The Polarography of Some Oxonium Ions in Methylene Chloride. Part I. Experimental Techniques and Results for Two Tertiary Ions

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The techniques used for the first polarographic measurements on oxonium ions in methylene chloride in the presence of tetra-n-butylammonium tetrafluoroborate supporting electrolyte are described. A three electrode polarographic cell was used with a dropping mercury working electrode, platinum counter-electrode, and silver iodide in methylene chloride reference electrode. The triethyl- and the ethyl(tetramethylene)-oxonium ions are reduced in a one-electron, irreversible step at half-wave potentials of −0.33 and −0.30 V, respectively. As the diffusion current is proportional to the concentration of the oxonium ion, polarography can be used to assay tertiary oxonium ions down to 10^{-4}M.

THE polarography of oxonium ions in non-aqueous solvents has not been attempted previously. We undertook it because in the light of experience with the polarography of carbenium ions[1] it seemed to offer a relatively simple method for the identification and estimation of oxonium ions, both of which are of interest in connection with studies on the polymerisation and other reactions of cyclic ethers and of 1,3-dioxacycloalkanes. Further, since the spectroscopic characteristics of most of the oxonium ions of current interest are such that they cannot be estimated conveniently at concentrations $<$ *ca.* 10^{-2}M at best, polarography appeared to be the most promising analytical method of adequate sensitivity for monitoring the concentration of propagating species in the polymerisations of cyclic oxygen compounds. The results to be described open up a new field whose theoretical implications and practical applications appear promising. In the present paper the techniques used and the results obtained with two tertiary oxonium ions, which are relatively easy to interpret, are described. In Part II the more complicated results obtained with different types of secondary oxonium ions will be presented.

EXPERIMENTAL

General.—The techniques are based on the experience accumulated at Keele concerning the polarography of carbenium ions under various conditions,[1] and the preparation and handling of carbenium [1d,e,2] and oxonium [3,4] salts.

Materials.—This section also includes some compounds which will only be mentioned in Part II. Methylene chloride was purified by standard methods and was stored under vacuum over calcium hydride. Tetra-n-butylammonium perchlorate (TBAP) and tetra-n-butylammonium tetrafluoroborate (TBAFB) were prepared by titrating 0.2M aqueous tetra-n-butylammonium hydroxide (BDH reagent grade) with 0.2M solutions of perchloric acid (BDH AnalaR grade) or fluoroboric acid (BDH technical grade), respectively, to pH 7. TBAP was recrystallised from aqueous acetone and TBAFB was recrystallised first from water and then from carbon tetrachloride–n-hexane. Both salts were dried under vacuum at 50° for several days and were stored over phosphoric oxide under vacuum. Tetra-n-butylammonium iodide (TBAI) (BDH reagent grade) was recrystallised from ethyl acetate–ethanol and stored over phosphoric oxide under vacuum. Triethyloxonium hexafluoroantimonate was obtained from phials of this salt prepared by Dr. F. R. Jones by standard high vacuum techniques. Ethyl(tetramethylene)oxonium hexafluoroantimonate was prepared under vacuum by standard techniques from 1-bromo-4-ethoxybutane (0.7 g) and silver hexafluoroantimonate (0.7 g) in methylene dichloride (20 cm^3). The mixture was treated as follows (all operations under vacuum). The solution was filtered to remove silver bromide, evaporated to remove solvent and most of the excess of ether, washed twice with n-hexane, and again evaporated to dryness to remove the last traces of the ether. The product was redissolved in methylene chloride and the solution was transferred to weighed phials,[5] the solvent was evaporated off, the phials were sealed, and stored at 0° until required. Diethyl ether, tetrahydrofuran, 1,3-dioxolan, and 1,3-dioxepan were purified by vacuum distillation from lithium aluminium hydride and were stored over this compound under vacuum. Stock solutions of anhydrous perchloric acid in methylene chloride were prepared as described [6] and were diluted with methylene chloride *in vacuo* as required. High purity nitrogen was dried by passing it through two spirals cooled with liquid nitrogen before use.

