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A Spectral and Conductance Study of Boron Halides and Boron Halide Complexes in Acetonitrile

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Conductance, infrared, and nuclear magnetic resonance measurements were used to study the nature of solute species in acetonitrile for a series of boron trihalides and phenyl-substituted boron halides and their complexes with acetonitrile and pyridine. In the series of boron trihalides, contrasting behaviors were observed. Boron trichloride and boron tribromide are weak electrolytes in acetonitrile. The bromide is more dissociated. Ionization occurs in these systems to produce a high concentration of $S_2BX_2^+,BX_4^-$ ion pairs. Boron triiodide, on the other hand, behaves as a strong 1:1 electrolyte with $S_2BI_2^+$ and I^- as the ionic species. Dichlorophenylborane forms a stable 1:1 adduct with acetonitrile and shows weak electrolytic behavior in acetonitrile. Chlorodiphenylborane and bromodiphenylborane behave as weak electrolytes and the conductance plots indicate multiple equilibria. The stable crystalline 1:1 molecular adducts of boron trichloride– and boron tribromide–pyridine retain their molecular structure in acetonitrile. Boron triiodide forms a crystalline 1:2 complex with pyridine which behaves as a strong 1:1 electrolyte in acetonitrile. The difference in behavior of the boron halides is discussed in terms of the relative donor strength of the halide ligands, pyridine, and the solvent molecules and the thermodynamic stability of the various solute species.

Introduction

The work reported herein is a continuation of our study of the nature of solute species in acetonitrile.[2–4] Although the thermodynamic stabilities of boron halide complexes have been studied[5] extensively and neutral $BX_3\cdot$(donor) molecular adducts as well as salts containing the BX_4^- anion and the (donor)$_2BX_2^+$ cation have been isolated,[6,7] only a few scattered reports have appeared which dealt with characterization of the boron halide solute species in nonaqueous solvents.[8,9] Consequently, the boron halides were chosen for detailed study.

Results

The measured molar conductances and corresponding concentrations for boron tribromide, boron triiodide, dichlorophenylborane, chlorodiphenylborane, and bromodiphenylborane are summarized in Table I.

Conductance measurements of boron tribromide solutions in acetonitrile show that it is a weak electrolyte although the Λ values are higher than those of boron trichloride[3] of comparable concentration.

The infrared spectrum of crystalline $CH_3CN\cdot BBr_3$ (Figure 1A) contains a broad asborption envelope in the 650–731-cm^{-1} region. This absorption is characteristic of the "BBr_3" vibrations in its molecular adducts.[10,11] The B–N bond vibration or a combination B–N, B–Br vibration is also expected to appear in this region.[12] It is not possible, therefore, to assign these frequencies unequivocally. The spectrum changes significantly when the solid is dissolved in acetonitrile (Figure 1B). The overlapping vibrational bands in the 650–700-cm^{-1} region become sharper with strong peaks at 664 and 693 cm^{-1}, and a strong new band appears at 596 cm^{-1}. This latter band is characteristic of the $\nu_3(T_d\ BBr_4^-)$ vibration.[13] Crystalline $(C_2H_5)_4NBBr_4$ shows a strong absorption band at 592 cm^{-1} (Figure 1C) which appears in the spectrum of its acetonitrile solution at 600 cm^{-1} (Figure 1D). The infrared data leave no doubt that the tetrabromoborate ion is a stable species in acetonitrile and that the tetrabromoborate ion is present in acetonitrile solutions of boron tribromide. The spectrum of the solid also contains an absorption band at 2330 cm^{-1}, which is readily assigned to the C≡N stretching vibration of coordinated acetonitrile.

The ^{11}B nmr data support the conclusion that the tetrabromoborate ion is a stable species in acetonitrile. The ^{11}B nmr spectrum of tetraethylammonium tetrabromoborate in acetonitrile consists of a single resonance band at 24.5 ± 0.2 ppm. This band appears at 24.1 ± 0.2 ppm in the spectrum of the salt in methylene chloride (23.9 ppm reported[14]).

