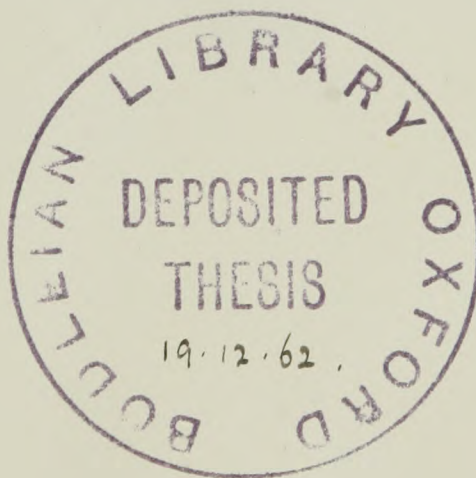


KINETICS OF CHEMICAL REACTIONS

THESIS SUBMITTED FOR THE DEGREE OF DOCTOR  
OF PHILOSOPHY IN THE UNIVERSITY OF OXFORD

BY

J. B. ROSSELL  
TRINITY COLLEGE



June 1962

The Physical Chemistry  
Laboratory

Abstract

General Introduction

Chapter I

General Survey of Kinetic Studies

Introduction

Experimental Errors

Reaction Series with Constant Concentration of  
Activator

Reaction Series in which the Concentration of  
Activator of Activation Varies

Structural Variations

Solvent Variations

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Chapter II

Experimental Methods

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ABSTRACT

The temperature dependence of most chemical reactions is accurately represented by the Arrhenius equation,

$$k = Ae^{-E/RT}$$

where  $k$  is the rate constant,  $A$  is a temperature independent entropy factor, often called the frequency factor, and  $E$  is the activation energy. This equation provides a useful method for the expression of results in a kinetic investigation.

It is found that when changes in rate are brought about through moderate variations of reactant structure, or of solvent medium, the values of  $A$  and  $E$  change, but not in a random manner. Three types of behaviour are found.

In some cases  $A$  remains constant while  $E$  varies as reactants are modified, this type of behaviour often being found when a substituent is separated from the reaction centre by a benzene ring. In other cases  $A$  and  $E$  vary together, and it is often found that large values of  $E$  are associated with large values of  $A$ , and vice versa, so that the resultant change in rate is less than that indicated by the variation of either parameter alone, and a sort of 'compensation' is found. The third type of behaviour, in which  $E$  remains constant while variations of  $A$  control the rate, is occasionally found when solvents are varied through a related series or when the structure of the solvent is varied by the application of pressure. The various types of behaviour are reviewed in section I of the thesis, together with some of the theories advanced in explanation. It is



suggested that the type of behaviour sometimes shown on solvent variation in which E remains constant while variations in A modify the rate, could arise from differences in the order of the pure solvent, and evidence is presented to support this view.

The experimental work reported in the thesis consists of a study of the formation and decomposition of quaternary ammonium salts based on dimethyl aniline, both in nitrobenzene solution and in solvents consisting of mixtures of chlorobenzene with nitrobenzene. Special attention has been given to the variations in rate brought about through changes in A and E by modifications in the structure of the reactants or in the solvent medium. The experimental methods used in following the reactions at different temperatures include measurement of the conductivity of the solutions, and the aqueous extraction of the quaternary salt from the reaction mixture, followed by the titration of ionisable halide by Volhard's method. These methods are discussed in section II of the thesis.

Section III contains an account of the problems connected with the kinetic behaviour of the reactions and the methods adopted to overcome difficulties arising from the unusual nature of this in some cases. It was found impossible satisfactorily, to represent the results for some of the reactions by a simple rate law, and this proved to be a major difficulty. The cause was traced to the decomposition of the salt first formed, together with the subsequent reaction of the decomposition products. These complications made it impossible in certain cases to use measured values of the reaction equilibrium in the calculation of the results. Two methods were used to overcome the difficulty, either



the drawing of an accurate initial tangent or, when this was not possible, graphical extrapolation of the simple second order constants back to zero reaction.

Some of the reactions, especially those in solvents of low polarity, were found to have equilibrium constants corresponding to very little reaction, a result sometimes obscured by reaction arising from the decomposition products.

Quaternary ammonium salts were found to be insoluble in some of the solvents used, and the product occasionally separated out from the solution, and the reactions became heterogeneous. This caused trouble in two ways. In some cases the experimentally measured rate corresponded to the rate of crystallisation, and not the rate of quaternization, whilst in other cases the surface of the solid product acted as a catalyst.

Section IV of the thesis contains the record and discussion of results for the reactions in nitrobenzene solution. Although structural changes in the reactants provide examples conforming to all three of the types of behaviour discussed in section I, the major effect is to change the rate through a variation of E. The value of A also varies, so that there is some degree of 'compensation'. This compensation effect is found when the alkyl groups attached to nitrogen are varied, when the halogen is varied, and in reactions with ethyl iodide, when ring substituents in the base are varied. When however, ring substituents in the base are varied in reactions of methyl iodide, the value of A does not change, and a comparison of the series of reactions for methyl and ethyl iodide throws doubt upon some established ideas about the stereochemistry of the transition complex.



Not all of the reactions were attended by troublesome subsequent or side reactions, and in some cases equilibrium constants could be measured, and the entropies and enthalpies of reaction calculated. Consideration of these lends support to the views of the transition complex obtained from the kinetic results.

Three of the quaternization reactions were studied in solvent mixtures containing nitrobenzene and chlorobenzene. The rate of the forward reaction proves to be mainly dependent on the activation energy, which rises as the solvent becomes progressively less polar, so that the rate in chlorobenzene is a little less than one seventh of the rate in nitrobenzene. The rate of the reverse reaction, is, however, greater in the solvents of low dielectric constant, as a result of the low stability of the salt. This leads to the unusual circumstance in which slower reactions have a shorter "half life" than faster ones.

The conclusions reached in the earlier sections are reviewed and collected in section VI, where some suggestions for additional work in this field are presented.





The temperature dependence of the rate of a large number of chemical reactions is accurately represented by the Arrhenius equation,

$$\text{i.e. } k = Ae^{-E/RT}$$

where  $k$  is the rate constant,  $A$  is a temperature independent entropy factor often called the frequency factor, and  $E$  is the activation energy. The equation provides a very useful method for the expression of results in a kinetic investigation, and it has been the subject of much theoretical interpretation and discussion (Gowenlock, 1960; R  tschi, 1958; Evans and Polanyi, 1938).

With moderate changes in the structure of the reactants, or of the solvent medium, variations in rate can be brought about through either a variation of  $E$ , or of  $A$ , or the simultaneous variation of both. In any particular series of reactions the variations in rate sometimes conform consistently to one of these types. Occasionally, however, it is found that some members of a series do not conform to such a generalisation, and this can often be traced to a distinct change in the reaction pattern. General aspects of the types of variation in  $A$  and  $E$  found in related reactions are reviewed in Section I of this thesis, where some ideas about the dependence of  $A$  on the structure of the solvent are advanced.

The experimental work reported in this thesis consists of a study of the formation and decomposition of quaternary ammonium salts based on dimethyl aniline. Special attention has been given to the variations in rate brought about through changes in  $A$  and  $E$  by



modifications in the structure of the reactants, or in the solvent medium. Several experimental techniques were employed during the investigation, and these are discussed in Section II.

Many reactions obey a rate law, which in the simplest of cases relates the rate to integral powers of the concentration of the reactants. Sometimes reactions are reversible, and the speed of the reverse reaction must then be taken into consideration before an accurate representation of the results can be obtained. In other cases side reactions or subsequent reactions complicate the picture, and it becomes difficult to find an equation that will adequately express the results. This has proved one of the difficulties met in the present work and Section III of the thesis is devoted to a discussion of the unusual behaviour of some of the quaternization reactions, and to the methods adopted to obtain accurate rate constants for them.

Kinetic results for the quaternization reactions in pure nitrobenzene are considered in Section IV, along with results for the reaction equilibria in cases where these could be measured reliably. Among these reactions examples conforming to all three of the types of behaviour discussed in section I have been found, and a comparison of the conditions under which these different phenomena occur leads to some interesting conclusions about the stereochemistry of the relevant transition complexes. When reliable equilibria could be measured it was possible to calculate the exothermicity and the total (thermodynamic) entropy change of the reactions. It was found that the fastest reactions were



also the most exothermic and suffered the largest entropy loss, probably connected with changes in the solvation sheaths.

Three of the reactions were studied in solvents consisting of mixtures of nitrobenzene and chlorobenzene, and results for these reactions are considered in section V. The rate of the forward reaction proves to be mainly dependent on the activation energy, which increases as the solvent becomes progressively less polar, so that the rate in chlorobenzene is lowered to a little less than a seventh of the rate in nitrobenzene. The rate of the reverse reaction, is, however, greater in solvents of low dielectric constant, as a result of the low stability of the salt and this leads to an unusual relation between the forward rate and the half life of the reaction as the solvent is varied.

The conclusions reached in the earlier sections are reviewed and collected in section VI, where some suggestions for additional work in this field are included.



## INTRODUCTION

The dependence of the rate of chemical reactions on temperature is empirically described by the Arrhenius equation,

$$k = Ae^{-E/RT}$$

(1)

where  $k$  is the rate constant,  $A$  is the pre-exponential factor,  $E$  is the energy of activation,  $R$  is the gas constant, and  $T$  is the absolute temperature.

This equation is derived from the theory of collision of atoms or molecules. The theory states that the rate of reaction is proportional to the number of collisions between molecules,  $Z$ , and the fraction of collisions,  $f$ , which are effective (i.e., which result in a reaction). The equation of collision theory is  $k = Zf$ , where  $Z$  is the number of collisions per unit time and  $f$  is the fraction of collisions which are effective. The equation of collision theory is  $k = Zf$ , where  $Z$  is the number of collisions per unit time and  $f$  is the fraction of collisions which are effective. The equation of collision theory is  $k = Zf$ , where  $Z$  is the number of collisions per unit time and  $f$  is the fraction of collisions which are effective.

## SECTION I

### GENERAL SURVEY OF ENERGY-ENTROPY RELATIONSHIPS

Another, a preliminary factor  $P$  is introduced, and the relationship becomes

$$k = PZf$$

In this equation,  $P$  is the probability factor, and  $f$  is the fraction of collisions which are effective. The equation of collision theory is  $k = PZf$ , where  $P$  is the probability factor, and  $f$  is the fraction of collisions which are effective.

The equation is derived from the theory of collision of atoms or molecules. The theory states that the rate of reaction is proportional to the number of collisions between molecules,  $Z$ , and the fraction of collisions,  $f$ , which are effective (i.e., which result in a reaction). The equation of collision theory is  $k = Zf$ , where  $Z$  is the number of collisions per unit time and  $f$  is the fraction of collisions which are effective. The equation of collision theory is  $k = Zf$ , where  $Z$  is the number of collisions per unit time and  $f$  is the fraction of collisions which are effective.

The above part is devoted to the general survey of energy-entropy relationships. In the interpretation of energy, the equation of collision theory is  $k = PZf$ , where  $P$  is the probability factor, and  $f$  is the fraction of collisions which are effective.

## INTRODUCTION

The dependence of the rate of chemical reaction on temperature is accurately represented by the Arrhenius equation,

$$k = Ae^{-E/RT} \quad (1)$$

where  $k$  is the rate constant,  $A$  is the so called frequency factor, and  $E$  is the energy of activation.

This can be written in several forms, the best known of which is perhaps that derived from the 'collision theory'. In this the rate constant is postulated to be equal to the product of the number of collisions between reactants,  $Z$  (easily derived from the kinetic theory) and  $e^{-E/RT}$ , the fraction of molecules having an energy in excess of the value  $E$ . Since in some reactions the colliding molecules may react only when they are in a specific orientation with respect to one another, a probability factor  $P$  is introduced, and the relationship becomes

$$k = PZe^{-E/RT} \quad (2)$$

In some reactions, involving simple molecules, this factor  $P$  is close to unity.

For reactions in solution the validity of using a collision number derived from the theory of gases is open to criticism and the splitting of the pre-exponential product into  $P$  and  $Z$  is often not attempted, the single constant  $A$  being used.

The simple form in equation (1) will be most used in the interpretation of results in this thesis.

An alternative interpretation of (1) has been



derived from a consideration of the activated collision complex, which is postulated to be in equilibrium with the reactants. The rate of reaction is dependent on the number of activated collision complexes present, and is therefore proportioned to the equilibrium constant  $K^\ddagger$  for their formation.

$$\text{i.e. } k = \text{const. } K^\ddagger \quad (3)$$

The equilibrium is temperature dependent, and will obey the van't Hoff isotherm,

$$\text{i.e. } \Delta F^\ddagger = -RT \ln K^\ddagger \quad (4)$$

where  $\Delta F^\ddagger$  is the free energy of activation. Substituting into (3),

$$k = \text{const. } e^{-\Delta F^\ddagger / RT} \quad (5)$$

$$= \text{const. } e^{\Delta S^\ddagger / R} \cdot e^{-\Delta H^\ddagger / RT} \quad (6)$$

where  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  are the entropy and enthalpy of activation respectively.

The theoretical evaluation of the product  $(\text{const. } \Delta S^\ddagger / R)$  in equation (6) has been the subject of some discussion, and it has been said that the approximations involved in this are equivalent to those involved in the evaluation of the probability factor  $P$  in equation (2) (Winkler and Hinshelwood 1936). The constant is usually equated to  $kT/h$ , the product of the vibrational partition function  $kT/h\nu$  and the frequency of vibration  $\nu$  in the reacting bond, while  $\Delta S^\ddagger$  is calculated from the product of the partition functions for the activated complex.



These calculations involve the assumption that the activated complex is similar to a stable molecule, and that its moment of inertia and vibrational partition functions are not widely divergent from those met with in stable molecules. This assumption is more or less the same as that made in the collision theory that collision diameters calculated from momentum transfer experiments (e.g. viscosity) are the same as those involved in chemical reactions, and that molecules must be in rather exact orientations and vibrational phases at the instant of collision.

It is better to regard the two approaches not as antagonistic, but as complementary, and to use either as the situation dictates. In this case it is possible to derive relationships between the quantities involved. Replacing the constant in equation (6) by  $kT/h$ ; and making the usual assumption that the number of activated complexes which decompose again to give the starting species are insignificant, equation (6) becomes;

$$k = \frac{kT}{h} \cdot e^{\left(\frac{\Delta S^\ddagger}{R}\right)} \cdot e^{\left(\frac{-\Delta H^\ddagger}{RT}\right)} \quad (7)$$

Equating (7) and (1);

$$k = Ae^{-E/RT} = \frac{kT}{h} \cdot e^{\left(\frac{\Delta S^\ddagger}{R}\right)} \cdot e^{\left(\frac{-\Delta H^\ddagger}{RT}\right)} \quad (8)$$

$$\text{i.e. } \ln.k = \ln.A - E/RT = \ln.(kT/h) + \Delta S^\ddagger/R - \Delta H^\ddagger/RT \quad (9)$$

$$\text{and, } \frac{d(\ln.k)}{dT} = \frac{E}{RT^2} = \frac{1}{T} - \frac{\Delta H^\ddagger}{RT^2} \quad (10)$$



$$\text{thus, } \Delta H^\ddagger = E - RT \quad (11)$$

Substituting from (11) into (9);

$$\ln A = \ln.(kT/h) + \Delta S^\ddagger/R + 1 \quad (12)$$

$$\therefore \Delta S^\ddagger = R.\ln.(A/T) - R.\ln.(k/h) - R \quad (13)$$

When A is expressed in seconds<sup>-1</sup>, and the constants are replaced by numerical values, this becomes

$$\Delta S^\ddagger = 4.576.\log_{10}(A/T) - 49.203 \quad (14)$$

In a series of related reactions involving moderate changes of structure, or variations in the solvent medium, entropies and enthalpies of activation (or reaction) vary, but not in a random manner. Three types of behaviour are found. In some cases  $\Delta S^\ddagger$  remains constant while  $\Delta H^\ddagger$  varies as reactants are modified, this type of behaviour often being found when a substituent is separated from the reaction centre by a benzene ring. In other cases  $\Delta H^\ddagger$  remains constant while variations in  $\Delta S^\ddagger$  modify the reaction rate, this type of behaviour occasionally being found when solvents are varied through a related series, or when the structure of a solvent is modified by an application of pressure. The most interesting type of behaviour is that in which  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  vary together, and it is often found that large values of  $\Delta H^\ddagger$  are associated with large values of  $\Delta S^\ddagger$ , and vice versa, so that the resultant change in rate is less than the variation of either quantity alone would indicate, and a sort of 'compensation' is found. At times this correlation, between the values



of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  approaches the precision of a linear relationship characteristic of the particular reaction series. It is frequently pointed out that this type of compensation could be caused by certain kinds of experimental error (Leffler 1955; Purlee, Taft and DeFazis 1955, Hammett p. 123), and it is appropriate to consider the effects of probable errors. The various types of behaviour will then be considered, with a few experimental examples, and their probable origins are discussed. That type in which  $\Delta H^\ddagger$  remains constant is kept until last, since it leads most naturally to some new ideas about solvent influence.

#### EXPERIMENTAL ERRORS

In considering changes in rate through a series of reactions, it is usual to seek examples giving as wide a variation in rate as possible, in order that this variation should be well outside the experimental error, but this can, in principle, introduce some error, as the slowest and fastest reactions may now be studied in different temperature intervals. Some carefully constructed Arrhenius plots do show a second order variation of activation energy with temperature, and a comparison of results obtained in different temperature ranges really involves an extrapolation outside the range in which the measurements were made. It is not easy to remove this difficulty, but it is probable that any errors introduced in this way are quite small, and less important than experimental errors.

There will be errors in the most carefully measured rate constants (and temperatures), leading to increased errors in the activation energy, which is calculated from



measurements over a range of temperature. Purlee, Taft and DeFazis (1955) have shown that an error of only 1% in the values of  $k$  leads to a maximum error in  $E$  of 0.26 k.cal./mole, if the temperature interval is only  $10^{\circ}\text{C}$ . This error can be reduced considerably by using a larger temperature interval, and is only 0.05 k.cal./mole for a temperature interval of  $60^{\circ}\text{C}$ , but this is still significant. The value of  $A$  is calculated from the rate at a given temperature, together with the value of  $E$ , and will also be subject to the same errors as  $E$ . In a series of reactions in which these two quantities are really constant, any error in  $E$  will lead to a corresponding error in  $A$ , and the type of behaviour known as 'compensation' will be apparent. This spurious correlation can be recognized by the small variation in  $k$ , together with the narrow band of activation energies obtained, and by a slope of  $2.303RT$  for the plot having  $E$  (in k.cal./mole) as ordinate, and  $\log_{10} A$  as abscissa.

Reaction series in which  $A$  remains constant, and changes in the reaction rate are brought about through changes in  $E$ , can be identified, provided that there is a reasonable spread of activation energies, random errors scattering the results about a line of constant  $A$ . When the reaction rate is determined by variations in  $A$ , and  $E$  remains constant, a similar situation is found, random variations merely scattering the results about a line of constant  $E$ .

If the values of  $E$  and  $A$  vary simultaneously, so that there is some compensation, the variations in  $k$ , as the reactants are modified, are not so great as the variations in either quantity alone would indicate, and great care must be used in interpreting



the results. Correlations can only be regarded as reliable when there is a sufficiently wide range of activation energies, and the rate constants are reliable, and at the same time spread over a smaller range than the variations in  $E$  alone would indicate.

#### REACTION SERIES WITH CONSTANT ENTROPIES OF ACTIVATION

For several series of reactions involving nuclear substituted benzene derivations, it is found that substituents in positions meta or para to the reaction centre modify the reaction rate in such a way that  $A$  remains constant, and all the change is due to variation in  $E$ . In some cases substituents in the ortho position also conform to this generalisation, but proximity effects often obscure the position. Reaction series in which this behaviour has been reported are the acylation of anilines, the alkaline hydrolysis of benzoic esters, the combination of methyl iodide with tertiary aromatic amines, and the chlorination of phenolic ethers.

Several workers have studied the acylation of substituted anilines, and it has been found that the variations in rate due to para or meta substituents in the aniline (or in a benzoylating agent) are due to changes in  $E$ . Venkataraman and Hinshelwood (1960) give results for the acylation of several nuclear substituted anilines with both benzoyl halides and aliphatic acyl halides;  $A$  remains almost constant for each acylating species used, and the large changes in rate are caused by correspondingly large variations in  $E$ . The variations in  $E$  due to the different substituents are almost independent of the acylating agent.



Stubbs and Hinshelwood (1949) studied the benzylation of twenty one disubstituted anilines, and found that the effect of the substituents was very close to the sum of their individual effects; it was also found that the frequency factor remained constant with ortho, as well as meta and para substituents. Williams and Hinshelwood (1934) showed that substituents in benzoyl chloride did not affect the near constancy of the pre-exponential factor.

The alkaline hydrolysis of benzoic esters was studied by Ingold and Nathan (1936), who found that  $A$  only varied by a factor of 2.5 in a series of reactions in which  $k$  varied by a factor of 5,000, the rate being dependent on variations in the energy of activation.

Several workers have studied the quaternization of tertiary aromatic amines with methyl iodide, and have reported that for meta and para substituents, variations in the frequency factor are very small, significant variations in the rate being due to a modification of the activation energy. Laidler (1938) studied the interaction of methyl iodide with six *m*- and *p*-substituted dimethyl anilines in nitrobenzene solution, and found that with five of them  $A$  changed by a factor of only 1.4, while  $E$  changed by 2.2 k.cal./mole. The sixth aniline (*m*-nitro dimethyl aniline) did not react. Evans, Watson and Williams (1939) followed the reaction between methyl iodide and eight meta and para substituted dimethyl anilines in methyl alcohol solution, and also found that  $A$  varied little, in contrast with the large variations in  $E$ .

Similar behaviour is reported (Bradfield, 1928, 1931) for the chlorination of phenolic ethers, where the



variations in  $A$  are again small in comparison with the variations in the activation energy.

These (and other) examples are usually taken as evidence that the energy of activation is mainly dependent on the electron availability at the reaction centre, provided that steric considerations do not cause complications. The substituents used are all separated from the reaction centre by a benzene nucleus, which can transmit the electrical effects caused by the substituent, without introducing any steric strain.

#### REACTION SERIES IN WHICH THE ENTROPIES AND ENTHALPIES OF ACTIVATION VARY TOGETHER

In a series of related reactions, involving moderate changes of structure, or systematic variations in the solvent in a mixed solvent system, the enthalpies and entropies of activation vary in a correlated manner, a large entropy of activation going with a large enthalpy of activation, and a small entropy with a small enthalpy. At times this correlation reaches the precision of a linear relationship characteristic of the particular reaction series. Many examples of such behaviour are known, in both first and second order reactions, and a few of these will be considered.

Although the correlated variation of entropy and enthalpy due to a variation in structure is similar to that which may accompany a systematic variation in the solvent, it is convenient to discuss them separately, as there are also several differences.

#### STRUCTURAL VARIATIONS

Blackadder and Hinshelwood (1958) give some results for the decomposition of a series of bisulphite compounds formed by the addition of sodium bisulphite to a number of aromatic and aliphatic aldehydes and



ketones. A good compensation effect is shown with the substituted benzaldehyde compounds, which is in some cases so pronounced that a compound of high activation energy can decompose faster than a compound of lower activation energy. The graph showing activation energy against  $\log A$  for the ortho substituted benzaldehyde compounds shows a fair degree of linearity, which is not so good, however, with the meta and para substituted compounds.

These plots are sometimes useful in identifying a change in reaction pattern, since the nature of the plot may very well vary with the reaction mechanism. An example is found in the hydrolysis of aromatic amides in aqueous ethanol, for which basic catalysis gives a good linear plot, whereas acid catalysis gives a curve concave toward the activation energy axis (Meloche and Laidler, 1951).

Sometimes the reactions of a series fall into two groups when the results are plotted in this manner, and the behaviour can often be explained by postulating some modification to the reaction mechanism. An example of this is the addition of hydroxylamine to alkyl thymyl ketones (Craft and Lester, 1951) which gives a good linear compensation plot as the alkyl group is varied. The value for methyl thymyl ketone lies appreciably to one side of this line, having a lower activation energy (or higher  $A$ ) than a corresponding point on the line. This can be understood on the basis that the methyl group imposes far less steric hindrance than the higher alkyl groups to the attacking reagent. This view is supported by the fact that the point for methyl thymyl ketone lies very close to the compensation line obtained when alkyl groups are varied in alkyl carvacryl ketones; the carvacryl ketones are isomeric with the thymyl ketones,



but offer less hindrance to the attacking hydroxylamine.

A further example of steric hindrance leading to a duality of compensation plots is in the unimolecular decomposition of substituted benzoyl peroxides in acetophenone, values for the meta and para substituted peroxides lying on one good line, while the values for the ortho substituted compounds lie on a line of slightly lower activation energy. This is possibly due to the higher steric strain in the ortho substituted compounds which raises their ground state potential energy, and thus aids the decomposition (Blomquist and Buselli 1951).

Similar correlations often exist between the total (thermodynamic) entropies and enthalpies of reaction, and Leffler (1955) has suggested that, since the correlations between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  ( $E$  and  $\log_{10} A$ ) or  $\Delta H$  and  $\Delta S$  frequently attain the precision of a linear relationship, this kind of relationship between the parameters has a theoretical basis, but that it is partly obscured by superimposed, independent variations. He defines the relationship;

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger \quad (15)$$

where  $\Delta H_0^\ddagger$  is a constant having the value of  $\Delta H^\ddagger$  when  $\Delta S^\ddagger$  is zero (it has no other significance) and  $\beta$  has the dimensions of temperature. The free energy of activation  $\Delta F^\ddagger$  is given by,

$$\Delta F^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad (16)$$

$$\text{and therefore, } \Delta F^\ddagger = \Delta H_0^\ddagger - (T - \beta) \Delta S^\ddagger \quad (17)$$



When  $T = \beta$ ,  $\Delta F^\ddagger = \Delta H^\ddagger$ , a constant for the series, and all the rate constants (or equilibrium constants) of reactions in the series will have the same value, within the limits of the relationship; that is to say, structure will have no effect upon rate or equilibrium. Since all the reactions have the same rate at the temperature  $\beta$ , Leffler calls it the 'isokinetic temperature'. He calls equation (15) the 'isokinetic relationship'.

If reactions were accidentally measured at the isokinetic temperature it would appear that the rate is independent of the changes in structure (or solvent) imposed, and this could easily lead to wrong conclusions. An example of this is the absence of rate changes due to solvent variation in the decomposition of phenyl azotriphenylmethane at  $36^\circ$ , even though there is an overall difference in activation energy of 4-5 K.cal./mole (Leffler and Alder, 1954).

Many organic chemists have found that a reaction is 'cleaner' at lower temperatures, that is there are less unwanted side products formed. Leffler suggests that this view should be modified slightly and that reactions are in fact cleaner at temperatures most removed from the isokinetic temperature, as it is at this temperature that the maximum number of isomers and side products will be formed.

This isokinetic relationship of Lefflers does not go any way toward explaining the causes of the effect, which is plausibly accounted for by Blackadder and Hinshelwood (1958). They observe that in unimolecular reactions  $A$  is often of the same order of magnitude as a bond vibration frequency, which implies that the



energy of activation is concentrated in a single bond in the transition complex, which has one critical vibrational degree of freedom. When  $A$  is appreciably higher than this, the interpretation is that the energy need only be more randomly distributed among several (say  $S$ ) degrees of freedom in the molecule. The probability of reaction is now increased by approximately  $(E/RT)^{S-1}/(S-1)!$ , which is manifested in an increased frequency factor. There is now a range of states of equal energy. The particular activation energy minimum, through which the reaction could take place by way of a single strictly defined state, is accompanied by a very low entropy. The number of molecules reacting is given by the product of the entropy and energy terms, and the observed reaction will not always correspond to the path of lowest activation energy, but it will correspond to the path giving the maximum product of these two terms. In a series of reactions various effects will displace the observed reaction toward, or away from, the path of lowest energy. As the mechanism is displaced toward the actual path of lowest activation energy, it will be accompanied by a lower frequency factor, and vice versa, so that a rough compensation will result.

The above model is strictly applicable to a unimolecular gas phase reaction, but it will also apply in essence to bimolecular reactions in solution, in which  $E$  is generally accepted to be a minimum when the approach of the attacking reactant is from a specific direction and in a specific orientation. The lowest value of the activation energy is thus accompanied by a low probability. It is convenient to denote this specific direction as the  $x$  axis, and the minimum



(relative) velocity of approach of the attacking species along this direction  $\dot{x}$ , in which case the lowest value of the activation energy will be related to  $\dot{x}^2$ . If the direction of approach is at an angle to the  $x$  axis the component of velocity along the  $x$  axis must still be at least  $\dot{x}$ . It will also have components of velocity at right angles to the  $x$  axis, say along the  $y$  and  $z$  axes and of magnitude  $\dot{y}$  and  $\dot{z}$ . Its actual velocity will be  $(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)^{\frac{1}{2}}$ , and the activation energy corresponding to this direction of approach will be related to  $(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$ , which is greater than  $\dot{x}^2$ , and the reaction will then have a higher activation energy.

Provided that the component of velocity along the  $x$  axis is not less than  $\dot{x}$ ,  $\dot{y}$  and  $\dot{z}$  can each take any value, and there is therefore a greater probability of reaction with an oblique approach, than for one strictly along the  $x$  axis.

The observed reaction will correspond to the values of  $\dot{x}$  and  $(\dot{y}^2 + \dot{z}^2)^{\frac{1}{2}}$  which give a maximum value to the energy-entropy product, and changes in the structure of the reactants will not only change  $\dot{x}$  directly, but they will also change the most favourable direction of approach, a rough form of compensation resulting.

It is also possible for solvation to cause a similar effect, especially in reactions where the activated collision complex is more (or less) solvated than the reactants. Spontaneous solvation (or desolvation) must now take place during the formation of the transition complex, with a resulting release (absorption) of energy, which lowers (raises) the observed activation energy. Since the solvent molecules are more constrained in a solvation sheath than they



are in the bulk solvent, the formation of a transition complex which is more solvated than the reactants will be accompanied by a loss of entropy, and vice versa.

The formation of a highly solvated transition complex is therefore accompanied by lowered energy and entropy of activation, whereas the formation of an only moderately solvated transition complex is accompanied by a higher energy and entropy of activation. These effects give a rough form of compensation.

A common type of reaction in which a large change of solvation occurs is one in which an ionic product is formed from non-polar reactants. When the reactants are modified, the polarity of the transition complex will also vary, as a result of the inductive influences of groups around the reaction centre. The transition complexes of greatest polarity will orientate most solvent molecules. There will then be a greater release of solvation energy, and a further lowering of the activation energy, but there will also be a further lowering of the activation entropy. The less polar transition complexes will orientate fewer solvent molecules, and their formation will therefore be accompanied by higher energies and entropies of activation.

Since an aromatic system can transmit the inductive effects of substituents, it is possible for substituents apparently remote from the reaction centre to modify its polarity, and thus cause a change in the solvation sheath, leading to compensating variations in  $A$  and  $E$ . Several reports have appeared in which substituents meta or para to the reaction centre cause correlated changes in  $A$  and  $E$  (Berliner and Altschul, 1952; Burkhardt, Horrex and Jenkins, 1936; Timm and Hinshelwood, 1938).



## SOLVENT VARIATIONS

The correlated variations of A and E, as solvents are varied systematically, have many features in common with the variations caused by structural changes in the reactants, but there are differences, in that there is now a possibility of large variations in the nature of the solvation sheath. The similarity between solvent and structural changes is nicely demonstrated in the results of Hegan and Wolfenden (1938) who studied the alkaline hydrolysis of two  $\gamma$ -lactones, each in four solvent mixtures. They obtained eight points, which lie on the same 'compensation' line.

Less satisfactory are the results of Hartley (1938), and Le Fevre and Northcott (1949, 1953) which show a large scatter. These results are for the cis-trans isomerism of azobenzene and p-chlorophenyl diazocyanide, in a wide range of solvents, ten solvents being used for the former reaction, and eight solvents for the latter.

There is also a wide scatter in the results reported for the reaction between methyl iodide and pyridine in various mixed solvents (Fairclough and Hinshelwood, 1937a; Raine and Hinshelwood, 1939) and quite complicated behaviour was found, the values of the activation energy sometimes passing through maxima and minima as the solvent composition was varied. This particular behaviour leads to the same activation energy at three different solvent compositions, the values of A at these compositions being obviously independent of the value of E, and only dependent on some property of the solvent. A smooth interpolation curve was therefore drawn through these points, and the overall variation of A corrected for this systematic dependence on the solvent. The resulting variation in A was strikingly similar to the



variation of E, with solvent composition. It was also found that in other mixed solvent systems the results could be adequately interpreted by postulating a dependence of A upon E, together with a dependence of A upon solvent polarity.

In order to obtain more information about this variation of A upon solvent polarity, Fairclough and Hinshelwood (1938) studied the Diels-Alder reaction between cyclopentadiene and benzoquinone, which has non-polar reactants and products, and presumably a non-polar transition state, results for six pure solvents being tabulated. In the reaction A varies with E in the usual manner, but it is found to be appreciably higher with the three polar solvents, than with the three non-polar solvents, again showing the increase of A with solvent polarity, and giving some support to a suggestion that the collision number may vary with solvent polarity.

A plausible theory which explains the variation of both A and E with the composition of certain mixed solvent systems is that of Venkataraman and Hinshelwood (1960). The theory has been applied to results for the acylation of substituted anilines in solvents consisting of mixtures of benzene and nitrobenzene, where it is found that the activation energy falls rapidly with increasing proportion of the polar solvent until the latter constitutes 25% of the whole, at which point the activation energy attains a constant value, and is insensitive to further addition of the polar solvent. The value of the frequency factor also falls sharply until the proportion of the polar solvent is 25%, at which point it passes through a minimum, and then rises again.



The theory postulates that in the two pure solvents there will be two different types of transition complex, each corresponding to different activation energies, and frequency factors, the transition complex in the polar solvent having a lower activation energy due to the greater stabilisation of the charges. As polar solvent is added to the non-polar solvent a very small number of transition complexes will be formed, giving a reaction rate with a low activation energy, but also with a low frequency factor reflecting the relative scarcity of these complexes. The observed rate, which is equal to the sum of the rates due to all the different mechanisms, will be governed more and more by these fast reacting complexes as the amount of polar solvent is increased, until when the polar solvent is present to the extent of 25% of the whole, reaction through this mechanism has completely swamped that due to the mechanisms of higher activation energy. From this point on there is no change in the activation energy, but as the proportion of polar solvent is increased, a larger number of these fast reacting intermediates are formed, leading to a rise in the pre-exponential factor  $A$ . The initial decrease in the pre-exponential factor is due to the progressively smaller contribution, to the total rate, of the relatively plentiful complexes of high activation energy, and the increasing contribution to the total rate of the scarce complexes of low activation energy. Numerical calculations based on this theory reproduce the shape of the experimental curves in a general qualitative manner.



REACTION SERIES IN WHICH THE ACTIVATION ENERGY REMAINS  
CONSTANT

The type of behaviour in which  $E$  remains constant, and variations in  $A$  determine the reaction rate, is known only from studies of a reaction in different pure solvents, of mixed solvent systems in some composition ranges, as mentioned above, and of the effect of pressure on reaction rate.

Pickles and Hinshelwood (1936) followed the formation of methyl pyridinium iodide in thirteen different solvents, and found that while the activation energy rose appreciably with some solvents of very low polarity, it was more or less constant for solvents of higher polarity, differences in reaction rate being caused by changes in  $A$  alone in these cases. The benzylation of *m*-nitroaniline, studied in eight solvents, also displayed this same effect, the value of  $A$  gradually rising with solvent polarity. The results of Grimm, Ruf and Wolf (1931) for the interaction of ethyl iodide and triethylamine in 17 aromatic solvents again show this type of behaviour. The aromatic solvents all correspond to similar activation energies, while two aliphatic solvents used were associated with much higher activation energies, and the variation in  $A$  alone accounted for the variation of rate in the aromatic solvents.

The effect of pressure on the rate of formation of quaternary ammonium salts has been studied by several workers, and here it is found that variations in  $A$  are of much greater importance than variations in  $E$ . Harris and Weale (1961) studied seven reactions in methyl alcohol solution, and one reaction in nitrobenzene solution, at pressures of up to 4,925 atmospheres.



The reaction rate is increased considerably by pressure, solely as a result of the increased value of  $A$ . In one case the value of  $A$  rises by a factor of 20, while  $E$  changes by only 0.1 k.cal./mole, which is less than the experimental error. The results of Gibson, Fawcett and Perin (1935) for the formation of quaternary ammonium salts in acetone solution also show a very great increase in  $A$  as the pressure is increased, although in these cases there is a slight rise in  $E$ .

A gradual variation in solvent character can be achieved with mixtures of two different liquids, and the dependence of the rate of the so called Menschutkin and similar reactions on the solvent has been studied in this way, as mentioned earlier. In these systems there is evidence for a general increase of  $A$  with solvent polarity, but the effect is partly masked by the dependence of the activation energy itself on solvent polarity.

