Ionic–Covalent Equilibria in Boron Trihalide Adducts. The $BF_2(hmpa)_2^+$ Cation

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The reaction 2 $hmpa{\cdot}BF_3 \rightleftharpoons BF_2(hmpa)_2^+ + BF_4^-$ occurs spontaneously in the hexamethylphosphoramide (hmpa)–BF_3 system. The degree of ionization for the above reaction is 0.13 in $CDCl_3$ solution at 27 °C. Factors favouring the relatively rare ionic form of boron trifluoride adducts are discussed.

DONOR–ACCEPTOR adducts between Lewis acids such as BF_3 and $SbCl_5$ and simple organic Lewis bases (D) are usually covalent with 1 : 1 stoicheiometry. However we have shown that in BF_3 adducts of tetramethylurea, tetramethylthiourea, and tetramethylselenourea there is an equilibrium between ionic and covalent forms of the adduct [1,2] [see equation (1)] which can be complicated by

$$2\,D{\cdot}BF_3 \rightleftharpoons D_2BF_2^+ + BF_4^- \qquad (1)$$

reaction of BF_4^- with an excess of BF_3[2] [see equation (2)].

$$BF_4^- + BF_3 \rightleftharpoons B_2F_7^- \qquad (2)$$

Ureas also form ionic adducts with $SbCl_5$[3] [equation (3)].

$$2\,D{\cdot}SbCl_5 \rightleftharpoons D_2SbCl_4^+ + SbCl_6^- \qquad (3)$$

Since ionic BF_3 adducts do not form spontaneously with most classes of simple donors, it would appear that particular structural features of the donor are necessary in order for the ionic form to become competitive. Since hexamethylphosphoramide [hmpa, $(Me_2N)_3P{=}O$] has features similar to tetramethylurea [*i.e.*, a grouping of the type $(Me_2N)_n\overset{\cdots}{-}E\overset{\cdots}{-}O$ (E = C or P)], the hmpa system was investigated in search of a further example of equilibrium (1). Previous n.m.r. studies of the hmpa-BF_3 system have noted its complexity without clarifying its behaviour.[4,5]

RESULTS

The $hmpa{\cdot}BF_3$ *System in the Presence of an Excess of* hmpa.—At 27 °C in $CDCl_3$ solution the main ^{19}F n.m.r. resonance, assigned to $hmpa{\cdot}BF_3$, is a fairly sharp doublet [chemical shift −148.5 p.p.m. from $CFCl_3$, $J(^{19}F-^{31}P) = 8.0$ Hz], both of the peaks also showing a splitting due to a $^{10}B-^{11}B$ isotope shift [6] of *ca.* 0.06 p.p.m., but with no splittings due to $^{11}B-^{19}F$ coupling. A resonance at −154.5 p.p.m. shows a 1-Hz coupling to ^{11}B as well as the $^{10}B-^{11}B$ isotope shift, and is assigned to BF_4^-.[7] A small broad quartet at lower field [−141.8 p.p.m., $J(^{11}B-^{19}F) = 12$ Hz] has the characteristic signal shape of a nucleus with spin ½ coupled to ^{11}B which is undergoing quadrupole relaxation at an intermediate rate; [8] no coupling to phosphorus is detectable. This signal is assigned to $BF_2(hmpa)_2^+$, by analogy with other oxygen-donor $D_2BF_2^+$ species [$BF_2(tmu)_2^+$, −146.0 p.p.m., $J(^{11}B-^{19}F) = 12.4$ Hz; $BF_2(dma)_2^+$, −144.2 p.p.m. (tmu = tetramethylurea and dma = dimethylacetamide)].[1] The relative peak areas were constant within experimental error up to BF_3 : hmpa ratios of 1 : 1 and were $hmpa{\cdot}BF_3$: $BF_2(hmpa)_2^+$: BF_4^- = 17.4 : 1 : 2.5.

A further very small ^{19}F peak (<1% of the total ^{19}F peak area) at −151.3 p.p.m. is apparently due to an impurity; its relative size differs in different samples but tends to increase with an increasing excess of donor.

