417. *Mechanism of Elimination Reactions. Part VII. Solvent Effects on Rates and Product-proportions in Uni- and Bi-molecular Substitution and Elimination Reactions of Alkyl Halides and Sulphonium Salts in Hydroxylic Solvents.*

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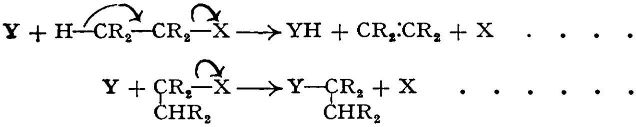
Consideration is given to the contribution of solvation energy to the activation energy of bimolecular and unimolecular elimination; and a theory is advanced by which it is possible to predict the direction of the effect of a change of solvent on the rate of a bimolecular, or of a unimolecular elimination. By the simultaneous use of a corresponding theory concerning solvent effects on bimolecular and unimolecular nucleophilic substitution, one can forecast the effect of solvent changes on the proportions in which substitutions and eliminations accompany each other.

In confirmation and illustration of these theoretical conclusions, a body of experimental data, some of it new, is assembled concerning solvent effects on the rates and product-proportions of reactions involving elimination. The reactions employed are the acid or alkaline decompositions undergone by alkyl halides and alkylsulphonium salts in water, or ethyl or *n*-propyl alcohol, or mixtures of these solvents.

In 1935 two of us advanced a theory concerning solvent effects in nucleophilic substitution. We have now to state and illustrate a similar theory of solvent effects in olefin eliminations.

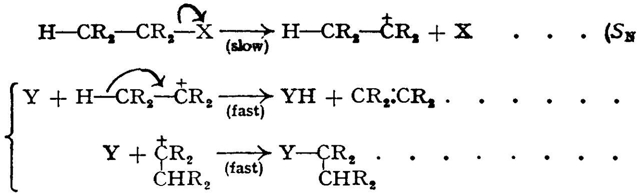
Nucleophilic substitutions and eliminations are so closely parallel in mechanism, and occur so often together, that it is hardly possible to consider one without the other. The bimolecular forms of the two reactions may be represented as follows :



$$\mathrm{Y} + \mathrm{H{-}CR_2{-}CR_2{-}X} \longrightarrow \mathrm{YH} + \mathrm{CR_2{:}CR_2} + \mathrm{X} \quad . \; . \; . \; . \; . \quad (E2)$$

$$\mathrm{Y} + \underset{\mathrm{CHR_2}}{\mathrm{CR_2}}{-}\mathrm{X} \longrightarrow \mathrm{Y}{-}\underset{\mathrm{CHR_2}}{\mathrm{CR_2}} + \mathrm{X} \quad . \; . \; . \; . \; . \; . \; . \quad (S_N2)$$

The electron transfers are similar but pass through a longer chain of atoms in the elimination than in the substitution. The unimolecular forms of the reactions may be expressed as follows :



$$\mathrm{H{-}CR_2{-}CR_2{-}X} \xrightarrow[\text{(slow)}]{} \mathrm{H{-}CR_2{-}\overset{+}{C}R_2} + \mathrm{X} \quad . \; . \; . \quad (S_N1 + E1)$$

$$\left\{\begin{array}{ll} \mathrm{Y} + \mathrm{H{-}CR_2{-}\overset{+}{C}R_2} \xrightarrow[\text{(fast)}]{} \mathrm{YH} + \mathrm{CR_2{:}CR_2} \; . \; . \; . \; . \; . \; . \; . \; . & (E1) \\ \mathrm{Y} + \underset{\mathrm{CHR_2}}{\mathrm{\overset{+}{C}R_2}} \xrightarrow[\text{(fast)}]{} \mathrm{Y}{-}\underset{\mathrm{CHR_2}}{\mathrm{CR_2}} \; . \; . \; . \; . \; . \; . \; . \; . \; . & (S_N1) \end{array}\right.$$

They have a common slow stage and the succeeding fast stages are similar, except that the electron transfer involves a larger number of atoms in the elimination than in the substitution.

