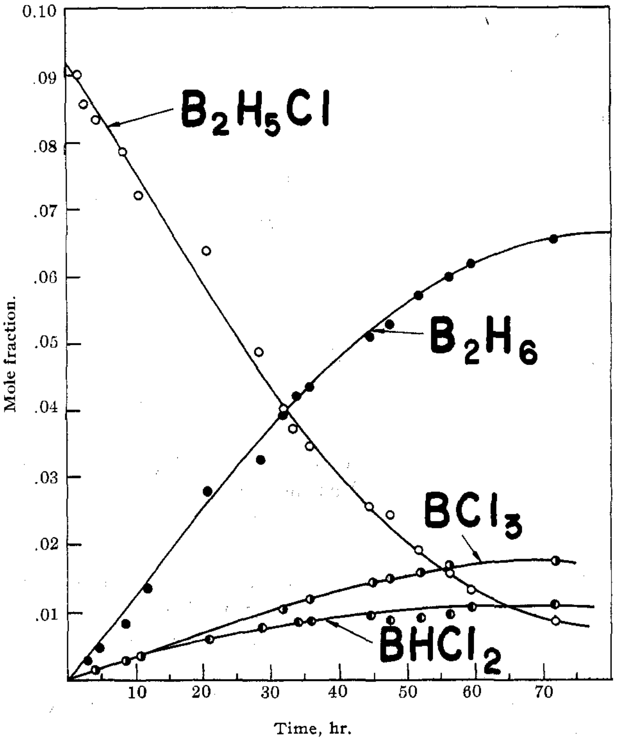

Fig. 3.—Decomposition of monochlorodiborane in nitrogen at 35°.

a 33 ft. × 0.25 in. stainless steel tube, containing 60–80 mesh firebrick coated with 20% (wt.) silicone oil (Dow Corning No. 703). With the column maintained at 0° and a 100 ml./min. He flow, B_2H_5Cl emerged as a pure fraction at 22.5 min. By using numerous samples of the mixture, quantities were selectively trapped in a section of the vacuum line at liquid nitrogen temperature. By infrared analysis, no traces of B_2H_6, BCl_3, or $BHCl_2$ were detected in the collected fractions.

Anal. Calcd. for B_2H_5Cl: B, 34.8; H, 8.1; Cl, 57.1. Found: B, 34.0; H, 8.4; Cl, 56.7.

Based on *PVT* measurements at 25°, a molecular weight corresponding to 60.5 was found (calculated = 62.1).

The infrared spectrum for monochlorodiborane at 8.8 mm. is given in Fig. 1. The cell path length was 10 cm. and the temperature was 25°.

Preparation of $BHCl_2$.—Preheated streams of H_2 and BCl_3 (in a 1:1 mole ratio) were passed through a quartz tube maintained at 900°. With a retention time of 1.7 sec., a 17% conversion of BCl_3 occurred to give a $BHCl_2$ yield of 97.3%. No traces of B_2H_5Cl, B_2H_6, or B_2Cl_4 were present in the gaseous product mixture. By condensing the $BHCl_2$ and BCl_3 at −111°, excess H_2 and HCl were removed from the mixture. Dichloroborane samples then were separated from BCl_3 by employing a preparative, low-temperature, gas chromatography column.[8]

Anal. Calcd. for $BHCl_2$: B, 13.1; H, 1.2; Cl, 85.7. Found: B, 12.6; H, 1.0; Cl, 87.1.

