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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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On the Nature of Coordination Compounds of Boron Halides and Diborane in Ether Solutions

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It is known that boron trifluoride and boron trichloride form molecular compounds with diethyl ether in a ratio of 1 : 1 ([1,2]), and the etherate BF_3 is very stable and can be distilled without decomposition. On this basis it could be assumed that, in ether solutions, boron trihalides exist in the form of monoetherates. We have recently found, however, that treatment of an ethereal solution of BCl_3 with ferric chloride gives a boronium salt–tetrachloroferrate of dichloro-bis(diethoxide)-boronium (I) ([3]). These

$$\{Cl_2B[O(C_2H_5)_2]_2\}FeCl_4 \tag{I}$$

data indicated the presence in solution of a complex salt with the cation $\{Cl_2B[O(C_2H_5)_2]_2\}^+$ and the anion Cl^- or BCl_4^-.

Fig. 1. Dependence of the equivalent electrical conductivity on concentration: $a–BCl_3$, $b–BBr_3$, $v–ClBH_2$, $g–BF_3$

Determination of the molecular weight of the etherate of boron trichloride in ether solution (concentration $\sim 0.15\,m$) by Ziegner' s method ([4]) gave values approximately 1.5 times higher than the molecular weight of $BCl_3O(C_2H_5)_2$ (found 303.4, 292.5; calculated 191.3). Thus, at this concentration about 55% of the etherate of boron trichloride is converted into a boronium salt of structure (II). The remaining portion of the etherate

$$\{Cl_2B[O(C_2H_5)_2]_2\}BCl_4 \tag{II}$$

may exist in solution in the form of a neutral complex (III), a boronium salt (IV), or their equilibrium mixture

$$BCl_3 \cdot O(C_2H_5)_2 + (C_2H_5)_2O \rightleftarrows \{Cl_2B[O(C_2H_5)_2]_2\}Cl. \tag{IV}$$

Fig. 2. Dependence of equivalent conductivity on concentration: 1 –(n-$CH_3C_6H_4)_2BCl$, 2 –(α-$C_{10}H_7$)BCl, 3 –$(C_6H_5)_2BCl$, 4 –(o-$CH_3C_6H_4)_2BCl$, 5 –(n-$C_4H_9)_2BCl$

Figure 2: Fig. 2. Dependence of equivalent conductivity on concentration: 1 –(n-$CH_3C_6H_4)_2BCl$, 2 –(α-$C_{10}H_7$)BCl, 3 –$(C_6H_5)_2BCl$, 4 –(o-$CH_3C_6H_4)_2BCl$, 5 –(n-$C_4H_9)_2BCl$

Analogous boronium salts are also formed in ether solutions by other boron trihalides–BF_3 and BBr_3. The etherate of boron trifluoride in an $\sim 0.2\,M$ ether solution is converted by ~ 40% into salt (V), whereas boron tribromide forms salt (VI) only by 20%. (Molecular weight of the etherate BF_3: found 193.5, 200.8; calculated 141.9; BBr_3: found 292.0, 292.2; calculated 250.0.)

$$\{F_2B[O(C_2H_5)_2]_2\}BF_4; \tag{V}$$

$$\{Br_2B[O(C_2H_5)_2]_2\}BBr_4. \tag{VI}$$

The ionic structure of the complexes of boron trihalides formed in ether solutions is confirmed by conductivity data. We investigated the conductivity of solutions of BF_3, BCl_3, and BBr_3 in diethyl ether. The measurements were carried out in an H-shaped vessel with four stopcocks (two for introducing nitrogen and two for draining the spent solution) and two platinized platinum electrodes (5). The capacity of the vessel at 18° was 13.2411 ohm^{-1}. To determine the conductivity, direct current with a stabilized voltage of 500 and 1000 V was used. It should be noted that in all cases the conductivity at 1000 V was twice as great as at 500 V. The readings of the microammeter did not change upon rapid reversal of the poles. The diethyl ether used as solvent was dried and distilled over phosphorus anhydride, and then over lithium hydride. The specific conductivity of the solvent prepared in this way at 18° was $< 4.2 \cdot 10^{-11}$ ohm^{-1} cm^{-1}. The halides under study were distilled before the solutions were prepared. The conductivity of the solutions was measured over a concentration range from 10^{-3} to $7 \cdot 10^{-1}$ mol/l. For each measurement in all series, a separate solution was prepared by diluting the standard (1 M) solution with the calculated amount of ether.