Sign-labels have been omitted from the above formulæ because there are several alternatives : the electron transfers alter the state of charge of the atoms involved. Therefore we commence the discussion of solvent effects in elimination, just as we commenced the former discussion of substitutions (*J.*, 1935, 244), by dividing the reactions under consideration into classes, four in all, according to whether the reagent is originally negative becoming finally neutral or is originally neutral becoming finally positive, and, independently, according as the expelled group is initially uncharged becoming ultimately negative, or is initially positive becoming ultimately neutral. The four types are here formulated and exemplified (Ar = p-$\mathrm{NO_2{\cdot}C_6H_4}$) :

Type 1 : $\bar{\mathrm{Y}} + \mathrm{H{-}C{-}C{-}X} \longrightarrow \mathrm{YH} + \mathrm{C{=}C} + \bar{\mathrm{X}}$

(Example) $\bar{\mathrm{O}}\mathrm{H} + \mathrm{H{\cdot}CH_2{\cdot}CHMe{\cdot}Br} \longrightarrow \mathrm{H_2O} + \mathrm{CH_2{:}CHMe} + \bar{\mathrm{Br}}$

Type 2 : $\mathrm{Y} + \mathrm{H{-}C{-}C{-}X} \longrightarrow \overset{+}{\mathrm{Y}}\mathrm{H} + \mathrm{C{=}C} + \bar{\mathrm{X}}$

(Example) $\mathrm{HOEt} + \mathrm{H{\cdot}CH_2{\cdot}CMe_2{\cdot}Cl} \longrightarrow \mathrm{H_2\overset{+}{O}Et} + \mathrm{CH_2{:}CMe_2} + \bar{\mathrm{Cl}}$

Type 3 : $\bar{\mathrm{Y}} + \mathrm{H{-}C{-}C{-}\overset{+}{X}} \longrightarrow \mathrm{YH} + \mathrm{C{=}C} + \mathrm{X}$

(Example) $\bar{\mathrm{O}}\mathrm{Et} + \mathrm{H{\cdot}CHMe{\cdot}CMe_2{\cdot}\overset{+}{S}Me_2} \longrightarrow \mathrm{HOEt} + \mathrm{CHMe{:}CMe_2} + \mathrm{SMe_2}$

Type 4 : $\mathrm{Y + H{-}C{-}C{-}\overset{+}{X} \longrightarrow \overset{+}{Y}H + C{=}C + X}$

(Example) $\mathrm{H_2O + H{\cdot}CHAr{\cdot}CH_2{\cdot}\overset{+}{N}Me_3 \longrightarrow H_3\overset{+}{O} + CHAr{:}CH_2 + NMe_3}$

There are four corresponding types of nucleophilic substitution. It is true of the eliminations and substitutions alike that the similarities between the four types are much more fundamental than their differences; but behaviour with respect to solvent changes, which is our present concern, happens to be one of the main ways in which, for either reaction, the four types differ.

All four types of elimination may proceed by the bimolecular mechanism $E2$. When we discuss solvent influence on this mechanism we shall be considering directly the effect on rate of bimolecular olefin formation. If we should wish to discuss the effect of solvent changes on the proportion in which the total bimolecular reaction yields olefin, it would be necessary to apply a parallel consideration to the corresponding bimolecular substitution S_N2, and make a comparison of the results.

The four types of elimination may also proceed by the unimolecular mechanism ($E1$). However, this and the unimolecular substitution mechanism (S_N1) have a common rate-determining stage, and it is therefore convenient to deal first with the effect of solvent changes on the rate of this stage, *i.e.*, on the rate of the total unimolecular reaction $S_N1 + E1$. Only two cases arise for consideration, because reactions of Types 1 and 2 are identical in form, and reactions of Types 3 and 4 are similarly identical, with respect to the rate-controlling stage of the unimolecular process. If we should seek the solvent effect on the proportion in which the total unimolecular reaction produces olefin, it would be necessary to compare the predicted solvent effects on the rates of the final rapid stages of the unimolecular mechanisms $E1$ and S_N1. Here again only two cases arise, because reactions of Types 1 and 3 are of the same form, and reactions of Types 2 and 4 are also of the same form, with respect to the rapid stages of the unimolecular processes.

The theory which we employ for the discussion of solvent effects is based on the simple picture of an ionising solvent as one whose molecules are attracted to electrically charged centres, and thus, by doing electrostatic work, reduce the energy of the system. Because of its intense local electric fields, water does this *par excellence;* and it is followed, in order of diminishing effectiveness, by the simpler alcohols, aprotic dipolar solvents, and non-polar solvents; *e.g.*, $\mathrm{H_2O > EtOH > Me_2CO > C_6H_6}$.

