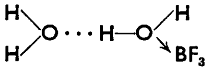
752. *Nuclear-resonance Spectra and the Structures of the Mono- and Di-hydrate of Boron Trifluoride.*

By P. T. Ford and R. E. Richards.

Proton and fluorine nuclear-resonance spectra are recorded for the mono- and the di-hydrate of boron trifluoride and for boron trifluoride dideuterate at 90° K. Different types of spectra are obtained when the samples are crystallised extremely slowly from those observed with rapidly cooled samples. In each case the results from the very slowly crystallised hydrates show that they crystallise in the un-ionised forms BF_3,H_2O and $BF_3,2H_2O$; the spectra are not consistent with the fully ionised structures $[BF_3{\cdot}OH]^-H_3O^+$ or $BF_3,[BF_3{\cdot}OH]^-H_3O^+$. The spectra of the rapidly cooled samples are consistent with a partially ionised structure similar to that prevailing in the pure liquids.

Klinkenberg and Ketelaar [1] showed that the *X*-ray diffraction pattern of the boron trifluoride dihydrate at −60° closely resembles those of ammonium fluoroborate and ammonium perchlorate and concluded that the compound is fully ionised in the solid state and should be written $[BF_3{\cdot}OH]^-H_3O^+$. Sowa, Kroeger, and Nieuwland [2] suggested that the compound might be regarded as $[H_2F]^+[BF_2(OH)_2]^-$, but Greenwood and Martin's conductometric work [3] on the liquid showed that ionic dissociation gives the oxonium and the hydroxyfluoroborate ion. The degree of ionic dissociation at 25° was found to be about 10% for the monohydrate and 20% for the dihydrate.

The majority of boron trifluoride compounds are in the 1 : 1 molecular ratio. There are, however, about twenty cases known in which boron trifluoride combines with two donor molecules, and it has been pointed out by Meerwein and Pannwitz [4] that in all these cases the donor molecules are associated liquids. They suggest that the structure of the 1 : 2 complexes could be explained in terms of hydrogen bonding, *e.g.*,



Greenwood and Martin [3] regard these substances as oxonium compounds. The 1 : 2 complexes, when they occur, are always more stable than the corresponding 1 : 1 complexes, and the extra stabilisation is ascribed to the energy of solvation of the proton, *e.g.*, $H^+[BF_3{\cdot}OH]^-$, $H_3O^+[BF_3{\cdot}OH]^-$.

The ionic and non-ionic structures for these complexes have different groupings of protons and fluorine atoms, and nuclear-resonance experiments were undertaken to discover which of these arrangements occur in the crystalline materials.

Experimental

The hydrates were prepared by passing the required amount of pure boron trifluoride (supplied by the Imperial Smelting Co.) into water. Both hydrates were purified by fractional crystallisation, at about 0°. The monohydrate is very readily supercooled, and it was therefore necessary to pre-freeze it at a very low temperature and then to warm it until only a small amount of crystalline material remained as a nucleus for the following crystallisations. Both pure hydrates formed large well-defined crystals. The monohydrate had m. p. 5·7°, d^{25} 1·779, and the dihydrate m. p. 6·3°, d^{25} 1·627. They cannot be distilled without risk of decomposition, so the pure liquids were poured into thin-walled Phoenix-glass ampoules and sealed off immediately.

Boron trifluoride dideuterate was prepared in a similar manner from 99·7% heavy water. A closed apparatus was used for the preparation and for the two fractional crystallisations;

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[1] Klinkenberg and Ketelaar, *Rec. Trav. chim.*, 1935, **54**, 959

[2] Sowa, Kroeger, and Nieuwland, *J. Amer. Chem. Soc.*, 1935, **57**, 454.

[3] Greenwood and Martin, *Quart. Rev.*, 1954, **8**, 1.

[4] Meerwein and Pannwitz, *J. prakt. Chem.*, 1934, **141**, 123.

the final product was sealed into an ampoule. The m. p. of the pure material was 11·2°. A sample of the gas released from the dideuterate by magnesium was analysed by a mass-spectrometer, and shown to contain 98·3% of deuterium.

