The Decomposition of Triethyloxonium Salts in Solution

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A kinetic study *in vacuo* of the decomposition of triethyloxonium salts $[OEt_3]A$ $\{A^- = (1)\ [BF_4]^-, (2)\ [PF_6]^-$ or, $(3)\ [SbF_6]^-\}$ in methylene dichloride has shown that the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values are strongly influenced by the presence in the solution of diethyl ether or 1,3-dioxolan. The decompositions, of first order, have been followed by monitoring the electrical conductivity or the formation of ethyl fluoride, or both. The mechanism of decomposition without and with the oxygen compound is discussed. A method of preparing and purifying (1) *in vacuo* is described.

THE thermal instability of oxonium salts was reported by Meerwein *et al.*[1,2] At the same time, Meerwein established that oxonium salts with simple anions could not be isolated and that the stability of those with complex anions decreased as follows: $[SbF_6]^- > [PF_6]^- > [SbCl_6]^- > [BF_4]^- > [FeCl_4]^- > [AlCl_4]^- > [SnCl_4]^-$. Dreyfuss and Dreyfuss[3] reported the spontaneous decomposition of oxonium salts with complex anions in the termination stage of the polymerisation of tetrahydrofuran initiated by triethyloxonium tetrafluoroborate (1). We also observed the spontaneous decomposition of (1) in CH_2Cl_2 when studying it as an initiator for the polymerisation of 1,3-dioxolan.[4] Quantitative information on this decomposition was lacking until our study which has been reported in outline.[5] Various points have been elucidated in the interval and we now report details of this work and the activation parameters and a mechanism for the reaction which can be represented as in equation (1) where Y = B, P, or Sb, R = alkyl group, X = F, and n = 4 or 6.

$$[OR_3]^+ + [YX_{n+1}]^- \longrightarrow OR_2 + RX + YX_n \quad (1)$$

The triethyloxonium salts containing $[BF_4]^-$ (1), $[PF_6]^-$ (2), and $[SbF_6]^-$ (3) were prepared and their decomposition studied in a vacuum apparatus. The decrease in the conductivity of solutions of these salts was monitored simultaneously with the evolution of EtF determined by g.l.c. Since the rate constant of decomposition obtained from conductance measurements (k_1') was the same, within experimental error, as that obtained chromatographically (k_1''), most of our results were obtained by recording the conductivity changes since this is an easier technique.

RESULTS

The g.l. chromatogram of the decomposition products from (1) had peaks with retention times equivalent to those of authentic samples of EtF and $OEt_2{\cdot}BF_3$. Salts (2) and (3) also decomposed with the evolution of EtF. Confirmation of these identifications was obtained by examining the ^1H n.m.r. spectrum of a solution of (1) in methylene dichloride which had been allowed to decompose at 348 K and was then transferred *in vacuo* to an n.m.r. tube. The resonances of EtF and $OEt_2{\cdot}BF_3$ were clearly visible (Figure 1). Similar results were obtained for a solution sealed *in vacuo* in an n.m.r. tube and aged for 1 week at 298 K. There were no unidentified peaks in either spectrum.

Figure 2 shows that the amount of EtF formed increases at a rate which is the same as that at which the conductance of the solution decreases. The same behaviour was found, independently of whether the solvent contained no oxygen compound or 1,3-dioxolan or OEt_2. Both measures give

