Effect of Alkyl Substituent Chain Length on the Ion-pair Dissociation Equilibria of Quaternary Ammonium Hexachloroantimonate Salts in Dichloromethane

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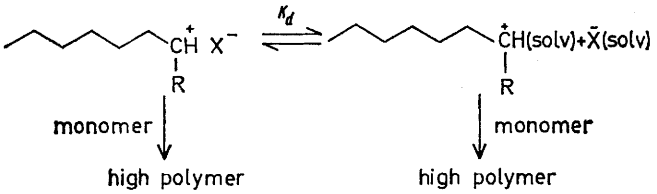
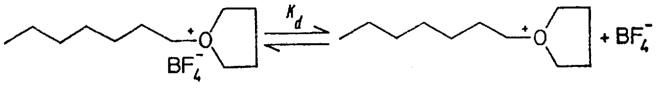
Ion pair dissociation constants K_d and molar conductances at infinite dilution λ_0 for a range of quaternary ammonium hexachloroantimonates in dichloromethane have been determined from conductance measurements. The values of K_d are virtually independent of the chain length of alkyl substituents on the ammonium ion, indicating that even an oligomeric substituent is unlikely to change K_d significantly. In contrast the corresponding Stokes' radii of the cations r_s^+ increase with increasing size of substituent, the relative values being consistent with a coiled conformation of the alkyl groups.

In the investigation of the reactivity of propagating ionic intermediates in the cationic polymerisation of vinyl monomers, a knowledge of the ion-pair dissociation constant, K_d, of the polymeric salt is required before a quantitative evaluation of kinetic data becomes possible.[1]



This is necessary because it is now well known that free ion and ion-paired species can have substantially different reactivities,[2] and the proportions of each entity present in a system must therefore be known. Unfortunately the high reactivity of carbocations, and in particular their propensity to isomerise and participate in transfer reactions in polymerisations,[1] has precluded the direct determination of dissociation constants from investigations of polymerising solutions.

In the case of the ring opening polymerisation of tetrahydrofuran the propagating cyclic oxonium ion is more stable, and under stringent conditions of purity ' living ' polymeric cations can be obtained.[3] Indeed Sangster and Worsfold [4] have succeeded in studying the dissociation of ' living ' oligomeric oxonium ion pairs directly, enabling them to make a comprehensive kinetic analysis of their polymerisations. In order to allow some progress to be made in investigations of corresponding vinyl systems, orders of magnitude for values of dissociation constants have been obtained by assuming comparibility with data for model cations, often the initiating species, with the same counterion as that used in polymerisation reactions.[5]



The present investigation was undertaken to determine whether or not the dissociation constants of quaternary ammonium ion pairs, with hexachloroantimonate as counterion, varied significantly as the chain length of one of the ammonium ion substituents was increased, with the hope that it might be possible to make some extrapolation to the situation of a polymeric chain as the substituent. A simple conductance technique was employed.[6,7]

EXPERIMENTAL

Materials.—Dichloromethane was purified and stored under vacuum as described previously.[6] Benzyldimethylphenylammonium hexachloroantimonate ($Me_2PhCH_2PhN^+SbCl_6^-$) was prepared as in the literature.[8] It was recrystallised from methanol and had m.p. 162° (decomp.) Benzyldimethyl-n-hexadecylammonium hexachloroantimonate ($Me_2PhCH_2C_{16}H_{33}N^+SbCl_6^-$) was prepared from the corresponding chloride (B.D.H.) by reaction with antimony pentachloride in carbon tetrachloride. Recrystallisation from methanol gave a white solid, m.p. 78—81°. Tetraethylammonium hexachloroantimonate ($Et_4N^+SbCl_6^-$) was obtained similarly from its chloride, and after recrystallisation from methanol it had m.p. 289—292° (decomp.). The chloride itself was prepared from the bromide (B.D.H.) using a slurry of silver chloride in methanol, the procedure being similar to that reported by Ford-Moore.[9] The remaining hexachloroantimonate salts were prepared by quaternisation of triethylamine with the appropriate alkyl bromide or iodide in dry acetone, followed by conversion to the chloride and finally the hexachloroantimonate derivatives. All these salts were recrystallised from methanol and m.p.s were 207—208, 142—144, 84—85, and 110—112° for the n-butyl, n-octyl, n-dodecyl, and n-hexadecyl derivatives respectively. Satisfactory elemental analyses were obtained and the results are summarised in Table 1.

