A Study of Atom and Radical Kinetics

A Thesis submitted for

the Degree of Doctor of Philosophy

by

M.A.Hanning–Lee

Jesus College

1990

Abstract

This thesis describes the measurement of rate constants for gas phase reactions as a function of temperature ($285 \leq T/\mathrm{K} \leq 850$) and pressure ($48 \leq P/\mathrm{Torr} \leq 700$). One or both reactants was monitored directly in real time, using time–resolved resonance fluorescence (for atoms) and u.v. absorption (for radicals). Reactants were produced by exciplex laser flash photolysis.

The technique was used to measure rate constants to high precision for the following reactions under the stated conditions:

- $H+O_2+He \longrightarrow HO_2+He$ and $H+O_2 \longrightarrow OH+O$, for $800 \leq T/\mathrm{K} \leq 850$ and $100 \leq P/\mathrm{Torr} \leq 259$. A time–resolved study was performed at conditions close to criticality in the H_2–O_2 system. The competition between the two reactions affected the behaviour of the system after photolysis, and the rate constants were inferred from this behaviour.

- $H+C_2H_4+He \rightleftharpoons C_2H_5+He$ ($T = 800$ K, $97 \leq P/\text{Torr} \leq 600$). The reactions were well into the fall–off region at all conditions studied. At 800 K, the system was studied under equilibrating conditions. The study provided values of the forward and reverse rate constants at high temperatures and enabled a test of a new theory of reversible unimolecular reactions. The controversial standard enthalpy of formation of ethyl, $\Delta H^0_{f,298}$ (C_2H_5), was determined to be 120.2±0.8 kJ mol^{-1}. Master Equation calculations showed that reversible and irreversible treatments of an equilibrating system should yield the same value for both thermal rate constants.

- $H+C_3H_5+He \longrightarrow C_3H_6+He$ ($T = 291$ K, $98 \leq P/\text{Torr} \leq 600$) and $O+C_3H_5 \longrightarrow$ products ($286 \leq T/\text{K} \leq 500$, $48 \leq P/\text{Torr} \leq 348$). Both reactions were pressure–independent, and the latter was also independent of temperature with a value of (2.0±0.2) $\times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

- $H+C_2H_2+He \rightleftharpoons C_2H_3+He$ ($298 \leq T/\text{K} \leq 845$, $50 \leq P/\text{Torr} \leq 600$). At 845 K, both reactions were in the fall–off region; rate constants were used to determine the standard enthalpy of formation of vinyl, $\Delta H^0_{f,298}$ (C_2H_3), as 293±7 kJ mol^{-1}. The value of this quantity has until recently been very controversial.

- $H+CH_4 \rightleftharpoons CH_3+H_2$. The standard enthalpy of formation of methyl, $\Delta H^0_{f,298}$ (CH_3), was determined by re–analysing existing kinetic data at $T = 825$ K and 875 K. A value of 144.7±1.1 kJ mol^{-1} was determined.

Preliminary models were examined to describe the loss of reactants from the observation region by diffusion and pump–out. Such models, including diffusion

and drift, should prove useful in describing the loss of reactive species in many slow–flow systems, enabling more accurate rate constants to be determined.

ACKNOWLEDGEMENT

I should like to thank some of the many people without whom this work could never have been written.

Firstly, my supervisor, Mike Pilling, for presenting such an interesting set of problems and for helping to solve them, even after going to Leeds to get away from me! Thanks also to Nick Green and to past and present members of the group, Martin, Jo, Simon, Kevin, Kay, and others for their generous help and encouragement. Special thanks must also go to Paul "So you want me to help you move house AGAIN?" Seakins and to Struan Robertson for their friendship and help.

I would also like to thank my friends in the Jesus College G.C.R., Paul, Ulrich, Seán, Jon, Marita, Anna, Bridget, Lisa, Chip and Jenny, and others, and my friends from Cambridge, for their support and encouragement.

I would like to thank those at King's School and at Cambridge who fanned my interest in science in general and this field in particular.

I am also grateful to Jesus College and to the S.E.R.C. for their financial support throughout my work, and to the technical and office staff of the P.C.L., for their enduring willingness to help.

Lastly, I should like to thank my mother, my brother, and the rest of my family for all their help and encouragement. I dedicate my thesis to them, and consider that other students will be fortunate to receive as much support as I have done.

Another damned, thick, square book! Always scribble, scribble, scribble! Eh? Mr. Gibbon?

Boswell: *Johnson*

Contents

1 INTRODUCTION **2**

1.1 AN OVERVIEW 2

1.2 PYROLYSIS AND CRACKING 3

1.3 OXIDATION AND COMBUSTION 4

1.4 PRESSURE–DEPENDENCE 5

1.5 THERMODYNAMIC DATA 8

1.6 OUTLINE OF THESIS 10

1.7 REFERENCES 11

2 APPARATUS AND DATA ANALYSIS **12**

2.1 INTRODUCTION 12

2.1.1 Systems 12

2.1.2 Reactant generation 14

2.1.3 Detection techniques 17

2.1.4 Outline of Chapter 19

2.2 EXPERIMENTAL DETAILS 22

2.2.1 Gas handling 22

2.2.2 Flow and pressure 23
2.2.3 Temperature control 24
2.2.4 Laser 25
2.2.5 Fluorescence production and detection 26
2.2.6 Absorption measurements 32
2.2.7 Data acquisition 35
2.3 ANALYSIS 38
2.3.1 Fit algorithms 40
2.3.2 Data weighting 43
2.3.3 Recovery of fitted data 44
2.4 REFERENCES 45

3 PHYSICAL LOSS PROCESSES IN AN EXPERIMENT 47
3.1 INTRODUCTION 47
3.1.1 Background 47
3.1.2 Outline of Chapter 49
3.1.3 Glossary 51
3.2 THE EXPERIMENT 52
3.2.1 Technique 52
3.2.2 Materials 55
3.3 FIRST–ORDER MODEL 55
3.3.1 Analysis of decay traces 55
3.3.2 Dependence of k_d on P and T 56
3.4 NON–FIRST–ORDER MODELS 62
3.4.1 Introduction 62

3.4.2 One–dimensional diffusion model 62
3.4.3 Two–dimensional diffusion models 71
3.4.4 Calculation of diffusion rate constants 77
3.5 CONCLUSION 78
3.6 REFERENCES 79

4 REACTIONS IN THE HYDROGEN–OXYGEN SYSTEM 80
4.1 INTRODUCTION 80
4.1.1 Outline of Chapter 82
4.2 PREDICTIONS OF SIMPLE SCHEME 84
4.3 EXPERIMENTAL 92
4.4 DATA FITTING 96
4.4.1 Simple scheme 96
4.5 FULL MECHANISM 101
4.5.1 Input data 101
4.6 SENSITIVITY ANALYSIS 113
4.6.1 Introduction 113
4.6.2 Input data 116
4.6.3 Sensitivity results 117
4.7 FLUX ANALYSIS 121
4.8 CONCLUSION 126
4.9 REFERENCES 127

5 RATE CONSTANTS FOR THE H+C_2H_4=C_2H_5 REACTIONS 129
5.1 INTRODUCTION 129

5.1.1 Outline of Chapter 132
5.1.2 Glossary 133
5.2 EXPERIMENTAL 133
5.3 DATA ANALYSIS 135
5.4 THE STANDARD ENTHALPY OF FORMATION OF C_2H_5 . . 142
5.4.1 Introduction 142
5.4.2 Calculation of entropies 143
5.4.3 Fit to ΔC_p^0 144
5.4.4 Calculation of $\Delta H_{f,298}^0$ (C_2H_5) 146
5.4.5 Estimated errors 146
5.4.6 Comparison to literature values 147
5.5 TROE FACTORIZATION OF k_{rec} 148
5.5.1 Introduction 148
5.5.2 H + C_2H_4 = C_2H_5 system 151
5.5.3 Conclusion 156
5.6 CONCLUSION 156
5.7 REFERENCES 157

6 MASTER EQUATION DATA TREATMENT 159
6.1 INTRODUCTION 159
6.1.1 Glossary 162
6.1.2 Relaxation rate constant, k_{rel} 164
6.2 MASTER EQUATION MODEL 165
6.2.1 Irreversible model for association 166
6.2.2 Reversible model for association 168

6.3 INPUT PARAMETERS 173
6.3.1 Rotational state densities 175
6.3.2 Vibrational state densities 177
6.3.3 Calculating k_i 179
6.3.4 Collisional probabilities, P_{ij} 183
6.3.5 Collision frequency, ω 185
6.3.6 Input distribution, $\mathbf{\Phi}$ 186
6.4 METHOD OF SOLUTION 186
6.4.1 Irreversible model 187
6.4.2 Reversible model 187
6.5 RESULTS AND DISCUSSION 188
6.5.1 Convergence tests 188
6.5.2 Checks on method 190
6.5.3 $\langle \Delta E \rangle_{down}$ 191
6.5.4 Thermal recombination rate constant 192
6.5.5 Population distributions 198
6.6 CONCLUSION 203
6.7 REFERENCES 205

7 A KINETIC STUDY OF THE REACTIONS H+ALLYL AND O+ALLYL 207

7.1 INTRODUCTION 207
7.1.1 Background 207
7.1.2 Glossary of Chapter 209
7.1.3 Outline of Chapter 209

7.2 THE EXPERIMENT 210
7.2.1 Technique 210
7.2.2 Sources of materials 215
7.3 ANALYSIS: SIMPLE SCHEME 215
7.3.1 Mechanism 215
7.3.2 Input data 218
7.3.3 Determination of k_{X+A} 219
7.3.4 Parameter recovery from simulated data: analytic solution 221
7.3.5 Sinks of allyl 225
7.3.6 Results and error analysis 226
7.4 ANALYSIS: FULLER SCHEME 228
7.4.1 Mechanism 228
7.4.2 Parameter recovery from simulated data 230
7.4.3 Fits to experimental data 234
7.4.4 Conclusion 235
7.5 CALCULATION OF k_{H+A} 236
7.5.1 Calculation of k_d (C_3H_6) 236
7.5.2 Calculation of k_{H+A} 237
7.6 CONCLUSION 238
7.7 REFERENCES 239

8 RATE COEFFICIENTS FOR THE H + C_2H_2 = C_2H_3 REACTIONS 241

8.1 INTRODUCTION 241
8.1.1 Previous work 241

8.1.2 Outline of Chapter 244
8.1.3 Glossary 245
8.2 THE EXPERIMENT 245
8.2.1 Ethyne photolysis 245
8.2.2 Procedure and materials 247
8.3 $H + C_2H_2 \longrightarrow C_2H_3$ 249
8.3.1 Data analysis 249
8.4 EQUILIBRATION STUDIES 251
8.4.1 Data analysis 251
8.4.2 Input data and results 253
8.4.3 Radical–radical reactions 254
8.4.4 Conclusion 257
8.5 THE STANDARD ENTHALPY OF FORMATION OF C_2H_3 . . 258
8.5.1 Introduction 258
8.5.2 Standard entropy of reaction 259
8.5.3 Change in molar heat capacity 260
8.5.4 $\Delta H^0_{f,298}(C_2H_3)$ 261
8.5.5 Estimated errors 261
8.5.6 Comparison to literature values 263
8.6 REFERENCES 265

9 A STUDY OF THE SYSTEM $H+CH_4 = CH_3+H_2$ 268
9.1 INTRODUCTION 268
9.1.1 Background 268
9.1.2 Glossary 270

9.1.3 Outline of Chapter 270
9.2 EXPERIMENTAL 271
9.3 DATA FITTING 272
9.3.1 Rate constants for escape 273
9.3.2 Determination of K 274
9.4 ENTHALPY OF FORMATION OF CH_3 278
9.4.1 Entropies and heat capacities 278
9.4.2 Enthalpies 282
9.5 SIDE REACTIONS 283
9.6 SUMMARY 285
9.7 REFERENCES 288

10 FUTURE WORK **290**
10.1 REFERENCES 291

Chapter 1

INTRODUCTION

1.1 AN OVERVIEW

The chemistry found in pyrolysis, cracking, combustion, or the atmosphere is complex, and computer modelling of the reaction can improve process control or provide insight about the mechanisms operating. Sensitivity analysis [1, 2, 3] identifies the most important reactions, which can then be measured to greater accuracy. Rate constants are often temperature–dependent, and must be measured over a range of temperatures.

Rate constants for formation and dissociation depend on pressure, and have been subject to many theoretical studies. If a rate constant has not been measured under the experimental conditions needed, it may be extrapolated from values at other conditions, although for many reactions extrapolation may be subject to significant error.

If a reaction has not been measured directly, its rate constant may also be

calculated from the reverse rate constant and the equilibrium constant. The latter may be calculated from thermodynamic data, but several important radicals have high uncertainties in their enthalpies of formation. Finally, many theories of chemical kinetics have been developed. Experimental measurements of rate constants provide a means of testing these theories.

1.2 PYROLYSIS AND CRACKING

Rice [4] proposed a general mechanism for pyrolysis of a hydrocarbon, RH. Reaction is initiated by the breaking of a C–C bond:

initiation	RH	$\longrightarrow$	$R_1 + R_2$
H transfer	$RH + R_1$	$\longrightarrow$	$R + R_1H$
radical decomposition	R_1	$\longrightarrow$	alkene + R_3
addition	alkene + R_3	$\longrightarrow$	R_1
radical isomerization	R_1	$\longrightarrow$	R_4
disproportionation	$R_1 + R_2$	$\longrightarrow$	R_1H + alkene
recombination	$R_1 + R_2$	$\longrightarrow$	RH

where R = H or alkyl. Allara *et al.* [5] have summarized kinetic data for reactions involved in the pyrolysis of *n*–alkanes up to pentane. At commercial cracking temperatures (1100–1200 K), large alkyl radicals decompose rapidly. As a result, the rate of cracking or the product spectrum can only be affected by reactions of H, CH_3, C_2H_3, C_2H_5, and C_3H_5. Lightfoot [6] showed that C_2H_3 reactions are also important in the cracking of ethane to high conversions. Since not all relevant reactions can be studied directly, accurate enthalpies of formation are needed for all these radicals, in addition to rate constants.

1.3 OXIDATION AND COMBUSTION

At low temperatures, oxidation is slow and many different products are formed. Complex phenomena such as autoignition and cool flames can occur, and have been explained by the formation and decomposition of a degenerate branching agent such as an alkyl hydroperoxide, ROOH.

At high temperatures reaction is rapid, and oxidation proceeds to completion if enough O_2 is present. Warnatz [7] and Westbrook *et al.* [8] noted that all alkanes and alkenes have combustion mechanisms dominated by a small set of reactions, and thus have similar laminar flame speeds. Large organic radicals decompose rapidly, and the reaction rate is largely determined by the competition between the two channels of the H + O_2 reaction:

$$\begin{aligned} H + O_2 &\longrightarrow HO_2{}^c \\ HO_2{}^c &\longrightarrow OH + O \\ HO_2{}^c + M &\longrightarrow HO_2 + M \end{aligned}$$

At low temperatures and high pressures, the collision complex $HO_2{}^c$ is stabilized by collision to the relatively unreactive radical HO_2, so that the overall rate of reaction is slow. At higher temperatures and lower pressures, two reactive radicals are formed (OH and O), and chain branching occurs.

The allyl radical, C_3H_5, is found in many systems, yet reacts slowly with O_2 and is resistant to thermal decomposition. Likely sinks include reactions with H and O, for which rate constants have not been measured.

1.4 PRESSURE–DEPENDENCE

For a general dissociation–recombination reaction:

$$\mathrm{A} \underset{k_{rec}}{\overset{k_d}{\rightleftharpoons}} \mathrm{B} + \mathrm{C}$$

the rate constants are related through the equilibrium constant:

$$\begin{aligned} K &= \frac{[\mathrm{B}][\mathrm{C}]}{[\mathrm{A}]} \\ K &= \frac{k_d}{k_{rec}} \end{aligned}$$

Thus a recombination reaction has the same pressure–dependence as the reverse dissociation reaction. Lindemann [9] explained this dependence: B and C combine to form the energized molecule, A^*, with a rate constant k_a. A^* may dissociate with rate constant k_d, or be stabilized by collision with rate constant k_s:

$$\mathrm{B} + \mathrm{C} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \mathrm{A}^* \xrightarrow{k_s[\mathrm{M}]} \mathrm{A}$$

At higher pressures, more collisions occur, and association is faster. At higher temperatures and the same particle density, more energy must be removed from A^*, so each collision is less efficient and association is slower (Figure 1.1).

The following simplified treatment gives the form of the low– and high–pressure limits. A^* is formed with a rate:

$$\frac{d}{dt}[\mathrm{A}^*] = k_a[\mathrm{B}][\mathrm{C}] - k_d[\mathrm{A}^*] - k_s[\mathrm{A}^*][\mathrm{M}]$$

In the steady–state approximation, $d\,[\mathrm{A}^*]/dt = 0$, and A is formed at a rate given by

$$\begin{aligned} k_s[\mathrm{A}^*][\mathrm{M}] &= \frac{k_a k_s[\mathrm{B}][\mathrm{C}][\mathrm{M}]}{k_d + k_s[\mathrm{M}]} \\ &= k_{rec}[\mathrm{B}][\mathrm{C}] \end{aligned}$$

Figure 1.1: Effect of T on fall–off

So the rate constant is

$$k_{rec} = \frac{k_a k_s[\mathrm{M}]}{k_d + k_s[\mathrm{M}]}$$

with low– and high–pressure limits:

$$\begin{aligned} k_{rec}^{0} &= \frac{k_a k_s[\mathrm{M}]}{k_d} \\ k_{rec}^{\infty} &= k_a \end{aligned}$$

At intermediate pressures, the reaction is said to be in the fall–off region (Figure 1.2). Many reactions important in pyrolysis, cracking, and combustion proceed at rates dependent on both temperature and pressure. These dependences must be characterized by experiment and expressed in a form convenient for modelling. Master Equation models provide a full description of falloff behaviour, but are time–consuming. Troe and co–workers [10, 11] have expressed rate constants in terms of parameters calculated from reactant and bath gas properties.

1.5 THERMODYNAMIC DATA

§ 1.2 identified CH_3, C_2H_3, and C_2H_5 as important species in many reaction systems. Since some rate constants for reactions of these species have not been measured, enthalpies of formation must be determined for all species.

As discussed in later Chapters, reported enthalpies of formation for each species cover a wide range, so rate constants derived in this way are not well–determined. This thesis presents new data for each radical.

Figure 1.2: Fall–off curve with low– and high–P limits

Entropies and heat capacities may be calculated, using Third Law methods, from vibrational frequencies and rotational constants. Pacansky *et al.* [12] have measured and calculated vibrational frequencies for many alkyl radicals, and made general observations about the radical frequencies compared to those of similar alkenes and alkanes.

1.6 OUTLINE OF THESIS

Brouard [13] described in detail the slow–flow apparatus and data analysis used to measure rate constants in this thesis. The apparatus employs laser flash photolysis, and species are detected by resonance fluorescence and absorption spectrometry. Chapter 2 summarizes his description, describes modifications made, and reviews other experimental techniques. Chapter 3 extends the Brouard model for the escape of reactive species from the observation zone. The latter process includes diffusion and pump–out; a fit to experimental data suggests that plug flow occurs through the cell.

Chapter 4 presents rate constants for both channels of the H + O_2 (+ M) reaction at $800 \leq T/\mathrm{K} \leq 850$. In Chapter 5, direct measurements are reported under equilibrating conditions for H + C_2H_4 $\rightleftharpoons$ C_2H_5 at 800 K, and $\Delta H^0_{f,298}$ (C_2H_5) is derived from the rate constants. Chapter 6 uses two Master Equation (ME) models to show that rate constants so measured are identical to those that would be measured under irreversible conditions.

In Chapter 7, the first rate constant measurements are reported for H + C_3H_5 $\rightleftharpoons$ C_3H_6 (where C_3H_5 = allyl) at 291 K. A joint study with Gutman and co–workers [14] determined the products and rate constant for O + C_3H_5 $\longrightarrow$ H +

CH_2=CHCHO over 286$\leq T/K \leq$500. Chapter 8 presents preliminary data for H + $C_2H_2 \longrightarrow C_2H_3$ at 298 K and 600 K, and for H + $C_2H_2 \rightleftharpoons C_2H_3$ at 845 K, from which $\Delta H^0_{f,298}$ (C_2H_3) is derived. Chapter 9 re–analyses the 825 K and 875 K data of McOwan [15] for the reactions H + $CH_4 \rightleftharpoons CH_3 + H_2$, to obtain an improved value for $\Delta H^0_{f,298}$ (CH_3).

1.7 REFERENCES

[1] R.I.Cukier, H.B.Levine, K.E.Shuler *J.Comput.Phys.* **26** 1 (1978)

[2] J.–T.Hwang, E.P.Dougherty, S.Rabitz, H.Rabitz *J.Chem.Phys.* **69** 5180 (1978)

[3] E.P.Dougherty, H.Rabitz *J.Chem.Phys.* **72** 6571 (1980)

[4] F.O.Rice *J.Am.Chem.Soc.* **53** 1959 (1931)

[5] D.L.Allara, R.Shaw *J.Phys.Chem.Ref.Data* **9** 523 (1980)

[6] P.D.Lightfoot, D.Phil. Thesis, Oxford University (1986)

[7] J.Warnatz 18th *Int.Symp.Comb.* 369 (1981)

[8] C.K.Westbrook, F.L.Dryer *Prog.Energy Combust.Sci.* **10** 1 (1984)

[9] F.A.Lindemann *Trans.Farad.Soc.* **17** 598 (1922)

[10] J.Troe *Ber.Bunsenges.Phys.Chem.* **87** 161 (1983)

[11] R.G.Gilbert, K.Luther, J.Troe *Ber.Bunsenges.Phys.Chem.* **87** 169 (1983)

[12] J. Pacansky, A.Gutierrez *J.Phys.Chem.* **87** 3074 (1983) and references therein

[13] M.Brouard D.Phil. Thesis, Oxford University (1986)

[14] I.R. Slagle, J.R. Bernhardt, D. Gutman, M.A. Hanning–Lee, M.J. Pilling *J.Phys.Chem.* **94** 3652 (1990)

[15] S.P.McOwan Part II Thesis, Oxford University (1985)

Chapter 2

APPARATUS AND DATA ANALYSIS

2.1 INTRODUCTION

To observe the kinetics of atoms with radicals or molecules, at least one species should preferably be monitored in real time. To simplify the kinetics, one species is usually present in large excess, so that the second is removed at a rate determined only by the concentration of the first. The rest of this Section will discuss methods to produce and detect active species, with emphasis on reactions that are important in combustion and cracking systems.

2.1.1 Systems

Discharge flow systems have been widely used at low pressures, and at near–ambient temperatures. Atoms are produced by a microwave discharge. One

species is present in excess throughout the flow tube: its constant concentration is often determined by titration. The other species may be stable, or may be generated by discharge, flash photolysis, or infrared multi–photon dissociation. Its concentration is measured as a function of distance along the tube, which is converted to time by assuming (usually) plug flow. To reduce the rate of atom recombination, pressures must be low (several Torr); since species reach the walls on the observation timescale, the rate of wall reactions must be measured.

Shock tubes have been used to measure rate constants at high temperatures ($>\approx$700 K) and pressures. A precursor–diluent mixture is shocked, and concentrations are measured for several μs within the shock front, before or after reflection from the end of the tube. The temperature and pressure are calculated from the properties of the diluent, and reactants are formed when the precursor dissociates thermally or is photolysed. In the former case, accurate dissociation rate constants are needed, if dissociation occurs on the same timescale as that of the target reaction(s). A shock tube apparatus can only perform single–shot experiments at a low repetition rate.

Static systems have also been used. If the system is in a steady state, information may be inferred from the concentrations. Flash photolysis may also be used to generate reactants, especially if only a little precursor is photolysed in each flash, or if the products are unreactive and are not dissociated by the flash. Data gathering is still restricted by the need to stop and change the gas mixture.

This thesis describes measurements made in a slow–flow system. Such systems are versatile, in that they can measure rate constants at a wide variety of pressures and temperatures. Marshall *et al.* [1] have measured rate constants up to 1800 K. Conditions found in cracking and combustion are readily accessible.

Reactants may be observed in real time over a wide variety of timescales, and generated at high repetition rates. Since products are steadily removed by pump–out, experiments may be repeated until enough information has been gathered. Species diffuse to the walls on a timescale longer than the residence time, so wall reactions need not be considered, and removal by pump–out is usually much slower than removal by reaction. If not, corrections may be made (Chapter 3).

2.1.2 Reactant generation

Unstable species may be produced by the steady or pulsed dissociation of a relatively stable precursor by electromagnetic or ionizing radiation. In thermal dissociation, a precursor may be heated by contact with a hot surface, or by a sensitizer (e.g. SF_6) which has absorbed infrared radiation from a pulsed laser. Kelly *et al.* [2] noted that incorrect rate constants will be obtained at short times after photolysis, since the more translationally excited species will disappear more rapidly from the observation zone. Thus the rate constant will depend on position and time. Gorensek *et al.* [3] noted that a reaction with a low activation energy will also deplete the more translationally excited molecules. A competing reaction will thus occur with too low a rate constant, unless a diluent gas is added to permit relaxation.

A precursor should have the following attributes:

- A photolytic precursor should not pyrolyse appreciably during the experiment, and should not be photolysed by monitoring radiation. Dissociation of a thermal precursor should either be complete before reaction starts, or occur with a well–determined rate constant.

- If the dissociation fragments are different, the other fragment should not interfere with the kinetics during reaction.
- The precursor and its fragments should not interfere with detection, e.g. by quenching excited states when fluorescence is used to detect a product or a reactant, or by absorbing at monitoring wavelengths.
- The precursor should be easy to handle: it should not react with the apparatus, and should contain no impurities that cannot readily be removed.
- The dissociation should be well–characterized. In photolysis, no long–lived excited states of precursor or products should be formed.
- It should be possible to vary each reactant concentration separately.

There is an optimum precursor concentration. Too low a concentration generates too little reactant and gives poor signal : noise. Too much precursor may absorb the monitoring radiation, quench the excited state in fluorescence, or affect the apparent rate constant by causing side–reactions.

The generation of species other than H will be discussed in each Chapter in turn.

H generation

Lightfoot *et al.* [4] validated N_2O photolysis at 193.3 nm in H_2 as a clean H source above 400 K, according to the following scheme:

$$
\begin{aligned}
N_2O &\xrightarrow{h\nu} O(^1D)+N_2 \\
O(^1D)+H_2 &\longrightarrow OH+H \\
OH+H_2 &\longrightarrow H_2O+H
\end{aligned}
$$

N_2O is thermally stable, easy to purify, does not attack or adsorb on the stainless steel reaction cell used in this work, and does not absorb too strongly at the H detection wavelength (121.6 nm). Photolysis is clean (>95% as shown [5]). Below 400 K, the reaction of OH with H_2 becomes slow: unless much H_2 is added, H is generated on the reaction timescale. The N_2 fragment is unreactive and does not interfere with detection. However, nascent N_2 might be vibrationally excited. Maricq *et al.* [6] showed that $N_2(v = 1)$ is deactivated slowly by He; $k = 5{\times}10^{-18}$ cm^3 molecule^{-1} s^{-1} at 291 K, and increases with temperature. Thus $N_2(v = 1)$ might survive long enough to pump reactants into vibrationally excited states.

Other H precursors were also used in this work: O_2–H_2 at 800–850 K (Chapter 4), C_2H_4 at 800 K (Chapter 5), 1,5–hexadiene (Chapter 7), and C_2H_2 (Chapter 8). Each is discussed in the relevant Chapter. None is as ideal an H atom source as N_2O–H_2.

Other precursors may absorb at different wavelengths. An exciplex laser may be run with different fills to produce the stated wavelengths / nm: KrCl (222), KrF (248), XeCl (308), and XeF (351).

Okabe [5] gives photolysis data for many compounds that dissociate to give H, or O or OH (which can form H by reaction with added H_2). However, HI, O_3, NO_2, HNO_2, and HNO_3 will all pyrolyse at the temperatures used in this work (up to $\simeq$800 K). Many compounds react with the species being observed; H_2S, NH_3, HNO_2, and HNO_3 would adsorb onto or corrode the stainless steel apparatus.

At 222 nm, N_2O or SO_2 might absorb strongly enough to be useful. Lightfoot *et al.* [4] validated N_2O–H_2 as a good source at 193.3 nm; N_2O has an absorption cross–section ten times lower at 222 nm than at 193.3 nm. Instead of $O(^1D)$, some $O(^3P)$ may be produced, which releases H from H_2 on the experimental timescale near ambient temperatures and complicates kinetic measurements. SO_2 fluoresces strongly and the SO produced may be very reactive.

At $\lambda \geq$248 nm, N_2O and SO_2 do not photodissociate appreciably.

Thus it is not trivial to identify a suitable H precursor for kinetic studies.

2.1.3 Detection techniques

The concentrations of reactants and products may be monitored by a wide variety of techniques, including those listed below. Pilling *et al.* [7] discuss the application of each of these techniques.

- Infrared absorption of the beam of a tunable diode laser. Multipass optics increase the pathlength and hence the sensitivity. Absolute cross–sections are not needed for a first–order decay.

- Ultraviolet (uv) absorption of continuous or pulsed sources. Several species may absorb at the same wavelength. Atoms can have large cross–sections and very sharp lines, so atomic resonance absorption spectroscopy has been widely used for kinetic studies. In Chapter 7, $[C_3H_5]$ was measured with a continuous uv source. In molecular modulation spectroscopy, sensitivity is increased by modulating the uv source and using phase–sensitive detection.

- Resonance fluorescence. If an atom is excited by radiation, it will re–emit at the same wavelength in all directions. Since non–radiative loss processes are rarely important, the quantum yield can be high, and low concentrations may be detected. The light source (a resonance lamp) is simple to build and maintain. For this thesis, H and O were detected at 121.6 and 130 nm respectively.

- Laser–induced fluorescence. Species are excited by the output of a pulsed laser: for small species ($\leq$4 atoms), it is possible that the quantum yield will be high in one wavelength band. Fluorescence occurs at longer wavelength, and filters remove the scattered laser light.

- Photo–ionization mass spectrometry has been used to determine radical concentrations for kinetic studies. Park *et al.* [8] and Slagle *et al.* [9] observed C_2H_3 and C_3H_5. Pressures in the detector must be low, so species must be sampled from the reaction cell.

- Multi–photon ionization (MPI) has also been used: a radical simultaneously absorbs more than one photon from an intense laser beam, and is ionized. Baravian *et al.* [10] determined absolute [H] with 364.7 nm radiation. The 3+1 REMPI transition of H was saturated, so all H atoms were ionized and the ion signal was independent of laser power. Goldsmith [11] used 2+1 MPI to measure [O] profiles in flames, with ppm limits of detection. This technique may prove more sensitive than resonance fluorescence for the systems studied here. A more sensitive technique would allow the use of lower $[H]_0$, and reduce the contribution of radical–radical reactions to the

measured rate constant. Very few precursors will absorb one photon of 365 nm radiation, and fine–tuning might avoid strong multi–photon absorption by the precursor.

- The optoacoustic effect can yield useful kinetic information. O'Connor *et al.* [12] irradiated the H_2–Cl_2 system with pulsed 488 nm radiation. The long chain lengths and highly exothermic reactions amplified the effect; the amplitude and phase clarified the mechanism of NO inhibition. A similar technique might prove useful for the H_2–O_2 system (Chapter 4), which can also show a highly exothermic chain reaction.

- Mass spectrometry may be used in steady–state (sampling from a flow system) or in time–resolved modes.

- In laser magnetic resonance, an absorption is Zeeman–shifted by a steady magnetic field into resonance with a laser frequency. If this is done inside the laser cavity, low concentrations may have a large effect on the laser gain, and the technique can be sensitive.

- Electron spin resonance may also be used to measure concentrations.

2.1.4 Outline of Chapter

The rest of this Chapter extends the description of the technique first given by Brouard [13] and emphasizes some new developments.

All experiments were performed in a slow–flow multiport stainless steel cell with optical detection of transient species. Figure 2.1 provides a schematic view.

The photolysis laser beam and absorption beam crossed at right–angles in a horizontal plane. Gas flowed at right–angles to this plane. The resonance lamp beam was also horizontal, at 135° to the laser beam. Fluorescence was detected at right–angles to the horizontal plane by a photomultiplier tube.

Figure 2.1: Experimental layout

§ 2.2.1, § 2.2.2, and § 2.2.3 describe the measurement and control of gas flows, pressure, and temperature. § 2.2.4 discusses the operating conditions and output characteristics of the exciplex laser used as a photolysis source. § 2.2.5 describes fluorescence detection. § 2.2.6 outlines the absorption measurements detailed in Chapter 7. § 2.2.7 describes the acquisition of data. Data analysis, using the Marquardt algorithm or numerical fit routines, is described in § 2.3.

2.2 EXPERIMENTAL DETAILS

2.2.1 Gas handling

Gases were flowed into the cell from cylinders or pre–mixed bulbs of $\simeq$1 litre volume. The latter were filled by pressure on a separate system, which was evacuated by an Edwards EO6 oil diffusion pump backed up by a rotary pump. Electrical heating tape speeded the evacuation.

Precursor or reactant was diluted in bath gas to allow accurate flow control and to reduce reactions in storage.

Pre–mixed bulbs could be stored for several months without change in measured rate constants, so reactions such as polymerization did not affect the bulb contents. If there had been a leak, effusion would have depleted the lighter bath gas and changed the bulb composition. Rate constants did not change while a bulb was in use, so faster effusion of the lighter bath gas did not fractionate the bulb contents. Formation of a monolayer on the inside of the bulb would not significantly deplete the precursor in the bulb.

Typically, 10 Torr of precursor was purified by freeze–pump–thaw cycles and

diluted with bath gas to 1000 Torr total pressure. For very low precursor : diluent ratios, precursor pressures too low for accurate measurements would be needed: in such cases, the line was filled with precursor and expanded to fill the bulb as well. The volume ratio (line : bulb + line) was determined separately with bath gas.

2.2.2 Flow and pressure

Each gas flow was measured and adjusted by MKS 260 electronic mass flow controllers. A capacitance manometer (0–1000 Torr, MKS Baratron 220 BHS–3AL) measured the pressure, which was controlled manually by adjusting the needle valve between the cell and the exhaust rotary pump. The cell could be evacuated (usually to 10^{-5} Torr) by an Edwards EO2 oil diffusion pump backed up by a rotary pump. Baffles reduced the backstreaming of oil from the diffusion pump to the cell.

Typical flows were 115 sccm (standard cm^3 per minute) of bath gas with 5 sccm each of diluted precursor and diluted reactant. The large excess of bath gas defined an effective third body and reduced temperature and pressure changes due to reaction. Each flow controller was calibrated against a bubble flow meter in series. Flow calibrations were performed with the usual shielding aluminium foil in place, to allow for errors caused by heat build–up near the thermal flow meters. There were independent uncertainties of 1% in calibration and 1% in any reading. The total flow uncertainty was dominated by that in the largest flow (1.4%).

Pressures covered the range 50–700 Torr. The capacitance manometer was

calibrated under vacuum and at atmospheric pressure, and could be read to 0.1 Torr. The uncertainty in pressure was thus negligible (<0.2%).

Since the cell had a volume of ≃1 litre, the residence time was ≃2 minutes (200 Torr, 600 K). Experiments were performed at a repetition rate slow enough for measured rate constants not to be changed by the accumulation of products. Chapter 3 presents some evidence for a jet of fast–flowing gas through the observation region, corresponding to plug flow. Flows and pressure took ≃5 minutes to settle.

2.2.3 Temperature control

The cell was heated by eight Watlow Firerod 200 W cartridge heaters. Observation windows were held by flanges against Teflon O–rings set into the cell. The O–ring holders were water–cooled to prevent damage to O–rings or windows. The maximum temperature was limited to 1000 K by the water–cooling capacity and by radiative heating of the uncooled centre portion of the windows. Temperatures of 286–850 K were used in this work.

Two type K (chromel–alumel) Thermocoax thermocouples in the gas flow measured the temperature. One lay upstream and the other downstream of the photolysis region, and both agreed to <3 K. A control unit provided temperature readout and control to 0.5 K, once the proportional, integral, and derivative settings were optimized to give rapid response without oscillation.

The manufacturer quoted an accuracy of ±2 K below 500 K and ±0.75% above, i.e. ± <6 K in the present work. Fontijn *et al.* [14] noted that an unshielded thermocouple may not be at the gas temperature: it may be heated by

radiation from the walls, or cooled by radiation through the cell windows to the surroundings. Such effects will be small at the lower temperatures used in this work. Including this independent uncertainty, the total temperature uncertainty was ±4 K.

2.2.4 Laser

The photolytic uv source was a Lumonics TE861S exciplex laser operated on ArF (193.3 nm).

Operating conditions

To improve pulse–to–pulse reproducibility, the manufacturer's recommended fill [15] was modified as recommended by Brouard [13]. The fill included 85 Torr 5% F_2–He (BOC) and 220 Torr Ar (BOC, 99.996%, <20 ppm N_2, <5 ppm O_2, <4 ppm H_2O), increased to 35 psi total pressure with He (BOC A grade, >99.995%, 2 ppm O_2, 1 ppm H_2, <2 ppm H_2O). This mixture was passed through a liquid N_2 trap, to prolong the life of a laser fill by removing impurities formed during lasing. A compressor (Compton D/416–2e with a PTFE cover) circulated the mixture.

The pulse energy was varied (10–130 mJ) by changing the fill pressure and operating voltage (V), or by attenuating the output with silica plates. Voltages below the maximum were used, to increase the lifetime of electrical components ($\propto V^{-9}$, [15]). Use of burn paper showed a reduced fluence near the edge of the pulse: a central rectangular region (0.5 cm × 2.0 cm) of more uniform fluence was selected inside the cell by two collimators (Figure 2.1). From measurements of the absorption pathlength (§ 2.2.6) the beam divergence was ≃0.01 rad, and the beam

was not focused. Pulse energy was normally measured at 10 Hz with a Scientech 354 power–energy meter: pulse–to–pulse reproducibility (4%) was measured with a Gentec energy meter. Signal averaging for $\geq$16 shots ensured that measured rate constants were not affected by poor reproducibility [16] or beam alignment [17]. The laser was fired at the highest repetition rate that did not affect measured rate constants by making reactive products accumulate: this rate was usually 3 Hz.

Since the precursor only absorbed a small fraction of the incident laser pulse, little attenuation would occur along the laser beam. In normal operation, an exciplex laser operates on many longitudinal modes, with output expected to cover the range 193.3$\pm$0.1 nm. The pulse had a FWHM of 10 ns [15]; since 100 mJ of 193.3 nm radiation = 10^{17} photons, the peak intensity was $\approx 10^{25}$ photons cm^{-2} s^{-1}. This intensity was too low to cause multi–photon processes in C_2H_2 (Chapter 8), and presumably in most other species.

The spark–gap switch and the laser discharge created copious radio frequency interference which was greatly reduced by shielding the gaps in the cabinet with aluminium foil.

2.2.5 Fluorescence production and detection

H or O resonance radiation was generated by a resonance lamp and directed into the cell. Fluorescence was detected at right–angles by a solar–blind photomultiplier. Control traces corrected to first–order for scattered laser light.

Resonance lamp

A flowing resonance lamp was supplied with He (BOC A grade, >99.995%, 2 ppm O_2, 1 ppm H_2, <2 ppm H_2O), or on 1% H_2–He or O_2–He mixtures from pre–mixed bulbs. In the latter case, H_2 (BOC CP grade, >99.9995%, 5 ppm N_2, 2 ppm H_2O, 1 ppm O_2) and He (BOC CP grade, >99.999%, 2 ppm each Ne, N_2) were passed through Oxisorb filters (Messer–Griesheim) to reduce O_2 and H_2O to 0.2 ppm. O_2 (BOC zero grade, 0.3% N_2, Ar) was used as received.

An inlet needle valve was adjusted manually to keep the pressure at 2–5 Torr, as measured on a Pirani thermal conductivity gauge. Lower pressures reduced the lamp output; higher pressures made the tuning difficult (i.e. >1 W reflected power). A microwave generator (Electromedical Supplies Microtron 200, Mark III) supplied 50 W of 2450 MHz radiation to the cavity. Lower powers reduced the lamp output, and higher powers rapidly discoloured the lamp windows, also reducing output. The cavity followed the $\lambda/4$ design of Fehsenfeld *et al.* [18]: it could easily be tuned or disassembled for lamp maintenance.

The lamp design was that of Lifshitz *et al.* [19] with separate MgF_2 windows at the end of the lamp and on the cell. The end window was attached by TorrSeal to the quartz outer tube; the latter was air–cooled to avoid damaging the TorrSeal. Fresh gas was injected near the end window through a capillary, which had to be quartz due to the high plasma temperature, and used gas was steadily pumped away. The pump had a ballast bulb to reduce pressure fluctuations which might modulate the lamp output. The microwave cavity surrounded the quartz outer tube. Output was directed into the cell, and collimated there by two circular collimators (Figure 2.1).

With a gas mixture of 1% H_2–He, the L_α line was strongly reversed with a FWHM of 0.005 nm [19]. Line profiles were explained [19] by a strongly self–absorbing plasma (at $\simeq$700 K for 50 W input power) with an absorbing layer at the same temperature next to the end window. Since the Doppler absorption profile of atoms in the cell was strongest in the centre, emission and absorption profiles would overlap poorly, little light would be absorbed in the cell, and fluorescence would be weak but would remain linear to high [H] or [O].

Kurylo *et al.* [20] found that fluorescence intensity $\propto$ [H] for [H] $< 3\times10^{12}$ cm^{-3}, using a lamp operated on pure He. The resonance lamp used here was operated on 1% H_2–He, and would thus be linear to even higher [H]. In the H_2–O_2 system (Chapter 4), both N_2O and O_2 were photolysed in early experiments to create O. Chain reactions provided so much [H] ($\gg[O]_0$) that the H signal saturated. This effect was avoided by omitting N_2O, so that less O was produced.

In use, the lamp output fell as the MgF_2 end window became covered by deposits, and darkened (in bulk) by uv radiation damage. The deposits were not removed by 12 h ultrasonic cleaning in 40% aqueous HF or trichloroethene, but could be removed by grinding. Darkening was removed by annealing for 3 h at 600 K. These treatments restored lamp output to the level of a new window.

Lamp spectra (Figure 2.2) were recorded on an evacuated McPherson 214 monochromator; a Channeltron detector (Mullard BL312) was attached to the exit slits, and the output pulses were fed via an amplifier to a chart recorder. The region 115–400 nm was surveyed: the L_α line and the O($^3S \longrightarrow {}^3P$) triplet at 130.2, 130.4, and 130.6 nm were emitted from any feed gas, perhaps because impurities were released from the lamp walls. The O radiation was effectively removed by air (Figure 2.2). Also present were emissions from N ($^2D_0 \longrightarrow {}^2P$ at 117.6 nm and

$^2P_0 \longrightarrow {}^2D$ at 131.10 nm), but these would not excite fluorescence in the reaction cell.

Figure 2.2: Resonance lamp spectra

The discharge emitted stray microwave radiation, which changed the readings of pressure and gas flow. Meters for the latter were covered with aluminium foil.

The resonance lamp beam might have had an output of 10^{14} photons s^{-1} [5] at the monitoring wavelength over a 1 cm^2 area. If the precursor had a concentration of 10^{14} molecule cm^{-3} and an absorption cross–section of 10^{-18} cm^2, precursor molecules would be photolysed at the rate of 10^{-10} molecule cm^{-3} s^{-1}, which would merely give a steady background signal from the reactant. Photolysis products would be pumped out steadily, so would not accumulate.

Detection

Fluorescence was viewed through two circular collimators to define the observation region, a MgF_2 window, and a flowing gas filter at 1 atm pressure and $\simeq$3 cm deep. To give a good H signal (if no O was in the cell), N_2 flushed out absorbing H_2O, CO_2, and O_2. To select H radiation in the presence of O, dry air filtered out the O radiation. To select O radiation in the presence of H, a CaF_2 window absorbed the L_α, and an N_2 filter ensured good O signal.

The signal from a solar–blind vacuum uv photomultiplier was passed into a 500 Ω–100k Ω load and amplified with a $\times$100 gain. Two different KBr photocathode tubes were used (Thorn EMI G26L314LF and its equivalent 9414), and also a CsI photocathode tube (Thorn EMI 9413), all with an RFI–B214FV housing and voltage divider. CsI was intrinsically more sensitive than KBr at the laser wavelength (193.3 nm), so a CsI tube would detect more scattered laser light. The KBr tubes were much more sensitive than specified at 193.3 nm, so scattered

laser light caused a strong signal. The distortion decayed with a time constant that increased with the amplifier load, so the distortion was worse for poor atom signal (because a high load was needed) and at short timescales.

Scattered light was reduced by long cell arms and a black–painted beam stop on the laser beam path. A 121.6 nm interference filter (7% peak transmittance and 11 nm bandpass) reduced the H signal too much and was not used. Electronic gating was also tried (the first dynode was switched off for 2 μs after the laser fired), but distorted the signal as much as the scattered light would have done. This too was not used.

For each set of experiments under identical conditions, one control trace was recorded with the resonance lamp switched off and all other settings the same. This control trace was subtracted from all experimental decays before analysis. Two control traces were extremely similar, so this technique provided first–order correction for scattered laser light, and extended kinetic measurements to shorter timescales than would otherwise be possible. The corrected data could be fitted more closely by the chemical model used.

2.2.6 Absorption measurements

Chapter 7 discusses further the monitoring of C_3H_5 by absorption. A Xe–Hg lamp provided the steady monitoring beam. The light transmitted to the cell was passed through a monochromator and detected by a photomultiplier; the output signal was amplified for recording.

Lamp

A 200 W Xe–Hg lamp (Canrad–Hanovia L5271000) was held in an Oriel 6137 housing placed next to the cell window. The housing included a 37 mm diameter f/1.0 fused silica lens, which condensed the beam to a divergence of $\simeq$0.1 rad. Two circular collimators of 5 mm diameter within the cell selected the brightest central portion of the beam, which was passed through the observation region.

The output was stable to $\simeq$0.4% on a millisecond timescale, and had a ripple of frequency $\approx$1 Hz and amplitude 2% of full scale. As a lamp aged, the ripple grew larger and the output decreased. When the laser fired, radio frequency interference affected the lamp power supply [13] and reduced the output for a few milliseconds. This could be interpreted as a spurious transient absorption, and was corrected as described below. The problem was worse at short times.

Detection

The transmitted light was focused by a Spectrosil lens (f = 10 cm) onto the entrance slit of a 0.5 m (Spex 1870) monochromator with a 1200 lines/mm grating. The dispersed light intensity (first–order) was monitored by a photomultiplier (RCA 1P28). The photomultiplier output was passed into a 1 or 5 kΩ load and amplified with a $\times$100 gain. Brouard [13] found a rise time of 5 μs for a 10 kΩ load.

The monochromator was calibrated frequently with the 214.440 nm line of a low–pressure Cd lamp. Scanning through the line gave a triangular waveform from which the calibration error and bandpass were found. Both slits were set to a width of 0.37 mm, and the bandpass was 0.63$\pm$0.01 nm FWHM (reproducible

to 0.02 nm). Thermal insulation of the monochromator reduced, to ≈0.02 nm, the fluctuation in the calibration error. Since the C_3H_5 δ absorption band is structureless with a FWHM of 10 nm [21], small shifts in the calibration error were not important.

For the kinetic analysis used here, C_3H_5 absorption must follow the Beer–Lambert Law:

$$-\ln\left(\frac{I}{I_{inc}}\right) = \Delta = \epsilon C l \tag{2.1}$$

where the incident and transmitted light intensities are I_{inc} and I, and Δ is the absorbance. If I_{inc} is too high, then non–linear effects will occur, and the Beer–Lambert law will break down. The path length is l, and there is a concentration C of species with absorption coefficient ϵ. Smith [17] showed that the Beer–Lambert law held to <1% for CH_3 with a bandpass of 0.6 nm (when $\Delta = 0.005$). For this work, C_3H_5 had a much wider absorption band than CH_3, and $\Delta < 0.002$, so the Beer–Lambert law would certainly hold.

Since the Xe–Hg and laser beams are perpendicular, l was equal to the width of the laser beam (of rectangular cross–section). The laser beam was not focused and had low divergence, so l was constant across the 5 mm diameter of the Xe–Hg beam. Burn paper was placed inside the cell along the absorption collimation, and the mean width of the burn mark from several pulses was taken to be l (2.1±0.05 cm). l appeared not to jitter from pulse to pulse.

The incident light intensity, I_{inc}, was measured between experiments by blocking the beam and using a digital voltmeter to measure the change in signal, V_{inc}. The detection system was linear ($V_{inc} \propto I_{inc}$, see below), so the accuracy

($\simeq$0.5%) was limited by the 2% ripple in I_{inc}.

To correct for the distortion caused by radio frequency interference (called "r.f.i."), a control trace was recorded for each set of experiments. The laser beam was blocked, so that no absorbing species would be generated in the Xe–Hg beam, and the control trace contained only the effect of r.f.i. This control trace was subtracted from each experimental transmitted–light trace before analysis. Two successive control traces were very similar. After correction, the experimental data followed the expected second–order decay more closely. Thus this technique provides a reproducible first–order correction for the removal of r.f.i. distortion, and allows absorbance to be measured at shorter times.

2.2.7 Data acquisition

The amplified signal(s) from the photomultiplier(s) were recorded by a digitizer (Gould Biomation 8100). Each trace had 2024 data points. The digitizer operated in pretrigger mode, in which information was recorded steadily until a trigger pulse was received. For this work, the trigger pulse (-200 V full scale) was taken from the laser and attenuated before use. Once the trigger pulse was received, recording continued for $\simeq$1600 points, so the pretrigger part of the trace contained $\simeq$424 points.

Successive points were separated by the sample interval δt; values of 1 μs – 2 ms were used in this work, corresponding to time constants of $\approx$ 0.5–1000 s^{-1}. If only fluorescence intensity data were recorded, every point would contain fluorescence data. Otherwise, alternate points corresponded to the two input channels for transmitted light and fluorescence, so points from any one channel

were separated by $2\delta t$.

Each shot was read from the digitizer by a microcomputer (Research Machines 380Z or Zenith PC compatible). After enough shots (100–2000) had been read, the trace was viewed and stored on disc. Analysis was performed on the microcomputer, the department Norsk ND–540, or the Oxford University VAX 8800, aided by the greater speed, filestore, and numeric range of the larger machines. Accuracy of transfer was checked by comparing files before and after transfer with utility or data reading programs.

Conversion of transmitted light intensity to absorbance

The absorbance Δ followed the Beer–Lambert law (Equation 2.1):

$$\Delta = -\ln\left(1 - \frac{\delta I}{I_{inc}}\right)$$

where an incident light intensity I_{inc} was reduced by an amount δI. For these experiments, δI <0.002 I_{inc}, so

$$\Delta \simeq \frac{\delta I}{I_{inc}}$$

δI and I_{inc} were detected by the absorption photomultiplier and amplifier; the output from the latter was recorded on a digitizer. I_{inc} corresponded to a signal voltage V_{inc} (measured on a digital voltmeter). δI corresponded to a reduction of δd digits in the digitizer reading. If the system was not saturated and was fully linear (see below), δd would depend only on δI and not on I_{inc}, so that $V_{inc} \propto I_{inc}$.

To calculate Δ, a conversion factor R had to be used, such that a change of one digit corresponded to a voltage change of R. R was measured by connecting

the voltmeter and digitizer inputs in parallel. A 10 s trace was recorded; after 5 s, a steady voltage was applied from a 1.5V battery and potential divider. The trace was analysed to find the mean change in digitizer reading, so $R =$ (change in voltmeter reading) / (change in digitizer reading). Chapter 7 gives typical values.

When δd was the result of a sum over N shots, the single–shot absorbance was

$$\Delta = \frac{R\,\delta d}{N V_{inc}}$$

For each transmitted light trace, δd was determined by subtracting the mean reading before the laser fired, and converted to absorbance.

Checks

The digitizer time base calibration was checked with a calibrated pulse generator. Both channels were accurate to <0.08% on all timescales.

§ 2.2.5 showed that fluorescence intensity was linear in concentration, and § 2.2.6 showed that the transmitted light intensity followed the Beer–Lambert law. Detection would only be linear if the digitizer reading was proportional to intensity. For fluorescence detection, the background and signal intensities were low, so the photomultiplier and amplifier should have been in their linear ranges. For absorption, small changes had to be measured against a large background, which might have saturated the instruments used. The linearity of the absorption photomultiplier and amplifier, and of each digitizer channel, was checked as follows.

A small change in intensity ($I_{inc} \longrightarrow I_{inc} + \delta I$) produced a small change

in digitizer reading, δd digits. If the system was linear, $\delta d/\delta I$ should be independent of I_{inc}. Light from the Xe–Hg lamp was divided into two beams with quartz flats (Figure 2.3). The transmitted light beam had an intensity I_{inc} that could be attenuated with other flats. The weak reflected beam had a constant intensity δI ($\simeq$0.7% of the intensity of the undivided beam). Both light sources were recombined and focused onto the entrance slit of the monochromator. The reflected beam was blocked with a piece of card.

The digitizer recorded a 10 s scan: after 5 s, the reflected beam was unblocked. The resulting trace was stored on disc and analysed to find δd. Four traces were recorded for each value of I_{inc}. Within experimental error ($\simeq$5%), δd was independent of I_{inc}, so detection was linear in I_{inc}. Channel B on the digitizer was slightly more linear and was therefore used for the fluorescence–only measurements. Brouard [13] also confirmed the linearity of the digital voltmeter.

2.3 ANALYSIS

In general, parameters in a chemical kinetic model are fitted to experimental data. In this work, some models predicted analytic forms for concentration–time curves, which were fitted by non–linear least squares programs. If no analytic form existed, the numerical integration package FACSIMILE [22] was used. Fitting to a large mechanism can be very slow: a mechanism of N species has $\simeq N^2/2$ possible bimolecular reactions. It would be useful to eliminate species and reactions which have little effect on the data under study. In Chapter 4, reactive flux and sensitivity analysis are used to identify and remove unimportant reactions from a mechanism.

Figure 2.3: Check of absorption linearity

The first $\simeq$7% of each trace ($\geq$100 μs) was discarded. This helped to reduce:

- effects from short–lived vibrationally excited species
- reactions much faster than the target reaction(s)
- uncorrected artefacts from scattered light or radio frequency interference
- some effects from diffusion and pump–out, which were strongly non–first–order at short times (Chapter 3).

Rate constants were insensitive to the exact proportion discarded. Several (usually four) experiments were performed under identical conditions, and each was fitted separately to give best–fit parameter values. The determinations were combined to give an overall best–fit estimate: error estimates were combined assuming independence. Performing one experiment with four times as many shots would not have showed any effects from e.g. gas flows not settling, and would have been more liable to interruption (e.g. if a bulb ran out).