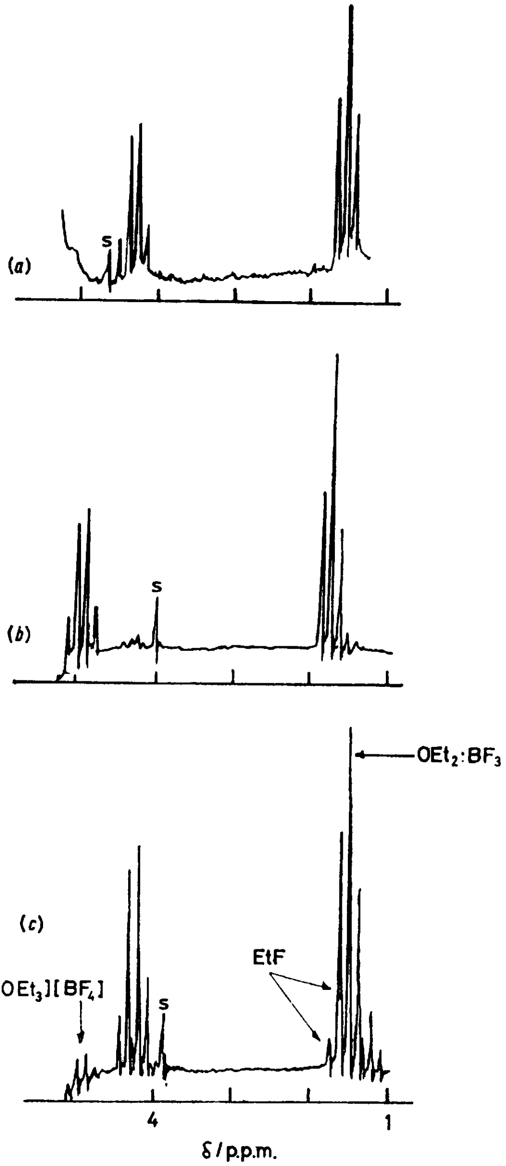


FIGURE 1 The ^1H n.m.r. spectra for (*a*) $OEt_2{\cdot}BF_3$, (*b*) $[OEt_3][BF_4]$, and (*c*) a 0.5 mol dm^{-3} solution of the decomposition products from $[OEt_3][BF_4]$ in CH_2Cl_2 (run 150). S = spinning side band

TABLE 1

The decomposition of $[OEt_3][BF_4]$ (1) in CH_2Cl_2 solution in the presence of OEt_2 or 1,3-dioxolan

Run no.	$10^2[(1)]$ [a] mol dm^{-3}	[Dioxolan] mol dm^{-3}	$[OEt_2]$ mol dm^{-3}	T/K	$10^4k_1'/s^{-1}$ [b]	$10^4k_1''/s^{-1}$ [c]	N [d]
120	1.1			298	0.05	0.056	4
141A	0.68			313	0.32		2
140	1.6			333	3.3		4
141B	0.1			343	6.0		3
112	1.33	1.0		298	0.28		1
122	1.0	1.0		298	0.22	0.28	3.5
146C	1.0	1.0		298	0.28		0.5
146A	4.2	1.0		313	1.72		1.5
142A	2.3	1.0		313	1.92		1.5
146B	2.0	1.0		323	7.5		1.5
146D	0.8	1.0		323	13.0		1.5
142B	0.54	1.0		333	8.3		2
135	1.15		1.0	298	0.044	0.047	4
145C	0.5		1.0	298	0.042		0.5
145A	2.2		1.0	313	0.44		0.3
143A	0.63		1.0	313	0.56		0.5
143B	0.45		1.0	333	6.9		2
145B	1.8		1.0	333	8.3		1.5
144B	0.35		3.0	298	0.056		0.05
144A	0.48		3.0	313	0.75		0.5
144C	0.29		3.0	333	10.6		3

[a] Estimated from κ (298 K) in CH_2Cl_2 except for the experiments with OEt_2 and 1,3-dioxolan designated B, C, or D. [b] From κ measurements. [c] From rate of EtF formation. [d] Number of half-lives recorded.

internally first-order reaction curves whose constants k_1' (from $-d\kappa/dt$) and k_1'' (from $d[EtF]/dt$) are similar for each system but differ from system to system. Tables 1 and 2 illustrate this point and also include values of k_1' at various temperatures. The Arrhenius plots of these results have been reported [5] so that we now only give the activation parameters calculable from these results (Table 3).

