294. *The Electrochemistry of Boron Trifluoride Co-ordination Compounds. Part II. Boron Trifluoride–Mono(acetic Acid).*

By N. N. GREENWOOD, R. L. MARTIN, and H. J. EMELÉUS.

The 1 : 1 compound of boron trifluoride and acetic acid, $BF_3,CH_3{\cdot}CO_2H$, has been isolated in a highly purified state as colourless crystals melting at 37·5°. The variation of electrical conductivity with composition in the boron trifluoride–acetic acid system has been studied at 25° and a minimum in conductivity found at a composition corresponding to the compound $BF_3,CH_3{\cdot}CO_2H$. At 25·0° the conductivity of stoicheiometric boron trifluoride–mono(acetic acid) is $\kappa_{25} = 2{\cdot}16_0 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$. The decomposition potential is temperature independent between 22° and 32° and has the value $D = 2{\cdot}5_0$ volt. Electrolysis at higher voltages results in the liberation of a mixture of hydrogen and boron trifluoride at the cathode, whereas the anodic gas contains oxygen, boron trifluoride, ethane, and carbon dioxide. The nature of the ions present in the molten complex is discussed and it is concluded that the compound is acetoxytrifluoroboric acid, $H(BF_3{\cdot}O{\cdot}CO{\cdot}CH_3)$.

IN Part I (Greenwood, Martin, and Emeléus, *J.*, 1950, 3030) the electrochemistry of pure liquid boron trifluoride–ethyl ether was investigated. The present paper is concerned with the results of a similar investigation on boron trifluoride–mono(acetic acid), $BF_3,CH_3{\cdot}CO_2H$.

The reaction between boron trifluoride and glacial acetic acid was first studied by Landolph (*Compt. rend.*, 1877, **85**, 39; *Ber.*, 1877, **10**, 1312) who concluded, on the bases of boiling point and smell, that some acetic anhydride was formed. The first evidence for compound formation between boron trifluoride and acetic acid, however, was not reported until 50 years later, when Meerwein (*Annalen*, 1927, **455**, 227) obtained a colourless, oily, slightly-fuming liquid to which he assigned the formula $(BF_3OCOCH_3)_3H$. This compound boiled at 59°/13 mm. and was said to be comparable in acidity to sulphuric acid. Recently, Booth and D. R. Martin ("Boron Trifluoride and its Derivatives," John Wiley and Sons, 1949, p. 65) suggested that this formula was a misprint and claimed that Meerwein's data on the physical properties of the compound indicated that it was $(BF_3OCOCH_3)H$, *i.e.*, boron trifluoride–mono(acetic acid). However, Booth and D. R. Martin are themselves in error for Meerwein's data, and his subsequent statements (*Ber.*, 1933, **66**, 411; Meerwein and Pannwitz, *J. pr. Chem.*, 1934, **141**, 123), as well as the results from Nieuwland's school, show that the compound was, in fact, boron trifluoride–di(acetic acid), $BF_3,2CH_3{\cdot}CO_2H$ (Bowlus and Nieuwland, *J. Amer. Chem. Soc.*, 1931, **53**, 3835; Sowa, *ibid.*, 1938, **60**, 654).

The occurrence of a 1 : 1 compound between boron trifluoride and acetic acid was reported by Meerwein and by Meerwein and Pannwitz (*locc. cit.*) who obtained rhombic crystals, m. p. 23—24°, by passing boron trifluoride into the di-complex. These communications appear to be the only papers published on the 1 : 1 compound. In the present investigation, boron trifluoride–mono(acetic acid) was synthesised gravimetrically by passing boron trifluoride into glacial acetic acid. The compound was obtained as a solid of accurately stoicheiometric composition and m. p. 37·3°. Repeated fractional crystallisation in dry air raised the m. p. to 37·5°, after which further fractionation effected no increase. This value is considerably higher than Meerwein's value of 23—24° but is similar to Swinehart's figure of 38—39° mentioned as a private communication by Booth and D. R. Martin (*loc. cit.*). The crystals of boron trifluoride–mono(acetic acid) were extremely unstable to moist air and hydrolysed immediately, with copious fuming, to a colourless liquid. It was found that slow crystallisation of the molten compound in a thermostat at 37·1° yielded well-formed single crystals of boron trifluoride–mono(acetic acid); one such crystal was obtained as a perfect hexagonal plate of dimensions 17 × 5 × 2 mm. The crystals were colourless, transparent, and sharp-melting.