2.3.1 Fit algorithms

In general, experimental data y_i of weight w_i are gathered at a series of evenly spaced times, t_i. A model of the experiment has several parameters a_j and predicts data $y(t_i, a_j)$. Fitting programs adjust the a_j to minimize some measure of the difference between the fit and experimental data: an often–used measure is the weighted sum of squares:

$$\chi^2 = \sum_i w_i[y_i - y(a_j, t_i)]^2$$

§ 2.3.2 describes the choice of the w_i. If y is linear in all the a_j, then there are analytic formulae to find the best–fit a_j. If y is non–linear, it can be linearized, but it may be hard to define the correct w_i [7]; it is better to fit y directly to the data.

The dependence of χ^2 on the a_j defines a hypersurface, and minimization of χ^2 may be viewed as a search for the lowest minimum on the hypersurface. Most searches are iterative, so the current best–fit values are used to predict the next. The search ends when successive estimates agree to within a given tolerance. There are several different search algorithms:

- Grid search, used by FACSIMILE. Each a_j is given a series of evenly spaced values. The set of values for all a_j defines a grid. χ^2 is evaluated at each grid point, and the next stage uses a finer grid in the region with the lowest χ^2.

- Gradient search. The derivatives of χ^2 with respect to each a_j ($\nabla\chi^2$) are calculated. Steps are taken along the path of steepest descent ($\parallel \nabla\chi^2$). This algorithm is efficient far from a minimum, but is slow near a minimum, where all gradients are small.

- Taylor expansion. χ^2 is linearized as a function of the a_j:

$$\chi^2(\mathbf{a} + \delta\mathbf{a}, t_i) \simeq \chi^2(\mathbf{a}) + \delta\mathbf{a}\,\nabla\chi^2(\mathbf{a})$$

  where $\mathbf{a}$ is the vector $\{a_j\}$, and $\delta\mathbf{a}$ is a general small step. The best $\delta\mathbf{a}$ to reduce χ^2 may be found by solving

$$\mathbf{B} = \delta\mathbf{a}\,\mathbf{A} \tag{2.2}$$

where $\mathbf{B}$ and $\mathbf{A}$ have elements

$$\begin{aligned} B_j &= \sum_i w_i[y_i - y(t_i)]\frac{\partial y(t_i)}{\partial a_j} \\ A_{jk} &= \sum_i w_i \frac{\partial y(t_i)}{\partial a_j}\frac{\partial y(t_i)}{\partial a_k} \end{aligned}$$

This method is most effective near the minimum, where the linear expansion is most accurate.

- Marquardt [23] combined the gradient search and Taylor expansion algorithms by modifying $\mathbf{A}$ to $\mathbf{A}'$:

$$\begin{aligned} A'_{jk} = &\quad A_{jk}(1+\lambda) \quad j = k \\ = &\quad\quad A_{jk} \quad\quad\; j \neq k \end{aligned}$$

where λ is real and positive. Equation 2.2 becomes

$$\mathbf{B} = \delta\mathbf{a}\,\mathbf{A}'$$

For large λ, $\mathbf{A}'$ is nearly diagonal, and the algorithm resembles a gradient search. For small λ, the procedure resembles a Taylor expansion. The derivatives $\partial y(t_i)/\partial a_j$ are evaluated analytically, or numerically:

$$\frac{\partial y(t_i)}{\partial a_j} \simeq \frac{y(t_i, a_j + h) - y(t_i, a_j - h)}{2h}$$

where h is a small change ($0.1a_j$). At the minimum, one iteration is performed with λ=0. In this case, $(\mathbf{A}')^{-1}$ is the error matrix $\mathbf{E}$, and the error in a_j may be found from E_{jj}.

2.3.2 Data weighting

For absorption decays, it is important to note that peak absorbance was small ($\Delta < 0.002$ in this work), so the light intensity did not depend on time. Most noise came from photomultiplier shot noise, which depended on intensity. Thus the noise did not depend on time. All data points were given a constant weighting $w = \sigma^{-1}$, where σ was taken as the variance of the 360 pretrigger points before the laser fired.

Fluorescence decays were recorded over several lifetimes, so the intensity and noise decreased with time. For non–first–order decays, a constant weighting factor ($w = \sigma^{-1}$) was used as for absorption data. For first–order decays, an initial fit was performed with $w = \sigma^{-1}$. The variance of each data point was then estimated from a quadratic best fit to the squared deviations:

$$\sigma_i \simeq a + bx_i + cx_i^2$$

$$x_i \;=\; [y_i - y(t_i)]^2$$

New weightings $w_i = \sigma_i^{-1}$ were used and a new fit was obtained.

2.3.3 Recovery of fitted data

The following tests (Table 1) showed that time constants were recovered correctly from simulated first–order data covering one, two, or three lifetimes (where a lifetime = k^{-1}). First–order fluorescence decay traces were simulated, random noise was added at typical experimental levels, and the decay was written to disc in the same format as an experimental data file, with a pretrigger baseline. Since all exponential decay curves have the same form, only the total number of decay lifetimes recorded could affect the shape of a decay trace, and hence the accuracy of parameter recovery. Data traces were generated over one, two, or three decay lifetimes, and analysed after discarding the earliest part of the decay, to correspond more closely to analysis of experimental data. Each trace had the same number of points as an experimental data file.

Table 1 shows that exponential data should be recorded over two or three lifetimes, even when the late part of the decay is partly obscured by noise on the baseline.

Fitted values of the pre–exponential (C) and k might have showed appreciable covariance, but the value of C had no chemical significance in this work.

Appendix B derives the general bi–exponential solution to the coupled rate equations of two species. Tests on simulated data (Chapter 4) identified conditions to recover both rate constants well. It was often more effective to fit rate constants

Lifetimes in data	% of decay discarded			
	3	6	9	13
1	1.7	1.7	1.4	1.7
2	1.1	1.2	1.0	1.2
3	0.4	0.7	0.7	0.7

Table 1: Recovery of experimental time constant k. Entry in table is the percentage by which the recovered value of k exceeded the value used to generate the data.

directly, rather than the four bi–exponential parameters. Chapter 5 demonstrates such a fit to equilibration data, and discusses the covariance of the fitted rate constants.

2.4 REFERENCES

[1] P.Marshall, A.Fontijn *J.Chem.Phys.* **85** 2637 (1986)

[2] K.Kelly, M.D.Kostin *J.Chem.Phys.* **85** 7318 (1986)

[3] M.B.Gorensek, M.D.Kostin *J.Chem.Phys.* **83** 2280 (1985)

[4] P.D.Lightfoot, M.J.Pilling *J.Phys.Chem.* **91** 3373 (1987)

[5] H.Okabe "Photochemistry of Atoms And Small Molecules", Wiley– Interscience, 1977

[6] M.M. Maricq, E.A. Gregory, C.T. Wickham–Jones, D.J. Cartwright, C.J.S.M. Simpson *Chem.Phys.* **75** 347 (1983)

[7] "Modern Gas Kinetics", Eds. M.J.Pilling, I.W.M.Smith, Blackwell's, Oxford

(1987)

[8] J.–Y.Park, M.C.Heaven, D.Gutman *Chem.Phys.Lett.* **104** 469 (1984)

[9] I.R.Slagle, F.Yamada, D.Gutman *J.Am.Chem.Soc.* **103** 149 (1981)

[10] G. Baravian, J. Jolly, P. Persuy, G. Sultan *Chem.Phys.Lett.* **159** 361 (1989)

[11] J.E.M.Goldsmith *J.Chem.Phys.* **78** 1610 (1982)

[12] M.T.O'Connor, R.B.Stewart, G.J.Diebold *J.Phys.Chem.* **90** 711 (1986)

[13] M.Brouard D.Phil. Thesis, Oxford University (1986)

[14] A.Fontijn, W.Felder *J.Phys.Chem.* **83** 24 (1979)

[15] "Lumonics TE861–S Operating Manual", Lumonics Inc., Ottawa, Canada (1980)

[16] J.M.Tulloch, M.T.Macpherson, C.A.Morgan, M.J.Pilling *J.Phys.Chem.* **86** 3812 (1982)

[17] M.J.C.Smith D.Phil. Thesis, Oxford University (1985)

[18] Type 5 of: F.C.Fehsenfeld, K.M.Evenson, H.P.Broida *Rev.Sci.Instrum.* **36** 294 (1965)

[19] Source C of: A.Lifshitz, G.B.Skinner, D.R.Wood *J.Chem.Phys.* **70** 5607 (1979); C.–C.Chiang, A.Lifshitz, G.B.Skinner, D.R.Wood *J.Chem.Phys.* **70** 5614 (1979)

[20] M.J.Kurylo, N.C.Peterson, W.Braun *J.Chem.Phys.* **53** 2776 (1970)

[21] N.Nakashima, K.Yoshihara *Laser Chem.* **7** 177 (1987)

[22] FACSIMILE: A.R.Curtis, W.P.Sweetenham "Release H User's Manual", Report AERE–R 11771, AERE Harwell (October 1985)

[23] D.M.Marquardt *J.Soc.Industr.Appl.Math.* **11** 431 (1963)

Chapter 3

PHYSICAL LOSS PROCESSES IN AN EXPERIMENT

3.1 INTRODUCTION

3.1.1 Background

Many experimental techniques in physics and chemistry generate species of short lifetimes in a small volume by the interaction of electromagnetic radiation with matter. These species are then studied further by a variety of methods.

In gas kinetics, infra–red multi–photon dissociation or exciplex laser flash photolysis may be used to generate reactive species for further study (Chapter 2). Species concentrations may be monitored in real time by techniques that probe a limited volume. For example, a pulsed laser beam may create species that are excited by a continuous light source: the emitted radiation may be detected by a photomultiplier.

The transient species produced may be lost by chemical reaction or by any process that moves the species away from the observation region. The latter processes may include bulk gas flow and diffusion. In a simple model, all gas is assumed to travel in the same direction with a single drift speed, μ. Diffusion is assumed to be isotropic and to follow Fick's second law:

$$\frac{\partial C}{\partial t} = D\nabla^2 C$$

which links concentration, C, to time, t, and position. For anisotropic diffusion, D would be replaced by a tensor.

The interaction of flow and diffusion creates a complex variation of C with time and distance. For kinetic studies, C is usually assumed constant throughout the observation region at all times; if the species of concentration C was only created in a limited volume, then $C = 0$ at $t = 0$ outside this volume. Within the observation region, C is only measured as a mean value, $\langle C \rangle$. $\langle C \rangle$ is often assumed to have a first–order time–dependence:

$$-\frac{d}{dt}\ln\langle C\rangle = k_d \tag{3.1}$$

where k_d is a time– and position–independent first–order rate constant. If physical processes are ignored altogether or are negligibly slow, $k_d = 0$.

Under certain conditions, the assumption of a constant k_d becomes invalid, and rate constants derived by using this assumption will be incorrect. Finite–element techniques may be applied [1], in which the whole reaction region is divided into small elements of space: changes in C within each element due to reaction and physical processes are formulated, and the coupled differential equa-

tions are integrated over time and space. For more than one spatial dimension, the solution of such equations can become very laborious.

This Chapter examines the escape, by diffusion and slow flow, of species generated in the laser flash photolysis–resonance fluorescence system used for kinetic studies in this thesis: the models can readily be generalized to similar experimental systems. Parameters of all models are fitted to experimental data, and the time–dependence of k_d is derived from the simplest model.

The escape of reactive species contributed to the kinetics of all reaction systems studied in this thesis. For most systems, escape was dominated by chemical processes, so the convenient first–order model provided acceptable accuracy. For the H_2–O_2 system of Chapter 4, the decay or growth of atom concentration was very sensitive to the escape of atoms, and more accurate non–first–order models were developed as described below. Chapter 4 describes the application of the simplest such model.

3.1.2 Outline of Chapter

To generate experimental data, H or O was produced by laser flash photolysis of suitable precursor–bath gas mixtures. § 3.2 describes the monitoring of $\langle C \rangle$ ($\langle [\mathrm{H}] \rangle$ or $\langle [\mathrm{O}] \rangle$) by resonance fluorescence, as the species was lost from the observation region by physical escape processes (diffusion and flow).

In § 3.3, these fluorescence decay traces are fitted to a single exponential of rate constant k_d. Results are presented for the dependence of k_d on temperature and pressure, and it is shown that the decay of $\langle C \rangle$ is only approximately first–order. The first–order approximation is inadequate to describe kinetics of systems

in which atom escape contributes strongly to observed decays.

§ 3.4 describes the one–dimensional model of Brouard [2] and fits model parameters to experimental data. The one–dimensional model is extended to two dimensions, using different approximations for the shape and orientation of the observation region, and these extended models are also fitted to data. Fitted values are related to possible gas flow patterns within the reaction cell, and further models are suggested.

3.1.3 Glossary

Symbol	Meaning
D	diffusion coefficient for reactive species in bath gas
C	concentration of reactive species at a point
$\langle C \rangle$	mean concentration in observation region
C_0	initial value of both C and $\langle C \rangle$
I	mean fluorescence intensity from observation region
I_0	initial value of I
k_d	effective first–order rate constant for decay of both I and $\langle C \rangle$
a, b	pressure coefficients of experimental k_d
b_0, m	temperature coefficients of b
μ	drift speed for bulk gas flow; models pump–out
h	half–depth of photolysis laser beam
w	half–width of laser beam
$\dot{V}$	volume flow rate of gas due to pump–out
x, y, z	Cartesian axes to describe experiment
x	Horizontal axis at right–angles to laser beam
y	Horizontal axis $\parallel$ laser beam
z	Vertical axis $\parallel$ direction of observation

3.2 THE EXPERIMENT

3.2.1 Technique

Chapter 2 discusses the generation and monitoring of H and O in more detail. N_2O was photolysed by a pulsed laser to produce $O(^1D)$. To create O, the N_2 bath gas rapidly quenched $O(^1D)$ to the ground state, $O(^3P)$. To create H in He or N_2 bath gas, H_2 was added: $O(^1D)$ reacted rapidly with H_2 to produce OH+H, and OH reacted rapidly to produce H_2O+H. In N_2 bath gas, some $O(^3P)$ was always formed, and reacted more slowly with H_2 to produce OH+H. Near ambient temperatures, the latter reaction occurred on a timescale only about five times shorter than that for H escape, even at large $[H_2]$.

The kinetic scheme includes He or N_2 bath gases as shown:

He or N_2	$N_2O \xrightarrow{h\nu} O(^1D)+N_2$	$(t = 0)$
N_2	$O(^1D)+N_2 \longrightarrow O+N_2$	$(t \approx 0)$
He	$O(^1D)+H_2 \longrightarrow OH+H$	$(t \approx 0)$
N_2	$O+H_2 \longrightarrow OH+H$	
He or N_2	$OH+H_2 \longrightarrow H_2O+H$	
He	$H \longrightarrow$ escape	k_d
N_2	$O \longrightarrow$ escape	k_d

H or O was monitored in real time by resonance fluorescence, with digitizer settings of 5–50 μs between points (covering a period of 8–80 ms after the laser fired). 250, 500, or 1000 shots were summed to give adequate signal : noise, and four experiments were performed in succession under identical conditions. Control traces with the resonance lamp switched off were sometimes recorded and sub-

tracted from the raw data before analysis, to remove to first order the distortion caused by scattered laser light. Such distortion was always small, because of the long timescales used. Figure 3.1 shows a typical decay for H in N_2.

Figure 3.1: Typical decay for H escape (file DH96)

Typical conditions: $[N_2O]$ = (0.27–7.4) $\times 10^{14}$ molecule cm^{-3}, $[H_2]$ = (0.81–8.8) $\times 10^{16}$ molecule cm^{-3}, laser energy $\approx$ 50–90 mJ. Flow rate = 115–120 standard cm^3 min^{-1} (= actual flow rate converted to 273 K, 1 atm pressure).

3.2.2 Materials

Manufacturers' specifications and typical impurity levels: N_2O (BOC preparative grade, 99.6%, impurities not given), H_2 (BOC CP grade, >99.9995%, 5 ppm N_2, 2 ppm H_2O), He (BOC CP grade, >99.999%, 2 ppm each Ne, N_2), N_2 (BOC CP grade, >99.999%, 1 ppm each O_2, CO_2, hydrocarbons, H_2).

N_2O was distilled at least three times from and to liquid N_2, discarding the most volatile fraction (entrained air), and least volatile fraction (water) each time. H_2 and He were passed through Oxisorb filters (Messer–Griesheim), to reduce O_2 and H_2O levels to 0.2 ppm. N_2 was used as received.

3.3 FIRST–ORDER MODEL

3.3.1 Analysis of decay traces

Raw data files were usually corrected for scattered laser light as described above. It was assumed that the fluorescence intensity, I, was proportional to the mean atom concentration, $\langle C \rangle$. In a first–order model:

$$\langle C \rangle_t \;=\; C_0 \exp(-k_d t)$$

$$I_t \;=\; I_0 \exp(-k_d t)$$

Each decay trace of I_t was fitted to the above expression, using the Marquardt algorithm for non–linear least squares fitting (Chapter 2) with analytic parameter derivatives. The first 7% of the decay was discarded, to ensure that all scattered laser light had been removed, and to remove any effects from the slow $O(^3P)+H_2$ reaction generating H at short times. I_0 and k_d were floated; the fit program recovered k_d satisfactorily from exponential decays with added noise.

Each of four experiments under identical conditions thus gave an estimate of k_d. These were assumed independent and combined to yield an estimate of k_d for a particular atom (H or O), bath gas (He or N_2), temperature, and pressure.

However, experimental traces were significantly non–exponential. Figure 3.2 shows the residuals (data − fit) from the exponential best fit to a trace: $\langle C \rangle$ decreases with time at first more quickly then more slowly than the best–fit exponential decay, so the effective value of k_d decreases with time. A bi–exponential model for $\langle C \rangle_t$ would be physically opaque, since there was no reason to postulate two different first–order loss processes on different timescales, and it might have proved difficult to interpolate between all four fitted parameters for different pressures.

3.3.2 Dependence of k_d on P and T

For a given atom, bath gas, and temperature, k_d will decrease at higher pressures, where diffusion is slower. For self–diffusion, kinetic theory shows that

$$D = \frac{3}{8n}\sqrt{\frac{k_B T}{\pi m}}\,\frac{1}{\sigma_{11}^2 \Omega_{11}^{(1,1)^*}(T_{11}^*)}$$

where n is the number density of molecules of mass m and collisional cross–section σ_{11} (Equation (5.150) of [3]). $\Omega_{11}^{(1,1)^*}$ is the collision integral. For diffusion of two dissimilar species, σ describes the cross–section for collision between them, and m should be replaced by their reduced mass μ. In an ideal gas at constant T, $n \propto P$, so $D \propto P^{-1}$. It might be expected that $k_d \propto P^{-1}$. In fact, plots of k_d against P^{-1} have a non–zero ordinate intercept:

Figure 3.2: Residuals of exponential fit to escape trace

$$k_d = a + b/P$$

Table 1 gives values for a and b for each atom, bath gas, and temperature. To derive a and b, k_d for each pressure was weighted by (variance)$^{-1}$ in a linear least squares fit. Figure 3.3 plots this relationship for experimental k_d for files DH1–30. The pressure–independent term, a, was ascribed [2] to the removal of gas by pump–out. a should therefore be species–independent, but this is not the case for the data in Table 1. For some data sets, a is actually negative. The total mass flow rate was fixed, so pump–out will in fact cause a flow rate that is not pressure–independent, but is $\propto P^{-1}$. This breakdown of the model suggests that a is not due solely to pump–out. Since the interaction region has complex geometry, a simple model for atom escape has proved inadequate.

For an ideal gas at constant P, $n \propto T^{-1}$, so the diffusion coefficient, D, should be $\propto T^{1.5}$. Lede *et al.* [4] discussed measurements of $D(T)$ and showed that $D \propto T^m$, where $m > 1.5$. They recommended $m = 1.72$ for D (H in H_2, 278–333 K). If $b \propto D$, then b for the data in Table 1 may be fitted to:

$$b = b_0(T/\mathrm{K})^m$$

Best–fit values for m and b_0 / Torr s^{-1} K^{-m} are: H in He: $m = 2.97$, $b_0 = 4.2\times10^{-5}$. H in N_2: $m = 1.67$, $b_0 = 0.115$. O in N_2: $m = 0.958$, $b_0 = 3.20$. Values of m are widely scattered due to the small range of data and to the breakdown of this simple model for atom escape.

X	M	T/K	P/Torr	Files	a / s^{-1}	b/Torr s^{-1}
H	He	601	51–311	AD5–28	23.3±0.4	8270±20
H	He	701	79–369	AD29–48	18.3±0.4	10330±40
H	He	800	53–335	AD49–68	9.1±0.5	19600±100
H	N_2	600	50–400	DH1–30	6.6±0.3	5363±52
H	N_2	700	50–352	DH31–60	4.1±0.3	6415±57
H	N_2	800	49–299	DH61–91	7.0±0.4	7904±82
H	N_2	825	103–178	DH96–99, DH108–123	−1.1±0.4	8142±180
H	N_2	850	152–269	DH124–147	−2.7±2.2	10567±546
O	N_2	403	49–401	DO37–61	5.4±0.3	952±68
O	N_2	500	49–97	DO76–85	8.2±1.0	1371±69
O	N_2	600	51–501	OD104–137	10.7±0.1	1425±13
O	N_2	700	50–500	OD73–103	11.2±0.2	1635±34
O	N_2	800	50–500	OD37–49, OD 58–72	15.0±0.3	1967±27

Table 1: Pressure and temperature dependence of k_d. Estimated internal errors (1σ) are shown. The atom X diffuses through the bath gas M.

Figure 3.3: k_d against P^{-1}, with best straight–line fit

3.4 NON–FIRST–ORDER MODELS

3.4.1 Introduction

Chapter 2 and Figure 3.4 describe the experimental layout in more detail. The laser beam, of rectangular cross–section, photolyses the precursor to create atoms. Since the medium is optically thin, little attenuation will occur, so the atom concentration will be constant along the laser beam, and zero outside.

Only some atoms are observed: the laser beam is probed by a resonance lamp beam at an angle of 135°. The probe beam lies in the plane of the laser beam, and is approximately cylindrical: a fraction of the atoms inside it are excited, and radiation is re–emitted. Some of this fluorescence is observed by a photomultiplier at right–angles to both beams. The photomultiplier has an approximately cylindrical field of view (defined by collimators), and gas flows parallel to the cylinder axis.

The observation region thus has a very complex shape. Atoms will disappear from it by gas flow and by diffusion into regions of lower concentration.

3.4.2 One–dimensional diffusion model

Brouard [2] neglected diffusion in the plane defined by the laser and resonance lamp beam axes, and postulated that the firing of the laser created a sheet of atoms of uniform concentration. The sheet had infinite length and width, and a depth of $2h$ in a direction parallel to the axis of observation of the photomultiplier. The latter direction defined the z axis in a set of Cartesian axes: x and y were in the plane defined by the laser and resonance lamp beams, and the origin was

chosen to lie in the mid–plane of the sheet.

Figure 3.4: Intersecting beam geometry

The initial rectangular distribution of atom concentration, $C(z, t = 0)$, was thus given by

$$\begin{aligned} C(z, t = 0) = &\quad 0 \quad |z| > h \\ = &\quad C_0 \quad |z| \leq h \end{aligned}$$

As time passed, the atoms diffused $\parallel z$ with diffusion coefficient D, so the initial rectangular distribution of atom concentration broadened. The centre of the distribution also drifted $\parallel z$ with speed μ, corresponding to steady gas flow.

The one–dimensional solution to the diffusion equation was taken from Equation 2.15 of Crank [6] for these boundary conditions, and modified by Brouard for a drift speed of μ:

$$C(z, t) = \frac{C_0}{2}[\operatorname{erf} z_+ + \operatorname{erf} z_-] \tag{3.2}$$

where

$$\begin{aligned} z_\pm &= \frac{-h \pm z + \mu t}{\sqrt{4Dt}} \\ \operatorname{erf} v &= \frac{2}{\sqrt{\pi}} \int_0^v \exp(-u^2)\, du \end{aligned}$$

where erf is the error function. μ models the constant rate of removal of gas by pump–out. Figure 3.5 shows concentration profiles for three times, 0, t_1, and $2t_1$, calculated from Equation 3.2.

Figure 3.5: 1-d diffusion. $D = 10$ cm^2 s^{-1}, $h = 0.5$ cm, $\mu = 60$ cm s^{-1}.

The observation region was taken to be the cube $\{-h \leq x, y, z \leq h\}$ with a volume of $8h^3$. Brouard considered a parallelepiped of sides d, d, and h, but the experimental information would have been inadequate to fit both d and h. In this region, the number of atoms was

$$\int_{-h}^{h}\int_{-h}^{h}\int_{-h}^{h} C(z,t)\,dx\,dy\,dz$$

or

$$4h^2\int_{-h}^{h} C(z,t)\,dz$$

since C was independent of x and y. Also, the number of atoms was $8h^3\langle C\rangle$, where $\langle C\rangle$ was the mean concentration:

$$\langle C\rangle = C_0 F_z \tag{3.3}$$

where

$$\begin{aligned} F_z &= \frac{g_t\sqrt{4Dt}}{2h} \\ g_t &= q(h_+) + q(h_-) - 2q(h_0) \end{aligned}$$

and

$$h_0 = \frac{\mu t}{\sqrt{4Dt}}$$

$$
\begin{aligned}
h_{\pm} &= \frac{2h \pm \mu t}{\sqrt{4Dt}} \\
&= \frac{2h}{\sqrt{4Dt}} \pm h_0 \\
q(v) &= \int \operatorname{erf} v \, dv \\
&= v \operatorname{erf} v + \frac{\exp(-v^2)}{\sqrt{\pi}} + \text{constant}
\end{aligned}
$$

Since g_t was symmetric in μ, the sign of μ was indeterminate — gas could be lost by flowing upwards or downwards. Equation 3.3 is antisymmetric in h (i.e. $\langle C \rangle(-h) = -\langle C \rangle(h)$), so the sign of h can be determined in fitting. Equation 3.3 has the correct short–time limit: as t approaches 0, $\langle C \rangle$ approaches C_0. For large t, numerical cancellation occurred in g_t, since $q(h_+) \approx q(h_-) \approx q(h_0)$. g_t may be rewritten in terms of the complementary error function, erfc, to enable more accurate calculation at large t:

$$
\begin{aligned}
g_t &= 2h_- + 2h_0 \ \operatorname{erfc} h_0 - h_+ \ \operatorname{erfc} h_+ - h_- \ \operatorname{erfc} h_- \\
&+ \left[\exp(-h_+^2) + \exp(-h_-^2) - \frac{2}{\sqrt{\pi}} \exp(-h_0^2)\right] \\
\operatorname{erfc} v &= 1 - \operatorname{erf} v
\end{aligned}
$$

If the detection system is linear, the fluorescence intensity, I, from the observation region will be proportional to the mean concentration, $\langle C \rangle$. Thus Equation 3.3 may be written in terms of I:

$$
\frac{I}{I_0} = \frac{g_t \sqrt{4Dt}}{2h} \tag{3.4}
$$

where I_0 is the initial fluorescence intensity. To fit data, D was estimated from literature values:

- A small amount (8%) of He was present in the N_2 from the pre–mixed bulb, so the gas mixture was not pure N_2. Diffusion coefficients were calculated for a mixture of 8% He, 92% N_2 using the expression of Sandler *et al.* [5]:

$$\frac{1}{D} = \sum_i \frac{x_i}{D_i}$$

where the ith component of a gas mixture has a mole fraction x_i, and diffusion of H through pure component i is described by a coefficient D_i.

- Khouw *et al.* [7] and Lede *et al.* [4] gave

$$\begin{aligned} D(\text{H in } N_2,\ 298\ \text{K}) &= 1.35 \pm 0.03\ \text{atm cm}^2\ \text{s}^{-1}\ /\ P \\ D(\text{H in He},\ 275\ \text{K}) &= 2.38\ \text{atm cm}^2\ \text{s}^{-1}\ /\ P \end{aligned}$$

- Near ambient temperatures, $D \propto T^{1.72}$ (§ 3.3.2). This dependence was assumed to hold up to the higher temperatures of the experiments modelled here. Thus:

$$\begin{aligned} D(\text{H in He}) &= 0.1153\ \text{Torr cm}^2\ \text{s}^{-1}\ (T/\text{K})^{1.72}\ /\ P \\ D(\text{H in } N_2\text{–He}) &= 0.0595\ \text{Torr cm}^2\ \text{s}^{-1}\ (T/\text{K})^{1.72}\ /\ P \end{aligned}$$

In analysis, D was fixed at the value calculated from the temperature and pressure. I_0, h, and μ were floated to fit the fluorescence decay trace to Equation 3.4, using the Marquardt algorithm for non–linear least squares fitting (Chapter 2). Since the experimental data only covered short timescales, g_t was expressed in terms of erf and not erfc.

The starting value of I_0 was set to the first fluorescence data point. To check that the fits were reproducible, h was started from 0.2 or 0.5 cm, and μ

from 5 or 10 cm s^{-1}: each trace converged to the same values from all four sets of starting conditions. Only I_0 and h were tested to determine convergence of a fit: between iterations, the fitted value of μ changed appreciably, so μ was not tested for convergence. Appendix A gives fitted values for h and μ.

Some attempts were made at joint analysis of a set of four traces (Chapter 4). h and μ were floated over all traces, and I_0 was optimized separately for each trace. Such analyses converged more slowly and to less reproducible minima than fits to isolated traces, and were abandoned.

Fitted values of h covered the ranges 0.3–1.1 cm in N_2–He, and 0.6–1.6 cm in He. These values are larger than the half–depth of the laser beam as measured experimentally (0.20±0.02 cm), perhaps due to model deficiencies. h did not depend systematically on pressure or temperature. The residuals of this fit were scattered evenly about 0, unlike those for the exponential model.

Fitted values of the drift speed, μ, were proportional to (T/P) as expected: on exit from the cell, the volume of gas would increase by a factor proportional to (T/P). Since the exit cross–sectional area and mass flow rate were constant, $\mu \propto (T/P)$. The flow rate of gas entering the cell was $\simeq 120$ cm^3 min^{-1} at 273 K and 1 atm pressure. At other temperatures and pressures, the volume flow rate, $\dot{V}$, was given by:

$$\begin{aligned} \dot{V} &= 120 \frac{T}{273\text{K}} \frac{1 \text{ atm}}{P} \text{cm}^3 \text{ min}^{-1} \\ &= 5.57 \text{ Torr cm}^3 \text{ s}^{-1} \text{ K}^{-1} \ (T/P) \end{aligned}$$

For plug flow through a cross–sectional area A:

$$\begin{aligned} \mu &= \dot{V}/A \\ &= 5.57 \text{ Torr cm}^3 \text{ s}^{-1} \text{ K}^{-1} \ (T/P)/A \end{aligned}$$

A plot of μ against (T/P) had a gradient = 5.57 Torr cm^3 s^{-1} K^{-1} / A. For N_2–He, the files DH1–147 were analysed, and a value of $A = 0.45 \pm 0.02$ cm^2 was found (gradient = 12.4±0.5 Torr cm^3 s^{-1} K^{-1}). For pure He, the files AD1–32 and AD37–68 were analysed, and a value of $A = 0.235 \pm 0.007$ cm^2 was found (gradient = 23.7±0.7 Torr cm^3 s^{-1} K^{-1}).

In this model, the drift speed derived from experimental data corresponds to plug flow through an area similar to that of the gas inlet and outlet tubing (0.31 cm^2). There might, therefore, be a narrow jet of gas flowing rapidly through the observation region, with much stagnant gas around it. Since photolysed gases could accumulate in the cell, this disturbing conclusion was checked with more sophisticated models.

3.4.3 Two–dimensional diffusion models

The Brouard model was modified to consider the finite width of the laser beam. Initially, a bar–shaped volume was filled with a concentration C_0 of atoms. The volume still extended indefinitely $\parallel y$ (in the direction of the laser beam), and had a depth of $2h$ and a width of $2w$ ($w > h$). This provided a better model of the initial atom distribution created by a laser beam of rectangular cross–section. The new initial boundary conditions were:

$$
\begin{aligned}
C &= 0 \quad |z| > h \quad \text{or } |x| > w \\
C &= C_0 \quad |z| \leq h \quad \text{and } |x| \leq w
\end{aligned}
$$

Diffusion $\parallel x$ was now included. Since there was no concentration gradient along the laser beam, diffusion $\parallel y$ could not occur. Diffusion was assumed to be isotropic. Gas flow still caused drift $\parallel z$; there was no drift $\parallel x$ or $\parallel y$.

Since the boundary conditions (see above) for this two–dimensional diffusion were separable in x and z, the solution was also separable:

$$C(x, z, t) = C(z, t) f(x, t)$$

$f(x, t)$ described diffusion $\parallel x$, without drift, and was taken from (2.15) of Crank [6]:

$$2f(x,t) = \text{erf}\left[\frac{-w+x}{\sqrt{4Dt}}\right] + \text{erf}\left[\frac{-w-x}{\sqrt{4Dt}}\right]$$

The observation region was still a cube of side $2h$ in $\{-h \leq z \leq h\}$. Two orientations of the cube with respect to x and y were considered. The orientations were named A and B; each is discussed below, and drawn in Figure 3.6. The observation region could also be modelled by the intersection of the cylindrical resonance lamp beam with the cylindrical field of view of the photomultiplier: simple shapes could include a cylinder or a sphere, but $\langle C \rangle$ would then be defined in terms of Bessel functions, and be more complicated to calculate.

Figure 3.6: Orientations A and B.

Orientation A

All edges of the cube were parallel to the axes (resonance lamp irradiation at 90° to the laser beam), so the cube was in $\{-h \leq x, y, z \leq h\}$ as before. The total number of atoms in the observation region was:

$$\begin{aligned} 8h^3\langle C\rangle &= \int_{-h}^{h}\int_{-h}^{h}\int_{-h}^{h} C(x,z,t)\,dx\,dy\,dz \\ &= 2h\int_{-h}^{h}\int_{-h}^{h} C(x,z,t)\,dx\,dz \\ &= 2h\int_{-h}^{h} f(x,t)\,dx\int_{-h}^{h} C(z,t)\,dz \end{aligned}$$

Integrating,

$$\begin{aligned} \langle C\rangle &= C_0 F_z F_x \\ F_x &= \frac{\sqrt{4Dt}}{2h}[q(w+) - q(w-)] \\ w_\pm &= \frac{w \pm h}{\sqrt{4Dt}} \\ q(v) &= v\ \operatorname{erf} v + \frac{1}{\sqrt{\pi}}\exp(-v^2) + \text{constant} \end{aligned}$$

The inclusion of diffusion $\parallel x$ thus multiplied the one–dimensional solution (Equation 3.3) by a dimensionless factor F_x. Assuming that the fluorescence intensity, I, was proportional to $\langle C\rangle$:

$$I = I_0 F_z F_x$$

Fluorescence decay traces were fitted to the above equation in the same way as for the one–dimensional model. w was set to the measured laser beam half–width (1.0 cm). F_x is symmetric in h; F_z and $\langle C \rangle$ are antisymmetric in h. Appendix A gives fitted values of h and μ. In this model, adding diffusion $\parallel x$ changed the best–fit values of h very little. Since a little of the observed loss was now ascribed to horizontal diffusion, a slightly lower vertical drift speed was needed to fit the observed rate of atom loss. The effect was small; since the laser beam was wide and shallow ($w > h$), vertical diffusion and drift removed atoms more quickly than horizontal diffusion.

μ was plotted against (T/P) to define an effective cross–sectional area, A, for plug flow. Since μ was less than in the one–dimensional case, A was slightly greater. In N_2–He, the files DH1–147 were analysed, and a value of $A = 0.46 \pm 0.03$ cm^2 was found (gradient = 12.0±0.8 Torr cm^3 s^{-1} K^{-1}). In pure He, the files AD1–32, AD37–44, and AD49–68 were analysed, and a value of $A = 0.303 \pm 0.007$ cm^2 was found (gradient = 19.34±0.07 Torr cm^3 s^{-1} K^{-1}).

Orientation B

The horizontal edges of the cube now lay at 45° to the x and y axes, corresponding to resonance lamp irradiation at 135° to the laser beam (Figure 3.6). The cube now occupied $\{-h \leq z \leq h,\ -h\sqrt{2} \leq x, y \leq h\sqrt{2}\}$, and the vertical faces were defined by the four planes $|x_v| = h\sqrt{2} - |y|$, where x_v was the value of x on a vertical face. The total number of atoms was now:

$$8h^3\langle C \rangle = \int_{-h}^{h} C(z,t)\,dz \int_{-h\sqrt{2}}^{h\sqrt{2}} dy \int_{-x_v}^{x_v} f(x,t)\,dx$$

$$= \qquad 2hC_0F_z \qquad \int_{-h\sqrt{2}}^{h\sqrt{2}} dy \int_{-x_v}^{x_v} f(x,t)\,dx$$

where $x_v = h\sqrt{2} - |y|$ and was non–negative. Integrating,

$$\begin{aligned}
\langle C \rangle &= C_0 F_z F_{xy} \\
F_{xy} &= \frac{Dt}{h^2}[h(y_+) + h(y_-) - 2h(y_0)] \\
h(v) &= \int\int \operatorname{erf} v\, dv \\
&= \int q(v)\, dv \\
&= (v^2 + 1/2)\operatorname{erf} v + v\, \exp(-v^2) + \text{constant} \\
y_0 &= \frac{w}{\sqrt{4Dt}} \\
y_\pm &= \frac{w \pm h\sqrt{2}}{\sqrt{4Dt}}
\end{aligned}$$

The inclusion of diffusion $\parallel x$ multiplied the solution for one–dimensional diffusion (Equation 3.3) by a dimensionless factor F_{xy}. This factor had a more complicated form than that of F_x in orientation A, because the limits on x and y were not independent. Once again, $\langle C \rangle$ is antisymmetric in h. Assuming that the fluorescence intensity, I, was proportional to $\langle C \rangle$:

$$I = I_0 F_z F_{xy}$$

Fits to fluorescence decay traces were attempted, but only for H in N_2–He. Some fits failed due to numeric overflow. Appendix A lists converged values. This model proved less satisfactory: converged values of h were more widely scattered

(–2.1 to 3.3 cm). A plot of μ against (T/P) had a gradient of 10.19±0.06 Torr cm^3 s^{-1} K^{-1}, corresponding to a cross–sectional area of 0.547±0.003 cm^2 for plug flow.

3.4.4 Calculation of diffusion rate constants

From Equation 3.1

$$k_d = -\frac{d}{dt}\ln\langle C\rangle$$

If the decay of $\langle C\rangle$ is not exponential, then k_d will depend on t. In the simpler one–dimensional model, Equation 3.3 shows that

$$\begin{aligned} k_d &= -\frac{d}{dt}\ln F_z \\ \ln F_z &= \frac{1}{2}\ln t + \ln g + \text{constant} \\ \Longrightarrow k_d &= -\frac{1}{2t} - \frac{d}{dt}\ln g \end{aligned}$$

Because

$$\begin{aligned} \frac{d}{dt}q &= \frac{d}{dt}\, v\ \mathrm{erf}\, v \\ \frac{d}{dt}h_0 &= \frac{h_0}{2t} \\ \frac{d}{dt}h_\pm &= -\frac{h_\mp}{2t} \end{aligned}$$

it may be shown that

$$-\frac{d}{dt}g = h_- \ \mathrm{erf}\, h_+ + h_+ \ \mathrm{erf}\, h_- + 2h_0 \ \mathrm{erf}\, h_0$$

$k_d(t)$ may therefore be expressed in terms of D, h, and μ at any time t.

3.5 CONCLUSION

In a flash photolysis–resonance fluorescence system, reactive species escape from the observation volume by diffusion and pump–out. For most kinetic studies, the escape could be modelled as first–order with a rate constant, k_d (even though the decay is not truly first–order). k_d has a component independent of pressure, which has been ascribed to pump–out. The other component of k_d is proportional to the diffusion coefficient for motion of the reactive species through the bulk gas. This latter component is, therefore, proportional to (pressure)$^{-1}$ at fixed temperature, and the constant of proportionality increases with temperature.

The first–order model was inadequate if escape contributed significantly to the kinetics. Brouard had included pump–out in the solution of the diffusion equation for a rectangular source. This solution was fitted to experimental data, and used to derive the time dependence of k_d. Two two–dimensional models were developed and fitted to data; these models were more complex, but described qualitatively similar processes for atom escape. For all these models, fits to experimental data suggested a very high drift speed.

This high drift speed suggests that escape of all species should be dominated by drift and not diffusion. Thus all species should be lost at the same rate from

the observation region, a conclusion which disagrees with experiment. The models used here are only simple approximations to the physical processes occurring in a region of complex shape (Figure 3.4), and thus yield poor results.

Models such as these may be used to predict the limit of spatial resolution in chemical kinetic studies: in small observation volumes, rapid loss of reactive species by physical processes will dominate reactive processes, and accurate kinetic studies will be impossible.

3.6 REFERENCES

[1] N.L.Schryer *J.Phys.Chem.* **81** 2335 (1977)

[2] M.Brouard D.Phil. Thesis, Oxford University (1986)

[3] G.C.Maitland, M.Rigby, E.B.Smith, W.A.Wakeham "Intermolecular Forces: Their Origin and Determination", Oxford University Press (1987)

[4] J.Lede, J.Villermaux *Chem.Phys.Lett.* **43** 283 (1976)

[5] S.I.Sandler, E.A.Mason *J.Chem.Phys.* **48** 2873 (1968)

[6] J.Crank "The Mathematics of Diffusion", 2nd Ed., Oxford University Press (1976)

[7] B.Khouw, J.E.Morgan, H.I.Schiff *J.Chem.Phys.* **50** 66 (1969)

Chapter 4

REACTIONS IN THE HYDROGEN–OXYGEN SYSTEM

4.1 INTRODUCTION

The reaction of H atoms with O_2 has long been recognized as important in the combustion of hydrogen or hydrocarbons [1]. Various workers have simulated the dynamics of the H+O_2 interaction, often on the well–defined Melius–Blint potential energy surface. Walch *et al.* [2] showed that the entrance barrier is negligible. Schechter *et al.* [3] demonstrated that the H inserts into the O–O bond at thermal collision energies. Miller [1] rejected any direct O–abstraction component to the reaction and asserted that reaction only proceeds via a long–lived complex. This HO_2 complex can dissociate to O+OH (net result H+$O_2 \longrightarrow$O+OH), or be sta-

bilized by collisions to the HO_2 radical ($H+O_2+M \longrightarrow HO_2+M$). The branching ratio between these channels depends sensitively on temperature and pressure, and is responsible for the second explosion limit in the H_2–O_2 system [4]. The dissociation channel of the $H+O_2$ reaction has an appreciable activation energy [5], compatible with an association–dissociation reaction. The rate constant for the association channel has a weak negative temperature dependence near ambient temperature [5], and this dependence would be expected to continue to higher temperatures.

Dougherty *et al.* [4] have studied the H_2–O_2 system to identify the reactions that most affect the behaviour. Their analyses (Green's function sensitivity and reaction flux) showed the dominance of the two reactions $H+O_2$ at the second explosion limit. The reaction $H+O_2 \longrightarrow O+OH$ causes chain branching since O and OH are both reactive species, whereas $H+O_2+M \longrightarrow HO_2+M$ converts reactive H into HO_2 (relatively unreactive at these temperatures), and thus causes chain termination.

At high temperature and low pressure, the branching channel dominates: chain carriers H, O, and OH accumulate and overall reaction is fast. Although heat is released, the ensuing explosion has mainly chain–branching rather than thermal character. At low temperature and high pressure, chain–carriers are converted into unreactive HO_2 and reaction is slow.

Using [M] to denote third–body concentration, the explosion can be crudely described by the branching ratio

$$R_b = \frac{k(\mathrm{H} + \mathrm{O_2})}{k(\mathrm{H} + \mathrm{O_2} + \mathrm{M})[\mathrm{M}]}$$

$R_b = 0.5$ represents the break–even point for radical generation; when one H reacts with O_2 to yield O+OH, subsequent reaction with H_2 produces three H. The other two H react with O_2 to yield HO_2 and are lost to further reaction. Thus R_b =0.5 represents conservation of the number of chain–carriers. When R_b <0.5, termination dominates chain–branching and reaction is slow. When R_b >0.5, branching dominates and causes explosion.

Previous work measured the H+O_2+M channel at low temperatures [5], or the H+O_2 channel at very high temperatures [6]. The position of the explosion limits has also been determined. There have been few direct measurements of either channel in the temperature range 700–900 K, where the balance between the channels is important [8]. Table 1 demonstrates the significant discrepancies found between several estimates of k(H+O_2+M) at 800 K.

The work described in this Chapter aimed to study the H_2–O_2 system close to the second explosion limit using time–resolved, laser–initiated techniques. This approach was chosen to examine a potentially sensitive direct method of investigating the interaction of the branching and terminating channels in the reaction of H with O_2.

4.1.1 Outline of Chapter

1. Initially, a simple kinetic scheme is adopted to determine the kinetics in a mixture of H_2 and O_2 following laser generation of low concentrations of O. The scheme predicts that the dependence of atom concentrations on time should be bi–exponential. The long–time behaviour is very sensitive to the interaction between k(H+O_2) and k(H+O_2+M) (Figure 4.1).

Source	M, k	T/K	Technique(s)
[5]	N_2 2.2	200–400	review (1986)
[6]	Ar 7.1	746–987	flash photolysis–shock tube, atomic resonance absorption spectroscopy (1989)
[7]	He 8.0, N_2 15.2, H_2O 71	298–639	discharge flow, titration (1989)
[8]	Ar 2.1, N_2 6.3, H_2O 53	231–512	flow, gas chromatography and mass–spectrometry (1983)
[9]	Ar 6.1, N_2 9.1	964–1176	induction time (1977)
[10]	Ar 9.0	300–2000	review (1990)

Table 1: k(H+O_2+M) / 10^{-33} cm^6 molecule^{-2} s^{-1} at 800 K. Some measurements have been extrapolated.

2. Measurements are described on the H_2–O_2 system at 100–243 Torr, 800–850 K. Photolysis of O_2 yielded O atoms to start the reaction cleanly. Subsequent reactions generated H, whose time evolution was probed by resonance fluorescence over periods of 0.16–3.2 s. To aid analysis, separate experiments on N_2O or N_2O–H_2 determined effective rate constants for H or O escape from the viewing zone, by diffusion and pump–out.

3. The simple scheme is shown to be unsatisfactory, and a fuller scheme is thus needed.

4. A fuller mechanism is derived, and used to analyse the data, in conjunction with sensitivity and flux analyses.

4.2 PREDICTIONS OF SIMPLE SCHEME

The scheme was:

O_2	$\xrightarrow{h\nu}$O+O	$(t = 0)$
O+H_2	$\longrightarrow$OH+H	k_1
H+O_2	$\longrightarrow$OH+O	k_2
H+O_2+N_2	$\longrightarrow$$HO_2$+$N_2$	k_3
H	$\longrightarrow$escape	k_4
OH+H_2	$\longrightarrow$H+H_2O	k_5
O	$\longrightarrow$escape	k_{30}

Figure 4.1: $[\mathrm{H}]_t$ for simple analytic scheme. $k_1' = 1468$, $k_2' = 116$, $k_4 = 39$, $k_{30} = 25$ s^{-1}. $k_3' = k$ $(\mathrm{H}{+}\mathrm{O}_2{+}\mathrm{M})[\mathrm{O}_2][\mathrm{M}]/\mathrm{s}^{-1}$.

where k_{30} is numbered in accordance with the fuller scheme of § 4.5. H and O were lost from the viewing zone by escape (diffusion and pump–out, Chapter 3). At experimental temperatures, $k_5 > 10k_1$ (Table 2), so OH was rapidly converted to H. Omitting H_2O, reactions 1 and 5 merge to:

$$O + 2H_2 \longrightarrow 2H \qquad k_1$$

To simplify the kinetics, the ratio $[H_2] : [O_2]$ was chosen to ensure that $k_5[H_2] \approx 120k_2[O_2]$ (Table 2), so OH from reaction 2 was rapidly converted to H. Since enough H_2 was present, the precise values of k_5 and $[H_2]$ were not significant. Omitting H_2O, reactions 2 and 5 become:

$$H + O_2 + H_2 \longrightarrow H + O \qquad k_2$$

At this stage, HO_2 was assumed inert and its reactions were neglected. The scheme then reduces to:

O_2	$\xrightarrow{h\nu}2O$	$(t = 0)$
$O+H_2$	$\longrightarrow 2H$	k_1
$H+O_2+H_2$	$\longrightarrow H+O$	k_2
$H+O_2+N_2$	$\longrightarrow HO_2+N_2$	k_3
H	$\longrightarrow$escape	k_4
O	$\longrightarrow$escape	k_{30}

Using k_1', k_2', k_3' to denote the pseudo–first–order rate constants $k_1[H_2]$, $k_2[O_2]$, $k_3[O_2][N_2]$, the differential equations describing the time–dependence of [H] and [O] were formulated:

Number	Reaction	k	k'/s^{-1}	Source
1	$O+H_2 \longrightarrow OH+H$	1.13×10^{-13}	1469	10
2	$H+O_2 \longrightarrow OH+O$	1.16×10^{-14}	116	10
$3N_2$	$H+O_2+N_2 \longrightarrow HO_2+N_2$	2.15×10^{-32}	495	5
$3H_2$	$H+O_2+H_2 \longrightarrow HO_2+H_2$	6.44×10^{-32}	8.4	5
$3O_2$	$H+2O_2 \longrightarrow HO_2+O_2$	2.15×10^{-32}	2.2	5
$3H_2O$	$H+O_2+H_2O \longrightarrow HO_2+H_2O$	1.07×10^{-31}	3.4×10^{-3}	5
4	$H \longrightarrow$ escape	38.5	38.5	this work
5	$OH+H_2 \longrightarrow H+H_2O$	1.05×10^{-12}	13650	10
6	$HO_2+H_2 \longrightarrow H+H_2O_2$	6.35×10^{-18}	0.083	5
7A	$H+HO_2 \longrightarrow H_2+O_2$	3.01×10^{-11}	39	5
7B	$H+HO_2 \longrightarrow 2OH$	1.64×10^{-10}	213	5
7C	$H+HO_2 \longrightarrow O+H_2O$	3.00×10^{-12}	3.9	5
$8N_2$	$H+OH+N_2 \longrightarrow H_2O+N_2$	8.96×10^{-32}	1.4×10^{-5}	5
$8H_2$	$H+OH+H_2 \longrightarrow H_2O+H_2$	2.69×10^{-31}	2.4×10^{-7}	5
$8O_2$	$H+OH+O_2 \longrightarrow H_2O+O_2$	8.96×10^{-32}	6.3×10^{-8}	5
$8H_2O$	$H+OH+H_2O \longrightarrow 2H_2O$	5.65×10^{-32}	1.3×10^{-11}	5
9	$O+OH \longrightarrow H+O_2$	2.80×10^{-11}	2.0×10^{-3}	L
10	$2OH \longrightarrow O+H_2O$	4.97×10^{-12}	3.5×10^{-4}	10
11	$OH+HO_2 \longrightarrow H_2O+O_2$	6.50×10^{-11}	85	10
12	$O+HO_2 \longrightarrow OH+O_2$	5.30×10^{-11}	67	5
13	$2HO_2 \longrightarrow O_2+H_2O_2$	8.85×10^{-13}	0.62	10
14	$H+OH \longrightarrow O+H_2$	1.12×10^{-13}	7.9×10^{-6}	5

Table 2: Typical experimental conditions. "L" denotes a fit to literature values. Units of k are cm, molecule, s.

Number	Reaction	k	k'/s^{-1}	Source
15	$OH+O_2 \longrightarrow O+HO_2$	4.15×10^{-25}	4.2×10^{-9}	5
16	$H+H_2O \longrightarrow OH+H_2$	4.59×10^{-16}	1.5×10^{-3}	10
17A	$H+H_2O_2 \longrightarrow HO_2+H_2$	2.83×10^{-13}	0.048	10
17B	$H+H_2O_2 \longrightarrow OH+H_2O$	1.87×10^{-12}	0.32	10
18	$O+H_2O_2 \longrightarrow OH+HO_2$	1.00×10^{-13}	0.017	10
19	$OH+H_2O_2 \longrightarrow H_2O+HO_2$	3.36×10^{-12}	0.57	10
$20N_2$	$H_2O_2+N_2 \longrightarrow 2OH+N_2$	1.12×10^{-19}	0.26	5
$20H_2$	$H_2O_2+H_2 \longrightarrow 2OH+H_2$	3.37×10^{-19}	4.4×10^{-3}	5
$20O_2$	$H_2O_2+O_2 \longrightarrow 2OH+O_2$	1.12×10^{-19}	1.1×10^{-3}	5
$20H_2O$	$H_2O_2+H_2O \longrightarrow 2OH+H_2O$	4.17×10^{-19}	1.3×10^{-6}	5
$21N_2$	$2H+N_2 \longrightarrow H_2+N_2$	2.42×10^{-33}	7.4×10^{-5}	5
$21H_2$	$2H+H_2 \longrightarrow 2H_2$	1.21×10^{-32}	2.0×10^{-7}	5
$21O_2$	$2H+O_2 \longrightarrow H_2+O_2$	2.42×10^{-33}	3.1×10^{-8}	5
$21H_2O$	$2H+H_2O \longrightarrow H_2+H_2O$	3.39×10^{-32}	1.4×10^{-10}	5
$22N_2$	$O+H+N_2 \longrightarrow OH+N_2$	1.58×10^{-32}	4.7×10^{-5}	5
$22H_2$	$O+H+H_2 \longrightarrow OH+H_2$	1.58×10^{-32}	2.6×10^{-7}	5
$22O_2$	$O+H+O_2 \longrightarrow OH+O_2$	1.58×10^{-32}	2.1×10^{-7}	5
$22H_2O$	$O+H+H_2O \longrightarrow OH+H_2O$	1.26×10^{-31}	5.2×10^{-10}	5
$23N_2$	$2O+N_2 \longrightarrow O_2+N_2$	5.92×10^{-34}	1.4×10^{-7}	5
$23H_2$	$2O+H_2 \longrightarrow O_2+H_2$	1.78×10^{-34}	2.3×10^{-10}	5
$23O_2$	$2O+O_2 \longrightarrow 2O_2$	9.28×10^{-33}	9.3×10^{-9}	5
$23H_2O$	$2O+H_2O \longrightarrow O_2+H_2O$	5.92×10^{-34}	1.9×10^{-13}	5
$24N_2$	$2OH+N_2 \longrightarrow H_2O_2+N_2$	2.85×10^{-32}	4.6×10^{-6}	5

Table 2 continued.

