

293. *The Electrochemistry of Boron Trifluoride Co-ordination Compounds. Part VII.* Degrees of Ionic Dissociation in the Molten State.*

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Evidence is presented which unequivocally establishes that the electrical conductivity of molten boron trifluoride complexes is due entirely to self-ionic dissociation of the co-ordination compounds. The percentage of ions free to conduct in a melt is shown to be numerically equivalent to the reduced conductivity, $\kappa = \mu\eta$, provided that the ratio of the activation energies of viscosity and conductivity, $m' = E_\eta/E_\mu$, is unity. This leads to values of the order of 10% for the degree of dissociation of the hydroxyl-containing complexes of boron trifluoride with water, alcohols, and acids, and 0.1% for the complexes with ethers, esters, and tertiary amines. The conduction characteristics of boron trifluoride complexes are compared with those of molten alkylammonium picrates and fused inorganic halides, to emphasize the conditions under which the calculations of the degree of ionic dissociation are valid.

BORON TRIFLUORIDE forms a number of organic and inorganic co-ordination compounds of varied catalytic activity (Booth and D. R. Martin, "Boron Trifluoride and its Derivatives," John Wiley & Sons, New York, 1949; Kästner, "Newer Methods of Preparative Organic Chemistry," Interscience Publ., New York, 1948). Discussions on the mechanism of catalysis in these liquids have, in the past, been largely speculative and often hampered by lack of precise information on the constitution of the molten phase;

* Part VI, *J.*, 1953, 757.

they have often assumed the existence of carbonium and other ions in the molten complex or reaction mixture and it has been the object of the present series of papers to investigate experimentally the hypothesis of ionic dissociation in boron trifluoride co-ordination compounds.

Preceding papers have demonstrated that the boron trifluoride compounds with water (Part IV, *J.*, 1951, 1915), alcohols (Part VI, *J.*, 1953, 757), ether (Part I, *J.*, 1950, 3030), acetic acid (Parts II and III, *J.*, 1951, 1328, 1795), and alkyl acetates (Part V, *J.*, 1953, 751) all conduct electricity. In addition, the electrical conductivities of boron trifluoride complexes with phenol (Sowa, Hinton, and Nieuwland, *J. Amer. Chem. Soc.*, 1933, 55, 3402), triethylamine (Greenwood, unpublished observations), pyridine (R. L. Martin, unpublished observations), orthophosphoric and pyrophosphoric acids (Topchiev, Paushkin, Vishnyakova, and Kurashov, *Doklady Akad. Nauk. S.S.S.R.*, 1951, 80, 381) are known (see Table I).

TABLE I. Boron trifluoride co-ordination compounds at 25°.

Compound	M. p.	$10^4\kappa$ (ohm ⁻¹ cm. ⁻¹)	μ (cm. ² ohm ⁻¹)	E_μ (kcal. mole ⁻¹)	E_η	m'	κ (cm. ² cp. ohm ⁻¹)	Ref.
BF ₃ .H ₂ O	6.0 ^b	245 †	1.17 †	3.7	3.8	1.0	10.5 †	Pt. IV
BF ₃ .2H ₂ O	6.2	779	4.98	3.2	4.1	1.3	17.2	Pt. IV
BF ₃ .MeOH ...	-18.6	124	0.883	3.1	3.2	1.0	2.22	Pt. VI
BF ₃ .2MeOH ...	-58.1	295	3.22	2.6	2.9	1.1	7.34	Pt. VI
BF ₃ .EtOH ...	-19	85.4	0.718	—	—	—	—	a
BF ₃ .2EtOH ...	—	106	1.46	2.8	2.9	1.0	4.13	b
BF ₃ .2Pr ⁿ OH ...	—	38	0.68	4.1	4.1	1.0	3.10	b
BF ₃ .PhOH.....	—	5.28	—	—	—	—	—	a
BF ₃ .2PhOH ...	—	11(50 ^c)	—	—	—	—	—	c
BF ₃ .AcOH ...	37.5	12.5 *	0.108 *	~8.5 *	~9.2 *	1.1	5.06 *	Pt. III
BF ₃ .MeOAc ...	65.5	6.74(65 ^c)	0.0766	6.4	5.0	0.8	0.175(65 ^c)	Pt. V
BF ₃ .EtOAc ...	32.5	1.24 *	0.0155 *	7.2 *	6.6 *	0.9	0.090 *	Pt. V
BF ₃ .Pr ⁿ OAc ...	14.7	0.938	0.0133	6.5	7.2	1.1	0.094	Pt. V
BF ₃ .Bu ⁿ OAc ...	17.9	0.319	0.0051	9.1	6.9	0.8	0.039	Pt. V
BF ₃ .Et ₂ O	-57.7	2.96	0.0374	3.4	3.1	0.9	0.071	Pt. I
BF ₃ .Et ₃ N	29.8	2.45 †	0.042 †	5.0	4.8	1.0	0.34 †	b
BF ₃ .C ₅ H ₅ N ...	48.4	5.09(50 ^c)	—	—	—	—	—	b
BF ₃ .H ₃ PO ₄ ...	-105	72.3	0.615	—	—	—	23	a
(BF ₃) ₂ .H ₄ P ₂ O ₇	-82	67	1.08	—	—	—	~105	a

