418. *Mechanism of Elimination Reactions. Part VIII. Temperature 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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A survey is made of the available data, including some new results, concerning temperature effects on rates and product-proportions in bi- and uni-molecular eliminations, and the accompanying nucleophilic substitutions, of alkyl halides and alkylsulphonium salts. The data are analysed in terms of the parameters of the Arrhenius equation, and the main regularities are pointed out. One is that, in both bi- and uni-molecular reactions of both alkyl halides and alkylsulphonium salts, the Arrhenius activation energy of elimination is higher than that of the accompanying substitution of the same molecularity. Another is that the substitutions and eliminations of organic ions have larger Arrhenius activation energies, and larger frequency factors, than do the corresponding reactions of neutral molecules; and that this effect of ionic character in the reactant is particularly marked for unimolecular reactions.

These relations may be consistently interpreted on the hypothesis that the differences of activation energy are largely due to differences of solvation energy, which can be theoretically treated as explained in the preceding paper. In the comparisons between simultaneous substitutions and eliminations the main distinction of theoretical importance relates to the solvation of the transition states of these processes. In the comparison between charged and neutral reactants, the emphasis is on the difference of solvation of the initial states. By a straightforward extension of the theory, it is possible to deal with the complementary question of the effect of solvation entropy on the frequency factors of the reactions compared.

We here report some new measurements on the temperature coefficients of reactions which are undergone in hydroxylic solvents by alkyl halides and sulphonium salts in conditions leading to the substantial formation of olefins. It is interesting to set the new data beside previous results of the same nature, and to treat the whole in relation to our division of nucleophilic substitutions and eliminations each into four types distinguished by charge distribution (preceding paper), and in relation to the two mechanisms, the bi- and the uni-molecular, which in principle are available to each of the four types.

(1) *Survey of the Observations.*—We shall first discuss the bimolecular decompositions. Since they are one-stage processes, we have to consider directly, and in the first instance separately, the temperature coefficients of the rates of the simultaneous bimolecular reactions of substitution and elimination, S_N2 and $E2$. If the temperature coefficients are different, then the difference will be reflected in the fact that the proportion in which the total bimolecular reaction produces olefin will shift as the temperature changes.

For the purpose of expressing the dependence of the rates on temperature, we use the Arrhenius equation, $k_2 = B_2 e^{-E/RT}$, where k_2 is the second-order rate constant. The known values of B_2 (in sec^{-1} g.-mol.$^{-1}$ l.) and E (in kilocals./g.-mol.) for bimolecular eliminations, and the bimolecular nucleophilic substitutions which accompany them, are given in Table I.

These data enable us to state that, so far as is known, the rates of the second-order eliminations which simple alkyl chlorides, bromides, and iodides undergo in aqueous and alcoholic solvents all have temperature coefficients corresponding to Arrhenius energies of activation * contained in the range 20—25 kilocals./g.-mol. The range for the second-order

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* In the case of the substitutions it is known that the Arrhenius energies of activation can be markedly changed by steric hindrance (Dostrovsky and Hughes, *J.*, 1946, 157).

TABLE I.

Arrhenius parameters for bimolecular elimination and the accompanying substitution reactions (S_N2 *and* E2) *in aqueous alcohol.*

Type.	Example.	Solvent.(a)	Substitution.		Elimination.	
			$\log_{10} B_2$.	*E.*	$\log_{10} B_2$.	*E.*
1(b)	$\mathrm{Pr^iBr} + \bar{\mathrm{O}}\mathrm{R}$	" 60% EtOH "	9·4	20·8	10·4	22·1
	$\mathrm{Pr^iI} + \bar{\mathrm{O}}\mathrm{R}$	,,	9·7	20·7	11·1	22·2
	$\mathrm{Pr^iCl} + \bar{\mathrm{O}}\mathrm{R}$	" 80% EtOH "	9·4	23·1	10·7	24·8
	$\mathrm{Pr^iBr} + \bar{\mathrm{O}}\mathrm{R}$	,,	10·1	21·7	10·9	22·6
	$\mathrm{Bu^tBr} + \bar{\mathrm{O}}\mathrm{R}$	" 100% EtOH "	—	—	10·1	19·7
3(c)	$\overset{+}{\mathrm{S}}\mathrm{Me_2Bu^t} + \bar{\mathrm{O}}\mathrm{R}$	" 100% EtOH "	—	—	14·9	24·0
	$\overset{+}{\mathrm{S}}\mathrm{Me_2{\cdot}[CH_2]_2{\cdot}Ph} + \bar{\mathrm{O}}\mathrm{R}$	,,	—	—	15·0	23·9
	$\overset{+}{\mathrm{S}}\mathrm{Me_2{\cdot}CHMePh} + \bar{\mathrm{O}}\mathrm{R}$	,,	—	—	16·0	26·2

