

#### 424. Mechanism of Elimination Reactions. Part XIV. Kinetics of Olefin Elimination from *tert.*-Butyl- and *tert.*-Amyl-dimethylsulphonium Salts in Alkaline and Acidic Alcoholic Media.

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Data are recorded to show the effect of homology on the rates of the constituent substitutions and eliminations which tertiary alkyl-dimethylsulphonium ions undergo in bimolecular reactions with ethoxide ions, and also in unimolecular reactions, in ethyl alcohol as solvent. It was readily possible to isolate each of these kinetic types of reaction. Dimethyl-*tert.*-butyl- and -*tert.*-amylsulphonium ions were studied, and the amylenes produced from the latter by each reaction mechanism were analysed, in order to permit a division of the elimination rates and proportions into those parts which apply to the establishment of the double bond along the separate branches of the tertiary alkyl groups.

The bimolecular eliminations of these ions in ethyl-alcoholic sodium ethoxide proceed considerably more rapidly than do the corresponding reactions of the simpler secondary alkyl, and much more rapidly than do those of the primary alkyl, dimethylsulphonium ions; and their speed is too great to permit the measurement of anything more than limits to the rates of the accompanying bimolecular substitutions. Bimolecular elimination proceeds less rapidly in the *tert.*-amyl than in the *tert.*-butyl group, and this is the total result of a large fall of rate for the establishment of the double bond in the alkyl branch which becomes lengthened, together with quite small decreases of rate for the entrance of the double bond into the alkyl branches which remain similar in the two homologues. In bimolecular elimination from the amylsulphonium ion the double bond enters mainly into the shorter branches of the tertiary alkyl group. These results contrast strikingly with those applying to bimolecular elimination from *tert.*-butyl and *tert.*-amyl bromides: they are discussed theoretically in Part XVI.

The rate of the overall unimolecular reaction is considerably greater for the *tert.*-amyl- than for the *tert.*-butyl-sulphonium ion. The rate of unimolecular substitution is increased, but the proportion of such substitution is decreased in the higher homologue. The rate, and the proportion, of elimination are increased in the amylsulphonium ion. The increase of elimination rate is due to a large increase in the rate of establishment of the double bond in the alkyl group which becomes lengthened, reinforced by smaller increases in the rate at which it enters the branches which remain similar in the two compounds. The increase in the proportion of elimination is the net result of a large increase in the proportion in which the double bond enters the lengthened alkyl branch, partly off-set by notable decreases in the proportions in which it enters the other alkyl branches. In unimolecular elimination from the *tert.*-amylsulphonium ion the double bond enters mainly into the long branch of the *tert.*-amyl group. These relations present marked contrasts to those shown by the bimolecular reactions of the sulphonium ions, but close similarities to those displayed by the unimolecular reactions of the analogous alkyl bromides. The theory of the matter is considered in Part XVI.

In this paper we are again concerned with the effects of structural modifications in an alkyl group on the kinetics of the substitutions and eliminations undergone by alkylsulphonium ions. The two preceding papers reported investigations on primary and secondary alkyl groups in alkyl-dimethylsulphonium ions; and the present paper records a corresponding study of tertiary alkyl groups in similar combination, *tert.*-AlkSMe<sub>2</sub>.

The work on the primary and secondary alkyl-dimethylsulphonium ions was restricted to the bimolecular decompositions which they undergo in the presence of a strongly nucleophilic reagent; for the unimolecular reactions of these substances are for the most part difficult to isolate in a mechanistically pure form, even those of secondary alkylsulphonium ions. On the other hand, the tertiary alkyl-dimethylsulphonium ions, although they still exhibit bimolecular reactions, which can be made to become the exclusive modes of decomposition by operating with a moderate concentration of a strongly nucleophilic reagent, also display unambiguous unimolecular reactions, which it is equally easy to isolate by avoiding the presence in considerable concentration of strongly nucleophilic reagents. Accordingly the opportunity has been taken to investigate the kinetics of both modes of reaction of these tertiary alkylsulphonium ions, with the main object of disclosing the effect of structure on the unimolecular, as well as on the bimolecular, reactions of elimination. As before, the bimolecular reactions which have been studied are the reactions between the alkyl-dimethylsulphonium ions and ethoxide ions in ethyl alcohol: the unimolecular reactions are those which the tertiary alkyl-dimethylsulphonium ions undergo in ethyl-alcoholic solvents in the absence of large amounts of alkali.

