SOME ONE ELECTRON TRANSFER REACTIONS

OF ORGANIC COMPOUNDS

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by

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ABBREVIATIONS.

The following abbreviations and units are used throughout.

k'	$sec.^{-1}$	Pseudo first order rate constant.
$k'_{corr.}$	$sec.^{-1}$	Pseudo first order rate constant corrected for self-decomposition of cobaltic ions.
k_2	$l.m.^{-1}sec.^{-1}$	Second order rate constant.
$k_a, k_b \ldots$	$sec.^{-1}$ or $l.m.^{-1}sec.^{-1}$	First or Second order rate constants for steps a,b....
C_o	$m.l.^{-1}$	Initial concentration of cobaltic ions.
C	$m.l.^{-1}$	Concentration of cobaltic ions at time t sec.
D		Optical density at time t sec.
D_∞		Optical density at completion of reaction.
E_a	$k.cal.m.^{-1}$	Arrhenius activation energy.
ΔH^*	$k.cal.m.^{-1}$	Enthalpy of activation.
ΔG^*	$k.cal.m.^{-1}$	Free energy of activation.
ΔS^*	e.u.	Entropy of activation.
μ	$m.l.^{-1}$	Ionic strength.
ϵ	$l.m.^{-1}cm.^{-1}$	Extinction coefficient.
DNP		2,4-Dinitrophenylhydrazone.
g.l.c.		Gas liquid chromatography.
ca., ~		Approximately.
v/v		By volume.
[ ]	$m.l.^{-1}$	Concentration.

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Abstract

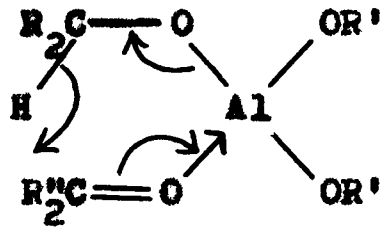
CHAPTER 1. INTRODUCTION.

The oxidation of an organic molecule can be formally regarded as involving transfer of an electron or electrons from that molecule to an acceptor, which is hence reduced. This oxidative process can occur by direct loss of an electron:

$$\text{e.g.}\quad ArO^- + M^{n+} \longrightarrow ArO^{\bullet} + M^{(n-1)+} \qquad (1.i.)$$

Alternatively, the electron transfer can be incorporated into the transfer of an atom or ion:

$$\text{e.g.}\quad RH + {}^{\bullet}OH \longrightarrow R^{\bullet} + H_2O \qquad (1.ii.)$$



$$\longrightarrow R_2C{=}O + Al(OR')_2OCHR''_2 \qquad (1.iii.)$$

$$RCHO + MnO_4^- \longrightarrow RCOOH + MnO_3^- \qquad (1.iv.)$$

Processes such as 1.iii. and 1.iv. involve the simultaneous transfer of two electrons, while in 1.i. and 1.ii. only a single electron is transferred at a time. Only processes involving one-electron oxidation were investigated in the present work.

It has been suggested that the true mechanism of oxidation may be identical to its formal definition, i.e. transfer of electrons.[1] The point of greatest electron availability in a molecule such as RCH_2OH is the hetero atom, and so the initial site of oxidative attack could well be at this centre, rather than involving adjacent hydrogen atoms. There has been some controversy as to whether proton transfer is an integral part of the electron transfer step,[2] or merely incidental to it.[3] Similar controversy has arisen[4] over whether inorganic redox reactions involve

direct electron transfer, or whether simultaneous transfer of some other group is necessary. The detailed steric and electronic requirements of both the organic molecule to be oxidised, and of the oxidant, must be considered for each oxidation reaction.

The present work has been concerned primarily with the oxidation of organic compounds by cobaltic perchlorate in aqueous perchloric acid. Transition metal ions have been employed as oxidising agents for many years, and there is now a large body of evidence concerning the stabilities and structures of the ions involved, and the way compounds of different structural types tend to be oxidised.[5,6] In general, only organic compounds are oxidised slowly enough for detailed kinetic study, and possible detection of transient intermediates. While these oxidations formally involve electron transfer from substrate to oxidant, the relative oxidative activities of transition metal ions show only slight correlation with their redox potentials. However, there appears to be better correlation between the activation energies for the one-electron oxidation of a compound by a series of transition metal ions, and the redox potentials of these ions, than for its oxidation by two-electron transfer, but lack of data prevents any extensive comparison.

Previous work has shown that cobaltic perchlorate is very reactive towards organic molecules. (Chapter 2). In perchloric acid solution, it has the very high redox potential of about 1.9 volts.[7] The valence states Co(I) and Co(IV) are unknown under these conditions.[8] It is safe to assume that a cobaltic ion will abstract one electron, or its equivalent, from a substrate molecule, producing an organic free radical which should then react rapidly with another cobaltic ion.[8] The liberation of free radicals

during cobaltic oxidations has recently been demonstrated.[9,10] Such one-electron oxidations hold considerable interest for both free radical and transition metal chemistry.[11]

The present work was undertaken to take advantage of this high reactivity of cobaltic perchlorate to extend the study of one-electron oxidation towards compounds much less reactive than those previously investigated. Aromatic hydrocarbons, and ethers, were selected as substrates for the following reasons:

a. There has been very little mechanistic study of the one-electron oxidation of either type of compound, (Chapters 3 and 4), although their reactions with free radicals have been well documented.[11]

b. Aromatic hydrocarbons are well known to form radical cations,[12] and to form charge transfer complexes with electron acceptors.[13] It was thought that with this very strong oxidant, oxidation by direct electron transfer, rather than by abstraction of hydrogen, might be observed.

c. Aromatic hydrocarbons were hoped to provide an interesting comparison with the ethers, from which some understanding might be gained of the effect of an electron rich hetero atom on the mechanism of oxidation.

d. The oxidation of toluene induced by alkyl radicals liberated by the cobaltic oxidation of carboxylic acids,[14] was investigated to see if similar processes are possible in the catalysis of autoxidation reactions by cobaltous ions.

Reaction mechanisms were investigated by kinetic methods and by detailed product studies. Cobaltic perchlorate was used as the oxidant throughout, to minimise any anion complexing in solution.

CHAPTER 2. PREVIOUS WORK ON OXIDATIONS BY COBALTIC SALTS.

The oxidation of organic compounds by cobaltic salts has been exhaustively reviewed recently.[8] However, a brief survey will be given here.

In 1934, cobaltic sulphate was found to oxidise a wide range of compounds,[15] some of them quantitatively to carbon dioxide. Bawn and his co-workers later made detailed studies of some of these oxidations. Their conclusions can be summarised as follows:

1). The reactions studied were considerably faster than the self-decomposition of cobaltic sulphate in aqueous solution. Hence cobaltic ions can oxidise organic molecules directly, rather than by first liberating hydroxyl radicals from the solvent.

2). The rate law for the oxidation of formic acid was:[16]

$$-d[Co^{III}]/dt = [Co^{III}][HCOOH](a + b/[H^+]) \qquad (2.i.)$$

Hence it was inferred that cobaltic ions can independently attack formic acid molecules and formate anions.

3). The oxidation of formaldehyde[17] yielded formic acid, and was second order with respect to oxidant at higher oxidiser concentrations, but first order at lower concentrations. The reversible formation of a cobaltic-formaldehyde complex, which decomposes to yield a formyl radical, was suggested.

4). The oxidations of ethanol[17] and n-propanol[17] showed complex reaction orders similar to that for the oxidation of formaldehyde, but the oxidation of methanol[17] was simply of first order with respect to oxidant. A general mechanism of alcohol oxidation, involving liberation of an alkoxy radical, followed by its oxidation to the aldehyde, was

suggested. Since the reactions were retarded by sulphuric acid, it was thought there was rapid oxidation of the alkoxide ion concurrent with the oxidation of the neutral molecule; or alternatively that the active neutral molecule could be removed as unreactive $R\overset{+}{O}H_2$ at high acidity.

5). Aliphatic olefins[18,19] yielded primarily the products of complete oxidative fission of the olefinic bond, together with traces of dienes. The oxidation rates were of first order with respect to each reactant, but were independent of sulphuric acid concentration, and they were much faster than the rates of olefin hydration. Direct attack on the olefin, to form the reactive intermediate $R\overset{\circ}{C} \text{——} \overset{+}{C}HR$, was proposed.

The acidity dependences for all the above oxidations by cobaltic sulphate, except for the oxidation of olefins, can be expressed as:

$$k_2 = a + b/[H^+] \qquad (2.ii.)$$

where $a \sim b$. Hoare and Waters[20] later suggested that the difference between oxidations by cobaltic sulphate and by cobaltic perchlorate, (when $b \gg a$), may be due to the formation of the complex $[Co(SO_4)\ aq]^+$, which is assumed to be inactive.

Bawn and co-workers have also investigated cobaltic acetate as an oxidant.[21,22] It does not oxidise olefins in glacial acetic acid solution,[23] and in glacial acetic - sulphuric acid mixtures shows oxidation kinetics quite different from those of cobaltic sulphate oxidations. The oxidation of benzaldehyde[19,24] in glacial acetic - sulphuric acid mixtures is of first order with respect to both cobaltic ions and the aldehyde. The rate step was thought to involve formation of a benzoyl radical, followed by its fast oxidation to benzoic acid.

Dewar[25] has oxidised a series of polynuclear aromatic hydrocarbons with cobaltic acetate, though he has given few details. The oxidation rates are slow, but increase markedly with increasing size of the

hydrocarbon. Anthracene yields a mixture of anthrone and hydroxyanthrone derivatives, together with anthraquinone. The initial oxidation rates follow the expression:

$$-\frac{d[Co^{III}]}{dt} = \frac{k[An]^{\frac{1}{2}}[Co^{III}]^2}{k'[Co^{II}] + k''[Co^{III}]} \qquad (2.iii.)$$

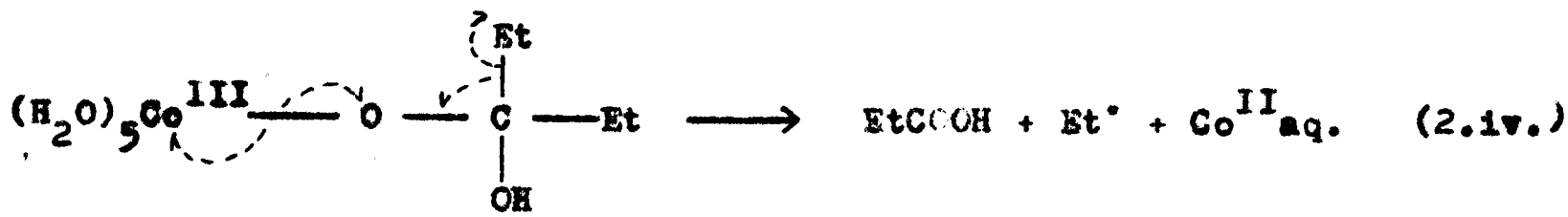
The half order dependence on anthracene concentration was thought to be caused by anthracene existing mainly as inert dimers in the solution.

The oxidation of a variety of organic compounds by cobaltic perchlorate has been studied in detail, mainly by Waters and his co-workers. These oxidations are all of first order with respect to oxidant, and, except for certain carboxylic acids, of first order with respect to substrate. The dependence of the oxidation rate on perchloric acid concentration follows equation 2.ii., where $k \gg k'$, in every case. These results can be summarised as follows:

1). Benzene[26,27] is reported by Baxendale and Wells to be oxidised to benzoquinone and muconic acid. Slow oxidation to $Ph^{\bullet}$ was assumed to occur in the rate step, followed by fast oxidation to phenol. No biphenyl was produced, and the reaction was unaffected by oxygen. No details of the actual rates have been given.

2). Cyclohexanone[28] is oxidised by both cobaltic perchlorate and cobaltic sulphate far faster than its rate of enolisation. The kinetic isotope effect of 0.9 at 25° indicates either direct electron transfer from the carbonyl group, with no concurrent fission in the rate step of C—H, or else slow formation of a cobaltic-ketone complex which rapidly decomposes. Diethyl ketone[20] is likewise oxidised by cobaltic sulphate much faster than its rate of acid catalysed enolisation. The extensive oxidation which occurs - one ketone molecule consumes about ten cobaltic ions, prevented elucidation by product studies of the initial point of

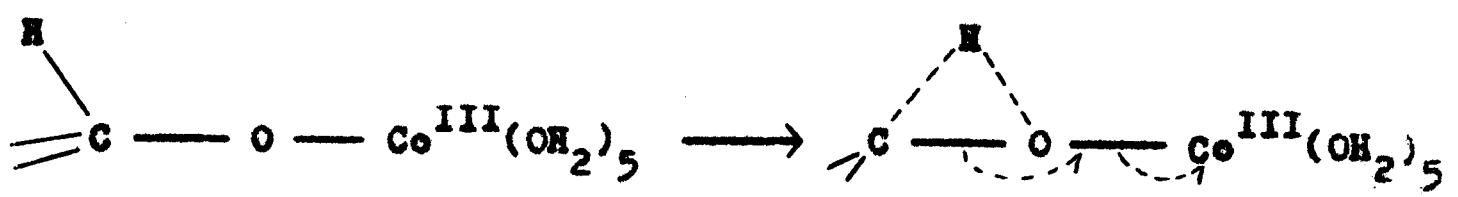
attack on the ketone. Oxidation through a ketone complex, or else through the gem-diol, was suggested.



(2.iv.)

3). Formaldehyde[29] is thought to be oxidised through its gem-diol. The kinetic isotope effect of 1.54 at 25° indicates homolysis of a C—H bond to form the carbon radical $HC^{\bullet}(OH)_2$.[30] A kinetic isotope effect of 2.3 at 10° was found for the oxidation of m-nitrobenzaldehyde,[31] indicating there is direct attack on the -CHO group to yield a benzoyl radical, which is then oxidised further to benzoic acid. p-nitrobenzaldehyde is oxidised faster than the meta- isomer, while benzaldehyde, which could not be studied accurately , is oxidised the slowest of the three. This accords with the greater stabilities of the substituted benzoyl radicals. Piperonal,[31] veratraldehyde,[31] and 1,2-methylenedioxybenzene,[31] are all attacked rapidly on the ether group.

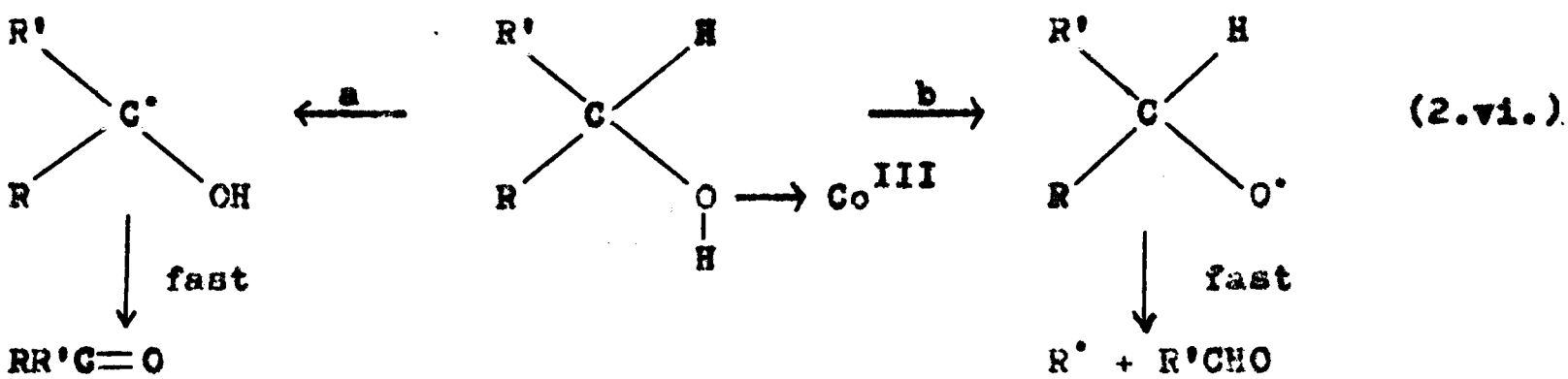
4). Cyclohexanol[32] is rapidly oxidised by cobaltic perchlorate. The kinetic isotope effect of 1.7 at 10° indicates formation of a carbon radical rather than an alkoxy radical, but because of its small value a rate step involving a concerted transfer was suggested:



(2.v.)

Cleavage experiments on other secondary alcohols[10] show that C—C fission competes with C—H fission. For example, methyl n-propyl carbinol gave almost equal amounts of acetaldehyde and methyl n-propyl ketone,

while <u>methyl isopropyl carbinol</u> yielded almost exclusively acetaldehyde. These ketone yields are reduced by the presence of acrylamide, showing that the ketone precursors are carbon radicals. The mechanism tentatively suggested was:



(2.vi.)

5). Tertiary alcohols are oxidised more slowly than are secondary alcohols.[22] The products obtained depend on the relative ease of elimination as radicals of the three β-alkyl groups;[9] thus <u>dimethyl ethyl carbinol</u> gave almost exclusively acetone, while <u>methyl ethyl isopropyl carbinol</u> gave almost exclusively methyl ethyl ketone. The ketone yields are unaffected by acrylamide, and so there is no carbon radical precursor of the ketones in this case. The scheme:

$$R'CR_2OH + Co^{III} \longrightarrow R'CR_2{-}O^{\cdot} \begin{cases} \longrightarrow R'^{\cdot} + R_2CO \\ \longrightarrow R^{\cdot} + R'COR \end{cases} \qquad \text{(2.vii.)}$$

was suggested, although these processes may be concerted to some extent.

6). <u>Benzoic acid</u> and its p-sulphonic derivative are oxidised very slowly by cobaltic perchlorate,[14] while <u>propionic</u>, <u>isobutyric</u>, <u>pivalic</u>, and <u>phenylacetic</u> acids react rapidly. Phenylacetic acid yields benzyl alcohol, benzaldehyde, and a trace of bibenzyl. The oxidations of propionic and phenylacetic acids show Michaelis-Menten kinetics,[33]

i.e. $$1/k = 1/k_1K[RCOOH] + 1/k_1 \qquad \text{(2.viii.)}$$

which indicates complexing of the cobaltic ions by the substrate in a fast pre-equilibrium. The concentration of the complex depended inversely on the acidity of the medium, while its decomposition rate was acid independent. The scheme:

$$RCOOH + \left[Co(OH_2)_6\right]^{3+} \rightleftharpoons \left[RCOO{-}Co(OH_2)_5\right]^{2+} + H_3O^+ \qquad (2.ix.)$$

$$\left[R{-}C(=O){-}O{-}Co(OH_2)_5\right]^{2+} \longrightarrow R^{\bullet} + CO_2 + Co^{II}aq. \qquad (2.x.)$$

accords with the secondary isotope effect of 1.24 at 15° observed for the oxidation of phenylacetic acid. Further evidence for the liberation of an alkyl radical was thought to be afforded by the rearrangement of neophyl radicals liberated from β-phenylisovaleric acid, and by the induced oxidation of toluene in systems containing carboxylic acids.[34] This work on the oxidation of carboxylic acids is important since it demonstrates the formation of a cobaltic complex which breaks down to yield a free radical.

7). The oxidation of <u>crotonic acid</u>[35] by cobaltic perchlorate is rather slower than that of propionic acid, and does not show Michaelis-Menten kinetics. <u>Cinnamic acid</u> is oxidised mainly to benzaldehyde, but some phenylacetaldehyde and phenylacetic acid are also obtained, indicating that oxidation occurs, at least in part, by attack on the carboxyl group.

The oxidations of 4-<u>phenylbutyric acid</u>, 5-<u>phenylvaleric acid</u>, and 6-<u>phenylhexanoic acid</u>[36] all yield benzaldehyde as the major carbonyl product.

The Oxidations of Inorganic Compounds by Cobaltic Salts.

The oxidations of Tl(I);[37] V(III) and V(IV);[38] Hg(I);[38] Ce(III);[39,40,41] Co(II);[42,43,44,45] Cr(II);[41] Fe(II);[46] and Ag(I)[47] ions, and of hypophosphorus acid,[48] have been investigated. The rate constants for all these reactions but the last two can be characteristically expressed by equation 2.ii., although the relative values of a and b vary.

The oxidation of water has been studied by several authors. This will be discussed in detail in Chapter 5. Hydrogen peroxide is very rapidly oxidised by cobaltic perchlorate.[49]

Reactions involving cobaltiamine complexes, which are substitutionally inert, have also been extensively studied.[4] Particularly important is the work of Taube and his collaborators, who have shown that electron transfer from the reducing agent to the cobaltic ion can occur through a variety of conjugated ligands;[50,51,52,53]

$$\text{e.g. } \left[(NH_3)_5Co \text{ —— } OOC.C_6H_4COOH\right]^{2+} + Cr^{2+} \longrightarrow Co^{2+} + 5NH_3 + C_6H_4(COOH)_2 + Cr^{3+} \qquad (2.xi.)$$

In this case electron transfer can be shown to occur both locally, i.e. by attack on the carboxyl group complexed to the metal ion, and through the ligand, by attack on the remote carboxyl group.

This outer sphere oxidation of the chromous ion contrasts the alternative inner sphere mechanism of oxidation by transition metal ions, in which the reductant first complexes the oxidant ion before the oxidative step occurs.[50] Such an inner sphere mechanism has been described previously for the oxidation of carboxylic acids by cobaltic perchlorate.

CHAPTER 3. THE OXIDATION OF AROMATIC HYDROCARBONS BY TRANSITION METAL IONS, AND RELATED REACTIONS.

Processes involving the oxidation of hydrocarbons are of great industrial significance. The complete range of these reactions is too large to be reviewed here.[54-58] However, previous work on the direct oxidation of aromatic hydrocarbons by transition metal ions in aqueous solution is relevant to the present study, and a brief survey will be made of this limited area, which appears to have received less attention than any other aspect of hydrocarbon oxidation. Autoxidation reactions catalysed by transition metal ions,[11,59] and heterogeneous oxidations,[55,57] will not be considered.

1. OXIDATION BY ONE-ELECTRON OXIDANTS.

Despite the wide use, as autoxidation catalysts,[11,59] of metal ions capable of gaining or losing one electron, there has been little mechanistic study of the direct oxidation of aromatic hydrocarbons by the higher valence states of these ions.

a. OXIDATION BY MANGANESE (III).[8]

Manganic sulphate oxidises toluene to benzaldehyde,[60,61] and p-xylene to p-methylbenzaldehyde,[62,63] at 20° to 35°. Manganic acetate in acetic acid[64] oxidises toluene slowly at 110° to benzaldehyde, benzyl acetate, bibenzyl, and a mixture of ring-methylated products. The reaction rate is independent of toluene concentration,[25] implying that there is slow oxidation of the solvent, liberating radicals which then attack the substrate. The oxidation of p-methoxytoluene to p-methoxybenzylacetate follows the rate law:

$$-\frac{d[Mn^{III}]}{dt} = \frac{k[ArMe][Mn^{III}]^2}{[Mn^{II}]} \qquad (3.i.)$$

Suggested mechanisms include:

$$2\ Mn^{III} \rightleftharpoons Mn^{II} + Mn^{IV} \qquad (3.ii.)$$

$$ArMe + Mn^{IV} \xrightarrow{slow} ArCH_2^+ + Mn^{II} + H^+ \qquad (3.iii.)$$

and $$ArMe + Mn^{III} \xrightarrow{slow} (ArMe)^{+\cdot} + Mn^{II} \qquad (3.iv.)$$

$$(ArMe)^{+\cdot} \longrightarrow ArCH_2^{\cdot} + H^+ \qquad (3.v.)$$

This oxidation exhibits a primary kinetic isotope effect, indicating that C—H fission is involved in the rate step. Manganic acetate also oxidises bibenzyl and triphenylmethane at 100°.[65]

The oxidations of toluene and dihydroanthracene by manganic acetate are catalysed by bromide ions.[64] The catalysed reactions follow the rate law: $$-d[Mn^{III}]/dt = k[Mn^{III}][ArH][Br^-]^2 \qquad (3.vi.)$$ and limiting rates are reached at high bromide ion concentrations. Catalysis by bromide ions is known for other transition metal oxidations.[66,67] The active intermediate is thought to be a species such as $Br^{-\cdot}$ [66] or HBr_2:[64] The catalysed oxidation of toluene yields no ring substituted products, and the products obtained from dihydroanthracene are anthrone, anthraquinone, and 10,10' - dioxodianthryl.

Polycyclic aromatic hydrocarbons are oxidised to acetates and quinones by manganic acetate at 50° to 100°.[65,68]

b. OXIDATION BY CERIC SULPHATE.[69]

Ceric sulphate oxidises p-xylene to p-tolualdehyde.[70] The reaction is of first order with respect to oxidant, but, since it was studied in an inhomogeneous system, the order with respect to hydrocarbon is not known. The apparent activation energy is 23.8 k.cal.mole.$^{-1}$

The oxidation of naphthalene by ceric sulphate in aqueous acetic-sulphuric acid solution[71] is first order dependent on each reagent. The

activation energy is 14 k.cal.mole.$^{-1}$, and initiation by hydroxylation of the substrate has been suggested. Ceric sulphate also oxidises anthracene.

c. OTHER ONE-ELECTRON OXIDATIONS.

Little is known of direct attack on aromatic hydrocarbons by Iron (III), although hydroxylation by Fenton's reagent has been investigated.[72] Boiling alkaline ferricyanide [73] has been used to oxidise toluene, xylenes, and their derivatives to the corresponding benzoic acids. The reaction is strongly autoinhibited by ferrocyanide,[25] and direct electron transfer from the ring has been postulated:

$$ArMe + Fe(CN)_6^{3-} \rightleftharpoons (ArMe)^{+\cdot} + Fe(CN)_6^{4-} \qquad (3.vii.)$$

$$(ArMe)^{+\cdot} + {}^{-}OH \longrightarrow ArCH_2^{\cdot} + H_2O \qquad (3.viii.)$$

The alcohol and aldehyde are intermediates in the oxidation of α-methylnaphthalene to naphthoic acid.[25]

The oxidations of benzene and anthracene by cobalt(III) have been mentioned previously. (Chapter 2). Aqueous vanadium(V) is not known to oxidise benzene, but polycyclic hydrocarbons are oxidised in aqueous acetic acid.[74]

2. OXIDATION BY CHROMIC ACID AND CHROMYL COMPOUNDS.[75,76]

The oxidation, by chromium(VI), of C—H bonds α to an aromatic ring, has been used widely in the preparation of arylcarboxylic acids and aldehydes, and in the determination of the orientation of alkyl groups attached to an aromatic nucleus. Regardless of its length, the alkyl group is finally oxidised to a carboxyl group.

The oxidations of diphenyl- and triphenyl- methanes in glacial acetic acid have been studied by Slack and Waters.[77] In both cases there is an initial fast reaction, which then slows off. The initial rate of

oxidation of diphenylmethane follows the expression:

$$-d\left[Cr^{VI}\right]/dt = k\left[Ph_2CH_2\right]\left[CrO_3\right]^2\left[H^+\right]^n \qquad (3.ix)$$

where n is not clearly defined, while the oxidation of triphenylmethane is of first order with respect to oxidant. Diphenylmethane is oxidised mainly to benzophenone. Small amounts of s- tetraphenylethane, indicating transient formation of $Ph_2\dot{C}H$, were ascribed to a side reaction. No benzhydrol or benzylacetate were detected. At later stages of the reaction there is some Ph—C fission leading to the formation of small quantities of benzoic and phenolic products. Similarly, the oxidation of triphenylmethane yields mainly triphenylcarbinol, and small amounts of benzophenone and phenol.

The oxidation of toluene[78] is similar to that of diphenylmethane. Electron attracting substituents decrease the oxidation rate, and the rate constants decrease slightly with increasing initial toluene concentration. Only the corresponding acids and a small amount of p-benzoquinone are formed.[79]

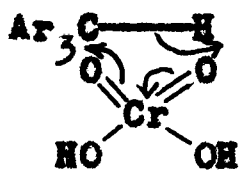
Wiberg and Evans[80] more recently examined the oxidation of diphenylmethane in 95% aqueous acetic acid with a swamping concentration of perchloric acid. These conditions are comparable to those used synthetically, and may lead to a different reaction from that described above. The rate law is:

$$-d\left[Cr^{VI}\right]/dt = k\left[CrO_3\right]\left[Ph_2CH_2\right]\ h_o \qquad (3.x.)$$

and k_H/k_D is 6.4 at 30°. Electron withdrawing groups cause a slight decrease, and electron donating groups a slight increase, in the rate. The oxidation product is benzophenone. Steric effects seem unimportant, since the relative rates are: cumene > ethylbenzene > toluene, and triphenylmethane > diphenylmethane. The oxidation rate is decreased by oxygen. Possible mechanisms for the rate step include:

$$Ar_3CH + Cr^{VI} \longrightarrow Ar_3C^+ + Cr^{IV} + H^+ \qquad (3.xi.)$$

$$Ar_3CH + Cr^{VI} \longrightarrow Ar_3C^\cdot + Cr^{V} + H^+ \qquad (3.xii.)$$



$$\longrightarrow Ar_3C{-}O{-}Cr^{IV}(OH)_3 \qquad (3.xiii.)$$

The small substituent effects, and small rate differences between toluene and triphenyl- and diphenyl- methanes, (0.16: 1 : 1.3), indicate that equation 3.xi. is probably incorrect. Considerably larger effects might be expected for a carbonium ion mechanism.[76] No distinction can be made between equations 3.xii. and 3.xiii. on available data. Either could account for preferential oxidation α to the benzene ring. If benzhydrol is an intermediate in the oxidation of diphenylmethane, it should be rapidly oxidised to benzophenone, since its oxidation rate is 3×10^4 that of diphenylmethane.[80]

No ring attack was seen under these milder conditions. Under more rigorous conditions it can compete with side chain oxidation,[81] but it is suppressed by lowering the acidity of the medium.

The oxidation of aralkyl hydrocarbons by aqueous dichromate occurs α to the ring, since t-butyl benzene is unreactive.[82] The mechanism is not known, but the oxidation of toluene to benzoic acid appears to occur through benzyl alcohol and benzaldehyde.[83]

The oxidation of arylalkanes by chromyl chloride is first order with respect to both oxidant and hydrocarbon.[84] The oxidations of toluene and diphenylmethane both show primary kinetic isotope effects,[85] and again the mechanism is thought not to involve carbonium ions.[86] The rate step probably involves radical formation, or else a cyclic

process, analogous to equations 3.xii. and 3.xiii.

Benzene is only very slowly oxidised by chromic acid in aqueous sulphuric acid, and forms only carbon dioxide. Polycyclic aromatic hydrocarbons are rapidly oxidised, generally to quinones.[87]

3. OXIDATION BY PERMANGANATE.[88]

Permanganate generally oxidises, to the carboxyl group, an alkyl group attached to an aromatic ring, more readily than it attacks the ring. The oxidations of substituted toluenes to the corresponding benzoic acids in acetic acid solution[89,90] show no simple rate laws, but are initially of the first order with respect to both substrate and oxidant. Electron withdrawing substituents decrease the reaction rate. The nature of the active oxidant is not clear, and permanganate ions and lower valence manganese, especially manganese(III), appear to be involved. Ethyl benzene[91] is attacked primarily at the α position, forming acetophenone as the first isolable product, which is slowly oxidised to benzoic acid. n-Propyl and iso-propyl benzenes react similarly.[92] There is little or no ring fission, and the overall reactivity varies in the sequence $\geq CH > \geq CH_2 > -CH_3$.

In sulphuric acid solution the three isomeric chlorotoluenes are extensively degraded to carbon dioxide.[93] This is thought to be caused by the action of permanganic acid.[88] In water,[94] or in acetic acid solution,[89] the corresponding benzoic acids are formed.

Benzene is slowly oxidised by boiling alkaline permanganate,[95] but it is stabilised by electron withdrawing substituents. Polynuclear

hydrocarbons are more easily oxidised, forming carboxylic acids.

4. OXIDATION BY LEAD TETRA-ACETATE.[96]

Lead tetra-acetate in acetic acid at 80° oxidises aromatic side chains to the corresponding acetates. Electron donating groups increase the oxidation rate, while electron withdrawing groups decrease it. It is not known whether benzyl radicals are reaction intermediates. Criegee[96] has redently reviewed these reactions, and concludes that there is evidence both for and against a radical chain mechanism. Dehydrogenation occurs in cases where an aromatic ring can be formed,[97] e.g. 1,4 - dihydronaphthalene gives naphthalene at 20°.

Benzene is stable towards lead tetra-acetate, but condensed aromatic polycycles react fairly easily. A variety of reactions can occur, leading to ring substitution, and to dimer and quinone formation.

NOTE: Since the completion of this Chapter, the oxidation of toluene and substituted toluenes by ceric ammonium nitrate has been reported.[230] The oxidations in aqueous acetic acid yield mainly benzaldehydes, and sometimes appreciable amounts of the benzyl alcohols. Nitro-toluenes are almost inert to oxidation, and methoxy-toluenes polymerise. In glacial acetic acid solution the corresponding benzyl acetates are obtained.

CHAPTER 4. THE OXIDATION OF ETHERS BY TRANSITION METAL IONS, AND RELATED REACTIONS.

The facile autoxidation of ethers, which is markedly catalysed by transition metal ions, is well known.[59,69,98] However, even less appears to be known of the direct oxidation of ethers by transition metal ions than of the corresponding oxidations of hydrocarbons. (Chapter 3). Ethers are easily attacked by free radicals at the α C——H bond, e.g.

$$Me_2CHOCHMe_2 + {}^{\bullet}OH \longrightarrow Me_2\dot{C}OCHMe_2 + H_2O \quad [99] \qquad (4.i.)$$

but only the strongest metallic oxidants will attack them directly. Ethers are considerably more resistant than are alcohols to one-electron oxidation. This is shown by the initial attack on the hydroxyl group of monomethylated glycols by vanadium(V)[100] and cobalt(III),[9] and by the use of ether groups to ascertain substituent effects for the oxidation reactions of other functional groups. Apart from the previously mentioned oxidations of piperonal, veratraldehyde and 1,2-methylenedioxybenzene by cobaltic perchlorate,[31] (Chapter 1), there appear to be no examples of the direct oxidation of ethers by one-electron metallic oxidants.

Di-isopropyl ether has been oxidised by chromic acid,[101] in aqueous sulphuric acid solution at 25°, to yield acetone, which is further oxidised to only a very small extent. The reaction occurs by direct attack on the unhydrolysed molecule. The second order rate constant decreases slightly with increasing total chromium(VI) concentration,

but the nature of the active oxidant has not been elucidated. The second order rate constant also increases slightly with increasing ether concentration, but increases markedly with increasing acidity. There is a primary kinetic isotope effect of 5.3, and direct attack by one chromic acid molecule on a tertiary C—H bond of the ether has been suggested, forming either the radical $Pr^{i}\dot{O}CMe_2$, or the ion $Pr^{i}\overset{+}{O}CMe_2$, which would rapidly form acetone and isopropanol. Isopropanol is oxidised about 1500 times per α hydrogen atom faster than is the ether.

Several aliphatic ethers have been oxidised slowly by permanganate-periodate mixtures,[102] but no details have been given.

Lead tetra-acetate readily oxidises ethers to the corresponding acylals,[96]

$$RCH_2OR' \xrightarrow{Pb(OAc)_4} RCH(OAc)OR' \qquad (4.11)$$

which hydrolyse to the aldehyde and the alcohol. Lead tetra-acetate - boron triflouride mixtures oxidise anisole, p-dimethoxybenzene, and 4,4' - dimethoxybiphenyl to the radical cations in anhydrous conditions.

Chapter 5: THE NATURE AND REACTIVITY OF THE COBALTIC SPECIES IN SOLUTION, AND THEIR SPONTANEOUS DECOMPOSITION.

A knowledge of the species present in aqueous solutions of cobaltic perchlorate is necessary to make possible detailed interpretation of the results from the present work. Only species occurring in aqueous perchloric acid solution will be considered. Sulphate, and other anions, are known to complex cobaltic ions in solution,[29,41] and for this reason cobaltic perchlorate was used throughout in the present investigation.

1. The Species Present in Aqueous Solution.

Solutions of cobaltic perchlorate in perchloric acid are thought to contain mainly the octahedrally co-ordinated species $\left[Co(OH_2)_6\right]^{3+}$.[104] There is no direct evidence for this species, but it is postulated by analogy with cobaltic ammine complexes and the aquo complexes of chromium (III) and iron (III), and from other indirect evidence.

There is no experimental evidence that either cobaltic or cobaltous ions are complexed by perchlorate anions in aqueous solution,[29,39,105] although this suggestion has been made in previous kinetic work.[43,48] It has been claimed, generally on spectrophotometric evidence, that several ions form perchlorate complexes in aqueous solution, but recent comprehensive

studies of this fundamental topic[106,107,108] showed that most of these claims are in error, and that there is little or no unequivocal evidence for such complexes in aqueous solution. Complexing of cobaltic ions by perchlorate anions will consequently be discounted for the conditions employed in the present work, although some ion pairing may occur.

Various hydrolysed and dimerised species have been suggested to exist in aqueous solutions of cobaltic salts. The variation of the absorption spectrum of cobaltic perchlorate solution with acidity, at acidities less than 1M., has been attributed[39,49] to the hydrolysis equilibrium:

$$H_2O + \left[Co(OH_2)_6\right]^{3+} \rightleftharpoons \left[CoOH(OH_2)_5\right]^{2+} + H_3O^+ \qquad (5.i.)$$

The following thermodynamic quantities were estimated:[39]

$K = 7.5 \times 10^{-3}$ m.l.$^{-1}$; $\Delta H^0 = 10 \pm 2$ k.cal.mol^{-1}.; $\Delta S^0 = 25 \pm 5$ e.u.

but measurements were difficult due to the rapid self-decomposition of cobaltic ions at low acidities. A more recent study[109] of the variation of the absorption spectrum with acidity, cobaltic ion concentration, and time of thermal decomposition, was interpreted in terms of a further <u>slow</u> equilibrium:

$$\left[Co(OH_2)_6\right]^{3+} + \left[CoOH(OH_2)_5\right]^{2+} \rightleftharpoons \left[(H_2O)_5\ Co - O - Co(OH_2)_5\right]^{4+} + H_3O^+ \qquad (5.ii.)$$

at cobaltic ion concentrations of about 5×10^{-3}M. This could cause the earlier measurements[39] to be in error, but the evidence for dimerisation was not conclusive, and the above thermodynamic values agree well with those expected by analogy with other metal ions.[44,110] A previous spectrophotometric study[29] found no evidence for polynuclear species over the cobaltic ion concentration range 5×10^{-4}M. to 10^{-2}M., which is about the range of cobaltic concentration used during the present work. Dimeric species have also been postulated to explain the kinetics of the self-decomposition of cobaltic ions in aqueous solution.[49,111] However, other interpretations of the kinetics are possible, (Section 3), and no other cobaltic oxidation shows kinetics necessitating dimer participation. (Chapter 2). The diamagnetism of cobaltic perchlorate solutions is not evidence for dimerisation, since the $\left[Co(OH_2)_6\right]^{3+}$ complex is thought to be of low spin.[109,112,113] Solid cobaltic alums are also diamagnetic,[113] and it would be difficult to fit a dimer into such a structure.

The absorbing species thought to correspond to the dimer in equation 5.ii. did not exist at acidities greater than 0.35M. Since this was the minimum acidity ever used in the present work, and the evidence for dimer formation is so scanty, it is very unlikely that dimeric species were ever involved in the oxidation reactions investigated. For a dimer to take part in the oxidation step a fast equilibrium with monomer would be required, which would not fit either the observed kinetics or the spectrophotometric evidence.[109] The dimeric form of at least one transition metal ion is known to be inactive as an oxidant.[114,153]

A striking feature of oxidations by cobaltic perchlorate is the inverse proportionality of their rates to the acidity of the medium. (Chapter 2). Since this relationship holds for a diverse range of substrates, it indicates that oxidation proceeds via a fast pre-equilibrium involving proton loss from a cobaltic species, and can be ascribed to the hydrolysis equilibrium 5.1.

2. Species Present in Aqueous Methyl Cyanide Solutions.

Previous work on cobaltic oxidations has always been carried out in solutions containing less than 50 per cent methyl cyanide by volume, and it was assumed that the cobaltic species present were identical to those in wholly aqueous solution. The insolubility of the substrates oxidised during the present work often necessitated the use of much higher methyl cyanide concentrations, up to 85 per cent by volume, in which other cobaltic complexes may be present.

Complexes of alkyl cyanides with both non-transition and transition metals have recently been exhaustively reviewed.[115] With only a very few exceptions,[116] these complexes can be isolated only under rigorously anhydrous conditions, and are readily decomposed by water, and on heating. Bonding is invariably by donation of the nitrogen lone pair electrons i.e. $M^{n+} \leftarrow N \equiv C - R$. No complexes of cobalt (III) have been reported, but cobalt (II) and iron (III) complexes have been investigated both in methyl cyanide solution and in the solid state.

The poor nucleophilic properties of methyl cyanide compared to water,[117] and the instability of methyl cyanide complexes to water,[115] suggest that methyl cyanide will not complex cobaltic ions in aqueous solution until it is present in very high concentration. Cobaltic perchlorate is blue-green in solutions of up to 50 per cent methyl cyanide (v/v), at an acidity of 1M. It becomes progressively more blue with more methyl cyanide, and then turns bright violet at about 80 per cent methyl cyanide. Above 90 per cent methyl cyanide it is bright cherry red. These changes occur at lower methyl cyanide concentrations when the acidity or ionic strength is increased.

The absorption spectrum of cobaltic perchlorate in aqueous solution shows two broad, weak bands at about 600 mμ and 400 mμ, and a very strong band at about 210mμ.[118] The variation of the visible spectrum with methyl cyanide concentration is shown in Table 5.1.

Table 5.1 Variation of the Visible Spectrum of Cobaltic Perchlorate with Methyl Cyanide Concentration.

$Co^{III} \sim 8 \times 10^{-3}$M. 1.0M $HClO_4$. 20°. μ ca. 1.05M.

Percentage MeCN(v/v)	mole fraction MeCN	λ_1 max mμ.	λ_2 max mμ.
0	0	616	402
12.5	.047	614	400
25	.095	612	399
38	.162	610	398
50	.24	606	396
60	.32	602	395
70	.42	592	392
80	.53	575	389
84	.60	561	382

Both the 400 mμ and 600 mμ bands move to shorter wave lengths, but this change is fairly small at concentrations up to about 60 per cent methyl cyanide, after which the shifts become larger. This agrees with the marked colour changes described above. These spectral changes indicate that at high methyl cyanide concentrations cobaltic ions are complexed by methyl cyanide. The weak visible bands have been ascribed to d - d transitions, and the strong band in the ultra-violet to charge transfer.[118,119,120]

Complexing by methyl cyanide would increase the ligand field splitting, since methyl cyanide is higher in the spectrochemical series than is water,[121,122,123] thus shifting the visible bands to shorter wavelength. No measurements were made of the ultra-violet absorption band. The enhancement of the spectral changes with increasing acidity or ionic strength could be due to the added acid or sodium perchlorate associating with water molecules rather than with methyl cyanide, forcing greater association between the cobaltic ions and methyl cyanide.

It can hence be concluded that, under some conditions employed during the present work, the cobaltic ions in solutions were complexed to some extent by methyl cyanide. This must be taken into account in interpreting the kinetic data.

3. The Self-Decomposition of Cobaltic Perchlorate in Aqueous Solution.

a. Previous Work on the Self-Decomposition Reaction.

In aqueous solution, cobaltic perchlorate decomposes spontaneously, evolving oxygen. The oxidations of organic substrates by cobaltic perchlorate previously studied, (Chapter 2), were much faster than the concurrent self-decomposition reactions, so that only a very small correction was necessary. The present work has been concerned with much less reactive and less soluble substrates, and has necessitated the investigation of systems in which the rate of self-decomposition is appreciable in comparison with the rate of the reaction under investigation. Consequently it is

necessary to discuss what is known of the mechanism of this self-decomposition.

The oxidation of water by cobaltic ions was first studied in 1903.[124] The data from this work were later re-interpreted[111] as showing a complex reaction order with respect to cobaltic ions, and an inverse acidity dependence.

Noyes and Deahl[125] found that the decomposition of cobaltic nitrate in aqueous nitric acid is initially of second order with respect to oxidant, but later tends towards first order. The reaction is slower at higher acidities, and faster in the presence of silver nitrate, although the kinetic form is unchanged. The reaction curves were thought to fit an expression of the form:

$$-\frac{d[Co^{III}]}{dt} = k_1 [Co^{III}] + k_2 \cdot \frac{[Co^{III}]^2}{[Co^{II}]^n} \quad (n = 1 \text{ to } 2) \quad (5.iii)$$

A tentative scheme involving the disproportionation:

$$2\ Co^{III} \rightleftharpoons Co^{II} + Co^{IV} \qquad (5.iv)$$

was suggested, Co^{IV} being the active oxidant.

Bawn and White[111] found that the self-decompositions of cobaltic sulphate and perchlorate both show complex kinetics. At an initial cobaltic ion concentration of about 10^{-2}M. the reaction is strictly second order with respect to oxidant:

$$-\frac{d[Co^{III}]}{dt} = \frac{k[Co^{III}]^2}{[H^+]^n} \qquad (5.v)$$

At lower initial cobaltic ion concentrations, the reaction is of intermediate order at constant pH:

$$\frac{-d\left[Co^{III}\right]}{dt} = k_1\left[Co^{III}\right] + k_2\left[Co^{III}\right]^2 \qquad (5.vi)$$

and the order changes markedly as the reaction proceeds. The rate of oxygen evolution corresponds to the rate of cobaltic ion consumption, and no retardation by cobaltous ions was found. The mechanism suggested involved the pre-equilibrium (5.i) followed by:

$$\left[Co\ OH\ (OH_2)_5\right]^{2+} + \overset{\bullet}{O}H \longrightarrow \left[Co\ OH\ (OH_2)_5\right]^{+} + \dot{O}H \qquad (5.vii)$$

which leads to an expression of the form:

$$\frac{-d\left[Co^{III}\right]}{dt} = \left[Co^{III}\right]\left\{\frac{a}{\left[H^+\right]} + \frac{b}{\left[H^+\right]^2}\right\} \qquad (5.viii)$$

This can at least explain the kinetics in very dilute solution. The bimolecular terms were suggested to be explicable in terms of binuclear cobaltic complexes or loose ion association groups in solution.

Baxendale and Wells[49] more recently examined the self-decomposition of cobaltic perchlorate solution. They found kinetics similar to those reported by Bawn and White, but showed in addition that as more samples of cobaltic perchlorate were decomposed in a given sample of water, the rate of reaction, and the curvature of the rate plots, decreased, until a limiting curve was reached. Cobaltous ions had no effect on the reaction rate however, indicating that the initial curvature was due to trace

impurities. The latter part of the reaction fitted the expression:

$$-\frac{d\left[Co^{III}\right]}{dt} = \frac{k\left[Co^{III}\right]3/2}{\left[H^{+}\right]^{2}} \qquad (5.ix)$$

and the suggested mechanism involved a dimeric cobaltic species:

$$CoOH^{2+} + \left[(H_2O)_5\ Co - O - Co(OH_2)_5\right]^{4+} \xrightarrow{\text{slow}} 3Co^{2+}\ aq. + \dot{O}OH \qquad (5x)$$

In agreement with the above evidence, other workers have found that the rate law for the self-decomposition of cobaltic perchlorate includes a term $\frac{k\left[Co^{III}\right]2}{\left[H^{+}\right]^{2}}$ which is irreproducible and depends on the past history of oxidant.[126]

These results show that the oxidation of water by cobaltic perchlorate is a complex reaction about which very little is understood. With reference to the present work, it is important to know whether free hydroxyl radicals, which could attack organic substrates in solution, are produced in the reaction. The initiation of vinyl polymerisation by decomposing cobaltic solutionsis not definite evidence for hydroxyl radical liberation, since increasing the acidity of the medium decreases the decomposition rate much more than the polymerisation rate.[49] The production of phenols by the addition of benzene and nitrobenzene to decomposing cobaltic solutions[127] could likewise be due to the direct oxidation of these hydrocarbons.