(*a*) " *x*% EtOH " means a mixture of *x* vols. of anhydrous ethyl alcohol with 100 — *x* vols. of water.
(*b*) Hughes, Ingold, and Shapiro, *J.*, 1936, 225; Hughes and Shapiro, *J.*, 1937, 1177; Hughes, Ingold, Masterman, and MacNulty, *J.*, 1940, 899; Dhar, Hughes, and Ingold, Part XI, this vol., p. 2065.

(*c*) Cf. Parts XII and XIII. The figures for $\overset{+}{\mathrm{S}}\mathrm{Me_2{\cdot}CHMePh}$ refer to a total reaction containing 40% of substitution and 60% of elimination.

elimination reactions of alkylsulphonium ions seems to lie somewhat higher, *viz.*, 24—26 kilocals./g.-mol. However, for any given pair of simultaneous bimolecular processes, the elimination has, in each of the investigated cases, an Arrhenius energy of activation which lies higher than that of the accompanying substitution by 1—2 kilocals./g.-mol. The elimination thus has always the larger temperature coefficient, so that a rise of temperature increases the proportions in which olefin is formed. This effect of temperature on the bimolecular reactions is illustrated in Table II.*

TABLE II.

Variation with temperature of the proportions in which olefins are formed in bimolecular substitution and elimination (S_N2 *and* E2).

Solvent : " 60% EtOH ".(a)			Solvent : " 80% EtOH ".(a)			Solvent : " 100% EtOH ".(b)		
Reaction.	Temp.	% Olefin.	Reaction.	Temp.	% Olefin.	Reaction.	Temp.	% Olefin.
$\mathrm{Pr^iBr} + \bar{\mathrm{O}}\mathrm{R}$	45°	53·2	$\mathrm{Pr^iCl} + \bar{\mathrm{O}}\mathrm{R}$	70°	57·1	$\mathrm{Et}\overset{+}{\mathrm{S}}\mathrm{Me_2} + \bar{\mathrm{O}}\mathrm{R}$	45°	12·0
,,	75	57·5	,,	90	60·6	,,	64	15·4
,,	100	63·6	$\mathrm{Pr^iBr} + \bar{\mathrm{O}}\mathrm{R}$	50	58·1	$\mathrm{Pr^i}\overset{+}{\mathrm{S}}\mathrm{Me_2} + \bar{\mathrm{O}}\mathrm{R}$	45	60·6
$\mathrm{Pr^iI} + \bar{\mathrm{O}}\mathrm{R}$	50	69·8	,,	80	61·2	,,	64	65·7
,,	70	72·7	,,	100	66·5			

(*a*) See Table I, footnotes *a* and *b*. (*b*) See Table I, footnotes *a* and *c*.

We shall now review the unimolecular reactions. They involve two stages, of which the first is rate-determining. Simultaneous substitution and elimination reactions of the same alkyl compound will have a common slow stage, *viz.*, the heterolysis of the alkyl compound : and

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* The substitutions with which the eliminations from sulphonium ions are in competition are themselves composite processes, since alternative alkyl groups can be displaced by substitution (cf. Parts XII, XIII, and XIV).

the rate of this process is the measured rate of the total unimolecular reactions, $S_N1 + E1$. Since this total rate thus has a simple mechanistic significance, it is natural to consider its temperature-dependence before discussing the temperature-variation of the rates of the separate reactions, S_N1 and $E1$.

Again we employ the Arrhenius equation $k_1 = B_1e^{-E/RT}$, where k_1 is now the first-order rate constant of the total unimolecular reaction. Table III contains the value of B_1 (in sec.$^{-1}$) and E (in kilocals./g.-mol.) for those unimolecular reactions in hydroxylic solvents which alkyl halides and sulphonium ions undergo giving known proportions of olefin.

TABLE III.