Apparatus.—The polarographic cell described previously [1d] was modified by replacing the mercury pool anode with a platinum gauze counter-electrode. The reference electrode described below was added to give a three-electrode polarography cell. The dropping mercury electrode (d.m.e.) had the following characteristics for a mercury height of 28.4 cm (corrected) and zero applied potential in 0.1M-TBAP in methylene chloride: $m = 2.507$ mg s^{-1}, $t = 3.18$ s. The reference electrode was a modification of the silver iodide reference electrode in methylene chloride of Holm *et al.*[7] and is shown in Figure 1. The electrolyte solution in compartment B was made by saturating 0.1M-TBAI in methylene chloride with silver iodide and tetra-n-butylammonium tetraiodotrisilver(I). The reference electrode compartment B was connected to the polarographic cell *via* the salt-bridge E which consisted of a 0.1M-TBAP solution in methylene chloride. The salt-bridge solution was changed regularly to prevent contamination of the solutions in the polarographic cell. This reference electrode was found to be stable over nine months to within ±5 mV and had a potential of $-0.370 \pm$

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[1] (*a*) M. I. James and P. H. Plesch, *Chem. Comm.*, 1967, 508; P. H. Plesch and I. Sestakova, *J. Chem. Soc.* (*B*) (*b*) 1970, 87; (*c*) 1971, 1337; (*d*) P. H. Plesch, A. Stasko, and D. Robson, *ibid.*, p. 1634; (*e*) P. H. Plesch and A. Stasko, *ibid.*, p. 2052.

[2] V. Bertoli and P. H. Plesch, *J. Chem. Soc.* (*B*), 1968, 1500.

[3] F. R. Jones and P. H. Plesch, *Chem. Comm.*, (*a*) 1969, 1230; (*b*) p. 1231; (*c*) 1970, 1018.

[4] O. Nuyken and P. H. Plesch, *Chem. and Ind.*, 1973, 379.

[5] P. P. Rutherford, *Chem. and Ind.*, 1962, 1614.

[6] E. Mathias and P. H. Plesch, *Chem. and Ind.*, 1971, 1043.

[7] F. Rohrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, 1966, **5**, 1542.

0.005 V relative to the saturated calomel electrode (aqueous) at 22 ± 3°. All polarograms were recorded with a Beckman Electroscan 30.

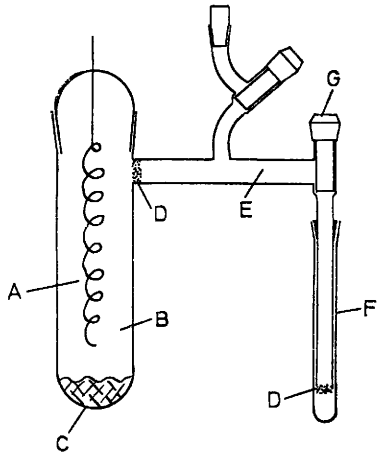

FIGURE 1 The reference electrode: A, silver-coated platinum wire; B, electrode compartment containing 0.1M-TBAP in methylene chloride; C, solid $(C_4H_9)_4NAg_3I_4$ and AgI; D, sintered glass disc; E, salt-bridge containing 0.1M-TBAP in methylene chloride; F, protecting sleeve containing same as E; G, Teflon taps. All e.m.f. values given in this paper are with respect to this electrode, except where stated otherwise

Technique.—All manipulations before the recording of the polarograms were carried out under vacuum. The polarographic cell, burettes for admitting the test solution, and solvent were assembled on the vacuum line as previously described [1d] and the counter-electrode was mounted in place of the mercury pool connection. Solid supporting electrolyte was weighed into the polarographic cell and the apparatus was then evacuated to $< 10^{-2}$ Pa for several hours. Freshly distilled solvent was added from the solvent burette. Nitrogen was admitted to the cell to a pressure in excess of atmospheric and the d.m.e. and the reference electrode were inserted through the appropriate ground-glass joints. After recording the polarogram of the supporting electrolyte, aliquot portions of the solution of oxonium salt were added from the burette (previously filled under vacuum).

When the secondary oxonium ions were being studied these were prepared *in situ* by mixing the oxygen compound with anhydrous perchloric acid in methylene chloride in the cell, each being added from a burette. For such systems the polarogram of the supporting electrolyte plus the ether or cyclic formal was recorded before the addition of the perchloric acid portions and this gave a base-current similar to that of the supporting electrolyte alone.

