STUDY OF HCN ELIMINATION FROM SOME POLYCYANO COMPOUNDS - ABDEL-REHIEM

STUDY OF HCN ELIMINATION FROM SOME POLYCYANO COMPOUNDS

by

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RESUME

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ETUDE DE L'ELIMINATION DE HCN DE QUELQUES COMPOSES POLYCYANO

L'élimination de HCN des composés N,N-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (I) et 2,6-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (II) a été étudiée dans du méthanol pur et dans un mélange HCl/méthanol à plusieurs températures. Les études cinétiques, les paramètres d'activation, les effets isotopiques et la catalyse par acide suggèrent un mécanisme ElcB de type-II pour ces éliminations.

La même réaction a été étudiée dans plusieurs mélanges de solvents, dont eau/méthanol, acétonitrile/méthanol et benzene/méthanol. Les rapports entre vitesse de réaction d'une part et constante diélectrique et la structure du milieu d'autre part, ont été examinés. Les mesures de moment dipolaire et de pK_a ont été faites.

Une étude comparative de l'elimination de HCN des composés N,N-dimethyl-4-(1,2,2-tricyanoethyl)aniline (III), 9-cyano-9-dicyano-methyl fluorene (IV) et 2-(p-N,N-dimethylaminophenyl)-2,3,3-tricyanopropionamide (V) dans du méthanol pur, a été faite en utilisant le composé (I) comme référence. Tandis que le composé (III) éliminait HCN par un mécanisme équilibre ElcB, le composé (IV) subissait la même réaction par un mécanisme chevauchant entre pré-équilibre et un mécanisme ElcB de type-II.

Le composé (V) n'éliminait pas de HCN dans les conditions des mesures cinétiques.

ABSTRACT

Ph.D. Ahmed G. Abdel-Rehiem Chemistry

STUDY OF HCN ELIMINATION FROM SOME POLYCYANO COMPOUNDS

The HCN elimination from N,N-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (I) and 2,6-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (II) has been studied in pure methanol and in HCl/methanol at different temperatures. Kinetic measurements, activation parameters, isotope effects and acid catalysis suggest an E1cB type-II mechanism for these eliminations.

The same reaction was studied in various water/methanol, acetonitrile/methanol and benzene/methanol solvent mixtures. The relationships between reaction rate and both dielectric constant and the structure of the medium were examined, and dipole moment and pK_a measurements made.

A comparative study was made of HCN elimination from N,N-dimethyl-4-(1,2,2-tricyanoethyl)aniline (III), 9-cyano-9-dicyanomethylfluorene (IV) and 2-(p-N,N-dimethylaminophenyl)-2,3,3-tricyanopropionamide (V) in pure methanol, taking compound (I) as reference. Whereas compound (III) underwent elimination via an equilibrium E1cB mechanism, compound (IV) underwent the same reaction via a mechanism on the borderline between pre-equilibrium and type-II E1cB mechanisms. Compound (V) failed to eliminate HCN under the conditions of kinetic measurements.

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For patience and encouragement throughout the course of this study, I express sincerest gratitude to my wife Zeinab.

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TO MY WIFE.

PREFACE

The aim of this work was to study the HCN-elimination from some polycyano compounds in different media, particularly methanol solution.

The thesis is divided into three parts, each of them being composed of four distinct chapters - introduction, experimental, data and discussion.

The first part deals with study of HCN-elimination from compounds N,N-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (I) and 2,6-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (II) in pure methanol. The introduction to this part is a general survey of β-elimination reactions and mechanisms with greatest emphasis on the ElcB mechanism because of its relevance to this work. The data obtained from the kinetic runs are listed in tables and accompanied by sample figures. In the discussion an attempt is made to interpret the results which are mentioned in the experimental section.

The second part deals with the effect of solvent on the rate and mechanism of HCN-elimination from compounds (I) and (II). The introduction gives a brief survey of the subject. Compounds and solvent preparation are as in the experimental section of part I. The discussion is composed of two sections; one of them illustrates the relationship between the dielectric constant and the rate and mechanism. The other shows an attempt to derive a free energy relationship between the structure and medium and the rate of elimination.

The third part is a comparative study of HCN-elimination from compounds N,N-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (I), N,N-dimethyl-4-(1,2,2-tricyanoethyl)aniline (III), 9-cyano-9-dicyanomethyl fluorene (IV) and 2-(p-N,N-dimethylaminophenyl)-2,3,3-tricyanopropionamide (V). The introduction is a survey of the use of kinetic hydrogen isotope effects as a tool to distinguish between different mechanisms of elimination, with emphasis on the E1cB mechanism. Data from the kinetic measurements are tabulated. In the discussion, compound (I) is used as the reference for the study and suitable mechanisms are suggested for the reactions of the compounds under investigation. Kinetic hydrogen isotope effects and exchange or "cross-over" experiments are used as the main criteria for such mechanisms.

Finally, a general discussion is included to summarise the work presented and to discuss the interrelationships between the three parts.

The experimental results reported here are those of three independent kinetic runs in which the reproducibility was within ±1%. Derived rate constants are accurate to only three significant figures. Accordingly activation energies and entropies are accurate to two significant figures.

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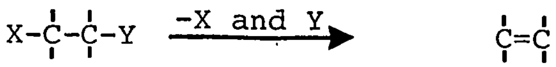
PART I :

Introduction

ELIMINATION REACTIONS

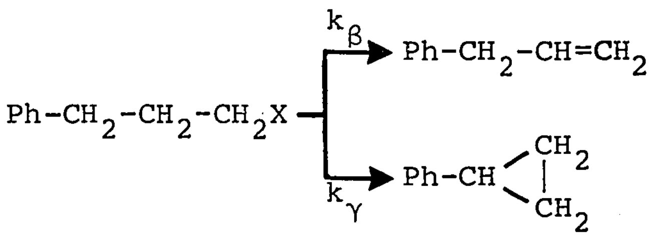
Elimination reactions are defined as processes in which two atoms or groups are removed from a molecule without being replaced by other atoms or groups. Various types of elimination reactions are recognized and are described by the position from which removal of the second atom or group occurs, i.e. α, β, γ, δ... eliminations.

β-Elimination reactions are the most common and involve the elimination of two groups from adjacent atoms with the formation of a multiple bond.



$$X-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Y \xrightarrow{-X \text{ and } Y} \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}$$

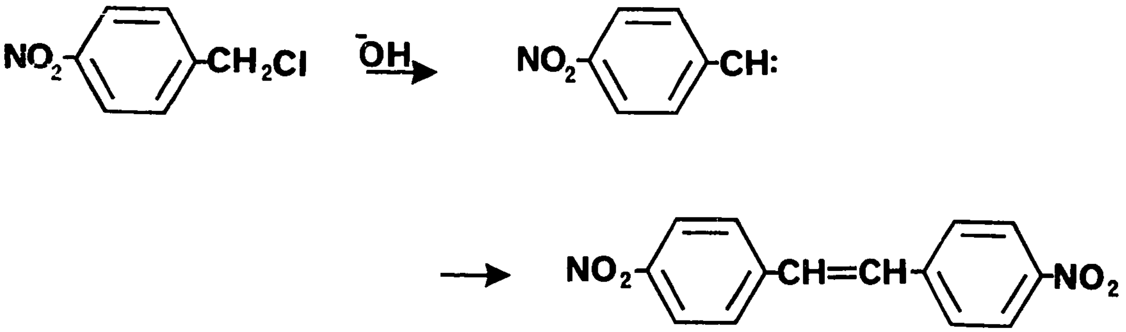
In a number of cases, γ-elimination may compete with β-elimination[1], resulting in the formation of either an olefin or a cyclic product[2], as illustrated in equation (1)



(1)

α-Eliminations yield intermediates that must be stabilized by rearrangement, dimerization or further decomposition[3], as shown in the following examples:

$$Ph_2C{=}CHBr \xrightarrow{\bar{N}H_2} Ph_2C{=}C: \longrightarrow Ph{-}C{\equiv}C{-}Ph \qquad (2)$$



(3)

$$CHCl_3 \xrightarrow{\bar{O}H} \ddot{C}Cl_2 \xrightarrow{H_2O} CO + HCOOH + Cl^- + H^+ \qquad (4)$$

δ-Elimination may give a stable species if bond migration enables the atomic octets to be preserved, i.e.

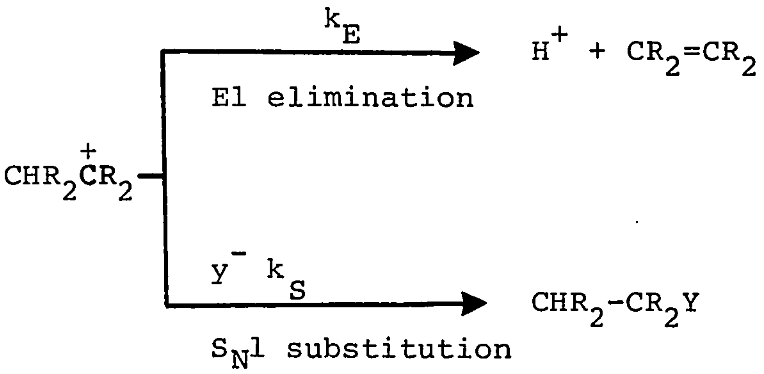
$$CH_3{-}CH{=}CH{-}CH_2Br \xrightarrow{\bar{O}H} H^+ + CH_2{=}CH{-}CH{=}CH_2 + Br^- \qquad (5)$$

The three basic mechanisms for β-elimination reactions are discussed in the following pages, namely the unimolecular (E1), the bimolecular (E2) and the carbanion (E1cB) mechanisms. The latter mechanism is discussed in the greatest detail as this is of major interest in connection with the work presented in this thesis.

A) The Unimolecular Mechanism (E1)

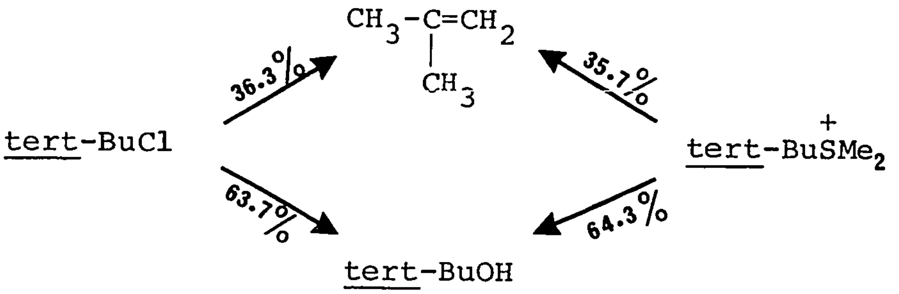
Unimolecular nucleophilic substitution reactions of secondary and tertiary alkyl halides were found to often be accompanied by olefin formation[4]. Hughes and Ingold[5] suggested a mechanism to account for this which involved a slow ionization step of the substrate to form the carbonium ion, followed by rapid decomposition of the carbonium ion as shown below. The rate determining step is the same as that for the nucleophilic substitution reaction, i.e. the ionization step.

$$CHR_2CR_2X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CHR_2\overset{+}{C}R_2 + X^- \qquad (6)$$



(7)

The carbonium ion formed is partitioned between elimination and substitution, the latter being the result of neutralization by solvent or any other available nucleophile. However, the proportion of olefin in the product is determined by the ratio of $k_E/(k_S+k_E)$. A reaction proceeding via this mechanism exhibits first-order kinetics and the rate is dependent upon the ease of carbonium ion formation. If a reaction is performed on two molecules which differ only in the leaving group (e.g. tert-BuCl and tert-Bu$\overset{+}{S}Me_2$) the rate will differ. However, once the carbonium ion is formed, if the solvent and the temperature are the same it should suffer the same fate in both cases, since the nature of the leaving group does not affect the second step. This means that the ratio of elimination to substitution should be the same. The compounds described above were solvolysed at 65.3° in 80% aqueous ethanol, with the following results[6]:



(8)

Although the rates were greatly different (as expected with such different leaving groups), the product ratios were the same (within 1%).

Unimolecular elimination is favoured by branching at the β-carbon atoms. tert-BuCl is solvolysed with only 16% elimination, whereas tert-BuC$(Et)_2$Cl with 90% elimination. Brown and Fletcher[7] explained this trend in olefin yield as being of steric origin. The fate of carbonium ion, once formed, is subject to steric influences in that if the carbonium ion loses a β-hydrogen (elimination), the bond angles about the β-carbon also increase, and the molecule becomes sterically less "crowded". If the carbonium ion becomes bound to another nucleophile (substitution), "crowding" is increased. Steric effects should therefore favour E1 over S_N1 reaction[8]. E1 reactions can best compete with S_N1 reactions in good solvating but poorly-nucleophilic media, such as sulfur dioxide and formic acid. Rearrangements typical of carbonium ion processes are usually observed in unimolecular reactions[9].

B) The Bimolecular Mechanism (E2)

Ingold[10] initiated a general mechanistic study of elimination reactions and proposed a mechanism for the decomposition of quaternary ammonium salts which was subsequently extended to other types of substrates. It is the most commonly observed elimination process and is formulated as:

$$Y + H\text{-}CR_2\text{-}CR_2\text{-}X \longrightarrow \overset{+}{Y}H + CR_2{=}CR_2 + X^- \qquad (9)$$

The reaction consists of abstraction of a proton from the β-carbon by base with the synchronous expulsion of X^- to form the elimination product. The reaction is of second-order kinetics, i.e. first order in each component.

$$\text{Rate} = k_2\ [Y]\ [H\text{-}CR_2\text{-}CR_2X] \qquad (10)$$

This mechanism predicts that substrate reactivity will vary with:

i) the strength of the base Y, as base strength measures the ability of the base to abstract a proton;

ii) the acidity of the abstractable hydrogen, i.e. the ability of β-carbon to stabilise negative charge, and

iii) the nature of the leaving group.

These conclusions for the bimolecular mechanism have been illustrated with respect to the formation of olefins from many systems, using a wide variety of nucleophilic reagents[11], with

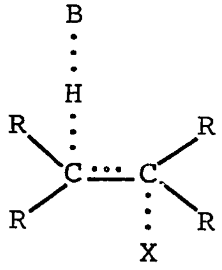
X and Y groups such as:

$X = -\overset{+}{N}R_3,\ -\overset{+}{P}R_3,\ -\overset{+}{S}R_2,\ -\overset{+}{O}H_2,\ -SO_2R,\ -NO_2,\ -Hal.,\ OSO_2R,\ -OCOR$

$Y = OH_2,\ NMe_3,\ \overset{-}{O}H,\ \overset{-}{O}R,\ \overset{-}{O}Ac,\ \overset{-}{O}Ar,\ \overset{-}{N}H_2,\ CO_3^{2-}$

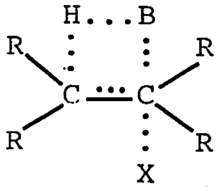
The E2 mechanism cannot usually be completely isolated from other side reactions, for under the elimination conditions the base may also act as a nucleophile towards the α-carbon atom and nucleophilic displacement reactions will accompany the elimination reactions.

Parker and Baile[12] suggested that there were three most probable transition states for the E2 mechanism:

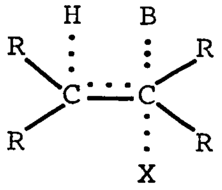


1

E2H



2

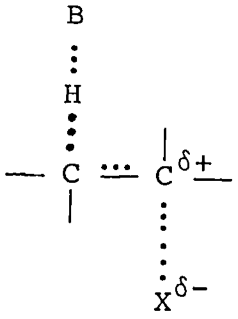


3

E2C

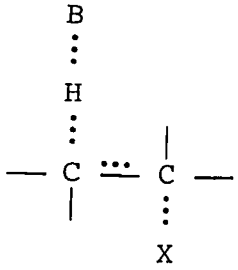
The actual position of any one E2 transition state in the spectrum between (1) and (3) will depend on the structure of the substrate, the nature of the base and the nature of the leaving group.

Recent developments of the theory of the bimolecular mechanism view this process as comprising a spectrum of sub-mechanisms, which differ subtly in transition state-character[13]. The theory postulates that the relative degrees of bond breaking of the C_α-X and C_β-H vary, in the transition state, from one extreme in which the former is extensively and the latter, but slightly, broken to an opposite extreme in which the C_α-X bond is almost but not wholly intact and the β-H is extensively transferred to the base[14]:



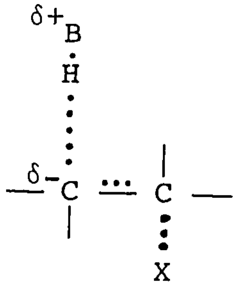
4

paenecarbonium



5

central



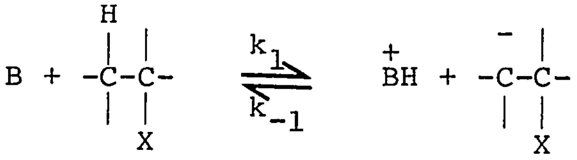
6

paenecarbanion

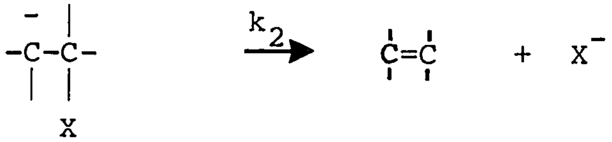
The former extreme approaches in character the transition state for the carbonium ion-forming step of the E1 mechanism, but differs in that it includes the base in a functional role, and Bunnett has termed this the paenecarbonium[14] extreme, represented by structure (4). The opposite, paenecarbanion extreme, represented by structure (6), approaches in character the transition state for the first step of the carbanion, or E1cB, mechanism of elimination. Between these two extremes lies a continuum of transition states of intermediate characters; in a strictly (central) transition state (5) the degrees of C_α-X and C_β-H bond rupture are equal, and the double bond character in the developing double bond is at a maximum.

C) The Carbanion Mechanism (ElcB)

Until fairly recently, this mechanism was often discussed but rarely observed. It differs from the more usual bimolecular (E2) mode of elimination in that it is a step-wise process, involving the intermediacy of a discrete carbanion. The ElcB mechanism[15] is represented by (11) and (12), illustrating the case for a neutral basic species:



$$B + -\overset{H}{C}-\underset{X}{C}- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overset{+}{B}H + -\overset{-}{C}-\underset{X}{C}- \qquad (11)$$



$$-\overset{-}{C}-\underset{X}{C}- \xrightarrow{k_2} C{=}C + X^- \qquad (12)$$

By assuming a steady state carbanion concentration, one obtains:

$$\text{Rate} = \frac{k_1 k_2\,[\text{Substrate}]\,[B]}{k_{-1}[\overset{+}{B}H] + k_2} \qquad (13)$$

The intermediate carbanion may react with $\overset{+}{B}H$ to give the starting material (or an isomer) or may lose a halide ion. Accordingly, two cases (assuming that both substrate and base concentrations are comparable) may arise:

a) The irreversible case, in which the first step is rate determining, being essentially the bimolecular irreversible formation of the carbanion, followed by the relatively rapid ejection of the leaving group from the α-carbon atom i.e. $(k_2 >> k_{-1}[\overset{+}{B}H])$. The reaction will be second order and the mechanism will be almost indistinguishable from the concerted process (E2).

b) The pre-equilibrium case in which the first step is a rapidly-attained equilibrium and the second, the unimolecular decomposition of the carbanion, is the rate determining step, i.e. $(k_{-1}[\overset{+}{B}H] >> k_2)$.

The existence of this mechanism was less firmly established than that of the E1 or E2 mechanisms because some of the experimental work used to support it has also been explained in other ways[16]; for example, the fact that cis-elimination is sometimes found in second-order reactions has been used to lend support to this mechanism but this has also been explained as a simple E2 cis-elimination process[17]. In the absence of considerable stabilisation, the carbanion in an ElcB reaction will be formed in an endo-energetic step so that the transition state leading to it should have carbanionic characteristics[4]. Thus structural and environmental effects will be similar to those expected for E2 reactions utilising paenecarbanion transition states, making experimental demonstration of the nature of the intervening species in an elimination reaction difficult[11]. The substrate will be more susceptible to elimination via the ElcB mechanism if the β-hydrogen is more acidic (and k_1 is high) and if the life-time of the carbanion increases when X is a poorer leaving group (k_2 is low).

D) Mechanistic Criteria for the E1cB Mechanisms

1) β-Hydrogen exchange accompanying elimination: If a pre-equilibrium carbanionic elimination is proceeding in a protic solvent, β-hydrogen atoms of the substrate will be exchanging with solvent protons at a rate which is rapid compared with that of olefin formation. Thus deuterotrichloroethylene[18] and several dichloroethylenes[19] undergo base-catalysed deuterium exchange at a rate considerably faster than their dehydrohalogenation [$k_{ex.} \gg k_{elim.}$].

Hine, Wiesboeck and Ramsey[20] have shown that 1,1,1-trifluoro-2,2-dihalogenoethanes are dehydrofluorinated much more slowly than they undergo hydrogen exchange[21] in alkaline methanol. The activating effect that the α-fluorines and β-halogens have on the β-hydrogen, together with the well-known reluctance of fluorine to depart as an anion from the saturated carbon (and more so from carbon bearing other halogens[22]), make the intermediacy of carbanions in these eliminations highly likely.

Iskander and Riad[23] studied the reaction of dilute alkalies on acids of the type $O_2N\text{-}C_6H_4\text{-}CH_2\text{-}CH_2SZ$. They reported that when $Z\text{=-}CH_2\text{-}COO^-$, E1cB mechanism is dominating as confirmed by hydrogen deuterium exchange. The carbanion formed reacts with the nitro-group to form the nitrone (brown acids).

Fedor[24] indicated that α-methylene proton exchange in deuterium oxide can be used as one of the criteria that the base catalysed β-elimination of methanol from β-methoxy ketones to give the corresponding α,β-unsaturated ketones, is likely to proceed via rapid general base catalysed enolate formation, followed by rate-determining loss of methoxide ion from the enolate anion.

O'Ferrall[25] observed that in solutions of methan[$^2H_1$]ol containing sodium methoxide, β-elimination of water from 9-fluorenyl-methanol occurs by an ElcB mechanism; the rate of β-hydrogen exchange was more than ten times that of the elimination rate.

In some other systems, the ElcB mechanism is the one likely to occur, but there is no hydrogen-exchange observed. Therefore, it must be pointed out that neither the positive nor the negative deuterium-exchange results constitute absolute proof of the existence or non existence of the ElcB elimination mechanism[16]. The mechanism may be occurring, and yet no exchange may be found, if the carbanion goes to product much faster than it reverses to starting material. On the other hand, it has been pointed out[26] that deuterium exchange could be taking place without the carbanion necessarily being the species which loses the leaving group.

2) Structural effects on elimination reactions: Rates of elimination of substrates bearing suitably substituted α-or β-bound phenyl groups can be correlated by the Hammett equation. For β-bound aryl groups, the value of the reaction parameter ρ increases as structural and environmental conditions are changed so as to shift E2 transition states in the ElcB direction[27]. Thus a high positive value of ρ is expected to obtain for a carbanionic elimination, since negative charge density on the β-carbon atom in the transition state will be at a maximum.

Therefore, in the elimination of acetic acid from 2-phenyl-2-acetoxyl-1-nitrocyclohexane, the isomer in which the H and OAc were cis reacted four times faster than the one in which these groups were trans[28]. Evidence against a cis E2 elimination in this case was that an increase in solvent polarity or ionic strength increased the rate of both reactions, arguing against a mechanism not involving ions, and that the Hammett ρ value was positive, and identical for the two substrates. The question of how high a ρ value to expect for an E1cB reaction is in doubt. DePuy et al[17] suggested that the value of 5.0, obtained from rates of carbanionic polymerisation, be used as a guide. Crosby and Stirling[29] obtained evidence that the base-induced elimination of phenoxide from β-substituted aryl ethyl ethers occurs by an E1cB mechanism. They obtained Hammett plots with a ρ value of $\sim$+2.

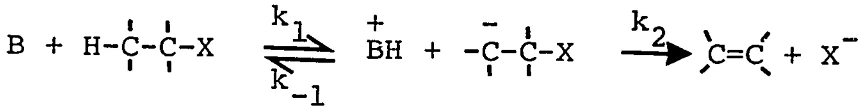
Another study was made[30] of the phenoxide elimination under basic conditions from a series of phenyl ethers of the type $X\text{-}CH_2\text{-}CH_2\text{-}OPh$. Good correlation is obtained between log $k_{elimination}$ and the parameter σ_{R^-}, but not σ or σ^*, indicating that the resonance stabilisation of a carbanionic species is an important component of activation in this system.

In Michael-type addition to C=C bonds, the first step of the reaction is nucleophilic attack. By the law of microscopic reversibility, those eliminations which are the reverse of Michael-type additions should start with the loss of a proton and hence be E1cB processes. Therefore, the decomposition of the Michael adduct of 4-nitrochalcone and malonitrile in neutral and acidic methanol exhibits kinetics that are consistent with a carbanion mechanism[31]. Similar results for the decomposition of 1,1,1,3-tetranitro-2-phenyl propane have been reported by Hine and Kaplan[32] and again the ElcB mechanism was invoked.

3) <u>Isotope effects:</u> Primary kinetic isotope effects are to be expected if there are bonding changes at the labelled atom in proceeding from reactants to the activated complexes (transition states). Therefore, it is one of the most powerful criteria to differentiate between E2 and ElcB mechanisms. A detailed review of kinetic isotope effects is given in the introduction to the third part of this dissertation.

E) Classification of the Carbanion Elimination Mechanism

Rappoport[33] suggested an extended range for the ElcB mechanism. He combined both of the previously mentioned[34] types of ElcB mechanism under one heading and termed this (type - I ElcB). This is the most studied case although it is only a limiting case in a series of ElcB mechanisms.



$$B + H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overset{+}{B}H + -\overset{-}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \xrightarrow{k_2} \rangle C=C\langle + X^- \qquad (14)$$

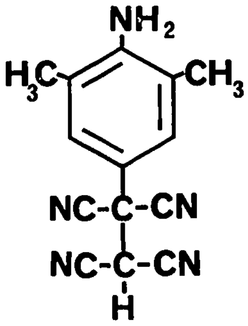
There is another limiting case, where (k_1/k_{-1}) becomes very high, using a substrate having a very acidic β-hydrogen and a relatively strong base B, while X^- leaves slower than halide ions (which were used quite often as leaving groups for [type-I] mechanism).

In one variant, HX is a stronger acid than the substrate, when [B]>[substrate], fast almost complete neutralisation takes place and [substrate] ≃ [carbanion] before the elimination starts. The elimination rate (= k_2[carbanion]) becomes first-order in substrate and zero-order in base. A stronger base would change the (k_1/k_{-1}) ratio, but not the elimination rate, since the concentration of carbanion remains constant.

If [B]<[substrate], then [carbanion] ≃ [B] and within a run the reaction is zero-order in base and first-order in substrate, if [HX] at the end of the reaction is taken equal to [B]. For different initial concentrations, the reaction is first-order in base at constant [substrate] and zero-order in substrate at constant [B].

When HX is weaker (e.g., by two pK units) than the substrate, competition between substrate and HX for B favours the former. With [B]>[substrate] the behaviour is similar to that discussed above. However, if [$\overset{+}{\text{BH}}$]<[substrate] the reaction is of zero-order in both B and substrate within a run, and when the concentrations become equal, the reaction is first-order in the remaining substrate. At constant [B] a zero-order dependency on the initial concentration of substrate is expected, while keeping [substrate] constant and changing [B] results in first-order dependency at low base concentration and zero-order dependency when [B]>[substrate]. Rappoport called this limiting case [type-II ElcB]. He predicted intermediate cases to be observed when substrate has a moderate acidity and the base has a gradually decreasing strength (when [substrate]<[B]). "Type-II ElcB" mechanism requires very strong electron attracting groups on the β-carbon, and if possible, on the α-carbon.

Rappoport and Shohamy[35] have described the amine catalysed elimination of HCN from 2,6-dimethyl-4-(1,1,2,2-tetracyanoethyl) aniline (7) as the first example of this type of mechanism.



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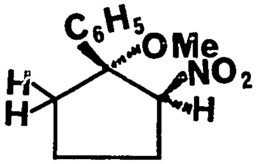
They found[35] that the amine catalysed elimination of HCN from (7) in chloroform goes to completion even if [substrate]>[amine]. With triethylamine and tri-n-butylamine the reaction is of zero-order in both substrate and the amine within a run, and of first-order in the amine for different runs when [amine]<[substrate], thus providing a typical example of an E1cB reaction of the second type.

Bordwell et al[36] studied the methoxide ion catalysed elimination of methanol from 2-phenyl-trans-2-methoxy-1-nitrocyclo pentane (8) and its cis-isomer.



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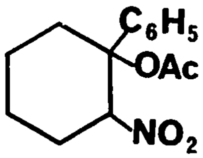
They showed that the overall reaction is an example of a first-order β-elimination involving a carbanion (nitronate ion) intermediate, and that the rate determining step is a first-order elimination of methoxide ion.

In another study[37], comparison has been made between the methoxide ion catalysed anti and syn β-elimination of acetic acid from nitroacetates (9) and the base-catalysed elimination of methanol from the corresponding methoxy compounds (10).



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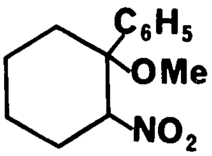

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The latter were shown to involve reversible nitronate ion formation with sodium methoxide-methanol mixture and irreversible nitronate ion formation with potassium tert-butoxide - tert-butanol mixture. Using comparisons of rate data, substituent effects, deuterium isotope effects and activation parameters for the acetoxy and methoxy compounds as criteria, they concluded that these eliminations involve steady-state formation of the carbanion intermediates.

Bordwell[37] also suggested that most base-(or solvent) initiated β-elimination reactions will proceed by two stage mechanisms and that the E2 mechanism will be relatively rare. This conclusion has not been universally accepted.

Experimental

A) Preparation of Materials

N,N-Dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (I):

This compound was prepared following the procedure adopted by Farrell and Wojtowski[38], by adding N,N-dimethylaniline (0.05 mole) in acetone (20ml) slowly to a cooled (-78°) and stirred solution of tetracyanoethylene (0.05 mole) in acetone (200ml), then stirring for 30 minutes. The solvent was rapidly evaporated under reduced pressure and the residue recrystallised twice from benzene to give light grey crystals, m.p. 120° (decomposition), (lit.[38,39] m.p.120° and 118°).

n.m.r. in $CDCl_3$: identical to that mentioned in lit.[39]

singlet $\delta = 3.08$ (6H)
singlet $\delta = 4.46$ (H) disappeared on deuteration.
quartet $\delta = 7.36$ (4H)

2,6-Dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (II):

This was prepared according to Rappoport's procedure[40], by adding a solution of tetracyanoethylene (0.01 mole) in acetonitrile (8ml) to a solution of 2,6-dimethylaniline (0.01 mole) in carbontetrachloride (10ml) at room temperature. The white product precipitated within 30 minutes. m.p. 160°; on slow heating decomposition occurred at 250°,(lit.[40] m.p. 160°, decomposition 250-280°).

n.m.r. in acetone-d_6: identical to that mentioned in lit.

singlet	$\delta = 2.30$ (6H)
broad singlet	$\delta = 4.73$ (2H)
singlet	$\delta = 7.28$ (2H)
singlet	$\delta = 7.25$ (1H)

N,N-Dimethyl-4-(1,1,2,2-tetracyano-2-$^{2}H_{1}$-ethyl)aniline (I-D):

Two methods were used to prepare this compound:

1) From the reaction of 4-monodeutero-N,N-dimethylaniline with tetracyanoethylene according to the procedure above for the preparation of the undeuterated compound. 4-Monodeutero-N,N-dimethylaniline was prepared according to Newton's procedure[41].

2) N,N-Dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (0.1g;0.0004mole) was dissolved in deuterated chloroform (10ml), then strongly shaken with three successive portions of deuterium oxide (3ml each). The organic layer was separated and then evaporated under reduced pressure and the residue obtained was collected and checked immediately for m.p. and n.m.r. then used for kinetic measurements.

m.p. 120° (decomposition).

n.m.r. in $CDCl_3$: The singlet characteristic of the dicyanomethyl proton "δ=4.46" disappeared completely.

(N,N-$^{2}H_{2}$)-2,6-Dimethyl-4-(1,1,2,2-tetracyano-2-$^{2}H_{1}$-ethyl)aniline(II-D):

The compound was prepared by shaking the solution of compound (II) in deuterated chloroform with deuterium oxide, as in procedure (2) for compound (I-D). decomposition at 250-260°.

n.m.r. in acetone d_6 : the broad peak at $\delta = 4.73$ disappeared and also the singlet at $\delta = 7.25$.

