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SHORT COMMUNICATION

The Electrolytic Conductance of Fluoromethylphosphoranes in Acetonitrile

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Previous studies of the conductance of compounds of type R_3PX_2 (R = organic group; X = halogen) in ionising solvents has been restricted to bromo- and chloro- compounds [1,2]. We now report the results of measurements of the electrolytic conductance in acetonitrile of the fluoromethylphosphorane $(CH_3)_3PF_2$ and the related derivatives $(CH_3)_2PF_3$ and CH_3PF_4 .

Each of these compounds dissolves readily in acetonitrile (dielectric constant, 36.7 at 25^o) producing solutions the specific conductances of which exceed that of the pure solvent by a factor of about one hundred. Measurements were made in the concentration range 0.006 - 0.033 mol dm^{-3} and the values of molar conductance (Λ_M) obtained were all less than 10 S cm^2 mol^{-1}. For comparative purposes values of molar conductance at 25^o and at concentration 0.01 mol dm^{-3} are given below for each compound:

Compound	Λ_M / $S\ cm^2\ mol^{-1}$
$(CH_3)_3PF_2$	9.2
$(CH_3)_2PF_3$	6.2
CH_3PF_4	3.7

The magnitude of the values found for Λ_M indicate that the fluoromethylphosphoranes are behaving as weak electrolytes in acetonitrile (for a strong 1:1 electrolyte in acetonitrile $\Lambda_M \sim 110-130\ S\ cm^2\ mol^{-1}$ in the concentration range used [3]). Therefore under the influence of the polar solvent of high dielectric constant the molecular phosphoranes are induced to undergo partial ionisation, thus, for example,

$$(CH_3)_3PF_2 \rightleftarrows (CH_3)_3PF^+ + F^-$$

The substituted phosphonium ion, $(CH_3)_3PF^+$, has been shown to be present in salts with the BF_4^- or AsF_6^- anions [4] (likewise the $(CH_3)_2PF_2^+$ ion has been reported as the PF_6^- and AsF_6^- salts [5]).

The relative magnitudes of the molar conductance values for the three phosphoranes are of considerable interest. It is found that for any given concentration within the range studied, the order of molar conductance is

$$(CH_3)_3PF_2 > (CH_3)_2PF_3 > CH_3PF_4$$

It has already been pointed out [6] that in the trigonal bipyramidal molecules of these compounds the P - F (axial) bond strengths follow the order

$$(CH_3)_3PF_2 < (CH_3)_2PF_3 < CH_3PF_4$$

This correlates well with the molar conductance trend and leads to the reasonable assumption that in the ionisation process an axial fluorine atom is released as fluoride ion. Since increasing the number of equatorial CH_3 groups leads to increased electron release to the central phosphorus atom causing a progressive weakening of the axial P-F bond, a parallel increase in the degree of ionisation of the phosphoranes in the ionising solvent would be expected thus leading to the observed variation in conductance.

It is relevant to draw attention here to the observation that changing the nature of R in R_nPX_{5-n} whilst keeping n and X the same can also produce changes in the electrolytic conductance behaviour of this type of compound. These changes may be large; for example $(C_6H_5)_3PCl_2$ is a fairly strong electrolyte in acetonitrile (Λ_M = 78 S cm^2 mol^{-1}; concentration = 0.01 mol dm^{-3}) [2] whereas $(C_6F_5)_3PCl_2$ is a very weak electrolyte (Λ_M = 0.5 S cm^2 mol^{-1}; concentration = 0.01 mol dm^{-3}) [7]. Likewise $(CH_3)_3PBr_2$ is a fairly strong electrolyte whilst $(CF_3)_3PBr_2$ is a very weak electrolyte [1,8]. There would appear, therefore, to be some correlation between the inductive effect of the organic group in R_nPX_{5-n} and the tendency for these compounds to undergo ionisation in polar solvents; the more strongly electronegative the group attached to the phosphorus atom the more likely it is that the phosphorane will be a weak electrolyte (that is the molecular form is favoured).

EXPERIMENTAL

The preparation of the fluoromethylphosphoranes has been described elsewhere [6,9]. Pure anhydrous acetonitrile for the conductance studies was prepared by Smith and Witten's method [10] (the specific conductance of the pure solvent was 10^{-7} S cm^{-1} at 25^o). For the conductance measurements use was made of a small dipping electrode type of cell which was adapted to enable introduction of solute and solvent by distillation in vacuo. The electrodes were of smooth platinum and readings of conductance were obtained using a Wayne Kerr universal bridge (B641).

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