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Studies on the Chemistry of Halogens and of Polyhalides. XXXII. The Bromine Trifluoride–Hydrogen Fluoride System[1,2]

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Raman, infrared, and electrical conductance studies were carried out on liquid mixtures of bromine trifluoride with hydrogen fluoride. The experimental data reveal the existence of a fluoride ion transfer equilibrium $BrF_3 + HF \rightleftharpoons BrF_2^+ + HF_2^-$. This reaction results in a maximum in the concentrations of BrF_2^+ at about 30 mol % BrF_3 where the ionic concentrations are 1.2, 0.5, and 0.7 *m* for the BrF_2^+, BrF_4^-, and HF_2^- ions, respectively. Both the specific conductivity and molar conductivity have been plotted against concentration and the results can be explained in terms of changing ionic species, their concentrations and mobilities, and the existence of a chain-conducting mechanism for electrical conductivity in both pure substances.

Introduction

The nature of the halogen fluoride–hydrogen fluoride mixtures has not been studied as yet with any degree of thoroughness. Some work has been done on the chlorine trifluoride–hydrogen fluoride system[3-7] and on the hydrogen fluoride–bromine pentafluoride system.[8] Rogers and Katz[9] studied the exchange of the radioactive ^{18}F isotope between BrF_3 and HF and found that at room temperature the exchange was complete in 10 min. They concluded that the exchange was due to the equilibrium $BrF_3 + HF \rightleftharpoons BrF_2^+ + HF_2^-$ which would indicate that HF acts as an acid (fluoride ion acceptor) in bromine trifluoride solutions.

It was of interest to us to investigate the nature of the BrF_3–HF system by spectroscopic and conductometric techniques in order to elucidate the nature of species present in the mixture and the equilibria between these species.

Experimental Section

Materials.—Commercial hydrogen fluoride was purified by the method of Runner, *et al.*[10] The product was allowed to react with sodium fluoride and the resulting $NaHF_2$ was then heated *in vacuo* at 150° to remove volatile impurities. Hydrogen fluoride was regenerated by heating the salt to 350–450° and distilled in a 125-cm polychlorotrifluoroethylene (Kel-F) still. The resulting anhydrous product had a specific conductance of less than 1×10^{-6} ohm^{-1} cm^{-1} at 0° as collected. (This corresponds to less than 1 ppm, on a molar basis, of water or any equivalent conducting impurity.[11]) Bromine trifluoride also was purified by distillation. Details have been discussed previously.[12] The conductivity exceeded 8.0×10^{-3} at 25°.[12] Potassium fluoride (Fisher Chemical Co.) was dried by heating at 120° for 24 hr. It was pretreated with bromine trifluoride before use.

Preparation of Solutions.—Solutions for spectral measurements were prepared in a tared Kel-F vessel attached to a metal vacuum line. Solutions of desired concentrations were prepared by condensing the appropriate amounts of HF and BrF_3 in the vessel, removing the vessel from the line, and weighing each compound.

A slight modification of the above method was used for the preparation of solutions for conductance studies since in this case a very small amount of impurities would affect the conductance of the system. Therefore, special precautions had to be taken to prevent the contamination of solutions with atmospheric impurities. A flow of helium was used to protect the surface of the line when a pot was removed from the line.

It was found that the HF–BrF_3 mixture attacked appreciably the platinum electrodes at room temperature. Because of this reactivity, the solutions were left in the cell for as short a time as possible. Since there was a slight change of conductance with time, measurements were taken at 5-min intervals and extrapolated to zero time. The actual correction, however, was less than 1% or within the experimental error of the measurement.

Equipment.—The vacuum line used for handling of the halogen fluorides and hydrogen fluoride as well as the conductivity cells have been described in previous publications.[12,13] The conductance measurements were made at 25° with a Wayne-Kerr autobalance precision bridge, Model B331, which has a nominal precision of $\sim\pm 0.01\%$. Overall conductivities, however, are probably good to $\pm 1\%$.