B) Product Analysis

Action of methanol on N,N-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline:

(0.1g ; 0.0004 mole) of the compound was dissolved in methanol (100ml) and kept under conditions identical to those used in kinetic measurements for more than ten half lives. Deep purple crystals precipitated. More precipitation occurred when the solvent was evaporated. The product was recrystallised from glacial acetic acid, m.p. 173-174° and proved to be N,N-dimethyl-4-(1,2,2-tricyanovinyl)aniline (lit.[42] m.p. 173-175) mixed m.p. 173-174°.

u.v. : $\lambda_{\text{max.(methanol)}} = 512$ nm. $\varepsilon_{\text{max.}} = 42,500$

Action of methanol on 2,6-dimethyl-4-(1,1,2,2-tetracyanoethyl) aniline:

This compound was treated as above to give, after working up, deep blue crystals which recrystallised from glacial acetic acid, m.p. 289° (decomposition) and proved to be 2,6-dimethyl-4-(1,2,2-tricyanovinyl)aniline (lit.[34] m.p. 289° (decomposition).

u.v. : $\lambda_{\text{max.(methanol)}} = 497$ nm. $\varepsilon = 26,000$

C) Purification of Solvents

The reactions were very sensitive to traces of moisture and basic or acidic impurities. Therefore, maximum degree of purity had to be achieved. All solvents used were Fisher's certified grade.

1) Purification of methanol: The method described by Vogel[43] was used. In a 1ℓ-round-bottomed flask, attached to a long water-condenser and drying tube, methanol (100ml) was added to magnesium turnings (3.8g). When the initial vigorous reaction subsided, a further 600ml of methanol were added and the reaction mixture refluxed for 30 minutes. The solvent was twice fractionally distilled using a two feet long fractionating column. The fraction boiling at 65.0° was collected and kept in clean dry polyethylene bottles. Freshly distilled samples were used for each set of experiments. Deuterated methanol (CH_3-OD) was doubly distilled before use.

2) Purification of acetone: In a 500ml round-bottomed flask attached to a water condenser and drying tube, acetone (300ml) was added to phosphorus pentoxide (5.9g) and refluxed for one hour. The dark brown mixture was fractionally distilled twice. Dry clean acetone was collected at 56.2° and kept in dry clean polyethylene bottles.

3) Purification of acetonitrile: The same procedure as used for acetone was employed. The redistilled acetonitrile was collected at 81.6°.

4) Purification of nitrobenzene: The compound was doubly distilled, using a fractionating column and air condenser. The

fraction boiling at 210.8° was collected and stored in a dry clean polyethylene bottle.

5) Purification of benzene: Benzene was kept above sodium wire for 24 hours, then doubly distilled using a fractionating column. The fraction boiling at 80.1° was collected and used immediately.

6) Preparation of the solvents used for the calibration of the dipole meter: The method described by Oehme and Wirth[44] was used. A chromatographic column with 40g of the usual 1/16 inch pellet form of molecular-sieve type 4A was covered by 50ml of the solvent. The closed column was inverted several times, the stopper replaced by a desiccant tube, and the liquid allowed to pass to the dipolemeter cell. This procedure was used to prepare benzene, cyclohexane and carbon tetrachloride.

7) Deionized water: Doubly distilled water was passed through an ion-exchange column (I 300 resin) to eliminate any traces of ions present, then used immediately.

D) Preparation of Standard Solution of Hydrochloric Acid

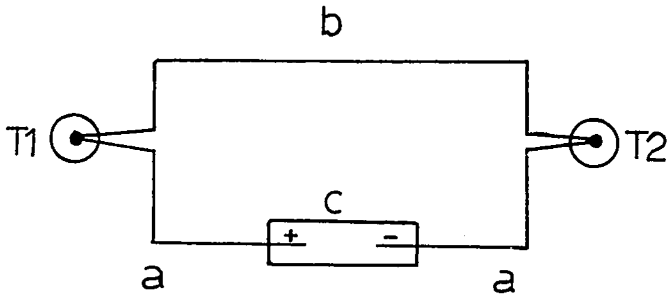
Fisher's concentrated standard hydrochloric acid was diluted to 1000 ml using deionised water. The solution was then volumetrically titrated against 10 ml of 0.0993N solution of sodium hydroxide. This had been standardized against an 0.1N solution of potassium hydrogen phthalate, using phenolphthalein as indicator. The process was repeated five times and three independent runs gave the same result.

Normality of HCl = 0.0995

To prepare a hydrochloric acid/methanol solution of known molarity, an exact volume of the 0.0995N solution was added to anhydrous methanol using an 'Agla' micrometer syringe and the volume was made up to 50 ml. with anhydrous methanol. (The molarity was assumed to be that of the corresponding hydrochloric acid/water solution.)

E) Thermocouple Technique for Temperature Measurements

The thermocouple circuit shown below was used to measure the temperature inside the thermostatted cell compartment of a Beckman DB spectrophotometer. It consisted of a) a copper wire b) a constantan wire and c) a potentiometer. Junction (T1) was kept at 0° by immersion in an ice bath. Calibration of the potentiometer readings was achieved by immersing the junction (T2) in water at different known temperatures. A linear relationship was obtained by plotting the e.m.f. vs temperature, fig (1).



Plot of temperature at junction T2 vs e.m.f. reading of the potentiometer of the thermocouple circuit.

T (°C)	e.m.f.(m.v.)
40.20	1.621
33.90	1.361
33.85	1.357
29.00	1.161
23.95	0.949

Fig. (1)

Figure 1 - Variation of e.m.f.(m.v.) with temperature °C.

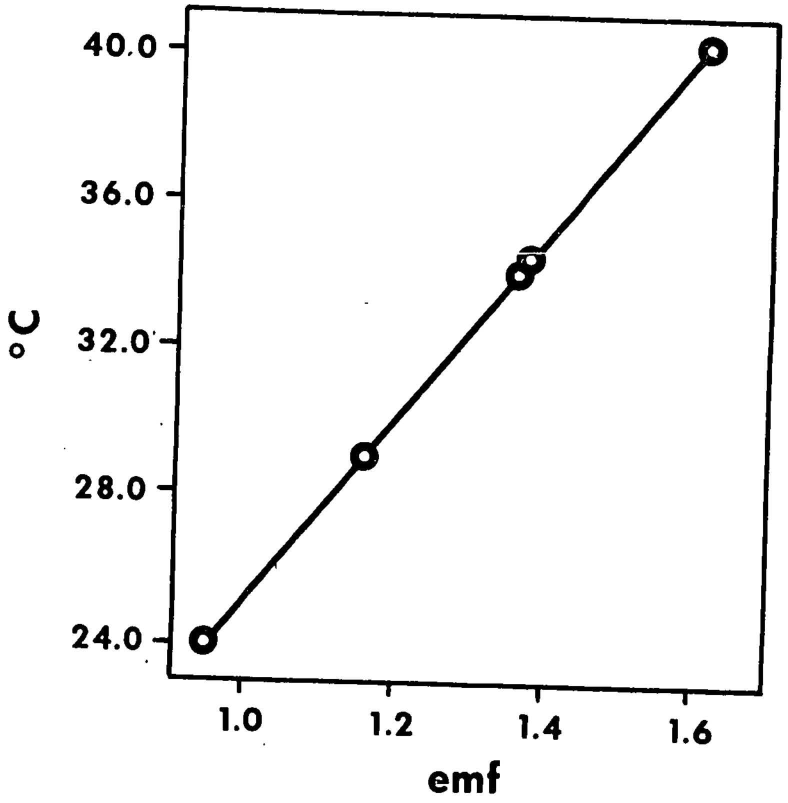


FIGURE 1

F) Dipole Moment Measurements

The determination of molecular dipole moments of compounds (I) and (II) was carried out using the dipolemeter type DM01 of Wissenschaftlich Technische Werkstätten and cell type MFL1. The experimental technique adopted by Oehme and Wirth[44] was used. The method is based upon the application of the following equation:

$$\mu^2 = \underset{(A)}{\frac{27kT}{4\pi N_\ell}} \cdot \underset{(B)}{\frac{1}{d_1(\varepsilon_1+2)^2}} \cdot \underset{(C)}{(a_\varepsilon - a_n)} \cdot \underset{(D)}{M_2}$$

which was used by Hedestrand[45]. In this equation, there are four terms:

A) A general constant term at constant temperature contains:

k	=	Boltzmann's constant	(1.381×10^{-16} erg.deg.$^{-1}$)
N_ℓ	=	Avogadro's number	(6.023×10^{23} mole^{-1})
T	=	Absolute temperature	

B) Solvent term contains:

d_1 = density of the solvent

ε_1 = dielectric constant of the solvent

C) Measured term, where:

$$a_\varepsilon = \frac{\varepsilon_{12} - \varepsilon_1}{w_2} \qquad \text{for one solution}$$

$$\text{and } a_n = \frac{n_{12}^2 - n_1^2}{w_2} \qquad \text{for one solution}$$

Here we have:

ε_{12} = dielectric constant of the solution.

w_2 = mole fraction of the solute.

n_1 = refractive index of the solvent.

n_{12} = refractive index of the solution.

A calibration graph for the capacitance reading on the dipolemeter and the dielectric constant of the corresponding solution in the cell was made by using purified solvents of known dielectric constants. A linear relationship was obtained fig. (2) and used to determine the dielectric constants of the solutions under investigation. At the same time, the refractive index of the solution was measured using an Abbé refractometer attached to the dipolemeter and thermostatted at the same temperature.

Results of the dipole moment measurements:-

At 25.0 ± 0.1°

Solvent	Capacitance	Dielectric constant	Refractive index
a) Calibration			
Cyclohexane	779.0	2.0148	1.4213
Carbon tetrachloride	1304.5	2.2263	1.4563
Benzene	1416.5	2.2725	1.4979
b) Measurement			
Solution (I) in benzene	1430.8	2.2860*	1.4962
Solution (II) in benzene	1426.5	2.2840*	1.4963

Fig. (2)

* Calculated from the graph.

Dipole moment of compound (I) = 3.32 Debyes

Dipole moment of compound (II) = 3.80 Debyes

Figure 2 - Variation of capacitance with dielectric constant (ε).

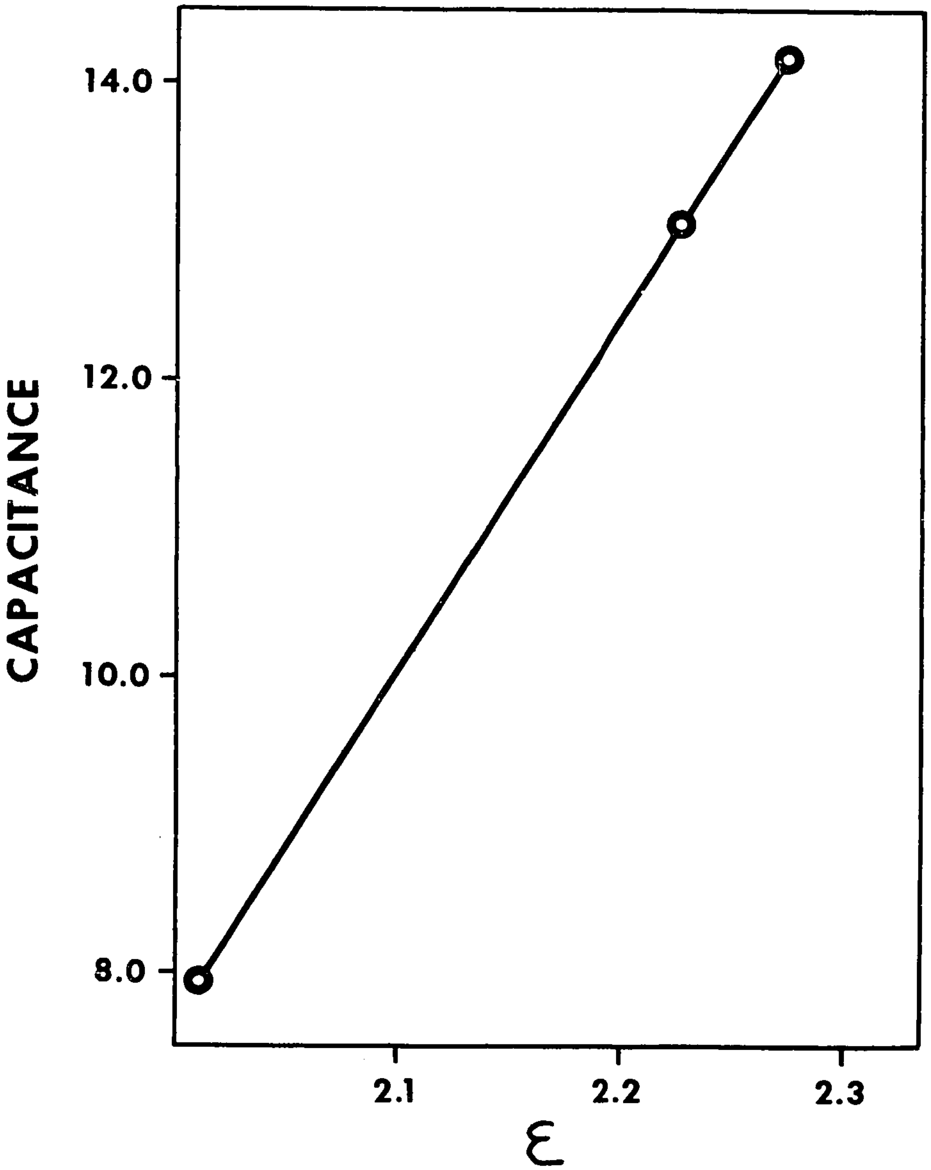


FIGURE 2

G) Kinetic Technique and Rate Measurements

The rates of reactions were measured by following the increase of absorbance of the products spectrophotometrically at an appropriate wavelength using a Beckman DB spectrophotometer connected to a thermostatted water bath and a Sargent recorder. Most of the measurements have been done at $\lambda_{max.}$ of the products. In a few cases, different wavelengths were used to allow measurements of the highest possible concentration of the products.

The desired volume of solvent (or mixture of solvents) was pipetted quantitatively into a flask which was then stoppered and thermostatted in a water bath at the reaction temperature. The proper amount of the compound under investigation was weighed and carefully transferred to a well closed stopper-like container. During mixing, this container was used as stopper for the flask containing the solvent to assure quantitative solution. At the moment of mixing, the recorder was switched on to start recording the time, then as soon as possible after the compound had dissolved, a sample of the reaction mixture was syringed into a clean dry quartz cell. The latter was then placed in the thermostatted cell compartment of the spectrophotometer. The recorder showed the continuous increase of the product absorbance (AB) with time.

For longer experiments, we preferred to leave the flask containing the reaction mixture in the thermostatted water bath and take samples at various intervals of time to check the absorbance of the product.

In most of the reactions, the results were measured till $\sim$ 80% of the reaction had occurred; deviation from linearity was observed after that. In a few cases, it was not possible to follow more than 15% of the reaction because the reactions were either very slow or the absorbance of the product was too high at the concentrations used, even with the smallest available light-path length.

The results recorded here are those of three independent runs in every case.

Rate measurements in aprotic solvents: Rate measurements of HCN elimination from compound (I) and from compound (II) in pure redistilled benzene, nitrobenzene, acetonitrile and in acetone at 34.7° were made. After more than 50 hours, less than 2% of reaction had occurred in each solvent.

Data

A) Rate measurements in pure methanol at different temperatures:-

(i) Reactions of Compound (I):

Initial concentration of the substrate = $1.0\text{x}10^{-4}$ M/ℓ

1 = 5mm

λ = 512nm.

Experiment(1):-

At 34.7° ± 0.1°

Time in minutes	(AB)
3	0.187
6	0.370
9	0.555
12	0.780
15	0.980
18	1.175
21	1.375
24	1.565

$k_\circ=5.013\text{x}10^{-8}$ mole $\ell.^{-1}$ sec.^{-1}

$k_1=5.013\text{x}10^{-4}$ sec.^{-1}

Fig. (3)

Experiment(2):-

At 30.0° ± 0.1°

Time in minutes	(AB)
5	0.180
10	0.356
15	0.535
20	0.717
25	0.900
30	1.090
35	1.264
40	1.440
45	1.610

$k_\circ=2.745\text{x}10^{-8}$ mole $\ell.^{-1}$ sec.^{-1}

$k_1=2.745\text{x}10^{-4}$ sec.^{-1}

Fig. (3)

1 = light-path length

λ = wave length

Figure 3 - Plots of absorbance (AB) against time for the reactions of compound (I) in pure methanol at different temperatures.

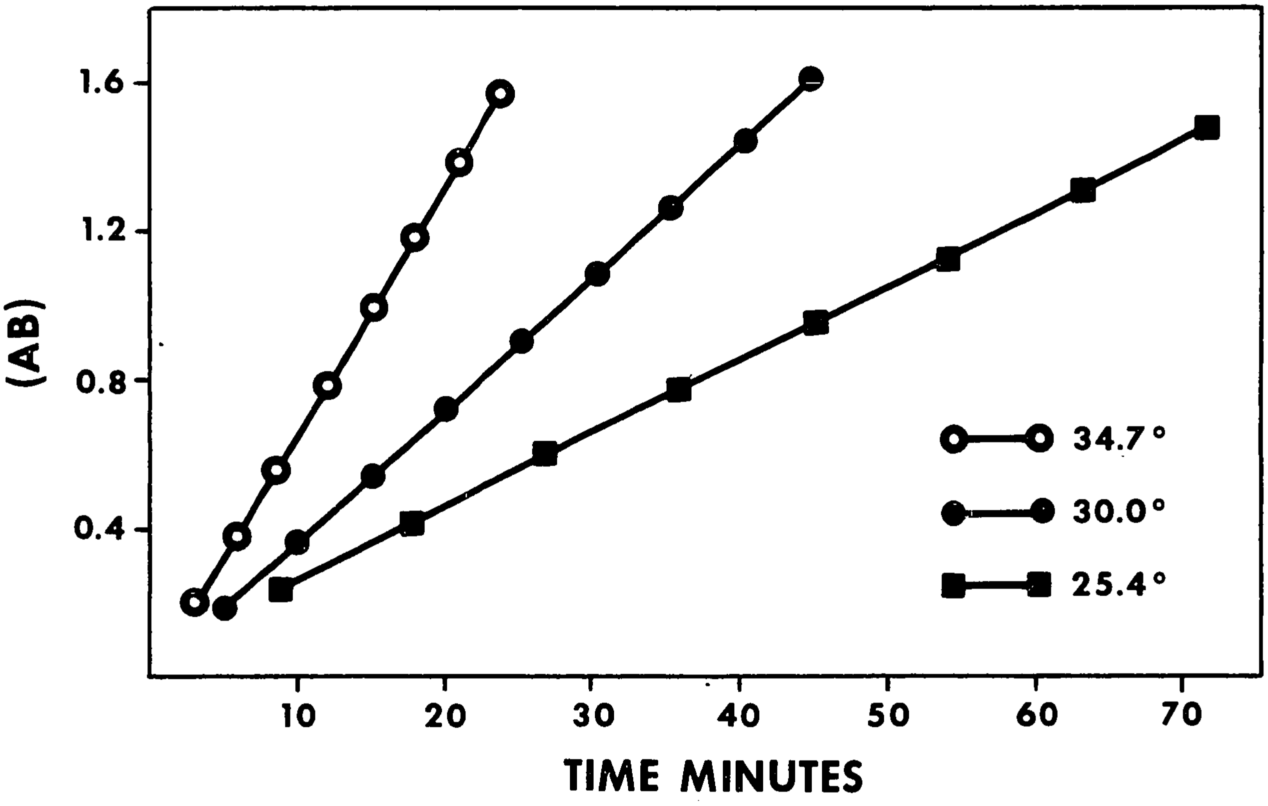


FIGURE 3

Experiment (3):-

At 25.4° ± 0.1°

Time in minutes	(AB)
9	0.225
18	0.408
27	0.590
36	0.765
45	0.943
54	1.120
63	1.295
72	1.470

$k_o = 1.504 \times 10^{-8}$ mole $\ell.^{-1}$ $\sec.^{-1}$

$k_1 = 1.504 \times 10^{-4}$ $\sec.^{-1}$

Fig. (3)

Calculation of the energy of activation (E_a)

Calculation of the energy of activation of the elimination reaction of (I) in methanol between 25.4° and 34.7°

Experiments 1, 2 and 3

$10^8 k_o$ mole $\ell.^{-1}$ sec.$^{-1}$	T(°C)	T(°K)	$(1/T)10^4$	8+log k_o
5.013	34.7	307.7	32.52	0.7001
2.745	30.0	303.0	33.00	0.4386
1.504	25.4	298.4	33.50	0.1772

$E_a = -$ slope x 2.303 x 1.987

$$= 10^4 \times \frac{0.522}{0.98} \times 2.303 \times 1.987$$

$= 24.43$ k cal. mole^{-1}

Fig. (4)

Figure 4 - Plot of log k against (1/T), T is in absolute degrees, for the reactions of compound (I).

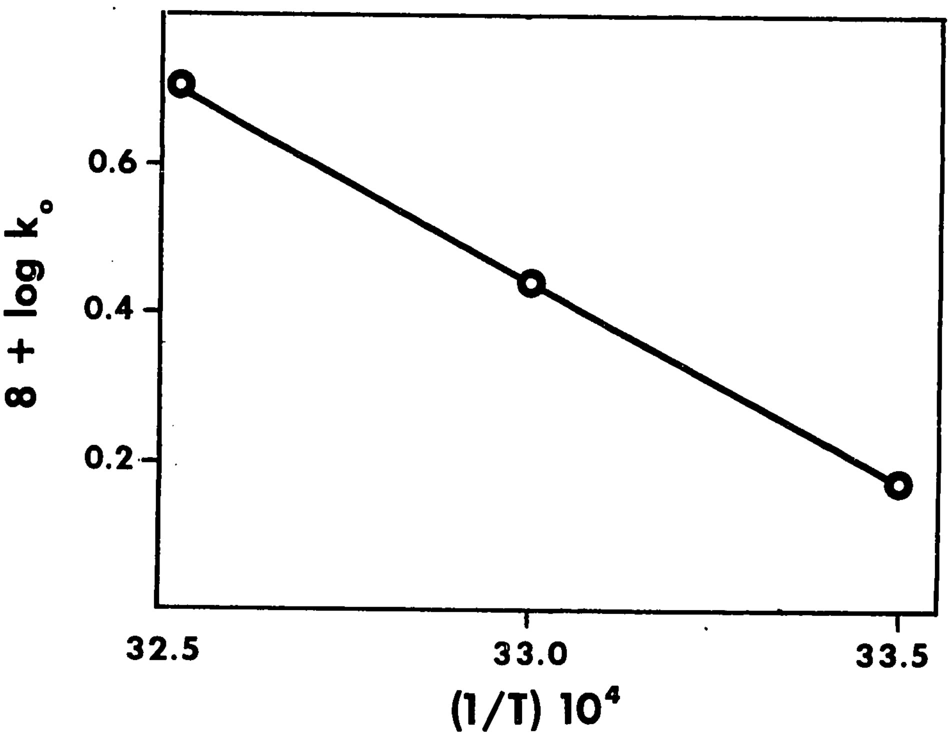


FIGURE 4

(ii) Reactions of compound (II):

Initial concentration of substrate = 1.0×10^{-4} M/ℓ

l = 5mm λ = 497nm.

<u>Experiment (4):-</u>

At 34.7° ± 0.1°

Time in minutes	(AB)
3	0.107
6	0.240
9	0.377
12	0.514
15	0.652
18	0.800
21	0.936

$k_o=5.949\times10^{-8}$ mole $\ell.^{-1}$ sec.$^{-1}$

$k_1=5.949\times10^{-4}$ sec.$^{-1}$

Fig. (5)

<u>Experiment (5):-</u>

At 30.0° ± 0.1°

Time in minutes	(AB)
4	0.112
8	0.226
12	0.335
16	0.447
20	0.550
24	0.667
28	0.778
32	0.889

$k_o=3.562\times10^{-8}$ mole $\ell.^{-1}$ sec.$^{-1}$

$k_1=3.562\times10^{-4}$ sec.$^{-1}$

Fig. (5)

Figure 5 - Plots of absorbance (AB) against time for the reactions of compound (II) in pure methanol at different temperatures.

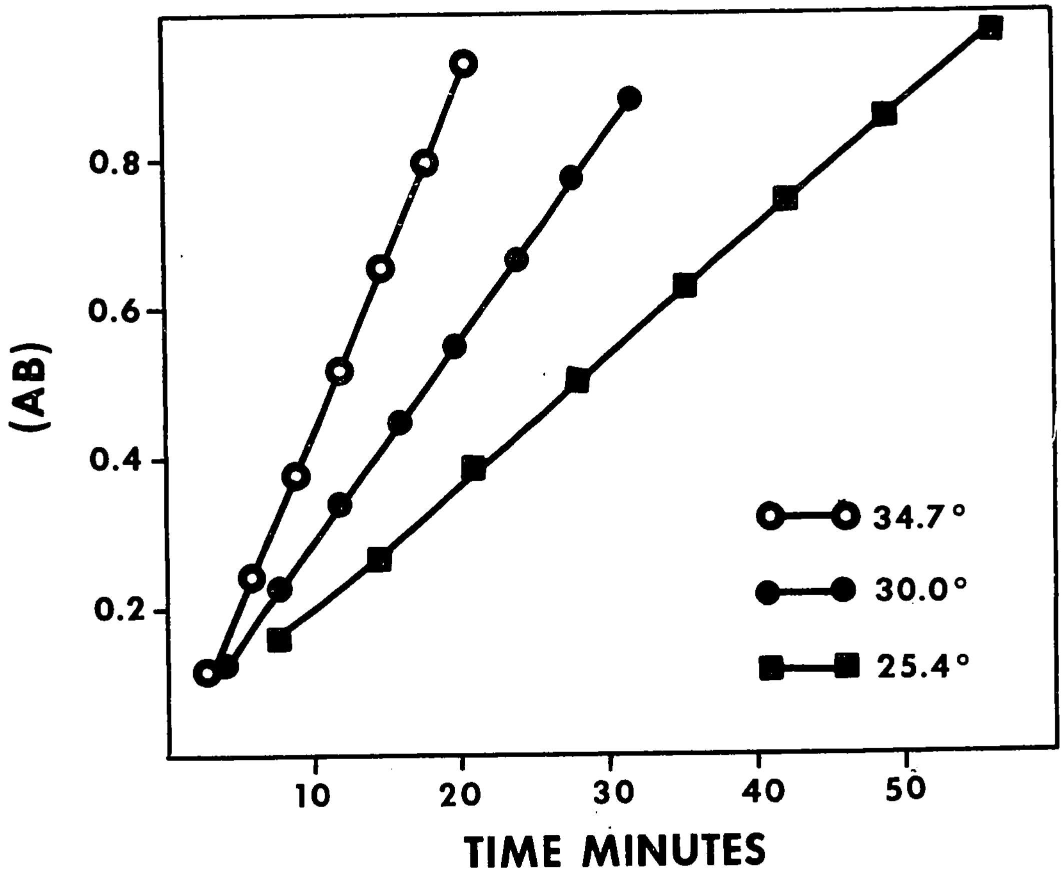


FIGURE 5

Experiment (6):

At 25.4° ± 0.1°

Time in minutes	(AB)
7	0.153
14	0.273
21	0.392
28	0.506
35	0.624
42	0.742
49	0.862
56	0.978

$k_o = 2.173 \times 10^{-8}$ mole $\ell.^{-1}$ $\sec.^{-1}$

$k_1 = 2.173 \times 10^{-4}$ $\sec.^{-1}$

Fig. (5)

Calculation of the energy of activation (E_a)

Calculation of the energy of activation of the elimination reaction of (II) in methanol between 25.4 and 34.7°

Experiments 4, 5 and 6

$10^8 k_o$ mole $\ell.^{-1}$ sec.$^{-1}$	T(°C)	T(°K)	$(1/T)10^4$	$8+\log k_o$
5.949	34.7	307.7	32.52	0.7743
3.562	30.0	303.0	33.00	0.5520
2.173	25.4	298.4	33.50	0.3375

$E_a = -\text{slope} \times 2.303 \times 1.987$

$= 10^4 \times \frac{0.4368}{0.98} \times 2.303 \times 1.987$

$= 20.44$ k cal. mole^{-1}

Fig. (6)

Figure 6 - Plot of log k against (1/T) for the reactions of compound (II).

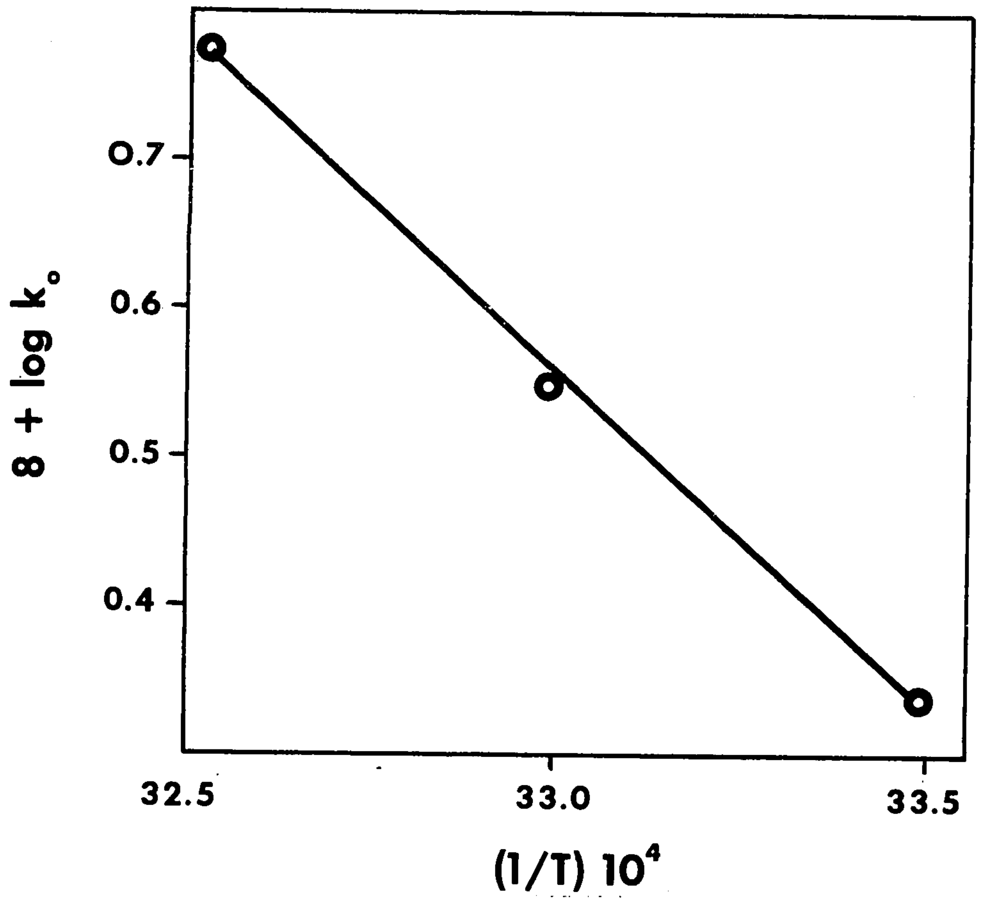


FIGURE 6

B) Rate measurements in pure methanol using different concentrations of the substrate at 30.0°:

(i) Reactions of compound (I):

l = 5mm. λ 512nm.