Polarograms were recorded at ambient temperature (22 ± 3°). The previously reported impurity wave [1d] was always present despite many attempts to eliminate it. This wave appeared to arise from impurities in the solvent as its height was independent of the amount and nature of the supporting electrolyte used. All potentials are reported relative to the ' silver iodide ' reference electrode described above and all currents are average currents corrected for residual current unless otherwise stated.

RESULTS AND DISCUSSION

The polarograms of triethyl- and of ethyl(tetramethylene)-oxonium hexafluoroantimonate in 0.05M-TBAFB in methylene chloride are shown in Figures **2** and **3** respectively. Both systems give a single reduction wave with the limiting current being diffusion controlled ($i_d \propto h^{\frac{1}{2}}_{\text{corr.}}$) and proportional to the concentration of the tertiary oxonium ion over the concentration ranges studied (Figure 4). The diffusion current constants, I_D $(= i_d/Cm^{2/3}t^{1/6})$, were **1.97** μA mM^{-1} mg$^{-2/3}$ s$^{\frac{1}{2}}$ for the triethyloxonium ion and **2.14** μA mM^{-1} mg$^{-2/3}$ s$^{\frac{1}{2}}$ for the ethyl(tetramethylene)oxonium ion, and the half-wave potentials were **—0.33** V (0.28mM) and **—0.296** ± 0.007 V (0.29—2.06mM), respectively. The plot of log $(i_d - i)/i$ against E had a slope of **49** mV for the triethyloxonium ion (0.28mM), and for the ethyl(tetramethylene)-, oxonium ion (0.29—2.06mM) two linear portions were obtained with slopes of **117** (first half of wave) and **78.5** mV (second half of wave) (values for 1mM). The onset of polarographic maxima at very low concentrations with the former compound made it difficult to obtain accurate values for the half-wave potential and the slope of the log plot, and it is difficult to attach significance to the value of **49** mV obtained. On the other hand, the reduction of the latter is obviously irreversible and the change in slope of the log plot at about the half-wave

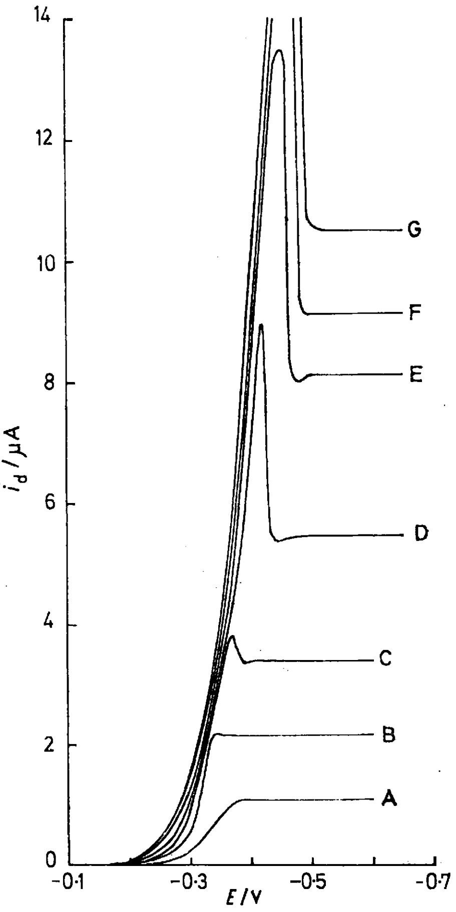

FIGURE 2 Polarograms at increasing concentrations of Et_3O^+; A, 0.276; B, 0.461; C, 0.716; D, 1.26; E, 1.76; F, 2.08; and G, 2.42mM in 0.05M-TBAFB in methylene chloride

potential may indicate a change in electrode mechanism at the more negative potentials.