Various schemes can be devised for the self-decomposition reaction. Oxidation of co-ordinated water or hydroxide by the central metal ion is

unlikely, since this process corresponds to that occurring in charge transfer band of the cobaltic absorption spectrum.[118,119,120] This absorption is at such short wavelengths that the charge transfer must require far too high an energy to occur without photochemical stimulation.[128] Furthermore, it has been shown[129,130] that the photochemical transition:

$$\left[Fe^{III}.\ \bar{O}H(OH_2)_5\right]^{2+} \rightleftharpoons \left[Fe^{II}.\ \dot{O}H(OH_2)_5\right]^{2+} \quad (\Delta H^{\circ}\ 90\ k.cal.mole^{-1}.) \qquad (5.xi)$$

is of much higher energy than oxidation via an ion pair:

$$Fe^{3+}aq + \bar{O}H \longrightarrow Fe^{2+}aq + \dot{O}H\ (\Delta H^{\circ}\ 40\ k.cal.mole^{-1}) \qquad (5.xii)$$

Thus such a mechanism can probably be discounted, unless it can be incorporated into some concerted process such as:

$$\left[Co\ OH(OH_2)_5\right]^{2+} + \left[CoOH(OH_2)_5\right]^{2+} \longrightarrow 2\ Co^{II}aq. + H_2O_2 \qquad (5.xiii)^{126}$$

where both metal ions act simultaneously as one-electron oxidants. Such a mechanism could explain the observed bimolecular term in the reaction kinetics, and avoids the formation of the high energy hydroxyl radical. A similar process has been proposed recently[131] for the production of oxygen from systems containing manganese (IV). The oxidation of co-ordinated water has been recently demonstrated[132] in the reaction of the complex $\left[(NH_3)_5\ Co.OH_2\right]^{3+}$ with a mixture of silver nitrate and acid persulphate. An intermediate Ag(II) or Ag(III) species is thought to interact with the cobaltic complex to form hydrogen peroxide, analogously to equation (5.xiii).

An alternative route for the self-decomposition reaction involves

outer-sphere oxidation of water or hydroxide ions:

$$Co^{III} + H_2O \longrightarrow Co^{II} + \dot{O}H + H^+ \qquad (5.xiv)$$

for which ΔH° = 34 k.cal.mole^{-1}, ΔS° = 31 e.u. and ΔG° = 25 k.cal.mole^{-1} [133]

and $$Co^{III} + \dot{O}H \longrightarrow Co^{II} + \dot{O}H \qquad (5.xv)$$

for which ΔH° = 21 k.cal.mol^{-1}, ΔS° = 59 e.u., ΔG° = 3 k.cal.mole^{-1}.

This could account for the observed first order term in the reaction kinetics.

The method of formation of the O — O bond to yield oxygen as the final product, is uncertain.[126] The dimerisation:

$$2\,\dot{O}H \longrightarrow H_2O_2 \qquad (5.xvi)$$

is possible, but unlikely since its rate would depend on the square of the very small hydroxyl radical concentration. The redox potential of the reaction:

$$\dot{O}H\ aq + H_2O \longrightarrow H_2O_2\ aq + H^+aq + e \qquad (5.xvii)$$

can be calculated from the standard free energies of formation of liquid water,[134] aqueous hydrogen peroxide,[134] and the gaseous hydroxyl radical,[134] and the free energy of solvation of the hydroxyl radical,[133] to be 0.83 volts. Hence the reaction:

$$Co^{III}.H_2O + \dot{O}H \longrightarrow Co^{II} + H_2O_2 + H^+ \qquad (5.xviii)$$

is thermodynamically favourable, and is likely to be rapid. Hydrogen peroxide is very rapidly oxidised to oxygen by cobaltic salts.[49]

It cannot be decided from the presently available evidence, whether or not the self-decomposition reaction liberates free hydroxyl radicals which

could attack organic substrates. However, this possibility should be taken into account when interpreting kinetic and product measurements.

b. The Self-Decomposition of Cobaltic Perchlorate in Aqueous Methyl Cyanide Solutions.

Since the self-decomposition of cobaltic ions in the aqueous methyl cyanide solutions used in the present work was often appreciable compared with rate of the reaction under investigation, it was necessary to make a systematic study of this background oxidation. Some representative kinetic runs at varying initial cobaltic ion concentrations are shown in Fig. 5.2. They are similar to those observed for the reaction in pure water. Table 5.3 shows that the rate of self-decomposition is reasonably independent of both the time of electrolysis of the cobaltous perchlorate solution, and the time of standing of the cobaltic perchlorate solution after electrolysis.

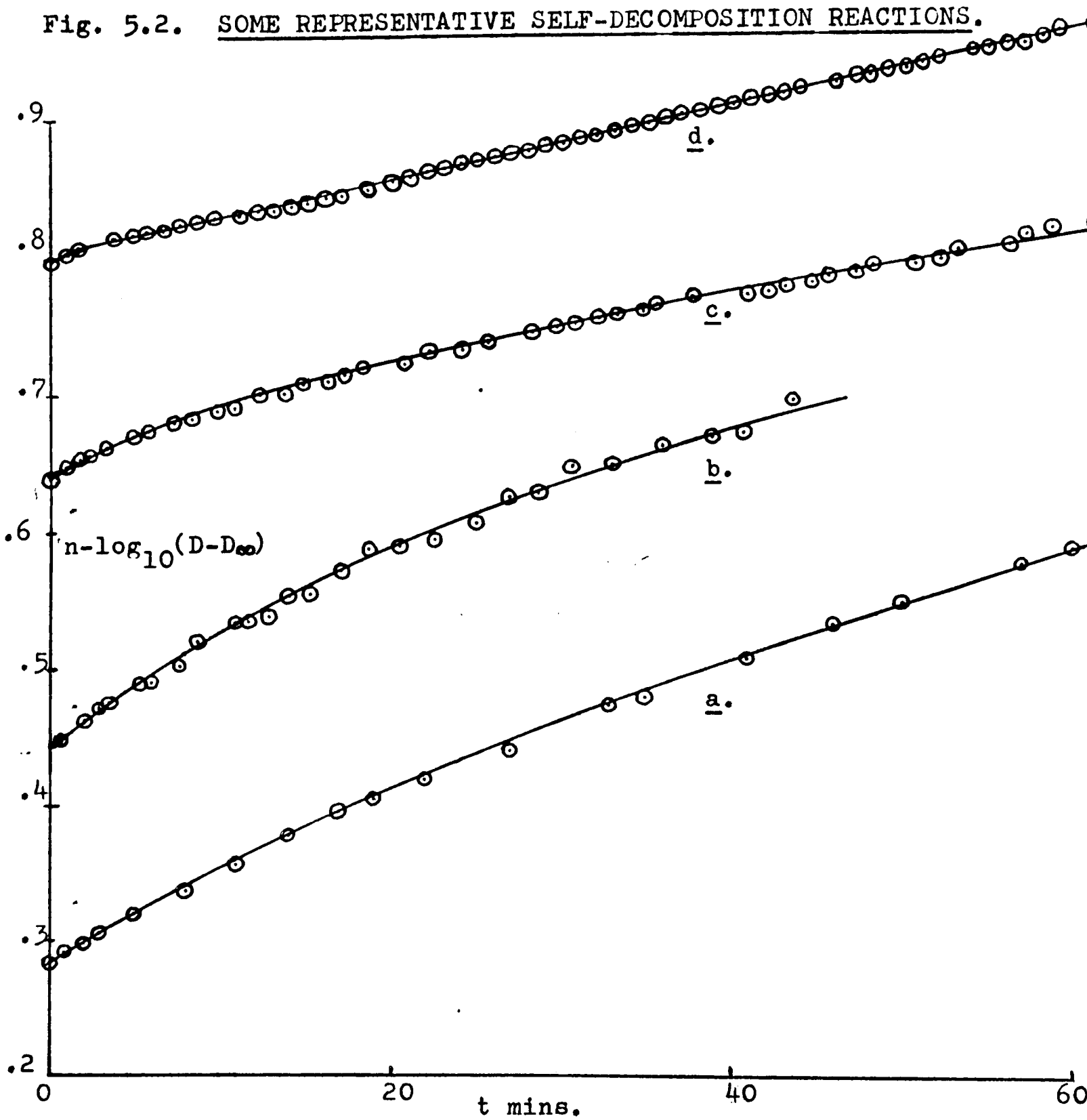
Table 5.3. Effect of Time of Electrolysis of Cobaltic Perchlorate, and Time of Standing after Electrolysis, on the Self-Decomposition Rate.

25°. $[HClO_4]$ 0.77M. 70 per cent (v/v) MeCN.

Time of electrolysis min.	Time of standing after electrolysis. min.	10^4 initial and final k' sec^{-1}. [a]	10^2 approx initial Co^{III}M
15	40	9.2 - 7.9	1.0
30	60	10.9 - 7.0	1.5
30	140	11.7 - 7.6	1.5
30	201	10.0 - 7.2	1.5
30	260	10.1 - 7.1	1.5
30	428	10.3 - 7.4	1.5
45	44	11.0 - 7.9	1.7
45	107	11.7 - 8.0	1.7
60	37	10.9 - 7.9	1.8
60	152	10.3 - 8.5	1.8

a. Measured by eye.

Fig. 5.2. SOME REPRESENTATIVE SELF-DECOMPOSITION REACTIONS.



a. 15° 60%MeCNv/v. 1.0M.$HClO_4$. $\mu\sim$ 1.0M. Initial $[Co^{III}] \sim 7\times10^{-5}$ M.
Initial $[Co^{II}] \sim 3\times10^{-5}$M.

b. As a. except $\mu\sim$ 1.01M., Initial $[Co^{III}] \sim 1.6\times10^{-3}$M. Initial $[Co^{II}] \sim 5\times10^{-4}$M.

c. As a. except $\mu\sim$1.05M., Initial $[Co^{III}] \sim 8\times10^{-3}$M. Initial $[Co^{II}] \sim 3\times10^{-3}$M.

d. As a. except $\mu\sim$1.1M. Initial $[Co^{III}] \sim 2.2\times10^{-2}$M. Initial $[Co^{II}] \sim 7\times10^{-3}$M.

n is an arbitrary number, selected to put all curves on the same part of the logarithmic scale.

Neither addition nor removal of oxygen had any effect on the rates, or the curvatures of the plots. Further purification of both methyl cyanide and water likewise had no effect, but the rate increased somewhat when the methyl cyanide was mixed with aqueous perchloric acid for more than half an hour before addition of the cobaltic perchlorate. (compare ref. 117). Consequently, solutions for kinetic work were made just before they were required for reaction.

Fig. 5.2 shows that there is no systematic variation in rate over about a 200 fold range of initial cobaltic ion concentration. Hence if the curvature of these plots is due partly to the oxidation of impurities, these must be present mainly in the electrolysed cobaltic perchlorate solution. Trace impurities could account for the variations shown in Table 5.3, and for the variation in self-decomposition rates measured under similar conditions but on different occasions, shown in Table 5.4.

Table 5.4 Some Representative Self-Decomposition Rates.

a. 20°. $[HClO_4]$ 1.00M. 50 per cent MeCN (v/v).		b. 15°. $[HClO_4]$ 1.00M. 60 per cent MeCN (v/v).	
10^3 approx initial $[Co^{III}]$ M.	10^4 initial and final $k'sec^{-1}$. [e]	10^3 approx initial $[Co^{III}]$ M.	10^4 initial and final $k'sec^{-1}$. [e]
2.8	1.2 - 1.0	0.1	2.7 - 1.5
4.6	2.9 - 2.5	1.6	3.8 - 1.8
5.1	1.7 - 1.2	2.0	1.9 - 0.9
5.6	1.9 - 1.7	2.2	3.6 - 1.1
6.0	1.7 - 1.5	2.5	2.5 - 1.4
6.2	2.4 - 1.6	2.7	1.0 - 0.8
6.8	1.5 - 1.1	2.7	3.8 - 0.9
7.4	2.9 - 1.2	3.3	1.2 - 0.6
7.4	2.7 - 1.3	8.1	2.6 - 0.9
9.2	1.7 - 1.3	21	1.5 - 1.1
14	2.1 - 1.7	22	3.6 - 1.1

e. Measured by eye.

Consequently self-decomposition rates were measured for each set of studies of substrate oxidation rates.

The curvature of the rate plots for the self-decomposition reaction prevents any accurate correction being made for this background oxidation during measurements of the oxidation rates of slowly reacting substrates. If the curvature is due to the oxidation of trace impurities, then the faster the reaction which is being studied, the more should the correction required approach the initial fast rate of the self-decomposition. Alternatively, if the curvature is due to a genuine complex reaction order with respect to cobaltic ions, then the required correction would be the mean self-decomposition rate over a similar range of cobaltic ion concentration to that followed during the reaction. This would be much less than the initial rate of self-decomposition. In practice the self-decomposition reactions were followed over time intervals rather longer than those followed for the actual oxidation reactions under investigation, and it was assumed that the true self-decomposition rate lay between the initial and final measured rates. The true rate of oxidation of the substrate should then lie between the two corrected values, assuming that no hydroxylation occurs. This necessarily makes rate measurements of very slow reactions rather approximate.

Chapter 6. THE OXIDATION OF AROMATIC HYDROCARBONS BY COBALTIC PERCHLORATE.

NOTE: Some of the results given in this Chapter, together with those of Chapter 7, have recently been accepted for publication in J. Chem. Soc.

The oxidation of a series of aromatic hydrocarbons by cobaltic perchlorate has been studied in aqueous perchloric acid. The insolubility and unreactivity of these substrates necessitated the use of high concentrations of methyl cyanide cosolvent, and the precision of the kinetic measurements was limited by the relatively high self-decomposition rates of cobaltic perchlorate in these solutions. (See Chapter 5). The decrease in cobaltic ion concentration with time was followed spectrophotometrically at 595-605 mμ. (See Chapter 11). Since this absorption band is weak, it was necessary to use fairly high concentrations of oxidant. Consequently it was often impossible to eliminate secondary oxidation of the more reactive products from the original hydrocarbon, and these secondary oxidations were a complication throughout the present work. The organic substrate was kept in effectively large excess over the oxidant, and reaction orders were evaluated as described in Chapter 11.

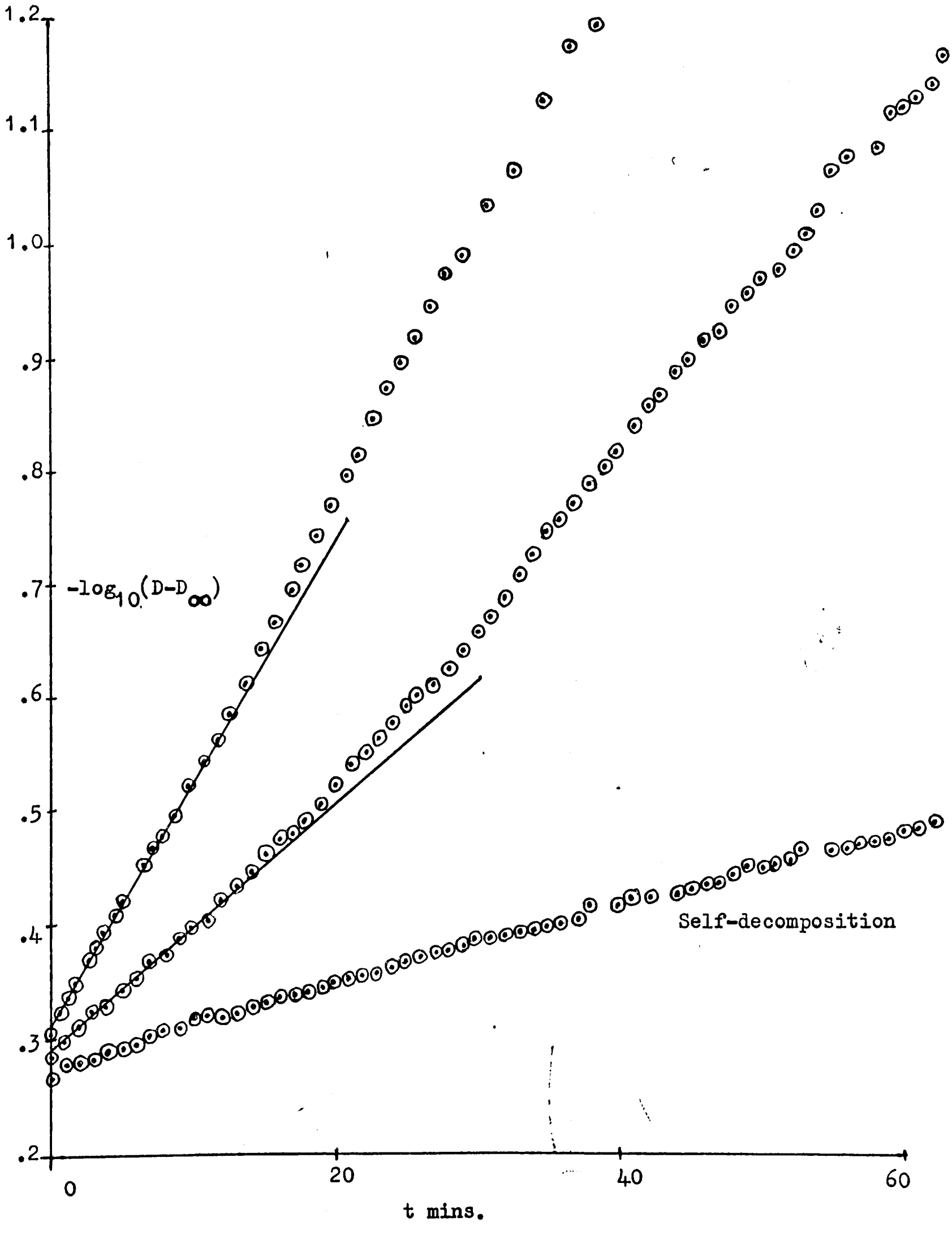
1. The Oxidation of Toluene.

a. Order with Respect to Substrate and Oxidant.

Typical plots of $\log_{10}(D-D_{\infty})$ against time, where D is the optical density at any instant and D_{∞} the optical density at the completion of the reaction, are shown in Figure 6.1. The reactions are first order with respect to cobaltic ions for up to one half life, but then deviate towards

FIG. 6.1 REPRESENTATIVE PLOTS FOR THE OXIDATION OF TOLUENE.

Conditions as for Table 6.2.



higher rates. This deviation can be ascribed, at least in part, to secondary oxidation of the more reactive products, (see the product studies below), but surprisingly it does not decrease regularly with increasing toluene concentration. However it was not difficult to measure the initial slopes, and hence to calculate the initial pseudo first order rate constants by:

$$k' = \frac{-2.30}{60} \frac{d \log_{10}(D-D_\infty)}{dt} \qquad (6.i.)$$

where t is in minutes and k' is in $sec.^{-1}$

The variation of the initial pseudo first order rate constants with toluene concentration is shown in Figure 6.2. These initial rate fall on a curve which cuts the axis at the top end of the range for the self-decomposition rate. Alternatively they could fit the dependence:

$$10^4 k' = 2.14 + 35.5 \left[PhMe\right] \qquad (6.ii.)$$

which has an intercept rather higher than the maximum self-decomposition rate. The interpretation of these two dependences will be discussed later. Many other substrates investigated in the present work were found to show similar behaviour i.e. dependences cutting the axis at the top of the self-decomposition range or at even higher values. The second order rate constants shown in Table 6.2. are hence calculated making use of the maximum self-decomposition correction. It was not possible to measure oxidation rates at toluene concentrations above about .23M, since the solutions became

FIGURE 6.2 THE DEPENDENCE OF OXIDATION RATE ON TOLUENE CONCENTRATION

Conditions as for Table 6.2.

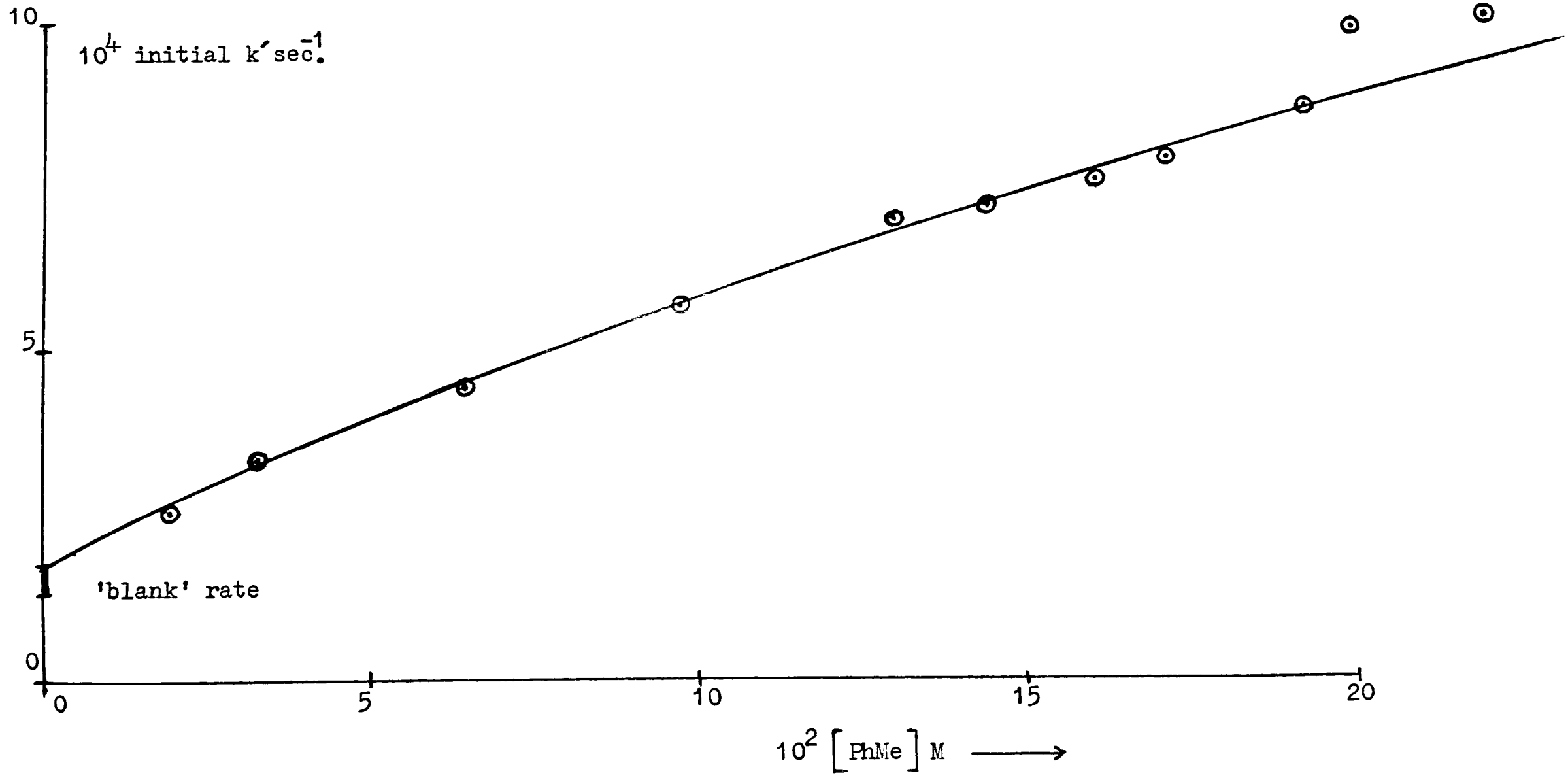


TABLE 6.2. DEPENDENCE OF OXIDATION RATE ON TOLUENE CONCENTRATION.

20.2° 50 per cent MeCN(v/v) 1.00M $HClO_4$. μ ca. 1.04M. Initial $[Co^{III}]$ ca. 7×10^{-3}M. Initial $[Co^{II}]$ ca. 2×10^{-3}M.

10^2 [PhMe] M.	10^4 initial k′ sec^{-1} [a]	10^3 k_2 $l.m.^{-1}$ $sec.^{-1}$ [b]	10^4 weighted mean k′ $sec.^{-1}$ [c]
0.0	[1.75-1.27] [d]	-	-
0.0	1.74-1.82	-	-
0.0	1.74-1.22	-	-
1.9	2.6	4.7	3.0
3.2	3.4	5.3	4.8
6.4	4.5	4.4	5.5
9.7	5.7	4.1	7.2
13.0	7.0	4.1	7.6
14.5	7.2	3.8	7.5
16.1	7.6	3.7	10.1
16.2	7.9	3.8	8.9
17.2	7.9	3.6	9.2
19.3	8.6	3.6	12.0
20.0	9.8	4.0	11.3
22.0	10.0	3.8	10.4

Equation 6.ii gives $k_2 = 3.5\times10^{-3}$ $l.m.^{-1}$ $sec.^{-1}$

a. Measured graphically.

b. Calculated from previous column taking k′ self decomposition= 1.7×10^{-4} $sec.^{-1}$

c. Calculated over 5-6 half lives (see Chapter 11). Without correction for self decomposition.

d. Initial and final rates measured graphically over similar time interval as taken for slowest run. (see Chapter 5).

turbid during the course of the reaction. Reactions were generally carried out using solutions degassed as much as possible under nitrogen, (Chapter 11), but deliberate addition of oxygen had no effect on the reaction rate. Likewise, leaving the reactions in the light beam at the wavelength used for kinetic measurements did not affect the rate.

b. Oxidation Products.

Yields of side-chain oxidation products, measured by the gas chromatographic method described in Chapter 10, are shown in Table 6.3. Within experimental error these products account for all the oxidant consumed showing there is very little fission of the aromatic nucleus. It is necessary to correct for the amount of oxidant used up by the simultaneous self-decomposition reaction to preserve this materials balance at lower toluene concentrations. Control experiments using cobaltous perchlorate showed there was no concurrent autoxidation of the toluene.

The general scheme for the oxidation is hence:

$$PhMe + Co^{III} \xrightarrow[k_a]{slow} PhCH^{\bullet}_2 + Co^{II} + H^+ \qquad (6.iii.)$$

$$PhCH^{\bullet}_2 + Co^{III}.OH_2 \xrightarrow{fast} PhCH_2OH + Co^{II} + H^+ \qquad (6.iv.)$$

$$PhCH_2OH + 2Co^{III} \xrightarrow{2k_b} PhCHO + 2Co^{II} + 2H^+ \qquad (6.v.)$$

$$PhCHO + 2Co^{III} + H_2O \xrightarrow{2k_c} PhCOOH + 2Co^{II} + 2H^+ \qquad (6.vi.)$$

Benzoic acid is much less reactive than is toluene under these conditions,

TABLE 6.3. PRODUCTS FROM THE OXIDATION OF TOLUENE.

Oxidations were carried out under N_2 at 20° in 5ml. of 50% MeCN v/v containing 1·00M. $HClO_4$. μ ca. 1.05M. $4.7 \pm 0.2 \times 10^{-5}$ moles Co^{III} added.

$10^2[PhMe]$M.	10^6 moles compound produced[a]				Product Ratios	
	$PhCH_2OH$	PhCHO	PhCOOH	$PhCH_2CH_2Ph$	$\frac{PhCHO}{PhCH_2OH}$	$\frac{PhCHO}{PhCOOH}$
22	.37	8.8	2.2	.07	24	4.0
16	.34	7.2	2.3	.05	21	3.1
11	.30	7.0	2.5	.03	23	2.8
5.1	.27	5.0	2.9	trace	18	1.7
1.9	.23	2.3	3.3	trace	10	0.7

a. Only minute traces of o-cresol and benzyl benzoate were detected, but no diphenylmethane.

$10^2[PhMe]$M.	Moles compound formed as % total side-chain attack			10^5moles Co^{III} accounted for as:			Mean[d] stoichiometry.
	$PhCH_2OH$	PhCHO	PhCOOH	Side-chain[b] attack	Self-decomp.[c]	Total	
22	1.5	71	27	4.9±.5	0.5-0.8	5.5±.7	4.3
16	1.6	67	33	4.3±.4	0.6-0.9	5.0±.6	4.4
11	1.4	64	34	4.4±.4	0.6-1.1	5.2±.7	4.5
5.1	1.4	53	45	3.8±.4	1.2-1.6	5.2±.6	4.6
1.9	1.6	32	69	2.9±.3	1.7-2.7	5.1±.8	5.0

b. Calculated as ($2PhCH_2OH + 4PhCHO + 6PhCOOH$).

c. Estimated from kinetic data, taking weighted mean rates for toluene oxidation, (Table 6.2.), and initial and final self-decomp. rates.

d. Mean no. of cobaltic ions consumed per toluene molecule oxidised.

and so is unlikely to be further oxidised. The production of small amounts of bibenzyl indicates that benzyl radicals are intermediates in the oxidation.

$$2PhCH_2^{\bullet} \longrightarrow PhCH_2CH_2Ph \qquad (6.vii.)$$

The variation of product ratios with toluene concentration, (Table 6.3), shows that the steps following the initial attack are not all fast. Reaction 6.vi. is much slower than reactions 6.iv and 6.v. Consequently, as benzaldehyde is produced during the reaction it will be oxidised away at an increasing rate, causing deviations, similar to those observed, from the strict first order dependence on cobaltic ions which might be expected for equation 6.iii. This effect of secondary oxidation should become relatively less important at higher toluene concentrations, when the average number of cobaltic ions consumed per toluene molecule oxidised decreases, as shown in Table 6.3. However, the scatter of the weighted mean rate constants in Table 6.2. shows no such systematic trend.

The tendency of the second order rate constants to decrease with increasing toluene concentration, as shown in Table 6.2., may be due to change in the stoichiometry of the initial reactions with toluene concentration. Similar behaviour has been observed[135] in other systems where secondary oxidation was comparable in rate to the initial attack. Other factors could also contribute to this variation. If hydroxyl radicals are liberated by the concurrent self-decomposition reaction, then their attack on the substrate could compete with their further oxidation to oxygen. Hydroxyl

radicals are known to rapidly attack toluene almost exclusively on the side chain:[72]

$$PhMe + {}^{\bullet}OH \longrightarrow PhCH_2^{\bullet} + H_2O \qquad (6.viii)$$

This reaction path involving attack on the toluene is likely to consume more oxidant subsequently than if the hydroxyl radical were simply oxidised to oxygen. This would correspond to a small increase in the self-decomposition rate in the presence of added substrate. The influence of this effect cannot be calculated at present, since it is not known if free hydroxyl radicals are liberated by the oxidation of water,(Chapter 5), and the relative rate constants for the attack of hydroxyl radicals on toluene and on cobaltic ions are not available. However, if the self-decomposition reaction were to produce appreciable numbers of hydroxyl radicals which attacked the toluene almost exclusively, a dependence of the form of equation 6.ii. might be expected. Alternatively, if the liberated hydroxyl radicals were partly consumed by cobaltic ions, then a curved dependence should be observed.

In order to evaluate further the influence of the secondary oxidations on the overall reaction process, it was attempted to measure directly the rates of reactions 6.v. and 6.vi. under conditions similar to those used for the oxidation of toluene. (Table 6.2.) Benzyl alcohol was oxidised much faster than mixing could be achieved, and so the second order rate constant, k_b, is not less than 50 $l.m.^{-1}sec.^{-1}$ The true value is probably greater than 100 $l.m.^{-1}sec.^{-1}$ (Compare ref.14). The rate of oxidation of benzaldehyde is shown in Table 6.4. The reaction is first order with respect to cobaltic ions over at least two half-lives.

TABLE 6.4 APPROXIMATE KINETICS FOR THE OXIDATION OF BENZALDEHYDE.

20.° 50 per cent MeCN v/v $[HClO_4]$ 1.00M.

Initial $[Co^{III}]$ ca. 1.5×10^{-2}M

Initial $[Co^{II}]$ ca. 5×10^{-3}M.

μ ca. 1.1M.

$10^2[PhCHO]$M.	$10^2 k'$ sec.$^{-1}$ [a,b]	k_2 l.m.$^{-1}$ sec.$^{-1}$ [a]
22	5.6	0.25
11	2.8	0.25
5.5	1.7	0.31

Initial $[Co^{III}]$ ca. 2.8×10^{-3}M.

Initial $[Co^{II}]$ ca. 1×10^{-3}M.

μ ca. 1.02M.

$10^2[PhCHO]$	$10^2 k'$ sec.$^{-1}$ [a,b]	k_2 l.m.$^{-1}$ sec.$^{-1}$ [a]
5.5	1.8	0.34
4.4	1.8	0.40
2.7	0.99	0.36
1.4	0.58	0.41

a. Corrected for rate of self decomposition of cobaltic perchlorate.

b. Slopes measured graphically.

Mean value of $k_c = \frac{k_2}{2} = .17$ l.m^{-1}. sec.$^{-1}$

The scatter in the derived second order rate constants is probably due to oxygen effects, and is in accordance with previous work on this oxidation, when no consistent results were obtained.[31,136]

Since benzyl alcohol is oxidised much faster than either toluene or benzaldehyde, then from equations 6.iii to 6.vi.:

$$-dC/dt = 4k_a[PhMe]C + 2k_c[PhCHO]C \qquad (6.ix.)$$

and
$$d[PhCHO]/dt = k_a[PhMe]C - k_c[PhCHO]C \qquad (6.x.)$$

Hence
$$\frac{dC}{d[PhCHO]} = -\left[\frac{4k_a[PhMe] + 2k_c[PhCHO]}{k_a[PhMe] - k_c[PhCHO]}\right] \qquad (6.xi.)$$

which, on integration, leads to:

$$C_o - C = \frac{-6k_a}{k_c}[PhMe]\log_e\left\{1 - \frac{k_c[PhCHO]}{k_a[PhMe]}\right\} - 2[PhCHO] \qquad (6.xii.)$$

The benzaldehyde concentration will reach a stationary value when

$$k_a[PhMe] = k_c[PhCHO] \qquad (6.xiii.)$$

This condition would give an indeterminate value for (C_o-C) from equation 6.xii. However, if 99 per cent of the stationary state concentration has been attained, then

$$.99k_a[PhMe] = k_c[PhCHO] \qquad (6.xiv.)$$

which leads to

$$C_o - C = 25.6\, k_a[PhMe]/k_c \qquad (6.xv.)$$

This equation then gives the amount of oxidant required for approximately

steady state conditions to be attained with respect to benzaldehyde. The analogous equation for determining approximately steady state conditions for benzyl alcohol is

$$C_o - C = 16.4\, k_a \left[PhMe\right] / k_b \qquad (6.xvi.)$$

Table 6.5 shows that for oxidations over the range of toluene and cobaltic ion concentrations studied, a stationary state concentration of benzyl alcohol, but not of benzaldehyde, should have been attained. However, Table 6.6 shows that the concentrations of benzaldehyde and benzyl alcohol actually produced by these reactions are in all cases higher than the calculated maximum stationary state concentrations, by a factor of at least 20 for the benzyl alcohol. The discrepancies are greater at lower toluene concentrations for both products, and so are unlikely to be simply due to erroneous k_b and k_c values.

These calculations suggest that some additional reaction may be intervening to enhance the yield of benzaldehyde and benzyl alcohol at the expense of benzoic acid. A possible process is

$$PhCHO + Co^{III} \longrightarrow Ph\dot{C}O + Co^{II} + H^+ \qquad (6.xvii.)$$

$$Ph\dot{C}O + PhMe \longrightarrow PhCHO + Ph\dot{C}H_2 \qquad (6.xviii.)$$

but this should be less noticeable at lower toluene concentrations, unless the relatively greater production of $Ph\dot{C}O$ radicals then outweighs the effect of the smaller substrate concentration. Radical transfer to the solvent is also conceivable:

$$Ph\dot{C}O + MeCN \longrightarrow PhCHO + {}^{\bullet}CH_2CN \qquad (6.xix.)$$

TABLE 6.5. CALCULATED COBALTIC PERCHLORATE CONCENTRATIONS REQUIRED FOR ATTAINMENT OF A STATIONARY STATE.

$10^2[PhMe]$ M.	$10^4 k_a[PhMe]$ sec.$^{-1}$ [a,b]	$10^2[Co^{III}]$ M.calc.[b,c,d] for steady [PhCHO]	$10^5[Co^{III}]$ M.calc.[b,c,e] for steady $[PhCH_2OH]$
22	2.1 ± 0.2	3.2 ± 0.3	1.0 ± 0.5
20	2.2 ± 0.1	3.3 ± 0.1	7.2 ± 0.3
19.3	2.2 ± 0.3	3.4 ± 0.4	7.4 ± 0.8
17.2	1.8 ± 0.1	2.7 ± 0.2	5.9 ± 0.3
16.2	1.7 ± 0.1	2.5 ± 0.2	5.5 ± 0.4
16.1	1.8 ± 0.2	2.8 ± 0.2	6.1 ± 0.5
14.5	1.4 ± 0.2	2.2 ± 0.2	4.7 ± 0.5
13.0	1.4 ± 0.1	2.1 ± 0.2	4.6 ± 0.3
11.0	1.2 ± 0.1	1.9 ± 0.1	4.1 ± 0.2
9.7	1.2 ± 0.1	1.8 ± 0.2	3.9 ± 0.4
6.4	.85 ± .05	1.3 ± 0.1	2.8 ± 0.2
5.1	.74 ± .04	1.1 ± 0.1	2.4 ± 0.2
3.2	.60 ± .12	0.9 ± 0.2	2.0 ± 0.4
1.9	.36 ± .10	.54 ± .15	1.1 ± 0.4

a. Calculated as :

$$\left[\frac{\text{(Weighted mean rate constant corrected for self-decomp. from Table 6.2)}}{\text{Mean stoichiometry from Table 6.3.}}\right]$$

b. Range is caused by uncertainty of weighted mean rates and of self - decomposition rates.

c. These figures do not include the amount of oxidant which would also be concurrently consumed by the self-decomposition reaction.

d. Calculated taking k_c = 0.17 l.m.$^{-1}$ sec.$^{-1}$ from Table 6.4.

e. Calculated taking k_b = 50 l.m.$^{-1}$ sec.$^{-1}$ (Its minimum value).

TABLE 6.6 COMPARISON BETWEEN KINETICALLY CALCULATED AND MEASURED CONCENTRATIONS OF OXIDATION PRODUCTS.

$10^2[PhMe]$ M.	$10^4[PhCHO]$ M		10^5 final $[PhCH_2OH]$ M	k_b calc.
	Calc. Stationary concentration[a]	Measured final concentration[b]	measured[b]	$l.m^{-1}.sec^{-1}$.
22	13 ± 1[d]	18	1.4±0.1[d]	7.4
20	13 ± 1	17	1.3±0.1	7.2
19.3	13 ± 2	17	1.2±0.2	7.1
17.2	10 ± 1	16	1.5±0.1	6.9
16.2	10 ± 1	14	1.4±0.1	6.8
16.1	11 ± 1	14	1.2±0.1	6.8
14.5	8.5±0.9	14	1.6±0.2	6.6
13.0	8.2±0.6	14	1.7±0.1	6.5
11.0	7.3±0.3	14	1.9±0.1	6.0
9.7	7.0±0.6	13	1.8±0.2	6.1
6.4	5.0±0.4	11	2.1±0.2	5.5
5.1	4.3±0.3	10	2.3±0.1	5.4
3.2	3.3±1.0	7.5	2.5±0.8	5.0
1.9	2.1±0.6	4.6	2.2±0.5	4.6

a. Calculated from Equation 6.xiii.

b. Derived from Table 6.3.

c. k_b calculated to give the measured concentration of $PhCH_2OH$.

d. Range due to uncertainty in $k_a[PhMe]$ values from Table 6.5.

$$\cdot CH_2CN + PhMe \longrightarrow PhCH_2^{\bullet} + MeCN \qquad (6.xx.)$$

The enhancement of the benzyl alcohol yield is so great that a stationary state concentration of this product is not likely to be reached immediately, in contrast to the prediction from the simple reaction scheme shown in Table 6.5. Hence the initial rate constants for the toluene oxidation given in Table 6.2. are less than $4k_a\left[PhMe\right]$. (Table 6.5.)

e. <u>The Influence of Perchloric Acid Concentration on the Oxidation Rate.</u>

The rate of oxidation of toluene was measured over a range of perchloric acid concentrations, while keeping the ionic strength of the medium constant by the addition of sodium perchlorate. Plots of $-\log_{10}(D-D_\infty)$ against time were again curved, (Fig. 6.1), and their curvature did not show any systematic change with acidity. Table 6.7 shows that the initial pseudo first order rate constants vary according to the expression:

$$10^3 k_{corr} = 1.21 + 4.0/\left[H^+\right] \qquad (6.xxi.)$$

at a toluene concentration of 0.11M. Equation 6.xxi is of the form found for all other oxidations of organic substrates by cobaltic perchlorate which have been investigated (Chapter 2). The very small intercept shown in Fig. 6.7 indicates that only an acid dependent path is involved in the oxidation to any appreciable extent.

This inverse acidity dependence can be explained by the rapid pre-equilibrium:

$$H_2O + \left[Co(OH_2)_6\right]^{3+} \rightleftharpoons \left[Co.OH(OH_2)_5\right]^{2+} + H_3O^+ \qquad (6.xxii.)$$

FIG. 6.7. INFLUENCE OF ACID CONCENTRATION ON THE RATE OF OXIDATION OF TOLUENE.

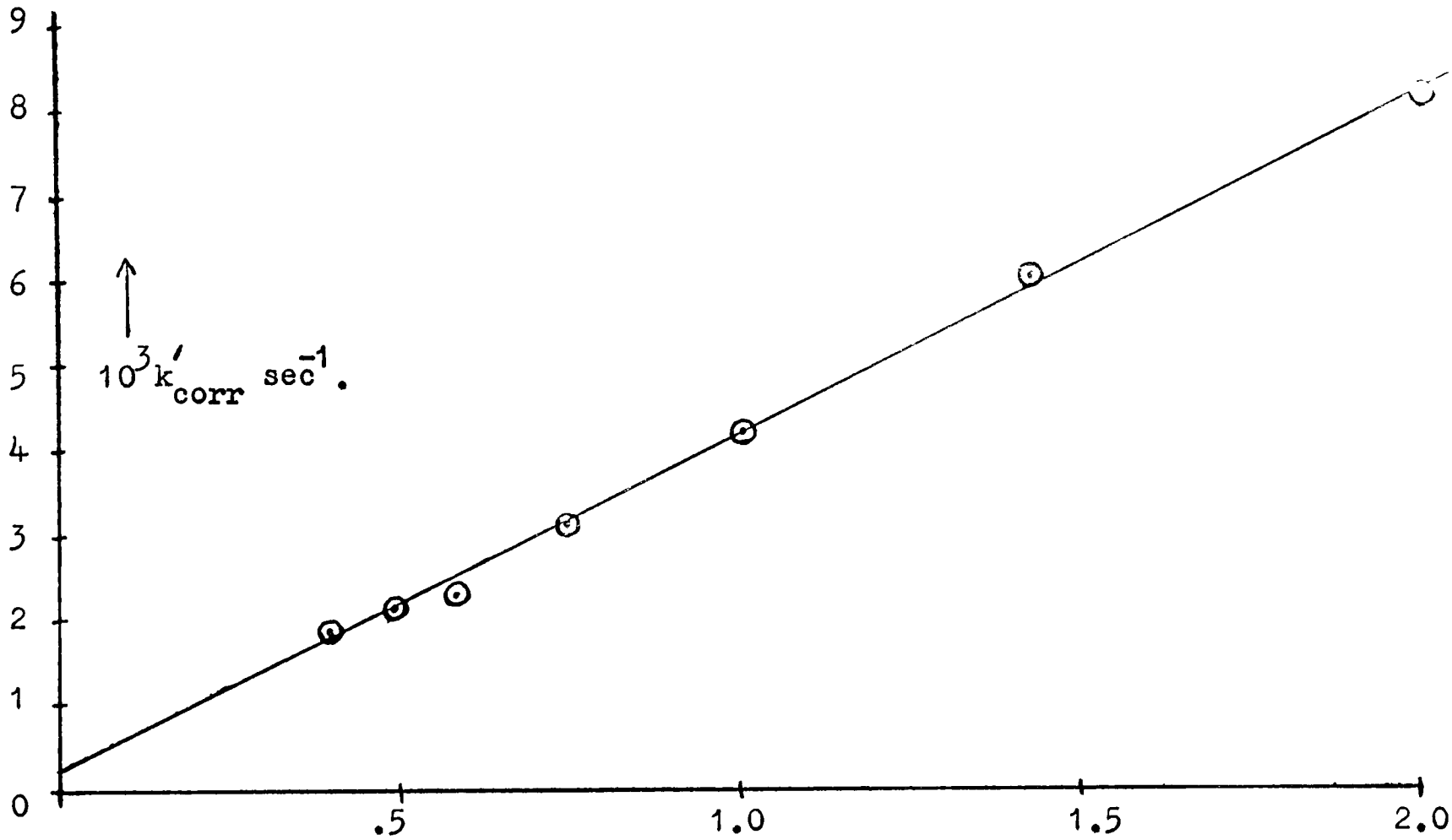


TABLE 6.7

20.2°. 50 per cent MeCN (v/v). μ ca. 2.6M. $[PhMe]$ .110M. initial $[Co^{III}]$ ca. 6×10^{-3}M. Initial $[Co^{II}]$ ca. 2×10^{-3}M

$[HClO_4]$M.	$1/[HClO_4]\bar{M}^1$	10^3 initial $k'sec^{-1}$.	[a] 10^3 $k'sec^{-1}$ for corresponding self-decomp.	[b] $10^3 k'sec^{-1}$ corr	$[H^+](10^3 k'_{corr}$ −0.21) mole l^{-1} sec^{-1}
2.56	0.39	2.2	.3 - .2	1.9	4.3
2.10	0.48	2.5	.4 - .2	2.1	4.0
1.75	0.57	2.8	.5 - .2	2.3	3.7
1.35	0.74	3.7	.6 - .3	3.1	3.9
1.00	1.00	4.9	.7 - .4	4.2	4.0
0.70	1.43	6.8	.8 - .4	6.0	4.1
0.50	2.00	9.3	1.2 - .5	8.1	3.9

a. Measured graphically

b. Calculated taking higher self-decomp, rate (c.f. Table 6.2)

before the formation of the activated complex in the rate step. The origin of the enhanced activity of the hydrolysed cobaltic species is still not certain. It will be discussed below for the separate cases of inner- and outer-sphere oxidation.

Oxidation by an Outer Sphere Mechanism.

An outer sphere process is more likely to occur in the oxidation of toluene than in the oxidation of compounds containing other functional groups possessing hetero atoms which can complex the cobaltic ion. In an outer sphere process the electron must, in effect, travel through the solvent sheath to the central ion, and the electron transfer will be the rate determining step. Magnetic data show that the unhydrolysed species $\left[Co(OH_2)_6\right]^{3+}$ is in the low spin state at room temperature.[112,113] Since the hydroxide ion is lower in the spectrochemical series than is water, the energy gap between the t_{2g} and e_g orbitals of the cobaltic ion should be smaller in the hydrolysed complex. Consequently, it has been suggested[32] that this species should contain a greater proportion of high spin complex than does the unhydrolysed species. In a low spin cobaltic complex the bonding orbitals of the central cation are filled. Any further electron added to this system must occupy an antibonding orbital, and will distort the co-ordination shell of the central cation by forcing one water molecule to lie farther away than the other five. This displacement will be partly achieved in the transition state and the energy required will be included in the activation energy of the reaction. The high spin cobaltic ion, in contrast, has

vacancies in its t_{2g} orbitals, and so can receive an electron without great distortion of its octahedral co-ordination shell. The activation energy for an electron transfer to a metal ion is lower the less change it produces in the ion structure.[137] Hence electron transfer to the high spin complex will be favoured over transfer to a low spin complex. If the hydrolysed species contains a greater proportion of high spin complex, this could explain its enhanced reactivity.

Unfortunately this explanation involving an outer sphere mechanism is not general. Hydrolysed metal ions are often more active in oxidation. $\left[FeOH(OH_2)_5\right]^{2+}$ is more reactive than $\left[Fe(OH_2)_6\right]^{3+}$,[138] and the hydrolysed manganic species is probably more active than the unhydrolysed species.[139] Both ferric and manganic ions have t_{2g} orbitals available in both high and low spin states and so the above argument cannot be applied in these cases. In addition, recent evidence[113] has indicated that the energy gap between the high and low spin states of the $\left[Co(OH_2)_6\right]^{3+}$ ion is about 15.k.cal.mol.$^{-1}$, a much higher value than previously thought to be the case.