Experiment (7):-

[I] = 2×10^{-4} M/ℓ

Time in minutes	(AB)
3	0.208
6	0.397
9	0.607
12	0.830
15	1.066
18	1.318
21	1.585
24	1.880

$k_o=6.172\times10^{-8}$ mole ℓ^{-1} sec^{-1}

$k_1=3.086\times10^{-4}$ sec^{-1}

Experiment (8):-

[I] = 1.6×10^{-4} M/ℓ

Time in minutes	(AB)
3	0.257
6	0.434
9	0.620
12	0.810
15	1.016
18	1.232
21	1.455
24	1.690
27	1.945

$k_o=5.332\times10^{-8}$ mole ℓ^{-1} sec^{-1}

$k_1=3.332\times10^{-4}$ sec^{-1}

Experiment (9):-

[1] = 0.8×10^{-4} M/ℓ

Time in minutes	(AB)
5	0.250
10	0.400
15	0.560
20	0.730
25	0.900
30	1.080
35	1.260
40	1.440

$k_o = 2.682 \times 10^{-8}$ mole $\ell.^{-1}$ $\text{sec}.^{-1}$

$k_1 = 3.352 \times 10^{-4}$ $\text{sec}.^{-1}$

Experiment (10):-

[1] = 0.5×10^{-4} M/ℓ

Time in minutes	(AB)
7	0.083
14	0.203
21	0.330
28	0.455
35	0.582
42	0.701
49	0.827
56	0.953

$k_o = 1.360 \times 10^{-8}$ mole $\ell.^{-1}$ $\text{sec}.^{-1}$

$k_1 = 2.720 \times 10^{-4}$ $\text{sec}.^{-1}$

Calculation of the first order rate constant of the reaction of (I) at 30.0°

Experiment no.	10^4[I] M/ℓ	10^8 k_o mole ℓ^{-1} sec^{-1}	10^4 k_1 sec^{-1}
7	2.0	6.172	3.086
8	1.6	5.332	3.332
2	1.0	2.745	2.745
9	0.8	2.682	3.352
10	0.5	1.360	2.720

k_1 (mathematically) = $10^{-4} \times 15.235/5$

= 3.047×10^{-4} sec^{-1}

k_1 (graphically) = slope

= 3.1943×10^{-4} sec^{-1}

Standard deviation of the slope = 0.0762

Correlation coefficient = 0.9942

Fig. (7)

Figure 7 - Variation of rate constants with [I].

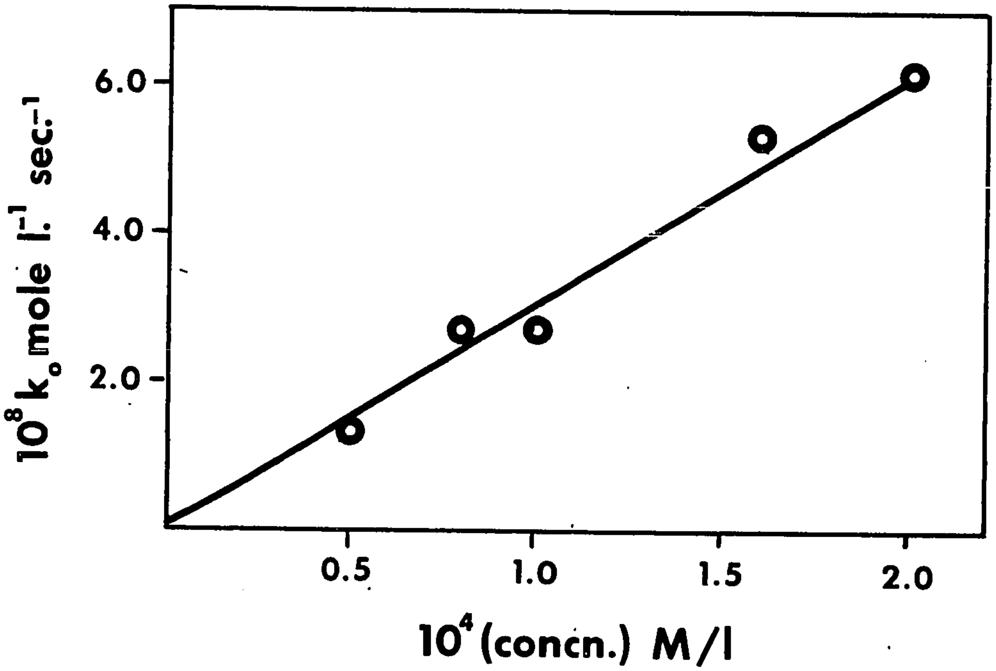


FIGURE 7

(ii) Reactions of compound (II):

l = 5mm.

λ = 497nm.

Experiment (11):-

[II] = 2×10^{-4} M/ℓ

Time in minutes	(AB)
4	0.208
8	0.396
12	0.594
14	0.695
16	0.800
20	1.016
24	1.212
28	1.448
32	1.725

$k_o = 6.730\times10^{-8}$ mole ℓ^{-1} sec^{-1}

$k_1 = 3.365\times10^{-4}$ sec^{-1}

Experiment (12):-

[II] = 1.6×10^{-4} M/ℓ

Time in minutes	(AB)
4	0.186
8	0.362
12	0.547
16	0.735
20	0.933
24	1.138
28	1.350
32	1.562

$k_o = 6.313\times10^{-8}$ mole ℓ^{-1} sec^{-1}

$k_1 = 3.946\times10^{-4}$ sec^{-1}

Experiment (13):-

[II] = 0.8×10^{-4} M/ℓ

Time in minutes	(AB)
5	0.082
10	0.182
15	0.286
20	0.402
25	0.516
30	0.635
35	0.752
40	0.870

$k_o = 2.923 \times 10^{-8}$ mole $\ell.^{-1}$ $\sec.^{-1}$

$k_1 = 3.654 \times 10^{-4}$ $\sec.^{-1}$

Experiment (14):-

[II] = 0.532×10^{-4} M/ℓ

Time in minutes	(AB)
5	0.079
10	0.150
15	0.222
20	0.297
25	0.370
30	0.442
35	0.513
40	0.583

$k_o = 1.862 \times 10^{-8}$ mole $\ell.^{-1}$ $\sec.^{-1}$

$k_1 = 3.500 \times 10^{-4}$ $\sec.^{-1}$

Calculation of the first order rate constant of the reaction of (II) at 30.0°

Experiment no.	10^4 [II] M/ℓ	10^{-8} k_o mole $ℓ.^{-1}$ $sec.^{-1}$	10^{-4} k_1 $sec.^{-1}$
11	2.00	6.730	3.365
12	1.60	6.313	3.946
5	1.00	3.565	3.565
13	0.800	2.923	2.654
14	0.532	1.862	3.500

k_1 (mathematically) = 10^{-4} x 17.030/5

= 3.406 x 10^{-4} $sec.^{-1}$

k_1 (graphically) = slope

= 3.5342 x 10^{-4} $sec.^{-1}$

Standard deviation of the slope = 0.3496

Correlation coefficient = 0.9923

Fig. (8)

Figure 8 - Variation of rate constants with [II].

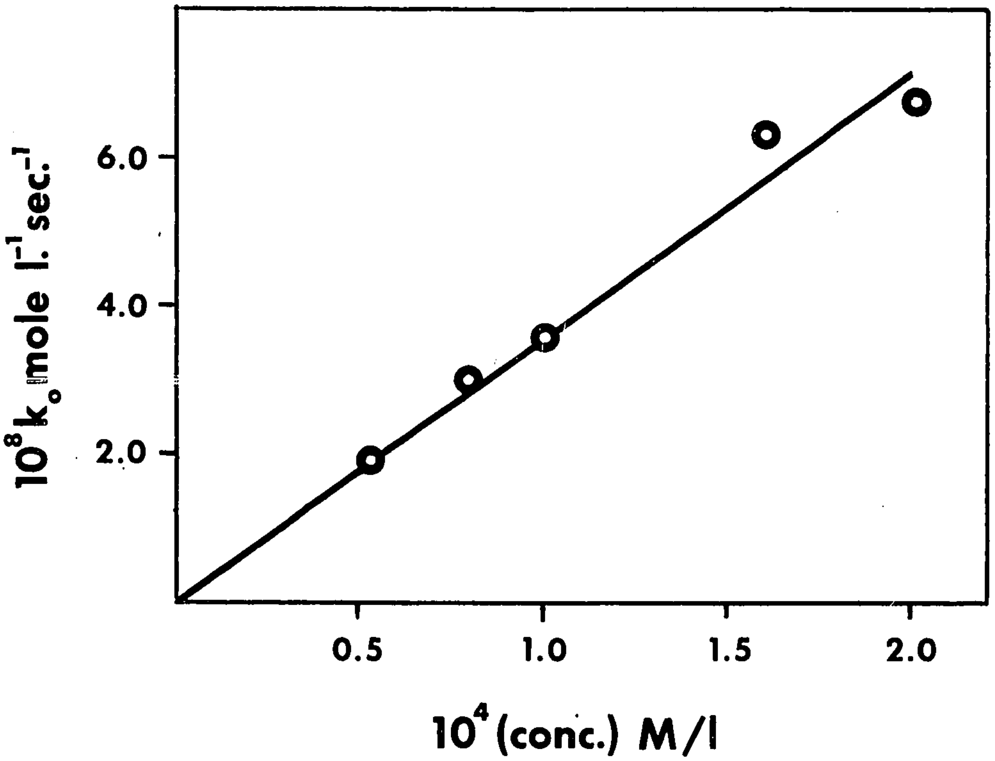


FIGURE 8

C) Rate measurements in acetone using constant concentration of the substrate and different concentrations of methanol at 30.0°:-

(i) Reactions of compound (I):

$[I] = 1.0\times10^{-2}$ M/ℓ

$\lambda = 550$nm (of $\varepsilon = 18{,}500$)

$l = 1$mm.

Experiment (15):-

$[MeOH] = 2\times10^{-2}$ M/ℓ

Time in hours	(AB)
2	0.731
3	0.953
4	1.171
5	1.393
6	1.592
7	1.828
7.5	1.945

$k_o = 3.395\times10^{-8}$ mole ℓ^{-1} sec^{-1}

Experiment (16):-

$[MeOH] = 1.0\times10^{-2}$ M/ℓ

Time in hours	(AB)
1	0.512
2	0.683
3	0.892
4	1.081
5	1.245
6	1.442
7	1.645
8	1.850

$k_o = 2.870\times10^{-8}$ mole ℓ^{-1} sec^{-1}

Experiment (17):-

[MeOH] = 0.5×10^{-2} M/ℓ

Time in hours	(AB)
1	0.485
2	0.640
3	0.795
4	0.930
5	1.090
6	1.240
7	1.401
8	1.556
9	1.712

$k_o = 2.315 \times 10^{-8}$ mole $\ell.^{-1}$ $\mathrm{sec}.^{-1}$

Calculation of the order (in methanol) of the reaction of compound (I)

Experiments 15, 16 and 17

[MeOH] 10^2 M/ℓ	3+log [MeOH]	10^{-8} k_o mole ℓ^{-1} sec^{-1}	8+log k_o
2	1.3010	3.395	0.5308
1	1.0000	2.870	0.4579
0.5	0.6990	2.315	0.3645

Order of the reaction (in methanol) = slope

= 0.276

Fig. (9)

Figure 9 - Variation of log k with log C, C is [MeOH] in mole $\ell.^{-1}$, for the reactions of compound (I).

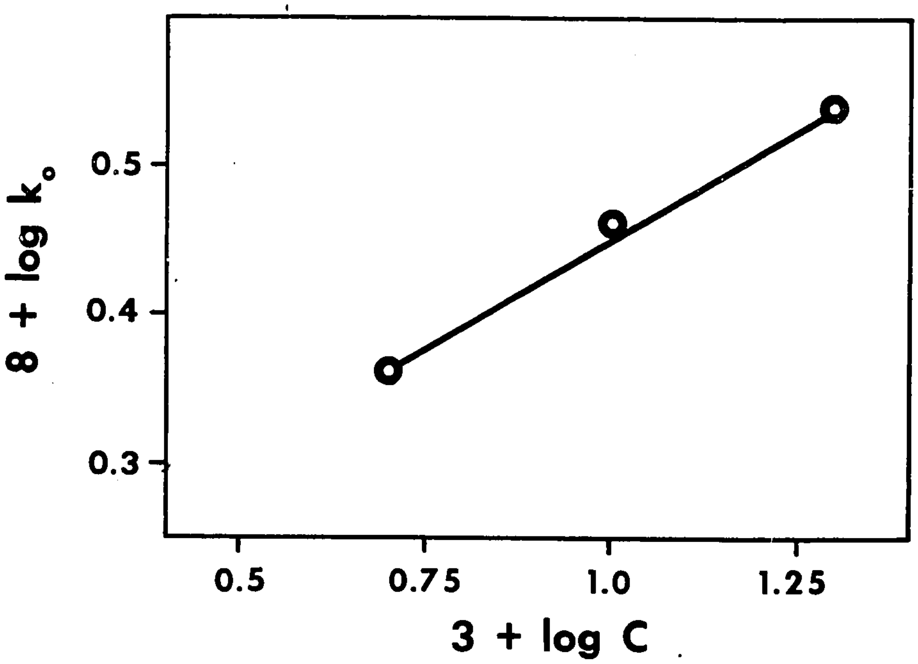


FIGURE 9

(ii) Reactions of compound (II):

$[II] = 1.0x10^{-2}$ M/ℓ

λ = 533nm (of ε = 11,400)

1 = 1mm.

Experiment (18):-

$[MeOH]\ 3x10^{-2}$ M/ℓ

Time in hours	(AB)
2	0.108
4	0.187
6	0.266
8	0.346
10	0.435
22	0.892
24	0.940
26	1.037
28	1.111
30	1.172
32	1.264
42	1.646
44	1.708
46	1.805
48	1.885
50	1.974

$k_o=9.330x10^{-9}$ mole $ℓ.^{-1}$ $sec.^{-1}$

Experiment (19):-

$[MeOH] = 2x10^{-2}$ M/ℓ

Time in hours	(AB)
1	0.090
3	0.145
5	0.210
10	0.353
23	0.830
25	0.854
27	0.932
29	0.992
31	1.093
34	1.185
37	1.273
47	1.660
49	1.753
51	1.805
53	1.852

$k_o=8.844x10^{-9}$ mole $ℓ.^{-1}$ $sec.^{-1}$

Experiment (20):-

[MeOH] = 1.0×10^{-2} M/ℓ

Time in hours	(AB)
3	0.122
6	0.202
9	0.292
12	0.372
22	0.680
24	0.731
26	0.805
28	0.855
30	0.902
34	1.020
48	1.423
50	1.471
52	1.560
54	1.610
58	1.738
61	1.835

$k_o = 7.026 \times 10^{-9}$ mole ℓ^{-1} sec^{-1}

Experiment (21):-

[MeOH] = 0.5×10^{-2} M/ℓ

Time in hours	(AB)
1	0.100
2	0.132
4	0.155
6	0.195
9	0.260
23	0.660
25	0.736
27	0.774
29	0.805
46	1.281
49	1.362
51	1.415
56	1.545
64	1.752
68	1.864
72	1.972

$k_o = 6.336 \times 10^{-9}$ mole ℓ^{-1} sec^{-1}

Calculation of the order (in methanol) of the reaction of compound (II)

Experiments 18, 19, 20 and 21

[MeOH] 10^2 M/ℓ	3+log [MeOH]	10^{-9} k_o mole ℓ^{-1} sec.$^{-1}$	9+log k_o
3	1.4771	9.330	0.9633
2	1.3010	8.844	0.9467
1	1.000	7.026	0.8467
0.5	0.6990	6.336	0.8018

Order of the reaction (in methanol) = slope

= 0.209

Fig. (10)

Figure 10 - Variation of log k with log C, C is [MeOH] in mole $\ell.^{-1}$, for the reactions of compound (II).

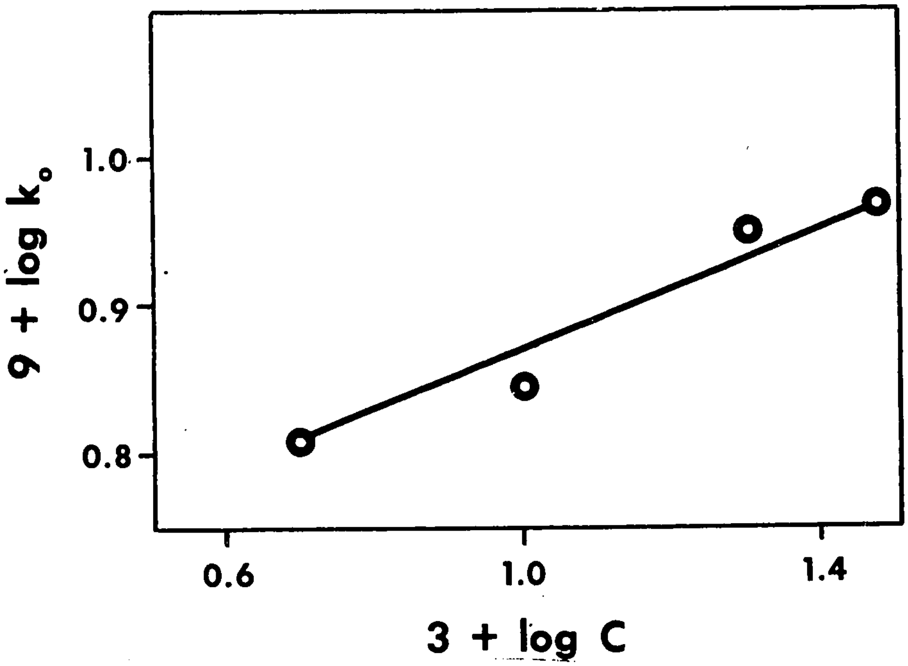


FIGURE 10

D) Rate measurements of DCN elimination from deuterated compounds in deuterated methanol at 34.7°

(i) Reaction of compound (I):

$[I\text{-}D] = 1.0 \times 10^{-4}$ M/ℓ

l = 5mm

λ = 512nm

Experiment (22):-

Time in minutes	(AB)
1	0.176
2	0.325
3	0.500
4	0.695
5	0.900
6	1.124
7	1.315
8	1.478
9	1.610

$k_o = 15.25 \times 10^{-8}$ mole ℓ.$^{-1}$ sec.$^{-1}$

$k_1 = 15.25 \times 10^{-4}$ sec.$^{-1}$

Kinetic isotope effect of the reaction:

$$k_H^H/k_D^D = \frac{5.013}{15.25}$$

$$= 0.3288$$

(ii) Reaction of compound (II):

$[II\text{-}D] = 1.0\times10^{-4}$ M/ℓ

l = 5mm

λ = 497nm

Experiment (23):-

Time in minutes	(AB)
1	0.159
2	0.255
3	0.351
4	0.448
5	0.540
6	0.636
7	0.730
8	0.828
9	0.919

$k_o=12.18\times10^{-8}$ mole $\ell.^{-1}$ $sec.^{-1}$

$k_1=12.18\times10^{-4}$ $sec.^{-1}$

Kinetic isotope effect of the reaction:

$$k_H^H/k_D^D = \frac{5.949}{12.18}$$

$$= 0.4888$$

E) Rate measurements of HCN elimination from the substrate in methanol in the presence of HCl at different temperatures:

$[HCl] = 0.5x10^{-4}$ M/ℓ

$l = 5mm$

Initial concentration of the substrate = $1.0x10^{-4}$ M/ℓ

(i) Reactions of compound (I):

$\lambda = 512nm$

Experiment (24):-

At 34.7° ± 0.1°

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
1	0.132	0.0507	0.9493	1.0534	0.232
2	0.265	0.1218	0.8782	1.1387	0.0566
3	0.387	0.1779	0.8221	1.2164	0.0849
4	0.503	0.2313	0.7687	1.3009	0.1142
5	0.610	0.2805	0.7195	1.3898	0.1430
6	0.710	0.3264	0.6736	1.4846	0.1718
7	0.803	0.3692	0.6307	1.5855	0.2003
8	0.886	0.4074	0.5926	1.6875	0.2274
10	1.046	0.4809	0.5191	1.9270	0.2850
12	1.183	0.5440	0.4560	2.1981	0.3420
14	1.300	0.5980	0.4021	2.4950	0.3972

$k_1 = 18.10x10^{-6}$ sec.$^{-1}$

Fig. (11)

Figure 11 - First-order plots for the reaction of (I) in methanol in the presence of HCl.

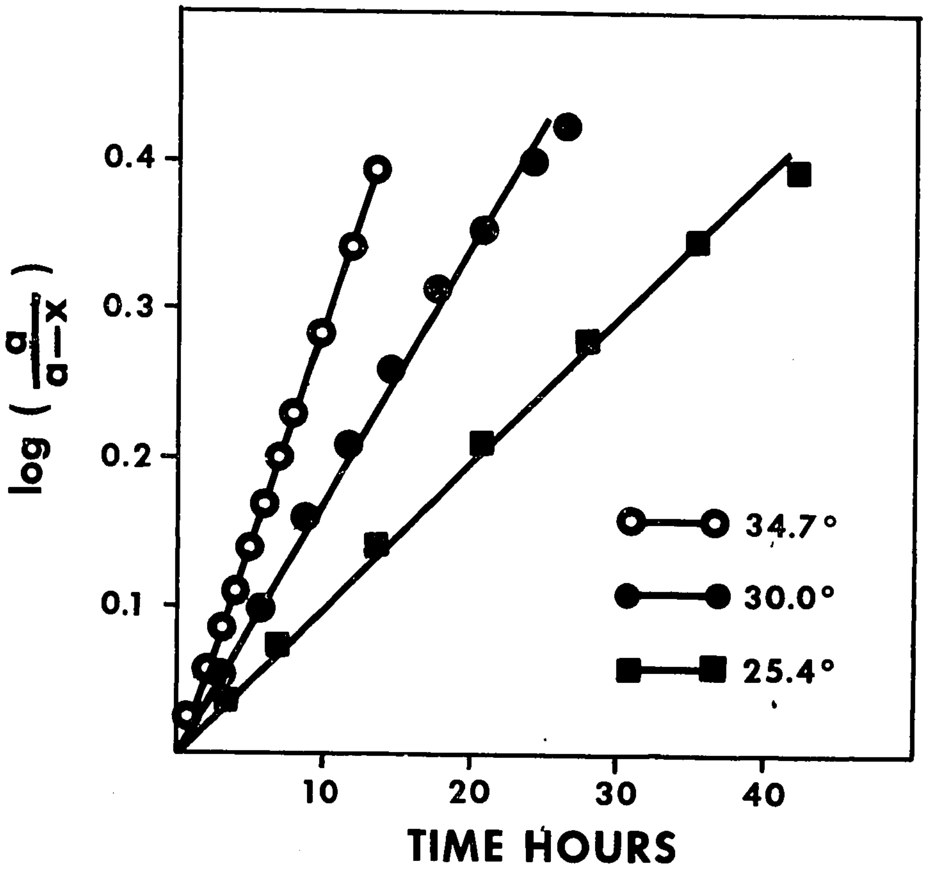


FIGURE 11

Experiment (25):-

At 30.0°

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
3	0.281	0.1248	0.8752	1.1426	0.0579
6	0.444	0.2025	0.7975	1.2539	0.0983
9	0.655	0.302	0.698	1.4327	0.1561
12	0.831	0.3825	0.6175	1.6194	0.2094
15	0.978	0.4500	0.5500	1.8182	0.2593
18	1.110	0.5110	0.4890	2.0450	0.3107
21	1.216	0.5590	0.4410	2.2676	0.3556
24	1.310	0.603	0.3970	2.5189	0.4012
26	1.362	0.627	0.373	2.6810	0.4283

$k_1 = 10.39 \times 10^{-6}$ sec.$^{-1}$

Fig. (11)

Experiment (26):-

At 25.4°

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
3.5	0.185	0.0851	0.9149	1.0930	0.0386
7	0.334	0.1538	0.8462	1.1802	0.0719
14	0.603	0.2770	0.7230	1.3831	0.1409
21	0.830	0.3816	0.6184	1.6170	0.2087
28	1.016	0.4671	0.5329	1.8765	0.2734
35	1.191	0.5469	0.4531	2.2020	0.3426
42	1.295	0.5954	0.4045	2.4722	0.3931
49	1.390	0.6391	0.3608	2.7716	0.4428
56	1.475	0.6781	0.3219	3.1066	0.4923

$k_1=6.119\times10^{-6}\ \text{sec.}^{-1}$

Fig. (11)

Calculation of the energy of activation (E_a)

Calculation of the energy of activation of the HCN elimination reaction from compound (I) in methanol in the presence of HCl between 25.4 and 34.7°

Experiments 24, 25 and 26

$10^6 k_1$ sec.$^{-1}$	T(°C)	T(°K)	$(1/T)10^4$	6+log k
18.10	34.7	307.7	32.52	1.2577
10.39	30.0	303.0	33.00	1.0166
6.119	25.4	298.4	33.50	0.7866

E_a = - slope x 2.303 x 1.987

= 22.05 k cal/mole

Fig. (12)

Figure 12 - Plot of log k_1 against (1/T); T°K.

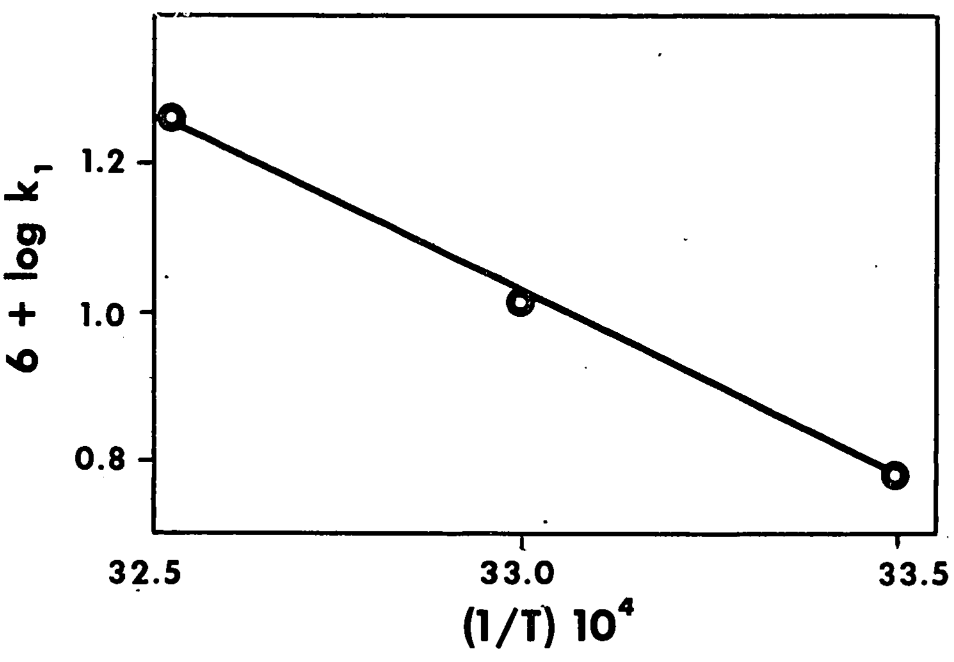


FIGURE 12

(ii) Reactions of compound (II):

λ = 497nm

Experiment (27):-

At 34.7° ± 0.1°

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
1	0.200	0.1538	0.8462	1.1817	0.0725
3	0.372	0.2862	0.7138	1.4009	0.1464
5	0.520	0.400	0.600	1.6667	0.2218
7	0.650	0.500	0.500	2.000	0.3010
9	0.766	0.5892	0.4108	2.4343	0.3863
11	0.870	0.6692	0.3308	3.0230	0.4804
13	0.956	0.7354	0.2645	3.7807	0.5776

$k_1=27.65\times10^{-6}$ sec.$^{-1}$

Fig. (13)

Experiment (28):-

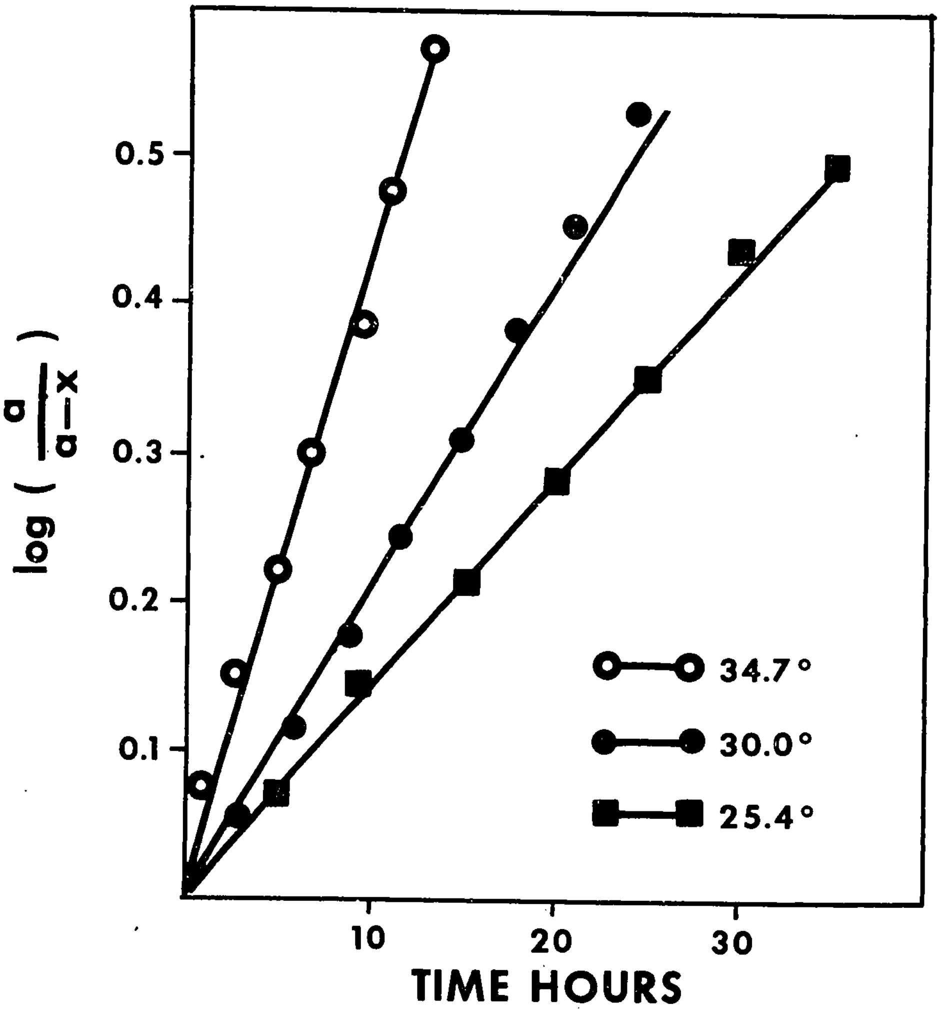
At 30.0° ± 0.1°

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
3	0.153	0.1177	0.8823	1.1334	0.0543
6	0.300	0.2308	0.7692	1.3000	0.1139
9	0.434	0.3338	0.6662	1.5010	0.1764
12	0.555	0.4269	0.5731	1.7449	0.2418
15	0.662	0.5092	0.4908	2.0375	0.3092
18	0.755	0.5808	0.4192	2.3855	0.3776
21	0.840	0.6462	0.3538	2.8265	0.4507
24	0.915	0.7038	0.2962	3.3761	0.5284

$k_1=13.80\times10^{-6}$ sec.$^{-1}$

Fig. (13)

Figure 13 - First-order plots for the reaction of compound (II) in methanol in the presence of HCl.



0.5
0.4
0.3
0.2
0.1
$\log\left(\frac{a}{a-x}\right)$
10
20
30
TIME HOURS
34.7°
30.0°
25.4°

FIGURE 13

Experiment (29):-

At 25.4° ± 0.1°

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
5	0.193	0.1485	0.8515	1.1744	0.0697
10	0.360	0.2769	0.7231	1.3829	0.1409
15	0.500	0.3846	0.6154	1.6250	0.2109
20	0.620	0.4769	0.5231	1.9117	0.2814
25	0.724	0.5569	0.4431	2.2568	0.3536
30	0.822	0.6323	0.3677	2.7196	0.4346
35	0.882	0.6785	0.3215	3.1131	0.4932

$k_1 = 9.023 \times 10^{-6}$ sec.$^{-1}$

Fig. (13)

Calculation of the energy of activation (E_a)

Calculation of the energy of activation of the HCN elimination reaction from compound (II) in methanol in the presence of HCl between 25.4 and 34.7°

Experiments 27, 28 and 29

$10^6 k_1$ sec.$^{-1}$	T(°C)	T(°K)	$(1/T)10^4$	$6+\log k_1$
27.65	34.7	307.7	32.52	1.4417
13.80	30.0	303.0	33.00	1.1400
9.023	25.4	298.4	33.50	0.9553

$E_a = -$ slope x 2.303 x 1.987

= 22.67 k cal/mole

Fig. (14)

Figure 14 - Plot of log k_1 against $(1/T)$; T°K.