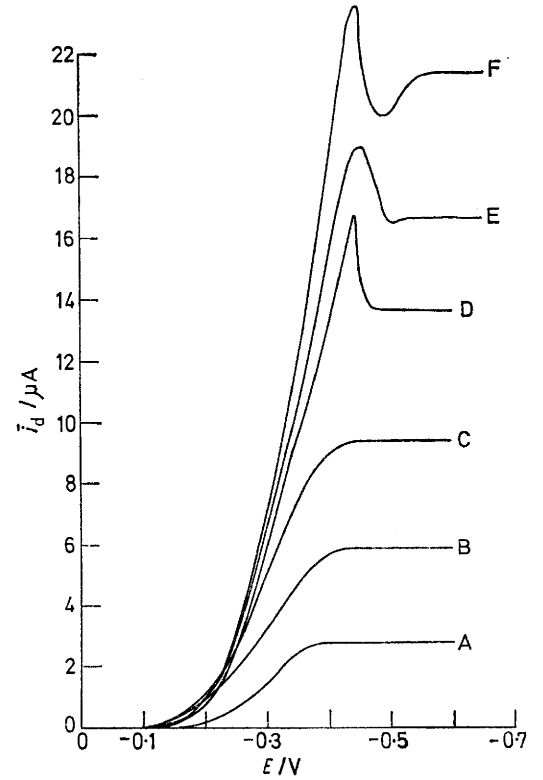

FIGURE 3 Polarograms at increasing concentrations of ethyl(tetramethylene)oxonium ion; A, 0.677; B, 1.31; C, 2.06; D, 2.96; E, 3.64; and F, 4.57mM in 0.05M-TBAFB in methylene chloride

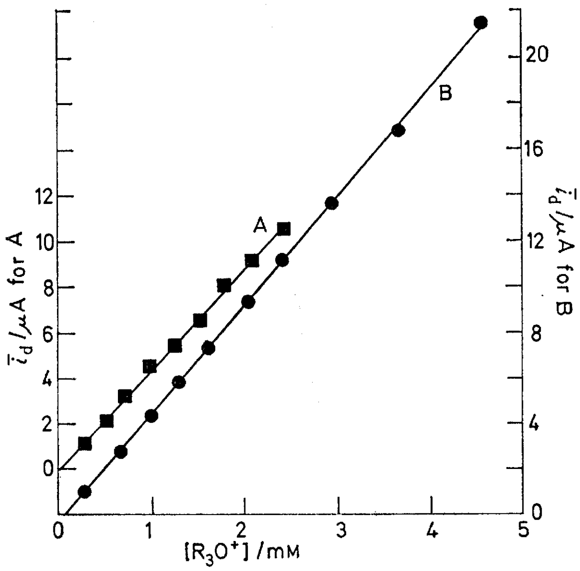

FIGURE 4 Plot of i_d against concentration of tertiary oxonium ion R_3O^+: (A) Et_3O^+; (B) $EtO^+[CH_2]_4$ in 0.05M-TBAFB in methylene chloride

The single reduction waves obtained for the triethyl- and ethyl(tetramethylene)-oxonium ions are consistent with a single one-electron reduction (1) of the oxonium ion to the radical. As no analysis of the product was

$$(C_2H_5)_3O^+ + e^- \longrightarrow (C_2H_5)_3O\cdot \longrightarrow \text{products} \qquad (1)$$

attempted, the fate of the immediate product of the electron transfer (the radical) is unknown.

We can show that the reduction waves are not only consistent with a one-electron process, but that they actually do represent such a process. This conclusion is based on a comparison with the polarographic waves for the reductions of the trityl cation and the tropylium cation which are known to be one-electron processes.[1d,2] The value of I_D for trityl hexafluoroantimonate in 0.1M-TBAP in methylene dichloride in our three-electrode cell was found to be 1.73 μA mM^{-1} mg$^{-2/3}$ s$^{1/2}$; there was only one wave ($E_{1/2} = +0.87$ V) which shows that the SbF_6^- ion is not reduced up to —0.6 V, the break-down potential of the base-electrolyte. The I_D for the tropylium ion was 2.5 μA mM^{-1} mg$^{-2/3}$ s$^{1/2}$ under similar conditions.

The question now arises, what is the state of the ion which is being reduced? Is it a free ion, a paired ion, or part of a triple ion? Whilst the nature of the species which is involved in the electron transfer step at the electrode surface cannot be ascertained from the present studies, a reasonable picture of the species present in the bulk of the solution can be obtained.

