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THE ALKALINE SOLVOLYSIS OF
ALLYL BROMIDE IN ALCOHOL-WATER SOLVENTS

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INTRODUCTION

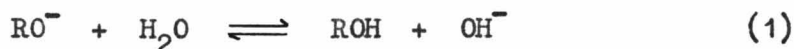
The influence of the solvent on the rates of the bimolecular nucleophilic reactions between basic anions and organic halides in alcohol-water mixtures, has been described, up till the present time, in terms of the effects of three phenomena: a change of nucleophile which occurs in alkaline alcohol-water mixtures, ion pair formation, and the Hughes-Ingold solvent effect.

If the individual effects of these could be separated then one could explain and predict changes in reaction rates, and also discover whether these three effects are adequate to explain the changes.

Factors affecting reaction rates in alcohol-water systems

1. Change of Nucleophile

In alcohol-water systems the rate of reaction of a substrate and an anionic base is influenced by the equilibrium:



where ROH is the alcohol. An apparent overall rate constant can be obtained by measuring the change in total base concentration during a reaction. In general the two bases - alkoxide and hydroxide ions - react at different rates, but

the individual rate constants cannot be evaluated unless the value of the equilibrium constant of equation (1) is known.

By definition of the thermodynamic concept of equilibrium

$$(\sum n_i G_i)_{\text{reactants}} = (\sum n_i G_i)_{\text{products}} \quad (2)$$

where n_i = the number of moles of compound i

G_i = the free energy of compound i

This equation can now be applied to the hydroxide-alkoxide equilibrium. The free energy of an ion cannot be defined absolutely, and so, for convenience, consider the general case where the electrolytes NaOR and NaOH are in equilibrium in a mixture of alcohol and water.



Now if A is one of the solvents,

$$\bar{G}_A = \bar{G}_A^{\circ} + RT \ln n_A f_A,$$

where \bar{G}_A° = free energy of A in pure A.

x_A = mole fraction of A.

f_A = activity coefficient of A.

and $x_A f_A = a_A$ = activity of A.

If MX is an electrolyte, then

$$\bar{G}_{MX} = \bar{G}_{MX}^{\circ} + RT \ln y_{MX} \cdot c_{MX}$$

where c_{MX} = concentration of MX in moles/l.

y_{MX} = activity coefficient of MX.

and $y_{MX} \rightarrow 1$ as $c_{MX} \rightarrow 0$.

i.e. \bar{G}_{MX}° = free energy of MX at infinite dilution in the given solvent.

i.e. \bar{G}_{MX}° is a function of the solvent composition.

Applying equation (2) to equilibrium (3)

$$\begin{aligned} \bar{G}_{H_2O}^{\circ} + RT \ln a_{H_2O} + \bar{G}_{NaOR}^{\circ} + RT \ln a_{NaOR} &= \bar{G}_{ROH}^{\circ} + RT \ln a_{ROH} + \bar{G}_{NaOH}^{\circ} + RT \ln a_{NaOH} \\ -\Delta G^{\circ} &= -\bar{G}_{ROH}^{\circ} - \bar{G}_{NaOH}^{\circ} + \bar{G}_{H_2O}^{\circ} + \bar{G}_{NaOR}^{\circ} \\ &= RT \ln \frac{a_{ROH} \cdot a_{NaOH}}{a_{H_2O} \cdot a_{NaOR}} \\ &= RT \ln K \end{aligned}$$

Now \bar{G}_{NaOH}° and \bar{G}_{NaOR}° depend on the solvent composition, and so

K will depend on the solvent composition, i.e.

$$K = \frac{c_{NaOH} \cdot a_{ROH}}{c_{NaOR} \cdot a_{H_2O}} \times \frac{f_{NaOH}}{f_{NaOR}} \text{ will vary as } x_{ROH} \text{ changes.}$$

However, in dilute solutions one may make the approximation

$f_{NaOH} = f_{NaOR}$ and so

$$K = \frac{c_{OH^-} \cdot a_{ROH}}{c_{OR^-} \cdot a_{H_2O}}$$

will be a constant as x_{ROH} changes.

Sometimes the expression

$$K' = \frac{c_{OH^-} \cdot x_{ROH}}{c_{OR^-} \cdot x_{H_2O}}$$

is evaluated, though, strictly, K' is constant only in ideal mixtures.

Assuming that the approximation $f_{NaOH} = f_{NaOR}$ is valid, so that K is a constant over the solvent range, there remains the problem of finding its value. The equilibrium constant is difficult to measure as there are few suitable reference properties associated with either the hydroxide or alkoxide ions. For example, consider a method of measuring K from kinetic work. If the hydroxide ion reacted at the same rate in alcohol-water mixtures as in water, then one could attribute any change in rate to a shift in the equilibrium, and so K could be found. However, the change in solvent also affects the reaction rate, and the relative effects of either cannot be separated. Thus in this, and in many other cases, the influence of a shift in equilibrium is overshadowed by some other effect.

Approximate values of the equilibrium constants, for the system in which the alcohol is ethanol or methanol, have been found by various workers and a brief description of some of the important methods is given below.

Koskikallio¹ measured the electromotive force of the cell,



using methanol-water mixtures as solvents.

He derived the expression

$$K_{\text{exp}} = K_1' \left(1 + \frac{a_{\text{MeOH}}}{a_{\text{H}_2\text{O}}} \cdot K_{\text{hm}} \right)$$

where K_{exp} = the measured apparent ionic product of methanol-water mixtures.

K_1' = ionic product of water in these mixtures.

$$\text{and } K_{ij} = \frac{[R_j O^-] \cdot a_{R_i OH}}{[R_i O^-] \cdot a_{R_j OH}}, \quad K_{ij}' = \frac{[R_j O^-] \cdot x_{R_i OH}}{[R_i O^-] \cdot x_{R_j OH}}$$

Using the symbols $h = \text{H}$, $m = \text{Me}$, $e = \text{Et}$

$$K_{\text{hm}} = \frac{[\text{MeO}^-] \cdot a_{\text{H}_2\text{O}}}{[\text{OH}^-] \cdot a_{\text{MeOH}}}$$

The values of K_1' were not known but it was assumed that they varied like the dissociation constant of acetic acid.

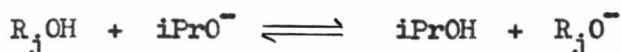
Murto² found further values for K_{hm} and K_{hm}' over a wide range of solvent composition, by using the known values of

1. J. Koskikallio, Suomen Kem, 30B, 1957, 111.

2. J. Murto, Ann. Acad. Sci. Fennicae, (A11), 117, 1962.

the dissociation constants of propionic, butyric and benzoic acids. Values of the equilibrium constants varied considerably, although when plotted against solvent composition the points for mixtures containing less than 50% methanol (by vol.) were close to a straight line. The extrapolated values for pure water were the same in each case: $K'_{hm} = 4.5$, $K_{hm} = 2.7$.

Hine and Hine³ determined the acidities of various alcohols in isopropyl alcohol. These were measured spectrophotometrically using 4-nitrophenylamine as indicator. They obtained values of K'_j for the reaction



$$\text{where } K'_j = \frac{[R_jO^-]}{[R_jOH][iPrO^-]}$$

From this it follows that

$$K'_{ij}(\text{isopropyl alcohol}) = \frac{[R_jO^-][R_iOH]}{[R_jOH][R_iO^-]},$$

for the equilibrium between R_iO^- and R_jO^- in isopropyl alcohol.

Values at 27°C were:

$$K'_{he} = 0.79 \text{ (in isopropyl alcohol)}$$

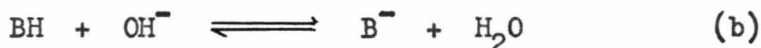
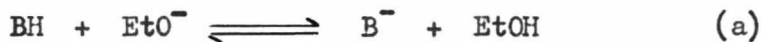
$$K'_{hm} = 3.3 \text{ (in isopropyl alcohol)}$$

Caldin and Long⁴ used a spectrophotometric method to measure the hydroxide-ethoxide equilibrium constant in ethanol-

3. J. Hine and M. Hine, J. Amer. Chem. Soc., 74, 1952, 5266.

4. E. F. Caldin and G. Long, J. Chem. Soc., 1954, 3737.

water mixtures containing 12.6%-4.7% water (by weight). If BH denotes the indicator (trinitrotoluene) the following are in equilibrium:



and the ratio of the corresponding equilibrium constants is equal to the equilibrium constant K'_{he} .

The concentration of B^- was determined spectrophotometrically, and K'_{he} was evaluated on the assumption that the equilibrium constant of equation (a) has the same value in ethanol-water mixtures as in absolute ethanol.

The mean of the values was $K'_{\text{he}} = 0.56 \pm 0.05$. K'_{he} varied irregularly but the standard error of the mean was less than 10% of the mean.

Ballinger and Long⁵ used a conductometric method to determine the constants

$$K'_{\text{HA}} = \frac{[\text{H}^+][\text{RO}^-]}{[\text{ROH}]}$$

for the reaction



in ethanol.

5. P. Ballinger and F. A. Long, J. Amer. Chem. Soc., 82, 1960, 795; 81, 1959, 1050.

By noting the ionic product of water, and its concentration in these solutions, Murto calculated the value

$$K'_{he} = 0.7$$

The three values of K'_{he} do not refer to exactly the same quantity. It has been pointed out that the measurements by Hine and Hine were made in isopropyl alcohol at 27°C and so will not apply precisely to the equilibrium constant in ethanol at 25°C. Finding the mean of the other two values 0.56 and 0.7:

$$K'_{he} = 0.63$$

Murto included the value of Hine and Hine and, by giving double weight to the value of Caldin and Long, found the mean of the three values to be $K'_{he} = 0.65$.

In order to compare any present work with the results of Murto the following values of the equilibrium constants have been taken:

$$K'_{he} = 0.65, \quad K'_{hm} = 4.5.$$

Once a value for K_{ij} , or K'_{ij} , has been established, one can calculate the proportion of the base present as hydroxide or alkoxide, in any particular solvent mixture.

For a binary mixture

$$K_{1i} = \frac{[R_i O^-] a_1}{[R_1 O^-] a_i} \quad (4)$$

where a_i = activity of $R_i OH$

$$\text{total base concentration } b_{\text{tot}} = \sum_{i=1}^2 [R_i O^-] \quad (5)$$

$$\text{proportion of base present as } R_i O^- = s_i = \frac{[R_i O^-]}{b_{\text{tot}}} \quad (6)$$

Substituting (4) and (5) into equation (6)

$$s_i = \frac{a_i K_{1i}}{\sum_{i=1}^2 a_i K_{1i}}$$

$$\text{by analogy } s_i = \frac{x_i K'_{1i}}{\sum_{i=1}^2 x_i K'_{1i}} \quad x_i = \text{mole fraction of } R_i OH$$

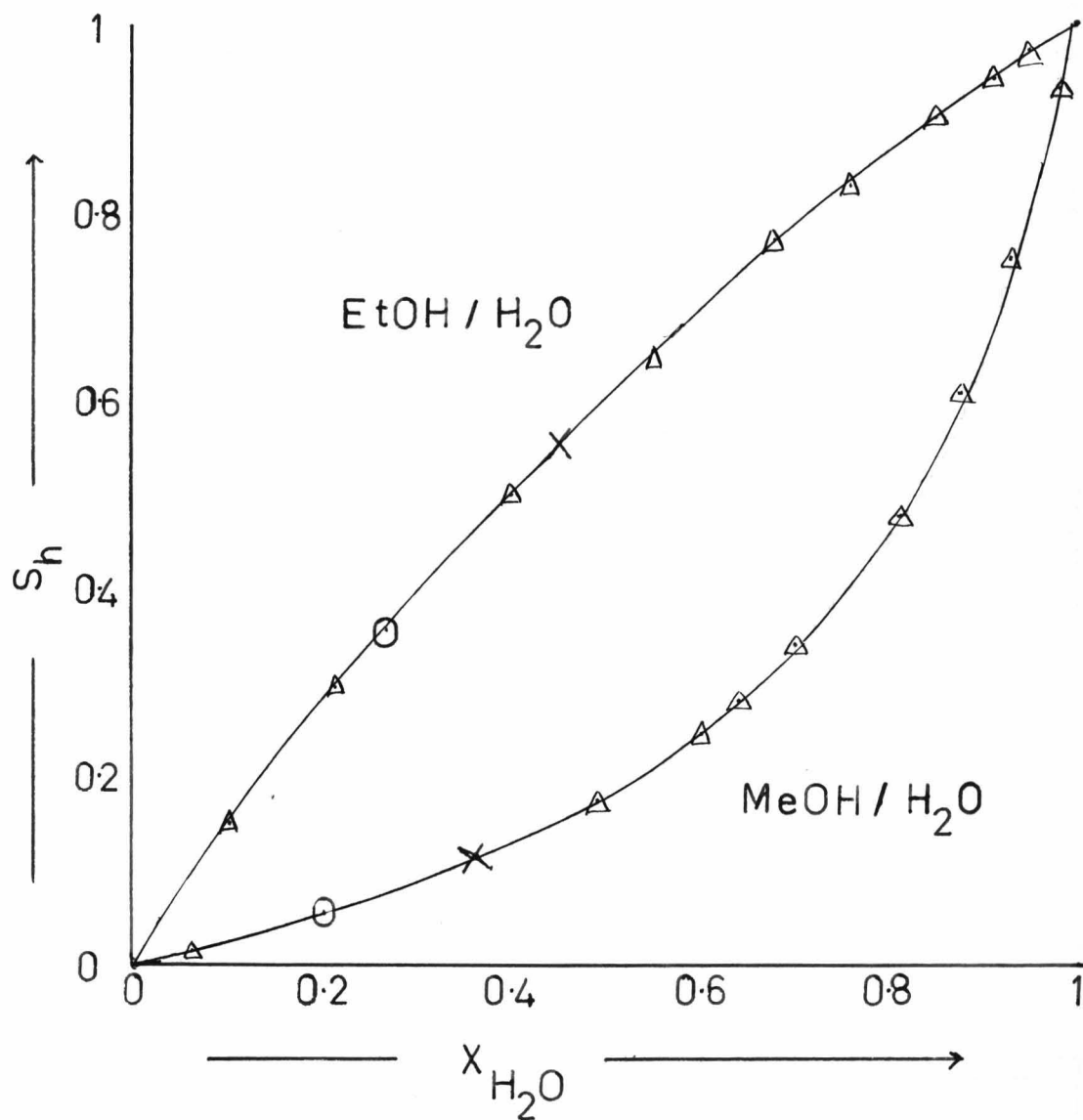
$$\text{i.e. } s_1 = \frac{x_1}{x_1 + x_2 K'_{12}}, \quad s_2 = \frac{x_2 K'_{12}}{x_1 + x_2 K'_{12}}$$

Using these equations for s_1 and s_2 , and the values of K'_{12} as above, one can find the variation of base composition with the solvent for methanol-water and ethanol-water mixtures. This is summarized in a graphical form in Figure I.

Although this graph is approximate it shows a distinction between alkoxide ion-hydroxide ion equilibria in aqueous ethanol and aqueous methanol. The addition of water to absolute ethanol causes a rapid conversion of the ethoxide ion to the hydroxide ion.

FIG. I

Base Composition in Alkaline
Alcohol-Water Mixtures.

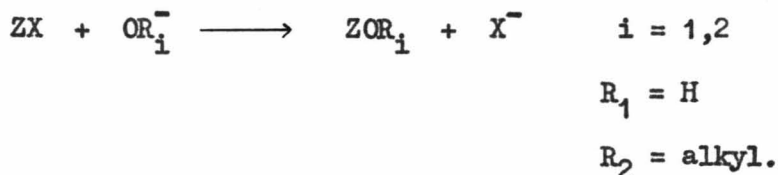


○ = 90% (by vol.) alcohol

X = 80% (by vol.) alcohol

In 90% and 80% (by volume) ethanol, the percentage of the base in the hydroxide form is 35% and 55% respectively. The corresponding solutions of methanol have only 5% and 11%, respectively, present in the hydroxide form.

