STUDY OF THE ELECTRICAL CONDUCTIVITY OF AQUEOUS AND NONAQUEOUS SOLUTIONS OF TRIFLUOROBORAZANE

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Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Abstract

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STUDY OF THE ELECTRICAL CONDUCTIVITY OF AQUEOUS AND NONAQUEOUS SOLUTIONS OF TRIFLUOROBORAZANE

Trifluoroborazane BF_3NH_3 is a typical representative of compounds with a donor-acceptor bond. Of great interest is the elucidation of the nature of the bond in such compounds between the donor and acceptor atoms. The available literature data on this question are very limited (1-3).

Thermochemical and spectroscopic studies have shown that the heat of reaction of gaseous boron fluoride and ammonia is

Fig. 1. Dependence of the electrical conductivity *(1)* and the concentration of hydrogen ions *(2)* of a 0.1 M solution of BF_3NH_3 in water on temperature

Fig. 2. Measurement of the electrical conductivity of aqueous and nonaqueous solutions of BF_3NH_3 with time at different temperatures. *a* —aqueous solutions, *b* —solutions in dimethylformamide, *c* —alcoholic solutions

27.5 kcal/g-mol (1) at 25° and that the force constant of the B—N bond in the trifluoroborazane formed is $4.4 \cdot 10^5$ dyn/cm (2). These data indicate a rather strong interaction between the boron and nitrogen atoms. A study of aqueous solutions of trifluoroborazane (4, 5) showed that its hydrolysis in neutral and weakly acidic solutions proceeds rather slowly and is observed only at temperatures above 25°.

We measured the electrical conductivity of solutions of trifluoroborazane in water, ethyl alcohol, and dimethylformamide. Figs. 1—4 give the results for aqueous and nonaqueous solutions of BF_3NH_3. Conductometry is a sensitive method for detecting highly conducting ions.

The characteristic family of curves shown in Fig. 2 indicates that a noticeable increase in electrical conductivity with time is observed only

Figure 3

Figure 2: Figure 3

above 25°. For a 0.1 M solution, the specific electrical conductivity at 25° is $3.16\cdot 10^{-4}\ \Omega^{-1}\cdot \mathrm{cm}^{-1}$. This value is of the same order as the electrical conductivity of aqueous solutions of ammonia and acetic acid of the same concentration. With increasing temperature, the conductivity of BF_3NH_3 solutions increases (see Fig. 1) and at 50° reaches $3.82\cdot 10^{-4}\ \Omega^{-1}\cdot \mathrm{cm}^{-1}$, and after an hour $7.95\cdot 10^{-4}\ \Omega^{-1}\cdot \mathrm{cm}^{-1}$. From 5 to 15° the electrical conductivity remains unchanged for a long time. This indicates the absence of hydrolysis at low temperatures.

But on the other hand (see Fig. 1), BF_3NH_3 solutions contain a considerable concentration of hydrogen ions, pH 3.5—3.6. Apparently, the source of the hydrogen ions, and consequently of the considerable conductivity, is the possibility of dissociation of trifluoroborazane in aqueous solutions by an acid mechanism, for example,

$$\mathrm{BF_3NH_3} \rightleftharpoons [\mathrm{BF_3NH_2}]^- + \mathrm{H}^+.$$

Thus, this phenomenon resembles the acid dissociation of platinum ammines with formation of amido derivatives, described in works (^{6,7}):

$$[\mathrm{Pt6NH_3}]^{4+} \rightleftharpoons [\mathrm{Pt5NH_3NH_2}]^{3+} + \mathrm{H}^+.$$

Fig. 3. Conductivity of aqueous solutions of trifluoroborazane upon dilution: 1—15°, 2—25°

Measurements of the electrical conductivity of BF_3NH_3 upon dilution (see Fig. 3) show that the dependence of the equivalent electrical conductivity λ on concentration in the coordinates λ—$\sqrt{C}$ is proportional in character and obeys Onsager' s law only in the concentration interval 0.1—0.003 g-equiv/l, after which a sharp increase in electrical conductivity is observed in the region of high dilutions. Indeed, solutions of weak electrolytes do not obey Onsager' s law, since at high dilutions the degree of dissociation increases, as a result of which the equivalent electrical conductivity rises sharply.