The ^{11}B nmr spectrum of boron tribromide in acetonitrile consists of a single band at 20.7 ± 0.2 ppm at 30°. Upon cooling to −40°, the position of the band shifts slightly to 19.5 ± 0.2 ppm. The presence of a single band is due certainly to exchange processes in-

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TABLE I

CONDUCTANCE OF BORON HALIDES IN ACETONITRILE AT 25°

BBr_3		BI_3		$(C_6H_5)BCl_2$		$(C_6H_5)_2BCl$		$(C_6H_5)_2BBr$	
10^2C	Λ	10^3C	Λ	10^3C	Λ	10^3C	Λ	10^3C	Λ
0.2953	8.13	0.1457	235	0.2363	12.6	0.3176	8.08	0.1151	37.1
0.3411	9.56	0.2087	229	0.9867	3.76	2.738	1.07	0.4493	14.0
0.4097	6.61	0.2348	227	2.681	1.55	3.344	1.42	0.7791	10.4
0.6032	4.46	0.2817	224	3.819	1.16	3.841	1.59	1.141	8.8
0.6630	5.52	0.3419	220	5.724	0.86	4.770	1.72	1.420	7.9
1.019	3.98	1.108	190	6.941	0.74	6.480	1.92	1.877	7.1
1.108	3.66	1.200	188	7.720	0.71	8.492	1.80	2.416	6.5
1.174	3.09	1.309	186	15.52	0.87	9.875	1.78	3.136	6.5
1.365	3.07	1.440	182	17.19	0.88	10.75	1.80	4.075	10.1
1.557	2.49	2.113	165	18.58	0.89	11.95	1.79	5.025	14.1
1.814	2.58	2.304	161	21.33	0.89	13.86	1.77	6.181	15.3
2.007	2.39	2.467	158	23.53	0.89	15.79	1.77	7.262	15.6
2.603	2.03	2.654	154	25.57	0.91			8.217	15.4
2.759	2.05	2.872	150	27.13	0.94				
3.486	1.86	3.084	145	28.18	0.95				
7.001	1.44	3.382	140	29.84	0.94				
8.122	1.38	3.744	133	41.51	0.98				
8.621	1.37	4.194	125	44.06	0.94				
9.270	1.47			46.07	0.97				
10.53	1.46			48.82	0.94				
11.67	1.46			51.34	0.97				
12.95	1.42			54.12	0.97				
15.06	1.37			57.25	0.97				
16.00	1.37			61.65	0.46				
17.05	1.35			69.92	0.92				
17.94	1.32			77.38	0.94				
19.26	1.31			80.38	0.95				
22.83	1.22			87.10	0.94				
27.32	1.08			101.0	0.95				

volving the bromide ion and/or the solvent. Thus, the observed chemical shift is an average for the various boron-containing species.

Boron triiodide behaves as a strong electrolyte in acetonitrile. Computer analysis of the conductance data gave a Λ_0 value of 240 ± 2. This behavior is in striking contrast to the weak electrolytic behavior exhibited by boron tribromide and boron trichloride.

The infrared spectrum of crystalline $CH_3CN \cdot BI_3$ shows a strong doublet with peaks at 585 and 606 cm^{-1} (Figure 1A). These bands are characteristic of the B–I asymmetric stretching frequencies for the two boron isotopes.[11] Two other bands of medium intensity appear in this region at 695 and 718 cm^{-1}. These are thought to be associated with the B–N absorption. In the acetonitrile solution spectrum of boron triiodide, the bands due to boron triiodide are indiscernible. This is due, in part, to the limited solubility of $BI_3 \cdot CH_3CN$ in acetonitrile. No evidence could be found in the spectrum for the presence of the BI_4^- ion. The instability of the BI_4^- ion in acetonitrile and its dissociation into BI_2^+ and two iodide ions has been established.[4]

The molar conductance values of dichlorophenylborane solutions in acetonitrile (Table I) are low and the shape of the Λ *vs.* $C^{1/2}$ plot is typical of a weak electrolyte. The curve rises asymptotically at low concentrations and levels off in the high-concentration region. The Λ values found for dichlorophenylborane are higher than those for boron trichloride at comparable concentrations.

Dichlorophenylborane reacts exothermally with acetonitrile to form the stable adduct $BC_6H_5Cl_2 \cdot CH_3CN$. The infrared spectrum of the solid shows strong absorption bands in the 650–750-cm^{-1} region. These overlapping bands are due to the phenyl and to the B–Cl vibrations. The C≡N frequency of the coordinated acetonitrile appears at 2320 cm^{-1}, 70 cm^{-1} higher than uncomplexed acetonitrile. When the adduct is dissolved in acetonitrile, the spectrum changes considerably in the 600–700-cm^{-1} region and resembles to a great extent the solution spectrum of $(C_2H_5)_4NBC_6H_5Cl_3$.[1] The $C_6H_5BCl_3^-$ ion has been shown by conductance measurements to be a stable species in acetonitrile.[4]

