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The Conductance of Some Haloborate and Boronium Salts in Acetonitrile at 25°

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The molar conductances of tetraethylammonium salts of phenyltrichloroborate, tetrabromoborate, and tetraiodoborate and of bis(pyridine)diphenylboronium bromide and boron triiodide–bis(pyridine) in acetonitrile are reported. Tetraethylammonium phenyltrichloroborate and tetraethylammonium tetrabromoborate behave as strong 1:1 electrolytes with no detectable ion-pair association. The ionization mechanism $(C_2H_5)_4NBI_4(s) = (C_2H_5)_4N^+ + BI_2(CH_3CN)_n^+ + 2I^-$ is proposed to account for the extraordinarily high limiting molar conductance for tetraethylammonium tetraiodoborate. Infrared spectral studies and other conductance data are presented to support this explanation. The molar conductances of bis(pyridine)diphenylboronium bromide and boron triiodide–bis(pyridine) are typical of strong 1:1 electrolytes. Limiting single-ion conductances are given for $(C_6H_5)BCl_3^-$, BBr_4^-, $(C_6H_5)_2B(C_5H_5N)_2^+$, and $BI_2(C_5H_5N)_2^+$.

Introduction

This communication is part of a systematic investigation of the character of boron-containing compounds in acetonitrile and deals specifically with electrolytic behavior. The behavior of typical 1:1 electrolytes in this solvent has been studied extensively.[3-7] Acetonitrile is a solvent of moderate dielectric constant ($\epsilon_{25°} = 36.01$) and weak but significant basic character.

The results of previous conductance studies indicate that salts composed of large symmetrical ions are not appreciably solvated in acetonitrile.[5,6] Moreover, the small values of the association constants derived from the conductance data of symmetrical electrolytes in acetonitrile indicate that ion-pair formation takes place only to a limited extent.[5] The objectives of this study were to characterize the boron-containing species in acetonitrile of tetraethylammonium haloborate salts and boron halide–pyridine complexes and to determine the extent of ion association.

Results and Discussion

The measured molar conductances and the corresponding concentrations for tetraethylammonium phenyltrichloroborate, tetrabromoborate, and tetraiodoborate are summarized in Table I. The data for bis(pyridine)diphenylboronium bromide and boron triiodide–bis(pyridine) are tabulated in Table II. The data for each compound represent a composite of no less than three separate runs. The results for tetraethylammonium tetrachloroborate have been reported elsewhere.[3] The conductance data were analyzed by the Fuoss–Onsager conductance equation[8-10] for unassociated electrolytes

$$\Lambda = \Lambda_0 - SC^{1/2} + EC \log C + JC \qquad (1)$$

and by the equation for associated electrolytes

$$\Lambda = \Lambda_0 - S(C\gamma)^{1/2} + EC\gamma \log C\gamma + JC\gamma - K_A C\gamma \Lambda f^2 \qquad (2)$$

The symbols in these equations have their usual definitions.[10] Analysis of the data was made with the aid of a least-squares program on a 7040 IBM computer.[11]

Initial values for Λ_0 were obtained from extrapolation of the Λ *vs.* $C^{1/2}$ plot or from a preliminary Shedlovsky plot of Λ_0 *vs.* C.[10] An initial value of J was calculated from an estimated value of the ion-size paramater, a_0. The viscosity coefficients for these solutions were unknown. This uncertainty does not have any effect on the computed value of Λ_0 or K_A. Only J and a_0 values were affected when viscosity corrections of 0.25–0.85 were used. Calculations were made using both unweighted values of Λ and Λ values weighted by C. Weighted data gave a better fit to the theoretical equation as evidenced by smaller values for standard deviations of individual conductances, $\sigma\Lambda$.

Tetraethylammonium Haloborates.—The results of the analysis of the weighted data for tetraethylammonium phenyltrichloroborate and tetrabromoborate are shown in Table III. The standard deviation of each parameter and the standard deviation of individual points are included. It should be mentioned that the Λ_0 values listed in Table III are consistently higher by 0.2–0.3 unit than those calculated from unweighted data. No parameters could be calculated for $(C_2H_5)_4NBBr_4$ when the data were analyzed by eq 2. This indicates a completely dissociated electrolyte. The small association constant and the high uncertainty in the K_A value for $(C_2H_5)_4NBC_6H_5Cl_3$ indicate that ion-pair formation is negligible. The small a_0 values resulting from these calculations cannot be considered reliable because of the uncertainty of the viscosity of these solutions.