Raman spectra were obtained with a Cary Model 81 Raman spectrometer, equipped with an He–Ne laser, and on an Ar ion laser spectrometer described elsewhere.[14] The infrared spectra were measured on a Beckman Model 12 infrared spectrometer employing a cell with diamond windows described in a previous publication.[15] In general, spectral scans were made in the 200–800-cm^{-1} region. In a few cases, Raman measurements were made to 2000 cm^{-1}. Attempts to use Irtran-2 windows for infrared measurements in the 1000–2000-cm^{-1} region were unsuccessful. It was found that while Irtran-2 does not react with bromine trifluoride or hydrogen fluoride alone, it does react with the mixture of the two fluorides.

A Du Pont curve resolver, Model 310, was employed to analyze

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the observed Raman spectra. The procedure and the identification of individual peaks is described in ref 12.

Results

Infrared and Raman Spectra.—A typical Raman spectrum of the BrF_3–HF mixture is shown in Figure 1.

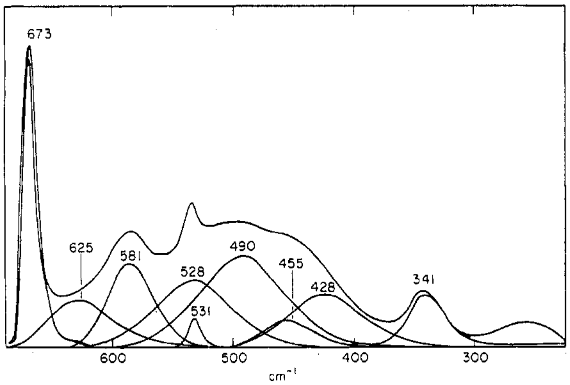

Figure 1.—Raman spectrum of BrF_3–HF mixture containing 0.424 mole fraction of BrF_3 (partially resolved).

The bands above 300 cm^{-1} are resolved and observed bands are tabulated in Table I. It should be noted that the ν_1 symmetric stretching vibration of the HF_2^- anion, which should occur at ~600 cm^{-1}, was not observed. It is quite possible that the band is so broad that it cannot be resolved. Woodward and Tyrell[16] did not observe a 600-cm^{-1} band in aqueous solutions containing HF_2^- ion. We tried to find this band in a 2 *M* potassium fluoride solution in HF without success.

TABLE I

RAMAN SPECTRUM OF BROMINE TRIFLUORIDE

Band location, cm^{-1}	Interpretation	Band location, cm^{-1}	Interpretation
673	ν_1 (a_1) BrF_3	455	ν_5 (b_{2g}) BrF_4
625	ν_1 (A_1) BrF_2^+	428	Polymer band
581	Polymer band	341	ν_5 (a_1) BrF_3
531	ν_2 (a_1) BrF_3	265	ν_6 (b_2) BrF_3
528	ν_1 (a_{1g}) BrF_4^-	249	ν_3 (b_{1g}) BrF_4^-
490	Possible dimer	236	ν_3 (a_1) BrF_3

In solution the HF_2^- is probably further solvated and it is perhaps not surprising that a discrete band is not observed in a mixture containing HF_2^-, $H_2F_3^-$, $H_3F_4^-$, etc., particularly if there are a number of acceptable alternative geometric arrangements for the solvated molecule. Since the actual distribution of each species is unknown, we use HF_2^- as equivalent to the equilibrium mixture of fluoride ions solvated with one or more hydrogen fluoride molecules.

In order to determine quantitatively the equilibria existing in BrF_3–HF mixtures it was necessary to obtain quantitative relations between the integrated intensities of the bands due to BrF_4^- and BrF_2^+ species and their concentrations. We first determined the concentration of these ions in pure bromine trifluoride by adding measured amounts of potassium fluoride to liquid BrF_3 and observing the change in the integrated areas of the 528- and 455-cm^{-1} bands characteristic of BrF_4^-. For example it was found that for a 0.91 *M* KF solution the intensities of the two bands were doubled.

