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Redistribution Reactions in Boron Trihalide Adducts of Carboxylic Esters. Mixed Boron Trihalide Adducts and Difluoroboron Cations

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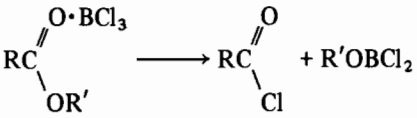
Boron trihalide adducts of acetate and benzoate esters readily exchange halogen to form mixed boron trihalide adducts $D{\cdot}BF_nCl_{3-n}$ *(n = 0–3). Benzoate esters, but not acetate esters, also form difluoroboron cations* $D_2BF_2^+$*, probably by displacement of chloride ion from the* BF_2Cl *adducts. In ester–*BF_3*–*BBr_3 *systems reaction of the bromine-containing adducts is competitive with halogen redistribution; a major decomposition product is the* $D_2BF_2^+$ *ion, in accord with bromide ion being a better leaving group than chloride ion.*

Introduction

Our studies of mixed boron trihalide adducts [1] have dealt with a number of different classes of organic donor molecule, but because of the complexities of exchange and decomposition reactions these studies have in most cases been restricted to the simplest available donor molecules of each class. Thus methyl acetate–mixed boron trihalide adducts have been studied in some detail [2, 3]. However the question of how much variation in the donor molecule substituents is necessary to produce marked changes in redistribution of substituents about boron has not previously been dealt with. We have now investigated differences in behaviour between acetate and benzoate ester adducts, in which the latter, but not the former, give rise to difluoroboron cations $D_2BF_2^+$ from the ester/BF_3/BCl_3 systems [4]. We now report a more detailed study of the effect of carboxylic ester substituents on exchange phenomena and NMR parameters of the mixed boron trihalide adducts.

Carboxylic esters are well established to be carbonyl oxygen donors to the boron trihalides [5, 6]. The BCl_3 adducts decompose slowly at room temperature [7, 8]:



$$RC(=O{\cdot}BCl_3)(OR') \longrightarrow RC(=O)Cl + R'OBCl_2 \qquad (1)$$

This reaction has been incorporated into a method of converting sterically hindered esters into the corresponding acids [9]. Ester–boron tribromide adducts decompose more rapidly in solution than the corresponding boron trichloride adducts, and this has limited our studies of halogen redistribution in bromine-containing systems.

Experimental

Methylene chloride, the boron trihalides, and the NMR reference compounds were purified as in previous work [10]. Methyl benzoate was purified by fractional distillation and drying over Molecular Sieves prior to use. Methyl *p*-nitrobenzoate, methyl *o*-chlorobenzoate, and methyl *p*-fluorobenzoate were prepared by the standard technique [11]. *p*-Fluorophenyl acetate was prepared from *p*-fluorophenol and excess acetic anhydride using pyridine as catalyst [12]. Methyl anisate, methyl *p*-toluate, *p*-tolyl acetate (Eastman), phenyl acetate, and methyl phenylacetate (Aldrich) were used without further purification.

The initial part of this work [13] was carried out using CW NMR instrumentation (^1H 60 MHz; ^{19}F, 56.4 MHz) described previously [10]. It was completed using a Bruker WP-60 Fourier Transform NMR spectrometer operating at the same frequencies, as described elsewhere [4]. ^{19}F chemical shifts reported in Table II are those obtained on the CW instrument using methylene chloride solvent and a temperature of −80 °C, and are similar, but not identical to those reported in ref. [4], for which the solvent was deuterochloroform and the temperature was −48 °C. (−80 °C chemical shifts in methylene chloride are 2.0 ± 0.5 ppm to higher field than the −48 °C chemical shifts in deuterochloroform). Note

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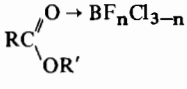
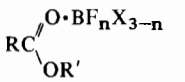
TABLE I. Donor Chemical Shifts[a] of Ester Adducts.



R	R'		Free Ester	D·BF_3	D·BF_2Cl	D·$BFCl_2$	D·BCl_3
CH_3	CH_3	CCH_3[b]	2.13	2.67	2.80	2.90	3.00
		OCH_3[b]	3.75	4.23	4.28	4.33	4.37
$C_6H_5CH_2$	CH_3	CH_2	3.77	4.33	4.50	4.62	4.75
		OCH_3	3.77	4.17	4.22	4.25	4.28
CH_3	C_6H_5	CH_3	2.30	2.80	3.02	3.12	3.23
CH_3	p-$C_6H_4CH_3$	$\overset{O}{\overset{\parallel}{C}}CH_3$	2.33	2.87	2.98	3.10	3.20
		p-CH_3	2.38	2.45	[d]	[d]	2.45
C_6H_5	CH_3	OCH_3	4.13	4.48	4.54	4.59	4.64
p-FC_6H_4	CH_3	F[c]	−106.0	−97.3	−96.3	−95.2	−94.5
CH_3	p-FC_6H_4	F[c]	−118.2	−113.9	[d]	[d]	−112.8