Conductance Technique.—Ion-pair dissociation constants K_d and molar conductances at infinite dilution λ_0 were obtained from measured conductances of salt solutions as a function of concentration. The cell used was a modified version of one described before [6] and is illustrated in Figure 1. Calibration was achieved with an aqueous 0.01M-KCl

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solution at 0°, the measured cell constant being 0.009 64 cm^{-1}.

An initial solution of a given salt was made up under vacuum in A (Figure 1) by distilling a known volume of solvent into a known weight of salt. The concentration chosen was arranged to be at the upper end of the range to be examined (*ca.* 10^{-3}M). The vessel was then isolated from the vacuum line by closing the greaseless tap B (J. Young Ltd.; type PQR/10 mm), and the conductance *G* of this solution measured at 0 and −45° using a Wayne Kerr universal bridge (model B224). The bridge's internal source and detector operating at 1 592 Hz were used in all measurements. A known volume of the solution was then removed *via* the vacuum burette C and greaseless tap D (J. Young Ltd.; type PQR/4 mm/RA). Finally the vessel was returned to the vacuum line and a second sample of solvent distilled in to complete the dilution procedure. This technique enabled the concentration range 10^{-3}—10^{-6}M to be covered conveniently in as many steps as required, though the range 10^{-3}—10^{-5}M in ten steps became standard, since data much below 10^{-5}M displayed poorer reproducibility.

TABLE 1

Elemental analyses of quaternary ammonium hexachloroantimonates

Quaternary ammonium ion	C (%) Found	C (%) Calc.	H (%) Found	H (%) Calc.	N (%) Found	N (%) Calc.	Cl (%) Found	Cl (%) Calc.
$Me_2C_6H_5CH_2PhN^+$	31.2	32.9	3.3	3.3	2.55	2.55	39.1	38.8
$Me_2C_6H_5CH_2C_{16}H_{33}N^+$	44.0	43.2	6.9	6.6				
Et_4N^+	21.2	20.7	4.5	4.3	2.9	3.0	44.8	45.8
$Et_3C_4H_9N^+$	25.4	24.4	5.1	4.85	3.4	2.85	42.4	43.2
$Et_3C_8H_{17}N^+$	31.1	30.6	6.05	5.85	2.25	2.55	37.7	38.8
$Et_3C_{12}H_{25}N^+$	36.1	35.6	7.1	6.6	2.15	2.3	2.3	35.2
$Et_3C_{16}H_{33}N^+$	41.7	40.0	7.6	7.25	1.95	2.1	30.4	32.2

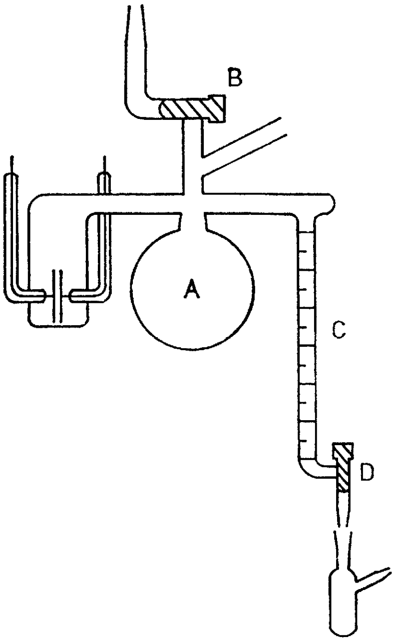

FIGURE 1 Conductance apparatus

In the operation of the bridge and the conductance vessel the standard precautions already described[6] were rigidly applied.

Treatment of Results.—Experimental conductance data *G* as a function of concentration were converted to molar conductances λ as before,[6] and again dissociation constants K_d were calculated from the Fuoss expression (I)[7] where

$$F(Z)/\lambda = 1/\lambda_0 + c\lambda f_{\pm}^2/[F(Z)\ K_d\ \lambda_0^2] \qquad (1)$$

F(*Z*) is the Fuoss correction function, *c* the salt concentration, $f_{\pm}$ the mean activity coefficient; λ the molar conductance at concentration *c*, and λ_0 the molar conductance at infinite dilution. An ICL 1904S computer was used for these evaluations, employing a program previously outlined.[6] A major improvement was made to the latter, however, by incorporating an iterative process to optimise values of λ_0 and K_d, thereby avoiding the manual procedure used before, of re-computing data in the light of previous λ_0 values generated by the computer.