Number	Reaction	k	k'/s^{-1}	Source
$24H_2$	$2OH+H_2 \longrightarrow H_2O_2+H_2$	8.55×10^{-32}	7.8×10^{-8}	5
$24O_2$	$2OH+O_2 \longrightarrow H_2O_2+O_2$	2.85×10^{-32}	2.0×10^{-8}	5
$24H_2O$	$2OH+H_2O \longrightarrow H_2O_2+H_2O$	1.06×10^{-31}	2.4×10^{-11}	5
$25N_2$	$H_2O+N_2 \longrightarrow H+OH+N_2$	8.24×10^{-37}	1.9×10^{-18}	5
$25H_2$	$H_2O+H_2 \longrightarrow H+OH+H_2$	2.47×10^{-36}	3.2×10^{-20}	5
$25O_2$	$H_2O+O_2 \longrightarrow H+OH+O_2$	8.24×10^{-37}	8.2×10^{-21}	5
$25H_2O$	$2H_2O \longrightarrow H+OH+H_2O$	5.19×10^{-36}	1.7×10^{-23}	5
$26N_2$	$HO_2+N_2 \longrightarrow H+O_2+N_2$	1.08×10^{-21}	2.5×10^{-3}	5
$26H_2$	$HO_2+H_2 \longrightarrow H+O_2+H_2$	3.25×10^{-21}	4.2×10^{-5}	5
$26O_2$	$HO_2+O_2 \longrightarrow H+2O_2$	1.08×10^{-21}	1.1×10^{-5}	5
$26H_2O$	$HO_2+H_2O \longrightarrow H+O_2+H_2O$	5.41×10^{-21}	1.7×10^{-8}	5
$27N_2$	$O+O_2+N_2 \longrightarrow O_3+N_2$	4.07×10^{-35}	0.94	k_{28}, K_c
$27H_2$	$O+O_2+H_2 \longrightarrow O_3+H_2$	1.22×10^{-34}	0.016	k_{28}, K_c
$27O_2$	$O+2O_2 \longrightarrow O_3+O_2$	4.59×10^{-35}	4.6×10^{-3}	k_{28}, K_c
$27H_2O$	$O+O_2+H_2O \longrightarrow O_3+H_2O$	2.04×10^{-34}	6.5×10^{-6}	k_{28}, K_c
$28N_2$	$O_3+N_2 \longrightarrow O+O_2+N_2$	6.19×10^{-16}	1424	5
$28H_2$	$O_3+H_2 \longrightarrow O+O_2+H_2$	1.86×10^{-15}	24	5
$28O_2$	$O_3+O_2 \longrightarrow O+2O_2$	6.99×10^{-16}	7.0	5
$28H_2O$	$O_3+H_2O \longrightarrow O+O_2+H_2O$	3.10×10^{-15}	9.9×10^{-3}	5
29	$O+H_2O \longrightarrow 2OH$	1.39×10^{-15}	4.4×10^{-3}	5
30	$O \longrightarrow$ escape	25	25	this work

Table 2 continued.

$$\begin{aligned}\frac{d}{dt}[\mathrm{H}] &= -k'_H[\mathrm{H}] + 2k'_1[\mathrm{O}] \\ \frac{d}{dt}[\mathrm{O}] &= k'_2[\mathrm{H}] - k'_O[\mathrm{O}]\end{aligned}$$

where k'_O is the rate constant for O atom loss ($k_{30}+k'_1$), and k'_H is the rate constant for H atom loss ($k_4 + k'_3$). These equations are solved (Appendix B) to yield:

$$[\mathrm{H}]_t = A_- \exp(\lambda_- t) + A_+ \exp(\lambda_+ t) \tag{4.1}$$

where A_+ and A_- are functions of $[\mathrm{O}]_0$, $[\mathrm{H}]_0$, k'_1, k'_2, k'_H, k'_O, and:

$$2\lambda_\pm = -k'_{loss} \pm \sqrt{(k'_{loss})^2 + 4(2k'_1k'_2 - k'_Ok'_H)} \tag{4.2}$$

where k'_{loss} is the total rate constant for atom loss ($k'_O + k'_H$). Typical values of k'_1, k'_2, k'_3, k_4, and k_{30} are given in Table 2. [O] decays with the same time constants but different pre–exponential factors.

$|\lambda_-|$ is larger than $|\lambda_+|$. The photolysis product O equilibrates with H on a short timescale described by λ_-, which is dominated by k'_{loss}, and hence by k'_1. On the much longer timescale described by λ_+, the chain–carriers (O and H) are then lost by conversion into less reactive HO_2 and by physical escape from the viewing zone, and replaced by the branching reaction (2). Typically, $|\lambda_-|$ was >1000 s^{-1}, and $|\lambda_+|$ ranged from 1–10 s^{-1}.

The long–time behaviour of the system is completely described in this model by λ_+, in which large pseudo–first–order chemical rate constants (k'_2, k'_3, and k_4) cancel to within 1%. Simulations (Figure 4.1) demonstrate that the long–term behaviour is very sensitive to small changes in k'_2 and k'_3, and hence is potentially

a good source of information about k_2 and k_3. If $\lambda_+ < 0$, the H atom signal decays exponentially, following a rapid rise described by λ_-. If $\lambda_+ > 0$, the H signal increases without limit and the system explodes. $\lambda_+ = 0$ is the explosion limit. λ_+ is very sensitive to small changes in experimental $[O_2]$, pressure, and temperature. For the long–time decay time constant, $-\lambda_+$, successive approximations to Equation 4.2 may be made:

$[H_2]$ is high and O escapes slowly, so $k'_1 > 50k_{30}$ (Table 2). Thus $k'_O \simeq k'_1$:

$$\begin{aligned} 2\lambda_+ &= -k'_{loss} + \sqrt{(k'_{loss})^2 + 4k'_1(2k'_2 - k'_H)} \\ \Longrightarrow \frac{2\lambda_+}{k'_{loss}} &= \sqrt{1 + [4k'_1(2k'_2 - k'_H)]/(k'_{loss})^2} - 1 \end{aligned}$$

Near the explosion limit, the term under the square root is $\simeq 1$, and a binomial expansion yields:

$$\lambda_+ = \frac{k'_1(2k'_2 - k'_H)}{k'_{loss}} \tag{4.3}$$

With sufficient H_2, k'_{loss} is dominated by k'_1, and

$$\begin{aligned} \lambda_+ &\simeq 2k'_2 - k'_H \\ &= 2k_2[O_2] - k_3[O_2][M] - k_4 \end{aligned}$$

With enough H_2, the decay time constant, $-\lambda_+$, is thus independent of $[H_2]$. The escape of H atoms from the viewing zone, k_4, leads to a dependence on $[O_2]$. A system with $2k_2[O_2] > k_3[O_2][M]$ can be stabilized by rapid H escape; as more

O_2 is added, escape becomes less important, and this stabilization becomes less effective. As the pressure rises, more HO_2 complexes are stabilized (k_3' increases). This dominates the falling escape rate constant (k_4), the system becomes less explosive, and a faster long–time decay is observed at higher pressures.

4.3 EXPERIMENTAL

Further details of apparatus, data collection, and analysis are supplied in Chapter 2. Reactants were diluted with He or N_2 to define the third–body species and to minimize temperature changes. H_2, O_2, and diluent were flowed through the heated stainless steel reaction cell. The conditions covered the ranges: pressure = 100–243 Torr, temperature = 800–850 K, $[H_2]$ = (0.9–1.6) $\times 10^{16}$ molecule cm^{-3}, $[O_2]$ = (3.5–11) $\times 10^{15}$ molecule cm^{-3}.

At high temperature, vibrationally excited ground state $O_2(\tilde{X}^3\Sigma_g^-)$ is photolysed at 193 nm to yield $O(^3P)$. At 800 K, Keiffer [11] found that $[O]_0 = 10^{-4}[O_2]$ for a laser energy of 110 mJ. In this experiment, the laser energy was 80 mJ, incident on the same area, so $[O]_0$ may be estimated at 5×10^{11} cm^{-3}. Production of electronically excited O is energetically impossible [12]. Since chain reactions occur, use of N_2O as an extra precursor produced so much O that the atom fluorescence signal saturated and distorted the decay traces; all experiments described here were performed with O_2 as the sole precursor.

H was detected by resonance fluorescence at 121.6 nm. Experimental $[H_2]$, and $[N_2]$ below 4×10^{18} molecule cm^{-3}, did not weaken the H fluorescence signal, since N_2 and the reactants neither quench $H(^2P)$ nor absorb at 121.6 nm. In contrast, experimental $[O_2]$ severely reduced the O fluorescence signal. Rao

et al. [13] have shown that $O_2(v = 1)$ absorbs 121.6 nm radiation strongly. At higher temperatures, $O_2(v = 1)$ will be more populated, and O_2 will absorb more strongly. To ensure good signal : noise ratio, all experiments had to be performed by detecting H. Figure 4.2 shows a typical decay.

Figure 4.2: Experimental decay trace. File is BANG350.

Temperature control proved crucial: a rise of 1 K could reduce the time constant for H loss from 10 s^{-1} to 1 s^{-1}, as the interaction between branching and termination is very temperature–sensitive. Using pure diluent at the same temperature and pressure as for kinetic experiments, the proportional, integral, and derivative settings on the temperature controller were adjusted to reduce oscillations to about 0.3 K. Pressure and temperature rises due to reaction were not observed.

Experiments near the explosion limit had to be performed at very slow laser firing rates (down to a frequency of 0.08 Hz); the laser firing sometimes had to be stopped until the H signal ceased, indicating the end of reaction and the final evacuation of reacted gases. Separate traces to cancel the distortion caused by laser light were not needed. The good H signal enabled use of low amplifier loads, so the fluorescence p.m. recovered rapidly. On these long timescales, the distortion had died away before the part of the trace to be analysed. As a check, laser spike traces were sometimes recorded and subtracted, but this correction made no difference to the results.

Gas purities are given below, with typical levels of the main contaminants taken from the manufacturer's analysis. O_2 (BOC zero grade, 0.3% N_2, Ar) and N_2 (BOC CP grade, 1 ppm each of O_2, CO_2, CO, H_2, H_2O, and hydrocarbons) were used as received. H_2 (BOC CP grade, 5 ppm N_2) and He (BOC CP grade, 2 ppm each Ne, N_2) were passed through Oxisorb filters (Messer–Griesheim) to reduce O_2 to 0.2 ppm.

4.4 DATA FITTING

4.4.1 Simple scheme

Escape by diffusion and flow

k_4 and k_{30}, the rate constants for atom escape from the viewing zone, were determined in separate experiments. N_2O was used as the precursor; 193 nm photolysis produced $O(^1D)$ cleanly (Chapter 2).

To determine k_{30}, N_2O was photolysed in N_2: $O(^1D)$ was quenched within a few μs by N_2 to $O(^3P)$, whose decay was fitted to a single exponential of rate constant k_{30}.

For k_4, H_2 was added to the N_2O–diluent mixture to convert $O(^1D)$ to OH+H: at these temperatures, the conversion of OH to H by reaction (5) was complete on a much faster timescale than that for H escape. H decays were fitted to a single exponential of rate constant k_4.

In N_2, k_4 is less than in He: the pure diffusion part of k_4 is reduced, to the extent predicted by kinetic theory, because N_2 has a greater mass and collision cross–section than He. It was thus decided to reduce the contribution of atom escape to the H decay by switching from He to N_2 (which is also a more relevant bath gas for combustion). N_2 is a much faster quencher of $O(^1D)$ to $O(^3P)$ than is He, so appreciable amounts of $O(^3P)$ were formed in N_2 but not in He. Even at $[H_2]$ large enough to quench the H fluorescence signal, the slow reaction of $O(^3P)$ to OH (and thence to H) formed H with a time constant only about five times faster than that for H escape. An exponential fit to the late part of the H trace was used to determine k_4.

Fits to bi–exponential models

It was hoped to fit observed H fluorescence decay traces to Equation 4.1, and thus to recover good rate constants. Fits were attempted to the pre–exponential factors and time constants using a bi–exponential model. The Marquardt algorithm for non–linear least squares fitting (Chapter 2) was used in this and all subsequent methods of fitting. The parameter derivatives

$$\frac{\partial y_{fit}}{\partial a_j}$$

were evaluated either analytically or numerically. Initial fits were performed to individual decay traces. Fits were attempted from a range of starting values for both the pre–exponential factors and the time constants.

Trials on simulated data showed that, for good parameter recovery, the time constants should differ by at least a factor of five. Also, adequate data should be available both for short timescales (dominated by the fast–time constant) and for long timescales (dominated by the slow–time constant). Experimental conditions were usually adjusted such that the long–time decay was in the range 0.1–1 s, i.e. such that the atom removal and branching rates were closely balanced. Thus, the time constants differed by such a large factor (at least 100) that a sample interval appropriate to the long–time behaviour missed the short–time information. Convergence from only a small range of starting values, and visual examination of residuals, confirmed that meaningful bi–exponential fits could not be made to single traces.

An attempt was made to combine the limited information available in different traces to obtain more chemical information. Knutson *et al.* [14] have shown

such procedures to be useful in analysing multi–exponential decays. Some parameters were floated locally (over just one trace) and others globally (constrained to be the same over all traces). However, fits only converged slowly, and the approach was abandoned.

Some traces differed merely by being gathered consecutively under identical conditions: combining up to five such traces increased the information available, but fit convergence was slow and short–time decay information was still lacking. The growth of [H] occurred on a timescale too fast to allow good data to be collected, so traces gathered on different timescales could not usefully be fitted together. Keiffer [15] suggested finding the long–time parameters (A_+, λ_+) from long–timescale data and fixing them in a bi–exponential fit to data gathered on an intermediate timescale. This process was considered too laborious, and was not used.

Fits to single exponential models

The main aim of the analysis is to study the interaction between reactions 2 and 3. The short–time behaviour is dominated by k_1 and the long–time behaviour by the balance between k_2, k_3, and k_4. It was therefore decided to observe only the long–time behaviour, which could be treated as a single exponential decay because of the large difference in magnitude of λ_+ and λ_-. Tests on simulated data with added noise showed that parameter recovery was optimized by collecting data over 2–3 decay times.

Data were gathered near the explosion limit, where the long–time decay constant was 1–10 s^{-1}. The initial plan was to limit the extent of side–reactions

by fixing laser energy and $[O_2]$: this would have fixed $[O]_0$ and thus the size of the radical pool. The pressure could then have been varied to pass through the explosion limit. However, the pressure (adjusted by a needle valve) would have settled more slowly than an individual gas flow, so it was decided to fix pressure and vary $[O_2]$. As $[O_2]$ was increased, the system approached the explosion limit, the long–time decay constant approached zero, and longer recording timescales were needed. Data were usually gathered for 0.16, 0.32, or 0.8 s after the laser fired: the longest timescale used was 3.2 s.

For each trace, the decay time constant $-\lambda_+$ was obtained, and was then processed to yield the rate constants k_2 and k_3, by using Equation 4.3. The effective third–body concentration [M] was taken as [diluent], since all other species were present in small amounts, and H_2 is a poor third–body for stabilizing HO_2 complexes.

It was attempted to derive both k_2 and k_3 from experimental decay time constants $-\lambda_+$. From Equation 4.3:

$$-\lambda_+ k'_{loss} = k'_1[O_2](k_3[M] - 2k_2) + k'_1 k_4$$

For each experiment, values of k'_1, k_4, and k'_{loss} were calculated. At fixed pressure a plot of $-\lambda_+ k'_{loss}$ against $[O_2]$ had a gradient of $k'_1(k_3[M] - 2k_2)$. The dependence of this gradient on [M] was found to give absurd values of k_2, k_3.

At these temperatures (800–850 K), k_2 is rather better determined than k_3. It was decided to substitute the CEC [10] value for k_2:

$$k_2(T) = 3.3 \times 10^{-10} \exp\left(\frac{-8460\ K}{T}\right)$$

in units of cm^3 $molecule^{-1}$ s^{-1} into another rearrangement of Equation 4.3:

$$k'_3 = 2k'_2 - k_4 - \frac{\lambda_+ k'_{loss}}{k'_1}$$

to yield values of k_3 which were only reasonable for some data sets. Thus it was not possible to extract reliable rate constants for reactions (2) and (3) by assuming this analytically soluble mechanism.

For this mechanism, error estimates are hard to propagate. A fuller analysis (see below) showed a positive covariance of k_2 and k_3 (data could be fitted by k_2 and k_3 both low or both high), which caused problems in this analysis as well.

The simple scheme also predicted decay rate constants very different from those found experimentally. Using typical concentrations and literature rate constants (Table 2), H should have decayed with a time constant, $|\lambda_+|$, of about 260 s^{-1}; the observed value was 1–10 s^{-1}, clearly indicating that this mechanism is inadequate. The problem may derive from reactions of HO_2, which have so far been neglected, on the long timescales investigated. Thus, it was decided to investigate a fuller mechanism. Inclusion of HO_2 reactions would yield a cubic in λ (not analytically soluble in general). If the cubic were solved numerically, the 3 roots would describe a tri–exponential time–dependence with six parameters. All six parameters could not be fitted to data.

4.5 FULL MECHANISM

4.5.1 Input data

All reactions among the set of species {H, O, H_2, OH, O_2, H_2O, HO_2, O_3, and H_2O_2, with third bodies M = N_2, H_2, O_2, and H_2O} were considered. Rate constants were drawn from the most recent evaluations, or sometimes estimated using thermodynamics and the literature value for the forward rate constant. Some were discarded as being too slow at experimental pressures and temperatures, or as having no net effect ($H+H_2 \longrightarrow H_2+H$). The rest are listed in Table 2, with the numbers used to identify the reaction and the value of the rate constant at 825 K. Where necessary, third body efficiency ratios were averaged from other reactions. In other cases they were estimated from matching of total masses and vibrational frequencies between the adduct and the third body.

Pseudo–first–order rate constants are presented for the usual conditions of an experiment: T = 825 K, $[N_2] = 2.3 \times 10^{18}$ molecule cm^{-3}, $[H_2] = 1.3 \times 10^{16}$ molecule cm^{-3}, $[O_2] = 10^{16}$ molecule cm^{-3} (calculated from gas flows, pressure, and temperature) and $[H] = 1.3 \times 10^9$ cm^{-3}, $[O] = 1.0 \times 10^8$ cm^{-3}, $[OH] = 7.0 \times 10^7$ molecule cm^{-3}, $[H_2O] = 3.2 \times 10^{12}$ molecule cm^{-3}, $[HO_2] = 1.3 \times 10^{12}$ molecule cm^{-3}, $[H_2O_2] = 1.7 \times 10^{11}$ molecule cm^{-3}. The latter concentrations are taken from simulations at 0.1 s with $[O]_0 = 5 \times 10^{11}$ cm^{-3} (§ 4.3). Pseudo–first–order rate constants refer to the removal of the first–named species by all others: thus in reaction 11, OH is removed by $[HO_2]$ with a time constant of 85 s^{-1}.

The mechanism was fed to the numerical fitting and simulation package FACSIMILE [16], which has been fine–tuned by the authors to make it efficient,

and has many user–friendly data handling and fitting routines.

To check that FACSIMILE simulation worked correctly, the analytic mechanism described above was used to generate [H]–time decay traces without added noise: the numerical approximation to the local time constant for H decay, $-\delta$ ln [H]$/\delta t$, was evaluated at several times, and agreed with the analytic $|\lambda_+|$ derived above.

To fit parameters to an observed data trace, FACSIMILE floated parameters to generate several simulated data traces. For each simulation, it calculated χ^2, the sum of squares of residuals, where the residual for time point j was defined as R_j = constant $\times$ (observed data point $j-$ calculated point $j/$ scale factor).

Calculated [H] were divided by the scale factor to relate them to the observed data (H fluorescence intensity). In an iterative process, the parameters were varied to minimize χ^2. The best–fit parameter values were printed, with an estimate of their errors taken from the sensitivity of χ^2 to small changes in the parameter values. The covariance between fitted parameters was also printed.

To check that FACSIMILE fitting worked correctly, the full mechanism was used to generate $[H]_t$ traces without added noise in the same file format as the experimental data, and fitting correctly recovered the parameter values used.

The full mechanism was also used to create concentration–time curves for species other than H. Figures 4.3 and 4.4 show concentration–time information for the typical conditions described above. On short timescales, O and OH decay together as they are converted to H. On longer timescales, H, O, and OH decay together as HO_2 and H_2O are formed. [H_2O_2] and [O_3] are always low, and [H_2] and [O_2] are unchanged (low extent of conversion).

Figure 4.3: FACSIMILE concentrations, typical conditions. Y axis = lg (concentration/molecule cm^{-3}).

Figure 4.4: FACSIMILE concentrations, typical conditions. Y axis = lg (concentration/molecule cm^{-3}).

Technique

Each experimental data file was transferred from the experimental microcomputer to the VAX; alternate points were discarded to reduce storage requirements, and pairs of (time, H fluorescence intensity) were written to an intermediate data file in compact format. The zero of time was taken as the experimental data file point at which the laser fired; since the digitizer trigger delay was fixed, the zero of time occurred at the same point in each experimental data file.

The rate constants k_2 for $H+O_2 \longrightarrow O+OH$, and k_{3N_2} for $H+O_2+N_2 \longrightarrow HO_2+N_2$, were required so these were floated. The rate constants for reaction 3 with other third bodies (k_{3O_2}, k_{3H_2}, k_{3H_2O}) were kept at constant ratios [5] to k_{3N_2} as the latter was floated. A voltage proportional to relative fluorescence intensity was actually measured: the apparatus sensitivity was defined as $Q = [H] : (H \text{ fluorescence intensity})$. Its units were concentration/digitizer digit, and $Q \approx 4{\times}10^7$ cm^{-3} digit^{-1}, after 250 shots had been summed. Q was floated, since it might have varied between experiments as the resonance lamp characteristics changed. The $[O]_0$ produced in the laser pulse was not known, yet might determine the extent of radical–radical reaction at long times; thus $[O]_0$ was also floated. The $[H]_t$ simulated by FACSIMILE at each stage was divided by the current best estimate of Q to match the intensity–time experimental data. Parameter recovery tests showed that fixing Q unduly constrained the fit and caused incorrect recovery of fitted rate constants.

Each parameter was given two starting values, differing by a factor of 10: $Q = 10^7$ or 10^8 cm^{-3} digit^{-1}, $[O]_0 = 10^{11}$ or 10^{12} cm^{-3}, $k_2 = 10^{-15}$ or 10^{-14} cm^3 molecule^{-1} s^{-1}, $k_{3N_2} = 10^{-33}$ or 10^{-32} cm^6 molecule^{-2} s^{-1}. Each of the 16 possible

combinations was used as a set of starting values: the 16 fits took 25 minutes CPU time on a VAX 8800.

Some attempted fits failed due to arithmetic overflow, non–convergence of some parameters, or non–convergence inside FACSIMILE's limit of 20 simulation runs per parameter fitted. Multiple minima in the χ^2 surface were rare. For each data file, the results of all converged fits were treated as independent estimates of the best–fit parameter values. They usually agreed to within 30%, and were combined to yield the best estimate of the best–fit values for that file. Four data files were gathered under each set of conditions: the results are presented in Appendix C.

Quality of Fit

FACSIMILE estimated the covariance between all pairs of fitted parameters. A given fluorescence signal strength could arise either from a low concentration and a sensitive apparatus (low $[O]_0$ and Q), or from a high concentration and an insensitive apparatus (high $[O]_0$ and Q). The observed atom loss rate could result from slow chain branching and termination (k_2 and k_{3N_2} low) or fast chain branching and termination (k_2 and k_{3N_2} high). So Q and $[O]_0$ had a positive covariance of 0.4 to 0.9, and k_2 and k_{3N_2} had a positive covariance of 0.3 to 0.8. Other covariances varied unsystematically.

For some fits, plots were obtained of the fit to the data (Figure 4.5), and of the residuals, $\propto$ (data $-$ fit), Figure 4.6. The residual–time plot was randomly scattered about zero, confirming that the mechanism was valid for all times covered by the experiment. As the H atoms were consumed, the signal decreased,

and hence the noise on the residuals decreased. The fit–data–time plot confirmed that the fit followed the data well.

Figure 4.5: Fit and data from FACSIMILE. File was BANG350.

Figure 4.6: Residuals from FACSIMILE fit. File was BANG350.

Effect of varying input parameters

$[O]_0$ is unknown, so H decays were simulated with $[O]_0$ set to different values (Figure 4.7). At low $[O]_0$ and low radical concentrations, radical–radical reactions are unimportant and the form of the H decay trace is independent of $[O]_0$, although the magnitude of [H] depends on $[O]_0$. Values of $[O]_0$ in accordance with estimates of O_2 photolysis (§ 4.3) are required in order to rationalize the long–time H atom decay. As $[O]_0$ is increased due to increasing the laser energy, radical–radical reactions replenish H at long times: H decays more slowly as reactions such as $H+HO_2 \longrightarrow 2OH$ turn the unreactive HO_2 radicals into OH, which is rapidly converted to H by reaction 5.

Input rate constants are uncertain (Table 3) and may affect fitted values. Fits were performed with some rate constants held at different values. § 4.6 presents the results of a sensitivity analysis. Table 4 shows that fitted values of k_2 and k_{3N_2} are moderately sensitive to the values used for these rate constants, but insensitive to errors in temperature measurement. k_{7c} was assumed to be uncertain by ±35%, and all other rate constants by ±10%. The uncertainty in these input rate constants was estimated to cause total uncertainties in k_2 of $\pm 0.40 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, and in k_3 of $\pm 0.60 \times 10^{-32}$ cm^6 molecule^{-2} s^{-1}. Figure 4.8 shows that different values for $k(H+HO_2)$ have little effect on the form of the H decay, even though these input rate constants do affect the recovered rate constants.

Figure 4.7: Effect of $[O]_0/cm^{-3}$ on $[H]_t$.

Figure 4.8: $[H]_t$. $[O]_0 = 10^{12}$ cm^{-3}. k_7 channels varied.

Number	Reaction	A	B/K	k	Error/%
4	H escape			63.8	10
6	$HO_2+H_2 \longrightarrow H+H_2O_2$	5×10^{-11}	13100	6.4×10^{-18}	10
7a	$H+HO_2 \longrightarrow H_2+O_2$	1.1×10^{-10}	1070	3.0×10^{-11}	10
7b	$H+HO_2 \longrightarrow 2OH$	2.8×10^{-10}	440	1.6×10^{-10}	10
7c	$H+HO_2 \longrightarrow O+H_2O$	3.0×10^{-12}	0	3.0×10^{-12}	35
30	O escape			31	10

Table 3: Uncertainty in input rate constants. The rate constant k equals $A\exp(-B/T)$, where A and k have cm, molecule, s units. Uncertainties are 2σ.

Some fits were also performed using a model for H atom escape (Chapter 3). FACSIMILE re–evaluated the effective pseudo–first–order rate constant

$$k_4 = \frac{-\delta \ln[\mathrm{H}]}{\delta t}$$

at each step in the integration, using escape parameters from fits to H decay traces under similar conditions.

4.6 SENSITIVITY ANALYSIS

4.6.1 Introduction

In many environments, computer models can be constructed by considering all possible reactions between all species. For N species, there will be $O(N^2)$ such reactions: in this model of the H_2–O_2 system, only 9 species are present, yet 62

Quantity	Old	4	6	30	7a	7b	7c	$20N_2$	T
Q	4.13±.12	+.04	−.11	−.26	−.38	−.56	−.37	−.08	+.00
$[O]_0$	7.12±.22	+.15	−.20	−.54	−.59	−.98	−.66	−.12	+.03
k_2	1.27±.02	+.21	−.01	−.05	+.28	−.20	−.04	+.01	+.01
k_{3N_2}	3.84±.11	+.08	+.04	−.27	+.39	−.23	−.27	+.04	+.04

Table 4: Dependence of fitted parameters on input parameters. Units are: $Q/10^7$ cm^{-3}, $[O]_0/10^{11}$ cm^{-3}, $k_2/10^{-14}$ cm^3 molecule^{-1} s^{-1}, and $k_{3N_2}/10^{-32}$ cm^6 molecule^{-2} s^{-1}. Input file was BANG350. For Old: all input values were unaltered, and a typical FACSIMILE estimate is given for the parameter uncertainty. For the rest, the specified rate constant was increased by 25% and the fits repeated; the fitted value changed by the amount shown. "T": the temperature was reduced by 4 K (the estimated error in measurement). FACSIMILE could not fit this data file with the simple scheme used above.

reactions were considered in the full kinetic model above. Such full models can use much computer time, yet any one observable (such as the concentration of one species, or the system temperature) will be determined by a mere handful of reactions.

Sensitivity analysis [17] aims to identify these crucial reactions, so that a simplified mechanism may be constructed. This simplified mechanism will use fewer computer resources (time and memory) to calculate the same system parameters. It can also indicate areas of weakness: a crucial rate constant may be poorly characterized, and thus worthy of further study. As mentioned above, Dougherty *et al.* [4] used sensitivity analysis to target the $H+O_2(+M)$ reactions, and provided some impetus for the study in this Chapter.

Methods used fall into two categories:

- Brute force method. A simulation run generates the parameter of interest (e.g. [H] at various times). One input term is then changed (e.g. $k(H+O_2)$ is doubled), and another simulation run is performed: the parameter of interest will change as a result. All other input terms may be changed successively. Hence sensitivity information is built up from many simulation runs. For example, the normalized sensitivity of a concentration to a reaction rate is defined as a function of time:

$$\frac{\partial \log [\text{species}]}{\partial \log k}$$

with all other input terms constant. k is changed at $t = 0$. The brute force method is conceptually simple, has been widely used [18], but requires much processing. Others have moved on to develop:

- Indirect methods. The kinetic solution (containing the parameter of interest) and all sensitivity information are calculated simultaneously. The computation is longer than a pure kinetic solution, but shorter than direct calculation of all sensitivity information by the brute force method. The Green's function method, as used by Dougherty *et al.*, is popular.

The Green's function method is coded in a package, CHEMSEN [19]. The system was assumed to have constant volume, pressure, and temperature (pressure and temperature rises from reaction will be negligible due to high dilution). An interpreter, CHEMKIN, takes a chemical mechanism (equations and thermal rate constants) and creates an intermediate file. CHEMSEN reads this file and a set of initial conditions (temperature, pressure, concentrations). For each output time, CHEMSEN yields the kinetic solution (species concentrations). Optionally, it also yields the normalized sensitivities to rate constants.

4.6.2 Input data

The full scheme, as used for FACSIMILE, was employed. CHEMSEN can calculate reverse rate constants, given forwards rate constants and its own thermodynamic database. Since reverse rate constants were usually available, this facility was only used for the unimportant reaction $O+O_2+M \longrightarrow O_3+M$ (27).

Escape processes were assumed to occur irreversibly with a pseudo–first–order rate constant. Equations of the form:

$$H \longrightarrow$$

do not balance chemically, and are unacceptable to CHEMKIN. Fake irreversible reactions were formulated:

$$H + N_2 \longrightarrow HN_2$$
$$O + N_2 \longrightarrow ON_2$$

and dummy data were provided for the imaginary species HN_2, ON_2. Each escape process was given a bimolecular rate constant; when CHEMSEN multiplied it by $[N_2]$, the correct pseudo–first–order rate constant was calculated.

4.6.3 Sensitivity results

Runs were performed for typical experimental conditions. The species concentrations as a function of time agreed well with FACSIMILE. Each output time took about 3.5 s CPU time on a VAX 8800: to generate the concentrations alone, FACSIMILE only needed about 0.3 s. Sensitivities of [H] to rate constants, defined as

$$S = \frac{\partial \ln [H]}{\partial \ln k} \tag{4.4}$$

are presented for all reactions in Table 5 at a time (0.16 s) corresponding to the middle of a typical experimental decay trace. $H+N_2 \longrightarrow HN_2$ denotes H escape, as discussed above.

Sensitivities are plotted for important reactions at all times in Figure 4.9. At all times of interest, [H] is mainly influenced by the target reactions $H+O_2 \longrightarrow$

Reaction number	Reaction	S
$3N_2$	$H+O_2+N_2 \longrightarrow HO_2+N_2$	-4.304
2	$H+O_2 \longrightarrow O+OH$	3.095
7b	$H+HO_2 \longrightarrow 2OH$	1.263
4	$H+N_2 \longrightarrow HN_2$	-5.330×10^{-1}
6	$HO_2+H_2 \longrightarrow H+H_2O_2$	5.006×10^{-1}
7a	$H+HO_2 \longrightarrow H_2+O_2$	-4.577×10^{-1}
$20N_2$	$H_2O_2+N_2 \longrightarrow 2OH+N_2$	4.371×10^{-1}
1	$O+H_2 \longrightarrow H+OH$	1.601×10^{-1}
30	$O+N_2 \longrightarrow ON_2$	-8.360×10^{-2}
$3H_2$	$H+O_2+H_2 \longrightarrow HO_2+H_2$	-7.285×10^{-2}
12	$O+HO_2 \longrightarrow OH+O_2$	-6.907×10^{-2}
13	$2HO_2 \longrightarrow O_2+H_2O_2$	6.162×10^{-2}
5	$OH+H_2 \longrightarrow H+H_2O$	4.542×10^{-2}
11	$OH+HO_2 \longrightarrow H_2O+O_2$	-4.405×10^{-2}
7c	$H+HO_2 \longrightarrow O+H_2O$	2.041×10^{-2}
$3O_2$	$H+2O_2 \longrightarrow HO_2+O_2$	-1.871×10^{-2}
$26N_2$	$HO_2+N_2 \longrightarrow H+O_2+N_2$	1.391×10^{-2}
$20H_2$	$H_2O_2+H_2 \longrightarrow 2OH+H_2$	7.410×10^{-3}
$20O_2$	$H_2O_2+O_2 \longrightarrow 2OH+O_2$	1.900×10^{-3}
9	$O+OH \longrightarrow H+O_2$	-1.063×10^{-3}
17a	$H+H_2O_2 \longrightarrow HO_2+H_2$	-2.757×10^{-4}

Table 5: Sensitivity of [H] to all rate constants at 0.16 s. Equation 4.4 defines S.

Reaction number	Reaction	S
$26H_2$	$HO_2+H_2 \longrightarrow H+O_2+H_2$	2.359×10^{-4}
17b	$H+H_2O_2 \longrightarrow OH+H_2O$	-2.091×10^{-4}
19	$OH+H_2O_2 \longrightarrow H_2O+HO_2$	-1.552×10^{-4}
$26O_2$	$HO_2+O_2 \longrightarrow H+2O_2$	6.049×10^{-5}
$8N_2$	$H+OH+N_2 \longrightarrow H_2O+N_2$	-3.190×10^{-5}
$22N_2$	$H+O+N_2 \longrightarrow OH+N_2$	-2.229×10^{-5}
$21N_2$	$2H+N_2 \longrightarrow H_2+N_2$	-2.111×10^{-5}
$3H_2O$	$H+O_2+H_2O \longrightarrow HO_2+H_2O$	-1.602×10^{-5}
18	$O+H_2O_2 \longrightarrow OH+HO_2$	-7.127×10^{-6}
$20H_2O$	$H_2O_2+H_2O \longrightarrow 2OH+H_2O$	1.461×10^{-6}
10	$2OH \longrightarrow O+H_2O$	-1.043×10^{-6}
$28N_2$	$O_3+N_2 \longrightarrow O+O_2+N_2$	-9.111×10^{-7}
$23N_2$	$2O+N_2 \longrightarrow O_2+N_2$	-8.307×10^{-7}
$21H_2$	$2H+H_2 \longrightarrow 2H_2$	-5.965×10^{-7}
14	$H+OH \longrightarrow O+H_2$	-5.646×10^{-7}
$8H_2$	$H+OH+H_2 \longrightarrow H_2O+H_2$	-5.408×10^{-7}
29	$O+H_2O \longrightarrow 2OH$	1.701×10^{-7}
$24N_2$	$2OH+N_2 \longrightarrow H_2O_2+N_2$	-1.597×10^{-7}
$8O_2$	$H+OH+O_2 \longrightarrow H_2O+O_2$	-1.387×10^{-7}
$22H_2$	$H+O+H_2 \longrightarrow OH+H_2$	-1.260×10^{-7}
$22O_2$	$H+O+O_2 \longrightarrow OH+O_2$	-9.692×10^{-8}

Table 5 continued.

Reaction number	Reaction	S
$21O_2$	$2H+O_2 \longrightarrow H_2+O_2$	-9.177×10^{-8}
$26H_2O$	$HO_2+H_2O \longrightarrow H+O_2+H_2O$	6.267×10^{-8}
$23O_2$	$2O+O_2 \longrightarrow 2O_2$	-5.664×10^{-8}
16	$H+H_2O \longrightarrow OH+H_2$	-5.564×10^{-8}
$28H_2$	$O_3+H_2 \longrightarrow O+O_2+H_2$	-1.545×10^{-8}
$28O_2$	$O_3+O_2 \longrightarrow O+2O_2$	-4.442×10^{-9}
$24H_2$	$2OH+H_2 \longrightarrow H_2O_2+H_2$	-2.722×10^{-9}
$23H_2$	$2O+H_2 \longrightarrow O_2+H_2$	-1.410×10^{-9}
$24O_2$	$2OH+O_2 \longrightarrow H_2O_2+O_2$	-6.942×10^{-10}
$21H_2O$	$2H+H_2O \longrightarrow H_2+H_2O$	-9.874×10^{-11}
$8H_2O$	$H+OH+H_2O \longrightarrow 2H_2O$	-6.376×10^{-11}
$22H_2O$	$H+O+H_2O \longrightarrow OH+H_2O$	-4.178×10^{-11}
15	$OH+O_2 \longrightarrow O+HO_2$	3.317×10^{-12}
$28H_2O$	$O_3+H_2O \longrightarrow O+O_2+H_2O$	3.823×10^{-13}
$24H_2O$	$2OH+H_2O \longrightarrow H_2O_2+H_2O$	-1.627×10^{-13}
$23H_2O$	$2O+H_2O \longrightarrow O_2+H_2O$	-7.117×10^{-14}
$25N_2$	$H_2O+N_2 \longrightarrow H+OH+N_2$	4.568×10^{-17}
$25H_2$	$H_2O+H_2 \longrightarrow H+OH+H_2$	7.767×10^{-19}
$25O_2$	$H_2O+O_2 \longrightarrow H+OH+O_2$	1.986×10^{-19}
$25H_2O$	$2H_2O \longrightarrow H+OH+H_2O$	2.591×10^{-22}

Table 5 continued.

O+OH, $H+O_2+N_2 \longrightarrow HO_2+N_2$, because these control the branching or terminating character of the system. Less important reactions are H escape (carefully measured in separate experiments), and the reactions of HO_2 with H and H_2 (rate constants taken from the best literature values [5]).

4.7 FLUX ANALYSIS

The method calculates the time–dependent flux for each reaction, defined as the rate constant multiplied by the concentrations of all reactants:

A$\longrightarrow$	products	Flux $= k$[A]
A+B$\longrightarrow$	products	Flux $= k$[A][B]
A+B+C$\longrightarrow$	products	Flux $= k$[A][B][C]

The concentration of a species is largely determined by those large–flux reactions in which it appears, so the flux quantifies the importance of each reaction. Table 6 presents fluxes for all H reactions at 0.16 s, for the same conditions as used for the sensitivity analysis.

Figure 4.10 presents the fluxes for the reactions $H+O_2(+N_2)$ and the escape of H, by diffusion and pump–out, for the three experimental timescales.

Figure 4.9: 5 largest normalized sensitivities from CHEMSEN. X axis: time/s for the three experimental timescales. Y axis: lg $|S|$, where Equation 4.4 defines S.

Figure 4.10: FACSIMILE fluxes, three experimental timescales. Y axis: lg (flux/molecule cm^{-3} s^{-1}).

Reaction number	Reaction	Flux
5	$OH+H_2 \longrightarrow H+H_2O$	1.18596×10^{12}
$3N_2$	$H+O_2+N_2 \longrightarrow HO_2+N_2$	6.39054×10^{11}
7b	$H+HO_2 \longrightarrow OH+OH$	4.20812×10^{11}
1	$O+H_2 \longrightarrow H+OH$	1.52144×10^{11}
2	$H+O_2 \longrightarrow O+OH$	1.50422×10^{11}
4	H$\longrightarrow$escape	1.41747×10^{11}
7a	$H+HO_2 \longrightarrow H_2+O_2$	7.70336×10^{10}
6	$HO_2+H_2 \longrightarrow H+H_2O_2$	4.46202×10^{10}
$3H_2$	$H+O_2+H_2 \longrightarrow HO_2+H_2$	8.41514×10^{9}
7c	$H+HO_2 \longrightarrow O+H_2O$	7.68556×10^{9}
$26N_2$	$HO_2+N_2 \longrightarrow H+O_2+N_2$	1.73274×10^{9}
$3O_2$	$H+2O_2 \longrightarrow HO_2+O_2$	9.77345×10^{8}
17b	$H+H_2O_2 \longrightarrow OH+H_2O$	5.18929×10^{8}
17a	$H+H_2O_2 \longrightarrow HO_2+H_2$	7.84838×10^{7}
$26H_2$	$HO_2+H_2 \longrightarrow H+O_2+H_2$	2.28169×10^{7}
16	$H+H_2O \longrightarrow OH+H_2$	6.37772×10^{6}
$3H_2O$	$H+O_2+H_2O \longrightarrow HO_2+H_2O$	5.24681×10^{6}
$26O_2$	$HO_2+O_2 \longrightarrow H+2O_2$	2.64998×10^{6}
9	$O+OH \longrightarrow H+O_2$	4.16320×10^{5}

Table 6: Fluxes of H reactions at 0.16 s. Units are molecule cm^{-3} s^{-1}.

Reaction number	Reaction	Flux
$8N_2$	$H+OH+N_2 \longrightarrow H_2O+N_2$	8.45705×10^{4}
$21N_2$	$2H+N_2 \longrightarrow H_2+N_2$	7.56022×10^{4}
14	$H+OH \longrightarrow O+H_2$	4.58259×10^{4}
$22N_2$	$H+O+N_2 \longrightarrow OH+N_2$	1.78042×10^{4}
$26H_2O$	$HO_2+H_2O \longrightarrow H+O_2+H_2O$	1.42263×10^{4}
$21H_2$	$2H+H_2 \longrightarrow 2H_2$	1.65923×10^{3}
$8H_2$	$H+OH+H_2 \longrightarrow H_2O+H_2$	1.11363×10^{3}
$8O_2$	$H+OH+O_2 \longrightarrow H_2O+O_2$	1.29339×10^{2}
$21O_2$	$2H+O_2 \longrightarrow H_2+O_2$	1.15623×10^{2}
$22H_2$	$H+O+H_2 \longrightarrow OH+H_2$	7.81493×10^{1}
$22O_2$	$H+O+O_2 \longrightarrow OH+O_2$	2.72291×10^{1}
$21H_2O$	$2H+H_2O \longrightarrow H_2+H_2O$	1.73750×10^{0}
$8H_2O$	$H+OH+H_2O \longrightarrow 2H_2O$	8.74878×10^{-1}
$22H_2O$	$H+O+H_2O \longrightarrow OH+H_2O$	2.33884×10^{-1}
$25N_2$	$H_2O+N_2 \longrightarrow H+OH+N_2$	7.15786×10^{-6}
$25H_2$	$H_2O+H_2 \longrightarrow H+OH+H_2$	9.42555×10^{-8}
$25O_2$	$H_2O+O_2 \longrightarrow H+OH+O_2$	1.09469×10^{-8}
$25H_2O$	$2H_2O \longrightarrow H+OH+H_2O$	7.40477×10^{-11}

Table 6 continued: Fluxes of H reactions at 0.16 s. Units are molecule cm^{-3} s^{-1}.

4.8 CONCLUSION

- The use of a laser method to probe the interaction between branching and termination in the O–H–H_2–O_2 system has been demonstrated.

- The long–time H decay could not be adequately represented by a simple mechanism which excluded HO_2 reactions.

- Inclusion of HO_2 provides the necessary extension of the timescale to reproduce the experimental data. In particular, the reactions $H+HO_2 \longrightarrow 2OH$ and $HO_2+H_2 \longrightarrow OH+H_2O$ are significant. The importance of the former, which is a radical–radical reaction, and is therefore sensitive to the overall radical concentrations, appreciably limits the use of this experimental technique to generate reliable rate constants for the $H+O_2$ branching and termination reactions.

- Best fit values are:

T/K	k_2	k_2 [10]	k_3	k_3 [5]
800	0.66±0.40	0.84	0.99±0.60	2.25
825	1.43±0.40	1.16	2.95±0.60	2.15
850	1.38±0.40	1.57	3.45±0.60	2.08

  where $k_2 = k(H+O_2 \longrightarrow OH+O)$ / 10^{-14} cm^3 molecule^{-1} s^{-1} and $k_3 = k(H+O_2+N_2 \longrightarrow HO_2+N_2)$ / 10^{-32} cm^6 molecule^{-2} s^{-1}. Literature values are presented for comparison. The errors are 1σ and include contributions from the overall uncertainties of each fit, and an assumed 10% uncertainty in each significant reaction of the full mechanism (but 35% for $H+HO_2 \longrightarrow O+H_2O$).

k_2 has a positive temperature–dependence as expected. k_3 has a strong positive temperature–dependence. As an association reaction, it would be expected to have a weak negative temperature dependence. Since k_2 and k_3 have a covariance of +0.3 to +0.8, the less well–determined k_3 may have been forced to follow the temperature–dependence of k_2. More accurate rate constants for HO_2 reactions might resolve this problem.

The results in Table 4 suggest that any inaccuracies in temperature measurement have little effect on the fitted values of k_2 and k_3.

- It is possible that spatial structure developed in this kinetic study, so that atom concentrations were not uniform in space.

- The analysis of the experimental data was greatly aided by the use of numerical integration coupled with sensitivity and flux analysis.

4.9 REFERENCES

[1] J.A.Miller *J.Chem.Phys.* **84** 6170 (1986)

[2] S.P.Walch, C.M.Rohlfing, C.F.Melius, C.W.Bauschlicher *J.Chem.Phys.* **88** 6273 (1988) *and erratum* **90** 7613 (1989)

[3] I.Schechter, R.D.Levine, R.B.Bernstein *J.Phys.Chem.* **91** 5466 (1987)

[4] E.P.Dougherty, H.Rabitz *J.Chem.Phys.* **72** 6571 (1980)

[5] W.Tsang, R.F.Hampson *J.Phys.Chem.Ref.Data* **15** 1087 (1986)

[6] A.N. Pirraglia, J.V. Michael, J.W. Sutherland, R.B. Klemm *J.Phys.Chem.* **93** 282 (1989)

[7] K.–J. Hsu, S.M. Anderson, J.L. Durant, F. Kaufman *J.Phys.Chem.* **93** 1018 (1989)

[8] G.L.Pratt, S.W.Wood *J.C.S.Farad.Trans.I* **79** 2597 (1983)

[9] M.W.Slack *Combust.Flame* **28** 241 (1977)

[10] D. Baulch, R.A. Cox, Th. Just, J.A. Kerr, M.J. Pilling, J. Troe, J. Warnatz, R.W. Walker, P.Frank submitted to *J.Phys.Chem.Ref.Data*

[11] M.Keiffer D.Phil. Thesis, Oxford University (1989)

[12] H.Okabe "Photochemistry of Atoms And Small Molecules", Wiley– Interscience, 1977

[13] V.S.Rao, G.B.Skinner *J.Chem.Phys.* **81** 775 (1984)

[14] J.R.Knutson, J.M.Beechem, L.Brand *Chem.Phys.Lett.* **102** 501 (1983)

[15] M.Keiffer private communication (1987)

[16] FACSIMILE: A.R.Curtis, W.P.Sweetenham "Release H User's Manual", Report AERE–R 11771, AERE Harwell (October 1985)

[17] R.Yetter, L.A.Eslava, F.L.Dryer, H.Rabitz *J.Phys.Chem.* **88** 1497 (1984)

[18] G.Rotzoll *J.Phys.Chem.* **90** 677 (1986)

[19] M.A.Kramer, R.J.Kee, H.Rabitz "CHEMSEN: A Computer Code For Sensitivity Analysis of Elementary Chemical Reaction Models", Princeton University.

Chapter 5

RATE CONSTANTS FOR THE $H+C_2H_4=C_2H_5$ REACTIONS

5.1 INTRODUCTION

The chemical industry uses the naphtha fraction of crude oil as a major feedstock. The favoured processing technique is cracking, in which the C_4–C_{12} hydrocarbons that constitute naphtha are pyrolysed at 1100 K and 2 atm pressure for about one second [1]. A major product, ethene, is processed into polymers (polyethylene, polyvinyl chloride) and into products such as ethan–1,2–diol, an anti–freeze. Naphtha cracking is a very large scale and expensive process, so it would be desirable to have a realistic chemical model to maximize the yield of those products that currently have the highest market value, and to compensate for the fluctuating composition of naphtha from different sources. By such computer simulations, the process conditions for a particular type of naphtha could be optimized.

Reaction chains in naphtha cracking are carried by gas–phase reactions of hydrocarbon radicals. At the high temperatures used, larger radicals decompose rapidly, and are unimportant as kinetic intermediates. Hence, only reactions of H, CH_3, C_2H_3, C_2H_5, and C_3H_5 radicals are significant (Chapter 1). Furthermore, rate constants for reactions with larger hydrocarbons can be estimated by additivity rules from those for smaller hydrocarbons.

To reduce the kinetic mechanism further, sensitivity analysis may be used to identify the most important reactions, as discussed in Chapter 4. A smaller mechanism containing only these crucial reactions should then reproduce all important observables of the system. At a certain time, the concentration of a species will be determined mainly by those reactions with the largest reduced sensitivity coefficients:

$$\frac{\partial \ln[\text{species}]}{\partial \ln k}$$

Lightfoot [1] modelled the cracking of ethane to high conversion at 1 atm pressure and 1118 K. He showed that the extents of ethane conversion and of methane production were most sensitive to the rates of various H atom addition–elimination reactions. These included the rate constants for the reactions:

$$C_2H_5 \underset{k_{rec}}{\overset{k_d}{\rightleftharpoons}} H + C_2H_4$$

To model cracking or combustion, accurate rate constants for these two reactions are needed at high temperatures and near–ambient pressures. Sometimes the theoretical models needed to supply such rate constants are poorly supplied with essential parameters. The rate constants for these reactions exhibit a strong

and complex dependence on temperature, pressure, and the nature of the bath gas. Many previous measurements have been made of one or both rate constants in several bath gases, using a variety of experimental techniques.

To obtain useful data for cracking simulations, the measurements should be made under conditions as close as possible to those used in cracking, or extrapolated from other conditions with the aid of well–characterized theoretical models. Only Lightfoot *et al.* [2] studied the pressure–dependence above 298 K. Teng *et al.* [3] and Cowfer *et al.* [4] measured k_{rec} using flow–tube techniques at pressures of 0.5–10 Torr, far below those encountered commercially. Photolysis or pulse radiolysis experiments on static systems have helped to extend the pressure range. Michael *et al.* [5] and Kurylo *et al.* [6] published falloff curves at room temperature in He from 1 to several hundred Torr. Lee *et al.* [7] and Sugawara *et al.* [8] measured the limiting high–pressure rate constant, k_{rec}^{∞}, between 198 K and 461 K. H atoms were produced by ethene flash photolysis, Hg–sensitized photo–decomposition of H_2, or pulse radiolysis, and measured by resonance fluorescence or resonance absorption. From these studies, k_{rec}^{∞} (198–461 K) appears to be quite well–determined.

The availability of accurate thermodynamic parameters allows the rate constant for a reverse reaction to be calculated from the measured forward rate constant. For example, rate constants for dissociation are strongly temperature–dependent, and can only be measured using a particular technique over a narrow range of temperature, yet the corresponding recombination rate constants are weakly temperature–dependent, and are often easier to measure.

There has long been controversy over the value of $\Delta H_{f,298}^{0}(C_2H_5)$: this Section aims to resolve this controversy using direct time–resolved measurements of

k_{rec}, k_d, and thus of K_p.

At the conditions prevailing in hydrocarbon cracking, the rate constants k_{rec} and k_d will be well into the falloff region, and extensive measurements are required above ambient temperatures. Lightfoot *et al.* [2] fitted k_{rec} by a technique based on the Troe factorization method. A similar analysis of direct measurements of k_{rec} at 800 K is presented here, to extend the database to temperatures closer to those encountered in commercial reactors.

5.1.1 Outline of Chapter

§ 5.2 describes the measurement of [H] by time–resolved resonance fluorescence, following 193.3 nm laser flash photolysis of C_2H_4, at 800 K and 48–600 Torr He. § 5.3 describes the mechanism to which the data were fitted, and the fitting procedure. Values are given for k_{rec}, k_d, and the equilibrium constant, $K_p = p(\mathrm{H})\ p(\mathrm{C_2H_4})\ /\ p(\mathrm{C_2H_5})$.

In § 5.4, K_p is combined with spectroscopic information to derive $\Delta H^0_{f,298}$ (C_2H_5), and the results are compared to those of Brouard *et al.* [9].

The experimental k_{rec} were fitted by Troe factorization. § 5.5 describes the procedure, and presents fitted values for k^0_{rec}, k^∞_{rec}, and F_{cent}.

5.1.2 Glossary

Symbol	Meaning
k_{rec}	rate constant for H + $C_2H_4 \longrightarrow C_2H_5$
k_d	rate constant for $C_2H_5 \longrightarrow$ H + C_2H_4
escape	removal of radical species by diffusion and pump–out
k_2	pseudo–first–order rate constant for escape of H
k_3	pseudo–first–order rate constant for escape of C_2H_5
$-\lambda_{\pm}$	slow and fast time constants for loss of H or C_2H_5
I	fluorescence intensity for H
E_l	energy of photolysis laser pulse
β	$(k_B T)^{-1}$
E	internal energy of molecule
k^0	limiting low–pressure rate constant
k^∞	limiting high–pressure rate constant
Q	ratio $k^0[\mathrm{M}]/k^\infty$
F_{cent}	Troe fall–off parameter
F^{SC}	Troe fall–off parameter
F^{WC}	Troe fall–off parameter

5.2 EXPERIMENTAL

Pre–mixed C_2H_4–He was further diluted with He, and flowed slowly through the stainless steel reaction cell, heated to 800 K. At this temperature, the yield of H from 193.3 nm photolysis of C_2H_4 was high enough to obviate use of N_2O–H_2 as an H source [2]. H was monitored by resonance fluorescence in real time. The

good H signal enabled use of low amplifier loads (0.5 or 1 kΩ: at higher loads, the H signal was clipped), so separate traces to record the laser light distortion were unnecessary. After each laser shot, H was typically monitored for 3.2 or 8 ms, and 250 or 500 shots were summed to give adequate signal : noise for analysis. [C_2H_4] covered a range of (0.47–8.0)$\times 10^{14}$ molecule cm^{-3}.

Experiments were conducted at various laser energies, and extrapolated to zero energy. Brouard *et al.* [9] showed that this procedure eliminates the effect of side reactions on the measured rate constants.

For analysis, a rate constant for the escape of H by diffusion and pump–out was needed; N_2O–H_2–He mixtures were photolysed at 193.3 nm. Chapter 3 discusses the chemistry. H fluorescence decay traces were recorded for 10–40 ms after the laser fired, over a range of pressures of 53–335 Torr. The laser energy was varied between 69 and 94 mJ. [N_2O] was (0.84–5.3)$\times 10^{14}$ molecule cm^{-3}, and [H_2] was (2.19–13.8)$\times 10^{16}$ molecule cm^{-3}. The long timescale obviated correction for distortion caused by scattered laser light, despite the lower signal and higher amplifier load (5 kΩ).

Gases were supplied with the following purities (from the manufacturer's analysis): He (BOC CP grade, 99.999%, 2 ppm each Ne, N_2); H_2 (BOC CP grade, 99.9995%, 5 ppm N_2, 2 ppm H_2O, 1 ppm O_2); N_2O (BDH, 99.6%, impurities not stated); C_2H_4 (BDH, 99.9%, 700 ppm CH_4 and C_2H_6). N_2O and C_2H_4 were distilled at least three times from and to liquid N_2, discarding the most volatile fractions (CH_4, C_2H_6, entrained air) and least volatile (entrained H_2O) each time.

