# **702.** *Addition Compounds of Boron Trifluoride with Orthophosphoric and Trideuterophosphoric Acids.*

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Fused orthophosphoric acid absorbs 1·084 moles of boron trifluoride at room temperature with considerable evolution of heat. Trideuterophosphoric acid behaves similarly. In both systems, addition of boron trifluoride was accompanied by a marked reduction in viscosity and electrical conductivity. These effects, which are the reverse of those normally observed when boron trifluoride is added to a ligand, are due to a progressive reduction in the extent of hydrogen bonding and to the replacement of a proton-switch conduction mechanism in the pure acids by one involving normal ionic migration in the molten complexes. The 1 : 1 compounds $BF_3,H_3PO_4$ and $BF_3,D_3PO_4$ are but poorly defined and solidify to glasses at about $-100°$. Nevertheless, it was possible to show that their properties were not markedly influenced by deuterium substitution and that the compounds were almost completely dissociated into ions.

THE experiments now reported were undertaken to discover whether the considerable influence which deuterium substitution has on the properties of phosphoric acid [1] persisted when the system was modified so as to render electrical conduction by proton jumps unlikely. The method chosen was to study the 1 : 1 addition compounds of orthophosphoric acid and trideuterophosphoric acid with boron trifluoride. Unfortunately, the physical properties of these complexes are difficult to determine accurately because the compounds cannot be purified either by distillation or by fractional crystallization; they decompose when distilled at atmospheric pressure, immediately lose some boron trifluoride when evacuated at room temperature, and solidify to a glassy mass when cooled to $-100°$. The data obtained are therefore necessarily less accurate than those obtained on more readily purified compounds, and a study of the influence of deuterium substitution depends for its reliability on the prior purification of the components and their accurate stoicheiometry on reaction. For this reason the properties of boron trifluoride–orthophosphoric acid which have already appeared in the literature [2] were redetermined under conditions identical with those used for the trideutero-compound, the two complexes having been synthesized to within one part in 10,000 parts by weight. The results, besides showing that complex formation removes the marked difference in properties between phosphoric and trideuterophosphoric acid themselves, are also relevant to a discussion of the catalytic properties of these compounds.

Boron trifluoride–phosphoric acid is one of the most powerful catalysts known for alkylation and polymerization of olefins, and its catalytic properties have been extensively studied by Topchiev and his collaborators during the past decade.[3] In an attempt to correlate this reactivity with the physical properties of the catalyst, these workers observed that, for a given batch of catalyst, the decrease in activity in successive runs was paralleled by a decrease in the electrical conductivity of the catalyst and that specific conductivity was a useful criterion for establishing when the catalyst was spent.[4] On the other hand, when several different catalysts were compared, there appeared to be no relation between conductivity and catalytic activity.[5] In particular, it was pointed out that, whereas the conductivity of phosphoric acid decreased substantially on addition of boron trifluoride,

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[1] Greenwood and Thompson, preceding paper.

[2] Topchiev and Paushkin, *Neftyanoe Khoz.*, 1947, **25**, No. 6, 54.

[3] *Idem*, " The Use of Boron Trifluoride and its Compounds as Catalysts in Alkylation and Polymerization Reactions," Moscow, Izdatel. Akad. Nauk, S.S.S.R., 1955, 53 pp.

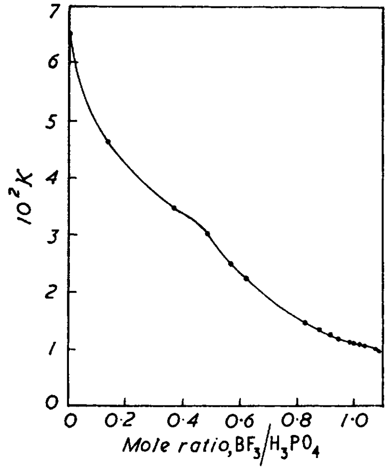
[4] Topchiev, Paushkin, Vishnyakova, and Kurashov, *Doklady Akad. Nauk, S.S.S.R.*, 1951, **80**, 611.

