## **372.** *Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XXI. Dynamics of the Elimination of the* tert.*-Butyl Group from Sulphonium Compounds.*

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In Part XVI (this vol., p. 526) the known facts concerning the reaction (B), which is exemplified by the formation of alcohols from quaternary ammonium hydroxides

$$\{\mathrm{R{\cdot}\overset{\oplus}{N}R'R''R'''}\}\overset{\ominus}{\mathrm{X}} \longrightarrow \mathrm{RX} + \mathrm{NR'R''R'''} \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \quad \mathrm{(B)}$$

were interpreted by the assumption of two complementary mechanisms. In the first of these, designated (B1), two stages were distinguished: it was assumed that the cation suffers fission without the intervention of the anion, which only subsequently combines with the ejected radical:

$$\left.\begin{array}{l} \mathrm{R\overset{\curvearrowright}{—}NR'R''R'''} \longrightarrow \overset{\oplus}{\mathrm{R}} + \mathrm{NR'R''R'''} \\ \quad\; \overset{\oplus}{\mathrm{R}} + \overset{\ominus}{\mathrm{X}} \longrightarrow \mathrm{RX} \end{array}\right\} \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \quad \mathrm{(B1)}$$

The equations represent a reaction which is of the first order with respect to the cation, of zero order with respect to the anion, and therefore of first order with respect to the ammonium compound. In the second mechanism, designated (B2), the intervention of the anion was assumed to be necessary for the disruption of the cation, the process taking place in a single stage as follows:

$$\{\mathrm{R'R''R'''\overset{\oplus}{N}\overset{\curvearrowright}{—}R}\}\overset{\curvearrowleft\ominus}{\mathrm{X}} \longrightarrow \mathrm{R'R''R'''N} + \mathrm{RX} \quad . \;\; . \;\; . \;\; . \;\; . \quad \mathrm{(B2)}$$

This mechanism requires that the reaction should be of the first order with respect to each ion, and therefore bimolecular with respect to the ammonium compound. Which of these two mechanisms operates in a given case was assumed to depend jointly on the cationic stability of the ejected radical and on the nucleophilic activity of the anion.

Amongst the facts concerning reaction (B) which were discussed on this basis was the circumstance that methyl and *tert.*-butyl alcohols are readily eliminated from quaternary ammonium hydroxides, whilst primary and secondary alcohols are not, the property of facile elimination in the form of alcohol evidently passing through a minimum in the series $CH_3$, $AlkCH_2$, $Alk_2CH$, $Alk_3C$. The interpretation suggested was that, from left to right in the series considered, the inductive effect ($+ I$) of the alkyl components produces a progressive increase in electron density at the point of attachment of the whole group. As the electron density is lowest in the methyl group, this group has the smallest cationic stability and the greatest affinity for an attacking anion: it undergoes elimination by mechanism (B2). The first effect of introducing alkyl components in place of hydrogen, and thus increasing the electron density at the point of attachment of the whole group, is to suppress mechanism (B2); and the known facts show that even a single alkyl group is highly effective for this purpose. Mechanism (B1), however, must be facilitated by alkyl substitution, so that the successive introduction of alkyl components must cause reactivity by this alternative mechanism to rise to an appreciable value at some stage during the substitution; and once this mechanism has taken control further alkyl substitution must enhance reactivity.

It will be evident that, in view of the distinctive dynamical requirements of mechanisms (B1) and (B2), the explanation advanced in order to account for the minimum property of the alkyl series implies that, whilst the elimination of methyl alcohol should be a bimolecular reaction, that of *tert.*-butyl alcohol should exhibit unimolecular dynamics. At the time at which the interpretation was advanced there was evidence that the elimination of methyl alcohol from quaternary ammonium hydroxides was of the second order; but nothing was known concerning the dynamics of the other elimination.

The above argument refers explicitly to ammonium compounds, but is obviously applicable without modification to the decompositions of sulphonium compounds also. From a practical viewpoint, it is more convenient to employ the latter for the purpose of dynamical investigations, and, as some unpublished experiments carried out in association with Mr. J. L. Gleave had confirmed for the sulphonium series the bimolecular character of the elimination of methyl alcohol, it was decided to test the predicted unimolecular elimination of the *tert.*-butyl group in reaction (B) by means of experiments on dimethyl-*tert.*-butylsulphonium hydroxide and its salts.

