54. *Mechanism of Substitution at a Saturated Carbon Atom. Part III. Kinetics of the Degradations of Sulphonium Compounds.*

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Recently, Hughes, Ingold, and Patel (J., 1933, 526)* considered the mechanism of substitutions of the form

$$\mathrm{Y} + \mathrm{Alk}\vdots\!-\mathrm{X} \longrightarrow \mathrm{Alk{-}Y} + \mathrm{X} \quad . \; . \; . \; . \; . \; . \; . \quad (\mathrm{S_N})$$

These substitutions are characterised, as the position of the dotted line in the equation indicates, by electron transfers from Y to Alk and from Alk to X; but, subject to this, no restriction is necessary concerning the states of electrification of the species involved. Thus, the reagent Y may be either negatively charged or neutral, and the group X either positively charged or neutral. Whatever the electrical distribution may be, the form of the change is the same, as may be seen by a comparison of such examples as the following :

$$(a)\ \overset{-}{\mathrm{O}}\mathrm{H} + \mathrm{Alk{\cdot}Br} \longrightarrow \mathrm{Alk{\cdot}OH} + \overset{-}{\mathrm{Br}}$$

$$(b)\ \mathrm{NMe_3} + \mathrm{Alk{\cdot}Cl} \longrightarrow \mathrm{Alk{\cdot}}\overset{+}{\mathrm{N}}\mathrm{Me_3} + \overset{-}{\mathrm{Cl}}$$

$$(c)\ \overset{-}{\mathrm{O}}\mathrm{H} + \mathrm{Alk{\cdot}}\overset{+}{\mathrm{S}}\mathrm{Me_2} \longrightarrow \mathrm{Alk{\cdot}OH} + \mathrm{SMe_2}$$

Evidently such differences in electrical distribution are trivial in relation to the fundamental analogy of the examples; consequently the essentials of any general theory of mechanism must apply to *all* substitutions covered by equation ($\mathrm{S_N}$), independently of the electrical distribution. There is reason to believe that the general applicability of the considerations

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* This paper will be referred to as Part I of the present series, and the subsequent paper by Hughes and Ingold (J., 1933, 1571) as Part II.

advanced by Hughes, Ingold, and Patel may have been obscured by the circumstance that all their illustrations related to substitutions having the distribution of charges shown in example (*c*). Therefore, we mention the matter at the outset, as the illustrations now to be considered continue to be drawn from the same field.

The essential characteristic of equation (S_N) is that the substituting agent is nucleophilic. The reactions collectively represented by this equation may conveniently be called " nucleophilic substitutions."

Concerning these substitutions, Hughes, Ingold, and Patel's main conclusions were (1) that two types of mechanism may operate, (2) that these may be distinguished kinetically, and (3) that it is possible to tell theoretically how the control of a particular substitution by one mechanism or the other should be affected by the chemical constitutions of the interacting species.

The first of the two mechanisms operates in a single stage, which may be formulated thus :

$$\overset{\curvearrowright}{Y}\ \ \mathrm{Alk}\overset{\curvearrowright}{-X} \longrightarrow Y\mathrm{-Alk} + X \quad . \ . \ . \ . \ . \quad (S_N2)$$

This is a bimolecular reaction. In the second mechanism the process becomes split up into two stages, thus :

$$\left.\begin{array}{l} \mathrm{Alk}\overset{\curvearrowright}{-X} \longrightarrow \overset{+}{\mathrm{Alk}} + X \\ \overset{\curvearrowright}{Y}\ \ \overset{+}{\mathrm{Alk}} \longrightarrow Y\mathrm{-Alk} \end{array}\right\} \quad . \ . \ . \ . \ . \ . \ . \quad (S_N1)$$

It is usually true that the second stage can be treated as instantaneous in comparison with the first, the whole reaction being of the first order. The two mechanisms were regarded as the extremes of a graded range.