Leffler (1955) has suggested that this dependence of  $A$  on the solvent may be caused by the need for partial desolvation of the reactants during the formation of the transition complex. In the ground state the reactants will be highly solvated, and some of the solvent molecules will need to be removed before the transition complex can be formed. As the solvent molecules are less constrained in the bulk of the solution, this dissolution will be accompanied by an increase of entropy, which will contribute to an increase in  $A$ . In polar solvents the solvation sheath is likely to be more tightly packed around the reactants, and there will be a larger increase of entropy on this partial desolvation, and a greater  $A$ . The desolvation will also be accompanied by an absorption of energy,



which is reflected in the fact that some highly polar solvents give higher activation energies to Menschutkin reactions, than do some less polar solvents. (Watanabe and Fuoss, 1956)

If this process is important, it could be argued that as the reactants become desolvated, and the solvating molecules are freed, there will be an increase of volume or a positive contribution to the volume of activation.

It is generally found that the total volume of activation is negative. This does not invalidate the view however, since the partial desolvation, although important, is not the whole story.

Another possibility is that the initial state of the pure solvent is important, solvents with strong dipoles being fairly ordered and of low entropy. In the results of Grimm, Ruf and Wolf (1931) the activation energies in the different aromatic solvents are all fairly close to a standard value, giving ground for the postulate that the activated complexes are all rather similar, with more or less equally ordered solvation sheaths. When solvent molecules become bound into this solvation sheath they have less freedom and a lower entropy than in the bulk of the solvent. The magnitude of the resulting entropy loss is dependent not only on the degree of order in the transition complex, but also on the degree of disorder in the bulk solvent. Very disordered solvents will sustain a much greater entropy loss in the formation of a solvated collision complex, and this circumstance will lead to a low frequency factor. On the other hand strongly polar solvents will, in general, be more ordered, and with these there will be a smaller entropy loss in the formation of the solvated transition complex, and thus a higher frequency factor.



An indication of the degree of order in a solvent is given by its freezing point, since solvents only just above their freezing points will have clusters of molecules arranged in a way similar to that of the solid crystal, whereas solvents at temperatures much higher than their freezing points will have lost this order. Solvents that freeze just below the working temperature will therefore be more ordered than those with very low freezing points, and will suffer a smaller entropy loss when they become bound into the highly ordered solvation sheath of a transition complex.

#### ENTROPIES OF ACTIVATION AND MELTING POINTS

There seems to be little or no discussion in the literature of this question of the order in the solvent itself, and a short investigation was accordingly made.

The view expressed above is supported by the plots of  $\log_{10} A$  against solvent freezing point shown in figures 1 and 2, where there is not only a definite trend in the predicted direction, but the plots give reasonable straight lines. In figure 1 the results of Grimm, Ruf and Wolf (1931) for the quaternization of triethylamine by ethyl iodide are plotted, whilst in figure 2 the results of Pickles and Hinshelwood (1936) for the quaternization of pyridine by methyl iodide are used. The latter workers did not publish values of  $A$ , but since the activation energies of the reaction are almost constant in the solvents used it is permissible to use  $\log_{10} k$  instead. The reaction between benzoyl chloride and *m*-nitro aniline, also studied by Pickles and Hinshelwood, has the same activation energy in several solvents, and gives the same type of plot as that shown in figure 2.



Figure I

Frequency factor against solvent freezing point

Freezing pt. of solvent, °C

for reaction  $\text{Et-I} + \text{Et}_3\text{N} \rightarrow \text{Et}_4\text{NI}$   
from Grimm,  $R_{\text{uf}} \propto \text{Wolf (1931)}$

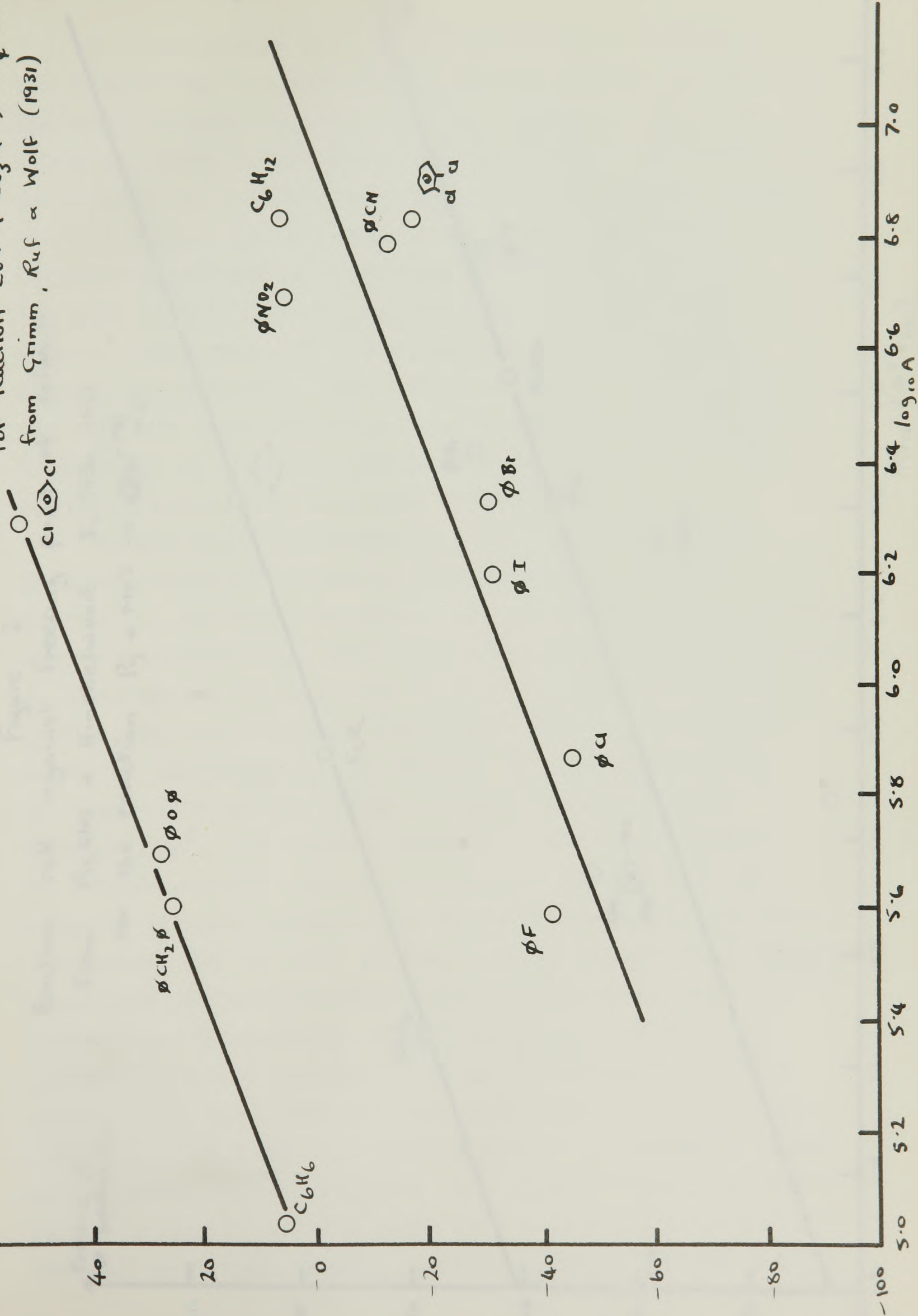




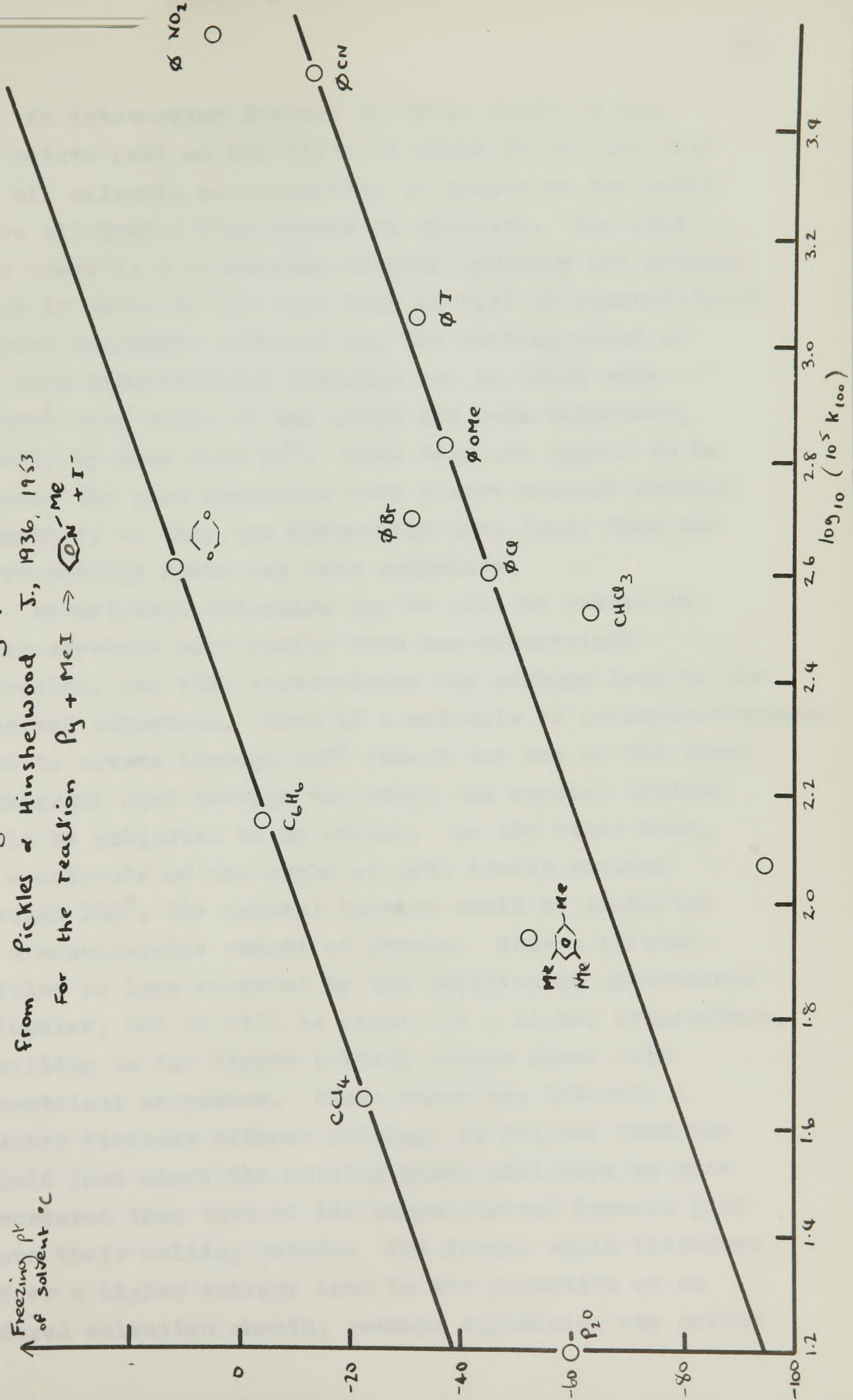
Figure 2

Reaction rate against freezing point of solvent

from Pickles & Hinshelwood J., 1936, 1953

for the reaction  $\text{Py} + \text{MeI} \rightarrow \text{Py-Me} + \text{I}^-$

Freezing pt  
of solvent °C





An interesting feature of these plots is that the points fall on two lines of equal slope, and that the six solvents corresponding to points on the upper lines all have a high degree of symmetry. The fact that there is a connection between symmetry and melting point is shown by the fact that of over 50 disubstituted benzene compounds referred to, the melting point of the para disubstituted compound was in every case greater than those of the ortho and meta compounds, usually by more than  $30^{\circ}$ . This does not appear to be because the para compounds have a more compact crystal structure, as they are frequently less dense than the corresponding ortho and meta compounds.

Symmetrical molecules may be able to rotate in their crystals more easily than non-symmetrical molecules, and this circumstance may perhaps lead to the observed behaviour. Thus if a molecule of p-dichlorobenzene were to rotate through  $180^{\circ}$  (about any one of the three orthogonal axes through the ring) the crystal lattice would be subjected to no strain. On the other hand, if a molecule of the ortho or meta isomer rotated through  $180^{\circ}$ , the crystal lattice would be subjected to a considerable amount of strain. Thus a crystal lattice is less weakened by the rotation of symmetrical molecules, and it will be stable at a higher temperature, resulting in the higher melting points found with symmetrical compounds. Since these can tolerate a greater disorder without melting, it follows that the liquid just above the melting point will also be more disordered than that of its unsymmetrical isomers just above their melting points. The former would therefore suffer a higher entropy loss in the formation of an ordered solvation sheath, perhaps explaining why points



corresponding to solvents of high symmetry lie on a different line to those of low symmetry in figures 1 and 2.

If this hypothesis has any validity the entropies and specific heats of symmetrical compounds should have features different from those of non-symmetrical compounds. Although no measurements appear to have been made on disubstituted benzene compounds, results have appeared for carbon tetrachloride and benzene, both of which correspond to points on the upper line of figure 2 (Davidson et al, 1948; Ubbelohde, 1950). In the case of carbon tetrachloride it is found that there are two crystal forms, a monoclinic low temperature form, and a cubic high temperature form. During the transition between the two forms there is a specific heat maximum, and a large entropy change, probably caused by the freeing of the fixed orientations enforced at lower temperatures. The entropy of fusion of the higher temperature form is therefore unusually low, and this has lead to the comment that crystals of carbon tetrachloride must be very 'liquid like' at temperatures a little below their melting point (Staveley, 1949). On the other hand no such transitions have been observed with solid benzene, which has a normal entropy of fusion.

Most organic solvents contract on freezing, showing that an increase of pressure raises the freezing point, and therefore makes the (liquid) solvent more ordered, indicating that reactions carried out at high pressures will have higher frequency factors than at atmospheric pressure. This is found in the results of Gibson, Fawcett and Perin (1935), and those of Harris and Weale (1961). The latter workers studied seven



quaternization reactions in methyl alcohol solution, and it was possible to calculate the freezing point of pure methanol at the pressures used (see Appendix I). The results lead to the graph shown in figure 3. Since the variations of activation energy that Harris and Weale report are less than those due to experimental error, a mean value of the activation energy has been taken for each reaction and frequency factors recalculated from the rate constants, sometimes for pressures at which a reaction had been studied at only one temperature. These recalculated values of A were used in the construction of figure 3, in which trends are again obtained in the sense predicted. The plots have only a slight curvature.

The gradients of the curves in figure 3 vary slightly from reaction to reaction, probably since the respective transition complexes incorporate differing numbers of solvent molecules. The most solvated transition complexes will be most sensitive to changes in the initial structure of the solvent, and will correspond to the shallowest plots. Thus, since in the reactions with dimethyl aniline, the one with methyl iodide has the steepest plot, the transition complex would here be the least solvated. Similarly, those formed in the reactions with ethyl or n-butyl iodide would be slightly more solvated, while there would be most solvation in the reaction with iso-propyl iodide, indicating that bulky alkyl groups actually favour solvation. The reactions of dimethyl aniline also show a uniform trend of activation energy, but in the opposite sense to that expected from the variation in solvation. The most solvated transition complex formed with iso-propyl iodide, is associated with the greatest activation energy, while the least solvated,

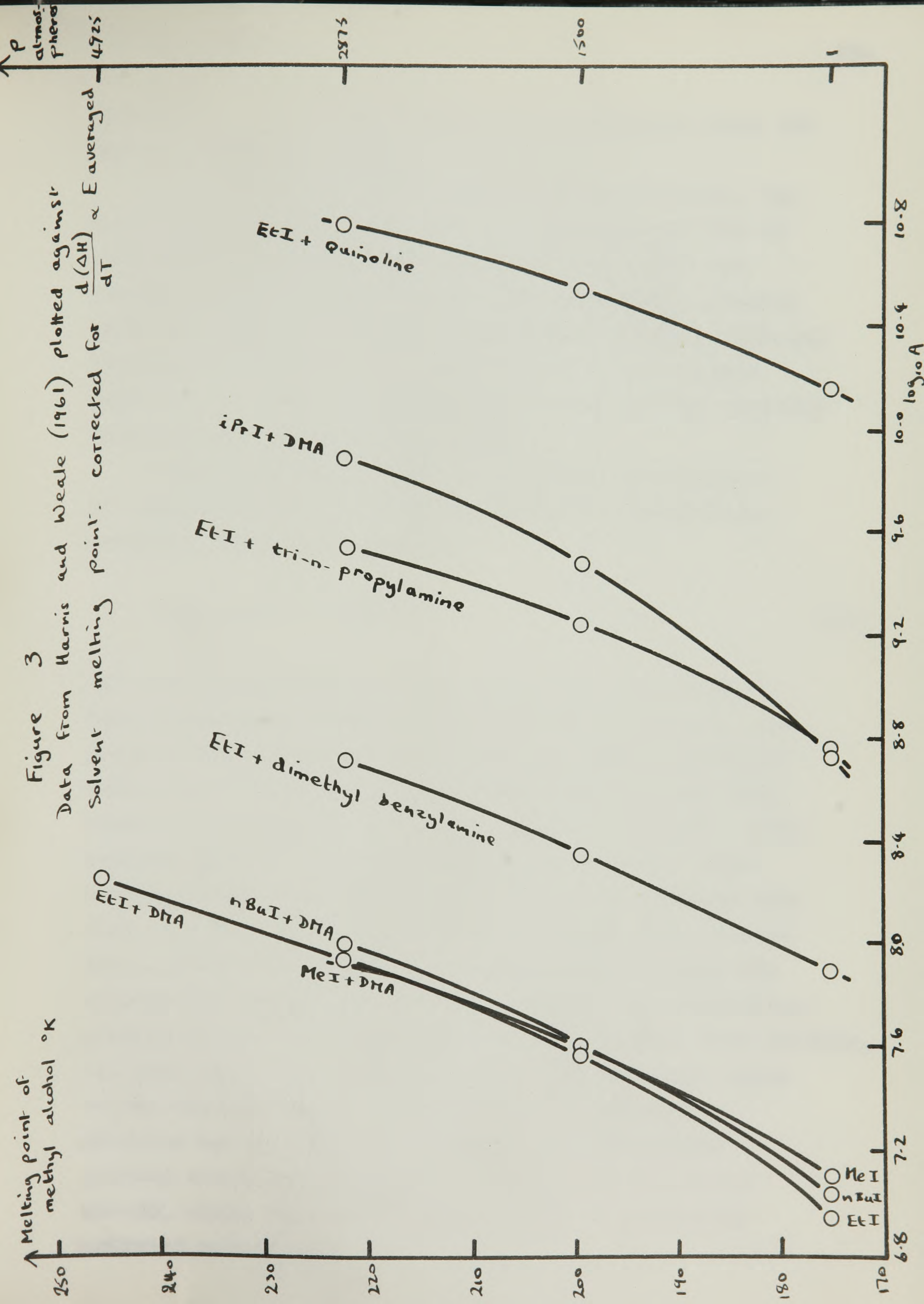


Melting point of methyl alcohol °K

Figure 3

Data from Harris and Weale (1961) plotted against Solvent melting point, corrected for  $\frac{d(\Delta H)}{dT} \propto E$  averaged

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that formed with methyl iodide, is associated with the lowest activation energy.

At pressures of more than 2,875 atmospheres, the variation in the values of A is also uniform, but at atmospheric pressure the reactions with ethyl and n-butyl iodides have somewhat lower frequency factors than that for the reaction with methyl iodide, although iso-propyl iodide is associated with a much larger value of A. This is surprising in view of the apparent trend in the degree of solvation.

Harris and Weale (1961) calculated the volumes of activation  $\Delta V^\ddagger$ , for the reactions at atmospheric pressure, from the equation,

$$d(\ln.k)/dP = -\Delta V^\ddagger/RT \quad (18)$$

and from comparison of these noted the same anomaly. They constructed models of the reaction products, and came to the conclusion that the unexpected behaviour arose from a balance of importance between what they term the primary and secondary solvation shells. They suggest that in the transition complex formed with methyl iodide four solvent molecules can approach very close to the positively charged nitrogen atom, but in those formed with ethyl and n-butyl iodides only two solvent molecules are capable of this. The transition complex formed with iso-propyl iodide is even more extreme, and here only one solvent molecule can approach close to the nitrogen atom. The reduced stabilization afforded by the primary solvation sheath demands greater stabilization from the secondary solvation sheath, which involves a large number of partially oriented molecules.



With methyl iodide there is a large entropy loss in the formation of the primary solvation sheath, but the high degree of stabilization given by this contributes to the low activation energy. The ethyl and n-butyl iodide reactions suffer a smaller entropy loss during the formation of the primary solvation sheaths, but this is offset by the increased order of the secondary solvation sheaths, so that the resulting value of  $A$  is slightly lower. The decreased stabilization now given to the changed complex contributes to the higher activation energy. Iso-propyl iodide reacts to form a transition complex in which the primary solvation sheath is very weak, and associated with a very small entropy loss. This is partly offset by the increased order of the secondary solvation sheath, but results in a much higher value of  $A$ . The low stabilization afforded to this transition complex contributes to the high activation energy.

From the foregoing discussion, it therefore appears that, provided the activation energy for a reaction remains constant, information about the interaction of the solvent and the transition complex can be obtained from the variation of frequency factor with the imposed pressure, or with the melting point of the solvents in a suitable series. It may then be possible to study the degree of solvation involved in related reactions by determining their reaction parameters in several solvents. Application of this view to the results shown in figures 1 and 2 suggests that the transition complex formed in the quaternization of pyridine by methyl iodide is more solvated than that involved in the formation of tetra-ethyl ammonium iodide, a not unreasonable conclusion. These graphs



also show that solvents with symmetrical molecules may give more precise information, since they have a better line.

From the above measurements (Table I), page 30, the boiling point of benzene at 1 atmosphere =  $175.2^{\circ}\text{F}$ .  
 Density of benzene at  $175.2^{\circ}\text{F}$  =  $0.6818 \text{ g./ml.}$   
 Specific heat of benzene,  $1.00 \text{ cal./g.}^{\circ}\text{C.}$   
 From International Critical Tables Vol. III, p. 401, the density of water at  $175.2^{\circ}\text{F}$  =  $0.9990 \text{ g./ml.}$   
 Density of liquid benzene at boiling point =  $0.6818 \text{ g./ml.}$

Using  $\Delta T = 1.00 \text{ cal./g.}^{\circ}\text{C.}$ , density of benzene (175.2) and that of water at  $175.2^{\circ}\text{F}$  by equation (1):

$$\text{Then } \frac{\Delta T}{\Delta T} = \frac{\Delta T}{\Delta T} \quad \text{or} \quad \frac{\Delta T}{\Delta T} = \frac{\Delta T}{\Delta T}$$

$$\therefore \frac{\Delta T}{\Delta T} = \frac{\Delta T}{\Delta T} = \frac{\Delta T}{\Delta T}$$

$$\therefore \frac{\Delta T}{\Delta T} = \frac{\Delta T}{\Delta T} = \frac{\Delta T}{\Delta T}$$

at  $175.2^{\circ}\text{F}$ ,  $\Delta T = 1.00 \text{ cal./g.}^{\circ}\text{C.}$ , then using (1):

$$\frac{\Delta T}{\Delta T} = \frac{\Delta T}{\Delta T} = \frac{\Delta T}{\Delta T}$$

The position of integration in equation (1) is then:

$$\text{Then } \frac{\Delta T}{\Delta T} = \frac{\Delta T}{\Delta T} = \frac{\Delta T}{\Delta T}$$

$$\text{Then } \frac{\Delta T}{\Delta T} = \frac{\Delta T}{\Delta T} = \frac{\Delta T}{\Delta T}$$



APPENDIX I

Calculation of the freezing point of pure methanol at high pressures.

From 'Selected Thermodynamic Properties' II, page 586;

Melting Point of methanol at 1 atmosphere =  $175.2^{\circ}\text{K}$

Latent heat of fusion,  $\Delta H = 757$  cal/mole.

Specific heat change,  $\Delta C_p = 4.2$  cal/mole.

From International Critical Tables; III, 45 and V, 181;

Density of solid methanol at melting point =  $0.9673$  gm/ml

Density of liquid methanol at melting point  
=  $0.90314$  gm/ml.

Giving  $\Delta V = 2.964$  ml/mole. Results of Bridgeman (1942) show that  $\Delta V$  is affected little by pressure.

$$\text{Now, } \frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \quad \text{or} \quad \frac{dP}{d(\ln.T)} = \frac{\Delta H}{\Delta V} \quad (1)$$

$$\therefore \frac{d^2 P}{dT \cdot d(\ln.T)} = \frac{1 \cdot d(\Delta H)}{\Delta V \cdot dT} = \frac{\Delta C_p}{\Delta V} \quad (\text{approx}) \quad (2)$$

$$\therefore \frac{dP}{d(\ln.T)} = \frac{\Delta C_p}{\Delta V} \cdot T + \text{const.} \quad (3)$$

at  $175.2^{\circ}\text{K}$ ,  $\Delta H = 757$  cal/mole, then using (1);

$$\frac{dP}{d(\ln.T)} = \frac{757}{2.964} \text{ cal/ml.} = 1.059 \times 10^4 \text{ atmospheres} \quad (4)$$

The constant of integration in equation (3) is thus,

$$\text{const.} = 280 \text{ atmospheres.}$$

$$\text{Then } \frac{dP}{d(\ln.T)} = \frac{\Delta C_p}{\Delta V} \cdot T + 280 \quad (5)$$



$$\frac{dP}{d(\ln.T)} = 58.88T + 280 \quad (6)$$

$$\text{i.e. } \frac{dP}{dT} = 58.88 + \frac{280}{T} \quad (7)$$

$$P = 58.88T + 280.\ln.T + \text{const.} \quad (8)$$

When  $P = 1$ ,  $T = 175.2^{\circ}$ , and the constant of integration in equation (8) is therefore  $-11,723$  atmospheres, then

$$P = 58.88T + 280.\ln.T - 11,723 \quad (9)$$

$$= 58.88T + 644.9.\log_{10} T - 11,723 \quad (10)$$

Substitution of suitable values for  $T$ , and evaluation of  $P$ , gave a graph of  $T$  against  $P$ , from which the following melting points were obtained,

$P = 1$ atmosphere	$T = 175.2^{\circ}\text{K}$
1,500 "	199.5 <sup>o</sup>
2,875 "	222.4 <sup>o</sup>
4,295 "	245.9 <sup>o</sup>



RESULTS

From the results of the tests, it was found that the rate of the reaction was not affected by the concentration of the reactants, but was affected by the temperature. The rate of the reaction increased with increasing temperature, and the activation energy was found to be 15.5 kJ/mol.

The results of the tests of the reaction of the reactants with the catalyst showed that the rate of the reaction was not affected by the concentration of the catalyst, but was affected by the temperature. The rate of the reaction increased with increasing temperature, and the activation energy was found to be 15.5 kJ/mol.

The results of the tests of the reaction of the reactants with the catalyst showed that the rate of the reaction was not affected by the concentration of the catalyst, but was affected by the temperature. The rate of the reaction increased with increasing temperature, and the activation energy was found to be 15.5 kJ/mol.

SECTION II

The results of the tests of the reaction of the reactants with the catalyst showed that the rate of the reaction was not affected by the concentration of the catalyst, but was affected by the temperature. The rate of the reaction increased with increasing temperature, and the activation energy was found to be 15.5 kJ/mol.

EXPERIMENTAL METHODS

The reaction was carried out in a 250 ml round-bottomed flask fitted with a magnetic stirrer and a thermometer. The reactants were weighed accurately and added to the flask. The flask was then sealed and placed in a water bath at the desired temperature. The reaction was allowed to proceed for a certain period of time, and the products were then analyzed. The rate of the reaction was determined by measuring the concentration of the reactants at different times. The activation energy was determined by plotting the natural logarithm of the rate constant against the reciprocal of the absolute temperature. The results of the tests showed that the rate of the reaction was not affected by the concentration of the reactants, but was affected by the temperature. The rate of the reaction increased with increasing temperature, and the activation energy was found to be 15.5 kJ/mol.



## APPARATUS

Grade 'A' burettes were used, whilst pipettes were grade 'B'. The latter were calibrated against both water and nitrobenzene. Special attention was given to the drainage time with nitrobenzene, and pipettes of the same capacity were chosen from ones with similar drainage times.

Thermometers were of the mercury in glass type, all were checked against thermometers calibrated at the National Physical Laboratory, and used under the specified conditions.

Thermostats at 6°, 25°, 40°, 60°, 80°, and 120°C were all electrically controlled, and were accurate to within 0.1°C. Electrically heated boilers were used at 100° and 140°, the former containing distilled water, and the latter m-xylene. Since the boiling points of these liquids vary slightly with barometric pressure, a close check was kept on them with thermometers.

The boiling water bath consisted of a lagged tank fitted with a drip feed constant head device, and with a false bottom above which the water had a uniform temperature. Reaction tubes were immersed directly in the liquid. The 140° boiler was fitted with a reflex condenser, and had pockets in which the ampoules were placed, good thermal contact being ensured by the addition of a little glycerine. As the pockets had a relatively low heat capacity it was found necessary to pre-heat the ampoules at 120°C for a brief time, a small empirical correction was then made to the time of reaction to compensate for this pre-heating.



MATERIALS

'Analytical Reagent' grade nitrobenzene and laboratory grade chlorobenzene were used throughout. Solvent mixtures were initially prepared by calculating the volumes of the two separate components needed to give the required weight percent mixture, and accurately pipetting these into a stock bottle. It was later found more convenient to mix weighed amounts of the two components. The density of the mixed solvents served as a check on the solvent preparation.

Dimethyl p-anisidine was prepared by the method of Bordwell and Boutan (1956). All other reactants were standard laboratory grade reagents. They were purified by distillation or recrystallisation and had the following melting and boiling points;

methyl iodide (MeI)	b.p. 42°C
ethyl iodide (EtI)	72°
ethyl bromide (EtBr)	38°
n-propyl iodide (n-PrI)	101.5°
n-butyl iodide (n-BuI)	130°
dimethyl aniline (DMA)	m.p. 2°C
dimethyl p-toluidine (DMpT)	209°
dimethyl p-anisidine (DMpA)	101° (10 mm. Hg) m.p. 46°
p-bromo dimethyl aniline (pBrDMA)	54.5°
dimethyl p-nitroso aniline (pNODMA)	85°
dimethyl m-toluidine (DMmT)	210°
dimethyl m-nitroaniline (mNDMA)	58°
dimethyl o-toluidine (DMoT)	184°
p-dimethylamino benzaldehyde (pDMAB)	74°
diethyl p-toluidine (DEpT)	229°
diethyl aniline (DEA)	215°
diethyl m-toluidine (DEmT)	229°
ethyl methyl aniline (EMA)	206°



In this list the letters in parenthesis are the abbreviations for the compounds used on some of the diagrams shown later.

Although some of the reactants were volatile, it was possible to prepare solutions of them of accurately known concentration by weighing them dissolved in the solvent, when their vapour pressures were quite low. 100 ml. of the solvent were pipetted into a clean, dry flask and accurately weighed. A suitable quantity of reagent was then added and the flask again weighed. The total quantity of solvent needed to give a solution of the required strength was calculated from the increase in weight and the solution was diluted accordingly by the use of pipettes and dropping tubes. 200 to 250 ml. quantities of  $M/5$  or  $M/10$  solutions were usually prepared. Solutions of solids were prepared by weighing a suitable quantity of the reagent into a beaker, and then adding the calculated volume of solvent. Since nitrobenzene is opaque to ultraviolet light, there was no photochemical decomposition of the reactant solutions.

The reaction rate measurements did not furnish a check on reagent concentration, and several attempts were made to analyse the initial solutions, but none of these proved fully reliable. In order, therefore, to guard against chance errors in preparation a comparison was always made with results obtained from an independently prepared batch of solution. Close checks were obtained, showing the precision of the preparations.

## TECHNIQUE

### Reactions

Equal quantities, usually 10 ml., of the two reactant solutions were pipetted into clean dry ampoules,



which were then sealed off in a blow torch flame and plunged into a thermostat tank. Ampoules used for short reactions at temperatures of  $40^{\circ}\text{C}$  or below were sometimes closed by corks. After a suitable time they were removed, cooled in an ice-water bath and washed prior to opening and analysis of the contents. Several reactions were very slow at room temperature, and no difficulties arose during the filling and sealing of the ampoules. Faster reactions were cooled in ice-water during the filling and sealing. For the fastest reactions partly filled ampoules were frozen in an ice-alcohol freezing mixture, and the second solution then added on top of the frozen mass. The ampoules were sealed without difficulty and then plunged into a thermostat tank and shaken, when melting and mixing quickly took place. With reactions at  $25^{\circ}$  and  $6^{\circ}$  the reactant solutions were immersed in the thermostat to attain the temperature of the bath before mixing.

#### ANALYSIS

The basic method of analysis was extraction of the quaternary ammonium salt from the reactant solution with water, and the Volhards titration of the ionisable halide with  $M/50$  silver nitrate solution.

Clean ampoules were opened, emptied into separating funnels and washed out with water, which dislodged remaining drops of reactant solution and extracted the salt from the thin film of solvent which sometimes adhered to the walls of the tube. The combined reactant mixture and aqueous washings were then shaken together in the funnel, and after settling, separated into beakers. The organic phase was shaken a further 3 times with water to give a total volume of roughly 200 ml.



A slight excess of M/50 silver nitrate solution was then run in from a burette and 5 ml. of ferric alum indicator added. The solution was frequently made strongly acid by the addition of 5-10 ml. of colourless 50% nitric acid, in order to intensify the end point, before the excess silver nitrate was back titrated with M/50 ammonium thiocyanate solution. At the end point the red colour formed with excess ammonium thiocyanate was just discharged by the addition of one drop of silver nitrate solution.

The small amounts of alkyl halides which dissolve in water do not react with silver nitrate at room temperature (Essex and Gelormini, 1926).

It was found that emulsions of nitrobenzene in water were formed during the extraction. These were stabilised by the quaternary ammonium salt, and the extractions took at least 15 minutes to complete, making it impossible to study fast reactions. When fine drops of the reaction mixture found their way into the titration solution the base dissolved in the acidic aqueous phase where it was oxidised to give a brown colouration, which obscured the end point of the titration. The oxidation was due to the combined effects of ferric alum and nitric acid, since both ferric sulphate and pure dilute nitric acid caused the colouration. A slight colouration was also formed by the photochemical decomposition of the precipitate in the presence of the reactant solution, but this caused little trouble. The oxidation, which appeared to be accelerated by the presence of halide ions, prevented the use of an acid to break the emulsions, or to stop the reaction by combination with the base, and it necessitated the accurate separation of organic



and aqueous phases if reliable results were to be obtained.

Emulsions can often be broken by the addition of a strong electrolyte, but no suitable electrolyte could be found. Alkalies could not be used for fear of hydrolysing the alkyl halide, and sulphates, fluorides, acetates, phosphates and borates are unacceptable since they reduce the sensitivity of the end point by reacting with the indicator to form complex ions. Several other salts are excluded because of their oxidising properties, or because they have coloured solutions.

The addition of small amounts of acetone (or ethanol) was found to reduce the stability of the emulsions, but this also increased the solubility of the base in the aqueous phase and was of no value.

Various methods of preventing further reaction of fast systems during the lengthy extraction were investigated. The first of these was extraction with ice cold water, but this had to be abandoned as in some cases the nitrobenzene froze in the separating funnel.

Another method used was extraction of the base with dilute perchloric acid, followed by the addition of alkali to release the aniline, and back extraction with ether. As the series of manipulations had to be performed very carefully to prevent loss of halide ion, it proved to be quite tedious.

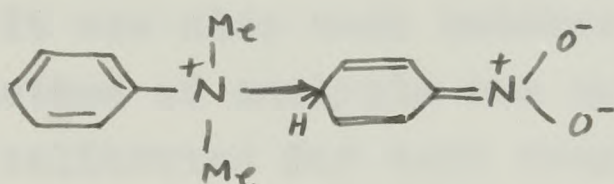
Dilution of the reactant solution with a non-polar solvent was next investigated, and after several attempts petroleum ether was found to be satisfactory. It not only stopped the reaction but prevented the formation of emulsions and lowered the solubility



of the salt in the organic phase, which now floated. The use of petroleum ether resulted in quicker and more accurate analyses, more than 95% of the salt now being removed in the first extraction.

Even so, the method of analysis was a little tedious, and above all it was of low accuracy in the earliest stages of the reaction. Some of the reactions studied did not go far at equilibrium, and in order to study these it was necessary to obtain accurate analyses of solutions containing about  $10^{-4}$  mole/litre of halide ion.

It had been noticed that many of the anilines gave strongly coloured solutions in nitrobenzene, due to the formation of addition compounds of the type (Bennett and Wain, 1936),



Solutions of quaternary ammonium salts in nitrobenzene are almost colourless, and the faint colour present could be due to the effect of the reverse reaction. There was thus a possibility that spectra might be of some help in analysing the solutions, but this was not so. Nitrobenzene is completely opaque at wavelengths of less than  $4,300\text{\AA}$ , and although there is an absorption peak at  $4,600\text{\AA}$  due to the addition compound formed between dimethyl p-toluidine and nitrobenzene, this was found to be very insensitive to the concentration of free base present during the reaction with ethyl bromide. In the visible range no new absorption peaks appeared with a solution that had undergone 10% reaction.



It had been found that the decomposition of the quaternary ammonium salts in nitrobenzene solution was not strictly unimolecular, indicating that they are slightly ionised, in which case the solutions should be electrically conducting. The use of conductivity as a method of following similar reactions has been mentioned by Chow and Fuoss (1958) and by Preston and Jones (1912).

