137. *Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XVIII. Thermal Decomposition of Sulphonium Hydroxides.*

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THE thermal decomposition of trimethylsulphonium hydroxide has been examined by Crum Brown and Blaikie (*J. pr. Chem.*, 1881, **23**, 395), who observed the elimination of methyl alcohol, and that of triethylsulphonium hydroxide by Alvisi (*Z. angew. Chem.*, 1897, **14**, 302), who reported the elimination of ethylene. The only previous record of simultaneous decomposition in two directions is due to von Braun, Teuffert, and Weissbach (*Annalen*, 1929, **472**, 121), who observed the formation of both decylene and methyl alcohol from dimethyl-*n*-decylsulphonium hydroxide.

A study of the decomposition of five sulphonium hydroxides of the form $\{AlkSMe_2\}^{\bullet}OH'$ has shown that the reaction in general pursues routes similar to those established for ammonium hydroxides :

$$\{R\cdot CH_2\cdot CH_2\cdot SMe_2\}^{\bullet}OH' \begin{cases} \rightarrow R\cdot CH{:}CH_2 + SMe_2 + H_2O & \quad . \quad . \quad . \quad (A) \\ \rightarrow R\cdot CH_2\cdot CH_2\cdot SMe + MeOH & \quad . \quad . \quad . \quad (B) \end{cases}$$

A notable distinction between the decompositions of the two types of compound consists in the more facile character of the mode of fission represented by reaction (B) in the case of the sulphonium hydroxides. This follows from the much smaller proportions of olefins obtained from the sulphonium compounds (see Table I), coupled with the perceptibly lower temperature of decomposition of these substances.

These differences apart, the variation in the proportions of reactions (A) and (B) as between one example and another in the sulphonium series is so closely parallel to the corresponding variation observed in the ammonium series (see Table I) that it appears a warrantable conclusion that similar mechanisms apply; thus we justify the assumption

TABLE I.

No.	Alk.	Proportions of olefin (mols. %). $\{AlkSMe_2\}\cdot OH'$ (this paper).	$\{AlkNMe_3\}\cdot OH'$ (Parts I and II*).
1	$CH_3\cdot CH_2\cdot$	27	95
2	$CH_3 \longrightarrow CH_2\cdot CH_2\cdot$	7·7	84
3	$CH_3 \longrightarrow CH_2 \longrightarrow CH_2\cdot CH_2\cdot$	3·8	79
4	$\begin{matrix}CH_3\searrow & \\ & CH\cdot CH_2\cdot \\ CH_3\nearrow & \end{matrix}$	1·5	63
5	$\begin{matrix}CH_3\searrow & \\ & CH\cdot \\ CH_3\nearrow & \end{matrix}$	63	*ca.* 100

* Part I, *loc. cit.*; Part II, Ingold and Vass, J., 1928, 3125.

that the mechanistic theory of Part I (Hanhart and Ingold, J., 1927, 997) as extended in Part XVI (Hughes, Ingold, and Patel, this vol., p. 526) applies without essential change in the sulphonium series also.

A further analogy with the ammonium series emerged from the study of three sulphonium hydroxides of a form, $\{AlkSMeEt\}\cdot OH'$, which permits the elimination of alternative olefins:

$$\begin{array}{llr} & \nearrow R\cdot CH{:}CH_2 + SMeEt + H_2O \quad . \quad . \quad . \quad . & (A') \\ \{R\cdot CH_2\cdot CH_2\cdot SMeEt\}\cdot OH' & \longrightarrow R\cdot CH_2\cdot CH_2\cdot SEt + MeOH \quad . \quad . \quad . \quad . & (B) \\ & \searrow R\cdot CH_2\cdot CH_2\cdot SMe + CH_2{:}CH_2 + H_2O \quad . \quad . & (A'') \end{array}$$

The results (see Table II, upper portion) indicate that the rule of the preferential elimination of ethylene is obeyed (Nos. 6 and 7) or disobeyed (No. 8) according to just the same principles as those which apply to ammonium hydroxides, and there can be no reasonable doubt that the explanation of these phenomena advanced in Part I (*loc. cit.*) in relation to ammonium hydroxides applies in the examples now considered.