Arrhenius parameters for total unimolecular reactions involving both substitution and elimination (S_N1 + E1) *in hydroxylic solvents.*

Type.	Example.	Solvent.[(a)]	Total reaction.	
			$\log_{10} B_1$.	E.
2	Bu^{t}Cl solvolysis[(b)]	" 50% EtOH "	13·4	22·9
	Bu^{t}Cl ,,	" 80% EtOH "	11·9	23·2
	Bu^{t}Br ,, [(c)]	,,	13·3	22·8
	Bu^{t}I ,, [(c)]	,,	13·4	22·4
	Am^{t}Cl ,, [(d)]	,,	11·9	22·9
	Bu^{t}Br ,, [(e)]	" 100% EtOH "	12·7	24·6
4	$\overset{+}{\text{S}}\text{Me}_2\text{Bu}^t$,,	Water	17·1	33·0
	$\overset{+}{\text{S}}\text{Me}_2\text{Bu}^t$,,	" 80% EtOH "	17·2	32·7
	$\overset{+}{\text{S}}\text{Me}_2\text{Am}^t$,,	,,	17·2	31·6

(*a*) Cf. Table I, footnote *a*.
(*b*) Hughes, *J.*, 1935, 255.
(*c*) Cooper and Hughes, *J.*, 1937, 1183.
(*d*) (Am^t = *tert.*-amyl) Hughes and MacNulty, *J.*, 1937, 1283.
(*e*) Hughes, Ingold, Masterman, and MacNulty, *J.*, 1940, 899; Dhar, Hughes, and Ingold, Part XI, this vol., p. 2065.

According to theory, the proportion in which olefin is produced in the unimolecular reaction depends on the relative rates of the final stages of the competing substitution and elimination. These final stages are immeasurably rapid, and the temperature coefficients of their rates are unknown; but any difference between the two temperature coefficients will be shown as a variation with temperature of the proportion in which olefin is formed. In the unimolecular reactions of both alkyl halides and alkylsulphonium ions the olefin proportion is, in fact, distinctly temperature-dependent, as is shown in Table IV.

TABLE IV.

Variation with temperature of the proportions in which olefins are formed in unimolecular nucleophilic substitution and elimination in ethyl alcoholic solvents (S_N1 *and* E1).

Solvolysis.	Solvent.	Temp.	% Olefin.	Solvolysis.	Solvent.	Temp.	% Olefin.
Bu^{t}Cl	" 80% EtOH "	25°	16·8[(a)]	Bu^{t}Br	" 100% EtOH "	25°	19·0[(c)]
,,	,,	50	23·7	,,	,,	55	27·9[(d)]
,,	,,	65	36·3	$\overset{+}{\text{S}}\text{Me}_2\text{Am}^t$	" 80% EtOH "	50	47·8
Am^{t}Cl	,,	25	33·0[(b)]	,,	,,	65	49·4
,,	,,	50	40·3[(b)]	,,	,,	83	53·7

(*a*) Cooper, Hughes, and Ingold, *J.*, 1937, 1280.
(*b*) Hughes and MacNulty, *J.*, 1937, 1283.
(*c*) Dhar, Hughes, and Ingold, Part XI, this vol., p. 2065.
(*d*) Hughes, Ingold, Masterman, and MacNulty, *J.*, 1940, 899.

The data of Tables III and IV furnish the following picture of temperature effects on the unimolecular reactions. First, the temperature coefficients of the total first-order reactions which alkyl chlorides, bromides, and iodides undergo in hydroxylic solvents are rather closely grouped, and, in the investigated cases, correspond to Arrhenius activation energies falling within the range 22—25 kilocals./g.-mol. Next, the temperature coefficients of the total first-order reactions of alkylsulphonium ions in hydroxylic solvents are also closely grouped in the examined examples; but the values are strikingly larger, and lead to Arrhenius energies of activation contained in the range 31—33 kilocals./g.-mol. These results, according to theory, apply to the first, slow stage of the unimolecular mechanism, *i.e.*, the heterolysis of the alkyl halide or alkylsulphonium ion. Finally, the proportion in which the total unimolecular reaction produces olefin always increases with rise of temperature. It is not remarkable that alkyl halides and sulphonium ions should be alike in this respect, since, according to theory, the effect arises from a difference in the energies of activation of the final, rapid stages of the simultaneous reactions of substitution and elimination, and these are both reactions of the separated carbonium ion. Interpreted in this way, the experimental results mean that the transference of a proton from the carbonium ion to the solvent with the formation of an olefin has an Arrhenius activation energy which is higher by about 2—4 kilocals./g.-mol. than that of the combination of the same carbonium ion with an anion extracted from the solvent. This follows if we apply the Arrhenius equation in parallel to the two rapid stages of each unimolecular reaction, taking the ratio of the amounts of the products as giving the ratio of the rates of the rapid stages, and using the data for different temperatures in order to eliminate the ratio of the frequency factors of the Arrhenius expression, and thus to isolate the difference of the activation energies.