Mean 1.0

* Supercooled liquid.

† Extrapolated.

a, Topchiev, Paushkin, Vishnyakova, and Kurashov, *Doklady Akad. Nauk. S.S.S.R.*, 1951, 80, 381; 1951, 80, 611. b, Greenwood and Martin, unpublished observations. c, Sowa, Hinton, and Nieuwland, *J. Amer. Chem. Soc.*, 1933, 55, 3402.

However, the existence of a measurable conductivity does not necessarily establish that the conducting entities are ions or that such ions are characteristic of the melt. Electrical conductivity may arise in any of the following ways: (i) self-ionic dissociation of the melt (*e.g.*, fused sodium chloride); (ii) ionic dissociation of dissolved impurities (*e.g.*, aqueous electrolytes); (iii) semi-conductivity (*e.g.*, fused lead sulphide); (iv) metallic conductivity (*e.g.*, liquid mercury); (v) various combinations of the preceding four mechanisms. That purified boron trifluoride co-ordination compounds conduct entirely by virtue of their *self-ionic dissociation* is consistent with the following evidence, which also eliminates the other four possibilities. (a) The compounds exhibit well-defined decomposition potentials, *D*, in the molten state (Parts I, II, IV, and VI); this eliminates all but (i), (ii), and (v). The value of *D* is characteristic for each complex; this renders (ii) and (v) unlikely. (b) Faraday's laws of electrolysis have been established (Parts II and IV); this eliminates all except (i) and (ii). (c) Electrolysis yields electrode products which are characteristic for each complex and are readily interpreted in terms of its empirical formula (Parts I, II, IV, and VI); this eliminates all except (i) and (v). (d) The shape of the conductivity-composition isotherms: reaction between two components of negligible conductivity ($<10^{-10}$ — 10^{-7} ohm⁻¹ cm.⁻¹) results in an immediate increase to values in the range 10^{-4} — 10^{-1} ohm⁻¹ cm.⁻¹. Minima in these isotherms correspond with 1 : 1 or 1 : 2 stoichiometric ratios of the components (Parts II, IV, V, and VI; Sowa, Hinton, and Nieuwland, *loc. cit.*;

Nieuwland, Vogt, and Foohey, *J. Amer. Chem. Soc.*, 1930, **52**, 1018); this eliminates all but (i) and, possibly, (iii). (e) The large increase in conductivity on melting (Parts III and IV); this eliminates (iii) and (iv). (f) The inverse relation between conductivity and viscosity (Parts I, III, IV, V, and VI); this eliminates (iii) and (iv). In short, electronic mechanisms are excluded by each of the six criteria, and of the two possible ionic mechanisms, (i) and (ii), conduction due to electrolytes present as impurity is eliminated by arguments (a), (c), and (d).

Degree of Ionic Dissociation.—The extent to which the molten complexes are dissociated into ions has not previously been evaluated. In this section, a method of estimating the degree of dissociation, α , is developed and the conditions under which it is reliable are examined. A distinction is drawn between ionization, which implies an appreciable separation of charge within a molecule, and ionic dissociation, which involves the separation of a molecule into anions and cations which are free to migrate under an applied potential. In this paper the extent to which kinetically free ions are formed is estimated: the structure of the undissociated form of the complex is not involved; it may or may not be ionized. In the same way, the mechanism of the dissociation process and the factors which influence the degree to which it occurs are not considered. The calculations merely determine the percentage of molecules which have undergone dissociation into ions in a given system.