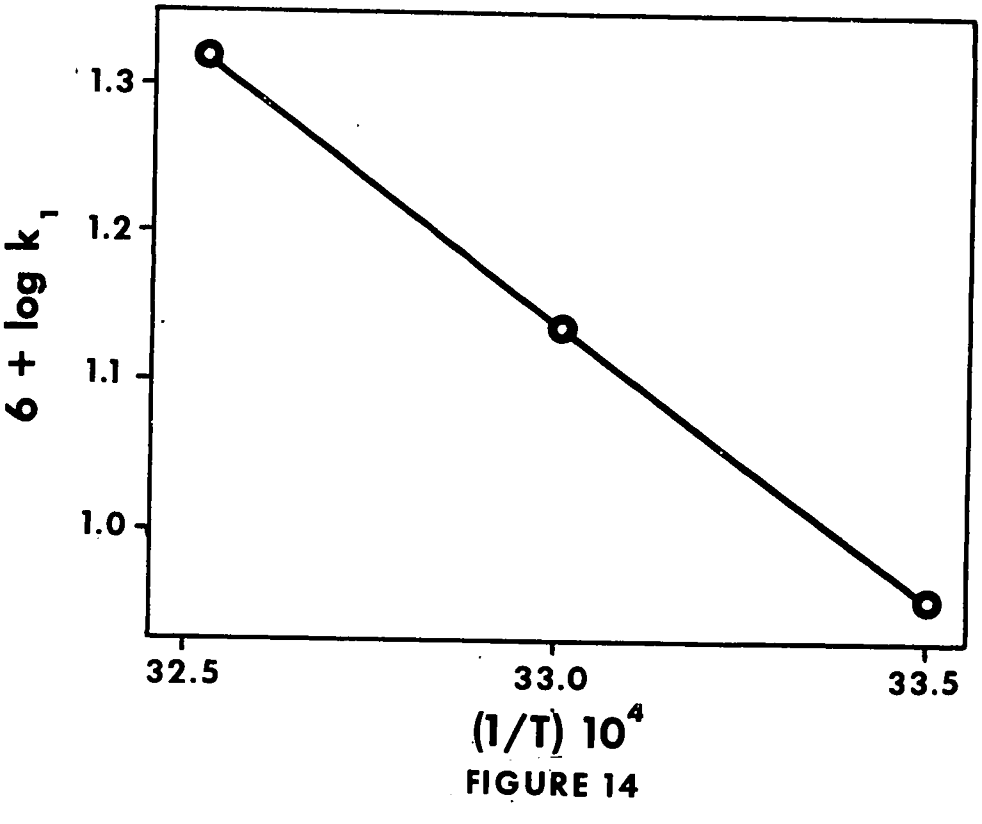


FIGURE 14

F) Rate measurements of HCN elimination from the substrate in methanol in the presence of different concentrations of HCl:

At 34.7° ± 0.10

Initial concentration of the substrate = 1.0×10^{-4} M/ℓ

l = 5mm

(i) Reactions of compound (I):

λ = 512nm

Experiment (30):-

[HCl] = 1.0×10^{-3} M/ℓ

Time in hours	(AB)	$(x)10^4$	$(a-x)10^4$	$\frac{a}{a-x}$	$\log\frac{a}{a-x}$
5	0.203	0.0933	0.9067	1.1029	0.0426
10	0.362	0.1664	0.8336	1.1996	0.0792
15	0.497	0.2284	0.7715	1.2962	0.1126
20	0.616	0.2832	0.7168	1.3951	0.1446
22.5	0.674	0.3100	0.6900	1.451	0.1620
25	0.750	0.3450	0.6550	1.528	0.1842
30	0.843	0.3880	0.6120	1.637	0.2141
35	0.964	0.4440	0.5560	1.799	0.2550

$$k_1=\frac{2.303}{60\times60}\times \text{slope}$$

$$= 4.478\times10^{-6}\ \text{sec.}^{-1}$$

Experiment (31):-

[HCl] = 1.0×10^{-4} M/ℓ

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
3	0.193	0.0889	0.911	1.098	0.0406
6	0.376	0.173	0.827	1.210	0.0828
9	0.537	0.247	0.752	1.330	0.1239
12	0.683	0.3145	0.6845	1.465	0.1629
15	0.810	0.373	0.627	1.595	0.2028
18	0.920	0.424	0.576	1.735	0.2339
21	1.010	0.465	0.535	1.870	0.2718
24	1.142	0.525	0.475	2.114	0.3251
27	1.232	0.567	0.433	2.310	0.3626

$$k_1 = \frac{2.303}{60\text{x}60} \text{ x slope}$$

$$= 8.559\text{x}10^{-6} \text{ sec.}^{-1}$$

<u>Experiment (32):-</u>

$[HCl] = 0.2x10^{-4}$ M/ℓ

Time in minutes	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
20	0.239	0.1099	0.8901	1.1235	0.0507
40	0.480	0.2207	0.7793	1.2832	0.1082
60	0.700	0.3218	0.6782	1.4745	0.1688
80	0.900	0.4138	0.5862	1.7059	0.2319
100	1.152	0.4845	0.5145	1.9411	0.2880
120	1.198	0.5509	0.4491	2.2285	0.3480
140	1.325	0.6092	0.3908	2.5588	0.4080
160	1.430	0.6575	0.3425	2.9200	0.4654

$k_1 = \frac{2.303}{60}$ x slope

$= 114.0x10^{-6}$ $sec.^{-1}$

Experiment (33):-

[HCl] = $1.333\text{x}10^{-5}$ M/ℓ

Time in minutes	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
15	0.210	0.09655	0.9035	1.1069	0.0441
30	0.418	0.1922	0.8078	1.2379	0.0927
45	0.612	0.2814	0.7186	1.3916	0.1436
60	0.794	0.3651	0.6349	1.5751	0.1973
75	0.955	0.4391	0.5609	1.7828	0.2511
90	1.085	0.4989	0.5011	1.9956	0.3011
105	1.206	0.5545	0.4455	2.2447	0.3512

$$k_1 = \frac{2.303}{60} \text{ x slope}$$

$$= 131.3\text{x}10^{-6} \text{ sec.}^{-1}$$

Experiment (34):-

$[HCl] = 1.0 \times 10^{-5}\ M/\ell$

Time in minutes	(AB)
6	0.182
12	0.363
18	0.593
24	0.805
30	1.006
36	1.203
42	1.395
48	1.573

$k_o = 2.6367 \times 10^{-8}$ mole $\ell.^{-1}$ $sec.^{-1}$

$k_1 = 263.7 \times 10^{-6}$ $sec.^{-1}$

(ii) Reactions of compound (II):

λ = 497nm

Experiment (35):-

[HCl] = $1.0\text{x}10^{-3}$ M/ℓ

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
5	0.182	0.1400	0.8600	1.1628	0.0656
10	0.337	0.2592	0.7408	1.3499	0.1303
15	0.467	0.3592	0.6408	1.5605	0.1934
20	0.577	0.4285	0.5715	1.7498	0.2430
25	0.675	0.5192	0.4808	2.0798	0.3181
30	0.758	0.5830	0.4170	2.4000	0.3802
35	0.824	0.6340	0.3660	2.7370	0.4373
40	0.884	0.6805	0.3195	3.1270	0.4952

$k_1 = \frac{2.303}{60\text{x}60}$ x slope

$= 8.050\text{x}10^{-6}$ sec.$^{-1}$

Experiment (36):-

[HCl] = 1.0×10^{-4} M/ℓ

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log\frac{a}{a-x}$
4	0.203	0.156	0.844	1.184	0.0734
8	0.373	0.287	0.713	1.402	0.1467
12	0.515	0.396	0.604	1.655	0.2188
16	0.636	0.489	0.511	1.956	0.2913
20	0.715	0.550	0.450	2.222	0.3466
24	0.828	0.637	0.363	2.758	0.4410
28	0.901	0.693	0.307	3.260	0.5132

$$k_1 = \frac{2.303}{60\times60} \times \text{slope}$$

$$= 11.76\times10^{-6} \text{ sec.}^{-1}$$

Experiment (37):-

[HCl] = 0.333×10^{-4} M/ℓ

Time in hours	(AB)
1	0.149
2	0.284
3	0.406
4	0.515
5	0.615
6	0.706
7	0.788
8	0.864
9	0.930
10	0.995

$k_o = 0.2468\times10^{-8}$ mole ℓ^{-1} $\sec^{-1}$

Calculation of k_1 for the first order part:

Time in hours	$10^4(x)$	$10^4(a)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log\frac{a}{a-x}$
0	0	0.5269	0.5269	1.000	0
1	0.070	0.5269	0.4569	1.1532	0.0618
2	0.1331	0.5269	0.3938	1.3380	0.1265
3	0.1915	0.5269	0.3354	1.5710	0.1962
4	0.2423	0.5269	0.2846	1.8514	0.2675
5	0.2923	0.5269	0.2346	2.2460	0.3514

$$k_1 = \frac{2.303}{60\times60} \times \text{slope}$$

$$= 45.11\times10^{-6} \sec^{-1}$$

Fig. (15)

Figure 15 - Zero- and first-order plots for the reaction of compound (I) in methanol in the presence of [HCl] = 0.333 x 10^{-4} mole $\ell.^{-1}$.

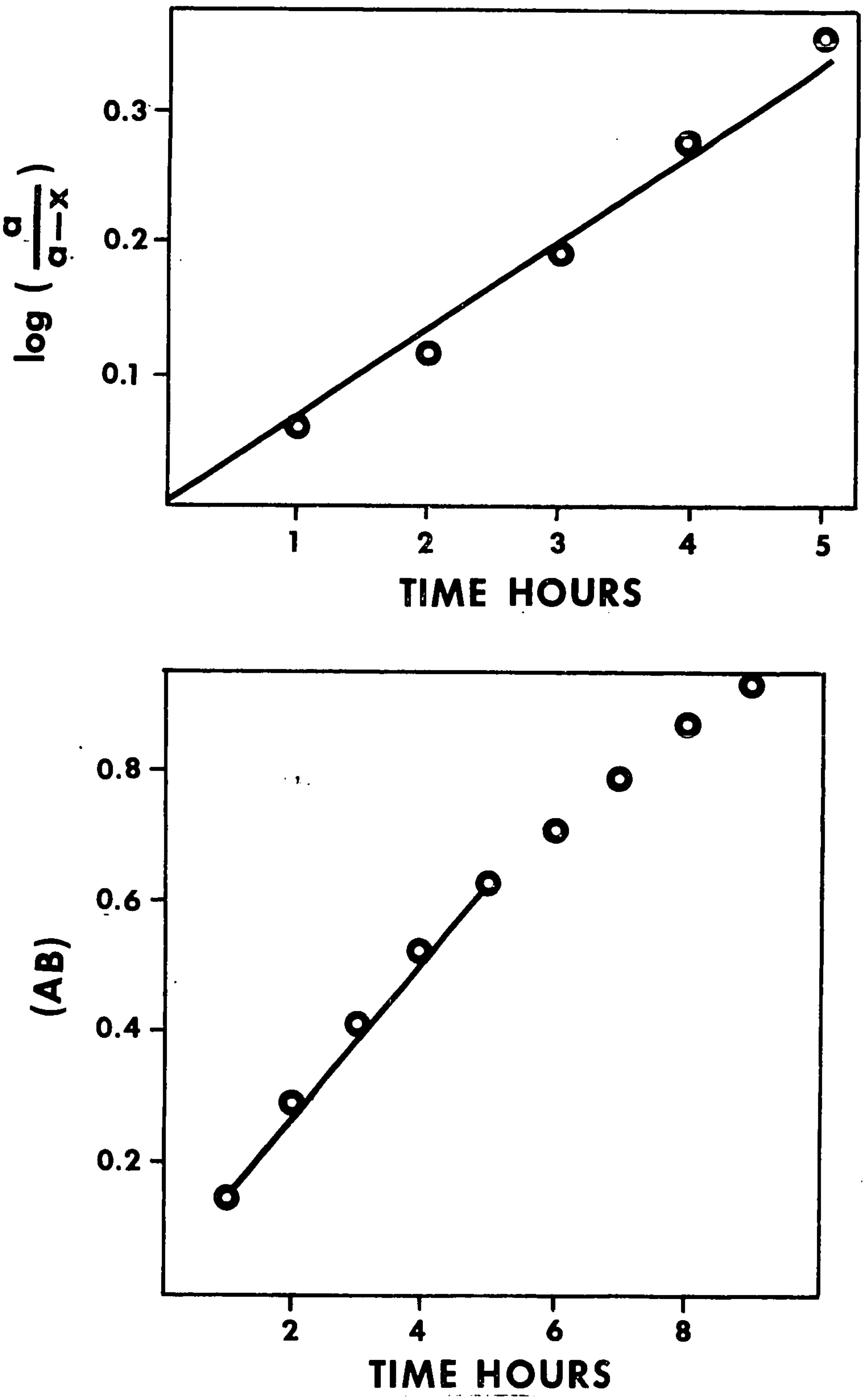


FIGURE 15

Experiment (38):-

[HCl] = 0.2×10^{-4} M/ℓ

Time in minutes	(AB)
20	0.128
40	0.282
60	0.423
80	0.554
100	0.675
120	0.790
140	0.893
160	0.987

$k_o=0.859\times10^{-8}$ mole $\ell.^{-1}$ $sec.^{-1}$

Calculation of k_1 for the first order part:

Time in minutes	$10^4(x)$	$10^4(a)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
0	0	0.4808	0.4808	1.000	0.000
20	0.0885	0.4808	0.3923	1.2256	0.0884
40	0.1677	0.4808	0.3131	1.5356	0.1863
60	0.2408	0.4808	0.2400	1.2003	0.3016

$k_1=\frac{2.303}{60}$ x slope

$=204.5\times10^{-6}$ $sec.^{-1}$

Experiment (39):-

[HCl] = 1.0×10^{-5} M/ℓ

Time in minutes	(AB)
5	0.110
10	0.245
15	0.388
20	0.532
25	0.678
30	0.824
35	0.968
40	1.108

$k_o=3.675\times10^{-8}$ mole $\ell.^{-1}$ $sec.^{-1}$

$k_1=367.5\times10^{-6}$ $sec.^{-1}$

Determination of pK_a of the substrate from the plot of log k_1 vs pH of the reaction medium.

(i) Reactions of compound (I)

[HCl] M/ℓ	pH	$10^6 k_1$ sec.$^{-1}$	6+log k_1	order
1.0×10^{-3}	3.0	4.48	0.6511	first
1.0×10^{-4}	4.0	8.56	0.9325	first
0.5×10^{-4}	4.30	18.10	1.2577	first
0.2×10^{-4}	4.70	114.0	2.0569	first
1.3×10^{-5}	4.87	131.3	2.1183	first
1.0×10^{-5}	5.0	263.7	2.4211	zero

pK_a of (I) in methanol = 4.5

Fig. (16)

Figure 16 - Variation of log k_1 with pH for the reactions of compound (I).

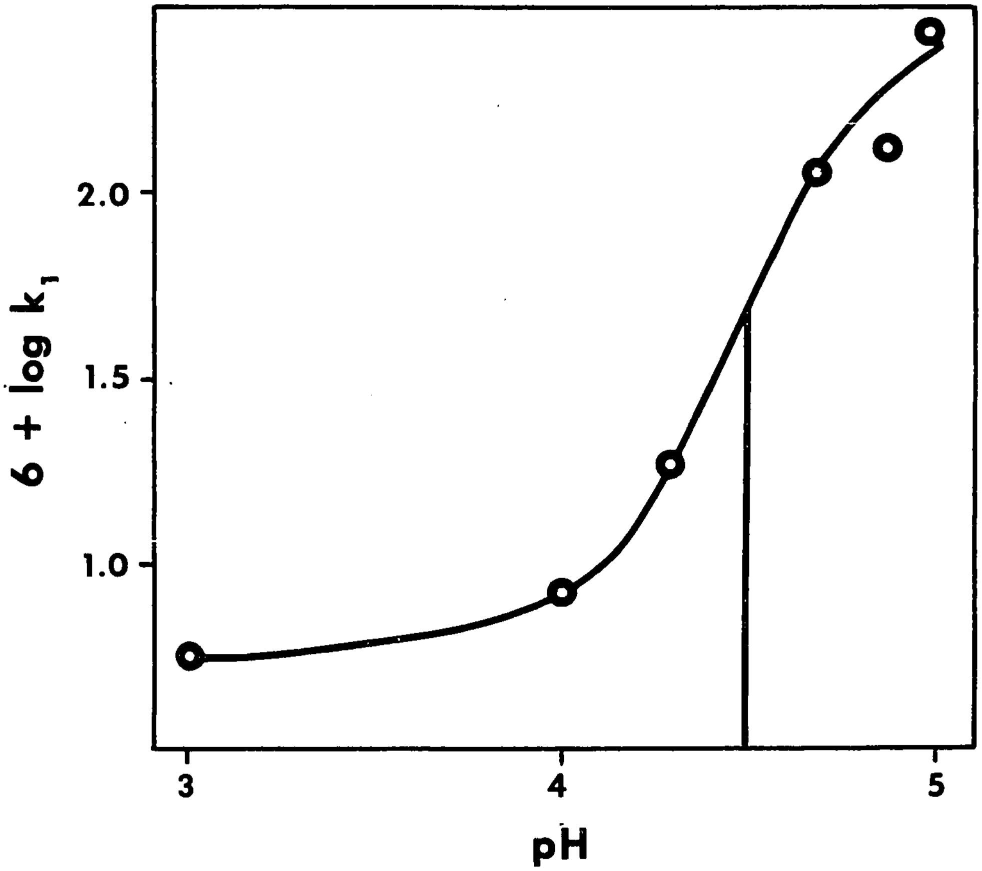


FIGURE 16

(ii) Reactions of compound (II)

[HCl] M/ℓ	pH	$10^6 k_1$ sec.$^{-1}$	6+log k_1	order
1.0×10^{-3}	3.0	8.05	0.9058	first
1.0×10^{-4}	4.0	11.76	1.0704	first
0.5×10^{-4}	4.3	27.65	1.4414	first
0.3×10^{-4}	4.48	45.11*	1.6543	zero-first
0.2×10^{-4}	4.70	204.5*	2.3107	zero-first
1.0×10^{-5}	5.0	367.5	2.5653	zero

pK_a of (II) in methanol = 4.5

Fig. (17)

* Values are taken for the first order part of the plot.

Figure 17 - Variation of log k_1 with pH for the reactions of compound (II).

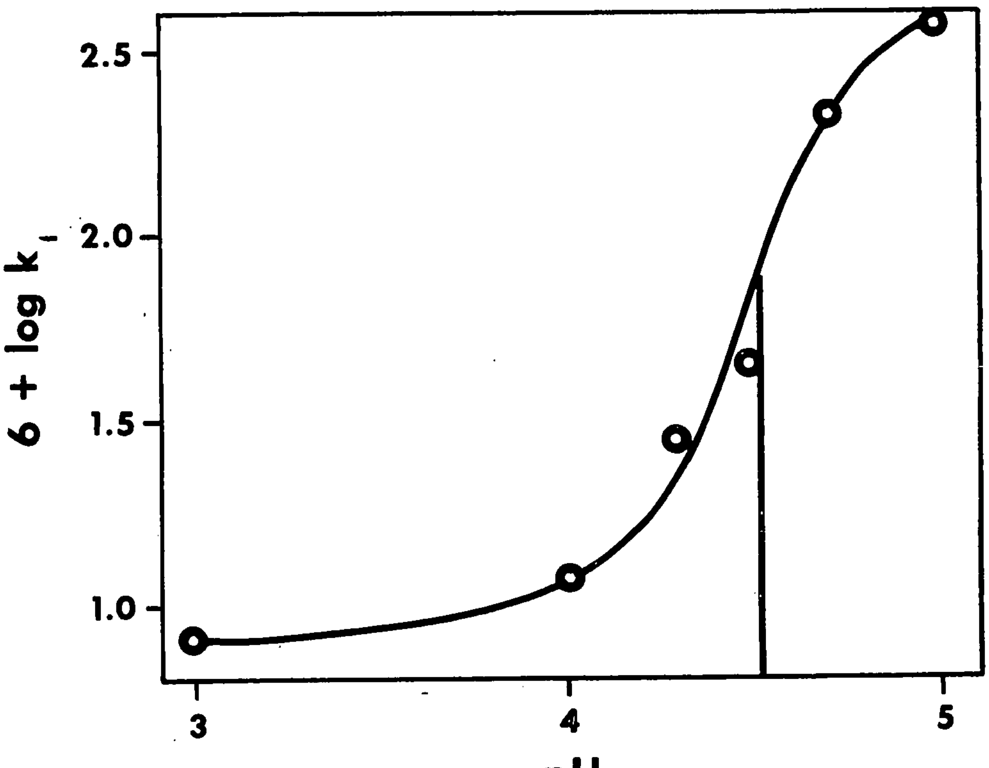
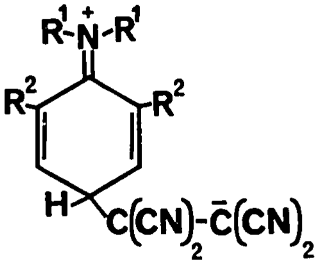


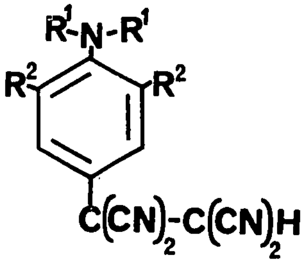
FIGURE 17

Discussion

A) Structural considerations: It was previously suggested that compound (I) has either a zwitterionic structure (11) or a neutral substituted ethane structure (12)[39]. Rappoport and Shohamy[40] proved, by studying the mass spectrum, i.r., u.v. and n.m.r. of compound (II), that it has structure (12).



11

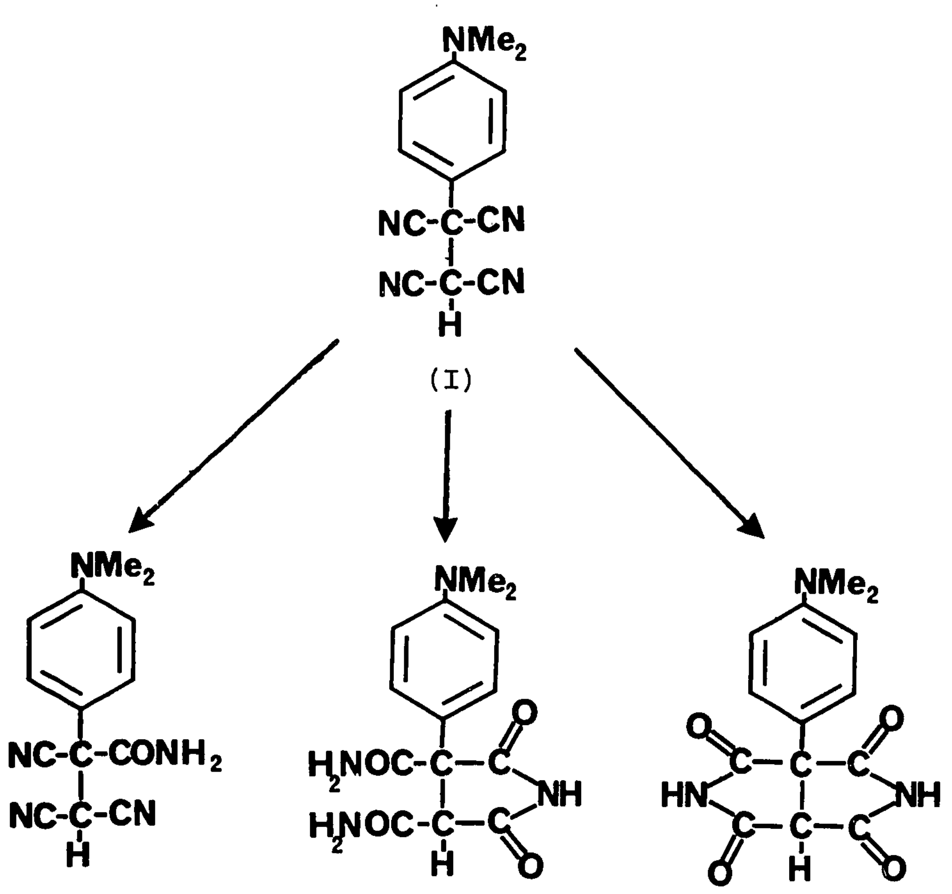


12

$R^1 = CH_3$, $R^2 = H$ compound (I)

$R^1 = H$, $R^2 = CH_3$ compound (II)

Later, Farrell and Wojtowski[38] did synthetic and spectroscopic studies on compound (I) and indicated that structure (12) is the correct one. They proved that by preparing certain derivatives, shown in the following scheme, containing the ethyl proton.



(I)

13 14 15

Hydroxylic bases slowly dissolve (I) at room temperature to yield 2,3,3-tricyano-2-(4-N,N-dimethylaminophenyl)-propionamide (13). Acid hydrolysis of (I) at room temperature results in the hydrolysis of all four cyano groups, to give 2,3-dicarbamoyl-3-(4-N,N-dimethylaminophenyl) succimide (14), which eliminates ammonia when heated to form 1-(4-N,N-dimethylaminophenyl) ethane-1,1,2,2-tetracarboxylic acid diimide (15). This also is formed directly from (I) by acid hydrolysis at 100°.

The presence of four electron-attracting cyano groups on the α- and β-ethyl carbons of compounds (I) and (II), which increase the acidity of the β-ethyl proton, combined with the fact that cyanide ion is a poor leaving group, provides an ideal system for studying, and confirming the existence, of the carbanion mechanism.

B) pK$_a$ calculations: The procedure adopted by Koshland[46], then later by Jencks and Sabato[47] was followed. The variation in rate with pH is used to determine the ionization constant of a reactant. This is particularly useful if the compound is too unstable to permit determination of its pK by ordinary methods. For a reaction in which the rate constants at pH values well above and below the pK are accurately known and there is no interference from additional kinetic terms, the pK of the reactant may be simply read from the midpoint of Δk, the difference in the rates of the reaction of the two species, in a plot of log $k_{obs.}$ against pH.

The HCN elimination reactions from (I) and from (II) were carried out in methanol in the presence of different concentrations of hydrochloric acid, ranging from [substrate]:[HCl] = 1:10 to 10:1. At these dilute concentrations of HCl [10^{-3} to 10^{-5} M/ℓ], the activity coefficient of the proton in methanol may be considered to be unity. One may therefore calculate the pH values of the solutions, knowing the exact concentration of HCl, assuming that it is completely dissociated. A plot of log k vs pH for the reaction medium has the appearance of a titration curve. The inversion point occurs at the pH corresponding to the pK$_a$ of the substrate. The pK$_a$ values calculated by this method for both compounds (I) and (II) in methanol were found to be identical (4.5). The estimated value for pK$_a$ (II) in water is 3.6[35]. pK$_a$ values of acetic acid at 25° in water, 10% and 20% aqueous methanol are 4.76, 4.90 and 5.08 respectively[48], showing that weak acids tend to be weaker in methanol than in aqueous solution. Therefore it is reasonable to find a difference in pK_a (II) = 0.9 between its value in water and that in methanol. pK_a (HCN) in water is 9.31[49]. Applying the same argument, one can calculate pK_a (HCN)-pK_a (substrate) ≈ 5.7 in methanol, suggesting that compounds (I) and (II) are much stronger acids than HCN, in methanol.

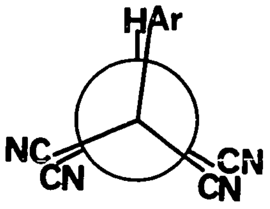
C) <u>Dipole moment measurements:</u> The dipole moment of compound (II) was measured by Rappoport[40] in dioxane at 25° and found to be 6.4D. This value may be inaccurate because dioxane is not considered one of the recommended solvents for dipole moment measurements. It has a powerful effect as an electron donor and also in the homogeneous field of a strong dipole, dioxane does not act as an unpolarised but as a quadrupolar medium[44].

Dipole moments for compounds (I) and (II) were measured at 25.0° in benzene and found to be 3.32D and 3.80D respectively.

Rappoport calculated the dipole moment of (II) by taking μ_{C-H}=0.30D and μ_{Ar}=1.63D, a 109° 28' angle of H and Ar with the central carbon-carbon bond, and assuming that the dipole moment of Ar is directed along the para-carbon nitrogen axis. $\mu_{[CH(CN)_2]}$=3.59D in the direction of the bisector was assumed, based on the observed value (3.59D) for malononitrile. Vectorial addition gave equation (15) where μ is the absolute value of the dipole moment for each conformer and α is the dihedral

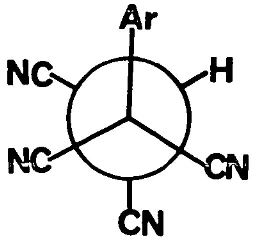
$$\mu = 5.36\sqrt{(1.06+\cos.\ \alpha)} \qquad (15)$$

angle between the projected planes of the two carbon atoms, being 0° in the eclipsed conformer (IIa). Calculated dipole moments for the two eclipsed (IIa, IIc), the gauche (IIb) and the trans-(IId) conformers are shown on the next page.



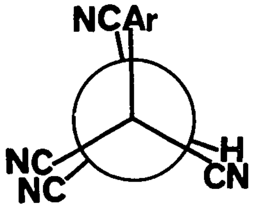
(IIa) α = 0°

μ = 7.7D



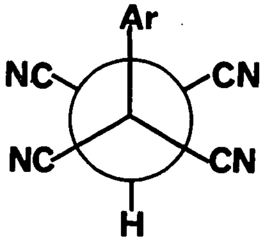
(IIb) α = 60°

μ = 6.7D



(IIc) α = 120°

μ = 4.0D



(IId) α = 180°

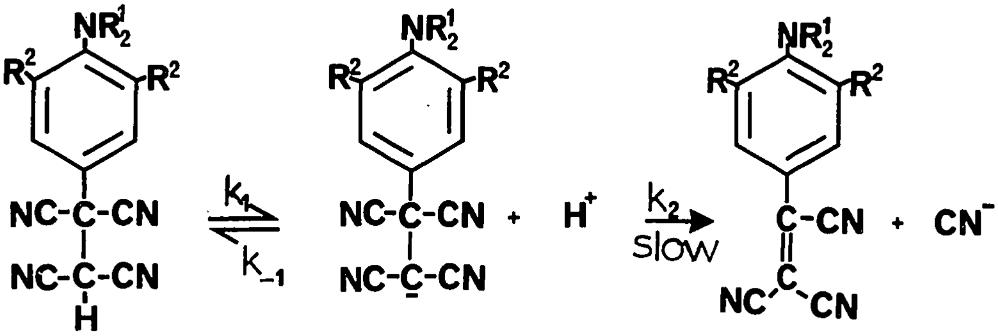
μ = 1.33D

The average value of the calculated dipole moments of the four conformers is 4.93D. The average value of the calculated dipole moments of conformers (IIb) and (IId) is 4.01D, which is closer to the experimental result for compound II, 3.80D. This suggests that the gauche (IIb) and (IId) conformers are more populated than the other eclipsed conformers. It further suggests that free rotation around the ethyl C-C bond is unrestricted and that conformer (IIb) is not the preferred one as was predicted by Rappoport[40].

D) Reaction and mechanism: The fact that there is no HCN elimination from substrate (I) in aprotic solvents, irrespective of the value of the dielectric constant, can be adduced as evidence that the reaction proceeds via an ElcB mechanism[40,41,50]. This also raises questions about the role of the conjugate base of the solvent as a species which can accelerate the proton-abstraction step, even though the pK_a of methanol is 15.

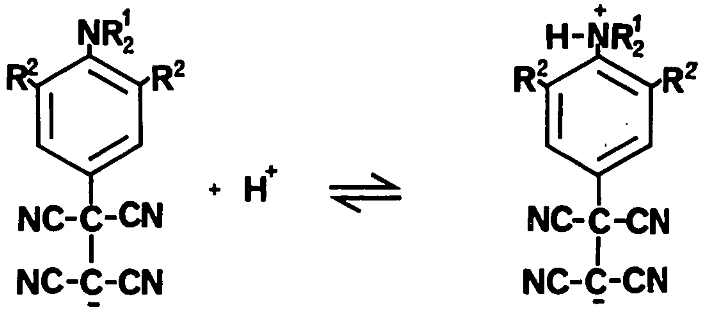
In pure methanol, the reaction was zero-order within the run to more than 80%, then deviation towards first-order behaviour was observed. Within a set of runs, for different concentrations of the substrate, the reaction was found to be first-order in the substrate. In acetone and in the presence of methanol in concentrations comparable to that of the substrate, a fractional-order in methanol, (0.276 and 0.209) for compounds (I) and (II) respectively, was observed, which indicates that methanol may act as a catalyst for HCN elimination reaction. In methanol as solvent, (dielectric constant = 30.15 at 35°) the formation of the conjugate base of the substrate in a large steady state concentration is enhanced and this is reflected by the pK_a value of 4.5. The carbanion formed is stabilised by the presence of the electron attracting cyanide groups. Therefore, the first step is a rapidly attained equilibrium which is highly shifted to the right. The second, rate determining, step is the departure of the cyanide ion. k_{-1} was found to be higher than k_2

(see below) as shown by the fact that the rate of hydrogen-deuterium exchange is much faster than elimination[51]. The following scheme illustrates a possible mechanism.