In Part I a number of predictions were made concerning the effect of constitutional changes on the mechanism and kinetics of nucleophilic substitutions. Illustrating in the series in which the group X is $\overset{+}{N}Me_3$, the effects were considered which are to be expected from independent variations of the group Alk and the reagent Y. The significant property of the group Alk was shown to be its electron-releasing power, and the effect of progressively increasing the electron repulsion, *e.g.*, by traversing the following series, was discussed :

$$CH_3\cdot \qquad CH_3{\rightarrow}CH_2\cdot \qquad \begin{array}{l} CH_3\searrow \\ \quad\quad CH\cdot \\ CH_3\nearrow \end{array} \qquad \begin{array}{l} CH_3\searrow \\ CH_3{\rightarrow}C\cdot \\ CH_3\nearrow \end{array} \quad . \quad \text{(Series i)}$$

This effect is evidently to impede the access of the reagent necessary for mechanism (S_N2),* and to facilitate the ionisation necessary for mechanism (S_N1). Accordingly, on traversing the series from left to right a change of mechanism in the sense $S_N2 \longrightarrow S_N1$ should be experienced if the range of variation of electron repulsion is sufficient. This change of mechanism should be detectable as a change in the reaction kinetics.

Similarly, the significant property of the reagent Y was shown to be its nucleophilic character, of which basicity may be taken as a sufficient indication. The more pronounced the nucleophilic character of the reagent, the more will mechanism (S_N2) be favoured at the expense of (S_N1). Therefore, if a series of reagents is arranged in order of decreasing basicity, *e.g.*,

$$OH' \qquad OPh' \qquad CO_3'' \qquad OAc' \qquad Cl' \qquad . \ . \ . \ . \quad \text{(Series ii)}$$

a change of mechanism in the sense $S_N2 \longrightarrow S_N1$ should be experienced on progressing through the series. This change also should be observable by means of the altered reaction kinetics.

It was also foreseen that these changes of mechanism should be associated with certain regular changes of velocity. Considering, first, constitutional variations in the molecule in which the substitution is to occur, the expected relationship is of the following kind. For given physical conditions (see below), the absolute velocity of reaction by mechanism

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* It must also impede extension of the vulnerable bond, but this effect is a minor one except for some highly extensible bonds such as are prone to participate in mechanism S_N1.

($\mathrm{S_N2}$) should continuously decrease, and the velocity of mechanism ($\mathrm{S_N1}$) should continuously increase on traversing series (i) from left to right. If the velocities are plotted as ordinates, the series of groups Alk being set out on the axis of abscissæ, the curves traced should have the general form indicated in Fig. 1. The point of intersection of the curves is the point of change of mechanism. The upper curve on either side of this point is the experimentally realisable curve (see, however, Part IV, p. 249), so that the observed velocity must pass through a minimum. Thus an approach towards the critical point from either side is associated with a continuous decrease of velocity.

The velocity relations determined by constitutional changes in the substituting agent Y are rather different. The form of the velocity diagram of series (ii) is shown in Fig. 2. The curve for mechanism ($\mathrm{S_N2}$) descends with decreasing basicity of the reagent, but in mechanism ($\mathrm{S_N1}$) the reagent is excluded from the slow stage, and the corresponding velocity curve is therefore horizontal. The point of intersection of the curves again marks the change of mechanism. Proceeding towards less basic reagents, the velocity decreases to the critical point, and thereafter remains constant.

It will be evident that in each of these series the precise location of the critical point will depend on the physical conditions; a high concentration must favour mechanism ($\mathrm{S_N2}$). The curves for mechanism ($\mathrm{S_N2}$) can obviously be displaced in a vertical direction by changing the concentration, although the practicable limits within which this is possible may not suffice to shift the critical point a whole place in the chemical series. Similarly, the solvent must exert a specific effect on each mechanism (see following paper), so the critical point should be capable of displacement by changing the solvent. Finally, it may be recalled that in border-line cases, in which the kinetics are intermediate or definitely dependent on the physical conditions, Hughes, Ingold, and Patel envisaged intermediate mechanisms, rather than a superposition of the extremes: there must be *degrees* of collaboration by the reagent in the process of expelling the substituent that is to be replaced.

FIG. 1.

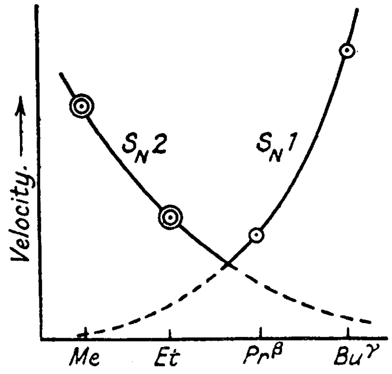
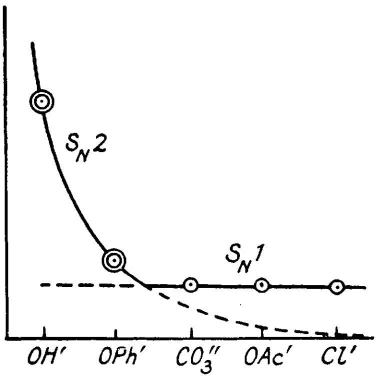


FIG. 2.