We will assume that in these solutions the small concentrations of hexafluoroantimonate ions do not affect the system and that the tertiary oxonium ions show no specific preference for participating in ion-pairs or triple ions. That is, to a first approximation, both cations and both anions can be considered to be uniformly distributed over the ion-pairs and triple ions present. If $[A^+] \equiv [R_3O^+] + [Bu_4N^+]$ and $[B^-] \equiv [SbF_6^-] + [BF_4^-]$, the equilibria involved can be represented by (2) and (3).

$$A^+ + B^- \rightleftharpoons A^+B^-, \quad K_2 \qquad (2)$$

$$\left.\begin{array}{l} A^+B^- + A^+ \rightleftharpoons A^+B^-A^+ \\ A^+B^- + B^- \rightleftharpoons B^-A^+B^- \end{array}\right\} K_3 \qquad (3)$$

If one makes the conventional assumption that $[A^+B^-A^+] = [B^-A^+B^-] \equiv [T]/2$, the relevant equilibrium constants are given by equations (4) and (5) where $[X] = [A^+]$ or

$$K_2 = \frac{[A^+B^-]}{[A^+][B^-]\gamma_\pm{}^2} \qquad (4)$$

$$K_3 = \frac{[T]\,\gamma_T}{2\,[A^+B^-][X]\gamma_X} \qquad (5)$$

$[B^-]$. The values of K_2 and K_3 were estimated as follows: Jones and Plesch[3c] obtained for Et_3O^+ PF_6^- in methylene chloride at 298 K $K_2 = 0.8 \times 10^5$ l mol^{-1}. Since in the present system the most abundant anion is BF_4^- which is smaller than PF_6^-, a value of 10^5 l mol^{-1} for K_2 is probably within a factor of 2 of the actual value. Triple ion formation constants K_3 are rare in the literature, but probably Beard and Plesch's value of $K_3 = 10^2$ l mol^{-1}, obtained for triethylmethylammonium iodide

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[8] J. H. Beard and P. H. Plesch, *J. Chem. Soc.*, 1964, 4075.

in methylene chloride at 298 K is as good a guide as can be found, because in the present system the most abundant cation is also a tetrahedral ammonium ion.[8] The values of the activity coefficients $\gamma_{\pm}$, γ_{T}, and γ_{X} can be estimated only very approximately by the Debye–Hückel equation for a solvent of such low dielectric constant as methylene chloride; the same value of 0.2 was calculated for all three.

From the K_2, K_3, and γ values the concentrations of the different species given in the Table were calculated for a typical solution containing 50mM of base electrolyte and 1mM of oxonium salt. Thus the dominant species in these solutions is the ion-pair, with the triple and single ions having approximately the same, much lower, concentrations; even relatively large variations in K_2 and K_3 would hardly affect this picture.

	$[A^+]$ or $[B^-]$(mM)	$[A^+B^-]$(mM)	$[T]/2$(mM)
All $\gamma = 1$	0.5	48	0.7
All $\gamma = 0.2$	4.1	39	2.8

Although the triple and the single ions are present in small but significant concentrations, only one polarographic wave was observed. Thus, either all species containing the oxonium ion are reduced at the same potential (which seems unlikely), or the equilibria between the electroactive species and other species containing oxonium ions are rapid enough for their conversion to the electroactive one to be completed in a time much shorter than the life of a mercury drop. Since the mercury drop is negatively charged at the potentials at which the reduction occurs, the most likely species present on the electrode surface, and hence most likely to be the electroactive species, would be the free oxonium ion.

Since for these tertiary oxonium ions the diffusion current is directly proportional to their total added concentration, they can be assayed polarographically at least down to 10^{-4}M with standard equipment. The half-wave potentials showed no significant variation with concentration so that they can probably be used for the identification of tertiary oxonium ions, at least according to type, although the presence of maxima at the higher concentrations is a complication. As expected, the unstrained, more stable triethyloxonium ion has a more negative $E_{\frac{1}{2}}$ than the ethyl(tetramethylene)oxonium ion, which is strained.

The much more complicated behaviour of some secondary oxonium ions will be described in Part II.

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