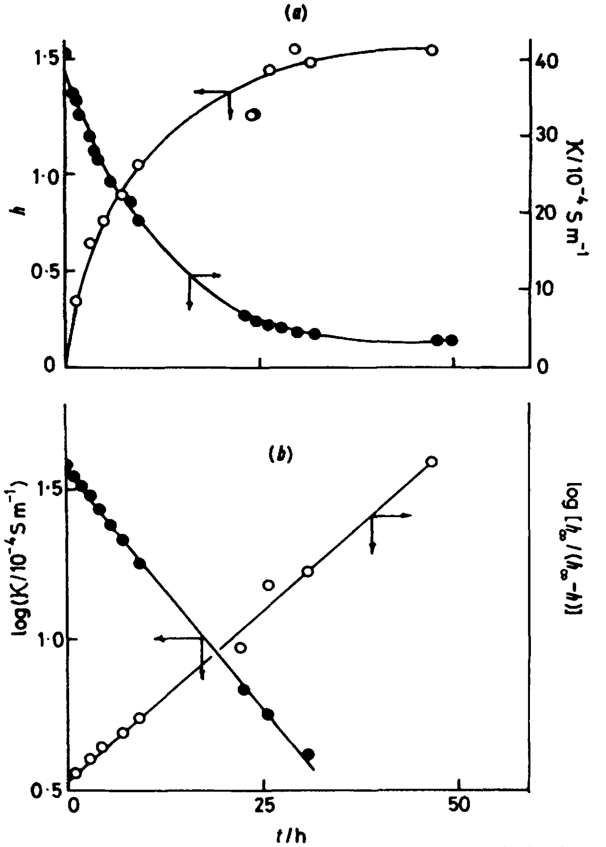


FIGURE 2 Decomposition of $[OEt_3][BF_4]$ in 1 mol dm^{-3} 1,3-dioxolan in CH_2Cl_2 at 298 K (run 122). (○), Relative height h of the EtF peak in the g.l.c. recorded under standard conditions for all experiments; (●), conductivity κ of the solution. (*a*) Reaction curves. (*b*) First-order plots for the evolution of EtF and the decrease in conductivity. h_∞ = Relative height of EtF peak when the reaction appeared to be complete and taken as 1.63 m

TABLE 2

The decomposition of $[OEt_3][PF_6]$ (2) in CH_2Cl_2

Run no.	$10^2[(2)]$/ mol dm^{-3}	T/K	$10^4k_1'/s^{-1}$	N
154A	0.54	298	0.024	0.5
158A	1.5	298	0.028	0.4
154B	0.34	313	0.12	0.5
158D	0.44	313	0.19	4
158C	1.0	333	0.69	1

TABLE 3

Activation parameters for the decomposition of $[OEt_3][BF_4]$ and $[OEt_3][PF_6]$ in CH_2Cl_2 solutions

Added oxygen compound	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
(*a*) $[OEt_3][BF_4]$		
	90 ± 2	−43 ± 7
1 mol dm^{-3} 1,3-dioxolan	97 ± 2	−8 ± 8
1 mol dm^{-3} OEt_2	120 ± 2	55 ± 6
3 mol dm^{-3} OEt_2	120 ± 2	75 ± 6
(*b*) $[OEt_3][PF_6]$		
	79 ± 2	−87 ± 8

The u.v. and visible spectra of the various solutions were examined, *in vacuo*, before and after decomposition at high temperatures. Experiments 140 and 143 with (1) (Table 1) and 158 with (2) (Table 2) gave solutions which showed no absorptions. When (1) in 1 mol dm^{-3} 1,3-dioxolan solution had been kept for 2 h at 313—333 K the solution did adsorb, but there are then other reaction products in the solution whose decomposition products could be responsible for the absorption.[4,6,7] A small amount of white precipitate produced in the decomposition of (2) was most probably $OEt_2 \cdot PF_5$.

In a single experiment with (3) a 2.4 × 10^{-2} mol dm^{-3} solution of it in CH_2Cl_2 was decomposed at 333 K. The initial conductivity decreased from 146 × 10^{-4} to 103.7 × 10^{-4} S m^{-1} in 70 h. The rate constant was 1.3 × 10^{-6} s^{-1}.

The solution had turned very slightly yellow after 46 h. The u.v. and visible spectra of the solution, taken after 10 h and when the cell had been opened to the atmosphere, showed two peaks (at 382 and 302 nm) which have not been identified.