The argument by which we deduce the effect of solvent changes on olefin elimination is similar to that previously applied to nucleophilic substitution. The effect of solvation on the rate of each activated process is assumed to arise from the difference between the solvation energy of the transition state and that of the initial state. The following postulates are made concerning the degree of solvation to be expected in the presence of electric charges : (1) solvation will increase with the magnitude of the charge; (2) solvation will decrease with increasing distribution of a given charge; (3) the decrease of solvation due to distribution will be less than the decrease due to destruction of the same amount of charge. By applying these rules differentially to the initial and transition states, we can deduce the effect of solvation on the energy of activation and hence on the rate. The direction of the effect being thus determined, we know that its magnitude will be greater the more ionising the solvent. The influence of entropy is here neglected, since it appears to be small in comparison with the energy effect of solvation. From a quantitative point of view this is a fault; but our theory could scarcely be elevated to a quantitative status without a much more detailed knowledge of solvation than we at present possess.

The application of these arguments to the bimolecular reactions is indicated in Table I. What happens to the charges on activation is shown in the middle three columns of the Table. The conclusions concerning the rates of bimolecular substitution and elimination (S_N2 and $E2$) are in the last column but one. It will be noted that the solvent effect on rate is always qualitatively the same for bimolecular substitutions and eliminations of the same type. The strong differences are those which occur between the types. The terms " large " and " small " are purely relative : they arise from the theory that the effect of the dispersal of a charge should be notably smaller than the effect of the creation or destruction of a charge (postulate 3 above).

In order to deduce the direction of the solvent effect on the proportions in which these bimolecular reactions produce olefin, it is necessary to be able to compare the qualitatively similar effects on the competing substitutions and eliminations. This we cannot do for those cases in which charges are created or destroyed by activation, since we have no means of comparing the amounts of charge created or destroyed by the two competing processes. But in those cases in which charges are dispersed, we can plausibly assume that they are more extensively dispersed in the transition state of elimination than in that of substitution. Thus we reach the conclusions indicated in the last column of Table I.

TABLE I.

Predicted solvent effects on the rates and proportions of bimolecular substitutions and eliminations (S_N2 *and* E2).

Type.	Reaction.	Disposition of charges.		Effect of activation on charges.	Effect of ionising medium on	
		Initial state.	Transition state.		reaction rates.	olefin proportion.
1	S_N2	$\bar{Y} + RX$	$\overset{\delta-}{Y}\ldots R\ldots\overset{\delta-}{X}$	Dispersed	Small decrease	Small decrease
	$E2$	,,	$\overset{\delta-}{Y}\ldots H\ldots C \mathrel{\underset{\cdots}{-}} C\ldots\overset{\delta-}{X}$			
2	S_N2	$Y + RX$	$\overset{\delta+}{Y}\ldots R\ldots\overset{\delta-}{X}$	Increased	Large increase	?
	$E2$	,,	$\overset{\delta+}{Y}\ldots H\ldots C \mathrel{\underset{\cdots}{-}} C\ldots\overset{\delta-}{X}$			
3	S_N2	$\bar{Y} + R\overset{+}{X}$	$\overset{\delta-}{Y}\ldots R\ldots\overset{\delta+}{X}$	Reduced	Large decrease	?
	$E2$	,,	$\overset{\delta-}{Y}\ldots H\ldots C \mathrel{\underset{\cdots}{-}} C\ldots\overset{\delta+}{X}$			
4	S_N2	$Y + R\overset{+}{X}$	$\overset{\delta+}{Y}\ldots R\ldots\overset{\delta+}{X}$	Dispersed	Small decrease	Small decrease
	$E2$	,,	$\overset{\delta+}{Y}\ldots H\ldots C \mathrel{\underset{\cdots}{-}} C\ldots\overset{\delta+}{X}$			

The corresponding argument for unimolecular reactions is given in Table II. The upper part of the Table is concerned with solvent effects on rates of total unimolecular processes, substitution plus elimination. These are the rates which measure the slow stage which is common to unimolecular substitution and elimination; and accordingly, the transition states of which we have here to take account are those of the slow initial stages of these reactions. The lower part of the Table deals with solvent effects on the proportions in which olefin is produced in these unimolecular reactions. The proportions are determined by the relative

TABLE II.