An alternative explanation is that an electron can be more easily conducted into the central metal ion through a hydroxide ion than through a less polarisable water molecule.[140] This would again lead to the observed inverse acidity dependence. The oxidation of toluene by an outer-sphere process could then occur by a mechanism such as:

$$PhCH_2 - H \cdots OH - Co^{III}(OH_2)_5 \longrightarrow PhCH_2^{\bullet} + Co^{II}(OH_2)_6 \quad (6.xxiii.)$$

which is essentially a hydrogen atom abstraction; or alternatively by abstraction of the electron from the π-electron cloud of the aromatic nucleus:

$$PhMe + \left[HO\text{-}Co(OH_2)_5\right]^{2+} \longrightarrow (PhMe)^{+\bullet} + \left[HOCo(OH_2)_5\right]^{+} \quad (6.xxiv.)$$

$$(PhMe)^{+\bullet} \longrightarrow PhCH_2^{\bullet} + H^{+} \quad (6.xxv.)$$

The proton could be transferred to a solvent water molecule in equation 6.xxv., and equations 6.xxiv. and 6.xxv. could be concerted. If the radical cation had a finite lifetime it could be attacked by solvent water, giving phenolic products which would consume large quantities of cobaltic perchlorate. However, Table 6.3. shows that the oxidation is exclusively of the side chain under these conditions, which indicates that if the route involving equations 6.xxiv. and 6.xxv. is followed, then electron and proton transfer occur virtually simultaneously.

Oxidation by an Inner Sphere Mechanism.

The oxidation of carboxylic acids by cobaltic perchlorate by an inner sphere mechanism[14] has demonstrated the substitutional lability of the active cobaltic species. In contrast to other low spin complexes which are generally substitutionally inert,[142] there is fast exchange of water between the solvent and the hydration shell of cobaltic perchlorate.[141] This may occur through a small proportion of the labile high spin complex. Alternatively it may be due to rapid exchange between the cobaltic and the labile cobaltous species.[42,43,44] More recent evidence[143] has shown that complexes containing π-bonding ligands such as $\bar{O}H$ are substitutionally

labile via an S_N1 type process, since there is stabilisation of the trigonal bipyramidal transition state.

Since substitution of the cobaltic ion is rapid the rate step is still probably electron transfer. If the hydrolysed species is substitutionally labile while the unhydrolysed species is inert, then the equilibrium concentration of the substrate complex will decrease with increasing acidity, which could account for the observed acidity dependence. This has been demonstrated recently for the oxidation of propionic acid.[14]

An inner sphere mechanism may be possible for the oxidation of toluene. Aromatic hydrocarbons are known to form complexes with some transition metal ions in aqueous solution, although none have been reported with cobaltic ions. If such a complex could be formed, then the removal of a π-electron could be concerted with removal of a side-chain proton by solvent water,(since the other cobalt ligands are unlikely to be favourably placed), and transfer of an electron from the side chain C-H to the benzene ring as the proton is being removed. This would be equivalent to the aromatic nucleus acting as a polarisable ligand through which the electron transfer can take place, to oxidise the side chain.

However, reaction through such a complex is likely to be much less favoured both sterically and geometrically than in other cases of cobaltic oxidations thought to take place by an inner sphere mechanism.[9,10,14,32]

d. The Variation of Oxidation Rate with Cosolvent Concentration.

The variation of the initial pseudo first order rate constant with methyl cyanide concentration over the range 35 per cent - 84 per cent (v/v) is shown in Table 6.8. The individual reactions showed the same deviations from first order dependence on oxidant noted previously, but the curvature appeared to decrease somewhat at higher methyl cyanide concentrations. Thus the oxidation in 84 per cent methyl cyanide was first order over two half lives. The increase in rate with methyl cyanide concentration is far too large to fit the expression

$$\log_{10} k' = M.(\%\ MeCN) \qquad (6.xxvi.)$$

which has been previously found satisfactory at lower cosolvent concentrations.[14] However, previous work on the oxidations of t-butanol and cyclohexanone has shown that these reactions also increase in rate more rapidly than is predicted by equation 6.xxvi. at methyl cyanide concentrations above about 60 per cent.[144]

The colours of the solutions obtained at the completion of the kinetic runs varied markedly with methyl cyanide concentration. Below 55 per cent methyl cyanide they were the pale pink colour usually obtained from cobaltic oxidations. Above this concentration they became a progressively deeper yellow. This yellow colour was extracted from the solution by dichloromethane, and was quite distinct from the slightly orange tint assumed by cobaltous perchlorate in high concentrations of methyl cyanide.

TABLE 6.8 THE INFLUENCE OF METHYL CYANIDE CONCENTRATION ON THE RATE OF OXIDATION OF TOLUENE.

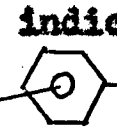
20.2°. $[HClO_4]$ 1.00M. μ ca. 1.04M. [PhMe] 5.2×10^{-2}M

Initial $[Co^{III}]$ ca. 6×10^{-3}M. Initial $[Co^{II}]$ ca 2×10^{-3}M.

% MeCN (v/v)	10^4 initial $k'sec^{-1}$. [a]	10^4 $k'sec^{-1}$ for corresponding self-decomp. [a]	10^4 $k'_{corr}sec^{-1}$ [b]
84	17.4	5.7 - 4.1	11.7
75	10.7	4.8 - 3.5	5.9
65	6.5	2.7 - 2.0	3.8
55	4.9	2.1 - 1.5	2.8
50[c]	4.1[c]	1.7 - 1.3[c]	2.4[c]
35	3.4	1.5 - 0.8	1.9

a,b. As for Table 6.7

c. Interpolated from Table 6.2

The spectrum of the dichloromethane extract of a large scale reaction showed no characteristic peaks in the visible region which would account for the yellow colour. It was attempted to analyse the concentrated extract on Kieselgel G and alumina thin layer plates, but in both cases the yellow compound reacted with the stationary phase and could not be moved up the plate or dissolved off again. On cellulose, using cyclohexane/60°-80° light petrol as eluting solvent, two bands were formed. The upper band, which was faintly yellow, moved nearly with the solvent front, and its mass spectrum showed large peaks at mass numbers 196,119 and 105, indicating that it probably contained some substituted benzophenones, PhCO--Me. [145] The carbonyl compounds from this fraction were converted to their 2,4-dinitrophenylhydrazones and separated on a Kieselgel G plate. (Chapter 10). In addition to benzaldehyde DNP, there was an upper band with an R_s value very similar to that of benzophenone DNP. This band yielded a red glue which would not crystallise, of which the mass spectrum showed a molecular ion peak at mass number 376, in agreement with the above.

The detection of these substituted benzophenones [177,83] supports the suggestion that reactions 6.xvii and 6.xviii. occur to produce the high yields of benzyl alcohol previously found.

The lower band on the cellulose thin layer plate remained on the base line. It was dissolved off with dichloromethane and after evaporation to dryness yielded a white polymeric material which would not redissolve,

and a very small amount of an ochre amorphous substance, the mass spectrum of which showed no characteristic peaks. This substance was not identified.

It can be concluded that at high methyl cyanide concentrations there is some new reaction leading to yellow products. This was confirmed by gas chromatographic measurement of the side chain oxidation products (Table 6.9). Two small new unidentified peaks with retention times close to that of bibenzyl appeared on the chromatograms, and at this higher methyl cyanide concentration large amounts of the oxidant consumed are not accounted for by side chain oxidation products. (Compare Table 6.3) Test oxidations of benzyl alcohol, benzaldehyde and benzoic acid under these conditions gave no yellow products, which must hence come from the initial oxidation of toluene. Even in the large scale reaction only a minute amount of the yellow compound was produced, despite the intensity of the colours formed.

Despite the large amounts of oxidant unaccounted for in Table 6.9., approximate calculations of the maximum stationary concentration of benzyl alcohol show that this is again much less than the measured value.

Kinetic measurements under similar conditions to those used for the product studies are shown in Table 6.10. The kinetic behaviour is similar to that found for the oxidation in 50 per cent methyl cyanide solution. (Fig. 6.1. and Table 6.2). Added oxygen did not affect the reaction rates or the colour of the products.

TABLE 6.9 PRODUCTS FROM THE OXIDATION OF TOLUENE IN 70 PER CENT METHYL CYANIDE SOLUTION.

Reactions carried out at 15° in 4 ml 70 per cent MeCN (v/v) $[HClO_4]$ 0.77M.

μ ca. 0.9M. Initial $[Co^{II}]$ ca. 9×10^{-3}M.

$1.03 \pm .05 \times 10^{-4}$ moles Co^{III} added in each case (i.e. Initial $[Co^{III}]$ 2.6×10^{-2}M)

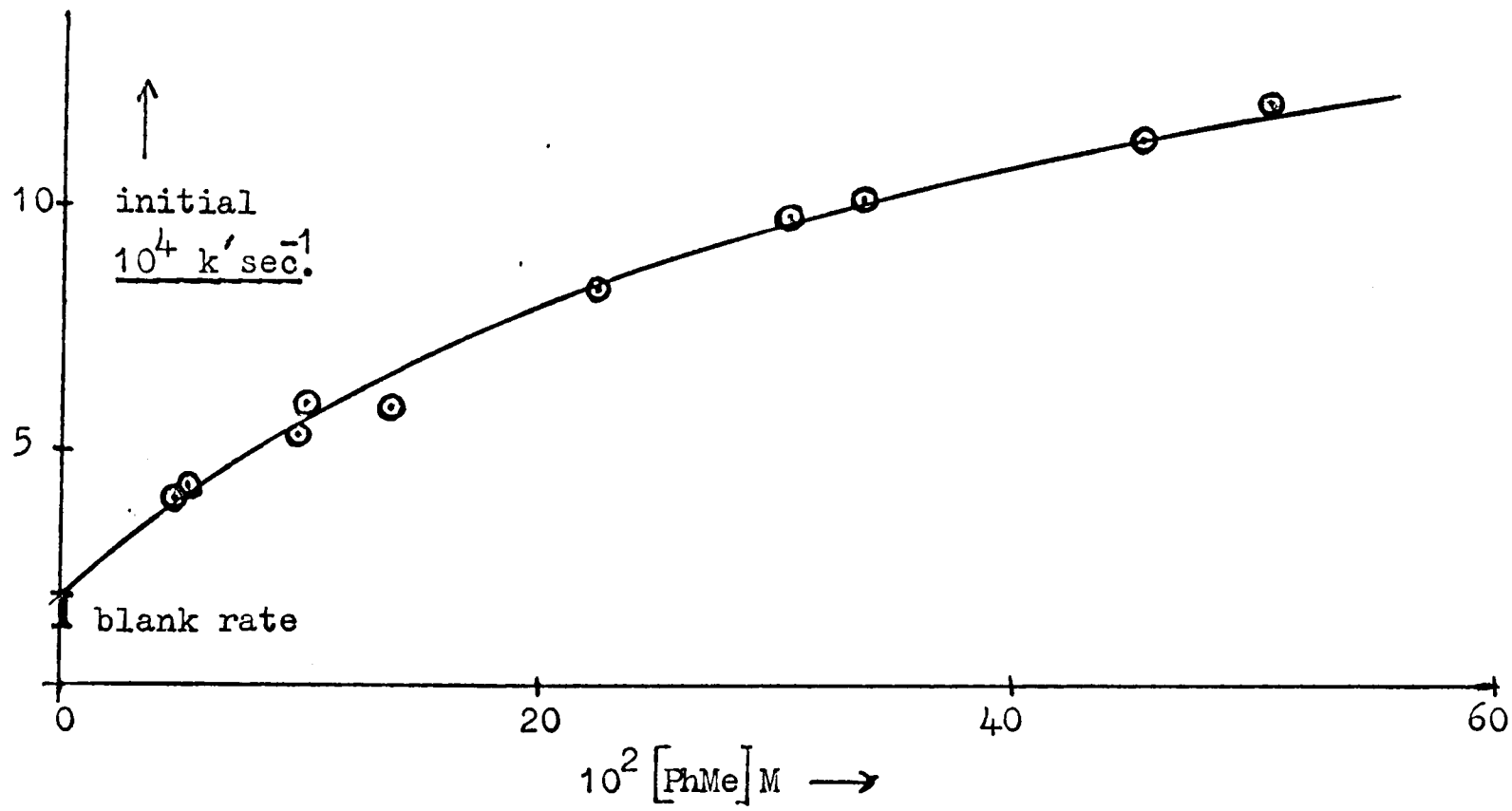
$10^2[PhMe]$M.	10^6 moles compound produced[a]				Product Ratios	
	$PhCH_2OH$	PhCHO	PhCOOH	$PhCH_2CH_2Ph$	$\frac{PhCHO}{PhCH_2OH}$	$\frac{PhCHO}{PhCOOH}$
21.5	.91	6.0	2.9	.05	6.6	2.1
16.6	1.0	4.9	2.9	trace	4.9	1.7
11.6	.88	4.4	2.6	.04	5.0	1.7
6.6	.60	2.8	2.5	.01	4.7	1.1

a. Only minute traces of o-cresol and benzyl benzoate, but no diphenylmethane, were detected.

$10^2[PhMe]$M.	Moles compound formed as % total side chain attack.			10^5 moles Co^{III} accounted for as:		
	$PhCH_2OH$	PhCHO	PhCOOH	b Side chain attack	c Self--decomp.	Total.
21.5	4.2	56	40	4.3±0.4	1.4-2.4	6.2±0.9
16.6	5.1	50	45	3.9±0.4	1.6-2.8	6.1±1.0
11.6	5.0	50	45	3.5±0.4	1.9-3.6	6.2±1.3
6.6	4.4	41	56	2.7±0.3	2.7-4.4	6.2±1.2

b,c. As for Table 6.3.

TABLE 6.10. RATE OF OXIDATION OF TOLUENE IN 70 PER CENT METHYL CYANIDE SOLUTION.



15°. $[HClO_4]$ 0.77M. μ ca. 0.9M. Initial $[Co^{III}]$ ca. 2×10^{-2}M. Initial $[Co^{II}]$ ca. 6×10^{-3}M.

10^2 [PhMe] M.	10^4 initial k′sec.$^{-1}$ [a]	10^3 k_2 l.m^{-1}. sec^{-1}. [b]	10^4 weighted mean k′sec^{-1}. [c]
0.0	[1.7-1.3] [d]	-	-
0.0	[1.9-1.5] [d]	-	-
4.8	3.9	4.2	3.9
5.1	4.1	4.3	4.5
9.9	5.2	3.3	5.8
10.2	5.9	3.9	6.4
13.7	5.8	2.8	6.1
21.5	8.3	3.0	8.3
30.4	9.8	2.6	11.3
33.7	10.2	2.5	10.2
45.2	11.4	2.1	12.6
50.6	12.1	2.0	14.0

a,c,d. As for Table 6.2.

b. Calculated from previous column, taking k′ self-decomposition = 1.9×10^{-4} sec^{-1}.

e. Variation of Oxidation Rate with Temperature.

Measurements of oxidation rates were made in solutions containing 50 per cent and 84 per cent methyl cyanide over the temperature range 0° to 30°. The variation of the initial pseudo first order rate constant with temperature is shown in Table 6.11. (Fig. 6.11.). The derived overall activation parameters are:

a) In 50 per cent methyl cyanide: $\Delta H^{\ddagger}$ = 27 k.cal.mole^{-1}; $\Delta G^{\ddagger}$ = 20 k.cal.mole^{-1}
$\Delta S^{\ddagger}$ = 24 e.u.

b) In 84 per cent methyl cyanide: $\Delta H^{\ddagger}$ = 22 k.cal.mol^{-1}; $\Delta G^{\ddagger}$ = 19 k.cal.mol^{-1}
$\Delta S^{\ddagger}$ = 9 e.u.

The activation enthalpies are not altered significantly by taking rate constants calculated using the lower self-decomposition rates.

The secondary oxidations occurring have second order rate constants greater than that for the initial step. Hence they are likely to have lower activation energies, and so to become relatively less important at higher temperatures, so that the apparent measured activation energy for the overall process may be rather lower than the true activation energy for the initial slow step. However, the individual rate plots did not become more linear with increasing temperature.

The $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ values shown in Table 6.11. apply to the overall reaction, and are calculated on the assumption that the overall oxidation is first order with respect to toluene. Their absolute values are thus

FIG. 6.11. INFLUENCE OF TEMPERATURE ON RATE OF OXIDATION OF TOLUENE.
Conditions as Table 6.11.

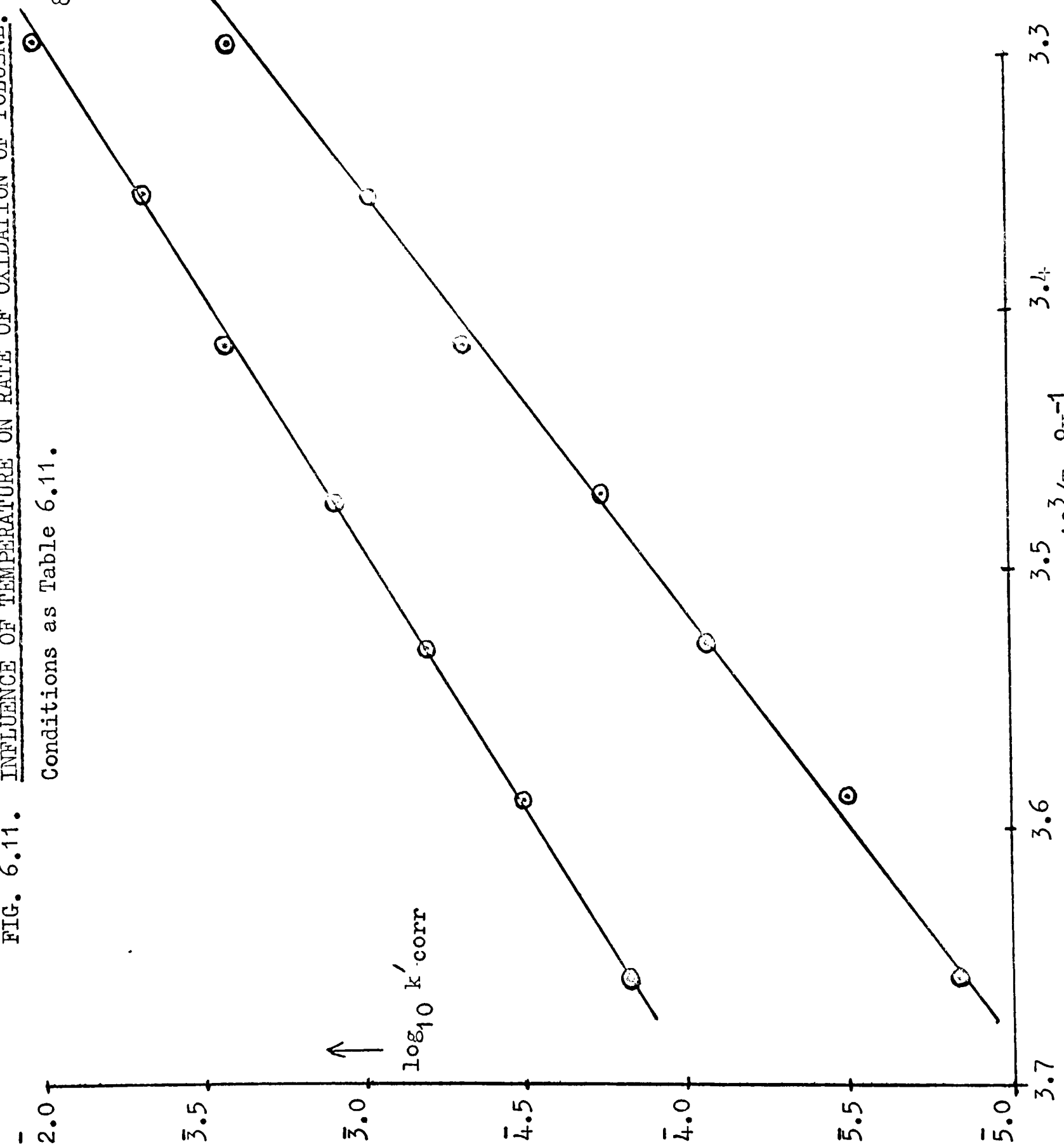


TABLE 6.11 INFLUENCE OF TEMPERATURE ON THE RATE OF OXIDATION OF TOLUENE.

$[HClO_4]$ 1.00M μ ca. 1.04M [PhMe] .121M. Initial $[Co^{III}]$ ca. 5 x 10^{-3}M. Initial $[Co^{II}]$ ca. 2 x 10^{-3}M. μ ca. 1.03M.

a. 50 per cent MeCN (v/v).

Temp °C.	$10^3/T$ K^{-1}.	10^4 initial $k'sec^{-1}$	10^4 $k'sec^{-1}$ for[a] corresponding self-decomp.	10^4 k'corr. sec^{-1}[b]	$4+\log_{10}$ k'corr.
0.3	3.66	0.30	0.15-0.12	0.15	$\bar{1}$.155
5.4	3.59	0.63	0.32-0.16	0.31	$\bar{1}$.491
10.3	3.53	1.50	0.67-0.34	0.83	$\bar{1}$.919
15.2	3.47	3.52	1.70-0.62	1.82	0.260
20.2[c]	3.41[c]	6.5[c]	1.7-1.3[c]	4.8[c]	0.681[c]
25.1	3.35	14.8	5.4-2.8	9.4	0.973
30.8	3.29	38.0	12.5-11.7	25.5	1.406

a,b. As for Table 6.7

c. Interpolated from Table 6.2.

Slope by least squares corresponds to E_a = 28 k.cal.mol^{-1}. Hence $\Delta H^{\ddagger}$ = 27 k.cal.mol^{-1} $\Delta G^{\ddagger}$ = 20 k.cal.$mole^{-1}$. $\Delta S^{\ddagger}$ 24 e.u.

b. 84 per cent MeCN.

0.3	3.66	1.98	0.47-0.36	1.51	0.179
5.4	3.59	4.1	1.0-0.7	3.1	0.491
10.3	3.53	8.4	2.0-1.3	6.4	0.806
15.2	3.47	15.5	3.3-2.0	12.2	1.086
20.2[d]	3.41[d]	-	5.7-4.1[d]	27.2[d]	1.435[d]
25.1	3.35	57	11 - 10	46	1.663
30.8	3.29	119	17	102	2.009

d. Extrapolated from Table 6.8., assuming first order dependence on toluene concentration.

Hence E_a = 23 k.cal.mol^{-1}. $\Delta H^{\ddagger}$ = 22 k.cal.$mole^{-1}$. $\Delta G^{\ddagger}$ = 19 k.cal.$mole^{-1}$. $\Delta S^{\ddagger}$ = 9 e.u.

likely to be rather approximate,[146,234] although the direction of their change with variation in solvent composition should be genuine.

The measured parameters do not differ markedly from those for other oxidations by cobaltic perchlorate, shown in Table 6.12, but it is difficult to make any critical comparison since the conditions used vary widely. The characteristic positive entropy of activation indicates some degree of solvent release around the ion in the formation of the dipolar transition state. The few activation measurements which have been reported for the oxidation of hydrocarbons by other metal ion oxidants are shown in Table 6.13.

The increase in the rate of oxidation of toluene with increasing methyl cyanide concentration is shown by Table 6.11 to be caused by a decrease in the activation energy, which outweighs the effect of the concomitant decrease in activation entropy. The marked rate increase above about 60 per cent methyl cyanide coincides with the marked spectral changes at similar cosolvent concentrations. (Chapter 5). Hence, it is possible that complexing of the cobaltic ions by methyl cyanide is producing cobaltic species which are more efficient oxidants, either by virtue of an increased redox potential, or by the methyl cyanide ligand providing an electron bridge into the central cation. Methyl cyanide is a weaker complexing agent than is water[117] and so the redox potential of a cobaltic-methyl cyanide complex might be higher than that of the wholly aquated complex. This suggestion has been used to interpret polarographic measurements[117,147] of the reduction

TABLE 6.12. ACTIVATION PARAMETERS FOR OXIDATIONS BY COBALTIC PERCHLORATE.

Substrate.	E_a k.cal.mole^{-1}	$\Delta S^{\neq}$ e.u.	Conditions.
Cyclohexanol	31.5	+43	$[HClO_4]$ 1.57M. in water.[10]
Diethylcarbinol	29.8	+38	$[HClO_4]$ 1.57M. 1.6% MeCN.[10]
Isopropanol	29.6	+35	$[HClO_4]$ 1.57M. in water.[10]
t-Butanol	32.1	+39	" " " "
p-Nitrobenzaldehyde	20.7	+13	$[HClO_4]$ 1.65M. 45% MeCN.[31]
m-Nitrobenzaldehyde	21.3	+14	" " " "
HCHO	22		$[HClO_4]$ 1M. $[ClO_4^-]$ 6M. in water.[29]
HCOOH	21.7		$[HClO_4]$ 1M. $[ClO_4^-]$ 4M. in water.[16]
EtCOOH	26.7	+21	$[HClO_4]$ 1.1M. $[NaClO_4]$ 2.04M. in water.[14]
Pr^iCOOH	22.6	+16	" " " "
Bu^tCOOH	18.7	+4	" " " "
$PhCH_2COOH$	21.4	+13	" " " "
Benzene	23		For acid dependent path.[16,17]
	40		For acid independent path.
$CH_3CH{=}CHCOOH$	24	+7	$[HClO_4]$ 1M. in water.[35]

TABLE 6.13. ACTIVATION PARAMETERS FOR OXIDATIONS OF AROMATIC HYDROCARBONS.

Reaction.	E_a k.cal.mole.$^{-1}$	$\Delta S^{\neq}$ e.u.	Conditions.
PhMe + $KMnO_4$	12.6	-23	50% acetic acid.[89]
p-xylene + Mn^{III} sulphate	31		in water.[62]
p-xylene + Ce^{IV} sulphate	24		5% H_2SO_4.[70]
Naphthalene + Ce^{IV} sulphate	14		Aqueous acetic acid-H_2SO_4.[71]
Ph_2CH_2 + Chromic acid	15.2	-21	95% acetic acid. 0.3M.$HClO_4$.[80]

of metal ions in methyl cyanide solutions. These reductions occur at more positive potentials in methyl cyanide than in water indicating that the ions are easier to reduce. However, the reductions also occur more quickly in methyl cyanide than in water[147] (i.e. the waves are more reversible), and so presumably the greater polarisibility of the methyl cyanide ligand is also influencing the reduction. More recent work[148,149] has shown that metal ions in benzyl cyanide solution are reduced at more positive potentials than in methyl cyanide, despite the better complexing properties of benzyl cyanide.[115] This indicates that the nitrile bridging is an important factor, since benzyl cyanide would be a better electron bridge than methyl cyanide. The conduction of an electron through a polarisable ligand to reduce the central cobaltic cation has been well authenticated by Taube.[50] Other metal ions are known to be more efficient oxidants and radical traps in methyl cyanide solution.[114,150] The large increase in the oxidation rate of toluene with increase in ionic strength, (compare Tables 6.2 and 6.7), could derive from the same cause as the spectral changes observed with variation in ionic strength. (p. 26).

The above considerations apply only to oxidation by an outer-sphere mechanism. The rates of oxidation of carboxylic acids, which are oxidised by an inner sphere mechanism,[14] have also been shown to increase with increasing methyl cyanide concentration (from 0 to 30 per cent). The change in solvent affected the rate of breakdown of the intermediate complex far more that the equilibrium constant for its formation. The cause of this is

not known. However, at higher methyl cyanide concentrations, when the methyl cyanide complexes the cobaltic ions, the complexed species could be substitutionally labile, similar to the $\left[Co.OH(OH_2)_5\right]^{2+}$ species, since methyl cyanide is known to be a π-bonding ligand in metal ion complexes.[123,178] Hence oxidation by an inner sphere mechanism may also show the marked rate increase with methyl cyanide concentration which was found experimentally. (Table 6.8).

2. The Oxidation of Substituted Toluenes.

The investigation of substituent effects on the oxidation of toluene is restricted to substituents which are not oxidised preferentially to the methyl group, and which do not complex the cobaltic ions.

a. The Oxidation of p-Nitrotoluene.

p-Nitrotoluene is oxidised only very slowly by cobaltic perchlorate. However, samples purified in several ways (Chapter 11) reacted at the same rate, showing that the oxidant was not being consumed by impurities. The plots of $-\log_{10}(D-D_{\infty})$ versus time are reasonably linear over two half lives (Figure 6.14.), and deviate much less from first order than the equivalent plots for toluene, although they tend to tail off slightly rather than speed up. Table 6.15, shows that the derived second order rate constants decrease sharply with increasing substrate concentration. However, in this case the decrease is less likely to be caused by changing amounts of secondary oxidation since the individual rate plots revealed no such effect. No rate

FIG. 6.14. REPRESENTATIVE PLOTS FOR THE OXIDATION OF p-NITROTOLUENE.

Conditions as Table 6.15.

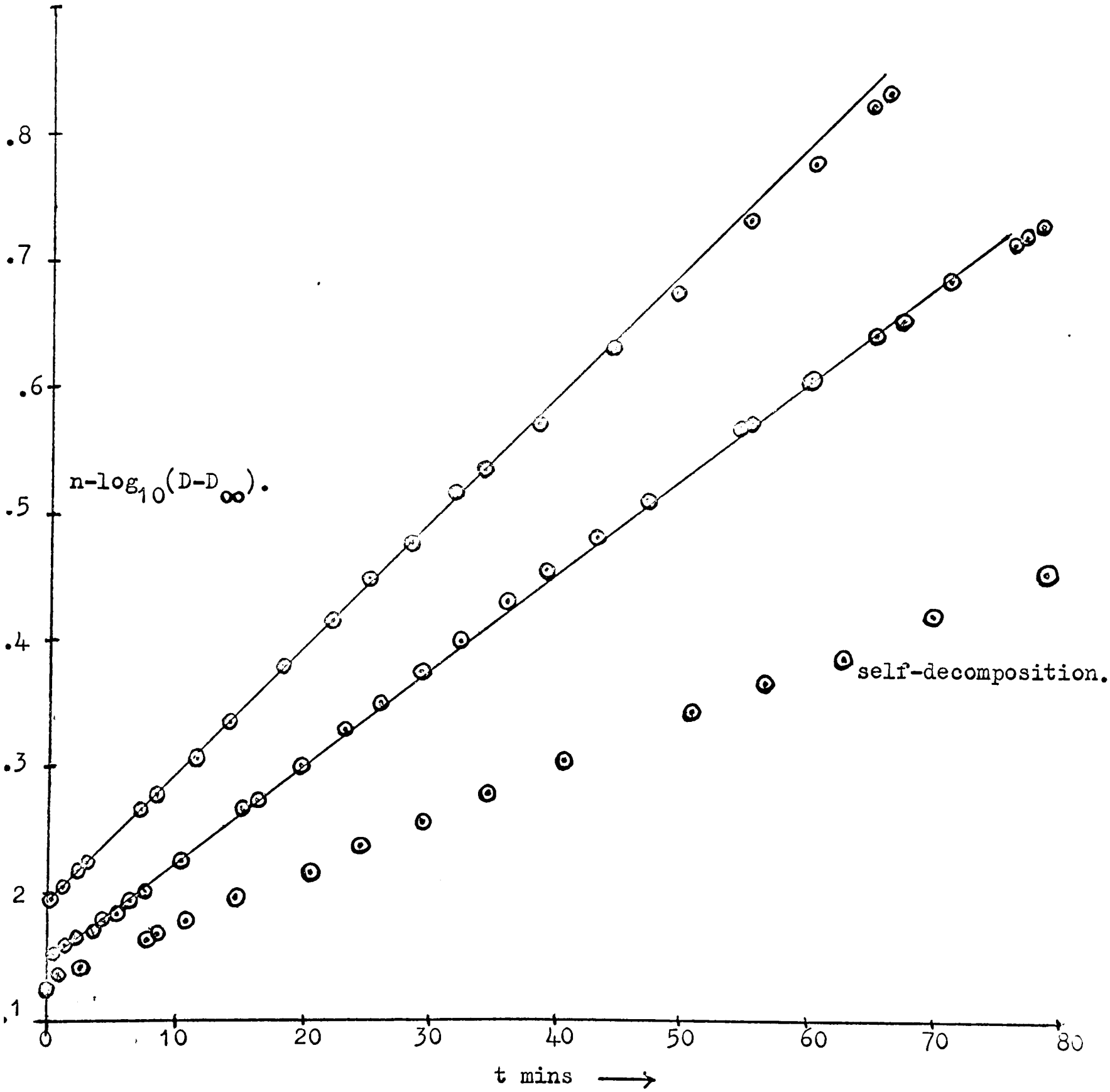


TABLE 6.15. OXIDATION OF p-NITROTOLUENE.

15.° 70 per cent MeCN (v/v). $[HClO_4]$ 0.77M. μ ca. 0.9M. Initial $[Co^{III}]$ ca. 2×10^{-2}M. Initial $[Co^{II}]$ ca. 6×10^{-3}M.

$10^2[p\text{-}NO_2PhMe]$M.	$10^4 k'$ sec^{-1}.[a]	$10^3 k_2$ l.m^{-1}. sec^{-1}.[b]	$10^4 k'_{corr}/[pNO_2PhMe]^{1/2}$ l.$^{-1/2}$mole$^{1/2}$. sec^{-1}.[b]
0.0	[1.8 - 1.5][c]	-	
0.0	1.6 - 1.5	-	
0.0	1.6 - 1.4	-	
3.8	2.5	1.8	3.5
4.4	2.5	1.6	3.0
4.6	2.5	1.5	3.1
6.8	2.7	1.3	3.4
10.6	3.0	1.1	3.5
12.2	2.9	0.90	3.1
12.6	3.1	1.0	3.5
18.0	3.1	0.72	3.0
21	2.9	0.52	2.4
24	3.1	0.54	2.6
30	3.4	0.53	2.9
31	3.5	0.55	3.1
39	3.8	0.51	3.2
43	3.7	0.44	2.9
48	3.8	0.42	2.9

a. Measured graphically over two half lives.

b. Calculated from previous column taking k' self-decomposition = 1.8×10^{-4} sec^{-1}.

c. Measured graphically.

constants are available for the oxidations of p-nitrobenzyl alcohol or p-nitrobenzaldehyde under the conditions used, but p-nitrobenzaldehyde is known to be oxidised about ten times faster than benzaldehyde[31] in 45 per cent methyl cyanide. Extrapolation of the data available leads to a second order rate constant of about 2 $l.m.^{-1}$ $sec.^{-1}$ for the oxidation of p-nitrobenzaldehyde under the conditions of Table 6.15. Since the oxidation of p-nitrobenzyl alcohol is likely to be very fast, the application of equation 6.xv. to the data in Table 6.15. indicates that a stationary state concentration of the p-nitrobenzaldehyde should be attained before, at the very maximum, 10 per cent of the oxidant has been consumed. p-Nitrobenzoic acid should hence be the major product and the mean stoichiometry should approach 6. This assumes that oxidation of the side chain is the major route.

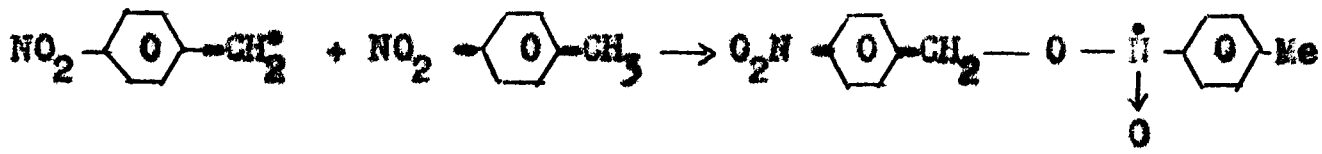
No quantitative measurements of reaction products were made, but qualitative analysis of the carbonyl products from a larger scale reaction, by conversion to their2,4-dinitrophenylhydrazones, (see Chapter 10), showed that only a minute amount of p-nitrobenzaldehyde was obtained, and no other carbonyl compound. Since the substrate is itself faintly yellow, it was difficult to tell if yellow products, analogous to those obtained from toluene under these conditions were being formed. However, the oxidised solution obtained was no different in colour from a control solution containing cobaltous perchlorate and the substrate.

There are several possible explanations specific to p-nitrotoluene

of the marked decrease in second order rate constant with substrate concentration shown in Table 6.15.:

a. The nitrotoluene may complex cobaltic ions through the nitro group, forming an inert adduct. Increasing the substrate concentration would deactivate a greater proportion of the oxidant, thus decreasing the apparent second order rate constant for oxidation. However, nitro aromatic compounds are not known to form stable complexes of this type, although they have been postulated[151] to explain the lower activity in nitrobenzene, than in benzene, of cobaltous stearate as an autoxidation catalyst.

b. Benzyl radicals are known to add to nitro-groups of aromatic compounds.[152] Hence the reaction:



(6.xxviii).

could compete with further oxidation of the nitrobenzyl radical. If this adduct were only slowly oxidised by cobaltic ions, the second order rate constant would decrease with increasing substrate concentration. However, it is doubtful whether the adduct would be resistant to oxidation.

c. The rate of oxidation of free radicals by cupric ions is known to be reduced markedly by electron withdrawing substituents in the radical.[153] If the oxidation of free radicals by cobaltic ions is similarly influenced, the p-nitrobenzyl radicals might dimerise rather than be oxidised further.

Increase in the substrate concentration, and hence the rate of production of benzyl radicals would influence the dimerisation, which depends on the square of the radical concentration, much more than it influences the rate of the competing further oxidation. Hence the apparent second order rate constants would decrease with substrate concentration. However, if this mechanism were operative, the individual rate plots should tail off sharply towards second order, and it is doubtful whether such a strong oxidant as cobaltic perchlorate would be greatly affected by the presence of the p-nitro group in the radical.

The decrease in the second order rate constants shown in Table 6.15. is so marked that the pseudo first order rate constants show a linear dependence on the square root of the substrate concentration. (Figure 6.16.) This could be explained by the substrate existing in the form of inert dimers in solution. A half order dependence on substrate concentration has been reported[25] for the oxidation of anthracene by cobaltic acetate. However, p-nitrotoluene is not known to form stable dimers in acid solution.

A similar inhibitory effect has been observed for the cobaltous stearate catalysed autoxidation of nitro-arylcarboxylic acids.[154]

FIG. 6.16 OXIDATION OF p-NITROTOLUENE.

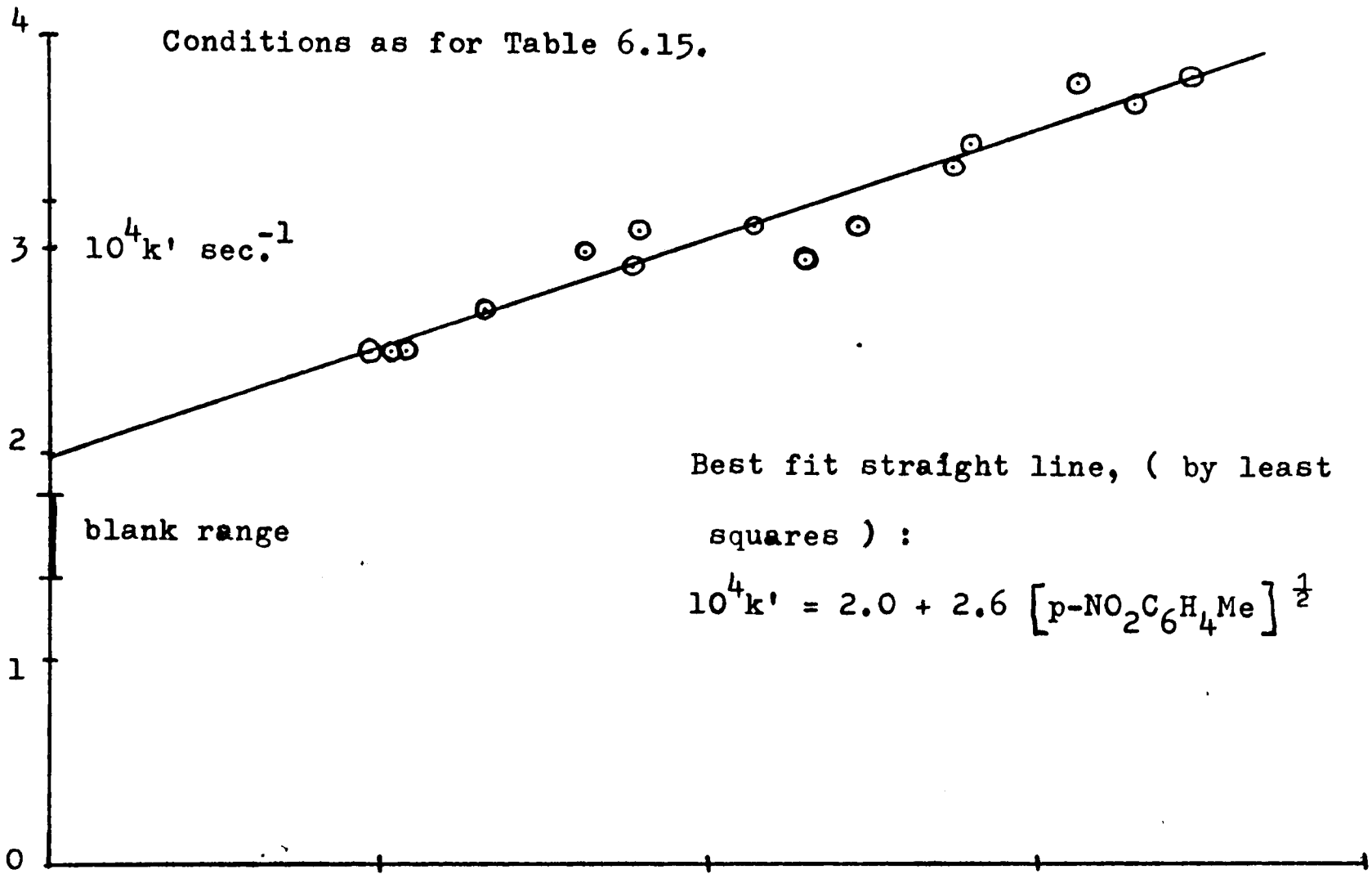


TABLE 6.17. OXIDATION OF p-t-BUTYLTOLUENE.

20°. $[HClO_4]$1.00M. 50% MeCN(v/v). μ ca.1.04M. Initial $[Co^{III}]$ca. 5×10^{-3}M. Initial $[Co^{II}]$ ca. 2×10^{-3}M.

10^2 $[p\text{-}Bu^tC_6H_4Me]$M.	10^4 initial k'sec.$^{-1}$ [a]	10^2 k_2 l.m.$^{-1}$ sec.$^{-1}$ [b]
0.0	1.9 - 1.6	-
1.04	5.5	3.5 - 3.8
1.39	6.9	3.6 - 3.8
1.73	8.1	3.6 - 3.8

a. Measured graphically.

b. Calculated from previous column taking initial and final self-decomp. rates.

Best fit straight line, (by least squares): $10^4k' = 1.6 + 380 \left[p\text{-}Bu^tC_6H_4Me\right]$

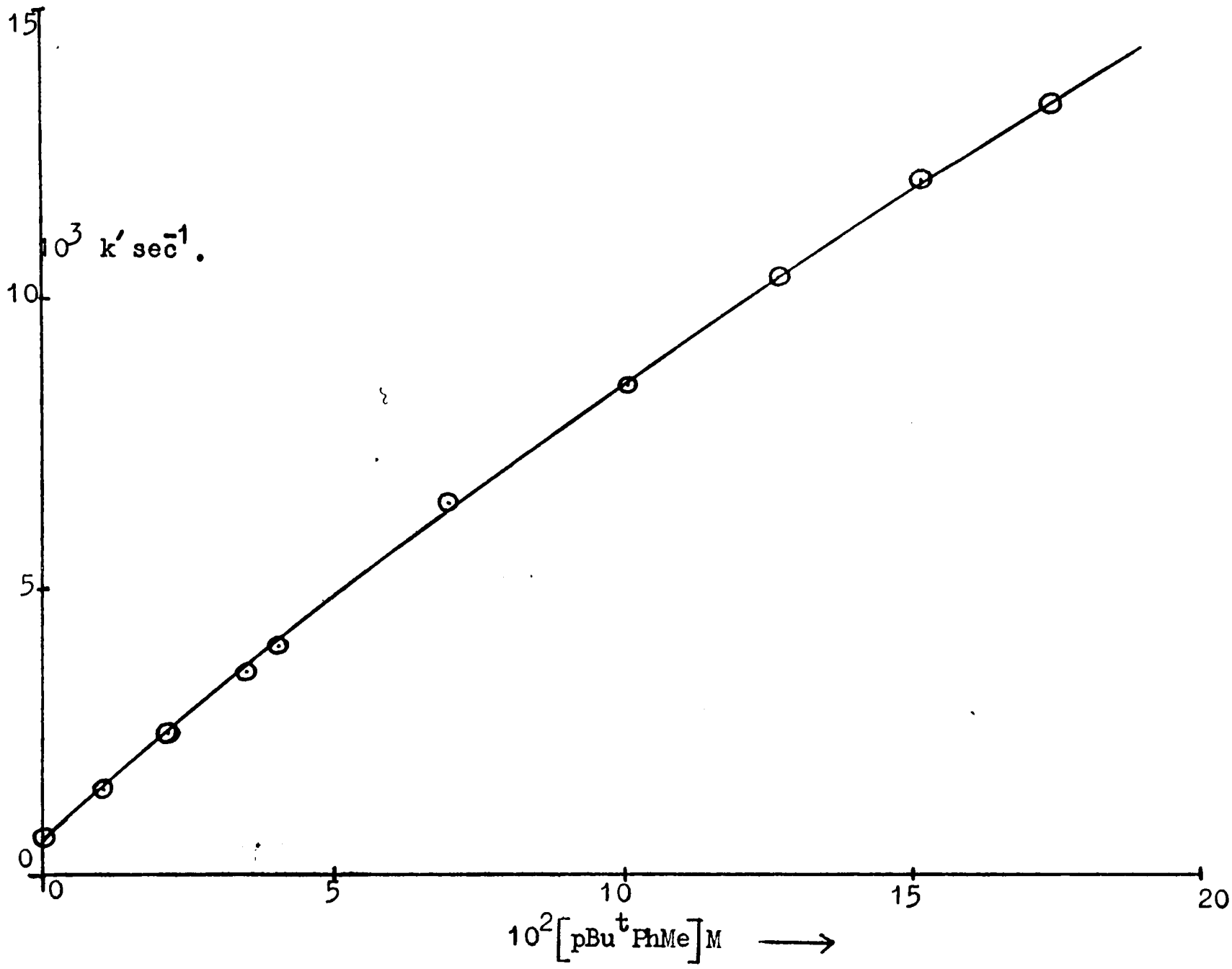
b. The Oxidation of p-t-Butyltoluene.

Plots of $-\log_{10}(D-D_{\infty})$ versus time for the oxidation of this compound in 50 per cent methyl cyanide solution are similar to those for the oxidation of toluene. (Fig. 6.1). The derived second order rate constants, (Table 6.17), are constant over the limited concentration range possible, but this range is too small to show whether there is any change of behaviour from that observed with toluene. The oxidation is much faster than that of toluene, and this acceleration by electron donating substituents and retardation by electron attracting substituents agrees with the substituent effects found for the oxidation of toluene, and other aromatic hydrocarbons, by other transition metal ions. (Chapter 3).

In 84 per cent methyl cyanide solution the reaction is accurately of the first order with respect to oxidant over two half-lives, but the second order rate constants still fall off slightly with increasing substrate concentration. (Table 6.18).

Only one carbonyl product was isolated from the reaction as its DNP. This was recrystallised from chloroform, yielding red crystals m.p. 251° - 252°. Its mass spectrum showed a molecular ion[155] at mass number 342, confirming that it was p-t-butylbenzaldehyde. (Lit. m.p. 250°-251°). The relatively large quantities of this compound obtained indicate that it is the major oxidation product. No peak corresponding to the alternative p-tolyl methyl ketone DNP was observed in the mass spectrum of either the

TABLE 6.18. OXIDATION OF p-t-BUTYLTOLUENE.



20.2° $[HClO_4]$ 1.00M. 85 per cent MeCN (v/v) μ ca. 1.05M. Initial $[Co^{III}]$ ca. 5×10^{-3}M. Initial $[Co^{II}]$ ca. 2×10^{-3}M.

10^2[p-Bu^{t}PhMe]M	10^3 k' sec^{-1} [a]	$10^2 k_2$ $l.m^{-1}.sec^{-1}$. [b]
0.0	[.55 - 59] [c]	-
1.04	1.48	8.6
2.08	2.40	8.7
3.5	3.5	8.3
4.0	4.0	8.5
7.0	6.5	8.4
10.1	8.6	7.9
12.7	10.4	7.7
15.1	12.0	7.5
17.3	13.6	7.5

a. Measured graphically over two half lives.
b. Calculated from previous column taking k' self-decomp. = 5.9×10^{-4} sec^{-1}.
c. Measured graphically.

p-t-butylbenzaldehyde DNP or of the 'acetone' band on the chromatoplate (Chapter 10). This lack of attack on the t-butyl group agrees with its inertness towards oxidation by other metal ions. (Chapter 3).