The latter workers studied quaternization reactions, in ethanolic solution, and they developed a conductivity method for the measurement of quaternization rates in ethanolic solution.

After a little research a similar method was developed for reactions in nitrobenzene, and it proved to be of great help in measuring very small amounts of salt. It was also much quicker than titration.

The method of analysis was not absolute, but had to be calibrated for each reaction. A clean, cooled, reaction ampoule was opened, carefully emptied into a cool 6 x 1½" test tube and washed out with water into a second test tube. The conductivity of the reaction mixture was then measured at 6°C, after which the conductivity electrode was rinsed in the water contained in the second test tube. This dislodged most of the reaction mixture, and extracted the quaternary ammonium salt from any that remained. The combined reactant solution and wash water were then analysed by the extraction and titration procedure.

After the conductivity and composition of several solutions had been obtained a graph was drawn showing conductivity against percentage reaction, for the reaction



studied, as illustrated in figure 1.

It can be seen that at first the conductivity of the solution is very sensitive to the concentration of product, and linearly dependent on it. At higher salt concentrations the proportionality falls off, and the method becomes less sensitive.

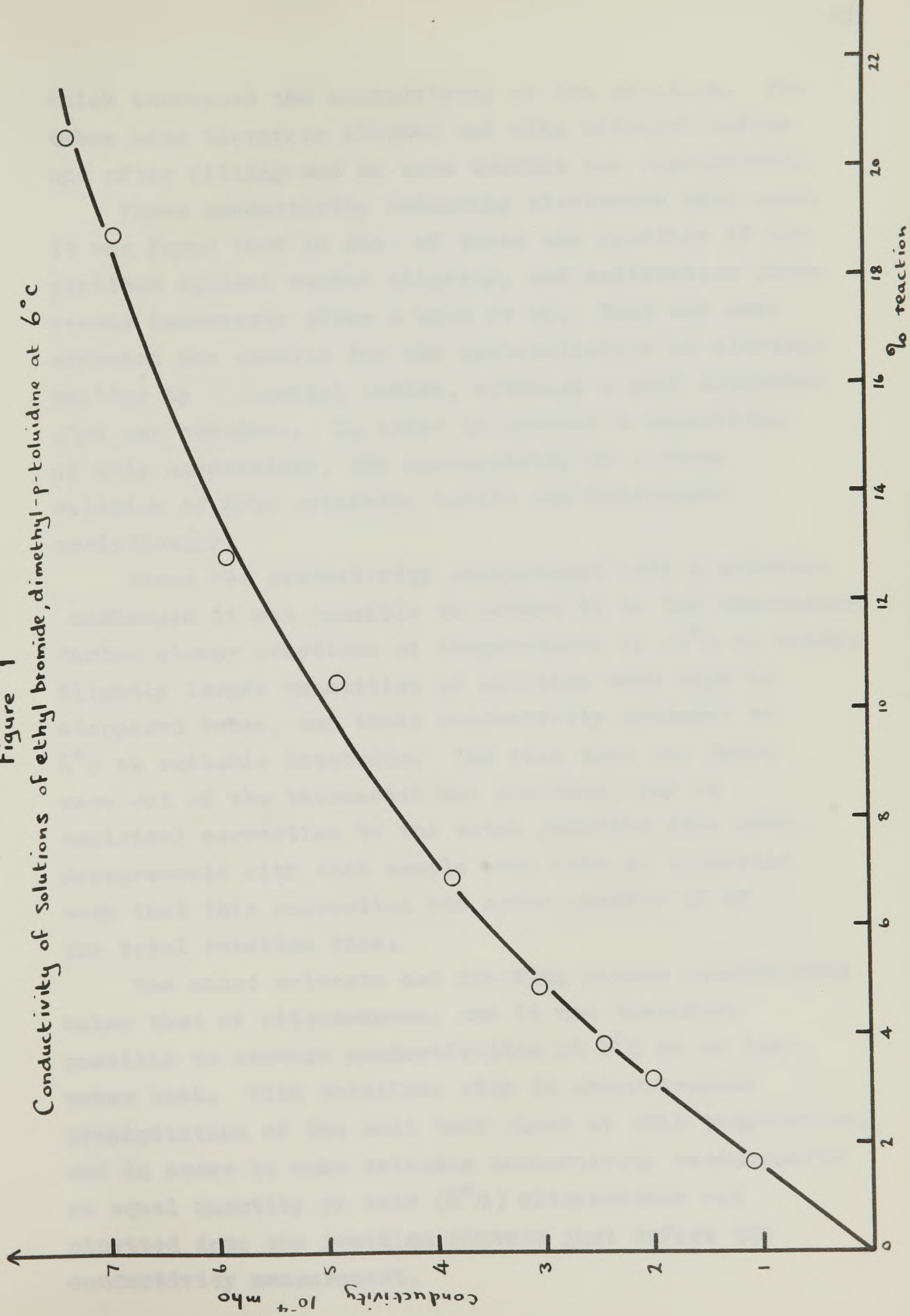
Once the calibration plot had been completed it was only necessary to measure the conductivity of a solution, and read off the corresponding percentage reaction. After each conductivity measurement the electrode was rinsed twice in acetone, and once in distilled water, ethanol and nitrobenzene respectively. It was shaken free from excess liquid between each rinsing, and blotted on a pad of clean filter papers. The reaction solution must have been diluted slightly by the nitrobenzene still adhering to the electrode, but since this was only a very small amount, and constant in both calibration and subsequent measurements, it introduced only negligible error.

The conductivity of the separate reactant solutions was extremely low, and outside the range of the conductivity bridge used. Several of these solutions were heated at  $80^{\circ}\text{C}$  for a few days, after which their resistance was still outside the range of the instrument. The conductivity of the unreacted solutions was accordingly presumed to be zero, and unaffected by heat. This was found to be so for solutions of ethyl iodide, methyl iodide and p-dimethyl aminobenzaldehyde (amongst others), but the calibration graphs for these systems were anomalous. The trouble was traced to the autoxidation of the benzaldehyde, in the presence of alkyl halide, to give small quantities of benzoic acid



Figure 1

Conductivity of solutions of ethyl bromide, dimethyl-p-toluidine at 6°C





which increased the conductivity of the solution. The tubes were therefore flushed out with nitrogen before and after filling and no more trouble was encountered.

Three conductivity measuring electrodes were used. It was found that in one of these the position of the platinum squares varied slightly, and calibration plots became inaccurate after a week or so. This may have affected the results for the quaternization of dimethyl aniline by *n*-propyl iodide, although a good Arrhenius plot was obtained. In order to prevent a repetition of this uncertainty, the conductivity of a stock solution of M/50 potassium iodide was determined periodically.

Since the conductivity measurement left a solution unchanged it was possible to return it to the thermostat during slower reactions at temperatures of 40°C or below. Slightly larger quantities of solution were kept in stoppered tubes, and their conductivity measured at 6°C at suitable intervals. The time that the tubes were out of the thermostat was recorded, and an empirical correction to the total reaction time made. Measurements with each sample were made at intervals such that this correction was never greater 1% of the total reaction time.

The mixed solvents had freezing points considerably below that of nitrobenzene, and it was therefore possible to measure conductivities at 0°C in an ice-water bath. With solutions rich in chlorobenzene precipitation of the salt took place at this temperature, and in order to make reliable conductivity measurements an equal quantity of cold (6°C) nitrobenzene was pipetted into the reaction mixture just before the conductivity measurement.



## SOLUBILITIES AND MELTING POINTS

The solubility of several salts in nitrobenzene at 25°C was measured by a modification of the titration procedure. Equal quantities of the two reactant solutions were mixed in an ampoule, which was then sealed off and thermostated at 25°C for several weeks, in which time crystals of a solid product often appeared. The tubes were quickly opened, dried and the contents filtered under suction into a thermostated receiver. Aliquots were then pipetted into beakers and analysed by extraction and titration, all determinations being made in triplicate. In cases where the reaction equilibrium at 25°C was not sufficiently favourable for precipitation of the salt to take place with reactant concentrations of M/10, solutions were prepared to give a concentration of M/5 after mixing. These were the most concentrated solutions used. Solubilities were only determined when no exchange reaction took place.

The residues after filtration were recrystallised to constant melting point from ethanol/petroleum ether, pure ethanol or aqueous ethanol, depending on the solubility and stability of the salt. Care had to be taken to minimise the decomposition of the salt in hot solutions.



### SECTION III

# GENERAL KINETIC RELATIONS IN PURE AND MIXED SOLVENTS



## INTRODUCTION

The quaternization of dialkyl anilines by alkyl halides has been studied in a variety of solvents, and in all but a few cases good second order rate constants have been reported. In polar solvents the reaction product sometimes remains in solution, and in several of these cases the reactions are reversible. In some of the work reported it has been necessary to take equilibrium constants into consideration when calculating rate constants.

The present work began with a study of the quaternization of dimethyl aniline by ethyl iodide in nitrobenzene solution, when it was found that the reaction was reversible, but contrary to previous reports equilibrium constants were of no help in calculating rate constants. The reason for this was traced to the decomposition of the quaternary ammonium salts, which were found to be capable of yielding several products. When allowances were made for this good rate constants were obtained.

Three reactions were also studied in a series of solvents consisting of mixtures of chlorobenzene and nitrobenzene. In the solvents containing 0-60% chlorobenzene use of the methods developed for reactions in pure nitrobenzene gave quite reasonable results, whilst in a solvent containing 80% chlorobenzene some difficulties were encountered. More serious difficulties were encountered in the solvents richest in chlorobenzene, since there appeared to be a modification to the characteristics of the reaction. This caused non linearity in the plots of the logarithm of the rate constant against the reciprocal of the absolute



temperature (Arrhenius plots). The difficulties were traced to three separate causes, the troublesome decomposition reaction met with in the reactions in pure nitrobenzene, the precipitation of a solid product which caused autocatalysis in some cases, and the effect of the solvent on the equilibrium constants.

#### REACTIONS IN NITROBENZENE SOLUTION

Hamman and Teplitzky (1956) and Evans, Watson and Williams (1939) used anhydrous methanol as solvent, whilst Clarke (1910), Thomas (1913) and Preston and Jones (1912) used anhydrous ethanol; Benkeser, DeBoer, Robinson and Sauve (1956) used pure acetone, and aqueous ethanol. Chow and Fuoss (1958) used propylene carbonate, Essex and Gelormini (1926) acetylene tetrachloride and benzyl alcohol. All found good second order constants. The last mentioned workers also followed the quaternization of dimethyl aniline by methyl iodide in nitrobenzene solution, and found that when an unimolecular reverse reaction was allowed for, good constants were obtained. Laidler (1938) also studied this reaction, but found that the reverse reaction had a slight contribution of second order character, showing that the quaternary salt is partially ionised. Harris and Weale (1961) report the reaction between ethyl iodide and dimethyl aniline in nitrobenzene, where the reaction equilibrium was used in the calculation of the rate constants, but they give no details.

The present work began with a study of the reaction of dimethyl aniline and ethyl iodide, in nitrobenzene solution. This reaction was shown to be reversible by the rapid fall of the simple second



order rate constants. Equilibria were accordingly measured at 60°, 80° and 100.7° (at 40° there was still reaction after 1,200 hours, and the equilibrium could not be determined) and equilibrium constants were calculated on the basis of an overall rate law,

$$\frac{dx}{dt} = k_1(a - x)^2 - k_2x \quad (1)$$

where  $a$  is the initial concentration of either reactant, and  $x$  is the concentration of the product at time  $t$ . If  $y$  is the concentration of product at equilibrium then,

$$K = \frac{k_1}{k_2} = \frac{y}{(a - y)^2} \quad (2)$$

Values of the equilibrium constant  $K$  were used to plot the logarithm of the equilibrium constant against the reciprocal of the absolute temperature, hereinafter called a "van't Hoff plot". A good straight line was obtained (see figure 1) substantiating the belief that the reverse reaction was predominantly of the first order. Integration of (1), and substitution from (2) gives (see Appendix II)

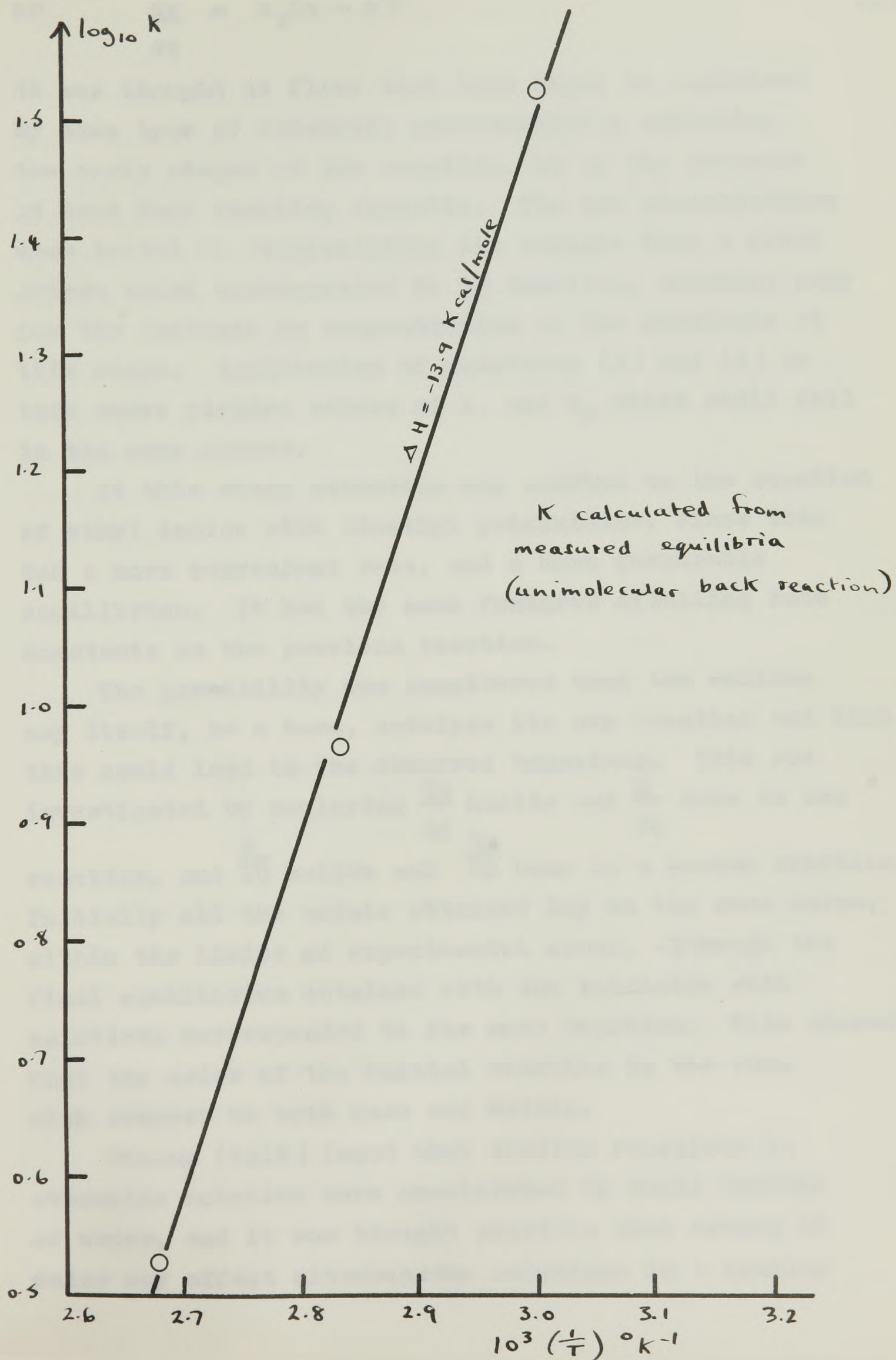
$$k_1t = \frac{2.303y}{(a^2 - y^2)} \cdot \log_{10} \left\{ \frac{(a^2 - xy)y}{a^2(y - x)} \right\} \quad (3)$$

Application of this equation to the results did not, however, yield good values of  $k_1$ , which fell during the reaction in a similar way to the simple second order constants  $k_3$  defined in the equations,

$$k_3t = \frac{x}{a(a - x)} \quad (4)$$



Figure 1  
EtI, DNA,  $\phi\text{NO}_2$  Van't Hoff Plot





$$\text{or } \frac{dx}{dt} = k_3(a-x)^2 \quad (5)$$

It was thought at first that this might be explained by some type of catalysis preferentially affecting the early stages of the reaction, or by the presence of some fast reacting impurity. The two possibilities were tested by recalculating the results from a false origin which corresponded to 5% reaction, allowing only for the decrease in concentration of the reactants at this stage. Application of equations (3) and (4) to this curve yielded values of  $k_1$  and  $k_3$  which still fell in the same manner.

At this stage attention was shifted to the reaction of ethyl iodide with dimethyl p-toluidine, since this had a more convenient rate, and a more favourable equilibrium. It had the same features of falling rate constants as the previous reaction.

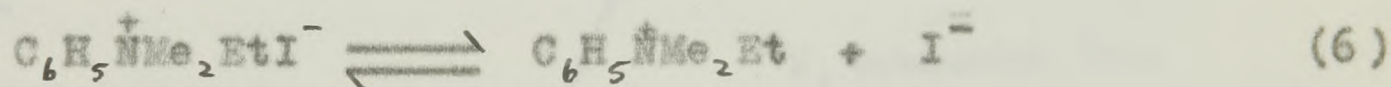
The possibility was considered that the aniline may itself, as a base, catalyse its own reaction and that this could lead to the observed behaviour. This was investigated by employing  $\frac{3M}{20}$  halide and  $\frac{M}{20}$  base in one reaction, and  $\frac{M}{20}$  halide and  $\frac{3M}{20}$  base in a second reaction. Initially all the points obtained lay on the same curve, within the limits of experimental error, although the final equilibrium obtained with the toluidine rich solutions corresponded to far more reaction. This showed that the order of the initial reaction is the same with respect to both base and halide.

Thomas (1913) found that similar reactions in ethanolic solution were accelerated by small amounts of water, and it was thought possible that traces of water may affect nitrobenzene solutions in a similar



way, and perhaps lead to the observed phenomena. Accordingly, a quantity of the solvent was rigorously dried over phosphorus pentoxide for several days, and fractionally distilled at reduced pressure. Use of this carefully dried solvent in a reaction at  $80^{\circ}\text{C}$  gave results differing from those previously obtained by less than 1%, showing that any traces of water contained in the solvent do not affect the reaction.

It is possible that dimethyl ethyl anilinium salts may be more highly ionised than the corresponding trimethyl anilinium salts, and this could lead to the reverse reaction having pronounced second order character. The initial ion-pair product would ionise as follows,



the ionisation constant being,

$$K_1 = \frac{[\text{C}_6\text{H}_5\text{N}^+\text{Me}_2\text{Et}][\text{I}^-]}{[\text{C}_6\text{H}_5\text{N}^+\text{Me}_2\text{EtI}^-]} \quad (7)$$

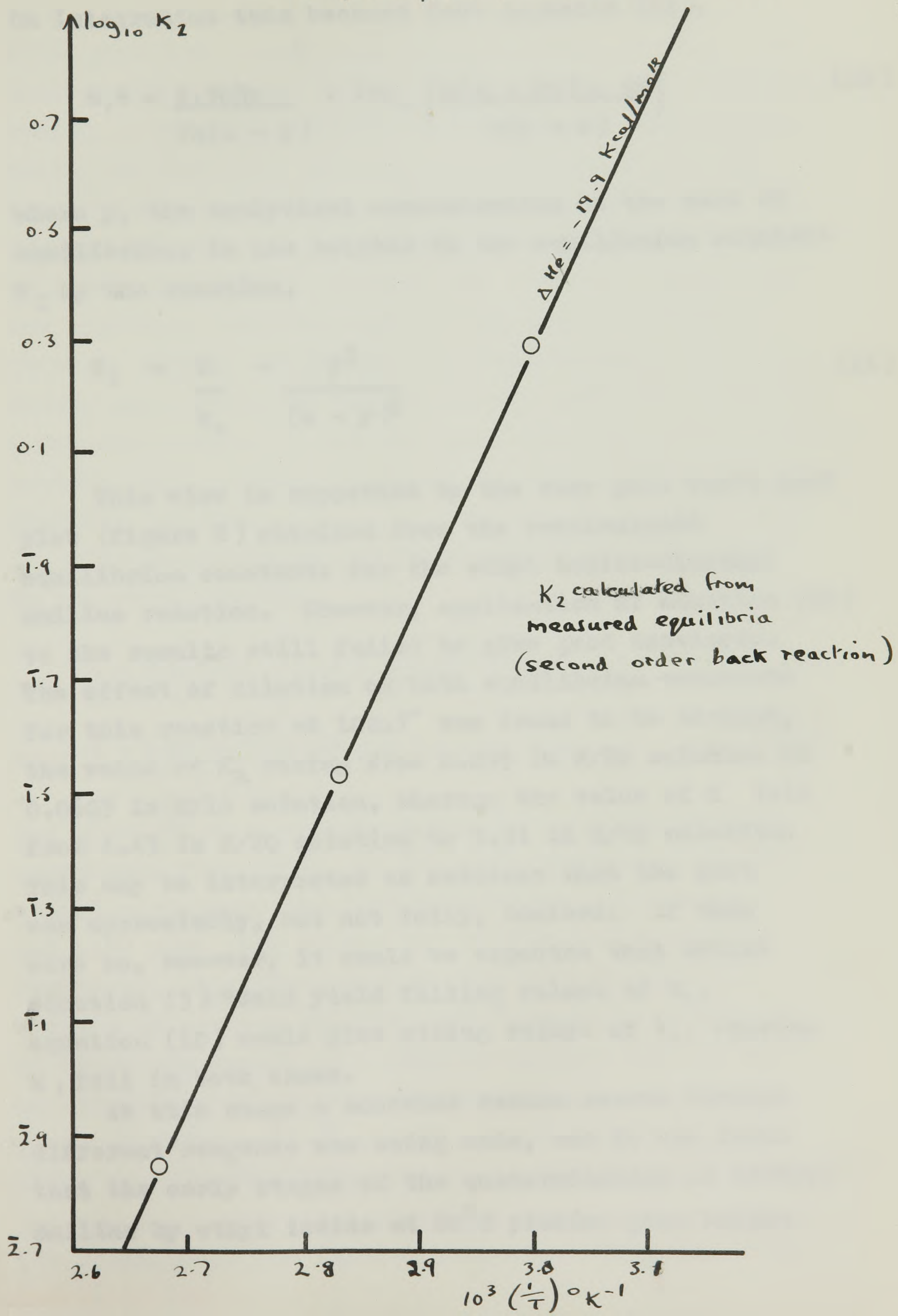
$$\text{i.e. } [\text{C}_6\text{H}_5\text{N}^+\text{Me}_2\text{EtI}^-] = [\text{C}_6\text{H}_5\text{N}^+\text{Me}_2\text{Et}][\text{I}^-]/K_1 \quad (8)$$

If the ionisation is appreciable, and a large amount of the salt is present in the form of free ions,  $x$  in equation (1) should be replaced by  $x^2/K_1$ , as shown by equation (8), giving,

$$\frac{dx}{dt} = k_1(a-x)^2 - \frac{k_2x^2}{K_1} = k_1(a-x)^2 - k_4x^2 \quad (9)$$



Figure 2  
ETI, DHA,  $\phi$  NO<sub>2</sub> - Van't Hoff Plot





On integration this becomes (see Appendix III),

$$k_1 t = \frac{2.303y}{2a(a-y)} \cdot \log_{10} \left\{ \frac{x(a-2y) + ay}{a(y-x)} \right\} \quad (10)$$

where  $y$ , the analytical concentration of the salt at equilibrium, is now related to the equilibrium constant  $K_2$  by the equation,

$$K_2 = \frac{k_1}{k_4} = \frac{y^2}{(a-y)^2} \quad (11)$$

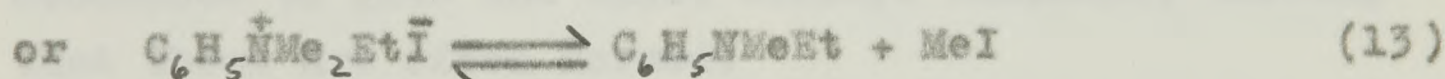
This view is supported by the very good van't Hoff plot (figure 2) obtained from the recalculated equilibrium constants for the ethyl iodide-dimethyl aniline reaction. However, application of equation (10) to the results still failed to give good constants. The effect of dilution on both equilibrium constants for this reaction at  $100.7^\circ$  was found to be serious, the value of  $K_2$  rising from 0.035 in M/20 solution to 0.0603 in M/10 solution, whereas the value of  $K$  fell from 4.43 in M/20 solution to 3.34 in M/10 solution. This may be interpreted as evidence that the salt was appreciably, but not fully, ionised. If this were so, however, it would be expected that whilst equation (3) would yield falling values of  $k_1$ , equation (10) would give rising values of  $k_1$ , whereas  $k_4$  fell in both cases.

At this stage a somewhat random search through different reagents was being made, and it was found that the early stages of the quaternization of diethyl aniline by ethyl iodide at  $80^\circ\text{C}$  yielded good values



of  $k_1$ , when equation (3) was used. Unfortunately, there was also a very slow side reaction, probably the decomposition of the salt to give olefine and hydrogen iodide, a reaction similar to the Hofmann degradation, making it difficult to obtain an accurate value for the equilibrium, which corresponded to only 9.3% reaction at  $80^\circ$ . This, in turn, caused errors in the velocity constants calculated for the later stages of the reaction, limiting work to the earlier stages, which in itself introduced some uncertainty. Even so, fairly good constants were obtained, and this indicated a possible cause for the strange behaviour in the previous systems, all of which employed an ethyl halide and a dimethyl aniline.

The decomposition of these salts can take place in two ways, namely,



and there is no a priori reason why (12) should have precedence over (13). If the salt decomposes by the second mechanism, the reagents evolved will react not only with each other, but also with the initial reactants. The final equilibrium will contain a mixture of several anilines and quaternary salts, in which the amount of ionisable halogen will be of no significance. During the early stages of the reaction there will be a very low concentration of these decomposition products in the reaction mixture, and the appearance of ionisable halogen will be due to the reaction of the initial reagents. Only the later



stages, and especially the equilibrium, will be effected by this exchange mechanism.

The proposed decomposition could therefore explain the results obtained with differing concentrations of base and halide, when it was found that the earlier stages of the reaction had the same order with respect to both halide and base, but that dimethyl p-toluidine rich solutions gave more reaction at equilibrium than did ethyl iodide rich solutions.

A search through the literature revealed that (13) is in fact the most favoured mechanism. Fahim and Galaby (1950) investigating the formation and decomposition of many dimethyl ethyl anilinium salts, found that decomposition leads to the N-ethyl N-methyl aniline in a large number of cases, and they suggest that this is a reliable method of preparation of these anilines. In a later paper Fahim and Fleifel (1951) found that diethyl methyl anilinium salts also decompose to give the mixed dialkyl anilines, showing that these are often formed.

Chow and Fuoss (1958) found that the reaction between dimethyl aniline and n-butyl bromide gave as a final product trimethyl anilinium bromide in poor yield, whereas methyl bromide and butyl methyl aniline gave butyl dimethyl anilinium bromide very easily. Two possibilities were considered for the abnormal reaction; either a rapid bimolecular, exchange between the butyl dimethyl salt initially formed and the unchanged dimethyl aniline, to give the trimethyl salt; or the unimolecular decomposition of the butyl dimethyl salt to give methyl bromide and butyl methyl aniline, followed by the reaction of the methyl bromide



with further dimethyl aniline. By means of infra-red spectra taken from the decomposition products of pure butyl dimethyl anilinium bromide, they show that the second possibility is in fact the correct one. This also explains the good yield of butyl dimethyl anilinium bromide from butyl methyl aniline and methyl bromide, as the proposed decomposition now regenerates the initial reactants.

This type of decomposition was also suggested by Clarke (1910), but was not substantiated.

With this evidence in mind several specific quaternizations were studied, and it was found that the earlier stages of the reaction between ethyl iodide and diethyl m-toluidine obeyed the kinetic law of equation (1), the later stages being slightly affected by a side reaction, perhaps the formation of olefine and hydrogen iodide. The reaction between methyl iodide and dimethyl aniline also gave good constants when equation (3) was applied to the results, as illustrated in figure 3. It was also found that the equilibrium constant for this reaction is not quite independent of reactant concentration when calculated on the basis of a unimolecular reverse reaction, showing that there is a slight ionisation of the salt, as reported by Laidler (1938). Further measurements were made with reactions employing unequal concentrations of methyl iodide and dimethyl aniline, these being  $2M/30$  and  $M/30$  respectively in one reaction, and vice versa in a second reaction. It was found that the equilibrium constants were the same in both cases, and that they were close to the values previously obtained.

In the reaction between ethyl iodide and dimethyl



Figure 3  
MeI, DMA 60°C

$k$  (litre mole<sup>-1</sup>, hour<sup>-1</sup>)

3.2

3.1

3.0

2.9

2.8

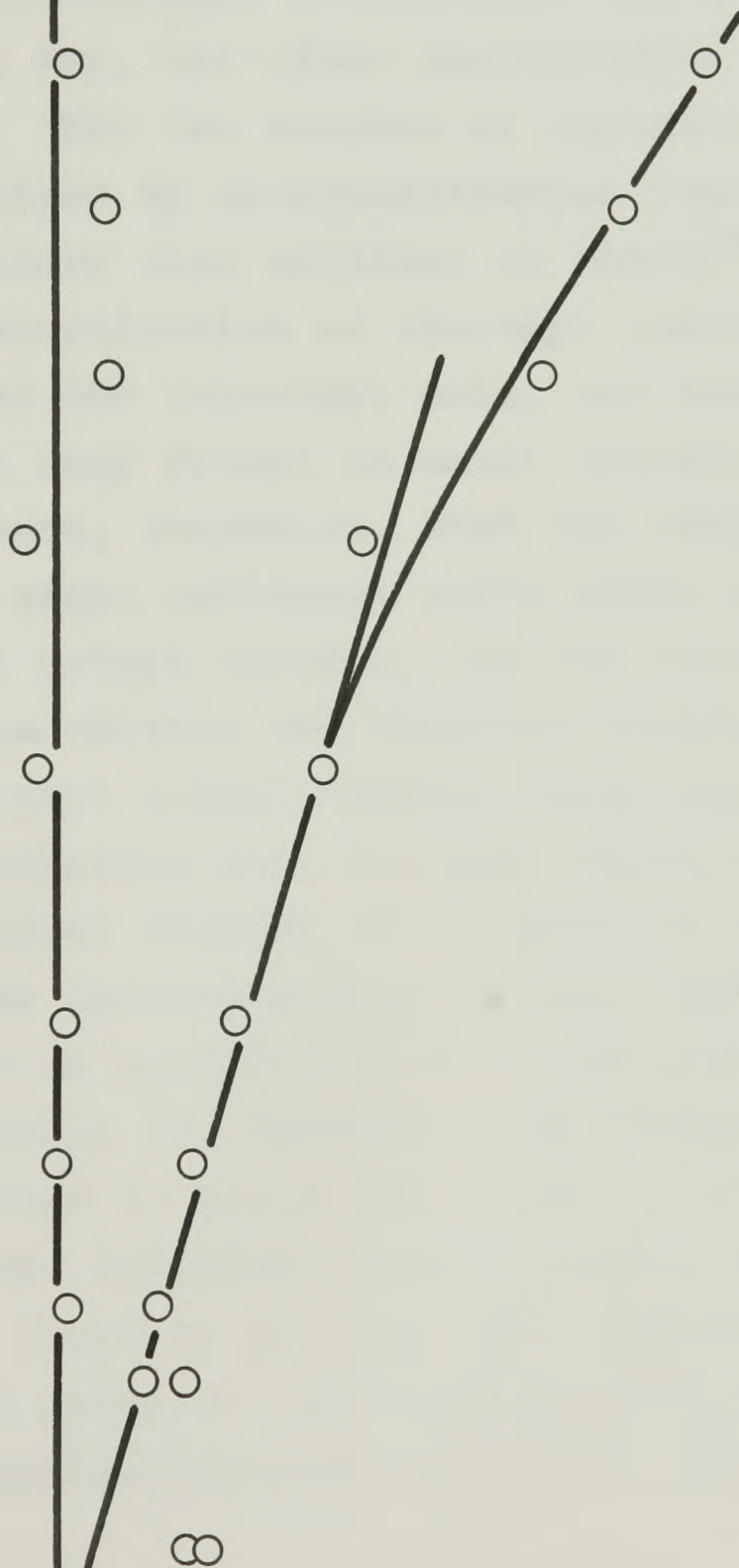
2.7

2.6

2.5

from  $\frac{dx}{dt} = k_1(a-x)^2 - k_2x$

from  $\frac{dx}{dt} = k_3(a-x)^2$



24 28 32 36 reaction



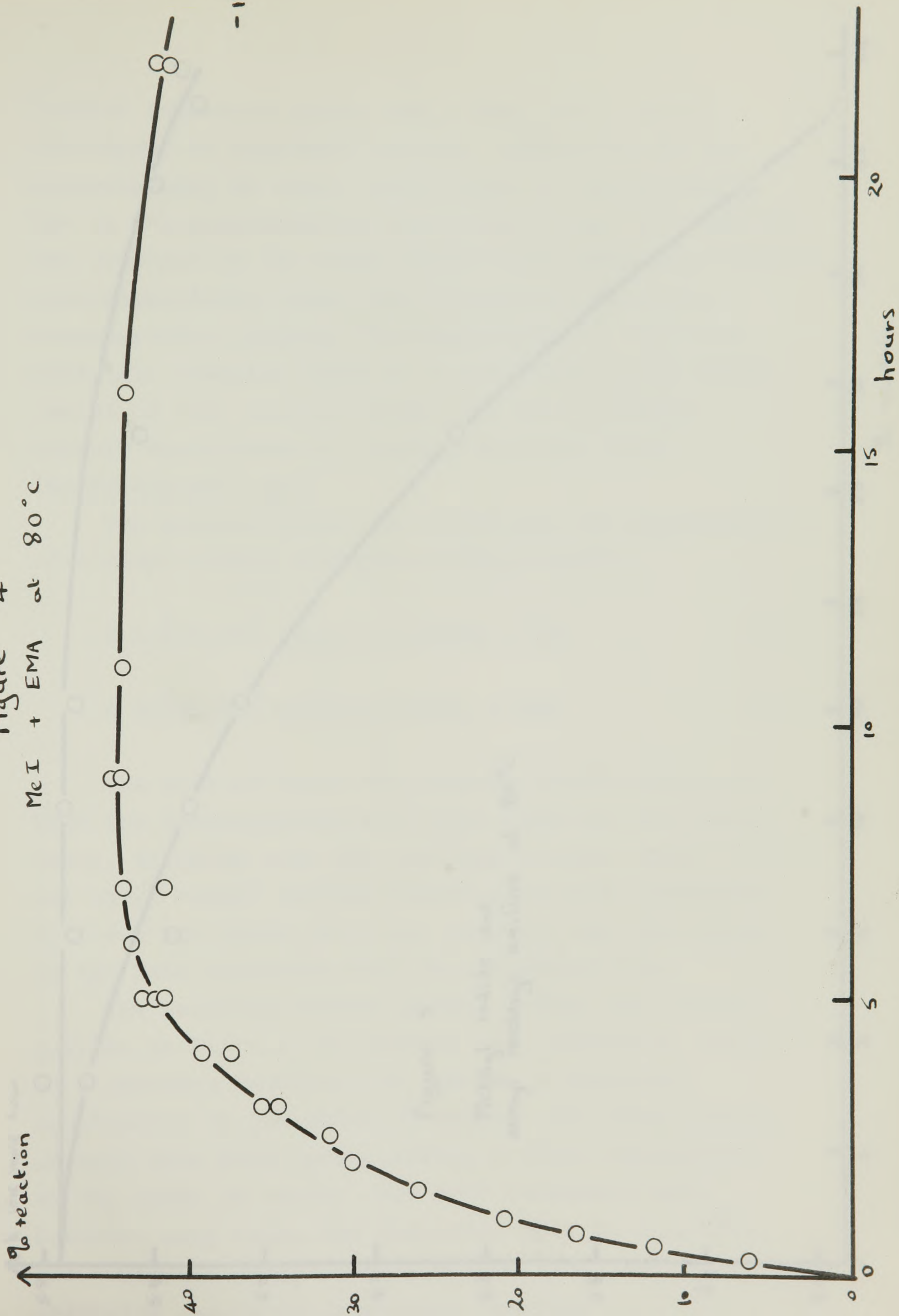
p-toluidine at 25°C, crystals of solid product were formed after a few days. These were filtered off and recrystallised, they sublimed at 210-11°C. Further recrystallisation had no effect upon the sublimation temperature, showing that the initial product was of reasonable purity. Trimethyl p-toluidinium iodide was prepared from dimethyl p-toluidine and methyl iodide in a similar way, and after purification it sublimed at 210-11°C. The two batches of crystals were intimately mixed by co-precipitation from hot ethanol, and this mixture also sublimed at 210-11°C. This shows that the quaternization of dimethyl p-toluidine by ethyl iodide gives the trimethyl salt, and that any other products are only formed in small amounts.