[5] *Idem, ibid.*, p. 381.

the catalytic activity of the system was considerably enhanced. From this it was concluded that catalytic activity was not related to the concentration of ions in the catalyst.[4,5] The apparent paradox in these two sets of observations arises from the misconception that electrical conductivity and ionic concentration are necessarily proportional to each other. However, conductivity depends not only on the number of ions but also on their mobility, which in turn normally depends to some extent on viscosity, so that no parallelism is to be expected between ionic concentration and specific conductivity in media of different viscosity. The situation is even more complex in the phosphoric acid system, since conduction in the pure acid occurs by a proton-switch mechanism[1] whereas, as will be shown below, the complex conducts by normal ionic migration. In addition, of course, there may well be specific chemical differences which obscure any simple correlation between conductivity and catalytic activity in the different systems.

## EXPERIMENTAL AND RESULTS

Boron trifluoride–orthophosphoric acid and boron trifluoride–trideuterophosphoric acid were synthesized on the 30 g. scale by direct absorption of boron trifluoride in the anhydrous acids until the theoretical increase in weight was obtained (±0·2 mg.). The complexes could not be crystallized but set to transparent glassy solids at about −100° (lit.[2] *ca.* −105°). As the compounds could not be evacuated without loss of boron trifluoride, they were poured directly into the conductivity cell and dilatometer and forced by pressure of dry nitrogen through a sinter into the viscometer. In other respects techniques were as previously described.[6] The properties were reproducible and the conductivity, in contrast to that of phosphoric acid,[1] showed no variation with time.



*Specific conductivity for the system* $BF_3$–$H_3PO_4$ *at* 40°.

Table 1 summarizes data on the density, viscosity, and conductivity of the two complexes between 25° and 40°. Densities can be represented by the equations

$$d_4^t\ (BF_3,H_3PO_4) = 1{\cdot}9087 - 1{\cdot}02 \times 10^{-3}t$$
$$d_4^t\ (BF_3,D_3PO_4) = 1{\cdot}9370 - 1{\cdot}25 \times 10^{-3}t$$

The calculated value of the density of the complex $BF_3,H_3PO_4$ at 20° is 1·8883, compared with values of 1·932[2] and 1·930[7] obtained on saturated solutions of boron trifluoride in phosphoric acid.

The viscosity of the phosphoric acid complex at 20° is given in the literature as 46·7 cP;[1] this is rather lower than the value of 54·1 cP obtained from a logarithmic extrapolation of the values in Table 1. The published conductivity,[4] $\kappa_{25} = 7{\cdot}227 \times 10^{-3}$ ohm$^{-1}$ cm.$^{-1}$, is also lower than the value of $8{\cdot}23 \times 10^{-3}$ ohm$^{-1}$ cm.$^{-1}$ obtained in this work. As both the viscosity and the conductivity of the parent acid are much higher than those of the complex, these figures suggest that the earlier data were obtained on samples containing more boron trifluoride than corresponded to the 1 : 1 complex. To test this, the conductivity of a sample of phosphoric acid was investigated at 40° as boron trifluoride was progressively added (see ref. 8 for design of cell). The results, shown graphically in the Figure, indicate that successive additions of boron trifluoride continuously lowered the conductivity of the system and that the 1 : 1 ratio was not characterized by any inflexion or discontinuity. Furthermore, boron trifluoride could be added up to a mole ratio of 1·084 at which point the conductivity was 14% lower than that of the 1 : 1 compound. A temperature run on the saturated solution led to a value of $\kappa_{25} = 7{\cdot}16 \times 10^{-3}$ ohm$^{-1}$ cm.$^{-1}$, in close agreement with the value of 7·227 ohm$^{-1}$ cm.$^{-1}$ given by Topchiev *et al.*[4] It can be assumed that their density and viscosity data also refer to a saturated solution rather than the 1 : 1 complex.

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[6] Greenwood and Thompson, *J.*, 1959, 3474.

[7] Topchiev, Paushkin, and Machus, *Doklady Akad. Nauk, S.S.S.R.*, 1947, **58**, 815.

[8] Greenwood, Martin, and Emeléus, *J.*, 1951, 1328.