Single-ion limiting conductances of $C_6H_5BCl_3^-$ and BBr_4^- ions were obtained by the application of Kohlrausch's law of independent migration of ions. Using

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[11] Dr. R. L. Kay of the Mellon Institute, Pittsburgh, Pa., kindly provided the program used in the analysis of these data.

Table I

Conductance of the Tetraethylammonium Haloborates in Acetonitrile at 25°

$(C_2H_5)_4NB(C_6H_5)Cl_3$		$(C_2H_5)_4NBBr_4$		$(C_2H_5)_4NBI_4$	
10^3C	Λ	10^3C	Λ	10^3C	Λ
0.8764	187.6	1.753	176.9	0.6154	349.0
1.036	186.2	1.842	175.6	0.7089	344.0
1.173	185.2	1.919	174.9	0.7660	338.6
1.458	182.8	2.094	173.6	0.8153	336.5
1.591	181.6	2.193	172.9	0.9472	327.6
1.750	180.9	2.303	172.2	1.002	326.4
1.974	178.9	2.424	171.1	1.068	325.2
2.158	177.8	2.559	170.2	1.101	316.6
2.426	176.8	2.709	169.2	1.124	320.9
2.587	176.2	2.879	168.1	1.177	313.2
2.835	175.5	3.071	167.4	1.215	317.5
3.089	174.2	3.227	166.8	1.227	315.0
3.477	172.8	3.290	166.1	1.277	308.5
3.537	171.6	3.543	164.4	1.360	306.2
3.727	171.4	3.569	165.6	1.399	308.9
3.901	170.5	3.813	164.5	1.550	301.8
3.984	169.9	3.838	162.8	1.554	297.8
4.202	169.5	4.158	162.4	1.680	293.2
4.416	166.9	4.195	160.3	1.708	291.2
4.691	166.1	4.545	160.7	1.801	287.6
5.046	165.5	4.606	158.6	1.850	285.1
5.367	164.6	4.999	158.2	2.018	278.3
5.711	163.9	5.765	153.3	2.220	270.4
6.190	162.4	6.399	147.6	2.466	260.9
6.933	159.7			2.775	251.3
				3.108	241.4

Table II

Conductance of Bis(pyridine)diphenylboronium Bromide and the Boron Triiodide–Bis(pyridine) Complex in Acetonitrile at 25°

$[(C_6H_5)_2B(py)_2]Br$		$[I_2B(py)_2]I$	
10^4C	Λ	10^3C	Λ
0.7832	129	0.1876	184
1.782	124	0.2068	183
2.890	119	0.2586	182
3.557	117	0.3069	181
4.623	115	0.5782	180
5.153	112	0.3939	179
6.121	111	0.4293	179
7.982	108	1.193	169
8.838	105	1.295	168
9.578	103	1.475	166
10.51	102	1.624	164
11.72	98.8	1.840	162
13.17	96.5	2.110	159
14.23	94.8	2.455	156
15.50	93.3		

Table III

Conductance Parameters for Acetonitrile Solutions of $(C_2H_5)_4NBC_6H_5Cl_3$ and $(C_2H_5)_4NBBr_4$ at 25°[a]

	Λ_0	a_0	K_A	S	J	$\sigma(\Lambda)$
$(C_2H_5)_4NB$-$C_6H_5Cl_3$	199.6 ± 0.3	1.24 ± 0.08		378.0	724.4	0.1
	200.9 ± 0.7	2 ± 1	10 ± 8	378.8	1387.4	0.6
$(C_2H_5)_4$-$NBBr_4$	198.1 ± 0.5	0.19 ± 0.04		376.9	869	0.1

[a] The first entry for each salt gives the value of the function obtained from eq 1. The second entry for $(C_2H_5)_4NBC_6H_5Cl_3$ gives the value of the function obtained from eq 2.

85.05 as $\lambda_0[(C_2H_5)_4N^+]$,[6] values of 114.5 and 113.0 were obtained for the single-ion limiting conductance of $C_6H_5BCl_3^-$ and BBr_4^-, respectively. The corresponding computed value for BCl_4^- ion is 95.2 ohm^{-1} cm^2 mol^{-1}.[8] The λ_0 values of the $C_6H_5BCl_3^-$ and BBr_4^- anions are approximately equal to one another and higher than that of the BCl_4^- ion. Such a relation is expected because the first two ions are of comparable size and larger than the BCl_4^- ion. The smaller, more polarizing tetrachloroborate ion would interact more strongly with the polar solvent than larger ions.