It appears, therefore, that the decomposition of dimethyl ethyl anilinium salts gives methyl iodide and an ethyl methyl aniline, and the interesting problem arose whether the reaction between methyl iodide and ethyl methyl aniline would obey the kinetic law. This reaction was, in fact, found to exhibit a rather curious feature as is shown in figure 4. Initially the quaternization is quite straightforward, and comes to an equilibrium at 44.5% after 7 hours. This equilibrium is, however, only transitory, for after a further 10 hours the amount of ionisable halogen in the solution begins to fall, and after a further 120 hours it is only 37%. Calculations based on the first stage of the reaction, and employing the transient equilibrium gave good rate constants (see figure 5).

The reversal of this reaction can only be explained by postulating that a large proportion of the initially formed salt decomposes to give the



Figure 4  
MeI + EMA at 80°C





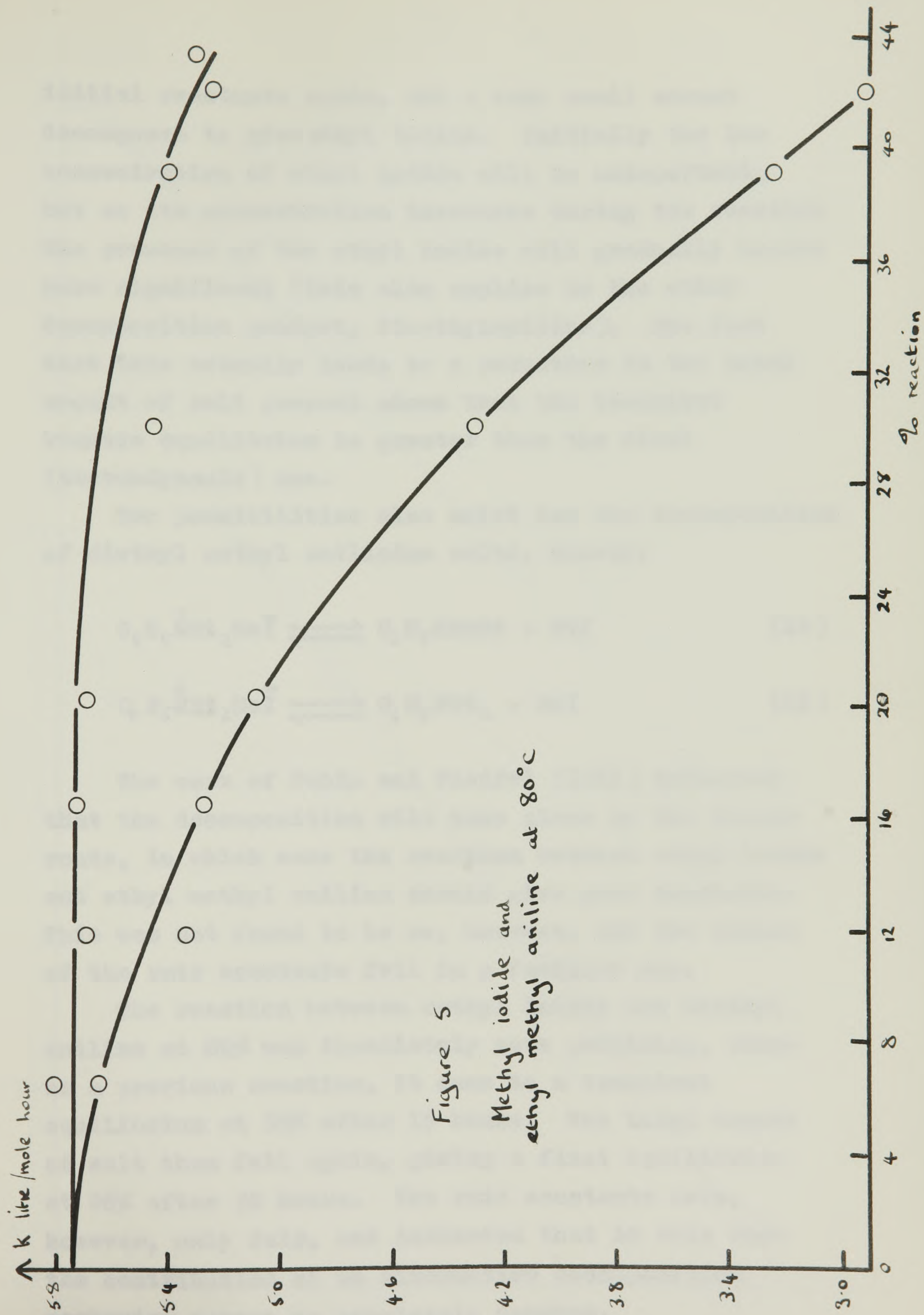


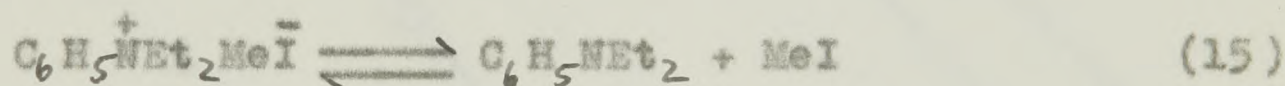
Figure 5

Methyl iodide and  
ethyl methyl aniline at 80°C



initial reactants again, and a very small amount decomposes to give ethyl iodide. Initially the low concentration of ethyl iodide will be unimportant, but as its concentration increases during the reaction the presence of the ethyl iodide will gradually become more significant (this also applies to the other decomposition product, dimethylaniline). The fact that this actually leads to a reduction in the total amount of salt present shows that the transient kinetic equilibrium is greater than the final (thermodynamic) one.

Two possibilities also exist for the decomposition of diethyl methyl anilinium salts, namely;



The work of Fahim and Fleifel (1951) indicates that the decomposition will take place by the former route, in which case the reaction between ethyl iodide and ethyl methyl aniline should give good constants. This was not found to be so, however, and the values of the rate constants fell in a familiar way.

The reaction between methyl iodide and diethyl aniline at 80% was immediately more promising, since as a previous reaction, it came to a transient equilibrium at 38% after 15 hours. The total amount of salt then fell again, giving a final equilibrium at 26% after 90 hours. The rate constants were, however, only fair, and indicated that in this case the contribution of an alternative decomposition mechanism cannot be completely ignored.



Figure 6  
Specimen Arrhenius Plots

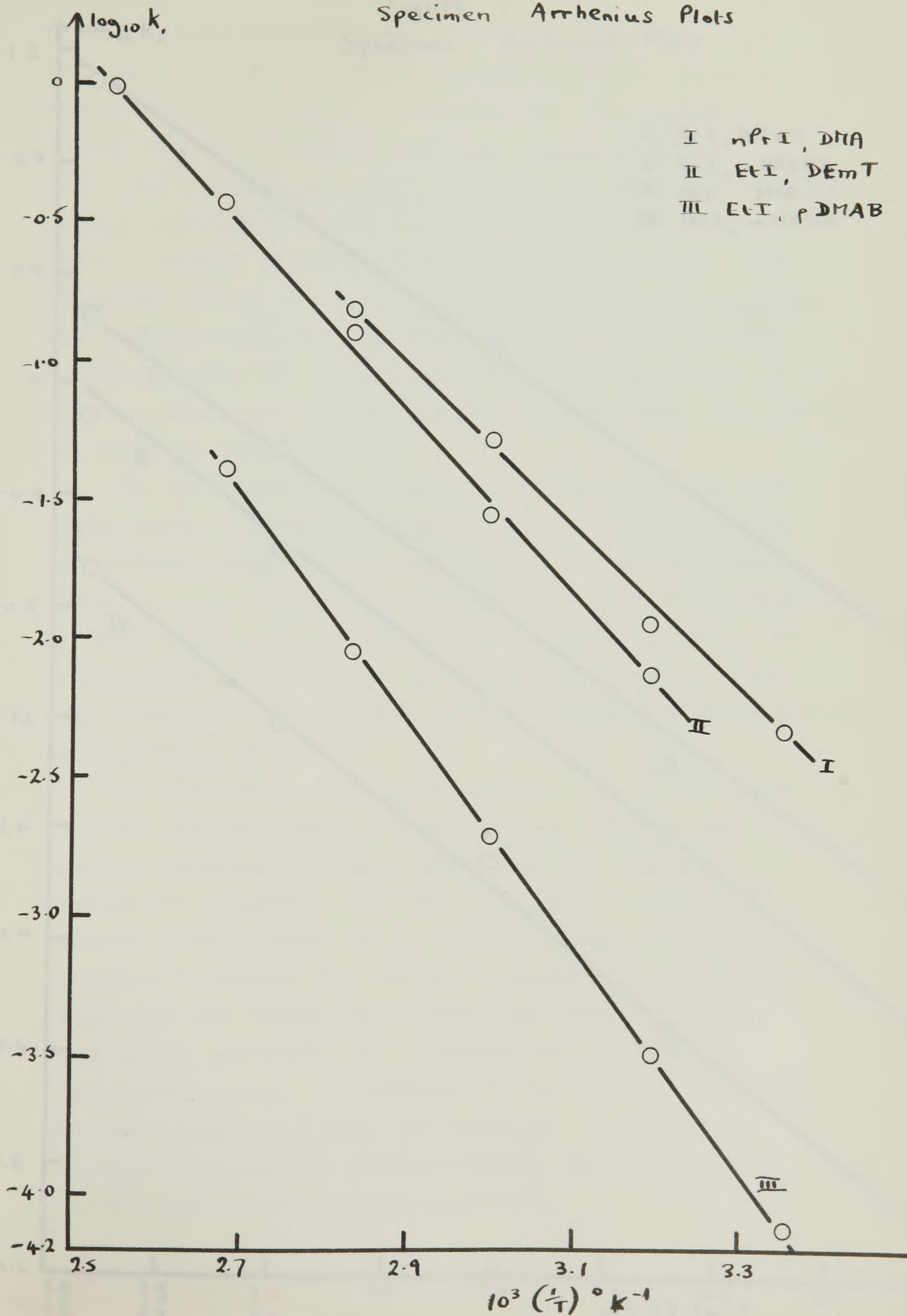
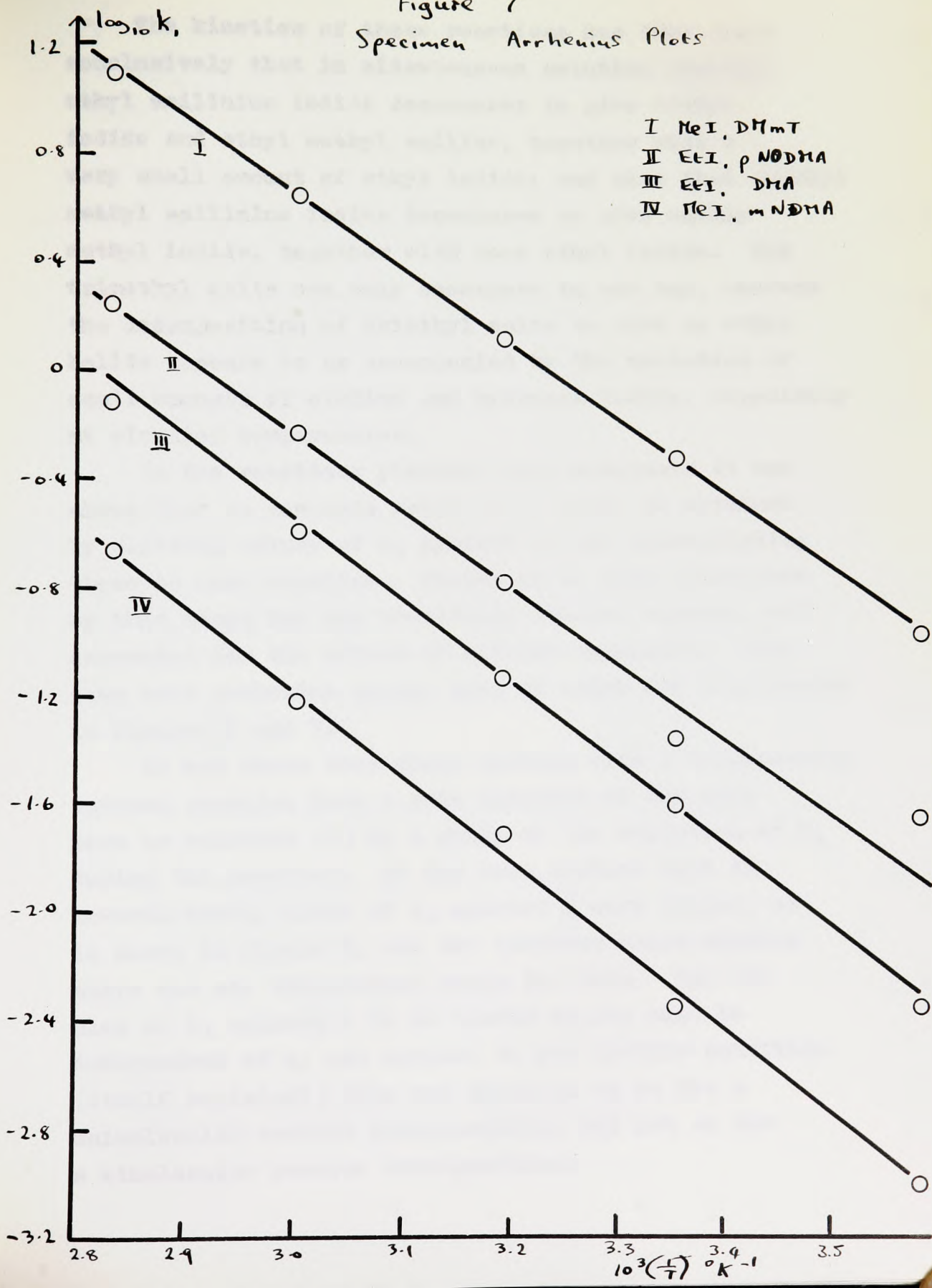




Figure 7  
Specimen Arrhenius Plots





The kinetics of these reactions has thus shown conclusively that in nitrobenzene solution dimethyl ethyl anilinium iodide decomposes to give methyl iodide and ethyl methyl aniline, together with a very small amount of ethyl iodide; and also that diethyl methyl anilinium iodide decomposes to give mainly methyl iodide, together with some ethyl iodide. The trimethyl salts can only decompose in one way, whereas the decomposition of triethyl salts to give an ethyl halide appears to be accompanied by the evolution of small amounts of olefine and hydrogen iodide, especially at elevated temperatures.

In the reactions yielding good constants it was shown that an accurate value of  $k_1$  could be obtained by plotting values of  $k_3$  against  $x$ , and extrapolating these to zero reaction. Values of  $k_1$  were calculated by this means for the previously studied systems, and corrected for the effect of solvent expansion. They gave good Arrhenius plots, some of which are illustrated in figures 6 and 7.

It was shown that those systems with a complicating reverse reaction have a rate equation of the same form as equation (1) by a study of the variation of  $k_3$  during the reaction. It had been noticed that in several cases, plots of  $k_3$  against  $x$  were linear, as is shown in figure 3, and the question arose whether there was any theoretical basis for this. For the plot of  $k_3$  against  $x$  to be linear  $dk_3/dx$  must be independent of  $x$ , and subject to one further condition (itself empirical) this was found to be so for a unimolecular reverse decomposition, but not so for a bimolecular reverse decomposition.



$$\text{If } k_3 t = x/a(a - x) \quad (4)$$

treating  $k_3$  as a variable, and differentiating with respect to  $t$ ,

$$\frac{tdk_3}{dt} + k_3 = \frac{1}{(a - x)^2} \cdot \frac{dx}{dt} \quad (16)$$

$$\text{i.e. } \frac{dx}{dt} = \frac{(a - x)^2 x}{ak_3(a - x)} \cdot \frac{dk_3}{dt} + k_3(a - x)^2 \quad (17)$$

$$\text{If } \frac{dx}{dt} = k_1(a - x)^2 - k_2 x \quad (1)$$

eliminating  $dx/dt$  between (1) and (17),

$$\frac{x(a - x)^2}{a(a - x)} \cdot \frac{d(\ln.k_3)}{dt} + k_3(a - x)^2 = k_1(a - x)^2 - k_2 x \quad (18)$$

$$\text{i.e. } \frac{x}{a(a - x)} \cdot \frac{d(\ln.k_3)}{dt} + k_3 = k_1 - \frac{k_2 x}{(a - x)^2} \quad (19)$$

If  $x$  is small, and can be neglected in comparison with  $a$ ,

$$\frac{x}{a^2} \cdot \frac{d(\ln.k_3)}{dt} + k_3 = k_1 - \frac{k_2 x}{a^2} \quad (20)$$

$$\text{i.e. } k_3 = k_1 - \frac{x}{a^2} \left\{ k_2 + \frac{d(\ln.k_3)}{dt} \right\} \quad (21)$$

$$\therefore \frac{dk_3}{dx} = \frac{1}{a^2} \left\{ k_2 + \frac{d(\ln.k_3)}{dt} \right\} - \frac{x}{a^2} \cdot \frac{d^2(\ln.k_3)}{dx \cdot dt} \quad (22)$$



Equation (22) shows that if  $d(\ln.k_3)/dt$  is independent of  $x$ ,  $dk_3/dx$  will also be independent of  $x$ . The possibility was tested by constructing plots of  $\log_{10}(k_3)$  against  $t$ , and several of these were found to be linear, although there is no theoretical reason for this. In these cases  $d(\ln.k_3)/dt$  is constant, and  $d^2(\ln.k_3)/dx.dt$  is zero. Equation (22) then reduces to,

$$\frac{dk_3}{dx} = \frac{1}{a^2} \left\{ k_2 + \frac{d(\ln.k_3)}{dt} \right\} \quad (23)$$

$$\text{i.e. } k_2 = -a^2 dk_3/dx - d(\ln.k_3)/dt \quad (24)$$

On the other hand, if the salt is significantly ionised, equation (1) must be replaced by,

$$\frac{dx}{dt} = k_1(a-x)^2 - k_4x^2 \quad (6)$$

using equation (17),

$$\frac{x}{a(a-x)} \cdot \frac{d(\ln.k_3)}{dt} + k_3 = k_1 - \frac{k_4x^2}{(a-x)^2} \quad (25)$$

$$\text{i.e. } k_3 = k_1 - \frac{k_4x^2}{(a-x)^2} - \frac{x}{a(a-x)} \cdot \frac{d(\ln.k_3)}{dt} \quad (26)$$

For small  $x$ ,

$$k_3 = k_1 - \frac{k_4x^2}{a^2} - \frac{x}{a^2} \cdot \frac{d(\ln.k_3)}{dt} \quad (27)$$



$$\therefore \frac{dk_3}{dx} = \frac{-2xk_4}{a^2} - \frac{1}{a^2} \cdot \frac{d(\ln.k_3)}{dt} - \frac{x}{a^2} \cdot \frac{d^2(\ln.k_3)}{dxdt} \quad (28)$$

Again, if the plot of  $\ln.k_3:t$  is linear  $d^2(\ln.k_3)/dx.dt$  is zero, and equation (28) becomes;

$$\frac{dk_3}{dx} = \frac{-2xk_4}{a^2} - \frac{1}{a^2} \cdot \frac{d(\ln.k_3)}{dt} \quad (29)$$

In cases where the plot of  $\log_{10}(k_3)$  against  $t$  was linear, the plots of  $k_3$  against  $x$  were also found to be linear. This proves that the reverse reaction is predominantly of the first order, since by equation (29), any appreciable contribution from a second order decomposition must destroy this linearity.

By use of equation (24) it is possible to obtain a value of  $k_2$  from the gradients of these plots, and thus gain the equilibrium constant. In reactions where there are no complications, it is possible to compare this value for the equilibrium constant with that obtained from a measured equilibrium. In some cases the values obtained were very close, for example in the reaction between ethyl iodide and diethyl aniline at  $100.7^\circ\text{C}$ , the values were 0.551 from equation (24), and 0.558 from the measured equilibrium, a difference of only 1.3%.

At one time it was hoped that it might be possible to construct van't Hoff plots for all systems by this method, even when the exchange reaction took place, but after several attempts in which poor van't Hoff plots were obtained, the method was abandoned. There are several possible reasons for the unreliability;



in neglecting  $x$  in comparison with  $a$  an error is introduced, and in some cases where the plot of  $\log_{10}(k_2)$  against  $t$  is not accurately linear a further error is introduced by neglect of the second order differential. It is also probable that there is a slight contribution of the second order mechanism, the importance of which will vary with temperature, evidence for this being the slight variation of equilibrium constant with reactant concentration, and the mediocre van't Hoff plots obtained when measured equilibria alone were used to calculate equilibrium constants. Above all, in the reactions between ethyl halides and dimethyl anilines, the reverse reaction does not regenerate the initial reactants, and the value of  $k_2$  obtained refers to a reaction different from the forward reaction. The ratios of  $k_1$  and  $k_2$  are therefore not equilibrium constants, and cannot be expected to obey the van't Hoff isochore.

Only two ways were used to calculate equilibrium constants, either the direct measurement of a valid equilibrium, or trial and error substitution of probable values into equation (3) until good values of  $k_1$  were obtained. These calculations were only made when it was known that the exchange reaction did not take place, but even so mediocre van't Hoff plots were obtained, probably because of a variation of the importance of the second order decomposition with temperature.

Whenever possible equation (3) was used to evaluate rate constants, using mainly measured values for the equilibrium. When this was impossible either because of the precipitation of the product before the equilibrium had been fully established,



or because of the effect of the exchange reaction, the values of  $k_2$  obtained from equation (4) were plotted against  $x$  and extrapolated back to zero reaction. When the conductivity method was used to measure very slow reactions at the lowest temperatures it was sometimes possible to draw accurate initial tangents. In one reaction, the quaternization of *p*-bromo dimethyl aniline by methyl iodide at 25°C the solubility of the salt is quite low, and precipitation took place almost immediately. This reaction obeyed the simple second order equation, and went to completion. There was no autocatalysis by the surface of the solid product.

#### REACTIONS IN MIXED SOLVENTS

In the range of solvents containing 0 to 60% chlorobenzene, use of the methods outlined above gave quite satisfactory results, whilst in a solvent containing 80% chlorobenzene some difficulties were met. More serious difficulties were encountered with the solutions richest in chlorobenzene, since there appeared to be a modification to the characteristics of the reactions, which caused non-linear Arrhenius plots. These plots gave highly improbable values for the reaction parameters, some composition - temperature ranges even appearing to show negative activation energies. The strange behaviour was traced to three already mentioned causes, namely extremely small equilibrium constants, the disturbance due to the exchange reaction, and the formation of a solid product, which appeared to cause autocatalysis in some cases.

The most troublesome of these phenomena was the effect of the solvent on the equilibrium, since



as the proportion of chlorobenzene in the solution was increased, the reaction equilibria became less and less favourable, so that in some cases the maximum conversion of the reactants was less than 1%. This made it difficult to obtain accurate rate constants, as the values derived from the simple second order formula fell rapidly when plotted against the concentration of product. If a valid equilibrium constant could be measured it was used in the calculation of the results, as with the reactions in pure nitrobenzene.

The equilibrium was found to be much more dependent than the forward reaction rate on the solvent composition. In fact the speed of the reverse reaction was actually increased by the addition of chlorobenzene to the solvent, as can be seen in the results given later. This meant that the time taken for the reaction to reach equilibrium fell as the proportion of chlorobenzene in the solvent was increased, and although the absolute reaction rate was lower in the solutions of low dielectric constant, the half life of the reaction was much shorter. Thus it fell from 35 minutes for the reaction between methyl iodide and dimethyl aniline in pure nitrobenzene at  $80^{\circ}\text{C}$  to a little less than 10 minutes for the same reaction in 40% nitrobenzene, and it was too short to measure in 20% nitrobenzene. A variation in reactant concentration was contemplated as a means of making the half life more favourable, but rough calculations showed that since the rate and equilibrium both depend on the initial concentration the half life would be almost unaffected.

The extremely small equilibrium constants also caused difficulties in another way in the reaction

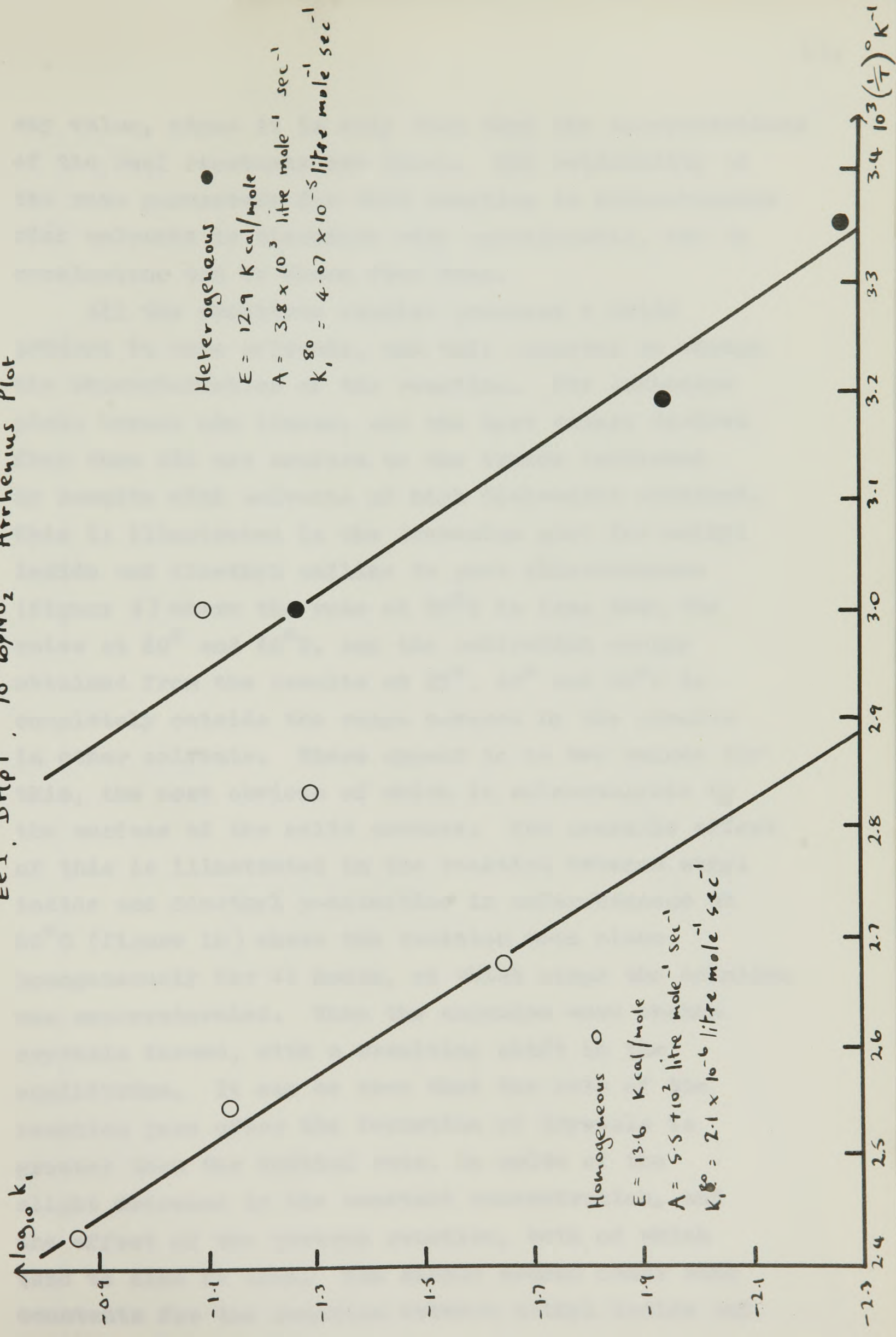


between ethyl iodide and dimethyl p-toluidine. Although this reaction had a somewhat more favourable equilibrium than the comparable reaction between methyl iodide and dimethyl aniline, the simple second order constants fell just as drastically. The reaction was, however, fairly slow in solvents containing high proportions of chlorobenzene, and could therefore be studied at a high temperature to prevent the formation of a solid product. Even so, the Arrhenius plots constructed with the results were very poor, as is shown in the example for the reaction in 10% nitrobenzene (figure 8). This non-linearity cannot be attributed to any influence of a solid product in the 5 cases where it does not form. The conductivity method was used to make very careful measurements on the reaction in a solvent containing 20% nitrobenzene, at 80°C, where crystals do not form, and it was found that an equilibrium corresponding to very little product (about 0.4%) was established in less than 10 minutes. The decomposition leads to the evolution of methyl iodide, which can then react with the unchanged base, giving rise to further reaction. The final equilibrium at 7.5% is reached after about 100 hours, and obscures the initial reaction, which had been missed when the less sensitive titration method of analysis was used.

Three stages are involved in the production of trimethyl p-toluidinium iodide; the initial formation of the dimethyl ethyl salt, its decomposition to yield methyl iodide, and the subsequent reaction of the methyl iodide. Only if the observed rate is governed by the initial reaction are the results of



Figure 8  
 $\text{EtI}$ ,  $\text{DHPT}$ ,  $10^3 \log k_1$  Arrhenius Plot





any value, since it is only then that the concentrations of the real reactants are known. The reliability of the rate parameters for this reaction in chlorobenzene rich solvents is therefore very questionable, and no conclusions can be drawn from them.

All the reactions studied produced a solid product in some solvents, and this appeared to change the characteristics of the reaction. The Arrhenius plots became non linear, and the best values derived from them did not conform to the trends indicated by results with solvents of high dielectric constant. This is illustrated in the Arrhenius plot for methyl iodide and dimethyl aniline in pure chlorobenzene (figure 9) where the rate at  $80^{\circ}\text{C}$  is less than the rates at  $60^{\circ}$  and  $40^{\circ}\text{C}$ , and the activation energy obtained from the results at  $25^{\circ}$ ,  $40^{\circ}$  and  $60^{\circ}\text{C}$  is completely outside the range covered by the results in other solvents. There appear to be two causes for this, the most obvious of which is autocatalysis by the surface of the solid product. The possible effect of this is illustrated in the reaction between ethyl iodide and dimethyl p-toluidine in chlorobenzene at  $60^{\circ}\text{C}$  (figure 10) where the reaction took place homogeneously for 44 hours, at which stage the solution was supersaturated. When the ampoules were shaken crystals formed, with a resulting shift in the equilibrium. It can be seen that the rate of the reaction just after the formation of crystals is greater than the initial rate, in spite of the slight decrease in the reactant concentration, and the effect of the reverse reaction, both of which tend to slow it down. The simple second order rate constants for the reaction between methyl iodide and



Figure 9  
Methyl Iodide, Di Methyl Aniline in Chlorobenzene  
Arrhenius Plot

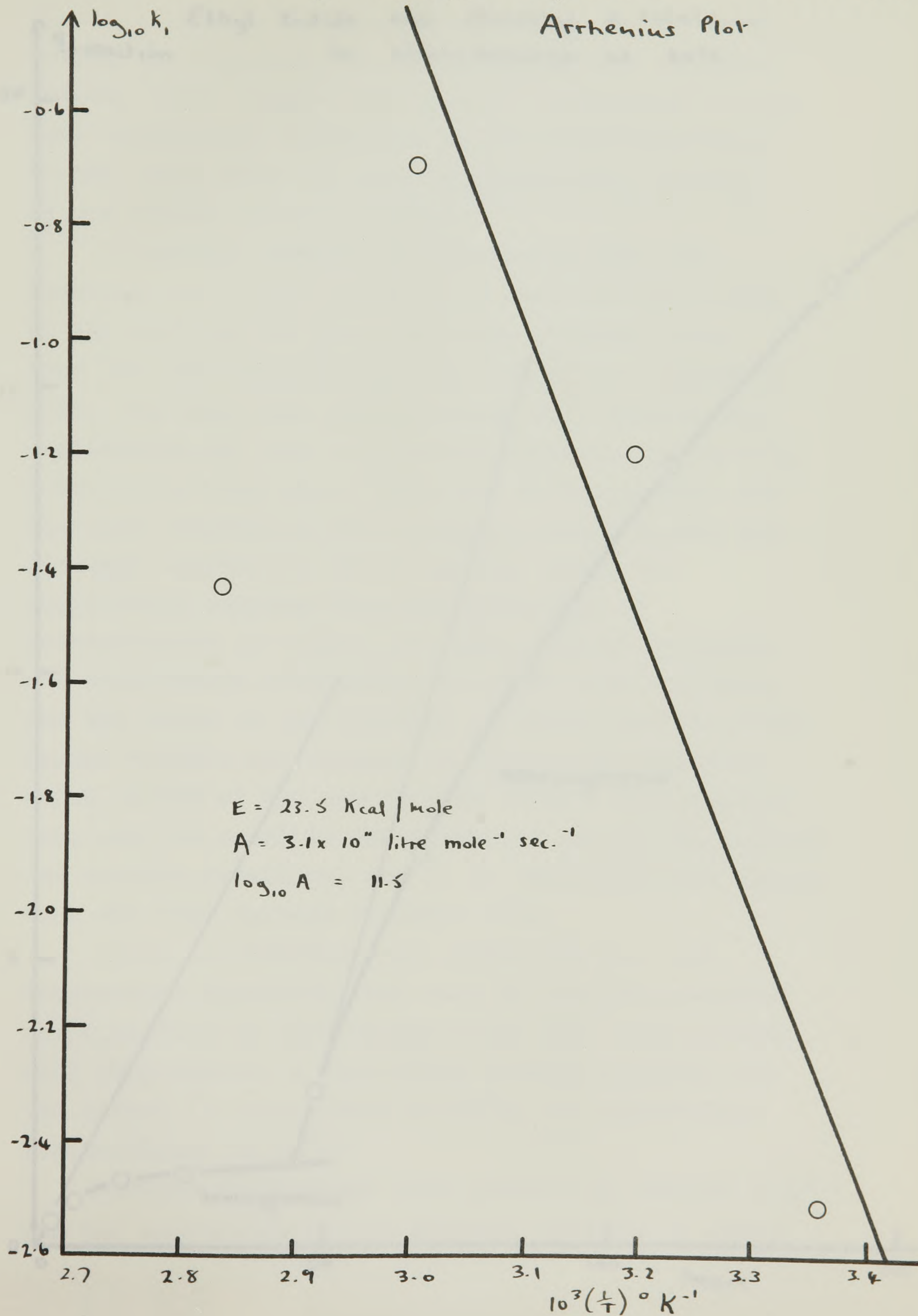
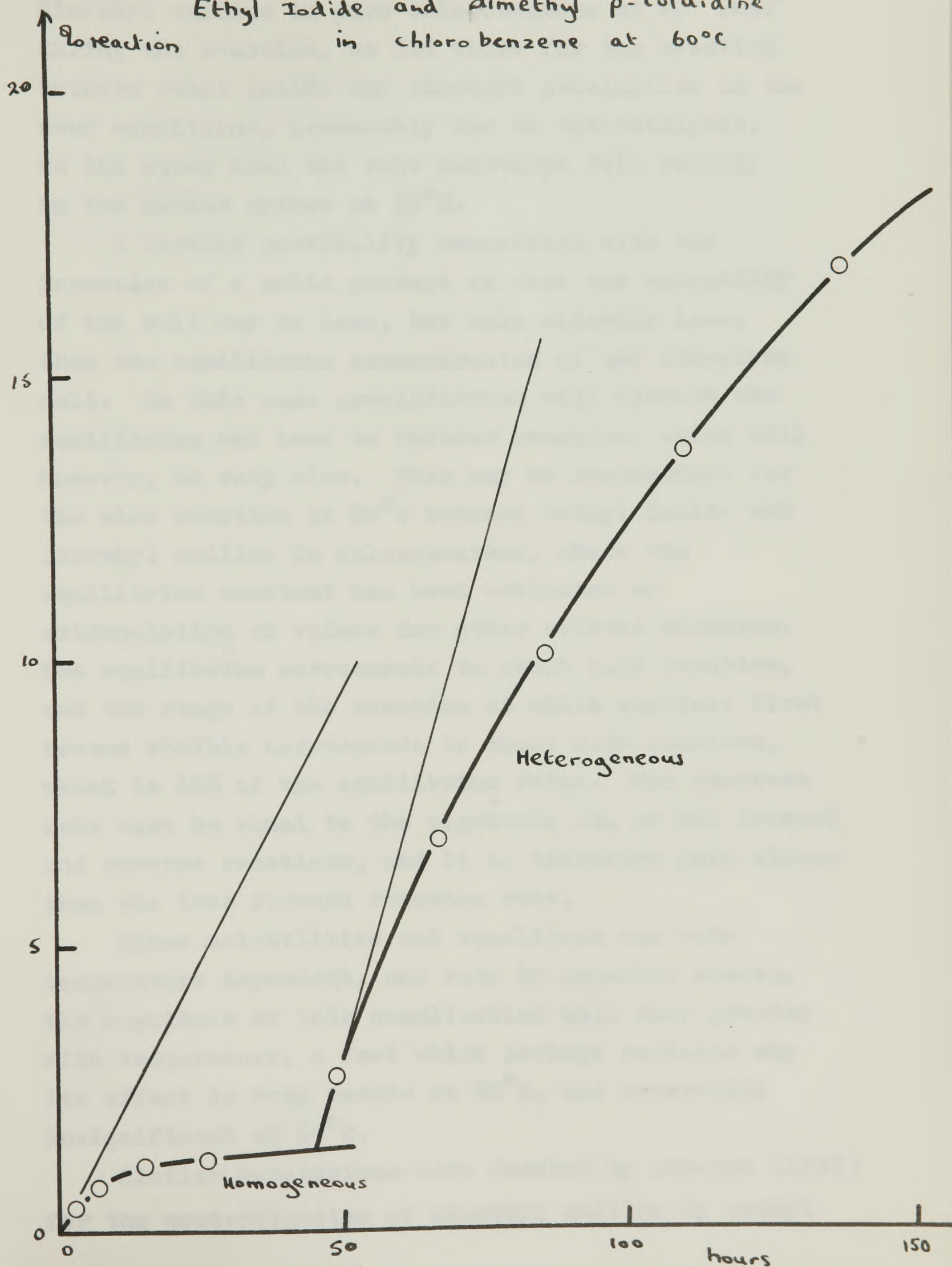




Figure 10

Ethyl Iodide and dimethyl p-toluidine  
in chloro benzene at 60°C





dimethyl aniline in pure chlorobenzene at  $40^{\circ}$  rose during the reaction, as did those for the reaction between ethyl iodide and dimethyl p-toluidine in the same conditions, presumably due to autocatalysis. On the other hand the rate constants fell rapidly in the former system at  $25^{\circ}\text{C}$ .