Consider the effect of this change of the nucleophile on the apparent rate of reaction. Suppose that a substrate, ZX, reacts simultaneously with alkoxide and hydroxide ions, according to the second order rate law, as follows:



If it is assumed that the products do not react further and that only one equivalent of base is consumed, then

$$\begin{aligned} \frac{dy_i}{dt} &= k_i^0 (a-x) (b-x) & x &= y_1 + y_2 \\ s_i &= \frac{[OR_i^-]}{[\text{total base}]} \end{aligned}$$

where k_i^0 is the specific rate constant for attack by OR_i^- , a , b are the initial concentrations of substrate and base, and y_i is the concentration of the i th reaction product. If the base fractions are not known then the apparent rate constant is

$$k_i = k_i^0 s_i$$

The total rate of reaction is measured by the change in the total concentration of products:

$$\frac{d\sum y_i}{dt} = \frac{dx}{dt} = (a-x)(b-x) \sum_{i=1}^2 k_i$$

so that the apparent overall rate constant is

$$k = \sum_{i=1}^2 k_i = k_1^{\circ} s_1 + k_2^{\circ} s_2$$

If all other factors were held constant the variation in the apparent overall rate constant, due to the change in nucleophile, would depend on the base fractions and the relative nucleophilicities of alkoxide and hydroxide ions. Suppose k_1° remains constant as the medium is changed from the alcohol to the aqueous alcohol. If $k_1^{\circ} < k_2^{\circ}$, i.e. if $k_H^{\circ} < k_R^{\circ}$, then an increase in s_1 , the fraction of base present as hydroxide ion, will cause a decrease in the apparent overall rate constant.

Determination of the relative nucleophilic strengths of OEt^- , OMe^- and OH^- , has been attempted. For attack at an aliphatic carbon atom in 100% dioxane⁶ the order is $\text{OEt}^- > \text{OMe}^- > \text{OH}^-$ in the ratio:

$$\text{OEt}^- : \text{OMe}^- : \text{OH}^- = 4.5 : 3 : 1$$

6. (Miss) I. Alet, M.Sc. Thesis, Victoria University of Wellington, 1959.

A similar order is observed for attack on an ester in water⁷, where the rate of attack is in the ratio:

$$\text{OEt}^- : \text{OMe}^- : \text{OH}^- = 4.17 : 1.59 : 1$$

This evidence indicates that the above order of nucleophilic strengths can be expected, although the actual ratios may depend on the substrate, solvent and temperature.

The assumption that $k_H^O < k_R^O$ is thus justified. From this it is deduced that the decrease in the apparent overall rate constant will be particularly great when water is added to an alkaline solution in ethanol, because of the rapid change in nucleophile.

An example of the influence of solvent composition on the overall rate constant comes from the work of Murto⁸ on the methyl iodide/sodium alkoxide (+ hydroxide) reaction in ethanol-water and methanol-water solvents. From his work it is possible to find the specific rate constants, k_i^O , over the solvent range.

In terms of the rate of increase of reaction products, the rate expression for the bimolecular substitution reaction of an organic halide and base is

$$\frac{dy_i}{dt} = k_i^O (a-x)(b-x) s_i$$

(symbols defined on page 10).

7. M. L. Bender and W. A. Glasson, J. Amer. Chem. Soc., 81, 1959, 1590.

8. Vide ref. 2.

Therefore
$$\frac{dy_i}{dy_k} = \frac{k_i}{k_k}$$

This means that the products are formed in a constant ratio throughout the reaction, and this has been verified experimentally⁹.

If $y_i = y_k = 0$ when $t = 0$, then by integration,

$$\frac{y_i}{y_k} = \frac{k_i}{k_k} = \frac{k_i^0 s_i}{k_k^0 s_k}$$

That is, the ratio of the concentration of products (or product ratio) is equal to the ratio of the apparent rate constants. Murto has found the product ratio for the methyl iodide/base reaction, and so the specific rate constants can be found by using the approximate values of the base fractions calculated with $K'_{he} = 0.65$, $K'_{hm} = 4.5$. The data for this reaction in the given solvents is shown in Tables 1 and 2, and the variation of $\log k_i^0$, and $\log k$ (overall rate constant), with solvent composition is shown in Figures II and III.

9. (i) C.A.L. de Bruyn and A. Steger, *Rec. Trav. Chim.*, 18, 1899, 41;
Z. physik. chem., 49, 1904, 333.
- (ii) E. Tommila and J. Murto, *Acta Chem. Scand.*, 16, 1962, 53.

Table 1

Reaction: The alkaline solvolysis of MeI in ethanol-water mixtures. k , k_i^o in units: $1.\text{mole}^{-1}\text{sec}^{-1}$.

Wt. % alcohol	$x_{\text{H}_2\text{O}}$	Moles % ether in product	$k \times 10^5$	$k_e^o \times 10^5$	$k_h^o \times 10^5$
100	0	100.0	157	157	
90.4	0.214	97.6	131	181.5	10.5
79.4	0.399	94.1	95.5	181.6	11.2
66.2	0.567	88.1	64.9	172.3	11.6
56.4	0.665	82.2	50.4	167.6	11.9
45.3	0.755	73.6	39.1	165.5	12.5
30.7	0.852	56.0	23.4	129.7	11.5
20.4	0.909	42.9	15.6	110.0	9.5
11.8	0.950	27.1	9.53	78.2	7.2
0.0	1.000	0.0	5.80	-	5.8

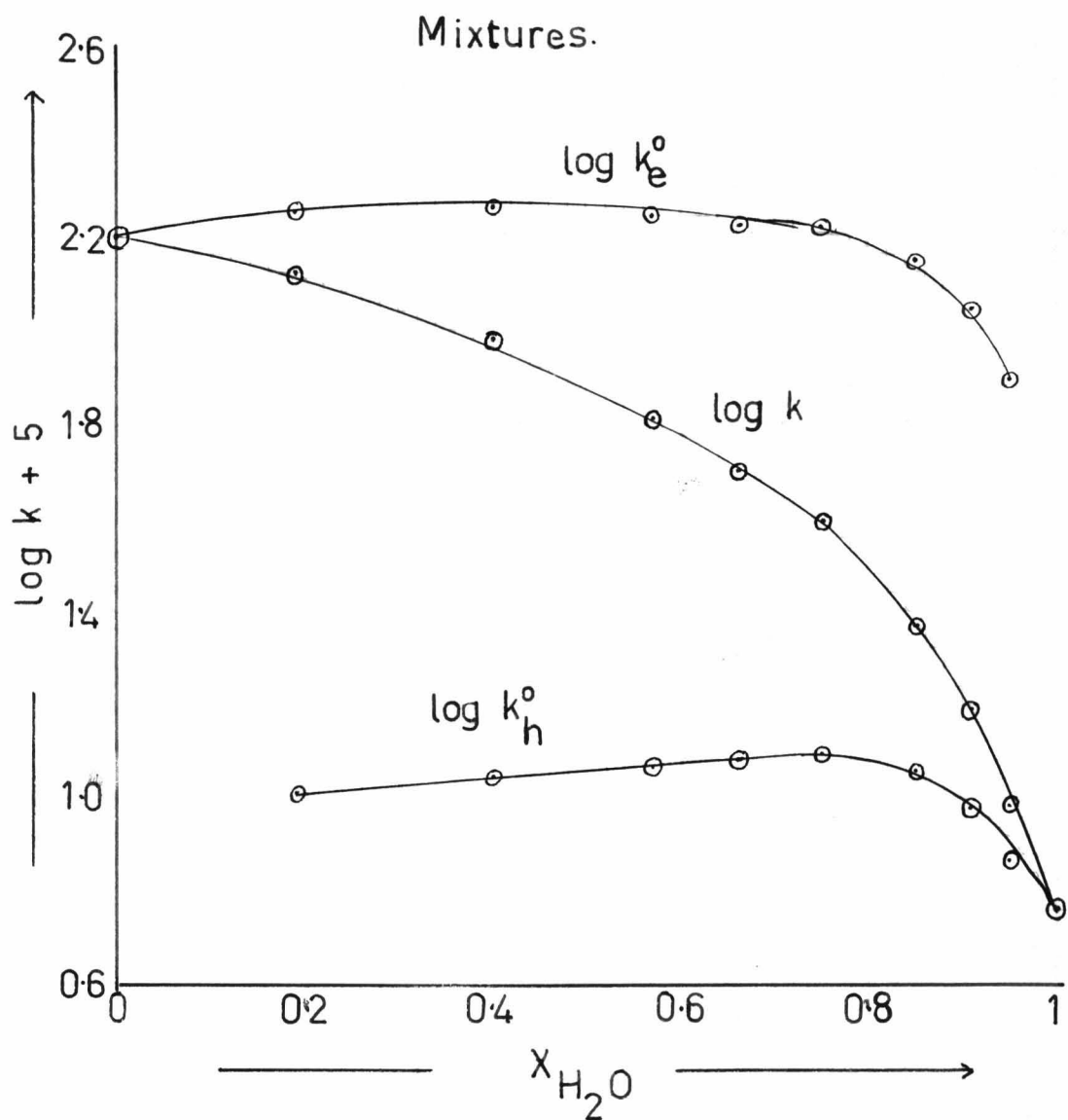
Table 2

Reaction: The alkaline solvolysis of MeI in methanol-water mixtures. k , k_i^o in units: $1.\text{mole}^{-1}\text{sec}^{-1}$.

Wt. % alcohol	$x_{\text{H}_2\text{O}}$	Moles % ether in product	$k \times 10^5$	$k_m^o \times 10^5$	$k_h^o \times 10^5$
100	0	100	27.8	27.8	
89.2	0.177	99.0	31.2	32.4	6.8
80.7	0.298	98.1	36.4	39.1	8.0
69.7	0.436	96.6	38.9	44.1	8.8
60.2	0.540	94.9	39.1	46.8	9.6
50.3	0.637	93.0	36.2	46.7	9.0
29.7	0.808	85.1	24.4	40.2	7.5
20.4	0.874	76.5	17.6	34.4	6.8
11.7	0.931	61.4	12.5	30.5	6.4
2.94	0.983	25.5	7.49	26.5	6.0
0.00	1.000	0.0	5.80	-	5.8

FIG. II

Variation of $\log k$, $\log k_i^0$ with
Solvent Composition in EtOH/H₂O

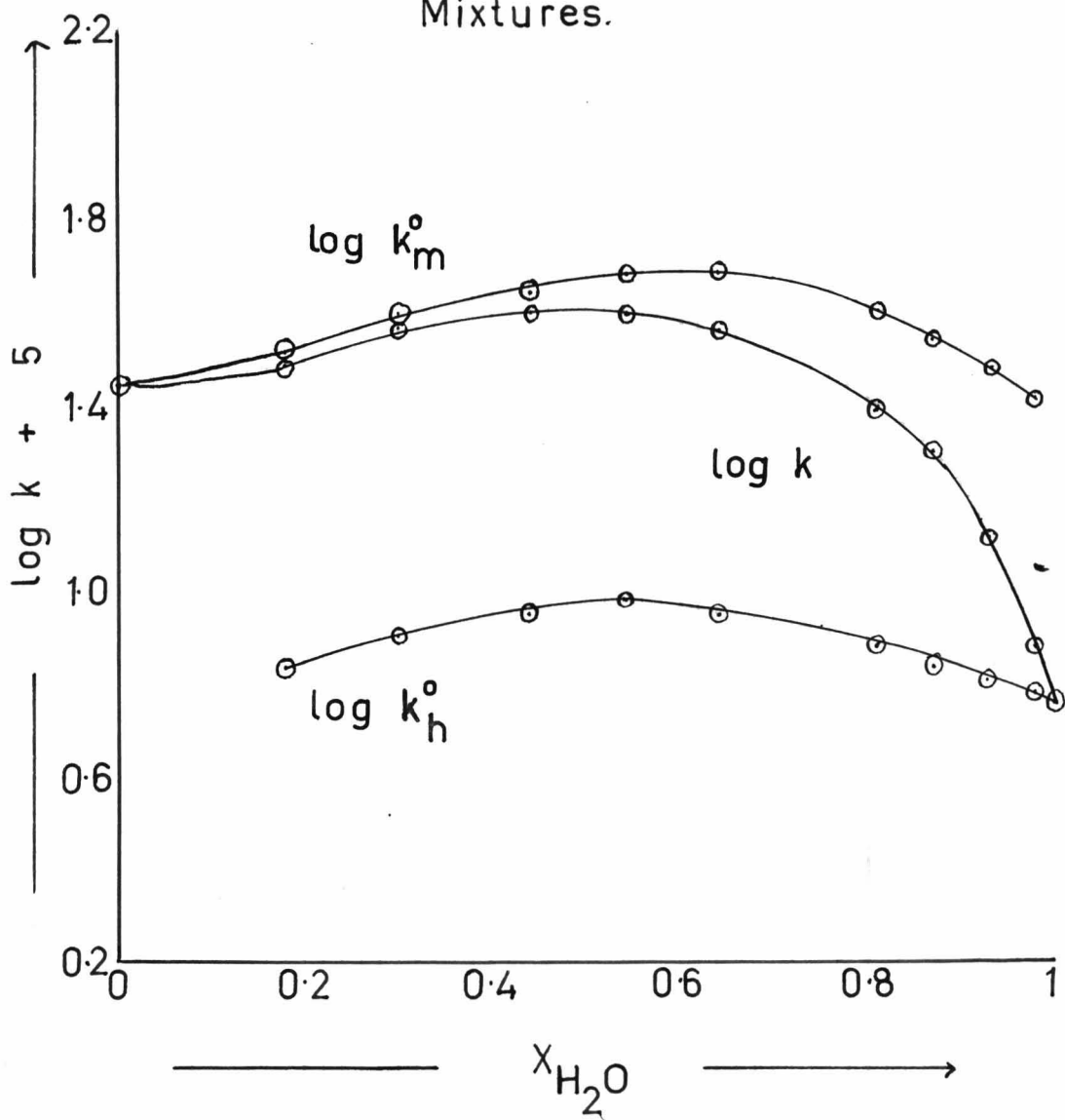


Substrate : Methyl iodide.

FIG. III

Variation of $\log k$, $\log k_i^\circ$ with
Solvent Composition in MeOH/H₂O

Mixtures.



Substrate : Methyl iodide

Although the values of s_i are approximate they show how k_i^0 varies with solvent composition. It appears that the specific rate constant, in every case, increases initially as water is added to the alcohol, and then decreases. Comparison of Figures II and III reveals that while the form of the overall rate constant is quite different for ethanol-water and methanol-water mixtures, the variation of k_i^0 is similar in the two solvent mixtures. The overall rate constant in methanol-water mixtures, and k_i in both solvent mixtures, increase initially as x_{H_2O} increases, but the more rapid change of nucleophile in ethanol-water mixtures causes the overall rate constant to decrease as x_{H_2O} increases.

2. Ion Association

A similar initial increase in second order rate constant, as the polarity of the solvent increased, was observed by Burns¹⁰ in the reaction of methyl iodide and thiophenoxide ions in aqueous alcoholic media. This is shown clearly in Table 3.

10. R. G. Burns, M.Sc. Thesis, Victoria University of Wellington, 1960.

Table 3

The Influence of Solvent Composition on the Methyl
Iodide/Sodium Thiophenoxide Reaction at 0°C

Solvent (Vol. % alcohol)	$10 k_2$ l.mole ⁻¹ sec. ⁻¹	$\frac{k_2^{\text{Aq}}}{k_2^{\text{Abs}}}$
Ethanol-water mixtures		
100	4.04	1
90	4.86	1.2
80	5.21	1.29
70	5.16	1.28
60	4.35	1.08
Methanol-water mixtures		
100	1.10	1
90	1.29	1.17
80	1.62	1.47
70	1.96	1.76
60	2.20	2.00

k_2^{Aq} = rate constant in aqueous alcohol

k_2^{Abs} = rate constant in absolute alcohol

Data from ref.10.

When sodium thiophenoxide is the attacking agent there should be no complicating effects of a change of nucleophile. Thiophenoxide ion is a relatively weak base¹¹ and so should not be susceptible to conversion to the hydroxide as the water content of the solvent increases. When methyl iodide is the substrate k_h^{O} is less than k_m^{O} or k_e^{O} , and comparison of the rate constants in

11. P.B.D. de la Mare and C. A. Vernon, J. Chem. Soc., 1956, 41.

Tables 1, 2 and 3, shows that the thiophenoxide ion is a much stronger nucleophilic reagent than the ethoxide or methoxide ions.

If a substantial change of nucleophile did occur as x_{H_2O} increased, then this would cause a decrease in the rate constant for the methyl iodide/sodium thiophenoxide reaction. However, the second order rate constant increased, and so this means that k_{PhS}^O increased, initially at least, as the solvent polarity was increased.

The dielectric constants of alcohols are lower in value than the dielectric constant of water, as is shown in Table 4.

Table 4

Solvent (Liquid at 25°C)	Dielectric Constant ¹²
Water	79
Ethanol	24.2
Methanol	31.5

Because of this, association of ions into ion pairs, and ion triplets, can occur to an appreciable extent in alcohols¹³. These ion aggregates are believed to react at a different (usually

12. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London, 1955, p.448.