Predicted solvent effects on the rates and proportions of unimolecular substitutions and eliminations (S_N1 *and* E1).

Type.	Reaction.	Disposition of charges.		Effect of activation on charges.	Effect of ionising medium on	
		Initial state.	Transition. state.		reaction rates.	olefin proportion.
			Effect on total rate.			
1 2	$S_N1 + E1$	RX	$\overset{\delta+}{R}\ldots\ldots\overset{\delta-}{X}$	Increased	Large increase	See below
3 4	$S_N1 + E1$	$R\overset{+}{X}$	$\overset{\delta+}{R}\ldots\ldots\ldots\overset{\delta+}{X}$	Dispersed	Small decrease	See below
			Effect on olefin proportion.			
1 3	S_N1	$\bar{Y} + \overset{+}{R}$	$\overset{\delta-}{Y}\ldots\ldots\ldots\overset{\delta+}{R}$	Reduced	Large decrease	?
	$E1$	,,	$\overset{\delta-}{Y}\ldots H\ldots C \mathrel{\underset{\cdots}{-}} \overset{\delta+}{C}$	,,		
2 4	S_N1	$Y + \overset{+}{R}$	$\overset{\delta+}{Y}\ldots\ldots\ldots\overset{\delta+}{R}$	Dispersed	Small decrease	Small decrease
	$E1$	,,	$\overset{\delta+}{Y}\ldots H\ldots C \mathrel{\underset{\cdots}{-}} \overset{\delta+}{C}$	,,		

rates of the competing fast stages of unimolecular substitution and elimination, and the relevant transition states are therefore those of the fast stages. We are unable to verify the predicted solvent effects of these fast reactions individually, but the relative effects on the competing process determine the effect on the proportion of olefin.

We shall now compare these theoretical expectations with experiment, using our measurements on the rates and product compositions of the reactions of various alkyl halides and sulphonium salts in acid or alkaline ethyl alcohol–water mixtures. In applying the theory we, of course, take water to be the more ionising solvent constituent.

The data for the rates of bimolecular reactions are assembled in Table III. The reactions of Types 1 and 3 are proved to be bimolecular by their kinetic order; and the constants tabulated are second-order rate constants. The reactions of Types 2 and 4 are solvolytic in character, and the tabulated constants are therefore first-order constants; but the reactions are believed to be essentially bimolecular, largely on account of the sensitivity of the rates to added bases. In the last column of the table the qualitative predictions are recapitulated for comparison with the figures. It will be noted that the effects are always in the expected directions. Furthermore, corresponding to the predicted distinction between " large " and " small " effects, there is a clear difference in the orders of magnitude of the effects observed. " Large " effects are illustrated by figures which indicate rate ratios for pure ethyl alcohol and pure water * of orders such as $10^4 : 1$ or $1 : 10^3$; whereas " small " effects are represented by data indicating ratios in the two pure solvents of the order of $10 : 1$ only.

TABLE III.

Observed solvent effects on the rate-constants (k_2 *in* $sec.^{-1}$ $g.$-$mol.^{-1}$ $l.$; k_1 *in* $sec.^{-1}$) *of the bimolecular substitutions and eliminations* (S_N2 *and* E2) *in aqueous ethyl alcohol.*

Type.	Rctn.	Example.	Rate const.	Temp.	Vol. % H_2O in aqueous EtOH. 0.	10.	20.	30.	40.	100.	Predicted effect.
1[a]	S_N2	$Pr^iBr + \bar{O}H$	10^4k_2	55°	0·60	—	0·49	—	0·30	—	Small decr.
	$E2$	,,	,,	,,	1·46	—	0·71	—	0·47	—	,,
2[a]	S_N2	$Pr^iBr + H_2O$	10^5k_1	,,	0·0173	—	0·236	—	0·667	—	Large incr.
3[b]	S_N2	$Me_3\overset{+}{S} + \bar{O}H$	10^4k_2	100	7240	—	178	—	15·1	0·369	Large decr.
	$E2$	$Et_3\overset{+}{S} + \bar{O}H$	,,	,,	—	—	205	—	21·0	0·242	,,
4[c]	$E2$	$Ar{\cdot}[CH_2]_2{\cdot}\overset{+}{N}Me_3 + H_2O$	10^5k_1	,,	—	20·95	—	13·96	—	3·88	Small decr.