The results agree fairly well with equation (1) if the degree of ionization is 0.13, although the BF_4^- peak is always somewhat greater than twice the size of the $BF_2(hmpa)_2^+$ peak. Contamination by traces of acidic impurities or water, with resulting BF_4^- formation, sometimes accounts for such discrepancies [9] but here it is excluded by the ^1H n.m.r. evidence described below. Formation of traces of $[BF(hmpa)_3][BF_4]_2$, in a further stage of donor-for-fluorine redistribution, is one possible cause. The ion $BF(hmpa)_3^{2+}$ would give a ^{19}F absorption only 0.125 times as intense as the two BF_4^- counter ions it requires, and the combination of very low intensity and broadening of the expected 1 : 1 : 1 : 1 quartet due to quadrupole relaxation of boron would make such a species difficult to detect by ^{19}F n.m.r. There is precedent for the existence of D_3BX^{2+} species where X is a heavier halogen.[10] A thorough but unsuccessful search was made for the ^{19}F resonance of this ion, which by application of pairwise interaction parameters [11] should have a chemical shift of *ca.* −132 p.p.m. and an $^{11}B-^{19}F$ coupling constant of *ca.* 26 Hz. Our inability to detect this signal does not prove the absence of the proposed species, which is still a possible explanation of the discrepancy of peak areas.

Boron-11 n.m.r. results are consistent with equation (1). While at 30 °C only a single resonance was observed, at −60 °C this was resolved into a large broad resonance [−19.9 p.p.m. from external $B(OMe)_3$; $\omega_{\frac{1}{2}}$ 33 Hz; $hmpa{\cdot}BF_3$] and a superimposed small sharper resonance (−19.5 p.p.m.; $\omega_{\frac{1}{2}}$ 5 Hz; BF_4^-). Small chemical-shift differences and the breadth of the peaks prevents resolution of the $BF_2(hmpa)_2^+$ resonance, which presumably is also broad and underlies the $hmpa{\cdot}BF_3$ peak. Assuming this, relative peak areas give a degree of ionization which is consistent with that determined by ^{19}F n.m.r. spectra.

At 27 °C separate ^1H 1 : 1 doublets are obtained for free donor [δ 2.66, $^3J(HP) = 9.6$ Hz] and the 1 : 1 adduct [δ 2.73, $^3J(HP) = 10.0$ Hz]. The adduct peaks are significantly broader than the free-hmpa peaks (peak width at half height *ca.* 0.6 Hz compared to *ca.* 0.3 Hz), indicating unresolved coupling to boron.

No separate ^1H signals are observed for $BF_2(hmpa)_2^+$, but the relative size of the signals ascribed to an excess of donor is larger than expected for free donor alone, and it appears that free hmpa and hmpa in the cation give a combined signal due to rapid exchange. This is consistent with the lack of splitting due to ^{19}F–^{31}P coupling in the ^{19}F n.m.r. spectrum of the cation, and is analogous to previous results for the hmpa·$SbCl_5$ and tetramethylurea·$SbCl_5$ adducts.[3] The degree of ionization can be estimated from the size deviation using equation (9) of ref. 3, which averaged over ten samples gives a value of 0.12 ± 0.04, in good agreement with the ^{19}F results. This corresponds to an equilibrium constant of 2×10^{-2} for autoionization [equation (1)].

Acidic impurities or water in systems such as hmpa–BF_3 give rise to ^1H signals at δ 7—16,[12] and in some samples a trace-impurity low-field ^1H peak, somewhat broadened and of varying size and chemical shift, could be detected after accumulation of 100 scans. However, there was no correlation between the size of this peak and the presence of ions as indicated by ^{19}F spectra, and it seems that acidic impurities can be ruled out as a cause of the behaviour observed.

The hmpa·BF_3 *System in the Presence of an Excess of* BF_3.—Solubility problems severely limited this study, suggesting that an ionic species predominates under conditions of an excess of BF_3. Dilute solutions ($\leqslant 0.3$ mol dm^{-3}) in a $CDCl_3$–CH_2Cl_2 solvent mixture could be studied down to -95 °C, but these solutions were metastable and deposited crystals on prolonged standing at -78 °C. Once formed, the crystals remained insoluble at ambient temperature. They are extremely sensitive to moisture and have not been studied further.