Confirmation is derived from the study (Table II, lower portion) of a further group of two sulphonium hydroxides of the form $\{AlkSMePr^{\beta}\}\cdot OH'$. This type also permits the elimination of alternative olefins, and the examples studied decomposed in three directions corresponding to equations (A'), (B), and (A''), with Pr^{β} written for Et and $CHMe{:}CH_2$ for $CH_2{:}CH_2$. One example (No. 9) illustrates expected violation of the ethylene rule, and in both cases the data are in complete conformity with the theoretical principles referred to in the preceding paragraph.

TABLE II.

No.	Alk in $\{AlkSMeEt\}\cdot OH'$.	Composition (mols. %) of olefin mixture. (A') $R\cdot CH{:}CH_2$.	(A'') $CH_2{:}CH_2$.
6	$CH_3\cdot CH_2\cdot CH_2\cdot$	20	80
7	$(CH_3)_2CH\cdot CH_2\cdot$	7	93
8	$C_6H_5\cdot CH_2\cdot CH_2\cdot$	97	3
	in $\{AlkSMePr^{\beta}\}\cdot OH'$.	(A') $R\cdot CH{:}CH_2$.	(A'') $CHMe{:}CH_2$.
9	$CH_3\cdot CH_2\cdot$	25	75
10	$(CH_3)_2CH\cdot CH_2\cdot$	6	94

One of the most difficult theoretical questions raised by the above results concerns the non-appearance of paraffinic decomposition, $\{SRR'R''\}^{\oplus}OH^{\ominus} \longrightarrow R'R''SO + RH$, since, according to Sidgwick's rule, sulphur, like phosphorus, should be able to form an electron decet, and should thus fulfil the condition which Fenton and Ingold regarded as essential to paraffinic degradation (Part V, J., 1929, 2342; cf. Hey and Ingold, preceding paper). However, the rule referred to is essentially permissive in character, and actually neutral sulphur in possession of a decet appears to be a rare and somewhat unstable form of this element, since Lowry and Jessop have shown that sulphur tetrachloride has no existence in solution (J., 1929, 1421; 1930, 762), so that sulphur tetrafluoride, described by Fischer and Jaenckner (*Z. angew. Chem.*, 1929, **42**, 810) as a reactive gas, quite unlike the stable hexafluoride, remains as the only authentic example. The known paraffinic decomposition of sulphones, $RR'SO_2 + OH^{\ominus} \longrightarrow R'SO_3^{\ominus} + RH$ (Part VIII, Ingold and Jessop, J., 1930, 708), is not regarded as an argument in the contrary sense, because the electrical dipoles in the sulphone group must considerably modify the stabilities of the possible configurations of electrons, and, indeed, there is a strong suggestion in the acid character of many sulphones of a definite tendency towards expansion in the valency electron group of the sulphone sulphur atom.

EXPERIMENTAL.

Preparation of Sulphonium Salts.—The route to salts of the type $\{RSMe_2\}^{\cdot}I'$ was in all cases the same, *viz.*, through RSH and RSMe; other routes led to the formation of more or less $\{SMe_3\}^{\cdot}I'$ in the final stage. (1) EtSH, prepared by Kleson's method (*Ber.*, 1887, **20**, 3411), was converted into EtSMe with NaOEt–EtOH and MeI, and the EtSMe was treated with MeI in the absence of a solvent. *Dimethylethylsulphonium iodide*, purified by pptn. from dry EtOH with Et_2O, was obtained as a very hygroscopic cryst. solid, m. p. *ca.* 110° (decomp.) (Found : I, 58·3. $C_4H_{11}SI$ requires I, 58·3%).

(2) $Pr^{\alpha}SH$ was prepared by adaptation of Kleson's method, and also as follows. A mixture of $Pr^{\alpha}Br$ (133 g.) and a soln. of NaOEt in EtOH (300 g.), prepared from Na (23·4 g.) and previously saturated with H_2S, was kept at room temp. for 24 hr., boiled under reflux for 0·5 hr., and poured into H_2O; the pptd. oil was dried (Na_2SO_4) (yield 50 g., b. p. 67—69°). $Pr^{\alpha}SMe$, b. p. 93—95° ($HgCl_2$-compd., cryst. from EtOH, m. p. 164—166°), was prepared from $Pr^{\alpha}SH$ (35 g.), NaOEt–EtOH (from Na, 10·7 g.), and MeI (66 g.) (yield 20 g.), and methylated with MeI in the absence of a solvent. *Dimethyl-*n*-propylsulphonium iodide* was too hygroscopic to permit an accurate determination of its m. p. (Found : I, 54·8. $C_5H_{13}SI$ requires I, 54·7%).