(*a*) Hughes, Ingold, and Shapiro, *J.*, 1936, 255; Hughes, Ingold, Masterman, and MacNulty, *J.*, 1940, 899.

(*b*) Gleave, Hughes, and Ingold, *J.*, 1935, 236.

(*c*) (Ar = *p*-$NO_2{\cdot}C_6H_4$) Hughes and Ingold, *J.*, 1933, 523. The alcoholic constituent of the solvent was *n*-propyl alcohol in this case.

Some figures for the rates of unimolecular reactions are given in Table IV. Here we have only two distinct reaction types, but their solvent effects differ strikingly in both direction and magnitude. Once again there is good agreement with qualitative theoretical prediction.

In Table V we present the evidence concerning the effect of solvent composition on the proportions of olefin produced from alkyl halides and sulphonium ions by reactions of those molecularities and types which have been studied in aqueous ethyl alcohol. The universal rule appears to be a moderate drop in the proportion of olefin as the solvent becomes more aqueous. This agrees with the theoretical predictions, where these are definite. In the case in which no prediction is made, the theoretical interpretation of the observed result would be that the loss of charge in the formation of the transition state is at least not smaller when the anion is attacking hydrogen than when it is attacking carbon.

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* These calculations can readily be made with the aid of Olson and Halford's formula (cf. Bird, Hughes, and Ingold, *J.*, 1943, 255, and papers there cited).

TABLE IV.

Observed solvent effects on the rate-constants (10^5k_1 *with* k_1 *in* $sec.^{-1}$) *of unimolecular substitutions and eliminations* (S_N1 *and* E1) *in aqueous ethyl alcohol.*

Type.	Rctn.	Example.	Temp.	Vol. % H_2O in aqueous EtOH.								Predicted effect.
				0.	10.	20.	30.	40.	50.	60.	100.	
1 & 2	S_N1 + $E1$	$\mathrm{Bu^tCl}$(a)	25°	—	0·171	0·914	4·03	12·6	36·7	129·4	—	Large increase
		$\mathrm{Bu^tBr}$(b)	25	0·45	—	37·0	—	—	—	—	—	
		,, (c)	55	19·8	—	1320	—	—	—	—	—	
		$\mathrm{Am^tCl}$(d)	25	—	—	1·45	—	14·8	—	—	—	
		$\mathrm{Am^tBr}$(e)	25	1·09	—	58·2	—	—	—	—	—	
3 & 4	S_N1 + $E1$	$\overset{+}{\mathrm{S}}\mathrm{Me_2Bu^t}$(f)	50	1·78	—	1·24	—	—	—	—	0·60	Small decrease
		,,	80	—	—	89·7	—	—	—	—	43·9	
		$\overset{+}{\mathrm{S}}\mathrm{Me_2Am^t}$(g)	50	15·0	—	6·66	—	—	—	—	—	
		,,	65·3	—	—	61·8	—	—	45·3	—	—	

(*a*) Hughes, *J.*, 1935, 255.
(*b*) Cooper and Hughes, *J.*, 1937, 1183; Cooper, Hughes, and Ingold, *J.*, 1937, 1280; cf. Part XI.
(*c*) Cooper and Hughes, *loc. cit.*; Hughes, Ingold, Masterman, and MacNulty, *loc. cit.*
(*d*) ($\mathrm{Am^t}$ = *tert.*-amyl) Hughes and MacNulty, J., 1937, 1283.
(*e*) *Idem. ibid.*, cf. Part XI.
(*f*) Cf. Parts VIII and XIV. The figure 1·78 for 10^5k_1 refers to EtOH with 3% H_2O. The figures 1·24 and 0·60 are calculated from measurements at other temperatures.
(*g*) Cf. Parts V, VIII, and XIV. The figure 15·0 for 10^5k_1 refers to EtOH containing 3% H_2O.

TABLE V.