Nuclear-magnetic-resonance measurements were made with the apparatus described by Richards and Smith[5] and Pratt and Richards.[6] A twin-T bridge method was used at frequencies near 12·2 Mc./sec. and derivatives of the absorption curves were obtained by automatic recording. The radiofrequency field was always reduced until no further change in the shape or width of the absorption line occurred; this ensures that the nuclear-resonance spectrum is not appreciably saturated.

Other Compounds.—Attempts were made to prepare pure samples of potassium hydroxyfluoroborate, $K^+[BF_3{\cdot}OH]^-$. The methods of Wamser[13] and of Ryss and Slutskaya[14] did not yield samples of satisfactory purity.

Paushkin and Topchiev[15] mention a compound of stoicheiometric formula H_2O,HF,BF_3, which might be $H_3O^+BF_4^-$. We were not able to obtain a compound of definite composition by passing boron trifluoride into an equimolar solution of hydrogen fluoride in water, although in one case a precipitate appeared when about 80% of the required BF_3 had been added which redissolved on increasing the amount of BF_3.

RESULTS

The absorption curves were obtained at 90° K and, for both the mono- and the di-hydrate, two types of spectra were observed according to the rate of cooling. If the samples were allowed to crystallise very slowly in the refrigerator for ≮24 hr., the proton-resonance spectra showed a doublet structure with a central minimum (see Figs. 1 and 2).

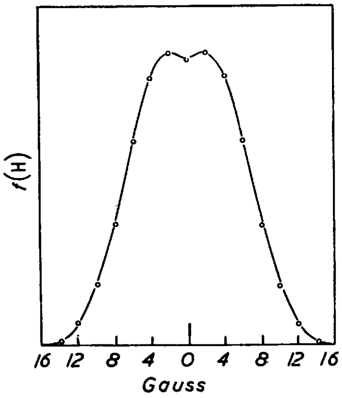

FIG. 1. *Proton resonance of* BF_3,H_2O *at* 90° K *after very slow cooling. Circles are theoretical points for pairs of protons* 1·62 Å *apart, with a broadening function* $\beta^2 = 7{\cdot}2$ *gauss*^{2}.

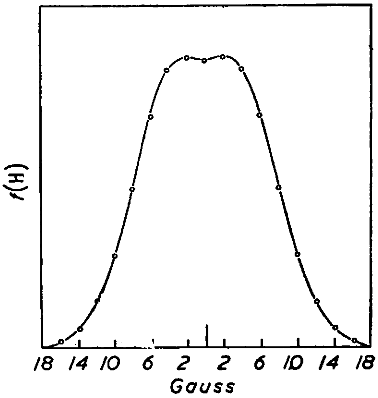

FIG. 2. *Proton resonance of* $BF_3,2H_2O$ *at* 90° K *after very slow cooling. Circles are theoretical points for pairs of protons* 1·54 Å *apart, with a broadening function* $\beta^2 = 9$ *gauss*^{2}.

If the samples were very rapidly frozen by immersion in liquid air, the proton-resonance spectra were found never to have the doublet structure, but always had a central peak (see Figs. 3 and 4).

	Proton resonance		Fluorine resonance	
Compound	Second moment (gauss²)	Line width (gauss)	Second moment (gauss²)	Line width (gauss)
BF_3,H_2O : slowly cooled	27·2 ± 1·4	13·2	21·8 ± 1·2	11·5
rapidly cooled ...	26·1 ± 2·0	11·9	20·5 ± 0·8	7·6
$BF_3,2H_2O$: slowly cooled ...	35·9 ± 2·1	15·6	25·0 ± 2·1	11·7
rapidly cooled ...	33·0 ± 1·8	14·3	20·3 ± 1·3	8·0
$BF_3,2D_2O$: slowly cooled ...	—	—	18·1 ± 1·5	9·3

The second moments and line widths obtained at 90° K are given in the Table. The second

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[5] Richards and Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261.