It should be made clear that the reason why unimolecular elimination is so much more prominent in the reactions of tertiary alkylsulphonium salts than in those of the analogous primary and secondary alkyl compounds is not that bimolecular elimination from tertiary alkyl groups in sulphonium ions is attended with any greater difficulty than from primary or secondary alkyl groups in such ions. On the contrary, we can establish that the facility of

such bimolecular eliminations increases from primary to secondary, and from secondary to tertiary, alkyl groups: the increases are, indeed, considerable. The prominence of unimolecular elimination in the reactions of the tertiary alkyl compounds is due to the circumstance that the increasing facility of unimolecular reactions from primary to secondary, and from secondary to tertiary, alkyl groups is found, wherever demonstration is possible, to be an extremely steep function of structure. We should expect this, if the influence of the alkyl groups is largely polar; for unimolecular rates depend on a polar bond-fission, which must require the more internal electrical compensation, and therefore must act the more strongly on a polarisable group, as there is no electrically countervailing, contemporaneous bond-formation.

Table I is given to illustrate the increase in the rate of bimolecular olefin elimination (*E2*) along the alkyl series primary, secondary, tertiary, in the reactions of alkyl-dimethylsulphonium ions with ethoxide ions. The second-order rate-constants,  $k(E2)$ , refer to the formation of ethylene, propylene, and isobutylene from dimethyl-ethyl-, -isopropyl-, and -*tert.*-butylsulphonium iodide, respectively, by reaction with ethyl-alcoholic sodium ethoxide. One observes that each additional methyl branch in the variable alkyl group increases the rate of bimolecular elimination by, roughly, 25-fold.

TABLE I.

*Second-order rate-constants, percentages of olefin formed, and separate rate-constants for bimolecular substitution,  $k(S_N2)$ , and elimination,  $k(E2)$ , (sec.<sup>-1</sup> g.-mol.<sup>-1</sup> l.) in the reactions of primary, secondary, and tertiary alkyl-dimethylsulphonium ions with ethoxide ions in dry ethyl alcohol at 45.08°.*

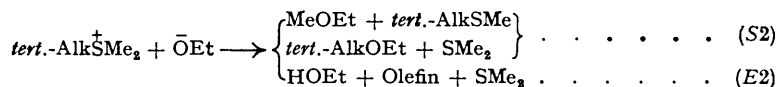
(Initially  $[AlkSM_e_2I] \sim 0.02$  and  $[NaOEt] \sim 0.095$ .)

Alk in $(AlkSM_e_2)^+I^-$	$10^5 k_2$	% Olefin.	$10^5 k(S_N2)$	$10^5 k(E2)$	Ref.
$CH_3 \cdot CH_2 \cdot$ .....	41.6	12.0	36.6	5.0	Part XII
$(CH_2)_2CH \cdot$ .....	187	61	73	114	„ XIII
$(CH_2)_3C \cdot$ .....	2930	100	> 90 *	2930	„ VIII

\* Based on an assumed maximum error in the olefin proportions of 3% for percentages in the neighbourhood of 100 (it is proportionately less for lower percentages—cf. Hughes, Ingold, Masterman, and MacNulty, *J.*, 1940, 900).