Observed solvent effects on the proportion of olefin (*expressed below as a percentage of the total decomposition*) *in bi- and uni-molecular reactions* (*substitution plus elimination*) *in aqueous ethyl alcohol.*

Type.	Reaction.	Example.	Temp.	% H_2O in aqueous EtOH.				Predicted effect.
				0.	20.	40.	100.	
1	S_N2 + $E2$	$\mathrm{Pr^iBr} + \bar{\mathrm{O}}\mathrm{H}$(a)	55°	71	59	54	—	Small decr.
2	S_N1 + $E1$	$\mathrm{Bu^tBr}$(b)	25	19·0	12·6	—	—	Small decr.
		$\mathrm{Am^tCl}$(c)	,,	—	33·0	25·7	—	
		$\mathrm{Am^tBr}$(d)	,,	36·3	26·2	—	—	
3	S_N2 + $E2$	$\overset{+}{\mathrm{S}}\mathrm{Et_3} + \bar{\mathrm{O}}\mathrm{H}$(e)	100	—	100	100	86	?
4	S_N1 + $E1$	$\overset{+}{\mathrm{S}}\mathrm{Me_2Am^t}$(f)	50	64·4	47·8	—	—	Small decr.
		,,	65·3	—	49·4	39·8(g)	—	

(*a*) See Table III, footnote *a*.
(*b*) ,, ,, IV, ,, *b*.
(*c*) ,, ,, ,, ,, *d*.
(*d*) See Table IV, footnote *e*.
(*e*) ,, ,, III, ,, *b*.
(*f*) ,, ,, IV, ,, *g*.
(*g*) The figure 39·8% is interpolated.

EXPERIMENTAL.

The methods used for the preparation of dimethyl-*tert.*-butyl- and -*tert.*-amyl-sulphonium salts, for following the kinetics of their hydrolysis or alcoholysis, and for estimating the production of olefin, were as described in Part VI. The main numerical results are included in the preceding Tables. Details of some of the experiments are given in Table VI. Other experiments are described in the accompanying papers, Parts VI, VIII, XI, and XIV.

TABLE VI.

*Illustrating determinations of rates of solvolysis of dimethyl-*tert.*-butyl- and -tert.-amyl-sulphonium ion in water and aqueous ethyl alcohol.*

(*a*) Solvent: water. Temp.: 80·1°. $[SMe_2Bu^tCl]$ initially 0·0593M. Solution initially neutral. Acidity, *y*, at time *t*, recorded in c.c. of 0·0592N-alkali per 10 c.c. sample. Mean $k_1 = 43{\cdot}9 \times 10^{-5}$ sec.$^{-1}$.

t (min.) (uncorr.)	0·0	5·5	10·0	14·8	20·0	25·05
y (uncorr.)	0·43	1·70	2·64	3·53	4·32	5·09
10^5k_1 (k_1 in sec.$^{-1}$)	—	43·1	43·6	43·9	43·4	44·2

t (min.) (uncorr.)	30·05	39·0	49·0	65·0	90·0	128·2
y (uncorr.)	5·69	6·60	7·47	8·32	9·11	9·69
10^5k_1 (k_1 in sec.$^{-1}$)	44·3	44·2	45·0	44·5	43·7	42·0

(*b*) Solvent: " 80% EtOH ", *i.e.*, a mixture of 4 vols. anhydrous ethyl alcohol with 1 vol. water. Temp. 80·1°. $[SMe_2Bu^tCl]$ initially 0·0637M. Solution initially neutral. Development of acidity, *y*, recorded in c.c. of 0·0500N-alkali per 10 c.c. sample. Mean $k_1 = 89{\cdot}7 \times 10^{-5}$ sec.$^{-1}$.

t (min.) (uncorr.)	0·0	5·05	8·00	14·5	17·5
y (uncorr.)	1·03	3·74	5·07	6·41	7·44
10^5k_1 (k_1 in sec.$^{-1}$)	—	86·6	88·2	89·2	90·9

t (min.) (uncorr.)	17·5	23·0	29·0	35·5	47·0
y (uncorr.)	8·19	9·44	10·26	11·05	11·65
10^5k_1 (k_1 in sec.$^{-1}$)	89·9	91·6	86·4	92·0	—

(*c*) Solvent: " 50% EtOH ", *i.e.*, a mixture of equal volumes of anhydrous ethyl alcohol and water. Temp. 65·3°. $[SMe_2Am^tCl]$ initially 0·05533M. Solution initially neutral. Acidity, *y*, at time *t*, recorded in c.c. of 0·0477N-alkali, and bromine, *x*, after absorption of part of it by olefin, in c.c. of 0·0492N-thiosulphate, each per 10 c.c. sample. Mean $k_1 = 44{\cdot}6 \times 10^{-5}$ sec.$^{-1}$.