TABLE 1. *Density, viscosity, and conductivity of* $BF_3,H_3PO_4$ *and* $BF_3,D_3PO_4$.

| Temp. | $d_4^t$ (g. cm.$^{-3}$) | | $\eta$ (cP) | | $10^3\kappa$ (ohm$^{-1}$ cm.$^{-1}$) | | $2\mu$ (ohm$^{-1}$ cm.$^2$ mole$^{-1}$) | | $2\mu\eta$ (ohm$^{-1}$ cm.$^2$ cP mole$^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | H | D | H | D | H | D | H | D | H | D |
| 25·0° | 1·8831 | 1·9058 | 46·16 | 48·51 | 8·23 | 8·20 | 1·449 | 1·454 | 66·9 | 70·5 |
| 30·0 | 1·8777 | 1·8990 | 39·27 | 41·66 | 9·29 | 9·25 | 1·641 | 1·646 | 64·4 | 68·5 |
| 35·0 | 1·8734 | 1·8933 | 34·36 | 35·85 | 10·41 | 10·37 | 1·848 | 1·853 | 63·4 | 66·4 |
| 40·0 | 1·8681 | 1·8870 | 30·35 | 31·11 | 11·85 | 11·50 | 2·105 | 2·062 | 63·9 | 64·3 |

Conductivity measurements on the stoicheiometric compounds were extended to lower temperatures, and Table 2 presents the results. The similarity in values between the two complexes persists down to −50°.

TABLE 2. *Electrical conductivity* ($10^3\kappa$ ohm$^{-1}$ cm.$^{-1}$) *below room temperature.*

| Temp. | −50° | −40° | −30° | −20° | −10° | −5° | 0° | +5° | 10° | 15° | 20° |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $BF_3,H_3PO_4$ ... | 0·259 | 0·551 | 1·046 | 1·745 | 2·718 | 3·288 | 3·951 | 4·676 | 5·46 | 6·32 | 7·24 |
| $BF_3,D_3PO_4$ ... | 0·238 | 0·505 | 0·995 | 1·690 | 2·634 | 3·232 | 3·888 | 4·607 | 5·38 | 6·26 | 7·19 |

## DISCUSSION

The molar volumes of the 1 : 1 complexes at 25° are 88·06 and 88·59 ml., the deuterium compound being the larger by 0·60% (cf. the phosphoric acids, 0·98% [1]). The diminished effect of deuterium substitution in the complexes is consistent [6] with a decrease in the number of hydrogen bonds when boron trifluoride is added to phosphoric acid but, in view of the difficulty of handling these compounds, it would be unwise to emphasise unduly these slight changes in molar volume.

A more direct indication of the reduction in the extent of hydrogen bonding comes from the viscosity. The data in Table 1 for the viscosity of the complexes at 25° (46·16 and 48·51 cP), when compared with those for the phosphoric acids themselves [1] (177·5 and 231·8 cP), show that the complexes are appreciably more mobile and that the influence of deuterium substitution in increasing the viscosity has been reduced from 30·6% to 5·1%. Furthermore, the activation energy of viscous flow, $E_\eta$, is also less in the complexes: 5·33 and 5·45 kcal. mole$^{-1}$ for $BF_3,H_3PO_4$ and $BF_3,D_3PO_4$ as compared with 8·03 and 8·51 kcal. mole$^{-1}$, respectively, for the parent acids. The complexes are therefore unique among the addition compounds of boron trifluoride since both viscosity and activation energy of viscous flow are normally greater for the complexes than for the ligands from which they are formed. Even the monohydrate and dihydrate of boron trifluoride have a higher viscosity than water itself, though the activation energies for the monohydrate and monodeuterate are less than for water and heavy water [9,10] where hydrogen bonding again leads to abnormally high values for the ligand.

The electrical conductivity also reflects the profound structural changes which occur when boron trifluoride is added to the phosphoric acids. The acids themselves have an abnormally large conductivity because of a proton-switch mechanism which involves the $H_2PO_4^-$ and $D_2PO_4^-$ ions.[1] There is no reason to suppose, however, that conduction in the complexes occurs by other than normal ionic transport. Consistently with this, the conductivity (Table 1) shows little change when deuterium replaces hydrogen, in contrast to the behaviour of phosphoric and sulphuric acids whose conductivity is appreciably lowered by deuteration.[1,6] Though part of this decrease, at least with sulphuric acid, is due to a change in the degree of ionic self-dissociation,[11] part is also due to the sensitivity of the conduction mechanism to replacement of protons by deuterons in the hydrogen bridges. By contrast, the slight change in ionic mass occasioned by deuteration of the complex will have little effect on the ionic migration velocity.[8,10]

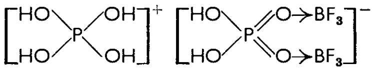
[9] Greenwood and Martin, *J.*, 1951, 1915.
[10] Greenwood, *J. Inorg. Nuclear Chem.*, 1958, **5**, 224, 229.
[11] Flowers, Gillespie, Oubridge, and Solomons, *J.*, 1958, 667.