(16)

The proton may be solvated by methanol, revert to the starting material or form the zwitterion:



(17)

The positive charge on the amino nitrogen will help to stabilise the carbanion intermediate. Factors which will determine the reaction of the proton are the pK_a of $Me\overset{+}{O}H_2$, pK_a of the substrate and the pK_a of the zwitterion. The pK_a of $Me\overset{+}{O}H_2$ is -2,[48],i.e. it is a very strong acid. The presence of strong electron withdrawing group in the para position of the anilinium ion increases its acidity[48]. Therefore, the pK_a of the zwitterion from (I) is less (stronger acid) than the

pK_a of N,N-dimethylanilinium ion (5.1 in water[48]), and also the pK_a of the zwitterion from (II) will be less than that of the 2,6-dimethylanilinium ion (3.95 in water[48]). Since the pK_a of the substrate in methanol is ca. 4.5, the equilibrium shown above is most likely to compete with that shown in equation (16).

In this mechanism, the starting material is used only as a reservoir to maintain the concentration of the carbanion (or zwitterion) constant.

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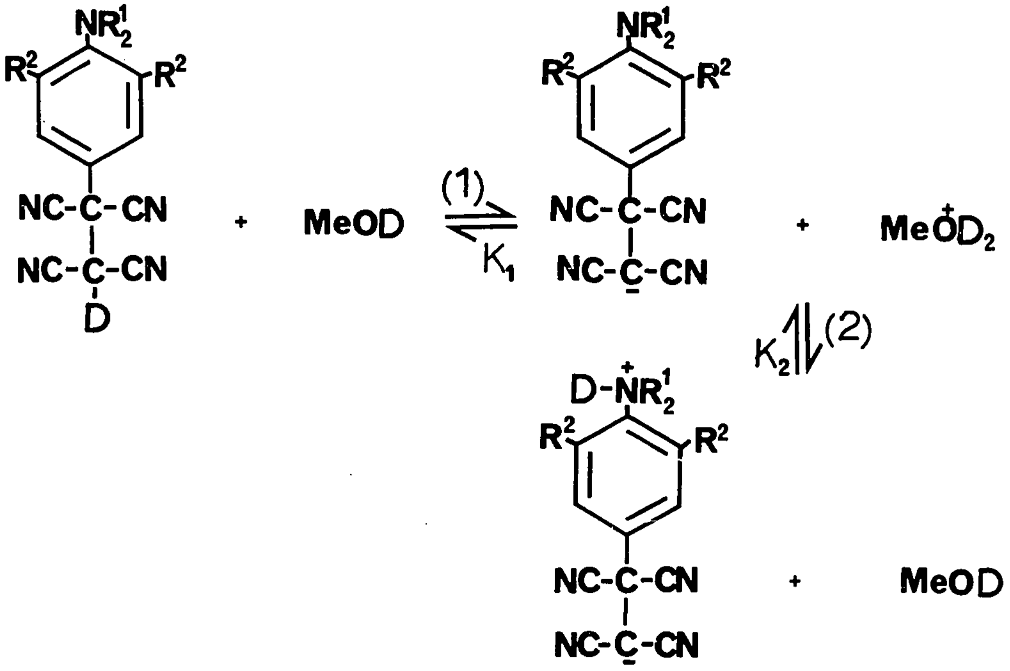
In this mechanism, the starting material is used only as a reservoir to maintain the concentration of the carbanion (or zwitterion) constant.

E) Kinetic isotope effects: The rates of DCN elimination from deuterated compounds (I-D) and (II-D) were measured in methan($^2H_1$)ol. The isotope effects, k_H^H/k_D^D, were found to be 0.329 and 0.489 for compounds (I) and (II) respectively. Rappoport[33] argued that there should be no kinetic hydrogen isotope effect for a type-II ElcB mechanism because the C-H bond-breaking is not involved in the rate determining step. Inverse kinetic hydrogen isotope effects have, however, been observed for ElcB type-II eliminations in other systems. Thus, Fedor[52] found that for the elimination of methanol from 4-methoxy-2-butanone and from 4-methoxy-4-methyl-2-pentanone, k_H^H/k_D^D = 0.87 and 0.77 respectively. Similarly, elimination of phenol from 2-phenoxyethyldimethylsulphonium iodide and 2-phenoxyethylsulphoxide gave k_H^H/k_D^D = 0.66 and 0.78 respectively[53]. In earlier work, Bird and Stirling[54] studied the elimination of HCl from aryl 3-chloropropyl sulphones with t-butoxide in t-butanol and found k_H^H/k_D^D = 0.5. The latter authors argued that this value eliminated the possibility of an E2 mechanism in their system and is a result of a solvent isotope effect. In all of the above mentioned cases, inverse isotope effects were interpreted on the basis of rapid internal return of the lyate ion between the labelled and the unlabelled solvents. This interpretation is not valid for this work because the elimination is carried out in pure methanol.

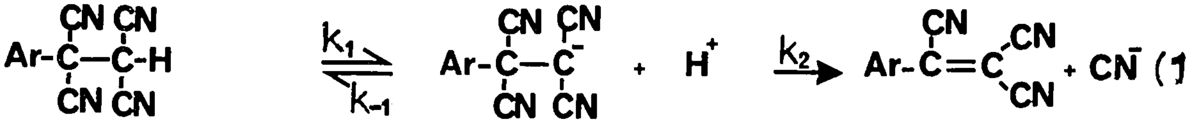
If there is a rapid equilibrium, in which a reactant is converted to its conjugate acid, the latter intermediate will generally be present in higher equilibrium concentration in the deuterated solvent as the dissociation of weak acids is generally smaller in the heavy medium[55]. For example, in aqueous systems the dissociation constants of acids are about four times as large in water as in deuterium oxide[54]. One might then expect a lower concentration of the carbanion in the deuterated than in the nondeuterated solvent and therefore a lower rate of elimination, opposite to what is observed. If the reactant-carbanion equilibrium is the controlling factor, then any kinetic hydrogen isotope effects should be the same for compounds (I) and (II), as they have identical pK_a's. This is not observed. A second possible equilibrium (2) involving the carbanion is shown below:



This equilibrium will be rapidly attained because proton (or deuterium) transfer is a diffusion controlled process . If (2) is the dominant equilibrium in the deuterated solvent, then the concentration of the substrate in the carbanion form could be higher than that in the protonated solvent. The rate determining step will still be cyanide-ion elimination from the carbanion and not from the zwitterion.

Measurements of the pK_a's of the deuterated substrates in deuterated methanol using the same technique adopted for pK_a measurements of the nondeuterated substrates will not be helpful in interpretation of the inverse kinetic hydrogen isotope effects. In the presence of H^+ (or D^+) the reaction is first-order and thus K_1 will be measured. This should be smaller in the deuterated than in the nondeuterated solvent. It will be of interest in the future to compare the pK_a's of deuterated and the nondeuterated compounds in pure methanol, pure methan($^2H_1$)ol and mixtures of them to study the solvent isotope effect on the pK_a's of these and other similar systems.

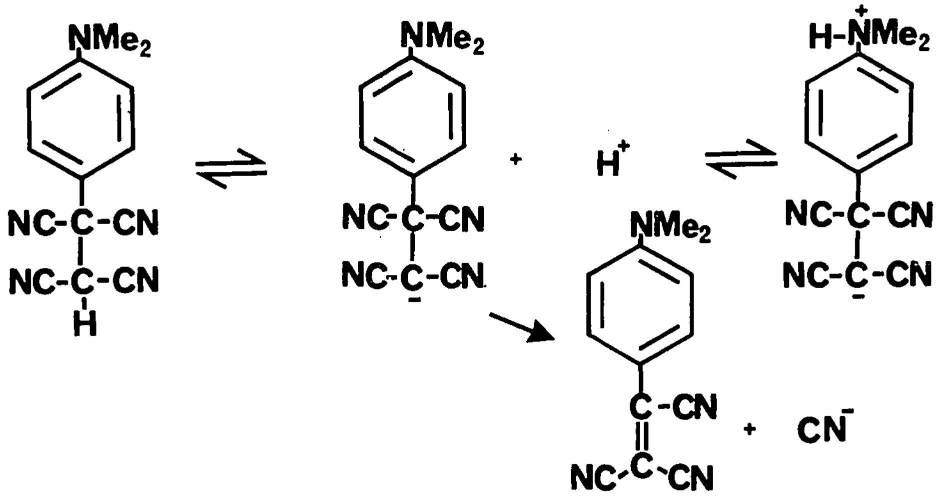
F) <u>Acid catalysis</u>: If the suggested mechanism is correct, one would observe a change in rate and in order on changing the hydrogen ion concentration in the reaction medium.



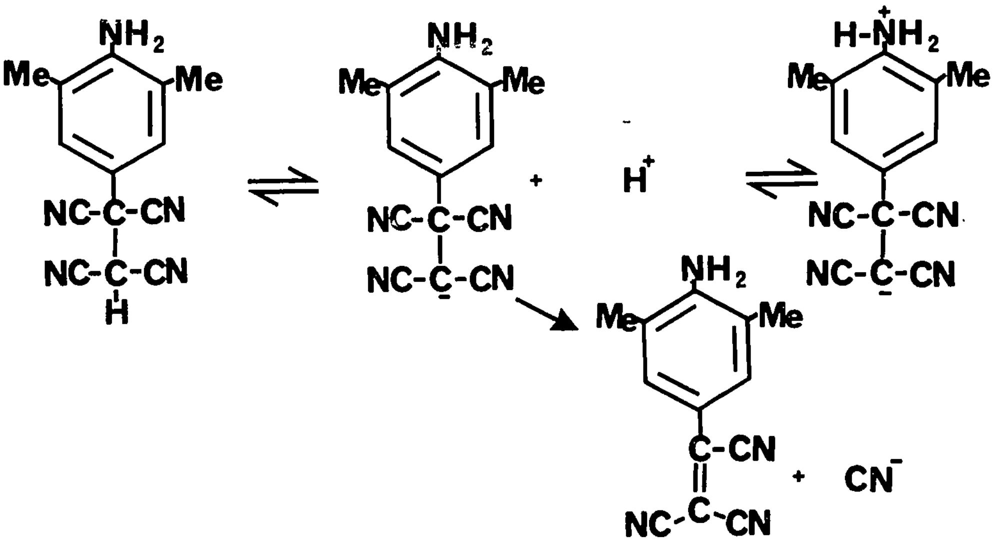
$$\mathrm{Ar{-}C(CN)_2{-}C(CN)_2{-}H} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ar{-}C(CN)_2{-}C^{-}(CN)_2} + \mathrm{H^+} \xrightarrow{k_2} \mathrm{Ar{-}C(CN){=}C(CN)_2} + \mathrm{CN^-} \quad (18)$$

According to Le Chatelier's principle, an increase in hydrogen ion concentration will shift the equilibrium to the left. This will have two effects: (1) a decrease in the rate of elimination, which is directly dependent on the carbanion concentration, and (2) a change in the elimination reaction from zero- to first-order kinetics, because of the lower steady-state concentration of the carbanion "or zwitterion".

A series of experiments were carried out in which increasing amounts of HCl were added to the reaction medium. The range of [substrate] : [HCl] was 10:1 to 1:10, i.e. two pH units. At the lowest hydrogen ion concentration,([substrate] : $[H^+]$ = 10:1) the rates for compounds (I) and (II) respectively were 0.525 and 0.615 times slower than the corresponding rates in pure methanol, but the reaction was still zero-order within the run. At the highest hydrogen ion concentration, ([substrate] : $[H^+]$ = 1:10) the rates for compounds (I) and (II) respectively were 8.92×10^{-3} and 13.5×10^{-3} times slower than the corresponding rates in pure methanol. In those cases, the reactions were first-order within the run. Within that range of hydrogen ion concentration a gradual decrease in rate with increasing concentration was observed. The reaction kinetics changed sharply from zero-order at $[H^+] = 1.0 \times 10^{-5}$ to first-order at $[H^+] = 1.333 \times 10^{-5}$ for compound (I), and continued as a first-order reaction at higher hydrogen ion concentration. The situation is slightly different for compound (II) as, instead of a sharp change in order, a gradual change from zero-order at $[H^+] = 1.0 \times 10^{-5}$ to first-order at $[H^+] = 0.5 \times 10^{-4}$ and higher was observed. There was thus a zone between $[H^+] = 0.2 \times 10^{-4}$ and $[H^+] = 0.333 \times 10^{-4}$ in which the reaction exhibited mixed-order kinetics. This difference in behaviour of the two compounds may be explained by the following considerations:



(19)



(20)

The presence of the zwitterion is enhanced by the relatively highly polar medium. In water, at 25° the pK_a of N,N-dimethylanilinium ion is 5.1[48] and that of 2,6-dimethylanilinium ion is 3.95[48]. This suggests a similar $\Delta pK_a \approx 1$ will exist between zwitterion from (I) and (II). Thus, the zwitterion from (II) should be a stronger acid than that from (I). Since the elimination of cyanide ion needs a higher concentration of negative charge on the β-carbon, this should occur via the carbanion rather than via the zwitterion. The carbanion from (II) will be in higher concentration than that from (I), and it is reasonable that compound (II) should react faster than compound (I). This is supported by the observation that, at pH = 4.699, the first-order rate constant of the elimination reaction of compound (II) is 1.79 times higher than that of compound (I).

TABLE (1)

HCN Elimination from (I) and from (II) in methanol

	25.4° 10^4k_1	30° 10^4k_1	34.7° 10^4k_1	E_a	$\Delta S^{\neq}$ a
1) In pure methanol					
I	1.504	2.745	5.013	24.43	-16.36
II	2.173	3.562	5.949	20.44	-28.87
2) In methanol and HCl (0.5×10^{-4} M/ℓ)					
I	0.0612	0.1039	0.1810	22.05	-22.05
II	0.0902	0.1380	0.2765	22.67	-14.50

First-order rate constants, k_1, are in sec.$^{-1}$ Activation energies, E_a are in kcal/mole. Entropies of activation, $\Delta S^{\neq}$, are in cal/mole/degree.

a $\Delta S^{\neq}/4.576 = \log_{10}k - 10.753 - \log_{10}T + (E_a/4.576T)$

G) Activation parameters: In table (1), the entropies of activation are highly negative and are more negative, for compound (II) than for compound (I). Hence the transition state from (II) has fewer degrees of freedom than that from (I), when compared with their ground states. This suggests the accumulation of negative charge in transition state from (II) is greater than that in the transition state from (I) and hence solvation of the former will be more favourable.

The highly negative entropies of activation are expected for both pre-equilibrium and type-II ElcB mechanisms. The transformation of p-nitrobenzyl chloride into p,p`-dinitrostilbene proceeds via the formation of a chlorocarbanion which reverts back to the original chloride faster than losing a chloride ion to give a carbene, and hence the stilbene. $\Delta S^{\neq}$ for this pre-equilibrium ElcB mechanism is -19.5 e.u.[56]

Rappoport[35] reported $\Delta S^{\neq}$ = -10.0 e.u. for the base initiated HCN elimination from compound (II) in chloroform which proceeds via a type-II ElcB mechanism. Our values are between ∿1.5-4 times his value and the greater difference is in solvation of the transition state.

Bordwell[36] studied the base-initiated elimination of methanol and acetic acid from several nitrocyclopentane derivatives in methoxide/methanol medium and found for these ElcB reactions that $\Delta S^{\neq}$ = -0.2 to -14.0 e.u.

Fedor[24] studied the base initiated elimination of methanol from two β-methoxy ketones in hydroxide/water medium in which $\Delta S^{\neq}$ for these reactions was -11.5 e.u. He suggested that the pre-equilibrium ElcB mechanism is the most probable pathway.

The energies of activation, in table (1), show that the transition state from (II) can be reached more easily than that from (I). This may be due to the fact that accumulation of the negative charge on the β-carbon of (II) is more favourable than that on the β-carbon of (I). The values found here range between 22.7 and 24.4 kcal/mole.

Rappoport[35b] suggested the value of 18.7 kcal/mole for the C-CN bond breaking, the same value that he obtained for the HCN elimination from (II) in chloroform. Bordwell[36] found a range of E_a values from 13.1 to 25.0 kcal/mole for base initiated methanol and acetic acid eliminations from nitrocyclopentane derivatives.

PART II :

Introduction

EFFECT OF PROTIC AND DIPOLAR-APROTIC SOLVENTS ON REACTION RATES

Protic solvents, such as fluoro-alcohols, hydrogen fluoride, water, methanol, formamide and ammonia are strong hydrogen-bond donors. Dipolar aprotic solvents are generally only weak hydrogen bond donors[57]. Solvents with hydrogen bound to carbon are poor hydrogen bond donors, normally weakly acidic and exchange very slowly, if at all, with D_2O. Solvents with hydrogen bound to more electronegative atoms, such as oxygen or nitrogen, exchange rapidly and form strong hydrogen bonds with suitable acceptors[58]. Only solvents of dielectric constant greater than ca. 15 are considered as dipolar aprotic solvents. This arbitrary choice[57] is made because in solvents of lower dielectric constant ion aggregation is so extensive that it becomes very difficult to observe the behaviour of solvent-separated ions. Common dipolar aprotic solvents[59] are dimethyl formamide (DMF), dimethyl acetamide (DMAC), dimethyl sulfoxide (DMSO), acetone, nitromethane, nitrobenzene, acetonitrile, benzonitrile, sulfur dioxide and propylene carbonate[60].

$$\overset{-}{Y}: + RX \rightleftharpoons [YR\overset{-}{X}]^{\neq} \longrightarrow \text{Products of substitution, elimination or addition} \qquad (21)$$

The distinction between protic and dipolar aprotic solvents, insofar as they influence rates of reaction (equation 21), is a sharp one[61]. Thus although N-methylformamide is one of the less protic solvents and nitromethane is one of the less dipolar aprotic solvents, many reactions (equation 21) are more than

100 times faster in nitromethane than in N-methylformamide[62]. The degree of solvent structure is often related to the ability of the solvent molecules to donate and accept hydrogen bonds, so that structure-making and structure-breaking interactions may be indirectly responsible for some of the protic-dipolar aprotic effects on rate[63].

The bulk properties as measured, the dielectric constant, molar polarisation and dipole moment of a solvent indicate how strongly it may interact electrostatically with a solute on the molecular level. One might therefore expect to find that the electrostatic interactions with a polar solvent decrease in the order:

$$\mathrm{DMF} > \mathrm{DMSO} > \mathrm{CH_3CN} > \mathrm{HCONH_2} > \mathrm{H_2O} > \mathrm{CH_3OH}$$

The important consideration is whether a solvent can effectively align its dipoles to obtain the maximum favourable interaction with a solute[64]. The positive hydrogen, in water, fits more closely about a negative centre than would positive charge localized on the nitrogen in DMF. The negative centre in DMSO is on a less hindered oxygen than that in methanol and interacts more strongly with positive centres.

Dispersion interactions are indicated by molecular polarizability and these are in the order[65]:

$$\mathrm{DMSO},\ \mathrm{DMF} > \mathrm{CH_3CN} \simeq \mathrm{HCONH_2} > \mathrm{CH_3OH} > \mathrm{H_2O}$$

Comparison of solvation of transition states with that of model solutes assumes that the former are in equilibrium with their surroundings. Ritchie, Skinner and Bodding[66] have pointed out that considerable solvent reorganization accompanies the progress from reactant to transition state. This assumption leads to a consistent model for the effects of solvents upon reaction rates.

Transition state structures may change more drastically with solvent transfer than do stable species, because a transition state can, in principle, exist at any point along the reaction coordinate. Its position should therefore change with solvent transfer[67].

Since anions, or intermediates of anionic characters, are of importance in this work, it is necessary to consider the effect of solvent variables, such as hydrogen-bonding capability, polarizability and dielectric constant on the solvation process of anions. It is almost impossible to completely isolate the effect of any one of these variables on the solvation process from the others, but generalisations as to how they affect the solvation process can be made.

Hydrogen bonding between solvent molecules and anions is highly dependent upon the size of the latter. A negative charge on a small atom, especially a first-row atom, which does not have electron-withdrawing substituents also attached to itself, results in an anion which is a strong hydrogen bond acceptor. Examples of this type are F^-, RO^-, Cl^-, R_2N^-, R_3C^-. Such anions have strong general hydrogen bonding interactions, rather than specific 1:1 interactions, with protic solvents[68]. Such interactions are absent in dipolar aprotic solvents. Dispersal of charge by electron-withdrawing groups or localization of charge on large atoms, e.g. I^-, produces anions which are weak hydrogen-bond acceptors. Such anions are less solvated by protic solvents than those in which the charge is highly localized.

Mutual polarizability plays an important role in solvating some anions in dipolar aprotic solvents. The latter are much more polarizable, in general, than protic solvents, so that strong solute-solvent interaction is possible for polarizable anions, I^-, ^-SCN in these solvents. This is one reason why anions such as picrate are more solvated by dipolar aprotic than by protic solvents. Therefore, in general, carbanions of high polarizability will be solvated better by dipolar aprotic solvents.

Ion-dipole electrostatic interactions are related to the solvent dielectric constant and the charge density of the anion[69]. In general, small anions with localized charge are more solvated in all solvents relative to the gas phase than are large anions, especially those with dispersed charge. Water and formamide have dielectric constant values of 78.5 and 109.5 respectively, at 25°, and thus solvate anions much more strongly than do solvents of lower dielectric constant. The electrostatic interaction between solute and solvent may be assumed to be similar for methanol and DMF because these solvents have similar dielectric constants, 32.6 and 36.7 respectively at 25°.

The products of an elimination reaction can sometimes be changed in a predictable way by changing the solvent, i.e. by changing the structure of the transition state. Froemsdorf and McCain[70] studied the products of the base-catalysed elimination of p-toluenesulfonic acid from different substrates in dimethyl sulfoxide and compared them with products obtained from the same reaction in ethanol. The results obtained demonstrated that it is possible in some elimination reactions to change from essentially Saytzeff products to Hofmann products without changing any of the steric requirements of base, leaving group or alkyl groups.

In part one it was concluded that compounds (I) and (II) eliminate HCN in pure methanol via an ElcB type-II elimination mechanism in which the cyanide ion is eliminated in a slow, rate determining, step. It was also found that compounds (I) and (II) did not eliminate HCN in dipolar aprotic solvents, presumably because of the instability of the carbanions in these media. Much work has been reported on the stability of carbanions in different media , but little on the effect of change from polar protic to dipolar aprotic solvent on the carbanion mechanism of elimination. This part is composed of two separate reactions. The first deals with the relationship between the rate of reaction and the change in dielectric constant function. The second section is an attempt to correlate the change in the rate of HCN-elimination with solvent composition and substrate structure.

Data

A) Rate measurements in benzene/methanol mixtures at 34.7°:

(i) Reactions of Compound (I):

Initial concentration of the substrate = 1.0×10^{-4} M/ℓ

l = 5mm

λ = 512nm.

Experiment (1):-

[MeOH] = 85% (by volume)

Time in minutes	(AB)
3	0.178
6	0.341
9	0.510
12	0.688
15	0.868
18	1.052
21	1.235
24	1.412
27	1.585

$k_o=4.539\times10^{-8}$ mole ℓ^{-1} sec^{-1}

$k_1=4.539\times10^{-4}$ sec^{-1}

Experiment (2):-

[MeOH] = 70%

Time in minutes	(AB)
5	0.220
10	0.457
15	0.700
20	0.945
25	1.200
30	1.445
35	1.675

$k_o=3.716\times10^{-8}$ mole ℓ^{-1} sec^{-1}

$k_1=3.716\times10^{-4}$ sec^{-1}

Experiment (3):-

[MeOH] = 50%

Time in minutes	(AB)
5	0.125
10	0.300
15	0.487
20	0.675
25	0.868
30	1.078
35	1.257
40	1.436
45	1.620

$k_o = 2.891 \times 10^{-8}$ mole $\ell.^{-1}$ $sec.^{-1}$

$k_1 = 2.891 \times 10^{-4}$ $sec.^{-1}$

Experiment (4):-

[MeOH] = 30%

Time in minutes	(AB)
6	0.150
12	0.342
18	0.533
24	0.730
30	0.925
36	1.115
42	1.300
48	1.490

$k_o = 2.444 \times 10^{-8}$ mole $\ell.^{-1}$ $sec.^{-1}$

$k_1 = 2.444 \times 10^{-4}$ $sec.^{-1}$

Experiment (5):-

[MeOH] = 10%

Time in minutes	(AB)
20	0.224
40	0.430
60	0.643
80	0.861
100	1.062
120	1.274
140	1.480
150	1.584

k_o=0.800x10^{-8} mole ℓ.$^{-1}$ sec.$^{-1}$

k_1=0.800x10^{-4} sec.$^{-1}$

Experiment (6):-

[MeOH] = 5%

Time in minutes	(AB)
20	0.208
40	0.385
60	0.566
80	0.744
100	0.922
120	1.086
140	1.251
160	1.411
180	1.565

k_o=0.6475x10^{-8} mole ℓ.$^{-1}$ sec.$^{-1}$

k_1=0.6475x10^{-4} sec.$^{-1}$

(ii) Reactions of Compound (II):

Initial concentration of the substrate = 1.0×10^{-4} M/ℓ

l = 5mm. λ = 496nm.

<u>Experiment (7):-</u>

[MeOH] = 85% (by volume)

Time in minutes	(AB)
3	0.100
6	0.204
9	0.317
12	0.432
15	0.548
18	0.665
21	0.782
24	0.902

$k_o=5.000\times10^{-8}$ mole ℓ^{-1} sec^{-1}

$k_1=5.000\times10^{-4}$ sec^{-1}

<u>Experiment (8):-</u>

[MeOH] = 70%

Time in minutes	(AB)
3	0.100
6	0.202
9	0.316
12	0.430
15	0.543
18	0.660
21	0.776
24	0.892

$k_o=4.900\times10^{-8}$ mole ℓ^{-1} sec^{-1}

$k_1=4.900\times10^{-4}$ sec^{-1}

Experiment (9):-

[MeOH] = 50%

Time in minutes	(AB)
5	0.108
10	0.224
15	0.345
20	0.463
25	0.580
30	0.700
35	0.823
40	0.942

$k_o = 3.068 \times 10^{-8}$ mole $\ell.^{-1}$ sec.$^{-1}$

$k_1 = 3.068 \times 10^{-4}$ sec.$^{-1}$

Experiment (10):-

[MeOH] = 30%

Time in minutes	(AB)
7	0.142
14	0.284
21	0.424
28	0.561
35	0.701
42	0.843
49	0.985

$k_o = 2.560 \times 10^{-8}$ mole $\ell.^{-1}$ sec.$^{-1}$

$k_1 = 2.560 \times 10^{-4}$ sec.$^{-1}$

Experiment (11):-

[MeOH] = 10%

Time in minutes	(AB)
20	0.138
40	0.276
60	0.422
80	0.565
100	0.707
120	0.852
140	0.990

$k_o=0.9083\text{x}10^{-8}$ mole $\ell.^{-1}$ sec.^{-1}

$k_1=0.9083\text{x}10^{-4}$ sec.^{-1}

Experiment (12):-

[MeOH] = 5%

Time in minutes	(AB)
40	0.155
80	0.285
120	0.413
160	0.543
200	0.672
240	0.802
270	0.902

$k_o=0.4133\text{x}10^{-8}$ mole $\ell.^{-1}$ sec.^{-1}

$k_1=0.4133\text{x}10^{-4}$ sec.^{-1}

(B) Rate measurements in acetonitrile/methanol mixtures at 34.7°

(i) Reactions of Compound (I):

Initial concentration of the substrate = $1.0\text{x}10^{-4}$ M/ℓ

1 = 5mm.

λ = 512nm.

Experiment (13):-

[MeOH] = 90% (by volume)

Time in minutes	(AB)
4	0.148
8	0.338
12	0.530
16	0.722
20	0.920
24	1.110
28	1.295
32	1.452
36	1.580

$k_\circ=3.662\text{x}10^{-8}$ mole $\ell.^{-1}$ sec.^{-1}

$k_1=3.662\text{x}10^{-4}$ sec.^{-1}

Experiment (14):-

[MeOH] = 80%

Time in minutes	(AB)
5	0.189
10	0.379
15	0.568
20	0.757
25	0.946
30	1.135
35	1.325
40	1.514

$k_\circ=2.905\text{x}10^{-8}$ mole $\ell.^{-1}$ sec.^{-1}

$k_1=2.905\text{x}10^{-4}$ sec.^{-1}

Experiment (15):-

[MeOH] = 60%

Time in minutes	(AB)
8	0.220
16	0.441
24	0.661
32	0.881
40	1.102
48	1.322
56	1.542
64	1.762

$k_o = 2.119 \times 10^{-8}$ mole $\ell.^{-1}$ sec.$^{-1}$

$k_1 = 2.119 \times 10^{-4}$ sec.$^{-1}$

Experiment (16):-

[MeOH] = 50%

Time in minutes	(AB)
10	0.210
20	0.452
30	0.680
40	0.895
50	1.135
60	1.341
70	1.580

$k_o = 1.750 \times 10^{-8}$ mole $\ell.^{-1}$ sec.$^{-1}$

$k_1 = 1.750 \times 10^{-4}$ sec.$^{-1}$

Experiment (17):-

[MeOH] = 40%

Time in minutes	(AB)
10	0.222
20	0.430
30	0.628
40	0.818
50	0.996
60	1.190
70	1.375
80	1.580

k_o=1.456x10^{-8} mole ℓ.$^{-1}$ sec.$^{-1}$

k_1=1.456x10^{-4} sec.$^{-1}$

(ii) Reactions of Compound (II):

Initial concentration of the substrate = 1.0×10^{-4} M/ℓ

l = 5mm.

λ = 496nm.

Experiment (18):-

[MeOH] = 90% (by volume)

Time in minutes	(AB)
3	0.074
6	0.177
9	0.294
12	0.408
15	0.568
18	0.688
21	0.810
24	0.940

$k_o=5.435\times10^{-8}$ mole ℓ^{-1} sec.$^{-1}$

$k_1=5.435\times10^{-4}$ sec.$^{-1}$

Experiment (19):-

[MeOH] = 80%

Time in minutes	(AB)
4	0.122
8	0.255
12	0.394
16	0.533
20	0.675
24	0.823
28	0.983

$k_o=4.583\times10^{-8}$ mole ℓ^{-1} sec.$^{-1}$

$k_1=4.583\times10^{-4}$ sec.$^{-1}$

Experiment (20):-

[MeOH] = 60%

Time in minutes	(AB)
6	0.137
12	0.275
18	0.410
24	0.546
30	0.682
36	0.820
42	0.956

$k_o = 2.782 \times 10^{-8}$ mole $\ell.^{-1}$ $sec.^{-1}$

$k_1 = 2.782 \times 10^{-4}$ $sec.^{-1}$

Experiment (21):-

[MeOH] = 50%

Time in minutes	(AB)
6	0.143
12	0.245
18	0.368
24	0.490
30	0.613
36	0.736
42	0.858
48	0.981

$k_o = 2.625 \times 10^{-8}$ mole $\ell.^{-1}$ $sec.^{-1}$

$k_1 = 2.625 \times 10^{-4}$ $sec.^{-1}$

Experiment (22):-

[MeOH] = 40%

Time in minutes	(AB)
8	0.138
16	0.276
24	0.414
32	0.552
40	0.690
48	0.828
56	0.966

k_o=2.215x10^{-8} mole $\ell.^{-1}$ sec.$^{-1}$

k_1=2.215x10^{-4} sec.$^{-1}$

C) Rate measurements in water/methanol mixtures at 34.7°

(i) Reactions of Compound (I):

$[I]_\circ$ = Initial concentration of (I)

l = 5mm. λ = 512nm.