3. The Oxidation of Homologues of Toluene.

a. The Oxidations of Ethyl Benzene and Diphenylmethane.

Both these oxidations in 70 per cent methyl cyanide solution are first order with respect to cobaltic ions over two half-lives, and are substantially of the first order with respect to hydrocarbon (Table 6.19). Neither reaction is influenced by added oxygen or by leaving it in the light beam of the spectrophotometer. The oxidised solutions from both substrates exhibit the yellow tint formed by the oxidation of toluene under these conditions. A similar colour develops when solid diphenylmethane is left in daylight for several months.

p,p'-dinitrodiphenylmethane was too insoluble for its oxidation to be investigated.

b. The Oxidation of Bibenzyl.

The plots of $-\log_{10}(D-D_{\infty})$ versus time for this oxidation were similar to those for the oxidation of toluene. (fig. 6.1.). The initial rates varied linearly with substrate concentration. (Table 6.20), but as in the case of p-t-butyl toluene, where similar behaviour was observed (Table 6.17), the possible range of substrate concentration was too small to show that there is any real change in behaviour from toluene.

FIG. 6.11. INFLUENCE OF TEMPERATURE ON RATE OF OXIDATION OF TOLUENE.
Conditions as Table 6.11.

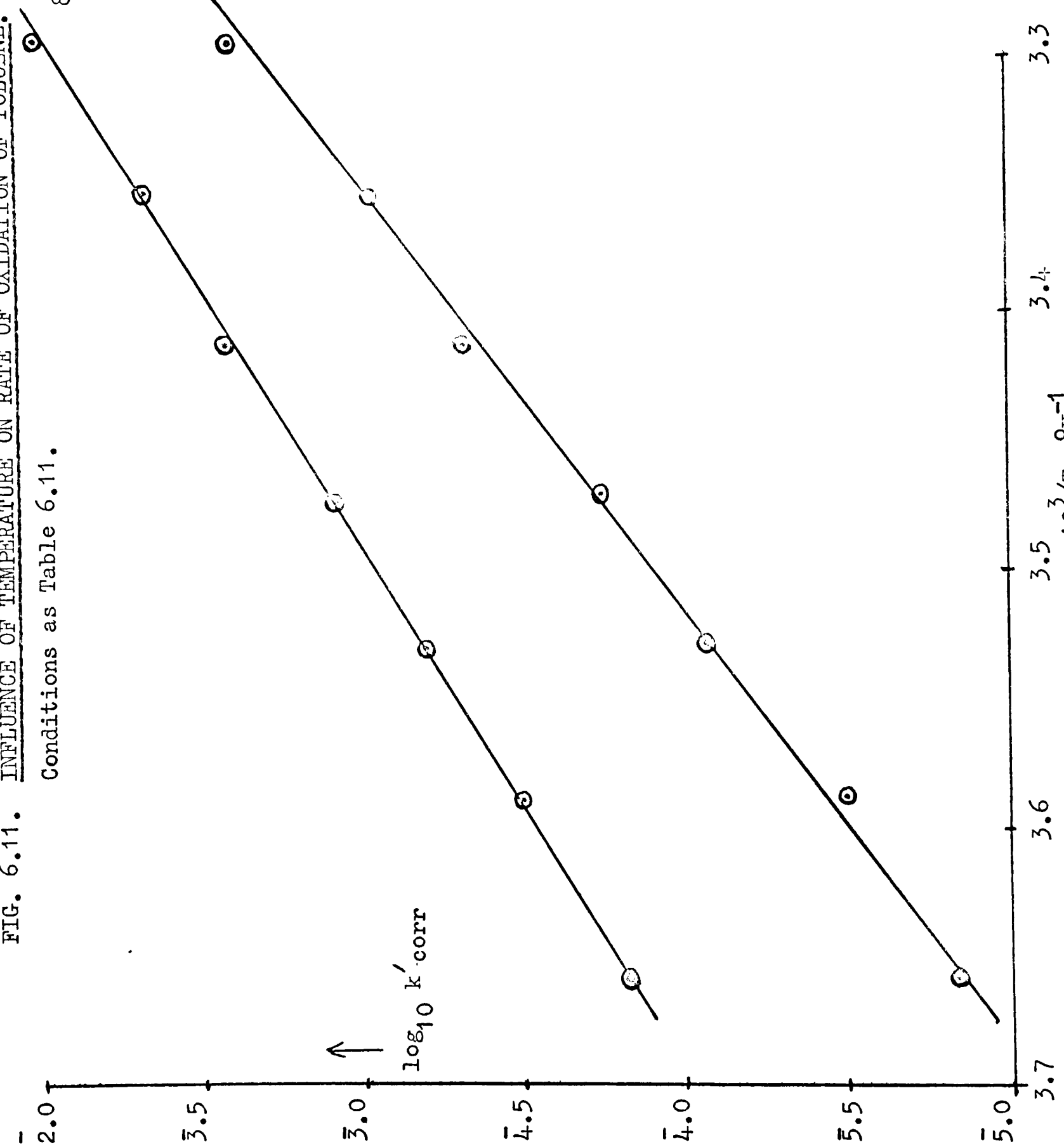


TABLE 6.19 THE OXIDATIONS OF ETHYL BENZENE AND DIPHENYLMETHANE.

Conditions as for Table 6.15.

$10^2[PhEt]$ M	10^4 k′ sec.$^{-1}$ [a]	$10^3 k_2$ l.m.$^{-1}$ sec.$^{-1}$ [b]	$10^2[Ph_2CH_2]$ M	10^4 k′ sec.$^{-1}$ [a]	$10^3 k_2$ l.m.$^{-1}$ sec.$^{-1}$ [b]
0.0	[1.68-1.34] [c]	-	0.0	[1.96-1.41] [c]	-
0.0	[2.05-1.46]	-	0.0	[1.75-1.63]	-
0.0	[1.45-1.34]	-	0.0	[2.14-1.82]	-
0.0	[1.45-1.32]	-	0.0	[2.04-1.83]	-
2.5	2.53	1.9-4.8	3.9	4.4	5.9-7.7
2.9	2.66	2.1-4.5	4.8	4.6	5.2-6.7
3.1	2.56	1.6-3.9	6.8	5.4	4.9-5.9
3.5	3.0	2.7-4.9	7.1	6.9	6.8-7.7
6.2	3.0	1.5-2.7	7.6	7.4	7.0-7.9
8.5	3.8	2.0-2.9	8.0	6.7	5.7-6.6
9.1	4.1	2.2-3.1	9.1	7.5	5.9-6.7
12.7	5.4	2.6-3.2	9.9	7.7	5.7-6.4
17.5	5.9	2.2-2.6	12.1	9.2	5.9-6.4
17.9	6.2	2.3-2.7	12.1	9.9	6.4-7.0
18.6	6.3	2.3-2.7	13.0	10.4	6.4-6.9
22.3	7.4	2.4-2.7	13.1	10.5	6.4-6.9
24.3	7.8	2.3-2.7	13.6	9.9	5.7-6.2
26.6	9.1	2.6-2.9	13.6	10.7	6.3-6.8
31.0	10.2	2.6-2.9	15.5	12.6	6.8-7.2
31.9	10.2	2.5-2.8	15.7	12.1	6.4-6.8
41.4	11.9	2.4-2.6	15.9	11.7	6.0-6.5
43.4	11.4	2.1-2.3	16.1	11.2	5.7-6.1
45.9	12.6	2.3-2.5	17.4	12.7	6.1-6.5
			17.6	13.1	6.2-6.6
			19.1	14.0	6.2-6.6

a. Measured graphically over two half lives.

b. Calculated from previous column taking initial and final self-decomp. rates.

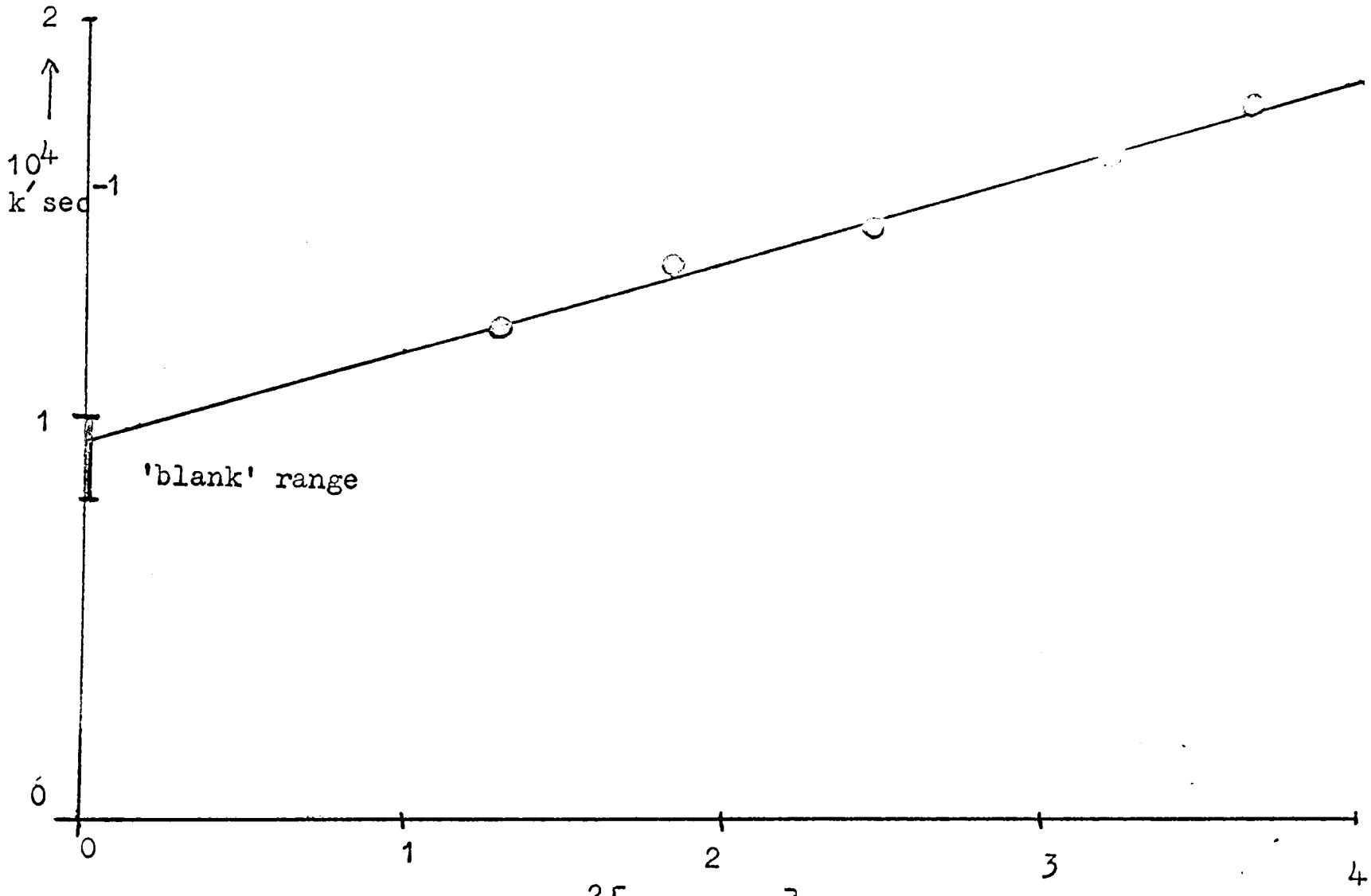
c. Measured graphically.

Best fit straight lines (by least squares): for ethyl benzene $10^4 k' = 2.0 + 24[PhEt]$

for diphenyl methane $10^4 k' = 1.8 + 64[Ph_2CH_2]$

TABLE 6.20 OXIDATION OF BIBENZYL.

~~Conditions as for Table 6.20.~~



15° $[HClO_4]$ 1.00M. μ ca. 1.02. 60 per cent MeCN. Initial $[Co^{III}]$ ca. 2×10^{-3}M. Initial $[Co^{II}]$ ca. 6×10^{-4}M.

10^2 [$Ph_2(CH_2)_2$] M	10^4 Initial k′ sec^{-1}. [a]	10^3 k_2 l.m^{-1} sec^{-1}. [b]
0.0	.79-1.0	-
1.28	1.23	1.8-3.4
1.82	1.38	2.1-3.2
2.46	1.49	2.0-2.8
3.19	1.66	2.1-2.7
3.65	1.79	2.2-2.7

a,b. As for Table 6.17.

Best fit straight line (by least squares) $10^4k' = 0.94 + 23[PhCH_2CH_2Ph]$

The oxidation rate is similar to that for toluene under similar conditions. No yellow products were formed only when high concentrations of oxidant and methyl cyanide were used.

c. Oxidation Products from Ethyl Benzene, Diphenylmethane and Bibenzyl.

The carbonyl products from the oxidation of all three compounds, were qualitatively analysed as their 2,4-dinitrophenyl hydrazones. (Chapter 10).

Diphenylmethane yields benzophenone and a trace of benzaldehyde. A check oxidation of benzylhydrol, which oxidises more quickly than diphenylmethane, but much more slowly than benzyl alcohol, yielded only benzophenone. Benzophenone is oxidised only very slowly by cobaltic perchlorate, and the oxidation of neither benzophenone nor benzhydrol forms yellow products. The oxidation of bibenzyl yields almost exclusively benzaldehyde, and only a small amount of benzyl phenyl ketone.

The products from the oxidation of ethyl benzene could not be investigated this way since the 2,4-dinitrophenylhydrazones of benzaldehyde and acetophenone were inseparable on Kieselgel G with the eluting solvents employed. The carbonyl products were analysed directly by gas chromatography, which showed that much more acetophenone than benzaldehyde, and no phenylacetaldehyde, was obtained. The oxidation of α-phenylethanol has been shown to yield only acetophenone.[36]

Carbon-carbon fission has been observed previously in the oxidations of secondary and tertiary alcohols by cobaltic perchlorate.[9,10,32] In the

present case the C–C fission could occur in the initial attack on the hydrocarbon:

$$PhCH_2R + Co^{III}.OH_2 \longrightarrow PhCH_2^{\bullet} + ROH + Co^{II} \qquad (6.xxix)$$

This would compete with C–H fission:

$$PhCH_2R + Co^{III} \longrightarrow Ph\dot{C}HR + Co^{II} + H^+ \qquad (6.xxx).$$

Equation 6.xxix is analogous to that proposed for the oxidation of β-phenylethanol to benzaldehyde by vanadium (V).[168] Alternatively the C–C fission may occur through the oxidation of the $Ph\dot{C}HR$ radical:[153,169]

$$Ph\dot{C}HCH_2Ph + Co^{III} \longrightarrow PhCH{=}CHPh + Co^{II} + H^+ \qquad (6.xxxi).$$

$$Ph\dot{C}HCH_3 + Co^{III} \longrightarrow PhCH{=}CH_2 + Co^{II} + H^+ \qquad (6.xxxii).$$

followed by rapid oxidation of the olefin formed to benzaldehyde.[18]

Either route could account for the almost exclusive production of benzaldehyde from the oxidation of bibenzyl, and for the much smaller amount of C–C fission occurring with ethyl benzene. However, the second route is unlikely to be available for the oxidation of diphenylmethane.
N.B. Further work shows $PhCH(OH)CH_2Ph \rightarrow PhCHO$ only.

4. The Oxidation of Some Other Aromatic Hydrocarbons.

a. The Oxidation of Biphenyl.

The rates of oxidation of biphenyl were investigated under two sets of condition similar to those used for the oxidation of toluene and of aromatic ethers (Chapter 8). In each case the reaction was of the first order with respect to both oxidant and substrate. (Tables 6.21 and 6.22).

TABLE 6.21. OXIDATION OF BIPHENYL.

20° $[HClO_4]$ 1.00M. 50 per cent MeCN (v/v). μ ca. 1.05M. Initial $[Co^{III}]$ ca. 8×10^{-3}M. Initial $[Co^{II}]$ ca. 2×10^{-3}M.

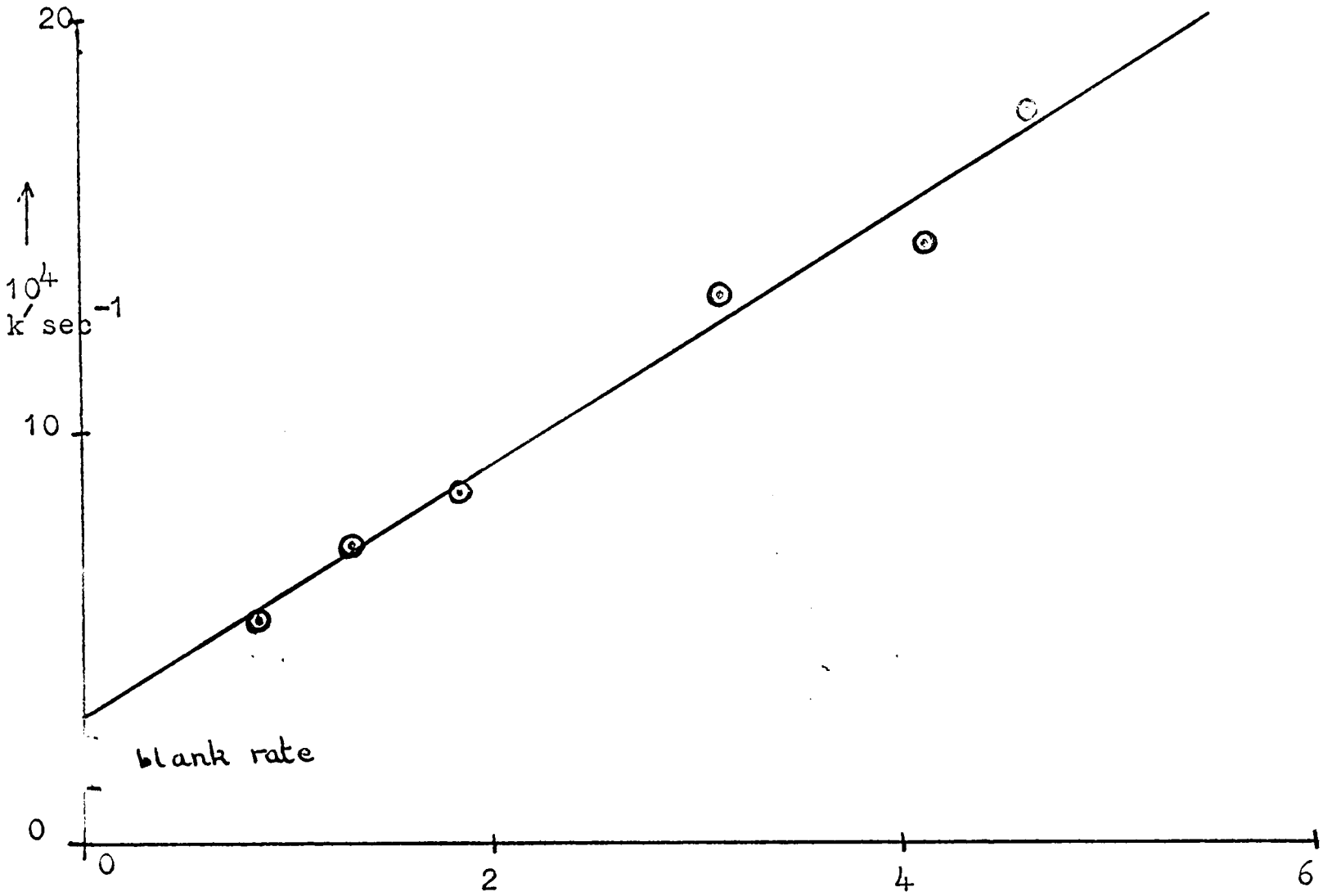
$10^2[Ph_2]$M.	10^3 k′sec^{-1} [a]	10^2 $k_2$1.m^{-1}.sec^{-1} [b]
0.0	0.15-0.13[c]	-
0.98	1.07	9.4-9.6
1.64	1.55	8.5-8.7
2.45	2.4	9.2-9.3

a,b,c. As for Table 6.19.

Best fit straight line $10^3k' = 0.14 + 91[Ph_2]$

TABLE 6.22. OXIDATION OF BIPHENYL.

Conditions as for Table 6.20.



$10^2[Ph_2]M \longrightarrow$ a

$10^2[Ph_2]M$.	$10^4 k' sec^{-1}$.	$10^2 k_2 l.m^{-1}.sec^{-1}$. [b]
0.0	2.5-1.4[c]	-
0.82	5.5	3.7
1.3	7.3	3.7
1.8	8.6	3.4
3.1	13.4	3.5
4.1	14.7	3.0
4.6	17.8	3.6

a,c. As for Table 6.19.

b. Calculated from previous column, taking k′self-decomposition = $2.5 \times 10^{-4} sec^{-1}$.
Best fit straight line $10^4 k' = 3.2 + 307[Ph_2]$

Bright yellow oxidised solutions were obtained. The yellow product was extracted into dichloromethane, and the absorption spectra of the extracts showed a peak at 370 mμ and a smaller one at 325 mμ. These appeared to correspond to the yellow product since they were least intense when the colour was least intense, i.e. in the extracts from those runs at the lowest substrate concentrations. In comparison, benzoquinone solution showed a broad band at 440 mu; while 3-3',5-5' - tetramethyldiphenoquinone, (which should have an absorption spectrum similar to that of diphenoquinone), showed a strong band at 422mu with a shoulder at about 398 mμ.

The infra-red spectrum of the extract showed no absorptions not shown either by the extract from a blank solution containing no substrate, or else by biphenyl,(which shows a large absorption which would obscure any quinone bands.[157])

A check oxidation of p,p'- dihydroxybiphenyl was very fast, forming a brown precipitate.[158] The resulting solution was only a very pale yellow, and its extract in dichloromethane showed no peaks above 300mμ. Hence it appears unlikely that the oxidation product from biphenyl is diphenoquinone, or that p,p'- dihydroxybiphenyl is an intermediate. However, it was not attempted to make any complete product study for this oxidation.

b. <u>The Oxidations of Naphthalene, Anthracene and Phenanthrene.</u>

All three compounds were oxidised too rapidly to be measured under conditions similar to those employed for the oxidation of toluene.

(Table 6.2.) Naphthalene was oxidised more slowly than phenanthrehe and anthracene, and the overall second order rate constant for its oxidation was about 50 $l.m.^{-1}sec.^{-1}$ Naphthalene and phenanthrene gave bright yellow, and anthracene, orange, products which may have been quinones, and the oxidation of naphthalene also yielded a buff coloured precipitate. These hydrocarbons are oxidised to quinones by other metal ion oxidants, (Chapter 3), although ring fission, leading to the production of dibasic acids, also occurs. Since the kinetics were immeasurable in the present case, no product studies were attempted.

5. Further Discussion.

The rates of oxidation of the aromatic hydrocarbons described in this chapter are in general essentially of the first order with respect to both substrate and oxidant. This is in agreement with previously investigated oxidations by cobaltic perchlorate. (Chapter 2). In many cases there are complications due to variation in the extent of secondary oxidation, which amounts essentially to changes in stoichiometry throughout the reaction. Where this causes the plots of $-\log_{10}(D-D_\infty)$ versus time to curve upwards to varying extents, then the derived second order rate constants usually correspondingly decrease with increasing substrate concentration. Where there is no deviation from a first order dependence on oxidant, then the second order rate constants are generally much less dependent on substrate concentration. However, comparison with the kinetic results from the oxidations of benzyl ethers, (Chapter 8), shows that there is little general correlation between the amount of

variation of secondary oxidation, and the extent of the deviation from a first order dependence on oxidant and/or substrate.

The oxidation of p-nitrotoluene is exceptional. Although it is first order with respect to oxidant and shows no signs of acceleration due to secondary oxidation, yet it shows the greatest deviation from a first order dependence on the substrate found for any reaction investigated. The possible causes of this deviation have been discussed on p. 72.

The inverse dependence of the rate of oxidation on the acidity of the medium, Table 6.7, has been interpreted in terms of the enhanced activity of the $\left[Co.OH(OH_2)_5\right]^{2+}$ species, while the increased oxidation rate in high methyl cyanide concentrations (Table 6.8) appears to be due to the enhanced activity of a cobaltic-methyl cyanide complex.

The oxidation of the toluenes, diphenyl methane, ethyl benzene and bibenzyl could occur by attack either involving the ring, or directly on the side chain. The oxidations of biphenyl and naphthalene, and the previously reported oxidation of benzene itself,[26,27] show that direct attack on the ring is a possible route. Unfortunately, no rate measurements for the oxidation of benzene have been given,[26,27] and so no direct comparison with the present measurements can be made. In order to test whether cobaltic perchlorate can react directly with an aliphatic side chain, the oxidation of cyclohexane was investigated.

The Oxidation of Cyclohexane.

Plots of $-\log_{10}(D-D_{\infty})$ for the oxidation of cyclohexane in 50 per cent methyl cyanide were similar to those for the oxidation of toluene. (Fig.6.1.) The variation of initial pseudo first order rate constant with substrate concentration is shown in Table 6.23. Only a very limited concentration range is possible since cyclohexane is much less soluble than toluene.

The overall rate of oxidation is rather higher than that for toluene at the same substrate concentration. However, product measurements by gas chromatography, (Table 6.24), show that the amounts of cyclohexanone and cyclohexanol produced account for only about a quarter of the oxidant consumed by the cyclohexane. This indicates that there is further oxidation of the cyclohexanone leading to ring fission products. (Compare ref.20.) Any adipic acid formed would not elute from the g.l.c. column employed. The stoichiometry of this reaction is hence much higher than that for the oxidation of toluene. Taking into account also the statistical factor that cyclohexane has 6 methylene groups while toluene has one methyl group, this indicates that the aliphatic chain in cyclohexane is attacked much more slowly by cobaltic perchlorate than is the methyl group of toluene. This agrees with the observed lack of attack on the t-butyl group of p-t-butyltoluene, and the β-methyl group of ethyl benzene.

It is hence unlikely that attack occurs directly on the aliphatic

TABLE 6.23 OXIDATION OF CYCLOHEXANE.

20^{o}. $[HClO_4]$ 1.00M. 50 per cent MeCN (v/v). μ ca. 1.05.

Initial $[Co^{III}]$ ca. 9×10^{-3}M. Initial $[Co^{II}]$ ca. 3×10^{-3}M.

$10^2[C_6H_{12}]$M.	10^4 initial $k'sec^{-1}$.[a]	$10^2 k_2$ $l.m^{-1}.sec^{-1}$.[b]
0.0	1.7-1.3	-
1.9	4.1	1.3
2.8	4.4	0.97
3.8	4.6	0.76

a. Measured graphically.

b. Calculated from previous column taking k' self- decomposition $1.7 \times 10^{-4} sec^{-1}$. Best fit straight line $10^4 k' = 3.6 + 26[C_6H_{12}]$

TABLE 6.24. OXIDATION PRODUCTS FROM CYCLOHEXANE.

Reaction performed at 20^{o} in total of 7.4 ml. solution containing 50 per cent MeCN (v/v).

$[HClO_4]$ 1.00M. $[C_6H_{12}]$ 2.8×10^{-2}M. 6.7×10^{-5} moles Co^{III} added.

	10^6 moles product[a] obtained	10^6 moles Co^{III} accounted for as: measured[b] products	self-decomp.	Total.
Cyclohexanone	2.0			
Cyclohexanol	0.29	8.6	1.8-2.4	10.4-11.0

a. No products of longer retention time were found.

b. Calculated as (2 cyclohexanol + 4 cyclohexanone).

side chain of the aralkyl hydrocarbons, unless the side chain is activated towards direct attack by the presence of the phenyl ring. This appears to occur in the oxidations of aralkyl hydrocarbons by chromic acid,[76,80] where there is thought to be direct attack on the C —— H bond α to the aromatic ring. (Chapter 3).

It is difficult to make any accurate assignment of relative reactivities towards cobaltic perchlorate of the various substrates studied, since an accurate knowledge of the stoichiometry is lacking for most of the reactions. However, the following general sequence can be derived:

$p\text{-}NO_2C_6H_4Me < PhCH_2CH_2Ph \sim PhMe \sim PhEt < Ph_2CH_2 < p\text{-}Bu^tC_6H_4Me$
$< PhPh <$ naphthalene $<$ anthracene, phenanthrene.

It must be noted that if p-nitrotoluene is acting as an inhibitor towards its own oxidation, (see p. 72), then extrapolation of the second order rate constant to zero substrate concentration may give a truer estimate of reactivity. This extrapolation would indicate that p-nitrotoluene is about as reactive as toluene.

The oxidations of aralkyl hydrocarbons by chromic acid have been compared previously [76,80] to attack by $Br^{\bullet}$ and $^{\bullet}CCl_3$ radicals, which show similar trends in reactivity. (Table 6.25). If oxidation by cobaltic perchlorate involves direct attack on the side chain by a route such as equation 6.xxiii., then the relative rates may parallel to some extent the relative rates of attack by hydroxyl radicals. Such data are not presently available, but comparable data which

TABLE 6.25. IONISATION POTENTIALS, STABILITY CONSTANTS FOR SILVER COMPLEXES, AND RELATIVE REACTIVITIES TOWARDS ATTACK BY FREE RADICALS, AND CHROMIC ACID, OF SOME HYDROCARBONS.

	Ionisation Potential. e.v.	K, M^{-1} for Ag^+ complex in aq. sol. at 25° μ=1.0 [159,161 / 162,163]	Relative rates of H atom abstraction by: $\cdot CCl_3$ [164,a]	Br· [164,165,a]	$Bu^t O\cdot$ [166,b]	Cl· [165,164,b]	Relative rates of oxidation by chromic acid [80]
Cyclohexane	9.1-9.9	-		.017	20	2.8	0.01
Benzene	9.24	2.41					
t-butylbenzene	8.68	2.3	0.24			0.22	
nitrobenzene	9.92	0.19					
Bibenzyl		8.0					
Toluene	8.82	2.95	1	1		1	0.16
Ethylbenzene	8.76		29 [d]	11 [c,d]	32	2.5	0.50
Diphenylmethane		3.46	29	7 [c]		2.0	1.0
Biphenyl	8.27	3.95					
Naphthalene	8.12	3.08					
Anthracene	7.2-7.8						
Phenanthrene	7.8-8.5	3.67					
Triphenylmethane			72	5.5		7.2	1.3

a. Per molecule.
b. Per C-H bond.
c. See also ref. 235.
d. See also ref. 236.

are available for some reactive radicals are given in Table 6.25. Attack by Br$^{\bullet}$, $\dot{C}Cl_3$ and BuO$^{\bullet}$, but not by Cl$^{\bullet}$, shows some similarity with the above sequence, especially since it has been shown[167] that Br$^{\bullet}$, and $\dot{C}Cl_3$ (and Cl$^{\bullet}$), attack toluenes and ethyl benzenes[236] substituted by electron donating groups faster than toluenes substituted by electron withdrawing groups. This implies that the dominant effect is availability of electronic charge on the α C-H group, rather than stabilisation of the radical produced.[233] However, a similar reactivity order would apply for removal of an electron from the benzene ring.

It has been suggested by Dewar[25] that the ease of oxidation, by cobaltic acetate, of a series of polycyclic aromatic hydrocarbons runs parallel to their ionisation potentials. This was thought to be evidence that oxidation occurs by direct electron transfer from a π-orbital of the organic substrate to the metal ion, since the measured ionisation potentials represent the energy required to abstract an electron from the highest filled π-orbital.[159] The ionisation potentials which are available for the substrates investigated are listed in Table 6.25. The decrease in these ionisation potentials approximately parallels the increasing reactivities of these substrates towards oxidation. Hence reaction could occur by abstraction of an electron from the ring.

The above parallelism does not rule out oxidation by an inner sphere mechanism. Aromatic hydrocarbons are known to form complexes with several metal ions in aqueous solution, but measurements of stability constants

have been made only for complexes with silver ions. These are given in Table 6.25. The stability constants show little relationship to either the ionisation potentials or the reactivity sequence given above. However, the stabilities of any transient cobaltic complexes need not necessarily vary in the same way as these of the silver complexes, and the stabilities of hydrocarbon complexes with other, non-transition metal, acceptors are known to parallel more closely the ionisation potentials of the hydrocarbons.[160]

It has been previously suggested, (p.54) that abstraction of an electron from a π-orbital may be concerted with formation of the benzyl radical. The evidence presented above appears to support, qualitatively, both attack on the side chain and attack on the ring. Hence, it is possible that both the ring and the side chain are involved simultaneously in the electron abstraction. This may take place from some more extended orbital involving both the ring and the α C-H bond (Compare ref. 10). The exact mechanism of electron transfer is unlikely to be the same when the conducting ligand is OH^- as when it is a nitrile group.[150] If the cobaltic-methyl cyanide complex performs its electron abstraction with less direct involvement of the side chain, then this may tend to form a transient radical cation which can be solvated in the ring by a water molecule. This would lead to the consumption of large amounts of oxidant to form quinonoid and possibly polymeric products. The oxidation of benzene also gives a yellow solution, indicating that similar products are also formed in this case. However, this should also apply to the oxidations of [redacted] p-t-butyl toluene,

which doesnot show any change of mechanism at high methyl cyanide concentrations.

The rate of oxidation of bibenzyl is anomalous. Whether attack occurs on the ring or on the side chain, then this substrate should react faster than toluene or ethyl benzene. Apart from the statistical factor, this oxidation is likely to have a rather higher stoichiometry than those of ethyl benzene and toluene, since it yields almost exclusively benzaldehyde, and very little benzyl phenyl ketone. The low rate of oxidation of bibenzyl is unlikely to be due to a steric effect since diphenyl methane is oxidised faster than either toluene or ethyl benzene. This is in contrast to the rates of oxidation of related alcohols, since benzhydrol is oxidised considerably more slowly than benzyl alcohol. Primary and secondary alcohols are thought to be oxidised by cobaltic perchlorate by an inner sphere mechanism.[9,10] The above reactivities of the alcohols indicates that steric effects may have a large influence on an inner sphere oxidation. This strongly suggests that the oxidations of the aromatic hydrocarbons are of an outer sphere type, since similar steric retardation is not observed. Cyclohexane is certainly oxidised by an outer sphere mechanism, which demonstrates that such a route is possible, even with a very unreactive substrate.

The oxidations of biphenyl, naphthalene, phenanthrene and anthracene,

which are very fast, almost certainly proceed by abstraction of an electron from a π orbital, to form a radical cation which can be hydrated and lead eventually to the formation of quinones, or polymers.[25] The alternative suggestion that there is fission of a C-H bond to give a σ radical has been made previously[26,27] for the oxidation of benzene. However this seems very unlikely since it is much easier to abstract an electron from a π orbital[159], and the incipient radical cation can be stabilised by solvation. Free aryl radicals are of much higher energy.

In conclusion, it is likely that several mechanisms are acting simultaneously in the oxidation of the aralkyl hydrocarbons. The foregoing arguments are necessarily speculative, and no definite decision can be made from the present evidence of whether oxidation is by an inner or outer sphere mechanism, although the latter is strongly favoured, or of whether attack is initially on the ring or on the side chain. Both the ring and the side chain appear to be involved simultaneously.

The results obtained from the oxidations of the hydrocarbons demonstrate that reaction mechanisms cannot be elucidated solely by the determination of the reaction kinetics. Accurate measurements of the reaction products are also necessary before the interpretation of the mechanism can be attempted.[3,195]

Chapter 7. THE INDUCED OXIDATION OF TOLUENE.

NOTE. The results given in this Chapter have recently been accepted for publication in J. Chem. Soc.

The oxidation of aliphatic acids by cobaltic perchlorate has been shown previously[14] to involve concerted fragmentation of a cobaltic-carboxylate complex, liberating a free alkyl radical and a carbon dioxide molecule.

$$R\text{-}COOH + \left[Co(OH_2)_6\right]^{3+} \rightleftharpoons \left[R\text{-}COO - Co(OH_2)_5\right]^{2+} + H_3O^+ \qquad (7.1.)$$

$$\left[R\text{-}C(=O)\text{—}O\text{-}Co(OH_2)_5\right]^{2+} \longrightarrow R^{\bullet} + CO_2 + Co^{II}_{aq} \qquad (7.11.)$$

Alkyl radicals can easily abstract a hydrogen atom from the side chain of a hydrocarbon such as toluene,[11,170] while the direct attack of cobaltic ions on aliphatic C-H bonds appears, from Chapter 6, to be a much slower process.

Previous exploratory measurements[34,171] showed that appreciable amounts of benzaldehyde were formed by the oxidation of mixtures of toluene and propionic, isobutyric, and pivalic acids, in aqueous methyl cyanide. However, the method employed for the measurement of these benzaldehyde yields, which involved separation of the 2,4 - dinitrophenyl-hydrazone by thin layer chromatography, was found to be unreliable during the course of the present work. This fact, together with the appreciable rate of direct oxidation of toluene, (Chapter 6), for which no correction was previously made, cast some doubt upon the earlier results. Benzaldehyde yields have now been measured much more extensively for these systems, (by Mr. D.J. Mills), by a more reliable modification of the former method, which was developed during the

present work, (Chapter 10). These measurements can be corrected for the benzaldehyde produced by the concurrent direct oxidation of toluene, as described in this Chapter, to show that induced oxidation of the toluene also occurs. This confirms that free radicals are liberated during the oxidation of aliphatic acids by cobaltic perchlorate.

The above conclusions have been substantiated by the present author, by analysis of the oxidation products from these systems by gas chromatography.

The combined oxidations of toluene and pivalic acid, and toluene and isobutyric acid, reached completion very quickly (< 2 mins), while reactions involving propionic acid were often much slower. The oxidations of all three acids in 50 per cent methyl cyanide were of first order with respect to cobaltic ions, as was found for their oxidations in water.[14] When toluene was added the reactions remained pseudo first order. Table 7.1. shows that the rates of the combined oxidations were approximately the sum of the separate rates of oxidation of the acid and the toluene. Hence the amount of oxidant consumed by the direct oxidation of toluene during the combined oxidations can be estimated from the weighted mean rate of oxidation for the relevant toluene concentration, extrapolated from Table 6.2., together with the rate constant for the appropriate acid, from Table 7.1. Since the points for the weighted mean rates for toluene oxidation are rather scattered (Table 6.2), the extrapolations were made using the line of the relatively

Table 7.1 Combined Oxidation of Toluene and Carboxylic Acids.

$[HClO_4]$ 1.0M. 50 per cent MeCN v/v 20°. μ ca 1.05 M. $[Co^{III}]$ initial ca 8×10^{-3} M. $[Co^{II}]$ initial ca 2×10^{-3} M.

Substrate	Initial pseudo first order* rate constant $sec.^{-1}$
None. (i.e. self decomposition of Co^{III}).	$1.7 - 1.3 \times 10^{-4}$
0.17M Toluene	7.9×10^{-4}
10^{-2} M Propionic Acid	1.2×10^{-3}
10^{-2} M Propionic Acid + .17 M Toluene	1.9×10^{-3}
10^{-1} M Propionic Acid	6.7×10^{-3}
10^{-1} M Propionic Acid + .17 M Toluene	7.4×10^{-3}
M Propionic Acid	2.3×10^{-2}
M Propionic Acid + .17 M Toluene	2.5×10^{-2}
10^{-2}M Isobutyric Acid	1.7×10^{-2}
10^{-2}M Isobutyric Acid + .17 M Toluene	2.0×10^{-2}
10^{-2}M Pivalic Acid	4.5×10^{-2}
10^{-2}M Pivalic Acid + .17 M Toluene	4.6×10^{-2}

10^{-1} M and M Isobutyric and Pivalic Acids were oxidised too fast to measure.

* Uncorrected for self decomposition of cobaltic ions.

higher mean rates, rather than the least mean square line through all the points. This ensured that the contribution from the direct oxidation of toluene was in no case underestimated, but was rather more likely to be an overestimate. The amount of benzaldehyde produced by this amount of oxidant attacking the toluene directly could then be estimated from the benzaldehyde yield at the relevant $(Co^{III}:\ toluene)$ ratio extrapolated from Table 6.3. These estimated yields from direct oxidation were subtracted from the measured yields to give data showing that carboxylic acids can promote the oxidation of toluene to benzaldehyde. This is shown, for propionic acid in Table 7.2., for isobutyric acid in Table 7.3., and for pivalic acid in Table 7.4.

The catalysis of toluene oxidation can be ascribed to the process:

$$R^{\bullet} + PhCH_3 \longrightarrow PhCH_2^{\bullet} + RH \qquad (7.iii.)$$

There will be competition for the alkyl radicals liberated in equation 7.ii. between toluene molecules (equation 7.iii.) and cobaltic ions:

$$R^{\bullet} + Co^{III}_{aq} \longrightarrow ROH + Co^{II}_{aq} + H^{+} \qquad (7.iv.)$$

The total yield of organic oxidation products will be proportional to the amount of available oxidant. However, reaction 7.iii is of zero order with respect to cobaltic ions while 7.iv. is first order in them. Hence the amounts of benzaldehyde produced from the induced oxidation should first increase with increasing initial oxidant concentration, and then decrease again as cobaltic ions remove the liberated alkyl radicals. However, the <u>percentage yield</u> of benzaldehyde from the induced oxidation should fall steadily with increasing initial cobaltic concentration. This has been found

Table 7.2: Induced Oxidation of Toluene Variation of Benzaldehyde Yield with $[Co^{III}]$ for Propionic Acid.

Reactions carried out at 20° in 2 ml. 50 per cent MeCN v/v. $[HClO_4]$ 1.10 M $[PhMe]$ .28 M. μ ca. 1.12 M.

A) M Propionic Acid

10^6 moles Co^{III} added	10^6 moles Co^{III} used by direct oxidation of toluene (a)	10^7 moles PhCHO produced by direct oxidation of toluene (b)	10^7 moles total PhCHO produced (c)	% yield Ph.CHO from induced oxidation (d)
2.8	0.17	0.41	0.67 0.60	
3.7	0.23	0.55	0.70 0.70	
5.6	0.34	0.80	0.94 0.93	
7.8	0.47	1.1	1.0 1.0	
9.3	0.56	1.3	1.1 1.1	

B) 10^{-1} M Propionic Acid

1.40	0.24	0.61	1.1	18
1.84	0.33	0.80	1.5 1.6	20
2.8	0.50	1.2	2.4 2.3 2.1	16-21
3.7	0.66	1.6	2.9 2.9	17
4.0	0.72	1.8	3.0	15
5.5	0.98	2.4	3.9 4.0 3.7	11-13
7.3	1.3	3.0	4.3 4.1	8.0
9.2	1.6	3.7	5.2 5.1	7.2

(a) Calculated as 10^6 moles Co^{III} added x $\left[\dfrac{\text{mean } k'_{\text{toluene}} - k'_{\text{self decomp.}}}{k'_{\text{PrCOOH}} + \text{mean } k'_{\text{toluene}} - k'_{\text{self decomp.}}}\right]$

k'_{EtCOOH} taken from Table 7.1. $k'_{toluene}$ by extrapolation from Figure 1.

(b) Estimated from previous column and variation of PhCHO yield with $\left[\dfrac{PhMe}{Co^{III}\ \text{added}}\right]$ ratio extrapolated from Table 6.3.

Footnotes to Table 7.2 continued

(c) Measured by [illegible] of 2:4-dinitro-phenyl-hydrazone, by Mr. D.J. Mills.

(d) Calculated as $\left[\frac{\text{4 x PhCHO produced by induced oxidation}}{\text{moles } Co^{III} \text{ not used by direct oxidation of toluene or by self decomposition.}}\right]$

Table 7.3. Induced Oxidation of Toluene.

Variation of Benzaldehyde Yield with $[Co^{III}]$ for Isobutyric Acid

Conditions and subscripts as for Table 7.2

(A) 10^{-1} M Isobutyric Acid

10^6 moles Co^{III} added	10^6 moles Co^{III} used by direct oxidation of toluene [(a)(e)]	10^7 moles PhCHO produced by direct oxidation of toluene [(b)]	10^7 moles total PhCHO produced [(c)]	% yield PhCHO from induced oxidation [(d)]
1.8	0.03	0.07	0.27 0.33	5.2
3.5	0.05	0.13	0.41 0.35	2.9
5.3	0.08	0.19	0.45 0.48	2.1
7.0	0.10	0.23	0.48 0.49	1.4

(e) Calculated on k' for 10^{-1} M. Pr^iCOOH ca. 10^{-1} sec.$^{-1}$ extrapolated from Table 7.1.

(B) 10^{-2} M Isobutyric Acid

1.6	0.14	0.34	0.79 0.77	12
1.8	0.16	0.39	0.97 0.95	14
3.2	0.28	0.68	1.2 1.2	6.9
3.5	0.30	0.73	1.4 1.4	8.7
4.8	0.41	1.0	1.8 1.9	8.3
5.3	0.46	1.1	2.2 2.1	8.8
6.4	0.55	1.3	2.1 2.1	5.4
7.0	0.60	1.4	2.1 2.1	4.4

Table 7.4 Induced Oxidation of Toluene.

Variation of Benzaldehyde Yield with $[Co^{III}]$ for Pivalic Acid

Conditions and subscripts as for Table 7.2.

(A) 10^{-1}N Pivalic Acid

10^6 moles Co^{III} added	10^6 moles Co^{III} used by direct oxidation of toluene (a)(e)	10^7 moles PhCHO produced by direct oxidation of toluene (b)	10^7 moles total PhCHO produced (e)	% yield PhCHO from induced oxidation (d)
1.3	0.01	0.02	1.2 1.2	35
1.6	0.01	0.03	1.0 1.0	26
2.7	0.02	0.05	1.4 1.4	21
3.2	0.02	0.06	1.2 1.1	14
4.0	0.03	0.07	1.4 1.3	13
4.7	0.03	0.09	0.86 0.87	6.9
5.4	0.04	0.10	0.86 0.88	6.0
6.3	0.04	0.10	0.96 0.96	5.5

(e) Calculated on k' for 10^{-1} pivalic acid ca. 2×10^{-1} sec.$^{-1}$ by extrapolation from Table 7.1.

(B) 10^{-2}M Pivalic Acid

0.60	0.020	0.05	1.3 1.3	86
0.90	0.029	0.07	1.8 1.8	81
1.3	0.042	0.10	2.3 2.3	71
1.6	0.051	0.13	2.0 2.0	50
2.2	0.071	0.19	2.2	38
3.0	0.097	0.24	2.2 2.9 2.9	28-36
3.2	0.10	0.25	2.8 2.9	33
3.7	0.12	0.28	2.4	24
4.7	0.15	0.37	2.1 2.1	15
6.3	0.20	0.49	2.1 2.1	11
8.9	0.29	0.66	2.4 2.4	7.9
11.1	0.36	0.82	2.4 2.3	6.1

to occur (Tables 7.2., 7.3., 7.4). Similar behaviour has been observed for the hydroxylation of benzene and toluene by Fentons' reagent.[72] When the cobaltic ion concentration is kept constant while the toluene concentration is increased, the yields of benzaldehyde from both direct and induced oxidation should increase. Table 7.5 shows this holds with pivalic acid, but that the extent of induced oxidation is marginal with propionic acid.

Table 7.5. INDUCED OXIDATION OF TOLUENE

Variation of Benzaldehyde Yield with Toluene Concentration

Conditions and subscripts as for Table 7.2.

(A) 10^{-2}M Pivalic Acid. Initial $[Co^{III}]$ 3.3×10^{-3}M.

[Toluene]M	10^6 moles[(a)] Co^{III} used by direct oxidation of toluene	10^7 moles PhCHO[(b)] produced by direct oxidation of toluene	10^7 moles[(c)] total PhCHO produced	% yield PhCHO[(d)] from induced oxidation
.094	0.09	0.18	0.84 0.88	4.1
.19	0.15	0.34	1.5 1.6	7.5
.23	0.18	0.41	2.0 2.0	10
.28	0.21	0.5	2.1 2.2	10-13
			2.5 2.6	

(B) M Propionic Acid. Initial $[Co^{III}]$ 2.8×10^{-3}M

.094	0.13	0.29	0.36 0.35	0.47
.19	0.24	0.56	0.73 0.73	1.3
.23	0.28	0.68	0.82 0.81	1.1
.28	0.34	0.80	0.94 0.93	1.0

Tables 7.2., 7.3., and 7.4., show that the induced oxidation yields decrease with increasing concentration of the organic acids. This would not be expected on the basis of the simple scheme outlined above, although the

yields would be expected to vary with the nature of the organic acid due to the varying extents of subsequent oxidation of the different aliphatic alcohols produced by equation 7.iv. Alkyl radicals have been shown to attack α C-H groups of carboxylic acids: [172]

$$R^{\bullet} + CH_3CH_2COOH \longrightarrow RH + \dot{M}eCHCOOH \qquad (7.v.)$$

and this could reduce the benzaldehyde yield with increasing carboxylic acid concentration. However, this explanation is not applicable to pivalic acid.

