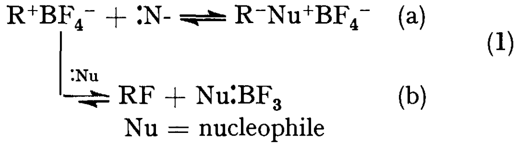
Ion-pair Dissociation Equilibria for Trityl Hexafluoro-arsenate and -antimonate in Polar Solvents

By **Wacław Gogolczyk, Stanisław Słomkowski,** and **Stanisław Penczek,*** Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, 90-362 Lodz, Poland

Dissociation constants (K_D) for $Ph_3C^+AsF_6^-$ and $Ph_3C^+SbF_6^-$ in CH_2Cl_2 and CH_2Cl_2–CH_3NO_2 were determined. The entropies and enthalpies of dissociation in CH_2Cl_2 (AsF_6^- ΔH −2.2 ± 0.2 kcal mol^{-1}, ΔS −25.1 ± 0.8 cal mol^{-1} K^{-1} SbF_6^- ΔH −2.2 ± 0.5 kcal mol^{-1}, ΔS −25 ± 2 cal mol^{-1} K^{-1}) are in agreement with the previously determined parameters for $SbCl_6^-$ anion, taking into account the larger diameter of the latter anion. The values of the Stokes radii of AsF_6^- and SbF_6^- ions (both 2.2 Å) as well as the effective interionic distances in both ion-pairs (equal to 7.1 Å) were evaluated. The values of K_D increase *ca.* 10^2 times at 25 °C on passing from CH_2Cl_2 to CH_3NO_2 as solvent. This gives an opportunity to study reactions with predominantly paired (in CH_2Cl_2) or free (in CH_3NO_2) cations.

IONIC reactions can proceed with ions in various states of aggregation: free, paired, and/or aggregated. Therefore, studies of the reactivities of these various forms are important for any structure–reactivity relationship. Indeed, differences in reactivities of *e.g.* free and paired ions coupled with different dissociation constants for two ionizable compounds under study can lead to meaningless conclusions if the overall rates of reactions of these two compounds with the same reactant are compared.

On the other hand, the chemical role of the counterions is sometimes overlooked. Some complex anions, such as BF_4^- or $SbCl_6^-$, were recently shown to be unstable and to decompose during the course of reaction (1). Therefore we looked for systems in which we could eliminate reactions like (1b) and in which we could vary over a large range the proportion between free and paired ions.



$$R^+BF_4^- + :N- \rightleftharpoons R^-Nu^+BF_4^- \quad (a)$$

(1)

$$\xrightarrow{:Nu} RF + Nu:BF_3 \quad (b)$$

Nu = nucleophile

In the present work we report on the determination of the dissociation constants (K_D) of $Ph_3C^+AsF_6^-$ and $Ph_3C^+SbF_6^-$ in CH_2Cl_2 as solvent. Studies were also extended to CH_2Cl_2–CH_3NO_2 as solvent and to CH_3NO_2 itself, because the much higher dissociation constant of trityl ion-pairs in these solvents allows almost separate reactions of paired and free ions to be studied, when CH_2Cl_2 (mostly ion-pairs) and CH_3NO_2 (mostly free ions) are used as solvent.

The dependences of K_D on $1/T$ and on the dielectric constant of the medium gave us further insight into the structure of the trityl ion-pairs. AsF_6^- and SbF_6^- anions were found to be the most stable, *i.e.* these anions do not disintegrate during chemical reactions, in contrast to BF_4^- and $SbCl_6^-$.

From previously published work on the dissociation of the trityl ion-pairs, only the following data are available (solvent in parentheses): $SbCl_6^-(CH_2Cl_2)$,[1,2] $Sb(OH)Cl_5(CH_2Cl_2)$,[1] $ClO_4^-(C_2H_4Cl_2)$.[3] For $Ph_3C^+AsF_6^-$ and $Ph_3C^+SbF_6^-$ only preliminary measurements of K_D in CH_2Cl_2 at room temperature have been reported.[4]

RESULTS AND DISCUSSION

The dissociation constants were measured in CH_2Cl_2, CH_2Cl_2–CH_3NO_2, and CH_3NO_2. Measurements in CH_2Cl_2 were carried out in the temperature range −25 to 25 °C for AsF_6^-, and −16 to 25 °C for SbF_6^-. Values of the dielectric constant, density, and viscosity, necessary for the evaluation of K_D, were taken from ref. 5. Concentrations of the trityl salts were corrected for the change in density.