Whereas tetraethylammonium tetrachloro-, tetrabromo-, and phenyltrichloroborates behave as typical 1:1 electrolytes in acetonitrile, the Λ values for the tetraiodoborate salt are exceptionally high. The data could not be fitted to the conductance equation derived for 1:1 electrolytes. Treatment of the conductance data by a simple least-squares program on a 1620 IBM computer gave a Λ_0 value of 436 ± 2 ohm^{-1} cm^2 mol^{-1}. These values indicate that this salt ionizes in solution to produce four conducting ions: $(C_2H_5)_4NBI_4(s) = (C_2H_5)_4N^+ + BI_2^+(solv) + 2I^-$. This conclusion is supported by the results of the conductance measurement of boron triiodide in acetonitrile.[12] Boron triiodide behaves as a strong 1:1 electrolyte and ionizes according to the equation

$$BI_3(solv) = [BI_2^+,I^-](solv) = BI_2^+(solv) + I^-$$

Solvation in the first coordination sphere of the boron species is unknown and is generalized in these equations. The limiting molar conductance of boron triiodide was calculated from eq 1 and found to be 240 ± 2 ohm^{-1} cm^2 mol^{-1}. The sum of the limiting molar conductances of boron triiodide and tetraethylammonium iodide (187.3)[5] in acetonitrile is 427 ± 2 ohm^{-1} cm^2 mol^{-1}, which is in good agreement with the Λ_0 value of 436 for tetraethylammonium tetraiodoborate.

The instability of the BI_4^- ion in acetonitrile can be deduced also from consideration of the infrared data. The spectrum of crystalline tetraethylammonium tetraiodoborate shows a strong band at 510 cm^{-1} which can be assigned to the ν_3 frequency of tetrahedral BI_4^- ion.[13,14] When the salt is dissolved in acetonitrile, this band disappears completely. The BCl_4^- and BBr_4^-, on the other hand, are stable in acetonitrile solutions as indicated by infrared data. The characteristic ν_3 frequencies of BCl_4^- and BBr_4^- ions appear at 664 and 692 cm^{-1} and at 592 cm^{-1}, respectively, in the spectra of their crystalline tetraethylammonium salts. The positions of these bands are only slightly shifted in the spectra of their acetonitrile solutions.

Boronium Halides.—The molar conductance values of bis(pyridine)diphenylboronium bromide are in the range of 1:1 electrolytes in acetonitrile. Analysis of the data by eq 1 gave a value 128 ± 4 ohm^{-1} cm^2 mol^{-1} for Λ_0. Thus, this compound behaves as a strong electrolyte in acetonitrile although the pure bromodiphenylborane is only slightly dissociated in acetonitrile.[12] A similar behavior was observed for chlorodiphenylboron and its 2,2′-bipyridine complex.[15] Several investiga-

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tions have suggested the presence of the solvated diphenylboronium ion in the solutions of chlorodiphenylborane in various solvents.[16,17] Attachment of a strongly basic ligand like pyridine would tend to stabilize the ion. The compound can be assigned the ionic structure $[(C_6H_5)_2B(py)_2{}^+]Br^-$. Earlier investigations had assigned ionic structures to similar compounds (*e.g.*, $[(C_4H_9)_2B(py)_2]Cl$,[18] $[(C_6H_5)_2Bbipy]Cl$,[19] and $[C_6H_5BH(py)_2]I$[20]). By using the value of 100 ohm^{-1} cm^2 mol^{-1} for $\lambda_0(Br^-)$[6], one obtains a value of 28 for λ_0 $(C_6H_5)_2B(py)_2{}^+$. This unexpectedly low value cannot be accounted for. It agrees generally with the λ_0 value of 23.7 ohm^{-1} cm^2 mol^{-1} reported for the closely related bipyridyldiphenylboronium ion measured in water at 25°.[19]

The 1:2 boron triiodide–pyridine complex behaves as a strong 1:1 electrolyte in acetonitrile as indicated by the high Λ values (Table II). Analysis of the data gave a Λ_0 value of 193 ± 4 ohm^{-1} cm^2 mol^{-1}. The most reasonable structure for the complex is $[I_2B(py)_2{}^+]I^-$. A similar conclusion on the structure of this complex was reached from molecular weight measurements in acetonitrile (312 *vs.* theoretical weight of 550) and other observations.[21] Recently, several boronium salts of the type $[H_2B(py)_2{}^+]I^-$ have been prepared and studied.[22] The single-ion limiting conductance of the bis(pyridine)-diiodoboronium ion was calculated to be 91 ohm^{-1} cm^2 mol^{-1} when a $\lambda_0(I^-)$ value of 102[5,6] was used.