Chlorodiphenylborane and bromodiphenylborane show weak electrolytic behavior in acetonitrile (Table I) and the Λ *vs.* $C^{1/2}$ plots show a minimum at ~0.002 *M* for the chloride and at ~0.0025 *M* for the bromide. A similar behavior was observed for the aluminum chloride–acetonitrile system and it was suggested that this behavior is due to multiple ionic equilibria.[3] It was not possible to isolate any acetonitrile complex of either borane. Whether the compounds ionize in acetonitrile to give the halide or the dihalodiphenylborate anions, the cation is considered to be the solvated diphenylboronium ion. Conductance measurements of chlorodiphenylborane in nitrobenzene[15] showed that it was a weak electrolyte, with Λ values lower than those found in acetonitrile. Ionization was enhanced by the addi-

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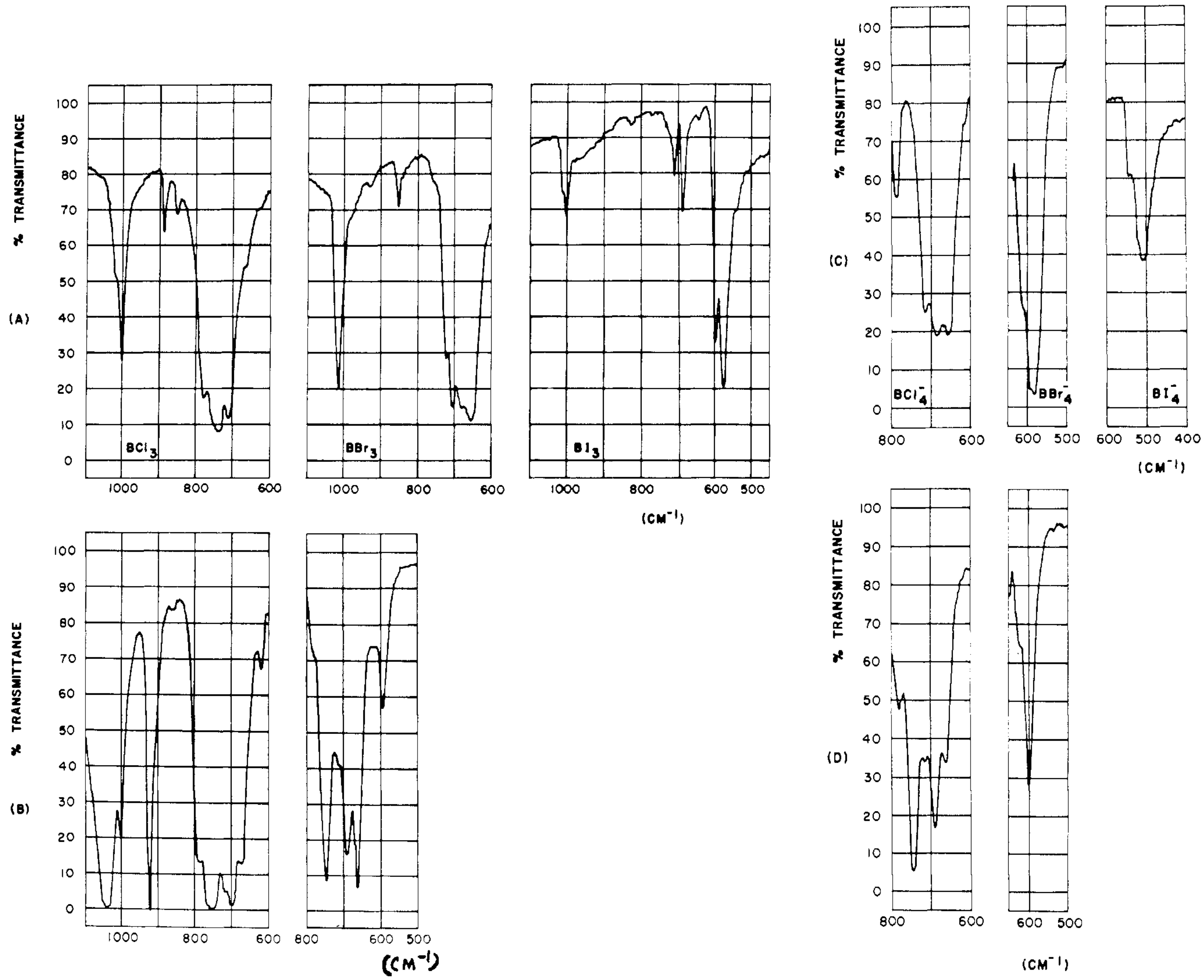

