The Association Constants of Triethyloxonium Salts and their Solvation by Diethyl Ether

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Summary From conductimetric measurements we have obtained the association constants of two tertiary oxonium salts in methylene dichloride solution, and also direct evidence for solvation of the cation by diethyl ether.

IN connection with our studies of the polymerisation of cyclic formals[1] by triethyloxonium hexafluorophosphate (I), and tetrafluoroborate (II), and of the decomposition of these salts,[2] we required information on their associative behaviour and their solvation by ethers. We report the results of conductimetric measurements on methylene dichloride solutions at 273·16°K and present here the first equivalent conductances and association constants of oxonium salts and direct evidence for solvation of the cation by an ether.

The salts (I) and (II) were obtained as described;[1,2] phials of diethyl ether were prepared *in vacuo* by standard methods. Conductivities were measured with a vacuum-cell fitted with bright platinum electrodes, a phial-breaking device, and a magnetic stirrer, and it was fused to the vacuum and solvent-dosing lines.

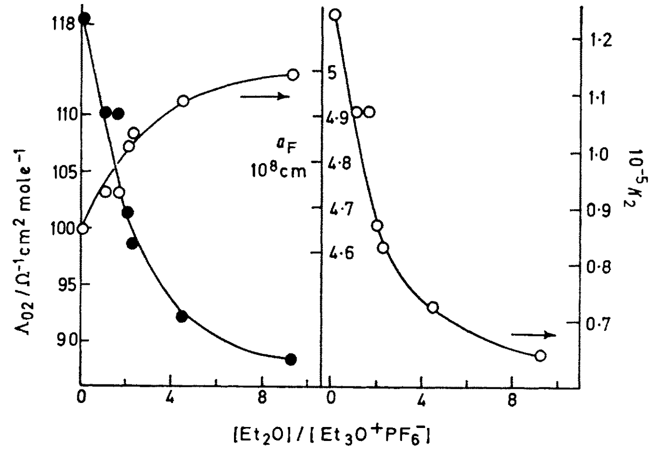

FIGURE. *The dependence of* Λ_{02} (●) *and* a_F (○) (*left*) *and of* K_2 (*right*) *on* $[Et_2O]/[Et_3O^+PF_6^-]$.

The conductivity of solutions of (I) was measured over a range of concentrations (c) from 10^{-2} to 8×10^{-6} M. The curves obtained for progressive dilution (by distilling solvent into the cell) were identical with those obtained by progressive concentration (by distilling solvent from the cell). The data for $c < 1·3 \times 10^{-3}$ M were analysed in terms of equation(I) by an iterative procedure.

$$F(z)/\Lambda = 1/\Lambda_{02} + [c\Lambda y_{\pm}^2/F(z)]K_2/\Lambda_{02}^2 \qquad (1)$$

where Λ_{02} is the equivalent conductance at $c = 0$, $y_{\pm}$ is the mean ionic activity coefficient, and K_2 is the binary association constant for the equilibrium

$$Et_3O^+ + X^- \rightleftarrows Et_3O^+X^-,\ X = PF_6 \text{ or } BF_4,$$

and is defined by the equation

$$K_2 = [Et_3O^+X^-]/[Et_3O^+][X^-]y_{\pm}^2 \qquad (2)$$

The values of $F(z)$ have been given by Fuoss.[3] The results are in the Table, where a_F is the distance of closest approach of the ions, calculated by Fuoss's equation.[4] The Table also contains the results of an analysis of our data ($c < 1·6 \times 10^{-4}$ M) by the method of Hanna, Pethybridge, and Prue[5] based on Fernåndez-Prini's[6] expansion of the Fuoss–Hsia equation; the results quoted, which give the best fit, correspond to an association distance of $2·67 \times 10^{-7}$ cm. An equally good fit was obtained in a similar manner using the Limiting Law (L.L. in the Table). The best values are probably $K_2 = (1·24 \pm 0·04) \times 10^5$ l mole^{-1} and $\Lambda_{02} = 118 \pm 1\ \Omega^{-1}$ cm^2 mole^{-1}.

The parameters derived from the conductance study of $Et_3O^+PF_6^-$ *in methylene dichloride at* 273·16°K ($\epsilon = 10·02$)

Equation	$10^{-5}K_2$ (l mole^{-1})	Λ_{02} (Ω^{-1}cm^{2}mole^{-1})	σ[a] (Ω^{-1}cm^{2}mole^{-1})	10^8a_F (cm)	No. of points
(1)	1·26	118·53	—	4·66	29
F.-H.[b]	1·195	117·00	0·36	—	16
L.L.[c]	1·269	118·53	0·36	—	16

[a] Standard deviation.
[b] K_2 calculated assuming $\Lambda_{02} = 117·00$ which is the value giving the best fit.
[c] K_2 calculated assuming the Λ_{02} given by equation (1).

The conductivity of solutions of (II) was measured for $c = 1·4 \times 10^{-2}$ to 3×10^{-4} M. Because of dosing difficulties and the relatively rapid decomposition of this salt in solution,[2] it was not possible to obtain reliable results at lower concentrations. The plot of $1/\Lambda$ against $c\Lambda$ (Ostwald) was strongly curved towards the $c\Lambda$-axis and the intercept gave an improbably small value of Λ_{02}. The Fuoss-Kraus plot for triple ions[7] ($\Lambda c^{1/2}$ against c) still had a slight curvature. From its linear part and an estimate of *ca.* 105 for Λ_{02}, and Λ_{03} (ternary ions) conventionally taken as $\Lambda_{02}/3$, approximate values of $K_2 \approx 2 \times 10^5$ l mole^{-1} and $K_3 \approx 10^2$ l mole^{-1} were obtained (K_3 is the mean association constant for formation of triple ions).

The solvation of oxonium salts by diethyl ether was investigated by applying equation (1) to results obtained on solutions of (I) in methylene dichloride containing up to

10 moles of diethyl ether per mole of (I), and thus determining Λ_{02}, K_2, and a_F for each solution. The results in the Figure show that as the ratio [ether]/[(I)] increases, Λ_{02} and K_2 decrease asymptotically to a limiting value; a_F increases only very slightly. We are aware of the criticisms expressed by various workers concerning the significance of a_F, but in the present instance at least its variation appears to be meaningful.

Since the concentration of diethyl ether was too small to affect the viscosity and the dielectric constant of the medium, and since it is unlikely that the anion would be solvated to any appreciable extent by the ether,[8] the observed changes must reflect the progressive solvation of the cation. Evidently, Λ_{02} and K_2 are average values for ion-pairs consisting of X^- with Et_3O^+ and X^- with $Et_3O^+(Et_2O)_n$, where n may vary with the ether concentration. The decrease of Λ_{02} reflects the increasing average size of the cations with increasing ether concentration, and the fall of K_2 must be due to the decrease in the charge-density of the cation due to solvation. The fact that a_F increases only slightly indicates that in the ion-pair the Et_3O^+ is sandwiched between the anion and the ether, and it suggests that $n = 1$.

We thank Dr. S. R. C. Hughes for carrying out the computations according to equation (1) and Dr. J. E. Prue for those by the F.–H. equation and the L.L. by means of their computer programs, and for helpful discussions.

(*Received, June* 18*th*, 1970; *Com.* 949.)

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