5.3 DATA ANALYSIS

A simple kinetic scheme was chosen to model the time–dependence of [H]:

$$\begin{aligned} C_2H_4 &\xrightarrow{h\nu} H + C_2H_3 && (t=0) \\ H + C_2H_4 &\longrightarrow C_2H_5 && k_{rec} \\ C_2H_5 &\longrightarrow H + C_2H_4 && k_d \\ H &\longrightarrow \text{escape} && k_2 \\ C_2H_5 &\longrightarrow \text{escape} && k_3 \end{aligned}$$

At zero time, $[H] = [H]_0$, $[C_2H_5] = 0$. At 800 K, dissociation of C_2H_3 to yield H proceeds more slowly than all other reactions involving H (Chapter 8). The scheme implies:

$$\begin{aligned} \frac{d}{dt}[H] &= -k'_H[H] + k_d[C_2H_5] \\ \frac{d}{dt}[C_2H_5] &= k'_{rec}[H] - k'_{Et}[C_2H_5] \end{aligned}$$

where $k'_{rec} = k_{rec}[C_2H_4]$, a pseudo–first–order rate constant; $k'_H = k'_{rec} + k_2$, the total first–order rate constant for loss of H; $k'_{Et} = k_d + k_3$, the total first–order rate constant for loss of ethyl. These equations were solved (Appendix B):

$$\begin{aligned} [H]_t &= A_+ \exp(\lambda_+ t) + A_- \exp(\lambda_- t) \\ 2\lambda_\pm &= -k'_{loss} \pm \sqrt{(k'_{loss})^2 + 4(k'_{rec}k_d - k'_H k'_{Et})} \\ &= -k'_{loss} \pm \sqrt{(k'_H - k'_{Et})^2 + 4k'_{rec}k_d} \\ k'_{loss} &= k'_H + k'_{Et} \end{aligned}$$

where k'_{loss} is the total first–order rate constant for loss of (H and C_2H_5). Since $k'_{rec} > 0$ and $k_d > 0$, the time constants are real, and concentrations cannot oscillate in time. The pre–exponential factors are:

$$\begin{aligned} A_{\pm} &= \frac{[\mathrm{H}]_0(-k'_H - \lambda_{\mp})}{\pm(\lambda_+ - \lambda_-)} \\ &= \frac{\mp[\mathrm{H}]_0(k'_H + \lambda_{\mp})}{\lambda_+ - \lambda_-} \end{aligned}$$

The fluorescence intensity, I, was assumed proportional to [H]. At zero time, $I = I_0$, so:

$$I_t = I_+ \exp(\lambda_+ t) + I_- \exp(\lambda_- t) \tag{5.1}$$

$$I_{\pm} = \frac{\mp I_0(k'_H + \lambda_{\mp})}{\lambda_+ - \lambda_-}$$

Each decay trace of H fluorescence was fitted to Equation 5.1, using the Marquardt algorithm for non–linear least squares fitting (Chapter 2). I_0, k'_{rec}, and k_d were floated. For greater speed, analytic parameter derivatives were used. The observed rate of H disappearance could be explained if H both added quickly to C_2H_4 and was released rapidly from C_2H_5 (k'_{rec} and k_d large) or if both reactions were slow (k'_{rec} and k_d small).

To check the procedure, fluorescence data were simulated according to Equation 5.1, random noise was added, and the whole decay was written to disc in the same format as an experimental data file. Input values (typical of an experiment) were: $k'_{rec} = 800$ s^{-1}, $k_d = 200$ s^{-1}, $k_2 = 87$ s^{-1}, $k_3 = 27$ s^{-1}, signal : noise = 25,

$I_0 = 5000$, and data were generated every 2 or 5 μs (till 3.2 or 8 ms after the simulated laser shot). Equation 5.1 predicted that:

$$I_t = 909 \exp(-38.444\text{s}^{-1} \times t) + 4091 \exp(-1075.5\text{s}^{-1} \times t) + \text{noise}$$

Simulated data were then analysed using the same values for k_2 and k_3. Recovered values for k'_{rec} and k_d were: 813±10 s^{-1} and 197±5 s^{-1} (1.6% high and 1% low) for data every 2 μs, 795±15 s^{-1} and 193±3 s^{-1} (0.6% and 3% low) for data every 5 μs. Thus k'_{rec} and k_d were recovered acceptably close to the input values under typical experimental conditions.

Separate experiments, photolysing N_2O–H_2–He mixtures, yielded k_2. Each H trace was fitted with the Marquardt algorithm to a single exponential decay of rate constant k_2 (Chapter 3). These values of k_2 were plotted against (pressure)$^{-1}$, giving

$$k_2(800\text{ K, He})/\text{s}^{-1} = (30 \pm 17) + \frac{17000 \pm 1500\text{ Torr}}{P}$$

C_2H_5 will diffuse more slowly than H: with any collision partner, C_2H_5 will have a higher reduced mass and collision cross–section, and a lower diffusion coefficient D. C_2H_5 was not detected directly, so k_3 had to be estimated. The pressure–independent part (30 s^{-1}) of k_2 was neglected. Lightfoot *et al.* [2] set k_3 equal to $k_2/7$ on the basis of cross–sections and masses for H, He, and C_2H_5. Values of k'_{rec} and k_d were only feebly sensitive to the value of k_3 used in the fit, so that little error was caused by neglecting the pressure–independent part of k_3.

Following the procedure of Brouard *et al.* [9], results from each set of four experiments under identical conditions were combined (assuming independence

for error estimates) to determine k'_{rec} and k_d for that laser energy, E_l, and $[C_2H_4]$. A value for the addition rate constant, k_{rec}, at each laser energy was obtained as the gradient of a linear plot of k'_{rec} against $[C_2H_4]$; to eliminate side–reactions, these values for k_{rec} were extrapolated to zero laser energy. k_d was extrapolated to zero $[C_2H_4]$ at each energy; these zero–$[C_2H_4]$ values were then extrapolated to zero laser energy. This procedure was validated by reference to the extended mechanism of Brouard *et al.* [9], and was considered to be simpler than a bilinear fit of the type

$$k_d = A + BE_l + C[C_2H_4]$$

k_{rec} depended weakly and linearly on E_l; k_d depended weakly and linearly on E_l and $[C_2H_4]$. Table 1 presents the results for k_{rec} and k_d, and Figures 5.1 and 5.2 present the falloff curves. Errors in k_{rec} and k_d are 1σ, taken from the uncertainties of the linear fitting program. Values of K_p, referred to a standard state of 1 atm total pressure, are also given in Table 1. Errors in K_p neglected the covariance of k_{rec} and k_d. There is no systematic dependence of K_p on pressure, so it would appear that the pressure–dependence of k_2 and k_3 has been modelled to sufficient accuracy.

P	$[C_2H_4]$	E_l/mJ	k_2	k_3	k_{rec}	k_d	ln (K_p/atm^{-1})
48	1.47–6.44	32–66	384	55	0.70±0.06	297± 9	9.99±0.08
97	0.65–1.61	35–71	205	29	1.97±0.32	220±17	11.32±0.18
157	1.05–4.03	38–77	138	20	2.51±0.08	201±12	11.64±0.07
204	1.37–3.38	38–77	113	16	2.83±0.21	174±29	11.90±0.18
258	0.82–3.45	35–72	96	14	3.12±0.24	222±28	11.76±0.15
295	0.94–3.96	27–56	88	13	3.06±0.06	281±19	11.51±0.07
374	1.23–4.93	38–77	75	11	3.64±0.04	378± 1	11.38±0.01
455	1.45–6.13	34–69	67	10	3.61±0.14	342±27	11.48±0.08
524	1.78–6.93	33–67	62	9	4.01±0.19	348± 7	11.56±0.05
600	2.00–8.07	26–53	58	8	4.66±0.21	356±16	11.69±0.06

Table 1: Pressure dependence of k_{rec} and k_d at 800 K in He. k_2 and k_3 were fixed in analysis. Units: P/Torr, $[C_2H_4]/10^{14}$ molecule cm^{-3}, k_2/s^{-1}, k_3/s^{-1}, $k_{rec}/10^{-12}$ cm^3 molecule^{-1} s^{-1}, k_d/s^{-1}.

Figure 5.1: Experimental k_{rec} (H+C_2H_4), 800 K, with Troe fit.

Figure 5.2: Experimental data for k_d (C_2H_5), 800 K.

5.4 THE STANDARD ENTHALPY OF FORMATION OF C_2H_5

5.4.1 Introduction

Estimates of the enthalpy of formation of C_2H_5 span a range of 108–120 kJ mol^{-1} (Table 2), which cause calculated rate constants to differ by a factor of four at 1000 K. Russell *et al.* [10] showed that the lower values, derived from a study of the C_2H_5 + $I_2 \rightleftharpoons C_2H_5I$ + I equilibrium, might be reconciled with the higher values using new information on the activation energy for the reaction $C_2H_5 + I_2 \longrightarrow C_2H_5I + I$. Brouard *et al.* [9] measured k_{rec} and k_d over the range 775–825 K at a total pressure of 200 Torr He, by the methods outlined in this Chapter. They combined their values for

$$K_p = \frac{k_{rec}}{k_d RT}$$

with entropies and heat capacities calculated from spectroscopic data, to yield $\Delta H^0_{f,298}(C_2H_5) = 118.7 \pm 1.7$ kJ mol^{-1}. Their error refers to 2σ, including internal and external uncertainties, but excluding errors in the entropy or heat capacity of C_2H_5.

This work extends the measurements of Brouard *et al.* [9] to other pressures at 800 K. The standard enthalpy of reaction for H + $C_2H_4 \rightleftharpoons C_2H_5$ was calculated from Equation (II) of [9]:

$$\frac{\Delta H^0_{298}}{T} = \Delta S^0_{298} - R \ln K_p + \int_{298}^{T} \Delta C^0_p \, d\ln T' - \frac{1}{T}\int_{298}^{T} \Delta C^0_p \, dT' \qquad (5.2)$$

5.4.2 Calculation of entropies

For each species, the total molecular partition function q was separated into translational, rotational, internal rotational, vibrational, and electronic components:

$$
\begin{aligned}
q &= q_T\, q_V\, q_R\, q_{IR}\, q_E \\
q_T &= \left(\frac{2\pi u M_R}{\beta h^2}\right)^{1.5} V \\
&= \left(\frac{2\pi u M_R}{\beta h^2}\right)^{1.5} \frac{1}{\beta P} \qquad \text{ideal gas} \\
q_R &= 1 \qquad \mathrm{H} \\
q_R &= \sqrt{\frac{\pi}{ABC}}\frac{1}{(hc\beta)^{1.5}\sigma} \qquad \mathrm{C_2H_4, C_2H_5} \\
q_{IR} &= \sqrt{\frac{\pi}{hc\beta(a_1+a_2)}} \qquad \mathrm{C_2H_5} \\
q_V^{-1} &= \prod_L 1 - \exp(-x_L) \qquad x_L = hc\beta\nu_L \\
q_E &= 2, 1, 2 \qquad \mathrm{H, C_2H_4, C_2H_5}
\end{aligned}
$$

where u is the unit of atomic mass, $\beta = (k_B T)^{-1}$, M_R is the relative molecular mass, and the subscript L specifies the harmonic oscillator of frequency ν_L (expressed in wavenumbers). The molecular entropy is:

$$
\begin{aligned}
S &= \frac{-1}{T}\left(\frac{\partial \ln q}{\partial \beta}\right)_{\text{volume}} + k \ln q \\
\frac{S}{k} &= -\left(\frac{\partial \ln q}{\partial \ln \beta}\right)_{\text{volume}} + \ln q
\end{aligned}
$$

Contributions to the molar entropy include:

Source	S^0/R	species
translational	$\ln\,(YM_R^{1.5})$	
	$Y = P^{-1}\left(\frac{e}{\beta}\right)^{2.5}\left(\frac{2\pi u}{h^2}\right)^{1.5}$	
rotational	$1.5 + \ln\,q_R$	(0 for H)
int. rotation	$0.5 + \ln\,q_{IR}$	(C_2H_5 only)
vibrational	$\sum_L \left\{\frac{x_L\,\exp(-x_L)}{1-\exp(-x_L)} - \ln[1-\,\exp(-x_L)]\right\}$	
electronic	$\ln\,2$	H, C_2H_5

Contributions to the molar entropy of reaction, $\Delta S^0_{298}/R$, include:

Source	Expression	Value/R
translational	$1.5\,\ln\left(\frac{29}{28}\right) - \ln Y$	-13.03
rotational	$\ln\left[\frac{Z(C_2H_4)}{Z(C_2H_5)}\right]$	1.74
	$Z = \sigma\sqrt{ABC}$	
int. rotation	$S^{ir}(C_2H_5)/R$	2.33
vibrational	$[S^{vib}(C_2H_5) - S^{vib}(C_2H_4)]/R$	0.23

Drawing values from Table 3, and Table 1 of Chapter 6, $\Delta S^0_{298} = -71.82$ J mol^{-1} K^{-1}. Brouard *et al.* [9] calculated a value of -86.06 J mol^{-1} K^{-1}. The discrepancy may be explained by their use of different physical parameters: in particular, they used a different symmetry number for C_2H_5. Chapter 6 explains that the symmetry number for C_2H_5 should probably be 6, rather than the value of 1 expected from the equilibrium geometry.

5.4.3 Fit to ΔC^0_p

The molar heat capacities at constant volume, C^0_v, are:

translational:	$1.5R$	all species
rotational:	$1.5R$	C_2H_4, C_2H_5
int. rotational:	$0.5R$	C_2H_5
vibrational:	$\sum_L \frac{Rx_L^2 \exp(-x_L)}{[1-\exp(-x_L)]^2}$	$x_L = hc\beta\nu_L$

All rotations were regarded as unquantized at and above 298 K. The largest rotational constant is $(a_1 + a_2)$, which describes the internal rotation of C_2H_5. Even at 298 K, $k_BT/[hc(a_1 + a_2)] = 12.4$, so high–temperature expressions were valid for all rotations. For $H+C_2H_4 \rightleftharpoons C_2H_5$,

$$\Delta C_v^0 = C_v^{0,vib}(C_2H_5) - C_v^{0,vib}(C_2H_4) - R$$

where the last term includes all non–vibrational degrees of freedom. At constant pressure:

$$\begin{aligned} C_p^0 &= C_v^0 + R \qquad \text{(perfect gases)} \\ \Delta C_p^0 &= \Delta C_v^0 - R \\ &= C_v^{0,vib}(C_2H_5) - C_v^{0,vib}(C_2H_4) - 2R \end{aligned}$$

In a procedure based on that of Brouard *et al.* [9], ΔC_p^0 was evaluated at 300, 310, ... 800 K and fitted to $\Delta C_p^0 = b_1 + b_2T$, where $b_1 = -17.35$ J mol^{-1} K^{-1} and $b_2 = 9.898\times10^{-3}$ J mol^{-1} K^{-2}, reproducing ΔC_p^0 to within 3% in this temperature range.

5.4.4 Calculation of $\Delta H^0_{f,298}$ (C_2H_5)

From Table 1 (excluding 48 Torr point), $\ln K_p = 11.58 \pm 0.12$ (2σ). In Equation 5.2, the terms $\int_{298}^{T} \Delta C_p^0 \, d \ln T'$ and $\frac{1}{T} \int_{298}^{T} \Delta C_p^0 \, dT'$ had simple polynomial forms. At 800 K, they took the values of -12.2 J mol^{-1} K^{-1} and -7.49 J mol^{-1} K^{-1} respectively. Thus $\Delta H^0_{298} = -138.24$ kJ mol^{-1}. Now

$$\Delta H^0_{f,298}(C_2H_5) = \Delta H^0_{298} + \Delta H^0_{f,298}(H) + \Delta H^0_{f,298}(C_2H_4)$$

Since $\Delta H^0_{f,298}(H) = 217.86$ kJ mol^{-1} [11] and $\Delta H^0_{f,298}(C_2H_4) = 52.47$ kJ mol^{-1} [12], $\Delta H^0_{f,298}(C_2H_5) = 132.09$ kJ mol^{-1}.

5.4.5 Estimated errors

Following the approach of Brouard *et al.* [9], the following random errors (2σ) were identified and propagated:

Quantity±uncertainty	Resulting error / kJ mol^{-1}
$\ln K \pm 0.12$	0.8
$T \pm 4$ K	0.2
$[C_2H_4] \pm 2\%$	0.03
$k_2 \pm 10\%$	0.05
ν (C_2H_5) = 840±100 cm^{-1}	0.15

The error was dominated by that in $\ln K$, so $\Delta H^0_{f,298}(C_2H_5) = 132.1 \pm 0.8$ kJ mol^{-1}, where the error refers to 2σ, and considered random errors only; it excluded uncertainty in the symmetry number of C_2H_5. The error in $\Delta H^0_{f,298}$ (C_2H_4) was assumed to be negligible.

Value	System	Reference (date)
120.2±0.8	H + C_2H_4⇌C_2H_5	This work (1990)
118.7±1.7	H + C_2H_4⇌C_2H_5	[9] (1986)
120±2.5	Br + C_2H_6⇌HBr + C_2H_5	[13] (1990)
120±3	Br + C_2H_6⇌HBr + C_2H_5	[10] (1988)
118.4	Cl + C_2D_6⇌DCl + C_2D_5	[14] (1989)
119±2	review	[15] (1978)
117	H + C_2H_6⇌H_2+ C_2H_5	[16] (1984)
117±4	R + C_2H_5I⇌RI + C_2H_5	[17] (1981)
108±5	HI + C_2H_5I⇌C_2H_6 + I_2	[18] (1969)

Table 2: Literature values for $\Delta H^0_{f,298}(C_2H_5)$ / kJ mol^{-1}.

5.4.6 Comparison to literature values

Perhaps vibration and internal rotation in C_2H_5 at 800 K effectively make equivalent all H at one end of the radical, increasing the effective symmetry number from 1 to 6. Rotational constants would change little, and ΔS^0_{298} would become more negative by R ln 6, thus $\Delta H^0_{f,298}(C_2H_5)$ = 120.2±0.8 kJ mol^{-1}, in close agreement with literature values. Table 2 quotes a selection of literature values for $\Delta H^0_{f,298}(C_2H_5)$.

5.5 TROE FACTORIZATION OF k_{rec}

5.5.1 Introduction

There are many models for pressure–dependent reactions. The mechanism of Lindemann–Hinshelwood [19], as extended in RRKM theory, postulated a process in which a reactant molecule, A, receives and loses energy in collisions with a bath gas, M:

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}(E)}{\overset{k_1(E)}{\rightleftharpoons}} \mathrm{M} + \mathrm{A}^* \overset{k_a(E)}{\longrightarrow} \text{products}$$

Molecules of A above a threshold energy E_0 have enough energy to decompose. Such molecules are described as "energized", written A^*, and decompose with an energy–dependent rate constant $k_a(E)$. The microcanonical rate constants depend on the energy E of A or A^*, and are denoted as $k_1(E)$ or $k_{-1}(E)$. At very high pressures, the overall rate of loss of A is only limited by the rate of decomposition of A^*, so the thermal rate constant, k^∞, is independent of pressure. At low pressures, collisional activation of A is rate–limiting, and reaction becomes second–order overall, with a rate constant k^0:

$$\begin{aligned} \text{High pressures: } -\frac{d}{dt}\ln[\mathrm{A}] &= k^\infty \\ \text{Low pressures: } -\frac{d}{dt}\ln[\mathrm{A}] &= k^0[\mathrm{M}] \end{aligned}$$

The Lindemann–Hinshelwood theory made the strong collision assumption that the energy of A before and after a collision was uncorrelated; in effect, a single collision was needed for deactivation. The theory predicted that:

$$\frac{k}{k^\infty} = F^{LH}$$

where:

$$\begin{aligned} F^{LH} &= \frac{Q}{1+Q} \\ Q &= \frac{k^0[\mathrm{M}]}{k^\infty} \end{aligned}$$

Troe *et al.* [20, 21, 22, 23] further developed the Lindemann–Hinshelwood model by multiplying F^{LH} by two factors. The first, F^{SC}, allows for the energy dependence of the microcanonical dissociation rate constant, k_a. The second, F^{WC}, allows for the weakness of collisions (each collision only removes or adds a little energy, so the energy after collision is correlated with the energy before collision). So:

$$\begin{aligned} \frac{k}{k^\infty} &= F^{LH} F \\ F &= F^{SC} F^{WC} \\ \lg F &= \frac{\lg F_{cent}}{1+X^2} \\ X &= \frac{\lg Q + c}{0.75 - 1.27 \lg F_{cent} - 0.14(\lg Q + c)} \\ c &= -0.4 - 0.67 \lg F_{cent} \end{aligned}$$

where F_{cent} is the value of F at the centre of the falloff curve:

$$F_{cent} = F_{cent}^{SC} F_{cent}^{WC}$$

$$
\begin{aligned}
\lg F_{cent}^{SC} &= \frac{-(1.06 \lg S_K)^{2.2}}{1 + f_1 S_K^{f_2}} \\
f_1 &= 0.1 \exp(2.5 b_k^{-1} - 0.22 b_k - 6 \times 10^{-10} b_k^6) \\
f_2 &= 1.9 + 4.6 \times 10^{-5} b_k^{2.8} \\
b_k &= \frac{W_r}{k_B T} \left(\frac{S_K - 1}{s - 1} \right)^{1.6} \\
S_K &= 1 + \frac{U_v^{\ddagger}}{k_B T}
\end{aligned}
$$

There are s harmonic oscillators, S_K is the effective number of oscillators, and $U_v^{\ddagger}$ is the mean thermal vibrational energy of the transition state. W_r is the Whitten–Rabinovitch correction for densities of states:

$$
\begin{aligned}
W_r &= E_0 + a(E_0) E_z \\
a(E_0) &= 1 - \frac{w(s-1)(s + r/2)}{s} \frac{\sum_i \nu_i^2}{(\sum_i \nu_i)^2} \\
E_z &= 0.5 \sum_i \nu_i \\
\lg w &= -1.0506 \left(\frac{E_0}{E_z} \right)^{\frac{1}{4}} \text{ if } E_0 > E_z \\
\frac{1}{w} &= 5 \frac{E_0}{E_z} + 2.73 \sqrt{\frac{E_0}{E_z}} + 3.51 \qquad \text{otherwise}
\end{aligned}
$$

E_z is the zero–point energy. There are r free internal rotors, and ν_i is the frequency of the ith harmonic oscillator. Also:

$$
\begin{aligned}
F_{cent}^{WC} &= [0.16 \lg \beta_c + 0.04 (\lg \beta_c)^2] \, [1 + (\lg F_e)^{2.2}] \\
\beta_c &= \left[\frac{\langle \Delta E \rangle_{down}}{\langle \Delta E \rangle_{down} + F_e k_B T} \right]^2
\end{aligned}
$$

where $\langle \Delta E \rangle_{down}$ is the mean energy removed in a deactivating collision. F_e is the correction for the energy dependence of the density of states, and is taken from Equation (9.10) of Troe [23], amended for a species with r free internal rotors:

$$F_e = \sum_{i=0}^{s-1} \frac{(s-1+r/2)!}{(s-1+r/2-i)!} \left(\frac{k_B T}{hc} \right)^i$$

If k^0, k^∞, and F_{cent} are known, the rate constant may be calculated under any conditions.

5.5.2 $H + C_2H_4 = C_2H_5$ system

The Troe factorization approach was used to fit data, assuming that relaxation measurements gave valid estimates of $k_{rec}(P)$.

Hase *et al.* [24] provided a model of the transition state, and collected vibrational frequencies and rotational constants for all species (Table 1, Chapter 6). Lightfoot *et al.* [2] studied the H + C_2H_4 reaction from 285 K to 604 K; they fitted data using F_{cent}^{SC} calculated using the Hase *et al.* model, and F_{cent}^{WC} calculated using $\langle \Delta E \rangle_{down} = 285$ cm^{-1}.

k_{rec}^0, k_{rec}^∞, and lg F_{cent} were varied to fit experimental data (Appendix D) for k_{rec} (800 K, P), taking model parameters from Hase *et al.* The value for k_{rec} (800 K, 48 Torr) was considered to be in error, and was omitted from the fit. Initially some parameters were fixed at calculated values, and a fit was performed using the Marquardt algorithm (Chapter 2); it was then found that all three parameters could be fitted simultaneously. Starting values for each parameter differing by a factor of 10 converged to the same results. Table 4 contains the fitted values, together with lg F_{cent} calculated as in the previous Section, and the result of a fit

with k_{rec}^{∞} fixed at the value of Lightfoot *et al.* [2].

Figure 5.3 presents four falloff curves for 800 K only. One was calculated using Troe parameters from the three–parameter fit to experimental data. Another was calculated with lg F_{cent} from the vibrational frequencies, and k_{rec}^{0}, k_{rec}^{∞} from a fit. A third was calculated with the same lg F_{cent}, and k_{rec}^{0}, k_{rec}^{∞} extrapolated from the lower–temperature expressions of Lightfoot *et al.* [2]. For a fourth, k_{rec}^{∞} was extrapolated from lower temperatures, and k_{rec}^{0} and lg F_{cent} were fitted to data (Table 4). The failure of the third fit suggests that low–temperature values for k_{rec}^{0} and k_{rec}^{∞} cannot readily be extrapolated to cracker temperatures, at least for the H + $C_2H_4 \longrightarrow C_2H_5$ reaction. Table 5 contains the best Troe fit to experimental k_{rec}.

Fit of k_{rec}^{∞}

k_{rec}^{∞} was fitted to

$$k_{rec}^{\infty} = AT^{n} \exp(-B/T)$$

Values were taken from this work and from the literature ([2,7,8]). Fitted values were: $A = 4.46 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $n = -0.0067$, and $B = 1064$ K.

Quantity	Value
ν_i, $C_2H_5^{\ddagger}$	3036, 3009, 2955, 2944, 1504, 1446, 1218, 1185, 944, 938, 869, 821, 399, 369 cm^{-1}
$\langle \Delta E \rangle_{down}$ for C_2H_5–He	285 cm^{-1}
0 K Reaction energy	151 kJ mol^{-1} = 12651 cm^{-1}
0 K Thresholds:	
$H + C_2H_4 \longrightarrow C_2H_5$	10.5 kJ mol^{-1} = 875 cm^{-1}
$C_2H_5 \longrightarrow H + C_2H_4$	162 kJ mol^{-1} = 13526 cm^{-1}

Table 3: Input data for Troe calculations.

Parameter/units	Fit (1)	Fit (2)	Literature
$k^0_{rec}/10^{-30}$ cm^6 $molecule^{-2}$ s^{-1}	6.60	7.61	not calculated
$k^\infty_{rec}/10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}	13.2	11.3	11.3
lg F_{cent}	−0.422	−0.409	−0.194?

Table 4: Troe quantities for $H + C_2H_4 \rightleftharpoons C_2H_5$ at 800 K. Fit (1) was a three–parameter fit to experimental data. Fit (2) was a two–parameter fit to experimental data, with k^∞_{rec} fixed at the extrapolated value of Lightfoot *et al.* [2]. To calculate "Literature" value, $\langle \Delta E \rangle_{down} = 285$ cm^{-1}.

P/Torr	k_{rec}^{expt}	$k_{rec}^{(1)}$	$k_{rec}^{(2)}$
97	1.97	1.96	2.00
157	2.51	2.45	2.47
204	2.83	2.75	2.76
258	3.12	3.05	3.05
295	3.06	3.23	3.23
374	3.64	3.57	3.57
455	3.61	3.89	3.88
524	4.01	4.13	4.11
600	4.66	4.37	4.34

Table 5: k_{rec}(H + C_2H_4, 800 K) / 10^{-12} cm^3 molecule^{-1} s^{-1}, experimental values and Troe fit. $k_{rec}^{(1)}$ and $k_{rec}^{(2)}$ corresponded to fits (1) and (2) of Table 4.

Figure 5.3: 800 K falloff curves

5.5.3 Conclusion

In the Troe approach, the rate constant k_{rec} is completely determined by the parameters k^0_{rec}, k^∞_{rec}, and F_{cent}. It was assumed that the Troe model could be extended to fit values for k_{rec}(800 K,P), obtained by a reversible analysis of kinetic data from the H + $C_2H_4 \rightleftharpoons C_2H_5$ system.

Satisfactory fits were obtained, and the fitted values were: $k^0_{rec} = 6.60 \times 10^{-30}$ cm^6 molecule^{-2} s^{-1}, $k^\infty_{rec} = 1.32 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and lg $F_{cent} = -0.424$. The value determined for k^∞_{rec}(800 K) was significantly higher than the value extrapolated from the low–temperature data of Lightfoot *et al.* [2], supporting theoretical models which predict an upward curvature of the Arrhenius plot at high temperatures.

The Troe model suffers from having many physically–opaque parameters, gleaned from fits to a variety of pressure–dependent reactions. The important parameter S_K is poorly–defined, since it is dominated by the uncertain low frequencies of the postulated transition state. β_c is also poorly–defined, since an accurate value for $\langle \Delta E \rangle_{down}$ is needed. Furthermore, the Troe model cannot be used to explore arbitrary reactant energy distributions or equilibrium systems: it is derived solely from measurements on thermalized reactants in irreversible systems. The next Chapter explores these points further.

5.6 CONCLUSION

- Laser flash photolysis of C_2H_4, followed by time–resolved observation of H resonance fluorescence, yielded satisfactory forward and reverse rate con-

stants for $H+C_2H_4 \rightleftharpoons C_2H_5$ at 800 K.

- From these rate constants:

$$\Delta H^0_{f,298}(C_2H_5) = 120.2 \pm 0.8 \text{ kJ mol}^{-1}$$

where the error is 2σ, and includes internal and external errors. The symmetry number of C_2H_5 was assumed to be 6, as all H at each end of C_2H_5 were made equivalent by internal motions (Chapter 6).

- Data for k_{rec}(800 K) were satisfactorily fitted by floating three parameters in the Troe factorization model:

$$\begin{aligned} k^0_{rec} &= 6.60\times10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \\ k^\infty_{rec} &= 1.32\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ \lg F_{cent} &= -0.424 \end{aligned}$$

5.7 REFERENCES

[1] P.D.Lightfoot, D.Phil. Thesis, Oxford University (1986)

[2] P.D.Lightfoot, M.J.Pilling *J.Phys.Chem.* **91** 3373 (1987)

[3] L.Teng, W.E.Jones *J.Chem.Soc.Farad.Trans. I* **68** 1267 (1972)

[4] J.A.Cowfer, J.V.Michael *J.Chem.Phys.* **62** 3504 (1975)

[5] J.V.Michael, D.T.Osborne, G.N.Suess *J.Chem.Phys.* **58** 2800 (1973)

[6] M.J.Kurylo, N.C.Peterson, W.Braun *J.Chem.Phys.* **53** 2776 (1970)

[7] J.H.Lee, J.V.Michael, W.A.Payne, L.J.Stief *J.Chem.Phys.* **68** 1817 (1978)

[8] K.Sugawara, K.Okazaki, S.Sato *Bull.Chem.Soc.Jap.* **54** 2872 (1981)

[9] M.Brouard, P.D.Lightfoot, M.J.Pilling *J.Phys.Chem.* **90** 445 (1986)

[10] J.J.Russell, J.A.Seetula, D.Gutman *J.Am.Chem.Soc.* **110** 3092 (1988)

[11] L.Wołniewicz *J.Chem.Phys.* **78** 6173 (1983)

[12] JANAF Thermochemical Tables, 2nd Ed., *Nat.Stand.Ref.Data Ser.*, NBS **37** 1971.

[13] P.W.Seakins, D.Phil. Thesis, Oxford University (1990)

[14] S.S.Parmar, S.W.Benson *J.Am.Chem.Soc.* **111** 57 (1989)

[15] W.Tsang *Int.J.Chem.Kin.* **10** 821 (1978)

[16] J–R.Cao, M.H.Back *Int.J.Chem.Kin.* **16** 961 (1984)

[17] A.L.Castelhano, P.R.Marriott, D.Griller *J.Am.Chem.Soc.* **103** 4262 (1981)

[18] D.M.Golden, S.W.Benson *Chem.Rev.* **69** 125 (1969)

[19] F.A.Lindemann *Trans.Farad.Soc.* **17** 598 (1922)

[20] J.Troe *Ber.Bunsenges.Phys.Chem.* **87** 161 (1983)

[21] R.G.Gilbert, K.Luther, J.Troe *Ber.Bunsenges.Phys.Chem.* **87** 169 (1983)

[22] J.Troe *J.Chem.Phys.* **66** 4745 (1977)

[23] J.Troe *J.Chem.Phys.* **66** 4758 (1977)

[24] W.L.Hase, H.B.Schlegel *J.Phys.Chem.* **86** 3901 (1982)

Chapter 6

MASTER EQUATION DATA TREATMENT

6.1 INTRODUCTION

Brouard *et al.* [1] measured the equilibrium constant K_c and the relaxation rate constant k_{rel} in the $H+C_2H_4 \rightleftharpoons C_2H_5$ system, and Chapter 5 describes similar observations over a range of pressures. From these measurements, the forward and reverse rate constants, k_{rec} and k_d, and $\Delta H^0_{f,298}$ (C_2H_5) were derived. The validity of such analyses needs to be examined in more detail. Quack [2] questioned the analysis of reversible unimolecular systems, in particular the relationship between such derived rate constants and the true irreversible rate constants. He concluded that:

> *"k_{rec} and k_d have no direct relationship to the true rate of reaction events and are best conceived to be a replacement of the measurable*

pair of quantities (k_{rel}, K_c) by a new pair of quantities (k_{rec}, k_d).”

Robertson [3] studied isomerization, and showed that back–reactions had to be included to derive true rate constants from the calculated k_{rec}, k_d. On a four–level system, he showed that this result arose from the steady–state approximation, i.e. the evolution of the system in time was characterized by one non–zero eigenvalue which had a much smaller magnitude than all other eigenvalues.

Davies *et al.* [4] used irreversible Master Equation (ME) models to fit experimental data for $2CH_3 \longrightarrow C_2H_6$, with a fixed mean energy transfer per deactivating collision, $\langle \Delta E \rangle_{down}$. It should be possible to fit $H+C_2H_4 \rightleftharpoons C_2H_5$ data, and perhaps to obtain good information on $\langle \Delta E \rangle_{down}$ for this system also. Such a fit could be performed with two different ME models. One might correspond to an irreversible reaction, and give the rate constant for addition directly. The other, relating to a reversible system, would yield the relaxation rate constant which could be related, via the conventional analysis questioned by Quack, to both the forward and reverse rate constants. A comparison of the two approaches should thus check the validity of the reversible system as a source of meaningful rate constants.

This Chapter develops methods to treat data according to reversible and irreversible ME models, and compares the two. A general equilibrating reaction with dissociation and association is:

$$\mathrm{A} \underset{k_{rec}}{\overset{k_d}{\rightleftharpoons}} \mathrm{B} + \mathrm{C}$$

Two ME models are formulated, in which all energy levels of a dissociative species (A or C_2H_5) are considered. In this work, they are grouped into grains,

and the coupled differential equations relating their populations are solved. Other sections describe the input data, detail the solution of each model, and state the results (thermal rate constant k_{rec} and C_2H_5 population distributions).

6.1.1 Glossary

Symbol	Meaning
ME	Master Equation
A	a general dissociative species, e.g. C_2H_5
B and C	dissociation products of A, e.g. H and C_2H_4
k_{rec}	thermal rate constant for B+C$\longrightarrow$A
k_d	thermal rate constant for A$\longrightarrow$B+C
k_{rel}	relaxation rate constant for B+C$\rightleftharpoons$A
K_c	equilibrium constant: [H] [C_2H_4] / [C_2H_5]
E	internal rovibrational energy of A
E_0	threshold energy. A cannot dissociate for $E < E_0$
cell	small region of energy space used to calculate density of states
grain	small region of energy space used in master equation calculations
δE	width of grain
i	index of grain. i=1, 2, ..., G
G	index of highest grain used
i_0	index of grain that includes energy E_0
c	index of cemetery state
S_i	number of states in grain i
N_i	density of states in grain i
n_i	concentration of molecules having energies in grain i

$\mathbf{n}$	vector of n_i
f_i	Boltzmann distribution in grain i; $N_i e^{-\beta E_i}$
ϕ_i	flux into grain i of A from reaction of B+C
$\mathbf{\Phi}$	vector of ϕ_i
k_i	first–order dissociation rate constant for grain i
$\mathbf{K}$	diagonal matrix of k_i
R_{ji}	collisional transition coefficient, grain i to j
P_{ji}	probability of collisional transfer, grain i to j
$\mathbf{P}$	matrix of P_{ji}
$\langle \Delta E \rangle_{down}$	mean energy transfer in a deactivating collision
α	$\langle \Delta E \rangle_{down}^{-1}$ (strictly, only at high E)
Y	ratio of $\langle \Delta E \rangle_{down}$ to E in model of Shi *et al.* [5]
ω	collision frequency
$\mathbf{Q}$	collision/reaction matrix, irreversible system
$\mathbf{M}$	collision/reaction matrix, reversible system
λ_k	kth eigenvalue of $\mathbf{M}$
$\mathbf{u_k}$	kth eigenvector of $\mathbf{M}$
ΔE_0^0	zero–point energy difference for A$\longrightarrow$B+C, equals $E_B + E_C - E_A$
$g(J,K)$	rotational degeneracy of molecular state
σ	rotational symmetry number
ILT	Inverse Laplace Transformation of $k(T)$ to k_i

6.1.2 Relaxation rate constant, k_{rel}

In a reversible system, the concentration of each reactant decays or rises exponentially to its equilibrium value (Appendix F). This Chapter considers a pseudo–first–order system with a large excess of C_2H_4:

$$\frac{d}{dt}\ln([\mathrm{H}]_t - [\mathrm{H}]_\infty) = -k_{rel} \tag{6.1}$$

where

$$\begin{aligned} k_{rel} &= k_d + k'_{rec} \\ k'_{rec} &= k_{rec}[\mathrm{C_2H_4}] \end{aligned}$$

and the relaxation rate constant, k_{rel}, is the sum of the first–order rate constants in each direction. k'_{rec} and k_d may be related to the equilibrium constant $K_c = [\mathrm{C_2H_4}][\mathrm{H}]\ /\ [\mathrm{C_2H_5}]$:

$$k_d = \frac{k_{rel}}{1 + [\mathrm{C_2H_4}]/K_c}$$

$$k'_{rec} = \frac{k_{rel}}{1 + K_c/[\mathrm{C_2H_4}]} \tag{6.2}$$

§ 6.2.2 shows that a reversible system of G grains shows a G–exponential decay; the non–zero time constant of smallest magnitude, $-\lambda_2$, may be identified with k_{rel}. K_c may then be used to decompose $-\lambda_2$ into two rate constants.

6.2 MASTER EQUATION MODEL

The model is:

$$\mathrm{H} + \mathrm{C_2H_4} \underset{k_d(E)}{\overset{k_{rec}(E)}{\rightleftharpoons}} \mathrm{C_2H_5}(E)$$

$$\mathrm{C_2H_5}(E) \underset{R(E,E')}{\overset{R(E',E)}{\rightleftharpoons}} \mathrm{C_2H_5}(E')$$

where E is the internal (rovibrational) energy of a single state. The collisional transition coefficients, $R(E', E)$ and $R(E, E')$, represent transfer of energy. C_2H_5 molecules with $E > E_0$, where E_0 is the threshold energy for reaction, dissociate with a rate constant $k_d(E)$. They are reformed, following a Boltzmann distribution calculated from detailed balance, with a rate constant k_{rec}. A coupled set of differential equations could be written for each state of C_2H_5: since there are very many states (3.4×10^{15} below 30000 cm^{-1}), calculation for every state is impractical! The individual levels may be grouped into energy bands, called grains. The grain of index i covers the energy range $\{(i-1)\delta E \leq\ E \leq\ i\delta E\}$. In terms of grains:

$$\frac{d}{dt}n_i = \phi_i - k_i n_i - \sum_j R_{ji} n_i + \sum_j R_{ij} n_j \tag{6.3}$$

where i is the grain index. n_i is the number per unit volume of C_2H_5 molecules which have internal energies in the range covered by grain i. Grain i is depopulated by dissociation with a first–order rate constant k_i, and is fed by reaction

of H+C_2H_4 with an input rate ϕ_i. R_{ji} is the transition coefficient for collisional transfer from grain i to grain j, and corresponds to $R(E, E')$ for a pair of states.

Grains with energies above E_{max} were assumed not to be significantly populated by reaction or collision, so only the lowest G grains were considered. To save calculation time, the lowest value of G was used that still produced convergence.

6.2.1 Irreversible model for association

In this model, it was assumed that H was supplied at a steady rate, with C_2H_4 at constant concentration. C_2H_4 was assumed to be in a Boltzmann distribution. H was assumed to have a Maxwellian velocity distribution, and has no internal states at thermal energies.

To simulate irreversibility, a cemetery state — an absorbing barrier placed below the dissociation energy — was introduced, at a grain of index c. This barrier was placed at a grain of C_2H_5 for which the probability of reactivation in one collision was $\simeq 0$ to any grain above the dissociation limit. The cemetery state was placed at the highest level for which the solution converged, to reduce calculation time and storage requirements.

Equation 6.3 can be rewritten in matrix form [6]:

$$\frac{d}{dt}\mathbf{n} = \mathbf{\Phi} - \mathbf{K}\mathbf{n} - \omega\mathbf{n} + \omega\mathbf{P}\mathbf{n} \tag{6.4}$$

where the vectors $\mathbf{n}$ and $\mathbf{\Phi}$ have elements n_i and ϕ_i. $\omega\mathbf{P}$ has elements R_{ij}. $\mathbf{K}$ is diagonal with elements k_i. Equation 6.8 shows that:

$$\frac{R_{ij}}{\omega} = P_{ij}$$

where P_{ij} is the probability that a C_2H_5 molecule is transferred from grain j to grain i on collision. $\mathbf{P}$ thus contains the probabilities of collisional transition between every pair of grains. Equation 6.4 was recast as:

$$\begin{aligned} \frac{d}{dt}\mathbf{n} &= \mathbf{\Phi} - \mathbf{Q}\mathbf{n} \\ \mathbf{Q} &= \mathbf{K} + \omega(\mathbf{I} - \mathbf{P}) \end{aligned}$$

where $\mathbf{I}$ is the identity matrix. It can be shown that there is a unique steady–state, i.e. there is just one non–trivial solution associated with a non–zero eigenvalue. When this steady–state is reached, $d\mathbf{n}/dt = \mathbf{0}$, and

$$\mathbf{\Phi} = \mathbf{Q}\mathbf{n}$$

so

$$\mathbf{n} = \mathbf{Q}^{-1}\mathbf{\Phi} \tag{6.5}$$

§ 6.3 describes each term. The cemetery state, of index c, was introduced as follows. For $i < c$:

$$\begin{aligned} P_{ji} = &\quad 1 \quad j = i \\ = &\quad 0 \quad j \neq i \end{aligned}$$

The net rate of stabilization of C_2H_5 was equal to the thermal first–order rate constant, $k'_{rec} = k_{rec}[C_2H_4]$, multiplied by [H]. This reactive flux equalled the difference between the total rates of formation and of loss of C_2H_5:

$$k'_{rec}[\mathrm{H}] = \sum_{i>c} \phi_i - \sum_{i>c} k_i n_i$$

It is also equal to the rate of stabilization into the cemetery state:

$$k'_{rec}[\mathrm{H}] = \sum_{i>c} P_{ci} n_i$$

§ 6.4.1 describes the solution.

6.2.2 Reversible model for association

The equilibrium system, which had been studied experimentally at 800 K, was also modelled. An initial [H] was prepared with constant excess $[C_2H_4]$ which was maintained in a Boltzmann distribution. Now the time–dependence of the grain concentrations n_i was considered, and the master equation was extended to allow [H] to vary with time. Since H has no low–lying internal energy levels, one element suffices to describe [H]. This element was added to **n**. The equation then accommodated formation of C_2H_5 by reaction out of this element to all grains $i \geq i_0$ of C_2H_5, where i_0 contained the threshold energy E_0, with rate constants (ϕ_i[H]) determined by the k_i and detailed balance. All grains $i \geq i_0$ of C_2H_5 filled the [H] element by dissociation to H+C_2H_4.

In summary, the vector **n** now included [H] and varied with time, in contrast to the irreversible case. Rate constants were obtained from the rate of relaxation of **n** to equilibrium and the equilibrium constant.

The collision–reaction matrix was called **M**, and is derived as follows: To calculate k_{rec}, the temperature and densities–of–states partition functions were used to calculate:

$$K_c = \frac{[\mathrm{H}][\mathrm{C_2H_4}]}{[\mathrm{C_2H_5}]}$$

Table 2 gives $K_c(T)$. The distribution was calculated:

$$n_i = \frac{[\mathrm{C_2H_5}]N_i e^{-\beta E_i}}{\sum\limits_i N_i e^{-\beta E_i}}$$

so that

$$\frac{n_i}{[\mathrm{H}]} = \frac{[\mathrm{C_2H_4}]}{K_c}\frac{N_i e^{-\beta E_i}}{\sum\limits_i N_i e^{-\beta E_i}}$$

The collision probability matrix **P** for $\mathrm{C_2H_5}$ was established and normalized. Collision and reaction were included. The resulting matrix was called **C**:

$$\begin{aligned} C_{ji} &= P_{ji} \qquad \text{if } j \neq i \\ C_{ii} &= P_{ii} - 1 - k_i/\omega \end{aligned}$$

where G grains of $\mathrm{C_2H_5}$ were considered. **C** was extended by one row and one column to include H: the new matrix was

$$\mathbf{M} = \begin{bmatrix} C_{11} & C_{12} & \dots & C_{1G} & \phi_1/\omega \\ C_{21} & C_{22} & \dots & C_{2G} & \phi_2/\omega \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ & & & & \\ & & & & \\ C_{G1} & C_{G2} & \dots & C_{GG} & \phi_G/\omega \\ k_1/\omega & k_2/\omega & \dots & k_G/\omega & -\sum_{i=1}^{G} \phi_i/\omega \end{bmatrix}$$

No new H was supplied after zero time, so

$$\frac{d}{dt}\mathbf{n} = \mathbf{M}\mathbf{n} \tag{6.6}$$

was solved. $\mathbf{M}$ was diagonalized:

$$\mathbf{U}^{-1}\mathbf{M}\mathbf{U} = \mathbf{\Lambda}$$

$\mathbf{\Lambda}$ is diagonal, with elements λ_k, the eigenvalues of $\mathbf{M}$. The kth column of $\mathbf{U}$ is $\mathbf{u_k}$, the kth right eigenvector of $\mathbf{M}$. $\mathbf{M}$, $\mathbf{\Lambda}$, $\mathbf{U}$ are all time–independent. Thus:

$$\begin{aligned} \frac{d}{dt}\mathbf{n} &= \mathbf{U}\mathbf{\Lambda}\mathbf{U}^{-1}\mathbf{n} \\ \mathbf{n} &= \mathbf{U}e^{\mathbf{\Lambda}t}\mathbf{U}^{-1}\mathbf{n_0} \end{aligned}$$

where $\mathbf{n_0}$ is the vector of grain concentrations at zero time. The matrix $e^{\mathbf{\Lambda}t}$ is diagonal with elements $e^{\lambda_k t}$. The concentrations in each grain, $\mathbf{n}$, therefore have a multi–exponential time–dependence, with time constants λ_k [6].

$$\mathbf{n} = \sum_{k=1}^{G+1} c_k e^{\lambda_k t} \mathbf{u_k}$$

where the c_k are determined by a superposition of the $\mathbf{u_k}$ to form the initial state $\mathbf{n_0}$. $\mathbf{M}$ has order $G+1$, since there are G grains for C_2H_5 and one element of [H]. If the eigenvalues are ranked in order of increasing magnitude, $\lambda_1 = 0$, and $\mathbf{u_1}$ describes the time–independent equilibrium (Boltzmann) distribution. It can be shown that $c_1 = 1$ by considering the $t \to \infty$ limit of $\mathbf{n}$. Since the system has a unique long–time limit, all other eigenvalues must be negative, and describe transients of varying durations. Most eigenvalues have large magnitudes, and represent very short–lived transients. λ_2 describes the longer–time behaviour of the grain concentrations. On long (experimental) timescales, the system relaxes exponentially with time constant λ_2 to the equilibrium distribution $\mathbf{u_1}$:

$$\mathbf{n} = \mathbf{u_1} + c_2 e^{\lambda_2 t} \mathbf{u_2} \tag{6.7}$$

If $\mathbf{n}_H$ is the [H] element of $\mathbf{n}$, then

$$[\mathrm{H}]_t = \mathbf{n}_H$$

or

$$[\mathrm{H}]_t = (\mathbf{u_1})_H + c_2 (\mathbf{u_2})_H e^{\lambda_2 t}$$

$$
\begin{aligned}
[\mathrm{H}]_{\infty} &= (\mathbf{u_1})_H \\
[\mathrm{H}]_t - [\mathrm{H}]_{\infty} &= c_2(\mathbf{u_2})_H e^{\lambda_2 t} \\
\frac{d}{dt}\ln([\mathrm{H}]_t - [\mathrm{H}]_{\infty}) &= \lambda_2
\end{aligned}
$$

Thus $\lambda_2 = -k_{rel}$ in Equation 6.1.

6.3 INPUT PARAMETERS

The following data are needed to solve the matrix equations 6.5 and 6.6. The calculation of each will be discussed in turn:

1. Densities of states, N_i, from vibrational frequencies, rotational constants and symmetry numbers (σ), for C_2H_4 and C_2H_5. Rovibrational energies were obtained by direct count, and vibrational densities of states by the Beyer–Swinehart algorithm. There are no low–lying electronically excited states; the spin degeneracies of H and C_2H_5 cancel in ratios of densities of states and partition functions.

2. Energy–dependent dissociation rate constants, k_i, by an Inverse Laplace Transform (ILT) of Arrhenius expressions for $k_{rec}^{\infty}(T)$. The zero–point energy difference, ΔE_0^0 (from the enthalpy of reaction and vibrational frequencies) is also needed, for the ILT and the equilibrium constant.

3. Collision probabilities, P_{ij}, for transitions between C_2H_5 grains. The P_{ij} depend on the mean energy removed from C_2H_5 in a deactivating collision, $\langle \Delta E \rangle_{down}$.

4. Lennard–Jones parameters s and ϵ for C_2H_5 and He to define the collision frequency, ω.

5. Input reactive flux, f_i, into C_2H_5 grains from reaction of H+C_2H_4.

C_2H_4 rotational constants/cm^{-1}	$A = 4.844$, $B = 0.906$
C_2H_4 σ	4
C_2H_4 frequencies/cm^{-1}	3105, 3103, 3026, 3021, 1630, 1440, 1342, 1220, 1073, 943, 949, 826
C_2H_5 rotational constants/cm^{-1}	$A = 3.90$, $B = 0.7128$, $a_1 = 10.51$, $a_2 = 6.204$
C_2H_5 σ	Values of 1 [9] or 6 were used: § 6.5.4
C_2H_5 frequencies/cm^{-1}	3112, 3033, 2987, 2920, 2842, 1440(2), 1439, 1366, 1186, 1175, 1138, 802, 540
C_2H_5 Lennard–Jones parameters	$s = 0.3497$ nm, $\epsilon/k_B = 46.95$ K

Table 1: Physical parameters for H, C_2H_4, C_2H_5 [8].

T/K	q_n (C_2H_4)	q_n (C_2H_5)	k_{rec}^{∞}	K_c
285	641	23445	0.972	4.363×10^{-6}
400	1219	55756	2.906	5.438×10^{2}
511	2174	118657	5.240	1.289×10^{7}
604	3503	217480	7.271	3.504×10^{9}
800	9435	743527	11.30	6.757×10^{12}

Table 2: Input data. q_n is the rovibrational partition function. Units of k_{rec}^{∞} are 10^{-12} cm^3 molecule^{-1} s^{-1}. In these units, $k_{rec}^{\infty} = 43.9 \exp(-755 \text{ cm}^{-1}/k_BT)$ [7]. Units of K_c are molecule cm^{-3}.

6.3.1 Rotational state densities

Vibrational and rotational data for C_2H_4 and C_2H_5 are presented in Table 1. The vibrational frequencies and rotational constants of C_2H_4 are well–known, as it is a stable species. The parameters for C_2H_5 are less well–known, since it is short–lived.

Numbers of states were calculated in small energy bands (cells) of width 1 cm^{-1}, which were then combined into 100 cm^{-1} grains for the master equation calculations.

For each species, the rotational energies were evaluated for all states lying below the maximum energy considered, E_{max}. The energy of each state was divided by the calculation cell size to yield the cell index j, and the number of states in cell j was increased by $g(J, K)$.

Ethene

C_2H_4 was treated as a rigid oblate symmetric top without centrifugal distortions. In this assumption, overall rotation is described by the quantum number J, with a component K about the symmetry axis, where $J \geq 0$ and $-J \leq K \leq J$. Each level has energy $E(J, K)$ and degeneracy $g(J, K)$:

$$\begin{aligned} E(J,K) &= BJ(J+1) + (A-B)K^2 \\ g(J,K) &= (2J+1) \qquad K = 0 \\ &= 2(2J+1) \qquad K > 0 \end{aligned}$$

where A and B are rotational constants assumed independent of vibrational state. For C_2H_4, $A > B$, so the smallest energy for a given J is that for $K = 0$. Hence the largest possible J (J_{max}) for an energy E_{max} will occur when $K = 0$, and is given by the positive root of:

$$BJ_{max}(J_{max} + 1) = E_{max}$$

In counting states, only values of J from 0 to J_{max} had to be considered. For each J, K was increased until the energy exceeded E_{max}, or until $K = J$.

Ethyl

Hase *et al.* [8] assumed that σ (C_2H_5) = 6, implying that the CH_3 group had threefold rotational symmetry, and the CH_2 group had twofold rotational symmetry, about the C–C axis. Pacansky and Schrader [9] showed that equilibrium C_2H_5 radical is actually less symmetric. Both CH_2 hydrogens lie off the C–C axis, and one of the CH_3 hydrogens is further from the axis than the other two. Hence σ of equilibrium C_2H_5 is only 1. Pacansky and Coufal [10] stated that C_2H_5 may be treated as having a free internal rotor.

All three rotational constants (A, B, C) of C_2H_5 are different, so it is an asymmetric top. However, B and C have similar values. Since the density of states is approximately inversely proportional to the product of the rotational constants, B and C should be combined as a geometric mean to create an effective constant:

$$B_f = \sqrt{BC}$$

C_2H_5 was thus approximated to a symmetric top with one free internal rotor

and rotational constants A, B_f, and B_f. This ignores centrifugal distortion due to overall or internal rotation, and the change in moments of inertia for different C_2H_5 conformations (the coupling of internal and overall rotation). Appendix G describes the calculation of its rotational density of states.

6.3.2 Vibrational state densities

The Beyer–Swinehart algorithm (Appendix E) provides a rapid way of evaluating vibrational sums and densities of states. For simplicity, the oscillators in C_2H_4 and C_2H_5 were treated as harmonic.