[6] Pratt and Richards, *ibid.*, 1953, **49**, 744.

moments are not corrected for the effects of inhomogeneity of the magnetic field or for the finite amplitude of the modulation field. In these experiments these effects are 0·1 and 0·5 gauss^2 respectively and so to obtain the corrected values for the second moments 0·6 gauss^2 must be subtracted from the values given.

Intermediate line shapes could be obtained for the proton and fluorine resonances if the conditions of cooling were chosen appropriately, so the conditions used in these experiments were chosen as carefully as possible to favour one extreme or the other.

After slow cooling the sample tube always cracked when allowed to warm to room temperature, whereas this never happened with the samples which had been rapidly cooled. It was therefore possible to study the same sample first after having been rapidly cooled and then after slow crystallisation, but the experiments could not be performed in the reverse order. The proton- and fluorine-resonance spectra of both slowly and rapidly cooled samples were measured without allowing the sample to warm. Experiments of this kind demonstrated that the differences observed in the spectra were due only to the different rates of crystallisation.

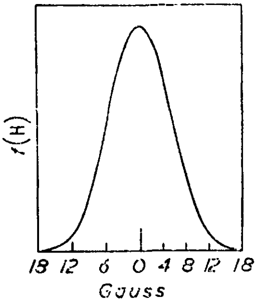

FIG. 3. *Proton resonance of* BF_3,H_2O *at* 90° K *after rapid cooling.*

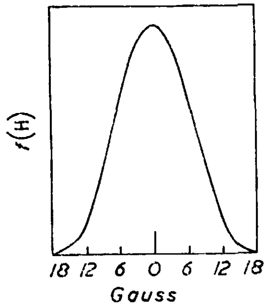

FIG. 4. *Proton resonance of* $BF_3,2H_2O$ *at* 90° K *after rapid cooling.*

DISCUSSION

When the hydrates were frozen very slowly the crystals obtained were presumably the most stable forms at the temperatures used, but rapid freezing is more likely to produce a solid having the same composition as the liquid at the melting point, or some composition between this and the stable crystalline form. The different nuclear magnetic resonance spectra obtained from slowly and rapidly cooled samples suggest that the liquid and the stable crystalline forms have different structures. A similar situation exists for liquid and crystalline nitric acid monohydrate.[5]

The Monohydrate. Slow Cooling.—Proton resonance. Fig. 1 shows the absorption curve obtained by taking the mean of five experimental curves. The central minimum is characteristic of a structure in which the protons are grouped in pairs. Very small traces of impurity in which the protons are not grouped in pairs will obscure this central minimum [7] and we believe that this must mean that the slowly cooled samples are pure materials. The circles in Fig. 1 were calculated for pairs of protons 1·62 Å apart, by use of a Gaussian broadening function [8] for which $\beta^2 = 7{\cdot}2$ gauss^2.

The close agreement between the experimental curve and the calculated points indicates strongly that the compound crystallises as the monohydrate, BF_3,H_2O. The H–H distance of 1·62 Å is quite consistent with a water molecule in which the O–H bond length and/or the HOH bond angle is very slightly increased from the values found in the gas. For example, if the HOH angle is 109° 30′, d_{OH} is 0·99 Å, and if the HOH angle is 105°, d_{OH} is 1·02 Å. The corresponding values [9] of the HOH angle and d_{OH} for water in the gas phase are 105° 3′ and $0{\cdot}956_8$ Å.

Increase in the O–H bond length or the HOH angle by these amounts might be easily

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[7] Deeley and Richards, *J.*, 1954, 3697.

[8] Pake, *J. Chem. Phys.*, 1948, **16**, 327.

[9] Herzberg, " Infrared and Raman Spectra," Van Nostrand, New York, 1945.

caused by the formation of strong hydrogen bonds or by co-ordination of the oxygen atom to the boron trifluoride molecule.