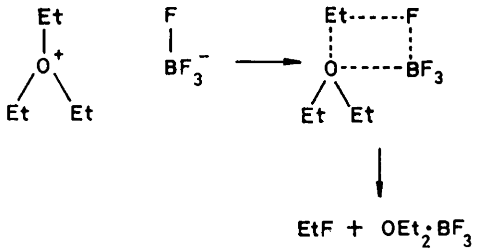
DISCUSSION

We determined the ion-pair association constant for (2) in CH_2Cl_2 solution at 273 K and showed that at concentrations less than 10^{-2} mol dm^{-3} triple-ion formation can be neglected.[8] Furthermore, since the decomposition is of first order with respect to the salt concentration, the decomposition of either kind of triple ion or the encounter of free ions cannot be rate determining. Therefore decomposition occurs through the ion pair according to equation (2) where k_1 is the first-

$$[OEt_3]^+ + [YF_{n+1}]^- \overset{K_A}{\rightleftharpoons} [OEt_3]^+[YF_{n+1}]^- \xrightarrow{k_1} EtF + YF_n + OEt_2 \quad (2)$$

order rate constant for decomposition. As shown in the Appendix, if the attainment of equilibrium between ions and ion pairs is rapid compared to the rate of loss of the ion pair, then $d[EtF]/dt = k_1''(s_0 - [EtF])$ where s_0 is the initial salt concentration, and $d\kappa/dt = -k_1'\kappa$, where κ is the conductivity at time t, and $k_1' = k_1'' = k_1$. This treatment provides the theoretical background for the observation that the first-order rate constant for the decomposition of triethyloxonium salts can be determined from the rate of evolution of EtF or from the rate of decrease of conductivity.

The activation parameters for the decompositions are shown in Table 3. For the reaction without ether we propose the mechanism of decomposition shown in (3).



(3)

That $\Delta H^\ddagger$ is relatively large probably reflects the dissipation of charge in going from a pair of small ions with concentrated charge and high coulombic energy to the transition-state complex with a lower charge density. That $\Delta S^\ddagger$ is negative is normal for this type of process.

TABLE 4

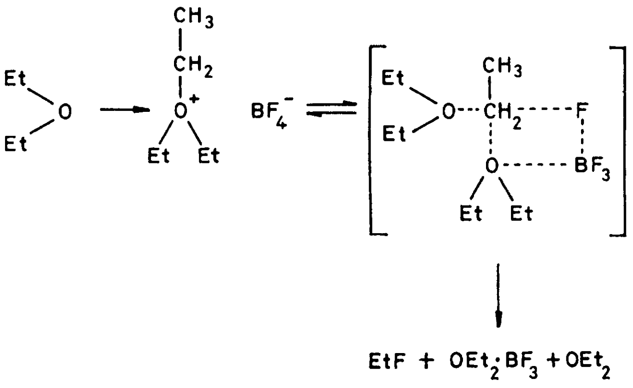
The ^1H n.m.r. peaks of 0.5 mol dm^{-3} triethyloxonium salts in the absence (*a*) and presence (*b*) of 1 mol dm^{-3} OEt_2 in CH_2Cl_2 solution at 308 K

		Chemical shift (δ/p.p.m.)					
		$[OEt_3]^+$			OEt_2		
$[YF_{n+1}]^-$		CH_3 *	CH_2 †	$\Delta\delta(CH_2)$	CH_3 *	CH_2 †	$\Delta\delta(CH_2)$
None	(*b*)				1.15	3.38	
$[BF_4]^-$	(*a*)	1.70	4.90				
	(*b*)	1.60	4.80	+0.1	1.10	3.50	−0.12
$[PF_6]^-$	(*a*)	1.70	4.90				
	(*b*)	1.65	4.85	+0.05	1.15	3.55	−0.17
$[SbF_6]^-$	(*a*)	1.70	4.90				
	(*b*)	1.70	4.90	0	1.2	3.50	−0.12

+ Represents an upfield shift, — a downfield shift.

* Triplets. † Quadruplets.

