

16. Mixed Tetrahalogenoborate Anions.

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Adducts of the type $\text{Ph}_3\text{CX}, \text{BY}_3$ (X or Y = F or Cl) contain triphenylmethyl carbonium ions, but infrared and nuclear magnetic resonance spectroscopy are not definite in showing the presence of mixed halogenoborate anions in the solid compounds. Tetrachloro- and tetrafluoro-borates undergo rapid halogen exchange in solution in methylene chloride, and a possible mechanism is presented for this reaction.

A NUMBER of adducts which might contain mixed halogenoborate ions are recorded in the literature although, apart from some recent work on a series of salts containing the BF_3Cl^- ion,¹ there has been no study of the physical properties of these compounds. Mixed boron trihalides are known but, owing to rapid disproportionation to the binary derivatives it is impossible to isolate the mixed species.²

Triphenylmethyl halides and boron trihalides give coloured adducts $\text{Ph}_3\text{CX}, \text{BY}_3$ ³ which might be expected to contain BXY_3^- anions. The infrared spectra of the adducts $\text{Ph}_3\text{CCl}, \text{BCl}_3$, $\text{Ph}_3\text{CCl}, \text{BF}_3$, and $\text{Ph}_3\text{CF}, \text{BCl}_3$ are in agreement with the presence of triphenylmethyl carbonium ions in the solid compounds. The infrared spectrum of the adduct $\text{Ph}_3\text{CCl}, \text{BCl}_3$ shows bands which are characteristic of the BCl_4^- anion and it is concluded that this compound may be formulated as $[\text{Ph}_3\text{C}]^+[\text{BCl}_4]^-$. Owing to the masking effects of the cation spectra it is impossible to be sure that the adducts $\text{Ph}_3\text{CCl}, \text{BF}_3$ and $\text{Ph}_3\text{CF}, \text{BCl}_3$ contain BF_3Cl^- and BFCl_3^- anions rather than the BF_4^- and BCl_4^- ions which would be expected if there were disproportionation upon crystallisation.

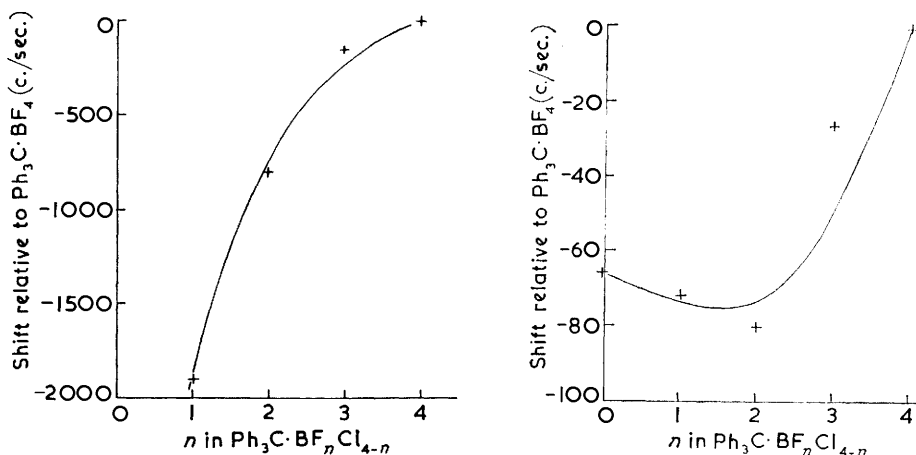
All these salts dissolve in methylene chloride to yellow solutions which contain the triphenylmethyl carbonium ion. Mixing methylene chloride solutions of triphenylmethyl tetrafluoroborate and tetrachloroborate causes immediate evolution of heat, and the nuclear magnetic resonance spectrum (¹⁹F or ¹¹B) of the solution shows a single peak. The position of this peak varies in a systematic manner (see Figures) with the relative amounts of tetrafluoro- and tetrachloro-borate which have been mixed together and it is inferred that there is rapid halogen exchange between the BF_4^- and BCl_4^- ions. It was not possible to detect

¹ Waddington and Klanberg, *Naturwiss.*, 1959, **46**, 578; *J.*, 1960, 2339.

² Long and Dollimore, *J.*, 1954, 4457; Coyle and Stone, *J. Chem. Phys.*, 1960, **32**, 1892.