A further possibility associated with the formation of a solid product is that the solubility of the salt may be less, but only slightly less, than the equilibrium concentration of the dissolved salt. In this case precipitation will disturb the equilibrium and lead to further reaction, which will however, be very slow. This may be responsible for the slow reaction at  $80^{\circ}\text{C}$  between methyl iodide and dimethyl aniline in chlorobenzene, where the equilibrium constant has been estimated by extrapolation of values for other solvent mixtures. The equilibrium corresponds to about 0.3% reaction, and the stage of the reaction at which crystals first became visible corresponds to about 0.2% reaction, which is 66% of the equilibrium value. The observed rate must be equal to the algebraic sum of the forward and reverse reactions, and it is therefore much slower than the true forward reaction rate.

Since solubilities and equilibria are both temperature dependent, and vary in opposite senses, the magnitude of this complication will vary greatly with temperature, a fact which perhaps explains why its effect is very marked at  $80^{\circ}\text{C}$ , and apparently insignificant at  $60^{\circ}\text{C}$ .

Similar conclusions were reached by Edwards (1937) for the quaternization of dimethyl aniline by methyl



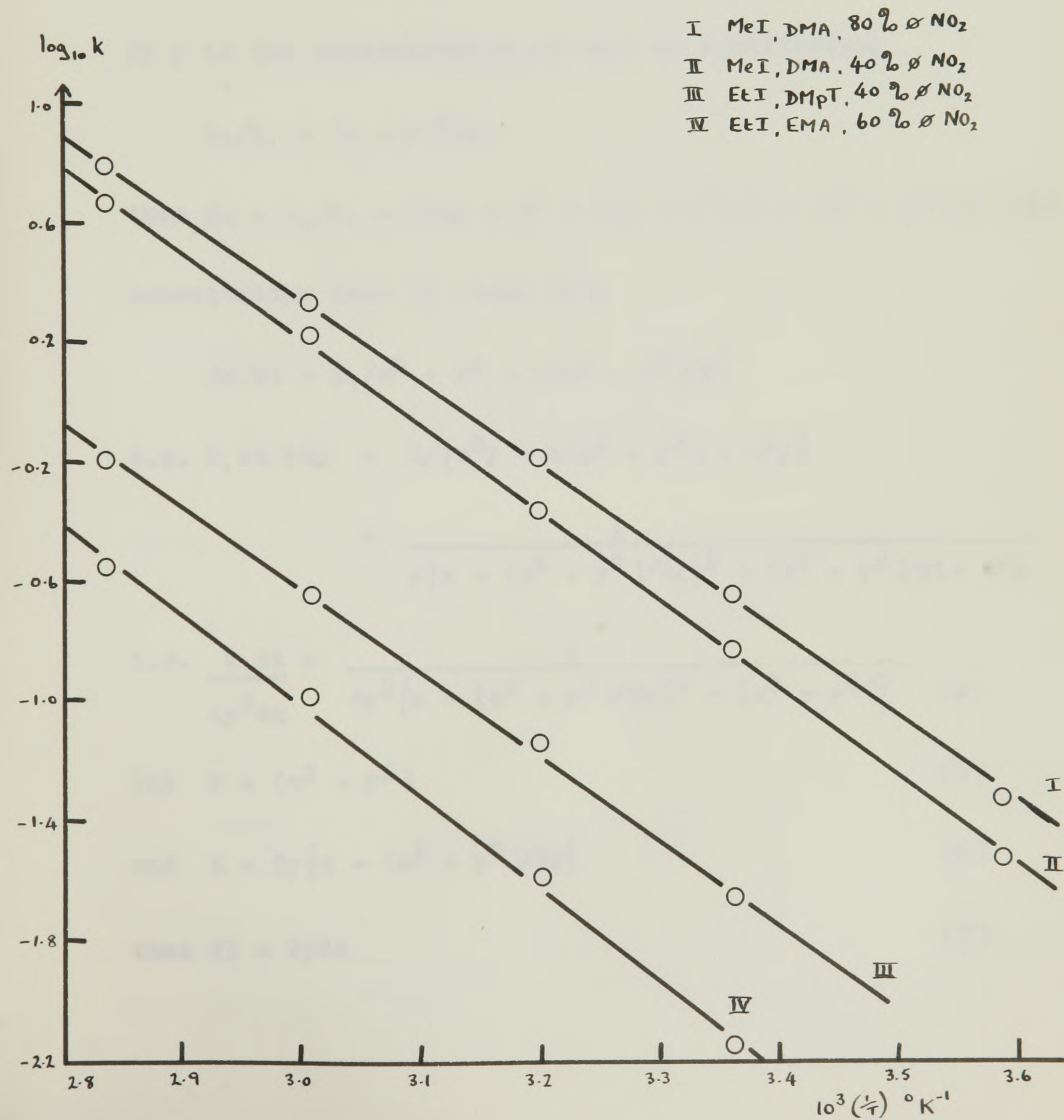
iodide in benzene solution. From the nature of the case more space has had to be devoted to the discussion of the difficult examples, but in spite of the complications involved in the determination of rate constants in some ranges, many good Arrhenius plots were obtained, and four specimens are included to illustrate this (figure 11).





Figure 11

Specimen Arrhenius Plots with mixed solvents





APPENDIX II

Integration of equation (1) section III.

$$dx/dt = k_1(a - x)^2 - k_2x \quad (1)$$

$$dx/dt = k_1\{a^2 + x^2 - x(2a + k_2/k_1)\} \quad (2)$$

If  $y$  is the concentration of salt at equilibrium;

$$k_2/k_1 = (a - y)^2/y$$

$$\text{then, } 2a + k_2/k_1 = (2ay + a^2 - 2ay + y^2)/y = (a^2 + y^2)/y \quad (3)$$

Substituting from (3) into (2);

$$dx/dt = k_1\{a^2 + x^2 - x(a^2 + y^2)/y\}$$

$$\text{i.e. } k_1 dt/y dx = 1/\{x^2y - x(a^2 + y^2) + a^2y\}$$

$$= \frac{1}{y\{x - (a^2 + y^2)/2y\}^2 - (a^2 + y^2)/y + a^2y}$$

$$\text{i.e. } \frac{k_1 dt}{4y^2 dx} = \frac{1}{4y^2\{x - (a^2 + y^2)/2y\}^2 - (a^2 - y^2)} \quad (4)$$

$$\text{Put } Y = (a^2 - y^2) \quad (5)$$

$$\text{and } X = 2y\{x - (a^2 + y^2)/2y\} \quad (6)$$

$$\text{then } dX = 2y dx \quad (7)$$



combining equations (4), (5), (6) and (7);

$$\frac{k_1 dt}{2y dX} = \frac{1}{X^2 - Y^2} \equiv \frac{A}{X - Y} + \frac{B}{X + Y} \quad (\text{say}) \quad (8)$$

$$\text{then } AX + AY + BX - BY \equiv 1$$

$$\therefore A = 1/2Y; \quad B = -1/2Y \quad (9)$$

Substituting equations (9) into (8);

$$\frac{k_1 dt}{2y} = \frac{dX}{2Y} \left\{ \frac{1}{X - Y} - \frac{1}{X + Y} \right\}$$

Integrating;

$$k_1 t = (y/Y) \ln. \left\{ \frac{X - Y}{X + Y} \right\} + \text{const.}$$

Using (5) and (6);

$$k_1 t = \frac{y}{(a^2 - y^2)} \ln. \left\{ \frac{xy - a^2}{xy - y^2} \right\} + \text{const.}$$

when  $t = 0$ ,  $x = 0$  and,

$$\text{const.} = - \frac{y}{(a^2 - y^2)} \cdot \ln. \left\{ \frac{a^2}{y^2} \right\}$$

$$\text{Giving, } k_1 t = \frac{y}{(a^2 - y^2)} \cdot \ln. \left\{ \frac{(a^2 - xy)Y}{a^2(y - x)} \right\} \quad (\text{III, 3})$$



APPENDIX III

Integration of equation (9), section III.

$$dx/dt = k_1(a - x)^2 - k_4x^2 \quad (1)$$

$$= k_1 \{ a^2 - 2ax + x^2(1 - k_4/k_1) \} \quad (2)$$

If  $y$  is the concentration of salt at equilibrium;

$$k_4/k_1 = (a - y)^2/y^2$$

$$1 - k_4/k_1 = (2ay - a^2)/y^2 \quad (3)$$

Substituting from (3) into (2);

$$\begin{aligned} y^2 dx/ak_1 dt &= ay - 2xy^2 + x^2(2y - a) \\ &= (x - y) \{ y(2y - a) - ay \} \end{aligned} \quad (4)$$

$$\text{Let } \frac{1}{(x - y) \{ y(2y - a) - ay \}} \equiv \frac{A}{(x - y)} + \frac{B}{x(2y - a) - ay} \quad (5)$$

$$\text{then } 2.Axy - Aax - Aay + Bx - By \equiv 1$$

$$\text{giving } A = 1/2y(y - a) \quad (6)$$

$$\text{and } B = -(2y - a)/2y(y - a) \quad (7)$$

Combining equations (4), (5), (6) and (7);

$$\frac{2ak_1(y - a)dt}{y} = \frac{dx}{x - y} - \frac{(2y - a)dx}{x(2y - a) - ay}$$



Integrating;

$$2a(y - a) k, t / y = \ln.(x - y) - \ln.\{x(2y - a) - ay\} + \text{const.}$$

$$\text{i.e. } k, t = \frac{y}{2a(y - a)} \cdot \ln.\left\{\frac{x - y}{x(2y - a) - ay}\right\} + \text{const.}$$

when  $t = 0$ ,  $x = 0$ , and

$$\text{const.} = \frac{y}{2a(y - a)} \cdot \ln.a$$

Then,

$$k, t = \frac{y}{2a(a - y)} \cdot \ln.\left\{\frac{x(a - 2y) + ay}{a(y - x)}\right\} \quad (\text{III, 10})$$



## INTRODUCTION

Many papers have appeared describing the effects of gas-liquid interfaces on the behavior of systems. Some have dealt with the effects of surface tension on the behavior of gas-liquid systems, while others have dealt with the effects of surface tension on the behavior of solid-liquid systems. The present paper deals with the effects of surface tension on the behavior of gas-liquid systems. The effects of surface tension on the behavior of gas-liquid systems have been studied by many investigators. Some have studied the effects of surface tension on the behavior of gas-liquid systems in general, while others have studied the effects of surface tension on the behavior of gas-liquid systems in specific cases. The present paper deals with the effects of surface tension on the behavior of gas-liquid systems in general.

## SECTION IV

### STRUCTURAL VARIATIONS

It is well known that the behavior of gas-liquid systems is affected by the structure of the interface. The structure of the interface is determined by the balance of forces acting on it. The forces acting on the interface are the forces of surface tension, the forces of adhesion, and the forces of cohesion. The structure of the interface is also affected by the nature of the gas and liquid phases. The structure of the interface is a complex phenomenon, and it is not yet fully understood. The present paper deals with the structural variations of the interface in gas-liquid systems.

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## INTRODUCTION

Many papers have appeared describing studies of quaternary ammonium salt formation, and several of these have dealt with the effects of a variation in the structure of one or both reactants. Relatively few, however, have considered the formation of salts based on dimethyl aniline. Studies have been made of the influence of ring substituents in the reactions of methyl iodide with dimethyl anilines, and Laidler (1938) and Evans, Watson and Williams (1939) found that the effect of ring substituents is to modify the rate of reaction through a variation of the activation energy alone, the frequency factor remaining more or less constant. Evans et al (1939a) also studied the effect of ortho substituents, and found that these cause a considerable retardation, again due to an increase in the energy of activation.

Chow and Fuoss (1958) studied the effect of structure on the quaternizations of several ditertiary amines based on diphenyl methane in propylene carbonate solution, but found it difficult to allocate a rate constant to the separate amino groups.

Thomas (1913) studied the effect of variations in the alkyl halide, in the groups attached to nitrogen, and in the aromatic nucleus, but as he made all the measurements at a single temperature the separate values of A and E cannot be determined. This limitation applies to the experiments of several other workers (Benkeser et al, 1956; Clarke, 1910; Davis and Lewis 1934; Hammann and Teplitzky, 1956; Long, 1911; Preston and Jones, 1912).

The present work was designed to remedy the deficiency. A study was made of reactions based on dimethyl aniline



and involving a variation of the alkyl groups in both base and in halide, of the halogen, and of the ring substituents in the aniline.

In general the effect of the structural modifications is to vary the rate through changes in the activation energy, but with concordant changes in the frequency factor which increases with the activation energy so as to give some 'compensation'.

Following the presentation of the results several of these phenomena reported by other workers, and also found in the present work, are discussed. In addition, the comparison of the values of  $E$  and  $A$  obtained when a single structural feature is varied reveals several unexpected phenomena. For instance, the quaternization of dimethyl aniline by *n*-propyl iodide is slower than with ethyl iodide, but the fall in rate is due to a fall in the value of  $A$ , while the activation energy retains the same value.

Another unexpected discovery was that although the reactions of methyl iodide with substituted dimethyl anilines do not display a 'compensation' effect, the reactions of ethyl iodide with the same anilines do. This comparison leads to some interesting conclusions about the stereo-chemistry of the activated complex in these reactions, and casts doubt upon some established views.

Dimethyl *o*-toluidine was quaternized with two alkyl halides, and it was found that the ortho methyl group causes considerable retardation. Reconsideration of previous discussions about the 'ortho effect' revealed that one rather important aspect has been hitherto overlooked. When this is taken into consideration, previously antagonistic views are reconciled.



Values are obtained for the entropy and enthalpy changes in some of the reactions, and consideration of these substantiates the views on the stereochemistry of the transition complex which were suggested by the kinetic results. The solubility of several of the salts was also measured, and a comparison of this with the entropy of reaction lends support to the view that the entropy of reaction can provide evidence about the degree of solvation.

### RESULTS

In the following tables results are given for the reactions studied in nitrobenzene. Measurements were made at at least four temperatures, and all rate constants were corrected for the thermal expansion of the solvent. The values for the percentage reaction are in all cases taken from smoothed curves.

The reliability of the constants ( $k_1$ ) obtained when a genuine equilibrium could be measured is illustrated by data for a few specimen runs, in which the falling values of the simple second order constants ( $k_3$ ) are included for comparison.

The subsequent tables (V to XXX) contain a summary of the temperature dependence of the reaction rates. The concentration of the reagents (after mixing) and the method of analysis used in each case are recorded, together with the method adopted to determine  $k_1$ , as this allows an estimate of the accuracy of the rate constant. The three methods of determining rate constants discussed in the last section were used as the situation dictated.

When a valid equilibrium could be measured (or estimated) it was used in the calculation of the rate



constant by the application of the formula (III, 3). This procedure is indicated by the letter 'a' in the following tables.

In some cases accurate initial tangents could be drawn, and this procedure will be signified by the letter 'b'.

When a back extrapolation procedure was used three cases arose, depending on the shape of the extrapolation plot. The simple second order rate constants ( $k_3$ ) fell during the reaction, and as has been mentioned previously the plot of  $k_3$  against  $x$  was frequently linear. This type of extrapolation gave a reliable value of  $k_1$ , and is signified by the letter 'c'.

Sometimes the gradient of the plot of  $k_3$  against  $x$  became more negative as  $x$  increased, so that the plot was concave toward the axes; this type of extrapolation has been designated by the letter 'd'.

In other cases the gradient of the extrapolation plot became less negative as  $x$  increased, so that the plot was convex toward the axes. The gradient of these plots therefore increased toward zero



concentration of product, and they correspond to the least reliable values of  $k$ . These extrapolations are signified by the letter 'e'.

Table XXXI contains a summary of the kinetic parameters. Values of the activation energies and frequency factors calculated by the method of least squares are recorded, together with the interpolated value of the rate constant at  $80^{\circ}\text{C}$ .

Table XXXII contains a summary of the thermodynamic reaction parameters obtained from van't Hoff plots when these could be constructed from valid equilibrium constants. Values of the interpolated equilibrium constants at  $80^{\circ}\text{C}$  are recorded together with values of the reverse reaction rate constant. In these cases only the entropy of activation (at  $80^{\circ}\text{C}$ ) was calculated from  $\log_{10} A$  using the equation,

$$\Delta S^{\ddagger} = 4.576 \cdot \log_{10} (A/T) - 49.203 \quad (\text{I, 14}).$$



At 80°C this becomes,

$$\Delta S_{\infty}^{\ddagger} = 4.576 \cdot \log_{10} A - 60.86 \quad (1)$$

The last table (XXXIII) contains the melting points of the solid salts prepared, together with their solubilities in nitrobenzene at 25°C.

### SPECIMEN RUNS

Table I

Ethyl iodide and diethyl aniline at 80°C

time (hours)	% reaction	$10^2 k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	$10^2 k_2$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )
0.5	0.36	7.55	7.23
1	0.71	7.25	7.15
2	1.41	7.45	7.15
3	2.04	7.50	6.95
4	2.62	7.52	6.86
5	3.17	7.57	6.83
6	3.60	7.41	6.05
25	7.75	6.49	3.35
47	8.58	4.89	1.99

Equilibrium 9.3%

Table II

Methyl iodide and dimethyl aniline at 80°C

time (minutes)	% reaction	$10^2 k_1$ (litre mole <sup>-1</sup> minute <sup>-1</sup> )	$10^2 k_2$ (litre mole <sup>-1</sup> minute <sup>-1</sup> )
5	3.6	15.05	14.8
10	6.9	15.4	14.8
20	12.3	15.3	14.0
30	16.9	15.6	13.1
45	21.8	15.4	12.4
60	26.0	16.0	11.7
75	28.8	16.1	10.8
90	30.8	16.15	9.9
120	33.8	17.1	8.5

Equilibrium 36.5%



Table III

Methyl iodide and dimethyl m-toluidine at 40°C

time (hours)	% reaction	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	$k_2$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )
2	11.6	1.32	1.31
4	20.7	1.31	1.31
6	28.4	1.34	1.32
8	34.9	1.36	1.34
12	43.9	1.34	1.30
16	50.5	1.33	1.27
22	58.3	1.37	1.28

Equilibrium 80%

Table IV

Methyl iodide and dimethyl m-nitro aniline at 80°C

time (hours)	% reaction	$10k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	$10k_2$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )
0.125	0.223	1.97	1.79
0.25	0.415	2.02	1.67
0.5	0.619	2.06	1.39
0.75	0.854	1.99	1.15
1	0.941	1.84	0.95
1.5	1.021	1.88	0.69

Equilibrium 1.2%



SUMMARY OF TEMPERATURE DEPENDENCE OF REACTIONSTable V

Methyl iodide and dimethyl aniline

Solutions M/20. Analysis by titration.

$T^{\circ}\text{C}$	K (litre/mole)	$k$ , (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k$ ,
80	17.7	9.85	a
60	66.7	3.19	a
40	123(?)	1.03	c
25		0.396	c

Table VI

Methyl iodide and p-dimethylaminobenzaldehyde

Solutions M/10. Analysis by conductivity.

$T^{\circ}\text{C}$	$k$ , (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k$ ,
80	$7.015 \times 10^{-2}$	b
60	$1.82 \times 10^{-2}$	b
40	$3.62 \times 10^{-3}$	b
25	$1.04 \times 10^{-3}$	b

Table VII

Methyl iodide and dimethyl m-nitro aniline

Solutions M/10. Analysis by conductivity

$T^{\circ}\text{C}$	K (litre/mole)	$k$ , (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k$ ,
80	0.129	$2.10 \times 10^{-1}$	a
60	0.220	$5.94 \times 10^{-2}$	a
40		$1.945 \times 10^{-2}$	a
25	0.434	$4.40 \times 10^{-3}$	a
6.0		$9.79 \times 10^{-4}$	a



Table VIII

Methyl iodide and p-bromo dimethyl aniline  
Solutions M/10. Analysis by titration.

$T^{\circ}\text{C}$	$k$ , (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k$ ,
80	1.97	d
60	$6.26 \times 10^{-1}$	d
40	$1.68 \times 10^{-1}$	d
25	$6.27 \times 10^{-2}$	c

Table IX

Methyl iodide and dimethyl o-toluidine  
Solutions M/10. Analysis by conductivity.

$T^{\circ}\text{C}$	$K$ (litre/mole)	$k$ , (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k$ ,
80	0.457	4.735	a
60	0.89	$1.15 \times 10^{-1}$	a
40		$2.98 \times 10^{-2}$	c
25		$7.3 \times 10^{-3}$	c
6.0		$2.92 \times 10^{-3} (?)$	e

Table X

Methyl iodide and dimethyl m-toluidine  
Solutions M/20. Analysis by conductivity.

$T^{\circ}\text{C}$	$K$ (litre/mole)	$k$ , (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k$ ,
80	8.74	12.5	a
60	137	4.53	a
40	406	1.34	a
25		$4.90 \times 10^{-1}$	a
6.0		$1.09 \times 10^{-1}$	second order



Table XI

Methyl iodide and ethyl methyl aniline  
Solutions M/20. Analysis by titration.

$T^{\circ}\text{C}$	K (litre/mole)	$k, \text{litre mole}^{-1}\text{hour}^{-1}$	determination of k,
80	28.9	6.04	a
60	77.5	1.92	a
40	291	$5.19 \times 10^{-1}$	a
25	-	$2.28 \times 10^{-1}$	c
5.0	-	$4.74 \times 10^{-2}$	e

Table XII

Methyl iodide and diethyl aniline  
Solutions M/10. Analysis by conductivity.

$T^{\circ}\text{C}$	K (litre/mole)	$k, \text{litre mole}^{-1}\text{hour}^{-1}$	determination of k,
80	13.9	1.005	a
60	28.0	0.2505	a
40	64.9	$6.57 \times 10^{-2}$	a
25	-	$1.71 \times 10^{-2}$	second order
6.0	-	$2.97 \times 10^{-3}$	second order

Table XIII

Ethyl iodide and diethyl aniline  
Solutions M/10. Analysis by titration.

$T^{\circ}\text{C}$	K (litre/mole)	$k, \text{litre mole}^{-1}\text{hour}^{-1}$	determination of k,
120.1	-	$4.77 \times 10^{-1}$	c
100.7	0.558	$3.03 \times 10^{-1}$	a
80	1.17	$9.02 \times 10^{-2}$	a
60		$2.23 \times 10^{-2}$	c
40		$2.61 \times 10^{-3}$	c



Table XIV

Ethyl iodide and diethyl m-toluidine  
Solutions M/10. Analysis by titration.

$T^{\circ}\text{C}$	K (litre/mole)	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
120.1	0.495	0.949	c
100.4	0.875	0.372	c
80	1.62	0.126	a
60		$2.815 \times 10^{-2}$	d
40		$7.47 \times 10^{-3}$	d

Table XV

Ethyl iodide and diethyl p-toluidine  
Solutions M/10. Analysis by conductivity.

$T^{\circ}\text{C}$	K (litre/mole)	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
120.1	0.741	1.40	a
100.3	1.49	$5.16 \times 10^{-1}$	a
80	-	$1.78 \times 10^{-1}$	a
60	-	$4.71 \times 10^{-2}$	a
40	-	$1.195 \times 10^{-2}$	a

Table XVI

Ethyl bromide and diethyl aniline  
Solutions M/10. Analysis by conductivity.

$T^{\circ}\text{C}$	K (litre/mole)	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
120.1	0.0458	$4.53 \times 10^{-2}$	d
99.7	0.0795	$1.54 \times 10^{-2}$	c
80	0.169	$3.92 \times 10^{-3}$	c
60	0.219	$7.80 \times 10^{-4}$	d
40	-	$1.85 \times 10^{-4}$	c



Table XVII

Ethyl iodide and ethyl methyl aniline

Solutions M/20. Analysis by conductivity.

$T^{\circ}\text{C}$	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
80	$5.42 \times 10^{-1}$	e
60	$1.57 \times 10^{-1}$	e
40	$4.48 \times 10^{-2}$	c
25	$1.49 \times 10^{-2}$	e

Table XVIII

Ethyl iodide and dimethyl aniline

Solutions M/10. Analysis by titration.

$T^{\circ}\text{C}$	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
80	$7.83 \times 10^{-1}$	d
60	$2.56 \times 10^{-1}$	c
40	$7.31 \times 10^{-2}$	c
25	$2.51 \times 10^{-2}$	c
6.0	$4.49 \times 10^{-3}$	d

Table XIX

Ethyl iodide and dimethyl m-nitro aniline

Solutions M/10. Analysis by conductivity

$T^{\circ}\text{C}$	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
80	$6.53 \times 10^{-3}$	b



Table XX

Ethyl iodide and dimethyl o-toluidine

Solutions M/10. Analysis by conductivity.

$T^{\circ}\text{C}$	$k$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k$ ,
80	$1.82 \times 10^{-2}$	b

Table XXI

Ethyl iodide and p-dimethyl aminobenzaldehyde

Solutions M/10. Analysis by conductivity.

$T^{\circ}\text{C}$	$k$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k$ ,
99.6	$4.00 \times 10^{-2}$	c
80	$8.94 \times 10^{-3}$	c
60	$1.92 \times 10^{-3}$	d
40	$3.14 \times 10^{-4}$	b
25	$7.55 \times 10^{-5}$	b

Table XXII

Ethyl iodide and p-bromo dimethyl aniline

Solutions M/10. Analysis by conductivity.

$T^{\circ}\text{C}$	$k$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k$ ,
80	$1.75 \times 10^{-2}$	c
60	$4.36 \times 10^{-2}$	b
40	$1.22 \times 10^{-2}$	e
25	$3.52 \times 10^{-3}$	b
6.0	$6.45 \times 10^{-4}$	b



Table XXIII

Ethyl iodide and dimethyl m-toluidine  
Solutions M/10. Analysis by conductivity.

$T^{\circ}\text{C}$	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
80	1.26	e
60	$3.96 \times 10^{-1}$	c
40	$1.04 \times 10^{-1}$	c
25	$4.03 \times 10^{-2}$	d
6.0	$9.62 \times 10^{-3}$	c

Table XXIV

Ethyl iodide and dimethyl p-toluidine  
Solutions M/10. Analysis by both conductivity  
and titration.

$T^{\circ}\text{C}$	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
80	2.74	e
60	0.955	c
40	0.317	c
25	0.116	c

Table XXV

Ethyl iodide and dimethyl p-anisidine  
Solutions M/20. Analysis by conductivity.

$T^{\circ}\text{C}$	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
80	4.25	e
60	1.65	c
40	0.510	c
25	0.205	c
6	$3.80 \times 10^{-2} (?)$	b



Table XXVI

Ethyl iodide and dimethyl p-nitroso aniline

Solutions M/10. Analysis by conductivity.

$T^{\circ}\text{C}$	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
80	1.76	c
60	$5.92 \times 10^{-2}$	e
40	$1.66 \times 10^{-1}$	c
25	$4.40 \times 10^{-2}$	c
6	$2.27 \times 10^{-2}$	c

Table XXVII

Ethyl bromide and dimethyl aniline

Solutions M/10. Analysis by titration.

$T^{\circ}\text{C}$	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
100.6	$3.49 \times 10^{-1}$	c
80	$7.99 \times 10^{-2}$	c
60	$2.22 \times 10^{-2}$	c
40	$5.21 \times 10^{-3}$	c

Table XXVIII

Ethyl bromide and dimethyl p-toluidine

Solutions M/10. Analysis by conductivity.

$T^{\circ}\text{C}$	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
80	$2.25 \times 10^{-1}$	c
60	$6.00 \times 10^{-2}$	d
40	$1.45 \times 10^{-2}$	b
25	$4.43 \times 10^{-3}$	d



Table XXIX

n-Propyl iodide and dimethyl aniline

Solutions M/10. Analysis by conductivity.

$T^{\circ}\text{C}$	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
80	$1.46 \times 10^{-1}$	e
60	$5.02 \times 10^{-2}$	e
40	$1.13 \times 10^{-2}$	e
25	$4.67 \times 10^{-3}$	e

Table XXX

n-Butyl iodide and dimethyl aniline

Solutions M/10. Analysis by conductivity.

$T^{\circ}\text{C}$	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
99.4	$3.32 \times 10^{-1}$	d
80	$1.18 \times 10^{-1}$	e
60	$3.25 \times 10^{-2}$	e
40	$7.64 \times 10^{-3}$	e
25	$2.11 \times 10^{-3}$	b



Table XXXI

## Summary of kinetic results

System	$\log k, ^{80}$ (litre mole <sup>-1</sup> second <sup>-1</sup> )	E(k.cal/mole)	$\log A$ (litre mole <sup>-1</sup> second <sup>-1</sup> )
MeI, DMA	-2.578	12.15	4.941
MeI, mNDMA	-4.226	14.25	4.5985
MeI, pDMAB	-4.710	16.08	5.246
MeI, pBrDMA	-3.286	13.16	4.859
MeI, DMOt	-3.886	15.63	5.789
MeI, DMmT	-2.443	12.54	5.319
MeI, EMA	-2.770	12.49	4.966
MeI, DEA	-3.5605	15.33	5.932
EtI, DEA	-4.719	16.10	5.243
EtI, DEmt	-4.502	15.64	5.184
EtI, DEpT	-4.327	14.59	4.704
EtI, EMA	-3.835	13.57	4.568
EtI, DMA	-3.641	13.55	4.745
EtI, mNDMA	-5.741	-	-
EtI, DMOt	-5.295	-	-
EtI, pDMAB	-5.581	18.50	5.886
EtI, pBrDMA	-4.3315	14.68	4.755
EtI, DMmT	-3.480	12.86	4.481
EtI, DMpT	-3.122	11.94	4.270
EtI, DMpA	-2.923	11.58	4.248
EtI, pNODMA	-3.362	11.99	4.058
EtBr, DMA	-4.631	15.95	5.243
EtBr, DEA	-5.207	17.10	5.399
EtBr, DMpT	-4.213	14.89	5.009
nPrI, DMA	-4.368	13.54	4.012
nBuI, DMA	-4.499	14.99	4.782



Table XXXII

## Summary of Thermodynamic Quantities

System	$\log K^{80}$ (litre/ mole)	$\Delta H$ (k.cal/ mole)	$\Delta S_{80}$ (cal/mole degree)	$\Delta S_{80}^\ddagger$ (cal/mole degree)
MeI, mNDMA	-0.89	-4.7	-17.5	-39.82
MeI, DMOt	-0.34	-7.8	-23.65	-34.36
MeI, DMmT	0.941	-18.5	-48.2	-36.54
MeI, DMA	1.25	-15.4	-37.9	-38.25
MeI, EMA	1.45	-12.7	-29.2	-38.13
MeI, DEA	1.14	-8.4	-18.8	-33.72
EtI, DEA	0.068	-8.3	-23.3	-36.87
EtI, DEmT	0.215	-8.1	-22.1	-37.14
EtI, DEpT	-0.131(120°)	-10.3	-25.6(120°)	-39.55(120°)
EtBr, DEA	-0.835	-8.0	-26.5	-36.15

Table XXXIII

## Solubilities and Melting Points

Salt	solubility (millimole/litre)	melting point
$C_6H_5^+NMe_3I^-$	24.7	200°(sub.)
p-Me- $C_6H_4^+NMe_3I^-$	20.2	210-211°(sub.)
p-MeO- $C_6H_4^+NMe_3I^-$	9.07	232°(sub.)
p-Br- $C_6H_4^+NMe_3I^-$	4.36	195°(dec.)
m-Me- $C_6H_4^+NMe_3I^-$	41.9	184°(sub.)
m-NO <sub>2</sub> - $C_6H_4^+NMe_3I^-$	1.46	203°
o-Me- $C_6H_4^+NMe_3I^-$	28.9	205-6°(sub.)
p-NO- $C_6H_4^+NMe_3I^-$	38	180°(?)



## DISCUSSION

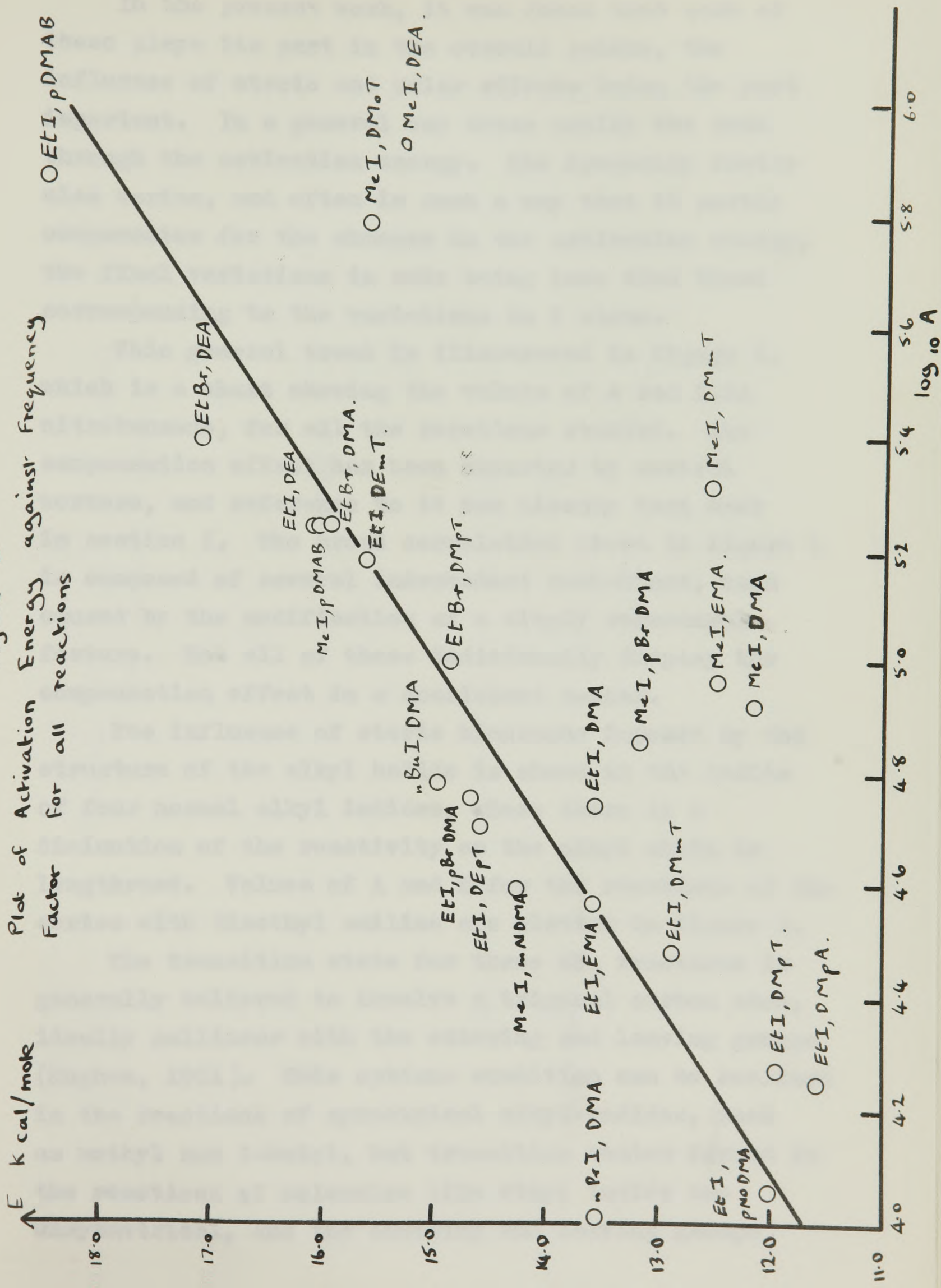
The quaternization of tertiary amines by alkyl halides involves an attack by the lone pair of electrons attached to the nitrogen atom upon the alkyl halide, displacing the halogen atom, which becomes a negative ion. The lone pair of electrons form a bond between the alkyl group and the nitrogen, and escape the full control of the nitrogen atom which therefore acquires a formal positive charge, becoming a cation with a tetrahedral bond distribution similar to that in inorganic ammonium salts. Although anilines contain more atoms than do the alkyl halides normally used in quaternization reactions, it is convenient to regard the former as the attacking species. An aniline is therefore occasionally referred to as the attacking, or entering, group, and the halogen atom as the leaving group.

In view of this the rate of quaternization of dialkyl anilines is dependent upon the availability of the lone pair electrons on the nitrogen atom. This is influenced by the inductive effects of groups attached to the nitrogen atom directly, or to the aromatic ring. A guide to the availability of the electrons is the basicity of the aniline, the most basic anilines generally showing the greatest reactivity.

The rate of quaternization is also dependent on the steric hindrance imposed by groups around the reaction centre, the strengths of the reacting bonds and the degree of solvent interaction, since this facilitates the reaction by stabilizing the charges as they develop.