Ambient-temperature ^{19}F n.m.r. spectra of freshly prepared solutions containing an excess of BF_3 showed a separate $BF_2(hmpa)_2^+$ resonance of similar size to that observed in samples containing an excess of hmpa. All of the remaining fluorides (hmpa·BF_3, BF_4^-, and BF_3) gave a single averaged resonance at *ca.* -145 p.p.m., which shifted somewhat to lower field with an increasing excess of BF_3. At -95 °C this peak separated into (*i*) an hmpa·BF_3 peak (-147.0 p.p.m.) still broadened by chemical exchange so that ^{19}F–^{31}P coupling was not visible, and (*ii*) a peak at *ca.* -145.8 p.p.m. assigned to $B_2F_7^-$.[13,*]

Under conditions of an excess of BF_3 only one ^1H doublet, having the same chemical shift as the 1 : 1 adduct doublet observed in solutions containing an excess of hmpa, is present. In contrast to the hmpa–$SbCl_5$ system[3] the doublet does not shift downfield with an increasing excess of Lewis acid.

DISCUSSION

Previous n.m.r. studies of the hmpa–BF_3 system can be reinterpreted in terms of equilibria (1) and (2). Elegant *et al.*[4] noted two ^{19}F absorptions but missed the broadened lower-field quartet of $BF_2(hmpa)_2^+$, so that the BF_4^- resonance was not correctly assigned. Hill[5] correctly identified the hmpa·BF_3 and BF_4^- ^{19}F resonances and detected two forms of adducted hmpa by ^1H n.m.r., using acetonitrile as solvent. From this he proposed ionization scheme (1). However, he too missed the $BF_2(hmpa)_2^+$ ^{19}F resonance, and he incorrectly attributed the formation of ionic species to the presence of water in the system. Gutmann and Imhof[15] have discussed autoionization of BF_3 adducts of various phosphoryl donors on the basis of conductance and n.m.r. data, but apparently did not attempt to observe the ions directly by ^{19}F n.m.r. They considered the ionic excess-of-BF_3 form of the adduct to involve a three-co-ordinate boron cation $R_3PO·BF_2^+$. We exclude this on the basis of various evidence, including the characteristic ^{19}F and ^{11}B chemical-shift ranges of trigonal and tetrahedral boron species, as discussed in our previous work.[1,2]

More recently, Vidal and Ryschkewitsch[16] observed weak co-ordination of further BF_3 to the 1 : 1 hmpa·BF_3 adduct, and considered nitrogen donation to a second BF_3 to be a possibility. They also reported that the stronger Lewis acid BCl_3 did not interact with hmpa beyond 1 : 1 proportions. This seems inconsistent with nitrogen donation, which should be equally effective with BCl_3, but is consistent with equations (1) and (2). The $B_2F_7^-$ ion is a well known species, stable at low temperatures but dissociated at ambient temperature,[13,14,17] whereas the analogous $B_2Cl_7^-$ ion has never been detected. Even if hmpa·BCl_3 is in equilibrium with the ionic form of the adduct, the apparent non-existence of $B_2Cl_7^-$ allows no means for further uptake of BCl_3, other than nitrogen donation. Incidentally, a previous report of nitrogen donation in ureas, quoted by Vidal and Ryschkewitsch as precedent for nitrogen donation in the hmpa–BF_3 system,[16] is in error.[9]

Thus previous studies of the hmpa–BF_3 system are consistent with equilibria (1) and (2) and with hmpa donating only through oxygen, its accepted site of co-ordination.[18] However, in contrast to the tetramethylthiourea–BF_3 system in which analogous equilibria have been established and are rapid,[2] an excess of BF_3 does not cause an immediate shift of equilibrium (1) to the right by removal of BF_4^- to form $B_2F_7^-$. The hmpa solutions with an excess of BF_3 are metastable; the conversion to the less soluble ionic species appears to be slow. Oxygen donor–BF_3 bonds are in general less rapidly broken than sulphur donor–BF_3 bonds[2,19] and this might slow down the covalent-to-ionic shift.