The products obtained from the oxidation of systems saturated with toluene in the presence of 10^{-2}M. propionic, isobutyric, and pivalic acids have also been investigated by gas chromatography by the method described in Chapter 10. These data, (Table 7.6.), confirm that benzaldehyde is the major oxidation product, and show that addition of the organic acid markedly changes the product ratios for benzyl alcohol, benzaldehyde, and benzoic acid.

The complexity of these systems, due to the many possible competing secondary reactions, and to mixing effects, and the fairly large scatter of the experimental results, precludes any more detailed analysis of the data. The observed catalysis of the oxidation of toluene, by carboxylic acids, agrees with previous work by Kooyman,[98,173] who showed that p-alkyl benzoic acids are very refractory towards cobaltous salt catalysed autoxidation except in the presence of compounds such as butyric acid which can be oxidised concurrently to liberate free radicals. It also agrees with the work

Table 7.6 INDUCED OXIDATION OF TOLUENE

Reactions performed at 20° in 10 ml. 50 per cent MeCN v/v saturated with toluene [PhMe] in solution ·30M. $[HClO_4]$ 1·10M. μ ca 1.14M.

Substrate acid	10^5 moles* Co^{III} added	10^6 moles compound produced** $PhCH_2OH$	PhCHO	PhCOOH	$PhCH_2CH_2Ph$	$\frac{PhCHO}{PhCH_2OH}$	$\frac{PhCHO}{PhCOOH}$	10^6 moles total side chain product expected from direct oxidation of toluene	10^6 moles total measured side chain oxidation product
10^{-2}M Propionic	6.7 (3.8)	1.2 (0.33)	14 (7.4)	0.91 (1.5)	trace	12	15	39	64
	8.1 (4.6)	0.52 (0.38)	16 (8.7)	0.72 (2.0)	0.1	31	22	48	70
	8.1 (4.6)	0.65 (0.38)	14 (8.7)	0.82 (2.0)	0.1	22	17	48	62
10^{-2}M Isobutyric	6.7 (0.55)	0.34 (0.07)	3.0 (1.2)	0.21 (0.09)	0.15	8.2	14	5.6	14
10^{-2}M Pivalic	6.7 (0.22)	0.34 (0.03)	2.0 (0.51)	0.25 (0.02)	0.008	5.9	8.0	2.2	10
	8.0 (0.27)	0.75 (0.03)	3.0 (0.60)	0.08 (0.03)	trace	4.3	40	2.7	15
	8.0 (0.27)	0.73 (0.03)	2.8 (0.60)	0.07 (0.03)	0.016	3.8	40	2.7	13

Traces of o-cresol were also found in each case, and only minute amounts of benzyl benzoate

* Figures in brackets represent the amount of Co^{III} estimated to be used by the direct oxidation of toluene (calculated as in subscript (a) Table 7.2).

** Figures in brackets represent the amount of the corresponding product expected from the direct oxidation of toluene, (calculated analogously to subscript (b) Table 7.2).

of Kochi,[153] who showed that while alkyl radicals are very rapidly oxidised by cupric ions, yet molecules such as hydrocarbons which can act as hydrogen donors can successfully compete for these radicals in solution.

The promotion by carboxylic acids of the cobaltic oxidations of other organic molecules is also of importance with regard to the interpretation of the mechanism of metal ion catalysed autoxidation reactions performed in solutions of organic acids. The catalytic process has previously been suggested to involve direct attack by the metal in its upper valence state on either the organic substrate or on a hydro-peroxide.[19,169,174,175,176,56] The present findings indicate that there is an alternative process involving liberation of alkyl radicals, which can then attack the substrate. i.e.

$$Co^{III}\text{—}OOCR \longrightarrow Co^{II} + CO_2 + R^{\bullet} \qquad (7.vi.)$$

$$R^{\bullet} + HX \longrightarrow RH + X^{\bullet} \qquad (7.vii.)$$

followed by the autoxidation chain:

$$X^{\bullet} + O_2 \longrightarrow XOO^{\bullet} \qquad (7.viii.)$$

$$XOO^{\bullet} + HX \longrightarrow XOOH + X^{\bullet} \qquad (7.ix.)$$

in preference to

$$Co^{III} + HX \longrightarrow Co^{II} + H^{+} + X^{\bullet} \qquad (7.x.)$$

This route provides an easy path for the catalysed autoxidation reaction, and could also provide some explanation of the lack of catalytic activity sometimes observed in the absence of carboxylic acids,[174,] and of the different efficiencies of different carboxylate salts as catalysts. Similar conclusions have recently been reached independently by Starnes[154] for the cobaltous catalysed autoxidation of aryl carboxylic acids.

Chapter 8. THE OXIDATION OF BENZYL ETHERS.

This Chapter describes an investigation of the oxidation of some benzyl ethers by cobaltic perchlorate. This was undertaken for comparison with the oxidation of hydrocarbons described in Chapter 6, and with previous work on radical attack on benzyl ethers. Kinetic measurements on these reactions were found to suffer from the same difficulties with regard to insolubility and secondary oxidation as were found with the aromatic hydrocarbons.

1. The Oxidation of Dibenzyl Ether.

a. Order with Respect to Each Reactant.

The rate of oxidation of dibenzyl ether in both 60% and in 85% methyl cyanide is first order with respect to cobaltic ions,(Figure 8.1.), and of first order with respect to ether. (Figure 8.2.) The addition of oxygen did not affect the reaction rate, but reactions were generally carried out under conditions as free from oxygen as possible. Likewise light of the wavelength employed for following the reaction did not affect the reaction rate. The pseudo first order rate constants shown in Fig. 8.2. fall on lines which cut the axis at the top end of their respective self-decomposition rate ranges. Similar behaviour was found for all the oxidations of ethers investigated, as well as for many of the oxidations of aromatic hydrocarbons described in Chapter 6. Hence the highest values of the self-decomposition rates were used to calculate the second order rate constants shown in Table 8.2.

FIGURE 8.1. REPRESENTATIVE FIRST ORDER PLOTS FOR THE OXIDATION OF DIBENZYL ETHER.

Conditions as for Table 8.2.

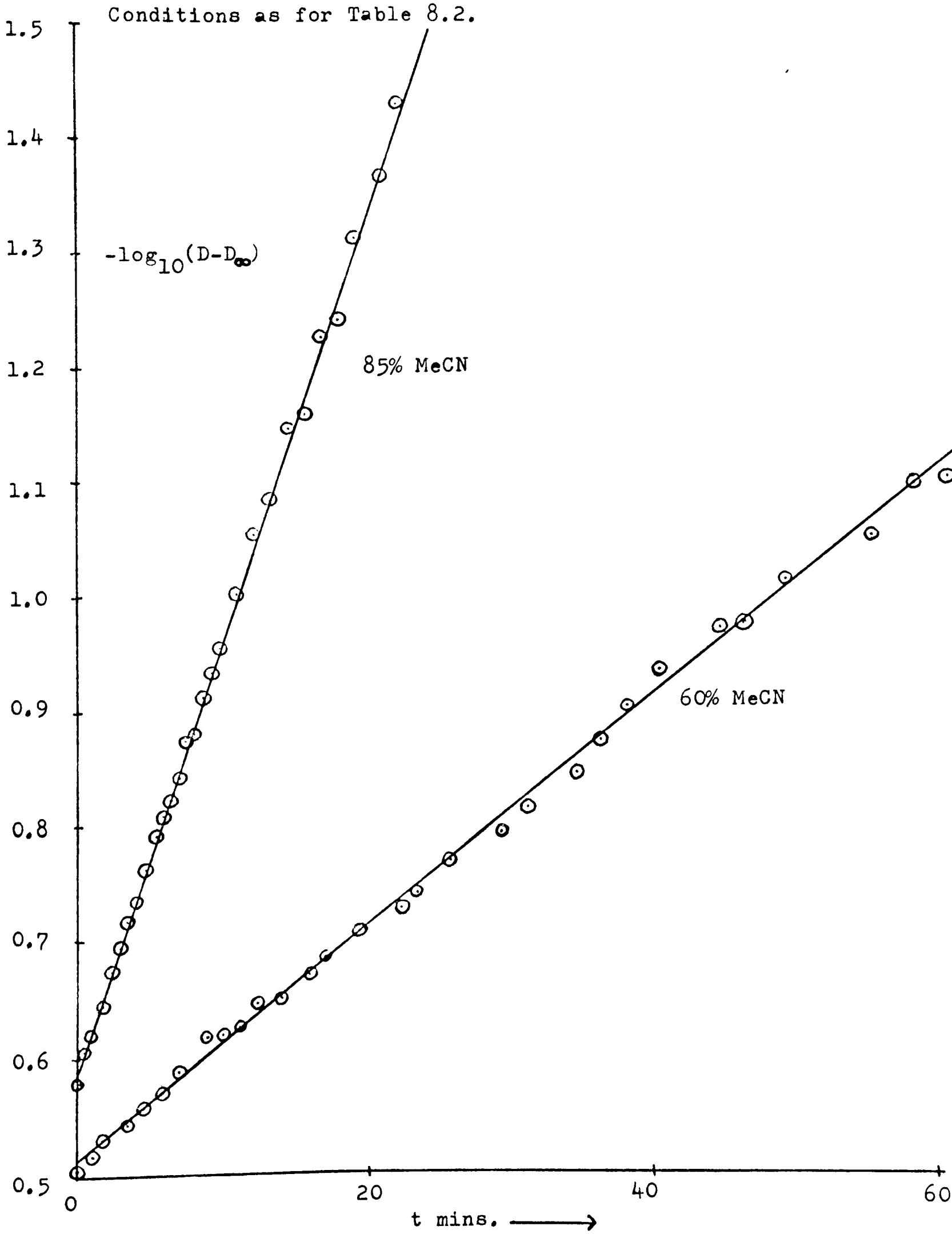


FIG. 8.2. OXIDATION OF DIBENZYL ETHER.

Conditions as for Table 8.2.

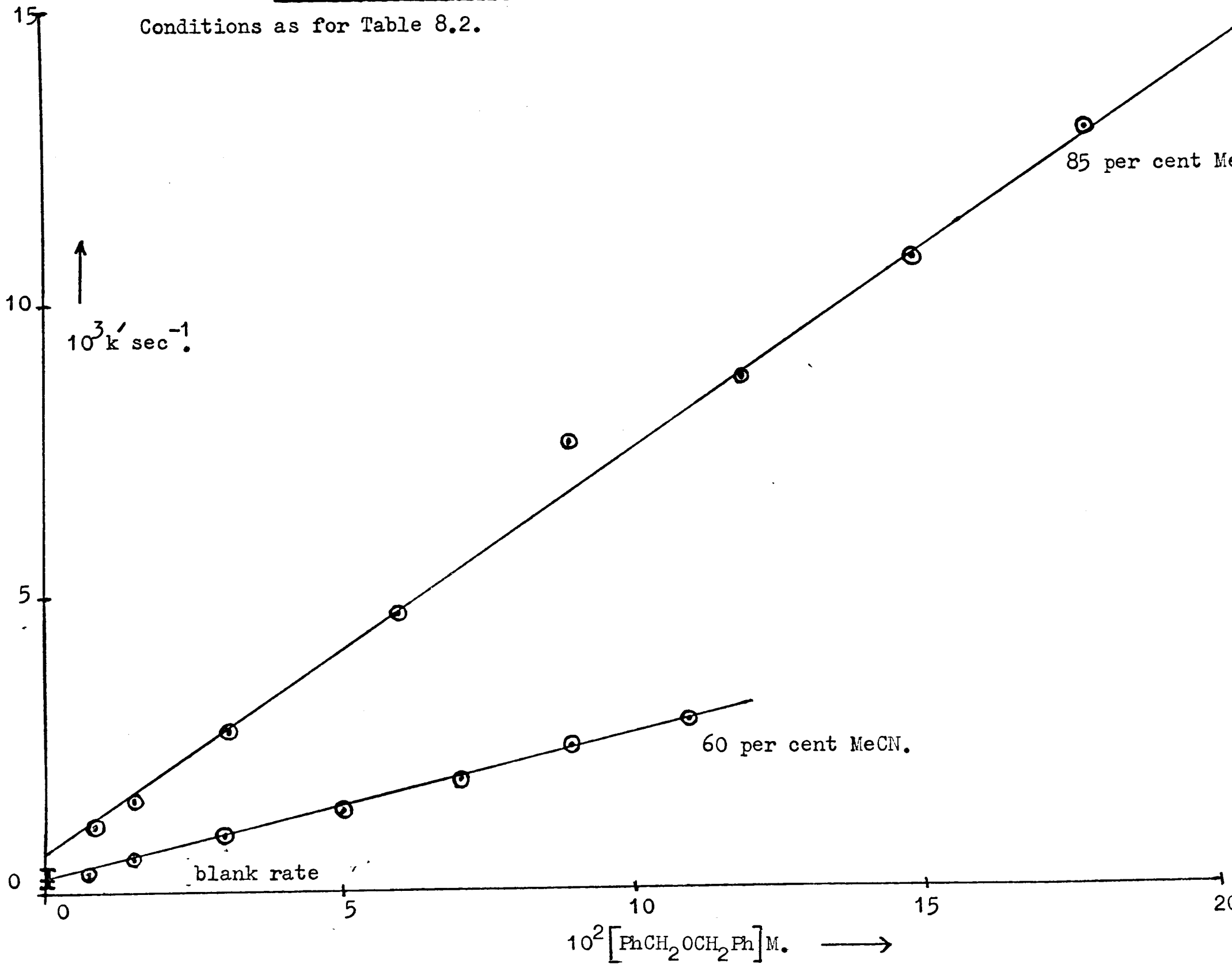


TABLE 8.2 THE OXIDATION OF DIBENZYL ETHER.

15.3°. $[HClO_4]$ 1.00M. μ ca. 1.0M. Initial $[Co^{III}]$M. ca. 2×10^{-3}M. Initial $[Co^{II}]$M. ca. 6×10^{-4}M.

A. 60 per cent MeCN v/v

$10^2[PhCH_2OCH_2Ph]$M.	10^4 k' sec^{-1}.[a]	10^4 k_2 $l.m^{-1}.sec^{-1}$.[b]
0.0	1.1 - .9[c]	-
0.70	3.7	2.6
1.5	5.3	2.3
3.0	9.7	2.6
5.0	13.5	2.3
7.0	18.2	2.3
9.0	24.2	2.5
11.0	28.3	2.4

Best fit $10^4k' = 1.9 + 240[PhCH_2OCH_2Ph]$ (by least squares).

B. 50 per cent MeCN.

$10^2[PhCH_2OCH_2Ph]$M.	10^3 k' sec^{-1}.[a]	10^2 $k_2 l.m^{-1}.sec^{-1}$.[b]
0.0	.39 - .19[c]	-
0.80	1.01	7.7
1.46	1.46	7.3
3.1	2.6	7.1
6.0	4.6	7.0
9.0	7.6	8.0
12.0	8.7	6.9
15.0	10.7	6.9
18.0	12.9	6.9
21.0	14.6	6.8

Best fit $10^3k' = 0.62 + 68[PhCH_2OCH_2Ph]$ (by least squares).

a. Measured graphically over two half lives.

b. Calculated from previous column taking higher self-decomposition rate.

c. Measured graphically.

b. Oxidation Products.

Yields of benzyl alcohol, benzaldehyde and benzoic acid, measured by gas liquid chromatography by the method described in Chapter 10, are shown in Tables 8.3 and 8.4. for oxidations in both 60 per cent and 85 per cent methyl cyanide. In both cases the cobaltic ions consumed by oxidation of the ether can be entirely accounted for by these oxidation products. Hence there can be little ring fission occurring. No yellow products were formed, even at high methyl cyanide concentration, from the oxidation of this, or any other, ether. This behaviour is similar to that for the oxidation of bibenzyl, but contrasts that found for the oxidation of toluene.

Benzyl ethers are more readily hydrolysed in acidic conditions than are aliphatic ethers,[179] though they are generally stable to dilute acids. Hence it was necessary to check that hydrolysis is not occurring to any large extent in the systems employed in the present study. Certainly hydrolysis is not the rate determining step, or the oxidation of dibenzyl ether would show a zero order dependence on the cobaltic ion concentration. Similarly there is unlikely to be a fast equilibrium:

$$H_2O + PhCH_2OCH_2Ph \rightleftharpoons 2PhCH_2OH \qquad (8.1.)$$

preceeding a rate determining attack on the alcohol, since the oxidation rate would then show a half order dependence on ether concentration. Hence there must be direct oxidation of the ether molecules by cobaltic ions. 'Blank' experiments using cobaltous perchlorate instead of cobaltic perchlorate were performed for each of the oxidation reactions for which product yields

are given in Tables 8.3 and 8.4. These blank runs were left for the same length of time as were the reaction runs, and worked up simultaneously with them. Analysis of the blank runs for the oxidations in 60 per cent methyl cyanide solution showed that only very small amounts of benzyl alcohol were produced by hydrolysis, compared with the amounts produced by the oxidation reactions, and there were no autoxidation products, i.e. benzaldehyde and benzoic acid. In order to minimise these side reactions throughout the present study, oxidation reactions were left only long enough for them to reach completion, (about eight half lives), before they were worked up for analysis. In 85 per cent methyl cyanide solution, the blank experiments showed appreciable but unreproducible amounts of benzyl alcohol (up to 15 per cent of that from the reaction runs), while the benzyl alcohol yields from the reaction runs were reproducible but suspiciously high. This may be partly attributed to hydrolysis in the working up procedure since it was very much more difficult to remove all the perchloric acid from these solutions of very high methyl cyanide concentration. These benzyl alcohol yields were hence discarded, although the measurements of benzaldehyde and benzoic acid are shown in Table 8.4. Neither of these products was found in the blank runs.

No correction for hydrolysis products was made, since it was not certain if hydrolysis occurred mainly under the reaction conditions or during the work up. Benzyl alcohol produced by hydrolysis during the reaction is likely to be largely oxidised to benzaldehyde, while this will

TABLE 8.3 PRODUCTS FROM THE OXIDATION OF DIBENZYL ETHER IN 60 PER CENT MeCN.

Reactions performed under N_2 at 15° in 4 ml 60 per cent MeCN (v/v). $[HClO_4]$ 1.00M. μ ca. 1.1M. 1.01×10^{-4} moles Ce^{III} added to each. (i.e. initial $[Ce^{III}] 2.52 \times 10^{-2}$M)

$10^2[PhCH_2OCH_2Ph]$M	10^6 moles compound produced.[a]			Product ratios PhCHO/$PhCH_2OH$	PhCHO/PhCOOH	average stoichiometry.
	$PhCH_2OH$	PhCHO	PhCOOH			
10.3	.104	36.1	4.3	347	8.4	4.3
6.8	.085	32.7	5.7	385	5.7	4.5
3.1	.052	28.1	6.4	540	4.4	4.6

a. Only trace quantities of bibenzyl and benzyl benzoate were detected.

$10^2[PhCH_2OCH_2Ph]$M	Moles compound formed as % total side chain attack:			10^5 moles Co^{III} accounted for: as side chain[b] attack	as self[c] decomp.	Total.
	$PhCH_2OH$	PhCHO	PhCOOH			
10.3	.24	81	19	8.9 ± .9	.7-.3	9.4±1.1
6.8	.19	75	26	8.8 ± .9	1.1-.5	9.6±1.2
3.1	.13	70	32	8.0 ± .8	2.1-1.0	9.6±1.4

b. Calculated as (2PhCHO + 4PhCOOH).

c. Calculated from Table 8.2A.

not happen for benzyl alcohol produced during the work up. In either case this does not invalidate the calculation that the oxidant consumed can be entirely accounted for in terms of the measured products. This calculation depends entirely on the yields of benzaldehyde and of benzoic acid, and two cobaltic ions are required to produce one benzaldehyde molecule whether

TABLE 8.4 PRODUCTS FROM THE OXIDATION OF DIBENZYL ETHER IN 85 PER CENT MeCN.

Reactions performed under N_2 at 15° in 5 ml. 85 per cent MeCN (v/v). $[HClO_4]$ 1.00M. μ ca. 1.04M. 3.00×10^{-5} moles Co^{III} added to each (i.e. initial $[Co^{III}]$ 6.0×10^{-3}M).

$10^2[PhCH_2OCH_2Ph]$ M	10^6 moles compound produced.[a]		Product ratio.
	PhCHO	PhCOOH	PhCHO/PhCOOH
21.3	14.6	.73	20
13.3	10.8	1.4	7.7
6.1	9.1	2.0	4.6
1.49	7.7	2.4	3.2

a. Only trace amounts of bibenzyl and no benzyl benzoate were detected.

$10^2[PhCH_2OCH_2Ph]$M.	Moles compound formed as % total side chain attack:		10^5 moles Co^{III} accounted for:		
	PhCHO	PhCOOH	as side chain[b] attack	as self[c] decomp.	Total
21.3	91	9.1	3.2±.3	.08-.04	3.2±.4
13.3	79	21	2.7±.3	.12-.06	2.8±.3
6.1	69	31	2.6±.3	.25-.12	2.8±.4
1.49	62	38	2.5±.3	.84-.41	3.1±.5

b. Calculated as (2PhCHO + 4PhCOOH).

c. Calculated from Table 8.2B.

this occurs by direct attack on the ether, or via the hydrolysis reaction. However, the mean stoichiometry of the reaction under these conditions, (85% MeCN) cannot be calculated in consequence.

The above product and kinetic measurements indicate that a general scheme

for the oxidation is:

$$PhCH_2OCH_2Ph + Co^{III} \longrightarrow PhCHOCH_2Ph + Co^{II} + H^+ \qquad (8.ii.)$$

$$PhCHOCH_2Ph \xrightarrow{fast} PhCH_2^{\bullet} + PhCHO \qquad (8.iii.)$$

$$PhCH_2^{\bullet} + Co^{III}H_2O \xrightarrow{fast} PhCH_2OH + Co^{II} + H^+ \qquad (8.iv.)$$

$$PhCH_2OH + 2Co^{III} \longrightarrow PhCHO + 2Co^{II} + 2H^+ \qquad (8.v.)$$

$$PhCHO + 2Co^{III} + H_2O \longrightarrow PhCOOH + 2Co^{II} + 2H^+ \qquad (8.vi.)$$

The isolation of traces of bibenzyl supports the view that benzyl radicals are intermediates in the reaction.

Reactions 8.ii and 8.iii could be concerted, but the detection of minute traces of benzyl benzoate from some of the reactions indicates that the intermediate $PhCHOCH_2Ph$ does have a transient existence, and can either break down as in reaction 8.iii, or can be oxidised by another cobaltic ion:

$$PhCHOCH_2Ph + Co^{III}.OH_2 \longrightarrow PhCH(OH)-OCH_2Ph + Co^{II} + H^+ \qquad (8.vii.)$$

followed by:

$$PhCH(OH)-OCH_2Ph + 2Co^{III} \longrightarrow PhC(=O)-OCH_2Ph + 2Co^{III} + 2H^+ \qquad (8.viii.)$$

This route could also produce benzaldehyde and benzyl alcohol since hemiacetals are readily hydrolysed under acid conditions

$$PhCH(OH)OCH_2Ph + H_2O \longrightarrow PhCH(OH)_2 + PhCH_2OH \qquad (8.ix.)$$

$$PhCH(OH)_2 \xrightarrow{fast} PhCHO + H_2O \qquad (8.x.)$$

Alternatively the oxidation of the radical $PhC^{\bullet}HOCH_2Ph$ could involve fission:

$$PhC^{\bullet}HOCH_2Ph + Co^{III}OH_2 \longrightarrow PhCHO + PhCH_2OH + Co^{II} + H^+ \qquad (8.xi.)$$

and this route could compete with equation 8.vii. Mixtures of benzyl alcohol, benzaldehyde and benzoic acid did not form either benzyl benzoate or dibenzyl ether under the conditions used. Such mixtures in benzene solution similarly do not form esters.[180]

The kinetic data in Table 8.2a., can be combined with the product measurements from Table 8.3. to make approximate stationary state calculations, analogous to those made for the oxidation of toluene (p.47.) These calculations show that a stationary state concentration of benzyl alcohol should be attained very quickly, but that a stationary state concentration of benzaldehyde should never be reached. However, the calculated maximum concentrations of benzyl alcohol are again very much lower than the actual yields obtained in 60% methyl cyanide solution.

TABLE 8.5. COMPARISON BETWEEN CALCULATED AND MEASURED CONCENTRATIONS OF BENZYL ALCOHOL FROM THE OXIDATION OF DIBENZYL ETHER IN 60%MeCN.

$10^2[PhCH_2OCH_2Ph]$ M.	Rate of prod. of $PhCH_2OH$ i.e. $10^4k_a[PhCH_2OCH_2Ph]$ [a]	$10^4[PhCH_2OH]$ M. [b] measured	approx. derived [c] k_b $l.m.^{-1}sec.^{-1}$
10.3	6	2.5	2.4
6.8	4	2.1	1.9
3.1	2	1.3	1.5

a. Approximately calculated as $k'_{corr}/4$.

b. Taken from Table 8.3.

c. Compare Table 6.6. and the true value of approx. 50 $l.m.^{-1}sec.^{-1}$ for k_b.

This enhancement in the benzyl alcohol yields may be due to the reaction:

$$PhC\dot{O} + PhCH_2OCH_2Ph \longrightarrow Ph\dot{C}HOCH_2Ph + PhCHO \qquad (8.xii.)$$

This is analogous to equation 6.xviii. which was a possible cause of the enhancement of the benzyl alcohol yields from the oxidation of toluene. (Table 6.6.)

Benzaldehyde yields from the oxidation of dibenzyl ether in 60% methyl cyanide have also been measured by thin layer chromatography of the 2,4-dinitrophenylhydrazone, by the method described in Chapter 10. These measurements are given in Table 8.6. Each reaction run was performed in duplicate, and several chromatoplates were prepared from each run. Blank reactions using cobaltous perchlorate instead of cobaltic perchlorate showed only a very small correction, even when the solutions were saturated with oxygen. However, added oxygen appeared to make the reaction product measurements more erratic, and so solutions as free from oxygen as possible were used for the other kinetic and product measurements described in this Chapter. These benzaldehyde measurements by thin layer chromatography agree reasonably well with those made on similar systems by the gas chromatographic method.(Table 8.3)

c. Variation of the Oxidation Rate of Dibenzyl Ether with Perchloric Acid Concentration.

The variation of the oxidation rate of dibenzyl ether with perchloric acid concentration in 60% methyl cyanide solution is shown in

TABLE 8.6. BENZALDEHYDE YIELDS FROM THE OXIDATION OF DIBENZYL ETHER.

Reaction performed at 15° in 1ml 60 per cent MeCN (v/v). $[HClO_4]$ 1.0 M.

a. Initial $[Co^{III}]$ 1.00×10^{-2} M. Under nitrogen. d

$10^2[PhCH_2OCH_2Ph]$	10^6 moles PhCHO produced	10^6 moles Co^{III} consumed by self-decomposition	% yield PhCHO e
14.5	3.9	.51 - .24	81 ± 1
11.6	3.8	.63 - .30	80 ± 2
8.7	3.7	.83 - .39	79 ± 2
5.8	3.5	1.19 - .56	77 ± 3
2.9	3.0	2.10 -1.00	72 ± 5
1.45	2.5	3.52 -1.67	69 ± 9

b. Initial $[Co^{III}]$ 1.22×10^{-2} M. With added oxygen.

13.1	4.6	.60 - .29	78 ± 1
9.1	4.5	.97 - .46	78 ± 2
6.1	3.8	1.4 - .67	68 ± 2
3.0	3.6	2.5 -1.2	70 ± 4
1.51	3.5	4.1 -2.0	77 ± 9

c. $[PhCH_2OCH_2Ph]$ .121M. In air.

10^6 moles Co^{III} added	10^6 moles PhCHO produced	10^6 moles Co^{III} consumed by self-decomp. d	% yield PhCHO e
18.4	5.9	1.1 - .53	66 ± 2
15.3	5.1	.78-.38	70± 2
9.2	3.3	.55- .26	76 ± 2
6.1	2.1	.37- .17	73 ± 2
3.1	1.1	.19- .09	75 ± 2

d. Calculated from Table 8.2A.

e. Corrected for self-decomposition of Co^{III}.

Figure 8.7. (Table 8.7).

TABLE 8.7. VARIATION OF RATE OF OXIDATION OF DIBENZYL ETHER WITH ACIDITY.

15°. 60 per cent MeCN (v/v). $[PhCH_2OCH_2Ph]$ = 5.4 x 10^{-2}M. Initial $[Co^{III}]$ ca. 2 x 10^{-3}M. Initial $[Co^{II}]$ ca. 6 x 10^{-4}M. μ ca. 2.89M.

$[HClO_4]$M.	$1/[HClO_4]^{M^{-1}}$.	10^4 k′ sec^{-1}. [a]	10^4 k′ for corresponding self-decomposition. [b]	10^4 k′ corr sec^{-1} [c]
2.86	0.35	5.8	1.4 - 0.5	4.4
2.40	0.42	8.6	1.2 - 0.6	7.4
2.05	0.49	12.4	1.2 - 1.0	11.2
1.65	0.61	17.9	2.2 - 1.3	15.7
1.30	0.77	25.4	2.7 - 1.6	22.7
1.00	1.00	39.6	3.6 - 2.2	36.0
0.70	1.43	63	7.2 - 3.8	55
0.50	2.00	91	6.6 - 3.4	84
0.35	2.86	133	10 - 6	123

a. Measured graphically over two half-lives.

b. Measured graphically.

c. Calculated taking higher self-decomposition rates.

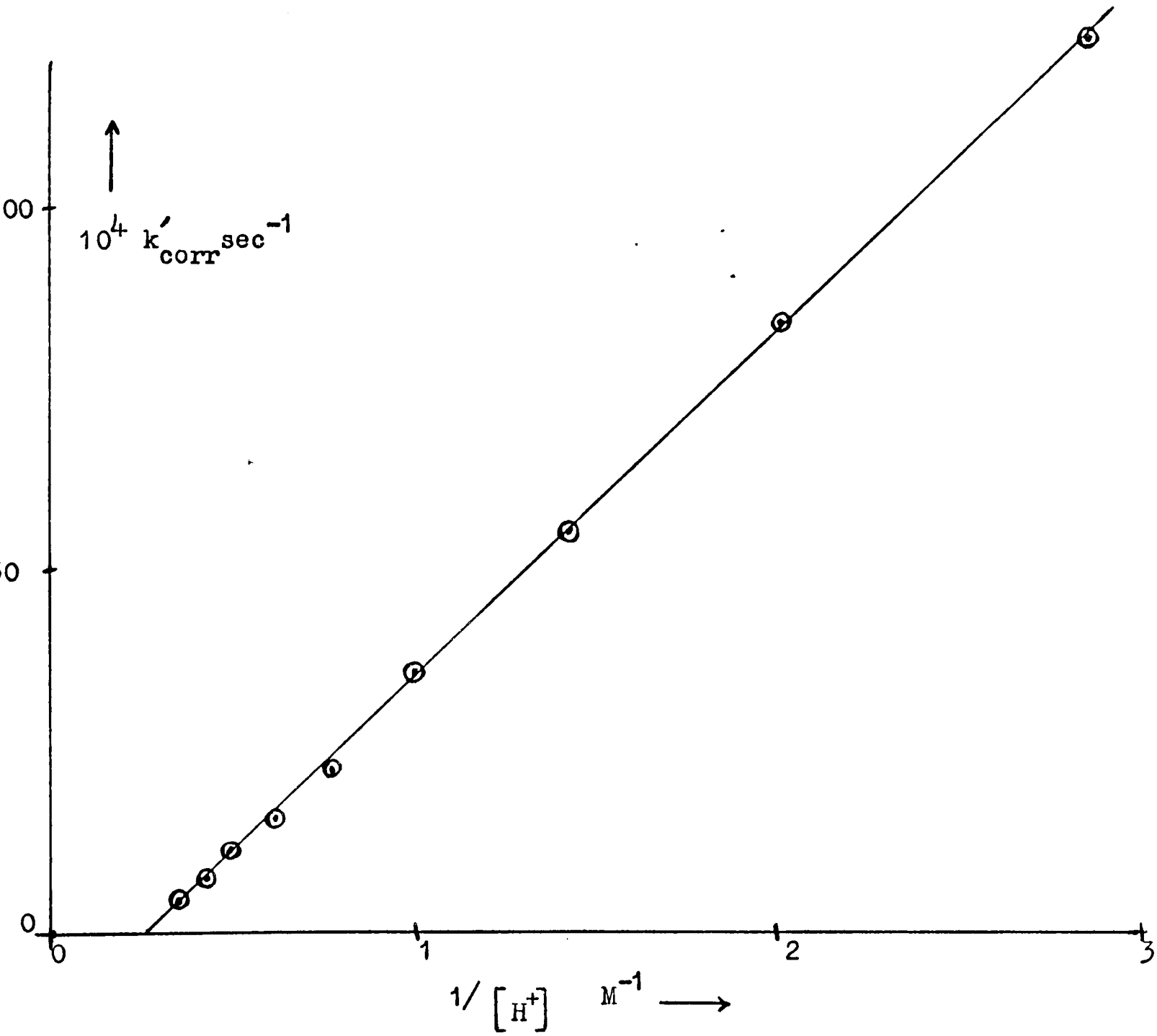
The pseudo first order rate constant follows the expression:

$$10^4\, k'_{corr.} = (47.6/[H^+] - 12.6) \qquad (8.xiii)$$

under the conditions given. A more realistic interpretation of Fig. 8.7 may be that some small terms in higher powers of $1/[H^+]$ cause the dependence to curve to make an intercept at the origin. However no mechanistic significance should be put upon this since the ionic strength was held constant, (with sodium perchlorate), only in the sense that the concentration of

FIG. 8.7. VARIATION OF RATE OF OXIDATION OF DIBENZYL ETHER WITH ACIDITY.

Conditions as for Table 8.7.



univalent ions was constant. This is only an approximation to the 'constant ionic strength' where the activity coefficients of all the species involved remain constant. Similar behaviour has been found for the oxidation of p-nitrobenzaldehyde in 45 per cent methyl cyanide solution,[31] and for the oxidations of t-butanol and cyclohexanol[32] in water. In the latter cases a dependence of the form:

$$k = a + b/h_o \qquad (8.xiv.)$$

was found to hold, where h_o is the Hammett acidity function.[181] No values are available for acidity functions of perchloric acid in methyl cyanide - water mixtures, and so no treatment of this sort could be applied in the present case.

Comparison of Table 8.7 with Table 8.2a shows that increasing the ionic strength of the medium markedly increases the reaction rate, as was noted previously for the oxidation of toluene.

This inverse acidity dependence and marked ionic strength effect can be interpreted in the way previously discussed for the oxidation of toluene.

2. The Oxidation of Benzyl Methyl Ether.

Benzyl methyl ether was investigated since the methyl group should be much less easy to split off as a free radical, than is the benzyl group in dibenzyl ether. (equation 8.iii). This factor could change the observed products.

a. Reaction Order with Respect to Each Reactant.

Plots of $-\log_{10}(D-D_\infty)$ against time were similar to those for the oxidation of toluene. (Fig. 6.1). The deviation from linearity may again be ascribed to the oxidation of secondary products. The variation of the initial pseudo first order rate constant with substrate concentration is shown in Figure 8.8 (Table 8.8). Deliberate addition of oxygen had no effect on the reaction rate, but kinetic and product studies were carried

FIGURE 8.8 OXIDATION OF BENZYL METHYL ETHER.

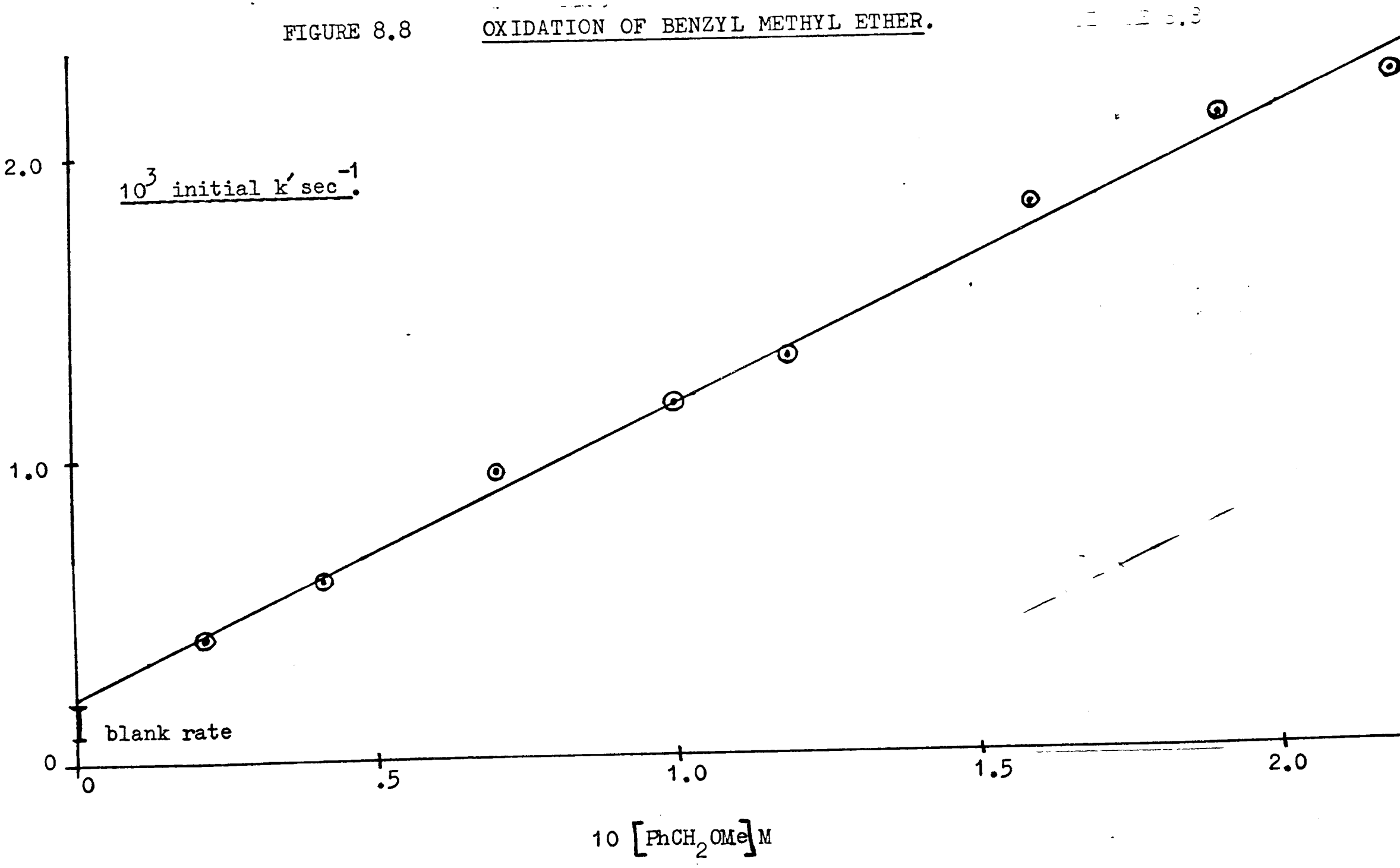


TABLE 8.8 OXIDATION OF BENZYL METHYL ETHER.

15° $[HClO_4]$ 1.00M. 60 per cent MeCN. Initial $[Ce^{III}]$ ca. 1.5×10^{-2}M. Initial $[Ce^{II}]$ ca. 5×10^{-3}M. μ ca. 1.1M.

$10[PhCH_2OMe]$M.	10^3 init k′ sec^{-1}. [a]	10^2 k_2 l.m^{-1} sec^{-1}. [b]	10^3 wtd. mean k′ sec^{-1}. [c]
0.0	[.19 - .09] [d]	-	-
0.21	0.40	1.00	0.54
0.40	0.58	0.98	0.71
0.70	0.94	1.07	1.31
1.00	1.15	0.96	1.48
1.19	1.31	0.94	1.73
1.60	1.80	1.01	2.18
1.92	2.09	0.99	2.51
2.20	2.22	0.92	2.91

Best fit line, (by least squares): $10^3 k' = 0.22 + 9.4[PhCH_2OMe]$.

a. Measured graphically; and computed by orthogonal polynomials as coefficient of for best fit weighted quadratic and cubic. Mean values taken.

b. Calculated from previous column taking k′ self-decomp = 1.9×10^{-4} sec^{-1}.

c. Computed by orthognal polynomials. (See Chapter 11). Without self-decomposition correction.

d. Measured graphically.

out under nitrogen.

b. Oxidation Products.

Yields of methyl benzoate, benzaldehyde and benzoic acid, measured by gas chromatography, are shown in Table 8.9. No bibenzyl was detected, and

only minute quantities of benzyl alcohol which were smaller than the amounts obtained from blank experiments using cobaltous perchlorate. These blank experiments showed that there was only a very small amount of ether hydrolysis under these conditions, and no autoxidation.

TABLE 8.9. AROMATIC PRODUCTS FROM THE OXIDATION OF BENZYL METHYL ETHER.

Reactions performed under N_2 at 15° in 10 ml 60 per cent MeCN (v/v). $[HClO_4]$ 1.0M. μ ca. 1.1M. 1.01×10^{-4} moles Co^{III} added.

$[PhCH_2OMe]$ M	10^6 moles compound produced.			Product ratios	
	PhCHO	PhCOOMe	PhCOOH	$\frac{PhCHO}{PhCOOMe}$	$\frac{PhCHO}{PhCOOH}$
.25	17.4	2.9	.62	6.0	28
.12	17.2	2.1	.48	8.2	36
.020	8.3	1.3	.97	6.4	8.6

No bibenzyl was detected.

$[PhCH_2OMe]$ M	10^{-5} moles Co^{III} accounted for as:		Total
	aromatic products[a]	as self-decomp.[b]	
.25	4.9 ± .5	.6 - .3	5.4 ± .7
.12	4.5 ± .5	1.1 - .5	5.3 ± .8
.020	2.6 ± .3	3.6 -1.7	5.3 ±1.3

a. Calculated as 2PhCHO + 4 PhCOOMe + 4 PhCOOH.

b. Calculated from wtd. mean rates in Table 8.8.

The non-production of benzyl alcohol by the oxidation indicates that attack is exclusively on the benzylic $-CH_2-$ group:

$$PhCH_2OMe + Co^{III} \longrightarrow \dot{P}hCHOMe + Co^{II} + H^+ \qquad (8.xv.)$$

and not on the methyl group. However, the production of large amounts of methyl benzoate shows that in this case oxidation of the intermediate $PhC\dot{H}OMe$ radical:

$$PhC\dot{H}OMe + Co^{III}H_2O \longrightarrow \underset{\underset{OH}{|}}{PhCHOMe} + Co^{II} + H^+ \qquad (8.xvi)$$

can compete effectively with its decomposition:

$$PhC\dot{H}OMe \rightarrow PhCHO + M\dot{e} \qquad (8.xvii)$$

and that oxidation of the hemiacetal:

$$\underset{\underset{OH}{|}}{PhCHOMe} + 2Co^{III} \longrightarrow \underset{\underset{O}{\|}}{PhCOMe} + 2Co^{II} + 2H^+ \qquad (8.xviii)$$

can compete successfully with its hydrolysis to benzaldehyde and methanol. Check experiments with solutions containing benzoic acid, benzaldehyde and methanol showed there is no ester or ether formation under these conditions, which agrees with previous work on similar mixtures in benzene.[180] Other checks showed the ester did not hydrolyse to any great extent under these conditions, and that its rate of oxidation was slower than that of the ether.

The methyl radical liberated by equation 8.xvii. should be oxidised rapidly to methanol by a further cobaltic ion, and then to formaldehyde and formic acid. Attempts to identify these products by GLC were unsuccessful, since neither formaldehyde nor formic acid would elute. No solvent could be found to separate formaldehyde 2,4 dinitrophenyl hydrazone from the DNP's of both benzaldehyde and 'acetone' (Chapter 10) However, after

separation of the benzaldehyde DNP by elution with benzene, the mass spectrum of the 'acetone' band showed a large peak at mass number 210, which was not present in the 'acetone' band from a 'blank' experiment. This peak corresponds to formaldehyde DNP. The presence of formaldehyde was confirmed by testing with veratrole and sulphuric acid by the method given by Feigl.[1,2] The reaction products gave the reddish-violet colour indicative of formaldehyde, while a control solution containing cobaltous perchlorate and unreacted substrate gave only a charred green colour.

c. Dependence of the Oxidation Rate of Benzyl Methyl Ether on Perchloric Acid Concentration.

The dependence of the rate of oxidation of benzyl methyl ether on the acidity of the medium, at constant ionic strength, was measured in both 20 per cent and 60 per cent methyl cyanide solutions. Lower concentrations of oxidant were used in these, and in later, kinetic measurements than were used for Table 8.E., in order to minimise secondary oxidation and hence the deviations from first order with respect to oxidant found in Section g. The pseudo first order rate constants followed the expressions:

a. In 60 per cent MeCN: $10^4\, k'_{corr} = 26.8/[H^+] - 6.28$ (8.xix)

b. In 20 per cent MeCN: $10^4\, k'_{corr} = 7.51/[H^+] + 0.42$ (8.xx)

under the conditions given. The plots of $-\log_{10}(D-D_{\infty})$ versus time were linear over one to two half lives, but their subsequent curvature showed no systematic variation with acidity.

FIG. 8.10 VARIATION OF RATE OF OXIDATION OF BENZYL METHYL ETHER WITH PERCHLORIC ACID CONCENTRATION

Conditions as for Table 8.10.

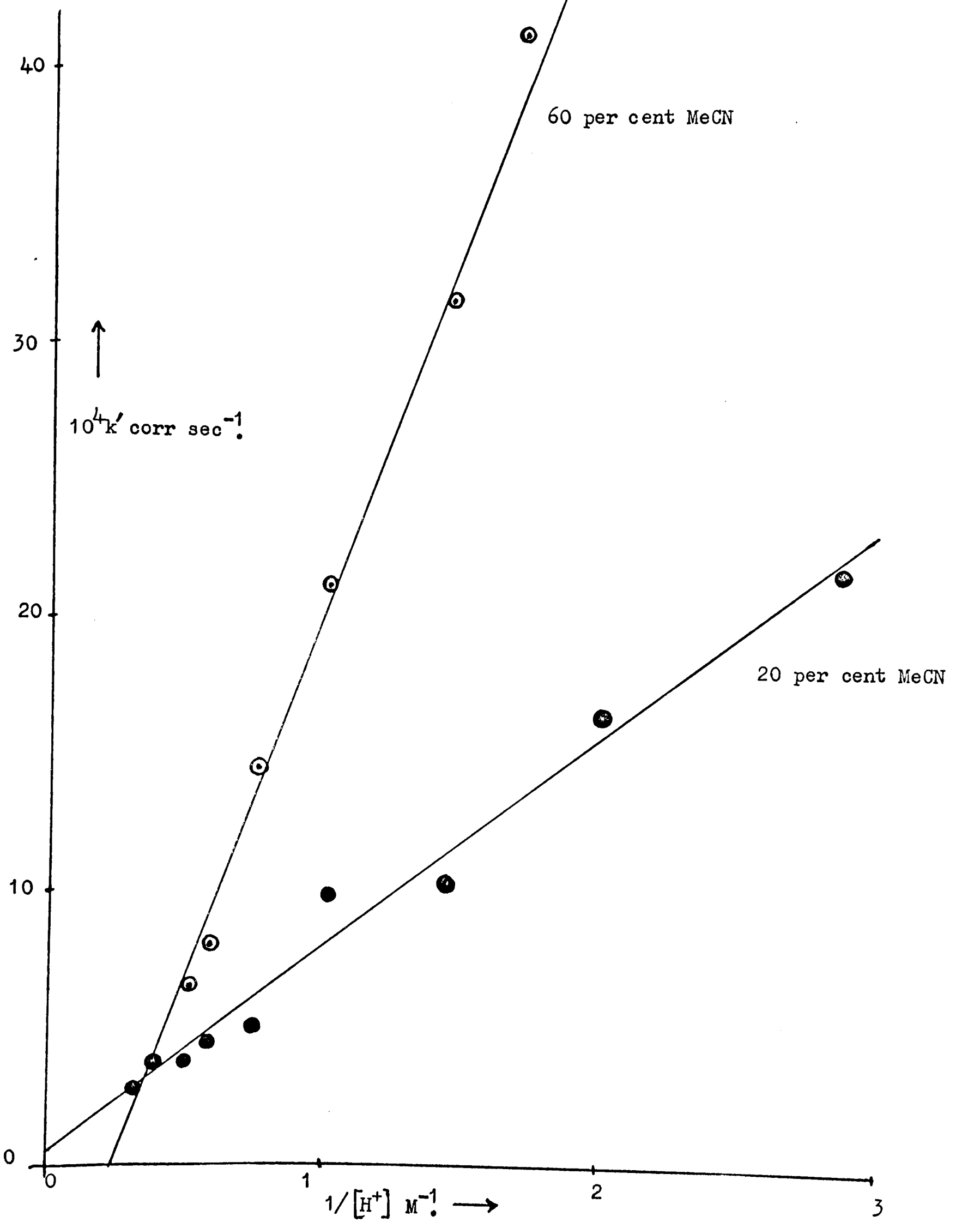


TABLE 8.10 VARIATION OF OXIDATION RATE OF BENZYL METHYL ETHER WITH PERCHLORIC ACID CONCENTRATION.