The relation $\kappa = nev$ between the specific conductivity (κ), the number (n) of charge carriers, their charge (e), and mobility (v) shows that, if κ and v could be measured, the number of charge carriers and hence the degree (α) of ionic dissociation could be calculated. It is difficult to devise methods for measuring ionic mobilities in pure melts, so that, in the absence of experimental values of v , calculation of α turns on an ability to estimate the mobility satisfactorily. The ensuing discussion is centred on finding valid conditions for estimating v ; this done, the degree of dissociation follows without difficulty.

In general, the specific conductivity, κ , and molar conductivity, $\mu = M\kappa d^{-1}$ vary exponentially with temperature:

$$\kappa = \kappa_0 e^{-E_\kappa/RT} \quad \dots \dots \dots (1)$$

$$\mu = \mu_0 e^{-E_\mu/RT} \quad \dots \dots \dots (2)$$

where M is the molecular weight, d the density, κ_0 and μ_0 are constants, and E_κ and E_μ are activation energies of ionic migration calculated on the basis of 1 ml. and 1 mole of compound, respectively. At room temperature E_κ and E_μ are very similar, differing only by about 0.1 kcal. mole⁻¹, but it has recently been shown that at higher temperatures the difference may be appreciable, and that use of E_μ rather than of E_κ is preferred for comparative purposes (R. L. Martin, to be published).

Frequently, the viscosity may also be represented by an exponential relation,

$$\eta = \eta_0 e^{E_\eta/RT} \quad \dots \dots \dots (3)$$

where E_η is the activation energy for the process of viscous flow. Elimination of T from equations (1) and (3) gives the relation

$$\kappa^m \eta = \text{constant} \quad \dots \dots \dots (4)$$

where $m = E_\eta/E_\kappa$. Similarly, from equations (2) and (3) it follows that

$$\mu^{m'} \eta = \text{constant} \quad \dots \dots \dots (5)$$

where $m' = E_\eta/E_\mu$. Values of E_μ , E_η , and m' calculated from the slopes of plots of $\log \mu$ against $1/T$ and $\log \eta$ against $1/T$ are presented in Table 1 for a number of boron trifluoride complexes.

It is important for the present argument to note that $m' \sim 1$ for all the complexes; its mean value is 1.0. These values should be compared with those given in Table 3 for molten salts where m' is frequently considerably greater than unity.

By inserting $m' = 1$ in equation (5) it is seen that $\mu\eta = \text{const.}$, *i.e.*, Walden's rule is experimentally established for boron trifluoride systems. The function $\mu\eta$ has been used by many authors to compare the relative conducting powers of electrolytes, because it is independent of molar concentration (or molar volume) and also makes allowance for

variation of mobilities caused by changes in viscosity. However, it has frequently been overlooked that this linear dependence of mobility on fluidity ($1/\eta$) implies that similar configurational changes occur in ionic migration and viscous flow, as shown by a similarity in the activation energies of the two processes. The function $\mu\eta$ has been termed the "reduced conductivity" (Part III) and is denoted by \mathfrak{K} . Reduction of the specific conductivity κ to a standard state of 1 mole and unit viscosity does, in fact, give an almost temperature-independent function (see Parts I and III—VI for experimental results).

In the case of a molten uni-univalent electrolyte the specific conductivity will be given by the formula

$$\kappa = n_+ e v_+ + n_- e v_- \quad \dots \quad (6)$$

As the number of cations and anions are equal, this becomes

$$\kappa = n e (v_+ + v_-) \quad \dots \quad (7)$$

where n is the number of charge carriers of one sign. The number of moles of compound per ml. is dM^{-1} so that the number of molecules is

$$n_0 = NdM^{-1} \quad \dots \quad (8)$$

where N is Avogadro's number. From (7) and (8) it follows that the ratio of the number of ions of one sign to the total original number of molecules is