The sulphonium hydroxide was found to decompose in two directions, (A) and (B), reaction (B), the centre of interest at present, predominating in aqueous solutions :

$$\{(CH_3)_3C{\cdot}SMe_2\}{\cdot}OH' \begin{array}{l} \nearrow (CH_3)_2C{:}CH_2 + SMe_2 + H_2O \quad . \; . \; . \quad (A) \\ \searrow (CH_3)_3C{\cdot}OH + SMe_2 \; . \; . \; . \; . \; . \; . \quad (B) \end{array}$$

There was no third simultaneous reaction.

The first evidence concerning the dynamics of reaction (B) was obtained in a series of experiments in which the hydroxide, in various initial concentrations, was allowed to decompose completely at constant volume, and the proportion in which reaction had pursued the two alternative paths was determined by measurements of the quantities of olefin produced. The results are contained (Expts. 1—6) in Table I, the first five cols. of which are self-explanatory. Col. 6 records the bromine equivalent of the olefin formed, in c.c. of 0·1*N*-thiosulphate, and col. 7 indicates the theoretical yield of olefin in the same units. The figures in col. 8, *i.e.*, the percentage in which decomposition occurs according to the reaction yielding the olefin, are obtained from the data of cols. 6 and 7.

TABLE I.

*Directions of Decomposition of Dimethyl*-tert.*-butylsulphonium Hydroxide and its Salts.*

| Expt. No. | Anion. | Initial concn. (*M*). | Solvent. | Vol. of soln. (c.c.). | Olefin, found. | Olefin, max. | $\frac{100\,A}{A + B}$. |
|---|---|---|---|---|---|---|---|
| 1 | OH′ | 0·966 | $H_2O$ | 10 | 72·05 | 193·2 | 37·3 |
| 2 | ,, | 0·720 | ,, | 10 | 44·20 | 144·0 | 30·7 |
| 3 | ,, | 0·483 | ,, | 15 | 32·60 | 144·9 | 22·5 |
| 4 | ,, | 0·362 | ,, | 15 | 20·85 | 108·6 | 19·2 |
| 5 | ,, | 0·241 | ,, | 20 | 14·25 | 96·4 | 14·8 |
| 6 | ,, | 0·120 | ,, | 40 | 9·10 | 96·0 | 9·5 |
| *7 | ,, | 0·120 | ,, | 40 | 20·65 | 96·0 | 21·5 |
| 8 | ,, | 0·240 | 75% EtOH | 20 | 80·00 | 96·0 | 83·3 |
| 9 | $CO_3''$ | 0·450 | $H_2O$ | 10 | 7·90 | 90·0 | 8·8 |
| 10 | I′ | 0·400 | ,, | 10 | 2·30 | 80·0 | 2·9 |
| 11 | ,, | 0·400 | 80% EtOH | 10 | 15·60 | 80·0 | 19·5 |
| 12 | ,, | 0·40 *ca.* | EtOH | 10 | 18·75 | 81·4 | 23·0 |

* Sodium hydroxide equivalent to 0·170*M* added.

These results are inter-related in precisely the way which is required by the hypothesis that reaction (A) is bimolecular, whereas reaction (B) is unimolecular. If $k_1$ is the coefficient of a unimolecular decomposition and $k_2$ that of a simultaneous bimolecular reaction of the same original substance, then, assuming that there is not a third reaction, it can be calculated * that the fraction $f_1$ of material undergoing change by the unimole-

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* If $x$ and $y$ are concentrations representing the progress of reaction by routes (A) and (B) respectively, the following differential equations may be set up :

$$(dx/dt) = k_2(a - x - y)^2; \quad (dy/dt) = k_1\,(a - x - y)$$

These equations require to be solved simultaneously with elimination of the independent variable, $t$. After the initial conditions, $x = 0$ and $y = 0$ when $t = 0$, have been used in order to evaluate the constant of integration, the result can be expressed in the form

$$y = K \log_e [(K + a)/(K + a - x - y)]$$

This relation is true at *all* times during the progress of the reaction, but, when $t = t_\infty$, $x + y = a$, and the equation then reduces to that given in the text.

cular route is given by $f_1 = (2{\cdot}3K/a) . \log_{10}(1 + a/K)$, where $K$ is written for $k_1/k_2$, and $a$ stands for the initial concentration. Table II illustrates the application of this formula, $K$ being given the value 0·70.