The variation of specific electrical conductivity with composition in the system boron trifluoride–acetic acid was determined at 25° and 1000 cycles A.C., in the conductivity cell shown in Fig. 1. The results are presented in Fig. 2 which incorporates the data obtained from five independent experiments.

It is seen that the conductivity passes through a maximum of $3{\cdot}17 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$ at a mole ratio of ~0·24. Further addition of boron trifluoride decreases the conductivity of the system until a minimum value of $\kappa_{25} = 1{\cdot}260 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$ is reached at the mole ratio of 1·000. At this point the compound is supercooled; the conductivity of the molten stoicheiometric compound at its melting point is $\kappa_{37\cdot5} = 2{\cdot}19_6 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$. It is only with difficulty that boron trifluoride can be absorbed beyond the stoicheiometric ratio at atmospheric pressure. A point of inflexion in the isotherm occurs at the mole ratio 0·5 (*i.e.*, $BF_3,2CH_3{\cdot}CO_2H$) for which $\kappa_{25} = 2{\cdot}13_4 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$. A further inflexion occurs at about 0·8.

The D.C. current–voltage curves on supercooled boron trifluoride–mono(acetic acid) at 22·5°, 25·1°, and 32·1° all gave a well-defined decomposition potential $D = 2{\cdot}5_0$ volts. This value is just twice that observed for boron trifluoride–ethyl ether (Greenwood, Martin, and Emeléus, *loc. cit.*) and, in contrast to the values for the latter compound, is temperature independent. The gases evolved during electrolysis of the stoicheiometric compound at higher voltages were collected and analysed in an apparatus similar to that described in Part I. By means of a copper coulombmeter it was established that, for each equivalent of electricity passed, one equivalent of hydrogen was liberated at the cathode, together with variable amounts of boron trifluoride. At the anode, a mixture of oxygen, boron trifluoride, ethane, and carbon dioxide was evolved, but this evolution was not quantitative, being extremely slow at first and accelerating as electrolysis proceeded. The observed ratios in which these gases were evolved, ethane being taken as unity, were $O_2 : BF_3 : C_2H_6 : CO_2 = 3{\cdot}4 : 1{\cdot}8 : 1{\cdot}0 : 2{\cdot}5$.

FIG. 1.
Conductivity–composition cell.

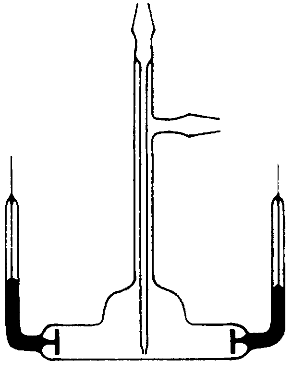


FIG. 2.
Conductivity–composition isotherm at 25·0°.

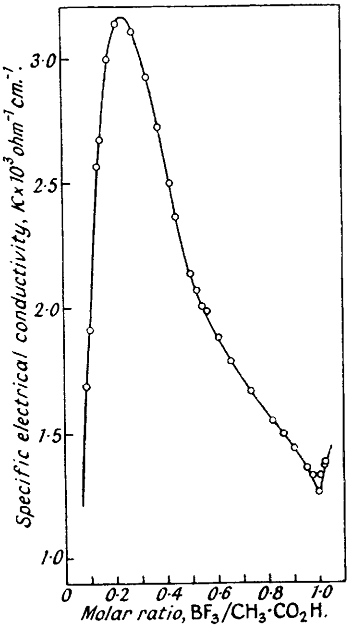
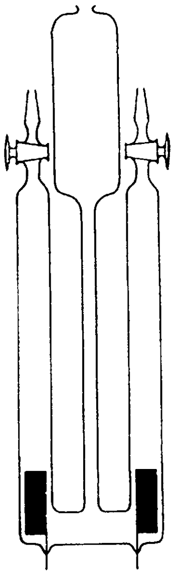


FIG. 3.
Electrolysis cell.



DISCUSSION.

It was pointed out in Part I that co-ordination of an organic molecule to boron trifluoride involves an electron displacement which confers on the complex a much higher degree of ionisation than exists in either the donor or the acceptor molecule alone. This enhanced ionisation is reflected in the large increase in electrical conductivity which accompanies co-ordination. In the present instance, the specific conductivity of glacial acetic acid, $\kappa_{25} = 1{\cdot}12 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$ (Rabinowitsch, *Z. physikal. Chem.*, 1926, **119**, 59), is raised to $1{\cdot}26 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$ by co-ordination to an equimolar proportion of boron trifluoride.

