Synthesis of $(C_6H_5)_2P(O)$–$P(O)(C_6H_5)_2$.—A sample of tetraphenylbiphosphine produced by the method outlined above was suspended in absolute toluene and cooled with an ice bath. Dry air was passed through the suspension for several hours. The temperature was then raised to the boiling point of toluene, and the solids dissolved. Upon cooling to room temperature white crystals formed which were filtered and dried under vacuum; m.p. 166–167° (lit. 167°). *Anal.* Calcd. for $(C_6H_5)_2P(O)P(O)(C_6H_5)_2$: C, 71.64; H, 5.01. Found: C, 70.97; H, 5.00.

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CONTRIBUTION FROM THE DEPARTMENT OF
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Difluorochlorinium Tetrafluoroborate

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Seel[2,3] has demonstrated that AsF_5 and SbF_5 dissolve in ClF_3 to give products formulated as $[ClF_2]^+[AsF_6]^-$ and $[ClF_2]^+[SbF_6]^-$ on the basis of conductivity and infrared studies. An adduct of PtF_5 with ClF_3 has also been described.[4] In the present study it has been found that BF_3 also reacts with ClF_3 upon warming from −78° to room temperature according to the equation

$$BF_3(g) + ClF_3(g) \rightleftharpoons BClF_6(s) \tag{1}$$

The compound $BClF_6$ is a colorless solid melting at 30°. The liquid has a marked tendency to supercool. The formula $[ClF_2]^+[BF_4]^-$ is consistent with conductivity and infrared data.

Vapor density measurements indicate that the compound is completely dissociated in the gas phase. The vapor pressure of $BClF_6(s)$ was measured over the range −30 to +20°. A plot of log *p vs.* 1/*T* gives the relation

$$\log p_{\text{mm}} = \frac{-(2576 \pm 16)}{T} + (12.00 \pm 0.06) \tag{2}$$

Experimental

Materials.—ClF_3 was obtained from the Matheson Co. and BF_3 from the Ohio Chemical and Mfg. Co. Both gases were purified by repeated low temperature sublimations.

Apparatus.—Preparation and purification were carried out in an all-nickel or Monel vacuum system similar to ones described elsewhere.[5] Pressure measurements were made with a Monel ACCO helicoid gage, 0–1500 mm. Temperatures above 0° were measured with a thermometer; below 0° constant temperature baths were used. Vapor density measurements were made in a thin-walled nickel weighing can fitted with a miniature brass Hoke valve. The melting point was determined in a thin-walled Kel-F tube.

Preparation of $BClF_6$.—The adduct was prepared by direct combination of the compounds between −78° and room temperature. Liquid ClF_3 at −78° rapidly absorbs BF_3 at first. The mixture begins to solidify as BF_3 is absorbed, slowing down additional absorption. It is preferable to warm a mixture of ClF_3 and excess BF_3 to room temperature in a closed nickel can. The mixture is then cooled to −78°, and the excess BF_3 is pumped off. The 1:1 adduct remaining behind can be easily sublimed and thus purified because of its high vapor pressure.

The apparent molecular weight of the gas determined by vapor density measurements was 81 ± 1. Since the expected molecular weight of an equimolar mixture of BF_3 and ClF_3 is 80.14, the compound appears to be totally dissociated in the gas phase.

Infrared Spectra.—Infrared spectra were obtained over the range 600–2000 cm.$^{-1}$ on a Perkin-Elmer Model 421 grating instrument. Vapor spectra were obtained in a 10-cm. nickel cell fitted with AgCl windows. The vapor spectra substantiated the conclusion obtained from vapor-density measurements that the compound was totally dissociated in the gas phase.

Solid spectra were obtained in a similar nickel cell fitted with an internal AgCl window which was an integral part of a liquid nitrogen reservoir. Spectra run with solid $BClF_6$ condensed on this window showed a broad peak centered at about 1030 cm.$^{-1}$. This band is characteristic of BF_4^-.[6] Spectra of solid BF_3 and ClF_3 run separately did not show this band.

Conductivity Measurements.—Measurements were carried out with a Model 216 B1 Industrial Instruments Co. conductivity bridge. The cell consisted of a Kel-F tee fitted with 0.25-in. platinum rods in the side arms. The other arm was connected *via* a 0.25-in. Kel-F U-tube to a Kel-F valve which was attached to the manifold. The compound, or a mixture of it with ClF_3, was condensed into the bottom of the U-tube and the valve was closed. The assembly was then detached from the manifold and immersed in a constant-temperature bath. After some time the assembly was inverted in such a way that the liquid flowed into the body of the cell so that conductivity measurements could be made.

Although ClF_3 did not attack the platinum electrodes, it was found that small amounts of platinum were dissolved off if in prolonged contact with $BClF_6$. After pumping off the compound, a small yellow residue, presumably PtF_4, remained in the U-tube. This residue dissolved in the solutions, but it had little effect on conductivity measurements as shown by the fact that when fresh ClF_3 was distilled into the cell, no increase in conductivity was detected.

Pure ClF_3 measured in our cell gave a specific conductance at 20° of $<10^{-6}$ ohm^{-1} cm.$^{-1}$. This is consistent with the value of $<10^{-9}$ ohm^{-1} cm.$^{-1}$ quoted in the literature.[7] Small amounts of BF_3 dissolved in ClF_3 raised the conductivity markedly. A 1 *M* solution of $BClF_6$ in ClF_3 possessed a specific conductance of 2.7×10^{-4} ohm^{-1} cm.$^{-1}$ at 20°. The specific conductance of molten $BClF_6$ at 31° was 1.5×10^{-2} ohm^{-1} cm.$^{-1}$. This remarkably high conductivity compares with the high values obtained with solutions of ClF_3–SbF_5 (6.65×10^{-3} ohm^{-1} cm.$^{-1}$ for a 0.564 *M* solution of ClF_3–SbF_5 in ClF_3 at 0°).

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