At the time of these predictions, no dynamical evidence was available in relation to either of the series illustrated (i and ii). We therefore undertook kinetic studies in each of the three fields of nucleophilic substitutions illustrated by equations (*a*), (*b*), and (*c*). As the measurements within field (*c*) have now reached a stage at which it is possible to give a complete confirmation of the predictions of Part I, we report them. The reactions studied are of the form $\bar{\mathrm{X}} + \mathrm{Alk{\cdot}\overset{+}{S}R_2} \longrightarrow \mathrm{X{\cdot}Alk} + \mathrm{SR_2}$, and we have not only observed the anticipated change of kinetics in series (i) and series (ii), but have also located the mechanistic critical point in each series, and verified the corresponding velocity relations.

In the series of experiments of which the object was to test the kinetic effect of varying the group Alk as in series (i), the reagent X was always the hydroxide ion: the compounds were trialkylsulphonium hydroxides.

The decomposition of trimethylsulphonium hydroxide is unidirectional, and the products are methyl alcohol and dimethyl sulphide. The kinetics were studied in aqueous solution at 100°. The reaction was shown to be bimolecular with respect to the sulphonium compound. The tests relating to initial velocity and half-life period were satisfied, and the bimolecular equation expressed the course of the change, except that the constant showed a slight upward drift. The magnitude of this is not greater than can be accounted for by the neglect of the activity correction appropriate to an interaction between unlike ions. Experiments carried out in the presence of additional hydroxide ions led to a more detailed specification of kinetics : they showed the reaction to be of the first order with respect to each of the ions of the sulphonium hydroxide. In contrast to an example considered later, the order of the reaction remained the same at the greatest dilutions for which accurate measurement was possible. The replacement of the solvent water by ethyl alcohol in successively increasing proportions led to large progressive increases in the reaction velocity.

It has already been shown (Ingold and Kuriyan, J., **1933**, 991) that triethylsulphonium hydroxide in aqueous solution decomposes in two directions, the products being ethyl alcohol and ethylene together with diethyl sulphide. The measurements now reported prove that the total decomposition is bimolecular, and is of the first order with respect to each of the participating ions. We may conclude that this statement applies to the component decompositions separately. The velocity of the total decomposition is increased when the solvent water is replaced by ethyl alcohol.

A comparison of the absolute rates of the decompositions considered in the two preceding paragraphs shows that the reaction leading to the formation of ethyl alcohol proceeds much more slowly than that yielding methyl alcohol.

In dilute aqueous solution methyldi*iso*propylsulphonium hydroxide decomposes substantially in a single direction, the products being *iso*propyl alcohol and the complementary sulphide. Kinetic investigation showed that this reaction is unimolecular. Furthermore, the addition of extraneous hydroxide ions had no effect on the speed ; and even the removal of these ions altogether by replacement with another anion (iodide) was without influence. It follows that the decomposition is of the first order with respect to the sulphonium cation, and that the rate-determining stage proceeds without intervention by the reagent anion. In more concentrated solution, and especially if part of the solvent water is replaced by alcohol, a bimolecular reaction supervenes, but at least a part of this is the elimination process leading to propylene.

The experimental particulars relating to the final member of the alkyl series have already been recorded (Part II, *loc. cit.*). The results show that dimethyl-*tert.*-butylsulphonium hydroxide in aqueous solution decomposes mainly in one direction yielding *tert.*-butyl alcohol and dimethyl sulphide, that this reaction is unimolecular even in moderately concentrated solution, and that the speed cannot be altered by the addition of extraneous hydroxide ions or by completely replacing these ions by different anions. This reaction also is accelerated by replacing water by alcohol as solvent.

A comparison of the absolute velocities of the decompositions referred to in the two preceding paragraphs shows that the reaction leading to *tert.*-butyl alcohol takes place very much more rapidly than that yielding *iso*propyl alcohol.

These four sets of experiments show that, for the reaction studied, the point of mechanistic change in series (i) lies between the ethyl and the *iso*propyl group. Moreover, the reaction velocities exhibit the expected relationship (Fig. 1) for a critical point in this position.

In the series of experiments to elucidate the effect of changing the substituting agent as in series (ii), the structure taken for substitution was always the trimethylsulphonium cation, its salts with different anions being investigated.