[a] ^1H chemical shifts: ppm to low field of internal tetramethylsilane, methylene chloride solution, −85 °C except methyl benzoate where the sample was supercooled to −113 °C. [b]Reference 2. [c] ^{19}F chemical shifts: ppm to low field of internal trichlorofluoromethane, methylene chloride solution, −80 °C. (Negative values are to high field of $CFCl_3$). [d]Not resolved.

TABLE II. ^{19}F Chemical Shifts[a] of Carboxylic Ester–Boron Trihalide Adducts:



	R	R'	D·BF_3	$D_2BF_2^+$	D·BF_2Cl	D·$BFCl_2$	D·BF_2Br	D·$BFBr_2$	Hammett σ_p values[e]
I[b]	CH_3	CH_3	−149.4	−144.2	−126.2	−112.0	−117.4	−101.0	
II[c]	CH_3	C_2H_5	−149.3		−125.9	−111.8	−117.9		
III	CH_3	C_6H_5	−147.6	−143.8	−125.1	−110.8	−117.3	−103.1	
IV	CH_3	p-$C_6H_4CH_3$	−147.7	−144.4	−125.1	−111.0	−117.5	−103.3	
V	CH_3	p-C_6H_4F	−147.3	−143.5	−125.0	−110.8	−118.3		
VI	$C_6H_5CH_2$	CH_3	−147.5	−141.6	−124.8	−110.5	−116.7	−99.8	
VII	C_6H_5	CH_3	−145.2	−136.8	−121.8	−107.4	−113.9		0.00
VIII	o-ClC_6H_4	CH_3	−144.8	−137.3	−121.7	−107.0	−114.2		
IX	p-FC_6H_4	CH_3	−144.9	−137.0	−121.5	[d]	−113.8		+0.06
X	p-$NO_2C_6H_4$	CH_3	−143.9	−135.3	−120.9	−106.7	−112.9		+0.78
XI	p-$CH_3OC_6H_4$	CH_3	−145.5	−138.4	−122.0	−107.6	−113.9		−0.27
XII	p-$CH_3C_6H_4$	CH_3	−145.4	−137.4	−121.7	−106.8	−113.8		−0.17

[a]Ppm to low field of internal trichlorofluoromethane, methylene chloride solution, −80 °C. (Negative values are to high field of $CFCl_3$). [b]Ref. 2. [c]Ref. 3. [d]Obscured by the *para*-fluorine resonance. [e]Ref. 18.

that ^{19}F chemical shifts to high field of $CFCl_3$ have *negative* signs, in accord with present practice [14] but in contrast to earlier papers of this series [2, 3, 10].

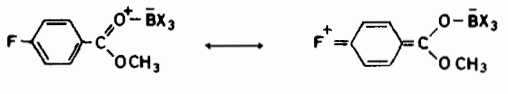
Results and Discussion

^1H and ^{19}F chemical shifts of the carboxylic esters and their boron trihalide adducts are given in Tables I and II. Splittings due to boron–fluorine coupling were not detected at the low temperatures at which ^{19}F spectra were obtained, and this is attributed to quadrupole relaxation of boron. Some adduct resonances did show such splittings when spectra were obtained at ambient temperature. However, neither boron–proton nor proton–fluorine coupling across the donor–acceptor bond could be detected. The BCl_3 and BBr_3 adducts have the low stability expect-

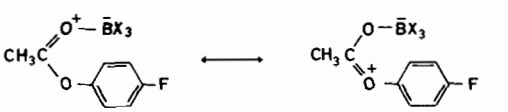
ed [7, 8], and chlorine and bromine-containing mixed boron trihalide adducts show similar behaviour. Decomposition is slow in the BF_nCl_{3-n} adduct systems, but is rapid in the BF_nBr_{3-n} adduct systems. Thus halogen redistribution could be studied without complications due to decomposition products in the BF_nCl_{3-n} systems. However further reactions of the bromine-containing adducts are competitive with halogen redistribution, and BF_2Br and $BFBr_2$ adducts are best formed at low temperatures by reacting the ester with an equilibrated mixture of BF_3 and BBr_3, in which the mixed boron trihalides are already present. Even under such conditions considerable reaction occurs, especially with adducts of the benzoate esters, as discussed below.