RESULTS AND DISCUSSION

Detailed experimental results for the salt $Et_3C_{16}H_{33}$-$N^+SbCl_6^-$ are shown in Table 2, while Figure 2 shows the corresponding initial manual extrapolations to infinite dilution. The Fuoss lines for this salt, generated by the computer after iteration, are shown in Figure 3, and the final values of K_d and λ_0 were obtained from the straight portions of these plots. A summary of the

TABLE 2

Conductance data for $Et_3C_{16}H_{33}N^+SbCl_6^-$ in CH_2Cl_2

T/°C	10^4[Salt]/M	10^6*G*/Ω^{-1}	λ */Ω^{-1} cm^2 mol^{-1}
0	10.5	2 910	26.9
0	4.18	1 520	35.1
0	2.50	1 050	40.4
0	2.00	885	42.7
0	1.59	752	45.5
0	1.27	636	48.2
0	1.01	541	51.5
0	0.403	282	67.4
0	0.155	141	87.5
0	0.0621	67.7	105
0	0.0207	31.9	148
−45	11.1	1 950	17.1
−45	4.42	1 010	22.1
−45	2.65	693	25.2
−45	2.11	585	26.7
−45	1.68	495	28.3
−45	1.35	415	29.7
−45	1.07	354	31.8
−45	0.427	180	40.7
−45	0.164	87.9	51.7
−45	0.0656	42.2	62.0
−45	0.0219	19.7	86.8

* λ = *KvG* where *K* is the cell constant, and *v* is the volume (cm^3) of solution containing 1 mole of the salt.

results from a similar treatment of data for all the salts is shown in Table 3.

The single ion conductance, λ_0^-, for the hexachloroantimonate ion in dichloromethane at 0° is known,[6] enabling the single ion conductances at 0°, λ_0^+, for all the ammonium ions to be calculated. Furthermore if the ions are regarded as rigid spheres immersed in a continous medium and are present only as tight ion-pairs or totally free of each other, then both the Stokes' radii[10] of the cations r_s^+ and the effective interionic distances a for each ion pair[11] can be evaluated.

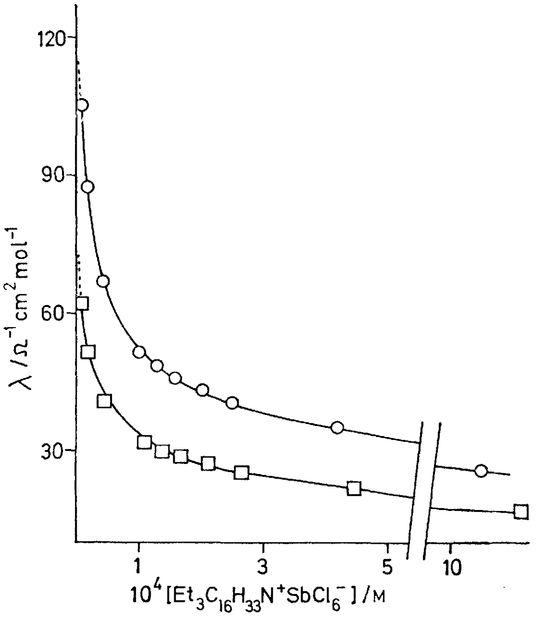

FIGURE 2 Molar conductance-concentration curves for the salt, $Et_3C_{16}H_{33}N^+SbCl_6^-$: ○, 0°; □, −45°

Data for ion pair dissociation constants in Table 3 are in good agreement with results from experiments involving other hexachloroantimonate salts in dichloromethane.[5,6] Good correlation also emerges with data for hexadecylammonium picrates and nitrates,[12] and trimethylarylammonium perchlorates[11] in 1,2-dichloroethane. The latter solvent is very similar in polarity to dichloromethane, and it is known that different anions influence dissociation to only a small extent providing they are large and diffuse.[5,13]