(2) *Discussion.*—While we have as yet no completely satisfactory theory of these effects of temperature, it may be noted that the more general of the differences to which attention has been called are in the direction in which they would be if solvation were the dominant cause, and if the apparent (Arrhenius) energy of activation were a good index of the real activation energy, *i.e.*, if the two varied in a parallel manner from case to case.

Thus, for the two bimolecular reactions, S_N2 and $E2$, of alkyl halides, the initial state is the same, whereas, of the two transition states, that corresponding to elimination is the less solvated because of its more widely distributed unit charge. This is equally true for the bimolecular reactions of the alkylsulphonium ions (cf. Table I of Part VII). Solvation would therefore operate in both cases to produce a greater activation energy for elimination than for substitution; and if this difference reappears in the apparent activation energies, as derived from the Arrhenius equation, then the elimination process would have the larger temperature coefficient, and an increase of temperature would increase the proportion of olefin, as is found experimentally.

A similar statement applies to the unimolecular reactions of both alkyl halides and sulphonium salts. Here the variation with temperature of the proportion of olefin is dependent on the relative temperature coefficients of the fast stages of the competing substitution and elimination, *i.e.*, the alternative reactions of the carbonium ion. In these reactions also, a unit charge, which is localised at the commencement of the reaction-stage, becomes distributed in the transition states, but more extensively in that of the process leading to elimination (cf. Table II of Part VII). Solvation would therefore reduce the energy of the transition state of the fast stage of the elimination less than it would reduce that of the fast stage of the substitution, that is, it would contribute more largely to the energy of activatian of the former reaction than to that of the latter; and if this difference were reflected in the Arrhenius activation energies, we should find that the proportion of olefin formed in unimolecular reactions increases with temperature, as in fact it does.

We may next consider the differences between the temperature coefficients of the bi- and uni-molecular reactions of alkyl halides on the one hand, and the temperature coefficients of the analogous reactions of alkylsulphonium ions on the other. From a theoretical point of view, the principal differences, due to solvation, between corresponding reactions of the two types of alkyl compound are probably those which relate to the initial states of the reactions; for in the initial state any ionic charges which are present are localised, and therefore have their maximum effectiveness in producing solvation. In the initial state of a bimolecular reaction of an alkyl halide, one of the reactants is electrically charged and the other is neutral; whereas in the initial state of a bimolecular reaction of a sulphonium ion both reactants are charged. In the initial state of a unimolecular reaction of an alkyl halide the single reactant involved in the rate-determining process is neutral, whereas in the corresponding reaction of a sulphonium salt the single reactant is charged. Now the solvation of a charged initial state must be a powerful factor tending to increase activation energy; and it may be the main factor determining the larger apparent activation energies of the bimolecular eliminations of sulphonium salts than of the bimolecular eliminations of the alkyl halides, as well as the considerably larger apparent activation energies of the overall unimolecular reactions of sulphonium salts than of the unimolecular reactions of the corresponding alkyl halides. We make this suggestion whilst realising that, where different types of link have to be broken, differences of activation energy are in any case to be expected, because we know of unimolecular reactions in which the bond broken is still the carbon–halogen bond, but the apparent activation energy is nevertheless increased to 29—33 kilocals./g.-mol., instead of retaining its usual value for secondary and tertiary alkyl halides of 22—25 kilocals./g.-mol.; and in these cases the special structural feature is, once again, that the sole reactant in the rate-determining stage is an ion. We are referring now to the unimolecular hydrolysis of the α-bromomethylmalonate ion and of several similar ions (Hughes and Taher, *J.*, 1940, 956; Gripenberg, Hughes, and Ingold, *Nature*, 1948, **161**, 480).

These considerations concerning the Arrhenius energies of activation require a slight extension in order to take account of the further fact that all the reactions, bimolecular and unimolecular, of the sulphonium salts have abnormally large B-factors. For the bimolecular reactions of sulphonium salts, the Arrhenius parameter B_2 is greater by several powers of ten than the theoretical collision frequency ($\log_{10}B_2$ is about 15, instead of the normal value of about 11, as observed, *e.g.*, in the corresponding reactions of the analogous alkyl halides). And for the unimolecular reactions of sulphonium salts, the frequency factor B_1 is of an altogether larger order of magnitude than molecular vibration frequencies ($\log_{10}B_1$ is about 17, instead of the common value of about 13, as illustrated, *e.g.*, in the corresponding reactions of alkyl halides). The unimolecular reactions of the bromomalonate ion and other bromo-anions give similarly large B-factors ($\log_{10}B_1$ is again about 17).