Proton NMR shows rapid donor–acceptor bond breaking in all of the ester adducts, as in other oxygen-donor boron trihalide adducts [2, 10]. In the presence of excess ester a single averaged ^1H resonance is obtained for each ester proton environment at room temperature. Separate ^1H resonances for individual acetate-ester adducts can be obtained at −85 °C. As the temperature is lowered, the heavier-halogen and mixed-halogen adduct resonances separate first, while the BF_3 adduct resonance remains coalesced with the uncomplexed-donor resonance to considerably lower temperatures. However the methyl resonances of individual methyl benzoate adducts are not resolved at −85 °C, indicating shorter donor–acceptor bond lifetimes. Only in one methyl benzoate/BF_3/BCl_3 sample in methylene chloride, which supercooled to −113 °C, could these resonances be resolved (Table I). As expected for donation from the carbonyl oxygen, acyl methyl resonances in the acetate series show larger complexation shifts than do O-methyl resonances.

Similarly, the *para*-fluorophenyl ^{19}F resonance undergoes a much larger complexation shift in methyl *p*-fluorobenzoate than in *p*-fluorophenyl acetate (Table I). In this case, proximity to the donor site is not as important as delocalization of the positive charge which is generated on the donor when the adduct is formed. An F^+, $B\bar{X}_3$ resonance form is possible in IX but not in V.



IX



V

Coalescence of the *para*-fluorine signals of the individual adducts is consistent with the ^1H studies of the CH_3 resonances in indicating rapid donor–acceptor bond breaking at ambient temperature. Once again, the BF_3 adduct of methyl *p*-fluorobenzoate exchanges Lewis acid faster with excess donor than do adducts containing even one chlorine atom. The complexation shifts of the BF_3 and BCl_3 adducts of methyl *p*-fluorobenzoate are similar to those reported by Taft and co-workers for the analogous *p*-fluorobenzophenone adducts [15], and indicate development of an appreciable positive charge on the fluorine. Transmission of electronic effects has been extensively studied by ^{19}F NMR in *p*-fluorophenyl systems by Taft and co-workers [16], although the validity of their conclusions has been questioned [17]. Difficulty in resolving the *p*-fluorine resonances of series of closely related adducts even at very low temperatures deterred us from making further use of this probe of charge distribution in the mixed boron trihalide adducts.

^{19}F chemical shifts of fluorine bonded to boron in the adducts are given in Table II. Acetate adducts of a particular BF_nX_{3-n} adduct (n = 1–3, X = Cl, Br) have a quite small range of chemical shifts. With a phenyl group in the R′ position (or in the α-position in methyl phenylacetate), there is a shift of a few ppm to low field in the BF_nCl_{3-n} adducts; however this is not observed in the BF_2Br and $BFBr_2$ adducts. The benzoates, too, are internally consistent in their chemical shifts for a given BF_nX_{3-n} adduct, with chemical shifts in all cases a few ppm to low field of the corresponding acetate adducts. Electron-withdrawing or -donating *para*-substituents affect the adduct ^{19}F shifts only slightly, compared to the much larger effects of the heavy halogens on boron. This is consistent with the known predominance of paramagnetic over diamagnetic shielding terms in determining ^{19}F chemical shift. The small changes that do occur with changes in the *para*-substituent are in the direction expected from Hammett σ constants [18]. Thus the *para*-nitro and *para*-methyoxy groups, which decrease and increase the donor strength, respectively, give adduct ^{19}F shifts to low field and to high field, respectively, of the corresponding adducts of methyl benzoate. The total range of chemical shifts is about 1.5 ppm for a given BF_nX_{3-n} adduct. The *para*-substituents have far more effect on the Lewis basicity of the esters than on ^{19}F chemical shifts of the adducts, as is shown when two of the esters are allowed to compete for a limited quantity of Lewis acid.

While halogen redistribution, donor–acceptor bond breaking reactions, and ^{19}F chemical shifts in these adducts are very similar to those observed in other oxygen-donor mixed boron trihalide adduct systems [2, 10, 19], the unusual feature is the occurrence of the reaction

$$D + D{\cdot}BF_2Cl \rightleftharpoons D_2BF_2^+ + Cl^- \qquad (2)$$

in the benzoate ester adduct systems but not in the acetate ester adduct systems. Benzoate ester/BF_3/BCl_3 systems have a resonance in the −137 to −140 ppm region (−135 to −139 ppm in $CDCl_3$ [4]) which cannot be assigned to a simple adduct. By reasoning that we have summarized previously [4], based on ^{19}F chemical shifts, this resonance is assigned to the $(ester)_2BF_2^+$ cation. This assignment has been confirmed by the observation of mixed-donor cations $DD'BF_2^+$ in samples containing more than one benzoate ester [4].