The absolute values of K_d for all the salts studied showed no significant variation with the chain length of alkyl substituent, an average value being 0.73×10^{-4}M at 0°. A similar lack of dependence has been reported previously,[14] though under aqueous conditions. There seems no reasonable grounds therefore to suppose that K_d would be substantially changed if considerably longer oligomeric or polymeric substituents were involved, and the assumption often made concerning comparibility of K_d data for polymeric ion pairs and small model systems seems totally justified.[5,15] Close similarity in the dissociation data for 'living' oligomeric oxonium

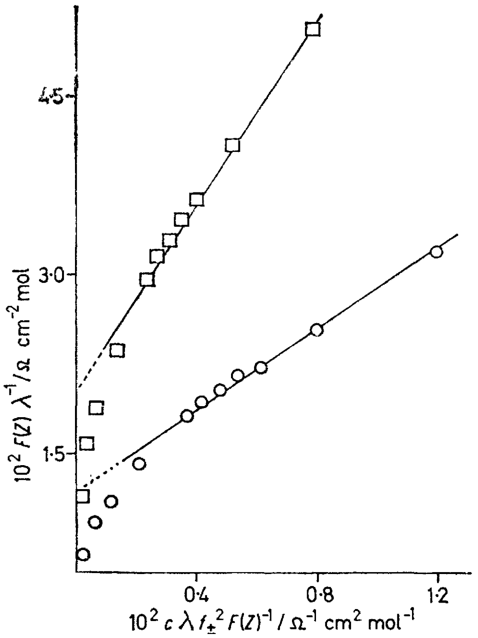

FIGURE 3 Fuoss plots for the salt, $Et_3C_{16}H_{33}N^+ SbCl_6^-$: ○, 0°; □, −45°

TABLE 3

Ion-pair dissociation equilibria for quaternary ammonium hexachloroantimonate salts in CH_2Cl_2

Quaternary ammonium ion	0°		−45°	
	10^4K_d/ l mol^{-1}	$\lambda_0/\Omega^{-1}cm^2$ mol^{-1}	10^4K_d/ l mol^{-1}	$\lambda_0/\Omega^{-1}cm^2$ mol^{-1}
$Me_2PhCH_2PhN^+$	0.49	102	0.51	59.3
$Me_2PhCH_2C_{16}H_{33}N^+$	0.54	80.8	0.71	46.2
Et_4N^+	0.84	113	1.02	64.8
$Et_3C_4H_9N^+$	0.69	110	0.86	64.0
$Et_3C_8H_{17}N^+$	0.80	97.4	0.79	60.4
$Et_3C_{12}H_{25}N^+$	0.60	99.9	0.76	58.7
$EtC_{16}H_{33}N^+$	0.72	87.5	0.88	51.6

TABLE 4

Single ion conductances and Stokes' radii for quaternary ammonium cations, and interionic distances of their hexachloroantimonate * ion pairs at 0° in CH_2Cl_2

Quaternary ammonium ion	$\lambda_0^+/\Omega^{-1}cm^2$ mol^{-1}	r_s^+/Å	a/Å	$(r_s^+ + r_s^-)$/ Å
$Me_2PhCH_2PhN^+$	51.5	3.0	6.2	6.0
$Me_2PhCH_2C_{16}H_{33}N^+$	30.0	5.1	6.2	8.1
Et_4N^+	61.7	2.5	6.5	5.5
$Et_3C_4H_9N^+$	59.2	2.6	6.4	5.6
$Et_3C_8H_{17}N^+$	46.6	3.3	6.5	6.3
$Et_3C_{12}H_{25}N^+$	49.1	3.1	6.3	6.1
$Et_3C_{16}H_{33}N^+$	36.7	4.2	6.4	7.2

* $\lambda_0^- = 50.8\Omega^{-1}$ cm^2 mol^{-1}, $r_s^- = 3.0$ Å.[6]

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tetrafluoroborate ion pairs derived from tetrahydrofuran, and those of triethyloxonium tetrafluoroborate [4] tends to confirm the generality of this conclusion.

As might be expected the Stokes' radii (Table 4) of the various cations increase as the size of alkyl substituent increases. Molecular models show that the relative values are consistent with a coiled rather than extended conformation of the alkyl substituents.

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