Rotational numbers of states, evaluated as above, were fed to the Beyer–Swinehart algorithm to yield the total rovibrational numbers of states in each cell. In this work, the cells had a size of 1 cm^{-1}.

The Beyer–Swinehart algorithm is more accurate with small cells. Master equation calculations are only practicable with a few hundred grains, which must therefore be much larger to cover the same energy range. The number of states, S_i, in each grain equalled the sum of the numbers of states, C_j, of all the cells within it, where j is a cell index. Each grain had an energy, E_i, given by a weighted sum of the cell energies, E_j:

$$\begin{aligned} S_i &= \sum_j C_j \\ S_i E_i &= \sum_j C_j E_j \end{aligned}$$

Correct weighting was more important for low energies, where the C_j in-

creased rapidly with energy. Thus an unweighted sum, corresponding to the mid–grain energy $(i - \frac{1}{2})\delta E$, was less than the true mean energy. For $i = 1$ and $\delta E = 100$ cm^{-1}, the respective energies were 50 and 66 cm^{-1}. For $E > \approx 500$ cm^{-1}, the difference was <1 cm^{-1}.

The S_i were divided by the grain size ($\delta E = 100$ cm^{-1}) to yield grain densities of states, N_i.

Testing state densities

The rovibrational partition functions, q_n, were evaluated from the densities of states for C_2H_4 and C_2H_5:

$$q_n = \sum_{i=0}^{\infty} S_i e^{-\beta E_i}$$

where grain i contains S_i states. In practice, grains above an energy E_{max} (subscript G) are considered to have negligible population, so:

$$q_n \simeq \sum_{i=0}^{G} S_i e^{-\beta E_i}$$

The number of states S_i in grain i equals the grain size, δE, multiplied by the density of states N_i:

$$q_n \simeq \delta E \sum_{i=0}^{G} N_i e^{-\beta E_i}$$

q_n was compared with the analytic approximation to the rovibrational partition function, $q_{rv} = q_{ir} q_r q_v$. The formulae for the rotational, internal rotational, and vibrational partition functions are stated in Chapter 5. For a free internal

T/K	C_2H_4		C_2H_5	
	q_{rv}	q_n	q_{rv}	q_n
285	646	641	23594	23445
400	1222	1219	55951	55756
511	2178	2174	119002	118657
604	3509	3503	218116	217480
800	9455	9435	746016	743527

Table 3: Partition functions: analytic and from state densities.

rotor, the moments of inertia of the free separated parts were combined according to Herzberg [11].

Table 3 contains q_n and q_{rv}, for the five experimental temperatures used. The agreement was considered acceptable, so q_n was used for all calculations.

6.3.3 Calculating k_i

In general terms:

$$\mathrm{A} \underset{k_{rec}}{\overset{k_d}{\rightleftharpoons}} \mathrm{B} + \mathrm{C}$$

where k_d and k_{rec} are canonical rate constants. Most theories calculate the microcanonical dissociation rate constant for each grain, k_i, but experiments more usually measure the canonical rate constants k_d and k_{rec}. At the high–pressure limit, the latter may be derived from a Boltzmann average of k_i, a cumbersome process.

For $C_2H_5 \rightleftharpoons H+C_2H_4$, a potential barrier on the reaction coordinate locates a constrained transition state: such a reaction is said to be of type I. A detailed RRKM model could be used to calculate k_i, but information about the transition state is limited for many reactions, including this one.

Slater [6] was the first to propose Inverse Laplace Transformation (ILT) of experimental dissociation data $k_d(T)$ to determine k_i, which can be more readily compared with theory, or used to test models:

$$\begin{aligned} k_d^\infty &= \frac{1}{q_{rv}} \int_0^\infty k_d(E) N(E) e^{-\beta E} dE \\ k_d(E)N(E) &= \mathcal{L}^{-1} \left\{ q_{rv}(\beta) k_d^\infty(\beta) \right\} \end{aligned}$$

where E is the rovibrational energy of A, $N(E)$ is the rovibrational density of states for A, q_{rv} is the rovibrational partition function of A, and $\mathcal{L}^{-1}$ is the ILT, with variable $\beta = (k_B T)^{-1}$.

Forst [12] and Pritchard [13] discussed ILT in more detail. ILT strictly applies to an infinite range of temperature, but the process will work well if $k_d(T)$ is measured over a wide range. However, dissociation reactions are strongly temperature–dependent, and only proceed at a measurable rate over a small range of temperatures using a specific technique. Recombination rate constants, on the other hand, are weakly temperature–dependent: B and C are often prepared by a temperature–independent method (e.g. flash photolysis), so recombination rates can be measured over a wide range of temperatures with one technique. Davies *et al.* [4] extended ILT to recombination rate constants at the high–pressure limit, $k_{rec}^\infty(T)$ (Appendix H). In terms of recombination:

$$k_d^{\infty}(T) = k_{rec}^{\infty}(T)\frac{q_b(T)q_c(T)}{q_a(T)}e^{-\beta\Delta E_0^0}$$

$$k_d(E)N(E) = \frac{2C'A_{rec}^{\infty}}{\sqrt{\pi}}\int_0^{E_A-E_{rec}^{\infty}-\Delta E_0^0} N_{BC}(E_{BC})\sqrt{E_A - E_{BC} - E_{rec}^{\infty} - \Delta E_0^0}\, dE_{BC}$$

where q denotes the total partition function, ΔE_0^0 is the zero–point energy difference, and C' comes from the translational part of q (Appendix H). If $k_{rec}^{\infty}(T)$ can be expressed in Arrhenius form, then A_{rec}^{∞} and E_{rec}^{∞} are the Arrhenius parameters. E_{BC} is the internal energy of (B+C) relative to their zero–point energy, and $N_{BC}(E_{BC})$ is the convolution of the rovibrational density of states for B and for C. The enthalpy of reaction of Brouard *et al.* [1] was corrected for the difference in the thermal vibrational energies of C_2H_4 and C_2H_5 to give ΔE_0^0. The association barrier, E_{rec}^{∞} [8], was added to yield the dissociation threshold. Lightfoot *et al.* [7] measured k_{rec}^{∞} for $285 \leq T/\mathrm{K} \leq 604$; their Arrhenius expression was assumed to hold for all temperatures used. Tsang *et al.* [17] gave a modified Arrhenius expression for k_{rec}^{∞}, which was used in § 6.5.4.

Testing k_i

For an energy range split into grains of subscript i, in the high–pressure limit:

$$k_d^{\infty} = \frac{\sum_{i=0}^{\infty} k_i N_i e^{-\beta E_i}}{\sum_{i=0}^{\infty} N_i e^{-\beta E_i}}$$

T/K	$k_d^\infty = K_c k_{rec}^{\infty,expt}$	k_d^∞ from k_i
285	4.16×10^{-18}	4.25×10^{-18}
400	1.56×10^{-9}	1.58×10^{-9}
511	6.68×10^{-5}	6.73×10^{-5}
604	0.0252	0.0254
800	75.8	76.1

Table 4: $k_d^\infty/\mathrm{s}^{-1}$ from q_n and k_i. K_c was calculated from partition functions.

In calculations, grains above an energy E_{max} (subscript G) are neglected. A cannot dissociate below the threshold energy, E_0 (grain i_0), so $k_i = 0$ for $i < i_0$:

$$k_d^\infty(T) \simeq \frac{\delta E}{q_n} \sum_{i_0}^{G} k_i N_i e^{-\beta E_i}$$

where δE is the grain size. These sums were evaluated at each experimental temperature, and are presented in Table 4, where they are compared with the values obtained directly from the experimental recombination rate constants via the equilibrium constant K_c. K_c was obtained from partition functions. Agreement was better than 2%, over a temperature range in which k_d^∞ changed by 19 orders of magnitude. Counting states with a 10 cm^{-1} cell size increased the error a little: consequently, a 1 cm^{-1} cell size was retained.

6.3.4 Collisional probabilities, P_{ij}

For weak collisions, the collisional transition coefficients for energy transfer, R_{ji} and R_{ij}, may be related to the probability P_{ij} that a molecule is transferred from grain j to grain i after a collision. If ω is the collision frequency,

$$\begin{aligned} R_{ij} &= \omega P_{ij} \\ R_{ji} &= \omega P_{ji} \\ \omega^{-1} \sum_j R_{ji} &= \sum_j P_{ji} \end{aligned}$$

Normalization requires that

$$\sum_j P_{ji} = 1$$

Thus

$$\sum_j R_{ji} = \omega \tag{6.8}$$

The principle of detailed balance relates the probability of transition between two grains at equilibrium:

$$P_{ji} f_i = P_{ij} f_j$$

$$\begin{aligned}\frac{P_{ji}}{P_{ij}} &= \frac{n_i}{n_j} \\ &= \frac{N_i}{N_j}\,\exp[-\beta(E_i - E_j)]\end{aligned}$$

where the f_i correspond to the normalized Boltzmann distribution. Calculated thermal rate constants depend only weakly on the form of P_{ij}. In this case, He is a weak collider, and an exponential–down form was assumed for P_{ij}:

$$\begin{aligned}P_{ij} = &\quad A_j\,\exp[-\alpha(E_j - E_i)] &\quad j > i \\ P_{ij} = &\quad \frac{A_i N_i}{N_j}\,\exp[-(\alpha+\beta)(E_i - E_j)] &\quad j \le i\end{aligned}$$

where $\alpha^{-1} = \langle\Delta E\rangle_{down}$, the mean energy transferred per downwards (deactivating) collision. The A_j were found by back–substitution.

Calculated k_{rec} were sensitive to $\langle\Delta E\rangle_{down}$; this was floated at each experimental temperature to obtain the best agreement between calculated and experimental k_{rec}. Below 800 K, the experimental k_{rec} were determined from an irreversible analysis [7]. At 800 K, C_2H_5 dissociation was significant, and a reversible analysis (Chapter 5) was used to determine experimental k_{rec}. The irreversible model was used to fit $\langle\Delta E\rangle_{down}$ at all temperatures, since the reversible model took about 15 times longer to compute the rate constants.

Shi *et al.* [5] examined the vibrational relaxation of excited azulene, and suggested that $\langle\Delta E\rangle_{down} \propto$ the internal energy E, so that $\langle\Delta E\rangle_{down}$ depends on the grain index i:

$$\alpha_i = \frac{1}{YE_i}$$

They argued that more efficient energy transfer is possible due to the higher density of states at higher energy. This hypothesis was tested in the irreversible model.

It was also considered possible that $\langle \Delta E \rangle_{down}$ was affected only by translational energy (and hence by temperature): as the reactant and bath gas collide with higher relative velocities, the molecules reach smaller separations and enter a region of stronger coupling, where more energy could be transferred.

6.3.5 Collision frequency, ω

Kinetic theory states that:

$$\begin{aligned} \omega &= \pi[\mathrm{He}] s^2 \Omega^{(2,2)} \sqrt{\frac{8 k_B T}{\pi \mu}} \\ \mu &= \frac{m(\mathrm{He}) m(\mathrm{C_2H_5})}{m(\mathrm{He}) + m(\mathrm{C_2H_5})} \end{aligned}$$

where μ is the reduced mass of the collision partners He and C_2H_5, and the collision integral $\Omega^{(2,2)}$ corrects from the hard–sphere value to the Lennard–Jones cross–section s. The expression of Neufeld *et al.* [14] was used:

$$\Omega^{(2,2)} = 1.16145 (T^*)^{-0.1487} + 0.52487 \exp(-0.7732 T^*) + 2.16178 \exp(-2.43787 T^*)$$

where $T^* = k_B T/\epsilon$. In Table 1, s and ϵ are the Lennard–Jones parameters for the collision of C_2H_5 with He. As recommended in [15], the cross–section s was the arithmetic mean, and the well depth ϵ was the geometric mean, of the separate values for C_2H_5 and He [15]. Data were not available for C_2H_5, so values for C_2H_6 [15] were used.

6.3.6 Input distribution, Φ

At equilibrium, rates of formation and dissociation are equal for each grain. Hence $\phi_i = k_i n_i$, where the n_i follow a Boltzmann distribution for C_2H_5. So

$$\phi_i = \text{constant } \times k_i N_i e^{-\beta E_i}$$

where each grain contributes to the canonical dissociation rate constant, k_d^∞. Summing,

$$\sum_i \phi_i = k_d^\infty$$

Thus

$$\phi_i = k_d^\infty \frac{k_i N_i e^{-\beta E_i}}{\sum\limits_i k_i N_i e^{-\beta E_i}}$$

6.4 METHOD OF SOLUTION

For all C_2H_5 grains from the lowest energy to the calculation limit of $E_{max} = 30000$ cm^{-1}, the grain energy E_i, state density N_i, and microcanonical dissociation rate constants k_i were written to an intermediate file for use by the ME programs.

§ 6.5.1 discusses the choice of grain size and E_{max}. The ME programs calculated the collision frequency, ω, from the Lennard–Jones parameters, pressure, and temperature.

6.4.1 Irreversible model

Two NAG routines [16] were used. F04ATF solved Equation 6.5 by Gaussian elimination and backward substitution. At each experimental temperature, E04ABF was used once to minimize

$$\sum_l [k_{rec,l}^{expt} - k_{rec}^{calc}(\langle \Delta E \rangle_{down})]^2$$

by varying $\langle \Delta E \rangle_{down}$ only, where k_{rec}^{expt} was measured at a series of pressures of index l. This process was performed with the cemetery state set to the bottom grain, to ensure that all C_2H_5 grains were considered.

6.4.2 Reversible model

The NAG routine F02AFF found the eigenvalues λ_k of $\mathbf{M}$, but not the eigenvectors. M01APF sorted the λ_k in order of increasing magnitude. Since $k_{rel} = -\omega\lambda_2$, Equation 6.2 was used to find k_{rec} from λ_2.

Cemetery state

In the matrix $\mathbf{M}$, the first c grains were made into cemetery states (from which C_2H_5 could not be reactivated by collision), for comparison with the irreversible model described above:

$$M_{ji} = 0 \qquad i \leq c$$

Since **M** was not inverted, it could be singular, and it did not matter that $M_{ii} = 0$. As C_2H_5 is rendered inactive by collisional deactivation, the system is no longer reversible. Any linear combination of the c cemetery states is an eigenvector of **M** with eigenvalue 0, so there are c zero eigenvalues. As before, the non–zero eigenvalue of smallest magnitude, λ_{c+1}, represents the long–term behaviour of the system, which is now the irreversible reaction $H+C_2H_4 \longrightarrow C_2H_5$:

$$k'_{rec} = -\omega\lambda_{c+1}$$

6.5 RESULTS AND DISCUSSION

6.5.1 Convergence tests

These tests were performed for $\sigma = 1$.

State densities were only calculated up to an energy E_{max} (§ 6.2). For each temperature, there will be a minimum suitable value of E_{max}. Lower values of E_{max} will omit populated grains and cause incorrect results. Higher values of E_{max} cause grains of very low population to be considered, and increase the calculation time, while conveying no new information. High grains will be most populated at the highest temperatures and pressures considered here (800 K, 600 Torr He); under these conditions, the largest E_{max} will be needed.

For each E_{max}, $\langle\Delta E\rangle_{down}$ was varied to fit experimental k_{rec}. This Chapter used E_{max} =30000 cm^{-1}, but E_{max} =27000 cm^{-1} sufficed even at 800 K and 600

E_{max}	Optimized $\langle\Delta E\rangle_{down}$	$-\lambda_2/\mathrm{s}^{-1}$
18000	61.96	1940.9
21000	73.63	2279.7
24000	74.71	2308.4
27000	74.76	2309.7
30000	74.76	2309.7

Table 5: Effect of E_{max} on results at 800 K and 600 Torr He. E_{max} and $\langle\Delta E\rangle_{down}$ have units of cm^{-1}.

Torr He. For E_{max} >27000 cm^{-1} and a 100 cm^{-1} grain size, the fitted $\langle\Delta E\rangle_{down}$, and λ_2 in the reversible model, were independent of E_{max} (Table 5). Irreversible rate constants changed by <0.05% for E_{max} >24000 cm^{-1} at 800 K.

Since the fitted $\langle\Delta E\rangle_{down}$ was always found to be less than the grain size (100 cm^{-1}), it was decided to check for convergence of rate constants by reducing the grain size at a typical temperature (511 K). As δE was reduced in 10 cm^{-1} steps, the fitted $\langle\Delta E\rangle_{down}$ decreased steadily (Table 6). Little difference was seen in the rate constants.

It was found that the height of the cemetery state, E_{cem}, affected the results by less than 0.01% if it lay more than about $15k_BT$ below the threshold: molecules of such low energy are unlikely to be reactivated before reaching the cemetery state.

δE	Fitted $\langle \Delta E \rangle_{down}$	$-\lambda_2/\mathrm{s}^{-1}$
100	38.17	1871.4
90	36.77	1869.4
80	35.17	1865.4
70	34.04	1866.5
60	32.75	1865.1
50	31.32	1861.5
40	30.25	1860.7

Table 6: Effect of δE on results at 511 K and 700 Torr He. δE and $\langle \Delta E \rangle_{down}$ have units of cm^{-1}.

6.5.2 Checks on method

In the irreversible model, the ME solution was accurate to the precision limits of the calculation (i.e. $\mathbf{Qn} = \mathbf{\Phi}$ to < 0.1 ppm). k_{rec}^{∞} was recovered correctly from the value used to calculate the k_i, for pressures $\leq 10^8$ Torr, at the temperatures considered here (Appendix D). k_{rec} calculated by the two different routes (see above) agreed to within 1 ppm.

If the cemetery state is removed, C_2H_5 is not scavenged, and the steady–state distribution corresponds to equilibrium. For each grain, the rates of formation and loss become equal, and the net reactive flux should be 0: it was indeed 0 to calculation precision.

In the reversible model, k_{rec}^{∞} was found to be 0.4% – 4% more than that used to calculate the k_i. One eigenvalue was always 0 to calculation precision, and all other eigenvalues were at least 1000 times larger than λ_2. The imaginary parts of

the eigenvalues were always very close to 0, as they should be:

$$\sum_k |\text{Im } (\lambda_k)| < 10^{-5}$$

When c cemetery states were used, the first c eigenvalues were 0, as expected.

6.5.3 $\langle \Delta E \rangle_{down}$

For $\sigma = 6$, fitted $\langle \Delta E \rangle_{down} = 182$ cm^{-1} at 800 K. This compares well with Tsang *et al.* [17], who fitted H+$C_2H_2 \rightleftharpoons C_2H_3$ with $\langle \Delta E \rangle_{down} = 100$ cm^{-1}. A larger value of $\langle \Delta E \rangle_{down}$ would be expected for the larger species C_2H_5. Table 7 presents values of Y from the Shi *et al.* model (§ 6.3.4), fitted to experimental data. Y also increased with T.

In this work, experimental k_{rec} could be fitted by assuming that $\langle \Delta E \rangle_{down}$ rose with T (Table 7 and Figure 6.1). This finding agrees with the results of Walther *et al.* [18] for $2CH_3 \longrightarrow C_2H_6$.

T/K	E_{cem}	$\langle \Delta E \rangle_{down}, \sigma = 1$	$\langle \Delta E \rangle_{down}, \sigma = 6$	$1000Y, \sigma = 1$
285	10000	25.37	43.58	1.803
400	9000	28.88	52.52	2.007
511	9000	38.17	78.30	2.598
604	7000	48.49	107.90	3.223
800	5000	74.76	182.37	4.720

Table 7: Parameters to solve Master Equation. The units of E_{cem} and $\langle \Delta E \rangle_{down}$ are cm^{-1}. Y is dimensionless.

6.5.4 Thermal recombination rate constant

Appendix D contains k_{rec} (H+C_2H_4) for the irreversible and reversible models at the experimental temperatures of 285, 400, 511, 604, and 800 K. k_{rec} was calculated at experimental pressures (50–700 Torr) for comparison to observed values. Results are also presented at the same temperatures for pressures of 10^{-3}, 10^{-2}, ... 10^{8} Torr, to compare the models over a wider range of pressure. All calculations were performed with the values of $\langle \Delta E \rangle_{down}$ and E_{cem} given in Table 7.

Figure 6.2 displays experimental and calculated k_{rec} for each temperature. Figure 6.3 compares the two values of k_{rec}, by plotting the ratio between them against lg (pressure).

Calculations were also performed with the following changes to input data or calculation techniques:

Figure 6.1: $\langle \Delta E \rangle_{down}$, Boltzmann distribution parameters against T. Plots vertically displaced for clarity.

- $\sigma(C_2H_5)$ was changed from 1 to 6. This corresponds to distorting the equilibrium geometry of Pacansky and Schrader [9] into one with full rotational symmetry about the C–C bond. Such distortion might be caused by internal rotation about the C–C bond, or by inversion at the radical centre. For simplicity, rotational constants and vibrational frequencies of C_2H_5 were unchanged. The increased symmetry reduced state densities by a factor of 6: microcanonical rate constants, k_i, increased by the same factor to fit experimental recombination rate data in the ILT. Since dissociation of energized C_2H_5 was faster, collisional deactivation had to be stronger to give the observed k_{rec}; thus the fitted $\langle \Delta E \rangle_{down}$ increased (Table 7). Once $\langle \Delta E \rangle_{down}$ had been fitted to experimental values, either value for σ gave identical k_{rec}. Chapter 5 shows that $\sigma = 6$ gives a value for $\Delta H^0_{f,298}$ (C_2H_5) nearer to other literature values, so $\sigma = 6$ values are to be preferred for this work.

- For 800 K only, all grains at and below an energy E_{cem} were made cemetery states in the reversible model. So long as $E_{cem} < 5000$ cm^{-1} (about $15k_BT$ below the threshold, E_0), k_{rec} was indistinguishable from values calculated by the irreversible model with a sufficiently low–energy cemetery state. Results remained similar with $E_{cem} = 8000$ cm^{-1} ($E_0 - 10k_BT$). Larger values of E_{cem} rapidly increased k_{rec}, as collisional reactivation and dissociation of C_2H_5 became less and less probable. The dependence of k_{rec} on E_{cem} was more pronounced than in the irreversible model.

Figure 6.2: Experimental and ME values for k_{rec} ($H+C_2H_4$). X axis: P / Torr. Y axis: k_{rec} / 10^{-12} cm^3 molecule^{-1} s^{-1}.

Figure 6.3: Two ME models for k_{rec}. X axis: lg (P / Torr). Y axis: k^{rev}/k^{irrev}.

- Chapter 5 showed that a Troe fit to k_{rec}^{∞} yielded a value 19% higher than that obtained by extrapolating the Arrhenius expression of Lightfoot *et al.* A_{rec}^{∞} was therefore increased by 19%, to fit $k_{rec}^{\infty}(800\text{ K})$, and new k_i were generated. When $\sigma = 1$, the fitted $\langle \Delta E \rangle_{down}$ changed to 68.63 cm^{-1}, and Appendix D presents the new k_{rec}. With the new A_{rec}^{∞}, more falloff was displayed.

- Tsang *et al.* [17] recommended that $k_{rec}^{\infty} = 6.97{\times}10^{-12}\ (T/300\text{ K})^{1.49}\ \exp(-347\text{ cm}^{-1}/k_BT)$ cm^3 molecule^{-1} s^{-1}. A different set of k_i was derived from this expression by ILT (Appendix H). This ILT was slower, so a 2 cm^{-1} cell size was needed. Correct k_d^{∞} were still recovered from these k_i (§ 6.3.3). Using $\sigma = 6$, new values of $\langle \Delta E \rangle_{down}$ were obtained. In order of increasing T: $\langle \Delta E \rangle_{down} = 30.90,\ 48.85,\ 76.48,\ 105.86,\ 174.75\ \text{cm}^{-1}$. The models still agreed well with each other.

Once $\langle \Delta E \rangle_{down}$ was adjusted to fit experimental k_{rec}, both theoretical models agreed well with experimental values (Figure 6.2). It appears that either model could be used to calculate k_{rec} for the $H+C_2H_4 \rightleftharpoons C_2H_5$ system at all temperatures and pressures within the experimental range. The irreversible model is faster, since no eigenvalues are calculated, and the use of a cemetery state reduces the size of the matrix to be handled. On a VAX 8800, the irreversible model needed 7–11 s CPU time per rate constant; at lower T, a higher E_{cem} could be used, and calculations were faster. The reversible model needed 2 minutes to find the eigenvalues.

The two models agreed well at all pressures of He considered, $\geq 10^{-3}$ Torr. At very high pressures, the irreversible model returned, to better than 0.03%,

the value of k_d^∞ used to calculate the k_i. The reversible model returned a value typically 1% higher.

6.5.5 Population distributions

Figure 6.4 shows the reactive distribution for C_2H_5 under Boltzmann conditions, $k_i N_i e^{-\beta E_i}$, normalized at two different temperatures. The plot does not extend below threshold (where $k_i = 0$).

Figure 6.5 shows the steady–state population vectors $\mathbf{n}$ for the irreversible model at constant collision frequency, ω. The value chosen for ω (3.11×10^9 s^{-1}) corresponds to the middle of the experimental range (300 Torr, 511 K). The cemetery state was set to the bottom grain. There was a peak above threshold, caused by reaction of H+C_2H_4 filling these C_2H_5 grains. At low temperatures, the input distribution was sharp (H+C_2H_4 cold) and collisional relaxation was slow ($\langle\Delta E\rangle_{down}$ small), so C_2H_5 molecules accumulated just above threshold. At high temperatures, the pile–up became broader (wider input distribution) and smaller in total area (molecules were relaxed faster).

In the reversible model at long times, the population vector is given by Equation 6.7:

$$\mathbf{n}(t) = \mathbf{u_1} + c_2 e^{\lambda_2 t}\mathbf{u_2}$$

The NAG routine [16] F02BCF found $\mathbf{u_2}$. Figure 6.6 shows the transient eigenvector of longest duration $\mathbf{u_2}$, also at $\omega = 3.11\times10^9$ s^{-1}. Just above threshold, the elements of $\mathbf{u_2}$ were negative, so population rose with time. Well above threshold, population fell with time. This process corresponded to a falling mean

energy as nascent C_2H_5 was thermalized.

Figure 6.4: Boltzmann reactive distribution: C_2H_5. $D(E) = k_i N_i e^{-\beta E_i}$.

Figure 6.5: Irreversible model, $\omega = 3.11 \times 10^9$ s^{-1}. Normalized steady–state populations.

Figure 6.6: Reversible model, $\omega = 3.11 \times 10^9$ s^{-1}. Longest–lived eigenvector, $\mathbf{u_2}$.

6.6 CONCLUSION

Two different models were examined, in which the reactant and product energy levels were divided into bands of energy, or grains. Coupled differential equations for the grain populations were formulated and solved.

In the irreversible model, it was assumed that H+C_2H_4 reacted at a constant rate, from a Boltzmann distribution of C_2H_4 and a Maxwellian velocity distribution of H, into all C_2H_5 grains above threshold. Collisional transition probabilities came from the exponential–down model and detailed balance. A cemetery state was added, from which C_2H_5 could not be reactivated by collisions. The grain populations reached a steady–state, in which collisional activation, deactivation, and reaction balanced for each grain. From the distribution, the thermal rate constant, k_{rec}, was derived. By varying just one parameter, $\langle \Delta E \rangle_{down}$, a good fit to experimental k_{rec} was achieved.

In the reversible model, the same value of $\langle \Delta E \rangle_{down}$ and the same probabilities were used to describe collisional transitions: the system was prepared with a non–equilibrium ratio of $[H] : [C_2H_5]$, and the approach to equilibrium was modelled. The evolution of grain populations with time was characterized by the eigenvalues of the matrix describing collision and reaction; the non–zero eigenvalue of smallest magnitude, λ_2, was decomposed with the aid of the equilibrium constant to yield k_{rec} and k_d. Robertson [3] has discussed the scheme for isomerization reactions.

$\langle \Delta E \rangle_{down}$ was fitted to experimental data of Lightfoot *et al.* [7] (285–604 K) and Chapter 5 (800 K). With $\sigma(C_2H_5) = 6$, values were obtained of 44 cm^{-1} at 285 K, rising to 182 cm^{-1} at 800 K. Once $\langle \Delta E \rangle_{down}$ had been fitted, both

models agreed well with experiment, and could be used to fit data throughout the temperature range. The two models agreed well at all pressures considered, $\geq 10^{-3}$ Torr of He.

Thus relaxation data, obtained by Lightfoot *et al.* [7] and in Chapter 5, may be decomposed to yield the true forward and reverse rate constants. These rate constants may then be used to calculate correct equilibrium constants and reaction enthalpies.

6.7 REFERENCES

[1] M.Brouard, P.D.Lightfoot, M.J.Pilling *J.Phys.Chem.* **90** 445 (1986)

[2] M.Quack *Ber.Bunsenges.Phys.Chem.* **88** 94 (1984)

[3] S.H.Robertson D.Phil. Thesis, Oxford University (1989)

[4] J.W.Davies, N.J.B.Green, M.J.Pilling *Chem.Phys.Lett.* **126** 373 (1986)

[5] J.Shi, J.R.Barker *J.Chem.Phys.* **88** 6219 (1988)

[6] N.B.Slater *Proc.Leeds Phil.Lit.Soc. Sci.Sect.* **6** 259 (1955)

[7] P.D.Lightfoot, M.J.Pilling *J.Phys.Chem.* **91** 3373 (1987)

[8] W.L.Hase, H.B.Schlegel *J.Phys.Chem.* **86** 3901 (1982)

[9] J.Pacansky, B.Schrader *J.Chem.Phys.* **78** 1033 (1983)

[10] J.Pacansky, H.Coufal *J.Chem.Phys.* **72** 5285 (1980).

[11] G.Herzberg "Molecular Spectra and Molecular Structure: Volume 2, Infrared and Raman spectra of Polyatomic Molecules", Van Nostrand Reinhold (1945)

[12] W.B.Forst *J.Phys.Chem.* **86** 1771 (1982)

[13] H.O.Pritchard "The Quantum Theory of Unimolecular Reactions", Cambridge University Press, 1984

[14] P.D.Neufeld, A.R.Janzen, R.A.Aziz *J.Chem.Phys.* **57** 1100 (1972)

[15] R.S.Reid, J.M.Prausnitz, T.K.Sherwood "The Properties of Gases and Liquids", McGraw–Hill, 3rd ed., 1987

[16] Numerical Algorithms Group, "NAG FORTRAN Library Manual", Mark 13, July 1988

[17] W.Tsang, R.F.Hampson *J.Phys.Chem.Ref.Data* **15** 1087 (1986)

[18] D. Walther, H.–H. Grotheer, J.W. Davies, M.J. Pilling, A.F. Wagner *23rd Int.Symp.Comb.* (1990, to be published)

[19] S.E.Stein, B.S.Rabinovitch *J.Chem.Phys.* **58** 2438 (1973)

Chapter 7

A KINETIC STUDY OF THE REACTIONS H+ALLYL AND O+ALLYL

7.1 INTRODUCTION

7.1.1 Background

Pyrolysis and oxidation of hydrocarbons involve many free radical intermediates. The allyl radical (3–propenyl, here referred to as C_3H_5 or A) has been identified as an important species in such systems [1, 2]. At high temperatures, most polyatomic hydrocarbon free radicals decompose thermally or react with O_2 [3]. C_3H_5 is resonance–stabilized, and is thus resistant to thermal decomposition [4] and reacts rather slowly with O_2 at high temperatures [1].

It was inferred that A is largely consumed by the atoms and free radicals

found in pyrolysis and combustion systems. Major sinks may include reaction with H, O, OH, and CH_3 [5] or HO_2 and CH_3O_2 [1]. No mechanisms or rate constants have been determined for these reactions. Kinetic models for pyrolysis and combustion systems have postulated products of reactions of A, and either estimated rate constants or adjusted them to fit experimental data. Tulloch *et al.* [6] have shown that A+A recombination proceeds at a rate comparable to that of an alkyl+alkyl recombination. Hence, it would seem that the resonance stabilization of A does not reduce its reactivity toward other radicals.

In this Chapter, results are presented of kinetic observations on the reaction of A with two important combustion species, H and O, at 48–600 Torr and 286–500 K. Observations on the O+A reaction were combined with the low–pressure observations of Gutman and co–workers, and the joint results have been published [7]. The mechanism and products of the O+A reaction were inferred from the combined low– and high–pressure observations.

7.1.2 Glossary of Chapter

Symbol	Meaning
A	allyl, 3–propenyl, C_3H_5
X	H or O
AH	propene, C_3H_6
A_2	1,5–hexadiene, C_6H_{10}
δt	digitizer sample interval
k_1	rate constant for recombination of A
k_{2X}	rate constant for the reaction X+A
k'_X	Pseudo–first–order rate constant for loss of X. Includes escape from the viewing zone, and reaction with A_2
Δ	Absorbance due to A
Δ_0	Δ at zero time
R	Change in digitizer input voltage required to produce unit change in output value
I	Fluorescence intensity from X
Q	Ratio of [X] to I

7.1.3 Outline of Chapter

§ 7.2 describes the time–resolved measurements of [X] and [A], where X = H or O. X was monitored by atomic resonance fluorescence, and A by absorption in its strong δ band. Nakashima *et al.* [8] found this band to be centred at 223 nm with a FWHM of 10 nm. The choice of suitable control experiments is shown to

reduce the distortion caused by scattered laser light, and by laser radio frequency interference, in the measurement of [X] and [A] respectively. 193.3 nm laser flash photolysis of C_6H_{10} created H and A; if N_2O was added, $O(^1D)$ was formed, and rapidly quenched to $O(^3P)$ by the bath gas.

§ 7.3 describes the determination of k_{X+A} from raw data for the time–dependence of fluorescence and transmitted light intensities. A simple kinetic scheme was assumed, which gave analytic forms for $[A]_t$ and $[X]_t$, and the sensitivity of fitted k_{X+A} to kinetic parameters was derived. § 7.3 and Appendix J present the fitted k_{X+A}; the values for k_{O+A} are compared to complementary low–pressure data [7] and the mechanism and products of the O+A reaction are discussed.

§ 7.3 also examines the kinetics of the X–A system, and shows that the simple kinetic scheme can return good rate constants, even under experimental conditions where the basic assumptions used to derive it may be incorrect. § 7.4 considers the effect of side–reactions, and applies small corrections to allow for them.

k_{H+A} is pressure–dependent: § 7.5 compares experimental values to those predicted by the Troe factorization method [9–12].

7.2 THE EXPERIMENT

7.2.1 Technique

N_2O and 1,5–hexadiene (A_2) were diluted with bath gas (He or N_2) and stored in separate bulbs. When required, extra bath gas was added, and the mixture

Products	Primary yield (%)
A + A	68
propene + allene	27
H + C_6H_9	2.5
CH_3 + C_5H_7	2.5

Table 1: Products from 193.3 nm photolysis of C_6H_{10}.

was flowed slowly through the reaction cell, which was maintained at the required temperature. The flowing gas was photolysed by 193.3 nm laser pulses. Chapter 2 describes all aspects of the technique.

Tulloch *et al*. [6] used gas chromatography to examine the products of 193.3 nm photolysis of A_2; their results are summarized in Table 1. They showed that 68% of photolysed A_2 splits into two A radicals, and that a minor channel (2.5%) produces H. Thus 193.3 nm photolysis of A_2 automatically produces both A and H, with an initial concentration ratio $[A]_0 : [H]_0 = 0.68{\times}2 : 0.025 \simeq 54$. A precursor such as C_3H_5Br would form a second reactive species. At experimental laser fluences, the H produced from A_2 photolysis gave good fluorescence signal, and it was found unnecessary to add N_2O–H_2 to produce more H.

For O+A studies only, N_2O was photolysed cleanly to $O(^1D)$ (Chapter 2), which was rapidly quenched by N_2 to $O(^3P)$. Schofield [13] quotes a rate constant of $(2.8{\pm}0.3){\times}10^{-11}$ cm^3 molecule^{-1} s^{-1} for the quenching process: at typical $[N_2]$ (Table 3), quenching was complete in 20 ns. The interval, δt, between a fluorescence point and the nearest transmitted light point was 1, 2, or 5 μs.

X was monitored by resonance fluorescence in real time: the resonance lamp was run on H_2–He or O_2–He to emit H or O resonance radiation. Lamp spectra (Chapter 2) showed that some resonance radiation from each atom was always present. When measuring k_{H+A}, O was absent from the reaction mixture, so no O fluorescence could be excited, and O resonance radiation did not have to be removed. When k_{O+A} was measured, C_6H_{10} photolysis always produced some H; a CaF_2 window in front of the fluorescence photomultiplier selectively absorbed the H fluorescence.

On the short timescales of these experiments, scattered laser light temporarily saturated the fluorescence photomultiplier. This effect was corrected (Chapter 2). Chapter 2 shows that small errors in wavelength calibration are unimportant, and that A absorbance follows the Beer–Lambert law. Chapter 2 also describes corrections made for the effect of radio frequency interference on the transmitted light signal.

Figure 7.1 shows a typical experimental decay.

Typical experimental conditions are given in Tables 2 and 3. For k_{H+A}, the bath gas was He. To measure k_{O+A}, $O(^1D)$ had to be quenched rapidly, so N_2 was used as the bath gas. For these calculations, it was assumed that $[H]_0 = [A]_0$ / 54, as explained above. Appendix I describes the calculation of $[O]_0$ from $[N_2O]$ and the laser energy.

Quantity / units	Range	Typical
T/K	291	291
P/Torr	98–600	350
[He] / 10^{18} cm^{-3}	3.2–19.8	10
[A_2] / 10^{13} molecule cm^{-3}	1.9–87	8
Laser pulse energy / mJ	22–135	70
$[A]_0$ / 10^{12} molecule cm^{-3}	0.6–170	5
$[H]_0$ / 10^{12} cm^{-3}	0.011–0.31	0.09

Table 2: Experimental conditions for k_{H+A} measurements.

Quantity / units	Range	Typical
T/K	286–500	402
P/Torr	48–348	170
[N_2] / 10^{18} molecule cm^{-3}	0.96–11.7	4.1
[A_2] / 10^{13} molecule cm^{-3}	1.1–20	6
[N_2O] / 10^{14} molecule cm^{-3}	1.8–10.4	4
Laser pulse energy / mJ	43–121	80
$[A]_0$ / 10^{12} molecule cm^{-3}	0.4–21	8
$[H]_0$ / 10^{12} cm^{-3}	0.007–0.38	0.15
$[O]_0$ / 10^{12} cm^{-3}	0.6–7.5	1.9

Table 3: Experimental conditions for k_{O+A} measurements.

Figure 7.1: O+allyl experimental data, file OALL440. A: allyl absorbance, Δ. B: O fluorescence in arbitrary units.

7.2.2 Sources of materials

Manufacturers' specifications and typical impurity levels

He (BOC CP grade, > 99.999%, 2 ppm each Ne, N_2), N_2 (BOC CP grade, >99.999%, 1 ppm each O_2, CO_2, hydrocarbons, H_2), 1,5–hexadiene (Aldrich, 98%, impurities not given), N_2O (BOC preparative grade, 99.6%, impurities not given).

Purification and storage

Successive freeze–pump–thaw cycles removed all impurities more volatile than C_6H_{10} at 77 K (mainly air). Those less volatile than C_6H_{10} would not be released into the gas phase when a bulb was prepared, and were considered irrelevant. C_6H_{10} is hygroscopic, and thus had to be stored over anhydrous $CaSO_4$. N_2O was distilled at least three times from and to liquid N_2, discarding the most volatile fraction (entrained air), and least volatile fraction (water) each time. He was passed through an Oxisorb filter (Messer–Griesheim), to reduce O_2 and H_2O levels to 0.2 ppm.

7.3 ANALYSIS: SIMPLE SCHEME

7.3.1 Mechanism

A simple scheme was postulated:

$$\begin{aligned} A_2 &\xrightarrow{h\nu} A+A \quad (t=0) \\ A_2 &\xrightarrow{h\nu} H+C_6H_9 \quad (t=0) \end{aligned}$$

For O+A only:

$$\begin{array}{rcll} N_2O & \xrightarrow{h\nu} & O(^1D)+N_2 & (t=0) \\ O(^1D)+N_2 & \longrightarrow & O+N_2 & (t \simeq 0) \end{array}$$

where O is in the electronic ground state (^{3}P). For H+A and O+A:

$$\begin{array}{rcll} A+A & \longrightarrow & A_2 & k_1 \\ X+A & \longrightarrow & \text{products} & k_2 \\ X+A_2 & \longrightarrow & \text{products} & k_3 \\ X & \longrightarrow & \text{loss by escape} & k_4 \end{array}$$

At this stage, reactions of C_6H_9 and other products were neglected. At zero time, $[A]_0 \gg [X]_0$ (Tables 2 and 3), so reaction (1) was assumed to be the main sink for A. § 7.3.5 examines the validity of this assumption. The term $k_2[X][A]$, which describes the loss of A due to reaction with X, was assumed to be much less than the term $2k_1[A]^2$, which describes the recombination of A. Thus:

$$\begin{aligned} \frac{d}{dt}[A] &= -2k_1[A]^2 \\ [A]_t^{-1} &= [A]_0^{-1} + 2k_1 t \end{aligned} \qquad (7.1)$$

and the decay of A follows a second–order model. At the monitoring wavelength, the absorbance of A is given by

$$\Delta = \epsilon l [A]$$

where ϵ is the absorption cross–section of A and l is the absorption path–length. Hence

$$\begin{aligned} \Delta_t^{-1} &= \Delta_0^{-1} + \frac{2k_1 t}{\epsilon l} \\ [\mathrm{A}]_0 &= \frac{\Delta_0}{\epsilon l} \end{aligned} \tag{7.2}$$

where Δ_0 is the zero–time absorbance. The time–dependence of Δ may be combined with k_1/ϵ to yield Δ_0, from which $[\mathrm{A}]_0$ may be calculated if ϵ is known.

This model predicts the following rate of reaction for X:

$$\begin{aligned} \frac{d}{dt}[\mathrm{X}] &= -k_2[\mathrm{X}][\mathrm{A}] - k'_X[\mathrm{X}] \\ k'_X &= k_3[\mathrm{A}_2] + k_4 \end{aligned}$$

Since $[\mathrm{X}] \ll [\mathrm{A}_2]$, k'_X is a pseudo–first–order rate constant for the removal of X by reaction with A_2 and by escape from the viewing zone. Because $[\mathrm{A}]_t$ has the closed form of Equation 7.1, Appendix K shows that:

$$\begin{aligned} \frac{[\mathrm{X}]_t}{[\mathrm{X}]_0} &= \exp(-k'_X t)\{1 + 2k_1[\mathrm{A}]_0 t\}^{\left(\frac{-k_2}{2k_1}\right)} \\ &= \exp(-k'_X t)\{1 + 2k_1[\mathrm{A}]_0 t\}^{\left(\frac{-k_2}{\epsilon}\frac{\epsilon}{2k_1}\right)} \end{aligned}$$

If the fluorescence system is linear, then the fluorescence intensity, I, is proportional to [X], and

$$\begin{aligned} \frac{I_t}{I_0} &= \exp(-k'_X t)\{1 + 2k_1[\mathrm{A}]_0 t\}^{\left(\frac{-k_2}{2k_1}\right)} \\ &= \exp(-k'_X t)\{1 + 2k_1[\mathrm{A}]_0 t\}^{\left(\frac{-k_2}{\epsilon}\frac{\epsilon}{2k_1}\right)} \end{aligned} \tag{7.3}$$

where I_0 is the value of I at $t = 0$. Tulloch *et al.* [6] only determined the *ratio* of k_1 to ϵ, so the X fluorescence data can only directly determine k_2/ϵ. A value of ϵ is needed to calculate k_2.

7.3.2 Input data

To obtain $[A]_0$, the transmitted light intensity had to be converted to the absorbance, Δ. Δ_t was calculated from δd_t (Chapter 2). The first 6% of the trace after the laser firing was discarded, to remove any uncorrected radio frequency interference distortion of the decay.

For C_6H_{10} photolysis, Tulloch *et al.* [6] showed that some absorbance remained after several milliseconds, long after A should have recombined, yet they could isolate no strongly absorbing species by gas chromatography. Gutman *et al.* [14] prepared A by 193.3 nm photolysis of C_6H_{10}: photo–ionization mass spectrometry revealed a product, of the same mass : charge ratio as hexadiene ($m : e = 82$) but a higher internal energy, with a life of several milliseconds. They therefore suggested that irradiation of C_6H_{10} produced a metastable isomer that reverted to the precursor on the timescale of gas chromatography, but was stable on the timescales of the present work. Clark [15] showed that this absorbance was $\simeq 0.02\Delta_0$. Thus Equation 7.2 was slightly modified to

$$\Delta_t = \left[\Delta_0^{-1} + \frac{2k_1 t}{\epsilon l}\right]^{-1} + 0.02\Delta_0$$

Tulloch *et al.* [6] measured k_1/ϵ with good precision over $293 \leq T/\mathrm{K} \leq 571$:

$$\frac{k_1}{\epsilon} = (296491 \pm 5263) \exp\left(\frac{132 \pm 13 \text{ K}}{T}\right) \text{cm s}^{-1}$$

The fitted Δ_0 had to be converted to $[A]_0$ which was equal to $\Delta_0/(\epsilon l)$, where l is the path–length and A has absorption coefficient ϵ at the monitoring wavelength. Chapter 2 describes the measurement of l. van den Bergh *et al.* [16] determined ϵ at 298 K. Nakashima *et al.* [8] showed that the δ absorption band of A is structureless, so ϵ was expected to have little temperature–dependence. They also reported a value for ϵ 34% higher than that of [16], and suggested that the latter workers had observed allyl radicals that were incompletely relaxed after their formation by photolysis. The value of [16] was used for analyses at all temperatures. Combining k_1/ϵ and ϵ:

$$k_1 = (1.69 \pm 0.03) \times 10^{-11} \exp\left(\frac{132 \pm 13 \text{ K}}{T}\right)$$

cm^3 molecule^{-1} s^{-1}. Table 4 contains input values for all experimental temperatures and pressures.

Slagle *et al.* [7] show that the O+A reaction produces 2–propenal (acrolein, C_3H_4O) as the sole detectable organic product. The absorption cross–section of 2–propenal has not been measured at 223 nm, but an extrapolation from the data of Blacet *et al.* [17] at slightly longer wavelengths suggests that $\epsilon \approx 2\times10^{-23}$ cm^2 molecule^{-1}, which is much less than the value for allyl. Thus 2–propenal will not interfere with detection of allyl by absorption.

7.3.3 Determination of k_{X+A}

No directly measured values were available for k_3(X+1,5–hexadiene), so it had to be estimated for each atom X. At temperatures similar to those studied here, Ohta [18] showed that each CH=CH$_2$ group in 1,5–hexadiene (A_2) would add OH

independently. If one CH=CH_2 were replaced by a group that would not add OH (e.g. H), then the rate constant would be approximately halved: k(OH+1,5–C_6H_{10}) = 2k(OH+1–butene) to within 7%. For want of direct measurements of k_3, the same relationship was postulated for H and O. Harris *et al.* [19] and Atkinson *et al.* [20] measured:

$$\begin{aligned} k(\text{H+1–butene}) &= (3.77\pm0.4)\times10^{-11} \quad \exp\left[-(942\pm94)\ \text{K}/T\right] \\ k(\text{O+1–butene}) &= 1.39\times10^{-11} \quad \exp\left[-(335\pm101)\ \text{K}/T\right] \end{aligned}$$

cm^3 $molecule^{-1}$ s^{-1}. To estimate k_3, these values were doubled:

$$\begin{aligned} k_3(\text{H}) &\simeq (7.54\pm0.8)\times10^{-11} \quad \exp\left[-(942\pm94)\ \text{K}/T\right] \\ k_3(\text{O}) &\simeq 2.78\times10^{-11} \quad \exp\left[-(335\pm101)\ \text{K}/T\right] \end{aligned}$$

cm^3 $molecule^{-1}$ s^{-1}. To measure k_4(O), the rate constant for diffusive loss and pump–out of O, mixtures of N_2O–N_2 were photolysed to create O(^{1}D) which was quenched to ground state O. The slow escape of O by diffusion and pump–out was fitted to an exponential of rate constant k_4(O).

To measure k_4(H), mixtures of N_2O–H_2–He were photolysed to create O(^{1}D), which reacted rapidly with H_2 to H+OH. OH reacted more slowly with H_2 to H+H_2O. The later part of the decay (after the OH reaction was complete) was fitted to an exponential of rate constant k_4(H) (Chapter 3).

For each atom, k_4 was fitted to a function linear in P^{-1} (Chapter 2):

$$k_4 = a + \frac{b}{P}$$

The time–dependence of the atom fluorescence intensity, I, was fitted to Equation 7.3 by the Marquardt algorithm (Chapter 2). The zero–time fluorescence

T/K	k_1/ϵ	k_1	k_3(H)	a(H)	b(H)	k_3(O)	a(O)	b(O)
286	470175	2.68	n	n	n	8.62	3.0	1091
291	466671	2.66	2.96	11	3383	n	n	n
402	412281	2.35	n	n	n	12.1	6.6	952
500	386070	2.20	n	n	n	14.2	8.2	1371

Table 4: Input data. a and b have units of s^{-1} and Torr s^{-1}. "n": no X+A experiments attempted. Temperature–independent: $\epsilon = 5.7\times10^{-17}$ cm^2 molecule^{-1}, l = 2.1±0.05 cm. R was remeasured frequently, and was typically 1.65 mV digit^{-1}. Temperature–dependent data: (k_1/ϵ) / cm s^{-1}, $k_1/10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_3/10^{-12}$ cm^3 molecule^{-1} s^{-1}.

intensity, I_0, and $(-k_2/2k_1)$ were floated: the respective initial estimates were the first fluorescence data point and -1. Analytic parameter derivatives were used for speed. The first 6% of the decay after the laser firing was discarded, to remove any uncorrected radio frequency interference or laser light distortion, and to match the portion of the decay from which $[A]_0$ was calculated. In the worst case, the first 25% of the decay might have to be discarded, causing the fitted rate constant k_2 to increase by ≃25%.

7.3.4 Parameter recovery from simulated data: analytic solution

The numerical integration package FACSIMILE [21] simulated fluorescence and transmitted–light traces according to the simple scheme of this Section. In this

simulation, the reaction of A with X was allowed to deplete A: the analysis of § 7.3.1 neglected such depletion. Any discrepancy between these assumptions will be most marked if $[X]_0 \approx [A]_0$, as in the O+A experiments (Table 3).

Noise with a Gaussian distribution was added to the data. For fluorescence data the standard deviation of the noise was $\propto \sqrt{\text{data}}$ (Poisson statistics). Even at peak absorbance (<0.01), the transmitted light intensity changed little, so it was assumed to possess noise of constant amplitude.

The simulated decays were then analysed by the normal fitting programs according to the scheme of the previous Sections. This procedure checked that parameters were recovered correctly, and examined the sensitivity of fitted parameters to uncertainties in the input data.

Values used for simulations corresponded closely to 500 K O+A experiments: $k_1 = 2.20\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_2 = 2.37\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, $k'_X = 681$ s^{-1}, $[A]_0 = 6.46\times10^{12}$ molecule cm^{-3}, $[X]_0 = 10^{12}$ cm^{-3}. To convert [A] to absorption: $\epsilon = 5.7\times10^{-17}$ cm^2 molecule^{-1}, $R = 1.65$ mV digit^{-1}, $V_{inc} = 2112$ mV, 1000 shots. δt (defined in § 7.2) was equal to 1, 2, or 5 μs.

Tables 5 and 6 present the parameters recovered on all three timescales. The units of $[A]_0$ and k_2 are 10^{12} molecule cm^{-3} and 10^{-10} cm^3 molecule^{-1} s^{-1}. § 7.2 defines δt. The simulated data traces were generated with $[A]_0 = 6.46$ and $k_2 = 2.37$ in these units. Case 1: Correct values used to analyse data, beginning $50\delta t$ after the start of reaction. Case 3: k_1/ϵ increased by 10% from the true value.

Table 5 only: Case 2: R increased by 10% from the true value. Case 4: Correct values used to analyse data, beginning $20\delta t$ after the start of reaction. Case 5: Correct values used to analyse data, beginning $80\delta t$ after the start of

reaction.

For Table 6, values of $[A]_0$ were carried over from the corresponding case in Table 5, and all analyses began $50\delta t$ after the start of reaction. Case 2: $[A]_0$ increased by 10% from the true value (which might, for example, be due to an incorrect value of R). Hence less C_6H_{10} left after laser fired, $k_3[A_2]$ reduced, and k'_X reduced to 680 s^{-1}. Case 3: Now a higher $[A]_0$, so k'_X similarly reduced to 680 s^{-1}. Case 4: k'_X increased by 10%, corresponding to incorrect values for k_3, $[A_2]$, or k_4.

$[A]_0$ was recovered adequately on all timescales by the assumption that the decay of A followed a second–order model. The recovered $[A]_0$ was most dependent on the apparatus sensitivity, R, and only depended weakly on k_1/ϵ and on the choice of start time for the analyses. k_2 was recovered very well at all experimental timescales, and more accurately than $[A]_0$. § 7.3.6 discusses the contribution of each quantity to the total error in k_2.

The analysis of § 7.3 assumed that reaction with X did not consume A significantly. For H+A experiments, $[H]_0 \ll [A]_0$, so more A recombines than reacts with H (Table 7), the assumption holds well, and k_2 should be recovered accurately. If $[X]_0 \approx [A]_0$, as in the O+A experiments simulated here, Table 7 shows that most of the initial A actually reacts with O, so the analysis of § 7.3 might be considered invalid. However, Table 6 shows that k_2 is still recovered to within 4% of the true value, if correct input values are used (Case 1).

δt	$[A]_0{}^1$	$[A]_0{}^2$	$[A]_0{}^3$	$[A]_0{}^4$	$[A]_0{}^5$
1	6.21	6.97	6.34	6.26	6.18
2	6.17	7.01	6.38	6.23	6.13
5	6.24	7.25	6.59	6.32	6.21

Table 5: Recovery of $[A]_0$ from simulated absorption data by analytic solution. See text for details.

δt	$k_2{}^1$	$k_2{}^2$	$k_2{}^3$	$k_2{}^4$
1	2.33	2.15	2.32	2.46
2	2.32	2.14	2.14	2.45
5	2.30	2.04	2.04	2.44

Table 6: Recovery of k_2 from simulated data. See text for details.

7.3.5 Sinks of allyl

The mechanism of § 7.3 was extended to show the fraction of A consumed by each reaction:

$A+A \longrightarrow A_2$	(1)	A recombination
$X+A \longrightarrow XA$	(2)	addition to X
$X+A_2 \longrightarrow$ products	(3)	
$X \longrightarrow$	(4)	

If X = H, XA is the stable species C_3H_6. If X = O, the adduct will dissociate, but dissociation was ignored for this calculation of channel branching ratios. If the amount of A that has reacted is denoted by δ[A], then some A will dimerize to A_2, and some will add to X:

$$\delta[A] = \frac{1}{2}([A_2] - [A_2]_{after}) + [XA]$$

The fraction of A that has reacted in each channel is $([A_2] - [A_2]_{after})$ / 2δ[A] and [XA] / δ[A] respectively, where $[A_2]_{after} = [A_2]$ immediately after the photolysis laser has fired. These ratios were calculated for the typical experimental conditions of Tables 2 and 3, and displayed in Table 7. For H+A, $[H]_0 \ll [A]_0$, and the assumption that A reacted exclusively by recombination held quite well even at short times: thus the analysis of this Section was validated. For O+A, $[X]_0$ was much higher, most A actually reacted with O, and the results of the simple–scheme analysis had to be re–examined by a fuller analysis.

t / ms	Recombination, %	Addition to H (O), %
1	80 (18)	20 (82)
2	85 (25)	15 (75)
3	88 (29)	12 (71)
4	89 (33)	11 (67)
5	90 (35)	10 (65)
6	91 (37)	9 (63)
7	91 (38)	9 (62)
8	92 (39)	8 (61)

Table 7: Sinks of A for H (or O)+A reaction.