Experiment (23):-

$[H_2O]$ = 2% (by volume)

$[I]_\circ = 1.0\text{x}10^{-4}$ M/ℓ

Time in minutes	(AB)
3	0.210
6	0.486
9	0.755
12	1.026
15	1.287
18	1.535
21	1.720

$k_\circ=6.690\text{x}10^{-8}$ mole $\ell.^{-1}$ $\sec.^{-1}$

$k_1=6.690\text{x}10^{-4}$ $\sec.^{-1}$

Experiment (24):-

$[H_2O]$ = 4%

$[I]_\circ = 1.0\text{x}10^{-4}$ M/ℓ

Time in minutes	(AB)
2	0.127
4	0.335
6	0.587
8	0.827
10	1.060
12	1.287
14	1.502

$k_\circ=8.630\text{x}10^{-8}$ mole $\ell.^{-1}$ $\sec.^{-1}$

$k_1=8.630\text{x}10^{-4}$ $\sec.^{-1}$

Experiment (25):-

$[H_2O] = 10\%$

$[I]_o = 0.8184\times10^{-4}$ M/ℓ

Time in minutes	(AB)
2	0.300
4	0.590
6	0.885
8	1.125
10	1.320
12	1.465
14	1.575
16	1.642

$k_o=11.20\times10^{-8}$ mole $\ell.^{-1}$ $sec.^{-1}$

For the first order part:

Time in minutes	$10^4(x)$	$10^4(a)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
0	0.000	0.4115	0.4115	1.000	0.0000
2	0.1103	0.4115	0.3012	1.3662	0.1354
4	0.2000	0.4115	0.2115	1.9456	0.2890
6	0.2667	0.4115	0.1448	2.8419	0.4536
8	0.3172	0.4115	0.0945	4.3637	0.6399
10	0.3480	0.4115	0.0635	6.4803	0.8117

$k_1=33.44\times10^{-4}$ $sec.^{-1}$

Experiment (26):-

$[H_2O] = 14\%$

$[I]_\circ = 0.8437 \times 10^{-4}$ M/ℓ

Time in minutes	(AB)
2	0.264
4	0.514
6	0.780
8	1.012
10	1.218
12	1.385
14	1.522
16	1.628
18	1.702

$k_\circ = 9.464 \times 10^{-8}$ mole ℓ.$^{-1}$ sec.$^{-1}$

For the first-order part:

Time in minutes	$10^4(x)$	$10^4(a)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
0	0.000	0.2837	0.2837	1.000	0.000
2	0.0768	0.2837	0.2069	1.3712	0.1367
4	0.1398	0.2837	0.1439	1.9715	0.2948
6	0.1885	0.2837	0.0952	2.9800	0.4742
8	0.2225	0.2837	0.0612	4.6356	0.6662

$k_1 = 34.43 \times 10^{-4}$ sec.$^{-1}$

Experiment (27):-

$[H_2O] = 20\%$

$[I]_\circ = 0.6253\text{x}10^{-4}$ M/ℓ

Time in minutes	(AB)
2	0.278
4	0.530
6	0.772
8	0.965
10	1.092
12	1.185
14	1.250

$k_\circ = 5.05\text{x}10^{-8}$ mole $\ell.^{-1}$ $\sec.^{-1}$

For the first-order part:

Time in minutes	$10^4(x)$	$10^4(a)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
0	0.000	0.2704	0.2704	1.000	0.000
2	0.888	0.2704	0.1816	1.4890	0.1729
4	0.1472	0.2704	0.1232	2.1948	0.3414
6	0.1999	0.2704	0.0705	3.8355	0.5838
8	0.2198	0.2704	0.0506	5.3439	0.7278

$k_1 = 37.08\text{x}10^{-4}$ $\sec.^{-1}$

(ii) Reactions of Compound (II):

$[II]_o$ = Initial concentration of (II)

l = 5mm. λ = 496nm.

Experiment (28):-

$[H_2O]$ = 2% (by volume)

$[II]_o = 1.0 \times 10^{-4}$ M/ℓ

Time in minutes	(AB)
2	0.078
4	0.173
6	0.282
8	0.392
10	0.506
12	0.618
14	0.730
16	0.843
18	0.954

$k_o = 7.150 \times 10^{-8}$ mole $ℓ.^{-1}$ $sec.^{-1}$

$k_1 = 7.150 \times 10^{-4}$ $sec.^{-1}$

Experiment (29):-

$[H_2O]$ = 4%

$[II]_o = 1.0 \times 10^{-4}$ M/ℓ

Time in minutes	(AB)
2	0.083
4	0.216
6	0.365
8	0.510
10	0.655
12	0.793
14	0.928

$k_o = 8.940 \times 10^{-8}$ mole $ℓ.^{-1}$ $sec.^{-1}$

$k_1 = 8.940 \times 10^{-4}$ $sec.^{-1}$

Experiment (30):-

$[H_2O] = 10\%$

$[II]_\circ = 0.985\times10^{-4}$ M/ℓ

Time in minutes	(AB)
1	0.080
2	0.184
3	0.310
4	0.438
5	0.563
6	0.682
7	0.795
8	0.897

$k_\circ=15.54\times10^{-8}$ mole ℓ^{-1} $\sec^{-1}$

$k_1=15.54\times10^{-4}$ $\sec^{-1}$

Experiment (31):-

$[H_2O] = 14\%$

$[II]_\circ = 0.930\times10^{-4}$ M/ℓ

Time in minutes	(AB)
1	0.123
2	0.234
3	0.370
4	0.510
5	0.650
6	0.781
7	0.906
8	1.028

$k_\circ=17.56\times10^{-8}$ mole ℓ^{-1} $\sec^{-1}$

$k_1=17.56\times10^{-4}$ $\sec^{-1}$

Experiment (32):-

$[H_2O] = 20\%$

$[II]_\circ = 0.938\text{x}10^{-4}$ M/ℓ

Time in minutes	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
1	0.335	0.258	0.680	1.379	0.1396
4	0.665	0.511	0.427	2.197	0.3418
7	0.895	0.688	0.250	3.752	0.5742
10	1.042	0.802	0.136	6.897	0.8386
13	1.125	0.865	0.073	12.85	1.1089
16	1.170	0.900	0.038	24.68	1.3923
19	1.195	0.919	0.019	49.37	1.6934

$k_1=36.26\text{x}10^{-4}$ sec.$^{-1}$

Discussion

A) Rate-dielectric constant function relationship: Kirkwood has calculated the frequency change resulting from a transfer of a dipole from a medium of dielectric constant unity to one having a dielectric constant ε, making the assumption that only electrostatic interactions are involved. As long as this is the major factor,

$$\Delta F_{el} = - \frac{\mu^2}{r^3} \left(\frac{\varepsilon-1}{2\varepsilon+1}\right) \qquad (22)$$

where μ is the dipole moment and r is the molecular radius (assuming the molecule to be spherical). The accuracy of this equation has been tested by equilibrium measurements, and for different compositions of mixed solvents the agreement is fairly good[72]. It was applied to the Menschutkin reaction in various mixtures of solvents and the correlation with the function is quite good[73]. This type of study has not been reported for an elimination reaction.

In the present work, the validity of the Kirkwood equation is examined by plotting log k_1 against $\left(\frac{\varepsilon-1}{2\varepsilon+1}\right)$ for the elimination reaction in benzene/methanol, water/methanol and acetonitrile/methanol mixtures.

In benzene/methanol mixtures, the reaction rate decreases with increasing benzene concentration, but still follows zero-order kinetics. A linear relationship was observed between log k_1 and $F(\varepsilon)$, where $F(\varepsilon) = \left(\frac{\varepsilon-1}{2\varepsilon+1}\right)$, up to 50% benzene/methanol by volume after which a change of slope was observed, table (1) fig. (1).

As the benzene/methanol ratio is increased, the dielectric constant of the medium decreases and therefore formation of ions

Variation of log k_1 with F(ε) in benzene/methanol solutions at 34.7°.

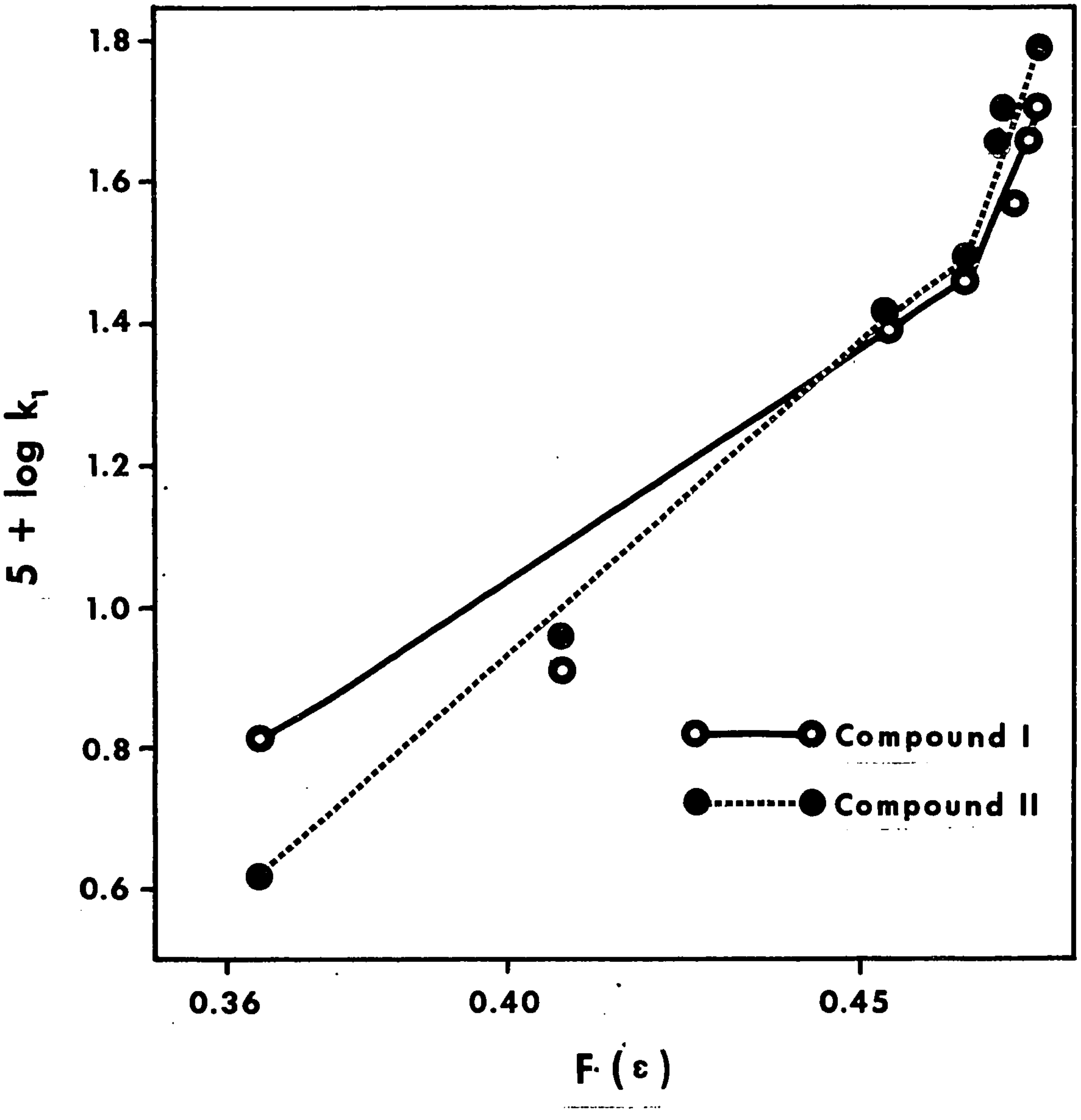
			Compound (I)		Compound (II)	
MeOH % by volume	ε *	F(ε)	10^4 k_1 sec.$^{-1}$	5+log k_1	10^4 k_1 sec.$^{-1}$	5+log k_1
100	30.15	0.4755	5.013	1.700	5.945	1.774
85	28.07	0.4738	4.539	1.656	5.000	1.699
70	25.58	0.4712	3.716	1.570	4.900	1.690
50	21.38	0.4657	2.891	1.460	3.068	1.487
30	15.72	0.4538	2.444	1.388	2.560	1.408
10	7.63	0.4077	0.800	0.903	0.908	0.958
5	5.04	0.3646	0.647	0.811	0.413	0.616

Table (1)

Fig. (1)

* The dielectric constants of the mixtures were calculated from $\varepsilon=\sum_i x_i \varepsilon_i$ where x_i = mole fraction of component i, having dielectric constant ε_i.

Figure 1 - Variation of log k_1 with $F(\varepsilon)$ for the reactions of compounds (I) and (II) in benzene/methanol mixtures.



5 + log k_1
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.36
0.40
0.45
F (ε)
Compound I
Compound II

Figure 1

becomes less favourable. The change in the slope may be explained by a medium effect on $\frac{\mu^2}{r^3}$,[74], i.e. the presence of an increased amount of benzene may deform the shape of the solvated dipole in the transition state.

In water/methanol mixtures, compounds (I) and (II) behave differently. Generally, the rate increased by increasing the water concentration. Compound (II) eliminated HCN in 2%, 4%, 10% and 14% (by volume) water/methanol solutions with zero-order kinetics, but with first-order kinetics in 20% water/methanol. Compound (I) eliminated HCN with zero-order kinetics in 2% and 4% water/methanol solutions, but when the water concentration increased to 10%, 14% and 20% by volume, the reaction rate increased and the reaction order changed from zero to mixed order. Change from 4% to 10% water, in the mixture, increased the rate of the elimination reaction of compound (II) four times. A plot of log k_1 against $F(\varepsilon)$ reflects this change in behaviour, table (2) and fig. (2). For compound (II), a linear relationship is observed for the four zero-order reactions, with one point off the line (the first-order reaction). For compound (I), two groups of points are observed, one for the zero-order reactions and another for the three mixed-order reactions. The solubility of the substrates decreased rapidly by increasing the water concentration. This prevented studies of solutions of higher water concentration.

The presence of water increases the dielectric constant of the medium and enhances the solvation of the negative charge, because of its greater capacity for hydrogen bonding. The

Variation of log k_1 with F(ε) in water/methanol solutions at 34.7°.

			Compound (I)		Compound (II)	
water % by volume	ε	F(ε)	10^4 k_1 sec.$^{-1}$	4+log k_1	10^4 k_1 sec.$^{-1}$	4+log k_1
2	32.11	0.4770	6.69	0.8255	7.15	0.8542
4	33.97	0.4782	8.63	0.8390	8.94	0.9515
10	39.07	0.4810	33.44	1.523	15.54	1.192
14	42.11	0.4824	33.83	1.530	17.56	1.245
20	46.23	0.4839	37.08	1.569	36.26	1.559

Table (2)

Fig.(2)

Figure 2 - Variation of log k_1 with F(ε) for the reactions of compounds (I) and (II) in water/methanol mixtures.

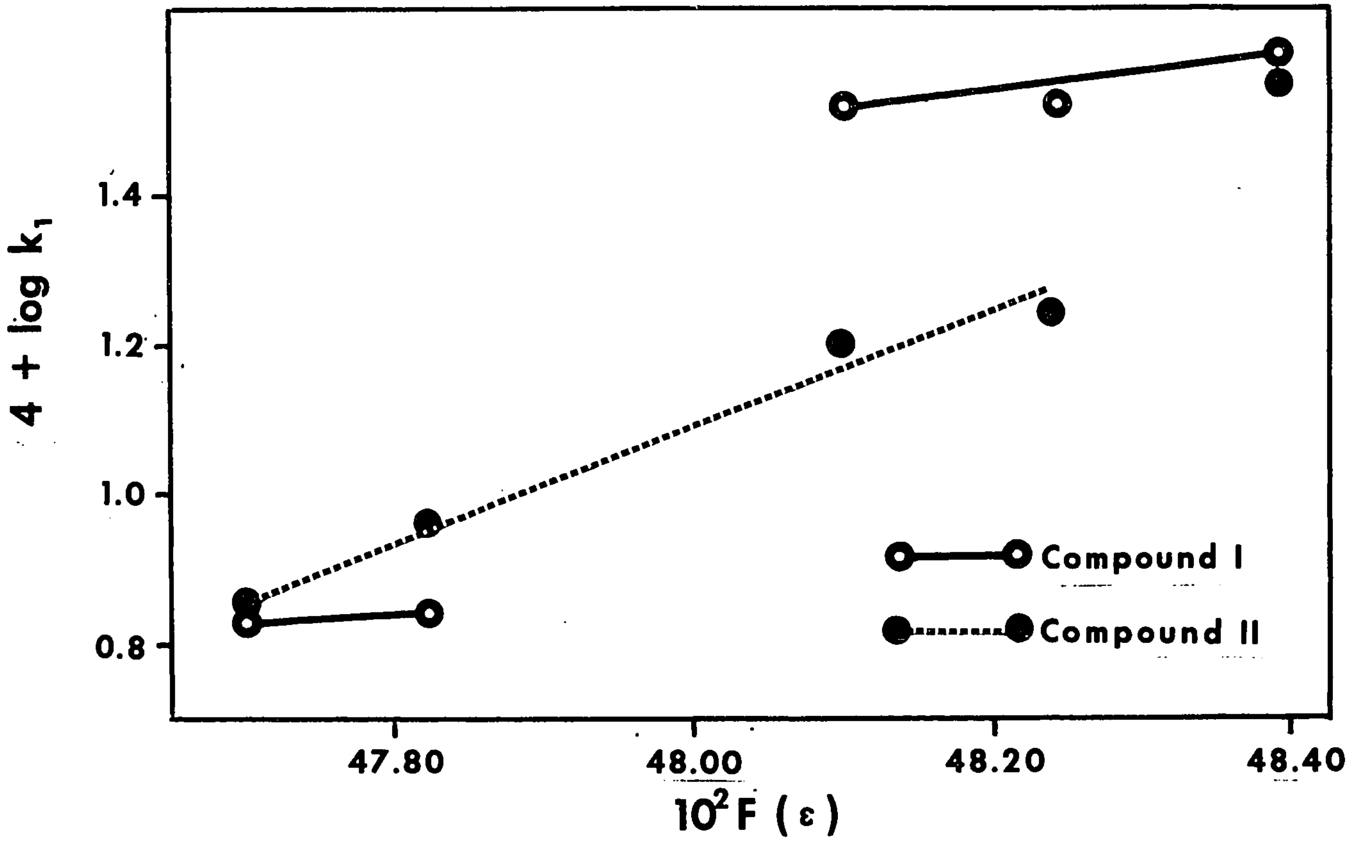
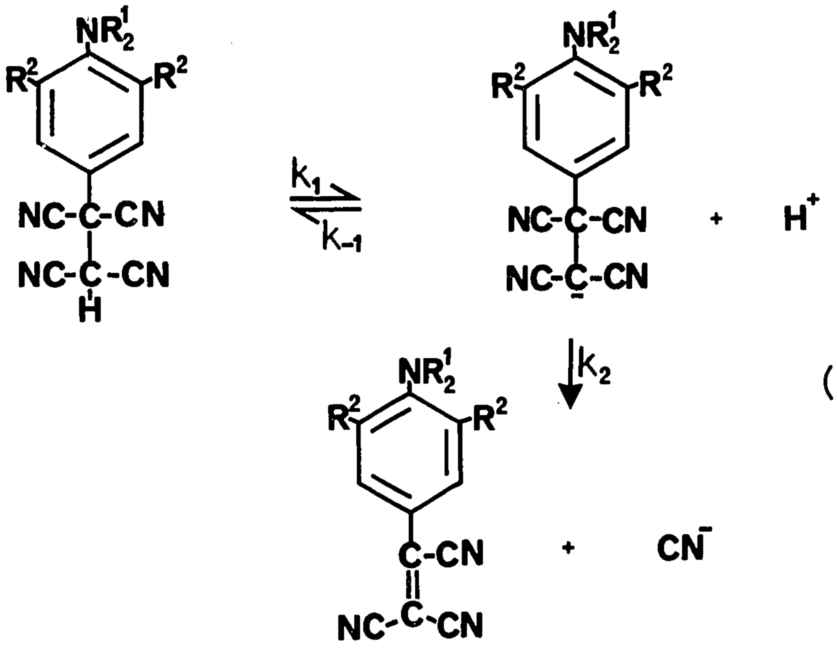

4 + log k_1
1.4
1.2
1.0
0.8
47.80
48.00
48.20
48.40
$10^2F(\varepsilon)$
Compound I
Compound II

Figure 2

formation of the zwitterion might be inhibited because this disperses the charges on the molecule; positive charge on a proton and a negative charge on carbanion are effectively greater than similar charges on a zwitterion. Therefore, in a medium of higher dielectric constant and higher solvating power, carbanion and proton formation will be enhanced, i.e. $k_1 >> k_{-1}$. In the second step of the reaction, olefin and cyanide ion formation will be enhanced because the presence of a strong relatively localized negative charge on the



(23)

cyanide ion will be more favoured by the medium than the dispersed charge on the carbanion. Therefore by increasing the water concentration in the medium, carbanion concentration may become very small, i.e. it will be in a steady state concentration and the rate will be directly dependent on the substrate; in this case $k_2 \approx k_{-1}$. This situation is rapidly attained by compound (II) and gradually reached by compound (I). A higher concentration of water should result in first-order kinetics for the reaction of compound (I).

Application of the general ElcB reaction scheme for the neutral species AH and B gives

$$\begin{tikzcd}
\text{A-H} + \text{B} \arrow[r, shift left, "k_1"] & \text{A}^- + \overset{+}{\text{HB}} \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2"] \\
 & \text{P} + \text{X}^-
\end{tikzcd} \qquad (24)$$

$$\frac{dP}{dt} = k_2\,[A^-]$$

If $$k_1\,[AH]\,[B] = k_{-1}\,[A^-]\,[\overset{+}{HB}] + k_2\,[A^-]$$

then $$[A^-] = k_1\,\frac{[AH]\,[B]}{k_{-1}[\overset{+}{HB}] + k_2}$$

Under the experimental conditions employed [B] is constant; also in methanol $\frac{k_1\,[AH]}{k_{-1}[\overset{+}{HB}]}$ is constant because of the equilibrium step. Therefore $\frac{dP}{dt}$ = constant, i.e. independent of the concentration of the substrate (zero-order). In water, $k_2 \sim k_{-1}$ and $k_2 \gg k_{-1}\,[\overset{+}{HB}]$ therefore $\frac{dP}{dt} = \frac{k_1[B]}{k_2}\,[AH]$, i.e. first-order dependency on the substrate.

In acetonitrile/methanol mixtures, table (3) fig. (3), the rate of reaction of both compounds was decreased by increasing the concentration of acetonitrile from 10% to 60% by volume. The reaction remained zero-order. A plot of log k_1 against $F(\varepsilon)$ gives reasonable linear relationships for compounds (I) and

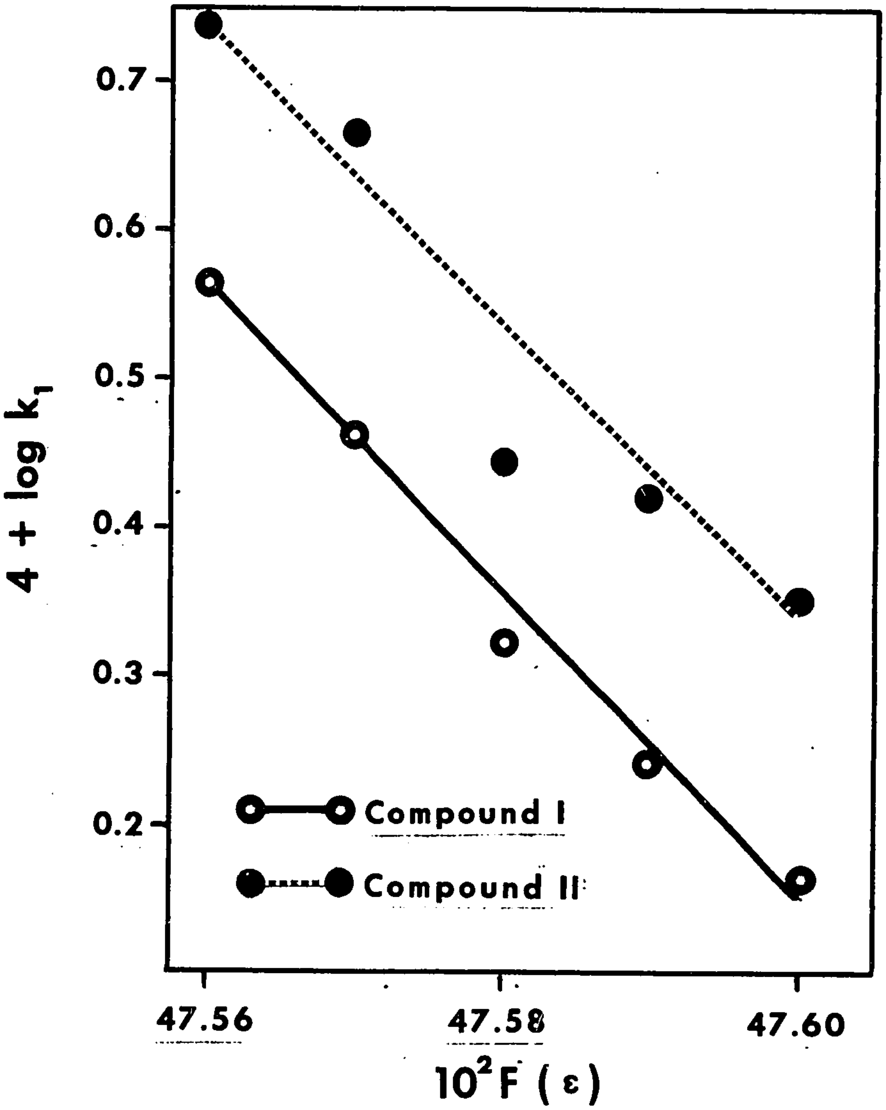
Variation of log k_1 with $F(\varepsilon)$ in acetonitrile/methanol mixtures at 34.7°.

			Compound (I)		Compound (II)	
MeOH % by volume	ε	$F(\varepsilon)$	$10^4 k_1$ sec.$^{-1}$	$4+\log k_1$	$10^4 k_1$ sec.$^{-1}$	$4+\log k_1$
80	30.24	0.4756	3.662	0.5637	5.435	0.7352
60	30.33	0.4757	2.905	0.4631	4.583	0.6602
50	30.52	0.4758	2.199	0.3240	2.782	0.4443
40	30.63	0.4759	1.750	0.2429	2.625	0.4191
20	30.74	0.4760	1.456	0.1631	2.215	0.3441

Table (3)

Fig. (3)

Figure 3 - Variation of log k_1 with $F(\varepsilon)$ for the reactions of compounds (I) and (II) in acetonitrile/methanol mixtures.



0.7
0.6
0.5
0.4
0.3
0.2
4 + log k_1
Compound I
Compound II
47.56
47.58
47.60
$10^2 F(\varepsilon)$

Figure 3

(II). Although acetonitrile has a dielectric constant higher than that of methanol, 37.5 and 32.6 at 25°[75] respectively, the rate of reaction became slower by increasing the acetonitrile concentration. For an increase in $\Delta\varepsilon$ of 0.59 the rate of reaction decreased to 0.29 times (for compound (I)) and 0.37 times (for compound (II)) the rate of reaction in pure methanol. This change corresponds to a change in $F(\varepsilon)$ of only 0.001, i.e. ∿ 0.2%. Therefore, it is obvious that the dielectric constant is not the major rate controlling factor in that mixture. Dipolar aprotic solvents, like acetonitrile, were found to enhance the reactions in which the transition states constitute dipoles[62]. In the present reaction the rate determining step is cyanide elimination from the carbanion. By increasing the acetonitrile concentration the carbanion solvation will be decreased, leading to a smaller concentration of this species and thus a slower rate of reaction.

In pure acetonitrile neither compound (I) nor compound (II) eliminates HCN, implying that carbanion formation is completely inhibited. This is supported by the fact that in acetonitrile organic acids are weaker than in methanol, e.g. benzoic acid has pK_a of 20.7 in acetonitrile and pK_a of 9.4 in methanol at 25°[76].

B) Linear free energy relationship: It was generally observed[77] that when the water concentration in a mixed solvent was increased, the rates of solvolyses of alkyl halides, tosylates and other similar compounds were also increased. With the same solvent mixtures, the change may be correlated reasonably well with changes in dielectric constant. However, this correlation is poor with other solvent mixtures and is generally poor when different solvents are compared[78].

It has also been observed that the changes in rate constant for one compound usually parallel those for other compounds. Grunwald and Winstein[79] were therefore led to suggest the use of a linear free energy equation of the type:

$$\log\left(\frac{k}{k_o}\right) = mY \qquad (25)$$

where k is the rate constant for the solvolysis of a compound in any solvent, k_o is the rate constant for the solvolysis of the same compound in the standard solvent (80% ethanol), Y is a measure of the ionising power of the solvent, and m gives the sensitivity of the substrate to changes in the medium. The application of the equation requires that the Y values be determined with respect to a standard compound, and this was chosen as t-butyl chloride ($m = 1.00$).

In this work, an attempt has been made to apply a similar of free energy relationship. This is the first attempt to study such a relationship for an elimination reaction.

$$\log\left(\frac{k}{k_o}\right) = xY \qquad (26)$$

The HCN-elimination reaction from compound (I) in benzene/methanol solution (50% by volume) is used as standard. x, a constant dependent on the substrate, is made equal to unity for compound (I). Y, a constant dependent on the medium, is made equal to zero for the reaction in 50% benzene/methanol mixture at 34.7°. k_o is the rate constant of the reaction in the standard solvent and k is the rate constant of the reaction in any other medium. Having $x = 1$ for compound (I), one may calculate Y for any medium by knowing the rate constant in that medium. Y thus reflects the effect of the medium on the rate of reaction as compared to that in 50% by volume benzene/methanol. A knowledge of Y for the HCN-elimination reaction in any medium, allows the calculation of x, the substrate constant, for any other compound undergoing the same elimination in the same medium, provided that the rate constants of the reactions in that medium and in 50% benzene/methanol mixture are known. Table (4) shows the values of Y for different solvent mixtures (of dielectric constant at 34.7° ranging between ∿ 16 and 46). (xY) values for the reaction of compound (II) in different media were calculated and the plot of Y against xY for compound (II) is shown in fig. (4). The slope gives x, the substrate-dependent constant. A reasonable linear relationship was obtained for the reaction mixtures ranging between 30% benzene/methanol to 4% water/methanol, i.e. covering a dielectric constant range between 16 and 34. x, for compound (II) was found to be 1.23, which means that the susceptibility of compound (II) to solvent polarity is greater than that of compound (I). At higher concentrations of water (between 10

VARIATION OF xY WITH Y

Compound (I) x = 1		Compound (II)	Medium
$4+\log k_1$	Y	$\log k/k_o=xY$	
1.569	+1.108	+1.071	water/methanol 20%
1.530	+1.069	+0.758	14
1.523	+1.052	+0.704	10
0.839	+0.378	+0.464	4
0.826	+0.365	+0.366	2
0.701	+0.239	+0.287	pure methanol
0.656	+0.195	+0.211	methanol/benzene 85%
0.570	+0.109	+0.202	70
0.461	0.000	0.000	50
0.389	-0.072	-0.080	30

Table (4)

Fig. (4)

Figure 4 - Plot of xY against Y.