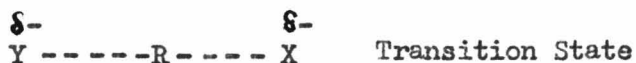
13. J. D. Reinheimer, W. F. Kieffer, S. W. Frey, J. C. Cochran and E. W. Barr, *J. Amer. Chem. Soc.*, 80, 1958, 164.

lower¹⁴⁾ rate than the free ions. Burns and England¹⁵ concluded that the above increase in rate constant with increasing water content of the solvent could be attributed to the progressive dissociation of the ion-pairs formed by the base.

3. Hughes-Ingold Solvent Effect

The general theory of solvent effects in alkoxylation reactions of alkyl halides was first put forward by Hughes and Ingold¹⁶. They divided nucleophilic substitution into two broad groups termed bimolecular (S_N2) and unimolecular (S_N1) substitutions¹⁷.

The bimolecular mechanism is a one stage process involving an electron transfer from the substituting agent to the seat of substitution, and from the latter to the displaced group. At the transition state of the reaction between an anion, Y^- , and substrate, RX , the negative charge is distributed over X and Y as follows:



14. S. Winstein, L. G. Savedoff, S. Smith, I.D.R. Stevens and J. S. Gall, Tetrahedron Letters, 9, 1960, 24.

15. R. G. Burns and B. D. England, *ibid.*, 24, 1960, 1.

16. E. D. Hughes and C. K. Ingold, J. Chem. Soc., 1935, 252.

17. C. K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, New York, 1953.

The unimolecular mechanism of nucleophilic substitution involves two stages: a slow heterolysis of the substrate followed by a rapid combination of the formed carbonium ion and the attacking agent.

These two types of substitution are then classified into "charge types"¹⁸ depending on the charges on the initial reactants.

Hughes and Ingold estimate the effects of solvation on the initial and transition states of these nucleophilic substitutions, and its contribution towards the activation energy for the reaction. They assume that solvation

1. increases with increasing magnitude of charge,
2. decreases with increasing dispersal of a given charge,
3. increases or decreases to a greater extent when a charge is created or destroyed.

Solvent polarity is assumed to

1. increase with the dipole moment of the solvent,
2. decrease in solvents where the dipole charge is shielded.

On this basis the effect on reaction kinetics is that a change to a more polar solvent will decrease or increase the heat of activation, according to whether the transition state is more or less polar than the initial state of the reactants.

18. Vide ref. 17, p.347.

For example, in the reaction of an uncharged substrate, RX , reacting with an anion, Y^- , the predicted effects of solvent changes are as follows:

Table 5

Predicted Solvent Effects on Rates of
Nucleophilic Substitutions

Disposition of Charges		Effect of activation on charges	Effect of increased polarity on rate
Initial State	Transition State		
(i) Bimolecular mechanism			
$Y^- + RX$	δ^- δ^- $Y \cdots R \cdots X$	Dispersed	Small decrease
(ii) Unimolecular mechanism			
RX	δ^+ δ^- $R \cdots X$	Increased	Large increase

Taken from C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, New York, page 347.

The methyl iodide/iodide ion reaction studied by Burns¹⁹ in alcohol-water solvents is free from any complicating change of nucleophile and shows the trend predicted by the Hughes-Ingold theory. Rate constants for the reaction are shown in Table 6.

19. Vide ref. 10.

Table 6

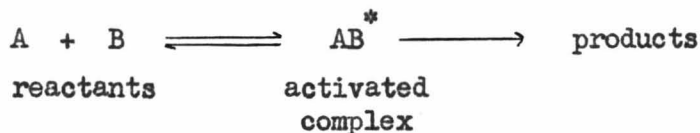
The influence of solvent composition on
the iodide exchange of MeI

Reaction: Methyl iodide/potassium iodide at 25°C.

Solvent (Vol. % methanol in aq. methanol)	$10^3 k_2$ 1.mole ⁻¹ sec. ⁻¹	$\frac{k_2^{\text{Aq}}}{k_2^{\text{Abs}}}$
100	7.64	1
90	6.98	0.914
80	6.39	0.836

There seems to be little other evidence that the Hughes-Ingold effect is in operation in the reactions discussed so far. In their treatment of solvent influences on activation energy, Hughes and Ingold neglected entropy effects, considering these to be negligible. To investigate the consequences of this omission it is necessary to define a few properties of the transition state for a reaction.

The transition state theory considers the activated complex as a chemical species in equilibrium with the reactants as shown.



For this one can define an equilibrium constant K^{++} :

$$K^{++} = \frac{[AB^{++}] \gamma_{AB^{++}}}{[A][B] \gamma_A \gamma_B}$$

where γ_i is the activity coefficient of i .

Since the reaction rate is proportional to the number of AB complexes passing through the transition state in the forward direction, the specific rate, k_r , is proportional to $[AB^{++}]$ which is proportional to K^{++} .

It is possible to show that²⁰

$$k_r = \frac{kT}{h} K^{++}$$

where k = Boltzmann's constant

T = absolute temperature

h = Plank's constant

Thermodynamic quantities defined are:

$$\begin{aligned} \text{Free energy of activation } \Delta F^{++} &= -RT \ln K^{++} \\ &= \Delta H^{++} - T \Delta S^{++} \end{aligned}$$

$$\text{Enthalpy of activation } \Delta H^{++} = R \frac{d \ln K^{++}}{d \left(\frac{1}{T} \right)}$$

$$\text{Entropy of activation } \Delta S^{++} = \frac{\Delta H^{++} - \Delta F^{++}}{T}$$

$R = Nk$ N = Avogadro's Number

The Arrhenius energy of activation, E_a , is defined as

$$\frac{d \ln k_r}{d \left(\frac{1}{T} \right)} = \frac{E_a}{R}$$

Entropy of activation is a measure of the difference in freedom of the initial and transition states of the reaction. For reactions in solution entropy effects also include changes in orientation of the solvent molecules as new species, requiring differing degrees of solvation, are formed from the reactants. If, in a reaction, the total number of molecules decreases, or if the molecules become more rigidly orientated, then the entropy of activation is negative. For a reaction in which a neutral molecule forms ions the charge separation begins in the transition state. The dipole becomes solvated with a sheath of molecules which are suitably orientated. This increase in orientation and restriction in the freedom of the solvent causes a decrease in entropy.

Murto²¹ has calculated the energies and entropies of activation for the alkaline solvolysis of methyl iodide in methanol-water and ethanol-water solvents. From these it can be seen that the decreases in the entropies of activation as the proportion of water in the solvent increased, were much larger than any changes in the energies of activation. Thus, Hughes' and Ingold's assumption that entropy effects are negligible is not valid.

From the relationships on page 22 a negative entropy of activation can retard a reaction. This means that the decrease

21. Vide ref. 2.

in the second order rate constant for the methyl iodide/potassium iodide reaction, as the alcoholic solvent becomes more aqueous, may be due to entropy effects rather than the Hughes-Ingold effect.

These entropy effects should be present in the alkoxylation reactions of alkyl halides, but it appears that they must be overshadowed by ion association effects, or some other effect yet to be determined.

Combination of these effects in the S_N2 reactions of primary alkyl halides

For any particular alkoxylation reaction in aqueous alcoholic media, the actual increase or decrease in rate, as the solvent changes, seems to depend on the balance in the effect of the phenomena already mentioned: the change in nucleophile, ion association, the Hughes-Ingold or entropy effects, as well as other possible effects of solvent change so far unrevealed.

Typical behaviour of a saturated, primary, aliphatic halide in this reaction can be taken to be that of methyl iodide and base in alcohol-water solvents.

Data for these reactions were given in Tables 1 and 2, and shown graphically in Figures II and III.

On the basis of known solvent effects, the form of the graphs can be explained in the following manner. The decrease in the overall rate constant in ethanol-water mixtures as x_{H_2O} increases, is attributed mainly to the large change in nucleophile from the ethoxide to the hydroxide ion which attacks the substrate more slowly.

The "methoxylation" reaction shows the initial rate increase which is thought to be due to the influence of ion pairing as explained on page 15. Similar effects must be operating in ethanol-water mixtures but their presence is not made obvious unless the specific rate constants k_i^0 are separated out.

These results are in qualitative agreement with the results of Burns²² and of de Bruyn and Steger²³ for the alkoxylation reactions of methyl iodide and ethyl iodide in ethanol-water and methanol-water mixtures. The alkaline ethanolysis and hydrolysis of n-propyl chloride²⁴ also shows the expected decrease in overall rate constant as the water content of the solvent increases.

The analysis of the overall rate constant into two specific rate constants, k_x^0 and k_h^0 , highlights the difficulties of trying to fit the former constants into any general theory of solvent action. Alkoxylation reactions in aqueous ethanolic and aqueous methanolic media appear to be very different when the overall

22. Vide ref. 10.

23. C.A.L. de Bruyn and A. Steger, *Rec. Trav. Chim.*, **18**, 1899, 311.

24. C.A. Vernon, *J. Chem. Soc.*, 1954, 4462.

specific rate constant is used as a criterion. Results from the work of Murto (see Figures II and III) indicate that similar effects are operating in both media. A variation in the relative nucleophilicity of OH^- and OR^- can cause the form of the graph of $\log k$ vs. $x_{\text{H}_2\text{O}}$ to change considerably as the substrate is changed.

In order to have a clearer idea of solvent effects in the $\text{S}_{\text{N}}2$ reactions of alkoxide and hydroxide ions it is necessary to have more information about product ratios, so that individual specific rate constants for each nucleophile can be separated and analysed.

Bimolecular reactivity of allylic halides

In the course of a study on nucleophilic substitution, Vernon²⁵ investigated the effect of a change in solvent polarity on the rate of the kinetically second-order reaction of an allylic halide and anionic base. He found that the rate of attack by base increased as the solvent was changed from ethanol to aqueous ethanol. These results can now be examined and compared with the usual behaviour of primary alkyl halides.

Contrary to expectations the apparent specific rate constants increased as the solvent polarity increased.

Table 7 shows the ratio $\frac{k_2 \text{ (aqueous solvent)}}{k_2 \text{ (pure solvent)}}$ for the reactions of some saturated alkyl halides, and some allyl chlorides, with ethoxide and hydroxide ions.

Table 7

Reactivity of some alkyl halides in ethanol-water
and dioxane/water mixtures

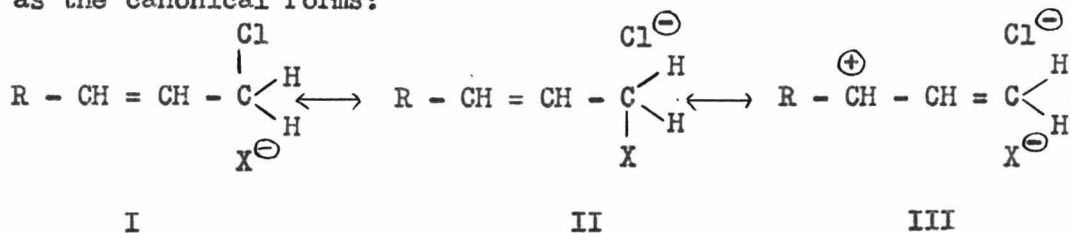
Substrate	T (°C)	Vol. % ethanol in aqueous ethanol	$k_2 \times 10^4$ l.mole ⁻¹ sec. ⁻¹	$\frac{k_2^{\text{Aq}}}{k_2^{\text{Abs}}}$	Ref.
CH ₂ =CH ₂ -CH ₂ Cl (allyl chloride)	44.6	100	1.57	1	24
		75	1.72	1.1	
		50	2.18	1.39	
CH ₂ =CH-CH ₂ -Cl (2-methyl allyl chloride)	44.6	100	1.58	1	24
		50	2.50	1.58	
CH ₂ -CH ₂ -CH ₂ Cl (n-propyl chloride)	101.6	100	9.07	1	24
		75	6.00	0.66	
		50	5.90	0.65	
CH ₃ I (methyl iodide)	25	100	15.9	1	26
		90	12.6	0.795	
		80	8.85	0.557	
		70	6.40	0.403	
		60	5.02	0.316	
		Vol. % dioxane in aq. dioxane			
CH ₂ =CH ₂ -CH ₂ Cl (allyl chloride)	64.9	60	6.07		24
		40	12.3		

Comparison of values of k_2 for the allyl halides with those for the saturated primary halides, indicates that in 50% alcohol the specific rate constants of the former compounds have increased by

approximately 50%, while the specific rate constants of the latter halides have decreased by a similar percentage.

Whatever phenomenon influences this rate increase it must be great enough to completely counteract the effect of the change of nucleophile which was a determining factor in the reactions of saturated primary alkyl halides (see page 1). According to the Hughes-Ingold classification (page 20) this change in reaction rate is more typical of an S_N1 reaction.

An attempt was made to find some explanation for this behaviour. Vernon suggested that the transition state for the nucleophilic attack on an allylic halide could be expressed as the canonical forms:



Form III is highly polar and therefore "when its contribution is considerable,, the reaction will take on the characteristics of an S_N1 reaction, i.e. it will be accelerated by suitably placed electron releasing substituents and by a change to a more polar medium".

With reference to the first comment, rate acceleration by electron releasing substituents, although a characteristic of S_N1 reactions, can also occur in normal S_N2 reactions. The effect

of electron withdrawing or releasing substituents on S_N2 reactions has been described by Hine²⁷, who says that there may be a variation in relative extent of bond making and breaking in the transition state of an S_N2 reaction. Thus transition states can be divided into categories.

- (a) The new bond is formed to a greater extent than the old one is broken - reactivity is increased by electron withdrawing substituents.
- (b) The old bond is broken to a greater extent than the new one is formed - reactivity is increased by electron withdrawing substituents.
- (c) Bond making and breaking have occurred to the same degree and so reactivity may be increased by either type of group.

A plot of reactivity against the electron withdrawing power of substituents²⁸, produces a curve with a minimum point which corresponds to a transition state of type (c).

Thus for a reaction proceeding by the S_N2 mechanism, the acceleration of rate by electron releasing groups corresponds to a transition state of type (b). In the allylic halide reactions this would merely imply that, at the transition state, the Cl atom was more loosely held than the X group.

27. J. Hine, Physical Organic Chemistry, McGraw-Hill, New York, 1956.

28. (i) J. W. Baker and W. S. Nathan, J. Chem. Soc., 1935, 1840.

(ii) C. S. Swain and W. P. Langsdorf, J. Amer. Chem. Soc., 73, 1951, 2813.

Consider the effect of a change in solvent polarity on relative energies of the allyl halide and anion X^- , and the transition state of the reaction as postulated by Vernon.

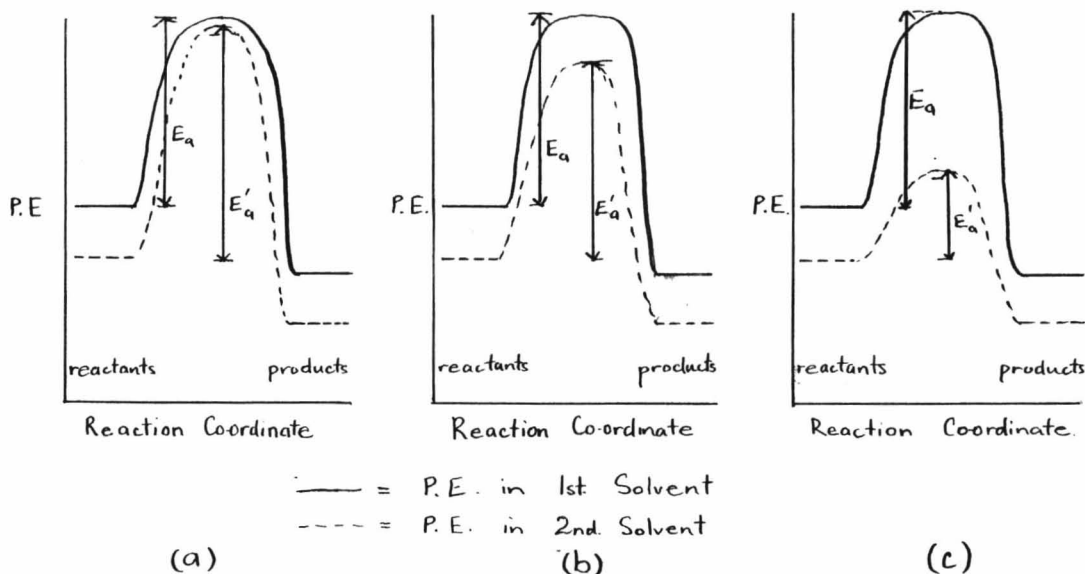
In a reaction in which charge is being created the largest entropy decrease occurs in the less polar solvents. Polar solvents are highly orientated so that any change in orientation will not be great.