7.3.6 Results and error analysis

The rate constants $k_2(\mathrm{H}) = k_{H+A}$ and $k_2(\mathrm{O}) = k_{O+A}$ were calculated using input data from Table 4. Appendix J presents the results, which are summarized in Table 8.

Uncertainty in the final value of k_2 may arise from the following quantities (all 1σ):

k_1/ϵ, determined to a precision of $\pm 2\%$ [6].

k_3, the rate constant for reaction of X with A_2. $k_3(\mathrm{X}) = 2k(\mathrm{X}{+}1\text{–butene})$, to an accuracy of $\pm 7\%$ [18]. $k(\mathrm{X}{+}1\text{–butene})$ was determined to a precision of $\pm 11\%$ [19, 20]. If these errors are independent, k_3 is known to $\pm 13\%$ accuracy.

$[A_2]$, the concentration of A_2 after the laser fired. Since $[\mathrm{A}]_0 \ll [\mathrm{A}_2]$ (Table 3), very little A_2 is removed by photolysis, and the uncertainty in $[A_2]$ is determined by

the following experimental quantities, with estimated accuracies: $P\pm1\%$, $T\pm1\%$, pre–mixed bulb ratio $\pm1\%$. Hence $[A_2]$ is known to an accuracy of $\pm \simeq 2\%$.

k'_X, the first–order loss rate constant for X, is usually dominated by the term $k_3[A_2]$ (Table 4), and thus will be uncertain by about 15%.

$[A]_0$ is proportional to the instrumental parameters R (which has only a small estimated uncertainty) and V_{inc} (voltage reading for full incident light, $\pm0.5\%$, Chapter 2). $[A]_0$ is also proportional to the absorption path–length l (Table 4, $\pm4\%$), and to the zero–time change in digitizer reading δd (Table 4, $\pm3\%$). Hence, the uncertainty in $[A]_0$ is $\approx \pm5\%$. An error is caused by the assumption that reaction with X does not deplete A, but § 7.3.4 shows that this error cancels out when k_2 is determined. Furthermore, fitted k_2/ϵ is insensitive to the value of ϵ used to calculate $[A]_0$. To show this, expand Equation 7.3 for short times:

$$\{1 + 2k_1[A]_0 t\}^{(-k_2/2k_1)} \simeq \ 1 - 2k_2[A]_0 t$$

if $2k_2[A]_0 t \ll 1$. So

$$\begin{aligned} 1 - 2k_2[A]_0 t &= 1 - \frac{\Delta_0}{\epsilon l}\frac{k_2}{\epsilon}\epsilon t \\ &= 1 - \frac{\Delta_0}{l}\frac{k_2}{\epsilon}t \end{aligned}$$

Thus, approximately, fitted $k_2 \propto \epsilon$.

Dependence of fitted k_2 on input data

From Case 3 of Tables 5 and 6, a 2% uncertainty in the value of k_1/ϵ should cause a 3% uncertainty in the final value of k_2/ϵ. From Case 2, a 5% uncertainty in $[A]_0$

should cause a 7% uncertainty in the final value of k_2/ϵ.

For each experimental analysis, the input value of k'_X was halved and the fit repeated. The results supported the conclusion of Case 4, Table 6 that

$$\frac{\delta k_2}{k_2} \simeq \frac{0.3\delta k'_X}{k'_X}$$

So a 15% uncertainty in k'_X would make k_2/ϵ uncertain by 5%.

Combining these factors, the final value of k_2/ϵ has an estimated uncertainty of 9%. The values of k_2 quoted in Table 8 include this estimated error and ignore the uncertainty in the literature value of ϵ.

7.4 ANALYSIS: FULLER SCHEME

7.4.1 Mechanism

C_6H_{10} is photolysed to A+A, AH+allene, H+C_6H_9, and CH_3+C_5H_7. If the O+A reaction were studied, O would also be generated at very early times from N_2O photolysis. All bimolecular reactions among the species (H, O, CH_3, A, AH, A_2, C_3H_4, C_5H_7, C_6H_9) were considered. Losses by diffusion and pump–out were considered for H and O, and other transient species were assumed to be removed with rate constants of 5 s^{-1}. The products of these reactions were considered unreactive, unless a species in the above set was produced. Table 9 presents the mechanism, with values for the rate constants at the typical conditions of Table 4.

The A radical is stabilized by conjugation, and will react more slowly than CH_3 with a given molecular reactant, Y. A ratio $k(\text{A+Y}) : k(\text{CH}_3\text{+Y})$ of 0.2 was assumed as an upper limit. For Y = AH, the ratio $k(\text{A+AH}) : k(\text{CH}_3\text{+AH})$ is

P/Torr	n	$[A_2]$	$[A]_0$	k_2(H+A)
98	33	1.87–11.8	2.5–8.2	2.67±0.24
200	45	8.50–87.0	8.3–155	1.44±0.13
300	19	5.06–11.2	1.1–1.6	3.96±0.36
400	46	10.3–21.7	2.9–8.2	3.81±0.34
600	42	6.39–14.5	1.2–5.6	7.38±0.66
T/K	P/Torr	n	$[A_2]$	k_2(O+A)
285	48–348	67	2.64–13.2	2.33±0.21
402	49–292	45	1.93–11.9	1.85±0.17
500	50–200	168	1.98–21.2	2.55±0.23

Table 8: Fitted values of k_{H+A} and k_{O+A}. Fitted values for $k_{H+A}/10^{-10}$ cm^3 molecule^{-1} s^{-1}. At each pressure, n experiments were performed, over the stated range of $[A]_0/10^{12}$ molecule cm^{-3}, and the results combined. $[A_2]$ is the pre–flash value/10^{13} molecule cm^{-3}. Errors are all 1σ.

only 0.01 [24]. For C_5H_7 and C_6H_9 reactions, it was assumed that $k(C_5H_7+Y) = k(C_6H_9+Y) = k(A+Y)$. C_3H_4 has two C=C bonds and AH only one, so it was assumed that $k(C_3H_4+P) = 2k(AH+P)$ for a general radical P. It was further assumed that $k(C_5H_7+C_5H_7) = k(C_6H_9+C_6H_9) = k(A+A)$, and that the mean–value rule would apply for reactions among hydrocarbon radicals R_1 and R_2:

$$k(R_1 + R_2) = 2\sqrt{k(R_1 + R_1)k(R_2 + R_2)}$$

7.4.2 Parameter recovery from simulated data

[A], and the fluorescence intensity from X, were simulated over experimental timescales using the mechanism of Table 9. Initial concentrations of [A], [O], and $[A_2]$ were taken from the typical values of Table 4, and those of all other species were derived from the photolysis ratios of Table 1.

The parameters $[A]_0$, Q, and k_2 were varied to fit both traces simultaneously, using FACSIMILE. Calculated [X] were divided by the time–independent parameter Q for comparison to experimental fluorescence intensity, which was expressed in digitizer digits. Other parameters were also adjusted to make calculated concentration–time curves fit the data as closely as possible. Initial values used: $[A]_0 = 10^{12}$ or 10^{13} molecule cm^{-3}, $Q = 10^7$ or 10^8 cm^{-3} digit^{-1}, $k_2 = 10^{-10}$ or 10^{-9} cm^3 molecule^{-1} s^{-1}. Thus $2^3 = 8$ starting values were attempted for each experiment, all of which usually converged.

Table 10 presents the results. With the full scheme, k_2 was recovered very accurately. $[A]_0$ and Q were always recovered with similar accuracy. It appears that $[X]_0$ has little effect on the accuracy of recovery of k_2, since the H+A and

Reaction	Stoichiometry	$k^{(1)}$	$k^{(2)}$	Source
1H	H+CH_3⟶	1.31×10^{-10}	5.54×10^{-11}	22
2H	H+A⟶AH	floated	2.00×10^{-10}	S
3H	H+AH⟶	1.34×10^{-12}	2.25×10^{-12}	23
4H	H+A_2⟶	2.96×10^{-12}	7.24×10^{-12}	S
5H	H+C_3H_4⟶A	2.68×10^{-12}	4.51×10^{-12}	S
6H	H+C_5H_7⟶	$= k_{2H}$	2.00×10^{-10}	S
7H	H+C_6H_9⟶A_2	$= k_{2H}$	2.00×10^{-10}	S
8H	H⟶	41.3	61.8	S
1O	O+CH_3⟶	N	1.40×10^{-10}	22
2O	O+A⟶H	N	floated	S
3O	O+AH⟶	N	4.70×10^{-12}	23
4O	O+A_2⟶	N	1.21×10^{-11}	S
5O	O+C_3H_4⟶	N	9.40×10^{-12}	S
6O	O+C_5H_7⟶	N	$= k_{2O}$	S
7O	O+C_6H_9⟶	N	$= k_{2O}$	S
8O	O⟶	N	12.2	S
1CH_3	CH_3+CH_3⟶	5.69×10^{-11}	5.41×10^{-11}	22
2CH_3	CH_3+A⟶	3.31×10^{-11}	3.31×10^{-11}	24
3CH_3	CH_3+AH⟶	1.45×10^{-18}	4.98×10^{-17}	24
4CH_3	CH_3+A_2⟶	2.58×10^{-18}	8.05×10^{-17}	24
5CH_3	CH_3+C_3H_4⟶	2.91×10^{-18}	9.95×10^{-17}	S
6CH_3	CH_3+C_5H_7⟶A_2	3.31×10^{-11}	3.31×10^{-11}	S

Table 9: Reactions in the H–O–A system. Units of k are cm, molecule, s. (1) denotes 291 K and 350 Torr, (2) denotes 402 K and 170 Torr.

Reaction	Stoichiometry	$k^{(1)}$	$k^{(2)}$	Source
$7CH_3$	$CH_3+C_6H_9\longrightarrow$	3.31×10^{-11}	3.31×10^{-11}	S
$8CH_3$	$CH_3\longrightarrow$	5	5	S
2A	$A+A\longrightarrow A_2$	2.66×10^{-11}	2.35×10^{-11}	6
3A	$A+AH\longrightarrow$	2.91×10^{-19}	9.95×10^{-18}	S
4A	$A+A_2\longrightarrow$	5.17×10^{-19}	1.61×10^{-17}	S
5A	$A+C_3H_4\longrightarrow C_6H_9$	5.81×10^{-19}	1.99×10^{-17}	S
6A	$A+C_5H_7\longrightarrow$	5.32×10^{-11}	4.69×10^{-11}	S
7A	$A+C_6H_9\longrightarrow$	5.32×10^{-11}	4.69×10^{-11}	S
8A	$A\longrightarrow$	5	5	S
6AH	$AH+C_5H_7\longrightarrow$	2.91×10^{-19}	9.95×10^{-18}	S
7AH	$AH+C_6H_9\longrightarrow$	2.91×10^{-19}	9.95×10^{-18}	S
8AH	$AH\longrightarrow$	5	5	S
$6A_2$	$A_2+C_5H_7\longrightarrow$	5.17×10^{-19}	1.61×10^{-17}	S
$7A_2$	$A_2+C_6H_9\longrightarrow$	5.17×10^{-19}	1.61×10^{-17}	S
$6C_3H_4$	$C_3H_4+C_5H_7\longrightarrow$	5.81×10^{-19}	1.99×10^{-17}	S
$7C_3H_4$	$C_3H_4+C_6H_9\longrightarrow$	5.81×10^{-19}	1.99×10^{-17}	S
$8C_3H_4$	$C_3H_4\longrightarrow$	5	5	S
$6C_5H_7$	$C_5H_7+C_5H_7\longrightarrow$	2.66×10^{-11}	2.35×10^{-11}	S
$7C_5H_7$	$C_5H_7+C_6H_9\longrightarrow$	5.32×10^{-11}	4.69×10^{-11}	S
$8C_5H_7$	$C_5H_7\longrightarrow$	5	5	S
$7C_6H_9$	$C_6H_9+C_6H_9\longrightarrow$	2.66×10^{-11}	2.35×10^{-11}	S
$8C_6H_9$	$C_6H_9\longrightarrow$	5	5	S

Table 9 continued: "N": there was no O under the experimental conditions described, so O reactions were omitted from the mechanism. Unreactive products are omitted. "S": this Section (measured or estimated).

O+A systems have very different $[X]_0$ but similar accuracy of recovery. Thus, an analysis based on a fuller mechanism can recover k_2 more accurately than one based on the analytic mechanism of the previous section.

The different accuracy of recovery of k_2 in the H+A and O+A systems might be due to either the different ratio $[X]_0 : [A]_0$ or the different mechanism. For the O+A system, recovery was also tested with $[O]_0$ reduced, by a factor of ten, to 2×10^{11} cm^{-3}. Recovered values of k_2 changed by $\leq$1% for full– or half–scheme fits. Thus, at low ratios of $[X]_0 : [A]_0$, k_2 can be recovered very accurately for the H+A or O+A systems.

The recovered value of k_2 may be sensitive to the value of $[X]_0$, which is needed to analyse files by FACSIMILE; for large $[X]_0 : [A]_0$, the rate of loss of A can be explained by a high $[X]_0$ and low k_2, or vice versa. Fits were also performed with $[O]_0$ fixed at a value four times lower than that used to generate the data. For files generated with the higher $[O]_0$, the fitted value of k_2 increased by $\simeq$7%; files generated with the lower $[O]_0$ were very insensitive to the $[O]_0$ used to analyse the data.

Since experimental $[O]_0$ is probably accurate to a factor of two, values of k_{2O} obtained from a full–scheme fit will have an uncertainty of $\simeq$3% from this source. For the H+A system, $[H]_0 \ll [A]_0$, so the actual value of $[H]_0$ is not important.

In the half–scheme, reactions of C_3H_4, C_5H_7, and C_6H_9 were omitted. It may be seen that omission of C_3H_4, C_5H_7, and C_6H_9 introduced a systematic error of 4–5% in the recovered value of k_2. There appears to be little advantage in using the half–scheme fit.

Results from the Marquardt algorithm fit to the simple scheme (§ 7.3) are also shown. For some of the latter fits, typical noise was added to the data before

System	δt	Full scheme	half–scheme	simple scheme	+noise
H+A	1	2.007±0.005	2.081±0.006	2.053	2.109
H+A	2	1.999±0.004	2.088±0.006	2.048	2.112
H+A	5	2.014±0.015	2.105±0.010	2.046	2.100
O+A	1	2.002±0.008	2.097±0.006	2.076	2.138
O+A	2	2.005±0.007	2.091±0.005	2.109	2.169
O+A	5	2.026±0.013	2.094±0.017	2.094	2.092

Table 10: Recovery of k_2. Units: $\delta t/\mu$s, $k_2/10^{-10}$ cm^3 molecule^{-1} s^{-1}. In these units, the input value of k_2 was 2, and $[O]_0 = 1.9\times10^{12}$ cm^{-3}.

analysis. When data traces were generated with $[O]_0 = 2\times10^{11}$ cm^{-3}, k_2 was recovered to within 2% of the true value (no noise added), or 5% (noise added to data).

7.4.3 Fits to experimental data

Traces of fluorescence and [A] were prepared from the raw experimental decay trace, and stored in an intermediate file with a format suitable for input to FACSIMILE. These intermediate files were analysed as above; almost all attempted fits from different starting values converged. Results from these experiments were combined to yield the best–fit value for k_2.

Table 11 presents fitted values. Values from the half–scheme are also presented, together with results of the simple–scheme fit (§ 7.3 and Appendix J). Fitted values of k_2 depended a little on other fitted values, so |covariance| was

Data files	full	half	simple	new k_O [25]
HALL210–215	3.81±0.28	3.96±0.31	4.13	(O absent)
HALL216–221	3.50±0.23	3.63±0.24	3.68	(O absent)
OALL432–437	2.66±0.15	2.76±0.17	2.68	2.76±0.17
OALL487–492	2.94±0.08	3.06±0.07	3.25	3.07±0.09

Table 11: Fits to experimental data from various schemes. k_2 has units of 10^{-10} cm^3 molecule^{-1} s^{-1}.

< 0.88. Cvetanović [25] quoted slightly different values for k_{3O}, k_{4O}, k_{5O}. The results are shown in the last column of Table 11.

The results of the previous Section would suggest that k_2 from a simple–scheme analysis of experimental data (Appendix J) are 0–8% too high, and should be reduced accordingly. k(H+A, 291 K, 600 Torr) seems very large; no clear reason can be suggested for this one result.

7.4.4 Conclusion

The use of an extended mechanism, incorporating all reactions between primary photolysis products, demonstrated that only small errors are introduced by using an analysis based on the simple scheme. The simple scheme results may be readily corrected and the corrections are relatively insensitive to $[X]_0$. Thus the rate constants of § 7.3 and Appendix J should be reduced slightly to allow for side–reactions. The uncorrected results of Appendix J were reduced by 5% for the H+A results and 6% for the O+A results, and are presented in Table 12.

When combined with the low–pressure data of Gutman and co–workers, it

T/K	P/Torr	H or O	N	k_2
291	98	H	33	2.5±0.2
291	200	H	45	1.4±0.1
291	300	H	19	3.8±0.2
291	400	H	46	3.6±0.1
291	600	H	42	7.0±0.2
285	48-348	O	67	2.2±0.1
402	49-292	O	45	1.7±0.2
500	50-200	O	168	2.4±0.1

Table 12: Recommended values of k(atom+allyl). N experiments were combined to yield each rate constant. k_2 has units of 10^{-10} cm^3 molecule^{-1} s^{-1}.

was inferred [7] that the only significant reaction channel of the O+A reaction is:

$$O+C_3H_5 \quad \longrightarrow \quad H+CH_2{=}CHCH{=}O$$

7.5 CALCULATION OF k_{H+A}

7.5.1 Calculation of k_d (C_3H_6)

Troe *et al.* [9–12] discussed the factorization of a pressure–dependent rate constant to allow for the effects of strong and weak collisions. Chapter 5 describes their approach in greater detail. In the Troe factorization, the rate constant k_{2H} is given by

$$\frac{k_{2H}}{k_{2H}^{\infty}} = \frac{F(k_{2H}^{0}[\mathrm{M}]/k_{2H}^{\infty})}{1 + (k_{2H}^{0}[\mathrm{M}]/k_{2H}^{\infty})}$$

where the limiting low–pressure rate constant for dissociation, k_d^0, was estimated from Troe ([12] and Appendix L): k_d^0(291 K, He) = 3.69×10^{-60} cm^3 molecule^{-1} s^{-1}.

7.5.2 Calculation of k_{H+A}

k_{2H}^0 is related to k_d^0:

$$\begin{aligned} k_{2H}^{0} &= k_d^0/K_c \\ K_c &= RT\ (K_p/\mathrm{atm}^{-1}) \\ &= RT\exp(-\Delta G_T^0/RT) \end{aligned}$$

where K_p is the equilibrium constant in terms of pressure for a standard state of 1 atm, and ΔG^0 is defined for the same standard state. Literature enthalpy and entropy values were used to calculate ΔG_{298}^0 = 26144 cm^{-1}, which was used as $\simeq \Delta G_{291}^0$. Thus K_c = 3.770×10^{-36} molecule cm^{-3}, and k_{2H}^0 = 9.79×10^{-25} cm^6 molecule^{-2} s^{-1}. k_{2H}^{∞} was estimated, from the experimental results at highest pressures, as 4×10^{-10} cm^3 molecule^{-1} s^{-1}.

The number of oscillators that affect reaction, S_K, can only be calculated exactly if all frequencies are known for the transition state. Troe gives an approximate expression:

$$S_K = \Delta s + E_{T,vib}^0/k_B T$$

where $E^0_{T,vib}$ is the mean thermal vibrational energy of the stable molecule C_3H_6 (not the transition state, $C_3H_6^{\ddagger}$) at temperature T, and Δs is a correction, which depends on the system being studied ($1 \leq \Delta s \leq 2$). If $E^0_{T,vib}$ were calculated from transition state frequencies, Δs would equal 1. From the formulae in Chapter 5, $F_{cent} = 0.664$ or 0.505 ($\Delta s = 1$ or 2).

At a typical experimental pressure (300 Torr) $k^0_{2H}[\mathrm{He}] \simeq 24000 k^{\infty}_{2H}$. For the H+$C_2H_4$ system of Chapter 5, $k^0_{2H}[\mathrm{He}] \simeq 2k^{\infty}_{2H}$ at typical experimental temperatures and pressures (300 Torr, 800 K). Thus experimental measurements for H+C_3H_5 are nearer the high–pressure limit, and less pressure dependence is seen, than for H+C_2H_4. For either value of Δs, $k_{2H} \geq 0.98 k^{\infty}_{2H}$ at all experimental pressures.

7.6 CONCLUSION

The rate constants for the reactions of H and O with allyl have been measured for $286 \leq T/\mathrm{K} \leq 500$, $48 \leq P/\mathrm{Torr} \leq 600$ by laser flash photolysis of C_6H_{10}–N_2O–bath gas mixtures. The atomic species and allyl were monitored by time–resolved resonance fluorescence and absorption respectively: traces were corrected for experimental distortion caused by scattered laser light or radio frequency interference. Fluorescence intensity and absorbance were fitted to a simple kinetic scheme. The inclusion of side–reactions among the primary photolysis products made little difference to the fitted values presented in Table 12. From this work, k(O+allyl) = $(2.0 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

A Troe factorization of k(H+allyl) showed that the reaction should not be pressure–dependent for $98 \leq P/\mathrm{Torr} \leq 600$, in disagreement with experimental re-

sults. The apparent pressure–dependence of the rate constant may be due to other side–reactions, not considered in this simple analysis.

7.7 REFERENCES

[1] R.D.Wilk, N.P.Cernansky, W.J.Pitz, C.K.Westbrook *Combust.Flame* **77** 145 (1989)

[2] D.Edelson, D.L.Allara *Int.J.Chem.Kin.* **12** 605 (1980)

[3] J.Warnatz, *18th Int.Symp.Comb.* 369 (1981)

[4] M.Narożnik, J.Niedzielski *J.Photochem.* **32** 281 (1986)

[5] C.K.Westbrook, W.J.Pitz *Combust.Sci.Technol.* **37** 117 (1984)

[6] J.M.Tulloch, M.T.Macpherson, C.A.Morgan, M.J.Pilling *J.Phys.Chem.* **86** 3812 (1982)

[7] I.R. Slagle, J.R. Bernhardt, D. Gutman, M.A. Hanning–Lee, M.J. Pilling *J.Phys.Chem.* **94** 3652 (1990)

[8] N.Nakashima, K.Yoshihara *Laser Chem.* **7** 177 (1987)

[9] J.Troe *Ber.Bunsenges.Phys.Chem.* **87** 161 (1983)

[10] R.G.Gilbert, K.Luther, J.Troe *Ber.Bunsenges.Phys.Chem.* **87** 169 (1983)

[11] J.Troe *J.Chem.Phys.* **66** 4745 (1977)

[12] J.Troe *J.Chem.Phys.* **66** 4758 (1977)

[13] K.Schofield *J.Photochem.* **9** 55 (1978)

[14] D.Gutman *et al.*, private communication (1988)

[15] D.Clark Part II Thesis, Oxford University (1988)

[16] H.E.van den Bergh, A.B.Callear *Trans.Farad.Soc.* **66** 2681 (1970)

[17] F.E.Blacet, W.G.Young, J.G.Roof *J.Am.Chem.Soc.* **59** 608 (1937)

[18] T.Ohta *J.Phys.Chem.* **87** 1209 (1983)

[19] G.W.Harris, J.N.Pitts *J.Chem.Phys.* **77** 3994 (1982)

[20] R.Atkinson, J.N.Pitts *J.Chem.Phys.* **67** 38 (1977)

[21] FACSIMILE: A.R.Curtis, W.P.Sweetenham "Release H User's Manual", Report AERE–R 11771, AERE Harwell (October 1985)

[22] D. Baulch, R.A. Cox, Th. Just, J.A. Kerr, M.J. Pilling, J. Troe, J. Warnatz, R.W. Walker, P.Frank submitted to *J.Phys.Chem.Ref.Data.*

[23] J.Warnatz in "Combustion Chemistry", ed. W.C.Gardiner (1984)

[24] D.L.Allara, R.Shaw *J.Phys.Chem.Ref.Data* **9** 523 (1980)

[25] R.J.Cvetanović *J.Phys.Chem.Ref.Data* **16** 261 (1987)

[26] J.Chao, B.J.Zwolinski *J.Phys.Chem.Ref.Data* **4** 251 (1975)

[27] S.W.Benson "Thermochemical Kinetics" 2nd Ed. Wiley–Interscience (1976)

[28] T.Takada, M.Dupuis *J.Am.Chem.Soc.* **105** 1713 (1983)

[29] C.F.Melius, private communication (1986)

[30] L.Wołniewicz *J.Chem.Phys.* **78** 6173 (1983)

Chapter 8

RATE COEFFICIENTS FOR THE H + C_2H_2 = C_2H_3 REACTIONS

8.1 INTRODUCTION

8.1.1 Previous work

Ethane is a major feedstock for the chemical industry. Homogeneous gas–phase pyrolysis (cracking) produces ethene as a major product, at temperatures approaching 1200 K, and ethane conversions of up to 90%. For this relatively simple system, global kinetic models have been used to simulate the cracking process (Chapter 5). All important reactions should be well–characterized at these conditions.

In cracking and combustion, larger radicals decompose rapidly. For hydro-

carbon species, only reactions of C_iH_j ($i \leq 3$) are rate–determining. Lightfoot [1] simulated high–conversion cracking and Cathonnet *et al.* [2] simulated fuel–rich combustion; both groups showed that the rate constants for the pressure–dependent reactions

$$H + C_2H_2 \underset{k_d}{\overset{k_{rec}}{\rightleftharpoons}} C_2H_3$$

influence the overall rate of reaction. For accurate modelling of the complex chemical systems found in industry, rate constants are needed for these reactions at high temperatures and at near–atmospheric pressures.

Below 700 K, dissociation of C_2H_3 is negligible, i.e. $k_d \simeq 0$. k_{rec} has been studied experimentally and theoretically at near–ambient temperatures. The limiting high–pressure rate constant, k_{rec}^{∞}, was measured over 300–400 K [3], 206–461 K [4], and 298–473 K [5].

At rather lower temperatures, others have investigated the dependence of k_{rec} on pressure. Payne *et al.* [6] used flash photolysis of C_2H_2–He mixtures to produce H, which was detected by real–time resonance fluorescence at 121.6 nm. They obtained fall–off curves for k_{rec} over the range 193–400 K and 10–700 Torr He. Keil *et al.* [7] covered the ranges 1–742 Torr, 298–306 K using two methods. At high pressures, Hg sensitized the photo–decomposition of H_2 in a static Hg–H_2–C_2H_2–He mixture; H was detected by resonance absorption. At low pressure (1–8 Torr), they used a discharge flow system. A hot filament dissociated H_2, and H was detected by mass spectrometry. Kowari *et al.* [8] produced H by pulse radiolysis of C_2H_2–He mixtures, and detected H by time–resolved resonance absorption. k_{rec} was thus determined at 300 K, 100–800 Torr. At such temperatures and near–

atmospheric pressures, k_{rec} is near the high–pressure limit, e.g. k_{rec}(400 K, 200 Torr He) $\simeq 0.8 k_{rec}^{\infty}$.

Transition state theory calculations have also been performed. Harding *et al.* [9] fitted experimental data with a 10 kJ mol^{-1} addition barrier, and a transmission coefficient κ of only $\simeq$0.1. Calculated values, of $\geq$26 kJ mol^{-1} and $\simeq$1 respectively, overestimated k_{rec}^{∞} by a factor of $\simeq$10 near ambient temperatures, mainly because the large value of κ caused a large Arrhenius A–factor to be derived. Nagase *et al.* [10] calculated that the transition state for addition was early and loose, with a *trans* geometry and a similar, unrealistically high addition barrier.

At very high temperatures, H abstraction (H + $C_2H_2 \longrightarrow C_2H + H_2$) can become significant. The literature rate constant [11] is

$$k = 10^{-10} \exp(-14000 \text{ K}/T)$$

cm^3 molecule^{-1} s^{-1}, so abstraction will be negligible even at 1200 K. Nagase *et al.* [10] postulated a linear, late, and tight transition state, with a high activation energy.

Rate constants may be calculated if accurate thermodynamic parameters are available for all species (Chapter 5). However, estimates of the standard enthalpy of formation of C_2H_3 at 298 K, $\Delta H^0_{f,298}(C_2H_3)$, range from 249 to 329 kJ mol^{-1} (Table 7). At 1200 K, rate constants so calculated will differ by a factor of 3050. This Chapter presents an attempt to resolve this controversy, using direct simultaneous measurements of k_{rec} and k_d at 845 K.

Some studies have been made of the pressure–dependence of k_{rec}. The literature [11] gives Troe factorization parameters for 200$\leq T/\text{K} \leq$400. Tsang

et al. [12] extrapolated lower–temperature measurements to cover the range 700≤ T/K≤2500, but such long extrapolations are often unreliable.

Experimental rates for H formation and loss may include contributions from side reactions among other species present. This Chapter examines this possibility further, and aims

- To determine k_{rec} and k_d directly at temperatures and pressures approaching those encountered commercially.
- To combine k_{rec} and k_d, derived from measurements under equilibrating conditions, to yield the equilibrium constant K and $\Delta H^0_{f,298}(C_2H_3)$.

8.1.2 Outline of Chapter

§ 8.2 describes the measurement of [H] by time–resolved resonance fluorescence, following 193.3 nm laser flash photolysis of C_2H_2 at 298 K, 600 K, and 845 K, in 50–600 Torr He.

At 298 K and 600 K, C_2H_3 dissociation is negligible. § 8.3 describes the mechanism to which the data traces were fitted, and the fitting procedure.

At 845 K, equilibration of H + C_2H_2 with C_2H_3 was observed; k_{rec}, k_d, and K were determined as described in § 8.4. § 8.4.3 presents literature values of rate constants for reactions among the photolysis precursor (C_2H_2), its primary photoproducts (H and C_2H), C_2H_3, and the main third body (He); radical–radical reactions appear not to affect k_{rec} or k_d when measured under the conditions of this work. § 8.5 combines K with other information to obtain $\Delta H^0_{f,298}(C_2H_3)$; the result is compared to literature values.

8.1.3 Glossary

Symbol	Meaning
k_{rec}	rate constant for H + $C_2H_2 \longrightarrow C_2H_3$
k_d	rate constant for $C_2H_3 \longrightarrow$ H + C_2H_2
escape	removal of radical species by diffusion and pump–out
k_2	pseudo–first–order rate constant for escape of H
k_3	pseudo–first–order rate constant for escape of C_2H_3
$-\lambda_{\pm}$	slow and fast time constants for loss of H or C_2H_3
I	fluorescence intensity from H
E_l	energy of photolysis laser pulse

8.2 THE EXPERIMENT

8.2.1 Ethyne photolysis

C_2H_2 is readily photolysed by ultraviolet radiation to yield a variety of excited and ground state products. Photolysis is discussed at several different wavelengths, corresponding to those of available exciplex laser transitions, and to the wavelength used to monitor H in this experiment.

At 222 nm, Herzberg [13] assigned the absorbing transition to $^1A_u \longleftarrow \tilde{X}\,^1\Sigma_g^+$. The absorption cross–section is small, and the photon energy can only generate ground state $C_2H(X^2\Sigma^+)$ + H(^{2}S).

For the kinetic study described in this Chapter, an exciplex laser operating in normal longitudinal multimode produced the photolysis pulse, with output over the range 193.3±0.1 nm. The pulse had a FWHM of 10 ns [14]. Typically, an

energy of 80 mJ was incident on a cross–sectional area of 1 cm^2, corresponding to 8×10^{24} photons cm^2 s^{-1}. The pulse was not focussed, so multi–photon processes were improbable; thus Wodtke *et al.* [15] needed intensities a factor of ten higher than used in this work for C_2H to be photolysed to C_2 + H during the laser pulse. They did not observe true two–photon production of C_2 + H_2, C_2 + 2H, or CH + CH.

At 193.3 nm, Wu *et al.* [16] measured σ (295 K) $\simeq 7\times10^{-20}$ cm^2 $molecule^{-1}$ for single–photon absorption. C_2H_2 is produced in the ^1B_u state [13] or in the ^1A_u state [17]. Wu *et al.* considered that energetically allowed products would include H + $C_2H(X^2\Sigma^+, A^2\Pi)$; Wodtke *et al.* considered one–photon production of C_2 + H_2 to be unlikely. It is possible that singlet C_2H_2 may undergo intersystem crossing to produce triplet C_2H_2 or H_2CC (vinylidene).

Fletcher *et al.* [17] studied emission from $C_2H(A^2\Pi)$ produced by 193.3 nm C_2H_2 photolysis; molecules in this excited state entered the ground state by intersystem crossing. Kanamori *et al.* [18] found that nascent C_2H is too vibrationally excited for the ν_3 band to be detected in absorption: several polyatomic species quenched C_2H efficiently, but He did not. Under the conditions of the present study (50 Torr He), C_2H was electronically and vibrationally relaxed by the time kinetic observation started ($\geq$2 ms).

Thus the 193.3 nm photolysis of ethyne was a complex process. Wu *et al.* observed a more diffuse (but still structured) spectrum as the temperature was increased from 155 K to 295 K. The yield of H depended on the cross–section, and would thus have a complex temperature–dependence. For this work, it was assumed that σ would not vary over the range $295\leq T/K\leq845$. Following Appendix I, $[H]_0$ was $\simeq$0.003 $[C_2H_2]$.

Ethyne absorbs more strongly at 121.63 nm, the wavelength at which H was monitored ($\sigma = 2\times10^{-17}$ cm^2 molecule^{-1} [19]). Since the fluorescence quantum yield is only $\simeq$0.05, most excited C_2H_2 would react, with a chemistry even more complex than at 193.3 nm. Thus Fahr *et al.* [20] prepared triplet vinylidene, $H_2CC(^3B_2)$, in good yield by 147 nm irradiation of ethyne. They estimated the threshold wavelength to be 136 nm for production of C + CH_2 in their electronic ground states. An appreciable amount of ethyne may be excited, dissociated, or isomerized by the resonance lamp beam, which might have had an intensity of 10^{14} photons s^{-1} [21]. Calculations similar to those in Appendix I show that C_2H_2 would absorb at the rate of 5×10^{11} molecule cm^{-3} s^{-1} throughout the length of the beam, but photolysis products would be pumped out steadily.

It may be seen that 193.3 nm photolysis of ethyne with 121.6 nm H detection was not ideal for isolation of the reactions H + $C_2H_2 \rightleftharpoons C_2H_3$. Chapter 2 attempts to identify a better H precursor, but few are suitable. Use of more sensitive H detection (Chapter 2) might enable use of lower $[H]_0$, so reducing the extent of radical–radical reactions. Use of a precursor other than ethyne would allow $[H]_0$ and $[C_2H_2]$ to be varied independently.

8.2.2 Procedure and materials

Chapter 2 describes the experimental procedure at greater length. Pre–mixed C_2H_2–He was further diluted with He and flowed slowly through the stainless steel reaction cell, which was maintained at the required temperature. At all temperatures, the yield of H from 193.3 nm photolysis of C_2H_2 was high enough to obviate use of N_2O–H_2 as an H source. H was monitored by resonance fluorescence

in real time. The good H signal meant that separate traces to record the laser light distortion were unnecessary. Amplifier loads ranged from 5–100 kΩ. After each laser shot, H was monitored for 32 or 80 ms, and 250–1000 shots were summed to give adequate signal : noise. The C_2H_2 concentration covered a range of (0.97–36.3)$\times 10^{14}$ molecule cm^{-3}, and laser pulse energies ranged from 9.5–115 mJ.

To analyse traces recorded under equilibrating conditions, the rate constant, k_2, for H atom escape was needed. Values were taken from Brouard [22] or Chapter 5, and extrapolated to higher temperatures as described in § 8.4.2.

Gases were supplied with the following purities (from the manufacturer's analysis): He (BOC CP grade, 99.999%, 2 ppm each Ne, N_2); H_2 (BOC CP grade, 99.9995%, 5 ppm N_2, 2 ppm H_2O, 1 ppm O_2); N_2O (BDH, 99.6%, impurities not stated); C_2H_2 (BOC Industrial Gases, $\geq$98.5% minimum, variable acetone and some air, S and P compounds <15 vpm). N_2O was distilled at least three times from and to liquid N_2, discarding the most volatile fractions (entrained air) and least volatile (entrained H_2O) each time.

The handling of ethyne posed several problems. C_2H_2 adsorbed strongly on glass, so the preparation line used to mix C_2H_2–He bulbs had to be wrapped in electrical heating tape to pump down below 10^{-4} Torr before use. Pure C_2H_2 is explosive [23], so was only available commercially in solution in acetone. Copper and some brass fittings could not be used, since explosive Cu_2C_2 could form [23]. Passage through an ice–salt bath (250 K) removed acetone. C_2H_2 was then distilled from liquid N_2 to solid CO_2–acetone (195 K), to avoid the build–up of large C_2H_2 pressures. The most volatile (C_2H_4, entrained air) and least volatile (acetone, water) fractions were discarded.

8.3 $H + C_2H_2 \longrightarrow C_2H_3$

At 298 K and 600 K, thermal dissociation of C_2H_3 was negligible, so k_d was neglected when analysing kinetic data gathered at these temperatures. $k_d^\infty < 0.7$ s^{-1} for $T \leq$600 K [11].

8.3.1 Data analysis

A simple kinetic scheme was chosen to model the time–dependence of [H]:

$$\begin{aligned} C_2H_2 &\xrightarrow{h\nu} H + C_2H \quad (t=0) \\ H + C_2H_2 &\longrightarrow C_2H_3 \quad k_{rec} \\ H &\longrightarrow \text{escape} \quad k_2 \end{aligned}$$

where a first–order model (Chapter 3) was used for escape — loss from the observation volume by diffusion and pump–out. The scheme implies:

$$\begin{aligned} \frac{d}{dt}\ln[H] &= -k'_H \\ k'_H &= k'_{rec} + k_2 \\ k'_{rec} &= k_{rec}[C_2H_2] \end{aligned} \tag{8.1}$$

where k'_H was the total first–order rate constant for loss of H, and k'_{rec} was a pseudo–first–order rate constant. Thus

$$[H]_t = [H]_0 \exp(-k'_H t)$$

where $[H] = [H]_0$ at zero time. The fluorescence intensity, I, was assumed proportional to [H]. At $t = 0$, $I = I_0$, and

$$I_t = I_0 \exp(-k'_H t) \tag{8.2}$$

Each decay trace of H fluorescence was fitted to the above equation, using the Marquardt algorithm for non–linear least squares fitting (Chapter 2). I_0 and k'_H were floated, using analytic parameter derivatives. Chapter 2 discusses the possible covariance of fitted k'_H and I_0.

To remove a possible effect of radical–radical reactions on measured rate constants, experiments were conducted at various laser energies, and k'_H was extrapolated to zero energy. Brouard *et al.* [24] used this procedure for the H + C_2H_4 system.

The zero–energy value of k'_H was plotted against $[C_2H_2]$. In the absence of side–reactions, the gradient should have been k_{rec}, as seen from Equation 8.1. From this approach, k_{rec}(298 K, 200 Torr He) = 8.1×10^{-14} cm^3 molecule^{-1} s^{-1}; Payne *et al.* [6] quoted $k_{rec} = 1.3\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at the same conditions. The disagreement was considered unacceptable, and a new approach was used.

To fix the extent of side–reactions, $[H]_0$ was held constant by fixing the product of laser pulse energy, E_l, and $[C_2H_2]$. A series of experiments was performed at different $[C_2H_2]$, and E_l was changed to ensure that $[H]_0$ was approximately constant. k_{rec} was taken to be the gradient of a plot of k'_H against $[C_2H_2]$.

Results are presented in Table 1: k_{rec}(298 K, 200 Torr) depends appreciably on $[H]_0$. For comparison, literature values are also shown. Agreement is encouragingly close, especially at 600 K. The ordinate intercept should have been k_2, and should have decreased with rising pressure (Chapter 3); no such trend was

apparent from these preliminary results.

8.4 EQUILIBRATION STUDIES

At 845 K, C_2H_3 was expected to dissociate at appreciable rates, and the kinetic scheme was modified accordingly.

8.4.1 Data analysis

The scheme now allowed for the loss of C_2H_3 by dissociation and escape, with rate constants k_d and k_3:

$$\begin{aligned}
C_2H_2 &\xrightarrow{h\nu} H + C_2H \qquad (t = 0)\\
H + C_2H_2 &\longrightarrow C_2H_3 \qquad k_{rec}\\
C_2H_3 &\longrightarrow H + C_2H_2 \qquad k_d\\
H &\longrightarrow \text{escape} \qquad k_2\\
C_2H_3 &\longrightarrow \text{escape} \qquad k_3
\end{aligned}$$

At 845 K, thermal dissociation of C_2H is negligibly slow. By analogy with Chapter 5, it was assumed that at zero time $[H] = [H]_0$ and $[C_2H_3] = 0$, and that the fluorescence intensity $(I) \propto [H]$. I was given by

$$\begin{aligned}
I_t &= I_+ \exp(\lambda_+ t) + I_- \exp(\lambda_- t)\\
I_\pm &= \frac{\mp I_0(k'_H + \lambda_\mp)}{\lambda_+ - \lambda_-}
\end{aligned}$$

Each decay trace of H fluorescence was fitted to the above equation. Chapter 5 details the procedures used to test the fitting program and to fit experimental data.

Files	T/K	P	N	$[H]_0$	k_{rec}	k_{rec} [6]	k_{rec} [11]	Int.	k_2
73–79	298	100	6	1.8	6.82	10.6	8.0	94.8	
65–72	298	200	8	1.0	6.52	13.0	10.2	62.5	
43–55	298	200	12	1.8	7.47	13.0	10.2	96.6	
56–64	298	200	8	4.0	8.19	13.0	10.2	98.5	
186–200	600	50	13	3.2	24.3		23.7	246	189
142–156	600	100	15	3.2	43.4		33.2	168	106
127–141	600	200	14	3.2	46.1		47.2	205	65
157–170,	600	300	29	3.2	46.4		58.0	254	51
215–229									
171–185	600	400	15	3.2	61.5		66.5	253	44
201–214	600	600	13	3.2	68.2		78.7	287	37

Table 1: Values of k_{rec} (298 K and 600 K). Filenames begin with MHAC. N experimental results were combined to produce each value of $k_{rec}(T, P)$. Units: P/Torr, $[H]_0/10^{10}$ cm^{-3}, $k_{rec}/10^{-14}$ cm^3 molecule^{-1} s^{-1}. Int. = ordinate intercept/s^{-1} of a plot of k_{rec} against $[C_2H_2]$. $[H]_0$ was estimated (see text). k_2/s^{-1} was evaluated from Table 1 of Chapter 3 (H in He, 600 K). Errors: experimental ±5%, ±10% [6], and factor of 2 [11].

8.4.2 Input data and results

Chapter 5 describes the measurement of the escape rate constant, k_2, and the calculation of k_3 for the H–C_2H_4–C_2H_5 system. For these experiments in He, k_2 was at first based on an extrapolation of the measurements of Brouard [22] to 845 K. k_2 was measured for the H + C_2H_4 work of Chapter 5 with the same collimator layout as used in this work. The pressure–dependent term was ascribed to diffusion, with a $T^{1.72}$ dependence (Chapter 3). The pressure–independent term was assumed to be caused by pump–out, with a rate $\propto T$. With the corrected expression,

$$k_2(845\text{ K, He})/\text{ s}^{-1} = (32 \pm 18) + \frac{19000 \pm 1700\text{ Torr}}{P}$$

and new, more appropriate, values of k_2 were calculated. k_2(100 Torr) increased from 131 to 222 s^{-1}, and k_2(200 Torr) from 78 to 127 s^{-1}.

k_3, the rate constant for escape of C_2H_3, was set to 10 s^{-1} for all temperatures and pressures. A more realistic estimate would include the 32 s^{-1} pressure–independent term of k_2, and a pressure–dependent term of $\simeq$20 s^{-1} (reduced to allow for the slower diffusion of C_2H_3 compared to H). Hence k_3 might be more accurately estimated at 50 s^{-1}, but values of k_{rec} and k_d were only feebly dependent on k_3.

k'_{rec} was extrapolated to $E_l = 0$ and plotted against C_2H_2 to obtain k_{rec}. To remove any possible effect of side–reactions, k_d was extrapolated to $[C_2H_2] = 0$. Tables 2 and 3 present the input values of k_2 and k_3 with the results for k_{rec} and k_d, together with

P	Filenames	N	$[C_2H_2]$	E_l	k_2	k_3
100	95–101, 114–116	10	1.92–9.52	19–110	131	10
200	102–113	12	2.95–12.2	26–115	78	10
200	117–123	7	4.75–12.3	32–113	78	10

Table 2: Conditions to fit k_{rec} and k_d (845 K, He). k_2 and k_3 were fixed in analysis. N traces were combined to yield values of k_{rec} and k_d. Units: P/Torr, $[C_2H_2]/10^{14}$ molecule cm^{-3}, E_l/mJ, k_2/s^{-1}, k_3/s^{-1}.

$$\begin{aligned} K_p &= \frac{[C_2H_3]}{[H][C_2H_2]} \\ &= \frac{k_{rec}}{k_d RT} \end{aligned}$$

since $K = (K_p/\text{atm}^{-1})$ for a standard state of 1 atm pressure. The error in K neglected any covariance between k_{rec} and k_d (Chapter 2). Values of K from the literature [11] depended weakly on pressure, perhaps due to incorrect Troe parameters for the rate constants.

8.4.3 Radical–radical reactions

Some early workers used large $[H]_0 : [C_2H_2]$ ratios; since C_2H_3 rapidly consumed H (Table 4), the rate of removal of H atoms exceeded that due solely to the H + C_2H_2 reaction. Their measured values of k_{rec} had to be divided by a stoichiometry factor between 1 and 2. In this work, $[H]_0 \ll [C_2H_2]$, so no such factor was needed.

C_2H_2 was photolysed to H and C_2H. Addition of H to C_2H_2 produced C_2H_3,

P	N	k_{rec}	k_d	ln (K_p/atm^{-1})	k_{rec} [11]	k_d [11]	ln (K_p/atm^{-1})
100	10	11.9	24.6	10.64	46.72	115.8	10.46
200	12	21.2	11.1	12.01	65.44	212.7	10.19
200	7	27.3	22.0	11.58	65.44	212.7	10.19

Table 3: Experimental and literature k_{rec} and k_d (845 K, He). Units: P/Torr, $k_{rec}/10^{-14}$ cm^3 molecule^{-1} s^{-1}, k_d/s^{-1}.

and recombination and dissociation reactions occurred, with He as the main third body. Thus, all possible reactions among the set of species {H, C_2H, C_2H_2, C_2H_3, and He} were considered. Table 4 presents literature values for the rate constants at typical experimental conditions (845 K, 200 Torr He, and $[C_2H_2] = 10^{15}$ molecule cm^{-3}). Reactions of C_2, and of all C_4 species, were neglected for this simple mechanism.

Pseudo–first–order rate constants are also presented. Concentrations of radical species were calculated at 0.04 s (the middle of an experimental decay trace) by the numerical integration package FACSIMILE [25]. $[H]_0$ was assumed to be $\approx 2\times10^{10}$ cm^{-3}, but this value would depend on the value of $\sigma(C_2H_2)$ used (§ 8.2.1). In a worst case, $[H]_0 = 2\times10^{11}$ cm^{-3}, and concentrations at 0.04 s would then be: $[H] = 2.2\times10^{10}$ cm^{-3}, $[C_2H] = 2676$ molecule cm^{-3}, and $[C_2H_3] = 9.1\times10^{10}$ molecule cm^{-3}.

Pseudo–first–order rate constants refer to the rate of removal of the first–named species by all other reactants in the rate equation: thus H is removed by addition to C_2H_2 with a time constant of 670 s^{-1}.

From the rate constants, the reaction H+H+He is insignificant. At 845 K,

Reaction	k	k'/s^{-1}	Reference
$H + H \longrightarrow H_2$	5×10^{-15}	1×10^{-4}	[11] (for M=Ar)
$H + C_2H \longrightarrow C_2H_2$	2×10^{-11}	5×10^{-8}	T
$H + C_2H \longrightarrow C_2 + H_2$	0	0	assumed
$H + C_2H_2 \longrightarrow C_2H_3$	6.7×10^{-13}	670	[11]
$H + C_2H_2 \longrightarrow C_2H + H_2$	6×10^{-18}	0.006	[11]
$H + C_2H_3 \longrightarrow C_2H_4$	10^{-15}	9×10^{-5}	estimated
$H + C_2H_3 \longrightarrow C_2H_2 + H_2$	2×10^{-11}	1.8	[11]
$H \longrightarrow$ escape	78	78	§ 8.4.2
$C_2H + C_2H \longrightarrow C_4H + H$	3×10^{-11}	8×10^{-8}	T
$C_2H + C_2H \longrightarrow$ other products	3×10^{-12}	8×10^{-9}	T
$C_2H + C_2H_2 \longrightarrow C_4H_2 + H$	5×10^{-11}	50000	[11]
$C_2H + C_2H_3 \longrightarrow C_4H_3 + H$	3×10^{-11}	2.7	T
$C_2H + C_2H_3 \longrightarrow$ other products	2×10^{-12}	0.18	T
$C_2H \longrightarrow C_2 + H$	0	0	assumed
$C_2H_2 + C_2H_2 \longrightarrow C_4H_3 + H$	2×10^{-34}	2×10^{-19}	T
$C_2H_2 + C_2H_3 \longrightarrow C_4H_4 + H$	9×10^{-18}	8×10^{-7}	[26]
$C_2H_2 \longrightarrow C_2H + H$	2×10^{-18}	2×10^{-18}	T
$C_2H_3 + C_2H_3 \longrightarrow C_4H_5 + H$	2×10^{-13}	0.018	T
$C_2H_3 + C_2H_3 \longrightarrow$ other products	2×10^{-11}	1.8	T
$C_2H_3 \longrightarrow C_2H_2 + H$	177	177	[11]
$C_2H_3 \longrightarrow$ escape	10	10	§ 8.4.2

Table 4: Rate constants at 845 K and 200 Torr He. The units are cm, molecule, s. "T" denotes an estimate from Tsang *et al.* [12], assuming that He has a collisional efficiency one quarter that of N_2.

the reaction $H+C_2H_2 \longrightarrow C_2H+H_2$ may be neglected, as may the thermal dissociation of C_2H and C_2H_2, and disproportionation of C_2H_2. The generation of H from $C_2H+C_2H_2$ is complete long before H observation begins, and should not interfere with the kinetics. From this cursory analysis, radical–radical reactions appear to contribute little to H decay, so it is unclear why the experimental k_{rec} and k_d are so much smaller than the literature values (Table 4). Errors in the rate constants for H or C_2H_3 escape seem inadequate to explain this discrepancy. Some errors may be caused by the presence of C_2H_2 or H_2CC in excited triplet states.

8.4.4 Conclusion

Ethyne was photolysed at 193.3 nm to produce H; photolysis may have produced many different species. H was detected by resonance fluorescence to measure k_{rec} and k_d directly. Preliminary results depend appreciably on $[H]_0$, perhaps due to side–reactions not considered in the simple scheme above. Further experiments and a more sophisticated kinetic analysis may isolate more accurate values of k_{rec} and k_d.

Photolysis of a different H precursor at a longer wavelength would reduce interference from side–reactions, since C_2H and excited C_2H_2 would not be generated. Choice of such a precursor appears to be difficult. Use of more sensitive H detection might enable use of a lower laser energy, so producing a lower $[H]_0$ and reduce mechanistic complications.

8.5 THE STANDARD ENTHALPY OF FORMATION OF C_2H_3

8.5.1 Introduction

For the H+C_2H_2⇌C_2H_3 system, estimates of the standard enthalpy of formation of C_2H_3, $\Delta H^0_{f,298}(C_2H_3)$, span a range of 249–329 kJ mol^{-1} (Table 7). Calculated rate constants would differ by a factor of 3050 at the temperature used for ethane cracking (≃1200 K). § 8.4 describes preliminary simultaneous measurements of the rate constants for

$$H + C_2H_2 \underset{k_d}{\overset{k_{rec}}{\rightleftharpoons}} C_2H_3$$

at 845 K in 100 or 200 Torr of He, from which the equilibrium constant, K, was calculated. The Master Equation calculations of Chapter 6 validate use of data gathered under reversible conditions to calculate an equilibrium constant.

In this Section, $\Delta H^0_{f,298}(C_2H_3)$ will be calculated from K, in an analysis which closely follows that of Chapter 5 for the H + C_2H_4⇌C_2H_5 system. The standard enthalpy of reaction at 298 K was taken from Equation (II) of [24]:

$$\frac{\Delta H^0_{298}}{T} = \Delta S^0_{298} - R\ln K + \int_{298}^{T} \Delta C^0_p \, d\ln T' - \frac{1}{T}\int_{298}^{T} \Delta C^0_p \, dT' \qquad (8.3)$$

Table 5 summarizes the data. For H + C_2H_2⇌C_2H_3, it should be noted that:

- Rotations were assumed to be at their high–temperature limits. This approximation was least valid when (k_BT/hcB) is smallest. Even for the lowest

temperature used (298 K) and largest rotational constant (C_2H_3, $A = 5.33$ cm^{-1}), $(k_BT/hcA) = 39$. This large value showed that the approximation was good.

- No species had an internal rotor.
- In calculating the entropy and enthalpy of reaction, the spin degeneracies of H and C_2H_3 cancelled.
- No species had an electronically excited state with significant thermal population at 845 K. In C_2H_3, the lowest electronically excited state ($^2A''$) lay at 17911 cm^{-1} [27]. The lowest excited state of C_2H_2 was *cis*–$^3B_2$, at 27665 cm^{-1}. If C_2H_2 isomerized to vinylidene (H_2CC), the lowest state of the latter would lie at 13853 cm^{-1} [28]. The H(1^2P) state lay at 82264 cm^{-1} [29].
- Most C_2H_3 frequencies had not been measured, so the calculated values of Harding *et al.* [9] were used instead.