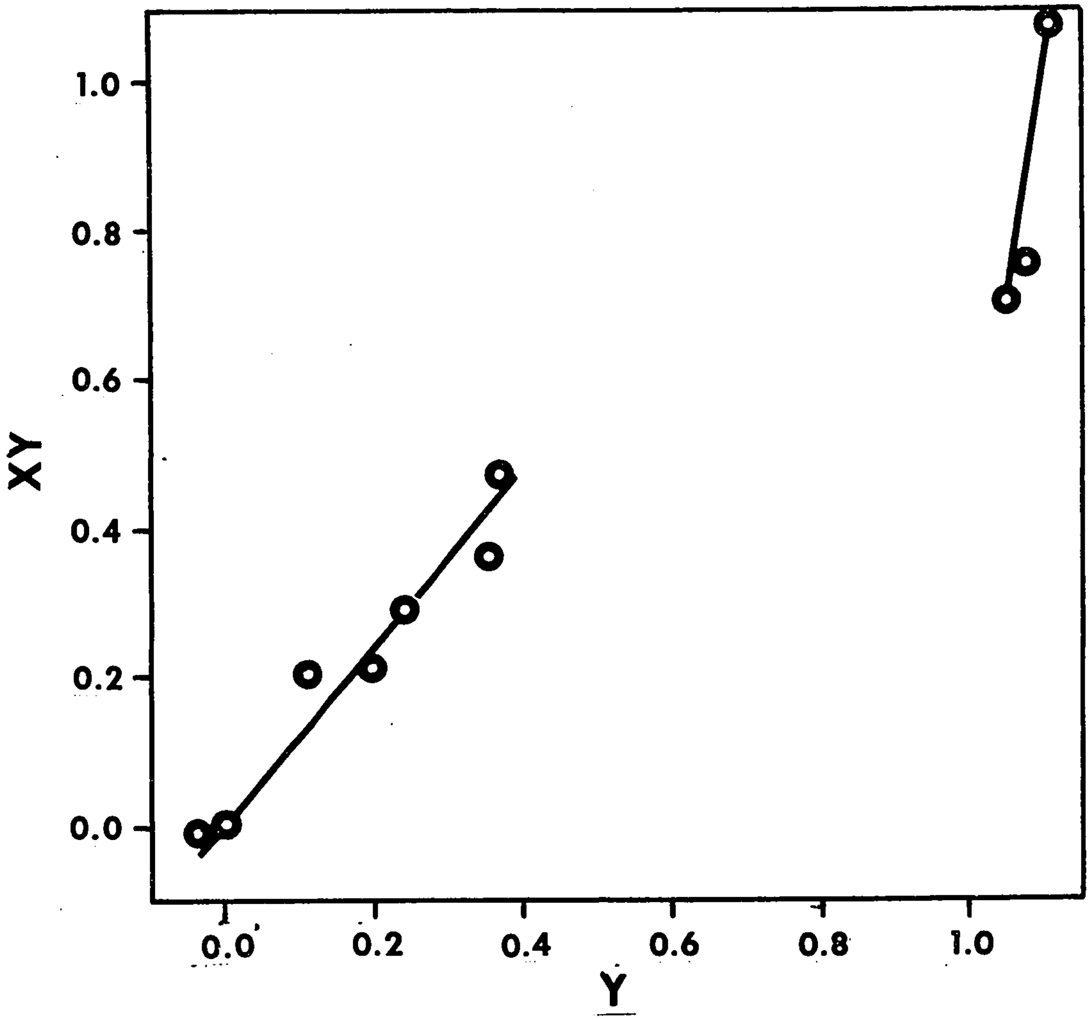


Figure 4

and 20% in methanol), a deviation from linearity was observed. This is as expected because of the drastic change in the solvation species of the transition state. For $\varepsilon = 36$ to 46, x is equal to 0.966 i.e. the strong solvating power of water diminishes the solvent effect difference on the rates of reaction.

PART III:

Introduction

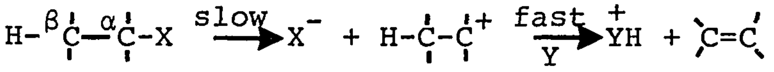
KINETIC ISOTOPE EFFECTS IN ELIMINATION REACTIONS

It has been frequently observed that isotopic substitution can change the rates of chemical reactions. When the isotopic change is made at an atom bound by the bond being broken (or formed) in the rate determining step, the rate change is termed a *primary* kinetic isotope effect. The difference in rate between the breaking of an A-B bond and an A-B* bond (perhaps by the attack of some reagent to form a new bond to one of the two atoms), where B and B* are isotopes, can be rationalized in terms of the conversion of the A-B stretching frequency in the transition state into translational modes due to bond breaking (or forming). *Secondary* isotope effects are those observed for cases where formal bond rupture or bond formation at the labelled position is not involved, but where bonding at the labelled atom is altered (as by hyperconjugation, hybridization changes, non-bonded steric interaction changes, etc.), in the rate determining step.

Studies of kinetic isotope effects may be considered as some of the most powerful tools for distinguishing between the three broad mechanistic classes of elimination reactions, i.e. E1, E2 and E1cB. Extensive studies have been carried out on the kinetic isotope effects in E1 and E2 elimination mechanisms using deuterium, tritium, ^{14}C, ^{37}Cl, ^{34}S and ^{14}N[80]; the results were consistent with the prediction that kinetic isotope effects are at a maximum when the bond formation (or rupture) is symmetrical at the transition state.

A brief survey is given here of kinetic hydrogen isotope effects, specifically involving deuterium, because this is of greatest relevance to this work.

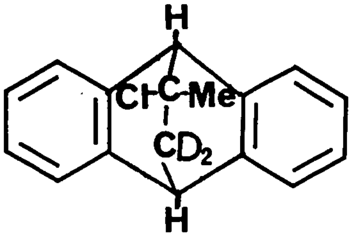
A) <u>Kinetic hydrogen isotope effects on E1 mechanism:</u> In this mechanism, equation (27), a primary kinetic isotope effect would not be expected for the β-hydrogen atoms, as the rate determining step is ionization to carbonium ion,



$$\mathrm{H}{-}{}^{\beta}\overset{|}{\underset{|}{\mathrm{C}}}{-}{}^{\alpha}\overset{|}{\underset{|}{\mathrm{C}}}{-}\mathrm{X} \xrightarrow{\text{slow}} \mathrm{X}^{-} + \mathrm{H}{-}\overset{|}{\underset{|}{\mathrm{C}}}{-}\overset{|}{\underset{|}{\mathrm{C}}}{}^{+} \xrightarrow[\mathrm{Y}]{\text{fast}} \overset{+}{\mathrm{Y}}\mathrm{H} + \rangle\mathrm{C}{=}\mathrm{C}\langle \qquad (27)$$

but secondary hydrogen isotope effects would be expected for α-hydrogen atoms and for properly oriented β-hydrogen atoms. Leffek et al[81] studied the solvolysis, in water, of the series ethyl bromide, isopropyl bromide, t-butyl chloride; replacement of β-CH_3 by β-CD_3 gave k^H/k^D, per CD_3 group values of 1.03, 1.15 and 1.37 respectively. This decrease in relative rate of solvolysis of protiated and deuteriated compounds with increasing number of β-CH_3 groups points to carbonium ion character at the α-carbon atom as being the origin of the secondary isotope effect. The main mechanism through which the carbonium ion centre exerts its influence is almost certainly hyperconjugation (delocalization of the sp^3 β-C–H σ-bond electrons into the developing p-orbital on the α-carbon). This results in 'looser' β-C–H bonding in the activated complex than in the reactants, and thus an isotope effect in the 'normal' direction. The β-C–H σ-orbital and the developing p-orbital on the α-carbon must be parallel for maximum overlap (electron delocalization), which leads to the conclusion that there will be conformational requirements for a β-hydrogen isotope effect. An illustration of this was provided by Shiner and co-workers[82].

Compound (11) undergoes E1-S_N1 solvolysis with $k^H/k^D = 1.14$, while its isotopic isomer (12), in which there can be no overlap of the β-C—D σ-orbital with the developing α-carbon p-orbital, has a k^H/k^D value of 0.986 (±0.01)



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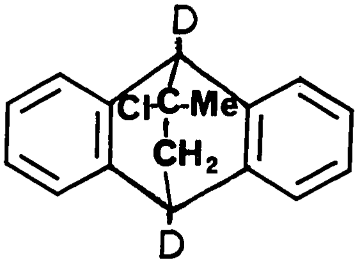

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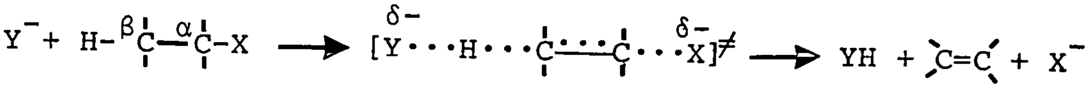
B) Kinetic hydrogen isotope effects in E2 mechanism: If we consider the ideal E2, concerted, mechanism, as in equation (28)

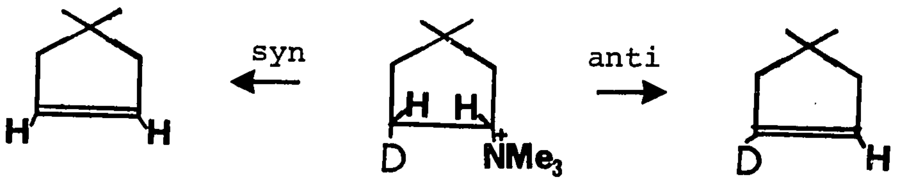


$$Y^- + H-\overset{\beta}{C}-\overset{\alpha}{C}-X \longrightarrow [\overset{\delta-}{Y}\cdots H\cdots C\cdots C\cdots \overset{\delta-}{X}]^{\neq} \longrightarrow YH + {>}C{=}C{<} + X^- \qquad (28)$$

then a primary kinetic isotope effect would be expected for the eliminated β-hydrogen atom and secondary effects might be found for any α-hydrogens and non-eliminated β-hydrogens.

One has to keep in mind that the activated complex, or transition state, of the E2 mechanism may possess carbonium ion, carbanion or 'central' character. In each case it can be also similar to either the starting material or the product. The position of the transition state along the reaction coordinate depends upon the nature of Y^-, X, the substituents on the substrate and the reaction medium[83]. Kinetic isotope effects are expected to vary according to the position of the activated complex in this spectrum. A primary kinetic isotope effect is expected to be at a maximum ($k^H/k^D \sim 7$ at 25°) considering only the stretching frequencies of the broken bonds, for the typical, central, E2 mechanism, and then tend towards lower values with increasing carbanionic or carbonium ion character in the transition state[80]. Ethyl trimethylammonium iodide, for example, dissociates in ethanol-ethoxide ion mixtures at 60° to give trimethylamine and ethylene. The β-hydrogen isotope effect k^H/k^D is ~ 6 (estimated from higher temperature data)[84]; for β-phenethyl trimethylammonium bromide the corresponding value is $k^H/k^D \sim 3$[85]. If the ethyl trimethylammonium ion is assumed to have an activated complex near the central position in the spectrum with the β-hydrogen about equally bonded to the β-carbon atom and to Y^-, then the replacement of β-hydrogen by phenyl would make the remaining β-hydrogen atoms more acidic. This would shift the activated complex towards the paenecarbanion[14] transition state, having greater transfer of hydrogen to Y^- with an accompanying reduction in the isotope effect.

Recently, the presence or absence of a primary β-hydrogen isotope effect has been used to help decide whether elimination in an E2 reaction takes place by a syn- or anti-mechanism. For instance, Coke and co-workers[86] have shown that syn-elimination is an important (sometimes predominant) path for the Hofmann elimination in 4-,5-,6- and 7-membered rings, where only cis-olefins can be formed. Saunders[87] extended the above research on 3,3-dimethylcyclopentyl trimethylammonium salts (as tosylate or iodide) (13), to other base/solvent systems such as NaOH/H_2O, NaOH/H_2O-DMSO, t-BuOK/t-BuOH, t-BuOK/t-BuOH-DMSO, and found that the amount of syn-elimination increased as the basicity of the medium increased. This might be due to the fact that as the basicity increases ion-pairing increases which leads to more syn-elimination. The values of k^H/k^D varied with base (1.17-1.92) but no clear mechanistically useful pattern is apparent from these results.



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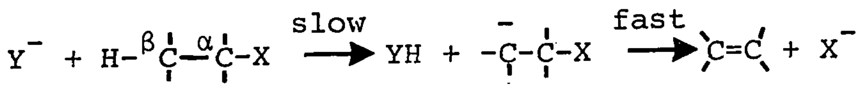
k^H/k^D = (1.17-1.92)

k^H/k^D = 1.0

C) Kinetic hydrogen isotope effects in E1cB mechanisms:

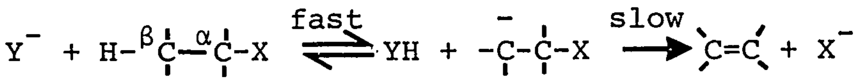
Two limiting types should be considered:

a) Irreversible E1cB mechanism:



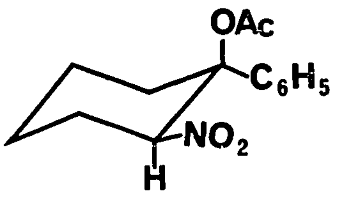
$$Y^- + H-{}^{\beta}\overset{|}{\underset{|}{C}}-{}^{\alpha}\overset{|}{\underset{|}{C}}-X \xrightarrow{\text{slow}} YH + -\overset{-}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \xrightarrow{\text{fast}} {>}C{=}C{<} + X^- \qquad (29)$$

and b) Pre-equilibrium E1cB mechanism:



$$Y^- + H-{}^{\beta}\overset{|}{\underset{|}{C}}-{}^{\alpha}\overset{|}{\underset{|}{C}}-X \overset{\text{fast}}{\rightleftharpoons} YH + -\overset{-}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \xrightarrow{\text{slow}} {>}C{=}C{<} + X^- \qquad (30)$$

If the formation of carbanion is rate determining, a primary kinetic hydrogen isotope effect would be expected upon replacement of the β-hydrogen atoms by deuterium. If the formation of the carbanion is rapid and reversible and its conversion to products is rate determining, an equilibrium isotope effect could be measured. Secondary isotope effects for α- and non-eliminated β-hydrogen atoms might be observed depending upon the change in hybridization of the β-carbon atom. Bordwell and co-workers[88] studied a good example of an irreversible E1cB reaction. They studied the base catalysed elimination of acetic acid from 2-phenyl-2-acetoxy-1-nitrocyclohexanes, (14) and (15) using piperidine as base in chloroform-ethanol solution. The ionic nature of the reaction was supported by the fact that an increase in solvent polarity caused an increase in rate. syn-Elimination



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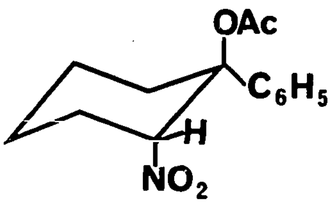

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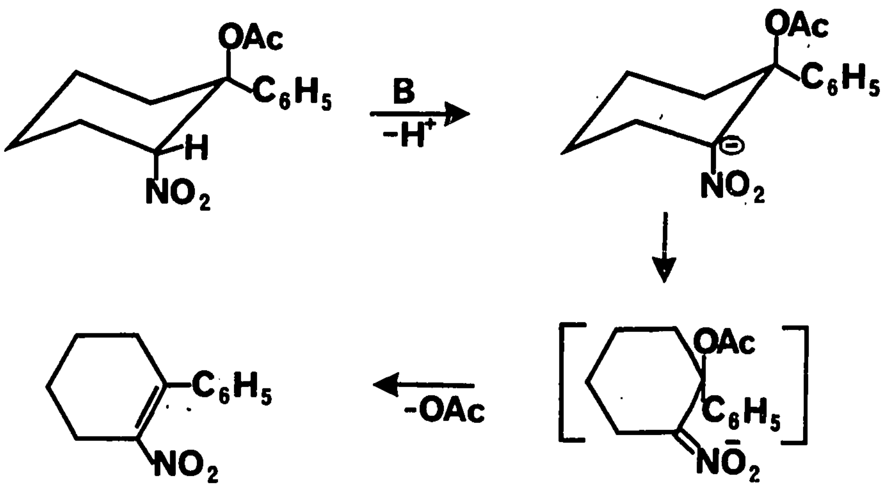
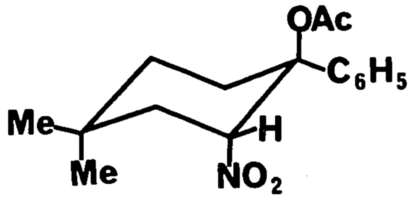
was faster than anti-elimination (3.5:1) The value of the kinetic hydrogen isotope effect, k^H/k^D was 4.9 in each case. Bordwell suggested an irreversible ElcB mechanism for these systems:



(31)

It was proposed that syn-elimination is faster as this relieves the steric hindrance of the axial nitro-group through planar nitronate ion formation. This was supported by the fact that the presence of an axial methyl group, e.g. in compound (16), increased the ratio of syn- : anti-elimination to 18:1



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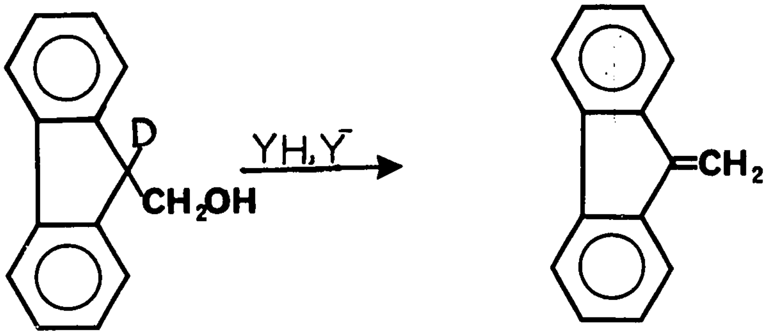
Another variant of the ElcB mechanism, suggested by Rappoport[33], is one in which effectively all of the substrate is converted by the base to the carbanion in a rapid reaction. Additional base will thus not increase the concentration of the carbanion and the reaction will become zero-order in base. Therefore, there would be no isotope effect since the isotopically substituted atom is no longer in the molecule in the rate-determining step. This behaviour was observed during the study of the HCN-elimination from compound (II) in chloroform using triethyl- and tri-n-butylamine; $k^H/k^D = 1.0 \pm 0.03$[35].

More O'Ferrall and Slae[89] have carried out an extensive isotope effect study of the β-elimination of water from 9-fluorenyl methanol to form dibenzofulvene. This reaction was investigated in water, t-butanol and mixtures of the latter two alcohols in the presence of the respective solvent conjugate bases. Hydroxide ion is a very poor leaving group as it is a strong base and the β-hydrogen atom in this compound is highly acidic because of the delocalized charge in the aromatic carbanion formed by its loss. Both factors favour an ElcB mechanism, and for all solvent systems the proposed mechanism was ElcB, carbanion formation being the rate determining step in t-butanol and carbanion decomposition being rate-determining in the other solvents.



(32)

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For water as solvent, the overall (solvent) isotope effect was $k_H^H/k_D^D = 0.92$. The corresponding value for solvent methanol was 0.36. Since hydrogen exchange is relatively rapid in this reaction, ionization of the substrate (17) to form the carbanion probably occurs in a pre-equilibrium step, and it seems likely that the dominant factor in the isotope effect is the free energy of transfer of the methoxide ion between methanol and deuterated methanol.

From this survey of the kinetic hydrogen isotope effect one can conclude that this effect is at maximum in the 'central' E2 mechanism and it decreases on going towards El or ElcB mechanisms.

In this part of the work the HCN-elimination from different polycyano compounds is discussed, and kinetic hydrogen isotope effects used as one of the important criteria to distinguish between the several types of E1cB mechanisms.

Experimental

A) Preparation of Materials

N,N-Dimethyl-4-(1,2,2-tricyanoethyl)aniline (III):

This compound was prepared following the procedure adopted by McKusick et al[90]. A mixture of 4-(N,N-dimethylamino) benzalmalonitrile (0.01 mole) and potassium cyanide (0.02 mole) in 50% aqueous ethanol (20ml.) was stirred on a steam bath until a homogeneous solution was obtained (four minutes). The solution was then filtered and diluted with 20ml. of water containing 2ml. of acetic acid. The product, N,N-dimethyl-4-(1,2,2-tricyanoethyl)aniline, precipitated and was separated by filtration, washed with water and dried, m.p. 125-130°. After recrystallisation from 50% ethanol the product had m.p. 138-139°, (lit.[90] m.p. 138°-139°).

n.m.r. in $CDCl_3$:

singlet $\delta = 3.15$ (6H)
quartet $\delta = 4.45$ (2H) changed to singlet (1H) by deuteration.
quartet $\delta = 7.40$ (4H)

9-Cyano-9-dicyanomethyl fluorene (IV):

This was prepared according to Hertzler's procedure[91]. A mixture of 9-dicyanomethylene fluorene[92] (0.01 mole) and sodium cyanide (0.02 mole) in 60% aqueous ethanol solution (30ml.) was stirred at room temperature. The system slowly became homogeneous. The yellow solution was cooled in ice and acidified with cold dilute hydrochloric acid. Filtration gave 2.41 g. of solid m.p. 142-146°. Rapid recrystallisation from ethanol gave white crystals m.p. 151-152° (lit.[91] m.p. 151.5-153°).

n.m.r. in $CDCl_3$:

singlet $\delta = 4.66$ (1H) disappeared on deuteration.
multiplet $\delta = 8.00$ (8H)

2-(p-N,N-dimethylaminophenyl)-2,3,3-tricyano propionamide (V):

The procedure adopted by Farrell and Wojtowski[38] was followed. N,N-Dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (0.008 mole) was mixed with a 5% aqueous solution of sodium hydroxide (50ml.) and stirred at room temperature until all the solid had dissolved. The resulting orange solution was cooled in ice, neutralized with hydrochloric acid at pH 6.6-6.8, and the blue precipitate filtered, washed with water and dried. The crude product was recrystallised from aqueous acetone and then from methanol and dried. The compound decomposed without melting above 190°. (lit.[38] decomposition above 190°).

N,N-Dimethyl-4-(1,2,2-tricyano-2-$^2H_1$-ethyl)aniline (III-D):

The compound was prepared by shaking a solution of compound (III) in deuterated chloroform with deuterium oxide. The organic layer was separated and then evaporated under reduced pressure and the residue obtained was collected and checked immediately for m.p. and n.m.r. then used for kinetic measurements. m.p. 138-139°.

n.m.r. in $CDCl_3$:

singlet δ = 3.15 (6H)
singlet δ = 4.60 (1H)
quartet δ = 7.40 (4H)

9-Cyano-9-(dicyano-$^2H_1$-methyl)fluorene (IV-D):

The compound was prepared using the procedure described above for compound (III-D). m.p. 151-152°

n.m.r. in $CDCl_3$:

multiplet δ = 8.00 (8H)

B) Product Analysis

Action of methanol on N,N-dimethyl-4-(1,2,2-tricyanoethyl aniline (III): 0.2g (0.0009 mole) of the compound were dissolved in methanol (50ml) and maintained under conditions identical to those used in kinetic measurements for more than ten half lives. Deep orange crystals precipitated. The solution was filtered and the solid collected, m.p. 184-186°, was identical with 4-dimethylamino benzalmalonitrile, yield (35%)

u.v. $\lambda_{\text{max.}(\text{methanol})} = 431$ nm. $\varepsilon_{\text{max.}} = 49{,}500$

Action of methanol on 9-cyano-9-dicyanomethyl fluorene (IV): This compound was treated as above to give, after working up, orange crystals of 9-dicyanomethylene fluorene, m.p. 230-232° (lit. m.p. 230-232°).

u.v. $\lambda_{\text{max.}(\text{methanol})} = 346$ nm. $\varepsilon_{\text{max.}} = 18{,}900$

Action of methanol on 2-(p-N,N-dimethylaminophenyl)-2,3,3-tricyano propionamide (V): 0.1g (0.0004 mole) of the compound were dissolved in methanol (100ml) and kept at room temperature for 15 days. A sample was examined spectrophotometrically for 3,3-dicyano-2-(p-N,N-dimethylaminophenyl)acrylamide at $\lambda = 476$ nm. Less than 2% reaction had occurred. The solvent was evaporated and the starting material recovered (97% yield).

Data

A) Rate measurements in pure methanol at different temperatures:-

(i) Reactions of Compound (III):

Initial concentration of the substrate = 1.0×10^{-4} M/ℓ

l = 5mm λ = 431nm.

Experiment (1):-

At 34.7° ± 0.1°

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
2	0.082	0.0331	0.9669	1.0342	0.0145
4	0.145	0.0586	0.9414	1.0622	0.0261
6	0.230	0.0929	0.9171	1.0903	0.0374
8	0.312	0.1261	0.8739	1.1442	0.0584
10	0.385	0.1556	0.8443	1.1844	0.0734
14	0.516	0.2085	0.7915	1.2634	0.1014
18	0.630	0.2545	0.7455	1.3413	0.1274
22	0.723	0.2921	0.7078	1.4128	0.1501
30	0.863	0.3487	0.6513	1.5352	0.1861
40	0.993	0.4012	0.5988	1.6700	0.2227
72	1.176	0.4752	0.5248	1.9054	0.2799
94	1.205	0.4869	0.5131	1.9489	0.2898
120	1.251	0.5055	0.4945	2.0222	0.3058
∞	1.301	0.5270	0.4730	2.120	0.3265

$$k_1 = \frac{2.303}{60\times60} \times \text{slope}$$

$$= 4.594\times10^{-6}\ \text{sec}^{-1}$$

$$K = \frac{(x_\infty)^2}{(a-x)_\infty}$$

$$= 5.872\times10^{-5}\ \text{mole}\ \ell^{-1}$$

Experiment (2):-

At 30.0° ± 0.1°

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
4	0.081	0.0327	0.9673	1.0338	0.0145
8	0.166	0.0671	0.9329	1.0719	0.0302
12	0.251	0.1014	0.8986	1.1128	0.0456
16	0.331	0.1337	0.8663	1.1543	0.0622
20	0.407	0.1644	0.8356	1.1967	0.0781
25	0.491	0.1984	0.8016	1.2475	0.0962
35	0.610	0.2465	0.7535	1.3271	0.1229
50	0.754	0.3046	0.6954	1.4380	0.1577
76.5	0.905	0.3657	0.6343	1.5765	0.1978
97.5	0.955	0.3859	0.6141	1.6284	0.2117
121	0.975	0.3940	0.6060	1.6502	0.2178
144	0.981	0.3964	0.6036	1.6567	0.2193
∞	0.995	0.4020	0.5980	1.6722	0.2232

$$k_1 = \frac{2.303}{60x60} \text{ x slope}$$

$$= 2.828 \times 10^{-6} \text{ sec.}^{-1}$$

$$K = \frac{(x_\infty)^2}{(a-x)_\infty}$$

$$= 2.702 \text{x} 10^{-5} \text{ mole } \ell.^{-1}$$

Experiment (3):-

At 24.6° ± 0.1°

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
4	0.040	0.0162	0.9838	1.0164	0.0069
8	0.089	0.0360	0.9640	1.0373	0.0158
12	0.135	0.0545	0.9445	1.0587	0.0247
16	0.178	0.0720	0.9280	1.0775	0.0325
20	0.222	0.0897	0.9103	1.0985	0.0409
24	0.260	0.1050	0.8950	1.1173	0.0480
28	0.300	0.1212	0.8788	1.1379	0.0562
32	0.333	0.1345	0.8655	1.1554	0.0626
40	0.402	0.1624	0.8376	1.1938	0.0769
52	0.483	0.1952	0.8048	1.2425	0.0943
78	0.609	0.2461	0.7539	1.3264	0.1227
128	0.739	0.2989	0.7011	1.4262	0.1541
164	0.752	0.3038	0.6962	1.4363	0.1571
∞	0.758	0.3062	0.6938	1.4413	0.1718

$$k_1 = \frac{2.303}{60 \times 60} \times \text{slope}$$

$$= 1.338 \times 10^{-6} \text{ sec.}^{-1}$$

$$K = \frac{(x_\infty)^2}{(a-x)_\infty}$$

$$= 1.351 \times 10^{-5} \text{ mole } \ell.^{-1}$$

Calculation of the energy of activation (E_a)

Calculation of the energy of activation of the elimination reaction of (III) in methanol between 24.6° and 34.7°

Experiments 1, 2 and 3

$10^6 k_1$ sec.$^{-1}$	T(°C)	T(°K)	$(1/T)10^4$	6+log k_1
4.594	34.7	307.7	32.50	0.6622
2.828	30.0	303.0	33.00	0.4514
1.338	24.6	297.6	33.60	0.1265

E_a = - slope x 2.303 x 1.987

$= 10^4 \times \frac{0.484}{1} \times 2.303 \times 1.987$

= 22.17 k cal. mole^{-1}

Calculation of the enthalpy (ΔH) of HCN elimination from compound (III) in methanol between 24.6 and 34.7°

Experiments 1, 2 and 3

10^5K mole $\ell.^{-1}$	T(°C)	T(°K)	$(1/T)10^4$	5+log K
5.872	34.7	307.7	32.52	0.7687
2.702	30.0	303.0	33.00	0.4317
1.351	24.6	297.6	33.60	0.1306

$\Delta H = -$ slope x 2.303 x 1.987 x 10^4

$= 27.09$ k cal. mole^{-1}

(ii) Reactions of compound (IV):

Initial concentration of the substrate = 1.0×10^{-4} M/ℓ

l = 5mm. λ = 346nm.

<u>Experiment (4):-</u>

At 34.7° ± 0.1°

Time in hours	(AB)
0.5	0.073
1.0	0.144
1.5	0.216
2.0	0.285
2.5	0.354
3.0	0.417
3.5	0.476
4.0	0.533
5.0	0.636
6.0	0.713
7.0	0.770
8.0	0.810
9.0	0.832

$k_o=4.130\times10^{-9}$ mole ℓ^{-1} $\sec^{-1}$

$k_1=4.130\times10^{-5}$ $\sec^{-1}$

continued....

For the first order part:

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
0.5	0.059	0.062	0.4963	1.1257	0.0525
1.0	0.116	0.123	0.4359	1.2817	0.1079
2.0	0.219	0.232	0.3267	1.7101	0.2333
3.0	0.296	0.313	0.2457	2.2739	0.3568
4.0	0.353	0.374	0.1847	3.0249	0.4807
5.0	0.383	0.405	0.1537	3.6350	0.5605
6.0	0.415	0.439	0.1197	4.6675	0.6691

$$k_1 = \frac{2.303}{3600} \times \text{slope}$$

$$= 7.17 \times 10^{-5} \text{ sec.}^{-1}$$

Experiment (5):-

At 30.0° ± 0.1°

Time in hours	(AB)
1	0.089
2	0.178
3	0.267
4	0.350
5	0.431
6	0.506
7	0.574
8	0.636
9	0.697
10	0.742
11	0.782
12	0.818

$k_o = 2.572 \times 10^{-9}$ mole $\ell.^{-1}$ $sec.^{-1}$

$k_1 = 2.572 \times 10^{5}$ $sec.^{-1}$

continued...

For the first order part:

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
0.5	0.035	0.0370	0.5651	1.0655	0.0275
1	0.075	0.0794	0.5227	1.1519	0.0614
2	0.143	0.1513	0.4508	1.3356	0.1259
3	0.205	0.2169	0.3852	1.5631	0.1939
4	0.266	0.2815	0.3206	1.8780	0.2736
5	0.311	0.3291	0.2730	2.2055	0.3435
6	0.351	0.3714	0.2307	2.6099	0.4166
7	0.387	0.4095	0.1926	3.1262	0.4950

$$k_1 = \frac{2.303}{3600} \text{ x slope}$$

$$= 4.435\text{x}10^{-5} \text{ sec.}^{-1}$$

Experiment (6):-

At 25.2° ± 0.1°

Time in hours	(AB)
2	0.103
4	0.205
6	0.304
8	0.397
10	0.485
12	0.562
14	0.630
16	0.685
18	0.732
20	0.766
22	0.795

k_{o}=1.499x10^{-9} mole $\ell.^{-1}$ sec.$^{-1}$

k_{1}=1.499x10^{-5} sec.$^{-1}$

continued...

For the first order part:

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
1	0.044	0.0466	0.5799	1.0804	0.0334
3	0.132	0.1340	0.4925	1.2721	0.1045
5	0.209	0.2212	0.4053	1.5458	0.1892
7	0.277	0.2931	0.3334	1.8791	0.2739
9	0.332	0.3513	0.2752	2.2765	0.3574
11	0.379	0.4010	0.2252	2.7783	0.4438
13	0.413	0.4370	0.1895	3.3061	0.5193
15	0.442	0.4677	0.1588	3.9452	0.5960

$$k_1 = \frac{2.303}{3600} \text{ x slope}$$

$$= 2.132 \text{x} 10^{-5} \text{ sec.}^{-1}$$

Calculation of the energy of activation (E_a)

Calculation of the energy of activation of the elimination reaction of (IV) in methanol between 25.2° and 34.7°

Experiments 4, 5 and 6

$10^9 k_o$ mole $\ell.^{-1}$ sec.$^{-1}$	T(°C)	T(°K)	$(1/T)10^4$	$9+\log k_o$
4.130	34.7	307.7	32.52	0.1758
2.572	30.0	303.0	33.00	0.4102
1.499	25.2	298.2	33.52	0.1758

$$E_a = -\text{ slope} \times 2.303 \times 1.987$$

$$= \frac{0.4402}{100} \times 2.303 \times 1.987$$

$$= 20.14 \text{ k cal. mole}^{-1}$$

B) Rate measurements of DCN elimination from deuterated compounds in deuterated methanol at 34.7°

(i) Reaction of compound (III):

[III-D] = 1.0×10^{-4} M/ℓ

l = 5mm. λ = 431nm.