Fig. 2. Dependence of equivalent conductivity on concentration:
1 –(n-$CH_3C_6H_4)_2BCl$,
2 –(α-$C_{10}H_7$)BCl,
3 –$(C_6H_5)_2BCl$,
4 –(o-$CH_3C_6H_4)_2BCl$,
5 –(n-$C_4H_9)_2BCl$.

All the solutions investigated conducted electric current. The curves constructed from the results obtained for the dependence of the equivalent conductivity (λ)

Fig. 3

Figure 3: Fig. 3

Fig. 4: plot of $\lg \lambda$ versus $\lg C$ for BCl_3 and $(C_6H_5)_2BCl$.

Figure 4: Fig. 4: plot of $\lg \lambda$ versus $\lg C$ for BCl_3 and $(C_6H_5)_2BCl$.

on concentration ($\sqrt{C}$) (Fig. 1) show that, in the region of very dilute solutions, with increasing concentration the equivalent conductivity decreases and then, after reaching a minimum, increases again. Apparently, in dilute solutions there exist mainly digaloido-bis(diethoxy)-boronium halides (salts of type IV), which, as the concentration is increased, rearrange into tetragaloidoborates of digaloido-bis(diethoxy)-boronium (II, V, VI), possessing a higher degree of dissociation.

Fig. 3

The ability to conduct current was also found for ether solutions of certain diarylboron chlorides ($(C_6H_5)_2BCl$, $(o\text{-}CH_3C_6H_4)_2BCl$, $(n\text{-}CH_3C_6H_4)_2BCl$, and $(\alpha\text{-}C_{10}H_7)_2BCl$) and di-*n*-butylboron chloride. Graphically, the dependence of the equivalent conductivity on the concentration of these compounds (Fig. 2) is expressed by a curve strongly concave toward the abscissa axis, which is characteristic of weak electrolytes. As can be seen from Fig. 2, organoboron chlorides, in the character of the depend—

λ from $\sqrt{C}$ differ from the boron trihalides. Evidently, this is explained by the fact that organoboron chlorides in ether solution are converted only into diaryl-bis-(diethoxy)-boronium chlorides and do not form salts with a more complex anion of the type BCl_4^-. This is consistent with the results of determinations of the molecular weights of diarylboron chlorides, whose values corresponded to the monomeric form (for $(C_6H_5)_2BCl$, found 208.0, calculated 200.5; for $(o\text{-}CH_3C_6H_4)_2BCl$, found 248.0, calculated 228.5).

We next investigated the electrical conductivity of an ether solution of chloroborane. As is seen from the curve shown in Fig. 1, an ether solution of chloroborane has approximately the same electrical conductivity as solutions of boron trihalides. This indicates the presence in solution of the cation $\{H_2B \cdot [O(C_2H_5)_2]_2\}^+$. In this connection it seemed of interest to investigate the electrical conductivity of ether solutions of diborane. Since diborane is relatively sparingly soluble in diethyl ether, the measurements were carried out in tetrahydrofuran solution. It turned out that the latter conducts electric current rather well (Fig. 3). Thus, diborane in tetrahydrofuran dissociates with formation of an ionic complex which, probably by analogy with "diborane diammoniate" (6), has the structure (VII):

$$B_2H_6 + 2C_4H_8O \rightleftharpoons [H_2B(OC_4H_8)_2]^+BH_4^-. \qquad \text{(VII)}$$

Fig. 4

The data obtained shed new light on the mechanism of various transformations of diborane occurring in ether solutions, in particular on the mechanism of hydroboration; in considering this mechanism it is now necessary to take into account not only the participation of boron etherate, as was done previously, but also the participation of the ionic complex (VII).