(3) $Bu^{\alpha}SH$ (40 g., b. p. 97—98°), prepared (yield 26%) by an adaptation of Kleson's method, was converted by treatment with NaOEt–EtOH (Na, 10·1 g.; EtOH, 200 c.c.) and MeI (63 g.) into $Bu^{\alpha}SMe$ (30 g., b. p. 122—123°), and the latter was methylated as usual. *Dimethyl-*n*-butylsulphonium iodide*, m. p. 82° (decomp.), was purified by pptn. from EtOH with Et_2O (Found : I, 51·7. $C_6H_{15}SI$ requires I, 51·4%).

(4) *iso*BuSH (46 g., b. p. 86—90°) was prepared from *iso*BuI (150 g.) by treatment with NaHS in EtOH as described for the prepn. of $Pr^{\alpha}SH$. *iso*BuSMe, b. p. 110—112°, prepared and methylated as in the previous examples, gave *dimethyl*iso*butylsulphonium iodide*, which, purified as usual, had m. p. 88—90° (decomp.) (Found : I, 51·4. $C_6H_{15}SI$ requires I, 51·4%).

(5) $Pr^{\beta}SH$, b. p. 53°, was obtained from $Pr^{\beta}Br$ exactly as described for the Pr^{α} isomeride, and was converted similarly into $Pr^{\beta}SMe$, b. p. 82—84°, which on methylation as usual gave *dimethyl*iso*propylsulphonium iodide*, very hygroscopic cubes (Found : I, 54·7. $C_5H_{13}SI$ requires I, 54·7%) from EtOH.

(6) $Pr^{\alpha}SEt$, prepared from NaSEt and $Pr^{\alpha}I$ (Stromholm, *Ber.*, 1900, **33**, 830), b. p. 115—117°, was methylated (10 g.) with MeI (14 g.) in cold $MeNO_2$ (25 c.c.) over-night. Addition of Et_2O pptd. an iodide from which was obtained *methylethyl-*n*-propylsulphonium picrate*, m. p. 94—96° (Found : C, 41·5; H, 5·0. $C_{12}H_{17}O_7N_3S$ requires C, 41·5; H, 4·9%).

(7) (With A. M. M. MANDOUR.) *Methylethyl*iso*butylsulphonium iodide* was prepared from MeSEt and *iso*BuI by maintaining the mixture with $MeNO_2$ at 70° for 1 week, cooling, and pptg. with Et_2O (Found : I, 48·7. $C_7H_{17}SI$ requires I, 48·8%).

(8) EtSH (31 g.) was added drop by drop under reflux to Na (11·5 g.) and Et_2O (25 c.c.). Towards the end of the reaction, EtOH (50 c.c.) was added, and the mixture was kept for 24 hr., treated with $CH_2Ph{\cdot}CH_2Cl$ (70 g.), kept a further 24 hr., and finally heated on the water-bath for 0·5 hr. The $SEt{\cdot}CH_2{\cdot}CH_2Ph$, isolated by pouring into H_2O, extraction with Et_2O, and drying ($CaCl_2$), had b. p. 113—115°/10 mm. (yield 50%). *β-Phenylethylmethylethylsulphonium iodide*, obtained from the sulphide and MeI in the absence of a solvent, had m. p. 84—85° (Found : I, 41·2. $C_{11}H_{17}SI$ requires I, 41·0%).

(9) $EtSPr^{\beta}$, b. p. 102—104°, prepared from dry EtSNa (27 g.), $Pr^{\beta}I$ (54 g.), and EtOH (100 c.c.) by boiling for 3 hr., pouring the product into H_2O, and collecting, drying and distilling the pptd. oil, was methylated (10·5 g.) with MeI (14 g.) in cold $MeNO_2$ (15 c.c.), and after 24 hr. Et_2O was added to ppt. the sulphonium iodide (hygroscopic crystals) from which *methylethyl*iso*propylsulphonium picrate*, cryst. from EtOH in needles, m. p. 173—175°, was prepared (Found : C, 41·6; H, 4·9. $C_{12}H_{17}O_7N_3S$ requires C, 41·5; H, 4·9%).