³ Paushkin and Osipova, *Doklady Akad. Nauk S.S.S.R.*, 1955, **103**, 439; Wiberg and Henbaum, *Z. anorg. Chem.*, 1935, **222**, 98; Peach and Waddington, *J.*, 1961, 1238.

fine structure in the nuclear magnetic resonance bands of the mixed solutions. This could be due to the fact that splitting of the ^{19}F resonance by the ^{11}B was too small to be observed under the present conditions of relative insolubility (the ^{11}B - ^{19}F splitting in the fluoroborate ion has been variously reported as 4.2 ± 0.3^4 and 2.0 ± 0.2^5 c./sec.), or, more probably in view of the rapid reaction between tetrafluoro- and tetrachloro-borate anions, to the fact that the solutions contain discrete BF_4^- and BCl_4^- ions which undergo rapid exchange through a series of mixed halogenoborate anions. The ^{11}B nuclear magnetic resonance spectra of solutions of the adducts $\text{Ph}_3\text{CCl}\cdot\text{BF}_3$ and $\text{Ph}_3\text{CF}\cdot\text{BCl}_3$ show single peaks at positions which correspond to the relative amounts of fluorine and chlorine implied by the empirical formulæ, but it is impossible to use the spectra as positive evidence for the presence of discrete BFCl_3^- and BF_3Cl^- ions in solution as there may be rapid exchange between other halogenoborate species to give the same result. The shielding of the ^{19}F nuclei in these solutions increases with an increase in the amount of fluorine



^{19}F Spectra (FIG. 1) and ^{11}B spectra (FIG. 2) of mixed solutions of triphenylmethyl tetrahalogenoborates.

present, as is observed in the ^{19}F nuclear magnetic resonance spectra of the isoelectronic chlorofluoromethanes,⁶ and of the mixed boron halides.² The ^{11}B spectra are in accordance with previous observations on the BF_4^- and BCl_4^- anions.⁷

Various experiments were carried out in attempts to obtain more information about the mechanism of halogen exchange between the BF_4^- and BCl_4^- anions. No ionic fluoride is known which is soluble in methylene chloride or other organic solvent. Triphenylmethyl fluoride is covalent in the solid state,⁸ and a solution in methylene chloride when mixed with a solution of triphenylmethyl fluoroborate shows two peaks in the ^{19}F nuclear magnetic resonance spectrum; one of these peaks is in the same position as that for a solution of triphenylmethyl fluoroborate alone and originates from the fluoroborate ion. A study of the ^{11}B - ^{19}F splitting of the fluoroborate ion in aqueous solution in the presence of fluoride ion⁵ indicates an absence of fast exchange between fluoride ions and fluoroborate ions in that solvent. A solution of triphenylmethyl chloride in methylene chloride is yellow and hence contains a quantity (unknown) of chloride ions; a mixture of such a solution and a solution of triphenylmethyl fluoroborate shows a single ^{19}F nuclear magnetic resonance absorption in the normal position for the fluoroborate ion. Simple chemical

⁴ Chambers, Clark, Reeves, and Willis, *Canad. J. Chem.*, 1961, **39**, 258.

⁵ Milner, unpublished observations.

⁶ Meyer and Gutowsky, *J. Phys. Chem.*, 1953, **57**, 481.

⁷ Landesman and Williams, *J. Amer. Chem. Soc.*, 1961, **83**, 2663.

⁸ Sharp and Sheppard, *J.*, 1957, 674.

tests show that boron trichloride reacts with triphenylmethyl fluoroborate in methylene chloride solution to give a product containing both chlorine and fluorine. Boron trichloride and tribromide both react with crystalline sodium fluoroborate to give mixed halogenoborates. The results appear to indicate a lack of reaction between fluoroborate and halide ions, but rapid reaction between fluoroborate anions and boron trihalides, and whilst it is impossible to discuss reaction mechanisms with any certainty in the absence of rate data it appears that a mechanism in which a tetrachloroborate ion dissociates to boron trichloride and chloride ion with subsequent attack of the boron trichloride upon tetrafluoroborate ions would be in agreement with the present observations on the reaction between chloroborate and fluoroborate ions.

EXPERIMENTAL

Triphenylmethyl fluoride was prepared from triphenylmethyl chloride (recrystallised from dry benzene) and anhydrous hydrogen fluoride;⁹ when recrystallised from light petroleum (b. p. 30—40°) it had m. p. 101° (lit.,⁹ 102—104°). Triphenylmethyl tetrafluoroborate, mixed chlorofluoroborates, and tetrachloroborate were prepared by condensing the appropriate boron trihalide on to a solution of triphenylmethyl fluoride or chloride in sodium-dried toluene. The reactants were allowed to warm to room temperature and the excess of boron halide and solvent were removed under a vacuum (Found, for triphenylmethyl chlorotrifluoroborate: Cl, 11.0. Calc.: Cl, 10.2. Found, for triphenylmethyl trichlorofluoroborate: Cl, 33.2. Calc.: Cl, 28.0. Found, for triphenylmethyl tetrachloroborate: Cl, 35.4: Calc.: Cl, 35.8%). Triphenylmethyl tetrafluoroborate was prepared by mixing ethereal solutions of triphenylmethyl chloride and silver fluoroborate.⁸