We found from conductance studies that oxonium ions are solvated by ether molecules and concluded that the cation appears to be sandwiched between the ether molecule and the anion.[8] In Table 4 we present further evidence for such solvation and for the formation of intimate ion pairs in which the charge has been largely dissipated. The ^1H n.m.r. spectra from 0.5 mol dm^{-3} solutions in CH_2Cl_2 of compounds (1)—(3) without and with 1 mol dm^{-3} OEt_2 showed small but significant upfield shifts for the methylene protons of the oxonium salts (1) and (2). In all three systems there was a corresponding downfield shift for the signal from the methylene protons of OEt_2. Since the spectrum of 1,4-dioxan was unchanged when recorded in the CH_2Cl_2 with and without diethyl ether, these effects are not a consequence of adding the ether but represent the different charge distributions within the ion pairs, which are the most abundant species in such solutions.[8] Since the chemical shift for the CH_2 protons of (3) is unchanged, whereas that of the CH_2 protons of OEt_2 is affected, we conclude that the oxonium ion is still solvated but that the larger $[SbF_6]^-$ ion is too far from the oxonium ion to affect its charge distribution. Therefore the upfield shift for the CH_2 protons of (1) in the presence of OEt_2 must be due to the $[BF_4]^-$ ion being so intimately associated with the oxonium ion that the charge density is further reduced. Thus we conclude that the solvated ion pair of (1) has a structure approaching that of the transition state shown in the Scheme. The $[PF_6]^-$ ion is intermediate in size and therefore intermediate in its behaviour in the presence of OEt_2.



SCHEME

We also confirmed the well known fact that when 1,3-dioxolan is present the decomposition of the salt is accompanied by ethylation of the dioxolan, and found that this is slow for compound (1) but much faster for (3). Because of the difference in size of the anions, the K_D for salt (3) is appreciably larger than for (1) and we therefore conclude that the alkylation is (mainly) by an ethyl transfer from an unpaired oxonium ion [6] (K_D = dissociation constant of ion pair).

The mechanism of the decomposition in the presence of OEt_2 is envisaged to be as shown in the Scheme.

The solvation of the oxonium ion by ether reduces its effective charge. In the transition state the ether is less strongly bound than in the initial state and this explains why $\Delta S^\ddagger$ is positive. The fact that the activation energy for the decomposition is higher than in the absence of ether is also explained by our scheme because more energy is required to form the transition state from the solvated than from the unsolvated ion pair. What has been written about OEt_2 also applies to 1,3-dioxolan, but its effect on the rate of decomposition is less than that of OEt_2 because it is less basic; 1,3-dioxolan has pK_b 6.81, OEt_2 has pK_b 5.65.[9]

The very considerable differences in the rate constants of decomposition are in the order established qualitatively by numerous other workers. From the results in Table 3 it follows that for $[BF_4]^-$ and $[PF_6]^-$ it is the change in $\Delta S^\ddagger$ and not that in $\Delta H^\ddagger$ which slows the reaction.

Anion	$[BF_4]^-$	$[PF_6]^-$	$[SbF_6]^-$
10^6k_1/s at 333 K	330	69	1.3

EXPERIMENTAL

Solvents and Reagents.—CH_2Cl_2 was purified conventionally, fractionally distilled through a 1.5 m column filled with nickel-gauze rings at a reflux ratio of 15 : 1, and stored over sublimed P_2O_5 or CaH_2 *in vacuo*. Diethyl ether was purified by the method of Vogel,[10] fractionally distilled from sodium metal, and stored *in vacuo* over $Li[AlH_4]$. 1,3-Dioxolan was heated under reflux over sodium metal, fractionally distilled through a 1 m column, and stored over $Li[AlH_4]$ *in vacuo*. Diethyl ether–boron trifluoride was fractionally distilled under nitrogen and the fraction boiling at 397 K (742 Torr) * was collected. This was then redistilled under reduced pressure (327 K, 20 Torr) with a nitrogen bleed. It was transferred quickly to a vessel attached to the vacuum line, frozen, degassed, and the vessel sealed. It was then distilled into a second flask, leaving a generous tail fraction. It was dosed through a series of breakseals into a burette and finally into the reaction vessel. Compound (1) was prepared on the vacuum line in the apparatus shown in Figure 3 by a method based on that of Meerwein *et al.*[1] as described below. Compound (2) was supplied by Dr. M. P. Dreyfuss and purified by three precipitations from solution by CCl_4 immediately before use, m.p. 414—415 K. Compound (3) was prepared by the silver salt method of Meerwein *et al.*[11]

$$Ag[SbF_6] + OEt_2 + EtBr \longrightarrow AgBr + [OEt_3][SbF_6]$$

from freshly purified EtBr, OEt_2, and silver(I) hexafluoroantimonate(V) (Ozark-Mahoning Co. Ltd.) in an evacuated cell and was distributed into phials as described for (1). Reprecipitation from CH_2Cl_2 solution with CCl_4 did not bring the melting point about 375—377 K (lit.,[12] 384 K) although a sample supplied by Dr. M. P. Dreyfuss had a melting point of 394—395 K.