Figure 1.—Infrared spectra of (A) crystalline boron halide–acetonitrile adducts, (B) boron halides in acetonitrile, (C) crystalline tetraethylammonium tetrahaloborates, and (D) tetraethylammonium tetrahaloborates in acetonitrile.

tion of an equivalent amount of aluminum chloride to the solution.[15] These results together with the uv spectrum of chlorodiphenylborane in ethyl methyl ketone indicated the presence of the diphenylboronium ion. The results of other investigations have suggested the presence of the solvated diphenylboronium cation in solution.[16,17]

Conductance and spectral studies were undertaken to determine what effect if any the replacement of weakly coordinating acetonitrile by the strong neutral complexing agent pyridine would have upon ionization of the $BCl_3\cdot$(donor) complexes. The 1:1 boron trichloride–pyridine and boron tribromide–pyridine complexes in contrast to the acetonitrile adducts are easily soluble in nonionizing solvents such as benzene or carbon tetrachloride and can be recovered from these solvents by the addition of water. Acetonitrile solutions of both boron trihalide–pyridine adducts show very weak electrolytic behavior. The infrared spectra of the acetonitrile solutions are identical with the spectra of the corresponding adducts in benzene,[18] a solvent in which the adduct has been shown to be molecular.[19] No evidence could be found for the presence of the BCl_4^- or BBr_4^- ions in these solutions.

Further evidence for the predominance of the molecular species in acetonitrile solutions comes from nmr data. A single resonance band appears at -8.0 ± 0.2 ppm (30°) and at -7.8 ± 0.2 ppm (−40°) in the ^{11}B nmr spectrum of the acetonitrile solution of $BCl_3\cdot py$. For the $BBr_3\cdot py$ adduct this band appears at 7.4 ± 0.2 ppm (30°). It is recognized that the appearance of a single ^{11}B resonance band does not necessarily indicate a molecular species. However, the appearance of a single band at -8.5 ± 0.2 ppm for $BCl_3\cdot py$ in methylene chloride, a nonionizing solvent, and a single band at 7.4 ± 0.2 ppm in the methylene chloride solution of the boron tribromide–pyridine adduct is consistent with the existence of a molecular species.

In view of the observed low conductance of the boron trichloride– and boron tribromide–pyridine adduct, it is possible that a small part of the adduct undergoes

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ionization to give solvated ion pairs $BCl_2(py)_2^+,BCl_4^-$ or BCl_2pyS^+,Cl^- and the corresponding ions in very low concentrations.

Discussion

There is a strong tendency for boron halides to interact with Lewis bases to form tetracoordinated species. There is no concrete evidence to indicate that the boron halides, in weakly basic solvents, have coordination numbers less than 4. Even in the nonpolar solvent, benzene, there is evidence for the formation of molecular addition compounds with boron tribromide.[20] Thus, boron halides provide systems uncomplicated by multiple coordination numbers, a characteristic which simplifies interpretation of experimental results.

In a previous study[3] it was shown that boron trichloride behaves as a weak electrolyte in acetonitrile. Because infrared spectral measurements indicate a high concentration of tetrachloroborate ion, it was suggested that boron trichloride is ionized according to the mechanism

$$2SBCl_3 \overset{K'_i}{\rightleftharpoons} [S_2BCl_2^+,BCl_4^-] \overset{K'_d}{\rightleftharpoons} S_2BCl_2^+ + BCl_4^-$$

with $K'_i \gg K'_d$. The symbol S refers to neutral solvent molecules.

This study shows that boron tribromide behaves in a manner similar to boron trichloride. The boron tribromide solutions are weakly conducting and contain a relatively high concentration of $S_2BBr_2^+,BBr_4^-$ ion pairs. Boron triiodide, on the other hand, behaves as a typical 1:1 strong electrolyte in acetonitrile to give $S_2BI_2^+$ and iodide ions.