8.5.2 Standard entropy of reaction

The standard entropy of reaction was

$$\Delta S^0_{298} = S^0_{298}(C_2H_3) - S^0_{298}(C_2H_2) - S^0_{298}(H)$$

Each degree of freedom contributed to S^0_T/R as follows:

translation	$\ln\left[P^{-1}(ek_BT)^{2.5}\left(2\pi uM_R/h^2\right)^{1.5}\right]$
rotation, C_2H_2	$1 + \ln\left(k_BT/hcB\sigma\right)$
rotation, C_2H_3	$1.5 + 1.5\ln\left[\sigma^{-1}\sqrt{\pi/ABC}\left(k_BT/hc\right)^{1.5}\right]$
vibration	$\sum_L \frac{x_L \exp(-x_L)}{1-\exp(-x_L)} - \ln[1-\exp(-x_L)]$

Chapter 5 identifies all symbols used. The components of $\Delta S^0_{298}/R$ had the following values: translational -13.02, rotational 8.33, vibrational -5.05. Thus $\Delta S^0_{298} = -80.94$ J mol^{-1} K^{-1}.

8.5.3 Change in molar heat capacity

Each degree of freedom contributed as follows to C^0_v, the molar heat capacity at constant volume.

Source	C^0_v/R
translation	1.5
rotation, C_2H_2	1
rotation, C_2H_3	1.5
vibration	$\sum_L \frac{x_L^2 \exp(-x_L)}{[1-\exp(-x_L)]^2}$

For H + $C_2H_2 \rightleftharpoons C_2H_3$:

$$\Delta C^0_v = C^{0,vib}_v(C_2H_3) - C^{0,vib}_v(C_2H_2) - R$$

where the last term included all non–vibrational degrees of freedom. By analogy with Chapter 5,

$$\Delta C^0_p = C^{0,vib}_v(C_2H_3) - C^{0,vib}_v(C_2H_2) - 2R$$

ΔC_p^0 was evaluated at 300, 310, ... 850 K and fitted to $\Delta C_p^0 = a_1 + a_2 T + a_3 T^2$, where $a_1 = -32.6 \pm 1.8$ J mol^{-1} K^{-1}, $a_2 = 0.0626 \pm 0.0066$ J mol^{-1} K^{-2}, and $a_3 = (-2.50 \pm 0.57) \times 10^{-5}$ J mol^{-1} K^{-3}, reproducing ΔC_p^0 to better than 0.6 J mol^{-1} K^{-1} in this temperature range. At 845 K, the terms in Equation 8.3, $\int_{298}^{T} \Delta C_p^0 \, d \ln T'$ and $(1/T) \int_{298}^{T} \Delta C_p^0 \, dT'$, had the values of -7.55 and -3.63 J mol^{-1} K^{-1} respectively.

8.5.4 $\Delta H_{f,298}^0(\mathbf{C_2H_3})$

From Table 3, the weighted mean of ln $K = 11.43 \pm 1.0$ (2σ), where the error was estimated from the scatter of values determined under similar conditions. From Equation 8.3, $\Delta H_{298}^0 = -152.00$ kJ mol^{-1}. Now

$$\Delta H_{f,298}^0(\mathrm{C_2H_3}) = \Delta H_{298}^0 + \Delta H_{f,298}^0(\mathrm{H}) + \Delta H_{f,298}^0(\mathrm{C_2H_2})$$

Since $\Delta H_{f,298}^0(\mathrm{H}) = 217.86$ kJ mol^{-1} [29] and $\Delta H_{f,298}^0(\mathrm{C_2H_2}) = 226.73$ kJ mol^{-1} [30], $\Delta H_{f,298}^0(\mathrm{C_2H_3}) = 292.59$ kJ mol^{-1}.

8.5.5 Estimated errors

Following Chapter 5, random errors (2σ) were identified and propagated to estimate the resulting uncertainty in $\Delta H_{f,298}^0(\mathrm{C_2H_3})$. The sensitivity of $\Delta H_{f,298}^0$ to uncertainty in k_2 was assumed to be the same as in Chapter 5. Table 6 presents the results.

The error was dominated by that in ln K, so $\Delta H_{f,298}^0(\mathrm{C_2H_3}) = 292.6 \pm 6.6$ kJ mol^{-1}, where the errors are 2σ and exclude uncertainty in $\Delta H_{f,298}^0(\mathrm{C_2H_2})$,

Species	Quantity / units	Value(s)	Reference
C_2H_2	B / cm^{-1}	1.1821	[31]
	σ	2	
	ν_i / cm^{-1}	3496, 3419, 1992, 764, 625	[31]
C_2H_3	A, B, C / cm^{-1}	5.33, 1.021, 0.857	[9]
	σ	1	
	ν_i / cm^{-1}	3311, 3295, 3178, 1774, 1357, 1176, 1174, 793, 791	[9]

Table 5: Physical parameters to calculate $\Delta H^0_{f,298}(C_2H_3)$.

Quantity±uncertainty	Resulting error/kJ mol^{-1}
ln K±1.0	6.6
T±4 K	0.2
[C_2H_2]±2%	0.03
k_2±60%	0.3
ν (C_2H_3)= 791±20 cm^{-1}	0.2

Table 6: Uncertainty in $\Delta H^0_{f,298}(C_2H_3)$

perhaps 1 kJ mol^{-1}. Including the latter independent uncertainty, $\Delta H^0_{f,298}(C_2H_3)$ = 293±7 kJ mol^{-1}.

8.5.6 Comparison to literature values

The advantage of the H + C_2H_2⇌C_2H_3 system to determine $\Delta H^0_{f,298}(C_2H_3)$ is that $\Delta H^0_{f,298}$ is particularly well–determined for all species other than C_2H_3. Because C_2H_2 was photolysed, some errors may have been caused by the presence of C_2H_2 or H_2CC in excited triplet states.

Equilibration could also be studied by photolysis of a precursor to produce C_2H_3 which would then dissociate. Fahr *et al.* [20] studied many such precursors: the compound chosen should be more thermally stable than C_2H_3 and should be unreactive towards H, C_2H_2, and C_2H_3: the other photolytic product (e.g. Cl from C_2H_3Cl) should be unreactive, or should be rapidly lost from the system before kinetic observations commence.

C_2H_3 could be monitored in absorption: Fahr *et al.* [32] measured the rate constant for C_2H_3+O_2 in this fashion.

Table 7 quotes some literature values for $\Delta H^0_{f,298}(C_2H_3)$. Sharma *et al.* [33] suggested that Lossing [34] and Harrison *et al.* [35] may have inadvertently observed excited states of C_2H_3 or $C_2H_3^+$, thus obtaining low values for $\Delta H^0_{f,298}$ (C_2H_3). No electronically excited states of C_2H_3 appear to have energies low enough to explain a 52 kJ mol^{-1} discrepancy. Raghavachari *et al.* [36] calculated the energies of $C_2H_3^+$ in linear or bridged structures: the order depended on the method of calculation, but the size of the difference was always <33 kJ mol^{-1}. Such a difference could cause much of the above discrepancy.

Value	System	Reference (date)
293±7	$H + C_2H_2 \rightleftharpoons C_2H_3$	This work (1990)
280±1	$C_2H_3 + HCl \longrightarrow Cl + C_2H_4$	[37] (1989)
≤297±13	$C_2H_3Br \xrightarrow{h\nu} C_2H_3 + Br$	[38] (1989)
277±2	$Cl + C_2H_4 \rightleftharpoons C_2H_3 + HCl$	[39] (1988)
255±8	$C_3H_6 \longrightarrow C_2H_3 + CH_3$	[40] (1988)
329	$C_2H_4 \xrightarrow{h\nu} C_2H_3 + H^+ + e$	[41] (1987)
301±8	$CH_4{}^+ + C_2H_2 \longrightarrow C_2H_3 + CH_3{}^+$	[33] (1985)
265±8	$C_4H_6 \longrightarrow 2C_2H_3$	[42] (1985)
265±8	$2C_2H_4 \longrightarrow C_2H_3 + C_2H_5$	[43] (1984)
299±9	$C_2H_4{}^+ + base \longrightarrow C_2H_3 + baseH^+$	[44] (1982)
295±8	review	[45] (1982)
249	$C_2H_3 + e \longrightarrow C_2H_3{}^+ + 2e$	[34] (1971)
289±8	$C_2H_3 + I_2 \rightleftharpoons C_2H_3I + I$, $C_2H_4 + I \rightleftharpoons C_2H_3 + HI$	[46] (1969)
264±13	$(C_2H_3)_2Hg \longrightarrow Hg + 2C_2H_3$	[47] (1961)
272±13	$C_2H_3 + e \longrightarrow C_2H_3{}^+ + 2e$	[35] (1960)

Table 7: Literature values for $\Delta H^0_{f,298}(C_2H_3)$/kJ mol^{-1}.

8.6 REFERENCES

[1] P.D.Lightfoot, D.Phil. Thesis, Oxford University (1986)

[2] M.Cathonnet, J.C.Boettner, H.James *18th Int. Symp. Combust.* 903 (1981)

[3] A.B.Callear, G.B.Smith *Chem.Phys.Lett.* **105** 119 (1984)

[4] K.Sugawara, K.Okazaki, S.Sato *Bull.Chem.Soc.Jap.* **54** 2872 (1981)

[5] R.Ellul, P.Potzinger, B.Reimann, P.Camilleri *Ber.Bunsenges.Phys.Chem.* **85** 407 (1981)

[6] W.A.Payne, L.J.Stief *J.Chem.Phys.* **64** 1150 (1976)

[7] D.G.Keil, K.P.Lynch, J.A.Cowfer, J.V. Michael *Int.J.Chem.Kin.* **8** 825 (1976)

[8] K.Kowari, K.Sugawara, S.Sato, S.Nagase *Bull.Chem.Soc.Jap.* **54** 1222 (1981)

[9] L.B. Harding, A.F. Wagner, J.M. Bowman, G.C. Schatz, K. Christoffel *J. Phys. Chem.* **86** 4312 (1982)

[10] S.Nagase, C.W.Kern *J.Am.Chem.Soc.* **101** 2544 (1979)

[11] D. Baulch, R.A. Cox, Th. Just, J.A. Kerr, M.J. Pilling, J. Troe, J. Warnatz, R.W. Walker, P.Frank submitted to *J.Phys.Chem.Ref.Data*

[12] W.Tsang, R.F.Hampson *J.Phys.Chem.Ref.Data* **15** 1087 (1986)

[13] G.Herzberg, "Molecular Spectroscopy and Molecular Structure III, electronic spectra and electronic structure of polyatomic molecules", Van Nostrand, Princeton, New Jersey (1966)

[14] "Lumonics TE–861S Operating Manual", Lumonics Inc., Ottawa, Canada (1980)

[15] A.M.Wodtke, Y.T.Lee *J.Phys.Chem.* **89** 4744 (1985)

[16] C.Y.R.Wu, T.S.Chien, G.S.Liu, D.L.Judge, J.J.Caldwell *J.Chem.Phys.* **91** 272 (1989)

[17] T.R.Fletcher, S.R.Leone *J.Chem.Phys.* **90** 871 (1989)

[18] H.Kanamori, K.Seki, E.Hirota *J.Chem.Phys.* **87** 73 (1987)

[19] M.Suto, L.C.Lee *J.Chem.Phys.* **80** 4824 (1984)

[20] A.Fahr, A.H.Laufer *J.Photochem.* **34** 261 (1986)

[21] H.Okabe "Photochemistry of Atoms And Small Molecules", Wiley– Interscience, 1977

[22] M.Brouard, D.Phil. Thesis, Oxford University (1986)

[23] "Matheson Gas Data Book", Matheson Gas Products (1971)

[24] M.Brouard, P.D.Lightfoot, M.J.Pilling *J.Phys.Chem.* **90** 445 (1986)

[25] FACSIMILE: A.R.Curtis, W.P.Sweetenham "Release H User's Manual", Report AERE–R 11771, AERE Harwell (October 1985)

[26] T.Tanzawa, W.C.Gardiner *J.Phys.Chem.* **84** 236 (1980)

[27] M.N.Paddon–Row, J.A.Pople *J.Phys.Chem.* **89** 2768 (1985)

[28] J.S.Binkley *J.Am.Chem.Soc.* **106** 603 (1984)

[29] L.Wołniewicz *J.Chem.Phys.* **78** 6173 (1983)

[30] R.A.Alberty, E.Burmenko *J.Phys.Chem.Ref.Data* **15** 1339 (1986)

[31] I.Suzuki, J.Overend *Spectrochimica Acta* **25A** 977 (1969)

[32] A.Fahr, A.H.Laufer *J.Phys.Chem.* **92** 7229 (1988)

[33] R.B.Sharma, N.M.Semo, W.S.Koski *Int.J.Chem.Kin.* **17** 831 (1985)

[34] F.P.Lossing *Can.J.Chem.* **49** 357 (1971)

[35] A.G.Harrison, F.P.Lossing *J.Am.Chem.Soc.* **82** 519 (1960)

[36] K. Raghavachari, R.A. Whiteside, J.A. Pople, P.v.R. Schleyer *J. Am. Chem. Soc.* **103** 5649 (1981)

[37] J.J.Russell, S.M.Senkan, J.A.Seetula, D.Gutman *J.Phys.Chem.* **93** 5184 (1989)

[38] A.M.Wodtke, E.J.Hintsa, J.Somorjai, Y.T.Lee *Israel J.Chem.* **29** 383 (1989)

[39] S.S.Parmar, S.W.Benson *J.Phys.Chem.* **92** 2652 (1988)

[40] G.A.Chappell, H.Shaw *J.Phys.Chem.* **72** 4672 (1968)

[41] H.Shiromaru, Y.Achiba, K.Kimura, Y.T.Lee *J.Phys.Chem.* **91** 17 (1987)

[42] J.H.Kiefer, H.C.Wei, R.D.Kern, C.H.Wu *Int.J.Chem.Kin.* **17** 225 (1985)

[43] G.Ayranci, M.H.Back *Int.J.Chem.Kin.* **15** 83 (1983)

[44] D.J.DeFrees, R.T.McIver, W.J.Hehre *J.Am.Chem.Soc.* **102** 3334 (1980)

[45] D.F.McMillen, D.M.Golden *Ann.Rev.Phys.Chem.* **33** 493 (1982)

[46] D.M.Golden, S.W.Benson *Chem.Rev.* **69** 125 (1969)

[47] A.F.Trotman–Dickenson, G.J.O.Verbeke *J.Chem.Soc.* 2580 (1961)

Chapter 9

A STUDY OF THE SYSTEM $H+CH_4 = CH_3+H_2$

9.1 INTRODUCTION

9.1.1 Background

Methane, CH_4, is an important fuel and chemical feedstock. In the cracking of CH_4 to C_2 compounds over a solid MgO catalyst, gas phase reactions such as

$$H + CH_4 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CH_3 + H_2$$

are significant. In general, rate constants may be calculated for rate constants for a reverse reaction, if the forward rate constant has been measured, and enthalpies and entropies are known for all species in the rate equation [1]. In non–isothermal systems, e.g. combustion, calculations of heat release need accurate values of the

enthalpy and entropy of important radicals.

In high–temperature combustion of all organic species, larger radicals decompose to yield C_1, C_2, and C_3 species. Therefore, it is essential that rate constants for reactions of such species should be well known. Because some rate constants for CH_3 reactions cannot be measured directly, an accurate value is needed for the standard enthalpy of formation of CH_3 at 298 K, $\Delta H^0_{f,298}(CH_3)$.

However, it has long been known that a discrepancy exists for the H+CH_4 $\rightleftharpoons$$CH_3$+$H_2$ equilibrium: the value for $\Delta H^0_{f,298}(CH_3)$ derived from k_f and k_b is 4 kJ mol^{-1} lower than that calculated from thermodynamic data [2]. Estimates cover the range 145–149 kJ mol^{-1} (Table 1), but a value of $\simeq$147.0$\pm$0.5 kJ mol^{-1} is now accepted. At 1000 K, rate constants calculated from extreme values will differ by a factor of 1.6. While $\Delta H^0_{f,298}(CH_3)$ is better–established than $\Delta H^0_{f,298}(C_2H_5)$ or $\Delta H^0_{f,298}(C_2H_3)$, this Chapter aims to improve the accuracy to which $\Delta H^0_{f,298}(CH_3)$ is known, using direct simultaneous measurements of k_f and k_b at 825 and 875 K, and to try to resolve the discrepancy described above.

9.1.2 Glossary

Symbol	Meaning
k_f	rate constant for $H+CH_4 \longrightarrow CH_3+H_2$
k'_f	$k_f[CH_4]$
k_b	rate constant for $CH_3+H_2 \longrightarrow H+CH_4$
k'_b	$k_b[H_2]$
k_2	rate constant for escape of H by diffusion and pump–out
k_3	rate constant for escape of CH_3 by diffusion and pump–out
D	gas diffusion coefficient
k_4	rate constant for $O(^1D)+H_2$
k_5	rate constant for $O(^1D)+CH_4$
k_6	rate constant for $OH+H_2$
I	fluorescence intensity from H
I_0	value of I at zero time
σ	rotational symmetry number

9.1.3 Outline of Chapter

McOwan [3] generated experimental data for this system. § 9.2 describes the experimental technique and data fitting. H was generated by laser flash photolysis of N_2O–H_2–CH_4–He mixtures at 825 K or 875 K, and monitored by time–resolved resonance fluorescence, as [H] and [CH_3] approached equilibrium.

§ 9.3 corrects the data analysis of McOwan, by considering the escape of CH_3 by pump–out and diffusion, to obtain new values for k_f and k_b at 825 K and 875 K. § 9.4 combines these rate constants with literature thermodynamic and

spectroscopic data to calculate $\Delta H^0_{f,298}(CH_3)$.

§ 9.5 extends McOwan's treatment of side–reactions to a more complete mechanism, and to the temperature at which experiments were actually performed.

9.2 EXPERIMENTAL

McOwan performed all experiments analysed here, using techniques described more fully in Chapter 2.

Mixtures of N_2O–H_2–CH_4–He were flowed slowly through the heated reaction cell and photolysed by the pulsed 193.3 nm (ArF) output of an exciplex laser. Experimental conditions: T = 825 K or 875 K, P = 200 Torr, [He] = (2.33 or 2.19)$\times 10^{18}$ cm^{-3}, [N_2O] = 2.2$\times 10^{14}$ molecule cm^{-3}, [H_2] = (1.1–11)$\times 10^{16}$ molecule cm^{-3}, [CH_4] = (0.52–3.9)$\times 10^{15}$ molecule cm^{-3}. The laser was fired at 3 Hz. Data were usually gathered for 32 ms after the laser fired.

Gas purities (from the manufacturers' catalogues): N_2O (BOC preparative grade 99.6%, impurities not given), H_2 (BOC CP grade, >99.9995%, 5 ppm N_2, 2 ppm N_2O, 1 ppm O_2), CH_4 (BOC, >99.995%, 40 ppm N_2+Ar), and He (BOC CP grade, >99.999%, 2 ppm each Ne, N_2). N_2O was distilled at least three times from and to liquid N_2, discarding the most volatile fraction (entrained air), and least volatile fraction (water) each time. CH_4 was purified in the same way. H_2 and He were passed through Oxisorb filters (Messer–Griesheim) to reduce O_2 and H_2O levels to 0.2 ppm.

Only N_2O absorbs at 193.3 nm: O(^{1}D) is produced cleanly (Chapter 2), and abstracts H from H_2 or CH_4 to form OH and H or CH_3. OH reacts rapidly with

H_2 at these temperatures to produce another H.

Time–resolved resonance fluorescence was used to detect H (121.6 nm). McOwan made no correction for distortion of the decay trace caused by scattered laser light, beyond discarding the first 6% of each trace. Experiments without CH_4 determined k_2, the rate constant for H escape by diffusion and pump–out.

9.3 DATA FITTING

The McOwan mechanism was extended to include CH_3 escape:

$$\begin{array}{rcll}
N_2O & \xrightarrow{h\nu} & O(^1D)+N_2 & (t=0) \\
O(^1D)+H_2 & \longrightarrow & OH+H & k_4 \ (t \simeq 0) \\
O(^1D)+CH_4 & \longrightarrow & CH_3+H & k_5 \ (t \simeq 0) \\
OH+H_2 & \longrightarrow & H+H_2O & k_6 \ (t \simeq 0) \\
H+CH_4 & \longrightarrow & CH_3+H_2 & k_f \\
CH_3+H_2 & \longrightarrow & H+CH_4 & k_b \\
H & \longrightarrow & \text{escape} & k_2 \\
CH_3 & \longrightarrow & \text{escape} & k_3
\end{array}$$

where escape denotes loss of H or CH_3 by diffusion and pump–out. At 825 K or 875 K, k_4, k_5, $k_6 \gg k_f$, k_b, k_2, k_3, so $O(^1D)$ and OH are converted to H and CH_3 long before observation of H commences. From the above mechanism,

$$\begin{aligned}
\frac{d}{dt}[H] &= -k'_H[H] + k'_b[CH_3] \\
\frac{d}{dt}[CH_3] &= k'_f[H] - k'_M[CH_3]
\end{aligned}$$

where $k'_H = k'_f + k_2$, $k'_M = k'_b + k_3$, $k'_f = k_f[\mathrm{CH_4}]$, and $k'_b = k_b[\mathrm{H_2}]$. k'_f and k'_b are pseudo–first–order rate constants. Appendix B details the solution. If the detection system is linear, the fluorescence intensity, I, is proportional to [H]:

$$I_t = I_+ \exp(\lambda_+ t) + I_- \exp(\lambda_- t) \tag{9.1}$$

$$\begin{aligned} \frac{I_\pm}{I_0} &= \frac{k'_H + \lambda_\mp + k'_M([\mathrm{CH_3}]_0/[\mathrm{H}]_0)}{\mp(\lambda_+ - \lambda_-)} \\ 2\lambda_\pm &= -k'_{loss} \pm \sqrt{(k'_{loss})^2 - 4(k'_H k'_M - k'_b k'_f)} \\ k'_{loss} &= k'_H + k'_M \end{aligned}$$

where I_0 is the value of I at zero time. From the short–time chemistry,

$$\frac{[\mathrm{CH_3}]_0}{[\mathrm{H}]_0} = \frac{k_5[\mathrm{CH_4}]}{2k_4[\mathrm{H_2}]}$$

Values of k_4 and k_5 were taken from [4] at room temperature; since both rate constants are near gas kinetic, they were assumed to have zero activation energy over the experimental temperature range $298 \leq T/\mathrm{K} \leq 875$. The previous equation was used to calculate $[\mathrm{CH_3}]_0/[\mathrm{H}]_0$ for each experiment.

9.3.1 Rate constants for escape

When $[\mathrm{CH_4}] = 0$, [H] decays exponentially with time constant k_2:

$$I_t = I_0 \exp(-k_2 t) \tag{9.2}$$

McOwan recorded fluorescence decay traces in the absence of $\mathrm{CH_4}$ at several temperatures and pressures to obtain $k_2(T,P)$, and used the Marquardt algorithm

(Chapter 2) to fit the fluorescence data I_t to Equation 9.2. I_0 and k_2 were floated, using analytic parameter derivatives.

For this work, the rate constant for CH_3 escape, k_3, was derived from k_2 by kinetic theory. In a simple treatment (Chapter 3), k_2 has a pressure–independent component (pump–out) which is the same for all gases, and a component which is proportional to the diffusion coefficient, D, for H diffusing through He. Thus $D(CH_3\text{–He})$ had to be calculated to convert k_2 to k_3.

CH_3 will diffuse more slowly than H through He because it is more massive and has a larger collisional cross–section. Collisional diameters were calculated: H–He = 0.134 nm (from diffusion coefficients [5]), CH_3–He = 0.31 nm (from mean free paths of He and NH_3 [6]). At a given temperature and pressure, $D(CH_3\text{–He}) = 0.094\ D(\text{H–He})$. The pressure–dependent part of k_2 was reduced in proportion:

$$k_3/\text{s}^{-1} = 0.094(k_2/\text{s}^{-1} - 25.6) + 25.6$$

at 825 K or 875 K, where 25.6 s^{-1} was the pressure–independent rate constant for pump–out of all gases in this system with this collimator arrangement [7].

9.3.2 Determination of K

Since $[CH_3]_0/[H]_0$, k_2, and k_3 were known, k'_f and k'_b were determined for each experiment by a fit to Equation 9.1, floating I_0, k'_f, and k'_b. Initially, I_0 was set to the first data point, and k'_f and k'_b were set to 99 s^{-1} (a value near all converged values). For each experiment, k_f, k_b, and K ($= k_f/k_b$) were calculated from fitted k'_f and k'_b. Parameter recovery was tested on data simulated by the above mechanism. For $[CH_3]_0/[H]_0 \leq 0.2$ (as in these experiments), K was recovered to

T/K	k_f	k_f [3]	k_f [8]	k_b	k_b [3]	k_b [8]
825	2.57±0.73	4.34±0.40	9.2	0.152±0.020	0.291±0.031	0.36
875	1.69±0.20	6.83±0.48	15	0.87±0.22	0.433±0.039	0.58

Table 1: Rate constants for $H+CH_4 \rightleftharpoons CH_3+H_2$. Values of k_f and k_b are uncorrected for side–reactions. Units are 10^{-14} cm^3 molecule^{-1} s^{-1}. Errors were taken from the fitting program. k_f [8] has an uncertainty factor of 1.6, and k_b [8] has an uncertainty factor of 2.

within $\leq$2% of the correct value. In contrast, McOwan plotted k'_f against $[CH_4]$ for all experiments to derive k_f.

Appendix M and Table 1 present the fitted k_f and k_b, together with the equilibrium constant, K. The values of k_f and k_b from this work agreed with those of McOwan to within experimental error. Simulations with a more complex mechanism (§ 9.5) show that this simple analysis underestimates K by $\simeq$18% due to the neglect of side–reactions, so the raw values of K are increased by 18% in Table 2. K increased somewhat as $[H_2]$ increased (Figure 9.1), and was insensitive to $[CH_4]$, laser energy, and $[CH_3]_0/[H]_0$. k_f and k_b were appreciably smaller than literature values [8], but K agreed with literature values within the error limits.

Uncertainties in K neglected the covariance, which could not readily be determined, of k_f and k_b. The following independent sources of uncertainty were identified and propagated:

- $[CH_4]$ and $[H_2]$ each ±3% (mainly due to flow uncertainties), so ln K had an error of ±0.04.

T/K	K	K [3]	K [8]
825	20.0±6.3	14.91±1.8	26
875	22.9±6.4	15.77±2.2	26

Table 2: Equilibrium constant for $H+CH_4 \rightleftharpoons CH_3+H_2$. K has been calculated from Table 1 and then increased by 18% to allow for side reactions (see text). The fractional error in K is from those in k_f and k_b.

- T±4 K. Since $(\ln K_{875} - \ln K_{825}) = 0.14$, $\ln K$ was only uncertain by ±0.01 due to errors in temperature measurement.

Figure 9.1: K against $[H_2]$ / 10^{16} molecule cm^{-3}.

- $k_2 \pm 4$ s^{-1}. Fits were repeated with different k_2, from which ln K had an error of ± 0.1.

  Including these errors, $K(825\text{ K}) = 20.0 \pm 6.6$ and $K(875\text{ K}) = 22.9 \pm 6.9$.

9.4 ENTHALPY OF FORMATION OF CH_3

$\Delta H^0_{f,298}(CH_3)$ has been measured by several workers, and results are presented in Table 3. Values of 145–149 kJ mol^{-1} have been measured, corresponding to rate constants that differ by a factor of 1.6 at 1000 K.

McOwan combined values for k_f and k_b to yield the equilibrium constant K and used literature data to derive $\Delta H^0_{f,298}(CH_3)$. This Section will follow the same approach, using values of K from McOwan and from re–analysing McOwan's raw data with a mechanism including the escape of CH_3. More recent literature data will be used, and the rotational entropy and heat capacity of H_2 will be treated exactly. The standard enthalpy of reaction for $H+CH_4 \longrightarrow CH_3+H_2$ was calculated from Equation (II) of [9]:

$$\frac{\Delta H^0_{298}}{T} = \Delta S^0_{298} - R \ln K + \int_{298}^{T} \Delta C^0_p \, d\ln T' - \frac{1}{T}\int_{298}^{T} \Delta C^0_p \, dT' \qquad (9.3)$$

9.4.1 Entropies and heat capacities

The formulae in Chapter 5 give the vibrational contributions to S^0_{298}, and hence to ΔS^0_{298}. No species has a low–lying electronically excited state (CH_3 has the lowest at 46205 cm^{-1} [19]), and no species has an internal rotor. Relevant phys-

Value	System	Reference (year)
146.5±1.0	$H+CH_4 \rightleftharpoons CH_3+H_2$	[3] recalculated, 825 K (1990)
144.3±0.9	$H+CH_4 \rightleftharpoons CH_3+H_2$	This work, 825 K (1990)
146.5±0.9	$H+CH_4 \rightleftharpoons CH_3+H_2$	[3] recalculated, 875 K (1990)
144.6±1.1	$H+CH_4 \rightleftharpoons CH_3+H_2$	This work, 875 K (1990)
147±2	$C_2H_6 \rightleftharpoons 2CH_3$	[13] (1989)
148±3	$CH_3+HBr \rightleftharpoons CH_4+Br$	[10] (1988)
145.6±1.3	$CH_3+HCl \rightleftharpoons CH_4+Cl$	[12] (1988)
146.7±0.4	$CH_3+HCl \rightleftharpoons CH_4+Cl$	[11] (1987)
145.3±1.0	$H+CH_4 \rightleftharpoons CH_3+H_2$	[3] 825 K (1985)
145.0±0.8	$H+CH_4 \rightleftharpoons CH_3+H_2$	[3] 875 K (1985)
145.7±0.8	review	[19] (1985)
145.6±1.0	alkane C–C homolysis	[14] (1984)
146.9	review	[15] (1982)
146.9±0.4	$CH_3+HCl \rightleftharpoons CH_4+Cl$	[16] (1981)
143.9±2.9	CH_3X photo–ionization	[17] (1981)
149	CH_4 photo–ionization	[18] (1968) corrected to 298 K

Table 3: Literature values of $\Delta H^0_{f,298}(CH_3)$ / kJ mol^{-1}.

Quantity/units	H	CH_4	CH_3	H_2
M_R	1.01	16.04	15.03	2.02
A, B, C/cm^{-1}	–	all 5.265	9.570, 9.570, 4.785	60.8904
σ	–	12	6	see text
ν_l/cm^{-1}	–	3018.7*3, 2916.5, 1534.0*2, 1306*3	3184*2, 3002, 1383*2, 606	4403.57
$S^{0,T}/R$	ln Y	ln $(M_R^{1.5}Y)$	ln $(M_R^{1.5}Y)$	ln $(M_R^{1.5}Y)$
$S^{0,R}/R$	0	1.5 + ln q_{rot}	1.5 + ln q_{rot}	see text
$C_v^{0,T}/R$	1.5	1.5	1.5	1.5
$C_v^{0,R}/R$	0	1.5	1.5	see text

Table 4: Parameters of H, CH_4, CH_3, H_2. The oscillator frequencies are ν_l. The degeneracy is also given. Y and q_{rot} are defined in Chapter 5. The superscripts T and R denote translational and rotational contributions. Source: [19] except for the 606 cm^{-1} frequency of CH_3 [20].

ical parameters are listed in Table 4, together with translational and rotational contributions to entropy and heat capacity.

In general, rotational entropy and heat capacity are given by

$$\begin{aligned} S_{rot} &= R \ln q_{rot} - C_v \\ \frac{-C_v}{R} &= \left(\frac{\partial \ln q_{rot}}{\partial \ln \beta} \right)_V \end{aligned}$$

where $\beta = (k_B T)^{-1}$. H_2 has a large rotational constant ($hcB/k_B = 86$ K), so that q_{rot} should be evaluated exactly over 298$\leq T/\mathrm{K} \leq$875:

$$
\begin{aligned}
q_{rot} &= \frac{1}{4}\sum_{J=0}^{\infty} g_j \exp[-\beta hcBJ(J+1)] \\
g_j &= 2J+1 \qquad J \text{ even} \\
&= 3(2J+1) \qquad J \text{ odd}
\end{aligned}
$$

At 298 K, $q_{rot} = 1.88$, $S^0_{rot} = 1.539R$, $C^0_v = 0.909R$; the high–temperature approximation predicts 1.70, $1.630R$, R respectively and is thus somewhat inaccurate. If the high–temperature limit is used for H_2 in the calculations below, the value in parentheses is obtained. Contributions to $\Delta S^0_{298}/R$ are: translational 0.942, rotational 1.679 (1.770), and vibrational 0.190. Thus $\Delta S^0_{298} = 23.37$ (24.13) J mol^{-1} K^{-1}.

Heat capacities

At any temperature,

$$\Delta C^0_p = C^{0,vib}_v(\mathrm{CH_3}) + C^{0,vib}_v(\mathrm{H_2}) + C^{0,rot}_v(\mathrm{H_2}) - C^{0,vib}_v(\mathrm{CH_4})$$

since $\Delta C^0_p = \Delta C^0_v$ (perfect gases), and non–vibrational terms in ΔC^0_v cancel. ΔC^0_p was calculated at 300, 310, ... 880 K, and fitted to <0.1 J mol^{-1} K^{-1} by

$$\Delta C^0_p = a + bT + cT^2 + dT^3$$

where: $a = 2.5075$ (4.0535) J mol^{-1} K^{-1}; $b = 0.071303$ (0.06775) J mol^{-1} K^{-2}; $c = -1.8357$ (-1.8003) $\times 10^{-4}$ J mol^{-1} K^{-3}; and $d = 1.1150$ (1.1368) $\times 10^{-7}$ J mol^{-1} K^{-4}. From these coefficients,

$$\begin{aligned}
\int_{298}^{825} \Delta C_p^0 \, d\ln T' &= 5.70(6.83) \\
\int_{298}^{875} \Delta C_p^0 \, d\ln T' &= 5.64(6.92) \\
\frac{1}{825 \text{ K}} \int_{298}^{825} \Delta C_p^0 \, dT' &= 2.88(3.66) \\
\frac{1}{875 \text{ K}} \int_{298}^{875} \Delta C_p^0 \, dT' &= 2.65(3.53)
\end{aligned}$$

J mol^{-1} K^{-1}. Numerical integration using NAG routines [21] proved impossible. Uncertainties in ΔS_{298}^0 and ΔC_p^0 might arise from uncertainties in the rotational constants or in low vibrational frequencies. Rotational constants are well–determined for these species. The lowest vibrational frequency is 606 cm^{-1} and is well–determined. Further uncertainty may arise when $\Delta C_p^0(T)$ is approximated to a polynomial. McOwan [3] used a fit of lower degree:

$$\Delta C_p^0 = a + bT + cT^2$$

Such a fit to the present $\Delta C_p^0(T)$ caused equal changes in each ΔC_p^0 integral, which cancelled in ΔH_{298}^0.

9.4.2 Enthalpies

For the reaction,

$$\Delta H_{298}^0 = \Delta H_{f,298}^0(\text{CH}_3) - \Delta H_{f,298}^0(\text{H}) - \Delta H_{f,298}^0(\text{CH}_4)$$

so

$$\Delta H^0_{f,298}(\mathrm{CH_3}) = \Delta H^0_{298} + \Delta H^0_{f,298}(\mathrm{H}) + \Delta H^0_{f,298}(\mathrm{CH_4})$$

Now $\Delta H^0_{f,298}$ (H) = 217.86 kJ mol^{-1} [22] and $\Delta H^0_{f,298}$ (CH_4) = -74.87 ± 0.34 kJ mol^{-1} [19], so

$$\Delta H^0_{f,298}(\mathrm{CH_3}) = \Delta H^0_{298} + (142.99 \pm 0.34) \text{ kJ mol}^{-1}$$

ΔH^0_{298} may be calculated with exact or high–temperature forms of $q_{rot}(H_2)$, from the McOwan data at 825 K or 875 K, and as analysed by McOwan or in this work. Using the exact expression for $q_{rot}(H_2)$, Equation 9.3 shows that

$$\begin{aligned} \Delta H^0_{298} &= -825 \text{ K} \times R \ln K_{825} + 21.61(22.52) \\ \text{or } \Delta H^0_{298} &= -875 \text{ K} \times R \ln K_{875} + 23.07(24.08) \end{aligned}$$

kJ mol^{-1}. Table 5 presents values of $\Delta H^0_{f,298}(CH_3)$, obtained from different K. From this work, the recommended value is 144.93±0.41 (19 results) or 144.40±2.21 (11 results) kJ mol^{-1} from 825 K or 875 K data. The mean, weighted by the number of results, is 144.7±1.1 kJ mol^{-1}. Values of K, and hence of $\Delta H^0_{f,298}(CH_3)$, have been reviewed elsewhere [2] and will thus not be reviewed here.

9.5 SIDE REACTIONS

McOwan used a restricted mechanism to explore the effect of side reactions in the N_2O–H_2–CH_4–He system at 700 K. Experiments were actually performed at 825 K and 875 K; at these higher temperatures, reactions with an appreciable activation

T/K	A	B	C	D	H
825	146.08±0.89	145.30±0.97	144.02±0.41	142.25	0.91
875	145.98±1.08	145.03±0.83	143.29±2.21	142.34	1.01

Table 5: Values of $\Delta H^0_{f,298}(CH_3)$/kJ mol^{-1}. For "A, C, D", K was calculated as follows: the K value of McOwan [3], but analysed as in this work; analysis of this work; reference [8]. "B" is taken from [3]. If the high–temperature limit for $q_{rot}(H_2)$ is used, the values increase by the amount under H.

energy will be more significant than indicated by the analysis of McOwan. It was therefore decided to repeat the checks of McOwan at 850 K with a fuller mechanism.

Initially, all reactions among {O(^{1}D), O, OH, H_2, CH_4, H, CH_3, and He}, where O denotes the electronic ground state O(^{3}P), were considered at 850 K in 200 Torr He. N_2O was assumed to be inert. Some reactions were deemed insignificant because they were slow, or involved species present only at low concentrations. All other reactions are presented in Table 6, together with the rate constant, k, and the pseudo–first–order rate constant, k'. For a general reaction

$$A + B(+C) \xrightarrow{k} \text{products}$$

k' is given by k[B] or k[B][C]. [H_2], [CH_4], and [He] were taken from typical experimental conditions. Following McOwan, [O(^{1}D)]$_0 = 10^{11}$ cm^{-3}. Higher initial concentrations are unlikely, so this represents the worst possible interference from radical–radical reactions. Radical concentrations were calculated by FACSIMILE [23], using the mechanism of Table 6, for a time of 0.01 s corresponding to the

middle of a typical experimental decay trace, and are as follows: $[O(^1D)] \simeq [O] \simeq [OH] \simeq 0$, $[H_2] = 5\times10^{16}$ molecule cm^{-3}, $[CH_4] = 2\times10^{15}$ molecule cm^{-3}, $[H] = 5.5\times10^{10}$ cm^{-3}, $[CH_3] = 6.1\times10^{10}$ molecule cm^{-3}, $[He] = 2.26\times10^{18}$ cm^{-3}.

The reaction of $O(^1D)$ with CH_4 produces $OH(0 \leq v \leq 4)$ [24], which will be removed by H_2 with rate constants similar to that for $v = 0$, and will not perturb the mechanism.

The mechanism of Table 6 was used to generate a decay trace on the experimental timescale with experimental levels of added noise. The decay was then analysed using the simple scheme of § 9.3. k_f was recovered 12% below, k_b 4% above, and K 18% below the true value.

9.6 SUMMARY

The decay traces of McOwan were re–analysed according to a kinetic scheme that included escape of CH_3. New values were obtained for the equilibrium constant, K, for $H + CH_4 \rightleftharpoons CH_3 + H_2$.

ΔS^0_{298} and $\Delta C^0_p(T)$ were recalculated from more recent literature data for all species. In a significant advance on the analysis of McOwan, the rotational partition function of H_2 was treated exactly, and the temperature dependence of ΔC^0_p was approximated more closely. Possible side–reactions do not contribute significantly to the depletion of H or CH_3. Recommended results are:

$$\begin{aligned} \Delta H^0_{f,298}(CH_3) &= 144.93\pm0.41 \text{ kJ mol}^{-1} \quad (825 \text{ K results}) \\ \Delta H^0_{f,298}(CH_3) &= 144.40\pm2.21 \text{ kJ mol}^{-1} \quad (875 \text{ K results}) \end{aligned}$$

or 144.7 ± 1.1 kJ mol^{-1} (combined 825 K and 875 K). In agreement with other

Reaction	k	k'/s^{-1}	Reference
$O(^1D) + H_2 \longrightarrow OH + H$	1.3×10^{-10}	6.5×10^{6}	k_4, [4]
$O(^1D) + CH_4 \longrightarrow OH + CH_3$	1.5×10^{-10}	300000	k_5, [4]
$O(^1D) + CH_4 \longrightarrow O + CH_4$	1.9×10^{-11}	38000	[25]
$O + OH \longrightarrow O_2 + H$	3.0×10^{-11}	0	[8]
$O + H_2 \longrightarrow OH + H$	1.4×10^{-13}	7000	[8]
$O + CH_4 \longrightarrow OH + CH_3$	2.8×10^{-13}	560	[8]
$CH_3 + O \longrightarrow HCHO + H$	1.4×10^{-10}	0	[8]
$OH + OH \longrightarrow H_2O + O$	5.2×10^{-12}	0	[8]
$OH + OH \longrightarrow H_2O_2$ (M = He)	5.5×10^{-13}	0	[8] (M = N_2)
$OH + H_2 \longrightarrow H + H_2O$	1.2×10^{-12}	60000	k_6, [8]
$OH + CH_4 \longrightarrow CH_3 + H_2O$	1.1×10^{-12}	2200	[8]
$H + OH \longrightarrow O + H_2$	1.3×10^{-13}	0	[2]
$H + OH + He \longrightarrow H_2O + He$	3.2×10^{-32}	0	[8]
$CH_3 + OH \longrightarrow$ products	9×10^{-11}	0	[2]
$CH_3 + H_2 \longrightarrow H + CH_4$	4.6×10^{-15}	230	k_f, [8]
$H + CH_4 \longrightarrow CH_3 + H_2$	1.2×10^{-13}	240	k_b, [8]
$H + H + He \longrightarrow H_2 + He$	2.1×10^{-33}	2.6×10^{-4}	[8] (M = Ar)
$H + CH_3 + He \longrightarrow CH_4 + He$	2.1×10^{-12}	0.13	[8]
$CH_3 + CH_3 \longrightarrow C_2H_6$ (M = He)	2.8×10^{-11}	1.7	[8] (M = Ar)
$H \longrightarrow$ escape	70	70	k_2, [3]
$CH_3 \longrightarrow$ escape	30	30	k_3, § 9.3.1

Table 6: Rate constants in the N_2O–H_2–CH_4–He system: 850 K, 200 Torr He. k has cm, molecule, s units. Pressure–dependent rate constants were not corrected from the stated third body to He.

studies, observation of this equilibrium produced a value rather lower than that found by other methods.

More accurate characterization of H escape, and more precise literature $\Delta H^0_{f,298}(CH_4)$, would further reduce the uncertainties. $H+CH_4 \rightleftharpoons CH_3+H_2$ equilibration could be studied by creating CH_3 in the presence of H_2 and CH_4. Acetone photolysis at 193.3 nm has been validated as a clean CH_3 source [7].

9.7 REFERENCES

[1] J.W.Davies, M.A.Hanning–Lee, M.J.Pilling, P.W. Seakins *Spectrochimica Acta* **46A** 581 (1990)

[2] W.Tsang, R.F.Hampson *J.Phys.Chem.Ref.Data* **15** 1087 (1986) and references therein

[3] S.P.McOwan, Part II Thesis, Oxford University (1985)

[4] K.Schofield *J.Photochem.* **9** 55 (1978)

[5] B.Khouw, J.E.Morgan, H.I.Schiff *J.Chem.Phys.* **50** 66 (1969)

[6] G.W.C.Kaye, T.H.Laby "Tables of Physical and Chemical Constants and some Mathematical Functions" (1953)

[7] M.Brouard, D.Phil. Thesis, Oxford University (1986)

[8] D.Baulch, R.A.Cox, Th.Just, J.A.Kerr, M.J.Pilling, J. Troe, J. Warnatz, R.W. Walker, P. Frank, submitted to *J.Phys.Chem.Ref.Data*

[9] M.Brouard, P.D.Lightfoot, M.J.Pilling *J.Phys.Chem.* **90** 445 (1986)

[10] J.J.Russell, J.A.Seetula, D.Gutman *J.Am.Chem.Soc.* **110** 3092 (1988)

[11] O.Dobis, S.W.Benson *Int.J.Chem.Kin.* **19** 691 (1987)

[12] J.J.Russell, J.A.Seetula, S.M.Senkan, D.Gutman *Int.J.Chem.Kin.* **20** 759 (1988)

[13] P.D.Pacey, J.H.Wimalasena *J.Phys.Chem.* **88** 5657 (1989)

[14] R.R.Baldwin, G.R.Drewery, R.W.Walker *J.Chem.Soc.Farad.Trans. I* **80** 2827 (1984)

[15] K.M.Pamidimukkala, D.Rogers, G.B.Skinner *J.Phys.Chem.Ref.Data* **11** 83 (1982)

[16] S.P.Heneghan, P.A.Knoot, S.W.Benson *Int.J.Chem.Kin.* **13** 677 (1981)

[17] J.C.Traeger, R.G.McLoughlin *J.Am.Chem.Soc.* **103** 3647 (1981)

[18] W.A.Chupka *J.Chem.Phys.* **48** 2337 (1968)

[19] JANAF Thermochemical Tables, *J.Phys.Chem.Ref.Data* **14**, Supplement **1** (1985)

[20] C.Yamada, E.Hirota, K.Kawaguchi *J.Chem.Phys.* **75** 5256 (1981)

[21] Numerical Algorithms Group, "NAG FORTRAN Library Manual Mark 13", July 1988

[22] L.Wołniewicz *J.Chem.Phys.* **78** 6173 (1983)

[23] FACSIMILE: A.R.Curtis, W.P.Sweetenham "Release H User's Manual", Report AERE–R 11771, AERE Harwell (October 1985)

[24] S.G. Cheskis, A.A. Iogansen, P.V. Kulakov, I.Yu. Razuvaev, O.M. Sarkisov, A.A. Titov *Chem.Phys.Lett.* **155** 37 (1989)

[25] S.T.Amimoto, A.P.Force, R.G.Gulotty, J.R.Wiesenfeld *J.Chem.Phys.* **71** 3640 (1979)

Chapter 10

FUTURE WORK

Sensitivity analysis, including the work of Turányi *et al.* [1], should be used to remove redundant species and unnecessary reactions from all mechanisms in this and future work.

Hall *et al.* [2] proposed the Maximum Likelihood Estimator as a more reliable best–fit criterion than χ^2. With any criterion, the residual autocorrelation should be checked to ensure that experimental data are randomly distributed about the best fit. Covariances between fitted parameters should be checked: FACSIMILE provides them automatically.

Complex fitting problems, where many parameters may be fitted to data, have been solved efficiently by advanced techniques. Bounds [3] reviewed genetic algorithms and optimization by simulated annealing, which can fit many parameters simultaneously and can be hundreds of times faster than conventional methods. Maximum entropy methods have also been used to fit multi–exponential decays [4]. Such approaches might be used to fit many rate constants at once to

the large body of kinetic data accumulated for the kinetic systems in this thesis.

Experimental technique might be improved by:

- more accurate modelling of the physical loss of reactive species from the observation zone. The models of Chapter 3 might be extended to consider the case where the beams are not fully aligned. Flow dynamics software might be used to study the flow patterns inside the cell.
- reducing scattered laser light;
- modifying the laser and microwave discharge to cause less interference, and shielding the Xe–Hg lamp power supply.

10.1 REFERENCES

[1] T.Turányi, T.Bérces, S.Vajda *Int.J.Chem.Kin.* **21** 83 (1989)

[2] P.Hall, B.Selinger *J.Phys.Chem.* **85** 2941 (1981)

[3] D.G.Bounds *Nature* **329** 215 (1987)

[4] A.K.Livesey, M.Delaye, P.Licinio, J.–C. Brochon *Faraday Disc.Chem.Soc.* **83** 247 (1987)

APPENDIX A: RESULTS OF FIT TO MODELS FOR ATOM ESCAPE

Chapter 3 describes the fitting of H fluorescence decays to three diffusion models. These include a one–dimensional model, denoted below by 1–d, and two two–dimensional models, 2–d(A) and 2–d(B).

For all these fits, the diffusion coefficient D was fixed at the value shown in Chapter 3, and the model parameters h and μ were floated. Fitted values are presented below. Since the models could not determine the sign of μ, only $|\mu|$ is given. Typical uncertainties from the fits were: $h\pm4\%$, $|\mu|\pm1\%$. Blanks indicate that fits did not converge. Units: $D/\mathrm{cm}^2\mathrm{s}^{-1}$, h/cm, $|\mu|/\mathrm{cm\ s}^{-1}$.

602–850 K, 49–400 Torr N_2

In the filenames column, 92–95 denotes the combined results from the data files DH92, DH93, DH94, and DH95.

Filenames	D	1–d	2–d(A)	2–d(B)
1–5	35.6	1.063	1.47	0.55
6–10	8.6	0.504	0.67	0.86
11–15	68.8	1.012	1.39	0.83
16–20	49.9	0.778	1.12	0.82
21–25	17.3	0.615	0.82	
26–30	11.4	0.566	0.80	
31–35	22.6	0.577	0.86	–0.72
36–40	12.8	0.347	0.37	
41–45	45.5	0.564	0.92	1.19
46–50	89.6	0.603	0.90	1.00
51–55	18.1	0.561	0.81	0.72
56–60	58.1	0.538	0.76	0.77
61–66	19.1	0.542	0.80	0.80
67–71	55.8	0.439	0.63	0.75
72–76	28.4	0.337	0.34	
77–81	35.4	0.322	0.34	

Fitted h.

Filenames	D	1–d	2–d(A)	2–d(B)
82–86	116.6	0.501	0.82	–2.1
87–91	80.4	0.505	0.80	–0.5
92–95	33.9	0.659	0.99	0.84
96–99	33.8	0.634	0.95	–0.3
100–103	33.7	0.610	0.93	0.75
104–107	33.7	0.597	0.91	0.83
108–111	47.0	0.627	0.95	3.3
112–115	40.0	0.596	0.90	0.84
116–119	58.5	0.756	1.08	0.79
120–123	51.9	0.667	0.97	0.72
124–127	23.6	0.492	0.72	
128–131	16.9	0.417	0.56	0.88
132–135	40.9	0.523	0.83	–0.95
136–139	20.6	0.462	0.64	
140–143	30.0	0.525	0.71	0.71
144–147	41.7	0.528	0.76	–0.02

Fitted h.

Filenames	D	1–d	2–d(A)	2–d(B)
1–5	35.6	96.3	100.2	106.7
6–10	8.6	21.2	17.5	30.2
11–15	68.8	150.6	141.3	175.0
16–20	49.9	103.4	91.1	136.6
21–25	17.3	39.2	31.5	
26–30	11.4	25.6	21.4	
31–35	22.6	43.4	34.4	64.1
36–40	12.8	36.0	27.7	
41–45	45.5	87.3	73.8	116.6
46–50	89.6	179.0	149.2	243.8
51–55	18.1	35.0	26.5	52.5
56–60	58.1	115.5	88.0	168.6
61–66	19.1	36.2	27.2	55.8
67–71	55.8	106.6	74.8	165.4
72–76	28.4	86.4	68.4	
77–81	35.4	109.4	88.7	

Fitted $|\mu|$.

Filenames	D	1–d	2–d(A)	2–d(B)
82–86	116.6	217.7	175.8	29.6
87–91	80.4	152.2	119.7	220.8
92–95	33.9	68.4	58.6	91.5
96–99	33.8	68.3	58.1	92.0
100–103	33.7	67.5	57.1	92.7
104–107	33.7	67.9	57.3	93.5
108–111	47.0	94.8	80.7	117.5
112–115	40.0	81.2	68.7	109.9
116–119	58.5	121.8	106.0	160.1
120–123	51.9	106.2	89.0	147.4
124–127	23.6	48.2	37.5	
128–131	16.9	34.6	24.0	56.6
132–135	40.9	79.2	64.7	109.3
136–139	20.6	42.6	31.5	
140–143	30.0	60.5	42.2	
144–147	41.7	80.7	59.0	124.6

Fitted $|\mu|$.

600–800 K, 51–369 Torr He

In the filenames column, 1–4 denotes the combined results from the data files AD1, AD2, AD3, and AD4.

Filenames	D	h, 1–d	h, 2–d(A)	$\|\mu\|$, 1–d	$\|\mu\|$, 2–d(A)
1–4	63.3	1.64	2.24	363	64
5–8	46.3	0.70	0.96	126	116
9–12	31.9	0.58	0.73	93	81
13–16	22.3	0.58	0.75	57	47
17–20	27.9	0.63	0.91	58	47
21–24	137.3	0.80	1.14	248	212
25–28	64.6	0.75	1.13	117	99
29–32	43.7	0.75	1.14	77	65
33–36	212.7				
37–40	175.5	0.91	1.59	322	243
41–44	114.2	0.83	1.24	206	179
45–48	88.6	0.82	1.23	157	2111
49–52	213.4	0.64	0.95	395	308
53–56	142.0	0.62	0.92	263	203
57–60	111.2	0.63	0.87	222	159
61–64	66.5	0.59	0.83	131	97
65–68	33.9	0.56	0.78	63	43

Fitted h and $|\mu|$.

APPENDIX B: Solution of Two Coupled Linear Ordinary Differential Equations

In a chemical system, concentrations of the species have time derivatives specified by differential equations such as:

$$\begin{aligned} \dot{a} &= Pa + Qb \\ \dot{b} &= Ra + Sb \end{aligned}$$

where a and b = [A] and [B]. $\dot{a}$ and $\dot{b}$ are their time derivatives da/dt and db/dt. P, Q, R, S are independent of time, and may be linear combinations of pseudo–first–order rate constants. Such paired differential equations may be solved as follows. Writing $\ddot{a}$ for d^2a/dt^2:

$$\begin{aligned} \ddot{a} &= P\dot{a} + Q\dot{b} \\ &= P\dot{a} + Q(Ra + Sb) \\ &= P\dot{a} + QRa + S(\dot{a} - Pa) \\ \Longrightarrow \ddot{a} &- (P + S)\dot{a} + (PS - QR)a = 0 \end{aligned}$$

A trial solution is:

$$\begin{aligned} a &= C\exp(\lambda t) \\ \dot{a} &= C\lambda\exp(\lambda t) \\ \ddot{a} &= C\lambda^2\exp(\lambda t) \end{aligned}$$

From the coefficients of exp (λt):

$$\lambda^2 - (P+S)\lambda + (PS - QR) = 0$$

This quadratic has two solutions $\lambda_\pm$:

$$\begin{aligned} 2\lambda_\pm &= (P+S) \pm \sqrt{(P+S)^2 + 4(QR - PS)} \\ &= (P+S) \pm \sqrt{(P-S)^2 + 4QR} \end{aligned}$$

If the system is not to oscillate, the roots must be real, so either $Q > 0, R > 0$ or $Q < 0, R < 0$.

$$a = A_+ \exp(\lambda_+ t) + A_- \exp(\lambda_- t)$$

To find the pre–exponential factors $A_\pm$, we use the boundary conditions. At zero time, $a = a_0$ and $b = b_0$, so $\dot{a} = Pa_0 + Qb_0$:

$$\begin{aligned} a_0 &= A_+ + A_- \\ Pa_0 + Qb_0 &= A_+\lambda_+ + A_-\lambda_- \end{aligned}$$

By subtraction:

$$A_\pm = \frac{a_0(P - \lambda_\mp) + Qb_0}{\pm(\lambda_+ - \lambda_-)}$$

Similarly, the time–dependence of b is:

$$b = B_+ \exp(\lambda_+ t) + B_- \exp(\lambda_- t)$$

with pre–exponential factors $B_{\pm}$:

$$B_{\pm} = \frac{b_0(S - \lambda_{\mp}) + Ra_0}{\pm(\lambda_+ - \lambda_-)}$$

APPENDIX C: Rate Constants for $H+O_2$, $H+O_2+N_2$

Results are presented here for each set of four H decay traces, gathered under identical conditions and analysed by FACSIMILE (Chapter 4).