It has already been noted that the decomposition of trimethylsulphonium hydroxide yields only methyl alcohol and dimethyl sulphide, that the reaction is bimolecular, and that the replacement of solvent water by successively increasing proportions of ethyl alcohol causes a marked increase of speed without any change of kinetic type. For experimental convenience the reaction in alcohol as solvent was taken as the starting point for the present comparisons.

Trimethylsulphonium phenoxide decomposes in a simple manner yielding anisole and dimethyl sulphide. The change was found to be bimolecular in ethyl alcohol, and was shown, by the addition of extraneous phenoxide, to be of the first order with respect to each of the participating ions. Comparison of the decompositions of trimethylsulphonium hydroxide and phenoxide shows that the latter compound reacts much more slowly than the former.

The decomposition of trimethylsulphonium carbonate in ethyl alcohol was found to be unimolecular, and the speed of reaction was not increased by addition of extraneous carbonate. It follows that the decomposition is of the first order with respect to the sulphonium cation, and that the rate-determining stage does not involve the anion.

The decomposition of trimethylsulphonium chloride was studied in ethyl alcohol and found to be unimolecular also. Von Halban examined the conversion of the bromide into ethyl bromide and diethyl sulphide in a large number of solvents (*e.g.*, alcohol, acetone) and observed unimolecular kinetics in all cases (*Z. physikal. Chem.*, 1909, **67**, 129). This result has been confirmed for a number of further solvents by Essex and Gelormini (*J. Amer. Chem. Soc.*, 1926, **48**, 882) and by Corran (*Trans. Faraday Soc.*, 1927, **23**, 605). Our experiments showed that, for the same temperature and the same solvent, the rates of decomposition of trimethylsulphonium carbonate, bromide, and chloride were identical to within the limits of experimental precision.

It follows from the last five sets of experiments that for the reaction examined the point of mechanistic change in series (ii) lies between the phenoxide and the carbonate ion. Furthermore, the absolute reaction velocities have the relationship expected (Fig. 2) for a critical point in this situation.

A summary of velocity coefficients is appended. The bimolecular coefficients, k_2, are in litres/mol.-hour, and, on account of the appreciable effect of ionic strength on this constant, are quoted for concentrations in the neighbourhood of 0·1*M*. The unimolecular coefficients, k_1, are in hours^{-1}.

Summary of Velocity Coefficients (*at* 100°).

Substitutions.

Cation series.
(Solvent: H_2O. Anion: OH′.)

Alcohol.	Cation.	k_2.	k_1.
MeOH	$Me_3S^{\cdot}$	0·133	—
EtOH	$Et_3S^{\cdot}$	0·014	—
$Pr^{\beta}OH$	$MePr^{\beta}_2S^{\cdot}$	—	0·0079
$Bu^{\gamma}OH$	$Me_2Bu^{\gamma}S^{\cdot}$	—	20·5 *

(* Part II, *loc. cit.*)

Anion series.
(Solvent: EtOH. Cation: $Me_3S^{\cdot}$.)

Anion.	k_2.	k_1.
OH′	2670	—
OPh′	48	—
CO_3''	—	0·265
Br′	—	0·279
Cl′	—	0·263

Solvent effect.
($Me_3S{\cdot}OH$ in aq. EtOH.)

EtOH, % by vol.	k_2.
0	0·133
60	5·44
80	64·0
100	2670

(Cf. also Part II.)

For $MePr^{\beta}_2SI$ in water, $k_1 = 0{\cdot}0071$.

Olefin eliminations.

(Solvent: Aqueous EtOH.)

Substance	EtOH, % by vol. 0	60	80	
$Et_3S{\cdot}OH$	0·087	7·55	73·8	k_2
$MePr^{\beta}_2S{\cdot}OH$	—	6·76	—	

EXPERIMENTAL.

Preparation of Materials.—Dimethyl sulphide, b. p. 37°, prepared by Klason's method (*Ber.*, 1887, **20**, 3412), and methyl iodide were allowed to react in absolute ethyl alcohol; the sulphonium iodide was precipitated with ether and crystallised several times from alcohol, m. p. 215° (decomp.) (Found: I, 62·3. Calc.: I, 62·6%); it was converted into the hydroxide, carbonate, chloride, or bromide by treatment with the corresponding silver salt. An alcoholic solution of the phenoxide was prepared from the chloride with the aid of alcoholic sodium phenoxide, the precipitated sodium chloride being removed.