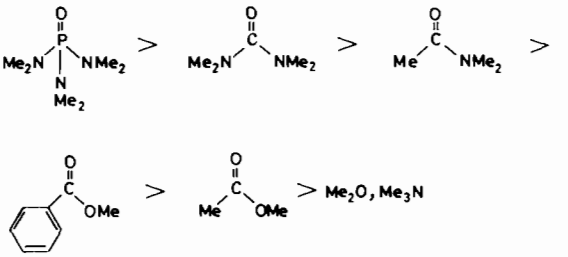
Relatively few $D_2BF_2^+$ cations are known, but they do form spontaneously in relatively small amounts from 'normal' BF_3 adducts of certain strong oxygen donors (tetramethylurea [19] and hexamethylphosphoramide [20]) in solution:

$$2D{\cdot}BF_3 \rightleftharpoons D_2BF_2^+ + BF_4^- \quad (3)$$

The $(ester)_2BF_2^+$ ions cannot be detected when only the BF_3 adduct is present, however. This is consistent with reaction (2), in which the benzoate esters are weaker donors than tetramethylurea or hexamethylphosphoramide, so that reaction is negligible unless chlorine is present to provide a good leaving group in the form of chloride ion. Our studies of tetramethylurea adducts support this interpretation. With tetramethylurea as donor, $D_2BF_2^+$ is only a minor species in the BF_3-only adduct system, whereas in the BF_nCl_{3-n} adduct system not only does $D_2BF_2^+$ become a major species, but it has been shown to form from $D{\cdot}BF_2Cl$ (Fig. 4 of ref. 19). Carboxylic esters are weaker Lewis bases than tetramethylurea, and this implies that they are also weaker nucleophiles. Hence reaction (2) should proceed to a lesser extent.

In accord with eqn. (2), and with bromide being a better leaving group than chloride, much larger amounts of the cations form in the benzoate ester/BF_3/BBr_3 systems than in the corresponding BF_3/BCl_3 systems. The major fluorine-containing species become the BF_3 adduct and the $D_2BF_2^+$ cation. The BF_2Br adduct signals are always small, and the $BFBr_2$ adduct signals have not been detected with certainty. Even the acetate esters, which give no evidence of formation of a $D_2BF_2^+$ cation from their BF_nCl_{3-n} adducts, do appear to undergo a similar reaction from their BF_nBr_{3-n} adducts. Although the BF_2Br and $BFBr_2$ adduct resonances are readily detectable with acetate esters, an additional resonance is present at 141–144 ppm which we assign to the $D_2BF_2^+$ cations by analogy with the benzoate-ester cations. The additional species is minor in excess-Lewis-acid samples, but becomes major in some excess-ester samples, in accord with eqn. (2) and the need for a nucleophile to drive off bromide ion. We are further investigating the scope of the reaction of donor molecules with pre-equilibrated BF_3/BBr_3 mixtures, containing all of the BF_nBr_{3-n} species, as a method of preparation of $D_2BF_2^+$ and $DD'BF_2^+$ cations. The reaction is analogous to that used in the preparation of $D_2BH_2^+$ cations from $D.BH_2X$ adducts [21].

$D_2BF_2^+$ cations form more readily from benzoate esters than from acetate esters as donors, consistent with the postulate that delocalization of positive charge from the donor atom throughout the donor molecule favours cation formation [20]. Donors can thus be arranged in their order of decreasing tendency to give $D_2BF_2^+$ cations as follows:



Adducts of bases such as Me_3N and Me_2O do not rearrange to give $D_2BF_2^+$ ions, although such cations may be available by other routes [22]. Steric as well as electron delocalization effects probably help to account for the absence of cation formation in such cases [20].

The benzoate ester BF_nCl_{3-n} systems differ from the corresponding tetramethylurea adduct system in that the $D_2BF_2^+$ cations form without any evidence for the corresponding formation of the $BF_nCl_{4-n}^-$ ions, which should be readily detectable by ^{19}F NMR [19, 23]. BCl_4^- alone is unlikely as a counterion sice it should undergo fluorine–chlorine exchange [23]. It seems more likely that the anion is chloride. This apparent difference in counterion in the two systems merits further investigation but is by no means unprecedented, being somewhat similar to the phosphorus pentahalides where structures change from molecular PF_5 to $PCl_4^+{\cdot}PCl_6^-$ to $PBr_4^+{\cdot}Br^-$. One possibility is that chloride ion is somewhat stabilized by a charge transfer complex with the aromatic ring, so that it is less likely to react further.

Acknowledgements

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