The ionic–covalent equilibrium (1) is not general but does occur in BF_3 adducts of ureas, thioureas, selenoureas, and dialkylamides as well as hmpa, all of which contain a grouping of the type $R_2N\underline{\cdots}E\underline{\cdots}X\rightarrow BF_3$ ($E = C$ or P; $X = O$, S, or Se). This grouping has the ability to delocalize the positive charge formed on the donor atom on adduct formation, shifting it further from the boron atom, and this probably makes the attack of a second donor molecule at boron less unfavourable. The greater equilibrium constant for equation (1) when the donor is hmpa rather than tetramethylurea (0.02 *vs.* 0.003) is

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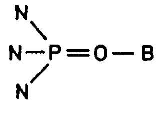
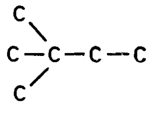
[*] The $B_2F_7^-$ ion is known to be dissociated to BF_4^- and BF_3 at ambient temperature but not at -95 °C (ref. 14). Above -140 °C only a single averaged ^{19}F resonance can be observed for $B_2F_7^- + BF_3$, or for $B_2F_7^- + BF_4^-$ (ref. 13).

consistent with the greater positive charge delocalization possible in hmpa, with its three rather than two NMe_2 groups.

However, steric effects should also be important, as in the better known case of symmetrical *vs.* unsymmetrical cleavage of diborane on adduct formation. For example, on reaction with B_2H_6, NH_3 (with low steric hindrance) forms primarily the ionic adduct $(H_3N)_2BH_2^{+}\cdot BH_4^{-}$ while the hindered NMe_3 forms only the covalent adduct $Me_3N\cdot BH_3$.[20] The hmpa group co-ordinated to boron could be considered a neohexyl analogue, and the terminal carbon of the neohexyl group has low steric hindrance. However Me_3N co-ordinated to boron could be considered a neopentyl analogue, and the terminal carbon of the neopentyl group has high steric hindrance.[21] This could explain the spontaneous formation of $D_2BF_2^{+}$ species with donors such as hmpa but the absence of analogous species with simpler donors such as the tertiary amines.





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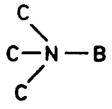

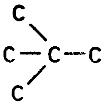

neopentyl

The adducts $[D_2BF_2][BF_4]$ can also be favoured when chelation provides an additional driving force,[22] but interestingly, ethylenediamine and tetramethylethylenediamine do not form such species.[23] A number of neutral BF_2 chelates are also known.[24] However, the class of non-chelated $D_2BF_2^{+}$ ions is still very restricted. We are presently investigating further examples, which appear to form as by-products in certain mixed boron trihalide adduct systems.[25]

EXPERIMENTAL

Purification of BF_3 has been described previously.[1] Hexamethylphosphoramide (Eastman Kodak) was vacuum distilled twice and dried over Lindé 4A molecular sieves; a high-gain ^1H spectrum of the purified compound showed no impurities. Deuteriochloroform (Merck, Sharp & Dohme) was transferred to, and stored in, a vacuum-line bulb after discarding the initial cut. Samples included the n.m.r. reference compounds $SiMe_4$, $CFCl_3$, and C_6F_6 and were prepared and sealed in flamed-out 5-mm medium-wall tubes by standard vacuum-line techniques. The hmpa was not transferred *in vacuo* but was added with a Hamilton syringe. The range of BF_3 : hmpa ratios studied was 0.2 : 1—1.5 : 1.

Nuclear magnetic resonance spectra were recorded on a Bruker WP-60 Fourier-transform n.m.r. spectrometer operating at 60 MHz (^1H), 56.4 MHz (^{19}F), and 19.25 MHz (^{11}B). Chemical shifts are given in p.p.m. to low field of the reference compound (^1H, internal $SiMe_4$; ^{11}B, external trimethoxyboron; ^{19}F, internal $CFCl_3$). For ^{19}F spectra, internal C_6F_6 was used as a secondary reference, with a chemical shift of -162.9 p.p.m. from internal $CFCl_3$ at 27 °C. When signal averaging was required 30° pulses were used, and a sufficient delay (10 s) was introduced between pulses to allow the spin system to return to thermal equilibrium so that distortions of relative peak areas would not occur. The transformed spectra contained 4K data points. Integration of spectra was performed digitally by computer. Broad-band proton-decoupled ^{13}C and ^{31}P spectra were obtained but because of a very small ^{13}C complexation shift (<0.1 p.p.m.), and broad ^{31}P signals ($\omega_{\frac{1}{2}} = 10$—30 Hz), these gave no useful information.

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