In order to determine the degree of ionization of boronium salts formed in ether solutions (for boron trichloride and diphenylboron chloride), we used the method proposed by Fuoss and Kraus(7) for calculating the dissociation constants of weak electrolytes. To obtain the additional data required for such a calculation, the electrical conductivity of these two chlorides was measured in very dilute solutions over the concentration range from 10^{-6} to $2 \cdot 10^{-4}$ mole/liter.

Graphically, the dependence of $\lg \lambda$ on $\lg C$ for BCl_3 and for $(C_6H_5)_2BCl$ is represented by a straight line (Fig. 4), which, as a first approximation for electrolytes with a low degree of dissociation, is an indication of the presence of an ordinary binary equilibrium. Deviation from linearity is observed at concentrations exceeding $2 \cdot 10^{-4}$ mole/liter. By successive threefold extrapolation of the experimental data expressing the dependence of λ on $\sqrt{C}$, and by subsequent calculations, the values of the equivalent electrical conductivity at infinite dilution (λ_0) and of the dissociation constant were found; they are, respectively, $9.80\ \Omega^{-1}\mathrm{cm}^2$ and $7.72 \cdot 10^{-9}$ for boron trichloride, and $12.05\ \Omega^{-1}\mathrm{cm}^2$ and $1.06 \cdot 10^{-9}$ for diphenylboron chloride.

The degree of dissociation, which in the most approximate form is expressed by the ratio λ/λ_0, proves at a concentration of $1 \cdot 10^{-6}$ mole/liter to be equal to 0.086 for BCl_3 and 0.041 for $(C_6H_5)_2BCl$. With increasing concentration these quantities fall rapidly and, at concentrations of the order of 10^{-4} mole/liter, amount to $6.5 \cdot 10^{-3}$ for BCl_3 ($C = 2 \cdot 10^{-4}$ mole/liter), and $3.67 \cdot 10^{-3}$ for $(C_6H_5)_2BCl$ ($C = 1 \cdot 10^{-4}$ mole/liter). From the calculation results given above it is seen that

for boron trichloride and diphenylboron chloride the values of λ_0 are quite close ($9.80\ \Omega^{-1}\ \mathrm{cm}^2$, $12.05\ \Omega^{-1}\mathrm{cm}^2$). On this basis one may quite justifiably assume that, for compounds of the same type as $(C_6H_5)_2BCl$, the values of λ_0 will differ little from $12\ \Omega^{-1}\mathrm{cm}^2$, and, consequently, the degree of dissociation of the boronium salts existing in ethereal solutions (at the same concentrations) decreases in the series:

$$\{(n\text{-}CH_3C_6H_4)_2B[O(C_2H_5)_2]_2\}Cl > \{(\alpha\text{-}C_{10}H_7)_2B[O(C_2H_5)_2]_2\}Cl >$$
$$> \{(C_6H_5)_2B[O(C_2H_5)_2]_2\}Cl > \{(o\text{-}CH_3C_6H_4)_2B[O(C_2H_5)_2]_2\}Cl >$$
$$> \{(n\text{-}C_4H_9)_2B[O(C_2H_5)_2]_2\}Cl.$$

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[1] N. Greenwood, R. Martin, *Quart. Rev.*, **8**, 1 (1954).
[2] W. Gerrard, M. Lappert, *Chem. Rev.*, **58**, 1081 (1958).
[3] B. M. Mikhailov, V. D. Sheludyakov, T. A. Shchegoleva, *Izv. AN SSSR, OKhN*, 1962, 1698.
[4] R. Signer, *Ann.*, **478**, 246 (1930).
[5] B. M. Mikhailov, K. N. Kurdyumova, *ZhOKh*, **25**, 1734 (1955).
[6] D. Schultz, R. Parry, *J. Am. Chem. Soc.*, **80**, 4 (1958).
[7] C. Gladstone, *Introduction to Electrochemistry*, IL, 1951, p. 223.

Note: Figure translations are in progress. See original paper for figures.

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