Diethyl sulphide, b. p. 92°, also prepared by Klason's method, was combined with ethyl iodide in nitromethane solution, and the sulphonium iodide, m. p. 150°, was purified by repeated precipitation first from ethyl alcohol and then from acetonitrile, by addition of ether (Found: I, 51·0. Calc.: I, 51·3%). The picrate had m. p. 149°. The hydroxide was prepared with the aid of silver oxide.

Di*iso*propyl sulphide, b. p. 118°, was prepared by a method, the details of which were kindly given to us by Dr. F. G. Mann. Its methiodide, prepared in nitromethane solution, and purified by repeated precipitation from acetone by means of ether, had m. p. 161° (Found: I, 47·9.

Calc. : I, 48·8%). The *picrate* had m. p. 161° (Found : C, 43·2; H, 5·3; N, 11·8. $C_{13}H_{19}O_7N_3S$ requires C, 43·2; H, 5·3; N, 11·6%).

Kinetic Measurements.—Methods. Four solvents were employed, *viz.*, water, 60% and 80% (by vol.) aqueous ethyl alcohol, and absolute ethyl alcohol. The alcohol was dried by Lund and Bjerrum's method (*Ber.*, 1931, **64**, 210). The temperature was 100° in all cases.

For each run a number of small, thin-walled, glass tubes, each containing measured portions of the original solution, were heated in a boiling water-bath, and at successive intervals of time a tube was removed, quickly cooled, and cleansed externally by washing with dilute hydrochloric acid (to remove any " hardness " deposited by the water-bath), water, and distilled water. Its contents were estimated volumetrically.

Hydroxides were titrated with phenolphthalein as indicator, phenoxides with lacmoid, and carbonates with Sofnol No. 1, these last estimations being carried out in a stream of air. Chlorides and bromides were titrated by Volhard's method. Iodides were estimated by allowing the alkyl iodide to hydrolyse completely and then titrating the hydriodic acid by means of alkali.

For reactions with half-change periods above 1 hr., the time of commencement of the reaction was taken to be the time at which the tubes were put into the bath; and the initial concentrations were taken to be those of the original solution. For reactions with half-change periods between 1 hr. and 4 mins., a time 1 min. after the moment of inserting the tubes was taken as the starting time; and at this time one tube was removed for an estimation the result of which gave the corresponding " initial " concentrations. For reactions of still lower half-change periods, a time 15 secs. after the moment of inserting the tubes was taken as the starting time, and at this moment a tube was removed, and shaken vigorously under cold water for a few seconds, for the estimation which was to provide the " initial " concentrations.

In the following tables concentrations, c, are in mols./litre, and the velocity coefficients are in the units specified on p. 240. These coefficients are defined in terms of time and concentration only, *viz.*, rate = k_2 [Cation] [Anion], and rate = k_1 [Cation], the activity factor being neglected for lack of an accurate data. The percentage of reaction is denoted by p;

Trimethylsulphonium hydroxide.

Solvent.	100% H_2O.						40% H_2O + 60% EtOH.			
Expt. No.	1		2		3		4		5	
$[Me_3S{\cdot}OH]_{p=0}$	0·2919		0·1607		0·1050		0·2117		0·2085	
$[NaOH]_{p=0}$	—		—		0·2464		—		0·1995	
	p.	k_2.	p.	k_2.	p.	k_2.	p.	k_2.	p.	k_2.
	12·1	0·118	17·8	0·134	11·9	0·132	8·1	5·02	14·4	4·20
	17·6	0·122	29·4	0·129	20·5	0·112	15·2	5·10	23·9	4·28
	22·8	0·120	38·1	0·127	29·7	0·117	21·4	5·15	33·0	4·33
	28·0	0·122	48·6	0·129	45·9	0·118	27·1	5·26	40·9	4·39
	34·2	0·127	56·0	0·135	53·1	0·118	31·4	5·18	47·0	4·34
	39·5	0·132	62·1	0·134	61·0	0·120	35·8	5·29	52·1	4·31
	44·1	0·131	64·2	0·135	66·8	0·118	43·6	5·48	61·4	4·36
	44·9	0·129	74·0	0·138	75·0	0·126	49·0	5·45	68·4	4·34
	53·0	0·134					53·2	5·42	73·9	4·36
	57·6	0·130					62·7	5·33	85·3	4·42
	63·6	0·133	Adopted value of k_2 for $c \sim$ 0·1, = *0·133*.				69·5	5·40	90·8	4·42
	67·9	0·133					74·7	5·54	94·9	4·58
	73·2	0·134					Adopted k_2 ($c \sim$ 0·1) = *5·44*			
	78·6	0·146								