Following Gripenberg, Hughes, and Ingold (*loc. cit.*) we regard these high B factors as due essentially to the ionic charges in the reactants (cf. Bell, *J.*, 1943, 629); and we believe the mode of dependence to be closely connected with the effect of the charges on the activation energies. In brief, our theory is that, relatively to co-ordinate axes fixed in the reactant molecules, certain solvent molecules are restricted by these charges to positions in the initial state which are geometrically close to the positions which solvating solvent molecules will be required to occupy in the transition state of the reaction. The result will be that their displacement from one set of positions to the other will not be accompanied by as large a decrease of entropy as would have been involved in the absence of the initial charges. The small distances through which the solvating solvent molecules would have to move will, however, be associated with large amounts of electrostatic work, because of the great strength of the forces in the immediate neighbourhood of an ion. Thus the change from the initial state to the transition state will require larger increases of energy than would have been needed in the absence of the initial charges. We shall not go further into these matters here, since the structural and environmental factors which affect the Arrhenius parameters of reactions in solution are being treated in a more general manner in another paper.

EXPERIMENTAL.

The methods used for the preparation of materials, for following the kinetics of hydrolysis and alcoholysis of the alkyl halides and sulphonium salts, and for estimating the proportion of olefin formed, 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 Tables V and VI. Other experiments are described in the accompanying papers, Parts VI, VII, XII, and XIII.

TABLE V.

Illustrating determinations of rates of bimolecular reactions of, and proportions of olefin formed from, alkylsulphonium ethoxide in dry ethyl alcohol.

(*a*) *Dimethyl*-tert.-*butylsulphonium Ethoxide* (*Total Rate : Expt. A*).—Solvent : EtOH. Temp. 19·98°. Initially [SMe_2Bu^tI] = 0·0200M and [NaOEt] = 0·0967N. Alkalinity, y, at time t expressed in c.c. of 0·01609N-acid per 5 c.c. sample. Rate-constant, k_2, in sec.$^{-1}$ g.-mol.$^{-1}$ l.

t (min.)	0	15	24	34	44	60	75
y (c.c.)	29·94	29·11	29·07	28·78	28·45	28·06	27·64
10^3k_2	—	(1·7)	1·10	1·07	1·11	1·08	1·12

t (min.)	117	140	160	180	200	240	∞
y (c.c.)	26·84	26·40	26·11	25·78	25·60	25·24	23·76
10^3k_2	1·09	1·12	1·13	1·17	1·15	1·14	—

(Mean 10^3k_2 = 1·12. Corrected for expansion of solvent, 10^3k_2 = 1·14.)

TABLE V (*continued*).

(*b*) *Dimethyl*-tert.-*butylsulphonium Ethoxide* (*Olefin Proportion: Expt. B.*)—Solvent: EtOH. Temp. 45·08°. Initially $[SMe_2Bu^tI] = 0{\cdot}0199$M and $[NaOEt] = 0{\cdot}0958$N. The alkali is expressed in c.c. of 0·01920N-acid per 5 c.c. sample, and the olefin is given by the amount of bromine, measured in c.c. of 0·02062N-thiosulphate, which survives out of a standard quantity added, in a 5 c.c. sample.

Initial readings.		Final readings.	
Alkali.	Bromine.	Alkali.	Bromine.
24·84	22·52	19·67	13·24, 12·98, 12·91, 12·75

(Olefin proportion: 97·2, 99·7, 100·6, 102·2%. Mean: 99·4%.)

Summary for $(\overset{+}{S}Me_2Bu^t)(\overset{-}{O}Et)$. In dry ethyl alcohol k_2 at 19·98° = 114 × 10^{-5}, and k_2 at 45·08° = 2930 × 10^{-5} sec.$^{-1}$ g.-mol.$^{-1}$ l. The following proportions of *iso*butylene at 45·08° are found: 100·5%, 99·4% (Mean proportion, 100%). Hence $k(E2)$ at 19·98° = 114 × 10^{-5}, and $k(E2)$ at 45·08° = 2930 × 10^{-5} sec.$^{-1}$ g.-mol.$^{-1}$ l.; and hence for the bimolecular elimination $B = 8{\cdot}5 \times 10^{14}$ sec.$^{-1}$ g.-mol.$^{-1}$ l. and E = 24·0 kilocals./g.-mol.

TABLE VI.