The tertiary alkylsulphonium ions which have been comparatively examined are the dimethyl-*tert.*-butylsulphonium and the dimethyl-*tert.*-amylsulphonium ions. In the first instance, they have been studied with respect to their bimolecular reactions with ethoxide ions in ethyl alcohol. In the presence of some tenths molar sodium ethoxide, these bimolecular reactions take place without sensible amounts of accompanying unimolecular processes; it can be calculated that the latter constitute a proportion of the order of 0.1% of the total reaction of the dimethyl-*tert.*-butylsulphonium ion. Thus the bimolecular reactions of these tertiary alkyl-sulphonium ions can be isolated much more clearly than can the corresponding bimolecular reactions of the tertiary alkyl bromides (cf. Part XI).

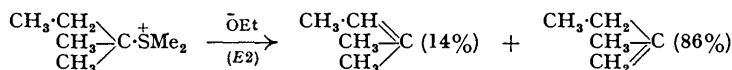
The bimolecular reactions of the tertiary alkylsulphonium salts may be formulated as follows:



There are thus two possible substitutions, but they are not accurately measurable, even together, in the presence of the much more rapid elimination. The total bimolecular rate, and the proportion of olefin formed, have, however, been measured. These data together provide the bimolecular elimination rate.

The elimination (*E2*) from the *tert.*-butylsulphonium ion is a single reaction, but the elimination from the *tert.*-amylsulphonium ion consists of two simultaneous processes; for the olefinic double bond can be formed along the longer branch, or along one of the two shorter branches of the *tert.*-amyl chain, to form trimethylethylene or 1-methyl-1-ethylethylene. It was important to determine the proportions of these products, since data for the orientation of any reaction capable of forming isomerides should be subject to the same theory as that by which the relative rates of the reaction in different compounds are interpreted. The

orientation ratio has therefore been determined by analysis of the formed amylenes, and on this basis the total bimolecular elimination rate has been split up into its components. Each of the amylenes has only a single stereoisomeric form, and hence the analysis could be simply performed by the measurement of a physical property: we used the refractive index. The results were as indicated :



These figures were obtained with the initial concentrations  $[\text{SMe}_2\text{AlkI}] \sim 0.09$  and  $[\text{NaOEt}] \sim 0.25\text{M}$ , in "97%" ethyl alcohol\* at  $24^\circ$ , *i.e.*, in conditions similar as to ionic strength, solvent, and temperature to those which relate to the rate-constants, and proportions of total olefins, listed and compared below. However, the ratio in which the isomeric amylenes are formed seems to be relatively insensitive to concentration changes within the range of those concentrations which give nearly pure bimolecular kinetics. The greatest observed variation was with  $[\text{AlkSMe}_2\text{I}] \sim 0.15$  and  $[\text{NaOEt}] \sim 2\text{M}$ , when the proportion of trimethylethylene fell to 10%. These proportions are widely different from those obtaining in the corresponding bimolecular reaction of *tert.*-amyl bromide (71% of trimethylethylene—cf. Part XI).

The principal data by means of which dimethyl-*tert.*-butyl- and *tert.*-amyl-sulphonium salts may be compared with respect to rates of their total bimolecular reactions with ethyl-alcoholic sodium ethoxide, and with respect to the proportions in which total olefins are formed in these reactions, are assembled in Table II.

TABLE II.

Second-order rate-constants ( $k_2$  in  $\text{sec.}^{-1} \text{g.-mol.}^{-1} \text{l.}$ ) and percentage of olefin formed in bimolecular reactions of tertiary alkyl-dimethylsulphonium iodides with sodium ethoxide in "97%" ethyl alcohol at  $24.0^\circ$ .

Alk in ( $\text{AlkSMe}_2\text{I}$ )	Initial concentrations.		$10^5 k_2$ .	% Olefin.
	$[\text{AlkSMe}_2\text{I}]$ .	$[\text{NaOEt}]$ .		
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 \\   \\ \text{C} \\   \\ \text{CH}_3 \end{array}$	{ 0.047	0.256	79.7	—
	{ 0.024	0.256	—	100
	{ 0.032	0.461	71.2	—
	{ 0.034	0.447	—	99
$\begin{array}{c} \text{CH}_3\text{-CH}_2 \\   \\ \text{CH}_3 \\   \\ \text{C} \\   \\ \text{CH}_3 \end{array}$	{ 0.091	0.234	58.1	—
	{ 0.085	0.233	—	96
	{ 0.091	0.430	50.9	—
	{ 0.047	0.449	—	98