This difference in behavior is best understood in terms of the coordination model.[21] Consider the equilibria

$$S + SBX_3 \overset{K_i}{\rightleftharpoons} S_2BX_2^+,X^- \qquad (1)$$

$$S_2BX_2^+,X^- \overset{K_d}{\rightleftharpoons} S_2BX_2^+ + X^- \qquad (2)$$

$$S_2BX_2^+,X^- + SBX_3 \overset{K'_i}{\rightleftharpoons} S_2BX_2^+,BX_4^- + S \qquad (3)$$

$$S_2BX_2^+,BX_4^- \overset{K'_d}{\rightleftharpoons} S_2BX_2^+ + BX_4^- \qquad (4)$$

The gas-phase ionization energy for the boron–halogen bonds in $>B-X(g) \rightarrow >B^+(g) + X^-(g)$ were calculated to be 186, 166, and 151 kcal mol^{-1} for BCl_3, BBr_3, and BI_3, respectively.[22] The increasing tendency for ionization (eq 1) in going from BCl_3 to BI_3 is governed in large measure by this diminishing B–X bond strength. The coulombic interaction between the ions formed in eq 1 diminishes in passing from boron trichloride to boron triiodide. As a result, dissociation occurs to an increasing extent in eq 2 as one goes from $S_2BCl_2^+,Cl^-$ to $S_2BI_2^+,I^-$.

Why boron triiodide does not ionize according to eq 1, 3, and 4 to give the tetraiodoborate ion is best understood in thermodynamic terms. The infrared studies and conductance measurements of the tetraethylammonium tetraiodoborate salt in acetonitrile[4] demonstrate that the tetraiodoborate ion is thermodynamically unstable in acetonitrile and dissociates into $S_2BI_2^+$ plus two iodide ions. The equilibrium $BX_4^- + S = SBX_3 + X^-$ and eq 1 and 2 have large equilibrium constants which favor displacement of the iodide ion by solvent molecules. Conductance and infrared studies[4] demonstrate that the BCl_4^- and BBr_4^- ions are stable in acetonitrile. In these systems the B–Cl and B–Br bonds are sufficiently strong to prevent the weakly basic acetonitrile molecules, though present in high concentration, from displacing the halide ions. The B–I bond energy is sufficiently small to allow displacement of iodide.

Blocking of the fourth coordination site of boron trichloride or boron tribromide with a strongly coordinated neutral ligand such as pyridine[23] serves to prevent ionization either by the process shown in eq 1 or by that shown in eq 3. The 1:1 adducts of pyridine and boron trichloride and of pyridine and boron tribromide are essentially nonconductors in acetonitrile. The infrared spectra of the solution are identical with the spectra of the corresponding crystalline material. It is concluded that the solvent acetonitrile is of insufficient donor strength to displace either the pyridine, the chloride, or the bromide ion from the boron adducts. In the case where the neutral ligand in the SBX_3 species is acetonitrile, the neutral ligand is displaced by the stronger bases chloride and bromide ion according to eq 3 to give a high concentration of $S_2BX_2^+,BX_4^-$ ion pairs.

In the case of boron triiodide, pyridine readily displaces the iodide ion as well as occupying the fourth coordination site to give the ionic 1:2 complex $[(C_5H_5N)_2BI_2^+][I^-]$. This compound behaves as a typical 1:1 electrolyte in acetonitrile.[4]

Substitution of a phenyl group for a halogen in the boron trihalides may be expected to weaken the remaining B–X bonds owing to the π interaction of the phenyl electrons with the partially empty p_z orbital of the boron.[24] The effect of this interaction is to reduce the π back-bonding of the halogen and thus to reduce the ionization energy of the B–X bond. The short B–C distance in dihalophenylboranes[25] from electron diffraction studies was attributed to the π bonding in the B–C bond. Molecular orbital calculations[26] on the dihalophenylboranes, however, indicate the electron density on boron arises mainly from the halogen–boron π orbitals. The contribution from the phenyl ring amounts only to about 5%. Moreover, it was indicated that the B–X bond order is higher than that of the B–C bond.

Our results indicate that the phenyl group does not

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(22) J. C. Lockhart, *J. Chem. Soc., A*, 809 (1966).

(23) The ΔH for phenol + donor = phenol–donor is −3.3 kcal mol^{-1} when the donor is acetonitrile and −8.07 kcal mol when pyridine is the donor. See ref 21, p 294.

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stabilize the boronium ions $C_6H_5BXS_2^+$ and $(C_6H_5)_2BS_2^+$ to any great extent. In the case of the diphenylhaloboranes the shape of the conductance curve suggests that all equilibria given in eq 1–4 are involved.

Experimental Section

Preparation and Purification of Reagents.—Boron tribromide (Alfa Inorganics) was purified by repeated vacuum distillation through traps at −45 and −63.5° until the vapor pressure was constant at 18.0 ± 0.2 mm at 0° (lit.[27] 18.5 mm at 0°).