Illustrating determinations of rates of unimolecular reactions of, and proportions of olefin formed from, alkylsulphonium salts and alkyl halides in water and aqueous alcohol.

(*a*) *Dimethyl*-tert.-*butylsulphonium Salt.*—Solvent: water. Temp. 65·35°. $[SMe_2Bu^tCl]$ initially 0·0593M. Solution initially neutral. Acidity, *y*, at time *t*, recorded in c.c. of 0·0592N-alkali for 10 c.c. sample.

t (hrs.) (uncorr.)	0·0	0·45	1·00	1·52	2·00	2·95
y (uncorr.)	0·10	0·98	1·93	2·70	3·50	4·60
10^5k_1 (k_1 in sec.$^{-1}$)	—	5·72	5·66	5·55	5·83	5·69
t (hrs.) (uncorr.)	3·75	4·80	5·80	6·80	7·80	11·50
y (uncorr.)	5·38	6·30	6·90	7·68	8·01	9·00
10^5k_1 (k_1 in sec.$^{-1}$)	5·64	5·66	5·53	5·72	5·69	—

Summary for $\overset{+}{S}Me_2Bu^tCl$. In water, k_1 at 65·35° = 5·67 × 10^{-5}, at 80·1° = 43·9 × 10^{-5}, and at 100·0° = 560 × 10^{-5} sec.$^{-1}$ (cf. Hughes and Ingold, *J.*, 1933, 1571). Hence $B_1 = 1{\cdot}22 \times 10^{17}$ sec.$^{-1}$, and E = 33·0 kilocals./g.-mol. In " 80% EtOH ", k_1 at 65·35° = 11·8 × 10^{-5}, and at 80·1° = 89·7 × 10^{-5} sec.$^{-1}$. Hence $B_1 = 1{\cdot}60 \times 10^{17}$ sec.$^{-1}$, and E = 32·7 kilocals./g. mol.

(*b*) tert.-*Butyl Chloride.*—Solvent: " 80% EtOH ". Temp. = 50·0°. $[Bu^tCl]$ initially 0·182M. Solution initially neutral. Acidity, *y*, at time *t*, recorded in c.c. of 0·0510N-alkali per 10 c.c. sample. Olefin, *x*, recorded in c.c. of 0·0493N-thiosulphate per 20 c.c. sample.

t (hrs.) (uncorr.)	0·00	0·32	1·02	2·00	5·20	22·0	72·4
y (uncorr.)	0·33	6·70	19·58	27·70	34·62	—	35·20
x (uncorr.)	0·30	7·32	19·26	27·46	31·80	19·52	6·51

The figures show that olefin hydration becomes considerable after 2 hours. The readings up to that time give figures which are included in the summary.

Summary for Bu^tCl. In " 80% EtOH ", k_1 at 25·0° = 0·854 × 10^{-5}, at 50·0° = 19·6 × 10^{-5}, and at 65·35° = 89·7 × 10^{-5} sec.$^{-1}$ (cf. Cooper, Hughes, and Ingold, *loc. cit.*). Hence $B_1 = 9{\cdot}8 \times 10^{11}$ sec.$^{-1}$, and E = 23·2 kilocals./g.-mol. The proportions of olefin at the above temperatures are given in Table IV.

(*c*) tert.-*Amyldimethylsulphonium Salt.*—Solvent: " 80% EtOH ". Temp. 82·7°. $[SMe_2Am^tCl]$ initially 0·0199M. Solution initially neutral. Acidity, *y*, at time *t*, expressed in c.c. of 0·0221N-alkali per 20 c.c. sample.

t (min.) (corr.)	1·0	2·0	3·0	4·0	6·0	30·0
y (corr.)	5·09	10·05	12·09	13·83	16·07	18·00
10^5k_1 (k_1 in sec.$^{-1}$)	554	671	618	608	619	—

Mean k_1 = 612 × 10^{-5} sec.$^{-1}$. There is no appreciable hydration of olefin in the first 6 mins., and independent determinations of the olefin proportion at 4—6 mins. gave 53·7%.

Summary for SMe_2Am^tCl. In " 80% EtOH ", k_1 for 50·0° = 6·66 × 10^{-5}, at 65·3° = 61·8 × 10^{-5}, and at 82·7° = 612 × 10^{-5} sec.$^{-1}$. Hence $B_1 = 1{\cdot}50 \times 10^{17}$ sec.$^{-1}$, and E = 31·6 kilocals./g.-mol. The proportions of olefin at the above temperatures are in Table IV.

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