15° $[PhCH_2OMe]$ = 6.0 x 10^{-2}M. Initial $[Co^{III}]$ ca. 3 x 10^{-3}M. Initial $[Co^{II}]$ ca. 1 x 10^{-3}M.

A. 60 per cent MeCN μ ca. 2.07M.

$[HClO_4]$M.	$1/[HClO_4]M^{-1}$.	10^4 initial k' sec^{-1}.[a]	10^4 k' sec^{-1} for corresponding self-decomp.[a]	10^4 k' corr. sec^{-1}.[b]	$[H^+]$ $(10^4 k'_{corr} + 6.28)$. moles l^{-1}. sec^{-1}.
2.04	0.49	7.2	0.8	6.4	26
1.75	0.57	9.3	1.4 - .6	7.9	25
1.35	0.74	16.0	1.6 - .7	14.4	28
1.00	1.00	24.6	3.5 - 1.6	21.1	27
0.70	1.43	36	4.2 - 3.4	32	27
0.59	1.69	46	4.7 - 2.9	41	28
0.50	2.00	51	6.0 - 3.2	45	26

Best fit line (by least squares): $10^4 k'_{corr} = -6.28 + 26.8/[H^+]$.

B. 20 per cent MeCN. μ ca. 3.23M.

					$[H^+]$ $(10^4 k'_{corr} - 0.42)$
3.2	0.31	3.0	0.3 - 0.1	2.7	7.4
2.6	0.38	4.0	0.3 - 0.1	3.7	8.6
1.75	0.57	6.3	1.9 - 0.5	4.4	7.0
2.1	0.48	4.9	1.2 - 0.3	3.7	6.9
1.35	0.74	6.7	1.7 - 0.5	5.0	6.2
1.00	1.00	11.5	1.8 - 0.9	9.7	9.3
0.70	1.43	13.9	3.8 - 1.3	10.1	6.8
0.50	2.00	20.6	4.3 - 2.2	16.3	7.9
0.35	2.86	27.7	6.2 - 4.6	21.5	7.4

Best fit line (by least squares): $10^4 k'corr = 0.42 + 7.51/[H^+]$

a. Measured graphically. b. Calculated using higher self decomp. rates.

The similarity between the acidity dependences in the two different solutions is noteworthy, since for the runs in 60 per cent methyl cyanide the oxidant was the violet 'complexed' colour, (Chapter 5), while in the 20 per cent methyl cyanide solution it was the 'uncomplexed' blue colour. This indicates that at constant ionic strength, the equilibrium concentration of the methyl cyanide-cobaltic complex is also inversely dependent on the acidity.

d. Dependence of the Oxidation Rate of Benzyl Methyl Ether on Methyl Cyanide Concentration.

The variation of the initial pseudo first order rate constant with methyl cyanide concentration, over the range 16.7 per cent to 85 per cent methyl cyanide (v/v), is shown in Table 8.11. The plots of $-\log_{10}(D-D_{\infty})$ versus time were linear over one to two half lives as before, and their curvature showed no systematic variation with methyl cyanide concentration.

A reaction was also performed in 91 per cent methyl cyanide solution, under which conditions the cobaltic perchlorate became a bright cherry red colour. The reaction run showed a fast initial rate which then altered to a lower rate after about one half life. The self decomposition reaction in 91 per cent methyl cyanide showed exactly similar behaviour, the fast initial rate being equal to that for the reaction run, then curving off to a rate lower than that for the reaction run. This behaviour may be due to some initial complexing reaction, but its origin was not investigated

further. High concentrations of methyl cyanide, in which the oxidant assumes this cherry red colour, were hence avoided for other measurements.

TABLE 8.11. EFFECT OF METHYL CYANIDE CONCENTRATION ON THE RATE OF OXIDATION OF BENZYL METHYL ETHER.

15°C. $[HClO_4]$ 1.0M. $[PhCH_2OMe]$ 6.03×10^{-2}M. Initial $[Co^{III}]$ ca. 3×10^{-3}M. Initial $[Co^{III}]$ ca. 1×10^{-3}M. μ ca. 1.02M.

Percentage MeCN	10^4 initial[a] k' sec^{-1}.	10^4 k' sec^{-1} for[a] self decomposition.	10^4 k'_{corr} sec^{-1}.[b]
85	26	2.7 - 1.6	23
78	23	2.0 - 1.2	21
69	11.9	2.2 - .9	9.7
60	5.9	2.0 - .9	3.9
51	4.5	1.7 - .4	2.8
33	3.3	1.2 - .3	2.1
25	3.1	.8 - .2	2.3
17	1.92	.13	1.8

a,b, as in Table 8.10.

e. Variation of the Rate of Oxidation of Benzyl Methyl Ether with Temperature.

The variation of the initial pseudo first order rate constant with temperature was measured in solutions containing 85 per cent, 60 per cent and 30 per cent methyl cyanide. These results are shown in Figure 8.12., (Table 8.12). The derived values for the activation parameters are:

FIGURE 8.12. VARIATION OF RATE OF OXIDATION OF BENZYL METHYL ETHER WITH TEMPERATURE.

Conditions as for Table 8.12.

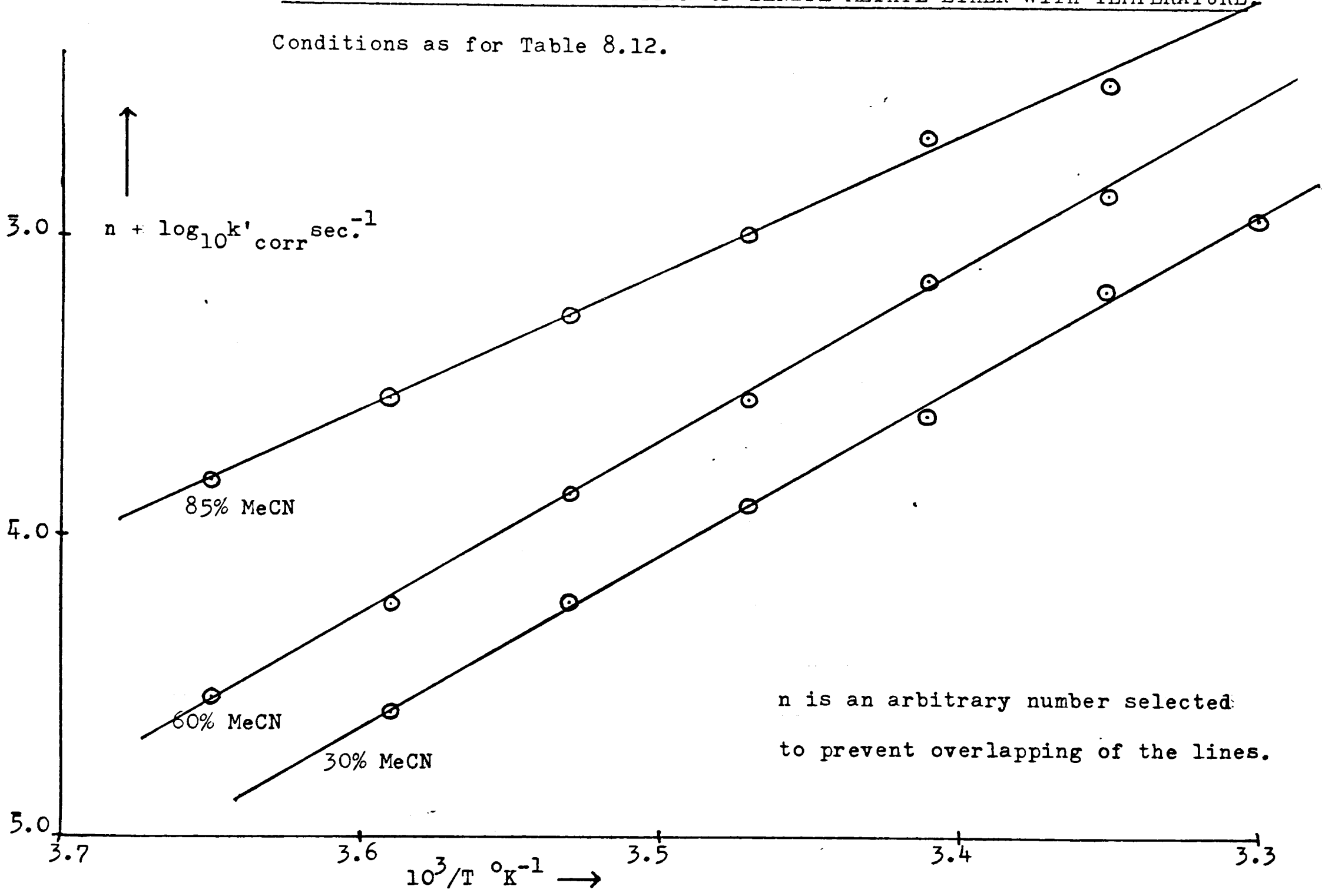


TABLE 8.12. VARIATION OF OXIDATION RATE OF BENZYL METHYL ETHER WITH TEMPERATURE.

$[HClO_4]$ 1.00M. Init. $[Co^{III}]$ ca. 2×10^{-3}M. Init. $[Co^{II}]$ ca. 6×10^{-4}M. μ ca. 1.01M.

A. 85% MeCN. $[PhCH_2OMe]$ 2.90×10^{-2}M.

Temp. °C.	$10^3/T$ °K^{-1}	10^4 initial[a] k'sec.$^{-1}$	10^4k'sec.$^{-1}$ for self-decomp.[a]	10^4k'corr.[b] sec.$^{-1}$	$4+\log_{10}$k'corr.
0.7	3.65	1.90	.38 - .26	1.52	0.182
5.6	3.59	3.2	.35	2.9	0.462
10.3	3.53	6.6	1.1 - 1.0	5.5	0.740
15.2[c]	3.47[c]	-	-	10.2[c]	1.009
20.2	3.41	25.8	3.8 - 2.3	22.0	1.342
25.1	3.35	39.8	6.3 - 4.0	33.5	1.525

Hence E_a = 21 k.cal.mole.$^{-1}$ ΔH^* = 20 k.cal.Mole.$^{-1}$; ΔG^* = 19 k.cal.mole.$^{-1}$ ΔS^* = 6 e.u.

a,b as for Table 8.10.

c. Extrapolated from Table 8.11.

B. 60% MeCN. $[PhCH_2OMe]$ 2.90×10^{-2}M.

0.7	3.65	0.41	.18 - .04	0.23	$\bar{1}$.362
5.6	3.59	0.88	.29 - .13	0.59	$\bar{1}$.771
10.3	3.53	1.90	.53 - .41	1.37	0.137
15.2[d]	3.47[d]	4.8[d]	1.9 - 0.9[d]	2.9[d]	0.462
20.2	3.41	11.0	3.7 - 1.7	7.3	0.863
25.1	3.35	20.8	6.6 - 2.6	14.2	1.152

Hence E_a = 27 k.cal.mole.$^{-1}$ ΔH^* = 27 k.cal.mole.$^{-1}$ ΔG^* = 19 k.cal.mole.$^{-1}$ ΔS^* = 26e.u.

d. Interpolated from Table 8.8.

TABLE 8.12. continued.

C. 30% MeCN. [$PhCH_2OMe$] 9.1 x 10^{-2} M.

Temp. °C.	$10^3/T$ °K^{-1}	10^4 initial[a] k'sec.$^{-1}$	10^4k'sec.$^{-1}$ for self-decomp.[a]	$10^4 k'_{corr}$ sec.$^{-1}$[b]	$4+\log_{10}k'_{corr}$
5.3	3.59	0.95	.13 - .08	0.82	$\bar{1}$.914
10.3	3.53	3.1	1.2 - 0.7	1.9	0.278
15.4	3.47	5.8	1.8 - 0.8	4.0	0.602
20.3	3.41	11.8	3.9 - 1.3	7.9	0.898
25.2	3.35	26.0	5.0 - 3.9	21.0	1.322
29.6	3.30	42.7	6.0 - 1.4	36.7	1.565

Hence E_a = 26 k.cal.mole.$^{-1}$; ΔH^* = 26 k.cal.mole.$^{-1}$; ΔG^* = 20 k.cal.mole.$^{-1}$

ΔS^* = 20 e.u.

A. In 85% MeCN. ΔH^* = 20 k.cal.mole.$^{-1}$ ΔG^* = 19 k.cal.mole.$^{-1}$

ΔS^* = 6 e.u.

B. In 60% MeCN. ΔH^* = 27 k.cal.mole.$^{-1}$ ΔG^* = 19 k.cal.mole.$^{-1}$

ΔS^* = 26 e.u.

C. In 30% MeCN. ΔH^* = 26 k.cal.mole.$^{-1}$ ΔG^* = 20 k.cal.mole.$^{-1}$

ΔS^* = 20 e.u.

These values show the same trend with varying methyl cyanide concentration as was found for the oxidation of toluene, (p.62), and can be interpreted

in a similar fashion. The corresponding values given for oxidation in 60 per cent and 30 per cent methyl cyanide are identical within experimental error.[234,146]

f. Affect of Chloride Ions on the Oxidation of Benzyl Methyl Ether.

Attempts were made to catalyse the oxidation of benzyl methyl ether with chloride ions, (compare refs. 64,66), by progressively replacing perchloric acid in the solution by hydrochloric acid. On addition of cobaltic perchlorate to the reaction solution containing chloride ions, (ca. 0·1M), the solution became immediately a golden yellow colour, and in addition a faint blue tint developed over the next few minutes. There was similar behaviour for blank solutions containing no organic substrate, except in the complete absence of chloride ions when the blank reaction slowly changed normally from blue to pink.

The yellow solution appeared to be quite stable. Its absorption spectrum showed peaks at 238, 314 and 362 mμ and a very faint absorption at 650-700 mμ, in contrast to the spectrum of cobaltic perchlorate (Chapter 5). The bluish tint and the long wave length absorption can be ascribed to cobaltous chloride, which shows a similar absorption in the visible region. It was not due to the production of chlorine gas since this absorbs at about 325 mμ, and the absorption of the solution was not altered by blowing through with nitrogen. The yellow compound appears to be a cobaltic-chloride complex. This has been formed previously as a stable species in flow reactions involving cobaltic ions and chloride ions.[183] The attempts at catalysis of oxidation were hence abandoned.

3. The Oxidation of Benzyl Cyclohexyl Ether.

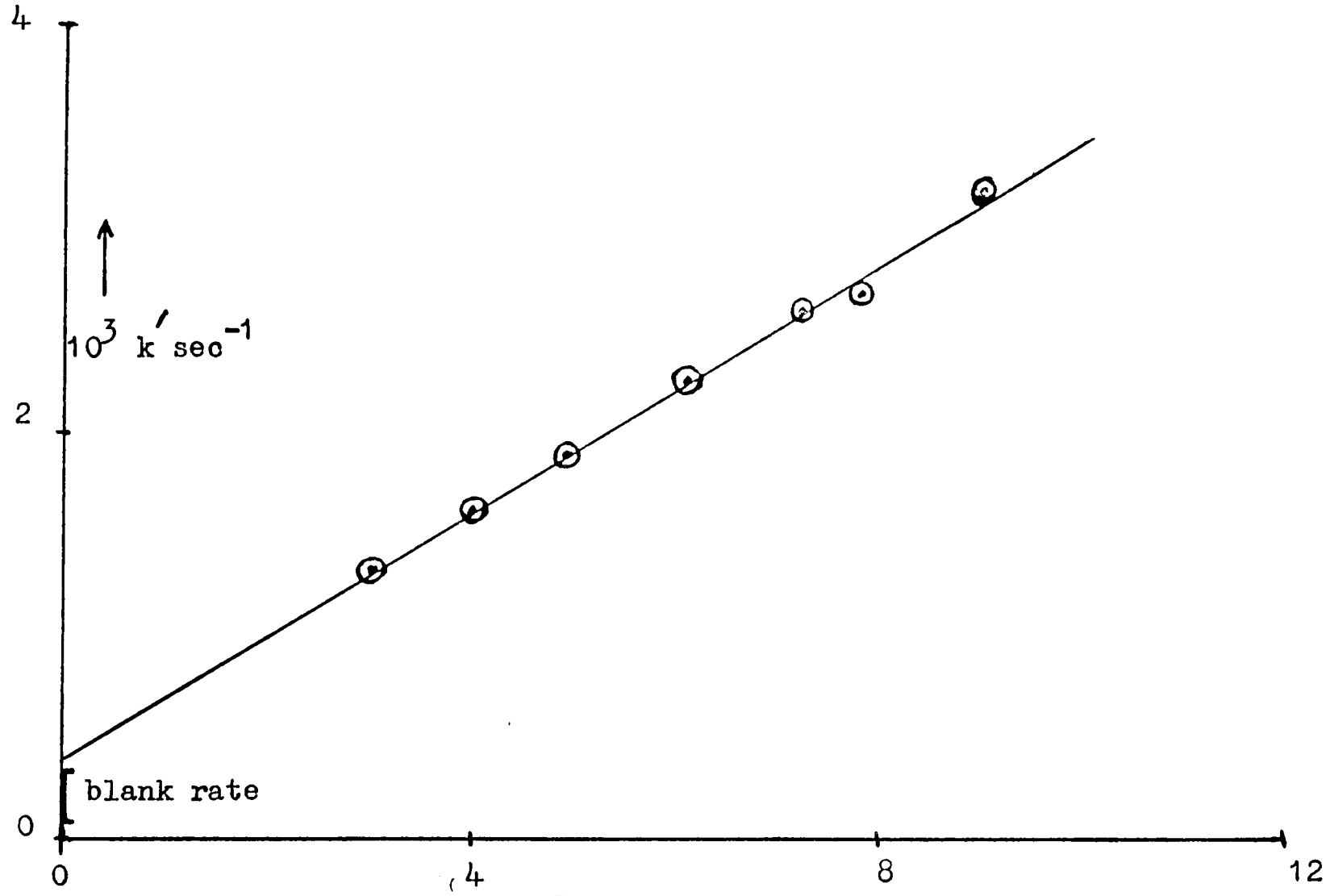
The oxidations of dibenzyl and benzyl methyl ethers described above show a marked difference with regard to ester formation. Hence, investigation was made of the oxidation of $\overset{\alpha}{\wedge}$benzyl ether containing a group of intermediate ability of being eliminated as a free radical. Benzyl cyclohexyl ether was chosen in preference to benzyl isopropyl ether since it was then possible to measure by GLC the oxidation products from both arms of the ether.

a. Order with Respect to Each Reagent.

The rate of oxidation of benzyl cyclohexyl ether was measured at 15° using initial cobaltic concentrations of about 2×10^{-2} M and 2×10^{-3} M. For each set of runs the plots of $-\log_{10}(D-D_{\infty})$ versus time were linear over at least two half lives. Added oxygen had no effect on the initial rates, but caused a marked decrease in rate towards the end of the reaction. Consequently all reactions were carried out under nitrogen, although reactions performed in air did not show this effect.

Table 8.13 shows that at the higher cobaltic ion concentration the reaction rate is first order dependent on substrate concentration. However at the lower initial cobaltic ion concentration, the plot of pseudo first order rate constant against substrate concentration was curved, (Figure 8.14), despite the fact that the individual runs for the ether oxidation were strictly of first order with respect to oxidant.

TABLE 8.13 OXIDATION OF BENZYL CYCLOHEXYL ETHER.



$10^2[PhCH_2OC_6H_{11}]$ M ⟶

15.2° $[HClO_4]$ 1.00M. 60 per cent MeCN. initial $[Co^{III}]$ ca. 2×10^{-2}M. Initial $[Co^{II}]$ ca. 6×10^{-3}M. μ ca. 1.1M Under N_2

$10^2[PhCH_2OC_6H_{11}]$ M	$10^3 k'$ sec^{-1} a	$10^2 k_2$ $l.m^{-1}.sec^{-1}$ b
0.0	.36 - .11 c	-
3.0	1.32	3.2
4.0	1.64	3.2
4.9	1.92	3.2
6.1	2.28	3.1
7.2	2.6	3.1
7.8	2.7	2.9
9.0	3.2	3.1

Best fit line (by least squares): $10^3 k' = 0.42 + 30.3\ [PhCH_2OC_6H_{11}]$

a,b,c as Table 8.2.

However the small change in rate on reducing the initial cobaltic ion concentration by a factor of ten, shown by Tables 8.13 and 8.14, confirms that the reaction is first order with respect to oxidant.

TABLE 8.14 OXIDATION OF BENZYL CYCLOHEXYL ETHER.

$[HClO_4]$ 1.00M. 60 per cent MeCN. initial $[Co^{III}]$ ca. 2×10^{-3}M. initial $[Co^{II}]$ ca. 6×10^{-4}M. μ ca. 1.01M under N_2.

A. 15.2°.

$10^2 [PhCH_2OC_6H_{11}]$ M	$10^3 k'$ sec^{-1} [a]	$10^2 k_2$ l.m.$^{-1}$ sec.$^{-1}$ [b]
0.0	.38 - .18°	-
0.88	0.69	3.5
2.8	1.56	4.2
4.8	2.12	3.6
7.2	2.70	3.2
9.1	3.23	3.1

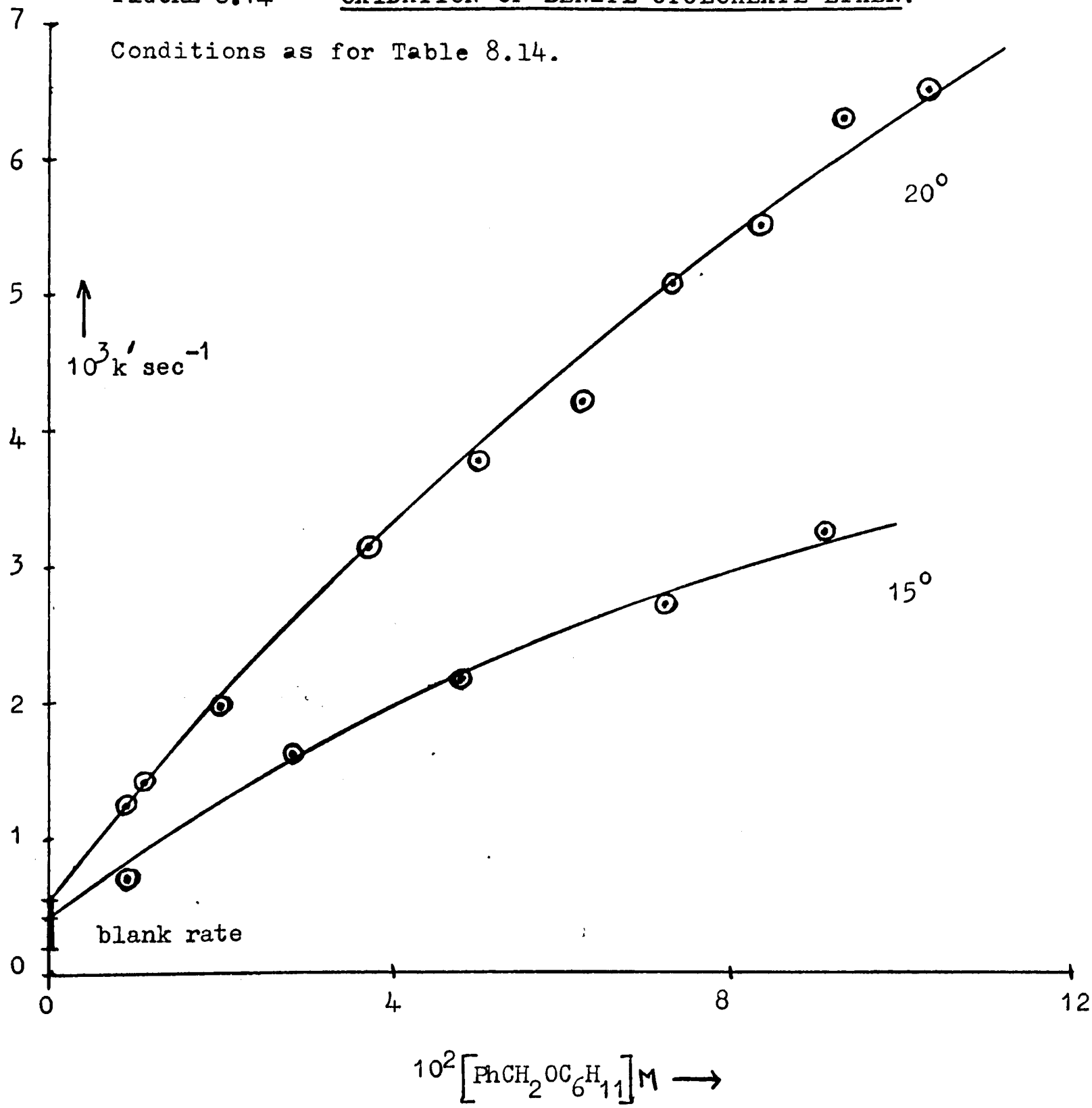
B. 20.2°

0.0	.50 - .17°	-
0.83	1.17	8.1
1.04	1.36	8.3
1.97	1.94	7.3
3.7	3.1	7.1
5.0	3.8	6.6
6.2	4.2	6.0
7.3	5.1	6.3
8.3	5.5	6.0
9.3	6.3	6.2
10.3	6.5	5.8

a,b,c, as for Table 8.2.

FIGURE 8.14 OXIDATION OF BENZYL CYCLOHEXYL ETHER.

Conditions as for Table 8.14.



b. Oxidation Products.

Yields of cyclohexanol, cyclohexanone, benzaldehyde, and benzoic acid are shown in Table 8.15. Blank experiments showed there were appreciable amounts of hydrolysis to benzyl alcohol and cyclohexanol under the reaction conditions; they also showed small amounts of bibenzyl and cyclohexyl benzoate which could not be removed completely from the ether by the purification method employed (Chapter 12). The benzyl alcohol yields obtained

from the oxidation reactions were much smaller than those obtained from the 'blank' reactions, which indicates that benzyl alcohol is not a major reaction intermediate. (Compare Table 8.3). However large amounts of

TABLE 8.15 OXIDATION PRODUCTS FROM BENZYL CYCLOHEXYL ETHER.

Reactions performed under N_2 at 15° in 5 ml. 60 per cent methyl cyanide solution containing 1.0% perchloric acid. 1.71×10^{-5} moles Co^{III} added to each (i.e. initial $[Co^{III}]$ 3.4×10^{-3}M)

$10^2[PhCH_2OC_6H_{11}]$ M	10^6 moles product obtained [a]			
	Cyclohexanone	cyclohexanol	PhCHO	PhCOOH
9.5	1.1	2.1	3.5	.27
7.0	.98	1.8	2.9	.34
4.9	1.1	1.2	2.6	.41
2.9	1.1	.94	2.6	.54

a. No bicyclohexyl was detected, and only small amounts of cyclohexyl benzoate.

$10^2[PhCH_2OC_6H_{11}]$ M	10^6 moles Co^{III} accounted for:		
	as measured products [b]	as self decomp. [c]	Total
9.5	10.3	2.0 - .9	12.3 - 11.2
7.0	9.1	2.4 -1.1	11.5 - 10.2
4.9	9.0	3.0 -1.4	12.0 - 10.4
2.9	9.6	4.1 -1.8	13.7 - 11.4

b. Calculated as (2 PhCHO + 2 cyclohexanone + 4 PhCOOH).

c. Calculated from Tables 8.13 and 8.14 A.

cyclohexanol were obtained, indicating that the primary attack was on the benzylic hydrogen rather than on the cyclohexyl hydrogen.

$$PhCH_2OC_6H_{11} + Co^{III} \longrightarrow \dot{P}hCHOC_6H_{11} \qquad (8.xxi.)$$

This is in agreement with previous work on the attack on this ether by t-butoxy radicals.[184] No correction was made for cyclohexanol and benzyl alcohol produced by hydrolysis, for reasons analogous to these given for the oxidation of dibenzyl ether. (p.112)

The yields of ester obtained from the oxidation reactions were larger than those from the control experiments, showing that ester is produced by the reaction. However, the amounts obtained after correction by the amounts shown by the control runs, were small and erratic and showed only that proportionately much less ester was formed than from the oxidation of benzyl methyl ether.

The amount of oxidant unaccounted for in Table 8.15 may be partly consumed by the production of the small amount of ester formed, and also by further oxidation of the cyclohexanone, since the measured products from the aliphatic arm of the ether are invariably less than those from the aromatic arm.

The product studies in Table 8.15 were performed under similar conditions of $^{C}o/$ [substrate] to the kinetic measurements shown in Table 8.14a. It is not possible from the measurements to accurately calculate the stoichiometry of the reaction, but there are marked changes in secondary oxidation with changes in ether concentration and so the variation of the derived second order rate constant with substrate concentration would be analogous to the behaviour found for the oxidation of aromatic

hydrocarbons. However, with these latter oxidations variation of the second order rate constant with substrate concentration was generally accompanied by deviation from first order dependence with respect to oxidant. This did not occur for the oxidation of benzyl cyclohexyl ether. The oxidation of benzyl methyl ether, in contrast, showed deviations from strict first order dependence with respect to oxidant, yet the second order rate constant did not vary with substrate concentration.

An approximate calculation for the production of cyclohexanol can be made using an equivalent equation to equation 6.xvi. k_b for the reaction: $C_6H_{11}OH + 2Co^{III} \xrightarrow{2k_b} C_6H_{10}O + 2Co^{II} + 2H^+$ (8.xxii.) was taken as 0.9 $l.m.^{-1}sec.^{-1}$ (extrapolated from data given in ref.10), and the average stoichiometry for the oxidation of benzyl cyclohexyl ether, under the conditions of Table 8.15. , was assumed to be between 3 and 5. These calculations, (Table 8.16.), show that under the conditions used for Table 8.15., a stationary state concentration of cyclohexanol is unlikely to have been attained, even at the lowest substrate concentration. However, for the kinetic runs at the higher initial cobaltic ion concentration, shown in Table 8.13., a stationary state concentration of cyclohexanol should be attained during the course of the oxidation.

Since a stationary state concentration of cyclohexanol is not likely to be reached under the conditions of Table 8.15.,

TABLE 8.16. CALCULATED PRODUCT YIELDS FROM THE OXIDATION OF BENZYL CYCLOHEXYL ETHER.

$10^2[PhCH_2OC_6H_{11}]$ M	$10^3[Co^{III}]$ M required to reach stationary state in cyclohexanol [a,b]	10^4[Cyclohexanol] M calc. stationary conc. [a,c]	measured final conc. [d]
9.5	14.6 ± 4.1	8.9 ± 2.5	4.2
7.0	11.3 ± 3.3	6.9 ± 2.0	3.6
4.9	8.9 ± 2.7	5.4 ± 1.6	2.4
2.9	6.5 ± 2.1	4.0 ± 1.3	1.9

a. Uncertainty caused by uncertainty in average stoichiometry.

b. This figure makes no allowance for the quantity of oxidant which will be concurrently consumed by self-decomposition.

c. Calculated as $(k_a[ether]/0.9)$M.

d. Derived from Table 8.15.

$10^2[PhCH_2OC_6H_{11}]$ M	10^4[PhCHO] M. calc. stationary conc. [e,a]	Measured final conc. [d]	10^3[Cyclohexanone] M calc. stat. conc. [a,f]	Meas.fin. conc. [d]
9.5	40 ± 10	7.0	80 ± 20	.22
7.0	34 ± 11	5.8	62 ± 16	.20
4.9	25 ± 7	5.2	47 ± 12	.22
2.9	18 ± 4	5.2	35 ± 7	.22

e. Calculated as $(k_a[ether]/.2)$M.

f. Calculated as $(k_a[ether]/10^{-2})$M. $k_b = 10^{-2}$ l.mol^{-1}.sec^{-1} extrapolated from ref. 144

it is even less likely to be reached for the other oxidation products, all of which are more slowly oxidised than cyclohexanol. Table 8.16 shows that the yields of the other products are well below the theoretical maxima.

c. Dependence of the Oxidation Rate of Benzyl Cyclohexyl Ether on Perchloric Acid Concentration.

This dependence was investigated in 60 per cent methyl cyanide solution at an ionic strength of 2.17M. The plots of $-\log_{10}(D-D_{\infty})$ versus time were again linear over two half lives, and showed no systematic change of curvature with acidity change. Fig. 8.17 shows that the pseudo first order rate constants follow the expression:

$$10^3 k'_{corr} = 5.10/[H^+] - 1.79 \qquad (8.xxii)$$

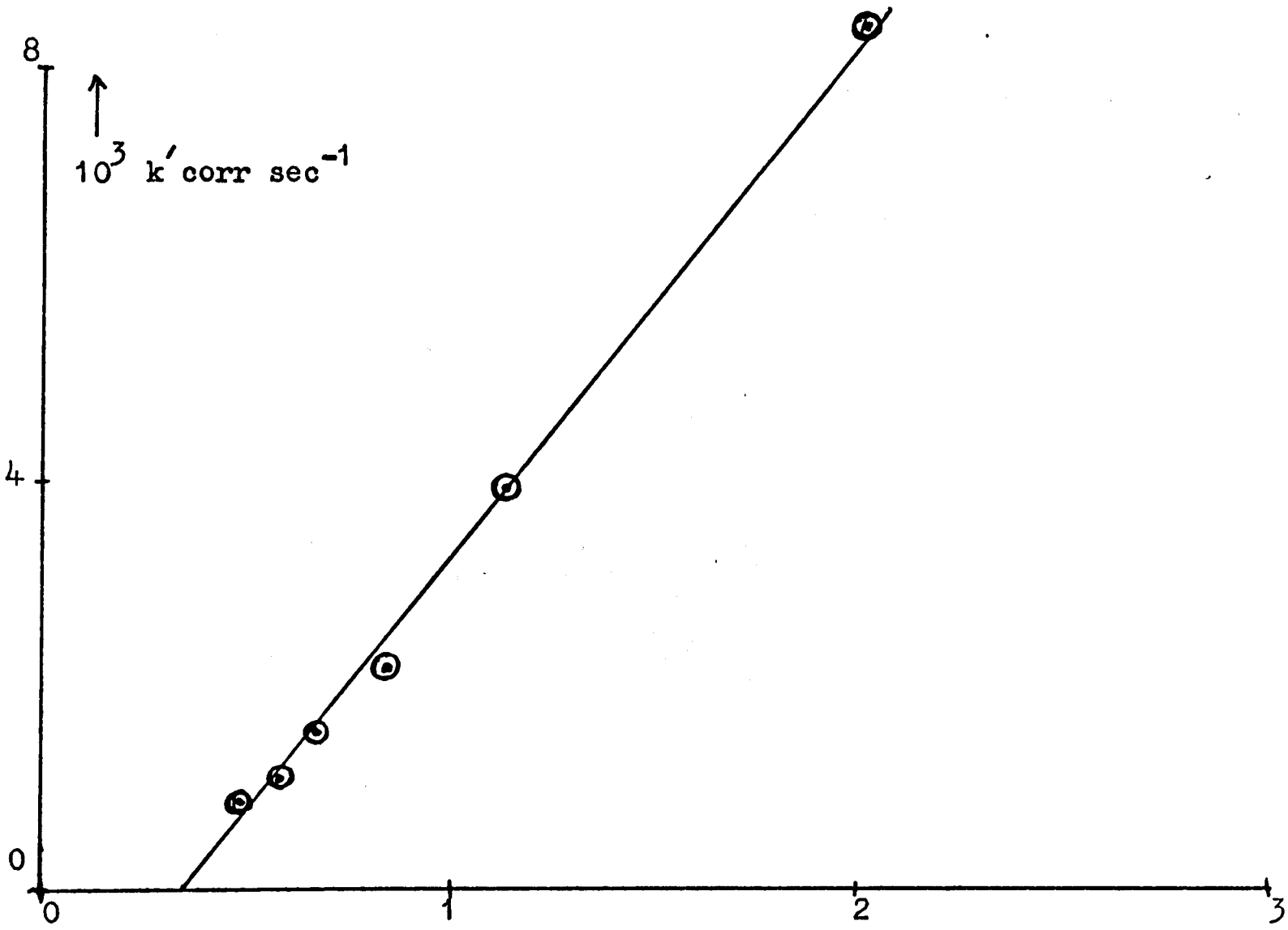
under the conditions given.

d. Variation of the Rate of Oxidation of Benzyl Cyclohexyl Ether with Methyl Cyanide Concentration.

Table 6.18 shows that there is again an increase in oxidation rate with increasing methyl cyanide concentration. Only a very limited range of cosolvent concentration could be investigated, due to the insolubility of the substrate.

No attempt was made to investigate the oxidations of α-substituted benzyl ethers, since these are known to be hydrolysed very much more easily than are benzyl ethers.[179]

TABLE 8.17 VARIATION OF OXIDATION RATE OF BENZYL CYCLOHEXYL ETHER WITH ACIDITY.



15.2° 60 per cent MeCN. $[PhCH_2OC_6H_{11}]$ = 4.8 x 10^{-2}M. Initial $[Co^{III}]$ ca. 2x10^{-3}M. Initial $[Co^{II}]$ ca. 6 x 10^{-3}M. μ ca. 2.17M.

$[HClO_4]$M.	$1/[HClO_4]M^{-1}$	10^3 k′ sec^{-1} [a]	10^3 k′ sec^{-1} for self-decomp. [b]	10^3 k'_{corr} sec^{-1} [c]
2.14	0.47	1.21	.36 - .21	0.85
1.79	0.56	1.50	.40 - .13	1.10
1.49	0.67	2.01	.43 - .26	1.58
1.20	0.83	2.84	.64 - .51	2.20
0.89	1.12	4.77	.79 - .36	3.98
0.50	2.0	9.7	1.2 - .9	8.5

a,b,c as Table 8.7.

Best fit line (by least squares): $10^3 k'_{corr} = -1.79 + 5.10/[H^+]$

TABLE 8.18 VARIATION OF OXIDATION RATE OF BENZYL CYCLOHEXYL ETHER WITH METHYL CYANIDE CONCENTRATION.

20.2°. $[HClO_4]$ 1.00M. $[PhCH_2OC_6H_{11}]$ 6.2×10^{-3}M. Initial $[Co^{III}]$ ca. 2×10^{-3}M. Initial $[Co^{II}]$ ca. 6×10^{-4}M. μ ca. 1.01M.

% MeCN	10^3 k' sec.$^{-1}$ [a]	10^3 k' sec^{-1} for self-decomp. [b]	10^3 k'_{corr} sec^{-1}. [c]
60[d]	4.2[d]	.50 - .17[d]	3.7[d]
68	7.0	.60 - .25	6.4
77	13.1	.77 - .35	12.3

a,b,c as Table 8.17

d. Taken from Table 8.14b.

4. Further Discussion.

The oxidations of all the three ethers investigated are essentially of the first order order with respect to both substrate and oxidant, and there is direct attack on the ether molecule by a cobaltic ion. Varying amounts of secondary oxidation of the primary oxidation products occur, but there appears to be no correlation between this, and the curvatures of the plots of $-\log_{10}(D-D_{\infty})$ versus time, and the variation of the derived second order rate constants with substrate concentration.

It is difficult to make any accurate comparison of the initial rates of attack on the ether molecules since the stoichiometries of the reactions are not known well enough. However the second order rate constants for the overall oxidations are:

$PhCH_2OC_6H_{11}$ 3.0×10^{-2} l.m.$^{-1}$sec.$^{-1}$; $PhCH_2OCH_2Ph$ 2.4×10^{-2} l.m.$^{-1}$sec.$^{-1}$ and

$PhCH_2OMe$ 0.94×10^{-2} l.m.$^{-1}$sec.$^{-1}$ These figures should be compared with the second order rate constants of 2.4×10^{-3} l.m.$^{-1}$sec.$^{-1}$ for the oxidation of bibenzyl, and ca. 100 l.m.$^{-1}$sec.$^{-1}$ for the oxidation of benzyl alcohol, under these conditions.

The product from the initial oxidative attack appears to be the radical $PhC^{\bullet}HOR$. This is in agreement with the attack on benzyl ethers by $Br^{\bullet}$,[185] $CCl_3^{\bullet}$,[185] $ROO^{\bullet}$,[186] $Bu^tO^{\bullet}$[185] and $Cl^{\bullet}$[232] radicals, all of which abstract an α hydrogen atom to give, eventually, the corresponding aldehydes. The relative rates of attack of some of these radicals on a series

of ethers, and on toluene and ethyl benzene, are shown in Table 8.19.

TABLE 8.19 RELATIVE RATES OF RADICAL ATTACK ON AROMATIC HYDROCARBONS AND ETHERS.

	H abstraction by:[185,187]		
	$Br^{\bullet}$ [a]	$^{\bullet}CCl_3$ [a]	$Bu^tO^{\bullet}$
PhMe	0.03	0.01	
PhEt	0.27	0.06	
$PhCH_2OMe$	1.0	1.0	1.0
$PhCH_2OEt$	1.1	1.3	1.1
$PhCH_2OPr^i$	1.5	1.3	1.3
$PhCH_2OBu^t$	1.7	1.8	1.8
$PhCH_2OCH_2Ph$	0.8	1.3	1.0

a. See also ref. 236.

It can be seen that there is some similarity between the reactivity series towards radical attack and towards oxidation by cobaltic perchlorate.

It has been suggested[187,188,189] that radical attack on benzyl ethers is governed by the stability of the intermediate radical formed. Extensive studies by Huang of the attack of t-butoxy radicals on a series of benzyl ethers showed that the $PhCHOR^{\bullet}$ radical was the primary product, which could then either dimerise, or decompose to benzaldehyde and $R^{\bullet}$ [184,190] The tendency to form dimers depended on the stability of $R^{\bullet}$. Thus there was mostly dimer formation when R was Me or Ph, and mostly decomposition when R was $PhCH_2$, Ph_2CH, or Bu^t, and both processes occurred when R was Et or Pr^i. This work was carried out using the neat ethers. Lovins, Andrews and Keeler,[185]

found, in contrast, that the attack of $Br^{\bullet}$, $CCl_3^{\bullet}$ and $Bu^tO^{\bullet}$ radicals on benzyl ethers in carbon tetrachloride solution gave only the decomposition products and no dimer, and that the benzaldehyde yield was insensitive to the nature of R. The present work shows results intermediate between the two types of behaviour described above, since esters were obtained in amounts varying with the nature of R, but much less ester was obtained than the amount of dimer found by Huang.

These results indicate that an outer sphere mechanism of oxidation , by direct attack on the benzylic $-CH_2-$ group is possible. Abstraction of an electron directly from the ring is also possible, since this could be concerted with the formation of the $PhC^{\bullet}HOR$ radical, or with elimination of the $R^{\bullet}$ radical. The much faster oxidation of the benzyl ethers, than the corresponding hydrocarbons, indicates that the ether oxygen atom is involved in the process, possibly by stabilising the incipient ether radical.[187]

An inner sphere mechanism is also possible, although unlikely. Aromatic ethers are known to complex via the oxygen atom rather than via the benzene ring.[191] However, ethers are in general very weak complexing agents, much weaker than are alcohols and water.[192] Although ether complexes are known, they are highly deliquescent, and immediately decomposed by water, except for some dioxan complexes which have been isolated from aqueous solution.[193]

In contrast to the oxidation of benzhydrol. (p.81), the oxidations of the benzyl ethers appears to be little influenced by steric effects. Also the rates of oxidation are slower by a factor of 10^4 than that of benzyl alcohol, which is thought to be oxidised by an inner sphere mechanism. This suggests that the benzyl ethers are oxidised by an outer sphere mechanism similar to that for the oxidation of the aralkyl hydrocarbons. (Chapter 6). The steric strain in a cobaltic-benzyl ether complex would be much greater than that in a similar complex of an alcohol.

5. <u>The Oxidation of Diphenyl Ether.</u>

The oxidation of diphenyl ether was attempted for comparison with the oxidations of benzyl ethers, and of aromatic hydrocarbons. (Chapter 6). Kinetic study was only possible at low substrate concentrations, since, in 60 per cent methyl cyanide solution, at substrate concentrations greater than 1.3×10^{-2}M, a brown precipitate was formed during the course of the reaction, although the substrate was itself fairly soluble in these solutions. Plots of $-\log_{10}(D-D_{\infty})$ versus time were approximately linear over two half lives, and the pseudo first order rate constants varied linearly with substrate concentrations. (Table 8.20).

Bright yellow solutions are formed, as well as the brown precipitate, and the yellow colour was most intense at the highest substrate concentration. The yellow colour was extracted into dichloromethane, but its absorption

TABLE 8.20 OXIDATION OF DIPHENYL ETHER

15°. 60 per cent MeCN $[HClO_4]$ 1.00M. Initial $[Ce^{III}]$ ca. 3×10^{-3}M. Initial $[Ce^{II}]$ ca. 1×10^{-3}M. μ ca. 1.02M.

10^2 [PhOPh]M.	10^4 k′ sec.$^{-1}$ [a]	10 k_2 l.m.$^{-1}$ sec.$^{-1}$ [b]
0.0	1.2 - 0.60[c]	-
0.50	6.4	1.03
0.81	8.8	.94
1.21	12.8	.96

Best fit line (by least squares): 10^4 k′ = 1.72 + 906 [PhOPh] .

a. Measured graphically over two half lives.

b. Calculated taking k′ self decomp. = 1.2×10^{-4} sec.$^{-1}$

c. Measured graphically.

spectrum showed only a weak maximum at 345mμ, and no other peaks not present in the spectrum of the extract of a blank solution containing cobaltous perchlorate and substrate. The infra-red spectrum of diphenyl ether showed peaks in the 1600 cm^{-1} region which would obscure the absorption of any quinone produced and the I.R. spectrum of the extract in dichloromethane showed no peaks not shown by a solution of the substrate in dichloromethane.

The brown precipitate was found to be insoluble in all the common solvents, and was presumed to be polymeric.[229] No attempt was made to characterise the oxidation products.

The second order rate constant for the oxidation of diphenyl ether is greater than that for the oxidation of biphenyl under similar conditions, and much higher than those for the benzyl ethers. However, it is not possible to make exact comparison of the relative rates of initial attack, since the steichiometries of the reactions are not known. The most likely route for the oxidation, by analogy with biphenyl, is direct abstraction of an electron from a π-orbital, to form a radical cation which can be hydrated and oxidised further.

Diphenyl ether is not cleaved by acid under the most stringent conditions,[179] and so is unlikely to hydrolyse in the present case.

CHAPTER 9. THE OXIDATION OF SOME ALIPHATIC ETHERS.