Fluorine resonance. The absorption spectrum of the slowly cooled material has a second moment of $21 \cdot 8 \pm 1 \cdot 2$ gauss^2. There is no satisfactory way to obtain the intermolecular broadening term, since the absorption line shows no structure and no *X*-ray measurements are available. However, this broadening can be roughly estimated at 7 gauss^2 because the intermolecular broadening found necessary for the proton-resonance spectrum was about 7 gauss^2. A large fraction of the intermolecular broadening is very likely to arise from H · · · F interactions in a lattice containing OH groups and F atoms.

If we estimate the intermolecular broadening of the fluorine resonance to be 7 gauss^2, this leaves about 15 gauss^2 as the intramolecular broadening of the BF_3 group. If this group were planar [10] with a B–F distance 1·30 Å, the intramolecular broadening would be 20·5 gauss^2, and if the FBF angle were tetrahedral with a B–F distance 1·43 Å (as in BF_4^-; Pendred and Richards [11]), then the intramolecular broadening would be 12·6 gauss^2. On the other hand, if the FBF angle were tetrahedral with a B–F distance 1·39 Å, as in BF_3,NH_3, $BF_3,NH_2{\cdot}CH_3$, and $BF_3,N(CH_3)_3$ (Hoard *et al.*[12]), the intramolecular broadening of the fluorine resonance would be 14·6 gauss^2.

The experimental value for the intramolecular term (with an assumed intermolecular broadening of about 7 gauss^2) is about 15 gauss^2, and so the fluorine resonance can be interpreted plausibly in terms of a BF_3 molecule with a co-ordinated water molecule.

We therefore conclude that both the proton- and the fluorine-resonance spectrum of the slowly cooled samples of the monohydrate show them to consist of un-ionised BF_3,H_3O molecules.

The Monohydrate. Rapid Cooling.—The proton resonance absorption curve (Fig. 3) shows no central minimum, and presumably this has been obscured by another curve which has a central maximum. This is readily understood if the rapidly cooled material is a mixture of BF_3,H_2O (giving the pair structure with a central minimum) and BF_3 with the ions $[BF_3{\cdot}OH]^-$ and $[H_3O]^+$, both ions giving curves with central maxima. Unfortunately quantitative calculations are not possible in this case, but the second moment of the proton resonance would be expected to be slightly reduced by the contribution of the $[H_3O]^+$ and $[BF_3{\cdot}OH]^-$ ions, which is in fact observed.

The fluorine resonance would also be expected to have a smaller second moment if some ions were present because in the tetrahedral ion $[BF_3{\cdot}OH]^-$ the B–F distance is likely to be longer than in BF_3 [cf. d_{B-F} in $BF_4^- = 1{\cdot}43$ Å (Pendred and Richards [11]); d_{B-F} in $BF_3,NH_3 = 1{\cdot}39$ Å (Hoard *et al.*[12])].

These results can be regarded as consistent with the presence of BF_3,H_2O together with a small amount of the ionised form. They are not consistent with the fully ionised form, which would give a proton-resonance signal with a sharp central maximum due to the presence of the odd hydrogen atom in the $[BF_3{\cdot}OH]^-$ ion. It seems likely therefore that, on rapid cooling, the slightly ionised structure of the liquid is retained.

The Dihydrate. Slow Cooling.—Fig. 2 shows the average proton-resonance absorption curve obtained from twelve derivative curves. It shows a central minimum, characteristic of a lattice in which the protons occur in pairs. The circles in Fig. 2 are calculated points and correspond to an H–H distance of 1·54 Å with an additional gaussian broadening, for which $\beta^2 = 9$ gauss^2 (Pake [8]).

This result suggests strongly that the protons in the slowly cooled samples are again present in water molecules, so that the structure of the solid should be written $BF_3,2H_2O$. If we assume that the two water molecules have the same dimensions, then for an O–H distance of 0·96 Å (as in water vapour) the HOH angle would be about 107°. The results would also be consistent with the presence of two water molecules in which the H–H

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[10] Levy and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 2085.