Thus, the difference in the entropy of activation for a reaction in two different solvents will depend on the magnitude of the change in solvation of the transition states in these solvents. If this is not large then the entropy of activation can be considered constant, and the main factor determining the relative rates of reaction will be changes in solvation energy.

Suppose, in estimating solvent effects on reaction rates, the assumptions made are the same as in the original theory of Hughes and Ingold - that is the main changes of the activation energy on changing the solvent come from the difference in the energy of solvation of the initial and transition states.

If one increases the polarity of the solvent, then both the initial state and transition state will be solvated to a greater extent, and so the potential energy of each will be decreased. The relative value of the activation energy in different solvents will depend on the fall in potential energy of both states.

The potential energy of reactants throughout the reaction can be represented diagrammatically as follows:



Curves a, b, and c, represent the situation in which the change in potential energy of the transition state is less, the same, or more, respectively, than the initial state. Relative values of the activation energy in the two solvents are marked on the diagram. For the activation energy to be lowered the fall in potential energy for the initial state must be less than that for the transition state.

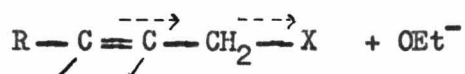
Now consider the mechanism postulated by Vernon, and the effect of solvation on the initial and transition states.

In the allyl bromide molecule the inductive effect of the Cl atom causes the C-Cl bond to be polar, and this effect is enhanced by the presence of the double bond from which the Cl atom

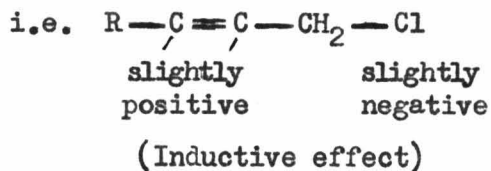
can draw electrons. As the other reactant, the ethoxide ion, approaches the α C atom its negative charge will tend to repel the electrons away from the α C atom, driving them back to the double bond and causing the C-Cl bond to lengthen.

This process can be shown in a molecular orbital picture:

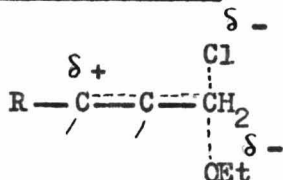
Initial state:



Arrows show the direction of the inductive effect of the X atom.



Transition state:



This shows that the separation of charges in the transition state is not as great as the Valence Bond representation may cause one to believe.

The effects of a change in solvent polarity on the two states, may now be estimated.

The initial state is that of a polar molecule and a negatively charged ion. As solvent polarity increases, the two entities, particularly the latter, will show quite a large decrease

in potential energy because of the increase in solvation. If a charge is dispersed the stabilization by solvation in a more polar solvent will be less than that for the original charge. Thus in the transition state the effect of the dispersal of the charge of the ethoxide ion is compensated by only a small charge separation. Therefore it seems unlikely that this transition state will show a larger decrease in potential energy in a more polar solvent, than the initial state of the reactants. As shown in diagram (c), page 31, this would have to occur for the reaction rate to be increased by more polar solvents.

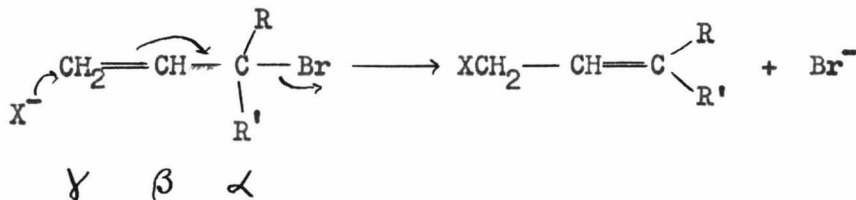
It appears that Vernon's explanation of the mechanism of allylic halide reactions is not quite adequate. Thus the object of the present work is to verify that this "allylic peculiarity" towards bimolecular substitution does occur over an extended solvent range, and to try to suggest some other explanation for its occurrence.

EXPERIMENTAL IKinetics of the alkaline solvolysis of allyl
bromide in alcohol-water solventsChoice of substrate

The purpose of the following work was to investigate the behaviour of the kinetically second order reaction of allyl compounds with alkoxide and hydroxide ions in alcohol-water mixtures. Allyl bromide was chosen as a substrate as it is

- (i) easily obtainable,
- (ii) does not appear to have any complicating side reactions such as the S_N2' , or elimination reactions:

(a) The S_N2' reaction¹, (abnormal bimolecular displacement), is one in which the nucleophile attacks the γ carbon atom, causing π -electrons to flow towards the β and α carbon atoms as the bromide ion is pulled off by the solvent.

The S_N2' reaction

This reaction is usually observed when the normal S_N2 reaction is hindered by the presence of alkyl groups attached

1. Review on the S_N2' reaction, R. H. de Wolfe and W. G. Young, Chem. Revs., 56, 1956, 769-784.

to the α carbon atom. In this case, if there are not any bulky groups attached to the γ carbon atom, the S_N2' reaction can proceed easily. The presence of an S_N2' reaction for allyl bromide has not been investigated, but one can argue by analogy with reference to α -methyl allyl chloride ($CH_2 = CH - \underset{\text{Cl}}{\overset{\text{Me}}{\text{CH}}}$).

Some workers² concluded that the nucleophilic attack of ethoxide ion in ethanol proceeded 100% by the normal S_N2 mechanism. Others³ suggested that more than 96% of the product resulted from normal displacement. England and Hughes⁴ investigated the S_N2' and S_N2 reactions of α -methyl allyl bromide with lithium bromide in acetone, and obtained the following rate constants at 25°C.

	<u>Mechanism</u>	<u>$10^6 k_2$ (1.mole⁻¹sec⁻¹)</u>
α -methyl allyl chloride	S_N2	879
and LiBr in acetone	S_N2'	14.9

That is, $\frac{\text{the specific rate constant of the } S_N2 \text{ reaction}}{\text{the specific rate constant of the } S_N2' \text{ reaction}}$

$$= \frac{879}{14.9} \approx \frac{59}{1}$$

The error in k_2 calculated by assuming only the S_N2 mechanism was operating would be less than 2%. In this compound the presence of the α -methyl group would favour the S_N2' reaction relatively,

2. A. G. Catchpole and E. D. Hughes, J. Chem. Soc., 1948, 4.
3. J. D. Roberts, W. G. Young and S. Winstein, J. Amer. Chem. Soc., 64, 1942, 2157.
4. (i) B. D. England and E. D. Hughes, Nature, 168, 1951, 1002.
(ii) B. D. England, J. Chem. Soc., 1955, 1615.

so that one can safely assume that in allyl bromide (in which attack at the α -carbon atom is not sterically hindered), any reaction occurring by the S_N2' mechanism is negligible.

(b) Vernon⁵ could not isolate any butenes from the reaction mixture, and so it can be assumed that no elimination occurs.

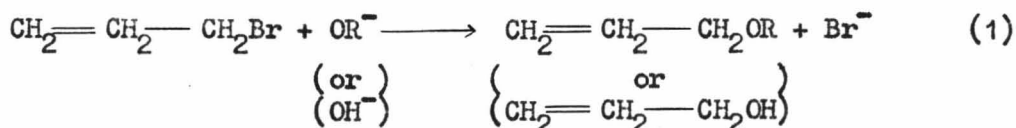
Preparation of Solvents

Ethanol and methanol were purified and dried as described in the section on reagents. The alcohol-water solutions were made up at 20°C by adding the required volume of distilled water to the dry alcohol. For example, a solution containing 80% alcohol was prepared by adding 20 volumes of water to 80 volumes of alcohol. Approximately 1000 ml. of each mixture were made up at one time in order to eliminate fluctuations in solvent composition which could have arisen if small volumes were prepared before each kinetic run.

Preliminary Discussion

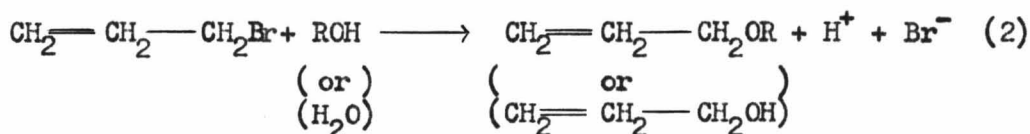
Without reference to mechanism the reaction of allyl bromide and base, in a given medium, can be represented as follows:

5. C. A. Vernon, J. Chem. Soc., 1954, 4462.



R = methyl or ethyl radical

Allyl bromide also takes part in solvolysis:



Let x be the concentration of bromide ion at any time

t, then

$$\frac{dx}{dt} = k_s(a-x) + k_2(a-x)(b-x) \quad (3)$$

where k_s is the rate constant for solvolysis, k_2 is the apparent overall rate constant⁶ for reaction (1), 'a' is the initial concentration of allyl bromide, and 'b' the initial concentration of base. If $k_s(a-x)$ is negligible compared with $k_2(a-x)(b-x)$ then

$$\frac{dx}{dt} \doteq k_2(a-x)(b-x) \quad (4)$$

Integration of (4) leads to the second order rate equation:

$$k_2 = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad (5)$$

In the absence of base

$$\frac{dx}{dt} = k_s(a-x)$$

or $\frac{dx}{dt} \frac{1}{(a-x)} = k_s$

i.e. $V_o \frac{1}{a} = k_s$ (6)

where V_o = the initial rate.

PART A: Kinetics of the bimolecular substitution
reaction by bromide ion analysis

Procedure

The allyl bromide solution (0.06 M) was prepared by dissolving a weighed amount of allyl bromide* in the appropriate solvent, and making it up to 100 ml. in a standard flask at 25°C. Methoxide and ethoxide solutions (0.12 M) were prepared as in the reagents' section.

Reactions were carried out at 25°C in a water bath thermostatically controlled by a toluene-mercury regulator. (Temperature variations were $\pm 0.02^\circ\text{C}$ or less). Evaporation of water from the bath was minimised by the presence of a thin film of paraffin on the surface of the water.

The reaction was followed by the "stoppered flask" technique. The alkoxide solution (100 ml., 0.12 M) and the allyl bromide solution (100 ml., 0.06 M), both at 25°C, were added to a reaction flask in the water bath. To prevent oxidation of the bromide ion to bromine the reaction flasks were painted black.

At various time intervals 10 ml. aliquots of the reaction mixture were removed and added to a slight excess of dilute nitric acid. About nine such samples, covering about 60%-85% of the reaction, were removed during an individual run. Zero time for the reaction was taken from the time of the removal of the first sample.

* See "Reagents".

Each sample was analysed for bromide ion by potentiometric titration against standard silver nitrate, using a Doran Potentiometer. The cell used for the analysis was:

$\text{Ag/AgBr, Br}^-(xM)/3\% \text{ Agar in } 0.1 \text{ M KNO}_3/\text{Calomel electrode}$

Indicator electrode Salt bridge Standard electrode

Alcohol was added to the mixture being analysed, in order to lower the solubility of the bromide ion and so produce a sharp end point to the titration. While the silver nitrate was being added the solution was stirred with a mechanical stirrer.

Details of typical runs are given in Tables 8 and 9. To obtain k_2 it was assumed that solvolysis was negligible (equation 5).

Table 8

Reaction: allyl bromide/sodium ethoxide (and hydroxide) in 80%
EtOH/20% H₂O at 25°C

[allyl bromide] = 0.0297 M

[base] = 0.0558 M

Time (sec.)	[Br ⁻] (in equivalent mls. of 0.0099 M AgNO ₃)	[allyl bromide]	[base]	$k_2 \times 10^3$ 1.mole ⁻¹ sec. ⁻¹
0	0	29.95	56.3	-
1200	2.65	27.30	53.65	1.41
2435	5.09	24.86	51.21	1.43
3600	7.03	22.92	49.27	1.42
4800	8.87	21.08	47.43	1.43
7200	11.93	18.02	44.37	1.43
9000	13.79	16.16	42.51	1.42
10810	15.49	14.46	40.81	1.44
12780	16.93	13.02	39.37	1.42
14400	18.07	11.88	38.23	1.43

Average $k_2 = 1.42 \times 10^{-3}$ 1.mole⁻¹sec.⁻¹

Table 9

Reaction: allyl bromide/sodium methoxide (and hydroxide) in
60% MeOH/40% H₂O at 25°C

[allyl bromide] = 0.0308 M

[base] = 0.0593 M

Time (sec.)	[Br ⁻] (in equivalent ml. of 0.0111 M AgNO ₃)	[allyl bromide]	[base]	k ₂ x 10 ³ l.mole ⁻¹ sec. ⁻¹
0	0	27.93	58.14	-
1260	4.08	23.85	54.06	2.20
2400	7.13	20.80	51.01	2.22
3720	10.02	17.91	48.12	2.23
4920	12.16	15.77	45.98	2.22
6000	13.77	14.16	44.37	2.21
7200	15.33	12.60	42.81	2.21
9000	17.24	10.69	40.90	2.20
10860	18.76	9.17	39.38	2.17
12620	20.23	7.70	37.91	2.21

Average k₂ = 2.21 x 10⁻³ l.mole⁻¹sec.⁻¹

Results

Results of the alkoxylation reactions of allyl bromide are summarised in Table 10.

Table 10

Reaction: allyl bromide/alkoxide (and hydroxide)
ions at 25°C

Solvent (Vol. % ethanol in aq.ethanol)	$k_2 \times 10^3$ 1.mole ⁻¹ sec. ⁻¹	$\frac{k_2^{\text{Aq}}}{k_2^{\text{Abs}}}$	Solvent (Vol. % methanol in aq.methanol)	$k_2 \times 10^3$ 1.mole ⁻¹ sec. ⁻¹	$\frac{k_2^{\text{Aq}}}{k_2^{\text{Abs}}}$
100	1.14	1	100	0.458	1
90	1.38	1.21	90	0.79	1.72
80	1.42	1.24	80	1.27	2.77
70	1.44	1.26	70	1.76	3.84
60	1.47	1.29	60	2.21	4.82
50	1.42	1.24			

In ethanol-water mixtures the overall rate constant increased initially reaching a maximum in 60% (by vol.) ethanol. The general increase in rate constant is in qualitative agreement with the results of Vernon⁷.

Reactions in methanol-water mixtures showed a more rapid increase in the overall rate constant as the water content of the solvent increased.

7. Vide ref. 5.

It was expected that, during an individual run, solvolysis of the allyl bromide might cause the calculated rate constants to drift. However, any drift was not apparent and values during each run varied by about 3% only. This indicates that any solvolytic action is not great but this will be investigated in the section on solvolysis.

PART B: Kinetics of the bimolecular substitution
reaction by analysis for alkali

As a check on the results in Part A a second method of analysis was used.

Procedure

Allyl bromide and ethoxide solutions were prepared as in Part A, and the same "stoppered flask" technique was used to carry out the reaction.

At various time intervals 10 ml. aliquots were removed from the reaction mixture and quenched with 25 ml. of approximately 0.03 N hydrochloric acid. To further quench the reaction the flask containing the acid and sample was chilled in an ice bath.

The excess of acid was measured by titration (under nitrogen) with standard sodium hydroxide (bromothymol blue indicator). From this the concentration of base in each sample could be calculated.

About 10 samples were removed during the reaction. Zero time for the reaction was taken as the time of the removal of the first sample.

Details of a typical run are given in Table 11.

Table 11

Reaction: allyl bromide/sodium ethoxide (and hydroxide) in
70% EtOH/30% H₂O at 25°C

$$[\text{allyl bromide}] = 0.0278 \text{ M}$$

$$[\text{base}] = 0.0585 \text{ M}$$

$$25 \text{ ml. of } 0.0401\text{N HCl} \equiv 26.2 \text{ ml. of } 0.0383\text{N NaOH}$$

Time (sec.)	excess [HCl] (in equivalent mls. of 0.0383N NaOH)	[base]	[allyl bromide]	$k_2 \times 10^3$ $\text{l.mole}^{-1}\text{sec.}^{-1}$
0	10.95	15.25	7.25	-
1200	11.50	14.70	6.70	-
2460	12.12	14.08	6.08	-
3665	12.80	13.40	5.40	1.46
5340	13.37	12.83	4.83	1.42
7140	13.90	12.30	4.30	1.40
8945	14.40	11.80	3.80	1.42
10760	14.80	11.40	3.40	1.41
12540	15.19	11.01	3.01	1.44
14350	15.46	10.74	2.74	1.41
16560	15.85	10.35	2.35	1.45

$$\text{Average } k_2 = 1.43 \times 10^{-3} \text{ l.mole}^{-1}\text{sec.}^{-1}$$

Results

Kinetic measurements were checked for 90%, 80% and 70% (by vol.) ethanol using this method. Results from the two methods of analysis are compared in Table 12. Differences amount to 2% or less.