Experiment (6):-

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
5	0.068	0.0274	0.9726	1.0281	0.0120
10	0.133	0.0537	0.9463	1.0567	0.0239
15	0.200	0.0808	0.9193	1.0879	0.0366
20	0.260	0.1050	0.8950	1.1173	0.0480
25	0.321	0.1296	0.8704	1.1488	0.0603
30	0.394	0.1591	0.8408	1.1893	0.0752
35	0.445	0.1797	0.8203	1.2190	0.0860
40	0.502	0.2028	0.7972	1.2543	0.0983
45	0.561	0.2266	0.7734	1.2929	0.1116
48.5	0.595	0.2404	0.7594	1.3164	0.1193
54.5	0.665	0.2686	0.7314	1.3672	0.1357

$$k_1 = \frac{2.303}{3600} \times \text{slope}$$

$$= 1.580 \times 10^{-6}\ \text{sec.}^{-1}$$

$$k_H^H/k_D^D = 2.908$$

(ii) Reaction of compound (IV):

[IV-D] = 1.0×10^{-4} M/ℓ

l = 5mm. λ = 346nm.

<u>Experiment (7):-</u>

Time in hours	(AB)
0.5	0.063
1.0	0.123
1.5	0.185
2.0	0.246
2.5	0.306
3.0	0.366
3.5	0.424
4.0	0.480

$k_o = 3.571 \times 10^{-9}$ mole ℓ^{-1} sec^{-1}

$k_1 = 3.571 \times 10^{-5}$ sec^{-1}

$k_H^H / k_D^D = 1.156$

C) Rate measurements of DCN elimination from deuterated substrates in methanol at 34.7°

(i) Reaction of compound (I-D):

$[I\text{-}D] = 1.0\times10^{-4}$ M/ℓ

l = 5mm. λ = 512nm.

Experiment (8):-

Time in minutes	(AB)
3	0.257
6	0.440
9	0.632
12	0.823
15	1.020
18	1.212
21	1.400
24	1.585

$k_o = 4.968\times10^{-8}$ mole $\ell.^{-1}$ $sec.^{-1}$

$k_1 = 4.968\times10^{-4}$ $sec.^{-1}$

(ii) Reaction of compound (III-D):

$[\text{III-D}] = 1.0\times10^{-4}$ M/ℓ

l = 5mm. λ = 431nm.

Experiment (9):-

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log\frac{a}{a-x}$
2	0.093	0.0376	0.9624	1.0390	0.0166
4	0.184	0.0743	0.9257	1.0802	0.0334
6	0.271	0.1094	0.8906	1.1228	0.0504
8	0.351	0.1418	0.8592	1.1638	0.0660
10	0.427	0.1725	0.8275	1.2084	0.0820
12	0.495	0.2000	0.8000	1.2500	0.0969
14	0.561	0.2266	0.7734	1.2929	0.1160
16	0.621	0.2509	0.7491	1.3349	0.1255
18	0.680	0.2747	0.7253	1.3787	0.1395

$$k_1=\frac{2.303}{3600}\times\text{slope}$$

$$=5.214\times10^{-6}\ \text{sec.}^{-1}$$

(iii) Reaction of compound (IV-D):

$[\text{IV-D}] = 1.0\times10^{-4}$ M/ℓ

l = 5mm. λ = 346nm.

Experiment (10):-

Time in hours	(AB)
0.5	0.065
1.0	0.134
1.5	0.196
2.0	0.258
2.5	0.318
3.0	0.375
3.5	0.428
4.0	0.476
4.5	0.523

$k_o=3.438\times10^{-9}$ mole ℓ^{-1} $\sec^{-1}$

$k_1=3.438\times10^{-5}$ $\sec^{-1}$

D) Rate measurements of DCN elimination from protiated substrates in deuterated methanol at 34.7°

(i) Reaction of compound (I):

$[I] = 1.0\times10^{-4}$ M/ℓ

$l = 5$mm. $\lambda = 512$nm.

Experiment (11):-

Time in minutes	(AB)
1	0.145
2	0.280
3	0.445
4	0.620
5	0.819
6	0.995
7	1.160
8	1.330
9	1.502
10	1.632

$k_{\circ}=16.58\times10^{-8}$ mole $\ell.^{-1}$ $\sec.^{-1}$

$k_1=16.58\times10^{-4}$ $\sec.^{-1}$

(ii) Reaction of compound (III):

[III] = 1.0×10^{-4} M/ℓ

l = 5mm. λ = 431nm.

Experiment (12):-

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
4	0.054	0.022	0.978	1.023	0.0099
8	0.109	0.044	0.956	1.046	0.0196
12	0.161	0.065	0.935	1.070	0.0294
16	0.215	0.087	0.913	1.095	0.0394
20	0.265	0.107	0.893	1.120	0.0492
24	0.314	0.127	0.873	1.146	0.0592
28	0.371	0.150	0.850	1.176	0.0693
32	0.413	0.167	0.833	1.200	0.0792
40	0.500	0.202	0.797	1.254	0.0983
50	0.604	0.244	0.756	1.327	0.1229

$$k_1 = \frac{2.303}{3600} \times \text{slope}$$

$$= 1.574\times10^{-6} \text{ sec.}^{-1}$$

(iii) Reaction of compound (IV):

$[IV] = 1.0\times10^{-4}$ M/ℓ

l = 5mm. λ = 346nm.

<u>Experiment (13):-</u>

Time in hours	(AB)
0.5	0.082
1.0	0.157
1.5	0.233
2.0	0.302
2.5	0.376
3.0	0.435
3.5	0.505
4.0	0.565

$k_o=4.263\times10^{-9}$ mole ℓ^{-1} sec^{-1}

$k_1=4.263\times10^{-5}$ sec^{-1}

E) Rate measurements of HCN elimination from substrates in 50% benzene-methanol solution at 34.7°

(i) Reaction of compound (III):

[III] = 1.0×10^{-4} M/ℓ

l = 5mm. λ = 431nm.

Experiment (14):-

Time in hours	(AB)	$10^4(x)$	$10^4(a-x)$	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$
5	0.052	0.0210	0.9890	1.0111	0.0047
10	0.116	0.0468	0.9532	1.0490	0.0208
15	0.180	0.0727	0.9273	1.0783	0.0326
20	0.237	0.0957	0.9043	1.1058	0.0437
25	0.290	0.1171	0.8829	1.1326	0.0543
44	0.445	0.1797	0.8203	1.2190	0.0860
50	0.480	0.1939	0.8061	1.2405	0.0937
76	0.605	0.2444	0.7556	1.3234	0.1216
97	0.675	0.2727	0.7273	1.3749	0.1383

$k_1 = \frac{2.303}{3600} \times \text{slope}$

$= 1.375 \times 10^{-6}\ \text{sec.}^{-1}$

(ii) Reaction of compound (IV):

[IV] = 1.0×10^{-4} M/ℓ

l = 5mm. λ = 346nm.

Experiment (15):-

Time in hours	(AB)
2	0.090
4	0.180
6	0.272
8	0.360
10	0.440
12	0.523
14	0.595
16	0.662

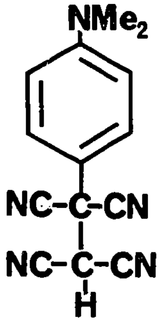
$k_o=1.323\times10^{-9}$ mole $\ell.^{-1}$ $sec.^{-1}$

$k_1=1.323\times10^{-5}$ $sec.^{-1}$

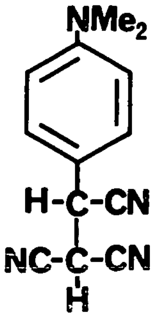
Discussion

A) <u>General considerations:</u> Recently, Bordwell[93] discussed the mechanistic classification of the β-elimination reactions, including E1, E2 and E1cB in one spectrum. E1cB mechanisms occupy a wide range of this spectrum, from the paenecarbanion E2 reaction (second-order anion) to the E1cB type-II reaction (first-order anion), passing through the pre-equilibrium ion pair and the pre-equilibrium anion reactions. The extent of β-C–H bond dissociation increases on going from the paenecarbanion to the E1cB type-II mechanism. Any reaction exhibiting E1cB mechanistic features can be placed at a point in this spectrum depending on the acidity of the β-hydrogen, the stability of the carbanion and the reaction medium.

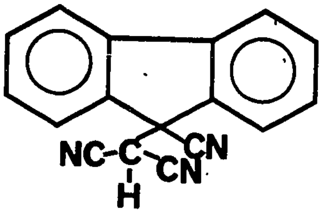
In the present work, a study of the HCN-elimination in pure methanol from compounds (III), (IV) and (V) was made.



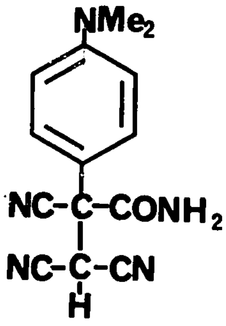
(I)



(III)



(IV)



(V)

Compounds (I), (III), (IV) and (V) have two things in common, the first is the presence of one cyano group on the α-carbon atom (leaving group), and the second is the presence of two cyano groups on the β-carbon atom.

These common factors suggest that the four compounds should easily form carbanions and then eliminate the cyanide ion with comparable rates and through similar mechanisms. However, this is not found to be the case.

The reactions were carried out for the compounds in methanol, protiated and deuterated compounds in both deuterated and nondeuterated methanol to study the kinetic hydrogen isotope effects and any solvent isotope effects. The reactions were also carried out for the compounds in 50% benzene/methanol solution at 34.7° to study the effect of the medium on the rate of reaction.

B) <u>Reactions and mechanisms:</u> In this discussion the HCN-elimination reaction from compound (I) is used as reference. It was concluded in the discussion of part I that compound (I) undergoes HCN-elimination via an E1cB type-II mechanism, in which the rate determining step is the cyanide ion elimination from the carbanion, this being present in a substantial concentration[94]. An inverse kinetic isotope effect was observed ($k_H^H/k_D^D = 0.33$). As shown in table (1) experiments on the labelled substrates in unlabelled solvent and vice versa indicate that the rate of hydrogen-deuterium exchange for compound (I) is much faster than the rate of elimination. This is shown by the fact that the labelled compound reacts in the unlabelled solvent at almost the same rate as the unlabelled compound.

TABLE (1)

	(I)	(III)	(IV)
$10^6\ k_H^H$	501.3	4.594	41.30
$10^6\ k_H^D$	496.8	5.214	34.40
$10^6\ k_D^H$	1658	1.574	42.60
$10^6\ k_D^D$	1525	1.580	35.70
k_H^H/k_D^D	0.33	2.91	1.16
order	zero	first	mixed
x	1.00	2.20	2.03
E_a	24.43	22.17	20.14
$\Delta S^{\neq}$	-16.3	-12.78	-15.12

At 34.7°:

k_H^H is the first order rate constant in sec.$^{-1}$ of undeuterated compound in undeuterated methanol

k_H^D is the first order rate constant in sec.$^{-1}$ of deuterated compound in undeuterated methanol

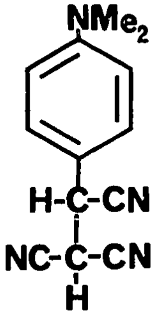
k_D^H is the first order rate constant in sec.$^{-1}$ of undeuterated compound in deuterated methanol

k_D^D is the first order rate constant in sec.$^{-1}$ of deuterated compound in deuterated methanol

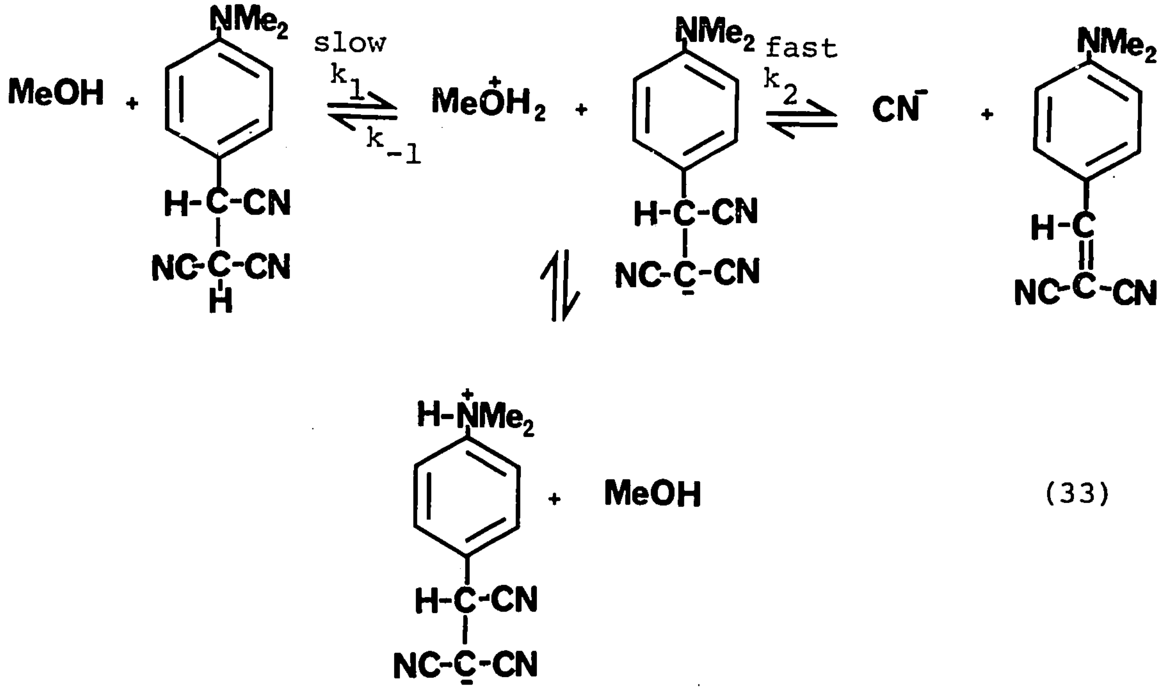
x calculated as $(\log k^1/k^{\circ}) = xY$

E_a, energy of activation in kcal. mole^{-1}, $\Delta S^{\neq}$ in e.u.

Compound (III) undergoes HCN-elimination at a rate which is more than 100 times slower than compound (I), table (1). The reaction shows first-order kinetics which level off to suggest that an equilibrium is reached when ∿ 53% of the reactant has been transformed into products at 34.7°. A kinetic hydrogen isotope effect of $k_H^H/k_D^D = 2.91$ was observed (for the undeuterated compound in methanol and deuterated compound in deuterated methanol). From the cross-over experiments (labelled compound in unlabelled solvent and vice versa) one can conclude that hydrogen exchange occurs faster than elimination, i.e. $k_{-1} > k_2$. Compound (III) has only one hydrogen which can undergo hydrogen-deuterium exchange, namely the dicyanomethyl hydrogen, as shown by n.m.r. studies in the experimental part. All the above results point to the following mechanism:



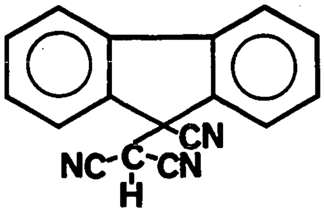
(III)



(33)

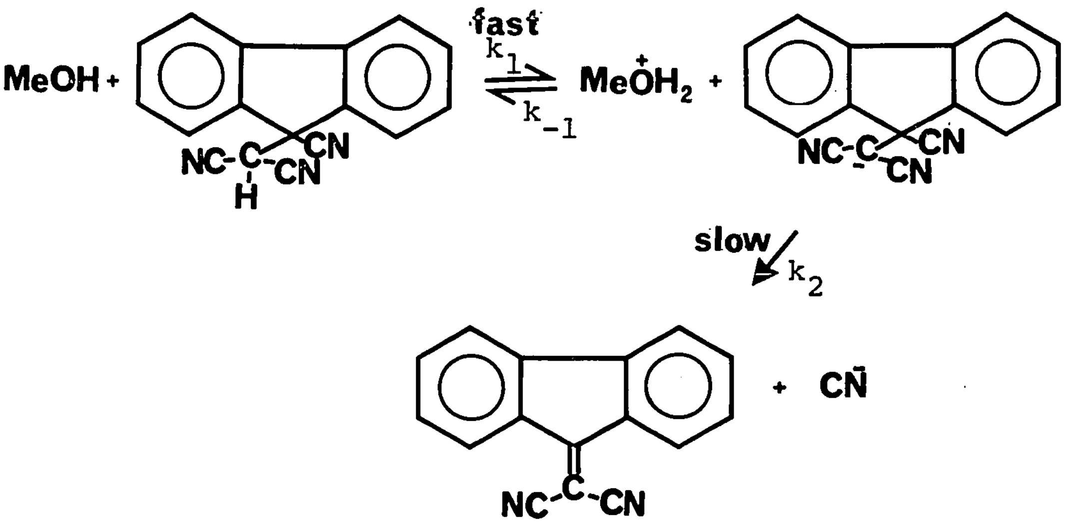
The first slow, rate determining, step is the formation of the carbanion. The high k_H^H/k_D^D value, 2.91, shows that the β-C—H bond breaking is occurring in the rate determining step. The carbanion is less stable than that of (I), presumably because of the absence of one cyano group on the α-carbon atom. The carbanion cannot therefore be accumulated and it rapidly goes to the product via first-order kinetics; in this case $k_1 << k_2 < k_{-1}$. Zwitterion formation may stabilize the carbanion, but this shows no effect on k_H^H/k_D^D because it is formed after the rate determining step. At ∿ 53% reaction at 34.7°, equilibrium is attained. This may be because the substrate can be simply prepared by HCN-addition to 4-(N,N-dimethylamino)-benzalmalonitrile[90] (product). Additional supporting evidence for this mechanism comes from the fact that x, which reflects the effect of medium change from 50% benzene/methanol to pure methanol on substrates undergoing HCN-elimination[95], has a value of 2.20 for compound (III). The rate determining step for HCN-elimination reaction from compound (I) is the second step, i.e. elimination of cyanide ion from the carbanion, a reaction in which there is no change in the net charge. The rate determining step for the elimination reaction of compound (III) is the first step i.e. the formation of the carbanion from the neutral substrate, which is accompanied by charge formation. In the latter case, the dielectric constant of the medium will have considerable effect on the rate of reaction, i.e. the higher the dielectric constant the greater the rate.

Compound (IV) eliminates HCN in methanol about 12 times slower than does compound (I). The reaction is zero-order for the first 40% reaction then it changes to first-order kinetics, above 90% a tendency to deviate from first-order is observed (equilibrium?). The kinetic isotope effect, k_H^H/k_D^D has the value of 1.16, table (1). From the cross-over experiments it appears that the elimination reaction of the deuterated compound has the same rate in methanol and in deuterated methanol and that is also observed for the undeuterated



(IV)

compound (within ± 2%). All the above mentioned results can be accommodated by the following mechanism:

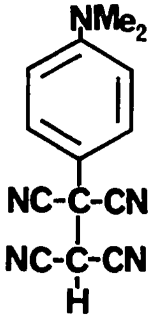


(34)

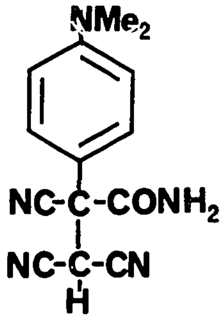
This reaction lies on the mechanistic border between the type-II and the pre-equilibrium ElcB mechanisms. For the first 40% of the reaction, a substantial concentration of carbanion is accumulated and the reaction appears to be zero-order within the run, i.e. independent of the [substrate]. Above 40% of reaction, a steady state concentration of the carbanion seems to be formed. The HCN-elimination reaction of compound (IV) is 12 times slower than that of compound (I). The replacement of one cyano group on the α-carbon atom by phenyl (effectively) and also the change in hybridization at the α-carbon atom destabilise the carbanion from (IV) relative to that from (I) and hence decrease its concentration. The reaction is also ∿ 9 times faster than that of (III), presumably because of the absence of the 4-(N,N-dimethylamino)-system, which is electron releasing, and the presence of the fluorenyl system which acts as a driving force to form the highly conjugated product. The fact that the reaction proceeds via mixed order kinetics eliminates the possibility of a (tight-ion)-type mechanism which may be proposed as an alternative, because the value of k_H^H/k_D^D is 1.16[93]. This observed hydrogen isotope effect could be interpreted by the fact that carbanion concentration is less in the labelled solvent. The suggestion that compound (IV) eliminates HCN in methanol by an ElcB mechanism which lies on the border of type-II and pre-equilibrium is enhanced by the value of x for this substrate. This is higher than that of compound (I) and lower than that of compound (III), table (1).

The value of energies and entropies of activation for the HCN-elimination reactions from compounds (I), (III) and (IV) in methanol are shown in table (1). The negative values for the entropies of activation (-16.30, -12.78 and -15.12 e.u. respectively) and the energies of activation (24.43, 22.17 and 20.14 Kcal. mole^{-1} respectively) reflect the differences between the reactants and transition states in the type-II and the pre-equilibrium mechanisms as described in the discussion of part I, page (110).

Compounds (V) and (I) have several common features. Compound (V) has a N,N-dimethylaminophenyl group on the α-carbon atom and two cyano groups on the β-carbon atom. It differs from compound (I) by having an amido group on the α-carbon atom instead of a cyano group. It is therefore surprising that compound (V) does not undergo HCN-elimination in pure methanol.

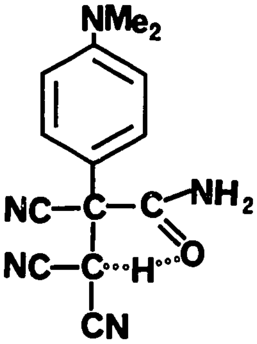


(I)

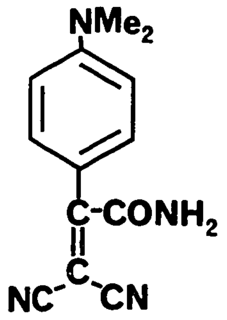


(V)

The reason for this behaviour may arise as a result of hydrogen bonding to the lone pair on the oxygen atom, since protonation of amides in dilute acid solution is predominantly oxygen protonation[96], but hydrogen bonding involving hydrogen bound to carbon is rare. A prerequisite for hydrogen bonding is that the distance between the two electronegative atoms be less than 9Å [97].



Models show that the closest distance between the carbonyl oxygen and the β-carbon atom is less than 3Å , i.e. hydrogen bonding could be effective and may prevent the molecule from dissociating. Some possible evidence[38] for hydrogen bonding may be that (V) undergoes HCN-elimination in methanol very rapidly on irradiation with 2537Å u.v. light to give 3,3-dicyano-2-(p-N,N-dimethylaminophenyl)-acrylamide (18). Irradiation of the sodium salt of (V) to give (18) proceeded extremely slowly, indicating that HCN-elimination from (V) by photolysis is probably a concerted process. However, the infrared spectrum of (V) shows no evidence of H-bonding in the solid state (KBr) and it is probable that this is not the reason for the failure of (V) to eliminate HCN. At present, there does not seem to be any simple explanation for this anomaly.



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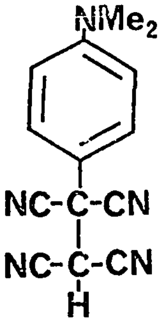
General Discussion

GENERAL DISCUSSION

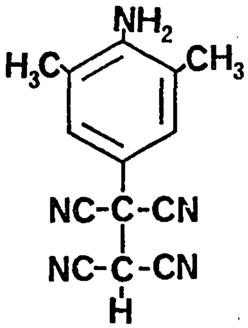
In a recent discussion of the mechanisms of β-elimination reactions, Bordwell[93] proposed a broad spectrum of mechanisms in which the concerted E2 mechanism is a special case rather than the normal mechanism. This is followed by several variants of E1cB and E1 mechanisms. He suggested that most of the base-initiated β-eliminations, in which there are electron-withdrawing groups attached to the β-carbon atoms, proceed via the stepwise rather than the concerted mechanism. The torsional strain introduced by eclipsing effects, the unfavourable entropy introduced into the transition state by freezing the rotation around three bonds of the substrate, and the energy requirements for such a transition state are the major reasons for his suggestion that the one-step β-elimination mechanism is probably uncommon. He proposed that E1cB mechanisms are the more probable modes of elimination for such systems.

Polycyano compounds proved to be good systems to study different variants of E1cB mechanism of elimination. The presence of one or more cyano groups on the β-carbon increases the acidity of the leaving proton, and cyanide ion, which is a poor leaving group, enhances the formation of the carbanion as an intermediate.

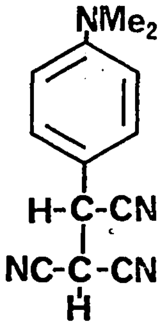
In this work, HCN-elimination from N,N-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (I), 2,6-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (II), N,N-dimethyl-4-(1,2,2-tricyanoethyl) aniline (III) and 9-cyano-9-dicyanomethylfluorene (IV) in methanol were studied.



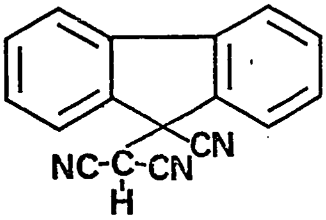
(I)



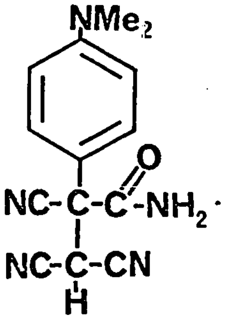
(II)



(III)



(IV)



(V)

The presence of two cyano groups on the β-carbon atom and one cyano (leaving) group on the α-carbon atom are the two common features between these compounds. Despite this, the compounds underwent HCN-elimination in methanol via different variants of the E1cB mechanism.

In part one of the thesis, the HCN-elimination reaction from (I) and (II) in methanol was discussed. pK_a values for these 'acids' were measured and showed that these compounds dissociate to give a proton and the conjugate base in methanol in a fast equilibrium step, thus forming a substantial concentration of the carbanion. Elimination of the cyanide ion occurred in the slow, rate determining step. This is supported by the fact that the reactions in pure methanol are of zero-order and change to first-order kinetics in the presence of hydrochloric acid. Negative values of entropies of activation provide additional support for this mechanism. An inverse hydrogen isotope effect was observed and in an attempt to interpret this phenomenon zwitterion formation was suggested. Acid catalysis provides evidence for zwitterion formation. On the basis of the experimental study it was concluded that compounds (I) and (II) eliminate HCN in methanol via an E1cB type-II mechanism.

In part two an attempt was made to study the solvent effects on the rates and mechanisms of HCN-elimination from compounds (I) and (II). Benzene/methanol, water/methanol and acetonitrile/methanol solvent mixtures were used as media for the reaction. The changes in rate were compared with the changes in Kirkwood's dielectric constant function.

$$\Delta F_{el} = - \frac{\mu^2}{r^3} \frac{(\varepsilon-1)}{(2\varepsilon+1)} \qquad (22)$$

Other functions, such as $\frac{1}{\varepsilon}$ and $(\varepsilon-1/\varepsilon+1)$ could be used and linear relationships were found between all of these different functions[98]. In benzene/methanol mixtures a linear relationship was observed. As the dielectric constant of the medium decreased, the rate of reaction decreased, supporting the ionic mechanism. In water/methanol mixtures, the rate of elimination increased as the water-ratio increased and also the kinetics of the reaction changed from zero- to first-order. These observations were also interpreted on the basis of the ElcB type-II mechanism. Water has a greater solvating power than methanol. Therefore it is expected to enhance the overall reaction, and especially the second step, i.e. cyanide ion expulsion. Thus at higher concentrations of water the carbanion was formed in a steady state concentration and the reaction became first-order in the substrate. The rate of solvation was clearly observed in the study of the reaction in acetonitrile/methanol mixtures. For a small increase in the dielectric constant, ($\Delta\varepsilon = 0.59$) the rate of elimination decreased threefold. This indicated that the solvation of the proton, and the carbanion, by pure methanol is the controlling factor in the reaction. This was supported by the fact that HCN-elimination from compounds (I) and (II) did not proceed in dipolar aprotic solvents such as acetone, acetonitrile and nitrobenzene.

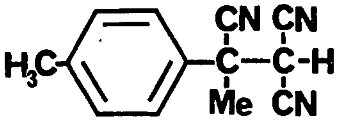
In an attempt to correlate structural medium changes with the rate of HCN-elimination from these systems, a free energy relationship of the form:

$$\log \frac{k}{k^{\circ}} = xY \qquad (25)$$

was employed, where x is a structure-dependent parameter and Y is a medium-dependent parameter. HCN-elimination from compound (I) in 50% benzene/methanol at 34.7° was taken as the standard reaction. This is the first time such a relationship has been applied to an elimination reaction. The values of x for these polycyano systems are expected to be always positive. Negative values of x mean that the rates of elimination in methanol are slower than in 50% benzene/methanol, which is highly unlikely for these substrates unless a non-ionic mechanism is involved. The higher the positive value of x, the greater the susceptibility of the substrate to change in the composition of the medium.

The fact that there are only few examples for HCN-elimination and also that methanol and benzene/methanol mixtures are unusual media for elimination reaction, without the presence of another base, puts considerable limitations on the use of this linear free energy relationship.

In part three, comparative study was made of the HCN-elimination reactions from compounds (III), (IV) and (V), taking the reaction of compound (I) as reference. Kinetic hydrogen isotope effects, cross-over experiments and the free energy relationship developed in part two were used as tools to study the reaction and mechanisms. The reactions of compound (III) provided an example of a new variant in the ElcB spectrum of elimination - an equilibrium ElcB mechanism. Recently, Rappoport[99] discussed the HCN-elimination from 2-tolyl-1,2,2-tricyanopropane (19) in acetonitrile in the presence of



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tri-n-butylamine as base, and he suggested an (equilibrium-ion pair) ElcB mechanism for this reaction. The activation parameters were in good agreement with those obtained for the reaction of compound (III) in pure methanol, $E_a = 19.4$ kcal. mole^{-1} and $\Delta S^{\neq} = -13$ e.u. for (19) while $E_a = 22.17$ kcal. mole^{-1} and $\Delta S^{\neq} = -12.78$ e.u. for compound (III). An ion pair mechanism was not suggested for the reaction of compound (III) because ion pair formation in pure methanol is unlikely because of the high solvating power of methanol and the ease with which the proton may be transferred between solvent molecules.

The reaction of compound (IV) provided an example of the mechanism which lies on the borderline between the pre-equilibrium and the type-II ElcB mechanisms. The mixed-order kinetics eliminate the possibility of either the ion-pair ElcB or the E2 mechanisms. The observed hydrogen isotope effect, $k_H^H/k_D^D = 1.16$, may be interpreted to imply that the carbanion concentration in deuterated methanol is less than in non-deuterated methanol.

Compound (V) did not eliminate HCN in methanol.

CONTRIBUTIONS TO KNOWLEDGE

The reaction and mechanism of HCN-elimination from compounds N,N-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (I) and 2,6-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline (II) were studied in pure methanol, water/methanol and benzene/methanol mixtures. Activation parameters, kinetic isotope effects and acid catalysis imply that the reaction proceeds via an ElcB type-II mechanism. Dipole moments and pK_a's of these compounds were determined.

A linear free energy relationship was applied for the first time for an elimination reaction to reveal the relationship between the effect of the medium and structural changes on the rate of reaction.

HCN-elimination from compounds N,N-dimethyl-4-(1,2,2-tricyanoethyl)aniline (III) and 9-cyano-9-dicyanomethyl fluorene (IV) were studied kinetically and mechanistically using the reaction of compound (I) as a standard. Kinetic hydrogen isotope effects and cross-over experiments were made to compare the rate of hydrogen-deuterium exchange and the rate of elimination. An equilibrium ElcB mechanism was suggested for HCN-elimination from compound (III) in methanol. A mechanism on the borderline between pre-equilibrium and type-II ElcB mechanisms was suggested for HCN-elimination from compound (IV) in methanol.

RESEARCH PROPOSALS

1) Study of HCN-elimination from compounds (I)-(IV) having ^{14}CN as leaving group.

2) Cross-over experiments in methanol-deuterated methanol mixture to throw some light on the inverse isotope effect observed in HCN-elimination from compounds (I) and (II).

3) A study of solvent effects upon the reaction transition state, activation parameters etc.

4) A study of HCN-elimination from compounds (I)-(IV) in dipolar aprotic solvents using different bases; also a study of the kinetic hydrogen isotope effect in this kind of solvent will help to explain the inverse isotope effect exhibited by compounds (I) and (II).

5) A study of HCN-elimination from other polycyano compounds having the same $\mathrm{CN}-\overset{\alpha\,|}{\underset{|}{\mathrm{C}}}-\overset{\beta}{\mathrm{C}}\mathrm{H(CN)_2}$ feature in methanol and in 50% benzene-methanol mixture to apply the linear free energy relationship ($\log \frac{k}{k^{o}} = xY$).

6) Study of the kinetics and mechanisms of HCN-elimination of compound (IV) in methanol by irradiation at 2537Å.

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