t (min.) (corr.)	10·0	20·0	30·0	40·0	∞
y (corr.)	2·6	4·6	5·9	7·2	11·6
10^5k_1 (k_1 in sec.$^{-1}$)	45·0	45·7	42·7	45·1	—

t (min.) (uncorr.)	0·0	0·0	0·0	20·0	20·0
y (uncorr.)	0·60	0·60	—	5·10	5·10
x (uncorr.)	13·85	13·9	13·95	10·85	10·60
[HCl] (units of *y*)	0·0	0·0	0·0	4·5	4·5
[Olefin] (units of *x*)	0·0	0·0	0·0	3·05	3·30

t (min.) (uncorr.)	20·0	20·0	40·0	40·0	40·0
y (uncorr.)	—	—	7·80	7·80	—
x (uncorr.)	10·90	10·80	9·90	10·00	9·66
[HCl] (units of *y*)	—	—	7·1	7·1	—
[Olefin] (units of *x*)	3·00	3·06	4·00	3·90	4·24

The mean proportion of olefin at $t = 20$ min. is 35·3%. The mean at $t = 40$ min. is lower, 28·4%, showing the incursion of olefin hydration.

(*d*) Solvent: " 50% EtOH ". Temp. 65·3°. $[SMe_2Am^tCl]$ initially 0·1042M. Solution initially neutral. Acidity, *y*, at time *t*, expressed in c.c. of 0·1059N-alkali per 10 c.c. sample. Mean $k_1 = 45{\cdot}7 \times 10^{-5}$ sec.$^{-1}$.

t (min.) (corr.)	5·0	10·0	15·0	20·0	30·0
y (corr.)	1·22	2·43	3·29	4·20	5·50
10^5k_1 (k_1 in sec.$^{-1}$)	44·5	47·9	45·9	47·1	46·3

t (min.) (corr.)	40·0	63·0	90·0	246	∞
y (corr.)	6·49	7·95	8·97	9·73	9·74
10^5k_1 (k_1 in sec.$^{-1}$)	45·8	44·9	43·4	—	—

(*e*) Solvent: " 50% EtOH ". Temp. 65·3°. $[SMe_2Am^tCl]$ initially 0·1182M. Solution initially neutral. Units of *y* and *t* as for expt. (*d*). Mean $k_1 = 45{\cdot}8 \times 10^{-5}$ sec.$^{-1}$.

t (min.) (corr.)	10·0	16·0	22·0	30·0	∞
y (corr.)	2·14	4·01	4·98	6·24	11·17
10^5k_1 (k_1 in sec.$^{-1}$)	46·9	46·3	44·7	45·5	—

(*f*) Solvent: " 80% EtOH " (cf. expt. *b*). Temp. 65·3°. $[SMe_2Am^tCl]$ initially 0·04425M. Solution initially neutral. Acidity, *y*, at time *t*, expressed in c.c. of 0·0406N-alkali, and residual bromine, *x*, after the uptake of part of it by the olefin, in c.c. of 0·0492N-thiosulphate, each per 10 c.c. sample. Mean $k_1 = 60{\cdot}3 \times 10^{-5}$ sec.$^{-1}$.

t (min.) (corr.)	5·0	10·0	15·0	20·0	24·0
y (corr.)	1·75	3·30	4·50	5·50	6·35
10^5k_1 (k_1 in sec.$^{-1}$)	—	60·1	59·2	58·5	60·7

TABLE VI (*continued*).

t (min.) (corr.)	30·0	35·0	40·0	60·0	100·0
y (corr.)	7·30	7·85	8·40	9·65	10·25
10^5k_1 (k_1 in sec.$^{-1}$)	61·6	60·6	61·0	60·1	—

Determined as in expt. *c*, the mean proportion of olefin at $t = 20$ min. was 48·5%. The mean at $t = 60$ min. was 40·0%, showing the incursion of olefin hydration.

(*g*) Solvent: "80% EtOH". Temp. 65·3°. [SMe_2Am^tCl] initially 0·02471M. Solution initially neutral. Mean $k_1 = 65·8 \times 10^{-5}$ sec.$^{-1}$. Mean proportion of olefin = 50·3%.

(*h*) Solvent: "80% EtOH". Temp. 65·3°. [SMe_2Am^tCl] initially 0·1250M. Solution initially neutral. Mean $k_1 = 59·5 \times 10^{-5}$ sec.$^{-1}$.

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