The results are divisible into two sets, those applying to initial alkali concentrations  $[\text{NaOEt}] \sim 0.25\text{M}$ , and those relating to the initial concentrations  $[\text{NaOEt}] \sim 0.45\text{M}$ . The rate-constants for each compound under these two conditions of concentration show that the reactions are subject to a negative salt effect. This is to be expected: the details of the phenomenon are being independently investigated. In the meantime it makes little difference which of the two common ionic strengths we choose for the purpose of comparing the results for the *tert.*-butyl-sulphonium salt with those for the *tert.*-amyl-salt. In Table III we make the comparison for the lower initial alkali concentration. One observes that the lower bimolecular elimination rate for the *tert.*-amyl compound than for the *tert.*-butyl compound is the total result of a large fall of rate for the establishment of the double bond along the alkyl branch which becomes lengthened in the *tert.*-amyl group, and of very small decreases of rate for the formation of the double bond in the branches which remain similar in the two homologues. The whole result forms a striking contrast to that which was obtained for the corresponding bimolecular reactions of *tert.*-butyl and *tert.*-amyl bromides. It was found that in this case the bimolecular elimination from the amyl group was faster, the increase being due entirely to the increased rate of establishment of the double bond along the alkyl branch which becomes lengthened in the *tert.*-amyl group (cf. Part XI). The theory of these relations will be discussed in Part XVI.

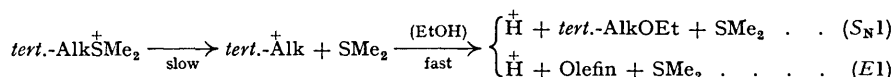
\* The alcohol-water mixture thus designated was made up to contain 2.8% by weight of water.

TABLE III.

*Analysis of kinetic data for the bimolecular reactions of tertiary alkyl-dimethylsulphonium iodides with sodium ethoxide (~0.25M) in "97%" ethyl alcohol at 24°, showing the dependence of the bimolecular elimination rate on alkyl structure.*

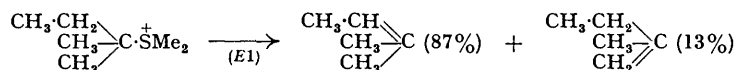
Alk in (Alk <sup>+</sup> SMe <sub>2</sub> ) <sup>-</sup> I.	10 <sup>5</sup> k <sub>2</sub> .	% Olefin.	10 <sup>5</sup> k(E2).	
			Total.	Each branch.
<i>tert.</i> -Butyl.....	79.7	100	79.7	$\left\{ \begin{array}{l} 26.6 \dots \text{CH}_3 \\ 26.6 \dots \text{CH}_3 \\ 26.6 \dots \text{CH}_3 \end{array} \right\} \text{C}.$
<i>tert.</i> -Amyl.....	58.1	96	55.8	$\left\{ \begin{array}{l} 7.8 \dots \text{CH}_3\text{-CH}_2 \\ 24.0 \dots \text{CH}_3 \\ 24.0 \dots \text{CH}_3 \end{array} \right\} \text{C}.$

When the ethoxide ion concentration falls below 0.01M, the unimolecular reactions of dimethyl-*tert.*-butyl- and -*tert.*-amyl-sulphonium ions become important. By working in very dilute alkaline, or in neutral or acidic, solution, these reactions can be isolated, the bimolecular processes being practically completely suppressed. The simultaneous reactions which now take place may be represented as follows :



Here there can be no second substitution process leading to a *tert.*-alkyl methyl sulphide, as there can be in bimolecular substitution, because the rate of the unimolecular heterolysis of the methyl group from the sulphonium ion will be altogether too small. Another contrast to the bimolecular decomposition is that the represented reactions of unimolecular substitution and elimination proceed at quite comparable rates. For both dimethyl-*tert.*-butyl- and -*tert.*-amyl-sulphonium ions we have measured the total unimolecular rates, and also the proportions of olefin formed under the conditions of the rate measurements, thus deriving the separate rates of unimolecular substitution and elimination.