The full data file name is formed with the prefix BANG. Thus 349–352 summarizes the results from files BANG349, BANG350, BANG351, and BANG352.

δt is the interval/10^{-4} s between successive points. $[H_2]$ = the initial concentration of $H_2/10^{16}$ molecule cm^{-3}. $[O_2]$ = the initial concentration of $O_2/10^{15}$ molecule cm^{-3}. k_2 = k ($H+O_2$) / 10^{-14} cm^3 molecule^{-1} s^{-1}; k_3 = k ($H+O_2+N_2$)/10^{-32} cm^6 molecule^{-2} s^{-1}. The bath gas is N_2. P is the pressure in Torr. T is the temperature/K.

As described in Chapter 4, each of four fitted parameters was given two different starting values to attempt a fit. Hence 16 fits were attempted per data file, and 64 per set of four files. Of those 64, N fits converged and were combined to yield the rate constants here. Chapter 4 discusses error limits and the covariance between fitted parameters. Blanks denote that no converged values were obtained.

Files	δt	P	$[O_2]$	$[H_2]$	N	k_2	k_3
241–244	1	157.9	7.03	1.63	32	0.750±0.006	1.35±0.02
245–248	2	158.5	7.57	1.64	18	1.00±0.03	1.03±0.06
249–252	2	157.85	7.66	1.63	14	1.04±0.02	2.09±0.07
253–256	5	158.1	7.96	1.63	2	0.79±0.05	0.98±0.02
257–260	1	243.2	7.53	1.57	38	0.412±0.003	0.48±0.02
261–264	1	243.5	8.26	1.57	27	0.44±0.01	0.61±0.03
265–268	2	244.3	9.49	1.57	13	0.43±0.02	0.57±0.04
269–272	2	241.0	10.1	1.53	9	0.61±0.02	0.89±0.04
273–276	5	241.7	10.7	1.53	9	0.41±0.01	0.44±0.05
277–280	5	241.6	10.4	1.53	11	0.44±0.02	0.55±0.04
281–284	1	199.2	6.96	1.26	34	0.645±0.009	1.06±0.02
285–288	2	197.1	6.04	1.30	41	0.90±0.03	1.49±0.06
289–292	1	197.85	7.59	1.30	33	0.564±0.002	0.79±0.01
293–296	2	197.58	8.59	1.30	12	0.808±0.008	1.28±0.02
297–300	5	197.85	8.79	1.30	6	0.53±0.01	0.68±0.01
425–428	1	253.3	3.35	0.0631	0		
429–432	1	258.65	6.51	0.0616	0		

800 K data. Fitted $[O]_0$ = 4–8 $\times 10^{11}$ cm^{-3}.

Files	δt	P	$[O_2]$	$[H_2]$	N	k_2	k_3
301–304	1	147.5	3.68	1.49	55	1.15±0.02	2.88±0.11
305–308	1	147.8	4.57	1.49	52	1.024±0.007	2.34±0.02
309–312	2	148.5	5.45	1.49	28	1.10±0.04	2.38±0.11
313–316	5	148.8	6.00	1.50	5	1.26±0.06	2.70±0.25
317–320	2	103.1	5.49	0.98	23	1.76±0.02	5.18±0.10
321–324	2	103.9	4.36	1.02	11	2.58±0.03	7.67±0.09
325–328	5	104.0	4.49	1.02	4	1.66±0.27	3.47±1.07
329–332	1	103.0	3.52	1.01	33	3.44±0.16	10.8±0.60
333–336	2	179.0	4.90	1.31	35	0.946±0.008	1.84±0.03
337–340	1	177.8	3.97	1.30	48	1.12±0.01	2.45±0.04
341–344	5	179.9	5.55	1.32	6	1.06±0.09	2.02±0.24
345–348	2	179.5	5.20	1.31	14	1.27±0.04	2.57±0.10
349–352	1	125.1	4.04	1.10	53	1.49±0.02	4.69±0.08
353–356	1	127.0	5.22	1.12	44	1.17±0.01	3.17±0.03
357–360	5	128.7	6.14	1.13	1	1.75	4.93
361–364	2	127.9	5.60	1.13	11	1.54±0.01	4.42±0.03

825 K data. Fitted $[O]_0$ = 5–11 $\times 10^{11}$ cm^{-3}.

Files	δt	P	$[O_2]$	$[H_2]$	N	k_2	k_3
365–368	1	99.6	5.17	0.862	24	2.01±0.02	6.53±0.10
369–372	2	99.9	5.56	0.863	7	1.96±0.02	6.15±0.12
373–376	5	99.9	5.69	0.864	0		
377–380	2	99.8	5.38	0.862	8	2.02±0.02	6.31±0.10
381–384	1	151.2	3.58	1.56	49	1.33±0.03	3.05±0.08
385–388	1	151.45	3.96	1.56	50	1.41±0.03	3.13±0.09
389–392	2	149.93	4.40	1.54	39	1.46±0.04	3.32±0.12
393–396	5	149.45	5.04	1.54	0		
397–400	1	127.83	4.20	1.21	46	1.62±0.03	4.23±0.10
401–404	2	127.95	4.61	1.21	27	1.57±0.01	3.97±0.02
405–408	2	127.8	4.75	1.21	21	1.62±0.02	4.03±0.06
409–412	5	127.9	5.06	1.21	4	1.89±0.06	5.02±0.16
413–416	1	175.55	4.65	1.64	45	1.12±0.02	2.96±0.10
417–420	1	176.1	5.15	1.64	46	0.945±0.006	2.12±0.02
421–424	2	176.2	5.69	1.64	31	0.80±0.02	1.52±0.05

850 K data. Fitted $[O]_0$ = 5–11 $\times 10^{11}$ cm^{-3}.

All results at the same temperature and pressure were weighted by N and combined:

Files	T	P	Total N	k_2	k_3
241–256	800	158	66	0.88±0.02	1.44±0.05
281–300	800	198	126	0.72±0.01	1.13±0.03
257–280	800	243	107	0.441±0.005	0.56±0.01
425–432	800	256	0		
317–332	825	104	71	2.66±0.12	8.08±0.43
349–364	825	127	109	1.37±0.02	4.05±0.08
301–316	825	148	140	1.10±0.01	2.57±0.05
333–348	825	179	103	1.08±0.01	2.23±0.04
365–380	850	100	39	2.003±0.003	6.42±0.02
397–412	850	128	98	1.617±0.006	4.15±0.02
381–396	850	151	138	1.396±0.005	3.16±0.01
413–424	850	176	122	0.97±0.01	2.28±0.05

All results at the same temperature were weighted by total N and combined:

Files	T	Total N	k_2	k_3
241–300	800	299	0.66±0.01	0.99±0.02
301–364	825	423	1.43±0.03	2.95±0.03
365–424	850	397	1.38±0.02	3.45±0.06

Including uncertainties in the rate constants fed into the full mechanism, the following errors result. k_2^t or k_3^t denote the values of Tsang *et al.* ([5] of Chapter 4):

Files	T	Total N	k_2	k_2^t	k_3	k_3^t
241–300	800	299	0.66±0.19	0.84	0.99±0.55	2.25
301–364	825	423	1.43±0.19	1.16	2.95±0.55	2.15
365–424	850	397	1.38±0.19	1.57	3.45±0.55	2.08

APPENDIX D: Experimental and Master Equation results for k_{rec}(H+C_2H_4)

Input parameters are discussed in Chapter 6. P = pressure He / Torr. $k = k_{rec}(\mathrm{H+C_2H_4})/10^{-12}$ cm^3 molecule^{-1} s^{-1}. In the reversible model, k is derived from k_{rel} (Chapter 6). $k^{(2)}_{irrev}$ was generated by defining $\langle \Delta E \rangle_{down} = YE_j$ in the model of Shi *et al.* [5, Chapter 6]. k^{TH} was calculated from the different k^{∞}_{rec} of Tsang *et al.* [17, Chapter 6]. To calculate $k^{(3)}_{irrev}$ (800 K), A^{∞}_{rec} was increased to fit k^{∞}_{rec}(800 K).

K_c was generated using partition functions from the calculated densities of states.

Experimental P:

T	P	k_{expt}	k_{irrev}	k_{rev}	$k_{irrev}^{(2)}$	k_{irrev}^{TH}	k_{rev}^{TH}	$k_{irrev}^{(3)}$
285	50	0.601	0.564	0.576	0.560	0.535	0.546	
285	100	0.698	0.680	0.694	0.681	0.662	0.675	
285	200	0.754	0.778	0.794	0.782	0.782	0.798	
285	400	0.779	0.851	0.869	0.856	0.885	0.904	
400	100	1.33	1.368	1.381	1.344	1.376	1.390	
400	200	1.79	1.714	1.730	1.710	1.708	1.726	
400	400	2.08	2.038	2.057	2.051	2.031	2.051	
400	600	2.11	2.206	2.226	2.227	2.205	2.228	
511	50	1.64	1.423	1.431	1.367	1.432	1.442	
511	100	2.04	1.946	1.958	1.910	1.934	1.947	
511	200	2.46	2.526	2.541	2.523	2.503	2.521	
511	400	2.92	3.119	3.138	3.153	3.108	3.130	
511	700	3.57	3.573	3.595	3.633	3.593	3.618	
604	50	1.62	1.552	1.558	1.478	1.532	1.544	
604	100	2.15	2.174	2.183	2.121	2.141	2.158	
604	200	2.83	2.903	2.915	2.889	2.875	2.898	
604	400	3.53	3.697	3.712	3.734	3.709	3.738	
604	600	4.38	4.168	4.186	4.237	4.225	4.259	
800	97	1.97	1.869	1.873	1.788	1.796	1.804	1.796
800	157	2.51	2.406	2.412	2.345	2.339	2.348	2.346
800	204	2.83	2.737	2.744	2.693	2.681	2.692	2.690
800	258	3.12	3.058	3.065	3.031	3.017	3.029	3.027
800	295	3.06	3.250	3.258	3.236	3.221	3.234	3.230
800	374	3.64	3.605	3.615	3.616	3.605	3.620	3.610
800	455	3.61	3.914	3.924	3.947	3.944	3.961	3.943
800	524	4.01	4.143	4.154	4.194	4.200	4.218	4.193
800	600	4.66	4.368	4.379	4.436	4.455	4.474	4.440

P	k_{irrev}	k_{rev}	$k_{irrev}^{(2)}$	k_{irrev}^{TH}	k_{rev}^{TH}
10^{-3}	1.843×10^{-4}	1.871×10^{-4}	1.499×10^{-4}	2.253×10^{-4}	2.293×10^{-4}
0.01	1.471×10^{-3}	1.495×10^{-3}	1.232×10^{-3}	1.814×10^{-3}	1.847×10^{-3}
0.1	0.0112	0.0114	9.654×10^{-3}	0.0125	0.0128
1	0.0693	0.0706	0.0627	0.0693	0.0707
10	0.291	0.297	0.280	0.271	0.277
100	0.680	0.694	0.661	0.662	0.676
10^3	0.913	0.932	0.917	0.988	1.010
10^4	0.965	0.985	0.965	1.100	1.123
10^5	0.971	0.991	0.971	1.118	1.142
10^6	0.972	0.992	0.972	1.120	1.155
10^7	0.972	0.992	0.972	1.121	1.145
10^8	0.972	0.992	0.972	1.121	1.145

285 K: $k_{rec}^{\infty} = 0.972$, $k_{rec}^{\infty,TH} = 1.121$.

P	k_{irrev}	k_{rev}	$k_{irrev}^{(2)}$	k_{irrev}^{TH}	k_{rev}^{TH}
10^{-3}	1.608×10^{-4}	1.611×10^{-4}	1.213×10^{-4}	3.132×10^{-4}	3.155×10^{-4}
0.01	1.381×10^{-3}	1.386×10^{-3}	1.069×10^{-3}	2.547×10^{-3}	2.568×10^{-3}
0.1	0.0115	0.0115	9.150×10^{-3}	0.0184	0.0186
1	0.0813	0.0818	0.0685	0.110	0.111
10	0.430	0.433	0.391	0.484	0.489
100	1.368	1.381	1.344	1.376	1.390
10^3	2.388	2.414	2.415	2.403	2.427
10^4	2.816	2.843	2.830	2.930	2.960
10^5	2.896	2.924	2.898	3.054	3.085
10^6	2.905	2.933	2.905	3.070	3.102
10^7	2.906	2.934	2.906	3.072	3.103
10^8	2.906	2.934	2.906	3.072	3.104

400 K: $k_{rec}^{\infty} = 2.906$, $k_{rec}^{\infty,TH} = 3.072$.

P	k_{irrev}	k_{rev}	$k_{irrev}^{(2)}$	k_{irrev}^{TH}	k_{rev}^{TH}
10^{-3}	1.858×10^{-4}	1.858×10^{-4}	1.410×10^{-4}	3.231×10^{-4}	3.248×10^{-4}
0.01	1.649×10^{-3}	1.647×10^{-3}	1.274×10^{-3}	2.690×10^{-3}	2.705×10^{-3}
0.1	0.0139	0.0140	0.0110	0.0202	0.0203
1	0.102	0.102	0.0853	0.127	0.128
10	0.564	0.567	0.510	0.607	0.611
100	1.946	1.958	1.911	1.934	1.947
10^3	3.840	3.864	3.911	3.889	3.917
10^4	4.935	4.965	4.987	5.276	5.313
10^5	5.202	5.234	5.212	5.722	5.762
10^6	5.237	5.269	5.239	5.794	5.835
10^7	5.241	5.273	5.241	5.802	5.843
10^8	5.242	5.273	5.242	5.803	5.844

511 K: $k_{rec}^{\infty} = 5.240$, $k_{rec}^{\infty,TH} = 5.803$.

P	k_{irrev}	k_{rev}	$k_{irrev}^{(2)}$	k_{irrev}^{TH}	k_{rev}^{TH}
10^{-3}	1.802×10^{-4}	1.801×10^{-4}	1.357×10^{-4}	2.745×10^{-4}	2.763×10^{-4}
0.01	1.632×10^{-3}	1.631×10^{-3}	1.247×10^{-3}	2.336×10^{-3}	2.352×10^{-3}
0.1	0.0139	0.0139	0.0110	0.0181	0.0182
1	0.104	0.104	0.0858	0.119	0.120
10	0.592	0.594	0.530	0.608	0.613
100	2.174	2.183	2.122	2.141	2.158
10^3	4.745	4.766	4.849	4.885	4.924
10^4	6.612	6.641	6.719	7.380	7.438
10^5	7.177	7.208	7.201	8.421	8.487
10^6	7.261	7.293	7.264	8.625	8.693
10^7	7.270	7.301	7.270	8.650	8.718
10^8	7.271	7.302	7.271	8.653	8.720

604 K: $k_{rec}^{\infty} = 7.271$, $k_{rec}^{\infty,TH} = 8.653$.

P	k_{irrev}	k_{rev}	$k_{irrev}^{(2)}$	k_{irrev}^{TH}	k_{rev}^{TH}
10^{-3}	1.119×10^{-4}	1.119×10^{-4}	8.292×10^{-5}	1.353×10^{-4}	1.358×10^{-4}
0.01	1.042×10^{-3}	1.042×10^{-3}	7.813×10^{-4}	1.200×10^{-3}	1.205×10^{-3}
0.1	9.136×10^{-3}	9.141×10^{-3}	7.040×10^{-3}	9.872×10^{-3}	9.911×10^{-3}
1	0.0711	0.0712	0.0575	0.0715	0.0718
10	0.441	0.442	0.386	0.420	0.422
100	1.900	1.905	1.826	1.827	1.835
10^3	5.253	5.266	5.397	5.490	5.513
10^4	9.056	9.081	9.369	10.86	10.91
10^5	10.88	10.91	10.99	14.69	14.75
10^6	11.25	11.28	11.26	15.89	15.96
10^7	11.29	11.32	11.29	16.08	16.15
10^8	11.29	11.32	11.29	16.10	16.18

800 K: $k_{rec}^{\infty} = 11.30$, $k_{rec}^{\infty,TH} = 16.10$.

P	k_{irrev}	$k_{irrev}^{(3)}$
10^{-3}	1.119×10^{-4}	9.322×10^{-5}
0.01	1.042×10^{-3}	8.700×10^{-4}
0.1	9.136×10^{-3}	7.722×10^{-3}
1.	0.0711	0.0615
10.	0.441	0.399
100.	1.900	1.828
10^3	5.253	5.427
10^4	9.056	10.02
10^5	10.88	12.54
10^6	11.25	13.12
10^7	11.29	13.19
10^8	11.29	13.19

800 K: $k_{rec}^{\infty} = 11.30$.

APPENDIX E: The Extended Beyer–Swinehart State Counting Algorithm

Stein *et al.* [19, Chapter 6] described the algorithm published by Beyer and Swinehart, and extended it for any type of degree of freedom. The following steps were used:

1. A cell size $\delta E = 1$ cm^{-1} and a total number of cells $G =$ (usually) 30000 were chosen: the highest energy was therefore $E_{max} = G\delta E =$ (usually) 30000 cm^{-1}.

2. An array T of length G was declared, and each element, corresponding to one cell, was filled with the cell's rotational degeneracy.

3. For each oscillator (index l), all its vibrational levels up to E_{max} were defined (by assuming it was harmonic). The level denoted by subscript k ($1 \leq k \leq G$) had an energy E_l, which was truncated to an integer R_l:

$$R_l = \text{int}\left(\frac{E_l}{\delta E}\right)$$

The highest level had a subscript G. For each k, the following operations were performed ($I = 1 \rightarrow G - R_l$):

$$T(R_l + I) = T(R_l + I) + T(I)$$

4. At the end, $T(I)$ was the degeneracy of cell I: division by δE gave the density of states. Since the vibrational frequencies were only given to 1 cm^{-1}, the rounding of E_l to R_l was exact, so the state-counting was also exact.

APPENDIX F: Relaxation rate constant for equilibrium A⇌B

Let the first–order rate constants be k_a and k_b:

$$\mathrm{A} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} \mathrm{B}$$

Without loss of generality, let initial concentrations of A and B be $[\mathrm{A}]_0$ and 0 respectively, and let the system evolve to equilibrium. At time t, concentrations are [A] and [B]:

$$[\mathrm{A}] + [\mathrm{B}] = [\mathrm{A}]_0$$

Consider kinetics of A:

$$\begin{aligned} \frac{d}{dt}[\mathrm{A}] &= -k_a[\mathrm{A}] + k_b[\mathrm{B}] \\ &= -k_a[\mathrm{A}] + k_b([\mathrm{A}]_0 - [\mathrm{A}]) \end{aligned}$$

or

$$\frac{d}{dt}[\mathrm{A}] = -k_{rel}[\mathrm{A}] + k_b[\mathrm{A}]_0 \qquad (.1)$$

where $k_{rel} = k_a + k_b$. At equilibrium ($t = \infty$), the concentrations are $[\mathrm{A}]_\infty$ and $[\mathrm{B}]_\infty$. The equilibrium constant is:

$$\begin{aligned} K &= [\mathrm{B}]_\infty/[\mathrm{A}]_\infty \\ &= [\mathrm{A}]_0/[\mathrm{A}]_\infty - 1 \end{aligned}$$

Also, $K = k_a/k_b$. Thus:

$$
\begin{aligned}
[\mathrm{A}]_0/[\mathrm{A}]_\infty - 1 &= k_a/k_b \\
k_b[\mathrm{A}]_0 - k_b[\mathrm{A}]_\infty &= k_a[\mathrm{A}]_\infty \\
k_b[\mathrm{A}]_0 &= k_{rel}[\mathrm{A}]_\infty
\end{aligned}
$$

At equilibrium

$$
\frac{d}{dt}[\mathrm{A}]_\infty = 0
$$

Substituting both expressions in Equation .1:

$$
\begin{aligned}
\frac{d}{dt}([\mathrm{A}] - [\mathrm{A}]_\infty) &= -k_{rel}([\mathrm{A}] - [\mathrm{A}]_\infty) \\
\frac{d}{dt}\ln([\mathrm{A}] - [\mathrm{A}]_\infty) &= -k_{rel}
\end{aligned}
$$

Thus the system relaxes to equilibrium, with a first–order rate constant k_{rel} equal to the sum of the opposing rate constants k_a and k_b. Rearranging:

$$
\begin{aligned}
k_a &= \frac{k_{rel}}{1 + K^{-1}} \\
k_b &= \frac{k_{rel}}{1 + K}
\end{aligned}
$$

APPENDIX G: Calculation of the density of states of a free internal rotor

Herzberg [11, Chapter 6] states that such a species is characterized by quantum numbers J, K, k_1, and k_2. K describes that component about the figure axis of the angular momentum J, and equals the sum of the components from the rotation of each end of the molecule:

$$k_1 + k_2 = \pm K$$

The rotational states have an energy:

$$E(J, K, k_1) \;=\; BJ(J+1) - BK^2 + a_1 k_1^2 + a_2 k_2^2 \qquad (.2)$$

where the single AK^2 term for a symmetric top has been replaced by separate terms for each end, $a_1 k_1^2$ and $a_2 k_2^2$. The rotational degeneracy of each state is

$$g(J, K, k_1) = (2J+1) g(K, k_1)$$

where $g(K, k_1) = 1$ if $K = k_1 = 0$: if $|K| > 0$ or $k_1 > 0$, two values of k_2 are possible, and $g(K, k_1) = 2$.

For each J state, the $K = 0$ case was considered first: k_1 was increased from 0, counting states, until the energy exceeded E_{max}.

When $K > 0$, the energy is a minimum at a value of k_1, k_{1min}, that may not be 0. To find this value, k_2 is replaced by $(K - k_1)$ in Equation .2, and E is differentiated with respect to k_1 at fixed J and K:

$$\left(\frac{\partial E}{\partial k_1}\right)_{J,K} = 2(a_1 + a_2) k_1 - 2 a_2 K$$

The case of $k_2 = -K - k_1$ corresponds to $K < 0$, and is included in the fact that $g(K, k_1) = 2$ if $|K| > 0$, so only $k_2 = K - k_1$ need be considered here. The derivative vanishes when $k_1 = k_{1min}$:

$$k_{1min} = \frac{a_2}{a_1 + a_2}$$

The second derivative then has the value:

$$\left(\frac{\partial^2 E}{\partial k_1^2}\right)_{J,K} = 2(a_1 + a_2)$$

This expression is strictly positive, so k_{1min} does represent a minimum energy. Analytic formulae (Chapter 6) were used to find the maximum J and K values to be considered. For a given J and K, the energy was evaluated with $k_1 = k_{1min}$: if this exceeded E_{max}, K was increased by 1 till its maximum value was reached. Otherwise, k_1 was decreased from k_{1min} to 0, and then increased from $(k_{1min} + 1)$, to count all states below E_{max}.

APPENDIX H: Inverse Laplace Transformation

Chapter 6 uses an Inverse Laplace Transformation (ILT) to determine the microcanonical rate constant for dissociation, k_i, from the limiting high–pressure rate constant for recombination, k_{rec}^{∞}. Davies *et al.* [4, Chapter 6] provided the following derivation, for A dissociating to B+C:

$$k_d(E)N(E) = \mathcal{L}^{-1}\{q_{rv}(\beta)k_d^{\infty}(\beta)\}$$

where all quantities refer to A. $\mathcal{L}^{-1}$ denotes an ILT with variable $\beta = (k_B T)^{-1}$, and Chapter 6 describes all other notation. The equilibrium constant may be used to consider recombination:

$$\begin{aligned} K_c &= \frac{q_b(T)q_c(T)}{q_a(T)} e^{-\beta \Delta E_0^0} \\ &= \frac{k_d^{\infty}(T)}{k_{rec}^{\infty}(T)} \end{aligned}$$

$$k_d^{\infty}(T) = k_{rec}^{\infty}(T) e^{-\beta \Delta E_0^0} \frac{q_b(T)q_c(T)}{q_a(T)}$$

where q denotes the total partition function. If $k_{rec}^{\infty}(T)$ can be expressed in Arrhenius form:

$$k_{rec}^{\infty} = A_{rec}^{\infty} e^{-\beta E_{rec}^{\infty}}$$

then

$$k_d(E)N(E) =$$

$$A_{rec}^{\infty} C' \mathcal{L}^{-1} \left\{ \int_0^{\infty} N_{BC}(E_{BC}) \beta^{-1.5} \exp[-\beta(E_{BC} + E_{rec}^{\infty} + \Delta E_0^0)] \, dE_{BC} \right\}$$

where

$$C' = \left(\frac{2\pi m_b m_c}{h^2 m_a} \right)^{1.5}$$

comes from the translational part of q, E_{BC} is the internal energy of (B+C) relative to their zero–point energy, and $N_{BC}(E_{BC})$ is the convolution of the rovibrational density of states for B and for C. From the ILT properties,

$$k_d(E)N(E) = A_{rec}^{\infty} C' \int_0^{\infty} N_{BC}(E_{BC}) \mathcal{L}^{-1}\{\beta^{-1.5} \exp[-\beta(E_{BC} + E_{rec}^{\infty} + \Delta E_0^0)]\} \, dE_{BC}$$

Inverting,

$$k_d(E)N(E) = \frac{2C' A_{rec}^{\infty}}{\sqrt{\pi}} \int_0^{E_A - E_{rec}^{\infty} - \Delta E_0^0} N_{BC}(E_{BC}) \sqrt{E_A - E_{BC} - E_{rec}^{\infty} - \Delta E_0^0} \, dE_{BC}$$

where E_A lies above the threshold for dissociation, so $E_A \geq E_{rec}^{\infty} + \Delta E_0^0$. If B+C are H+$C_2H_4$, H has no internal states at moderate energies, so $N_{BC}(E_{BC})$ is just $N_{C_2H_4}(E_{C_2H_4})$.

If $k_{rec}^{\infty}(T)$ has a modified Arrhenius form

$$k_{rec}^{\infty} = A_{rec}^{\infty} \left(\frac{T}{300 \text{ K}} \right)^{n^{\infty}} e^{-\beta E_{rec}^{\infty}}$$

where $n^{\infty} > -1.5$, then it may be shown that

$$\begin{aligned} k_d(E)N(E) &= Q \int_0^{E_A - E_{rec}^{\infty} - \Delta E_0^0} N_{BC}(E_{BC}) X \, dE_{BC} \\ Q &= \frac{C' A_{rec}^{\infty}}{(300 k_B)^{n^{\infty}} \Gamma(1.5 + n^{\infty})} \\ X &= [E_A - E_{BC} - E_{rec}^{\infty} - \Delta E_0^0]^{(n^{\infty} + 0.5)} \end{aligned}$$

APPENDIX I: $[O]_0$ PRODUCED BY N_2O PHOTOLYSIS

Pulse energy of 80 mJ covered an area of 0.7 cm × 2.2 cm before collimation; fluence = 52 mJ cm^{-2}.

At 193.3 nm, the 3 mm thick Spectrosil "B" cell window may absorb 10%, and will reflect 4% from each surface at normal incidence. Fluence inside cell = 43 mJ cm^{-2} = 4.3×10^{16} photons cm^{-2} (one 193.3 nm photon has energy of 10^{-18} J).

298 K absorption cross-section of N_2O = 1.1×10^{-19} cm^2 $molecule^{-1}$ (Okabe, [5] of Chapter 2). If $[N_2O]$ = 4×10^{14} molecule cm^{-3}, then $\sigma\times$ $[N_2O]$ = 4.4×10^{-5} cm^{-1}.

Number of photons absorbed per cm = $\sigma\times$ $[N_2O]$ × photon fluence = 1.9×10^{12} cm^{-1}. The quantum yield for $O(^1D)$ production is >0.97 [Okabe], so $[O(^1D)]_0$ = 1.9×10^{12} cm^{-3}.

For the O+allyl experiments, $k(O(^1D) + N_2)[N_2] \gg k(O(^1D) + C_6H_{10})$ $[C_6H_{10}]$, so almost all $O(^1D)$ is quenched to $O(^3P)$ before it can be removed by C_6H_{10}. Hence $[O(^3P)]_0 \simeq [O(^1D)]_0$.

APPENDIX J: RATE CONSTANTS FOR THE REACTIONS H + ALLYL, O + ALLYL

Chapter 7 defines δt, the sample interval / μs. n is the number of converged fits from each set of (usually) four experiments. $[A_2]$ is the pre–flash [1,5–hexadiene] / 10^{13} molecule cm^{-3}. E is the laser pulse energy / mJ. $[A]_0$ is the fitted value of zero–time [allyl] / 10^{12} molecule cm^{-3}. k_2 is the fitted value of k(atom+allyl) / 10^{-10} cm^3 molecule^{-1} s^{-1}. Errors are taken from the fitting program. Each set of data files includes four decay traces and (usually) two control experiments (Chapter 7). Unless otherwise stated, the laser was fired at 3 Hz.

H+ALLYL

All measurements were performed at 291 K in He. The filenames begin with HALL: 292–297 summarizes the results from HALL292 to HALL297 inclusive.

HALL	n	$[A_2]$	E	$[A]_0$	k_2
292–297	2	1.87	97	3.8	2.39
305–310	3	4.78	98	3.7	3.64
311–316	4	4.80	70	2.5	2.64
317–322	4	7.68	109	4.8	2.57
323–328	4	7.65	87	4.4	2.94
329–334	4	7.64	63	2.6	3.91
335–340	4	11.3	126	8.2	1.11
341–346	4	11.3	95	7.7	1.92
347–352	4	11.3	62	4.9	3.03

98 Torr, $\delta t = 2\mu$s. $k_2 \pm \simeq 0.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

HALL	δt	n	$[A_2]$	E	$[A]_0$	k_2
141–145	0.5	4	33.3	86	78	1.40
146–149	0.5	4	33.3	86	59	1.66
150–154	0.5	4	33.3	45	32	2.28
155–159	0.5	4	33.3	25	16	1.99
160–165	0.2	5	87.0	80	151	1.39
166–169	0.2	4	87.0	80	155	1.10
170–174	0.2	4	87.0	39	70	1.20
185–189	1	4	8.50	77	13	1.23
190–194	1	4	8.50	43	8.3	0.84
200–204	1	4	19.3	59	20	1.63
205–209	1	4	19.3	33	11	1.13

200 Torr, $k_2\pm \simeq 0.15 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. No radio frequency interference control experiments were recorded. 146–149 and 166–169 were performed at a laser repetition rate of 1 Hz.

HALL	n	$[A_2]$	E	$[A]_0$	k_2
425–430	3	5.06	117	1.2	2.89
431–436	2	5.08	89	1.1	4.24
437–442	4	5.08	61	1.2	4.28
461–466	4	11.2	104	1.6	4.21
467–472	2	11.2	83	1.6	5.19
473–478	4	11.2	58	1.6	3.43

300 Torr, $\delta t = 5\mu$s. $k_2\pm \simeq 0.35 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

HALL	n	$[A_2]$	E	$[A]_0$	k_2
210–215	4	10.3	80	3.1	4.13
216–221	4	10.3	84	3.7	3.68
222–227	4	10.3	80	3.5	4.01
228–233	3	10.3	107	3.3	3.92
234–239	4	10.4	90	2.9	4.62
240–245	3	10.4	73	3.3	4.36
246–252	4	15.7	93	5.8	2.93
253–258	4	15.7	75	3.8	4.32
259–264	4	15.7	57	4.6	3.53
265–271	4	20.7	113	5.0	4.69
277–284	4	21.7	77	6.4	2.52
285–291	4	21.7	79	8.2	3.32

400 Torr, $\delta t = 2\mu$s. $k_2 \pm \simeq 0.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. 216–221 and 285–291 were performed at 2 Hz, 222–227 at 1 Hz.

HALL	n	$[A_2]$	E	$[A]_0$	k_2
359–364	4	6.39	90	1.18	8.57
365–370	4	6.40	70	1.38	6.09
371–376	3	6.42	118	1.81	6.22
377–382	4	7.88	92	1.77	6.19
383–388	3	7.88	67	1.46	7.62
389–394	4	11.5	116	3.7	6.67
395–400	4	11.4	90	2.8	8.20
401–406	4	11.5	66	5.6	9.25
407–412	4	14.5	112	3.03	7.44
413–418	4	14.4	86	2.84	6.06
419–424	4	14.5	58	2.93	8.65

600 Torr, $\delta t = 2\mu$s. $k_2\pm \simeq 0.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

All measurements at the same pressure were averaged (using values from individual experiments). Values are not corrected for side–reactions (Chapter 7):

P / Torr	HALL	n	$[A_2]$	E	$[A]_0$	k_2
98	292–297, 305–352	33	1.87–11.8	62–126	2.5–8.2	2.67±0.19
200	141–209	45	8.50–87.0	25– 86	8.3–155	1.44±0.07
300	425–442, 461–478	19	5.06–11.2	58–117	1.1–1.6	3.96±0.23
400	210–271, 277–291	46	10.3–21.7	57–113	2.9–8.2	3.81±0.13
600	359–424	42	6.39–14.5	58–118	1.2–5.6	7.38±0.23

O+ALLYL

All measurements were performed in N_2. The filenames begin with OALL. $[N_2O]$ is the pre–flash value / 10^{14} molecule cm^{-3}. P is the pressure / Torr.

OALL	P	δt	n	$[A_2]$	$[N_2O]$	E	$[A]_0$	k_2
57– 61	195	2	3	4.97	3.3	91	3.06	2.69
62– 67	195	2	3	7.55	3.3	91	4.70	2.89
68– 73	105	5	2	2.64	3.47	91	1.52	1.63
74– 79	105	5	4	5.46	3.47	91	5.12	1.20
80– 85	106	2	4	8.02	3.47	91	6.85	1.53
86– 91	107	2	4	10.3	3.47	91	10.4	1.94
92– 97	107	2	4	13.2	3.47	91	12.4	2.06
98–102	292	5	1	7.28	3.2	85	3.31	2.21
103–108	292	1	4	3.58	3.78	93	1.88	1.99
109–114	292	1	4	5.46	3.78	93	4.35	3.67
115–120	292	1	4	9.43	3.78	93	5.28	4.64
121–126	293	1	3	11.4	3.78	93	6.10	1.64
127–131	294	1	3	13.2	3.78	93	5.84	2.66
132–137	348	2	4	6.50	2.94	93	2.62	2.32
138–143	348	2	2	8.96	2.94	93	3.25	1.72
156–161	203	5	3	5.10	3.16	87	1.88	1.30
162–167	48	5	4	2.43	2.86	87	2.10	1.69
168–173	48	1	4	3.38	2.80	94	2.79	2.41
174–179	48	1	3	4.64	2.80	94	4.56	3.20
180–185	48	1	4	5.80	2.80	94	5.33	1.15

286 K, $k_2 \pm \simeq 0.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

OALL	P	δt	n	$[A_2]$	$[N_2O]$	E	$[A]_0$	k_2
186–191	201	2	4	5.58	2.24	93	6.26	2.27
192–197	203	2	4	9.33	2.24	93	9.35	3.99
198–203	204	1	2	12.8	2.24	93	12.9	1.17
247–252	202	5	1	1.94	2.25	75	2.05	1.82
259–264	201	2	3	6.02	2.25	75	5.12	1.61
265–270	201	1	4	8.10	2.25	75	8.06	2.09
271–276	203	1	4	10.1	2.25	75	13.4	2.40
277–282	291	5	4	5.85	2.29	83	6.88	1.16
283–288	291	2	4	8.83	2.29	83	5.05	4.97
289–294	49	2	4	1.93	2.09	81	4.79	1.17
295–300	49	2	3	2.84	2.09	81	4.35	2.26
301–306	49	1	4	3.70	2.09	81	7.36	1.74
307–312	49	1	4	4.65	2.09	81	8.36	1.55
313–318	293	1	4	11.9	2.29	61	41.1	0.47

402 K, $k_2 \pm \simeq 0.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

OALL	δt	n	$[A_2]$	$[N_2O]$	E	$[A]_0$	k_2
320–324	5	4	1.98	2.11	68	3.73	1.34
325–330	5	4	4.99	2.11	68	6.76	1.44
557–562	1	4	7.22	1.75	73	9.80	2.06
563–568	1	4	7.23	1.75	94	8.19	2.68
576–580	1	3	7.18	1.75	65	8.31	4.25
581–586	1	4	10.9	2.09	72	15.2	1.89
587–592	1	4	10.7	2.09	93	9.88	3.07
593–598	1	4	10.8	2.09	53	11.8	2.89
599–604	1	4	10.9	2.09	71	9.40	2.62
605–610	1	3	10.8	2.09	70	10.2	2.60
611–616	1	3	5.16	2.10	98	3.92	4.13
617–622	1	4	5.13	2.10	79	11.3	2.41
623–628	1	4	5.21	2.10	57	5.90	2.66
629–634	1	3	2.08	2.10	110	5.94	1.77
635–640	1	4	2.06	2.10	89	5.08	2.30
641–646	1	4	2.06	2.10	56	3.24	2.15

500 K, 50 Torr, $k_2 \pm \simeq 0.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. 576–580 and 599–604 were performed at a laser repetition rate of 2 Hz, and 605–610 at 1 Hz.

OALL	δt	n	$[A_2]$	$[N_2O]$	E	$[A]_0$	k_2
331–336	5	4	2.32	2.31	68	3.31	1.21
337–342	5	4	5.67	2.31	68	4.39	1.38
343–348	2	4	4.90	1.98	75	5.60	1.96
349–354	2	4	7.78	1.98	75	9.80	1.13
355–360	5	3	2.01	1.98	75	3.49	1.35
361–366	1	4	10.7	1.98	75	17.8	1.56
367–372	1	4	4.96	2.00	68	8.99	1.86
373–378	1	4	4.97	2.00	62	10.0	2.07

500 K, 100 Torr, $k_2\pm \simeq 0.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. 373–378 were performed at a laser repetition rate of 1 Hz.

OALL	δt	Rate	n	$[A_2]$	$[N_2O]$	E	$[A]_0$	k_2
397–402	1	3	3	21.2	10.1	61	17.2	1.13
403–408	1	3	4	21.2	10.1	86	18.2	1.87
409–411	1	1	1	21.2	10.1	71	16.5	2.45
412–418	2	3	4	2.05	10.3	76	1.11	2.06
419–424	2	1	2	2.05	10.3	74	1.24	3.56
425–431	2	3	3	2.05	10.3	115	0.75	8.23
432–437	1	3	4	10.2	4.83	62	9.37	2.68
448–454	1	3	4	11.1	4.87	108	9.06	4.71
455–461	1	3	4	11.1	4.87	89	7.65	2.74
462–467	1	3	4	11.1	4.87	71	15.4	1.73
468–474	1	3	4	11.3	4.93	73	9.40	3.62
475–480	1	2	4	11.3	4.93	72	10.0	3.69
481–486	1	1	1	11.2	4.93	71	8.08	4.59
487–492	1	3	4	7.90	4.91	66	6.83	3.25
493–499	2	3	5	4.87	4.91	108	4.48	1.56
500–505	2	3	4	4.91	4.91	85	39.7	0.59
506–511	2	3	4	4.93	4.91	68	3.91	1.65
512–518	1	3	4	7.92	4.93	67	9.22	2.69
519–525	1	2	4	7.93	4.93	75	12.5	2.00
526–532	1	1	2	7.92	4.93	63	5.52	3.20
537–543	1	3	4	7.84	4.88	101	4.97	6.58
544–549	1	3	4	7.88	4.88	92	7.51	3.97

500 K, 200 Torr, $k_2 \pm \simeq 0.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. "Rate" is the laser repetition rate / Hz. Two consecutive radio frequency interference control experiments were sometimes performed (Chapter 7).

All measurements at the same pressure were averaged (using values from individual experiments). Values are not corrected for side–reactions (Chapter 7):

OALL	T/K	P	n	[A_2]	k_2
162–185	285	48	15	2.80–2.86	2.44±0.21
68– 97	285	106	18	2.64–13.2	1.68±0.15
57– 67, 156–161	285	200	9	4.97–7.55	2.30±0.31
98–131	285	293	19	3.58–13.2	2.96±0.38
132–143	285	348	6	6.50,8.96	2.12±0.39
289–312	402	49	15	1.93–4.65	1.64±0.11
186–203, 247–252, 259–276	402	202	22	1.94–12.8	2.36±0.25
277–282, 313–318	402	292	8	6.02–11.9	0.82±0.19
319–330, 557–568, 576–646	500	50	60	1.98–10.9	2.47±0.11
331–378	500	100	31	2.01–10.7	1.57±0.08
397–437, 448–532, 537–549	500	200	77	2.05–21.2	3.01±0.20

All measurements at the same temperature were then averaged (using values from individual experiments). Values are not corrected for side–reactions (Chapter 7):

OALL	T/K	P	n	[A_2]	k_2
57–143, 156–185	285	48–348	67	2.64–13.2	2.33±0.14
186–203, 247–252,	402	49–292	45	1.93–11.9	1.85±0.16
259–282, 289–318					
320–378, 397–437, 448–532,	500	50–200	168	1.98–21.2	2.55±0.11
537–549, 557–568, 576–646					

APPENDIX K: TIME–DEPENDENCE OF [ATOM] IN ATOM + ALLYL REACTIONS

As in Chapter 7, the allyl radical is called A, and the atom X. At $t = 0$, [A] = $[A]_0$, and [X] = $[X]_0$. Chapter 7 shows that:

$$\frac{d}{dt}[X] = -k_2[X][A] - k'_X[X] \tag{.3}$$

where:

$$\begin{aligned} k'_X &= k_3[A_2] + k_4 \\ [A]^{-1} &= [A]_0^{-1} + 2k_1 t \end{aligned}$$

and $[A_2]$ is constant. The last equation may be rearranged:

$$[A] = \frac{[A]_0}{1 + 2k_1[A]_0 t}$$

and substituted into Equation .3:

$$-\frac{d}{dt}\ln[X] = \frac{k_2[A]_0}{1 + 2k_1[A]_0 t} + k'_X$$

Integrating,

$$\begin{aligned} \ln[X] &= -\frac{k_2}{2k_1}\ \ln(1 + 2k_1[A]_0 t) - k'_X t \\ \Longrightarrow \frac{[X]_t}{[X]_0} &= \exp(-k'_X t)\left\{1 + 2k_1[A]_0 t\right\}^{(-k_2/2k_1)} \end{aligned}$$

as stated in Chapter 7.

APPENDIX L: TROE CALCULATION OF k_d^0(H+allyl)

The reactions are:

$$C_3H_6 \underset{k_{2H}}{\overset{k_d}{\rightleftharpoons}} H + C_3H_5$$

where $k_{2H} = k_d/K_c$, and k_d^0 is factorized according to Troe [12, Chapter 7]:

$$k_d^0 = \beta_c \, Z \, f(E_0) \, F_e \, F_{anh} \, F_{rot}$$

Internal rotation is treated as a vibration. Table 1 lists all input data, and each term in k_d^0 is calculated in turn.

β_c

β_c allows for the weakness of collisions, and is given by

$$\beta_c = \left[\frac{\langle \Delta E \rangle_{down}}{\langle \Delta E \rangle_{down} \; + F_e k_B T} \right]^2$$

F_e is defined below. At 291 K, k_BT = 202 cm^{-1} and F_e = 1.099. From Chapter 6, $\langle \Delta E \rangle_{down}$ = 44 cm^{-1} at 285 K for C_2H_5 in He. A larger value would be expected for the larger species C_3H_6, so $\langle \Delta E \rangle_{down}$ was set to 60 cm^{-1}, and β_c = 0.0452.

Z

The collision rate constant, Z, was calculated as in Chapter 6. For the collision pair C_3H_6–He, s = 0.3615 nm (arithmetic mean of separate values), ϵ = 55.3 K

Species	Quantity / units	Value(s)	Reference
C_3H_6	internal rotors	0	
	no. of oscillators	21	
	ν_i / cm^{-1}	3091, 3022, 2991, 2973, 2953, 2932, 1653, 1459, 1443, 1414, 1378, 1298, 1178, 1045, 990, 935, 919, 912, 575, 428, 188 (torsion)	[26]
	$\Delta H^0_{f,298}$ / cm^{-1}	1711	[26]
	S^0_{298} / J mol^{-1} K^{-1}	266.9	[27]
	s / nm	0.4678	[15]
	(ϵ/k_B) / K	298.9	[15]
C_3H_5	ν_i / cm^{-1}	3412, 3407, 3327, 3318, 3314, 1661, 1632, 1556, 1370, 1204, 1093, 1051, 1040, 786, 761, 596, 562, 476	[28]
	$\Delta H^0_{f,298}$ / cm^{-1}	12454	[29]
	S^0_{298} / J mol^{-1} K^{-1}	265.3	[27]
H	$\Delta H^0_{f,298}$ / cm^{-1}	18216	[30]
	S^0_{298} / J mol^{-1} K^{-1}	114.6	[27]
He	s / nm	0.2551	[15]
	(ϵ/k_B) / K	10.22	[15]

Table 1: Quantities used to calculate k^0_d (291 K, He). References: see Chapter 7.

(geometric mean), $\Omega^{(2,2)} = 0.916$, and $\mu = 168\text{u}/46$. At 291 K, $Z = 4.888\times10^{-10}$ cm^3 molecule^{-1} s^{-1}.

$\mathbf{f(E_0)}$

For this reaction, there will be no barrier to recombination, and the threshold energy, E_0, is equal to the zero–point energy difference, ΔE_0^0. $f(E_0)$ includes the density of vibrational states from which reaction occurs:

$$f(E_0) = \frac{k_B T n^{vib}(E_0)}{q^{vib}} \exp\left(\frac{-E_0}{k_B T}\right)$$

where $E_0 = \Delta E_0^0$. At a temperature T:

$$\begin{aligned} \Delta E_T^0 \quad &= \quad E_T^0(\mathrm{C_3H_5}) + E_T^0(\mathrm{H}) - E_T^0(\mathrm{C_3H_6}) \\ \Longrightarrow \Delta E_0^0 \quad &= \Delta E_T^0 \quad + [E_T^0(\mathrm{C_3H_6}) - E_0^0(\mathrm{C_3H_6})] \\ &\qquad\quad - [E_T^0(\mathrm{C_3H_5}) - E_0^0(\mathrm{C_3H_5})] \\ &\qquad\quad - [E_T^0(\mathrm{H}) - E_0^0(\mathrm{H})] \end{aligned}$$

The internal energy of C_3H_5 and C_3H_6, E, has components from whole–body rotation and vibration:

$$E_T^0 = 1.5 k_B T + E_T^{0,vib}$$

So

$$\begin{aligned} E_0 = \Delta E_T^0 &+ [E_T^{0,vib}(\mathrm{C_3H_6}) - E_0^{0,vib}(\mathrm{C_3H_6})] \\ &- [E_T^{0,vib}(\mathrm{C_3H_5}) - E_0^{0,vib}(\mathrm{C_3H_5})] \end{aligned}$$

For ideal gases, $\Delta E_T^0 = \Delta H_T^0 + k_B T$, and

$$\begin{aligned} E_0 = \Delta H_T^0 + k_B T &+ [E_T^{0,vib}(\mathrm{C_3H_6}) - E_0^{0,vib}(\mathrm{C_3H_6})] \\ &- [E_T^{0,vib}(\mathrm{C_3H_5}) - E_0^{0,vib}(\mathrm{C_3H_5})] \end{aligned}$$

$\Delta H_{298}^0 = 28959$ cm^{-1}, $E_{298,vib}^0$ ($\mathrm{C_3H_6}$) $-$ $E_0^{0,vib}$ ($\mathrm{C_3H_6}$) $= 190$ cm^{-1}, and $E_{298,vib}^0$ ($\mathrm{C_3H_5}$) $-$ $E_0^{0,vib}$ ($\mathrm{C_3H_5}$) $= 189$ cm^{-1}. Thus $E_0 = 29162$ cm^{-1}.

$\mathbf{n^{vib}(E_0)}$

This is the density of vibrational states. In the Whitten–Rabinovitch approximation,

$$\begin{aligned} k_B T\ n^{vib}(E_0) &\approx \frac{k_B T\ (E_0 + a(E_0)E_z)^{s-1}}{(s-1)! \prod_{i=1}^{s} h\nu_i} \\ &= \frac{(hcW_R/k_B T)^{s-1}}{(s-1)! \prod_{i=1}^{s} hc\tilde{\nu}_i/k_B T} \end{aligned}$$

where $W_R = (E_0 + a(E_0)E_z)/hc$, and there are $s = 21$ oscillators. Now

$$E_z = \frac{1}{2}\sum_{i=1}^{s} \tilde{\nu}_i$$

$$a(E_0) = 1 - \frac{w\ (s-1)\ \sum_{i=1}^{s} \nu_i^2}{\left(\sum_{i=1}^{s} \nu_i\right)^2}$$

$$\lg w = -1.0506 \left(\frac{E_0}{E_z}\right)^{0.25}$$

where the zero–point energy of C_3H_6 = E_z = 16889 cm^{-1}, w = 0.0625, and $a(E_0)$ = 0.920. At 291 K, W_R = 44700 cm^{-1}, the vibrational partition function (q^{vib}) = 2.106, so $f(E_0) = 3.558 \times 10^{-52}$.

F_e

F_e corrects for the energy dependence of n^{vib}, and is given by

$$F_e = \sum_{i=0}^{s-1} \frac{(s-1)!}{(s-1-i)!} \left(\frac{k_B T}{hcW_R}\right)^i$$

At 291 K, F_e = 1.099.

F_{anh}

F_{anh} corrects for the anharmonicity of vibrational modes lost in dissociation, and is calculated from Equation 9.9 of Troe:

$$F_{anh} = \left(\frac{s-1}{s-1.5}\right)^m$$

where $m = 3$ modes are lost, and F_{anh} = 1.079.

F_{rot}

Rotation will enhance dissociation, and F_{anh} describes this effect. From Equation 9.12 of Troe:

$$F_{rot} = \frac{(s-1)!}{(s+0.5)!} \frac{W_R^{1.5}\, y}{y - 1 + W_R/(s+0.5)k_B T}$$

$$y = 2.15 \left(\frac{E_0}{k_B T}\right)^{\frac{1}{3}}$$

Since $\Gamma(21.5) = 1.108 \times 10^{19}$, $F_{rot} = 396$.

$\mathbf{k_d^0}$

k_d^0 is thus given by

$$k_d^0 = 0.0452 \times\ 4.888 \times 10^{-10}\ \times 3.558 \times 10^{-52}\ \times 1.099\ \times 1.079\ \times 396$$

which equals 3.69×10^{-60} cm^3 molecule^{-1} s^{-1}.

APPENDIX M: RATE CONSTANTS FOR $H+CH_4 = CH_3+H_2$

Filename	$[CH_4]$	$[H_2]$	k_f	k_b	K	k_f	k_b	K
16	0.518	1.07	14.2	0.239	59.4	14.0	0.237	59.1
17	0.985	1.07	5.49	0.341	16.1	5.35	0.332	16.1
18	1.45	1.07	1.95	0.246	7.93	1.82	0.228	7.98
19	1.92	1.07	1.01	0.181	5.58	0.912	0.155	5.88
20	2.39	1.07	0.422	0.136	3.10	0.377	0.094	4.01
22	0.985	1.09	4.79	0.250	19.2	4.65	0.242	19.2
23	1.38	1.34	2.54	0.227	11.2	2.42	0.216	11.2
24	1.93	1.62	1.21	0.121	10.0	1.14	0.110	10.4
25	2.40	1.89	0.880	0.114	7.72	0.812	0.102	7.96
26	2.88	2.17	0.764	0.075	10.2	0.716	0.067	10.7
27	3.35	2.44	0.522	0.061	8.56	0.487	0.053	9.19
28	1.45	1.07	2.47	0.259	9.54	2.33	0.242	9.63
29	1.45	2.69	2.51	0.080	31.4	2.46	0.078	31.5
30	1.45	4.57				(4.06	0.002	2030)
32	1.45	8.35				(3.84	0.002	1920)
33	1.45	10.2				(4.00	0.002	2000)
34	1.45	11.2	(3.30	0.005	660)	(3.29	0.005	658)
35	3.41	11.0	(1.56	0.009	173)	(1.55	0.009	172)
70	0.985	1.09	5.42	0.238	22.8	5.27	0.231	22.8
71	1.46	1.48	2.57	0.247	10.4	2.45	0.187	13.1
72	1.93	1.88	1.28	0.140	9.14	1.22	0.137	8.91
73	2.40	2.30	0.974	0.066	14.8	0.928	0.097	9.57
74	2.88	2.99	0.960	0.049	19.6	0.923	0.046	20.1
75	3.77	3.41	0.641	0.036	17.8	0.618	0.033	18.7

Filenames begin with METH. The forward and reverse reactions had rate constants of k_f and k_b respectively. [CH_4] and [H_2] are expressed in units of 10^{15} and 10^{16} molecule cm^{-3} respectively. k_f and k_b are expressed in units of 10^{-13} cm^3 molecule^{-1} s^{-1}. $K = k_f/k_b$. A blank indicates that the fit did not converge. Values in parentheses excluded from mean K. The first set of results were found by assuming that $[CH_3]_0 = 0$. For the second set, $[CH_3]_0/[H]_0$ was calculated from [CH_4] and [H_2]. K (825 K) = 15.5 or 15.6±2.9 (19 values).

Filename	[CH_4]	[H_2]	k_f	k_b	K	k_f	k_b	K
54	0.977	1.06	3.97	0.290	13.7	3.51	0.276	12.7
55	1.45	1.47	1.82	0.132	13.8	1.73	0.122	14.2
56	1.91	1.87	1.30	0.091	14.3	1.45	0.085	17.1
57	2.38	2.28	1.30	0.057	22.8	1.25	0.053	23.6
58	2.86	2.70	1.51	0.042	36.0	1.46	0.039	37.4
59	3.34	3.11	1.33	0.034	39.1	1.29	0.032	40.3
60	3.81	3.52	1.19	0.027	44.1	1.16	0.025	46.4
61	1.21	1.27	2.41	0.143	16.9	2.31	0.134	17.2
62	1.68	1.67	1.62	0.107	15.1	1.54	0.099	15.6
63	2.15	2.08	1.59	0.058	27.4	1.54	0.054	28.5
64	2.62	2.49	1.44	0.044	32.7	1.40	0.041	34.2
65	2.62	4.58	(1.87	0.024	77.9)	(1.84	0.023	80)
66	2.63	6.67	(2.40	0.017	141)	(2.38	0.017	140)
67	2.63	8.76	(2.86	0.015	191)	(2.84	0.015	189)
68	3.87	10.8	(1.19	0.015	79.3)	(1.18	0.015	78.7)

K (875 K) = 25.1±3.4 or 26.1±3.6 (11 values).