Table 12

Comparison of rate constants from
two methods of analysis

The allyl bromide/alkoxide (and hydroxide) ion reaction at 25°C.

<u>Vol. % ethanol</u> <u>in aqueous ethanol</u>	$\frac{k_2 \times 10^3}{\text{l.mole}^{-1}\text{sec.}^{-1}}$	
	$[\text{Br}^-]$ analysis	alkali analysis
90	1.38	1.40
80	1.42	1.42
70	1.44	1.43

For an individual run the values for the overall rate constant, calculated from the alkali concentration, varied more than those obtained in Part A. During the titrations for bromide ion concentration the solution being analysed was acidic, and so the reaction was quenched from the beginning to the end of the analysis. However, in Part B, the excess of acid was titrated against alkali and so at the end point of the titration the solution would have been neutral. Any excess of alkali would have

reacted with the allyl bromide, thus causing an error in finding the actual end point of the titration, and also in calculating the values for the rate constant.

In Part A it was assumed that the bromide ion liberated during the reaction was also a measure of the alkali used up. In Part B it was assumed that the alkali used up corresponded to the amount of allyl bromide that had reacted. The results from the two methods are the same within the experimental error, and so the assumptions made are consistent. That is, equivalent amounts of allyl bromide and sodium alkoxide or hydroxide react together.

PART C: Solvolysis of allyl bromideProcedure

To measure the rates of solvolysis in alcohol-water solvents, the procedure in Part A was repeated with sodium perchlorate replacing the sodium alkoxide. The concentration of the sodium perchlorate was the same as that of the sodium alkoxide so that the solvolysis rate would be measured in solutions of the same ionic strength as the original solutions.

The solvolytic reaction was followed by analysis of the bromide ions produced. Solvolysis of allyl bromide produces ions which increase the ionic strength of the solution. This causes the rate of solvolysis to change and so initial rates of solvolysis were determined.

From equation 6:

$$\left. \frac{dx}{dt} \right)_{t=0} \frac{1}{a} = k_s \quad \text{or} \quad \frac{V_0}{a} = k_s$$

Results

Values of k_s (the solvolysis rate constant) are shown in Table 13. For comparison, values of k_2 are given also.

Now from equation 3, the total rate of reaction, in the alkaline solvent, is given by

$$\frac{dx}{dt} = k_s(a-x) + k_2(a-x)(b-x)$$

Table 13

The alkaline solvolysis of allyl bromide in alcohol-
water mixtures at 25°C

Solvent (Vol. % ethanol)	$k_2 \times 10^3$ (l.mole ⁻¹ sec. ⁻¹)	$k_s \times 10^6$ (sec. ⁻¹)
100	1.14	-
90	1.38	-
80	1.42	1
70	1.44	2.6
60	1.47	3.6
50	1.42	4.4
(Vol. % methanol)		
100	0.458	-
90	0.79	-
80	1.27	-
70	1.76	3.5
60	2.21	4.6

From the magnitude of k_s in each case it can be seen that $k_2(b-x)$ is much greater than k_s . That is, the proportion of the reaction due to solvolysis is very small. This is the reason for the constancy of the values of k_2 during any specific run (Part A).

In the calculation of k_2 one may therefore neglect any solvolytic contribution to the reaction rate.

As an extra test, corrections to the second order overall rate constants were calculated as in the Appendix, but as the corrections made a change of only 1%-2%, the operation was not considered necessary.

Conclusions

It has been verified that the influence of the solvent on the apparent overall rate constant for the bimolecular nucleophilic substitution of allyl bromide, is different to its effect on the reaction of a typical aliphatic halide⁸.

Many of the other allylic halides which might have been investigated for the "allylic peculiarity" towards bimolecular substitution are not suitable. Some react by the S_N1 mechanism while for others the kinetics are complicated by the presence of an S_N2' reaction⁹.

However, benzyl bromide and allyl bromide are a similar type of compound. Both have a centre of unsaturation in conjugation with the bromine atom. Thus the investigation of the kinetics of the alkoxylation reactions of benzyl bromide might be valuable.

8. Vide page 14.

9. C. A. Vernon, J. Chem. Soc., 1952, 3326; *ibid.*, 1954, 423; 4462.

EXPERIMENTAL II

Kinetics of the alkaline solvolysis of benzyl bromide in alcohol-water solvents

Procedure

The alkoxylation reactions of benzyl bromide were studied at 25°C using the "stoppered flask" technique described earlier.

The benzyl bromide solution (0.06 M) was prepared by dissolving a weighed amount of benzyl bromide* in the appropriate solvent and making it up to 100 ml. in a standard flask at 25°C.

Sodium ethoxide was prepared and standardized as before.

The extent of the reaction was measured by analysis for the concentration of alkali.

Each 10 ml. aliquot of the reaction mixture was quenched with hydrochloric acid (25 ml., approximately 0.3 N), and the excess of acid titrated against standard sodium hydroxide.

Results

A second order rate constant was obtained for the reaction in absolute ethanol, but in solvents containing water the reaction was first order. Details of a run in absolute ethanol and another in an aqueous solvent, are given in Tables 14 and 15.

Results are shown in Table 16.

* See Reagents.

Table 14

Reaction: Benzyl bromide/sodium ethoxide in 100% ethanol at 25°C

$$[\text{benzyl bromide}] = 0.0291 \text{ M}$$

$$[\text{base}] = 0.0524 \text{ M}$$

$$25 \text{ ml. of } 0.0306 \text{ N HCl} \quad \equiv \quad 20.79 \text{ ml. of } 0.0368 \text{ N NaOH}$$

Time (sec.)	excess [HCl] (in equivalent ml. of 0.0368 N NaOH)	[base]	[benzyl bromide]	$k_2 \times 10^3$ $\text{l.mole}^{-1}\text{sec.}^{-1}$
0	6.59	14.20	7.89	-
870	7.24	13.55	7.24	1.98
1800	7.86	12.93	6.62	1.97
2460	8.21	12.58	6.27	1.92
3000	8.53	12.26	5.95	1.96
3600	8.83	11.96	5.65	1.96
4400	9.16	11.63	5.32	1.92
5460	9.62	11.17	4.86	1.95
7200	10.21	10.58	4.27	1.93
7800	10.38	10.41	4.10	1.92

$$\text{Average } k_2 = 1.97 \times 10^{-3} \text{ l.mole}^{-1}\text{sec.}^{-1}$$

Table 15

Reaction: Benzyl bromide/ethoxide (and hydroxide) ions in
70% EtOH/30% H₂O at 25°C

[benzyl bromide] = 0.0590 M

[base] = 0.0281 M

25 ml. of 0.0334 N HCl = 24.27 ml. of 0.0344 N NaOH

Time (sec.)	excess [HCl] (in equivalent ml. of 0.0344 N NaOH)	[base]	[benzyl bromide]	$k_1 \times 10^4$ (sec. ⁻¹)
0	7.15	17.12	8.15	-
600	7.80	16.47	7.50	1.25
1210	8.28	15.99	7.02	1.24
1800	8.81	15.46	6.49	1.27
2400	9.27	15.00	6.03	1.26
3040	9.70	14.57	5.60	1.23
3600	10.10	14.17	5.20	1.25
4200	10.42	13.85	4.88	1.22
4740	10.78	13.49	4.52	1.24
6090	11.36	12.81	3.84	1.24

Average k_1 = 1.24×10^{-4} sec.⁻¹

Table 16

Reaction: Benzyl bromide/alkoxide (and hydroxide)
ions in ethanol-water mixtures at 25°C

Solvent (Vol. % ethanol in aqueous ethanol)	$k_2 \times 10^3$ l.mole ⁻¹ sec. ⁻¹	$k_1 \times 10^4$ sec. ⁻¹
100	1.97	-
90	-	1.12
80	-	1.21
70	-	1.24

Conclusion

It seems that the nucleophilic substitution with benzyl bromide is bimolecular in absolute alcohol, but unimolecular in aqueous solvents. The transition from one mechanism to the next is not gradual enough for one to be able to observe a stage in which both mechanisms are competing.

Thus, benzyl bromide is not suitable for the investigation of the "allylic-type peculiarity".

EXPERIMENTAL IIIProduct Analysis

In the introduction it was suggested that the individual specific rate constants for attack by hydroxide or ethoxide ions are more reliable than overall rate constants as an estimate of solvent effects on the rate of alkoxylation reactions¹⁰.

From the equations¹¹:

$$k = k_h + k_r = k_h^o s_h + k_r^o s_r$$

and $\frac{y_h}{y_r} = \frac{k_h}{k_r},$

specific rate constants, k_i^o , can be calculated from the apparent specific rates. These, in turn, can be obtained from a knowledge of the apparent overall rate constant and the product ratios for the reaction.

For the reaction of allyl bromide and base the products are allyl alcohol and an ether-allyl ethyl ether in ethanol-water mixtures and allyl methyl ether in methanol-water mixtures. A suitable and convenient method for the analysis of these products would be by gas chromatography.

10. Vide page 25.

11. Vide pages 11 and 13.

PART A. Analysis using the Argon ionisation
detector

An attempt was made to analyse the reaction mixtures with the Argon chromatograph manufactured by W. G. Pye and Co. Ltd, Cambridge.

The Detector

The operation of an Argon ionisation detector is described in the literature¹².

The presence of small quantities of water vapour in a sample has a marked quenching action on the sensitivity of the detector. As the reactions were carried out in aqueous solvents it was necessary to try to eliminate the water from the solutions.

O'Brien¹³ has carried out similar analyses and eliminated water from the samples by means of a precolumn. This was a modification of a method used by Swaboda¹⁴.

The precolumn, opens into the usual analytical column and the fixed phases of each are different. In principle the precolumn contains a material from which water is eluted very slowly.

The Fixed Phases

The precolumn (6" long) contained 20% diglycerol on celite and the analytical column (4'6" long) contained 10% polyethylene glycol 400

12. J. E. Lovelock, J. Chromatography, 1, 1958, 35.

13. L. E. O'Brien, M.Sc. Thesis, Victoria University of Wellington, 1962.

14. P.A.T. Swoboda, Chemistry and Industry, 41, 1960, 1262.

on celite. The packing material was prepared as follows.

The required amount of the diglycerol or polyethylene glycol 400 was weighed out into a beaker and dissolved in methanol. A weighed quantity of celite was then added together with sufficient methanol to make a sludge. After thorough stirring the material was dried out in an oven at 100°C.

Packing the column

With a piece of glass wool as a plug at the base of the column, the packing material was poured slowly through a funnel into the column. During the filling process the base of the column was tapped steadily to ensure even packing.

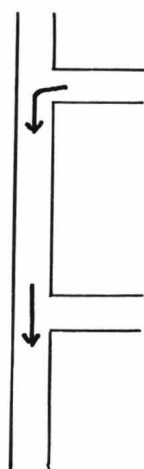
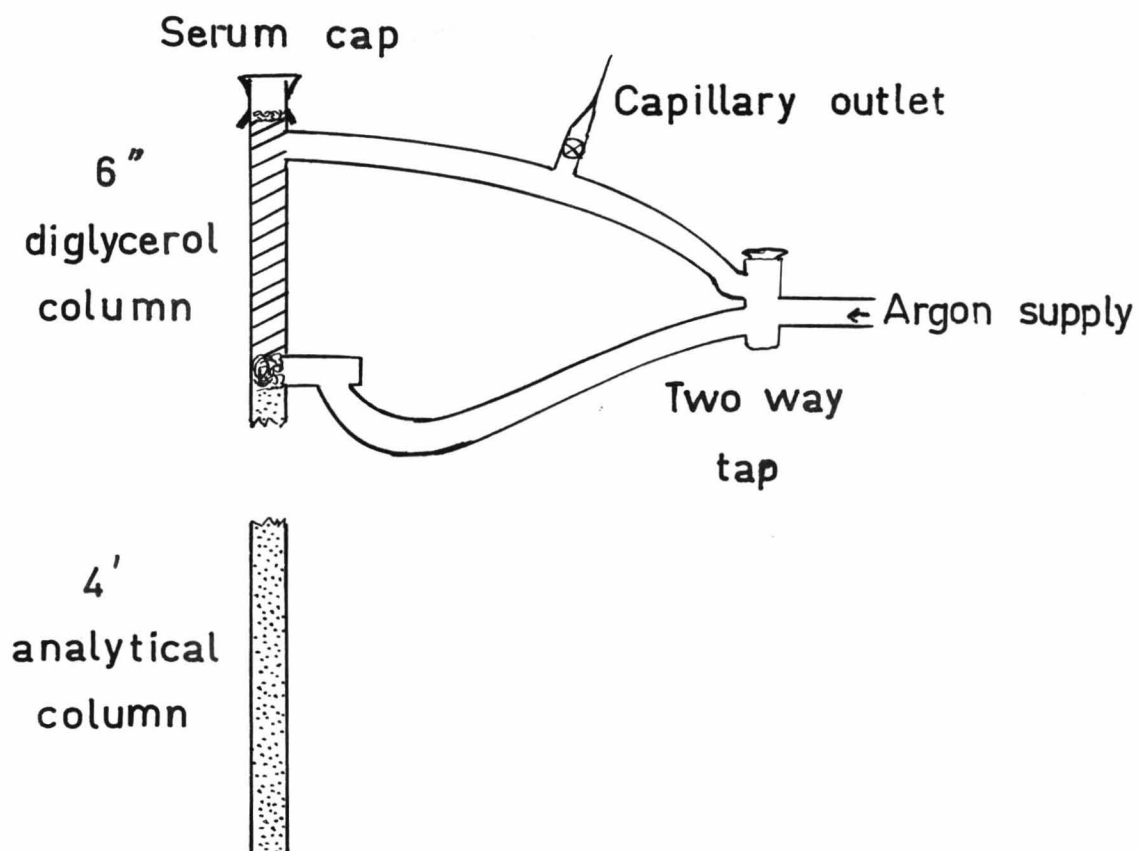
When the side arm at the top of the analytical column was reached, a piece of glass wool was inserted to prevent the packing material from coming out. The precolumn was then packed with the 20% diglycerol on celite.

Procedure

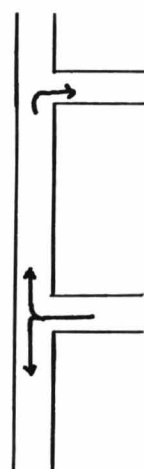
A diagram of the column is shown in Figure IV. By means of a two-way tap the flow of carrier gas, argon, could be adjusted to enter the column at the top of the precolumn or at the beginning of the analytical column.

With the argon flow as in position I, a sample of liquid (0.4 microlitres) was injected, from a microlitre syringe, on to

FIG. IV



Position I



Position II

the top of the precolumn. (Alcohols and ethers are eluted from diglycerol before water). The carrier gas was then adjusted to position II and water was flushed back out of the precolumn and escaped into the atmosphere through a capillary tube.

The method was tested using samples of the reacted mixture of allyl bromide and alkali in aqueous alcoholic solvents.

Results

Even by carefully varying the time between turning the gas flow from position I to position II, it was impossible to completely eliminate water vapour from the column. This water vapour caused the detector to behave erratically and give poorly defined chromatograms.

Conclusion

It is necessary to use another type of detector such as a katharometer or flame ionisation detector¹⁵, whose responses to other components are not affected by water vapour, if the solutions are to be analysed by gas chromatography.

- 15.a) D. Ambrose and B. A. Ambrose, Gas Chromatography, Newnes Ltd, London, 1961.
- b) I. G. McWilliam and R. A. Dewar, Gas Chromatography, Butterworths, London, 1958, p.142.

PART B. Analysis using a katharometer detector

Reaction products were analysed with a Perkin-Elmer 154-C gas chromatograph fitted with a katharometer whose responses depended on the difference in thermal conductivity between the emerging vapour and the carrier gas - helium. The column contained 5% β - β' dipropionitrile on chromosorb, and was one metre long and 0.6 cm. in diameter.

As the flow rate and temperature could not be accurately reproduced it was necessary to do a complete set of the analysis of the calibration solutions and samples on the same day. The operating conditions were as follows:

1. For the analysis of the samples in ethanol-water mixtures the temperature was 40°C, and the rate of flow of the carrier gas was 52 ml/min. (at 21°C and 760 mm).
2. For the analysis of the samples in methanol-water mixtures the temperature was 42°C and the flow rate was 44 ml/min. (at 21°C and 760 mm).

Samples, approximately 0.4 microlitres in volume, were injected into the column from a microlitre syringe.