Whilst unimolecular olefin elimination (E1) from the *tert.*-butylsulphonium ion is a single process, the corresponding reaction of the *tert.*-amylsulphonium ion proceeds in two directions, just as does bimolecular elimination, producing a mixture of trimethylethylene and 1-methyl-1-ethylethylene. We have determined the proportions of these isomerides with the following results :



These figures refer to nearly neutral solution in "97%" ethyl alcohol at 50°, *i.e.*, to conditions corresponding to those under which the total unimolecular rate constants and the proportions of total olefins, have been measured as recorded below. However, the ratio in which the two isomerides are produced in unimolecular elimination does not seem to be greatly affected by the conditions. For instance, in "50%" ethyl alcohol (a mixture of equal volumes of alcohol and water), and at 65.3°, conditions corresponding to some measurements of the total unimolecular rate, and of the proportion of total olefin, which are recorded in Part VII, the trimethylethylene was found to constitute 85% of the total amylenes, the difference between this figure and the above-recorded 87% being almost within the normal experimental error. It will have been noticed that the proportions in which the isomeric amylenes are produced in the unimolecular elimination stand in marked contrast to those in which they are formed in bimolecular elimination from the dimethyl-*tert.*-amylsulphonium ion (14% of trimethylethylene). On the other hand, the proportions given by the unimolecular elimination are quite similar to those obtained for the corresponding unimolecular reaction of *tert.*-amyl bromide (82% of trimethylethylene—*cf.* Part XI).

Table IV contains the observational data by means of which dimethyl-*tert.*-butyl- and -*tert.*-amyl-sulphonium ions may be compared with respect to both the rates of their total unimolecular decompositions and the proportions in which total olefins are formed in these reactions.

TABLE IV.

First-order rate-constants ( $k_1$  in  $\text{sec.}^{-1}$ ) and proportions of olefin formed in unimolecular reactions of tertiary alkyl-dimethylsulphonium iodides in "97%" ethyl alcohol at 50.0°.

Alk in $(\text{AlkSMe}_2)\text{I}$ .	Initial concn. [AlkSMe <sub>2</sub> I].	$10^5k_1$ .	% Olefin.
<i>tert.</i> -Butyl	0.034	1.78	—
	0.020	—	50.5
<i>tert.</i> -Amyl	0.034, 0.032	15.1, 14.8	—
	0.058	—	64.5

These results are analysed in Table V, which records, for the two alkylsulphonium ions, the rates of the separate unimolecular reactions of substitution and of elimination, and also the rates with which the olefinic double bond is established in these eliminations along each of the three branches of the tertiary alkyl chains. In the theory of unimolecular reactions, a simple significance attaches to the rate of the total reaction, for this is identified with the rate of the common slow stage; and also to the proportions in which the olefins are formed, since these are interpreted as giving directly the ratios of the rates of the fast stages. Therefore these figures also are given in the Table, including the proportions in which the alkyl groups accept a double bond in each of their three branches.

TABLE V.

Analysis of kinetic data for the unimolecular reactions of tertiary alkyl-dimethylsulphonium ions in "97%" ethyl alcohol at 50°, showing the dependence of unimolecular elimination on alkyl structure.

Alk in $(\text{AlkSMe}_2)$ .	$10^5k_1$ .	$10^5k(S_N1)$ .	$10^5k(E1)$ .		% Subn.	% Elimination.	
			Total.	Per branch.		Total.	Per branch.
$\begin{array}{c} \text{CH}_3 \\   \\ \text{C} \\   \\ \text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	1.78	0.88	0.90	$\begin{cases} 0.30 \\ 0.30 \\ 0.30 \end{cases}$	49.5	50.5	$\begin{cases} 16.8 \\ 16.8 \\ 16.8 \end{cases}$
$\begin{array}{c} \text{CH}_2\text{-CH}_3 \\   \\ \text{C} \\   \\ \text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	14.95	5.33	9.67	$\begin{cases} 8.41 \\ 0.63 \\ 0.63 \end{cases}$	35.5	64.5	$\begin{cases} 56.1 \\ 4.2 \\ 4.2 \end{cases}$