An infrared spectrum of the compound is shown in Fig. 2. The tracing was obtained at a total gas pressure of 16 mm. in a 5.0-cm. path length at −10°. By placing 0.6 mm. of BCl_3 in an identical 5.0-cm. reference cell at 30°, absorption due to this impurity was "blanked" from the spectrum. The resulting spectrum agrees well with the absorption peaks reported by other investigators.[5,9,10]

Conversion of $BHCl_2$ to B_2H_5Cl.—A solution (300 ml.) containing 3.93% (mole) $BHCl_2$ in liquid BCl_3 reached an equilibrium vapor pressure of 599.6 mm. at 0.5° in a 2-l. vacuum-jacketed, glass chamber. Samples of the vapor phase, which contained 21.20% (mole) $BHCl_2$, were raised slowly to 40° under autogenous pressure while gas chromatograms and infrared spectra were recorded. The first analysis, at 10°, showed that 0.91% B_2H_5Cl (but no B_2H_6) was present in the mixture. A concentration of 2.54% B_2H_5Cl was reached before traces of B_2H_6 appeared.

Reaction of B_2H_5Cl with Excess BCl_3.—A 0.214-mmole sample of B_2H_5Cl was condensed in a vacuum-line trap with 50.23 mmoles of BCl_3 and allowed to stand at 30° for 4 hr. (liquid BCl_3 was present). The mixture was vaporized completely into a large known volume and analyzed by infrared, gas chromatography, and gasometry. The B_2H_5Cl had diminished to 0.132 mmole while 0.391 mmole of $BHCl_2$ had formed in the mixture. No quantities of B_2H_6, HCl, or H_2 were detected. After 1 week at 20°, an identical mixture showed that all the B_2H_5Cl had reacted to form $BHCl_2$.

Disproportionation of B_2H_5Cl.—Under a pressure of 760 mm., a gas mixture containing 9.1% B_2H_5Cl in nitrogen was maintained at 35° in a 2-l. glass chamber. Over a 70-hr. period, small samples were removed for analyses by gas chromatography, gasometry, and infrared spectrometry. The results are shown in Fig. 3.

Reaction of B_2H_5Cl with B_2O_3.—A 1.0-g. (14.36 mmoles) sample of −100 mesh B_2O_3 was placed in the U section of a cold trap attached to the side of an infrared gas cell. A 0.306-mmole sample of B_2H_5Cl was admitted to the gas cell and the spectrum recorded. Liquid nitrogen was placed around a remote tip of the U-trap, causing all the B_2H_5Cl to condense there. As the tip was warmed to 25°, the gas returning to the cell passed through the B_2O_3 a second time. The infrared spectrum then showed only B_2H_6 (0.235 mmole) to be present in the gas cell. After evacuating the B_2H_6, the B_2O_3 was heated to 100° as an infrared scan was recorded. A spectrum of BCl_3 then was observed. After evacuating the BCl_3, analysis of the resulting B_2O_3 showed no Cl to be present.

Reaction of B_2H_5Cl with Excess HCl.—To a 0.415-mmole sample of B_2H_5Cl contained in an infrared gas cell, a 5.302-mmole sample of HCl was introduced at 25°. An infrared scan of the 1500 to 1650 cm.$^{-1}$ region was begun and showed that B_2H_5Cl had immediately disappeared. Gas chromatographic and gasometric analysis of the mixture showed 2.052 mmoles of H_2 and 0.851 mmole of BCl_3 to be present in the remaining HCl.

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CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS,
WASHINGTON, D. C., AND THE DEPARTMENT OF CHEMISTRY
OF THE UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

The Nature of the Compound Obtained from Aqueous Cesium Chloride Solution and Hydrogen Chloride

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In 1957 one of us reported the preparation of a new compound from aqueous cesium chloride solution saturated with hydrogen chloride.[1] On the basis of partial

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[1] R. West, *J. Am. Chem. Soc.*, **79**, 4568 (1957).

analysis this substance was formulated as $CsHCl_2$. Recently Valleé and McDaniel have shown by means of more complete analyses that the correct formula for the compound is $CsCl\cdot{}^3/_4HCl\cdot{}^3/_4H_2O$.[2] The same workers also have prepared the compound $CsHCl_2$ and established that it is stable only at very low temperatures or high hydrogen chloride pressures.[2] These findings make it seem unlikely that the compound obtained from aqueous solution contains the hydrogen dichloride anion HCl_2^-, but leave unsettled the question of the actual nature of the substance. In this paper infrared spectral evidence will be presented which indicates that the compound is probably a mixed oxonium salt, $4Cs^+Cl^-\cdot 3H_3O^+Cl^-$.