The variation of conductivity with composition in the boron trifluoride–acetic acid system indicates that compound formation occurs at 1 : 1 and possibly also 1 : 2 proportions. The minimum in conductivity observed at the molar ratio 1·000 is strong evidence for the existence of the compound $BF_3,CH_3{\cdot}CO_2H$. Such evidence is desirable to confirm Meerwein's deduction of compound formation from the results of analyses, particularly as he showed that the liquid could not be distilled without change in composition. The conductivity minimum in conjunction with the m. p. maximum at 37·5° provides an unequivocal demonstration of the existence of boron trifluoride–mono(acetic acid) as a stoicheiometric compound. The existence of boron trifluoride–di(acetic acid) is already well established by the work of Meerwein and of Nieuwland (*locc. cit.*) and a detailed discussion of its properties falls outside the scope of the present paper. It may be mentioned, however, that the absence of a minimum at the ratio 0·500 is not inconsistent with the formation of the 1 : 2 compound, for the work of Bloom and Heymann (*Proc. Roy. Soc.*, 1947, *A*, **188**, 392) has demonstrated that inflexion in a conductivity isotherm may well resolve into a minimum at sufficiently low temperatures.

The possible modes of ionic dissociation in the highly conducting compound boron trifluoride–mono(acetic acid) may be written in the following ways, depending on whether dissociation involves rupture of the carbon–oxygen, carbon–hydrogen, or oxygen–hydrogen bond:

$$BF_3,CH_3{\cdot}CO_2H \longrightarrow CH_3{\cdot}CO^+ + BF_3,OH^- \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$BF_3,CH_3{\cdot}CO_2H \longrightarrow H^+ + BF_3,CH_2{\cdot}CO_2H^- \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$BF_3,CH_3{\cdot}CO_2H \longrightarrow H^+ + BF_3,CH_3{\cdot}CO_2^- \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Electrolysis at 100—105 volts results in the cathodic liberation of one equivalent of hydrogen for each faraday of electricity passed so that mechanism (1) is definitely eliminated, and the compound is not to be considered as acetyl hydroxytrifluoroborate, $CH_3{\cdot}CO[BF_3{\cdot}OH]$. Of the remaining two mechanisms, equation (3) is preferred, as it involves dissociation at a point nearer that of the primary electron displacement induced by the formation of the donor–acceptor bond. In this way it may be seen that boron trifluoride–mono(acetic acid) is, in fact, acetoxytrifluoroboric acid, $H[BF_3{\cdot}O{\cdot}CO{\cdot}CH_3]$. This compound should not be confused with "acetoxyboron fluoride," $(CH_3{\cdot}CO{\cdot}O{\cdot}BF)_2$, obtained by Kroeger, Sowa, and Nieuwland (*J. Amer. Chem. Soc.*, **1937**, **59**, 965) by acetylation of dihydroxydifluoroboric acid with acetyl chloride.

The evolution of boron trifluoride at the cathode is presumably a secondary reaction, as the amount of gas evolved varied in different experiments. The possibility of catalytic reduction to a less stable complex such as boron trifluoride–acetaldehyde with consequent liberation of boron trifluoride must be eliminated in view of the quantitative evolution of hydrogen at the cathode.

The anode reactions are of a more complicated character, but it is possible to formulate a plausible mechanism to account for both the nature of the gases evolved and their relative proportions. The somewhat speculative nature of the following considerations, however, in no way detracts from the fundamental demonstration of the mode of dissociation as determined from the cathode analysis. It is suggested that the primary anodic discharge gives rise to acetoxytrifluoroborate radicals which have a long life in acetoxytrifluoroboric acid on account of regeneration by solvent exchange (Waters, "The Chemistry of Free Radicals," Clarendon Press, 1946, p. 19).

$$BF_3,CH_3{\cdot}CO_2^- \longrightarrow BF_3,CH_3{\cdot}CO_2 + e^-$$

$$BF_3,CH_3{\cdot}CO_2 + HO{\cdot}CO{\cdot}CH_3,BF_3 \longrightarrow BF_3,CH_3{\cdot}CO_2H + O{\cdot}CO{\cdot}CH_3,BF_3$$