We may direct attention to the following relations. The rate of the total unimolecular reaction is considerably greater for *tert.*-amyl than for the *tert.*-butyl compound; and the difference is greater for the reactions of these sulphonium ions than it is for the corresponding reactions of the analogous tertiary alkyl halides (Part XI). The rate of unimolecular substitution is considerably increased, but the proportion of unimolecular substitution is decreased, in the *tert.*-amyl compound as compared with its lower homologue. The rate of unimolecular elimination is much greater for the *tert.*-amyl than for the *tert.*-butyl compound; and this is the total result of a large increase in the rate at which the olefinic double bond is established in that branch which becomes lengthened in the higher homologue, together with smaller increases in the rates at which it enters the branches that remain similar in the two compounds. The proportion of unimolecular elimination is greater for the *tert.*-amyl than for the *tert.*-butyl compound; and this is the net result of a considerable increase in the proportion in which the double bond is accepted into the lengthened chain of the amyl structure, partly counterbalanced by quite large decreases in the proportion in which it is established in the branches that remain similar in the two homologues. At almost every point, these relationships present marked contrasts to those which apply to the corresponding bimolecular reactions. On the other hand, except for the quantitative difference mentioned above, these relationships agree at every point with those which apply to the unimolecular reactions of *tert.*-butyl and *tert.*-amyl bromides (cf. Part XI). The theory of the matter will be considered in Part XVI.

## EXPERIMENTAL.

*Materials.*—Freshly decolourised and distilled *tert.*-butyl iodide or *tert.*-amyl iodide was kept for 2 days at 20° in the dark with an equivalent of dimethyl sulphide in about 2 vols. of nitromethane as

solvent. The salt which first crystallised was washed with dry ether, and purified by partial precipitation from solution in ethyl alcohol by the addition of ether. Dimethyl-*tert.*-butylsulphonium iodide gave  $I = 51.9\%$  (Calc. :  $I = 51.6\%$ ); dimethyl-*tert.*-amylsulphonium iodide gave  $I = 48.8\%$  (Calc. :  $I = 48.8\%$ ). It was not advantageous to attempt to obtain further crops of these salts from the mother liquors, since the material thus recovered contained trimethylsulphonium iodide (cf. Part XII). The benzyl iodide employed in some of the separations was crystallised from alcohol at a low temperature, and thus obtained as colourless needles, m. p.  $24^\circ$ .

*Methods for Measurement of Rates and Olefin Proportions.*—These were as described in Part XII. The extraction method was used for the determination of isobutylene, and of the combined amylenes, aqueous mercuric chloride being employed for the purpose of removing organic sulphides (cf. Part VI). For unimolecular runs in acid solution, the formed olefin was determined at various times during the course of reaction, in order to control possible error arising from the acid-catalysed combination of the olefin with the solvent (cf. Part X). For runs in alkaline solution, and hence for all bimolecular runs, it was sufficient to determine the olefin formed towards the conclusion of the reaction.

*Results of Measurements of Rates and Olefin Proportions.*—The results of the principal series of measurements are given in Table I. In illustration of the experimental basis of these figures, we give in Tables VI, VII, and VIII the record of one bimolecular rate run, one unimolecular rate run, and one olefin determination. (As to the meaning of "97%" EtOH, see footnote, p. 2086).

TABLE VI.