Under the given conditions in the chromatograph, the ether, which emerged first, was recorded in a sharp, almost symmetrical peak. The peaks for the alcohols and finally for

water, were unsymmetrical and showed considerable "tailing". The amount of ether present was determined by using di-isopropyl ether as an internal marker. This was added in a known constant concentration to the mixture under analysis. Calibration solutions contained the same concentration of di-isopropyl ether and various known concentrations of the allyl ether.

Interpretation of chromatograms

Quantitative interpretation of a differential chromatogram is based on peak heights or peak areas. The peak area is proportional to the amount of that component present and a quantitative analysis would be obtained by measurement of the areas of all the peaks.

If these areas are A_1, A_2, A_3, \dots , the concentration c_x of any component x is given by¹⁶:

$$c_x = \frac{a_x A_x}{\sum_i a_i A_i}$$

where a_i are calibration constants. The values of a_i are usually different for different components, as the response of the detector does not bear any simple relationship to molecular weight or weight concentration of the component.

Areas can be determined in various ways:

16. Vide ref. 15a, p.161.

- (a) by a planimeter;
- (b) by cutting out the peak from the chart and weighing the paper;
- (c) by a method of geometrical approximation, for example, by supposing that the area is proportional to the peak height by the width at half height (BD x HJ in Figure a).

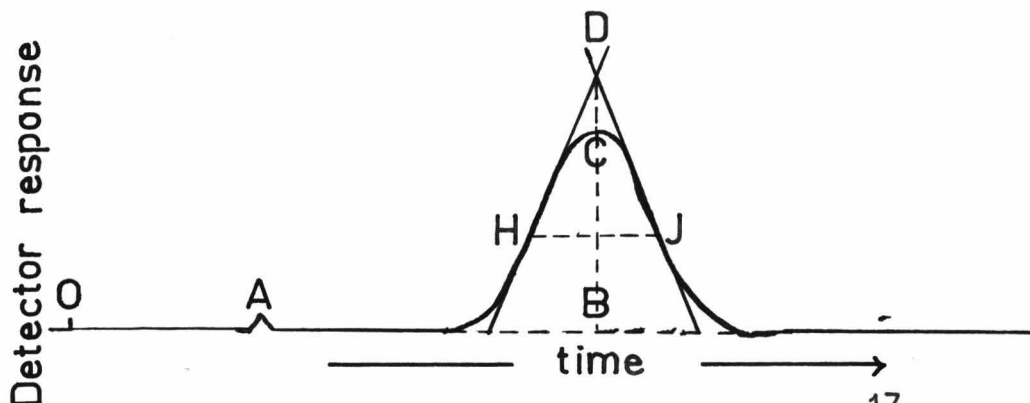


Fig. a. Chromatogram of a single solute¹⁷.

The time corresponding with the distance OB is the elution or retention time t_R , and this is a characteristic of the component. The retention volume, V_R is given by

$$V_R = t_R F_c \quad (7)$$

where F_c is the volumetric flow rate of the carrier gas measured at the outlet pressure and at the temperature of the column.

17. E. Heftmann, Chromatography, Reinhold Pub. Co., New York, p.165.

With the methods a, b and c it is difficult to make accurate measurements if the peaks are very narrow or have a moderate overlap.

The problem of determining the areas of resolved and partially resolved chromatography peaks has been reviewed by Bartlett and Smith¹⁸. They point out that symmetrical peaks approximate to a normal or Gaussian distribution curve. The equation for this type of curve is given by Goulden¹⁹ as

$$Y = \frac{N}{\sigma \sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x}{\sigma}\right)^2}$$

where Y is the height of the curve measured at a distance x from the mean, N is the number of variants (taken as area, A) and σ is the standard deviation. At the centre of the peak $x = 0$, $Y = h$ the peak height, and so the equation becomes:

$$h = \frac{A}{\sigma \sqrt{2\pi}}$$

$$\text{or } A = 2.507 h \sigma \quad (8)$$

For a normal distribution curve σ bears a relationship to the peak widths at various fractions of the peak heights.

18. J. C. Bartlett and D. Morison Smith, Can. J. Chem., 38, 1960, 2057.

19. C. H. Goulden, Methods of Statistical Analysis, 2nd ed., John Wiley & Sons, Inc., New York, 1952, p.30.

Bartlett and Smith have calculated these relationships from Sheppard's Tables of the Probability Integral²⁰, and these are shown in Figure b.

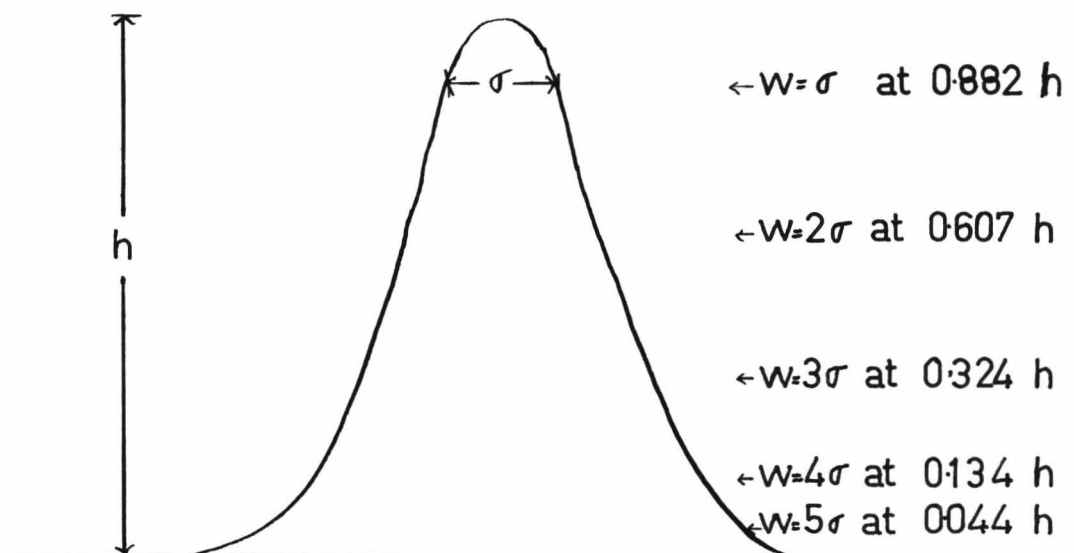


Fig. b. A normal distribution curve.

As a test for whether a peak shows the Gaussian distribution one can measure the peak width at the given heights. To satisfy the conditions the σ obtained should be nearly constant to a peak width of 4σ .

It has also been shown that the σ for different peaks is a linear function of retention time t_R , i.e. $\sigma = kt_R$.

Therefore for two components P, Q which produce peaks showing the above properties -

20. Biometrika Tables for Statisticians, Vol. 1, Cambridge University Press, London. 1954, p.104.

$$A_P = 2.507 h_P \sigma_P \text{ using equation 8.}$$

$$= 2.507 h_P k t_{R(P)} \text{ using equation 7.}$$

$$\text{Similarly } A_Q = 2.507 h_Q k t_{R(Q)}$$

$$\text{Thus } \frac{A_P}{A_Q} = \frac{h_P}{h_Q} \times \frac{t_{R(P)}}{t_{R(Q)}}$$

and as $\frac{t_{R(P)}}{t_{R(Q)}}$ is a constant,

$$\frac{A_P}{A_Q} \propto \frac{h_P}{h_Q}$$

$$\text{But } \frac{A_P}{A_Q} \propto \frac{\text{conc. P}}{\text{conc. Q}} \text{ (molar concentration)}$$

$$\therefore \frac{\text{conc. P}}{\text{conc. Q}} \propto \frac{h_P}{h_Q}$$

Analyses

If the solutions used for analysis are too dilute it is difficult to measure very accurately the required volumes of substrate necessary to make up the solution. For only a small quantity of substrate the differences in the amount of ether produced in each reaction will not be great, and so the differences in response of the detector will not be great.

To eliminate some of these errors the reactions were carried out using approximately 0.24 M allyl bromide and 0.3 N sodium ethoxide or hydroxide.

The allyl bromide solution was prepared by dissolving the allyl bromide (2 ml. or 1.442 g.) and di-isopropyl ether* (3 ml. or 2.183 g.) in the appropriate solvent and making it up to 50 ml. in a standard flask at 25°C. The alkoxide solution was prepared at 25°C. also.

Each solution (25 ml.) was pipetted into a blackened reaction flask which was then firmly closed by a ground glass stopper. These reaction mixtures were made up in 100, 90, 80, 70, 60 and 50% (by vol.) ethanol solutions, and 100, 90, 80, 70, and 60% (by vol.) methanol solutions. The reaction flasks remained in the 25°C thermostat for two weeks.

To make up a standard solution, a weighed quantity of allyl ethyl ether* or allyl methyl ether*, and di-isopropyl ether* (1.5 ml. or 1.0915 g.) were dissolved in the dry alcohol and made up to 50 ml. at 25°C. The standards were kept in blackened flasks at 25°C for several days.

* See Reagents.

Table 17Amount of ether in each standard solution

	Gm. of ether/50 ml.	Molarity	$\frac{\text{Molarity}}{0.238} \times \frac{100}{1}$
allyl ethyl ether			
1.	1.0299	0.240	100.6
2.	0.9973	0.232	97.45
3.	0.9480	0.220	92.6
4.	0.8817	0.205	86.2
5.	0.8281	0.193	80.9
6.	0.7421	0.173	72.5
allyl methyl ether			
7.	0.8568	0.238	100
8.	0.8395	0.233	98
9.	0.8255	0.228	96.3
10.	0.8071	0.224	94.2
11.	0.7855	0.218	91.7

As the original concentration of allyl bromide in the reaction flasks was 0.238M, the third column expresses the amount of ether as a percentage of the concentration of the allyl bromide.

Results: Ethanol-water mixtures.

The allyl ethyl ether and di-isopropyl ether peaks conformed to the conditions for a Gaussian distribution curve. (Values of σ were approximately constant to a peak width of 4σ). Thus the ratio of the concentration of ether to the concentration of the marker was found by measuring the peak heights.

$$\frac{h_{\text{allyl ether}}}{h_{\text{dip. ether}}} \propto \frac{\text{conc. allyl ether}}{\text{conc. dip. ether}} \propto \frac{\frac{\text{conc. allyl ether}}{0.238} \times \frac{100}{1}}{\text{conc. dip. ether}}$$

Therefore $\frac{h_{\text{allyl ether}}}{h_{\text{dip. ether}}} \propto \% \text{ allyl ether in product}$

as the concentration of di-isopropyl ether was a constant.

From the standard solutions a graph of % ether in the product vs. the ratio of peak heights was obtained. Values for the solutions under analysis were read off from the graph. Results are shown in Table 18.

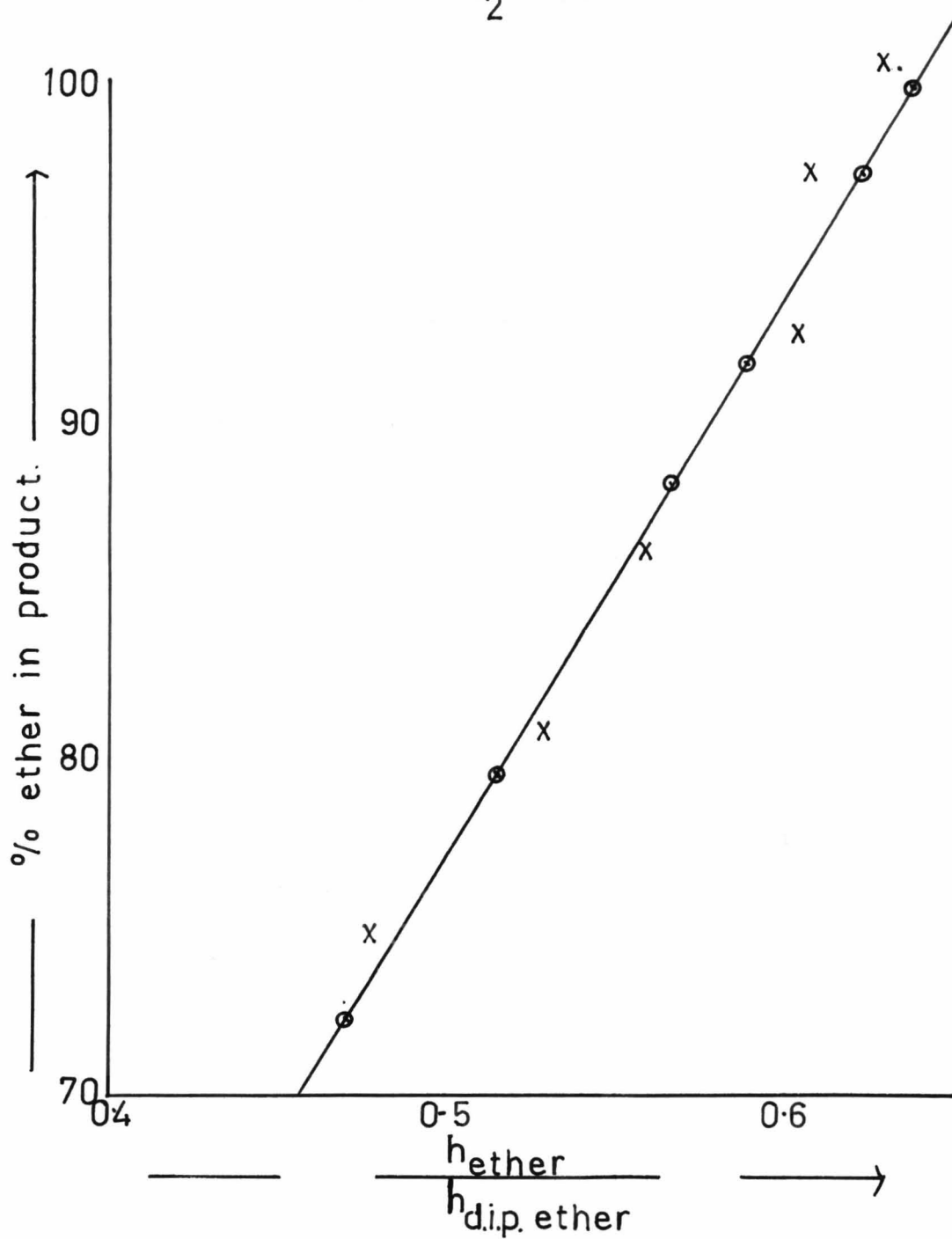
Table 18

Solution	$\frac{h_{\text{ether}}}{h_{\text{dip. ether}}}$	Sample solns. (Vol. % ethanol)	$\frac{h_{\text{ether}}}{h_{\text{dip. ether}}}$	% ether in product
1	0.628	100	0.636	99.9
2	0.608	90	0.622	97.2
3	0.604	80	0.588	91.8
4	0.557	70	0.566	88.2
5	0.528	60	0.515	79.5
6	0.477	50	0.470	72.2

FIG. V.

Product Composition in

EtOH / H₂O Mixtures.



d.i.p. = di isopropyl

x = Standard solution

o = Reaction solution

Methanol-water mixtures:

In these solutions the two ether peaks were not completely resolved. This situation has been treated by Bartlett and Smith²¹ who have calculated the height of the curve due to one component at the position of the other peak. To simplify corrections to peak heights they have drawn a graph showing the relationship between the distance between the two peaks, in terms of σ of the first peak, and the % correction to be made. If the separation is greater than 4σ the correction is considered negligible. For the allyl methyl ether and di-isopropyl ether peaks the separation was 5σ to 6σ and so no correction was necessary.

Results are shown in Table 19.

