The Decomposition of Triethyloxonium Salts

By F. R. JONES and P. H. PLESCH*

(*Department of Chemistry, The University, Keele, Staffordshire* ST5 5BG)

Summary The rate of decomposition of triethyloxonium salts $Et_3O^+YF_n^-$ in solution to Et_2O, EtF, and YF_{n-1} depends on Y and is strongly affected by the presence of ethers.

IN the preceding communication[1] we summarised our findings on the polymerisation of cyclic formals by triethyloxonium tetrafluoroborate (I) and hexafluoroantimonate (IV).† It appeared that (I) decomposed in solution; because triethyloxonium salts are used extensively as catalysts, we studied this reaction for (I) and also for other triethyloxonium salts. During the course of this work other groups of workers reported to us on the instability of (I) in solution (although the pure solid seems to be quite stable when prepared under vacuum), but there appear to be no publications on this subject.

Experimental details and procedures were as described.[1] Triethyloxonium hexafluorophosphate (V) was a gift from Dr. M. P. Dreyfuss; it was re-precipitated thrice from methylene dichloride solution by carbon tetrachloride before being introduced into the conductivity cell, where it was thoroughly evacuated. Salts (I) and (IV), having been prepared and filled into phials *in vacuo*, did not require this treatment.

By n.m.r. spectroscopy and g.l.c. we ascertained that the stoicheiometry of the decompositions is that shown in eqn. (1):

$$Et_3O^+YF_n^- \rightarrow Et_2O + EtF + YF_{n-1}, \qquad (1)$$

where Y = B, P, or Sb, and n = 4 or 6. This reaction is analogous to the decomposition of simple triethyloxonium salts described by Meerwein.[2]

The most obvious phenomenon signalling the decomposition is the decrease in the electrical conductivity of the salts olutions with time, which is of first-order (k_1') for (I), (IV), and (V). The rate of formation of ethyl fluoride [studied for (I) only] is also of first-order (g.l.c. measurements) and the rate constant is approximately the same as k_1'. The rate constants at various temperatures for the decomposition of (I), (IV), and (V) are shown in the Figure.

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† We retain the numbering used in ref. 1 for ease of reference.

The presence of diethyl ether in the reaction mixture changes the slope of the Arrhenius plot, and its effect increases with concentration (Figure).

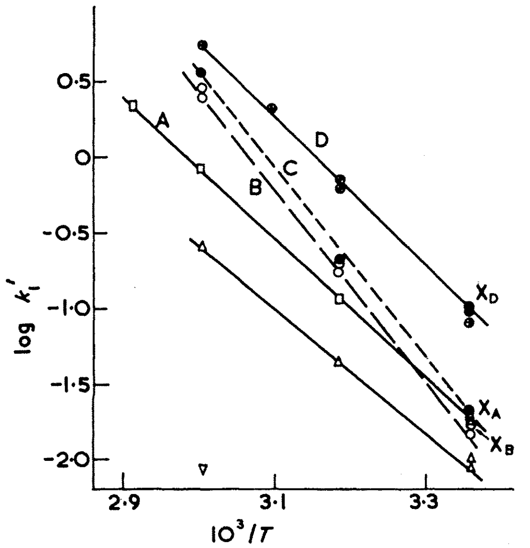
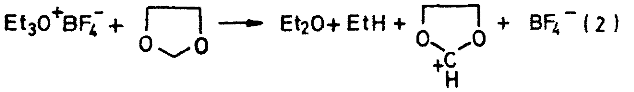


FIGURE. *The decomposition of triethyloxonium salts in methylene dichloride solution, and the effect of various ethers and of temperature on the first-order rate constant* k_1' (hr.$^{-1}$). □, ○, ⊕, ● *represent experiments with* BF_4^-. *The points marked* X *are g.l.c. measurements*: A, *no ether*; B, 1M-*diethyl ether*; C, 3M-*diethyl ether*; D, 1M-*dioxolan*. △, PF_6^-; ▽, SbF_6^-.

If 1,3-dioxolan (II) is added to a solution of (I) under conditions of temperature and concentration such that there is no polymerisation (above ceiling temperature and below "floor" concentration),[3] a part of the oxonium ions reacts rapidly by reaction (2):



This is shown by the formation of ethane, the amount of which does not increase after the first 2 min. of reaction. That reaction (2) occurs also under polymerisation conditions has been mentioned.[1] It is the analogue of the reaction between (I) and 2-phenyl-1,3-dioxolan[4] and of that between methoxymethyl perchlorate and (II).[5] The subsequent decrease in conductivity and formation of ethyl fluoride are of first-order and the rate constants are significantly greater than in the absence or presence of diethyl ether (Figure).

The kinetics of the conductivity increase and of the ethyl fluoride evolution suggest that the decomposition is a unimolecular reaction, and it seems likely that ion-pairs and both types of triple-ion may undergo this. Therefore, the observed rate constants are probably composite, so that their detailed interpretation must wait until we have clarified the electrochemical conditions in the reaction mixtures; for this reason we also refrain at present from deriving activation parameters from the temperature-dependence of the rate constants.

The reasons for the effect of ether and (II) on the rate of decomposition of the salt are not entirely clear at present. However, since the dielectric constants of diethyl ether and (II) are less than that of methylene dichloride, the effect of these compounds may be due, at least partly, to the change in polarity of the medium, and also partly to solvation of the oxonium ion as suggested in the preceding communication.[1]

The stability of the salts in solution depends strongly on the nature of the cation, and increases in the order $BF_4^- < PF_6^- << SbF_6^-$. When we have a reliable interpretation of the rate constants, it will be possible to interpret this gradation in terms of the activation parameters and to attempt a correlation of these with the properties of the anions.

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[1] Preceding Communication.
[2] H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, and E. Pfeil, *J. prakt. Chem.*, 1937, **147**, 257.
[3] P. H. Plesch and P. H. Westermann, *J. Polymer Sci., Part C, Polymer Symposia*, 1968, **16**, 3837.
[4] H. Meerwein, V. Hederich, H. Morschel, and K. Wunderlich, *Annalen*, 1960, **635**, 1.
[5] V. Jaacks, H. Frank, E. Gruenberger, and W. Kern, *Makromol. Chem.*, 1968, **115**, 290.