TABLE II.

*Reaction Orders in Decomposition of Dimethyl-*tert.*-butylsulphonium Hydroxide.*

| Expt. No. | $a$. | $f_1$ (calc.). | $f_1$ (found). | Expt. No. | $a$. | $f_1$ (calc.). | $f_1$ (found). |
|---|---|---|---|---|---|---|---|
| 1 | 0·966 | 0·628 | 0·627 | 4 | 0·362 | 0·805 | 0·808 |
| 2 | 0·720 | 0·687 | 0·693 | 5 | 0·241 | 0·858 | 0·852 |
| 3 | 0·483 | 0·760 | 0·775 | 6 | 0·120 | 0·922 | 0·905 |

Table I contains some additional evidence which supports our view that reaction (A) is of the first order with respect to each ion, and therefore bimolecular as a whole,* whilst reaction (B) is unimolecular, depending on the cation only. A comparison of the results of Expts. 6 and 7 shows that extraneous hydroxide ions produce a relative increase in the rate of reaction (A). Expts. 9 and 10 relate to the decomposition of the sulphonium carbonate and *iodide* respectively, and a comparison of the proportions of olefin formed with those obtained for the hydroxide under comparable conditions of concentration (Expts. 3 and 4) shows that reaction (A) is suppressed relatively to reaction (B) when the strongly basic hydroxide ion is replaced by the less basic carbonate ion or the much less basic iodide ion. These relationships are evidently to be expected from our hypothesis concerning the dynamics of these reactions. The remaining experiments (Nos. 8, 11, and 12) are concerned with the effect of replacing water by ethyl alcohol as solvent, a matter to which further reference is made below.

If the hypothesis be accepted by which the above results have been interpreted, it follows from Expts. 5 and 6 that the decomposition should pursue a unimolecular course to the extent of about 90% under conditions convenient for the direct observation of the kinetics of the change. We therefore traced the velocity–time relation experimentally, and, as the data in Table III show, the course of the decomposition can be represented by the unimolecular equation, $k_1 = (2{\cdot}3/t)\log_{10}\{a/(a - x)\}$, to the degree of accuracy expected. It will be observed that the downward drift of the " constant " is smaller in Expt. 14 than in Expt. 13; that is because in Expt. 14 the initial concentration is smaller, and therefore the proportion of reaction (A) is relatively less (compare Tables I and II). In Expt. 15 the downward drift is hardly perceptible; the reason for that is that in this experiment extraneous sodium hydroxide was added, the effect of which is to buffer the hydroxide-ion concentration throughout the change, and thus to render the dynamics of the bimolecular side reaction more closely similar to those of a unimolecular change. Actually, in all three cases the downward drift of the unimolecular constant is somewhat smaller than would have been anticipated from the amount of the accompanying bimolecular reaction calculated in accordance with the data given in Tables I and II; but this is because the reactions are subject to a correction for activity which, if applied, would tend to produce a small upward drift in the constant. Apart from such minor variations, it is seen that the unimolecular constant adequately describes the results, and is independent of the initial concentration and of any extraneous hydroxide ions. Of the three experiments recorded in Table III, No. 14 must be least affected by the bimolecular side-reaction, and so the true value of the unimolecular constant may best be estimated by observing the limit to which the calculated constant tends in this experiment at great dilution. For the temperature employed, 100°, the velocity coefficient of reaction (B) may be taken as about 0·36 min.$^{-1}$.

If the dynamics of reaction (B) have really no concern with the anion, it follows that not only the sulphonium hydroxide but also its salts should exhibit a unimolecular reaction, and, furthermore, that in aqueous solution at the same temperature the hydroxide

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* There is one previous observation of the bimolecular character of the olefinic decomposition of sulphonium hydroxides [reaction (A)]. Masson (J., 1886, **49**, 233) showed that dithian methohydroxide, $\{S(CH_2{\cdot}CH_2)_2SMe\}^{\cdot}OH'$, decomposed to give a neutral oil which Mansfeld (*Ber.*, 1886, **19**, 696, 2658) and V. Meyer (*ibid.*, p. 3262) showed to be the dehydration product, $MeS{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH{:}CH_2$. Green and Sutherland (J., 1911, **99**, 1174) proved that the reaction followed a bimolecular course.