Figure I





In the present work, it was found that each of these plays its part in the overall scheme, the influence of steric and polar effects being the most important. In a general way these modify the rate through the activation energy. The frequency factor also varies, and often in such a way that it partly compensates for the changes in the activation energy, the final variations in rate being less than those corresponding to the variations in  $E$  alone.

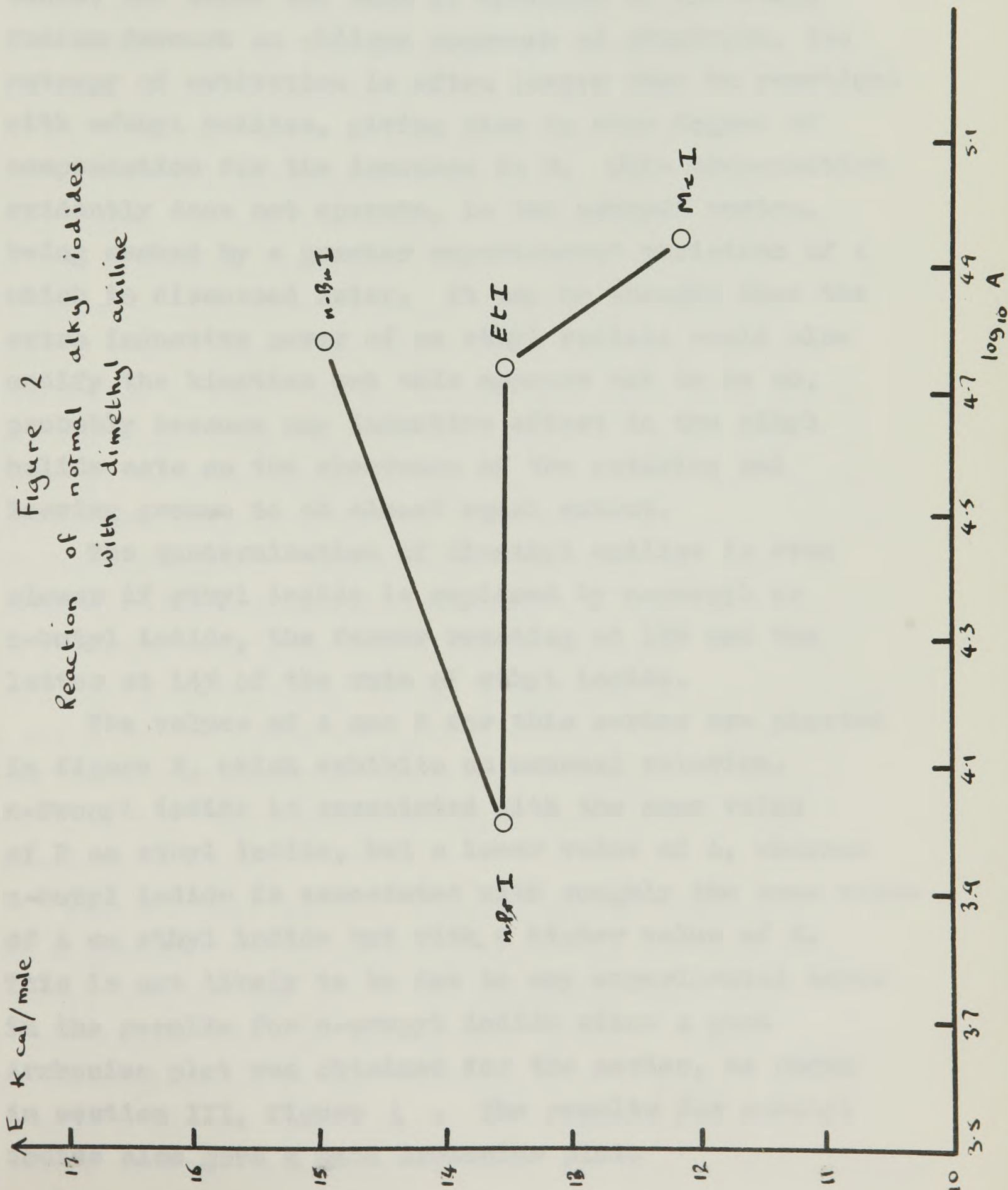
This general trend is illustrated in figure 1, which is a chart showing the values of  $A$  and  $E$  in nitrobenzene, for all the reactions studied. The compensation effect has been reported by several workers, and reference to it has already been made in section I. The broad correlation shown in figure 1 is composed of several independent variations, each caused by the modification of a single structural feature. Not all of these individually display the compensation effect in a consistent manner.

The influence of steric hindrance imposed by the structure of the alkyl halide is shown in the series of four normal alkyl iodides, where there is a diminution of the reactivity as the alkyl chain is lengthened. Values of  $A$  and  $E$  for the reactions of the series with dimethyl aniline are plotted in figure 2.

The transition state for these  $SN_2$  reactions is generally believed to involve a trigonal carbon atom, ideally collinear with the entering and leaving groups (Hughes, 1951). This optimum condition can be realised in the reactions of symmetrical alkyl iodides, such as methyl and *t*-butyl, but transition states formed in the reactions of molecules like ethyl iodide are unsymmetrical, and the entering and leaving groups



Figure 2  
Reaction of normal alkyl iodides  
with dimethyl aniline





are subjected to a sideways force, pushing them out of line with the central carbon atom. This leads to an increase in the activation energy in the transition from methyl to ethyl halides as shown in figure 2. Since the activated complex formed with ethyl iodide has bent bonds, and since the lack of symmetry of the ethyl radicle favours an oblique approach of reactants, the entropy of activation is often larger than in reactions with methyl halides, giving rise to some degree of compensation for the increase in  $E$ . This compensation evidently does not operate, in the present series, being masked by a greater superimposed variation of  $A$  which is discussed later. It may be thought that the extra inductive power of an ethyl radicle would also modify the kinetics but this appears not to be so, probably because any inductive effect in the alkyl halide acts on the electrons of the entering and leaving groups to an almost equal extent.

The quaternization of dimethyl aniline is even slower if ethyl iodide is replaced by *n*-propyl or *n*-butyl iodide, the former reacting at 19% and the latter at 14% of the rate of ethyl iodide.

The values of  $A$  and  $E$  for this series are plotted in figure 2, which exhibits an unusual relation. *n*-Propyl iodide is associated with the same value of  $E$  as ethyl iodide, but a lower value of  $A$ , whereas *n*-butyl iodide is associated with roughly the same value of  $A$  as ethyl iodide but with a higher value of  $E$ . This is not likely to be due to any experimental error in the results for *n*-propyl iodide since a good Arrhenius plot was obtained for the series, as shown in section III, figure 6. The results for *n*-butyl iodide also gave a good Arrhenius plot.



A similar contrast between the behaviour of ethyl and n-propyl halides has been reported by other workers (Winkler and Hinshelwood, 1935; Dunbar and Hammett, 1950), and has been attributed to the lower number of conformations available to the n-propyl group in the transition state (Magat et al., 1950). The observed rate is due to the sum total of all possible mechanisms, but when one in particular yields the major proportion of the product, this is the mechanism that the experimentally determined quantities most nearly represent. It will correspond to the maximum product of the energy and entropy terms in the Arrhenius equation. It appears that with n-propyl iodide this maximum occurs when E has a low value in a strictly defined transition state. The fact that the activation energy has the same value for the reactions of both ethyl and n-propyl iodides suggests that the entering and leaving groups are subjected to the same amount of steric strain in the two cases. Models show that this can only be so if the terminal methyl group in the n-propyl radicle is directed away from the reaction centre. This would reduce the probability of the transition state to roughly a third of its value with ethyl iodide, and therefore lead to a corresponding reduction in  $\log_{10} A$  of roughly 0.5 ( $\log_{10} 3$ ). This value compares with an observed reduction of 0.73.

The configuration of minimum steric hindrance has a somewhat lower probability in the reaction with n-butyl iodide, and it is not surprising that there is a compromise, whereby the maximum product of the energy and entropy terms is now associated with higher values of both A and E. The transition, from n-propyl to n-butyl iodide, thus shows a clear example of the working



of the compensation effect.

The importance of steric hindrance in explaining changes caused by structural alterations in the tertiary amino group is shown in figure 3. Although the basicity increases in the transition from dimethyl to diethyl aniline, the rate of reaction decreases. The increase of basicity is illustrated by the following acidity constants for the anilines in water (Taylor, 1958).

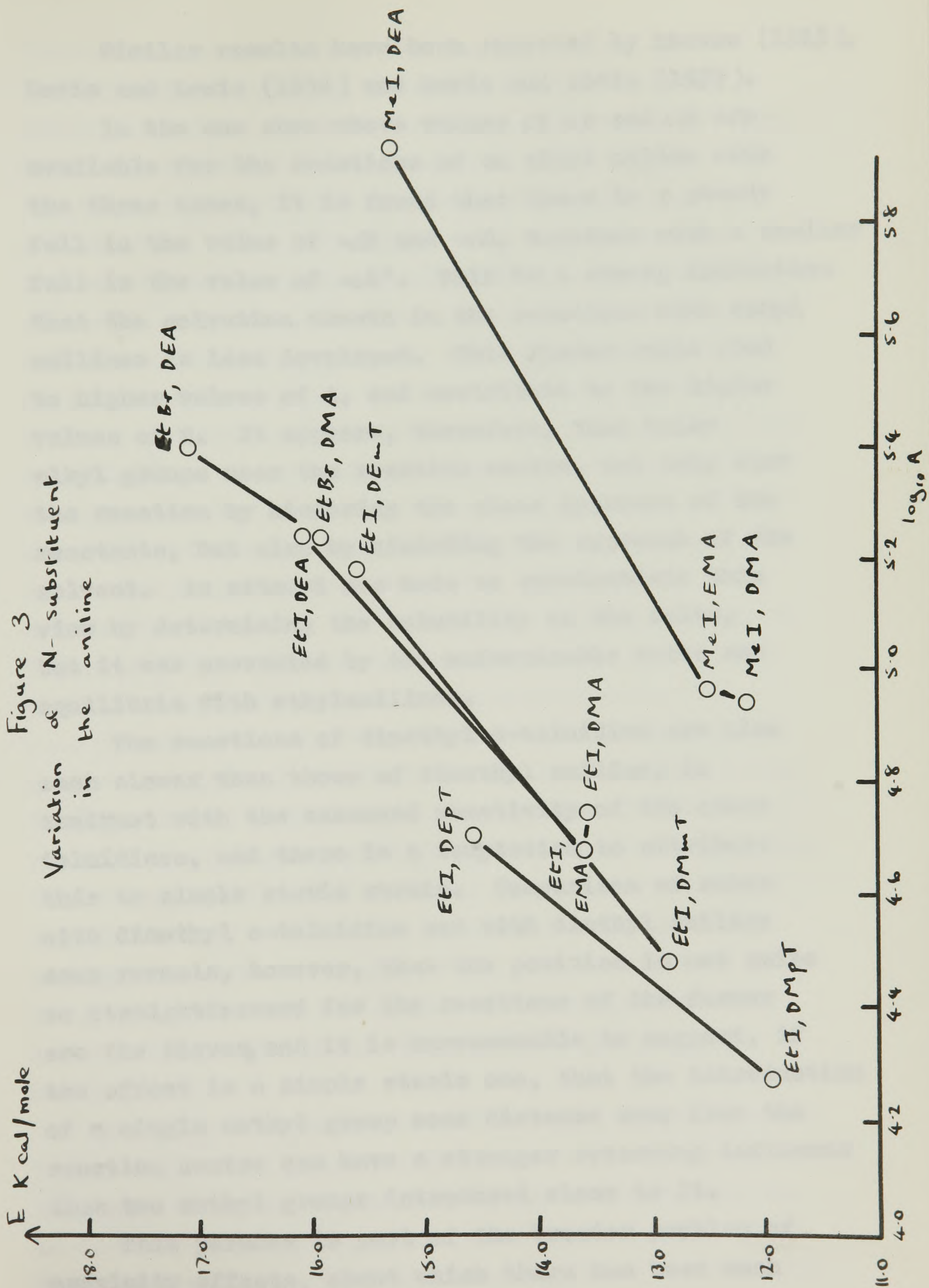
dimethylaniline       $pK_a$  at  $25^\circ C = 5.98$

diethylaniline       $pK_a$  at  $25^\circ C = 6.56$

The replacement of one N-methyl group by an ethyl group lowers the rate only slightly. It achieves this in different ways in the two reactions studied, by lowering A in the reaction with ethyl iodide, and by raising E in the reaction with methyl iodide. The small influence is probably due to a rather fine balance between the enhanced basicity, and the increased steric retardation. The enhanced basicity may also explain why the value of the equilibrium constant for the reaction of methyl iodide with ethyl methyl aniline is the greatest of this particular series.

When the second N-methyl group is also replaced by an ethyl group, there is a much greater retardation, and the rate generally falls to about a tenth of its value with dimethyl aniline. With ethyl bromide however, the rate with diethyl aniline is a quarter of the rate with dimethyl aniline. In all cases the retardation is brought about through a rise in the value of E. The value of A also rises in a correlated way, and partly compensates for the change of E.







Similar results have been reported by Thomas (1913), Davis and Lewis (1934) and Davis and Addis (1937).

In the one case where values of  $\Delta S$  and  $\Delta H$  are available for the reactions of an alkyl halide with the three bases, it is found that there is a steady fall in the value of  $-\Delta H$  and  $-\Delta S$ , together with a smaller fall in the value of  $-\Delta S^\ddagger$ . This is a strong indication that the solvation sheath in the reactions with ethyl anilines is less developed. This factor would lead to higher values of  $A$ , and contribute to the higher values of  $E$ . It appears, therefore, that bulky alkyl groups near the reaction centre, not only slow the reaction by hindering the close approach of the reactants, but also by hindering the approach of the solvent. An attempt was made to substantiate this view by determining the solubility of the salts, but it was prevented by the unfavourable rates and equilibria with ethylanilines.

The reactions of dimethyl o-toluidine are also much slower than those of dimethyl aniline, in contrast with the enhanced reactivity of the other toluidines, and there is a temptation to attribute this to simple steric strain. Comparison of rates with dimethyl o-toluidine and with diethyl aniline soon reveals, however, that the position is not quite so straightforward for the reactions of the former are the slower, and it is unreasonable to suggest, if the effect is a simple steric one, that the introduction of a single methyl group some distance away from the reaction centre can have a stronger retarding influence than two methyl groups introduced close to it.

This paradox is part of the broader problem of proximity effects, about which there has been much



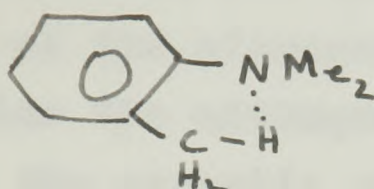
discussion. Brown and Fried (1943) studied the quaternization rates of several bicyclic tertiary amines, and came to the conclusion that ortho groups force the tertiary amino group out of the plane of the ring, and that this is responsible for the retardation. They considered that an alternative explanation of hydrogen bonding in the activated collision complex could not explain the fact that in a series of bicyclic amines  $C_6H_4-C_nH_m-NMe$  there is no retardation when  $n = 2$  or  $3$ , but when  $n = 4$ , and a seven membered ring is formed, there is considerable retardation. The tertiary amino group is held in the plane of the ring only when  $n = 2$  or  $3$ , and they consider this to be evidence in favour of the non-coplanarity hypothesis. The view is further substantiated by the fact that when a methyl group is introduced into the remaining o-position in N-methyl tetrahydroquinoline there is no retardation.

The view is also supported by the lower dipole moments recorded for anilines with ortho substituents (Hughes, 1948; Smith, 1961), and by the reduced reactivity of the p-position in condensation reactions (von Braun, 1916, 1918). These facts can be readily explained by a combination of steric hindrance and reduced mesomerism brought about if the tertiary amino group twists out of the plane of the ring, but they are difficult to explain on the basis of hydrogen bonding.

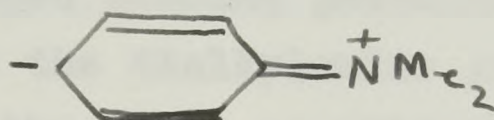
On the other hand, several workers (Evans et al., 1939a; Fahim and Galaby, 1950; Watson p. 241) have suggested that the effect is due to hydrogen bonding in the activated transition state. Watson considers that the available evidence supports the view that the



dialkylamino group in dimethyl o-toluidine remains more or less in the plane of the ring, and that hydrogen bonds form in the activated transition state with a possible structure;



The fact that the ortho effect increases both A and E is considered contradictory to the view that the dialkylamino group is twisted out of the plane of the ring. In unsubstituted dimethyl aniline there is some mesomerism which activates the para position and involves canonical forms such as;



Watson postulates that if this type of mesomerism were prevented by the twisting of the dialkylamino group out of the plane of the ring, it would lead to a greater freedom of the lone pair electrons attached to the nitrogen atom, which would in turn lower the activation energy. On the other hand hydrogen bonding would reduce the availability of the lone pair and thus raise the activation energy, it would also give the nitrogen atom a more positive charge than that given to it by the mesomeric effect alone, and by analogy with the large values of A found in reactions involving an ion, this would raise A. The partial binding of the electrons in the hydrogen bond may also reduce the intensity of the mesomeric effect, and thus explain the reduced reactivity of the para position.



Reduced mesomerism may also explain the smaller dipole moments found when substituted anilines are compared with isomeric o-toluidines and 2:6-xylidines.

An aspect which appears to have been overlooked in the discussions so far is the electronic configuration of the nitrogen atom. In unsubstituted dimethyl aniline the nitrogen atom is trigonal and coplanar with the aromatic ring. The pair of non-bonding electrons are in a p-orbital perpendicular to the plane of the ring, which partially overlaps with the aromatic  $\pi$  bond system, giving rise to the mesomerism and enhanced reactivity at the para position.

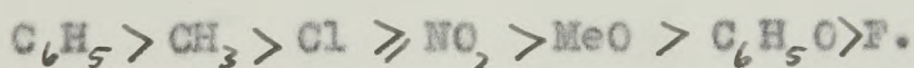
Models show that when a substituent (such as methyl) is introduced into the ortho position, it is impossible for the hydrogen bonding postulated by Watson to take place, unless the dialkylamino group twists out of the plane of the ring, as otherwise the electrons in the p-orbital are too far away from the hydrogens of the ortho group for any interaction to take place. If the amino group is twisted out of the plane of the ring, by the repulsion of the ortho substituent, overlap of the p-orbital with the  $\pi$ -bond system is reduced, and the nitrogen atom will probably revert to a tetrahedral configuration. The structure of lowest strain is now found to be that in which the two N-alkyl groups are pointing away from the ortho methyl group, at one of the hydrogen atoms on which the lone pair electrons, now in an  $sp^3$ -orbital, are directed.

The discussion as to whether the ortho effect is due to hydrogen bonding in the transition state, or to non-coplanarity of the amino group and the aromatic ring is therefore rather pointless. The postulated hydrogen bonding cannot take place if the amino group



is coplanar with the ring, and if the amino group is not coplanar with the ring some form of hydrogen bonding is extremely likely.

Hydrogen bonding of this type is obviously not possible when a halogen or oxygen atom is attached at the ortho position, but it may now be possible for some type of interaction to take place between the ortho atom and one of the hydrogens of the N-methyl groups, forming a six membered ring which may help to keep the tertiary amino group coplanar with the aromatic ring, and offset the steric force tending to force the amino group out of the plane of the ring. If non-coplanarity and hydrogen bonding in the transition state both retard quaternization this could explain the observed trend in magnitude of the ortho effect. This is (Evans et al., 1939a)



It is nevertheless possible that hydrogen bonding in the transition state may cause some charge separation as postulated by Watson. This may promote the formation of a small solvation sheath, in which case the subsequent formation of the fully solvated transition complex would be accompanied by a smaller entropy loss, resulting in the higher value of A. A more probable explanation of the rise in A, is that the transition complex has a stereochemistry modified by the fact that the initial reactant now has a nitrogen atom in a tetrahedral electronic configuration, instead of the planar (trigonal) configuration in meta or para isomers.

The arguments advanced by Brown and Fried (1943) are also open to criticism, since in the tertiary bicyclic amines studied it is not only impossible for the dialkyl amino group to twist out of the plane of



the ring, but, because of this, it is also impossible for hydrogen bonds to form.

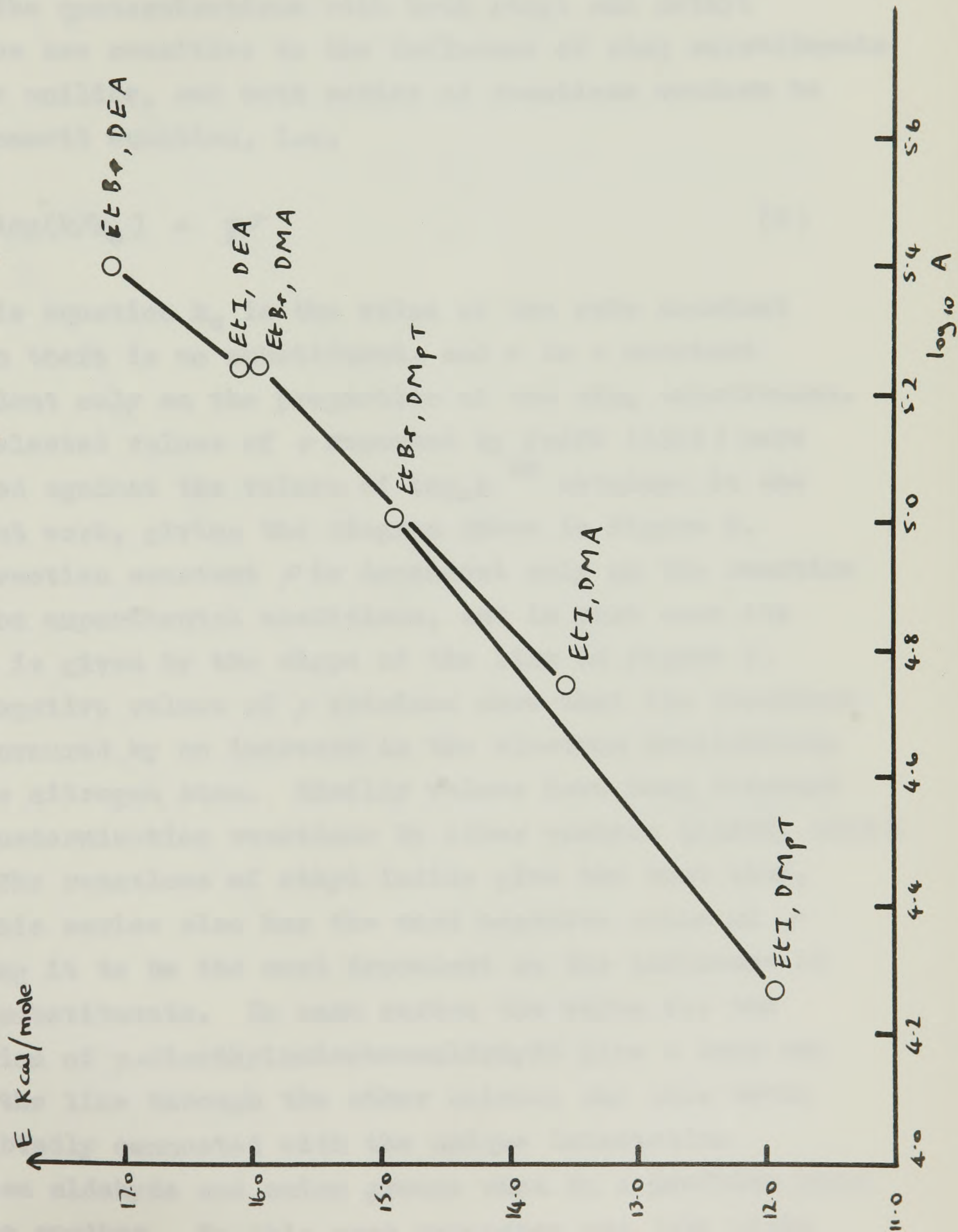
The quaternization reactions are also sensitive to a variation of the halogen, iodides reacting faster than bromides. This is the usual type of behaviour and was reported by Hammann and Teplitzky (1956). It can be correlated with the respective carbon-halogen bond strengths which are (Finar, p. 80) 45.5 k.cal/mole for carbon-iodine and 54 k.cal/mole for carbon-bromine. Since bromine is a little more electronegative than iodine ( $\text{Br} = 2.8$ ,  $\text{I} = 2.5$ ) alkyl bromides are slightly more polar than the corresponding iodides, but this will have little effect upon the reactivity.

The relevant reaction pairs are shown in figure 4, where it can be seen that the rate is mainly dependent on the activation energy. The value of  $A$  also changes, so that there is the familiar type of compensation effect. This compensation could arise in two ways, either a change in the polarity of the transition complex with a resulting change of solvation, or a modification of the steric requirements. The problem is in fact quite similar to one met later in the discussion of the effect of ring substituents in the aniline and is best left to be discussed in conjunction with this.

In the reactions of diethyl aniline with the two alkyl halides the equilibrium constant with the bromide corresponds to the smaller amount of reaction. This can be correlated with the greater strength of the carbon-bromine bond. Surprisingly, the two halides have equally exothermic reactions, although the reaction with ethyl bromide corresponds to the greater



Figure 4  
Variation of halogen in ethyl halides





entropy loss. This must be connected with the influence which the properties of the reacting bonds exert on the solvation sheath.

The quaternizations with both ethyl and methyl iodides are sensitive to the influence of ring substituents in the aniline, and both series of reactions conform to the Hammett equation, i.e.

$$\log(k/k_0) = \rho\sigma \quad (2)$$

In this equation  $k_0$  is the value of the rate constant  $k$  when there is no substituent, and  $\sigma$  is a constant dependent only on the properties of the ring substituent. The selected values of  $\sigma$  reported by Jaffé (1953) were plotted against the values of  $\log_{10} k^{80}$  obtained in the present work, giving the diagram shown in figure 5.

The reaction constant  $\rho$  is dependent only on the reaction and the experimental conditions, and in each case its value is given by the slope of the line in figure 5. The negative values of  $\rho$  obtained show that the reactions are favoured by an increase in the electron availability at the nitrogen atom. Similar values have been obtained for quaternization reactions by other workers (Jaffé, 1953).

The reactions of ethyl iodide give the best line, and this series also has the most negative value of  $\rho$  showing it to be the most dependent on the influence of ring substituents. In each series the value for the reaction of *p*-dimethylaminobenzaldehyde lies a long way from the line through the other points, and this seems undoubtedly connected with the unique interaction between aldehyde and amino groups when in a position para to one another. In this case resonance can take place with a quinone structure, e.g.



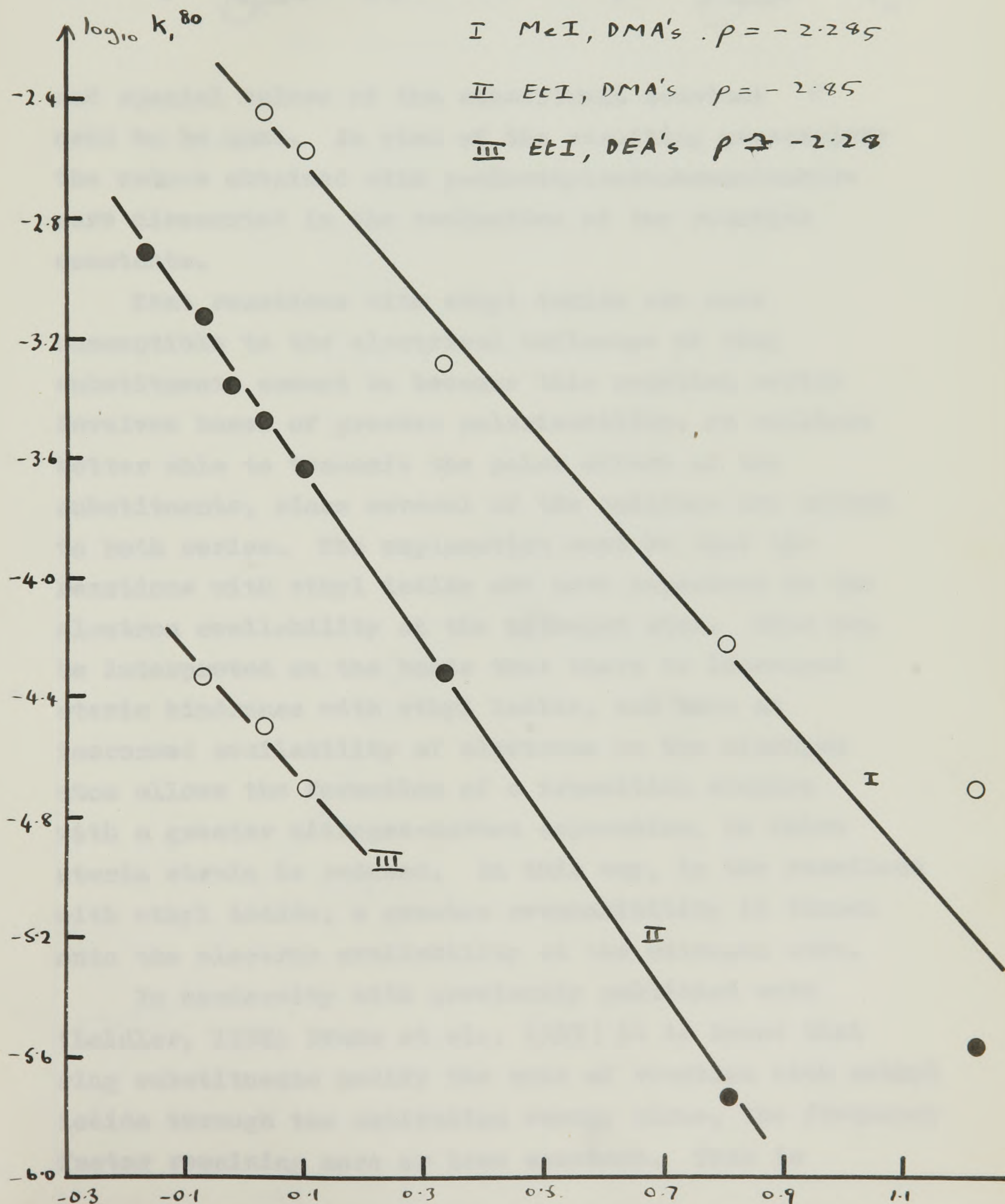
Figure 5

Plot of  $\log_{10} k, ^{80}$  against Hammett substituent constants for three reaction series

I MeI, DMA's  $\rho = -2.285$

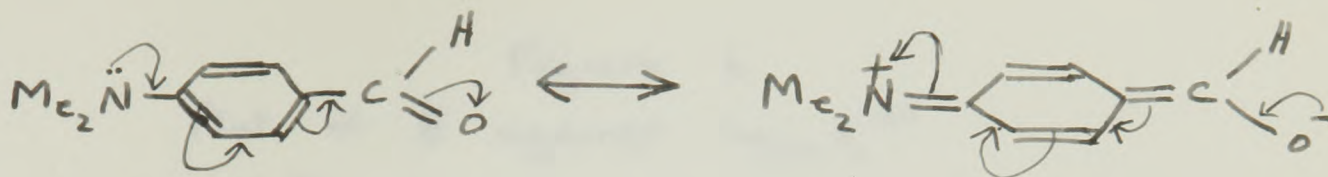
II EtI, DMA's  $\rho = -2.85$

III EtI, DEA's  $\rho = -2.28$





e.g.



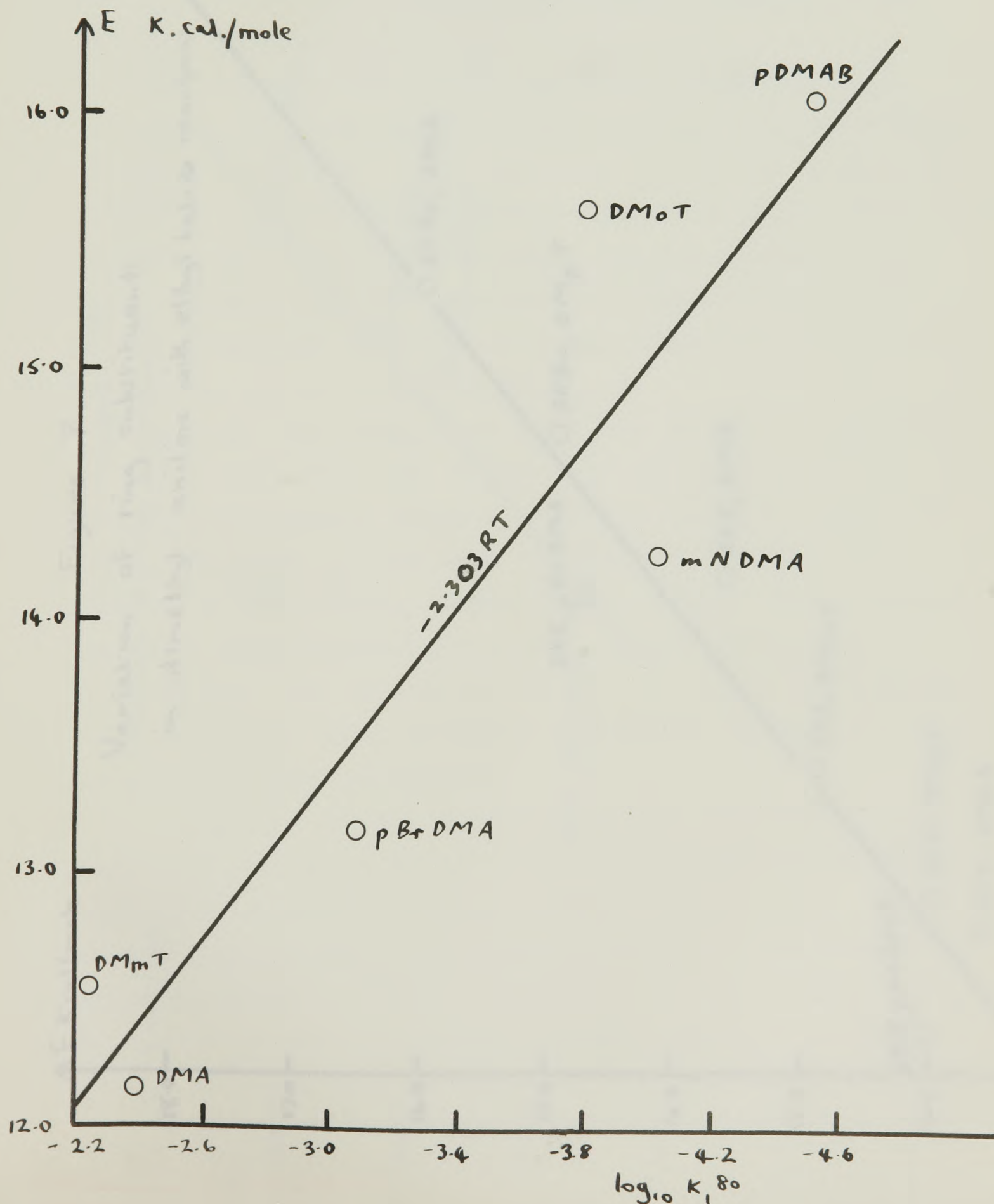
and special values of the substituent constant  $\sigma$  need to be used. In view of the resulting uncertainty the values obtained with p-dimethylaminobenzaldehyde were discounted in the evaluation of the reaction constants.

That reactions with ethyl iodide are more susceptible to the electrical influence of ring substituents cannot be because this reaction series involves bases of greater polarisability, or anilines better able to transmit the polar effect of the substituents, since several of the anilines are common to both series. The explanation must be that the reactions with ethyl iodide are more dependent on the electron availability at the nitrogen atom. This can be interpreted on the basis that there is increased steric hindrance with ethyl iodide, and that an increased availability of electrons on the nitrogen atom allows the formation of a transition complex with a greater nitrogen-carbon separation, in which steric strain is reduced. In this way, in the reactions with ethyl iodide, a greater responsibility is thrown onto the electron availability at the nitrogen atom.