Solvent.	20% H_2O+80% EtOH.		100% EtOH.		" 60% Aqueous EtOH." *			
Expt. No.	6		7		8		9	
$[Me_3S{\cdot}OH]_{p=0}$	0·1885		0·0590		0·00273		0·00232	
$[NaOH]_{p=0}$	—		—		—		0·00622	
	p.	k_2.	p.	k_2.	p.	k_2.	p.	k_2.
	15·6	59·1	17·6	2600	12·7	10·8	9·8	12·8
	27·5	60·5	32·4	2620	25·9	12·7	18·2	12·2
	37·1	62·0	43·5	2900	32·2	11·5	23·5	11·3
	44·9	63·5	48·2	2830	38·9	11·6	29·9	11·1
	50·1	64·0	53·7	2830	48·6	11·7	34·1	10·6
			60·1	2440	52·4	11·4		
	Adopted k_2 for $c \sim$ 0·1, = *64·0*		66·7	2710	67·2	12·5		
			70·3	2420				
			Mean k_2 = *2670*		Mean k_2 = *11·7*		Mean k_2 = *11·6*	

* See p. 242.

the corresponding values of k_2 or k_1 are those calculated from the above formulæ after integration for the range 0 to p.

The bimolecular character of the reaction is confirmed by the approach to equality of the products of the period of half-change and the initial concentrations, *viz.*, 7·6 and 7·7 for Expts. 1 and 2 respectively. The variation of the bimolecular coefficient with ionic strength can be seen from the values for a single run (Expts. 1, 2, 4, 6), or by comparing different runs in the same solvent (Expts. 1, 2, 3; or 4, 5); the change is in the right direction, and is of the order of magnitude to be expected for activity effects in reactions between univalent ions of unlike charge. The experiments conducted in the presence of added sodium hydroxide (Nos. 3, 5, 9) show that the reaction is of the first order with respect both to the sulphonium cation and to the anion. In Expts. 3 and 5 the ionic strength is comparatively large but buffered, and accordingly the coefficients are low but comparatively constant. Expts. 8 and 9 were carried out after the others, and with a separate sample of aqueous alcohol of approximately the composition shown (it cannot be assumed that this solvent has exactly the same composition as that used for Expts. 4 and 5). These experiments prove that the reaction remains of the first order with respect to each ion at the greatest dilutions for which accurate measurement was possible. Owing to the large dilutions, the coefficients do not drift appreciably, nor do they become changed by the addition of excess of sodium hydroxide; they should be within a few units per cent. of the constants appropriate to infinitesimal ionic strength.

Trimethylsulphonium phenoxide.

Expt. No. 10. Solvent: 100% EtOH. $[Me_3S{\cdot}OPh]_{p=0}$ = 0·1311. $[NaOPh]_{p=0}$ = 0·0078.

p ………	8·9	14·8	21·7	28·2	33·2	38·2	49·5	53·0	65·1	73·3	78·4	81·1
k_2 ………	47·8	41·6	(32·8)	43·8	42·9	45·2	46·7	48·0	51·2	55·5	56·8	55·3

Mean k_2 ($c \sim 0{\cdot}1$) = *48·6*

Expt. No. 11. Solvent: 100% EtOH. $[Me_3S{\cdot}OPh]_{p=0}$ = 0·0949. $[NaOPh]_{p=0}$ = 0·1610.

p ………	13·7	24·5	34·9	43·6	48·6	54·0	61·8	65·0	73·3	84·2	89·9	94·0
k_2 ………	36·0	35·0	36·4	37·1	35·0	34·5	37·6	36·2	37·6	37·0	35·2	35·6

Mean k_2 ($c \sim 0{\cdot}2$) = *36·1*

These two experiments, in one of which a substantial excess of phenoxide ions was present, show the reaction to be of the first order with respect both to the sulphonium cation and to the anion. The difference between the two mean constants is in the direction, and of the order of magnitude, to be expected from the omission of corrections for activity.

Trimethylsulphonium carbonate.

Solvent, 100% EtOH.