Boron triiodide was prepared according to the procedure described by Klanberg and coworkers.[28] The colorless crystalline boron triiodide readily undergoes photochemically induced dissociation. In order to avoid the difficulty of purifying and storing pure samples of boron triiodide, samples of the boron triiodide–acetonitrile adduct were prepared from slightly impure samples of boron triiodide. The crystalline adduct is easily purified by recrystallization from acetonitrile. Consequently, all conductance studies of the boron triiodide system were carried out using the boron triiodide–acetonitrile adduct.

Dichlorophenylborane was prepared by the method described by Burch, *et al.*[29] The resulting deep red liquid was fractionally distilled under reduced pressure and the colorless fraction [bp 49–52° (5 mm)] was collected in an ampoule with a breaker side arm. Further purification was obtained by repeated vacuum distillation through traps at −80 and 0°. The final product has a vapor pressure of 78 mm at 23°.

Samples of bromo- and chlorodiphenylboranes were kindly provided by Mr. B. Laube. The slightly discolored chlorodiphenylborane was fractionally distilled under reduced pressure and the center cut boiling at 98–100° (1 mm) [lit. bp 94–96° (0.1 mm),[30] 106–108° (3–4 mm)[31]] was retained. Bromodiphenylborane was fractionally distilled under reduced pressure and the fraction boiling at 84–85° (0.01 mm) [lit.[30] bp 112–115° (0.05 mm)] was collected.

Boron Halide–Acetonitrile Adducts.—The crystalline 1:1 adducts of acetonitrile with BCl_3, BBr_3, and BI_3 were prepared by standard procedures[1,32] and purified by vacuum sublimation at 60–70°. The adduct of dichlorophenylborane was prepared by the direct addition of acetonitrile to a solution of dichlorophenylborane in carbon tetrachloride and was purified by vacuum sublimation at 70° (1 mm). The white crystalline product melts at 118–121° in a sealed ampoule (lit.[22] mp 118.5–120.5°).

Boron Halide–Pyridine Adducts.—These were prepared by the direct addition of pyridine to a cooled solution (−80°) of the halide in methylene chloride and were purified by vacuum sublimation.

The purified $BCl_3 \cdot py$ adduct melts sharply at 113.0–113.5° (lit.[33] mp 113–114°). *Anal.* Calcd for $C_5H_5BCl_3N$: C, 30.58; H, 2.55; Cl, 54.22; N, 7.14. Found: C, 30.55; H, 2.42; Cl, 54.04; N, 7.27.

Crystalline $BBr_3 \cdot py$ melts sharply at 127.0–127.5° (lit. mp 127–128°,[19] 128–129°[32]). *Anal.* Calcd for $C_5H_5BBr_3N$: C, 18.20; H, 1.50; Br, 72.72; N, 4.25. Found: C, 18.64; H, 1.48; Br, 72.50; N, 4.31.

The preparation of $BI_3 \cdot 2py$ has been described elsewhere.[4]

The apparatus and procedure for conductance measurements were described before in detail.[1,3,4] The ^{11}B nmr spectra were taken with a Varian Model HA-100 high-resolution spectrometer operated at 32.083 Mc using the boron trifluoride–diethyl ether adduct as the external reference. The infrared spectra were recorded on a Beckman Model IR 10 spectrophotometer.

Acknowledgment.—The assistance of Mr. Robert Thrift in taking the ^{11}B nmr spectra and the generosity of the University of Illinois in making its instruments available are gratefully acknowledged.

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Reactivity of Boroxine. Reactions with Azomethane and Azoethane[1]

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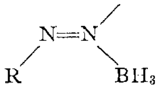
A product of the reaction of boroxine with azomethane and azoethane has been identified as a 1:1 azoalkane–borine addition compound. Structural information based on infrared and nuclear magnetic resonance data indicate that the product has the unsymmetrical configuration



Introduction

Previous investigations of the chemistry of boroxine ($H_3B_3O_3$) have shown this compound to be reactive with a series of simple reagents: O_2,[2] CO,[2] BX_3,[3] and PF_3.[4] In the reactions with CO and PF_3 boroxine behaves as an effective source of BH_3, to form simple addition-type products, while in the reaction with O_2 cyclic $H_2B_2O_3$ is produced. From these observations it was anticipated that azo compounds should react with boroxine either to yield new cyclic derivatives through the N=N linkage or to form addition products. This paper is the result of a series of studies of the reactions of boroxine with azomethane and azoethane.

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