In conformity with previously published work (Laidler, 1938; Evans et al., 1939) it is found that ring substituents modify the rate of reaction with methyl iodide through the activation energy alone, the frequency factor remaining more or less constant. This is



Figure 6  
 Plot of  $E$  against  $\log_{10} k_1^{80}$   
 for reactions with methyl iodide





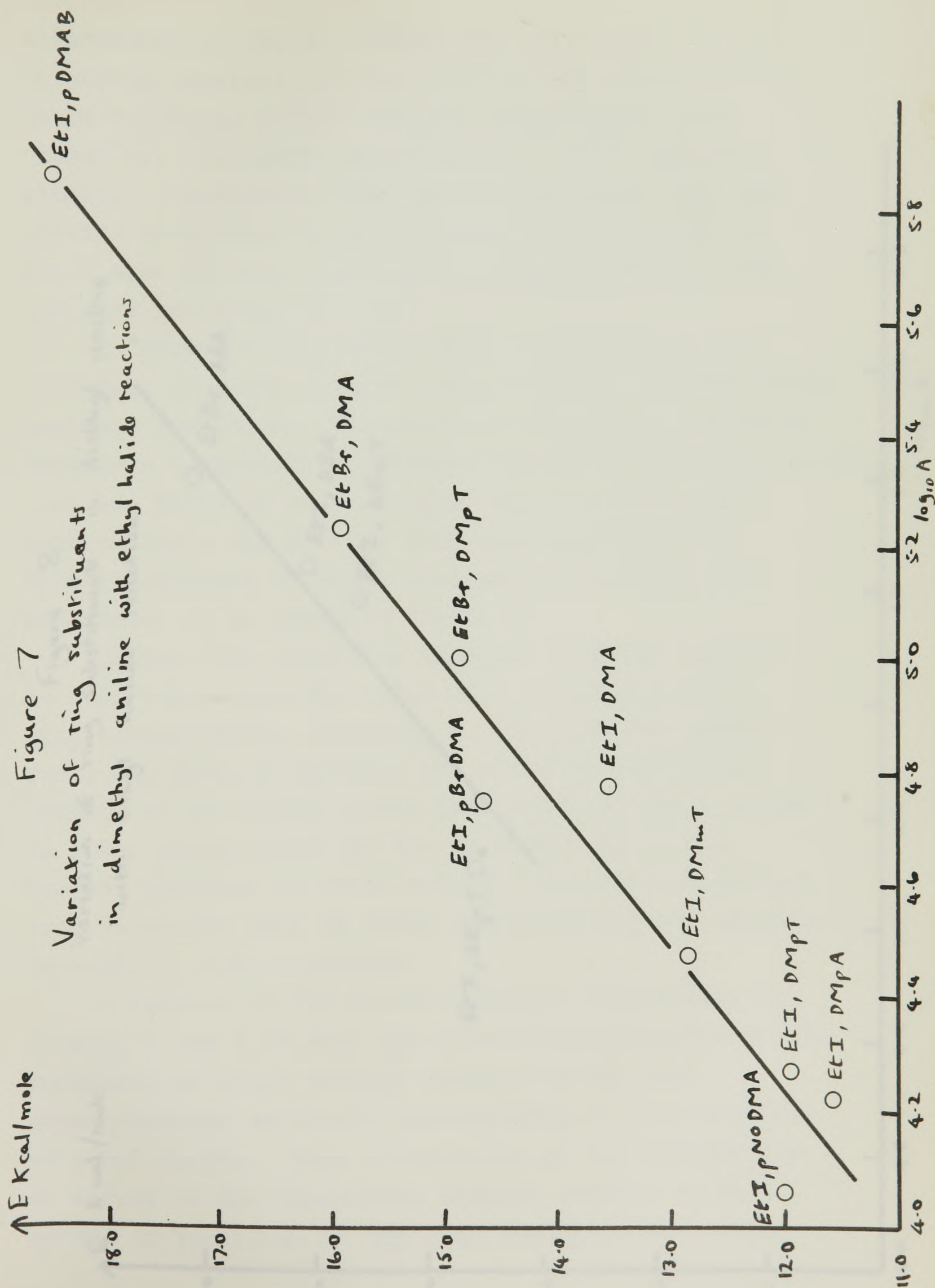
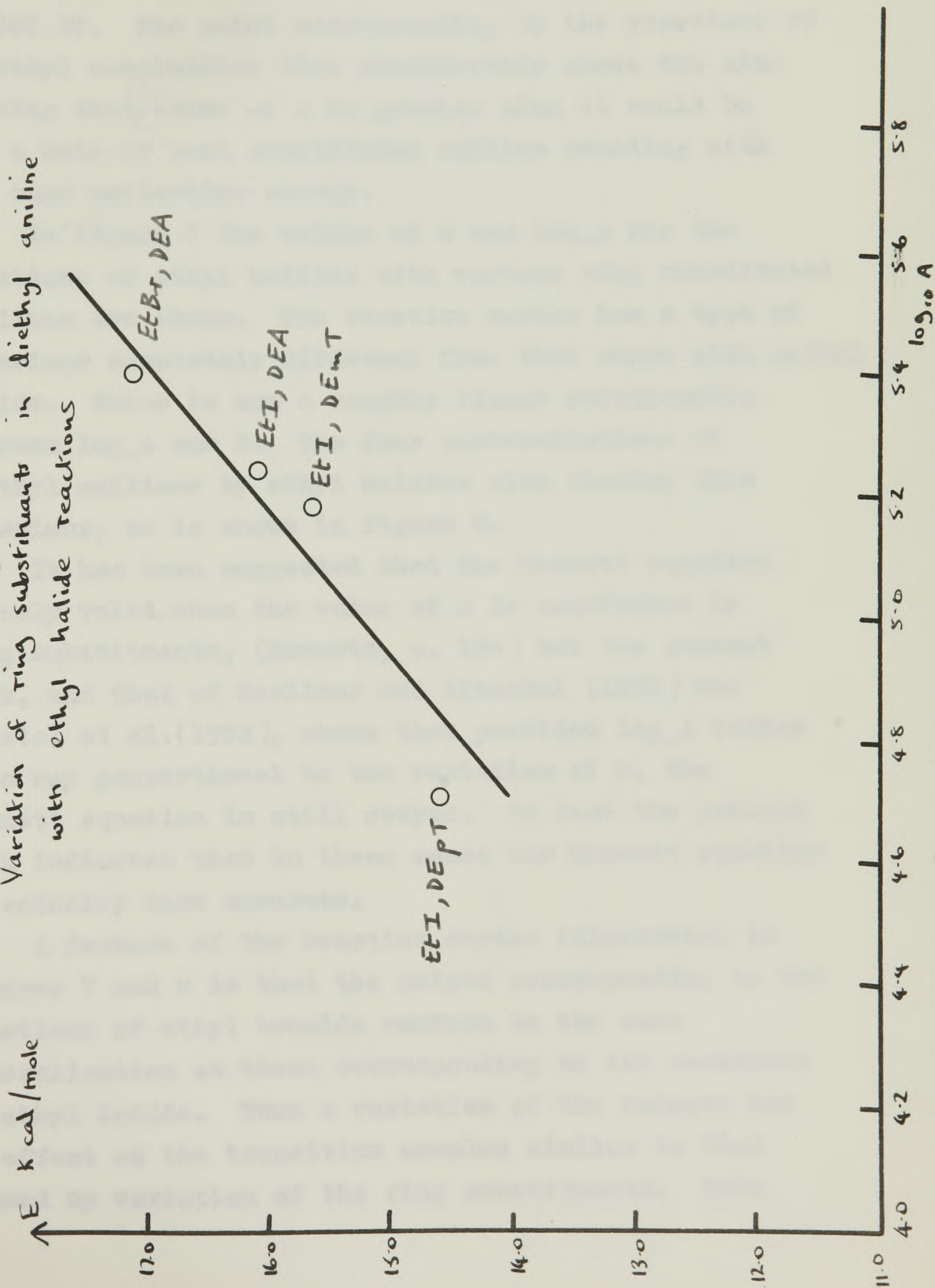




Figure 8

Variation of ring substituents in diethyl aniline  
with ethyl halide reactions





illustrated in figure 6 where the activation energy is plotted against the logarithm of the rate constant at  $80^{\circ}\text{C}$ , giving a line with the theoretical slope of  $-2.303 \text{ RT}$ . The point corresponding to the reactions of dimethyl o-toluidine lies considerably above the line showing that <sup>the</sup> value of A is greater than it would be for a meta or para substituted aniline reacting with the same activation energy.

In figure 7 the values of E and  $\log_{10} A$  for the reactions of ethyl halides with various ring substituted anilines are shown. The reaction series has a type of behaviour completely different from that shown with methyl iodide. There is now a roughly linear relationship between  $\log_{10} A$  and E. The four quaternizations of diethyl anilines by ethyl halides also display this behaviour, as is shown in figure 8.

It has been suggested that the Hammett equation is only valid when the value of A is unaffected by ring substituents, (Hammett, p. 194) but the present work, and that of Berliner and Altschul (1952) and Cristol et al. (1952), shows that provided  $\log_{10} A$  varies in a way proportional to the variation of E, the Hammett equation is still obeyed. In fact the present work indicates that in these cases the Hammett equation is actually more accurate.

A feature of the reaction series illustrated in figures 7 and 8 is that the points corresponding to the reactions of ethyl bromide conform to the same generalisation as those corresponding to the reactions of ethyl iodide. Thus a variation of the halogen has an effect on the transition complex similar to that caused by variation of the ring substituents. This



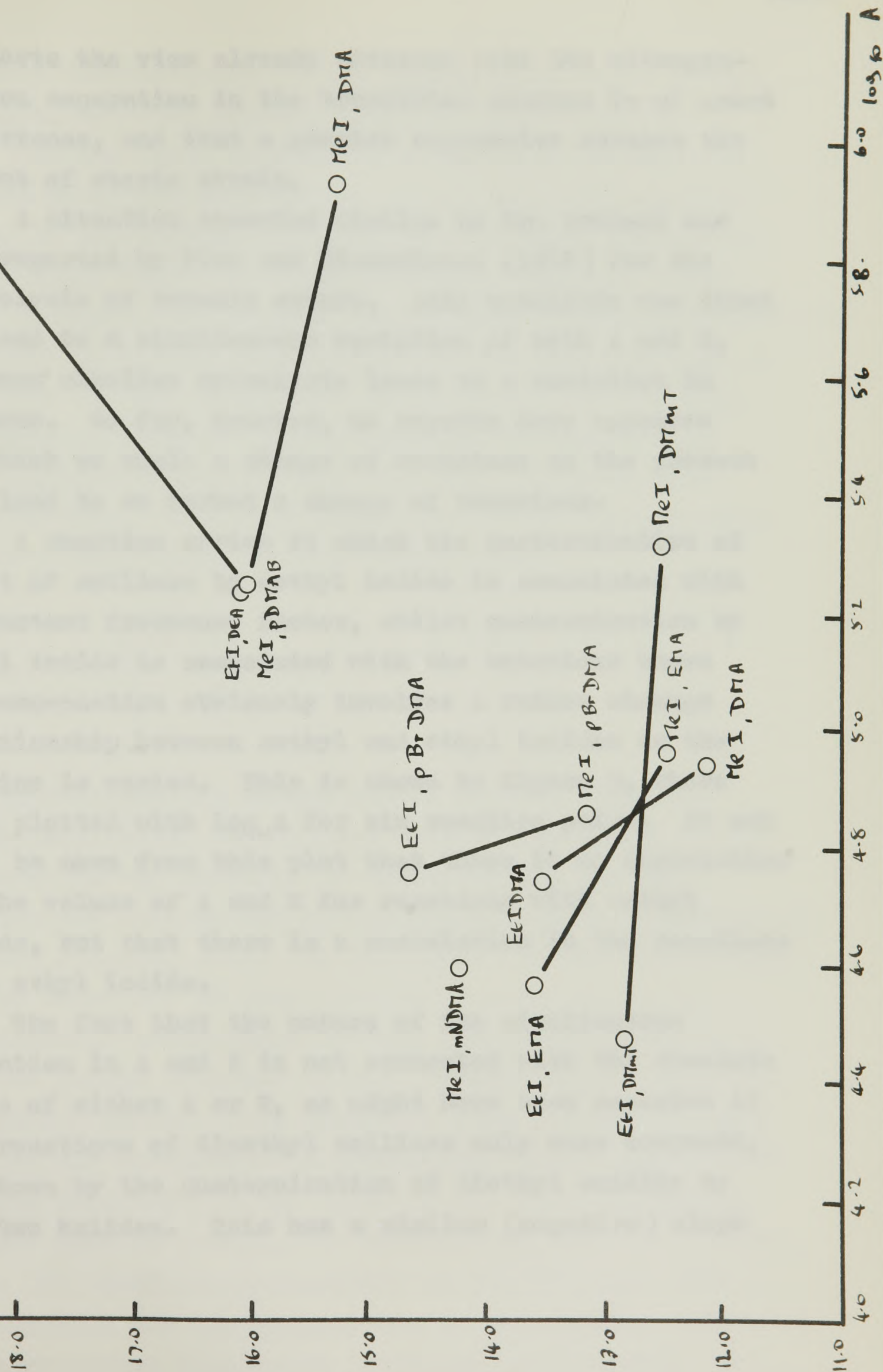
Figure 9

## Relations

$\Delta E$  Kcal/mole

between ethyl  $\alpha$  methyl iodide

O ETI, DYAB





supports the view already advanced that the nitrogen-carbon separation in the transition complex is of great importance, and that a greater separation reduces the amount of steric strain.

A situation somewhat similar to the present one was reported by Timm and Hinshelwood (1938) for the hydrolysis of benzoic esters. Acid catalysis was found to lead to a simultaneous variation of both A and E, whereas alkaline hydrolysis leads to a variation in E alone. So far, however, no reports have appeared in which so small a change of structure as the present one lead to so marked a change of behaviour.

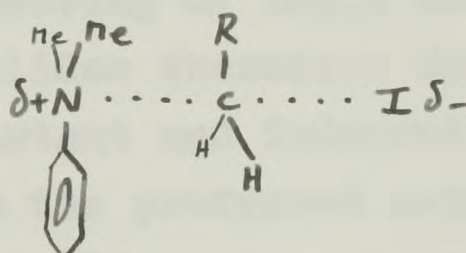
A reaction series in which the quaternization of a set of anilines by methyl iodide is associated with a constant frequency factor, whilst quaternization by ethyl iodide is associated with the behaviour known as compensation obviously involves a rather strange relationship between methyl and ethyl iodides as the aniline is varied. This is shown in figure 9, where E is plotted with  $\log_{10} A$  for six reaction pairs. It can also be seen from this plot that there is no correlation in the values of A and E for reactions with methyl iodide, but that there is a correlation in the reactions with ethyl iodide.

The fact that the nature of the simultaneous variation in A and E is not connected with the absolute value of either A or E, as might have been expected if the reactions of dimethyl anilines only were compared, is shown by the quaternization of diethyl aniline by the two halides. This has a similar (negative) slope



to that corresponding to the reactions of ethyl methyl aniline, but much greater values of both A and E.

The observed relations can, however, be explained by the following hypothesis. It is generally accepted that, in the transition state, the reacting carbon atom of an alkyl halide is trigonal-planar (Hughes, 1951) with attacking and leaving groups more or less symmetrically situated on either side of it. If the nitrogen atom in the base is also postulated to be planar, as it is in the ground state of dimethyl aniline (Smith, 1961), the transition complex will have the following type of structure, where R is either  $\text{CH}_3$  or H, corresponding to ethyl and methyl halides respectively;



In the reactions of methyl iodide ( $R = \text{H}$ ) there is relatively little interaction between the groups attached to the nitrogen or carbon atoms, and the complex can take up any of the conformations corresponding to free rotation about the N-C axis. On the other hand, in the reactions of ethyl iodide ( $R = \text{Me}$ ) there is considerable interaction between the methyl group at R and the groups attached to the nitrogen atom, especially the phenyl group. This prohibits many (apparently about 4/5) of the conformations previously allowed and thereby results in a fall in the value of A. When activating groups, such as methyl, are substituted into the aniline ring, the electron availability at the nitrogen atom is increased and the complex can be constituted with a nitrogen-carbon separation increased sufficiently for



there to be much less steric strain. The activation energy is then only slightly altered on the transition from methyl to ethyl halide. As the ring substituents are changed, however, the electron availability at the nitrogen atom may diminish and so demand a closer approach, resulting in a greater interference between the alkyl groups concerned and a rise in the activation energy. This lowers the rate corresponding to the strictly oriented transition state until it becomes comparable with that corresponding to other routes with higher values of both  $E$  and  $A$ . These probably involve the oblique approach of reactants and the bending of bonds.

The lowering of  $\log_{10} A$  on transition from methyl to ethyl halides therefore appears to be initially roughly constant and independent of the value of  $E$ . It reflects the preferred orientations in the reactions with ethyl iodide. Superimposed upon this is a correlated increase of both  $\log_{10} A$  and  $E$ , due to the contribution of the reaction taking place by other routes in which there is more steric strain. The transition is therefore represented roughly in the equation,

$$\log_{10} A^{\text{Et}} \simeq \log_{10} A^{\text{Me}} - \text{const.} + 0.3(E^{\text{Et}} - E^{\text{Me}}) \quad (3)$$

The rough applicability of the equation is shown by the following values of the constant necessary to make the equation fit in each case;



diethylaniline	constant =	0.93
dimethyl m-toluidine		0.93
ethyl methyl aniline		0.72
dimethyl aniline		0.62
dimethyl p-bromo aniline		0.57
p-dimethylaminobenzaldehyde		0.11

In equation (3) the factor 0.3 expressing the proportionality between  $E$  and  $\log A$  was obtained from the gradient of the general trend shown on the overall chart in figure 1. Five of the six reaction pairs conform to the generalisation reasonably well, but the reactions of p-dimethylaminobenzaldehyde are a good way out. This may be due to the special features of this reactant previously mentioned, or to the greater experimental uncertainty associated with the extremely slow reactions.

Superimposed upon the relationship expressed in equation (3) will be changes in  $A$  caused by different solvation patterns with the two halides. The solvation sheath is likely to have a lower entropy in the reactions with methyl iodide, since in this case more solvent molecules can approach close to the reaction centre. In the reactions of ethyl iodide fewer solvent molecules can approach close to the reaction centre because of the hindrance of the longer alkyl chain. This effect may well become more pronounced as the nitrogen-carbon distance in the transition state is reduced, which may explain the trend in the values of the constants. If this is so, and since the carbon-nitrogen separation is related to the activation energy, it is suggested that the effect of solvation considerably increases the factor of proportionality between  $\log A$  and  $E$ .



If the factors were doubled, for example, the relationship would become

$$\log_{10} A^{\text{Et}} \simeq \log_{10} A^{\text{Me}} - \text{const.} + 0.6(E^{\text{Et}} - E^{\text{Me}}) \quad (4)$$

The constants required to make this equation fit in each case are as follows,

diethyl aniline	1.17
dimethyl m-toluidine	1.02
ethyl methyl aniline	1.04
dimethyl aniline	1.02
dimethyl p-bromo aniline	1.03
p-dimethylaminobenzaldehyde	0.84

It can be seen that the agreement with equation (4) is quite good and gives general support to the idea that, in the transition state, the nitrogen atom of the aniline has a trigonal-planar configuration and that in this case the transition state is more like the initial reactant than the final salt. This conclusion is at variance with the views expressed elsewhere (e.g. Glasstone, Laidler and Eyring, p. 419) that the transition state is rather similar to the final product. This view is based on the observation that the values of  $\Delta S^\ddagger$  and  $\Delta S$  are similar in the reaction between methyl iodide and dimethyl aniline, a similarity that has been confirmed in the present work. Comparison of these quantities for other reactions, however, shows that this similarity is the exception rather than the rule, since in all other reactions the two entropies are dissimilar,  $\Delta S^\ddagger$  being sometimes greater and sometimes smaller than  $\Delta S$ . In this respect the early availability of results for the reaction of methyl iodide with dimethyl aniline



(Essex and Gelormini, 1926) may have been misleading.

#### TOTAL ENTROPIES AND ENTHALPIES OF REACTION

When true equilibria could be measured at more than one temperature, van't Hoff plots were constructed and the enthalpies and entropies of reaction calculated. These are shown along with equilibrium constants and rate constants for the reverse reaction in table XXXII.

Several equilibrium constants were obtained for the reactions of nuclear substituted anilines, but these gave a poor Hammett plot. This may be due to the slight ionisation of the quaternary salts, the extent of which probably varies from reaction to reaction, so changing the effective reaction order of the reverse decomposition in each case. This must reduce the accuracy of the entropies and enthalpies, but the values are still qualitatively interesting.

It is clear that the fastest reactions are also the most exothermic, suffer the largest entropy loss and have the most favourable equilibria. Changes in equilibrium are not overwhelming due to variation of either the forward or reverse reaction rate. In this respect the situation is <sup>unlike</sup> that found with the reactions in mixed solvents reported in the next section, where a large variation in the reverse reaction rate is mainly responsible for the variation of equilibrium constant.

The entropy of reaction  $\Delta S$  often depends largely on the change in solvation during a reaction, and the negative values here indicate that the products are more solvated than the reactants. Since none of the reactants used in this study will be heavily solvated, the value of  $\Delta S$  can be used as an indication of the solvation of the final product. The conclusions drawn on this basis are supported by the measured solubilities,



in so far as the most soluble salt is associated with the greatest entropy loss, and vice versa.

The enthalpy of reaction varies roughly in parallel with the entropy of reaction, and this can be understood on the basis that the heat of solvation of the product contributes in no small way to the total exothermicity of the reaction. The properties of the solvation sheath seem to be determined by the polarity of the quaternary amino group, and not by any direct interaction between a substituent and the solvent. Otherwise the introduction of a nitro group into trimethyl anilinium iodide would be expected to increase the solubility of the salt in nitrobenzene, which is contrary to the observed facts.



## DISCUSSION

In the present work, the reaction of the solvent with the solute has been studied. The solvent used was a mixture of the solvent and the solute. The reaction was studied at a constant temperature, and the rate of reaction was measured. The results show that the reaction is first order with respect to the solute and zero order with respect to the solvent. This is in agreement with the results of other workers. The activation energy of the reaction was found to be 10.5 kcal/mole. This is also in agreement with the results of other workers. The reaction is believed to be a simple bimolecular reaction.

## SECTION V

### EFFECT OF THE SOLVENT MEDIUM ON RATE AND EQUILIBRIA

It is well known that the rate of a chemical reaction is affected by the nature of the solvent medium. In the present work, the effect of the solvent medium on the rate and equilibrium of the reaction has been studied. The results show that the rate of reaction increases with increasing polarity of the solvent. This is in agreement with the results of other workers. The equilibrium constant of the reaction also increases with increasing polarity of the solvent. This is also in agreement with the results of other workers. The reaction is believed to be a simple bimolecular reaction.

The results of the present work are summarized in Table I.



## INTRODUCTION

It was mentioned in the general discussion of energy-entropy relationships that a variation of the solvent often causes a modification in the kinetics of a chemical reaction, through the activation energy and frequency factor, similar to that caused by moderate structural variations in one of the reactants. Studies of the so-called Menschutkin reaction have been reported by several workers, with different reactant and solvent systems. In most of these it was found that a change of solvent, within a related group, modified the reaction rate mainly through the frequency factor, the activation energy remaining more or less unaffected. On the other hand, the use of solvents of widely differing properties often causes variations in both  $E$  and  $A$ , and the compensation effect previously discussed is sometimes found.

Grim, Ruf and Wolf (1931) studied the reaction between triethylamine and ethyl iodide in fifteen aromatic solvents and two aliphatic solvents (*n*-hexane and cyclo-hexane) determining the activation energies and frequency factors in all but three aromatic solvents. The activation energies in the aromatic solvents all lie close to a mean value of 12.3 k.cal./mole, the greatest departure being only 1.7 k.cal./mole. In contrast, the activation energies with the two aliphatic solvents are widely divergent, being 16.0 k.cal./mole with *n*-hexane, and 17.1 k.cal./mole with cyclo hexane. Similar results were obtained by Pickles and Hinshelwood (1936) for the reaction between pyridine and methyl iodide in thirteen solvents, nine of which were aromatic.

The results of Essex and Gelormini (1926) for the



quaternization of dimethyl aniline by methyl iodide in three solvents show a dependence on A of the reaction rate. There is a correlation between E and A, the highest value of A going with the highest value of E, but in this case also the variation of A is the more important, and is sufficiently large to offset the simultaneous variation of E.

In contrast, the results of Hawkins (1922) show a similar correlation, but the rate is principally governed by a large variation in the activation energy. Hawkins studied the reaction between pyridine and allyl bromide in seven solvents, five of which were oxygen-containing compounds, and two of which were aromatic hydrocarbons (benzene and toluene). For the five oxygen-containing solvents there is a fair correlation of E and A, and in this case the rate is mainly dependent on the large variations of E. Hawkins also studied this reaction in two solvent mixtures, but as he only made measurements at a single temperature, the separate variations of A and E cannot be determined.

Solvent mixtures are easier to treat theoretically, than a series of individual pure solvents, as it is difficult to represent changes in the latter by a satisfactory variable. Several workers have therefore confined their attention to studies of a reaction in solvent mixtures. Such a study was made by Fairclough and Hinshelwood (1937a), who followed the reaction between methyl iodide and pyridine in five solvent mixtures. They found that there is a rough correlation of A and E, together with a tendency for A to increase with solvent polarity, in such a way that the changes in reaction rate could not be attributed to the variation of either parameter alone. This type of behaviour



was also found by Raine and Hinshelwood (1939), who studied the formation of three quaternary ammonium salts in a series of mixed solvents containing benzene and nitrobenzene.

The quaternization of 4-picoline by n-butyl bromide in a series of solvents containing propylene carbonate and diphenyl ether was studied by Watanabe and Fuoss (1955), who found that the rate was greatest in the propylene carbonate rich solutions of high dielectric constant. However, the activation energy is also greatest in these mixtures of high dielectric constant, the rate being dependent on the variations of A. There is therefore a rough correlation of A and E, high values of A going with high values of E.

The present study was undertaken in order to extend the knowledge of the dependence of quaternization reactions on the solvent medium. Three reactions were studied in solvents containing mixtures of nitrobenzene and chlorobenzene; ethyl methyl aniline and dimethyl p-toluidine were each quaternized with ethyl iodide, and dimethyl aniline with methyl iodide. The rate of these reactions proved to be mainly governed by the activation energy, variations of the frequency factor being relatively unimportant. The variation of the equilibrium constant with solvent composition was also studied, and this was found to be more sensitive to solvent composition than the rate constant.

As discussed previously (Section III) the results were quite satisfactory in the range of solvents containing 0-60% chlorobenzene, while in a solvent containing 80% chlorobenzene some difficulties were met. More serious difficulties were encountered with reactions in the solvents richest in chlorobenzene, and several



reactions had to be abandoned. For theoretical purposes, however, values of the reaction parameters for solvents rich in chlorobenzene were obtained by extrapolation of values for other mixtures.

### RESULTS

In the following tables results are given for the three reactions studied, the solvent compositions being given in the weight per cent of nitrobenzene. Detailed results for the reactions in pure nitrobenzene have been excluded since they are contained in the previous section.

The percentage reaction was in each case taken from a smooth curve, and all the rate constants are corrected for the thermal expansion of the solvent. The expansion corrections for mixed solvents were estimated by interpolation between the corrections calculated for the pure components.

The reliability of the rate constants ( $k_3$ ) obtained when a valid equilibrium could be measured is illustrated by data for a few specimen runs, in which the falling values of the simple second order constants ( $k_3$ ) are included for comparison. Specimen runs for the ethyl iodide dimethyl p-toluidine reactions are also given to illustrate the rapidly falling values obtained.



The subsequent tables contain a summary of the temperature dependence of the reactions. The methods used in the last section for the determination of rate constants have also been used here, and the same notation is employed. Thus the letter 'a' signifies that equation (III, 3) has been used in the calculations, while the letter 'b' means that an initial tangent was drawn. Back extrapolation of the simple second order constants ( $k_3$ ) to zero reaction was often employed, and when the extrapolation plot was linear the letter 'c' is given. Some of the plots of  $k_3$  against  $x$  had a gradient that became more negative as  $x$  increased, a curve concave toward the origin being obtained. These extrapolations are signified by the letter 'd'. The least reliable extrapolations, denoted by the letter 'e', correspond to a gradient which became less negative as  $x$  increased, giving a line convex toward the origin. The method of analysis used is recorded in each case, together with the concentration of the reactants after mixing.

The final tables contain values of the activation energies and frequency factors at each solvent composition, together with interpolated values for the rate constants at 80°C. These quantities were calculated from the Arrhenius equation by the method of least squares. Values of the entropy of activation at 80°C ( $\Delta S_{80}^\ddagger$ ) are given for the reactions of methyl iodide with dimethyl aniline, these were calculated from  $\log A$  by the method used in the last section. Activation energies and frequency factors corresponding to reactions that took place heterogeneously, have been excluded from these final tables as they are of little value.

A table is also given containing a summary of the entropies and enthalpies of reaction, calculated from



van't Hoff plots, for the quaternization of dimethyl aniline by methyl iodide.

The values given in parenthesis in these tables are those obtained by extrapolation, or interpolation as the case may be, of results obtained at other solvent compositions.

### SPECIMEN RUNS

Table I

Methyl iodide-dimethyl aniline in 80% nitrobenzene at 60°C.

time (hours)	x%	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	$k_2$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )
0.25	2.48	2.05	2.035
0.5	4.9	2.105	2.06
1	9.0	2.06	1.98
2	15.9	2.07	1.89
5.75	31.96	2.28	1.64

Equilibrium 42.1%

Table II

Methyl iodide-dimethyl aniline in 60% nitrobenzene at 80°C.

time (hours)	x%	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	$k_2$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )
0.125	3.20	6.09	5.21
0.25	5.25	5.81	4.43
0.5	7.82	5.79	3.39
0.75	9.04	5.63	2.65
1	9.60	5.31	2.12

Equilibrium 10.4%



Table III

Ethyl iodide-dimethyl p-toluidine in 80% nitrobenzene at 60°C.

time (hours)	x%	$k_3$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )
0.25	4.00	1.67
0.5	6.90	1.48
1	11.05	1.24
2	17.21	1.04
4	24.80	0.82

Table IV

Ethyl iodide-dimethyl p-toluidine in 20% nitrobenzene at 80°C.

time (hours)	x%	$10^2 k_3$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )
1	0.56	5.64
2	1.04	5.25
4	1.65	4.20
8	2.52	3.23
15	3.55	2.45
30	5.08	1.78
70	7.05	1.08
100	7.5	0.81

Temperature Dependence of Reaction Rates.

Reactions of methyl iodide with dimethyl aniline.

Table V

80% nitrobenzene. Analysis by conductivity. Solutions M/20.

T°C	K(litre/mole)	$k_1$ (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of $k_1$
80	7.1	6.04	a
60	25.0	2.13	a
40		0.636	c
25		0.217	c
5.93		0.0457	b



Table VI

60% nitrobenzene. Analysis by conductivity. Solutions M/20.

$T^{\circ}\text{C}$	$K(\text{litre/mole})$	$k, (\text{litre mole}^{-1}\text{hour}^{-1})$	determination of $k$ ,
80	2.74	6.04	a
60	8.76	2.14	a
40		0.5955	c
25		0.210	d
5.93		0.0429	b

Table VII

40% nitrobenzene. Analysis by conductivity. Solutions M/20.

$T^{\circ}\text{C}$	$K(\text{litre/mole})$	$k, (\text{litre mole}^{-1}\text{hour}^{-1})$	determination of $k$ ,
80	0.87	4.63	a
60	(2.51)	1.64	c
40		0.422	c
25		0.1445	c
5.93		0.0284	b

Table VIII

20% nitrobenzene. Analysis by conductivity. Solutions M/20.

$T^{\circ}\text{C}$	$K(\text{litre/mole})$	$k, (\text{litre mole}^{-1}\text{hour}^{-1})$	determination of $k$ ,
60	0.66	1.038	a
40		0.192	b
25		0.0768	c
5.93		0.0161	b

Table IX

10% nitrobenzene. Analysis by titration. Solutions M/20.

$T^{\circ}\text{C}$	$k, (\text{litre mole}^{-1}\text{hour}^{-1})$	
40	ca. 0.5	(solid product visible)



Table X

0% nitrobenzene. Analysis by titration. Solutions M/10.

$T^{\circ}\text{C}$	$k, (\text{litre mole}^{-1}\text{hour}^{-1})$	determination of $k,$
80 (heterogeneous)	0.0348	e
60 (heterogeneous)	0.201	e
40 (heterogeneous)	0.0639	(autocatalysis)
25 (heterogeneous)	0.00305	e

$$E = 23.5 \text{ k.cal./mole}$$

For values at 60, 40,  $25^{\circ}\text{C}$  {  $A = 3 \times 10^4 \text{ litre mole}^{-1}\text{second}^{-1}$   
 $k_{80} = 7 \times 10^{-4} \text{ " " "}$

Reactions between ethyl iodide and dimethyl p-toluidine

Table XI

80% nitrobenzene. Analysis by conductivity. Solutions M/10.

$T^{\circ}\text{C}$	$k, (\text{litre mole}^{-1}\text{hour}^{-1})$	determination of $k,$
80	2.06	e
60	0.722	e
40	0.191	c
25	0.0875	e

Table XII

60% nitrobenzene. Analysis by conductivity. Solutions M/10.

$T^{\circ}\text{C}$	$k, (\text{litre mole}^{-1}\text{hour}^{-1})$	determination of $k,$
80	0.953	e
60	0.329	e
40	0.0920	c
25	0.0337	e



Table XIII

40% nitrobenzene. Analysis by conductivity. Solutions M/10.

$T^{\circ}\text{C}$	$k, (\text{litre mole}^{-1}\text{hour}^{-1})$	determination of $k,$
80	0.640	e
60	0.2215	e
40	0.0699	e
25	0.0216	e

Table XIV

20% nitrobenzene. Analysis by titration and conductivity.

Solutions M/10

$T^{\circ}\text{C}$	$k, (\text{litre mole}^{-1}\text{hour}^{-1})$	determination of $k$
80	0.0680	e
60	0.299	e
40	0.0681	e
25	0.0228	e

Solid product visible at 25, 40 and  $60^{\circ}$ . Using these values only:  $E = 14.8 \text{ k.cal./mole}$

$$A = 4.57 \times 10^5 \text{ litre mole}^{-1}\text{second}^{-1}$$

$$k^{80} = 3.16 \times 10^{-3} \text{ " " "}$$

Table XV

10% nitrobenzene. Analysis by titration. Solutions M/10.

$T^{\circ}\text{C}$	$k, (\text{litre mole}^{-1}\text{hour}^{-1})$	determination of $k,$
138.8	0.138	e
120.1	0.0734	e
100.6	0.0282	e
80	0.0510	e
60(homogeneous)	0.0801	e
60(heterogeneous)	0.05	e
40(heterogeneous)	0.0114	d
25(heterogeneous)	0.00537	e



Table XV contd.

Using results for homogeneous reactions at 100, 120 and 140°

$$\left\{ \begin{array}{l} E = 13.6 \text{ k.cal./mole} \\ A = 5.5 \times 10^2 \text{ litre mole}^{-1} \text{second}^{-1} \\ k_{80} = 2.1 \times 10^{-6} \text{ " " "} \end{array} \right.$$

Using results for heterogeneous reactions at 25, 40 and 60°

$$\left\{ \begin{array}{l} E = 12.9 \text{ k.cal./mole} \\ A = 3.8 \times 10^3 \text{ litre mole}^{-1} \text{second}^{-1} \\ k_{80} = 4.07 \times 10^{-5} \text{ " " "} \end{array} \right.$$
Table XVI

0% nitrobenzene. Analysis by titration. Solutions M/10.

T°C	k, (litre mole <sup>-1</sup> hour <sup>-1</sup> )	determination of k,
138.6	0.0562	e
120.1	0.0653	e
100.7	0.0223	c
80	0.00819	c
60	0.0120	c
60 (heterogeneous)	0.0336	d
40 (heterogeneous)	0.00581	autocatalysis

Using 80, 100, 120° results

$$\left\{ \begin{array}{l} E = 14.05 \text{ k.cal./mole} \\ A = 1.12 \times 10^3 \text{ litre mole}^{-1} \text{second}^{-1} \\ k_{80} = 2.19 \times 10^{-6} \text{ " " "} \end{array} \right.$$

Using 40, and 60° results for heterogeneous reactions

$$\left\{ \begin{array}{l} E = 18.1 \text{ k.cal./mole} \\ A = 6.5 \times 10^6 \text{ litre mole}^{-1} \text{second}^{-1} \\ k_{80} = 3.89 \times 10^{-5} \text{ " " "} \end{array} \right.$$



## Reaction between ethyl iodide and ethyl methyl aniline

Table XVII

60% nitrobenzene. Analysis by conductivity. Solutions M/10.

$T^{\circ}\text{C}$	$k, (\text{litre mole}^{-1}\text{hour}^{-1})$	determination of $k,$
80	0.278	c
60	0.0980	c
40	0.0253	e
25	0.00711	e

## General Summary of Solvent Dependence

Table XVIII

Kinetic results for reaction of methyl iodide with dimethyl aniline

% nitrobenzene	$E$ (k.cal./mole)	$\log_{10} A$ (litre mole <sup>-1</sup> second <sup>-1</sup> )	$\log_{10} k^{80}$ (litre mole <sup>-1</sup> sec. <sup>-1</sup> )	$\Delta S_{80}^{\ddagger}$ (cal.degree <sup>-1</sup> mole <sup>-1</sup> )
100	12.15	4.942	-2.578	-38.25
80	12.91	5.238	-2.754	-36.89
60	13.08	5.346	-2.755	-36.40
40	13.51	5.501	-2.865	-35.68
20	13.98	5.476	-3.078	-35.79
0	(14.5)	(5.62)	(-3.38)	(-35.15)

Table XIX

Equilibrium results for reaction of methyl iodide and dimethyl aniline

% nitrobenzene	$\Delta H$ (k.cal./mole)	$\log_{10} k^{80}$ (litre mole <sup>-1</sup> second <sup>-1</sup> )	$\log_{10} K^{80}$ (litre/mole)	$\Delta S_{80}$ (cal.degree <sup>-1</sup> mole <sup>-1</sup> )
100	-15.4	-3.83	1.248	-37.9
80	-15.4	-3.575	0.81	-39.8
60	-14.5	-3.15	0.37	-39.3
40	(-11.7)	-2.825	-0.61	(-33.4)
20	(-7.5)	(-2.62)	(-0.46)	(-21.4)
0	(-0.1)	(-2.49)	(-0.89)	(-4.4)



Table XX

Reaction between ethyl iodide and dimethyl p-toluidine			
% nitro-benzene	E (k.cal./mole)	$\log_{10} A$ (litre mole <sup>-1</sup> second <sup>-1</sup> )	$\log_{10} k^{80}$ (litre mole <sup>-1</sup> second <sup>-1</sup> )
100	11.94	4.269	-3.122
80	12.20	4.301	-3.252
60	12.75	4.320	-3.574
40	12.75	4.156	-3.739
20	-	-	-4.723
10	13.6	2.74	-5.68
0	14.0	3.05	-5.66

Table XXI

Reaction between ethyl iodide and ethyl methyl aniline			
% nitro-benzene	E (k.cal./mole)	$\log_{10} A$ (litre mole <sup>-1</sup> second <sup>-1</sup> )	$\log_{10} k^{80}$ (litre mole <sup>-1</sup> second <sup>-1</sup> )
100	13.57	4.568	-3.335
60	13.96	4.568	-4.075

DISCUSSION

Some of the results, in chlorobenzene rich solvents, are not reliable, and caution must be exercised in drawing conclusions from them. Fortunately, the results for the reactions between methyl iodide and dimethyl aniline in solvents of intermediate composition give smooth curves when plotted against composition, as shown in figures 1-5. These curves have been carefully extrapolated to give values for the reaction parameters in pure chlorobenzene, and these extrapolations all yield consistent values. It may be objected that these parameters refer to a reaction which has not been proved to take place at all in pure chlorobenzene, but they are still of theoretical interest.