Logarithmic plots of the specific conductivity and molar conductivity ($\mu = \kappa V_M$) against the reciprocal of the absolute temperature are linear between 5° and 40° and lead to the following activation energies (in kcal. mole$^{-1}$):

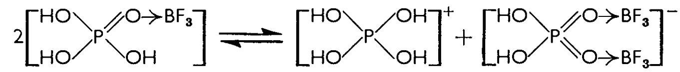
| | | | | |
|---|---|---|---|---|
| $BF_3,H_3PO_4$ | : | $E_\kappa$ 4·24, | $E_\mu$ 4·34; | cf. $E_\eta$ 5·33 |
| $BF_3,D_3PO_4$ | : | $E_\kappa$ 4·24, | $E_\mu$ 4·35; | cf. $E_\eta$ 5·45 |

At lower temperatures the values rise steadily until, at −50°, $E_\kappa$ is 7·65 kcal. mole$^{-1}$. It is seen that deuterium substitution has no significant effect on the activation energies of conduction. This is entirely consistent with conduction by means of ionic migration but does not, by itself, unambiguously establish this mechanism since the activation energy of conduction by the proton-switch mechanism is also apparently insensitive to deuterium substitution.[1,6]

Boron trifluoride–phosphoric acid has been formulated [12] as $[H^+]_3[PO_4,BF_3]^{3-}$, but this cannot be reconciled with the compound's monomeric molecular weight in molten phenol.[2] The simplest structure which is consistent with this fact and also with the high electrical conductivity of the compound is inset. Moreover, this structure provides a simple interpretation of the stoicheiometry of the compound since it implies donor–acceptor bonding by both "phosphoryl" oxygen atoms but by none of the hydroxylic oxygen atoms. A compound containing half this amount of boron trifluoride is also conceivable and its formation may be indicated by the slight irregularity in the conductivity–composition graph at the mole ratio 0·5. By contrast, it is not clear why the phosphate ion in a compound such as $[H^+]_3[PO_4,BF_3]^{3-}$ should absorb only one mol. of boron trifluoride, especially as the compounds $[Na^+]_3[PO_4,3BF_3]^{3-}$ and $[K^+]_3[PO_4,3BF_3]^{3-}$ are known.[13] The structure now proposed, $[P(OH)_4]^+\ [(OH)_2P(OBF_3)_2]^-$, also indicates clearly why addition of boron trifluoride to phosphoric acid represses electrical conduction by the proton-switch mechanism since, first, the boron atoms occupy co-ordination positions on the phosphoryl oxygen atoms formerly available to protons in hydrogen bridges, and secondly, donor–acceptor bond formation so reduces the electron density around the oxygen atoms that there is little chance of forming hydrogen bridges of sufficient strength at the remaining oxygen co-ordination position for proton transfer to occur.



On the basis of this structure and the simple theory of ionic mobilities in molten complexes [14] it is possible to calculate approximately the extent to which the complex exists in the ionic form:



As two moles of complex are required to produce a uni-univalent electrolyte, the appropriate measure of the percentage degree of ionic dissociation, $\alpha$, is $2\mu\eta$ and this quantity is tabulated in the last column of Table 1. The values obtained lie in the range 60—70%. In view of approximate nature of the calculation and the assumption necessarily made about the absolute magnitude of the ionic mobilities, these figures may well indicate that the complexes are virtually completely dissociated into ions.

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[12] Paushkin, *Zhur. priklad. Khim.*, 1948, **21**, 1199.
[13] Baumgarten and Hennig, *Ber.*, 1939, **72**, 1743.
[14] Greenwood and Martin, *J.*, 1953, 1427.