The equivalent conductance Λ was evaluated from the measured conductances. The dissociation constant K_D was determined from the dependence of the equivalent conductance on concentration (c), according to Fuoss' method.[6,7] First, from the dependence of Λ on $c^{1/2}$ the approximate value of the equivalent conductance at infinite dilution (Λ_0) was determined and then for each experimental point the correction factor F(z) was evaluated. Afterwards, from the dependence (2) where

$$F(z)/\Lambda = 1/\Lambda_0 + c\gamma^2\Lambda/[\Lambda_0^2 K_D] \qquad (2)$$

γ is the activity coefficient, the corrected Λ_0 and K_D values were determined.

Determined in this way K_D and Λ_0 values in CH_2Cl_2 solution are given in Table 1.

The values of the dissociation constants measured for $Ph_3C^+AsF_6^-$ and $Ph_3C^+SbF_6^-$ are close to these determined by Szwarc[1] for $Ph_3C^+SbCl_6^-$ (1.4×10^{-4} mol l^{-1} at 25 °C in CH_2Cl_2) and Ledwith[2] (1.9×10^{-4} mol l^{-1}). The equivalent conductances are however, slightly larger than for $SbCl_6^-$ (Λ_0 100.0[1] and 108 Ω^{-1} cm^2,[2] respectively). This is expected, because the smaller anions should have higher mobilities reflected by higher equivalent conductances at infinite dilution.[8] This would not be true for highly solvating media, because the smaller the ion the higher the tendency to solvation

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[1] N. Kalfoglou and M. Szwarc, *J. Phys. Chem.*, 1968, **72**, 2233.

[2] P. M. Bowyer, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc.* (*B*), 1971, 1511.

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[5] M. Szwarc, 'Carbanions, Living Polymers, and Electron Transfer Processes,' Interscience, New York, 1968.

[6] R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 476.

[7] R. M. Fuoss and F. Accascina, 'Electrolytic Conductance,' Interscience, New York, 1959.

[8] D. F. Evans and M. A. Matesich, 'Techniques of Electrochemistry,' eds. E. Yeager and A. J. Salkind, Wiley–Interscience, New York, 1973, vol. 2, p. 18.

and the larger the effective radius of the ion: however methylene chloride does not seem to be a good solvating agent for anions.

From the plot of $\ln K_D$ on the reciprocal of the absolute temperature for both $Ph_3C^+AsF_6^-$ and $Ph_3C^+SbF_6^-$ the enthalpy and entropy of dissociation were determined (Table 2).

TABLE 1

The dissociation constants K_D and equivalent conductances at infinite dilutions Λ_0 for $Ph_3C^+AsF_6^-$ and $Ph_3^+SbF_6^-$ in CH_2Cl_2 solution

T/K	10^4K_D/mol l^{-1}	Λ_0/Ω^{-1} cm^{-2}
(*a*) $Ph_3C^+AsF_6^-$		
248	2.9	70.9
273	1.9	96.9
282	1.9	104.2
293	1.4	137.6
298	1.4	126.9
298 *	2.2	95.8
(*b*) $Ph_3C^+SbF_6^-$		
257	3.1	81.7
270.5	2.2	100.9
273	2.4	97.1
286	2.5	96.8
287	1.9	116.7
293	2.0	116.8
295.5	1.5	118.4
298	1.6	124.6
298 *	2.5	84.8

* Ref. 4.

TABLE 2

Salt	$-\Delta H_D$/kcal mol^{-1}	$-\Delta S_D$/cal mol^{-1} K^{-1}
$Ph_3C^+AsF_6^-$	2.2 ± 0.2	25.1 ± 0.8
$Ph_3C^+SbF_6^-$	2.2 ± 0.5	25 ± 2

The only thermodynamic parameters for dissociation available in the literature for trityl salts were determined by Szwarc[1] and Ledwith[2] for $Ph_3C^+SbCl_6^-$ (Table 3).