*Illustrating determinations of total second-order rate-constants ( $k_2$  in  $\text{sec.}^{-1} \text{ g.}^{-1} \text{ mol.}^{-1} \text{ l.}$ ): Dimethyl-*tert.*-amylsulphonium iodide (Expt. A).*

(Solvent : "97%" EtOH. Temp.  $24.0^\circ$ . Initially  $[\text{SMe}_2\text{Am}^+\text{I}] = 0.0910\text{M}$  and  $[\text{NaOEt}] = 0.234\text{M}$ . In the table  $[\text{SMe}_2\text{Am}^+\text{I}]$  and  $[\text{NaOEt}]$  are each expressed in c.c. of 0.2365N-acid per 15 c.c. sample.)

$t$ (sec.).	$[\text{NaOEt}]$ .	$[\text{SMe}_2\text{Am}^+\text{I}]$ .	$10^5 k_2$ .	$t$ (sec.).	$[\text{NaOEt}]$ .	$[\text{SMe}_2\text{Am}^+\text{I}]$ .	$10^5 k_2$ .
0	24.72	9.60	—	3582	21.19	6.07	59.5
509	24.23	9.11	56.4	4531	20.60	5.48	58.5
1143	23.30	8.18	58.9	5700	19.90	4.78	59.1
1812	22.78	7.61	56.8	9271	18.49	3.37	57.2
2403	22.13	7.01	59.4	12909	17.51	2.39	56.8

(Mean  $k_2 = 58.1 \times 10^{-5} \text{ sec.}^{-1} \text{ g.}^{-1} \text{ mol.}^{-1} \text{ l.}$ )

TABLE VII.

*Illustrating determinations of total first-order rate-constants ( $k_1$  in  $\text{sec.}^{-1}$ ): Dimethyl-*tert.*-amylsulphonium iodide (Expt. A).*

(Solvent : "97%" EtOH. Temp.  $50.0^\circ$ . Initially  $[\text{SMe}_2\text{Am}^+\text{I}] = 0.0340\text{M}$ . Solution initially neutral. Developed acid expressed in c.c. of 0.01655N-alkali per 10 c.c. sample.)

$t$ (sec.).	Acid.	$10^5 k_1$ .	$t$ (sec.).	Acid.	$10^5 k_1$ .	$t$ (sec.).	Acid.	$10^5 k_1$ .
0	0.78	—	1926	6.07	15.5	6776	13.97	15.1
294	1.68	14.2	2614	7.52	15.8	8124	15.19	14.9
580	2.51	15.2	3802	10.63	17.1	9521	16.28	14.7
855	3.33	15.5	5811	12.45	14.4	$\infty$	21.35	—

(Mean  $k_1 = 15.1 \times 10^{-5} \text{ sec.}^{-1}$ .)

TABLE VIII.

*Illustrating determinations of proportion of olefins formed : Total amylenes formed in unimolecular decomposition of dimethyl-*tert.*-amylsulphonium iodide.*

(Solvent : "97%" EtOH. Temp.  $50.0^\circ$ . Initially  $[\text{SMe}_2\text{Am}^+\text{I}] = 0.0582\text{M}$ . Preliminary experiments had shown that after 30 minutes in these conditions a quantity of olefin convenient for measurement had been formed, but that it had not yet reacted to an appreciable extent with the solvent. Estimations of acid and olefin were therefore made at the time-zero and 30 minutes later. Samples of 15 c.c. were titrated with alkali, and, after addition of a standard quantity of bromine, with thiosulphate. The alkali and thiosulphate were standardised with reference to the same solution of potassium bi-iodate,  $\text{KHI}_2\text{O}_6$ ; 25 c.c. of this required 4.97 c.c. of alkali, whilst 10 c.c. required 43.34 of the thiosulphate.)

Initial readings.		Readings after 30 mins.	
Alkali.	Thiosulphate.	Alkali.	Thiosulphate.
0.09	32.16	12.99, 12.93	2.30, 1.91
0.10	32.26	13.13	1.71

(Acid produced = 12.92 c.c. alkali. Olefin formed = 30.24 c.c. thiosulphate. Proportion of olefin = 64.5%.)