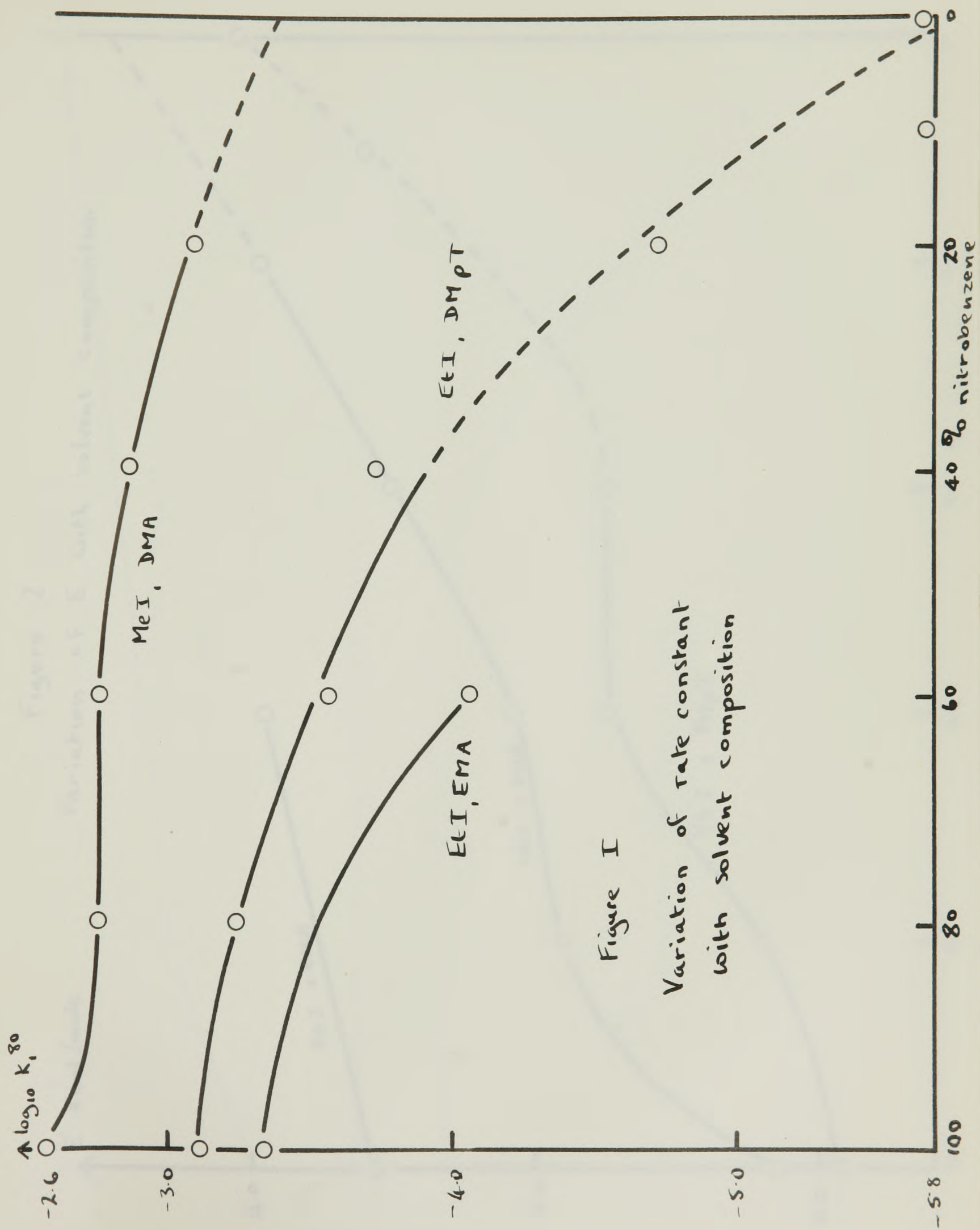
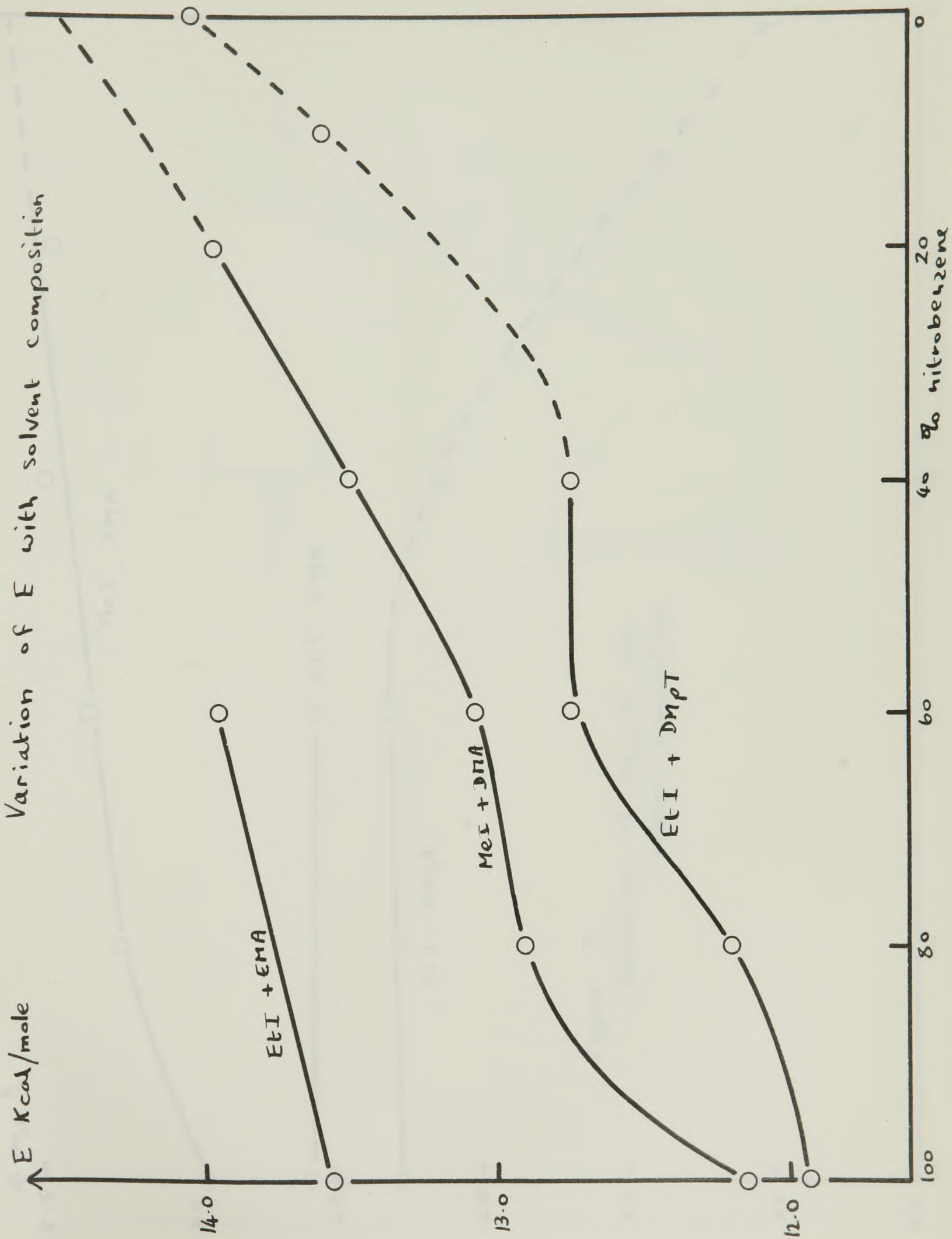




Figure 2  
Variation of E with solvent composition





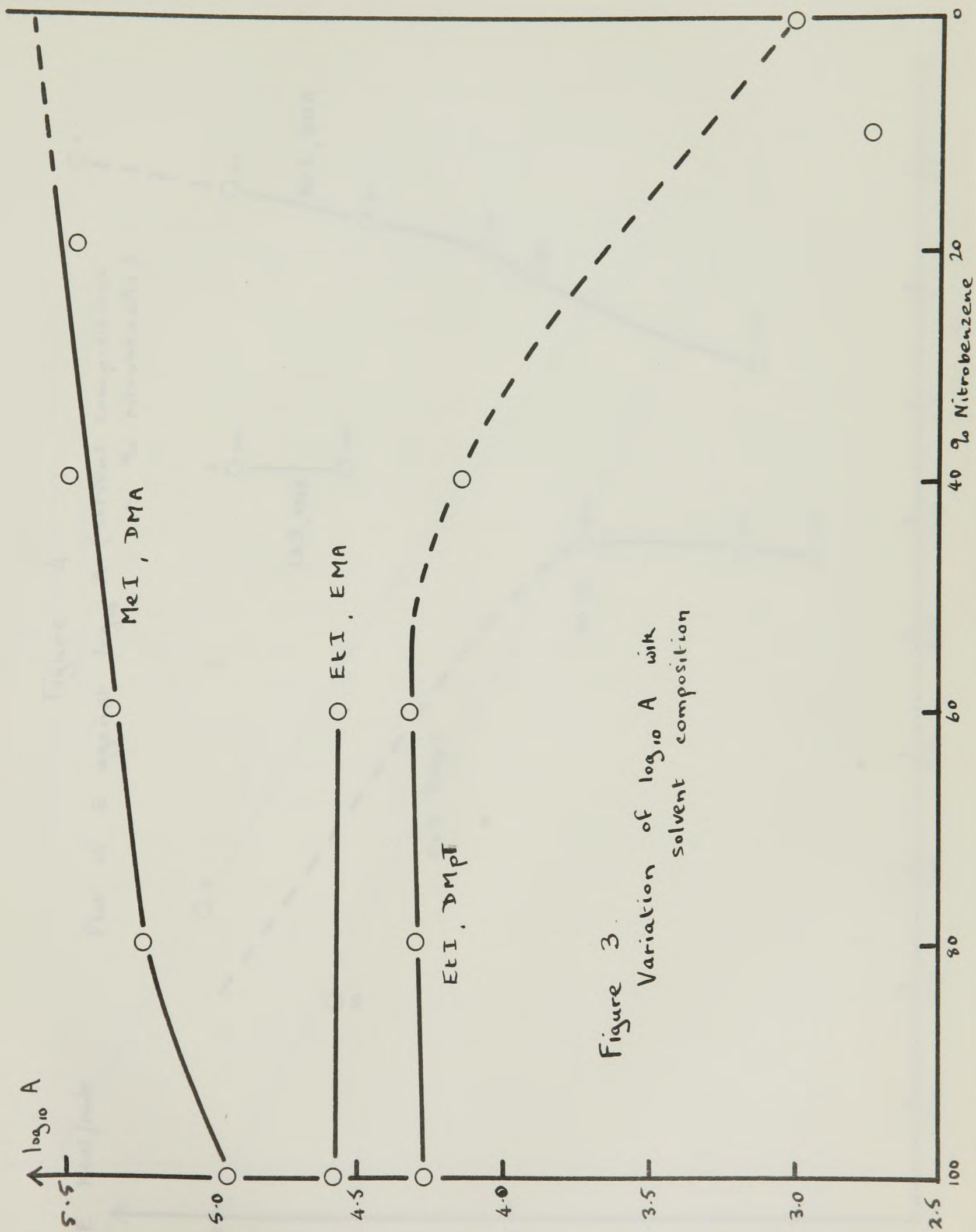


Figure 3  
Variation of  $\log_{10} A$  with  
solvent composition



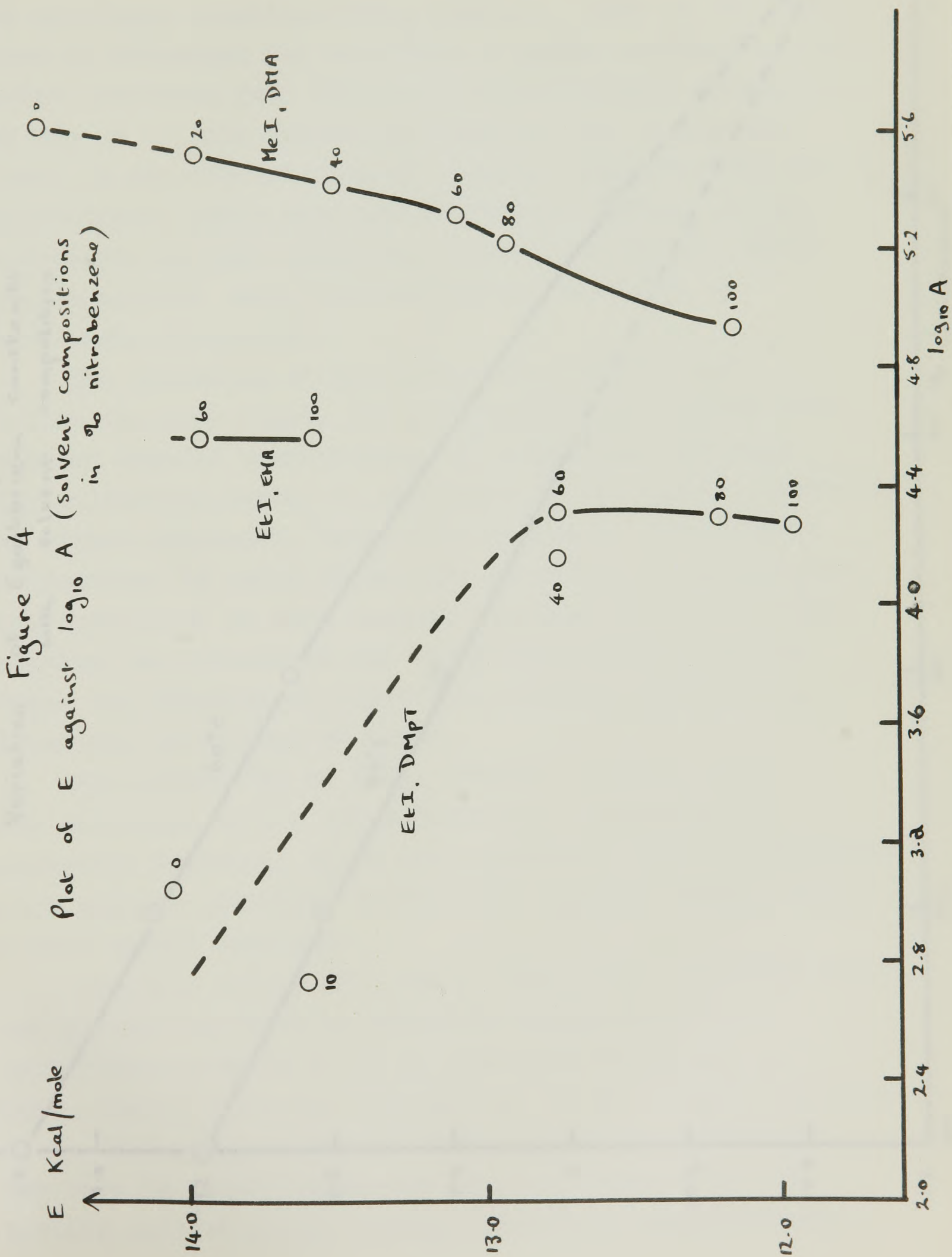
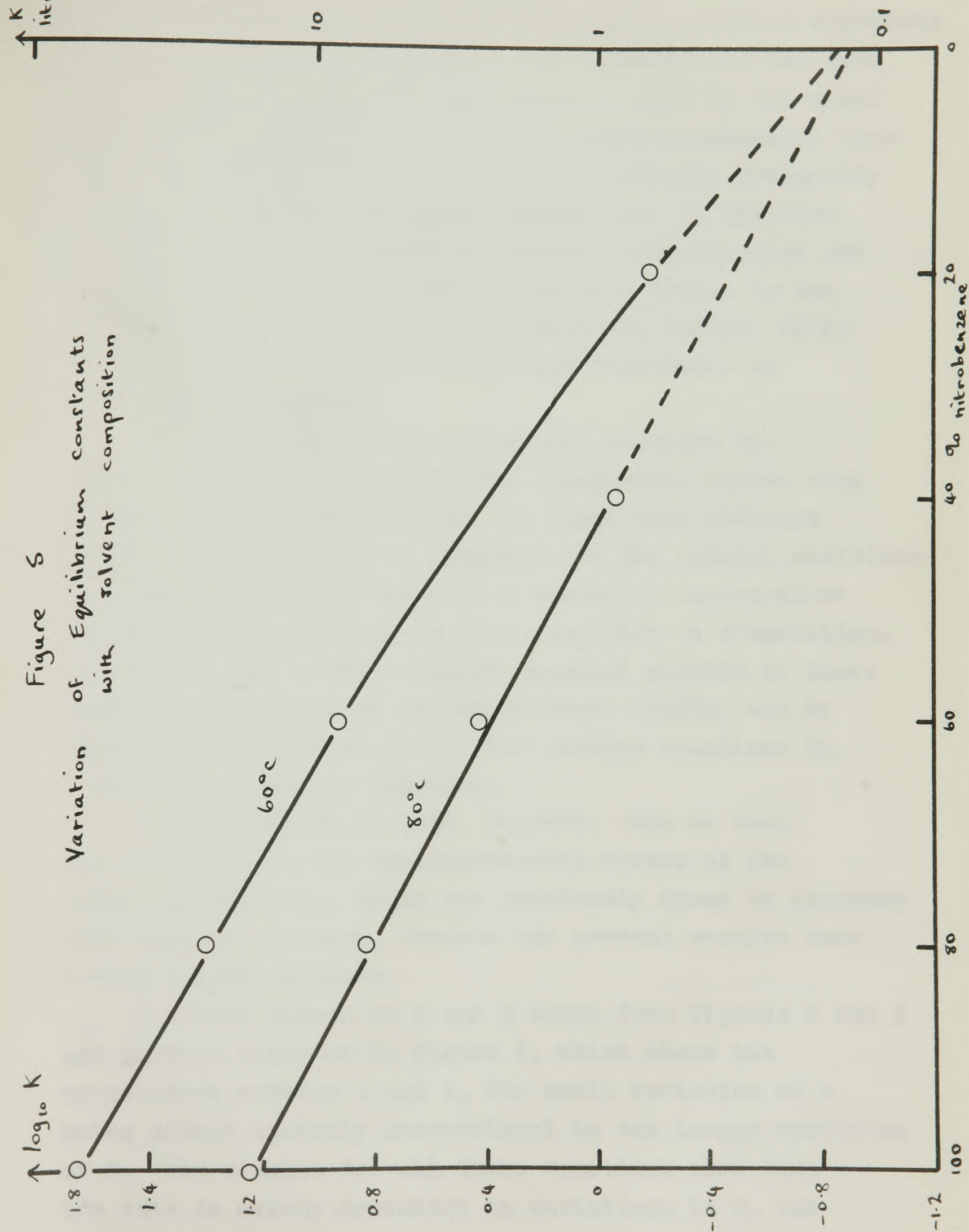




Figure 5  
Variation of Equilibrium constants  
with solvent composition





Several trends are apparent. In the transition from nitrobenzene to chlorobenzene the rate of reaction decreases by a factor of at least seven, the variation in the rate of all three reactions being similar. This is the usual type of behaviour for reactions in which essentially non-polar reactants give rise to a polar product, presumably by way of a polar transition complex, and it has been found in the benzylation of anilines (Venkataraman and Hinshelwood, 1960; Bose and Hinshelwood 1958), in the hydrolysis of acyl chlorides (Archer and Hudson, 1950) and in several amine quaternization reactions, as previously discussed.

The variation of the activation energies all follow the same trend, and give interesting curves when plotted against composition. It seems that although the activation energy is sensitive to the initial additions of either component, there is a region of intermediate composition in which it is less sensitive to composition. The curves are in this respect somewhat similar to those obtained by Fairclough and Hinshelwood (1937a) and by Raine and Hinshelwood (1939) for similar reactions in a variety of solvent mixtures.

The similarity is lost, however, when we turn our attention to the non-exponential factor of the Arrhenius equation, which was previously found to increase with solvent polarity, whereas the present results show a very slight decrease.

Smoothed values of A and E taken from figures 2 and 3 are plotted together in figure 4, which shows the correlation between A and E, the small variation of A being almost linearly proportional to the larger variation of E. The results for all three reactions show that the rate is mainly dependent on variations in E, the smaller variations in A being relatively insignificant.



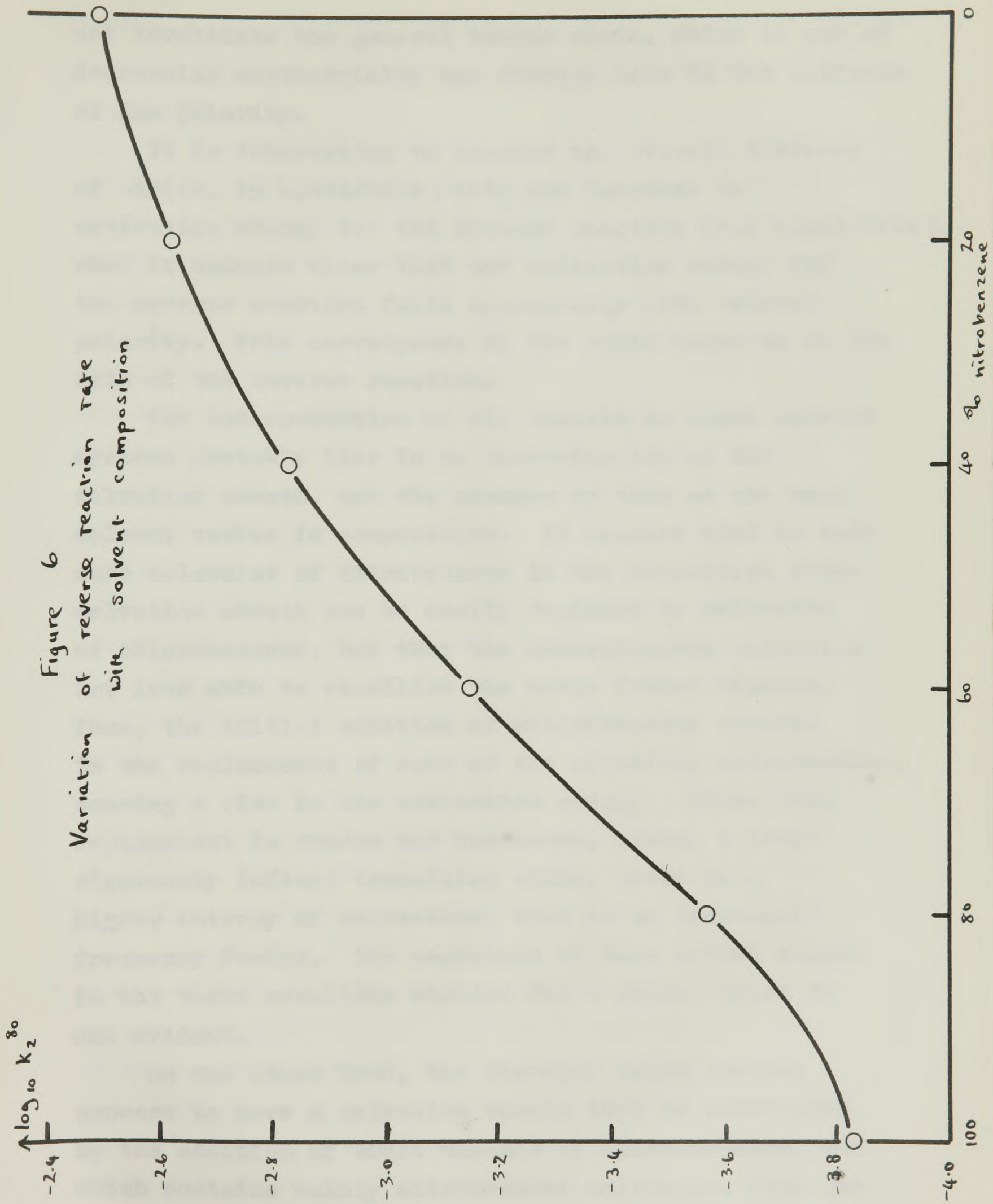
It was possible to measure equilibrium constants for one reaction at two temperatures, and the results obtained are shown plotted against solvent composition in figure 5. The equilibrium constant is extremely dependent on solvent polarity, and falls to very low values. Although the extrapolations to pure chlorobenzene are doubtful, it is unlikely that the equilibrium constants at either temperature will be greater than 0.1 mole/litre, which corresponds to less than a third of one per cent reaction.

Smoothed values of  $\log K^{80}$  were taken from figure 5, and used to calculate reverse reaction rates, which are shown plotted against composition in figure 6. The reverse rate is very sensitive to changes in composition, much more so than the forward rate, and in contrast to this the addition of non-polar solvent actually accelerates the decomposition of the salt, and accounts for the rapid change of the equilibrium constants with solvent composition. This behaviour contrasts with that found in the reactions in pure nitrobenzene, where equilibrium constants were not especially dependent on the rate of the reverse reaction.

Smoothed values of the equilibrium constant at  $60^{\circ}\text{C}$  were also read off from figure 5, and, in conjunction with those obtained at  $80^{\circ}\text{C}$ , used to estimate the values of  $\Delta H$  and  $\Delta S$  for the reaction in each solvent mixture, the values of  $\Delta S$  being calculated for  $80^{\circ}\text{C}$ . Although a smooth trend is obtained, this is no indication that the values are accurate, since it is a consequence of using smoothed values for the equilibrium constants themselves. Any slight error in the interpolations and extrapolations of the equilibrium constants will be magnified in the calculation of  $\Delta H$  and  $\Delta S$ , but this does



Figure 6  
Variation of reverse reaction rate  
with solvent composition





not invalidate the general trends shown, which is one of decreasing exothermicity and entropy loss in the solvents of low polarity.

It is interesting to compare the overall decrease of  $-\Delta H$  (ca. 15 k.cal/mole) with the increase in activation energy for the forward reaction (2.4 k.cal/mole), when it becomes clear that the activation energy for the reverse reaction falls appreciably with solvent polarity. This corresponds to the rapid increase in the rate of the reverse reaction.

The interpretation of all results in mixed solvent systems probably lies in an understanding of the solvation sheath, and the changes in this as the bulk solvent varies in composition. It appears that in this case molecules of nitrobenzene in the transition state solvation sheath can be easily replaced by molecules of chlorobenzene, but that the chlorobenzene molecules are less able to stabilise the newly formed dipoles. Thus, the initial addition of chlorobenzene results in the replacement of some of the solvating nitrobenzene, causing a rise in the activation energy. Since this replacement is random and unordered, giving a less rigorously defined transition state, there is a higher entropy of activation, that is an increased frequency factor. The magnitude of this effect varies in the three reactions studied for a reason which is not evident.

On the other hand, the strongly polar product appears to have a solvation sheath that is unaffected by the addition of small amounts of chlorobenzene, and which contains mainly nitrobenzene molecules, with the result that the exothermicity of the reaction does not vary. Since there is less nitrobenzene in the mixed



solvents, however, the solvated product now has a lower probability, and the entropy of reaction becomes more negative.

At intermediate solvent compositions the activation energy is less sensitive to changes, and this is probably caused by some compromise between the energy and entropy terms in the rate equation. Transition complexes can form with relatively large numbers of chlorobenzene molecules in the solvation sheath. These correspond to higher values of  $A$ , but since the newly formed dipoles are less stabilised there is also a high energy of activation. The complexes which form with a larger proportion of nitrobenzene have a lower value of  $A$ , but they also have a lower value for the activation energy, and on account of this they give rise to the most reaction. It is, therefore, to this route that the experimental results most nearly conform.

The solubility of the salt was found to be dependent on the solvent composition, and ranged from almost complete insolubility in pure chlorobenzene (ca. 0.2 millimole per litre at  $80^{\circ}\text{C}$ ) to a quite reasonable solubility in nitrobenzene (24.7 millimole per litre at  $25^{\circ}\text{C}$ ). This must be the result of a diminishing solvation sheath in the least polar solvents, which is also responsible for the fall in the exothermicity of the reaction, and the less negative entropy of reaction. In the last section the transition complex was stated to be somewhat similar to the final product, and therefore a diminishing solvation sheath in the final product gives a strong presumption for a diminishing solvation sheath in the transition state.

Solvation results in a loss of entropy, that is the entropies of reaction and activation are negative.



A diminished solvation sheath therefore results in a smaller loss of entropy and a higher frequency factor. The diminished solvation also results in a lower stabilisation of the changes, and causes the higher activation energy in the least polar solvents.



## SECTION VI

## CONCLUSIONS



It has been shown that in nitrobenzene solution dimethyl ethyl anilinium iodide decomposes to give mainly methyl iodide and ethyl methyl aniline, and also that diethyl methyl anilinium iodide decomposes to give mainly methyl iodide and diethyl aniline. This latter discovery appears contrary to that reported by Fahim and Fleifel (1951), but this is not surprising, since they studied decompositions under completely different conditions.

The decomposition of trimethyl anilinium iodide takes place by a single route, but since the salts are slightly ionised in nitrobenzene solution the kinetics of the reverse reaction are not strictly of the first order, which results in a little uncertainty in the quantities calculated from the measured equilibria.

The decomposition triethyl anilinium iodide appears to give rise to small amounts of olefine and hydrogen iodide, especially at elevated temperatures (above  $100^{\circ}\text{C}$ ), and this introduces further uncertainty into values derived from measured equilibria. Even so, this does not prevent the determination of accurate rate constants and many good Arrhenius plots are obtained, rendering possible the calculation of reliable values of  $E$  and  $A$ .

The main influence of structural, or solvent variations on the rate is achieved mainly through a change in the activation energy. Lengthening the carbon chain of either the alkyl halide, or nitrogen substituent, raises the activation energy, as does replacing iodine by bromine in the alkyl halide. On the other hand when electron releasing substituents are attached to meta or para positions in the aromatic



ring the value of the activation energy is lowered, because of the resulting increase in the electron availability at the nitrogen atom.

Attention has been given to variations in the frequency factor,  $A$  both in the general survey of energy-entropy relationships in section I, and in the discussion of the experimental results. Examples have been given in which  $\log_{10} A$  varies in a way roughly proportional to  $E$ , and it was shown that this can arise either through the effect of the polarity of the transition complex on the solvation sheath, or that of steric strain on the reaction path.

A correlated rise in both  $A$  and  $E$  has also been found for reactions in solvents of decreasing polarity and it has been shown that this is due to the lower stabilization afforded to the transition state dipoles in chlorobenzene rich solvents, together with the somewhat higher probability associated with the less solvated transition complex.

The equilibrium constant of one reaction has been found to be very sensitive to the solvent medium, because of the low stability of the salt in non-polar solvents. This leads to the unusual circumstance in which slower reactions have shorter half lives than faster ones.

Examples are known where  $A$  remains constant and  $E$  alone varies under the influence of ring substituents in an aromatic reagent, and it is found, in conformity with previously published work, that the reactions of methyl iodide with nuclear substituted dimethyl anilines display this behaviour.

It is also possible for  $A$  to vary while  $E$  remains constant, a type of behaviour usually confined to the



effect of the solvent medium on the reaction characteristics, but two cases have been found in the present work where steric requirements modify  $A$  without affecting  $E$ .

The variation of  $A$  alone, found with a suitable series of solvents, has been shown to depend on the degree of order in the initial solvent. Several cases have been found in which  $\log_{10} A$  is linearly related to the melting point of the solvent. A similar phenomenon is that reported by Venkataraman and Hinshelwood (1960) for reactions in a mixed solvent system, when for part of the solvent range the value of  $\log_{10} A$  is linearly dependent upon the solvent composition, while  $E$  remains constant. In part of this range the variation of melting point is also linearly dependent upon solvent composition (International Critical Tables IV, 176).

It is suggested that the sensitivity of the frequency factor to the melting point of a solvent may be a guide to the degree of solvent interaction. A way of testing this would be to use several solvents with symmetrical molecules in a study of a series of reactions in which the degree of solvation accorded to the transition state could be predicted with reasonable confidence from other information, say the volume or entropy of activation.

The present work shows that steric requirements can also cause a variation in the value of  $A$  independent of a variation in  $E$ . This arises when a structural modification enforces rather strict geometric configurations on the transition state, thus reducing the probability of reaction without affecting  $E$ . This is equivalent to the need for rather exact orientation of the reactants with respect to one another, and conforms to early ideas about the probability factor.



In one of these cases it is necessary to postulate that in the transition state the nitrogen atom has a trigonal electronic configuration, a suggestion at variance with the accepted view. The latter is based mainly on the similarity between the entropies of activation and reaction observed in the quaternization of dimethyl aniline by methyl iodide. Comparison of these quantities for other reactions, both in nitrobenzene and in mixed solvents, reveals however, that this similarity is the exception rather than the rule, and casts further doubt upon the earlier views. It may be objected that as the entropies of reaction are known to be somewhat inaccurate, because of the slightly second order character of the reverse reaction, they cannot be expected to compare well with the entropies of activation. Nevertheless, there is no reason to suppose that the values for the reaction of methyl iodide with dimethyl aniline in pure nitrobenzene are any different in this respect, or to accept the results for this reaction in preference to the results for the other reactions.

The present view leads to the prediction that the frequency factors corresponding to the reactions of substituted dimethyl anilines with a *t*-butyl halide should be not less than those corresponding to the reactions of methyl iodide, since the *t*-butyl radical is symmetrical about the reaction centre in the transition state (Ingold, 1957), and there will be no preference for any particular orientation. Configurations will exist corresponding to free rotation about the N-C axis. On the other hand, reactions with *t*-butyl iodide will be subjected to more steric strain than those with methyl iodide, and this circumstance may cause a correlated



rise in E and A sufficiently large to obscure any slight reduction in the value of A which might have taken place because of a restriction of rotation.

The behaviour of iso-propyl iodide in this series is harder to predict, since although models show that the reactants can be so oriented that steric strain is only a little more than that associated with ethyl iodide, the configuration is so strictly defined that it corresponds to a very low value of A. This may reduce the amount of reaction taking place by this route to such an extent that it is completely masked by mechanisms of higher activation energy, and which correspond to free rotation about the N-C axis. In this circumstance the reactions of iso-propyl iodide will be similar to those of t-butyl iodide.

The series of iodides, methyl, ethyl, iso-propyl and t-butyl, may therefore be associated with variations of A and E somewhat similar to those found with the straight chain isomers, and a comparison of the two series might yield further information about the stereochemistry of the transition complex.

An extension of this topic would be to study the reactions of higher alkyl or aryl halides, such as hexyl, cyclo-pentyl or benzyl, or the influence of ring substituents on the reaction of benzyl halides, although the present work indicates that the rate would be almost independent of such ring substituents.

Further information about the stereochemistry of the activated collision complex, could be obtained by repeating the present work with a different solvent, since not all of the variation of A with E is attributable to steric effects alone, and it has been postulated that the steric effects are reinforced by solvation effects.



That is to say, in the transition from methyl to ethyl iodide, the correlated increase of A and E has a proportionality factor different from that expected. This is perhaps due to changes in the solvation sheath. A study with a different solvent would both check the present results, and show how much the solvent affects the proportionality between E and A.

The values of A and E obtained when the halogen is varied have been found to lie on the same 'compensation line' as the quantities corresponding to a variation of ring substituent, and it has been suggested that this may be because the main effect of changing the halogen is to alter the carbon-nitrogen separation in the transition state, thus modifying the amount of steric strain. If this is so, then frequency factors associated with methyl bromide will probably have the same value as those associated with methyl iodide, quantities corresponding to both reactions lying on the same line when E is plotted against  $\log k$ .

An extension of this theme would be to study the reactions not only of alkyl chlorides, but also of pseudo-halogens compounds. The formation of quaternary salts with bases other than ammonia derivatives has been reported, an example being the formation of quaternary phosphonium and arsonium salts (Davis and Lewis, 1934), but so far, little or no attention has been given to the formation of anions other than those of the halogens. Methyl thiocyanate is a typical pseudo-halogen, and it can be readily incorporated into the standard Volhard's titration for ionisable halide ion. If this compound quaternizes dimethyl aniline its reaction would probably yield interesting results.



Thomas (1913) discovered that derivatives of acetanilide react with alkyl halides, apparently to give a quaternary salt. The reaction product was not characterised, however, nor were activation energies and frequency factors determined, and it is not certain that the observed reaction gave a quaternary salt. This aspect is also worthy of further study.



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