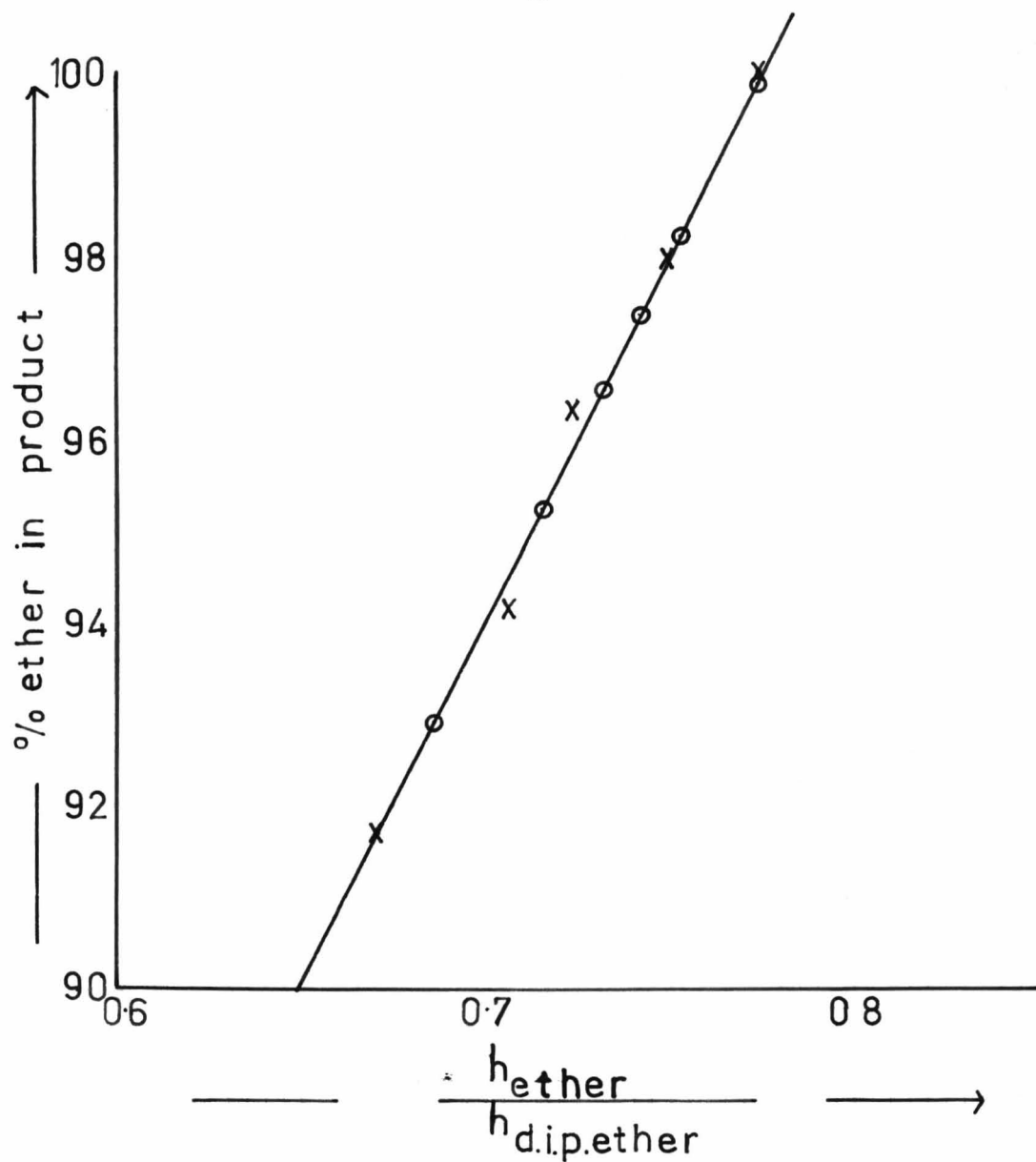
Table 19

Solution	$\frac{h_{\text{ether}}}{h_{\text{dip.ether}}}$	Sample solution (Vol. % methanol)	$\frac{h_{\text{ether}}}{h_{\text{dip.ether}}}$	% ether in product
7	0.775	100	0.774	99.9
8	0.75	90	0.753	98.5
9	0.723	80	0.742	97.3
10	0.706	70	0.715	95.3
11	0.671	60	0.686	92.9

21. Vide ref. 18.

FIG. VI.

Product Composition in
MeOH / H₂O Mixtures.



d.i.p. = di isopropyl

x = Standard solution

o = Reaction solution.

Analysis of Results

Specific rate constants for attack by hydroxide or alkoxide ions were calculated using $K_{he}^! = 0.65$ and $K_{hm}^! = 4.5^{22}$. The variation of k_i^0 with solvent composition is shown in Table 20. A plot of $\log k$ and $\log k_i^0$ vs. the mole fraction of water (x_{H_2O}) in the solvent is shown in Figures VII and VIII.

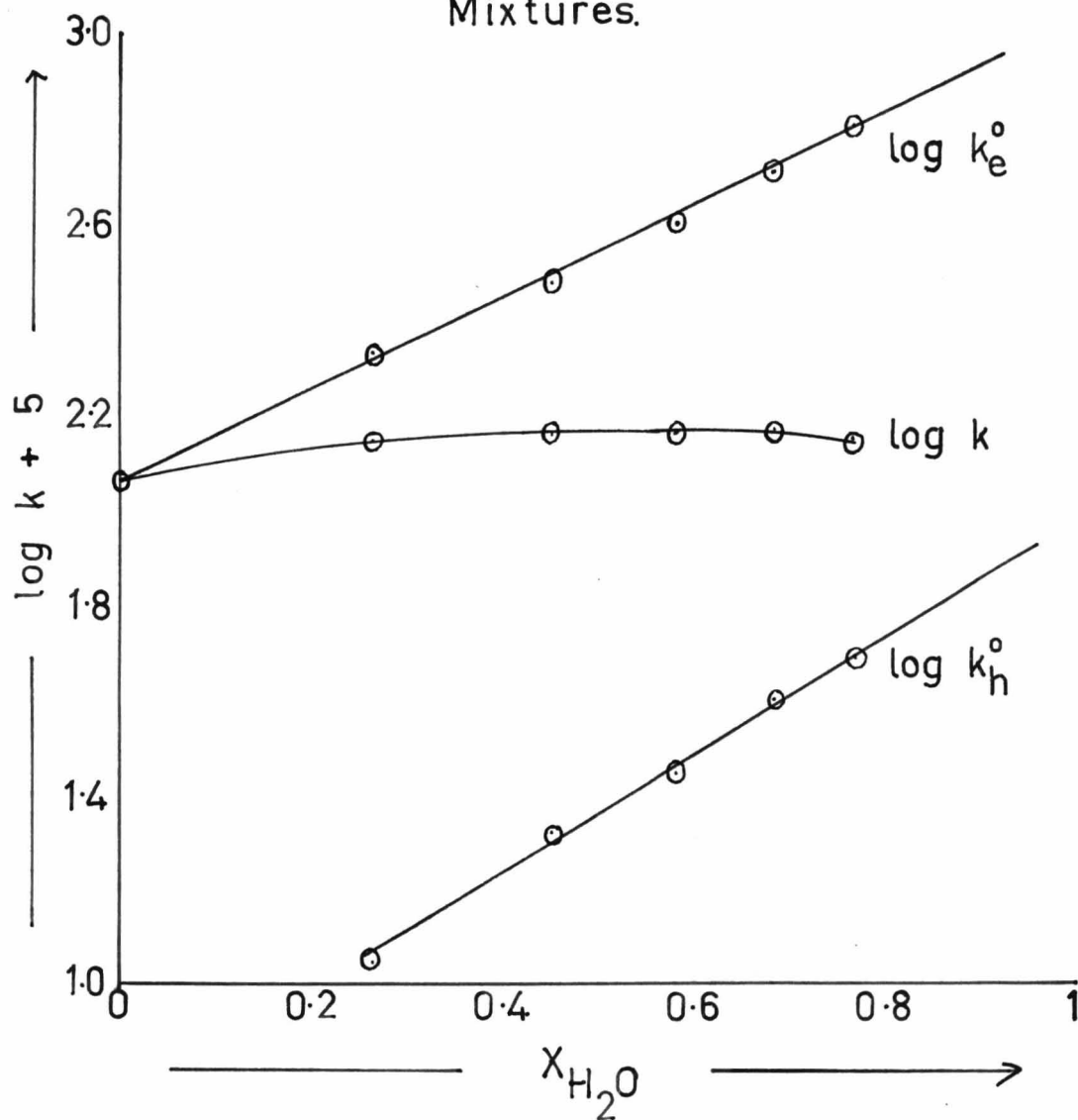
Table 20

Vol. % alcohol in solvent	x_{H_2O}	$k_2 \times 10^5$ (l.mole ⁻¹ sec. ⁻¹)	$k_h^0 \times 10^5$ (l.mole ⁻¹ sec. ⁻¹)	$k_r^0 \times 10^5$ (l.mole ⁻¹ sec. ⁻¹)
<u>ethanol</u>				
100	0.00	114	-	114
90	0.264	138	11	208
80	0.448	142	21	293
70	0.581	144	28	392
60	0.683	147	39	504
50	0.764	142	48	618
<u>methanol</u>				
100	0.00	45.8	-	45.8
90	0.199	79	23	82
80	0.359	127	31	139
70	0.490	176	47	204
60	0.599	221	64	272

FIG. VII.

Variation of $\log k$, $\log k_i^0$ with
Solvent Composition in EtOH/H₂O

Mixtures.

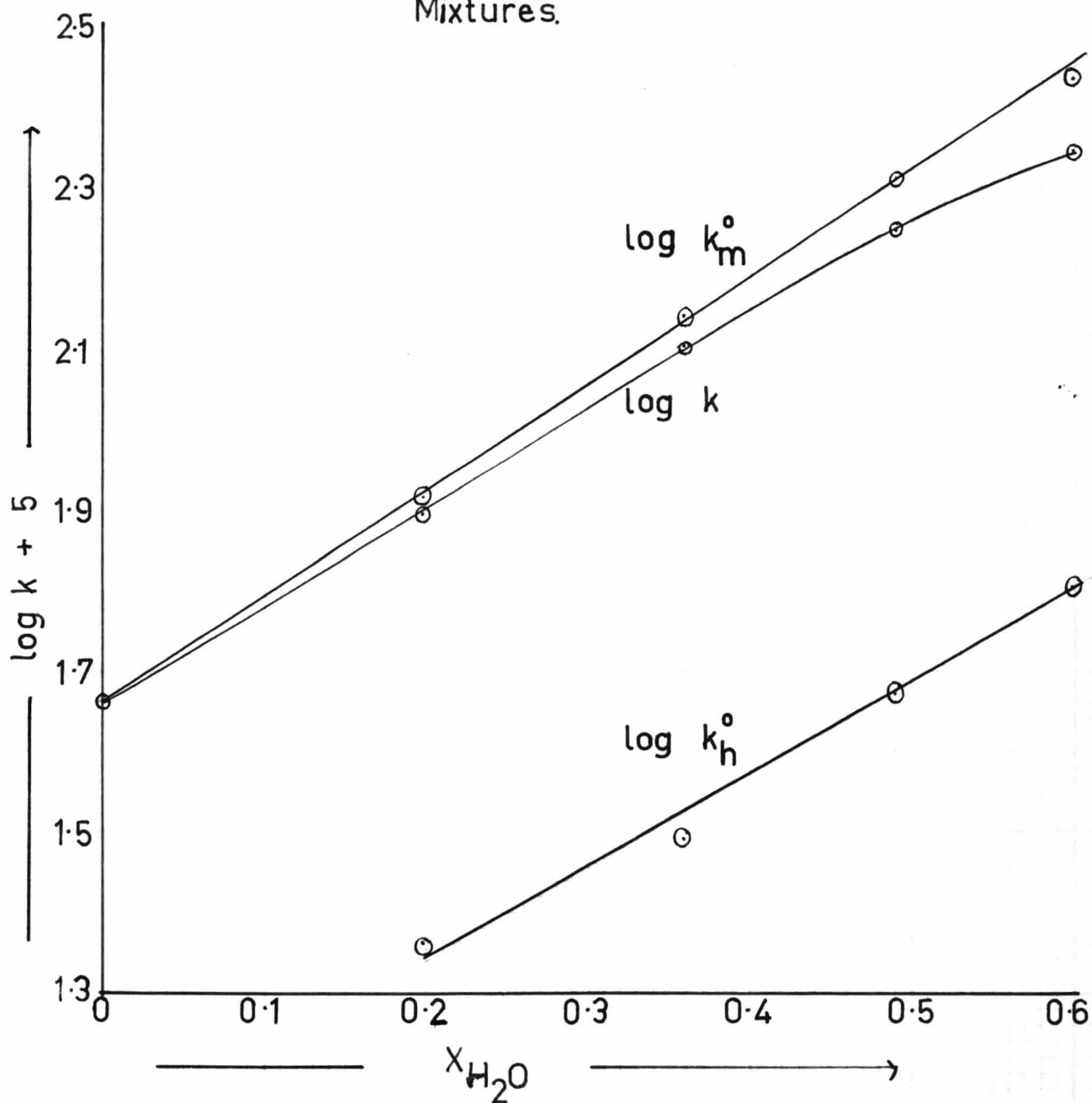


Substrate: Allyl bromide.

FIG. VIII.

Variation of $\log k$, $\log k_i^\circ$ with
Solvent Composition in MeOH/H₂O

Mixtures.



Substrate: Allyl bromide

Although the apparent overall rate constant reaches a maximum in ethanol-water mixtures the specific rate constants increase as $x_{\text{H}_2\text{O}}$ increases. Comparison with Figures II and III shows that the increases in specific rate with increased solvent polarity is much greater when the substrate is allyl bromide than when it is methyl iodide.

Murto has analysed the products from the reaction of methyl iodide and base in alcohol-water solvents, and expressed them as a function of the weight % of alcohol in the solvent. By converting weight % to volume % using the densities²³ at 20°C,

<u>Liquid</u>	<u>Density (g./ml.)</u>
Methanol	0.7928
Ethanol	0.7893
Water	0.9982

the results for the products from methyl iodide and allyl bromide can be compared.

23. Handbook of Chemistry, N. A. Lange, McGraw-Hill, 1961.

Table 21Product composition.Substrate: methyl iodide or allyl bromide

Vol. % alcohol in solvent	% ether in product	
	Methyl iodide reaction	Allyl bromide reaction
alcohol = ethanol		
100	100	99.9
90	97	97.2
80	92.6	91.8
70	87.4	88.2
60	80.7	79.5
50	72.5	72.2
alcohol = methanol		
100	100	99.9
90	98.8	98.0
80	97.5	97.3
70	95.8	95.2
60	93.9	92.9

Within the limits of error the ratios, ether: alcohol, are the same for the two substrates. As

$$\frac{y_i}{y_k} = \frac{k_i}{k_k} = \frac{s_i k_i^0}{s_k k_k^0}$$

this implies that the relative reactivities of hydroxide ion and ethoxide ion are the same in the two reactions.

Conclusion

The results imply that the effect causing the increase in specific rate must be much greater than just ion pairing of the nucleophile which is thought to influence the methyl iodide reaction.

DISCUSSION

According to the discussion on Vernon's¹ explanation, the presence of a polar transition state is not sufficient to account for the observed changes in reactivity of allyl compounds.

The rate of hydrolysis of allyl chloride in alkaline aqueous dioxane solution increases with increasing water content of the solvent². This suggested that the reactivity changes of allyl compounds could be a property of the behaviour of the hydroxide ion. However, from the analysis of the product ratios of the alkaline solvolysis of allyl bromide, it is clear that the rate of attack by alkoxide and hydroxide ions increased to the same extent.

Table 22 shows a comparison of the first order and second order reactivities of some allyl compounds³.

1. C. A. Vernon, J. Chem. Soc., 1954, 4462.
2. H. Pourrat and R. Schmitz, Bull. Soc. Chim., 1952, 505.
3. Vide ref. 1.

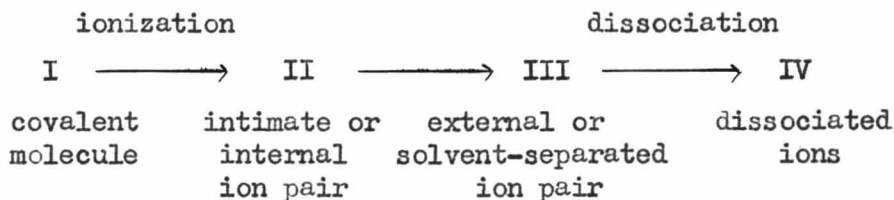
Table 22

Kinetic data for the alkaline solvolysis of allylic chlorides in ethanol and 50% aqueous ethanol at 44.6°C

Substrate	Ethanol		50% Aqueous Ethanol	
	$k_1 \times 10^5$ (sec. ⁻¹)	$k_2 \times 10^4$ (l.mole ⁻¹ sec. ⁻¹)	$k_1 \times 10^5$ (sec. ⁻¹)	$k_2 \times 10^4$ (l.mole ⁻¹ sec. ⁻¹)
CH ₂ :CH.CH ₂ Cl		1.57		2.18
CH ₂ :C(CH ₃)CH ₂ .Cl		1.58		2.50
CH ₃ .CH:CH.CH ₂ Cl		4.68	27.8	-
CH ₂ :CH.C(CH ₃)Cl		0.09	14.3	-
(CH ₃) ₂ .C:CH.CH ₂ Cl		26.8	155	-
CH ₂ :CH.C(CH ₃) ₂ .Cl	20	-	~167	-

This comparison reveals that 1-methyl allyl chloride (structure $\text{CH}_2 = \text{CH}_2 - \underset{\text{Cl}}{\overset{\text{Me}}{\text{CH}}}$) reacts mainly by the S_N1 mechanism and has relatively little reactivity in a kinetically second order mechanism. It is difficult to believe that the allyl halide reacts entirely by a covalent mechanism and 1-methyl allyl chloride largely by an ionic mechanism. This suggests that the allyl halide might react by a mechanism involving partial ionization.