Reaction of Boron Trihalides with Tetrafluoroborates.—Boron trichloride was purified by distillation and was condensed on to a solution of triphenylmethyl tetrafluoroborate in methylene dichloride. The reactants were allowed to warm to room temperature, and after 20 min. the excess of boron trichloride and the solvent were removed under a vacuum. Analysis (Found, for the residue: Cl, 28.5%) corresponds closely to that required for $\text{Ph}_3\text{C}\cdot\text{BCl}_2\text{F}$ and it is apparent that the excess of chlorine found in the product from the reaction Ph_3CF plus BCl_3 resulted from displacement of some of the fluorine as boron trifluoride by the boron trichloride. Boron trichloride or tribromide in excess was treated with sodium fluoroborate in a Carius tube for ~2 days (Found, for the reaction involving boron trichloride: Cl, 6.3. Found, for the reaction involving boron tribromide, Br, 27.1%).

Infrared spectra were recorded for Nujol and hexachlorobutadiene mulls (prepared in the dry-box) on a Perkin-Elmer model 21 spectrophotometer fitted with rock salt or potassium bromide optics. The infrared spectra of the triphenylmethyl compounds confirmed the existence of triphenylmethyl ions in the solid state. Spectra were recorded as follows (in cm^{-1}).

$\text{Ph}_3\text{C}\cdot\text{BF}_4$:⁸ 3080w, 2910w, 2850w, 1587s, 1565w,sh, 1490s, 1454s, 1364m, 1313w, 1299s, 1195w, 1172w, 1117s, 1105s, 1090s, 1065w, 1059w, 1038m, 1015—1027m,* broad, 995w, 983w, 953w, 917m, 847w,sh, 833s, 809s, 782w,sh, 700s, 670w,sh, 658w, 622s, 611s, 577s,* 520s,* 470s.

$\text{Ph}_3\text{C}\cdot\text{BF}_3\text{Cl}$: 2930w, 1575s, 1490s, 1450s, 1360m, 1295s, 1195w, 1170w, 1116s, 1103s, 1080w, 1067w, 1058w, 1052w, 1028w, 1017w, 1010w, 1005w,sh, 996w,sh, 928w, 889m, 843m, 818w, 805w, 753s, 740s, 693s, 661w, 622s, 614w,sh, 500w.

$\text{Ph}_3\text{C}\cdot\text{BFCl}_2$: 2930w, 1577s, 1485s, 1448s, 1365w, 1300w, 1185m, 1166w, 1118s, 1102s, 1090s, 1063s, 1032w, 1008m, 998m, 979m, 950w, 916m, 895w, 838s, 805s, 768s, 738w, 727w, [695s, 685w,sh, 662s, broad], 622s, 609s, 462w.

$\text{Ph}_3\text{C}\cdot\text{BCl}_3$: 2950w, 1580s, 1480s, 1451s, 1359s, 1297s, 1180m, 1117s, 1102s, 1095s, 1063s, 1041w, 1012m, 998s, 978s, 949m, 916m, 838s, 804s, 767s, 726w, [700s, 662s, broad],* 621s, 603s, 462m.

KBF_4 : 1058, 1032,¹⁰ 534, 521.

KBCl_4 :¹¹ 1447, 1382, 1261, 703, 668.

* Anion spectrum.

⁹ Swain and Mosely, *J. Amer. Chem. Soc.*, 1955, **77**, 3727.

¹⁰ Côté and Thompson, *Proc. Roy. Soc.*, 1951, *A*, **210**, 217.

¹¹ Kynaston, Larcombe, and Turner, *J.*, 1960, 1772.

Nuclear magnetic resonance spectra were recorded by using a Varian high-resolution instrument working at 56.4 Mc./sec. (for ^{19}F) and 10 Mc./sec. (for ^{11}B). The boron and fluorine resonances of the tetrafluoroborate ion were used as standards, and signals were referenced by replacement; all measurements were made at $21^\circ \pm 1^\circ$. The results for the mixed solutions containing tetrafluoro- and tetrachloro-borate are shown graphically. The principle uncertainty in these results arises in the measurement of concentrations since it is impossible to make precise measurements on such moisture-sensitive materials. The presence of triphenylmethanol does not influence the position of the tetrafluoroborate or other signals. ^{11}B nuclear magnetic resonance shifts recorded for adducts were (p.p.m.): $\text{Ph}_3\text{C}\cdot\text{BF}_4$, 0; $\text{Ph}_3\text{C}\cdot\text{BClF}_3$, -26; $\text{Ph}_3\text{C}\cdot\text{BCl}_2\text{F}$, -72; $\text{Ph}_3\text{C}\cdot\text{BCl}_4$, -66; 1:1 mixture $\text{Ph}_3\text{C}\cdot\text{BF}_4$ and $\text{Ph}_3\text{C}\cdot\text{BCl}_4$, -80.

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