TABLE 3

	Ref. 1	Ref. 2
ΔH_D/kcal mol^{-1}	-0.8 ± 0.3	-2.0
ΔS_D/cal mol^{-1} K^{-1}	-17	-23

The exothermicity of dissociation comes mostly from the heat of solvation. For the same energy of solvation ΔH_D for AsF_6^- and SbF_6^- should be less negative than for $SbCl_6^-$, because the dissociation of the larger $SbCl_6^-$ anion should be easier due to the weaker Coulombic attraction. Actually, dissociation of salts with AsF_6^- and SbF_6^- seems to be slightly more exothermic and this effect may account for the higher energy of solvation for these anions, overshadowing the differences in the Coulombic attraction.

From the dependence of K_D on temperature the effective interionic distance could be determined, by using the Denison–Ramsey[9] approach, based on the sphere in continuum ' model, which for the dissociation constant for 1 : 1 electrolytes gives formula (3) (e =

$$K_D = \exp[-e^2/(kT\varepsilon a)] \qquad (3)$$

electron charge, k = Boltzmann constant, T = absolute temperature, ε = dielectric constant, and a = effective interionic distance). From formula (3) we calculated a 7.1 (AsF_6^-) and 7.3 Å (SbF_6^-) at 0 °C. Ledwith[2] determined at the same temperature a 7.6 Å for $Ph_3C^+SbCl_6^-$

Our values for the interionic distances can also be compared with the same values calculated on the basis of the Stokes radii of the components of the ion-pairs. Remembering that equation (4) holds where η =

$$r_s^- = 0.820/\eta\Lambda_0^- \qquad (4)$$

viscosity in poises, r_s^- = Stokes radius for an anion, and Λ_0^- = the equivalent conductance at the infinite dilution for the anion, and that equation (5) where Λ_0

$$\Lambda_0 = \Lambda_0^+ + \Lambda_0^- \qquad (5)$$

is the measured equivalent conductance at the infinite dilution we could determine r_s^- for AsF_6^- and SbF_6^- from both formula (4) and (5). Λ_0 is known from experiment, Λ_0^+ for Ph_3C^+ cation was determined previously (Λ_0^+ 31.3 Ω^{-1} cm^2).[2] Thus (*cf.* Table 1), at 0 °C in CH_2Cl_2 Λ_0^- is 65.6 for AsF_6^- and 65.8 Ω^{-1} cm^2 for SbF_6^-. Thus, $r_s^-(AsF_6^-,SbF_6^-) = 2.2$ Å. Since r_s^+ = 4.9 Å,[2] the interionic distance ($a = r_s^+ + r_s^-$) becomes 7.1 Å, in agreement with the value determined from equation (3).

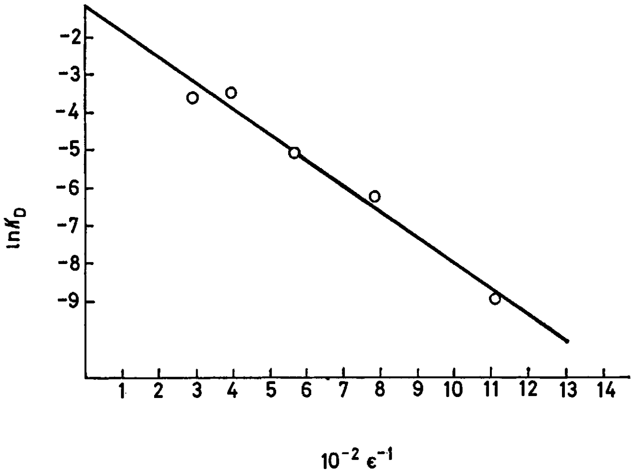

FIGURE 1 Linear dependence of $\ln K_D$ (dissociation constant) on the reciprocal of the dielectric constant for $Ph_3C^+AsF_6^-$ in mixed CH_2Cl_2–CH_3NO_2 solvent at 25 °C

The dependence of $\ln K_D$ on $1/\varepsilon$, measured for CH_2Cl_2–CH_3NO_2, is linear (*cf.* Figure 1), indicating that there are no side reactions involving nitromethane and upsetting the ion-pair–free ions equilibrium.