Experimental Section

Purification of Acetonitrile.—Acetonitrile (Fisher Certified reagent) was purified by the method recommended by Coetzee.[6,23] The specific conductances of samples purified by this method were less than 5×10^{-8} ohm^{-1} cm.$^{-1}$

Preparation and Purification of Reagents. Tetraethylammonium Phenyltrichloroborate.—Tetraethylammonium chloride (Eastman Kodak White Label) was dried in the oven at 120°. A 3.2-g (20-mmol) sample of the chloride was suspended in 100 ml of 1,2-dichloroethane in a round-bottomed flask and a slight excess of dichlorophenylborane was distilled into the flask which had been cooled to −80°. The mixture was heated to ∼50°, the temperature at which all solid materials dissolved. When the mixture was cooled to −80°, a white solid separated. The solid was filtered, washed with chilled solvent, and dried under vacuum overnight. The white solid melted with decomposition at 99–103° (sealed ampoule).

Anal. Calcd for $C_{14}H_{25}BCl_3N$: C, 51.76; H, 7.76; Cl, 32.76; N, 4.31. Found: C, 51.64; H, 7.79; Cl, 32.06; N, 4.18.

Tetraethylammonium Tetrabromoborate.—In addition to a procedure similar to the one described above, this salt was prepared by the following method. A 6.1-g (29-mmol) sample of dried tetraethylammonium bromide (Matheson Co.) was dissolved in 100 ml of methylene chloride and added dropwise to a solution of 7.5 g (30 mmol) of boron tribromide in 50 ml of methylene chloride at −80° with continuous stirring. Fine white crystals formed. The solid was filtered, washed with chilled solvent, and dried at 80° under vacuum overnight. The compound melted with decomposition to a brown liquid at 278–280°. On storage in a desiccator, the white solid turned slightly yellow.

Anal. Calcd for $C_8H_{20}BBr_4N$: C, 20.86; H, 4.37; Br, 69.01; N, 3.04. Found: C, 21.46; H, 4.62; Br, 69.42; N, 3.38.

Tetraethylammonium Tetraiodoborate.—This compound was prepared by both methods described above. The final product was a highly crystalline, dark yellow solid which melted at 238–240° with decomposition in a sealed ampoule. The solid developed a brown coloration on exposure to light for about 2 weeks.

Anal. Calcd for $C_8H_{20}BI_4N$: C, 14.81; H, 3.11; I, 78.25; N, 2.16. Found: C, 14.69; H, 3.29; I, 78.00; N, 2.06.

Bis(pyridine)diphenylboronium Bromide.—A solution of 1.0 g (2.5 mmol) of bromodiphenylborane in 50 ml of 1,2-dichloroethane was added dropwise to a solution containing excess pyridine in the same solvent. A vigorous reaction occurred and a white solid precipitated immediately. The mixture was filtered and the solid was washed with the solvent and dried under vacuum for 24 hr. Upon heating, the solid began to contract at 165°. The compound finally melted with decomposition at 219–220° in a sealed ampoule.

Anal. Calcd for $C_{22}H_{20}N_2BBr$: C, 65.50; H, 4.96; N, 6.95; B, 2.74; Br, 19.84. Found: C, 65.22; H, 5.00; N, 6.89; B, 2.88; Br, 19.75.

Boron Triiodide–Bis(pyridine).—Boron triiodide was dissolved in 50 ml of methylene chloride, and a solution of excess pyridine in 50 ml of the same solvent was added dropwise to it. A yellow precipitate separated immediately. The solid was filtered, washed with chilled methylene chloride, and dried under vacuum at 60°. The final product was a bright yellow, crystalline substance. Upon heating, the solid turned brown at 190–200°, began decomposing at 218–220°, and then melted with decomposition at 239–240° (to a dark brown liquid) in a sealed ampoule.

Anal. Calcd for $C_{10}H_{10}N_2BI_3$: C, 21.90; H, 1.83; N, 5.11; I, 69.20. Found: C, 22.01; H, 1.84; N, 5.20; I, 69.08.

Apparatus and Procedure.—All conductances were measured with a Leeds & Northrup Direct Reading mho–ohm conductance bridge, Model 4959, operated at 1000 cps. Readings were considered accurate to within 0.5%. The conductance cells have been described elsewhere.[1,24] The cell constants were checked periodically with freshly prepared dilute aqueous potassium chloride solutions. Conductance measurements were made with the cell immersed in a constant-temperature water bath held at 25.00 ± 0.01°.

The procedure for conductance measurements reduces contact of the reagents with air and atmospheric moisture to a minimum and is described in detail elsewhere.[1]

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