23. *Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XII. Decomposition of Quaternary Ammonium Alkoxides.*

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Previous studies of quaternary ammonium compounds have shown that the proportion in which thermal decomposition proceeds according to the reaction (B) whereby a radical from the cation appears in association with the anion, or according to the alternative reaction (A), in which a radical from the cation is eliminated as an olefin, is strongly dependent on constitutional influences. In particular it is known that a general change in reaction-direction in the sense B ⟶ A is observed on passing from an ammonium compound with a very feebly basic anion such as chloride towards one in which the anion has the strong basicity of the hydroxide ion, the cation being the same throughout. The hydroxide ion is the most basic of those hitherto investigated in this connexion, and the present experiments were undertaken in order to determine whether the aforesaid change in the direction of decomposition continues to progress in the same sense when the basicity of the anion is further increased, beyond that of hydroxide, to that of methoxide and ethoxide.

Accordingly we have prepared trimethylethylammonium and trimethyl*iso*butylammonium methoxide and ethoxide. The four compounds decompose to give, on the one hand ethylene or *iso*butylene, and on the other a methyl or an ethyl ether, together with the complementary amine in each case (cf. Achmatowicz, Perkin, and Robinson, J., **1932**, 500). The proportion of reaction A, far from being notably greater than in the case of the ammonium hydroxides, was actually a few units % smaller (Table), and it appears that the replacement of reaction B by reaction A on increasing the basicity of the anion of the ammonium compound does not continue for anions more basic than hydroxide.

The principal products of decomposition of benzyltrimethylammonium ethoxide are trimethylamine and benzyl ethyl ether.

Table : Percentage of Reaction A.

Cation.	Anion.........	$OH^{\ominus}$.	$OMe^{\ominus}$.	$OEt^{\ominus}$.
$C_2H_5{\cdot}NMe_3$		94	90	88
iso-$C_4H_9{\cdot}NMe_3$		63	57	55

EXPERIMENTAL.

Ethyl- and *iso*butyl-trimethylammonium bromides (0·1 g.-mol.) were converted *via* the hydroxides into the chlorides, which after thorough drying were added to an equiv. of a solution of NaOMe or NaOEt in the appropriate Ca-dried alcohol. After filtration of the NaCl with precautions against access of moisture the solutions were completely distilled through the following train, *viz.*, a condenser, a cooled flask containing dil. HCl, a reflux condenser, a second flask of dil. HCl, a second reflux condenser, a cooled flask containing Br, a second similar flask, a drying-tube, and an aspirator. At the end of the distillation the apparatus was swept through with 10 vols. of dry air whilst the liquid in the HCl traps was kept gently boiling under reflux. The excess of Br was destroyed with ice and SO_2, and the olefin bromide extracted with light ligroin, washed with $NaHCO_3$ aq. and H_2O, and distilled. The figures in the two right hand columns of the table are based on concordant triplicate determinations of the yield of olefin bromide, and the figures under the heading $OH^{\ominus}$ are taken from Ingold and Vass's data (J., **1928**, 3125). Amines and ethers could not be isolated quantitatively.

Benzyltrimethylammonium ethoxide, prepared from the directly formed chloride, yielded 65% of rectified benzyl ethyl ether, b. p. 185°, a large amount of trimethylamine, and a small amount of a less volatile base, presumably benzyldimethylamine.

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