$$\frac{n}{n_0} = \frac{M\kappa}{Nde(v_+ + v_-)} = \frac{M\kappa}{2Nde v} \quad \dots \quad (9)$$

where v is now the average mobility of cations and anions in a medium of viscosity η . From the experimental fact established above that $m' = 1$, this mobility may be related to a standard reference mobility v_0 in a medium of unit viscosity (1 cp.) by using the relation

$$v = v_0 \eta^{-1} \quad \dots \quad (10)$$

In a uni-univalent electrolyte, the number of ions of one sign equals the number of dissociating molecules, so that equations (9) and (10) give the percentage degree of ionic dissociation as

$$\alpha = \frac{n}{n_0} = \frac{M\kappa\eta}{d} \cdot \frac{100}{2Nev_0} \quad \dots \quad (11)$$

Values of v_0 are limited to a very narrow range of mobilities. Thus, reference to tables of ionic mobilities in aqueous or non-aqueous solutions (Kortüm and Bockris, "Textbook of Electrochemistry," Elsevier Publ. Co. Inc., 1951, p. 701) indicates that in any particular solvent *all mobilities are within a factor of ten of each other*. In water, for which the viscosity at 20° is 1.00 cp., all ions except hydrogen and hydroxyl have mobilities in the range 2.5×10^{-4} to 10×10^{-4} cm.² sec.⁻¹ volt⁻¹, so that a value $v_0 = 5 \times 10^{-4}$ cm.² sec.⁻¹ volt⁻¹ represents all mobilities to within a factor of 2. Because of the established relation between mobility and viscosity it is also valid to use this figure as a plausible standard average mobility in boron trifluoride complexes when reduced to unit viscosity. With this figure, the numerical value of the term $100/2Nev_0$ in equation (11) becomes unity, so that the percentage degree of ionic dissociation is given directly by the reduced conductivity :

$$\alpha \sim \mu\eta = \mathfrak{K} \quad \dots \quad (12)$$

In this way, the values of \mathfrak{K} listed in Table I give a useful indication of the extent to which boron trifluoride complexes dissociate into ions. The compounds with water, alcohols, and acetic acid are 2—20% dissociated into ions. The compounds with ortho- and pyro-phosphoric acid are also highly dissociated, but it is not possible to identify \mathfrak{K} with α here as it has not been established whether the compounds dissociate into uni-univalent or uni-multivalent ions. It will be noted that all these compounds contain a hydroxyl group in the molecule. On the other hand, complexes with ethyl ether and the esters are only weakly dissociated; values of α vary between 0.04 and 0.2%, indicating that their melts are predominantly molecular. These conclusions are consistent with the chemical behaviour of the various complexes.

It is stressed that these are order-of-magnitude calculations only. For this reason too much weight should not be placed on the apparently systematic decrease of α with

increasing chain length of the alcohols and esters. It would be safe to conclude, though, that the acetate complexes are considerably less dissociated than the acetic acid complex. The viscosity correction is not likely to introduce serious error for the reasons discussed earlier, but the arbitrary value of v_0 used for all complexes might introduce some error as it is based on data for infinite dilution. Many of the complexes considered have ionic concentrations of the order of 1 molar and for these more highly dissociated compounds, estimates of α are likely to be low. (The number of moles per litre is $1000dM^{-1}$ of which $\alpha\%$ are ionized; hence there are $10\alpha dM^{-1}$ moles per litre as free ions.)

Comparison with Other Molten Systems.—The conclusions deduced in the preceding section are supported by a re-analysis of the data of Walden, Ulich, and Birr (*Z. physikal. Chem.*, 1927, **130**, 495; 1928, **131**, 1, 21) for 22 molten picrates, with κ as a basis for estimation of the degree of ionic dissociation. Although these authors did not represent their conductivity and viscosity results in exponential form, their data do, in fact, conform to such equations and, when plotted in this way, lead to the values of E_μ , E_η , and m' given in Table 2. Here again the proximity of m' to unity permits an interpretation of the reduced conductivity in terms of the degree of ionic dissociation.

From Table 2 the average value of α_{150° for primary alkylammonium picrates is 36% and for secondary alkylammonium picrates, 37%. This is consistent with these authors' conclusions from other arguments (*ibid.*, 1928, **131**, 31; Walden, *ibid.*, 1931, **157**, 389) that primary and secondary alkylammonium picrates are incompletely dissociated.