Expt. No.	12			13		14		15		16	
$[(Me_3S)_2CO_3]_{p=0}$	0·0362			0·0314		0·0680		0·1155		0·1712	
$[(NEt_4)_2CO_3]_{p=0}$	—			0·0287		—		0·0545		—	
	p.	k_2.	k_1.	p.	k_1.	p.	k_1.	p.	k_1.	p.	k_1.
	11·7	7·3	0·250	13·4	0·266	12·5	0·267	22·1	0·250	14·1	0·303
	21·1	7·4	0·237	25·5	0·271	18·6	0·246	31·5	0·251	25·9	0·298
	30·4	8·1	0·243	35·7	0·271	32·7	0·264	39·3	0·250	36·1	0·297
	38·2	8·6	0·241	44·5	0·270	41·1	0·264	46·2	0·247	45·4	0·301
	45·2	9·2	0·242	52·1	0·272	48·0	0·261	52·5	0·248	53·1	0·302
	51·4	9·8	0·242	58·1	0·268	54·2	0·270	63·2	0·250	66·5	0·301
	61·7	11·2	0·240	69·0	(0·227)	65·0	0·263	71·1	0·248	75·0	0·308
	70·1	13·1	0·242			79·1	0·262	78·1	0·260		
	76·4	15·0	0·242			88·4	0·269	86·5	0·250		
	Mean k_1 = *0·242*			Mean = *0·270*		Mean = *0·263*		Mean = *0·250*		Mean = *0·301*	

In the record of Expt. 12 the bimolecular coefficient is included for comparison: the variation exposed is typical for the series. The constancy of the unimolecular coefficients, and the circumstance that they are unaltered by the addition of extraneous carbonate (Expts. 13 and 15), show the reaction to be of the first order with respect to the sulphonium ion and of zero order with respect to the anion. In contrast to the bimolecular coefficients of the previous sections, these unimolecular coefficients do not vary greatly with the ionic strength of the solution, and this is consistent with the theory of ionic strength effects on reaction velocity. The mean value of k_1 is *0·265* hr.$^{-1}$.

Trimethylsulphonium bromide.

An initial velocity only was determined:

Expt. No. 17. Solvent, 100% EtOH. $[Me_3S{\cdot}Br]$ = 0·1047. k_1 = *0·279*.

Trimethylsulphonium chloride.

Expt. No. 18. Solvent, 100% EtOH. $[Me_3S{\cdot}Cl]_{p=0}$ = 0·0480. Mean k_1 = *0·263.*

p	12·2	22·8	32·1	40·8	48·0	55·1	65·3	72·4	79·0
k_1	0·261	0·259	0·259	0·262	0·261	0·267	0·270	0·262	0·262

Triethylsulphonium hydroxide.

Solvent.	100% H_2O.			40% H_2O + 60% EtOH.		20% H_2O+ 80% EtOH.
Expt. No.	19	20	21	22	23	24
$[Et_3S{\cdot}OH]_{p=0}$	0·1905	0·3619	0·2955	0·1847	0·1817	0·1535
$[NaOH]_{p=0}$	—	—	0·3600	—	0·2347	—
Range of p	11·1—65·4	18·2—79·0	16·2—74·0	10·4—75·5	33·0—98·0	14·4—49·1
Range of k_2	0·098—0·109	0·099—0·107	0·060—0·094	7·47—8·06	6·17—7·54	66·0—76·0
k_2 ($c \sim 0{\cdot}1$)	Adopted (from Expt. 19) *0·101*			Adopted *7·55*		Mean *73·8*

These results are given in summary as they are very similar to those for trimethylsulphonium hydroxide. The products of the periods of half-change and the initial concentrations for Expts. 19 and 20 are 9·9 and 10·0 respectively, in conformity with the bimolecular character of the reaction, which is also shown by the invariance of the coefficients within the limits permitted by the variations of ionic strength.

The reaction in water proceeds to the extent of 86% in the direction of the elimination leading to ethylene, and 14% in the direction of the substitution giving ethyl alcohol (cf. Ingold and Kuriyan, J., 1933, 991). The corresponding constants ($c \sim 0{\cdot}1$) are therefore k_2 (elimination) *0·087* and k_2 (substitution) *0·014*. The reactions in 60% and 80% alcohol go wholly in the direction leading to the olefin.