Apparatus.—Ultraviolet and visible spectra were recorded with a Beckman DB spectrophotometer thermostatted at 298 K. The spectra of solutions *in vacuo* were obtained with the apparatus described [13] which is related to the devices shown in Figure 4. Hydrogen-1 n.m.r. spectra were recorded on a Perkin-Elmer R10 machine with ^1H resonance at 60 MHz, thermostatted at 308 K; $SiMe_4$ (δ = 0 p.p.m.) was used as an external standard. For measurements *in vacuo* a sample tube was fused to a device similar to that in Figure 4 and sealed off after filling. Gas–liquid chromatographic analyses were run on a Perkin-Elmer F11 instrument fitted with a dual-column analyser, a flame ionisation detector, and two 3-m silicone oil SE-30 [Chromosorb P (100—120 mesh)] columns. For the conductivity measurements. the cells were of the type shown in Figure 4. Either a Chandos Linear conductivity meter operating at 1 000 Hz or a Wayne-Kerr B221 Universal Bridge operating at 1 582 Hz was used to measure conductivities. The cell constants were determined conventionally.[14]

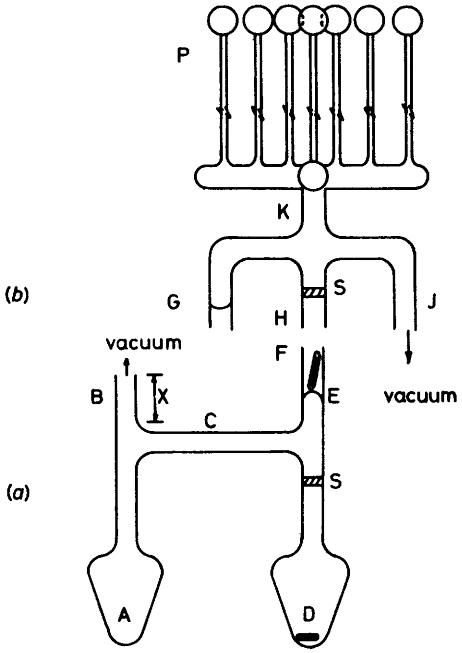


FIGURE 3 Vacuum apparatus for the preparation of $[OEt_3][BF_4]$. E and G are breakseals, P are phials, and S are sintered-glass filters

Preparation of (1).—The apparatus is shown in Figure 3. The preparation assembly (*a*) was fused to the vacuum and reagent supply line at B and pumped out for *ca.* 3 h. The three reagents (3 mol epichlorohydrin, 4 mol $OEt_2{\cdot}BF_3$, and 16 mol OEt_2) were then distilled into flask D. With the contents of D frozen, the apparatus was sealed off from the line at B. The reactants were then thawed and mixed by stirring them magnetically. A precipitate was formed which was a viscous oil at room temperature. The oil crystallised after *ca.* 12 h at 273 K. However, the time can be reduced by washing the oil. Washing was carried out by filtering the solution into flask A through the sintered filter S, and distilling the excess of OEt_2 back into flask D by cooling it. Whereas the by-product boric acid ester is soluble in OEt_2, compound (1) is insoluble. After crystal-

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* Throughout this paper: 1 Torr = (101 325/760) Pa.

lisation it was washed with the ether about ten times as described above. For this process it is important that X is long enough to hold all the filtrate. Filtration can be accomplished easily by slightly warming or cooling the appropriate flask. When washing was complete, the glass above S was washed by refluxing the ether in this part of the apparatus. This was best accomplished by stroking the glass with cotton wool soaked in liquid nitrogen. The contents of A were frozen to distil the remaining ether into it and then A was sealed off at C.