[11] Pendred and Richards, *Trans. Faraday Soc.*, 1955, **51**, 468.

[12] Hoard, Geller, and Owen, *Acta Cryst.*, 1951, **4**, 405.

[13] Wamser, *J. Amer. Chem. Soc.*, 1948, **70**, 1209.

[14] Ryss and Slutskaya, *J. Gen. Chem. U.S.S.R.*, 1952, **22**, 41.

[15] Paushkin and Topchiev, *ibid.*, 1949, **19a**, 657.

distances were slightly different—one more than 1·54 Å, and one less. This H–H distance is consistent with the presence of water molecules in the lattice, although it is clear that at least one water molecule must have bond lengths and/or angles different, beyond experimental error, from those in BF_3,H_2O. This might occur if the dihydrate crystallised with one water molecule co-ordinated to the BF_3 (as in BF_3,H_2O) and other included in the lattice, probably with hydrogen bonds. These two water molecules might well have slightly different H–H distances. If the structure were $H_3O^+,BF_3\cdot OH^-$, then the absorption curve would have a strong central maximum, quite different from that observed.

The second moment of the fluorine resonance is 25 ± 2·2 gauss^2. This value is 3 gauss^2 higher than in the monohydrate, probably owing to increased intermolecular interaction from the protons of the second water molecule and also, possibly, to a slightly different FBF angle in the BF_3 group. The result is quite consistent, however, with the presence of BF_3 to which a water molecule is co-ordinated, and would be less consistent with a tetrahedral $[BF_3\cdot OH]^-$ ion, for which the B–F distance was 1·43 Å as in BF_4^-.

The Dihydrate. Rapid Cooling.—The proton-resonance absorption curve (Fig. 4) shows a broad central maximum, and the second moment is reduced from 36 to 33 gauss^2. This is consistent with the presence of some of the ionic species $[BF_3\cdot OH]^-$ and $[H_3O]^-$, both of which have proton arrangements which would contribute an absorption curve with a sharp central peak, thus obscuring the central dip due to the proton pairs.

The second moment of the fluorine resonance is decreased to 20 gauss^2 in the rapidly cooled sample. This may be attributed to the presence of the ionic form, of which the second moment of the fluorine resonance would be nearer 12·9 than 25 gauss^2. The lowering of the second moment is entirely consistent with a degree of ionisation of 20% (Greenwood and Martin [3]).

The Dideuterate. Slow Cooling.—The second moment of the fluorine resonance is 18 gauss^2. Since the deuterons have very small nuclear magnetic moments, most of this broadening must arise from interactions between fluorine atoms and between fluorine and boron atoms. The intermolecular broadening between fluorine atoms is probably quite small, with the two D_2O molecules disposed in some way about the BF_3 group, so we estimate the intramolecular broadening for the BF_3 group to be about 15 gauss^2, similar to the value estimated in connexion with BF_3,H_2O. This would correspond to a B–F distance of about 1·38 Å and a tetrahedral FBF angle.

Conclusion.—The measurements described above show that in the stable crystalline state obtained by very slow cooling, the monohydrate and dihydrate of boron trifluoride have hydrogen atoms grouped only in pairs, and this must mean that their structures should be written as BF_3,H_2O and $BF_3,2H_2O$.

If the samples are not frozen extremely slowly different results are obtained which can be interpreted in terms of the presence of small amounts of ionic species such as $[BF_3\cdot OH]^-$ and $[H_3O]^+$. This would be expected if the samples were frozen before the change from the partially ionised liquid to the stable un-ionised crystals could be completed.

The behaviour of these substances may be contrasted with that of nitric acid monohydrate (Richards and Smith [5]). The boron trifluoride hydrates and the nitric acid hydrate are both partially ionised in the liquid state. Whereas the former crystallises in the wholly un-ionised form, the latter crystallises in the completely ionised form. Very rapid freezing of the nitric acid monohydrate gave a solid having a composition corresponding to that of the liquid, just as has been found for the BF_3 hydrates.

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