### TABLE III.

*Dynamics of Decomposition of Dimethyl*-tert.*-butylsulphonium Hydroxide in Water at* 100°.

| Expt. 13 ($a = 0·207$). | | | Expt. 14 ($a = 0·117$). | | | Expt. 15 ($a = 0·0565$; [NaOH] $= 0·1175$). | | |
|---|---|---|---|---|---|---|---|---|
| $t$ (mins.). | $a - x$. | $k_1$. | $t$ (mins.). | $a - x$. | $k_1$. | $t$ (mins.). | $a - x$. | $k_1$. |
| 0·5 | 0·1695 | 0·399 | 0·5 | 0·0965 | 0·385 | 0·5 | 0·0465 | 0·389 |
| 1·0 | 0·1410 | 0·384 | 1·0 | 0·0800 | 0·380 | 1·0 | 0·0385 | 0·383 |
| 1·5 | 0·1155 | 0·389 | 1·5 | 0·0665 | 0·376 | 1·5 | 0·0320 | 0·379 |
| 2·0 | 0·0965 | 0·381 | 2·0 | 0·0555 | 0·373 | 2·0 | 0·0260 | 0·387 |
| 2·5 | 0·0805 | 0·378 | 2·5 | 0·0450 | 0·382 | 3·0 | 0·0180 | 0·381 |
| 3·0 | 0·0670 | 0·376 | 3·0 | 0·0380 | 0·374 | 4·0 | 0·0130 | 0·367 |
| 4·0 | 0·0450 | 0·381 | 4·0 | 0·0270 | 0·366 | 5·0 | 0·0085 | 0·379 |
| 5·0 | 0·0315 | 0·376 | 5·0 | 0·0185 | 0·369 | 6·0 | 0·0055 | 0·388 |
| 6·0 | 0·0225 | 0·369 | 6·0 | 0·0125 | 0·372 | | | |
| 7·0 | 0·0150 | 0·375 | 7·0 | 0·0090 | 0·366 | | | |
| 8·0 | 0·0105 | 0·372 | | | | | | |

and all its salts should decompose at the same speed. We have therefore studied the dynamics of the decomposition of the sulphonium carbonate and iodide in aqueous solution at 100°, and the results are in Table IV. Owing to the smaller amount of side reaction (A) accompanying these decompositions (see Table I) the unimolecular coefficients show a more accurate constancy than was observed in the experiments with the hydroxide. Their values are 0·33 min.$^{-1}$ for the carbonate, and 0·34 min.$^{-1}$ for the iodide, which, in view of the neglect of activity corrections, are in satisfactory agreement with each other and with the value 0·36 min.$^{-1}$ obtained for the hydroxide.

### TABLE IV.

*Dynamics of Decomposition of Dimethyl*-tert.*-butylsulphonium Salts in Water at* 100°.

| (Expt. 16.) Carbonate ($a = 0·342$). | | | | | | (Expt. 17.) Iodide ($a = 0·268$). | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $t$ (mins.). | $a - x$. | $k_1$. | $t$ (mins.). | $a - x$. | $k_1$. | $t$ (mins.). | $a - x$. | $k_1$. | $t$ (mins.). | $a - x$. | $k_1$. |
| 1 | 0·245 | 0·334 | 5 | 0·067 | 0·326 | 1 | 0·192 | 0·333 | 5 | 0·047 | 0·348 |
| 2 | 0·180 | 0·321 | 6 | 0·045 | 0·338 | 2 | 0·135 | 0·342 | 7 | 0·024 | 0·344 |
| 3 | 0·129 | 0·325 | 8 | 0·024 | 0·332 | 3 | 0·095 | 0·345 | 9 | 0·012 | 0·345 |
| 4 | 0·094 | 0·323 | | | | 4 | 0·070 | 0·335 | | | |

The above results are considered to establish the truth of our prediction (*loc. cit.*) that, although the elimination of the methyl group by reaction (B) is bimolecular, the elimination of the *tert.*-butyl group by the same reaction would be found to be unimolecular.*