The behaviour of the tertiary salts showed them to be the weakest electrolytes and this is consistent with the present evaluation of their reduced conductivity which is equivalent to an average degree of dissociation of 12%. The best-conducting picrates were the quaternary ammonium salts and it was concluded that these were practically completely dissociated into ions. The present concepts give a formal value of 48% as the average for salts in this class.

TABLE 2. Alkylammonium picrates at 150°.

Compound (Pic = picrate)	M. p.	$10^4\kappa$ (ohm ⁻¹ cm. ⁻¹)	μ (cm. ² ohm ⁻¹)	E_μ (kcal. mole ⁻¹)	E_η	m'	κ (cm. ² cp. ohm ⁻¹)
Et·NH ₃ Pic	169·8 ^a	80 *	1·67 *	7·6	7·9	1·0	~45 *
Pr ⁿ ·NH ₃ Pic	144	61·1	1·31	9·6	11·7	1·2	40·6
Bu ⁿ ·NH ₃ Pic	150·3 d	50·3	1·16	9·7	10·3	1·1	33·0
Bu ^t ·NH ₃ Pic	150·3 d	48·2	1·11	9·8	12·0	1·2	41·1
<i>n</i> -C ₅ H ₁₁ ·NH ₃ Pic	143·5	42·5	1·07	10·1	11·8	1·2	31·4
<i>iso</i> -C ₅ H ₁₁ ·NH ₃ Pic ...	132·8	35·6	0·888	11·3	12·5	1·1	33·4
<i>n</i> -C ₇ H ₁₅ ·NH ₃ Pic	124·2	30·1	0·864	10·7	11·8	1·1	25·7
Me ₂ NH ₂ Pic	160—161	19 *	3·75 *	6·0	8·4	1·4	~60 *
MeEtNH ₂ Pic	96·8	156·3	3·36	7·4	8·7	1·2	47·4
Et ₂ NH ₂ Pic	70·7	131·5	3·12	6·9	6·9	1·0	29·7
Pr ⁿ ₂ NH ₂ Pic	98·6	91·2	2·48	7·7	7·7	1·0	29·1
(<i>n</i> -C ₅ H ₁₁) ₂ NH ₂ Pic ...	94·5	40	1·39	8·7	9·2	1·1	19·3
Et ₃ NHPic	174·5	70 *	1·88 *	7·9	7·4	0·9	~20 *
Pr ⁿ ₃ NHPic	114—115	41·4	1·35	9·0	7·4	0·8	10·3
(<i>iso</i> -C ₅ H ₁₁) ₃ NHPic ...	124·6	12·4	0·546	9·8	8·9	0·9	5·1
Me ₂ Pr ⁿ ₂ NPic	93	176·5	5·36	7·0	8·1	1·2	48·4
Et ₂ Pr ⁿ ₂ NPic	144·2	165·1	5·23	6·9	6·7	1·0	50·1
Et ₃ Pr ⁿ ₂ NPic	79·8	171·5	5·66	6·8	7·6	1·1	48·0
MePr ⁿ ₃ NPic	82·2	156·7	5·29	7·2	7·8	1·1	46·2
EtPr ⁿ ₃ NPic	107·2	151·1	5·33	7·4	7·9	1·1	45·9
Pr ⁿ ₄ NPic	119·6	139·8	5·19	7·2	7·9	1·1	45·2
(<i>iso</i> -C ₅ H ₁₁) ₄ NPic	87·0	59·6	3·10	7·1	9·5	1·3	47·0

Mean 1·1

 * Extrapolated. d = with decomp.

Instructive comparisons may also be drawn from the field of high-melting inorganic salts. Table 3 presents a representative selection of the data available on these salts, recalculated where necessary to evaluate the quantities required by the present analysis. It will be noted that values of κ lie between 141 for molten potassium bromide and 361 for molten silver iodide and it might be thought that this argues against the identification of the reduced conductivity with the degree of ionic dissociation as developed above.