These radicals may dimerise to the boron trifluoride complex of diacetyl peroxide in preference to immediate decomposition, and this would account for both the slow initial evolution of gas at the anode and the fact that the evolution of gaseous products at this electrode is not quantitative. Such behaviour is paralleled by the well-known stability of acetate radicals and of diacetyl peroxide in glacial acetic acid at temperatures similar to those used in the present experiments (*ca.* 30°) (Waters, *loc. cit.*; Kharasch and Gladstone, *J. Amer. Chem. Soc.*, 1943, **65**, 15). As the electrolysis proceeds, decomposition of the peroxide complex will occur in two ways. Complete disruption may take place in accord with the classical experiments of Kolbe, to give boron trifluoride, ethane, and carbon dioxide:

$$(BF_3,CH_3{\cdot}CO_2)_2 \longrightarrow 2BF_3 + C_2H_6 + 2CO_2$$

Alternatively disproportionation of the peroxide compound may give oxygen and the boron trifluoride complex of acetic anhydride. It is difficult to construct an equation for this reaction as the constitution of the latter compound is still a matter of some doubt (cf. Bowlus and

Nieuwland, *loc. cit.*; Morgan and Taylor, *J. Soc. Chem. Ind.*, 1931, **50**, 869; Meerwein, *loc. cit.*; Meerwein and Vossen, *J. pr. Chem.*, 1934, **141**, 149). The discussion shows, however, that the observed anodic gases may well be evolved by discharge of the anion of acetoxytrifluoroboric acid.

The variation of the electrical conductivity, viscosity, and density of boron trifluoride–mono(acetic acid) as a function of temperature forms the subject of a subsequent paper.

EXPERIMENTAL.

Boron Trifluoride.—The gas used was a pure-grade material supplied by courtesy of the Imperial Smelting Company. The purity was checked tensimetrically and by molecular-weight determination. The vapour pressure was measured in the range −133° to −112° by use of a calibrated ethylene thermometer, and the results agreed with the data of Pohland and Harlos (*Z. anorg. Chem.*, 1932, **207**, 242). The molecular weight of the gas was 67·6 (Calc. for BF_3 : *M*, 67·8).

Boron Trifluoride–Mono(acetic Acid).—This compound was prepared gravimetrically to 1 part in 2000 by passing boron trifluoride through " AnalaR " glacial acetic acid contained in an all-glass water-cooled reaction vessel. The bubble rate was controlled by means of a subsidiary valve inserted in the copper lead from the storage cylinder, and a copper-to-glass ground joint from the valve to the reaction vessel prevented access of water vapour during the preparation. The complex crystallised completely at room temperature leaving no mother-liquor (cf. Meerwein and Pannwitz, *loc. cit.*), and the melting point, as determined by the cooling curve procedure, was 37·3°. Further purification of the compound was effected by fractional crystallisation in a sealed vessel in the presence of dry air. The compound was melted at 39° and, when slowly recrystallised at 37·1°, gave well-formed single crystals in the form of colourless, transparent, hexagonal plates. After 5 recrystallisations the m. p. had risen to 37·5° and subsequent fractionation effected no further increase. The temperature was measured with a calibrated thermometer graduated in tenths of a degree.

Carbon and hydrogen micro-analyses confirmed the identity of the recrystallised compound (Found : C, 18·5; H, 3·24. Calc. for $BF_3,CH_3{\cdot}CO_2H$: C, 18·8; H, 3·13%).

Conductivity of the Boron Trifluoride–Acetic Acid System.—The design of the cell used to determine the variation of electrical conductivity with composition of the boron trifluoride–acetic acid system is shown in Fig. 1. The cell was of the conventional type in soda glass, with platinum electrodes, but modified by the addition of an internally sealed tube by means of which boron trifluoride could be led into the system. The cell was enlarged above the plane of the electrodes to accommodate the increase in volume which accompanies complex formation. Mixtures of the desired composition were thus prepared *in situ* and their conductivities at 1000 cycles A.C. measured using the Wheatstone-type network described in Part I. The inlet and outlet tubes were provided with ground glass stoppers to minimise access of moisture. Platinum leads were sealed into the side-arms of the cell to prevent evaporation of mercury with consequent change in weight of the cell. The volume of liquid required was ~6 ml. and the cell constant was 1·857 cm.$^{-1}$. Thermostatic control was obtained to ±0·05° by using the apparatus described in Part I. To reduce losses resulting from evaporation of the acetic acid, and to guard against thermal decomposition of the compound, the conductivity–composition experiments were carried out at 25°. It was found unnecessary to supercool to lower temperatures.