(10) $Pr^{\beta}SH$, b. p. 57—60°, was prepared from $Pr^{\beta}I$ and EtOH–KHS as described by Claus (*Ber.*, 1872, **5**, 659), converted into $Pr^{\beta}SNa$ by treatment with Na in Et_2O, and the dry Na compound methylated with MeI in EtOH. $Pr^{\beta}SMe$, b. p. 93—95° (4 g.), *iso*BuI (9 g.), and $MeNO_2$ (10 c.c.) were kept for 20 hr. at 80—90° with excess of suspended Ag_2SO_4. The sulphonium

sulphate pptd. with Et_2O yielded *methyl*iso*propyl*iso*butylsulphonium picrate*, long needles, m. p. 49—50° (Found : C, 44·6; H, 5·4. $C_{14}H_{21}O_7N_3S$ requires C, 44·8; H,.5·6%), from hot H_2O.

General Method of Decomposing Sulphonium Hydroxides.—The hydroxide solutions were prepared as usual from the iodides and CO_3''-free Ag_2O [except in the case of No. 10, where the sulphate and $Ba(OH)_2$ were used] with minimal exposure to air. They were distilled (bath temp. 120—130°, except that with No. 8 the final temp. was made higher in order to drive over the styrene) from a flask fitted with a N inlet tube through an efficient condenser into a train consisting of an empty trap at 0°, three traps containing $HgCl_2$ aq. at room temp., and a graduated aspirator. The first trap caught H_2O, MeOH, a mixture of sulphides, and in one case styrene also. The small amounts of volatile sulphides (chiefly Me_2S) which escaped this trap were held by the $HgCl_2$ aq., from which the cryst. additive compound was pptd. Gaseous products went into the aspirator into which a current of N swept the contents of the apparatus at the end of the reaction. The contents of the first trap were separated by distillation into a mixture of sulphides and an aq. solution of MeOH, and the sulphides were either partly or completely separated by distillation according to the separation of their b. p.'s. They were usually identified by their b. p.'s and by the I content of their methiodides. The identification of small amounts of Me_2S in mixtures consisting mainly of higher sulphides depended on the small solubility of $\{Me_3S\}^{\cdot}I'$ in cold MeOH, for methylation of the mixture and extraction of the methiodides with this mixture effected an almost quant. separation of the lower homologue. The gas in the aspirator was measured and samples were analysed (Bone–Wheeler). Olefins were further identified in the form of their bromides.

Results (quantitative results are given in the introduction).—(1) *Dimethylethylsulphonium hydroxide.* MeOH was separated from the aq. distillate as *p*-nitrobenzoic ester (m. p. and mixed m. p. 94—96°). Me_2S after partial separation was identified by the prep. of $\{Me_3S\}^{\cdot}I'$, m. p. 208° (decomp.) (Found : I, 61·8. Calc. : I, 62·2%), and MeEtS was similarly identified as $\{Me_2EtS\}^{\cdot}I'$, m. p. and mixed m. p. 110° (decomp.) (Found : I, 58·0. Calc. : I, 58·3%). Gas analysis indicated the presence of a C_2-hydrocarbon, completely absorbable in Br to give $C_2H_4Br_2$, b. p. 130—131° (Found : C, 12·5; H, 2·2. Calc. : C, 12·7; H, 2·1%).

(2) *Dimethyl-*n*-propylsulphonium hydroxide.* MeOH was identified as in (1) (*p*-nitrobenzoate, m. p. 94°, mixed m. p. 93—96°). Me_2S, separated by distillation in a nearly pure form, gave $\{Me_3S\}^{\cdot}I'$, m. p. 207—209° (decomp.) (Found : I, 62·3. Calc. : I, 62·2%). $Pr^{\alpha}SMe$, b. p. 93—95°, was converted into its methiodide (Found : I, 54·7. Calc. : I, 54·7%). The gaseous C_3-hydrocarbon was completely absorbed in Br to give $C_3H_6Br_2$, b. p. 140° (Found : C, 17·0; H, 3·0. Calc. : C, 17·8; H, 3·0%).