*Experiments on the Isolation of Amylene Mixtures.*—The first attempts to separate in a perfectly pure condition the amylenes formed from dimethyl-*tert.*-amylsulphonium salts, without disturbance

to the proportions of the isomerides, involved extracting the amylenes with tetrachloroethylene, after the addition of water to the alcoholic solution, and then removing the accompanying sulphides by extraction with aqueous mercuric chloride. This method failed, because it was found difficult to filter so great a bulk of the mercury compound without losses of, and therefore alterations to the composition of, the amylenes. The modification was therefore introduced of combining the sulphides with benzyl iodide, removing the easily filtered sulphonium salt, and then eliminating the last traces of sulphides by the use of mercuric chlorides. The combination of benzyl iodide with the sulphides in the tetrachloroethylene solution was found to be considerably accelerated by the addition of some nitromethane. The experiment described below (Control No. 7) is one of several by which the reliability of this method was established.

Trimethylethylene has  $n_D^{20}$  1.38774, and 1-methyl-1-ethylethylene has  $n_D^{20}$  1.37774 (cf. Part XI). A mixture, 10 c.c., having  $n_D^{20}$  1.38242, was added to 16 g. of dimethyl sulphide, 200 c.c. of ethyl alcohol, and 200 c.c. of water. The mixture was extracted with three 30 c.c. portions of tetrachloroethylene, and the combined extracts were mixed with 10 c.c. of nitromethane and 62 g. of benzyl iodide. The mixture was kept at 13° in the dark for 17 hours, and then filtered with the help of a pump, a liquid-air trap being used as a precaution against loss of the olefin. The salt on the filter was washed with a little pre-cooled tetrachloroethylene, and the combined filtrates were kept with 10 g. of mercuric chloride at -10° overnight. Some calcium chloride was then added, and the mixture was kept at the same temperature for a further day, and then filtered through glass-wool. The filtrate was distilled, with a fairly high reflux ratio, through a well-lagged, 30 cm. column of Vigreux type, having only a small hold-up. The distillate up to 40° was collected. It had  $n_D^{20}$  1.38231, and this figure was exactly repeated after the sample had been refluxed with, and distilled from, sodium-potassium alloy.

*Analysis of Amylenes from the Bimolecular Reaction of Dimethyl-tert.-amylsulphonium Ethoxide.*—The results have already been given, and the following details of one experiment are added as a description of method. A solution, 1.5 l., in "97%" ethyl alcohol, 0.090M with respect to dimethyl-tert.-amylsulphonium iodide and 0.250N with respect to sodium ethoxide, was kept at 24° for 4 hours. It was then cooled to 0°, mixed with an equal quantity of water at 0°, and extracted with tetrachloroethylene, this procedure, and the subsequent treatment of the extract with nitromethane and benzyl iodide, and later with mercuric chloride and with calcium chloride, following exactly the lines of the control experiment already described. The distillate from the Vigreux column had  $n_D^{20}$  1.37912. It was boiled under reflux for 30 minutes with sodium-potassium alloy, and again distilled. It then had  $n_D^{20}$  1.37913, which corresponds to the composition, 14% trimethylethylene, 86% 1-methyl-1-ethylethylene.

*Analysis of Amylenes from the Unimolecular Reaction of Dimethyl-tert.-amylsulphonium Iodide.*—The following description illustrates the method used in these experiments. A solution, 1.5 l., in "97%" ethyl alcohol, 0.255M with respect to dimethyl-tert.-amylsulphonium iodide, was coloured with cresol-red and heated at 50° for 7 hours in a flask fitted with a mercury-sealed stirrer, a reflux condenser, and a dropping funnel. A liquid-air trap was placed above the reflux condenser as a precaution against loss of olefin. A solution, about 1N with respect to sodium ethoxide, in "97%" ethyl alcohol was run into the rapidly stirred solution of the sulphonium salt at such a rate as to maintain it either neutral or very faintly acid. At the end of the period mentioned the solution was cooled to 0°, and the amylenes were isolated as in the preceding example. The final product had  $n_D^{20}$  1.38546, which corresponds to the composition 87% trimethylethylene, 13% 1-methyl-1-ethylethylene.

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