The tipping device (*b*) was sealed to the vacuum line at J and flask D containing (1) was sealed to it at H–F. The whole assembly down to the breakseal E was pumped out for *ca.* 3 h before E was broken. The pumping was continued for another 2 h, CH_2Cl_2 (10 cm^3) was distilled into D from a reservoir attached to the vacuum line, and then the whole assembly was sealed off at J. The solution of (1) in CH_2Cl_2 was then distributed into the phials P. The apparatus was, once again, attached to the vacuum line *via* the breakseal G, with the phials at the bottom, and pumped for another 3 h. During this stage the phials were cooled to 273 K. A plug of CH_2Cl_2 was frozen at K, the breakseal G was broken and the CH_2Cl_2 was distilled out of the phials into a receiver, leaving the solid behind. When this process was complete some solid remained in the necks of the phials and this was washed back into the phials by condensing some solvent in the necks of the phials as described. The process was repeated until all the solid was collected in the phials in a dry state. It was then evacuated for 1 or 2 h before the phials were sealed off.

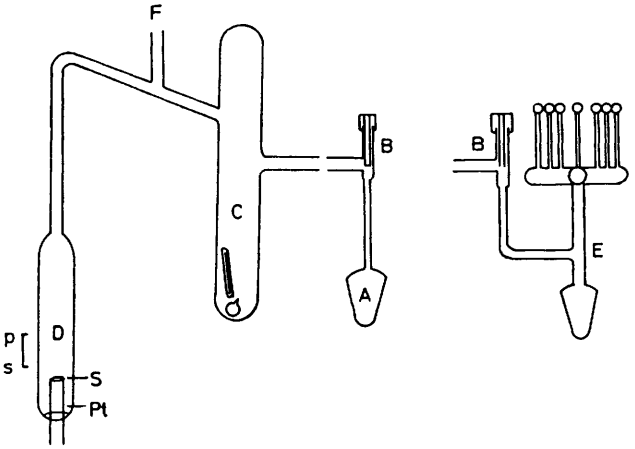

FIGURE 4 Vacuum conductivity and sampling cells for following the decomposition of oxonium salts in solution. D is a conductivity cell with platinum electrodes Pt held together with a soda-glass bead S and sealed through soda glass and attached to the Pyrex apparatus with a Pyrex-to-soda glass graded seal p–s. C is the charging arm containing the phial of oxonium salt. For conductivity studies flask A was attached to C *via* the tap B. For simultaneous sampling the tipping device E replaced A

The solid can be distributed into phials by this method provided that there is not more than 0.1—0.2 g in each phial. With larger quantities the distillation of solvent from the phials becomes too time-consuming and difficult. The quantity in each phial was determined by the midpoint method [15] (error ±5 mg). The yield was almost 90%. Since salt (1) is hygroscopic, the melting point was determined by strapping a phial to a thermometer and warming them slowly in an oil-bath, m.p. 364—365 K (lit.,[1] m.p. 364 K). Phials containing smaller quantities of (1) were prepared by diluting the contents of a phial in the device described.[16] The solid salt was then obtained by a process similar to that described above.

The midpoint method,[15] normally used for weighing 0.1 to *ca.* 1.5 g of solution, is not really sufficiently accurate for weighing small quantities of solid. Therefore the amount of (1) used in each experiment was calculated from its conductivity in CH_2Cl_2 by means of a calibration curve obtained by diluting the contents of a phial containing a relatively large quantity of salt. The calibration curve was linear over the normal concentration range required.

The salt (1) prepared by our method is stable for several weeks at 273 K. However, after *ca.* 3—4 months a small quantity of oil was observed in some of the phials, in particular those containing large amounts. It has been shown by Magagnini and his co-workers [17] in a very elegant study that the alleged polymerisation of *N*-vinylcarbazole by (2) was in fact initiated by PF_5 which accumulated in the phials containing solid (2) due to decomposition of the solid salt.

Decompositions. The salt concentration was determined at the start of each run from the conductivity of (1) in CH_2Cl_2 solution, as mentioned above.

Diethyl ether or 1,3-dioxolan was distilled into the flask A of the device ABCD in Figure 4 and the Teflon tap B was closed. After pumping for a short time, CH_2Cl_2 was run into the side arm C containing a phial of salt. With the solvent frozen, the device was sealed off from the vacuum line at F. The phial was broken and the solution tipped into the conductivity cell D, equilibrated at 298 K, and the conductivity recorded. With the tap B open, the OEt_2 or 1,3-dioxolan was mixed with the solution and the apparatus totally immersed in the thermostat.