Theoretically, the mechanism of dissociation of BF_3NH_3 in aqueous solutions proposed above can be explained as follows. The strong electronegativity of fluorine enhances the acceptor ability of the BF_3 group. Its electron unsaturation and the tendency of boron toward the coordinatively saturated tetravalent state lead in the BF_3NH_3 molecule to a considerable shift of electron density from the donor atom to the acceptor atom. This, in turn, causes the appearance of a certain negative charge ($\delta-$) at boron and positive charge ($\delta+$) at nitrogen. As a result, the hydrogen atoms bonded to nitrogen atoms become more "acidic," i.e., electron-deficient, in comparison, for example, with the original ammonia. Trifluoroborazane itself becomes capable of dissociating in polar media with elimination of a proton, i.e., according to the acid type. The presence of a positive charge at the nitrogen atom contributes to this to an even greater extent.

Some literature data also support the proposed mechanism of dissociation of BF_3NH_3. Thus, Brown and Johnson (^{8}) established the existence not only of the di- and triammine, but also of the tetraammine of boron fluoride, assigning the latter the following structure:

$$\begin{array}{c} \mathrm{H \cdots NH_3} \\ \mathrm{F_3B \leftarrow N{-}H \cdots NH_3} \\ \mathrm{H \cdots NH_3} \end{array}$$

The authors explain the existence of ammoniates of higher order by the protonic character of hydrogen in trifluoroborazane and by the possibility of the formation of hydrogen bonds through the free electron pair of nitrogen in ammonia.

It is interesting that in liquid ammonia trifluoroborazane also has conductivity (^{9}), and it is of the same order as the conductivity of aqueous solutions of acetic acid. Moreover, Kinan and McDowell (^{10}) found an energetic interaction of metallic potassium with a solution of BF_3NH_3 in liquid ammonia, accompanied by the evolution of hydrogen. These facts confirm the acid dissociation of BF_3NH_3 solutions in liquid ammonia. Apparently, in this case as well the dissociation mechanism is similar to that given above for aqueous solutions:

$$\mathrm{BF_3NH_3 + NH_3 = [BF_3NH_2]^- + NH_4^+}.$$

For clarification of the behavior of trifluoroborazane in solutions with different dielectric constants ε, we also carried out measurements of the electrical conductivity of BF_3NH_3 in ethyl alcohol and dimethylformamide. The data for a $0.1\,M$ solution at 20° are given in Fig. 2. The specific electrical conductivity in ethyl alcohol is $4.2 \cdot 10^{-5}$ $\mathrm{ohm^{-1} \cdot cm^{-1}}$, and in dimethylformamide, $7.2 \cdot 10^{-5}$ $\mathrm{ohm^{-1}cm^{-1}}$. The low values of electrical conductivity are explained by the low polarity of the solvents. Figure 4 gives the dependence of the specific electrical conductivity on the dielectric constant. A sharp increase in conductivity is seen on going from alcohol ($\varepsilon = 26.4$) and dimethylformamide ($\varepsilon = 37.6$) to water, for which $\varepsilon = 78.3$. Measurements of electrical conductivity were carried out on an apparatus whose schematic diagram is described in work (^{11}). The concentration of hydrogen ions was determined with an LPU-01 instrument.

Fig. 4. Dependence of the electrical conductivity of BF_3NH_3 solutions on the dielectric constant of the solvents

The synthesis of trifluoroborazane was described previously ([12]). The product obtained was purified by double recrystallization from water. The purity of the preparation was monitored by elemental analysis and spectroscopically.

Thus, the study of aqueous and nonaqueous solutions of trifluoroborazane has shown that BF_3NH_3 belongs to the class of weak electrolytes and is capable of dissociating by an acid mechanism.

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