*Methyldi*iso*propylsulphonium hydroxide.*

Solvent.	100% H_2O.				40% H_2O + 60% EtOH.			
Expt. No.	25		26		27		28	
$[MePr^{\beta}_2S{\cdot}OH]_{p=0}$	0·00290		0·00290		0·1331		0·1246	
$[NaOH]_{p=0}$	—		0·00326		—		0·1257	
	p.	$100k_1$.	p.	$100k_1$.	p.	k_2.	p.	k_2.
	6·6	0·753	7·6	0·817	13·4	6·94	34·3	6·58
	15·9	0·666	13·4	0·742	26·5	(9·13)	42·8	6·66
	20·8	0·776	20·1	0·767	33·4	7·48	48·6	6·45
	29·4	0·798	28·6	0·772	38·0	6·90	54·4	6·43
	37·3	0·912	37·2	0·910	43·0	6·77	64·2	6·44
	42·4	0·757	42·3	0·757	50·4	6·52	70·1	6·17
	52·5	0·795	53·5	0·815	60·1	6·74	81·0	6·04
					63·7	6·52		
					71·2	7·45		
Mean $100k_1$		*0·779*		*0·797*	74·6	6·60	Adopted k_2 (for $c \sim 0{\cdot}1$; from Expt. No. 27) : *6·76*	
					77·0	6·04		
Range of k_2	2·69—6·11		1·06—1·49		81·1	6·45		

Expts. Nos. 25 and 26 show that the reaction in dilute aqueous solution is unimolecular, dependent on the sulphonium cation, and independent of the anion. There is no elimination of olefin under these conditions : the reaction under observation is the substitution leading to *iso*propyl alcohol. For this reaction k_1 = *0·00788*. Expts. 27 and 28 prove that the decomposition in 60% alcohol is bimolecular. In this case also the reaction proceeds in a single direction : it is the elimination process leading to propylene.

*Methyldi*iso*propylsulphonium iodide.*

Expt. No. 29. Solvent, 100% H_2O. $[MePr^{\beta}_2S{\cdot}I]_{p=0}$ = 0·04425. Mean k_1 = 0·00631.

p	6·0	11·6	16·6	23·7	30·5	36·0	45·9
$100k_1$	0·626	0·604	0·601	0·650	0·640	0·635	0·634

(Range of k_2 = 0·144—0·191)

Expt. No. 30. Solvent, 100% H_2O. $[MePr^{\beta}_2S{\cdot}I]_{p=0}$ = 0·00236. Mean k_1 = 0·00710.

p	7·1	13·4	19·0	27·2	34·3	40·8	50·0
$100k_1$	0·741	0·716	0·705	0·704	0·701	0·699	0·696

(Range of k_2 = 3·26—4·25)

The reaction is shown to be unimolecular by the approximate constancy of k_1 in contrast to the 20-fold variation of k_2 between the two experiments. The value of k_1 for the less concentrated solution approximates to that obtained for the hydroxide at a comparable dilution.

Examination of Reaction Products.—In order to supplement the data obtained by Ingold and Kuriyan (*loc. cit.*), the following determinations were made of the proportion of olefin eliminated from sulphonium hydroxides containing ethyl or *iso*propyl groups.

The sulphonium hydroxide solutions were heated in closed tubes at 100° for a sufficient time, and the tubes then broken under carbon tetrachloride in a stoppered bottle. Titration of the aqueous layer with acid yielded the extent to which reaction had occurred. The carbon tetrachloride layer was shaken with saturated mercuric chloride solution to remove sulphides, washed with water, treated with excess of standard bromine solution, and then titrated with thiosulphate in the presence of potassium iodide. The results were as follows:

Compound.	*c.*	Solvent.	Reaction, %.	Olefin, %.
$(Et_3S)OH$	0·0630	60% aq. EtOH	100	97·5, 101·5, 101·0
$(MePr^{\beta}_2S)OH$	0·0062	H_2O	50	0·0
,, ...	0·0616	60% aq. EtOH	100	98·3, 100·2

Part of the solution used for Expt. 10 (50 c.c.) was heated at 100° for 24 hours, and then distilled. No volatile ether was obtained. The crude anisole fraction weighed rather more than the theoretical (0·61 g.); the fraction rectified for analysis weighed 0·32 g. and had b. p. 154—155° (Found: C, 76·2; H, 7·4. Calc.: C, 75·6; H, 7·2%).

The *iso*propyl alcohol formed in the decomposition of methyldi*iso*propylsulphonium hydroxide in water was identified by oxidation in aqueous solution by means of chromic acid to acetone, which was detected by the iodoform reaction and by Tschelinzev and Nikitin's colour test (*J. Gen. Chem. Russ.*, **1933**, **3**, **317**), and isolated as its 2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p. 127°).

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