The rate of decomposition is so low that at $\leqslant 313$ K most reactions were measured over about one quarter-life. This meant that much of the salt remained in solution after such a measurement and further measurements could be made on the same solution at several different temperatures. Since our cells were evacuated we could use temperatures above the boiling point of CH_2Cl_2. At 333 and 343 K (and occasionally at 313 K) there was sometimes distillation from D into C. In order to establish that the conductivity change was not caused by distillation, the device was removed from the constant-temperature bath, the contents mixed, and the conductivity measurements continued after the cell had been replaced in the bath. Although the cell was out of the bath for < 1 min, a break in the first-order plot was observed, but the first-order plots before and after mixing had the same gradient.

The evolution of EtF. This was monitored simultaneously with the conductivity by means of the vacuum sampling cell. In this cell, flask A (in Figure 4) was replaced by the tipping device (E). Once the salt solution had been prepared, some of it was collected in E and isolated by closing tap B, sealed off, thawed, and tipped into phials which were sealed off as described above and stored at the required temperature. The dead volume in the phials was kept to a minimum. These phials were opened after set periods for analysis by g.l.c. The reaction was assumed to have been interrupted by the cooling operation.

APPENDIX

Consider the ' drained ' equilibrium (2). Let $[OEt_3^+] = [YF_{n+1}^-] \equiv y$, $[OEt_3^+YF_{n+1}^-] \equiv p$, and $[EtF] \equiv e$. Then we obtain (A1) and (A2). From a mass balance the initial concentration of salt s_0 is given by (A3); since $y \ll p$,

$$K_2 = p/y^2 \qquad \text{(A1)}$$

$$\mathrm{d}p/\mathrm{d}t = 2K_2y\mathrm{d}y/\mathrm{d}t \qquad \text{(A2)}$$

$$s_0 = y + p + e \qquad \text{(A3)}$$

equation (A3) becomes (A4). If we consider the reaction at

$$s_0 \simeq p + e \qquad \text{(A4)}$$

low conversion, we can write (A5). From (A1) and the

$$\mathrm{d}s_0/\mathrm{d}t = 0 = (\mathrm{d}p/\mathrm{d}t) + (\mathrm{d}e/\mathrm{d}t) \qquad \text{(A5)}$$

definition of k_1 [equation (2)], equation (A6) follows.

$$\mathrm{d}e/\mathrm{d}t = k_1K_2y^2 \qquad \text{(A6)}$$

Therefore substitution of (A2) and (A6) into (A5) gives (A7)

$$0 = 2yK_2\mathrm{d}y/\mathrm{d}t + k_1K_2y^2 \qquad \text{(A7)}$$

$$\mathrm{d}y/\mathrm{d}t = -k_1y/2 \qquad \text{(A8)}$$

and thence (A8). By substituting (A4) into (A1) and re-

$$y = (s_0 - e)^{\frac{1}{2}}/K_2^{\frac{1}{2}} \qquad \text{(A9)}$$

arranging we get (A9), and by substituting (A9) into (A6) we

$$\mathrm{d}e/\mathrm{d}t = k_1(s_0 - e) \qquad \text{(A10)}$$

obtain (A10). This means that the formation of EtF is of first order with respect to the salt concentration with a contant k_1, and therefore $k_1 = k_1''$.

For the conductivity κ we have $\kappa = \Lambda s$ where Λ is the molar conductivity and s the concentration of salt at any time. Since $s = p + y$ and $y \ll p$, $s \simeq p$, and (A11)—(A13) follow from equation (A1) and the definition

$$s = K_2y^2 \qquad \text{(A11)}$$

$$\kappa = \Lambda K_2y^2 \qquad \text{(A12)}$$

$$\mathrm{d}\kappa/\mathrm{d}t = 2\Lambda K_2y\mathrm{d}y/\mathrm{d}t \qquad \text{(A13)}$$

of κ. Substitution of (A8) into (A13) gives (A14), and substitution of (A12) into (A14) gives (A15). Therefore

$$\mathrm{d}\kappa/\mathrm{d}t = -\Lambda K_2k_1y^2 \qquad \text{(A14)}$$

$$\mathrm{d}\kappa/\mathrm{d}t = k_1\kappa \qquad \text{(A15)}$$

the decay of conductivity with time is of first order with respect to the conductivity, with a rate constant k_1, and therefore $k_1' = k_1$, and a comparison of (A10) with (A15) shows that $k_1' = k_1'' = k_1$.

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