Reference may be made, in conclusion, to the remarkable effect of replacing water by ethyl alcohol in these decompositions. As the results in Table V show, one effect is to cause a great increase in the speed of both decompositions. This result is normal; for an electrovalent compound is giving rise to covalent compounds, and the reactions should therefore be favoured by a medium of low cohesion (Richardson and Soper, J., 1929, 1873). The other main effect is to cause a selective facilitation of reaction (A). This is shown clearly by the results of Expts. 8, 11, and 12 in Table I, and by the strong downward drift of the unimolecular velocity coefficients in Table V. In the case of the decomposition of the hydroxide, it might be supposed that in alcoholic solutions ethoxide ions intervene to the assistance of reaction (A), but this explanation will not embrace the reaction of the iodide, and it therefore seems clear that a true solvent influence operates selectively on the simultaneous reactions. The direction of the selectivity also has a

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* Reference to the same paper (*loc. cit.*, p. 530) will make it clear that the same difference of dynamics was expected to apply to the production of primary alcohols and of *tert.*-butyl alcohol in the alkaline hydrolysis of alkyl halides. It is known (Grant and Hinshelwood, this vol., p. 258) that the formation of primary alcohols in this reaction is bimolecular. Experiments by one of us (E. D. H.) have now shown that the formation of *tert.*-butyl alcohol by the hydrolysis of the chloride is a unimolecular process the results will be published in conjunction with other investigations now in progress on the hydrolysis and alcoholysis of alkyl halides.

natural explanation; for reaction (A), which involves an encounter between two oppositely charged ions, must inevitably be more sensitive to the cohesion (dipole moment, dielectric constant) of the solvent than reaction (B), which involves only a single ion together with the neutral solvent.

TABLE V.

*Effect of Medium on Speed of Decomposition of Dimethyl*-tert.*-butylsulphonium Hydroxide at* 100°.

| (Expt. 18.) 40% EtOH ($a$ = 0·0460). | | | (Expt. 19.) 70% EtOH ($a$ = 0·1935). | | | (Expt. 20.) 80% EtOH ($a$ = 0·0485). | | |
|---|---|---|---|---|---|---|---|---|
| $t$ (mins.). | $a - x$. | $k_1$. | $t$ (mins.). | $a - x$. | $k_1$. | $t$ (mins.). | $a - x$. | $k_1$. |
| 0·5 | 0·0350 | 0·546 | 0·25 | 0·0785 | 3·60 | 0·25 | 0·0132 | 5·20 |
| 1·0 | 0·0280 | 0·496 | 0·50 | 0·0375 | 3·28 | 0·50 | 0·0045 | 4·75 |
| 1·5 | 0·0215 | 0·507 | 0·75 | 0·0230 | 2·84 | 0·75 | 0·0018 | 4·39 |
| 2·0 | 0·0170 | 0·497 | 1·00 | 0·0140 | 2·62 | | | |
| 3·0 | 0·0100 | 0·508 | 1·25 | 0·0065 | 2·71 | | | |
| | | | 1·50 | 0·0030 | 2·77 | | | |

(Expt. 21.) In 90% EtOH the value of $a - x$ fell to zero in 0·25 min.

## EXPERIMENTAL.

*Dimethyl*-tert.*-butylsulphonium Iodide*.—*tert.*-Butyl iodide (1 mol.), prepared from *tert.*-butyl alcohol and hydriodic acid (Norris, *Amer. Chem. J.*, 1907, **38**, 641), and freshly distilled under reduced pressure, was mixed with dimethyl sulphide (1 mol.) in nitromethane. The crystals which had separated after 3 days at room temperature were collected and shown to consist of pure *dimethyl*-tert.*-butylsulphonium iodide* (decomposes and disappears at 160°) (Found, after crystallisation from alcohol: C, 29·3; H, 6·2; I, 51·5; S, 13·1. $C_6H_{15}IS$ requires C, 29·3; H, 6·1; I, 51·6; S, 13·0%).

The salt subsequently deposited was contaminated with trimethylsulphonium iodide, and in the later stages of reaction this substance only was precipitated. It was identified by analysis after crystallisation from dilute alcohol (Found: C, 17·6; H, 4·6; I, 62·4; S, 15·7. Calc.: C, 17·6; H, 4·4; I, 62·3; S, 15·7%). *Dimethyl*-tert.*-butylsulphonium picrate*, prepared from the iodide and sodium picrate, separated from alcohol in large needles, decomp. 132° (Found: C, 41·7; H, 5·0; N, 12·0; S, 9·3. $C_{12}H_{17}O_7N_3S$ requires C, 41·5; H, 4·9; N, 12·1; S, 9·2%).