D.C. Measurements.—The current–voltage curves for different samples were determined by using a standard circuit which incorporated a microammeter and voltmeter. At 22·5°, 25·1°, and 32·1° well-defined decomposition potentials were obtained, the value in each case being 2·50 v. The first visible evolution of gas was at the cathode at an applied potential of 4 v.; no gas appeared at the anode. At much higher potential differences, of the order of 100 v., there was copious evolution of cathodic gas; the anodic evolution was slow initially but after the electrolysis had proceeded for some time the rate increased and eventually exceeded that at the cathode.

Identification of Cathode Gases.—The apparatus used for generation and identification of the gaseous products of electrolysis was similar to that described in Part I. About 150 ml. of boron trifluoride–mono(acetic acid) were electrolysed at ~100 v. in the cell sketched in Fig. 3. A copper coulombmeter of standard design was inserted in series with the cell. The gas evolved under these conditions was led into the vacuum system and passed through a trap which was kept immersed in liquid oxygen. The number of moles of non-condensable gas was calculated from the pressure in a constant-volume manometer. In successive experiments on different samples, 3·0 and 4·1 millifaradays liberated 1·5 and 2·1 millimoles of non-condensable gas. Experimental determinations of the molecular weight of the gas gave 2·9 and 2·0 respectively. The gas was sparked with air in a Hempel apparatus and confirmed as hydrogen.

The fraction condensable in liquid oxygen weighed 40·2 mg. and 134·6 mg. respectively in the two experiments. Molecular-weight determinations gave 66·7 and 66·0 (Calc. for BF_3 : 67·8). The vapour pressure of this fraction, measured manometrically between −133° and −114°, corresponded with Pohland and Harlos's data (*loc. cit.*) for boron trifluoride.

Identification of Anode Gases.—In the first electrolysis experiment only ~3 ml. of anode gas were evolved in the first hour compared with 50 ml. at the cathode. The gas amounted to 0·1 millimole and was not condensable in liquid oxygen. This quantity was too small for molecular-weight and Hempel analysis to be carried out. The second experiment followed the course of the first, but the anodic evolution rapidly increased during the second hour and ~50 ml. of gas were collected. This was fractionated by passage through a trap immersed in liquid oxygen. The non-condensable fraction (0·75 millimole) had a molecular weight of 32·9, and its absorption by alkaline pyrogallol confirmed its identity as oxygen.

The fraction condensable in liquid oxygen weighed 58·6 mg. and had a molecular weight of 51·7 (Calc. for the mixture $2BF_3 + C_2H_6 + 2CO_2$: 50·7). The b. p.s of these constituents were too close to permit quantitative vacuum-fractionation of the mixture, but their separation was accomplished by chemical means. The gas was condensed into a reaction bulb and shaken with distilled water until absorption was complete. The residual gas was distilled through a trap at the temperature of melting alcohol, $-112°$, into the molecular-weight bulb and weighed. In this way boron trifluoride was removed in the form of its hydrate. Carbon dioxide was then estimated by absorption in 10% aqueous sodium hydroxide. The residual gas weighed 6·7 mg. and a molecular-weight determination on this small quantity gave a value ~34 (Calc. for ethane : 30). The identity of the gas was confirmed by explosion in a Hempel pipette. The analysis therefore indicates that the condensable gas liberated at the anode under the present conditions of electrolysis are :

Constituent.	Weight, mg.	Mole ratio. Exptl.	Mole ratio. Calc.
Boron trifluoride	27·2	1·8	2
Carbon dioxide	24·7	2·5	2
Ethane	6·7	1·0	1
Total	58·6		
Wt. of anode gas taken	58·6 mg.		

The amount absorbed in water and alkali totalled 51·9 mg. (calc., 51·7 mg.); this suggests that the hydrate of boron trifluoride decomposes slightly under high vacuum, thereby rendering the boron trifluoride figure low and that for carbon dioxide high.

Two of the authors (N. N. G. and R. L. M.) thank the Commissioners of the Exhibition of 1851 for the award of Overseas Studentships during the tenure of which this work was carried out.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, February 5th*, 1951.]