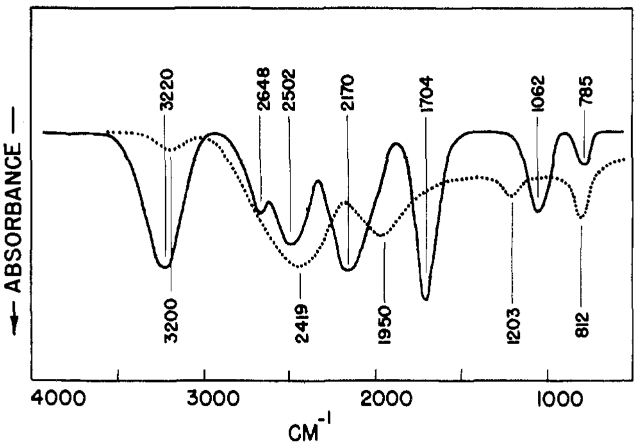

Fig. 1.—Infrared spectra of $4CsCl\cdot 3H_3OCl$ (solid line) and $4CsCl\cdot 3D_3OCl$ (dashed line) as mulls in Nujol. Nujol bands have been deleted.

Experimental

The compound $CsCl\cdot{}^3/_4HCl\cdot{}^3/_4H_2O$ was prepared by the originally published procedure.[1] The deuterium analog was obtained in an analogous manner from DCl in 97% D_2O. Infrared spectral examination of the water liberated upon decomposition of the deuterium compound indicated that deuteration was more than 95% complete.

Infrared spectra were determined for both substances as mulls in Nujol, using a Beckman IR-7 double-beam grating-prism spectrometer which was flushed with dry air. Typical spectra are shown in Fig. 1.

Results and Discussion

The spectrum consists of a series of broad bands, all shifted to lower frequency in the deuterium compound. The positions of absorption all correspond to bands previously reported for H_3O^+ and D_3O^+ compounds studied at low temperatures, and the over-all agreement of the spectra with those of H_3O^+ and D_3O^+ is very good.[3,4] The spectra are quite unlike those for typical ionic substances containing hydrate water, and bands characteristic of HCl and DCl are also absent.[5] The spectrum of $(CH_3)_4N^+HCl_2^-$ has been studied by Waddington, who attributed bands at 1565 and 1180 cm.$^{-1}$ to the HCl_2^- ion.[6] These also are absent in the spectrum of the cesium compound. Of the likely absorbing species, only oxonium ion seems to be present, and hence the spectral evidence suggests that the compound is actually $4CsCl\cdot 3H_3OCl$. This structure is entirely reasonable, for it is known that HCl transfers a proton to water in its solid monohydrate, forming $H_3O^+Cl^-$.[3] However, the stabilization of the oxonium ion by cesium chloride in $4CsCl\cdot 3H_3OCl$ is remarkable.

Some variability was noted in the spectra of different mulls of the same sample of cesium compound. The two bands at about 2650 and 2500 cm.$^{-1}$ occasionally appear as a single broad band centered near 2630 cm.$^{-1}$. The intensity and position of the 2170 cm.$^{-1}$ band is somewhat variable, and the intensity of the 785 cm.$^{-1}$ band changed markedly. Some of the variability may be due to differences in particle size and hence in the amount of scattered light. However, the results also suggest preferred orientation of crystallines in certain mulls, and variability in absorption depending on crystal orientation.

Some experiments to determine the presence of HCl_2^- ion in water also have been carried out, with negative results. It was found that the presence of up to 8 *M* lithium chloride does not alter the infrared or Raman spectrum of hydrochloric acid solutions of various concentrations.

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