1. The Oxidation of Di-isopropyl Ether.

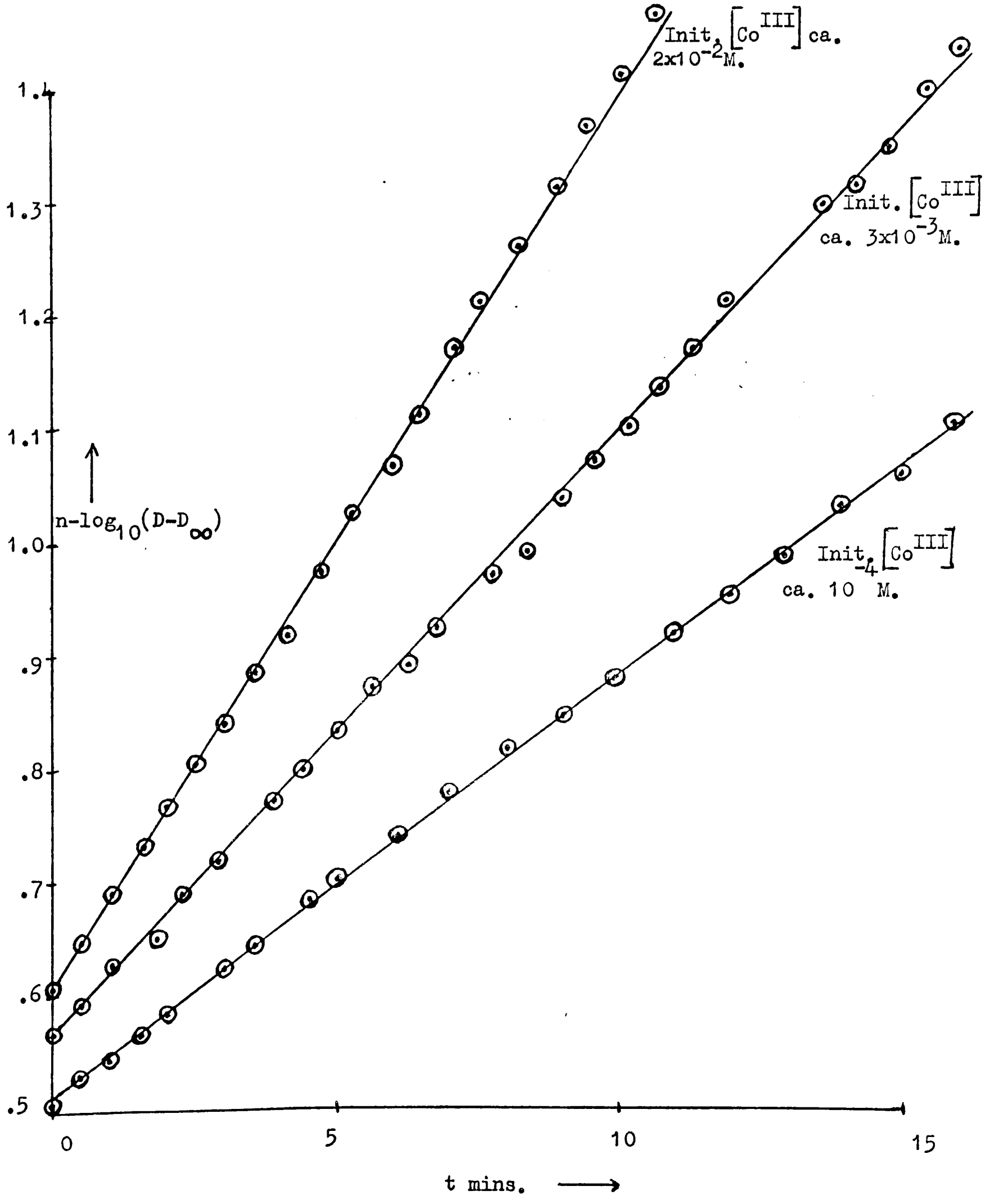
The oxidation of di-isopropyl ether by cobaltic perchlorate was investigated for comparison with its oxidation by chromic acid,[101] (Chapter 4), since this is the only previously reported mechanistic study of the oxidation of an ether by a transition metal ion.

a. Order with Respect to each Reactant.

The oxidation rate of di-isopropyl ether was found to be first order with respect to cobaltic ions over at least two half-lives. Fig. 9.1 shows that this first order dependence holds over the range of initial cobaltic ion concentration from 10^{-4}M to 2×10^{-2}M. However, at the higher initial cobaltic concentration the reaction accelerates slightly after about two half lives, especially at low ether concentrations. This can be ascribed to the greater amount of secondary oxidation occurring with higher initial concentrations of oxidant. The rates of reaction using higher initial cobaltic ion concentrations were followed spectrophotometrically at 595-605 mμ., as before. However, the runs using 10^{-4}M initial oxidant concentration were followed at 240 mμ., and, once it had been confirmed that these reactions were of the first order with respect to oxidant, they were often analysed kinetically by the Guggenheim method[194] to avoid the long wait for the reaction to come to completion.

FIGURE 9.1 REPRESENTATIVE FIRST ORDER PLOTS FOR THE OXIDATION OF DI-ISOPROPYL ETHER.

Conditions as for Table 9.2



The variation of the pseudo-first order rate constant with ether concentration is shown in Fig. 9.2. In contrast to the first order dependence on cobaltic ion concentration found from the individual runs, these rate constants increase with increasing initial cobaltic ion concentration, and the derived second order rate constants also decrease sharply with increasing ether concentration.

The rate of oxidation was not affected by added oxygen, nor by light of either of the two wave lengths used for following the reaction.

b. Oxidation Products.

Yields of acetone from the oxidation were measured by a modification of the Behre-Benedict salicylaldehyde method, described in Chapter 10. These measurements (Table 9.3), indicate that acetone is a major oxidation product. Hence the general oxidative sequence is:

$$Pr^iOPr^i + Co^{III} \xrightarrow{k_a} Me_2\dot{C}OPr^i + Co^{II} + H^+ \qquad (9.i.)$$

$$Me_2\dot{C}OPr^i \xrightarrow{k_b} Me_2CO + Pr^i\cdot \qquad (9.ii.)$$

$$Pr^i\cdot + Co^{III}H_2O \xrightarrow{k_c} Pr^iOH + Co^{II} + H^+ \qquad (9.iii)$$

Reactions 9.i and 9.ii could be concerted.

The ether radical $Me_2\dot{C}OPr^i$ has been detected in flow systems from the attack of hydroxyl radicals on di-isopropyl ether.[99,196] This implies that the radical is relatively long-lived in solution, before breaking down as in equation 9.ii. Such ether radicals are also known to

Fig. 9.2. THE OXIDATION OF DI-ISOPROPYL ETHER.

Conditions as Table 9.2.

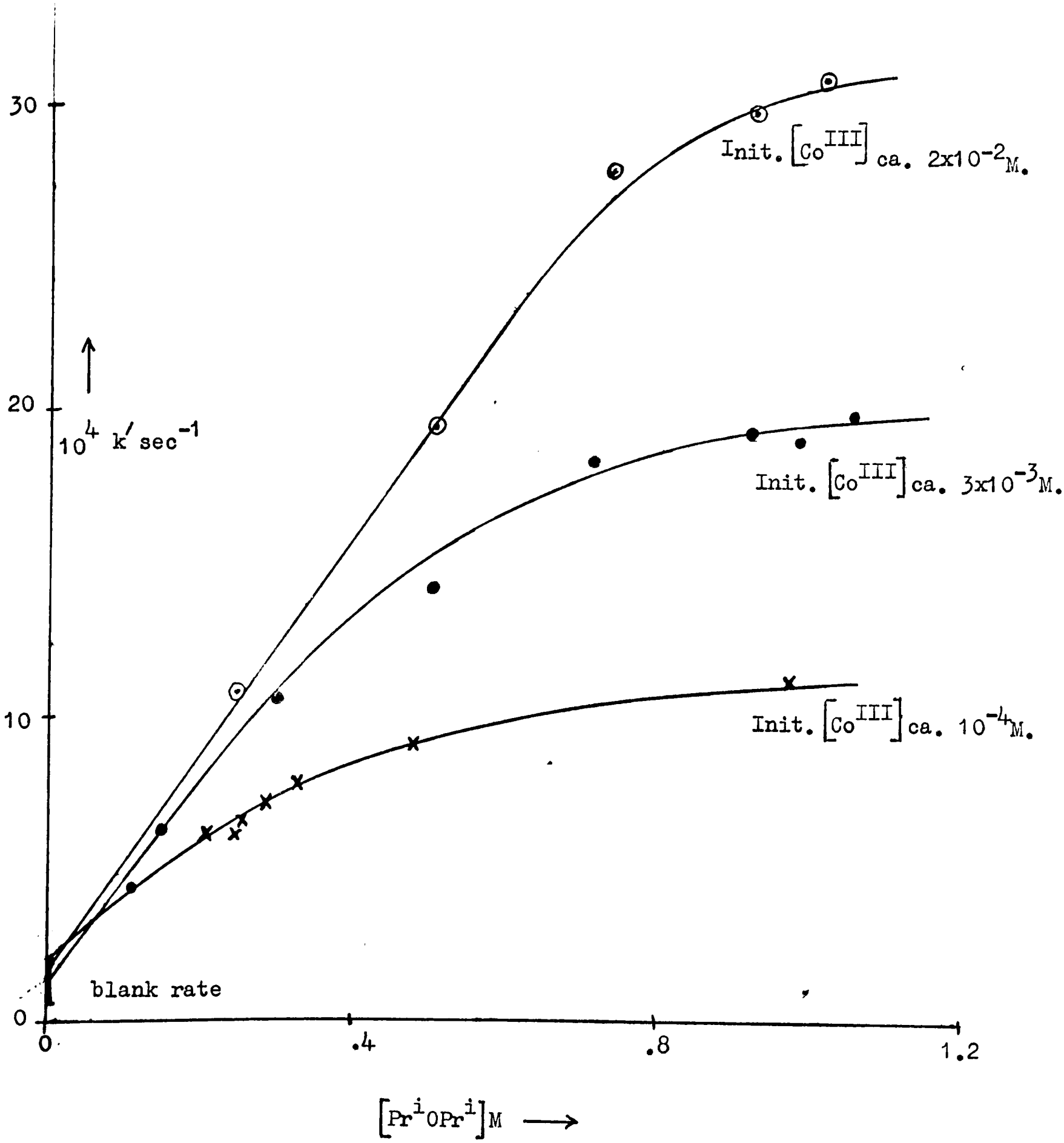


TABLE 9.2. THE OXIDATION OF DI-ISOPROPYL ETHER

15°C. 50 per cent MeCN (v/v). $[HClO_4]$ 1.00M.

A. Initial $[Co^{III}]$ ca. 2×10^{-2}M. Initial $[Co^{II}]$ ca. 6×10^{-3}M			B. Initial $[Co^{III}]$ ca. 3×10^{-3}M Initial $[Co^{II}]$ ca. 1×10^{-3}M			C. Initial $[Co^{III}]$ ca. 10^{-4}M. Init. $[Co^{II}]$ ca. 3×10^{-5}M.		
$[Pr^iOPr^i]$M	$10^4k'$ sec^{-1} [a]	10^3k_2l.m.$^{-1}$sec^{-1} [b]	$[Pr^iOPr^i]$M	$10^4k'$ sec^{-1} [a]	10^3k_2l.m.$^{-1}$sec^{-1} [c]	$[Pr^iOPr^i]$M	$10^4k'$ sec^{-1} [a]	10^3k_2l.m.$^{-1}$sec^{-1} [d]
0.0	1.6 - .8	-	0.0	1.2 - .7	-	0.0	2.0 - 1.6	-
.24	10.8	3.8	.10	4.4	3.2	0.0	2.0 - 1.4	-
.50	19.6	3.6	.14	6.2	3.6	.20	6.1	2.0 - 2.4
.73	28	3.6	.29	10.6	3.2	.24	6.1	1.7 - 2.0
.92	30	3.0	.50	14.2	2.6	.25	6.5	1.8 - 2.0
1.05	31	2.8	.71	18.5	2.4	.28	7.1	1.8 - 2.0
			.92	19.4	2.0	.32	7.8	1.8 - 2.0
			.98	19.2	1.8	.48	9.1	1.5 - 1.6
			1.05	20.0	1.8	.97	11.1	.94 -1.0

a. Measured graphically over two half-lives

b. Calculated from previous column taking k' self-decomp. = 1.6×10^{-4} sec^{-1}

c. Calculated from previous column taking k' self-decomp. = 1.2×10^{-4} sec^{-1}.

d. Calculated from previous column taking highest and lowest self-decomp. rates.

decompose only slowly in the gas phase.[197,198] Hence there is likely to be competitive oxidation of the ether radical:

$$Me_2\dot{C}\text{-}OPr^i + Co^{III}H_2O \xrightarrow{k_d} Me_2C(OH)\text{-}OPr^i + Co^{II} + H^+ \qquad (9.iv.)$$

This is analogous to the scheme previously postulated for the oxidation of benzyl ethers.

Further oxidation of the isopropanol can also occur:

$$Pr^iOH + 2Co^{III} \xrightarrow{2k_e} Me_2CO + 2Co^{II} + 2H^+ \qquad (9.v.)$$

Measurements of the rate of oxidation of isopropanol under similar conditions are shown in Table 9.4. The reaction is first order with respect to both substrate and oxidant. From the above scheme, the yield of isopropyl alcohol must be $\leq \left[\frac{C_e}{2}\right]$. Taking the value for k_2 given in Table 9.4., this shows that for the lowest initial cobaltic ion concentrations employed, 10^{-4}M, secondary oxidation of the isopropanol should be negligible, while at the highest cobaltic ion concentration there should be considerable amounts of secondary oxidation. Similar calculations show that the secondary oxidation of acetone is negligible for all the initial cobaltic ion concentrations employed. k_2 for the oxidation of acetone was taken as 2×10^{-4} $l.m.^{-1}sec.^{-1}$, (extrapolated from ref 199). Table 9.5 shows that a stationary state with respect to isopropanol is unlikely to be attained, even at the highest initial cobaltic ion concentration employed in the present work. However, the occurrence of appreciable amounts of secondary oxidation at high initial cobaltic ion concentrations may explain, in part, the

TABLE 9.4. OXIDATION OF ISO-PROPANOL.

15° $[HClO_4]$ 1.00M. 45 per cent. MeCN initial $[Co^{III}]$ ca. 10^{-4}M. μ ca. 1.00M.

$10^2[Pr^iOH]$M.	10^3 k' sec^{-1}	10 k_2 l.m.$^{-1}$ sec^{-1}
0.0	.29 - .26	-
.92	2.8	2.7
2.0	5.4	2.6
3.7	10.0	2.6

mean k_2 = 0.26 l.m.$^{-1}$ sec^{-1}.

TABLE 9.5. CALCULATED AMOUNTS OF OXIDANT REQUIRED TO ATTAIN A STATIONARY CONCENTRATION OF ISOPROPANOL.

$[Pr^iOPr^i]$M.	10^4 k_a[ether] sec^{-1} [a]	$10^2[Co^{III}]$M. Calc. for [b] attainment of stationary state.
.20	2.0	2.2
.24	2.0	2.2
.25	2.2	2.4
.28	2.6	2.8
.32	2.9	3.2
.43	3.6	3.9
.97	4.6	5.0

a. Calculated from Table 9.2.e. taking mean stoichiometry = 2.

b. Calculated from $C_o - C = 16.4\ \frac{k_a[ether]}{k_e}$ where k_e ca. 0.15 l.m.$^{-1}$ sec^{-1} c.f. equation 6.xvi.

variation of pseudo-first order rate constants with initial oxidant concentration.

From the above kinetic scheme the ratio $C_o/$[acetone produced] should

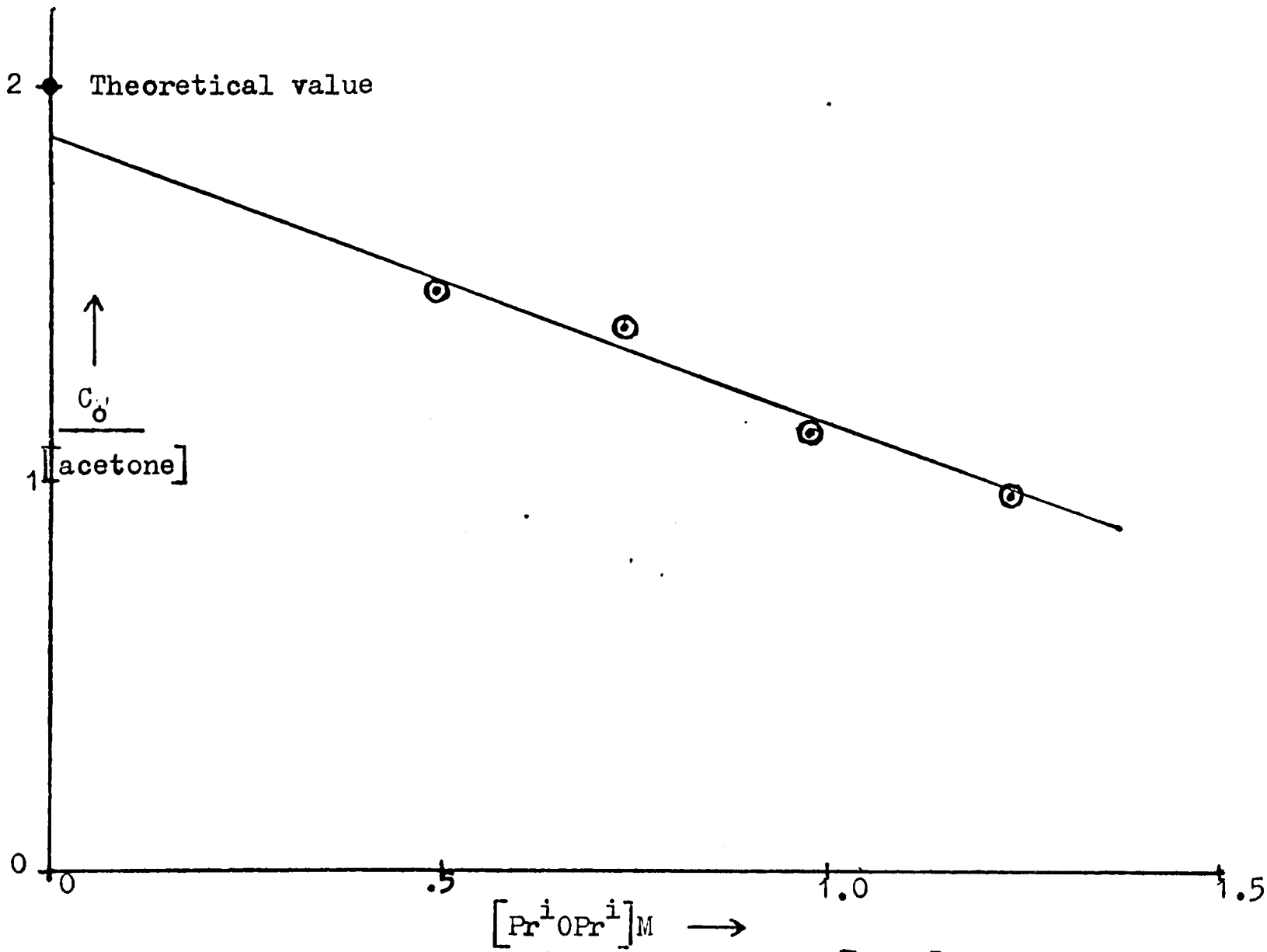
remain constant at 2, with varying ether concentration. This should be true whether there is secondary oxidation of the isopropanol or not. However, Table 9.3. shows that the measured $\delta/[\text{acetone}]$ ratio is always less than 2, and decreases approximately linearly with increasing ether concentration. Extrapolation of these values to zero ether cuts the axis at about the theoretical value of 2. This indicates that there is some other reaction, involving the ether, which produces acetone without consumption of cobaltic ions. Blank experiments, using cobaltous perchlorate and substrate, and using cobaltic perchlorate but no substrate, were performed for all the product measurements shown in Table 9.3, and showed this enhanced yield was not due either to autoxidation of the ether, or to oxidation of the solvent system. Nor was it due to peroxides in the system, since only ether free from all peroxides was used, (Chapter 11), and a check oxidation of an old sample of ether, (which contained peroxides), produced a much smaller yield of acetone, although the oxidation rate was much higher.

Hence there is probably a short regenerative chain:

$$Pr^{i\bullet} + Pr^{i}OPr^{i} \xrightarrow{k_f} Me_2\dot{C}OPr^{i} + C_3H_8 \qquad (9.vi)$$

This is an internal induced oxidation of the isopropyl ether. (c.f. Chapter 7). Similar reactions have been postulated to explain the production of hydrocarbons from the radiolysis of ethers,[200] and could also explain the production of propane in the thermal decomposition of di-isopropyl ether catalysed by isopropyl iodide or iodine.[201]

TABLE 9.3. ACETONE YIELDS FROM THE OXIDATION OF DI-ISOPROPYL ETHER.



Reactions performed in 2 ml. 15°. 50 per cent MeCN $[HClO_4] = 1.00M$.
4.7×10^{-5} moles Co^{III} added in each case i.e. init. $[Co^{III}]$ $2.34 \times 10^{-2}M$.

$[Pr^iOPr^i]M$.	$10^2[Me_2CO]M$ produced	$10^2[Co^{III}]M$ consumed by self-decomp.	$\frac{[Co^{III}]\text{ consumed by ether}}{[Me_2CO]\text{produced}}$
1.22	2.29	.12	.97
.97	1.97	.12	1.13
.73	1.57	.14	1.40
.49	1.46	.19	1.47

Best fit line (by least squares): $C_o/[Me_2Co] = 1.86 - 0.73[Pr^iOPr^i]$.

The chain propagation step, 9.vi, must compete with further oxidation of the isopropyl radical, (equation 9.iii). However, such a scheme should still show first order kinetics with respect to both substrate and oxidant, if secondary oxidation of the isopropanol is ignored:

$$-dC/dt = k_a C\left[Pr^iOPr^i\right] + k_d C\left[Me_2\dot{C}OPr^i\right] + k_e C\left[Pr^i\right] \qquad (9.vii.)$$

$$\frac{d\left[Me_2\dot{C}OPr^i\right]}{dt} = k_a C\left[Pr^iOPr^i\right] - k_d C\left[Me_2COPr^i\right] - k_b\left[Me_2\dot{C}OPr^i\right]$$

$$+ k_f\left[Pr^{i\bullet}\right]\left[Pr^iOPr^i\right] = 0 \qquad (9.viii)$$

$$\frac{d\left[Pr^{i\bullet}\right]}{dt} = k_b\left[Me_2\dot{C}OPr^i\right] - k_e C\left[Pr^{i\bullet}\right] - k_f\left[Pr^{i\bullet}\right]\left[Pr^iOPr^i\right] = 0 \qquad (9.ix.)$$

Hence $k_a C\left[Pr^iOPr^i\right] - k_d C\left[Me_2\dot{C}OPr^i\right] - k_e C\left[Pr^{i\bullet}\right] = 0 \qquad (9.x.)$

and $$\frac{-dC}{dt} = 2\,k_a C\left[Pr^iOPr^i\right] \qquad (9.xi.)$$

This is in agreement with the observed first order dependence on cobaltic ion concentration found from the individual reaction runs.(Fig. 9.1) It does not explain the variation of rate constant with initial cobaltic concentration shown in Fig. 9.2. However the rate constant increases at the most by a factor of 3 when the initial cobaltic ion concentration increases by a factor of 200. Hence the individual log plots would not deviate appreciably from linearity.[214] The cause of the decrease in rate constant with increase in ether concentration is not known. The values given in Table 9.2. fit neither a Michaelis-Menten dependence nor a half-order dependence

on ether. Di-isopropyl ether is not known to complex transition metal ions strongly in aqueous solution,[193] (although complexes are known for dioxan), and the hydrolysis of di-isopropyl ether is much slower than that of the benzyl ethers.[179,202] (Chapter 8).

The production of acetone from the oxidation was confirmed by preparing the 2,4-dinitrophenylhydrazone (Chapter 10), purifying by thin layer chromatography and then recrystallising from chloroform/60°-80° petrol. Orange crystals were obtained, melting sharply at 124°. An authentic sample melted at 126.5° and the mixed melting point was 125-126°. The 'blank' solution with cobaltous perchlorate instead of cobaltic, gave a very weak 'acetone' band in comparison, and recrystallisation of this gave a product melting over a wide range.

Attempts made to analyse the products by gas chromatography failed since the large amounts of di-isopropyl ether and methyl cyanide present obscured any acetone and isopropanol respectively which were formed. However, no products with longer retention times were observed, indicating that there is little isopropyl acetate formed.

Attempts made to trap the intermediate radicals failed since acrylamide was oxidised faster than the ether under the conditions of Table 9.2., and also m-dinitrobenzene, and s-trinitrobenzene were too insoluble to be employed as radical traps.

From equations 9.i to 9.vi.

$$+\frac{d[Me_2CO]}{dt} = [Me_2\dot{C}OPr^i][k_b + k_dC] \qquad (9.xii.)$$

Hence

$$\frac{d[Me_2CO]}{dC} = -\frac{(k_eC + k_fA)(k_b + k_dC)}{2C(k_bk_e + k_ek_dC + k_dk_fA)} \qquad (9.xiii.)$$

From this equation it should be possible to find the absolute values for all the four rate constants, k_b, k_e, k_d, k_f by measurement of the variation of acetone concentration with the variation of cobaltic ion concentration along a single reaction run. However, it was found to be impossible to measure the acetone produced by the method previously used, since all the methods of quenching which were tried interfered with the method of measurement. (See Chapter 10). It was not possible to measure the acetone spectrophotometrically at about 280 mμ since the cobaltous ions also absorbed in this region. This investigation was hence abandoned.

c. Variation of Rate of Oxidation with Methyl Cyanide Concentration.

This dependence was measured at a constant ether concentration of 0.34M. with initial cobaltic ion concentration 2×10^{-2}M. (Table 9.6). There is the usual marked rate increase at high methyl cyanide concentrations. Measurements over a variety of ether and methyl cyanide concentrations using initial cobaltic ion concentration ca. 10^{-4}M. are shown in Table 9.7. These confirm the variation of rate constant with ether concentration found

TABLE 9.6. VARIATION OF THE OXIDATION RATE OF DI-ISOPROPYL ETHER WITH METHYL CYANIDE CONCENTRATION.

15.0 $[HClO_4]$ 1.00M. Initial $[Co^{III}]$ ca. 2×10^{-2}M. Initial $[Co^{II}]$ ca. 6×10^{-3}M.
μ ca. 1.0M. $[Pr^iOPr^i]$ .34M.

% MeCN	10^4 k' sec.$^{-1}$ [a]	10^4 k' sec.$^{-1}$ for corresponding self decomp. [b]
84	38	4.5 - 4.3
75	19.0	4.0 - 3.4
57	14.5	2.3 - 1.5
48	11.3	1.3 - 1.0
39	8.2	1.5 - .7
30	6.0	.9 - .5

a. Measured graphically over two half-lives.

b. Measured graphically.

in 50 per cent methyl cyanide solution. (Table 9.2.)

2. The Oxidation of Diethyl Ether.

Accurate measurements of the order of reaction with respect to diethyl ether were not attempted due to the difficulty of making up standard solutions of the substrate. However, oxidations performed in water at 15° and a perchloric acid concentration of 1M. indicated that the second order rate constant, assuming the reaction to be first order with respect to ether, was about 1×10^{-3} l.m.$^{-1}$ sec.$^{-1}$ This indicates that the reaction is similar in rate to the oxidation of di-isopropyl ether.

TABLE 9.7. OXIDATION OF DI-ISOPROPYL ETHER.

15° $[HClO_4]$ 1.00M. init. $[Ce^{III}]$ ca. 10^{-4}M. init. $[Co^{II}]$ ca. 3×10^{-5}M.

A. 60 per cent MeCN

$[Pr^iOPr^i]$ M	$10^4k'$ sec^{-1} [a]	10^3k_2 l.m.$^{-1}$ sec^{-1} [b]
0.0	2.6-1.6	-
0.0	2.9-2.5	-
0.0	3.6-2.4	-
.083	5.0	1.7
.10	5.8	2.2
.13	6.3	2.1
.16	8.0	2.8
.19	6.9	1.7
.21	8.0	2.1
.21	8.3	2.2
.25	8.8	2.1
.31	9.5	1.9
.42	10.6	1.7
.42	11.0	1.8
.58	12.4	1.5
.75	14.1	1.4
.92	14.9	1.2

B. 45 per cent MeCN

$[Pr^iOPr^i]$ M.	$10^4k'$ sec^{-1} [a]	10^3k_2 l.m.$^{-1}$ sec^{-1} [b]
0.0	2.9-2.6	-
.062	3.5	0.97
.065	4.0	1.7
.074	3.8	1.2
.18	6.0	1.7
.18	5.6	1.5
.26	7.0	1.6
.33	7.9	1.5
.49	8.8	1.2
.51	9.1	1.2
.59	9.6	1.1

C. 40 per cent MeCN

0.0	1.9-1.3 [a]	- [b]
0.0	1.6-1.1	-
.081	3.7	2.2
.21	5.2	1.6
.24	5.4	1.5
.31	6.2	1.4
.48	7.4	1.1
.61	7.5	.92

D. 30 per cent MeCN

0.0	1.2- .9 [a]	- [b]
0.0	1.4-1.0	-
0.0	1.3-1.1	-
0.0	1.3-0.9	-
.085	3.1	2.0
.13	3.9	1.9
.15	3.7	1.2
.17	4.4	1.8
.24	5.3	1.6
.29	5.0	1.2
.35	6.1	1.3

a. Measured graphically over two half-lives.

b. Derived from previous column taking higher self-decomp. rate.

3. The Oxidation of 2,2' - Dichlorodiethyl Ether.

The oxidation of this ether was found to be autocatalytic. The plots of $-\log_{10}(D-D_\infty)$ versus time were markedly curved, Figure 9.8., and this curvature was so great that the variation of $(D-D_\infty)$ with time was also an accelerating curve. The dependence of the initial pseudo first order rate constant on ether concentration is shown in Table 9.9. This shows that the initial oxidation is first order with respect to ether.

The oxidised solutions all showed a positive test for chloride ion with nitric acid and silver nitrate. The white precipitate formed was soluble in excess ammonia. No chloride ions were liberated from blank solutions made up with cobaltous perchlorate instead of cobaltic perchlorate and left for the same length of time, or from the self-decomposition reaction. Hence chloride ions must be produced during the oxidation of the ether, but at concentrations very much smaller than those used in the attempt to catalyse the oxidation of benzyl methyl ether. (p. 134). Chloride ions are also liberated in the oxidation of chloral by vanadium(V).[203] A possible reaction scheme is:

$$ClCH_2CH_2OCH_2CH_2Cl + Co^{III} \longrightarrow ClCH_2\dot{C}HOCH_2CH_2Cl + Co^{II} + H^+ \quad (9.xiv.)$$

$$ClCH_2\dot{C}HOCH_2CH_2Cl \longrightarrow ClCH_2CH_2^{\bullet} + ClCH_2CHO \quad (9.xv.)$$

$$ClCH_2CH_2^{\bullet} + Co^{III}OH_2 \longrightarrow ClCH_2CH_2OH + Co^{II} + H^+ \quad (9.xvi.)$$

Further oxidation of the chlorohydrin could then release chloride ions, since it has been shown that radicals such as $ClCH_2\dot{C}HOH$ can rearrange rapidly to $^{\bullet}CH_2CHO$ and HCl.[204,196] Alternatively, chloride ions might be released from the primary ether radical. The autocatalysis of the

FIG. 9.8 REPRESENTATIVE PLOTS FOR THE OXIDATION OF 2,2′-DICHLORO-DIETHYL ETHER.

Conditions as for Table 9.9

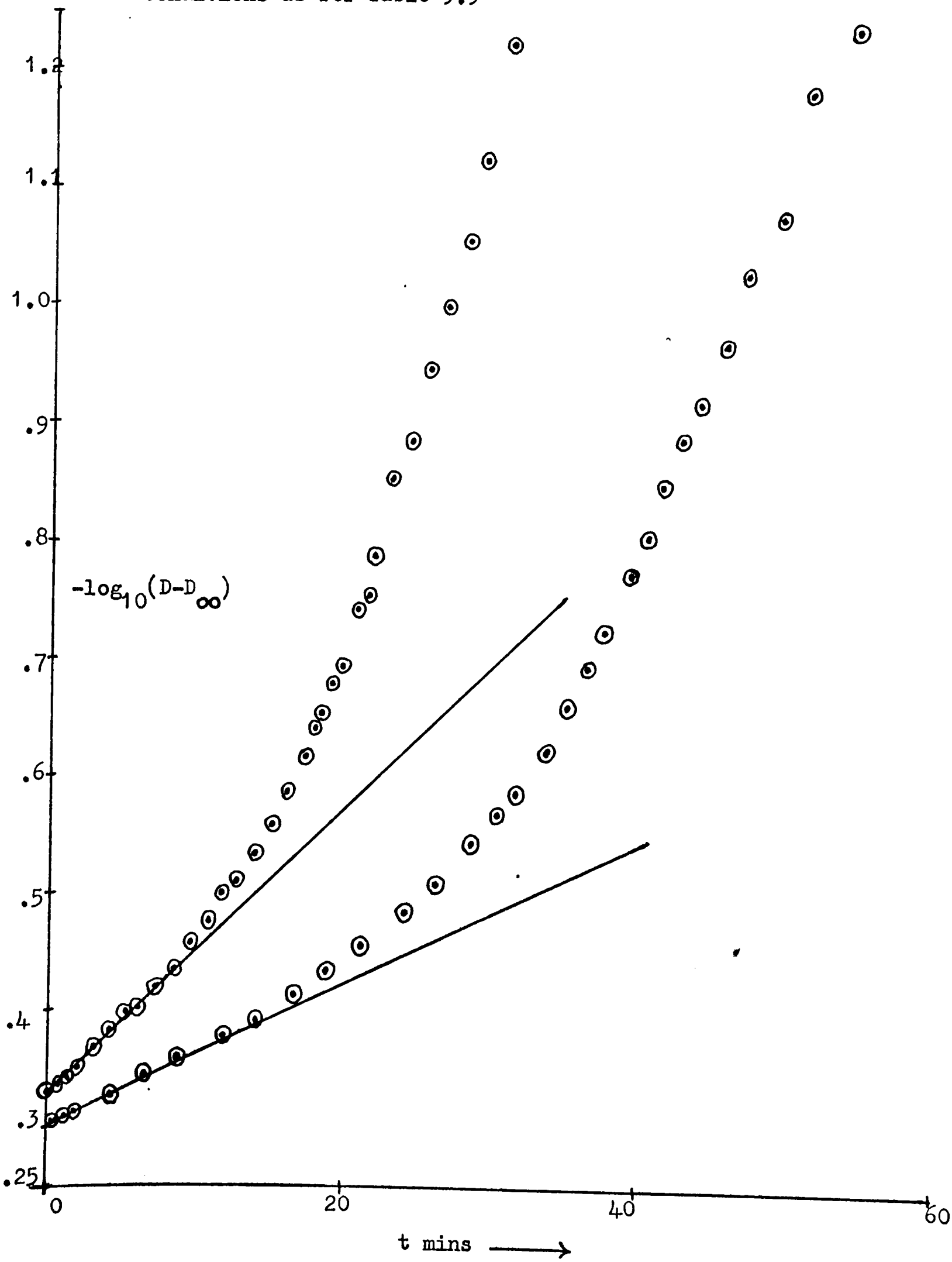
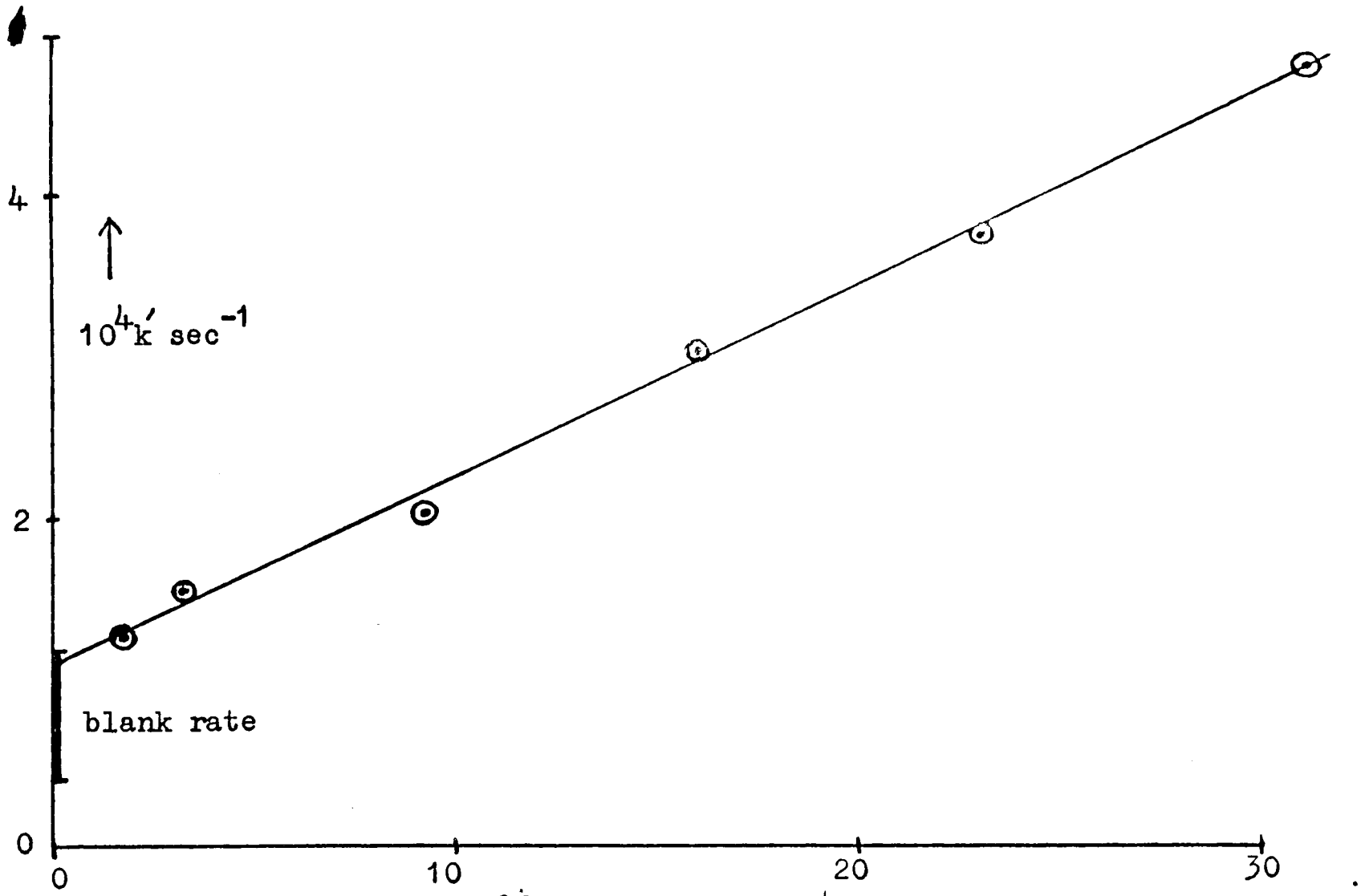


TABLE 9.9 OXIDATION OF 2,2′ - DICHLORODIETHYL ETHER.



15°$[HClO_4]$1.00M. 40 per cent MeCN. init. $[Co^{III}]$ ca. 8×10^{-3}M. Init. $[Co^{II}]$ ca. 3×10^{-3}M. μ ca. 1.04M.

$10^2[(ClCH_2CH_2)_2O]M$	10^4 initial k' sec^{-1} [a]	$10^4 k_2$ l.m.$^{-1}$ sec^{-1} [b]
0.0	1.2- .4	-
1.7	1.3	5.9
3.1	1.6	12.9
9.2	2.1	9.8
15.9	3.1	11.9
23	3.8	11.3
31	4.8	11.6

Best fit line, (by least squares): $10^4 k' = 1.14 + 11.8[ClCH_2CH_2OCH_2CH_2Cl]$

a. Measured graphically

b. Calculated from previous column taking k' self-decomp. = 1.2×10^{-4}sec^{-1}.

oxidation could then be caused by:

$$Cl^- + Co^{III} \longrightarrow Cl^{\cdot} + Co^{II} \qquad (9.xvii.)$$

$$Cl^{\cdot} + ClCH_2CH_2OCH_2CH_2Cl \longrightarrow ClCH_2\dot{C}HOCH_2CH_2Cl + HCl \qquad (9.xviii.)$$

This is another internal induced oxidation. Alternatively, the reaction:

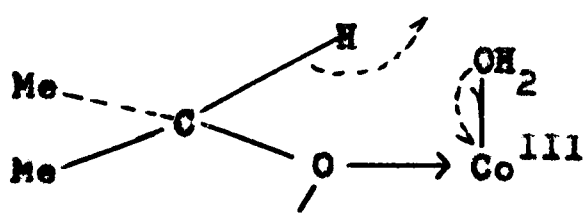
$$ClCH_2\dot{C}HOCH_2CH_2Cl \longrightarrow Cl^{\cdot} + CH_2{=}CHOCH_2CH_2Cl \qquad (9.xix.)$$

has been suggested to occur in the thermal decomposition of 2,2' - dichlorodiethyl ether.[205] However, this reaction is considerably endothermic, and is less likely to occur in solution at low temperatures.

A reaction such as 9.xix. could not occur with the α chloro ether. However, no attempt was made to study the oxidation of the α chloro ether, since it is known to hydrolyse rapidly.[206]

4. Further Discussion.

The rate of oxidation of di-isopropyl ether is considerably slower than those of the benzyl ethers, (Chapter 8), but similar to the rate of oxidation of toluene. Isopropanol is oxidised about 200 times per α C—H bond faster than di-isopropyl ether, but this is not nearly as great as the difference in oxidation rates of benzyl alcohol and the benzyl ethers. Either an inner or an outer sphere mechanism is possible for the oxidation of di-isopropyl ether. If an intermediate complex is formed, this should give rise to a cyclic transition state for the oxidative step:



$$\longrightarrow Me_2\dot{C}OPr^i + Co^{II} + H^+ \qquad (9.xx.)$$

analogous to that possible for the oxidation of isopropanol.[32] However, there should be considerable steric repulsion against forming such a complex, and this may explain the large reactivity difference between the ether and the alcohol. Alternatively, oxidation may occur by an outer sphere mechanism. The difference between the oxidation rates of di-isopropyl ether and the benzyl ethers reflects the influence of the phenyl ring in activating the α C-H towards attack by either mechanism. No firm decision as to the detailed mechanism can be made on the evidence presently available.

Chapter 10. METHODS OF PRODUCT ANALYSIS.

A large part of the present work was concerned with devising methods to measure quantitatively the products from the oxidation reactions studied. Consequently, these methods will be described in some detail.

1. The Estimation of Acetone.

The acetone yields from the oxidation of di-isopropyl ether, (Chapter 9), were measured by a modification of the Behre-Benedict salicyladehyde method which is specific for acetone.[207] This method has been modified previously by Mino et al.[208] to measure acetone yields from the ceric oxidation of pinacol, but their method was found to give irreproducible results in systems containing di-isopropyl ether and methyl cyanide. The method finally found to give satisfactory results was as follows:

Reactions were performed in 2 ml. of solution. After completion of the reaction, (ca. 10 half-lives), 0.20 ml salicylaldehyde was added from a microsyringe, followed by 1 ml. saturated potassium hydroxide solution (from a pipette). The two phase system formed was churned with a glass rod and left for 20 minutes. The red mixture was then diluted to 10 ml with 40 per cent ethanol-water (v/v), stirred up and left a further 20 mins. It was then centrifuged for five minutes and 1 ml. of the clear red solution was made up accurately to 10 ml. with ethanol/water and left a further five minutes. The optical density of the solution was then measured at 520 mμ. in a 1 cm. cell. This optical density reading was taken 55 mins after the initial addition of the

alkali. The time intervals were critical since the optical density increased with time, and so all measurements had to be made under standard conditions. Addition of alkali to the reaction solution before addition of the salicylaldehyde gave irreproducible results. (Compare ref. 208). A corresponding blank solution containing cobaltous perchlorate was made for each reaction solution, and developed in parallel with it. Only small 'Blank' corrections to the measured reaction yields were necessary.

The method was calibrated using solutions containing known amounts of Analar acetone, and the same amounts of water, methyl cyanide, perchloric acid and cobaltous perchlorate as used in the 'blank' runs. The presence of di-isopropyl ether in the calibration solution had little effect on the measured optical density. The calibration curve is shown in Fig. 10.1 This indicates that the method is accurate to about ± 7 per cent.

Several metal ions were found to interfere with the method since they chelated the salicylaldehyde.[209] Consequently the oxidation reactions could not be quenched by addition of metal salts. (p.163). The quenching method employed by Mino et. al.,[208] where the oxidant was precipitated out by the addition of excess alkali, gave irreproducible results.

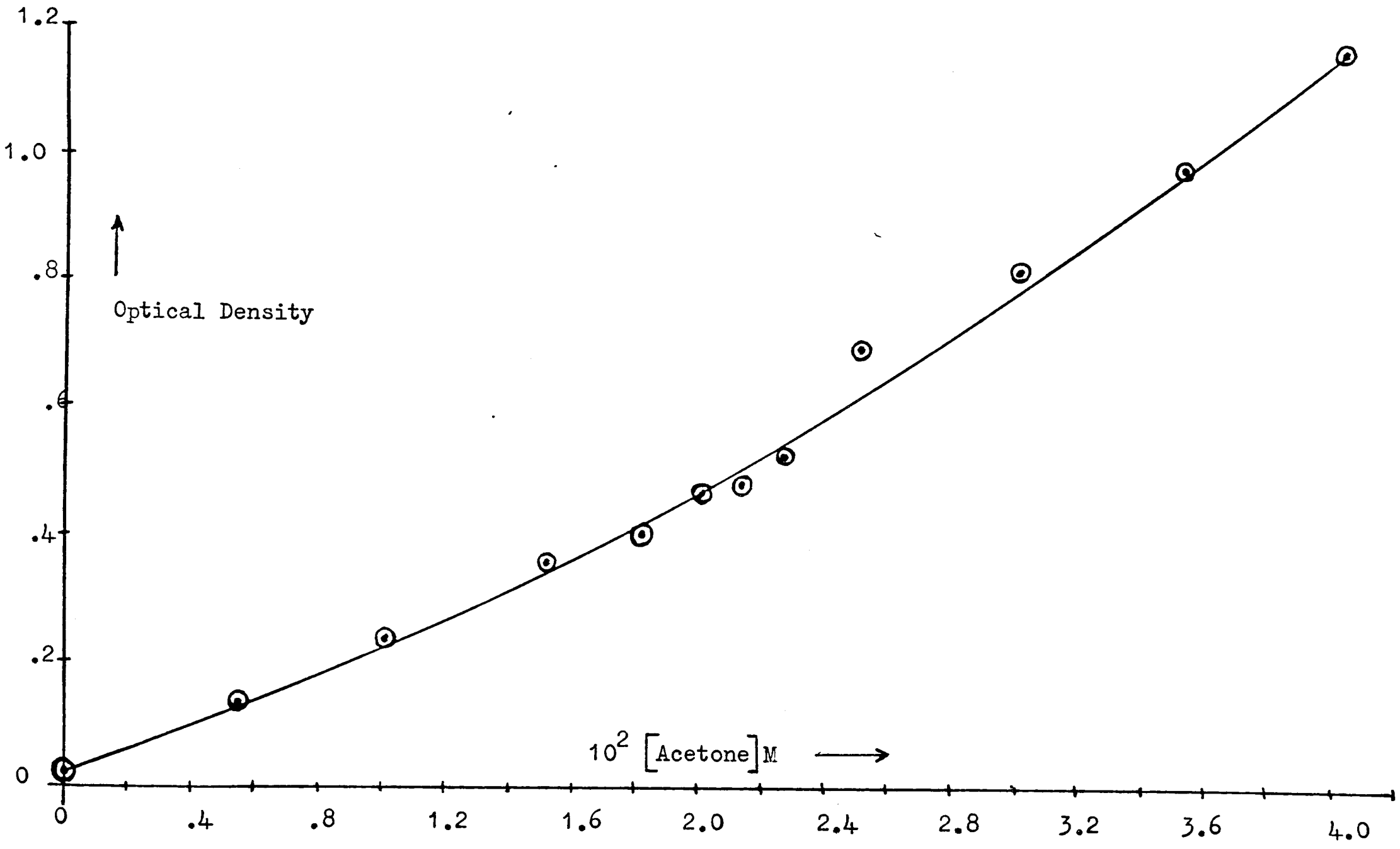
2. <u>The Estimation of Benzaldehyde as its 2,4 - Dinhenylhydrazone.</u>

This was first attempted, using the method given by Clifford and Waters[14], as follows:

Reactions were performed in a total of 1 ml. of solution. Excess

FIG 10.1 CALIBRATION CURVE FOR THE ESTIMATION OF ACETONE.

$[HClO_4]$ 1.00M. $[Co^{II}]$ca. 0.03M. 50 per cent MeCN (v/v).