It has been suggested by Winstein⁴ and co-workers that in the hydrolysis of a compound, RX, one can consider a system of progressive ionization:



(internal ion pair - two ions of opposite charge in contact).

There may be some variation in the furthest stage of ionization/dissociation which is reached in any reaction involving the ionization of RX. Reaction products may arise from more than one of the varieties of carbonium ion, depending on the various rates of ionization and reaction. The rate of the product forming reaction of II, say, may exceed the rate of progression to the next stage III. It is thought that the intimate ion pair II is able to give rise to solvolysis products in the solvolysis of α,α -dimethyl allyl chloride⁵, in trans-2-acetoxycyclohexyl-p-toluene sulphonate⁶, t-butyl chloride⁷ and 2-octyl sulphonates⁸.

4. S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, J. Amer. Chem. Soc., 78, 1956, 328.

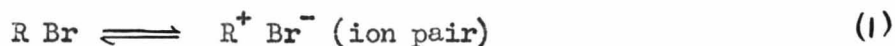
5. W. G. Young, S. Winstein and H.L. Goering, J. Amer. Chem. Soc., 73, 1951, 1958.

6. S. Winstein and R. Heck, *ibid.*, 74, 1952, 5584.

7. S. Winstein, E. Grunwald and H.W. Jones, *ibid.*, 73, 1951, 2700.

8. H. Weiner and R. A. Sneen, Tetrahedron Letters, 20, 1963, 1309.

From this one can advance a mechanism for the alkoxylation of allyl bromide as follows:



where R is $\text{CH}_2 = \text{CH}_2 - \text{CH}_2^-$.

The first stage is the rapidly established equilibrium between allyl bromide and the ion pair, the second the rate-determining attack of OR'^- on the ion pair. Hence the overall rate measured by the increase in bromide ion concentration is

$$\begin{aligned} \frac{d[\text{Br}^-]}{dt} &= k_2 [R^+ \text{ Br}^-] [\text{OR}'^-] \\ &= k_2 K_{\text{eq}} [R\text{ Br}] [\text{OR}'^-] \quad \text{where } K_{\text{eq}} = \frac{[R^+ \text{ Br}^-]}{[R\text{ Br}]} \\ &= k_2' [R\text{ Br}] [\text{OR}'^-] \end{aligned}$$

(On the assumption that equilibrium (1) is rapidly established the K_{eq} is approximately constant).

That is, the reaction will exhibit second order kinetics. The position of the initial equilibrium will depend on the polarity of the solvent. In more polar solvents the proportion of ion pair ($R^+ \text{ Br}^-$) will be greater, and so the apparent specific rate constant k_2' will increase. This prediction of a second order rate constant

which increases as solvent polarity increases, is in agreement with the present experimental work.

In general, carbonium ions are very reactive and would not be involved in a rate determining stage. However, it has been noted, in cases where the carbonium ion formed has some stability (e.g. triphenyl methyl carbonium ion)⁹, that the rate determining step is the attack of the nucleophile on the carbonium ion. An allyl carbonium ion is not as stable as the ϕ_3C^+ (as shown by the fact that 1-Me allyl chloride reacts mainly by a normal S_N1 mechanism) but there is the possibility of the formation of a relatively stable ion pair which would react in the manner suggested above.

Winstein¹⁰ justifies the distinction between the two types of ion pairs by suggesting that there is an energy barrier between the two. The intimate ion pair is peripherally solvated only, so that the solvent shells of the two ions are incomplete, and powerful electrostatic and perhaps other forces are present in stabilizing the species.

If one accepts a basis of progressive ionization then the kinetics of nucleophilic attack on other allylic halides can be explained.

9. D. Bethell and V. Gold, J. Chem. Soc., 1958, 1905.

10. S. Winstein and J. C. Robinson, J. Amer. Chem. Soc., 86, 1958, 169.

Suppose that ionization of R Br proceeds to stage IV.

Once it is formed, the carbonium ion will react quickly with the nucleophile and the overall rate of reaction will depend on the rate of formation of the carbonium ion. The reaction will be kinetically of the first order. For example the alkoxylation of 1-Me allyl chloride in 50% ethanol-water occurs by the S_N1 mechanism.¹¹

If two entities, say III and IV are reacting with the nucleophile - IV by a first order reaction and III by a second order reaction - then the reaction rate can be separated into first order and second order components. This situation could exist if the rate of formation of the carbonium ion from the ion pair is comparable to the rate of attack of the nucleophile on the ion pair.

Finally, the ion pair may be the only reacting species, and so the reaction kinetics will be second order as in the case of allyl bromide.

If this interpretation is correct then these compounds which react partly or completely by a bimolecular mechanism cannot be clearly defined as belonging to either the S_N1 or S_N2 type mechanisms.

The rate determining stage is bimolecular as in the S_N2 mechanism, but the reacting species is ionic which is characteristic of the S_N1 mechanism, and so this mechanism can be referred to as belonging to the borderline region.

11. Vide ref. 1.

Though the existence of a borderline region has been recognized for some time there is still much discussion on the actual mechanism in operation. Hughes and Ingold usually discuss these reactions in terms of separate S_N1 and S_N2 mechanisms, but suggest that there must be some intermediate mechanism¹². In general¹³ they favour the conclusions of Winstein¹⁴ and others^{15,16}, that the individual acts of substitution take on characters intermediate to various degrees between the two extremes of mechanism. Winstein¹⁷ demonstrated this for the solvolysis of isopropyl bromide using the free energy relationship

$$\log k = \log k_o + mY$$

where k = specific solvolysis rate constant for R Br in a given solvent.

k_o = specific solvolysis rate constant for R Br in the standard solvent - 80% ethanol.

Y is a measure of the ionizing power of the solvent and is set equal to $\log k - \log k_o$ for *t*-butyl chloride.

m is characteristic for a substrate and shows the sensitivity of the reaction to the ionizing power of the solvent. From examples when the mechanism is known it appears that, for S_N1 reactions, values of m are of the same magnitude which is different from that characteristic of an S_N2 reaction. Using this Winstein shows that

12. M.L.Dhar, E.D.Hughes and C.K.Ingold, J. Chem. Soc., 1948, 2058.

13. E.D. Hughes and C.K. Ingold, *ibid.*, 1954, 634.

14. Vide ref. 7.

15. C.G.Swain and W.P.Langsdorf, J. Amer. Chem. Soc., 73, 1951, 2813.

16. D.A. Brown and R.F. Hudson, J. Chem. Soc., 1953, 3352.

17. Vide ref. 7.

if the solvolysis of iso-propyl bromide was distributed between the two extreme mechanisms, then there should be an upward curvature in the $\log k$ vs. Y plot. This curvature would correspond to a change in mechanism but it was not observed. Therefore Winstein considers that the solvolysis cannot be described as a concurrence of extreme mechanisms and suggests that some intermediate mechanism may be operating.

Similar conclusions have been reached by Kornblum and co-workers¹⁸, and Swain¹⁹ and Hudson²⁰ but they have not gained universal acceptance²¹.

Recently Casapieri and Swart²² reported an example of simultaneous S_N1-S_N2 exchange between diphenyl methyl chloride and chloride ions in dimethyl formamide. However, they reached this conclusion on the basis of being able to separate distinct first order and second order rate constants. It has been suggested on page 77, that the existence of a second order rate constant does not necessarily imply that a true S_N2 reaction is taking place.

18. N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, J. Amer. Chem. Soc., 77, 1955, 6269.

19. Vide ref. 15.

20. Vide ref. 16.

21. V. Gold, J. Chem. Soc., 1956, 4633.

22. P. Casapieri and E. R. Swart, *ibid.*, 1961, 4342.

From the present work it seems that while a given reaction may occur by more than one mechanism, and that evidence of this can be given by separating distinct rate constants, the mechanisms involved need not be the usual S_N1-S_N2 mechanisms.

Further information may be disclosed by investigating those reactions in which distinct first order and second order constants can be separated. Then by testing the properties of the second order component by changing factors such as solvent polarity, one might be able to advance more definite mechanisms for the borderline region.

REAGENTSReactantsAllyl bromide:

The "L. Light & Co." product was dried over anhydrous CaCl_2 , decanted off and then distilled through a Vigreux column. The distillate was then stored in a brown flask.

B.P. 70°C (cf. Heilbron p.55, B.P. $70^\circ\text{--}71^\circ\text{C}$)

$n_D^{20} = 1.4655$ (cf. Heilbron p.55, $n_D^{20} = 1.4655$)

Benzyl bromide:

The "L. Light & Co." product was purified as above.

B.P. 196°C at 753 mm. (cf. Heilbron p.271, B.P. 198°C).

Sodium Alkoxides:

B.D.H. sodium was cut into small pieces (about 0.5 g. to 1 g.) under paraffin, dried with filter paper, washed quickly with S.V.R. alcohol, absolute alcohol and the appropriate solvent, and transferred to a flask containing about 50 ml. of this last solvent. When using aqueous alcoholic solvents, the flask was cooled in water until the sodium had finished reacting.

The cooled alkaline solution was standardized against standard hydrochloric acid (bromothymol blue indicator). To prepare a dilute solution of the alkoxide, the required volume of concentrated solution was diluted with the appropriate solvent. This solution was then standardized against hydrochloric acid.

ProductsAllyl ethyl ether:

This was formed by the direct action of sodium ethoxide on allyl bromide.

Some sodium (12 g.) was dissolved in 120 ml. of absolute ethanol to form the ethoxide solution. Allyl bromide (40 g.) was then added dropwise to bring about the spontaneous precipitation of sodium bromide.

The solution was refluxed for 30 mins., to ensure complete reaction, and followed by a distillation from which a fraction boiling between 60°-76°C was collected. This was then fractionally distilled in a 24" Vigreux vacuum jacketed column giving a major cut between 66°C and 67°C at 756 mm. pressure.

The fraction was washed with water to remove traces of alcohol and dried over anhydrous CaCl_2 . The dry allyl ether was then distilled from quinol (to remove the peroxide impurities) under nitrogen and stored in a black flask under nitrogen.

B.P. = 66-67°C (cf. Beilstein 66-67°C, 741 mm.)

n_D^{25} = 1.3881

Allyl methyl ether:

This was synthesized using the above method, i.e. the action of sodium methoxide (in absolute methanol) on allyl bromide.

B.P. = 44°C, 753 mm. (cf. Heilbron, B.P. = 46°C).

Di-iso propyl ether:

Peroxides were first removed from the "L. Light and Co." product by treatment with an acidified solution of a ferric salt.

Ferric salt:

Crystalline FeSO_4 (10 g.) was dissolved in conc. H_2SO_4 (1 ml.) and distilled water (20 ml.). 100 ml. of the ether were then shaken with 1-2 ml. of the solution diluted with 10 ml. of water.

The ether was then separated off, dried with anhydrous CaCl_2 and distilled.

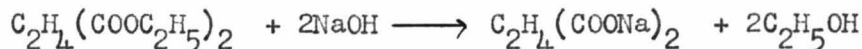
B.P. = 68.5°C (cf. Heilbron p.264, B.P. 69°C).

n_D^{25} = 1.3640.

SolventsEthyl alcohol:

Commercial absolute alcohol was dried by method 2 in Vogel p.166.

Sodium reacted with the absolute alcohol and then sodium hydroxide was removed by allowing it to react with a high boiling point ester-ethyl phthalate and dry ethyl alcohol was obtained:



One litre of absolute ethanol and 7 g. of sodium were placed in a 2 litre round bottomed Pyrex flask. When the sodium had reacted 27.5 g. of ethyl phthalate was introduced and the mixture was refluxed

gently for 2 hours. The mixture was then distilled through a short column and the dry alcohol was stored in a tightly stoppered bottle.

$$n_D^{25} = 1.3598 \quad (\text{cf. Heilbron p.487 } n_D^{25} = 1.3595).$$

Methyl alcohol:

Methyl alcohol was dried by Method 1, Vogel p.166.

A mixture of 10 g. of clean dry magnesium turnings, 1 g. of iodine and 150 ml. of alcohol were warmed in a flask until the iodine had disappeared, and the magnesium was converted into the methyrate. Two litres of alcohol were then added, the mixture was refluxed for 30 minutes and then distilled off through a short column.

$$n_D^{25} = 1.3279 \quad (\text{cf. Heilbron p.291, } n_D^{25} = 1.3276).$$

Reagents

Sodium hydroxide:

This was prepared using procedure B for carbon dioxide-free sodium hydroxide, Vogel, page 234.

Sodium hydroxide pellets (about 20 g.) was dissolved in distilled water (20 ml.) in a Pyrex flask which had a well fitting stopper covered with tin foil. This was allowed to stand until the supernatant liquid was clear. For a 0.03 N solution of sodium hydroxide, 2.2 ml. of the conc. solution was withdrawn carefully

and diluted quickly with 1 litre of freshly boiled water. This solution was then standardized against standard potassium hydrogen phthalate solution (bromothymol blue indicator).

Potassium hydrogen phthalate:

A.R. potassium hydrogen phthalate was dried at 120°C for several hours.

Hydrochloric acid:

Pure concentrated hydrochloric acid (3 ml.) was diluted to one litre with distilled water. This gave a solution approximately 0.03 N which was then standardized against standard sodium carbonate (screened methyl orange indicator).

Sodium carbonate:

A.R. sodium carbonate was dried at 260° for 1 hour.

Silver nitrate:

A.R. silver nitrate was dried (150°C) for 2 hours and cooled in a desiccator. A 0.10 N solution was then made up and standardized against NaCl (potentiometric titration).

Sodium chloride:

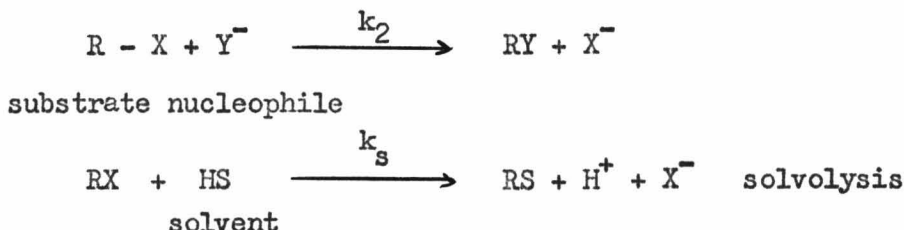
A.R. sodium chloride was dried at 250°C for 1-2 hours.

References:

- A. I. Vogel, A Textbook of Practical Organic Chemistry, Longmans, Green and Co., 1948.
I. Heilbron and H. M. Bunbury, Dictionary of Organic Compounds, Eyre and Spottiswoode, London, 1953.

APPENDIXCalculation of the Second-Order Rate Constant

Given two reactions occurring simultaneously as follows:



If x is the concentration of X^- at any time t and a, b are the initial concentrations of RX and Y^- respectively, then

$$\frac{dx}{dt} = k_2(a-x)(b-x) + k_s(a-x)$$

$$\text{Define } K_2 = \frac{1}{t} \int_0^x \frac{dx}{(a-x)(b-x)} = \frac{1}{t} \cdot J$$

From the definition,

$$K_2 = \frac{1}{t} \frac{1}{b-a} \log_e \left\{ \frac{b(a-x)}{a(b-x)} \right\}$$

Here K_2 is a function of t and x . From a plot of K_2 vs. t one can find $\frac{tdK_2}{dt}$ for any t .

$$\begin{aligned}
 \text{Then } K_2 + \frac{tdK_2}{dt} &= \frac{dJ}{dt} = \frac{dJ}{dx} \cdot \frac{dx}{dt} \\
 &= \frac{1}{(a-x)(b-x)} \cdot \frac{dx}{dt} \\
 &= k_2 + \frac{k_s}{(b-x)}
 \end{aligned}$$

$$\text{Therefore } k_2 = K_2 - \frac{k_s}{(b-x)} + \frac{tdK_2}{dt}$$

If k_s is known then k_2 can be found using this relationship.

ABSTRACT

The rate of the alkaline solvolysis of allyl bromide has been measured in various ethanol-water and methanol-water mixtures. This has been found to increase with increase in solvent polarity. An attempt was made to explain this behaviour in terms of partial ionisation of the substrate.

It has been suggested that in nucleophilic substitution the individual specific rate constants for attack by alkoxide or hydroxide ions are a better indication of solvent effects than the apparent overall rate constant.

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