These molten salts, however, in contradistinction to the systems with boron trifluoride and the picrates, do not fulfil the essential condition that m' equals unity. In such melts, where m' is very different from unity, there is little justification for assuming that use of the reduced conductivity κ (*i.e.*, $\mu\eta$) effects an adequate viscosity correction [cf. equation (5)]. In fact, the disparity between E_η and E_μ is a clear indication that in these melts different structural processes are involved in viscous flow on the one hand and ionic migration on the other. This is frequently (Bloom and Heymann, *Proc. Roy. Soc.*, 1947, *A*, **188**, 392; Frenkel, "Kinetic Theory of Liquids," Clarendon Press, Oxford, 1946) taken to indicate that, whereas viscous flow involves a breakdown of the configuration of both anions and cations and will depend mainly on the resistance to shear of the larger ions (usually the anions), electrical conductance will be primarily determined by the freedom of movement of the smaller ions (usually the cations) through the interstices between the larger ions. This is reflected, for example, in the distinct increase in E_μ and corresponding decrease in μ which is observed on passing from lithium chloride to caesium chloride, whilst E_η remains approximately constant. Similarly the conductivity of silicate melts is increased by addition of metal oxides, the greatest increase being produced by oxides of univalent metals with small cationic radii (Bockris, Kitchener, Ignatowicz, and Tomlinson, *Trans. Faraday Soc.*, 1952, **48**, 75).

Despite the large values of m' in many inorganic melts, which arise from the differences between E_η and E_μ , it is possible to effect a partial correction for the influence of viscosity on mobility. This results from the general relation that, when both molar conductivity and viscosity vary exponentially [equations (2) and (3)], they must themselves be connected by equation (5), *viz.*, $\mu^{m'}\eta = \text{const.}$ or $\mu\eta^{1/m'} = \text{const.}$ This suggests that, in the general case, reduction of conductivities to a standard state of unit viscosity should be made by using $\eta^{1/m'}$ rather than η itself. The derivation leading to equation (12) would then give the percentage of ionic dissociation as $\alpha \approx \mu\eta^{1/m'}$. Values of this function are listed in Table 3. The value of $\mu\eta = 141$ for potassium bromide now reduces to $\mu\eta^{1/m'} = 109$, and the value of $\mu\eta = 361$ for silver iodide becomes $\mu\eta^{1/m'} = 121$. These calculations, therefore, confirm that the particular molten salts in Table 3 are completely ionized, yielding numerical values as close to 100% as may be expected in view of the approximations involved.

TABLE 3. *Molten inorganic halides at their m. p.**

Compound	M. p.	κ (ohm ⁻¹ cm. ⁻¹)	μ (cm. ² ohm ⁻¹)	E_μ (kcal. mole ⁻¹)	E_η (kcal. mole ⁻¹)	m'	κ (cm. ² cp. ohm ⁻¹)	$\mu\eta^{1/m'}$
NaCl	800°	3.54	134	2.70	9.4	3.5	196	149
KCl	768	2.12	104	3.26	7.8	2.4	157	123
NaBr	740	2.93	129	2.58	10.6	4.1	185	141
KBr	728	1.61	90	3.42	7.9	2.3	141	109
AgCl	455	3.77	112	1.20	5.3	4.4	333	143
AgBr	422	2.75	92	0.99	~5.0	5.1	348	119
AgI	552	2.36	99	0.90	5.8	6.4	361	121
						Mean	4.0	

* Data from Biltz and Klemm (*Z. anorg. Chem.*, 1926, **152**, 267), Ward (*Trans. Faraday Soc.*, 1937, **33**, 88), and Bloom and Heymann (*Proc. Roy. Soc.*, 1947, *A*, **188**, 392). In some instances the m. p. is appreciably below the accepted value.

A comprehensive review of data is not the present purpose. However, the general methods developed in this paper have been found to apply with equal success to the many compounds for which specific conductivity, viscosity, and density are known over a range of temperature and for which it has been established that conduction is due to an ionic transport mechanism.

The authors acknowledge with gratitude the awards of a Senior Harwell Fellowship (to N. N. G.) and a Senior 1851 Studentship (to R. L. M.). This paper is published by permission of the Director, A.E.R.E.

ATOMIC ENERGY RESEARCH ESTABLISHMENT, HARWELL,
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[Received, January 24th, 1953.]