2,4 - dinitrophenyl hydrazine in 5% sulphuric acid and a known amount of cyclohexanone DNP in s-tetrachloroethane were added to the oxidised solutions, and mixed thoroughly. 1 ml. of chloroform was added and shaken, and the aqueous layer removed. The chloroform layer was washed twice with 5% sulphuric acid to remove excess 2,4 - dinitrophenyl hydrazine, dried with anhydrous potassium carbonate, filtered through cotton wool, and the filtrate concentrated to ca. 0.3 ml. Some of this solution was then placed in a line onto an unbaked Kieselgel G chromatoplate with a fine capillary. The plate was developed with 60/40 benzene/cyclohexane in a tank constructed so that the top of the chromatoplate just emerged through the lid, allowing continual evaporation of the solvent to draw the dinitrophenyl hydrazones up the plate. The benzaldehyde DNP and cyclohexanone DNP bands were then separately scraped off into funnels fitted with cotton wool plugs and the DNP's dissolved from the silica with s-tetrachloroethane. These solutions were made up to 2 ml. with s-tetrachloroethane and their optical densities measured at 365 mμ in 2 m.m. cells. The yield of benzaldehyde is then given by:

$$\text{Moles PhCHO} = M_s \cdot \frac{D_b}{D_s} \cdot \frac{\varepsilon_s}{\varepsilon_b} \qquad (10.i.)$$

where M_s is the moles of standard (cyclohexanone) DNP added, D_b and D_s are the optical densities of the benzaldehyde DNP and standard DNP solutions, and ε_b and ε_s are the extinction coefficients of the benzaldehyde DNP and standard DNP at 365 mμ.

This method was found to give high and erratic results. The cause

of these errors was eventually traced to the cyclohexanone DNP in acid solution hydrolysing in preference to the benzaldehyde DNP, even in the presence of excess 2,4 - dinitrophenyl hydrazine. The method was therefore modified. The modification found to give the best results followed a procedure very similar to that given above, except that benzophenone DNP in benzene solution was added as the standard DNP. The solutions were extracted with benzene, and benzene was used as the eluting solvent for developing the chromatoplates. The benzaldehyde DNP and benzophenone DNP were carefully dissolved from the silica with benzene, and made up to 2 ml in benzene, and their optical densities were measured in benzene solution in 2 m.m. cells. The extinction coefficients of these two DNP's were measured separately in benzene solution using the same cells. (Table 10.2). At least two plates were made from each reaction solution and mean values taken. The amount of standard DNP added was similar to the amount of benzaldehyde expected from the reaction so that the bands on the plates were of comparable intensities.

This modified method is shown by Table 10.3 to give very accurate results. It was used as described above by D.J. Mills for the estimation of benzaldehyde yields from the oxidation of toluene induced by the oxidation of carboxylic acids. (Chapter 7).

The presence of dibenzyl ether in the reaction solutions was found to interfere with the development of the chromatoplates. Hence it was necessary

TABLE 10.2 R_s VALUES, AND EXTINCTION COEFFICIENTS OF SOME 2,4-DINITROPHENYLHYDRAZONES.

DNP	R_s [a]	$10^{-4}\varepsilon$ [b]
Ph_2CO [c]	1.00	2.48
PhCHO [c]	.87	2.64
PhCOMe [f]	.83	-
pBu^{t}PhCHO	.78	-
Cyclohexanone [e]	.58	2.05
Me_2CO [e]	.50	-
MeCHO	.50	-
HCHO [e]	.50	-
pNO_2PhCHO [d]	.22	-
$PhCH_2COPh$ [c]	1.0	-

a. Relative to Ph_2CO DNP on unbaked Kieselgel G eluted with dry benzene.
b. In benzene solution at 365 mμ.
c. Identified by R_s, m.p., m.m.p., and mass spectrum.
d. Identified by R_s value only.
e. Identified by R_s and mass spectrum only.
f. Identified by m.p. and mass spectrum only.

to evaporate off, on a water bath, all the benzene from the dried benzene extracts from the reaction solution, and then to remove all the dibenzyl ether by evaporating to dryness at 110° at a pressure of < 0.3 m.m. (Allowing the temperature to rise above 130° caused partial decomposition of some of the DNP's, giving black products. When this happened low values were given for the amount of benzaldehyde DNP present). The dry residue was then redissolved in a small amount of chloroform, and analysed as before. The results obtained from this method were still very accurate. (Table 10.3).

TABLE 10.3 ESTIMATION OF BENZALDEHYDE BY THIN LAYER CHROMATOGRAPHY.

Benzaldehyde DNP used in each case 6.03×10^{-4} moles.

Procedure	10^4 moles PhCHO found	Mean
1. PhCHO DNP and Ph_2CO DNP mixture in benzene solution separated on plate.	5.87 5.87	5.87
2. As 1 but using mixture in 50 per cent MeCN/H_2O solution (v/v). Extracted with benzene etc. as described in text.	5.72 5.76	5.74
3. As 2 but in solution containing 1M. perchloric acid.	5.57 5.76	5.68
4. As 3 but with excess 2, 4-dinitrophenylhydrazine in 5M. sulphuric acid.	6.01 6.04	6.03
5. As 4 but in 60 per cent MeCN/water containing ca. .1M. dibenzyl ether. (Ether removed under vacuum before analysis).	5.98 5.96	5.97

4. and 5. simulate the conditions obtaining in the analysis of the final oxidised solutions from toluene and dibenzyl ether respectively.

A spurious band with an R_s value corresponding to that of acetone DNP always appeared on the chromatoplate whatever the extracting solvent used. (Compare ref 14). This was not removed by first refluxing the

benzene solvent over Brady's reagent before use, or by recrystallising the 2,4-dinitrophenylhydrazine from benzene. This band was dissolved from the plate with chloroform, and the solid obtained after evaporation of the chloroform melted over a 25° range, even after recrystallisation from chloroform /60°-80° petrol. Its mass spectrum[155] showed that it consisted largely of acetone DNP, and there was also some higher molecular weight material, but no acetaldehyde DNP.

The other bands on the chromatoplates were generally identified (a) by comparison of their R_s values with those of authentic samples, and (b) by taking the m.p., mixed m.p. with an authentic sample, and the mass spectrum[155] of material collected from the same bands on different plates and recrystallised from chloroform/60°-80° petrol.

The modified method was used qualitatively (i.e. without adding the standard DNP), to analyse carbonyl products from the oxidations of bibenzyl, diphenyl methane, benzhydrol, p-nitrotoluene, p-t-butyl toluene, and toluene. In cases where benzophenones or acetophenones were expected the mixture of the oxidised reaction solution and the 2,4-dinitrophenylhydrazine solution was warmed for about 10 minutes at 70°, since these ketones are known to form DNP's rather slowly. The method was also employed to confirm the production of cyclohexanone and benzaldehyde from the oxidation of benzyl cyclohexyl ether, and the production of benzaldehyde from the oxidation of benzyl methyl ether. In the latter case formaldehyde DNP was

also detected in the mass spectrum of the 'acetone' DNP band. Both these ethers had to be removed under vacuum before the DNP's were put on the chromatoplate, since they interfered with development of the bands.

The chromatoplates used during this work were prepared by Mr. R. Prior of the Dyson Perrins Laboratory.

3. The Estimation of Products by Gas Chromatography.

Yields of benzaldehyde, benzyl alcohol, bibenzyl and benzoic acid from the oxidations of toluene and dibenzyl ether were measured simultaneously using a Perkin Elmer F11 Gas Chromatograph with a flame ionisation detector. The column used was 2m. x 1/8" O.D. stainless steel packed with diethyleneglycol polyadipate, penta-erythritol and phosphoric acid on 80-100 mesh chromosorb W (25:2:73). (Perkin Elmer DD035F). The carrier gas was nitrogen. The procedure finally found to be the most satisfactory was as follows:

After completion of the oxidation reaction, (about 8 half lives), 0.2 ml of an accurately known solution of about 0.017g biphenyl in 10 ml. methyl cyanide was added from a microsyringe, followed by about 30 mg of p-methoxyphenol inhibitor. This inhibitor was necessary to prevent autoxidation of the benzaldehyde, (and of the benzyl ethers), before measurements were made.[210] p-Methoxyphenol was found to be suitable for this, since it did not react with any of the products and had a suitable retention time on the gas chromatograph. After thorough mixing of the solution,

an equal volume of dichloromethane was added, and the whole was thoroughly shaken, centrifuged, and the aqueous layer carefully removed. Water, equal to half the volume of the added dichloromethane, was then added to the organic layer, shaken, centrifuged, and the aqueous layer again carefully removed; this was repeated. The organic phase was then dried with about 1g. of very dry magnesium sulphate, (this had been kept in an oven at 110°), and filtered through cotton wool. This procedure, carefully carried out, was found to remove all the perchloric acid from the mixture. This was checked with pH universal indicator paper which remained neutral. The filtrate was carefully evaporated to 0.3 ml with a stream of nitrogen, (too much evaporation made the solution turn brown), and 10 µl was injected into the gas chromatograph for each analysis. The solutions were not evaporated down until required immediately for analysis, and were kept in the dark under nitrogen both before and after evaporation. The analyses were completed as quickly as possible to avoid keeping the extracted solutions too long.

Dichloromethane was found to be the most suitable extracting solvent. Ether is ineffective since it is too basic, too miscible with water, and tends to extract the cobaltous perchlorate.[211] Benzene forms emulsions which are difficult to break, and cannot be easily evaporated down with a nitrogen stream. (It was thought undesirable to heat solutions containing both benzaldehyde and the phenol inhibitor). Dichloromethane was preferred to chloroform since it is more volatile, and had less tendency to form emulsions.

Temperature programming was necessary for all the components of the mixture to have convenient retention times. A typical chromatogram is as follows:

Start at 130°, N_2 pressure 13 p.s.i.

	Retention time mins	Sensitivity	peak wt. (g)	$\frac{\text{peak wt.}}{Ph_2 \text{ peak wt.}}$ = area ratio
PhCHO	20	10×10^2	.0503	2.61
Set 150°				
$PhCH_2OH$	44	20 x 1	.0972	.101
o-cresol	54	20 x 1	.0166	.017
Ph-Ph	66	2×10^2	.0964	1.00
Set 160°				
$PhCH_2CH_2Ph$	86	20 x 1	.0564	.058
Set 170°				
PhCOOH	120	50 x 1	.0754	.196
$pMeO.C_6H_4OH$	140			

Toluene eluted out with the solvent peak, dibenzyl ether after the inhibitor peak. The aliphatic acids employed in the induced oxidations, (Chapter 7), had shorter retention times than benzaldehyde, (11-12 minutes), and did not interfere.

Three chromatographs were made of the extract from each reaction solution, and mean values taken. Peak areas were compared by weighing. A check of this method by cutting out and weighing squares of chart paper showed that the error involved was very small. The product yields were then given by:

$$\text{moles product} = \text{area ratio} \times \text{calibration const.} \times \text{moles } Ph_2 \text{ added} \qquad (10.11.)$$

A 'blank' run containing cobaltous perchlorate instead of cobaltic perchlorate was made up to parallel each reaction run, with which it was simultaneously developed. This allowed checks to be made for concurrent autoxidation and hydrolysis.

Product measurements for other systems (Chapter 6 and 8), were made in analogous manner. For the oxidation of benzyl cyclohexyl ether, durene was used as standard since biphenyl overlapped with the ether. Cyclohexanone, cyclohexanol, durene and benzaldehyde eluted in this order at 100° and nitrogen pressure 13 p.s.i.; then benzyl alcohol, benzyl cyclohexyl ether and bibenzyl at 150°; cyclohexyl benzoate at 160°; and benzoic acid and inhibitor at 170°. For the oxidation of benzyl methyl ether, the ether, followed by benzaldehyde and methyl benzoate eluted at 125°; then benzyl alcohol and biphenyl at 150°; and benzoic acid and inhibitor at 170°. The reaction solutions containing ethers were left only 8 half-lives before working up to minimise hydrolysis. It was especially important in these cases to remove every trace of perchloric acid, since checks in which the acid was deliberately not all removed produced large amounts of benzyl alcohol.

Calibration constants were measured simultaneously for each component by making up simulated final reaction solutions containing the correct

amounts of cobaltous perchlorate, perchloric acid, methyl cyanide and water, together with known amounts of the reaction products similar to those actually found, and following the whole extraction procedure given above. The calibration constant is then given for each component by (mole ratio / area ratio). These calibration constants were not altered significantly by varying the amount of the components, or the amount of drying agent used. Those measured for the oxidation of toluene did not vary with toluene concentration. However, they did vary with the methyl cyanide and acid concentrations of the reaction solutions, and so calibration constants were measured for each set of product runs performed. This was carried out directly after the measurement of the reaction products had been completed, using exactly the same conditions for the extraction procedure and the temperature programming. Some specimen calibration constants are shown in Table 10.4. These figures are from different chromatograms of two identical extracted calibration solutions, and indicate that the method is capable of giving results reproducible to within about 5 per cent for benzaldehyde and about 10 per cent for benzyl alcohol and benzoic acid. However, the product measurements from the oxidation of the benzyl ethers seemed rather less reproducible than those from the oxidation of toluene.

For the runs carried out in 85 per cent methyl cyanide solution (p. 114) the extraction procedure had to be modified since the dichloromethane formed a homogeneous solution with the other components. 1ml. of

TABLE 10.4 CALIBRATION CONSTANTS FOR GAS CHROMATOGRAPHIC ANALYSIS.

For solutions containing 60 per cent MeCN (v/v) and 1M $HClO_4$.

		Mole ratio/area ratio		
	10^6 moles added	Solution 1	Solution 2	Mean
PhCHO	20.1	2.35 2.40	2.44 2.51	2.43 ± .08
$PhCH_2OH$	.51	2.70 2.95	2.55 2.60	2.70 ± .25
Ph_2	2.16	1.00 1.00	1.00 1.00	1.00
$PhCH_2CH_2Ph$	.22	.83 .82	0.86 0.84	0.84 ± .02
PhCOOH	1.91	2.22 2.13	2.35 2.17	2.29 ± .16

water was added to this homogeneous solution, which converted it into a two phase system, and the extraction was then carried out as described previously.

The identity of the measured peaks was checked on several stationary phases by showing that only the measured peak increased in size when some of the pure authentic compound was added to the solution. Qualitative analyses were made on columns containing: Apieson L on chromosorb P; Fluorosilicone oil on HMDS chromosorb W; Carbowax 1500 on chromosorb W; and Carbowax 20M on chromosorb W. This confirmed the identity of all the peaks except for benzoic acid which would not elute from the latter four columns. These tests also showed that in the oxidation of toluene, minute traces of m- and/or p- cresols, (these two compounds do

not resolve), are formed in addition to o-cresol, but that in the quantitative chromatograms they are hidden by the biphenyl peak. The assignments of identity were checked for the carbonyl compounds by making the 2,4-dinitrophenylhydrazones. (Section 2).

CHAPTER 11. FURTHER EXPERIMENTAL METHODS.

1. KINETIC STUDIES.

The kinetic measurements described in Chapters 6,8 and 9 were made by following the decrease in cobaltic ion concentration with either a Unicam S.P. 500 or S.P. 800 spectrophotometer. The reactions were carried out at constant temperature by circulating water from a toluene-mercury thermostat, (accurate to $\pm$ 0·1°), through the copper cell block of the spectrophotometer. With the S.P. 500, temperature was measured with a mercury-in-glass thermometer, (previously calibrated against an NPL standard thermometer), standing in the copper block. With the S.P. 800 the temperature of the thermostat bath was measured with a calibrated thermometer, and the difference in temperature between the bath and the cell block was measured with a calibrated thermocouple. For temperatures below 10°, a dry air current was blown continuously through the cell block housing to prevent condensation on the optical faces of the cells. A cell block designed to take four sample cells was employed in the S.P. 800, so that four kinetic runs could be performed simultaneously,

a. Choice of Wavelength.

Kinetic studies of cobaltic oxidations have often been made by following a shoulder of the large ultra-violet absorption of the cobaltic ion.[9,10,14] Except for the oxidations of the aliphatic ethers, this was impossible in the present work[31], since the aromatic substrates absorbed strongly in the ultra-violet over a range completely blanketing the cobaltic ion absorption. Consequently, the cobaltic ion concentration

was followed using the weak absorption band at 595-605 mu., (Chapter 5). Cobaltous ions show a very weak absorption at about 515mu., which does not interfere. The low extinction coefficient of the absorption band used,[38] compared with that for the ultra-violet absorption,[18] imposes several limitations on the method:

i. A high concentration of cobaltic ions, (ca. 10^{-2}M.), and hence also of substrate, was necessary. Use of a scale expander on the S.P. 800 enabled the initial cobaltic ion concentration to be reduced to about 2×10^{-3}M., but at higher expansion factors the noise level was too high. (Plots at these lower initial oxidant concentrations show the greatest scatter due to the higher background noise). However, this facility is not available for the S.P. 500. Since the S.P. 800 was not available until about half way through the present work, the oxidations of the aromatic hydrocarbons, (Chapter 6), were not all investigated under uniform conditions.

This high concentration of reagents, and the slow rate of oxidation of the substrates investigated, necessitated the use of high methyl cyanide concentrations, which increased both the complexity of the reactions and the rate of self-decomposition of cobaltic ions.(Chapter 5).

ii. 10m.m. stoppered cells were necessary. This increased the difficulty of rapid and accurate thermostatting, and required large quantities of purified reagents. 2·4 or 2·7 ml. of solution were used in each case.

b. Preparation of Solutions.

A solution of cobaltic perchlorate was prepared prior to each set of

experiments, and kept at 0°. Oxygen was removed before use by blowing through with a stream of nitrogen. Other reagents, except the ethers, which autoxidised, could be stored.

Solutions for kinetic work were made up using a glass syringe, (Agla), fitted with a micrometer head, and a glass needle; (cobaltic perchlorate oxidises stainless steel needles.) This delivered volumes reproducible to ± 0·2% in 0·1 ml. In order to minimise the heat of mixing of the components, and any hydrolysis of the methyl cyanide, and to achieve good thermostatting, the solutions were generally made up in two parts:

i. containing water, perchloric acid, cobaltic perchlorate, and sometimes part of the methyl cyanide.

and ii. containing a solution of the organic compound in methyl cyanide. The two portions were separately thermostatted before mixing, which initiated the reaction. In cases where only a small amount of oxidant was used, the other components were all mixed and thermostatted in the same tube, and the cobaltic perchlorate was injected to initiate the reaction. After initiation the solution was poured quickly into a silica cell fitted tightly into the cellblock of the spectrophotometer. This ensured the best possible thermostatting. The first optical density was usually measured within ten seconds of mixing. Reactions with half lives down to about 5 seconds could be followed on the S.P. 800, but only reactions with half lives greater than 15 seconds could be followed on the S.P.500. The final optical density reading, (D_∞), was taken after about ten half lives.

Kinetic and product studies were generally carried out in solutions largely freed from dissolved oxygen. No attempt was made to create completely anerobic conditions, since cobaltic perchlorate decomposes to evolve oxygen, and oxygen is liberated in the dilution of the cobaltic perchlorate when making up the reaction solutions. However, most of the oxygen was removed from the system by degassing the cobaltic perchlorate solution and the water by blowing through with nitrogen, and by refluxing and then cooling the methyl cyanide in an atmosphere of nitrogen, and keeping sealed under nitrogen. Many of the substrates used were also kept under nitrogen. Solutions were made up in nitrogen filled tubes, thermostatted under nitrogen, and the reaction performed under nitrogen. The effect of oxygen was tested by carrying out reactions in solutions saturated with oxygen. However, oxygen was found to have little effect on any of the reactions studied, except for that of benzaldehyde.[31,136] This is in agreement with previous studies of cobaltic oxidations.[212] Although the above procedure does not remove catalytic amounts of oxygen, it should reduce the oxygen concentrations in the reaction solutions to about 10^{-5}M.[213] which is small in comparison to the cobaltic ion concentrations generally employed. In cases where the reaction solutions were deliberately saturated with oxygen, the oxygen concentration was about 10^{-3}M.[213]

c. ANALYSIS OF KINETIC DATA.

Cobaltic perchlorate solution is unstable. Consequently, the initial optical density reading varied slightly between kinetic runs, although

the same volume of cobaltic perchlorate solution was used for each run in any one set of runs. First Order kinetics with respect to oxidant were demonstrated by showing that the plots of $-\log_{10}(D-D_\infty)$ versus time were linear over about two half lives.[195] This method demonstrates a general first order dependence on oxidant, but can conceal small variations.[214] A knowledge of the exact initial cobaltic ion concentration was hence unnecessary, since it would not affect the slope of the first order plots. The pseudo first order rate constants are given by:

$$k' = -(2{\cdot}30/60)(d\log_{10}(D-D_\infty)/dt) \text{ sec.}^{-1} \qquad (11.i.)$$

The final optical density, (D_∞), is necessary, since $(D-D_\infty)$ measures the cobaltic ion concentration at any instant.[38] No reference cell was employed.

Deviations from first order dependence on oxidant were seen by deviations from linearity of the plots of $\log_{10}(D-D_\infty)$ versus time. Except for the oxidation of 2,2'-dichlorodiethyl ether , these deviations were quite small, and the reactions remained essentially of the first order. Initial slopes were taken in these cases, and it was checked in several instances that varying the cobaltic ion concentration by a large factor caused no correspondingly large variation of the initial pseudo first order rate constant.

Those oxidations of di-isopropyl ether which were followed at 240mμ., (initial oxidant concentration ca. 10^{-4}M.), were shown to be accurately of the first order with respect to oxidant by the above method. Once this had been established, the kinetic data were often analysed by the Guggenheim Method[194,195] to avoid the long wait for D_∞. This was done by taking a set of readings $D_1, D_2 \ldots$ at times $t_1, t_2 \ldots$,

and another set $D_1-\Delta D_1$, $D_2-\Delta D_2$.... at times $t_1+\Delta$, $t_2+\Delta$ ...., where Δ is a constant time interval from one to two half lives. The plot of $\log_{10}\Delta D_1$, $\log_{10}\Delta D_2$ .... against t_1, t_2 .... is then linear for a first order reaction, and its slope gives k' as above. Several values for Δ were taken, and the mean value of k' found. (This method is rather insensitive to changes in reaction order, and so it is necessary to ensure previously that the reaction is of first order with respect to oxidant.)

The order with respect to organic substrate was found in all cases by measuring the pseudo first order rate constants over a range of (excess) substrate concentrations. These runs were not performed in order of substrate concentration, but in a more random fashion.

The slopes of the plots of $-\log_{10}(D-D_\infty)$ versus time were measured graphically. Where there was deviation from first order, initial rates were also measured graphically. These measurements were often checked by fitting the best weighted curve to the data by the method of orthogonal polynomials,[215] using Autocode Program 1000 on the Leo-Marconi KDF9 Computer. The initial rate is given by the coefficient of x in the best fit quadratic or cubic equation. These coefficients were generally very similar to each other and to the graphically measured initial rate.

For the above purpose, and for finding the weighted mean rate of a first order plot which deviated from linearity, the measured $\log_{10}(D-D_\infty)$ values were weighted using the corresponding $(D-D_\infty)$ values as weighting factors. This placed proportionately more importance on those points corresponding to the consumption of the greatest amounts

of oxidant. The weighted mean rates used for calculations in Chapters 6,7 and 8 were taken as the coefficient of x of the linear equation approximating best to the measured curve.

The slopes and intercepts of the best straight lines to fit the dependences on substrate concentration, acidity etc. were also calculated using Autocode Program 1000. Each point was given equal weight, since differential weighting in these cases would be quite arbitrary.

2. PRODUCT STUDIES.

Reactions for product studies were carried out under nitrogen in thermostatted tubes fitted with ground glass stoppers. The extraction procedure and centrifuging could then be carried out in these same tubes. Solutions containing all components except the oxidant were made up and thermostatted, and the cobaltic perchlorate solution was added from a microsyringe. The strength of the stock cobaltic perchlorate solution was measured immediately afterwards. Equivalent 'blank' runs containing cobaltous perchlorate were performed together with the reaction runs.

3. THE USE OF ORGANIC COSOLVENT.

Methyl cyanide was used as the organic cosolvent throughout the present work in order to obtain homogeneous solutions containing both the organic substrate and the oxidant. Methyl cyanide was selected since it is miscible with water in all proportions, and is oxidised only very slowly by cobaltic perchlorate. The volume contraction on

mixing of methyl cyanide and water is very small,[216] and so the convention adopted in this thesis of describing methyl cyanide concentration by ' % methyl cyanide v/v ' is very similar to the actual volume composition of the mixed solutions.

Previous work on oxidations by cobaltic perchlorate has been carried out using methyl cyanide concentrations of less than 50%, when it could be assumed that the species present and the reactions occurring were essentially the same as in pure water. (Chapter 5). In the present work it was necessary to employ higher methyl cyanide concentrations, and its complexing properties and very low basicity[217,231] and low dielectric constant[216] compared to water, may all have complicated the results from the kinetic and product studies. In every case there was a marked increase in rate with increasing methyl cyanide concentration, and sometimes a distinct change of mechanism. However, concentrations of methyl cyanide up to 70% have been shown previously [218] to have little effect on the stoichiometry of the cobaltic oxidation of t-butanol to acetone. This indicates that there are no side reactions involving attack by intermediate radicals on the methyl cyanide, which is present in far greater excess than any organic substrate, to produce the $^{\bullet}CH_2CN$ radical, which could consume large amounts of oxidant.

4. FURTHER ANALYTICAL METHODS.

a. Determination of Cobalt (III).

The strength of cobaltic perchlorate solutions produced by electrolysis was measured volumetrically. A known amount, (0·1ml. to 0·5ml.), was added from a microsyringe to excess ferrous sulphate solution, (ca. 0·01M. in 5% sulphuric acid). A volume, equal to the volume of ferrous sulphate solution, of syrupy phosphoric acid was then added, and four drops of barium diphenylaminesulphonate indicator. The excess ferrous sulphate was then back titrated against ca. 0·01M. ceric sulphate solution from a burette. The indicator turns purple at the end point. Equal volumes of ferrous sulphate to those used above were then titrated (separately) against the ceric sulphate solution and a primary standard of 0·01N. potassium dichromate solution. This was made up by dissolving a known weight of Analar potassium dichromate (ground up and dried at 150° for two hours), in water. These titrations were repeated several times and the mean values taken. The molarity of the cobaltic perchlorate solution could then be calculated to within an accuracy of about 5%.

These titrations were carried out for each set of product studies, so that the amount of oxidant added was accurately known. It was necessary to restandardise the ferrous and ceric sulphate solutions on each occasion.

b. Detection of Organic Peroxides.

Many of the substrates oxidised in the present work undergo very facile autoxidation, and the peroxides formed are oxidised more rapidly

than the substrate by cobaltic perchlorate. (Chapter 9). Consequently it was necessary to ensure that all substrates were free from every trace of peroxides. This test was made by the method given by Egerton et al.[219] which can detect about 10^{-6}M. peroxides. The test solution was made up as follows: 2g. ammonium thiocyanate, 2g. ferrous sulphate and ½ml. concentrated sulphuric acid were dissolved in 50ml. water. This solution was shaken with four or five portions of n-pentanol, until all the red colour was removed in the organic layer. 2ml. of the solution was then added immediately to 3 drops of the organic substrate in ca. 1ml. methyl cyanide, and shaken. 2ml. of the reagent was also added to a reference solution of methyl cyanide and water. The development of a red colour indicated the presence of peroxides. Substrates found to contain peroxides were discarded.

c. Determination of Acidity.

The acidities of the cobaltous perchlorate, perchloric acid and sodium perchlorate solutions were found by titration against N/10 standard sodium hydroxide solution using screened methyl orange indicator.

d. Determination of Cobalt (II).

The cobaltous perchlorate stock solution was estimated gravimetrically by precipitation as $Co(C_5H_5N)_4(CNS)_2$.[220]

e. Determination of Sodium Perchlorate Solution.

This was performed gravimetrically by slow evaporation of a known volume to dryness at 140°, and then weighing the solid perchlorate. The stock solution was then diluted to the required concentration.

CHAPTER 12. METHODS OF PREPARATION AND PURIFICATION OF MATERIALS.

1. INORGANIC COMPOUNDS.

a. Cobaltous Perchlorate.

Saturated potassium bicarbonate solution was added to a solution of Analar cobaltous chloride, (14g.), in distilled water, (150ml.), until precipitation was complete. The purple precipitate was coagulated by warming, filtered off, and redissolved in aqueous 2M. perchloric acid. This precipitation was repeated three times until the perchloric acid solution gave no precipitate with silver nitrate.solution. The reagents were added slowly and minimum quantities were used. Finally the basic cobalt carbonate was dissolved in 8M. perchloric acid, (Analar), filtered through sintered glass to remove insoluble potassium perchlorate, and the solution cautiously evaporated until it fumed. Cooling then yielded a mass of pink crystals which were dried by suction. This cobaltous perchlorate was made up into an approximately 0·25M. solution in 6M. perchloric acid.

b. Cobaltic Perchlorate.

Cobaltic perchlorate was prepared by electrolysis of the stock cobaltous perchlorate solution at 0°. The electrolytic apparatus consisted of a vertically held platinum disc anode, and a small square platinum cathode contained in a separate compartment formed by a glass tube with a sintered glass disc at the lower end. The anode current density was kept below 0·1 $A.cm.^{-2}$, and the electrolyte was stirred

rapidly during electrolysis. As cobaltous ions were oxidised to the cobaltic state, the solution changed from pink to deep blue-green, (except in the cathode compartment). The current efficiency decreased with the cobaltous ion concentration, so pure solutions of cobaltic perchlorate were unobtainable. After about 20 minutes electrolysis the solution was about 0·1M. in cobaltic ions. The solution deteriorated very quickly even at 10°, and so fresh electrolysis was necessary for each set of kinetic runs and product studies.

Oxygen was always evolved during electrolysis, and on standing as the solutions decomposed. It was removed before use of the cobaltic perchlorate solution by blowing through with nitrogen. The electrolysed solution was kept at 0°, and was covered to prevent absorption of moisture from the atmosphere.

c. Water.

Laboratory distilled water was redistilled from alkaline permanganate, and then distilled twice more. It was freed from oxygen by blowing through with nitrogen before use.

d. Perchloric Acid.

Analar 70% perchloric acid was diluted to about 6M. with pure water, and standardised against sodium hydroxide solution.

e. Sodium Hydroxide.

M/10 sodium hydroxide solution was prepared from a B.D.H. volumetric ampoule.

f. Sodium Perchlorate.

Commercial sodium perchlorate contains impurities which are not

removed by recrystallisation from water, and which are rapidly oxidised by cobaltic perchlorate. Hence pure sodium perchlorate was prepared by neutralising Analar perchloric acid with the theoretical quantity of Analar sodium carbonate, evaporating the solution, washing the crystals obtained with water, and drying at 50°.

2. METHYL CYANIDE.

B.D.H. reagent grade methyl cyanide contains small quantities of hydrolysis products.[221] These would react rapidly with cobaltic perchlorate. It was necessary to make the methyl cyanide spectroscopically pure in order to minimise the spontaneous decomposition in the solvent mixture. The following method was found to be satisfactory:

To the methyl cyanide,(500ml.), was cautiously added ,with cooling, concentrated sulphuric acid,(50ml.), and then potassium permanganate, (65g.), slowly and in portions. The mixture, which was quiescent at first and then boiled spontaneously, was refluxed for 3 hours, filtered, dried over potassium carbonate, and refluxed three times over phosphorus pentoxide for 3 hours. It was then fractionated through a 60 cm. lagged Fenske ring column at a reflux ratio of 20:1 and collected at 81·5°. Methyl cyanide purified in this way was spectroscopically pure, and gave only one peak on analysis by gas chromatography.

3. HYDROCARBONS.

Many of the organic substrates investigated in the present work were oxidised only very slowly by cobaltic perchlorate. Hence it was necessary to rigorously pufify these substrates. Purifications by

Preparative gas chromatography were carried out on an F and M 770 preparative gas chromatograph operated by Mr. C.J. Ball of the Dyson Perrins Laboratory.

a. Toluene, (Analar), was shaken with concentrated sulphuric acid until no yellow colours were formed, then with aqueous potassium carbonate and finally with water. It was kept over clean mercury for 2 days, dried over magnesium sulphate, fractionated from phosphorus pentoxide, b.p. 110°, refractionated, and stored in the dark under nitrogen. Analysis by g.l.c. showed it contained no benzyl alcohol, cresols, benzaldehyde, biphenyl, bibenzyl or benzoic acid.

b. p-Nitrotoluene, (B.D.H.), was purified in two ways. Both purified samples were oxidised at the same rate, showing that the measured reaction was not oxidation of impurities.

i. p-Nitrotoluene was recrystallised four times from ethanol, eluted twice from an alumina Grade H column with 1:5 60°- 80° petrol / benzene as eluting solvent, (it could be detected in the eluate by warming with titanous chloride and methanol), recrystallised from benzene and ethanol, and sublimed at atmospheric pressure. This yielded long, almost colourless needles, which melted very sharply at 52° without sweating.

ii. p-Nitrotoluene was sublimed four times at atmospheric pressure to yield crystals melting sharply at 52°.

c. p-t-Butyltoluene, (Eastman Kodak), was shaken with concentrated sulphuric acid, then with water, with aqueous sodium hydroxide, and again with water, dried over magnesium sulphate, and stood over clean mercury for two days. It was then further purified by preparative g.l.c.

on a 15% carbowax 6000 column at 100°. (60% recovery). Analysis by g.l.c. then showed a maximum of 0.2% impurities, probably other hydrocarbons.

d. Ethyl Benzene, (B.D.H.), was shaken with concentrated sulphuric acid until no yellow colours were formed, then with potassium carbonate solution, and with water, dried over magnesium sulphate, stood over clean mercury for three days, fractionated from phosphorus pentoxide, b.p. 134°, and carefully refractionated. It was then partially frozen with liquid nitrogen and the liquid portion poured off.[222] This was done four times. The solid portion was remelted, dried over magnesium sulphate, and stored in the dark. This material was oxidised at the same rate as a sample which was further purified by preparative g.l.c. on a 15% Apiezon L column.

e. Diphenylmethane, (B.D.H.), was fractionated once at atmospheric pressure , b.p. 262°, and then three times at reduced pressure, b_{10} 128°, to yield colourless crystals, m.p. 27°, which were stored in the dark in the cold. Analysis by g.l.c. showed only one peak.

f. Bibenzyl, (B.D.H.), was recrystallised from ethanol , and then sublimed twice at 14m.m. pressure, to yield white crystals m.p. 52°.

g. Biphenyl, (B.D.H.), was sublimed twice at its m.p. at 14m.m. pressure, to yield white crystals, m.p. 71°.

h. Naphthalene, (B.D.H.), was sublimed twice at 25° at 11m.m. pressure, to yield white crystals m.p. 80°.

i. Cyclohexane, (B.D.H. spectroscopically pure), was fractionated bp.81°

Analysis by g.l.c. showed it contained no cyclohexanol, cyclohexanone, benzene, phenol or cyclohexene.

j. Benzene, for extraction and elution was Analar dried over sodium wire. Analysis by g.l.c. showed it contained no benzaldehyde, benzyl alcohol or benzoic acid.

4. ETHERS.

All purified ethers were carefully checked for peroxides before use.

a. Dibenzyl Ether, (B.D.H.), was dissolved in diethyl ether and washed with aqueous ferrous sulphate, water, aqueous sodium bisulphite, water, aqueous sodium hydroxide and again with water, and dried over magnesium sulphate under nitrogen. It was then filtered through Woelm Basic I alumina, the diethyl ether evaporated off, and carefully fractionated in vacuo. $b_{0.3}$ 106°. A colourless, almost odourless oil was obtained. It was kept cold, under nitrogen, in the dark, and used very quickly.

This procedure was shown by g.l.c. to remove all impurities except for small traces of bibenzyl, and samples purified in this manner were used for kinetic work. Samples for product study were purified by preparative g.l.c., to remove the bibenzyl, prior to fractionation.

b. Benzyl Methyl Ether, (B.D.H.), was purified as described for dibenzyl ether, except that the final purification was by preparative g.l.c. instead of by fractionation. Preparative g.l.c. was performed on a 15% carbowax 6000 column, (recovery 90%). The main impurities, which were collected and identified, were benzaldehyde and methyl benzoate. (This supports the assignment of peaks given in Chapter 10).

The pure ether, analysed by g.l.c., contained negligible amounts of

impurities. It was kept cold, in the dark, under nitrogen, and used very quickly.

c. Benzyl Cyclohexyl Ether, (kindly donated by Mr. G.C.Mitchell), was purified as described for dibenzyl ether. ($b_{0.7}$ 88°) It was kept cold, under nitrogen in the dark, and used very quickly.

Analysis by g.l.c. showed that this procedure did not remove small traces of bibenzyl and cyclohexyl benzoate. Attempts to remove these impurities by preparative g.l.c. failed, since the ether pyrolysed in the exhaust manifold of the chromatograph. The cyclohexyl benzoate impurity also pyrolysed in the manifold, and a good yield of benzoic acid was collected. (Benzoic acid would not, itself, elute from the column employed).

d. Diphenyl Ether, (B.D.H.), was sublimed twice at 14m.m. pressure, to yield white crystals, m.p. 27°. It was kept in the dark.

e. Di-Isopropyl Ether, (Eastman Kodak, alcohol free), was shaken with aqueous ferrous sulphate, water, aqueous sodium bisulphite, water, aqueous sodium hydroxide, and again with water, and dried over magnesium sulphate. It was then stood over sodium wire under nitrogen, filtered, and carefully fractionated in an atmosphere of nitrogen, using a Fenske ring column and a reflux ratio of 50:1. (b.p.68°). This procedure reduced the ultra-violet cut off to a very low wavelength, (220 mμ), and analysis by g.l.c. showed it was free from isopropanol, [redacted]. It was kept cold, under nitrogen, in the dark, and used very quickly.

NOTE. It is extremely dangerous to attempt fractionation of di-isopropyl ether directly, without first removing the peroxides.[223] Isopropanol and water must also be removed before fractionation, since

they form azeotropes with the di-isopropyl ether.[224]

f. 2,2'-Dichlorodiethyl Ether,(B.D.H.), was shaken with concentrated hydrochloric acid, water, aqueous sodium hydroxide, and again with water, dried over magnesium sulphate and stood over sodium wire for two days. It was then filtered through glass wool, and fractionated three times, b.p. 177°, to yield a colourless liquid with a faintly sweet odour. It was checked to be free from chloride ion, and analysis by g.l.c. showed only one peak. This ether was found to be stable, even in air, but it was kept in the dark.

g. Diethyl Ether, was B.D.H. absolute anaesthetic grade, used without further purification.

5. OTHER ORGANIC COMPOUNDS.

a. Benzaldehyde,(Bush), was stood over anhydrous potassium carbonate in the dark for several days. Analysis by g.l.c. showed it was free from benzyl alcohol and benzoic acid.

b. Benzyl Alcohol,(B.D.H.), was dissolved in ether, washed with aqueous sodium bisulphite, water, aqueous sodium hydroxide, and again with water, and dried over magnesium sulphate. After removal of the ether, it was fractionated at reduced pressure, b_{15} 103°., and kept in the dark. Analysis by g.l.c. showed it contained only a very small amount of benzaldehyde, even after keeping for about a month.

c. Benzoic Acid,(Analar), was recrystallised from water, m.p.122°.

d. Pivalic Acid,(B.D.H.), was recrystallised from water, m.p.35°.

e. Isobutyric Acid,(B.D.H.), was dried over sodium sulphate, and fractionated with a reflux ratio of 10:1. b.p. 154°.

f. Propionic Acid,(B.D.H.), was dried over sodium sulphate, and then refluxed for four hours over potassium permanganate, and fractionated as above, b.p. 140°. Analysis by g.l.c. showed that the above acids contained only very small amounts of impurities.

g. p-Methoxyphenol,(B.D.H.), was recrystallised from 40°- 60° petrol, then sublimed at its m.p. at 14m.m. pressure, to yield white crystals, m.p. 53°. It was kept in the dark.

h. Dichloromethane,(B.D.H.), was stood over potassium carbonate, and then fractionated, b.p. 41°. It was kept in the dark.

i. 2,4-Dinitrophenylhydrazine,(B.D.H.), was recrystallised from Analar benzene, and then made up to an approximately 10^{-2}M. solution in 5M. sulphuric acid.

j. 2,4-Dinitrophenylhydrazones,were prepared by the usual method,[225] and recrystallised from benzene, chloroform or chloroform/petrol. Cyclohexanone DNP was purified by dry column chromatography[226] on silica deactivated with 3% water, and then recrystallised from ethanol. m.p. 160°. DNPs were stored in the dark.

k. Isopropanol,(B.D.H.), and Methyl Benzoate,(B.D.H.), were dried over magnesium sulphate, and fractionated.

l. Cyclohexanol,(B.D.H.), and Cyclohexanone,(B.D.H.),were purified by preparative g.l.c.

m. Cyclohexyl Benzoate, was prepared by the method given by Berlin and Gibbs.[227] To a mixture of 5ml. cyclohexanol, 10ml. pyridine, and 15ml. benzene, was added 7ml. benzoyl chloride. Reaction occurred immediately, and continued for about 10 minutes. The solution was then filtered, washed with water, dried over magnesium sulphate and the benzene evapor-

ared off. The mixture was then fractionated at reduced pressure to yield cyclohexyl benzoate. $b_{0.7}$ 121°

n. Benzhydrol, (B.D.H.), was recrystallised from ether/60°-80° petrol, then sublimed m.p. 68°.

o. Acrylamide, (B.D.H.), was sublimed twice at 14m.m. pressure, to yield white crystals, m.p. 85°.

p. Barium Diphenylamine Sulphonate Indicator, (B.D.H.), was made up in 0·2% aqueous solution.[228]

All melting points were taken on a Kofler block. In those cases where fractionation was employed in the above purifications, fractions were generally taken over a boiling range of 1° or less.

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ABSTRACT.

The oxidation of a series of aromatic hydrocarbons and ethers by cobaltic perchlorate has been investigated. This was undertaken a. to extend the range of known one-electron oxidations of organic compounds to include much less reactive molecules than those previously investigated; and b. to investigate the possibility of oxidation by direct electron transfer, rather than by the homolytic fission of a C——H bond.

The oxidations studied were generally much slower than any previously investigated cobaltic oxidations, so that the self-decomposition of the cobaltic ions in solution was often of comparable rate. The latter reaction shows no simple order with respect to cobaltic ions, and is not accurately reproducible.

The oxidations of a series of aromatic hydrocarbons approximately follow the rate law:

$$-d[Co^{III}]/dt = k_2[Co^{III}][ArH]/[H^+] \qquad (i.)$$

In many cases the kinetic form is complicated by variations in the extent of secondary oxidation. However, there is no exact comparison between the deviations from a first order dependence on substrate and oxidant, and the variation of stoichiometry with substrate concentration. The approximate reactivity order is:

$p\text{-}NO_2C_6H_4Me < C_6H_{12} < PhCH_2CH_2Ph \sim PhMe \sim PhEt < Ph_2CH_2 < p\text{-}Bu^tC_6H_4Me$
$< Ph_2 <$ naphthalene $<$ phenanthrene, anthracene.

This order can be correlated with both the ionisation potentials of the compounds, and their relative rates of attack by several free radicals.

No firm conclusion can be reached concerning the point of initial attack on the aralkyl hydrocarbons, but it is suggested that both the aromatic ring and the side chain can be involved. The slow oxidation of cyclohexane demonstrates that cobaltic ions can oxidise a paraffin chain. The reactivity order shows little steric influence, which supports an outer sphere mechanism for the oxidations. It contrasts with the reactivity order of related alcohols, which are thought to be oxidised by an inner sphere mechanism, and which do show marked steric retardation. Polycyclic hydrocarbons such as biphenyl and naphthalene, which possess no side chain, are oxidised rapidly. It is suggested that in these cases there is direct electron transfer from a π-orbital.

The side chain oxidation products from toluene, (benzyl alcohol, benzaldehyde, and benzoic acid), were accurately estimated by a gas chromatographic method developed during the course of the work. In 50% methyl cyanide solution, these products account for all the oxidant consumed. At higher co-solvent concentrations there is less side chain oxidation, and yellow products are formed. It is suggested that there is oxidation of the aromatic ring under these conditions. Stationary state calculations for the side chain oxidation show that the measured yields of benzyl alcohol are much greater than the theoretical maxima. This suggests the occurrence of some additional reaction, possibly:

$$\dot{PhCO} + PhCH_3 \longrightarrow PhCHO + \dot{PhCH_2} \qquad \text{(ii.)}$$

The production of $\dot{PhCO}$ radicals is supported by the detection of methyl benzophenones in the oxidation products. A similar conclusion is reached for the oxidation of dibenzyl ether.

C——C fission is a major process in the oxidation of bibenzyl, and occurs to lesser extents in the oxidations of diphenylmethane and ethyl benzene. Thus the oxidation of bibenzyl yields benzaldehyde, and not benzyl phenyl ketone.

The oxidation of p-nitrotoluene is exceptional since it appears to be inhibited by the substrate. Explanations for this involving the complexing of cobaltic ions by the nitro- group, or the nitro- group acting as a trap for intermediate radicals, are tentatively suggested.

The results obtained from the direct oxidation of toluene are used to analyse mathematically detailed kinetic and product studies of the oxidation of systems containing toluene and a carboxylic acid. The oxidation of toluene is promoted by several aliphatic acids, and this is ascribed to the reactions:

$$RCOOH + Co^{III} \longrightarrow R^{\bullet} + CO_2 + Co^{II} + H^{+} \quad \text{(iii.)}$$

$$R^{\bullet} + PhMe \longrightarrow PhCH_2^{\bullet} + RH \quad \text{(iv.)}$$

The significance of such processes with regard to the catalysis of autoxidation reactions by carboxylate salts of transition metals is discussed.

The oxidations of a series of benzyl ethers are faster than the oxidations of similar hydrocarbons, but much slower than the oxidation of benzyl alcohol. The overall reactivities, which are in the sequence:

$$PhCH_2OMe < PhCH_2OCH_2Ph < PhCH_2OC_6H_{11} < PhOPh$$

are not governed by steric effects. Oxidation occurs by direct attack on the ether rather than by its prior hydrolysis, and an outer sphere mechanism similar to that for the aralkyl hydrocarbons is suggested. Quantitive measurements, by gas chromatography, of the oxidation products,

indicate a reaction scheme such as:

$$PhCH_2OR + Co^{III} \longrightarrow Ph\dot{C}HOR + Co^{II} + H^+ \qquad (v.)$$

$$Ph\dot{C}HOR \longrightarrow PhCHO + R^\cdot \qquad (vi.)$$

$$Ph\dot{C}HOR + 3Co^{III} + H_2O \longrightarrow PhCOOR + 3Co^{II} + 3H^+ \qquad (vii.)$$

$$R^\cdot + Co^{III}.OH_2 \longrightarrow ROH + Co^{II} + H^+ \qquad (viii.)$$

The formation of an ester can be correlated with the ability of the R group to be eliminated as R$^\cdot$. The detailed kinetic behaviour is similar to that found for the oxidation of the aralkyl hydrocarbons.

The oxidation of di-isopropyl ether is slower than the oxidations of the benzyl ethers. Larger yields of acetone are obtained than can be explained by the stoichiometry of a reaction scheme analogous to that shown in equations v. to viii. This indicates that there is a short regenerative chain:

$$Me_2\dot{C}OPr^i \longrightarrow Me_2CO + Pr^{i\cdot} \qquad (ix.)$$

$$Pr^{i\cdot} + Me_2CHOPr^i \longrightarrow Me_2\dot{C}OPr^i + C_3H_8 \qquad (x.)$$

which can produce acetone without consumption of cobaltic ions.

The oxidation of 2,2'- dichlorodiethyl ether is autocatalytic, and liberates chloride ions. The autocatalysis is ascribed to the rearrangement of an intermediate radical to yield chloride ions which are then oxidised to Cl$^\cdot$, or else to elimination of Cl$^\cdot$ from the primary radical. The Cl$^\cdot$ radicals can then attack the substrate ether.

The substrates which have been investigated are all rather insoluble, and so solutions containing high concentrations of methyl cyanide co-solvent were necessary. The increase in the oxidation rates of the

hydrocarbons and ethers with increasing methyl cyanide concentration is far too large to fit the expression:

$$k = k_o e^{MX} \quad \text{(where X is \% methyl cyanide v/v)} \qquad \text{(xi.)}$$

which has been previously found satisfactory for solutions of up to 50% methyl cyanide. Spectral changes indicate that a cobaltic- methyl cyanide complex, which is an active oxidant, is formed. Its enhanced reactivity is due to a decrease in the energy of activation for the oxidations, which outweighs the effect of a less favourable activation entropy.

In general, the thesis shows that reaction mechanisms cannot be elucidated solely from a knowledge of reaction kinetics. Accurate measurements of reaction products are also necessary before any interpretation of mechanism can be attempted. Thus, similar kinetic behaviour is found a. when the same substrate is oxidised to give different products under different conditions; and b. when similar substrates are oxidised by quite different routes.