(3) *Dimethyl-*n*-butylsulphonium hydroxide.* The first runnings obtained on distillation of the mixed sulphide were methylated and $\{Me_3S\}^{\cdot}I'$ was isolated, m. p. 208 (decomp.), by use of cold MeOH (Found : I, 62·8. Calc. : I, 62·7%). $Bu^{\alpha}SMe$ had b. p. 123—124°; its identity was confirmed by conversion into its $Bu^{\alpha}SMe_2I$ (Found : I, 51·5. Calc. : I, 51·4%). The gaseous C_4-hydrocarbon was completely sol. in Br, giving an oily bromide in quantity too small for distillation.

(4) *Dimethyl*iso*butylsulphonium hydroxide.* The first few drops obtained on distilling the sulphides gave on methylation $\{Me_3S\}^{\cdot}I'$ in quantity too small for purification; identification is based on the m. p., 204° (decomp.), of the crude salt and on its insolubility in cold MeOH. *iso*BuSMe had b. p. 110—112°; its identity was confirmed through its methiodide (Found : I, 51·6. Calc. : I, 51·4%). MeOH was identified by its *p*-nitrobenzoate, m. p. and mixed m. p. 95—96°. The gaseous C_4-hydrocarbon was completely sol. in Br, giving an oily bromide in quantity too small to distil.

(5) *Dimethyl*iso*propylsulphonium hydroxide.* The sulphides were divided into fractions, b. p. 40—55° and 55—76°. The former on treatment with MeI yielded $\{SMe_3\}^{\cdot}I'$, m. p. 210° (decomp.) (Found : I, 62·1. Calc. : I, 62·2%), and the latter gave methiodides which on lixiviation with cold MeOH and pptn. with Et_2O yielded $\{Pr^{\beta}SMe_2\}^{\cdot}I'$ (Found : I, 54·6. Calc. : I, 54·7%). The C_3-hydrocarbon was wholly sol. in Br, giving $C_3H_6Br_2$, b. p. 138—140° (Found : C, 18·1; H, 3·0. Calc. : C, 17·8; H, 3·0%).

(6) *Methylethyl-*n*-propylsulphonium hydroxide.* The mixture of $Pr^{\alpha}SMe$ and $Pr^{\alpha}SEt$, b. p. 85—112°, could not be separated. MeOH was detected as usual, and EtOH by the CHI_3 reaction. Gas-analysis indicated hydrocarbons equiv. to $C_{2\cdot 20}$, and these were wholly sol. in Br, giving a mixture of $C_2H_4Br_2$ and $C_3H_6Br_2$, b. p. 130—140°.

(7) (With A. M. M. MANDOUR.) *Methylethyl*iso*butylsulphonium hydroxide.* The mixture of sulphides could not be separated. Alcohols were detected as in the preceding case. Analysis of the gaseous products indicated hydrocarbons equiv. to $C_{2\cdot 14}$, $C_{2\cdot 13}$, and were wholly sol. in

Br to give a mixture of bromides from which $C_2H_4Br_2$, b. p. 131°, was separated by distillation (Found: Br, 86·5. Calc.: Br, 86·0%).

(8) β-*Phenylethylmethylsulphonium hydroxide.* The sulphide fraction of b. p. below 100°, consisting of crude MeSEt, was identified as such by conversion into SMe_2EtI (Found: I, 58·2. Calc.: I, 58·3%). Styrene, b. p. 140—143°, was identified through its dibromide, m. p. and mixed m. p. 73—74°. The gaseous C_2-hydrocarbon was wholly sol. in Br, giving an oily bromide in quantity too small for distillation.

(9) *Methylethyl*iso*propylsulphonium hydroxide.* The sulphides were not separated. Analysis of the gaseous products indicated hydrocarbons equiv. to $C_{2\cdot75}$, $C_{2\cdot75}$, and these were wholly sol. in Br, giving bromides, b. p. 130—140°, evidently a mixture of $C_2H_4Br_2$ and $C_3H_6Br_2$.

(10) *Methyl*iso*propyl*iso*butylsulphonium hydroxide.* The sulphides were not separated, and gas-analysis indicated hydrocarbons equiv. to $C_{3\cdot07}$. These were completely sol. in Br, giving bromides, b. p. 140—150°, from which $C_3H_6Br_2$, b. p. 140—141°, was obtained by distillation (Found: C, 18·0; H, 3·2. Calc.: C, 17·8; H, 3·0%).

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