*Products of the Decomposition of Dimethyl*-tert.*-butylsulphonium Hydroxide*.—The hydroxide solution, prepared from the iodide by means of carbonate-free silver oxide, was standardised by titration in the cold with phenolphthalein as indicator, and was heated in a flask connected to a condenser, a receiver, and a succession of wash vessels, three containing saturated aqueous mercuric chloride and two containing bromine. Decomposition occurred rapidly below the b. p. of the solution, which was partly distilled, the receiver being kept above the b. p. of dimethyl sulphide. At the conclusion of the distillation, the products were swept through the apparatus by means of a current of air, and the distillate was shown to consist of aqueous *tert.*-butyl alcohol by conversion into *tert.*-butyl chloride by saturation with hydrogen chloride. The chloride, which separated as an oil, was washed with water and sodium hydrogen carbonate, dried with calcium chloride, and identified by its b. p., 51°, and by analysis (Found: C, 51·8; H, 9·7; Cl, 37·7. Calc.: C, 51·9; H, 9·7; Cl, 38·4%). Tests with mercuric chloride showed that the *tert.*-butyl-alcoholic distillate contained no sulphides, which had passed completely into the mercuric chloride traps. Analysis of the unpurified precipitate obtained from these traps showed the sulphide to consist substantially wholly of dimethyl sulphide [Found: C, 5·2; H, 1·3; Cl, 22·2; S, 6·9. Calc. for $2(CH_3)_2S,3HgCl_2$: C, 5·1; H, 1·3; Cl, 22·7; S, 6·8%], and the yield was 93% of that calculated on this basis. The contents of the bromine traps were decolorised with sulphur dioxide and the olefin bromide was extracted with light petroleum, washed, and distilled. The main fraction, b. p. 148—150°, was identified as *iso*butylene dibromide (Found: Br, 73·3. Calc.: Br, 74·1%), the small less volatile fraction containing a bromine substitution product of this.

*Proportion of Olefin formed by Decomposition of Dimethyl*-tert.*-butylsulphonium Hydroxide and its Salts. Effects of Concentration, of the Addition of a Common Anion, and of the Nature of the Anion and the Solvent*.—Solutions of the sulphonium compounds of known concentration were heated at constant volume until decomposition was complete, and the volatile products were swept in a current of air through the train of wash-flasks previously described. The flasks which had previously contained bromine were in the present experiments charged with an accurately measured volume of a standard solution of bromine in chloroform. The whole of the sulphide was found to be retained in the first two of the three mercuric chloride traps, and the quantity of bromine destroyed by the olefin was estimated iodometrically. The results are recorded in Table I.

*Dynamics of the Decomposition of Dimethyl-*tert.*-butylsulphonium Hydroxide, Carbonate, and Iodide in Aqueous Solution at* 100°.—Several measured portions (5·00 c.c.) of standardised solutions of the hydroxide, carbonate, or iodide were separately enclosed in glass tubes, plunged into boiling water, shaken vigorously to facilitate the attainment of thermal equilibrium and, after known time intervals, were withdrawn, quickly cooled, and titrated. In the case of the hydroxide the residual alkali was titrated with 0·05*N*-hydrochloric acid using phenolphthalein as indicator. In the experiments with the carbonate the solutions were titrated with 0·1*N*-hydrochloric acid in the presence of Sofnol No. 1 as indicator, the carbon dioxide being expelled with carbon dioxide-free air. The reaction of the iodide was followed by taking advantage of the circumstance that *tert.*-butyl iodide is decomposed by hot water, yielding the stoicheiometric quantity of hydriodic acid, which was titrated with 0·1*N*-sodium hydroxide. For the purposes of calculation, the concentration of sulphonium compound present one minute after introduction into the boiling water-bath was taken as the initial concentration, and the corresponding time as the initial time. The results are in Tables III and IV.

*Effect of Replacing Water by Ethyl Alcohol as Solvent on the Speed of Decomposition of Dimethyl-*tert.*-butylsulphonium Hydroxide at* 100°.—The method was the same as that described in the previous paragraph except that in the experiment with 40% aqueous alcohol the observation made 0·5 min. after the introduction of the tube into the boiling water-bath, and that in the experiments with 70% and 80% alcohol the observations at 0·25 min. after the introduction of the tubes were treated as the initial observations. The results are in Table V.

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