The mobilities of ions decrease (as judged on the basis of Λ_0 values for $Ph_3C^+AsF_6^-$) when passing from CH_2Cl_2 (Λ_0 126.9 Ω^{-1} cm^2) to CH_3NO_2 (Λ_0 118.8 Ω^{-1} cm^2), indicating the stronger solvation power of CH_3NO_2. The dissociation constants increase (Figure 1) by two orders of magnitude; thus in CH_2Cl_2 solvent at 25 °C $K_D = 1.4 \times 10^{-4}$ and in CH_3NO_2 2.4×10^{-2} mol l^{-1}. Thus, if the concentration range of the trityl cation is

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[9] J. T. Denison and J. B. Ramsey, *J. Amer. Chem. Soc.*, 1955, **77**, 2615.

from 10^{-4} to 10^{-3} [region of concentration used, because of the molar extinction coefficient of Ph_3C^+ ($\varepsilon_{max.}$ 3.95×10^4)], then the proportions of free and paired ions are as shown in Table 4.

TABLE 4

Proportion (mol %) of free ions in CH_2Cl_2 and CH_3NO_2 solutions calculated for $Ph_3C^+AsF_6^-$ at 25 °C

	Concentration	
Solvent	10^{-3}M	10^{-4}M
CH_2Cl_2	~20	~50
CH_3NO_2	~50	~90

Thus, our work shows that solutions of trityl salts in nitromethane behaves 'normally,' *i.e.* there are no chemical reactions decreasing the concentration of ions; this is in agreement with our u.v.–visible studies which show that $\varepsilon_{max.}$ in both CH_2Cl_2 and CH_3NO_2 are the same.

The high degree of the dissociation of the trityl salts in CH_3NO_2 and the low degree in CH_2Cl_2 enables the studies of reactivities of free ions and ion-pairs.

EXPERIMENTAL

Materials.—Trityl salts (AsF_6 and SbF_6^-) (Ozark Mahoning) were purified by several recrystallisations by additions of CCl_4 to solutions in CH_2Cl_2.[10] This procedure was repeated until no more traces of Ph_3CH or Ph_3COH could be detected by g.l.c. in the solvent after precipitation. The salts have $\lambda_{max.}$ (CH_2Cl_2) 408 ($\varepsilon_{max.}$ 3.95×10^4) and 435 (3.95×10^4) nm. Methylene chloride, rigorously purified essentially as described by Cheradame and Sigwalt,[11] was stored in ampoules over a sodium mirror below 0 °C. Nitromethane after treatment with $CaCl_2$ was heated with CaH_2 and fractionated twice under reduced pressure of nitrogen. Final purification and storage involved treatment with sodium mirrors under vacuum, as described for methylene chloride. A white precipitate which forms at the earlier stages of treatment of CH_3NO_2 with sodium mirror should be handled with special care; to avoid explosions it is recommended that it is dissolved carefully in isopropyl alcohol.

Instrumentation and Measurement of K_D.—Taking advantage of the availability of the Teflon–glass stopcocks, measurements applying high vacuum technique were performed in the apparatus shown in Figure 2, instead of completely sealed apparatus, as usually used for conductivity measurements for ions sensitive to water or oxygen.[5]

Our apparatus consists of two vessels, upper (A) and bottom (B), connected through the Teflon (Rotaflo) stopcocks and a calibrated tube. The conductivity cell (C) was sealed to vessel B. Solutions with known concentrations of the trityl cations were prepared separately in a vessel attached by a ground joint and stopcock to the apparatus. After distilling the known amount of solvent to the bottom vessel B and closing the corresponding stopcocks, the required amount of the substrate solution was transferred to the calibrated tube. Solutions for measurements (concentration 10^{-5}—10^{-3}M) were prepared by introducing measured amounts of the substrate solution from the calibrated tube into the known amount of solvent in vessel B.

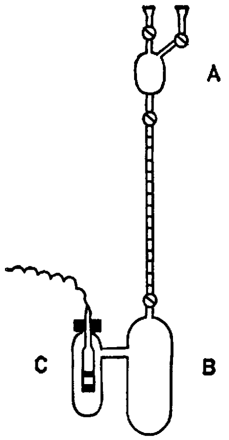

FIGURE 2 Apparatus for conductivity measurements

Conductivity measurements were performed with a Radelkis conductometer OK 102/1. In the region 0.1—500 μS the conductivity cell was fed with a 60 Hz alternating current, and in the region 500 μS—0.5 S with 3 kHz alternating current.

[6/2192 *Received*, *29th November*, 1976]

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[11] H. Cheradame, M. Mazza, Nguyen Anh Hung, and P. Sigwalt, *Eur. Polymer J.*, 1973, **9**, 375.