Consequently it was assumed that the concentration of BrF_4^- and, therefore, the concentration of BrF_2^+ ions in pure BrF_3 was about 0.9 *M*, the integrated intensity of the 625-cm^{-1} band, taken to be characteristic of BrF_2^+, and the 528-cm^{-1} band, taken to be representative of BrF_4^-, corresponding to 0.9 *M* concentration. It was further assumed that the concentration of the species in any solution is directly proportional to the integrated intensities of these Raman bands, measured under the same conditions.

The concentrations of BrF_4^- and BrF_2^+ were, therefore, calculated for each of the solutions prepared, and assuming electric neutrality, the concentration of HF_2^- was taken as the difference between these. The concentrations so calculated are tabulated in Table II.

TABLE II

CONCENTRATION OF SPECIES PRESENT IN BROMINE TRIFLUORIDE–HYDROGEN FLUORIDE MIXTURES

Initial concn			Ionic concn, *M*		
Mole fraction	BrF_3, *M*	HF, *M*	BrF_2^+	BrF_4^-	HF_2^-
1.00	20.5	0.00	0.91	0.91	0.00
0.93	19.9	1.6	1.00	0.83	0.17
0.82	19.8	4.5	1.04	0.86	0.18
0.73	17.8	7.6	1.07	0.83	0.24
0.53	15.0	13.2	1.14	0.68	0.46
0.52	14.8	13.8	1.16	0.71	0.45
0.43	13.1	17.8	1.19	0.57	0.62
0.37	12.0	20.4	1.18	0.51	0.67
0.35	11.5	21.5	1.21	0.48	0.73
0.29	10.2	24.7	1.12	0.46	0.66
0.18	7.0	32.5	0.98	0.38	0.60
0.113	4.8	37.7	0.78	0.25	0.53
0.109	4.7	38.1	0.78	0.28	0.50
0.065	2.9	42.2	...	0.15	...

It is seen that the concentration of the BrF_4^- anion decreases steadily upon the addition of hydrogen fluoride. The concentration of the BrF_2^+ ion increases from pure BrF_3 to solutions containing ~30 mol % BrF_3. At lesser concentrations of BrF_3, the BrF_2^+ concentration begins to decrease although the fraction of the BrF_3 which is ionized continues to increase.

Pure BrF_3 contains not only the ionic species but also a number of polymers.[12] Our experimental evidence suggests that until at least an equal mole fraction of HF is added, the un-ionized fraction of bromine trifluoride remains essentially constant. Accordingly for the equilibrium

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^- \qquad (1)$$

we have assumed the ion product $[BrF_2^+][BrF_4^-] = 0.8$.

From the data given in Table II it is possible to calculate the equilibrium constant for the reaction

$$BrF_3 + HF \rightleftharpoons HF_2^- + BrF_2^+ \qquad (2)$$

for nearly the entire gamut of the BrF_3–HF mixtures. Equilibrium constants for the reaction mechanism in

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the BrF_3–HF system at different concentrations have been calculated on the basis of the ionic concentrations obtained from the Raman data and are given in Table III. It seems that the agreement is about as good as can be expected from the measurements and the values at least indicate the correct order of magnitude for the equilibrium constant. It should be noted that, obviously, no activity corrections are at present possible with this system and this fact may well account for the observed variation of equilibrium constant values with concentration. The method fails, however, for solutions containing less than 10 mol % BrF_3 since at these concentrations the 625-cm^{-1} band due to BrF_2^+ ion solvated by BrF_3[12] is noticeably changed in shape and broadened. It appears to be possible to resolve this band into two components at 625 and 662 cm^{-1}, respectively. It may be that these changes are a consequence of BrF_2^+ ion solvation by HF molecules.

TABLE III

EQUILIBRIUM CONSTANTS FOR THE BROMINE TRIFLUORIDE–HYDROGEN FLUORIDE SYSTEM

Mole fraction BrF_3	10^3K^a	Mole fraction BrF_3	10^3K^a
0.925	6.14	0.371	3.71
0.821	2.33	0.349	4.12
0.729	2.09	0.293	3.40
0.533	2.97	0.177	3.08
0.518	2.87	0.113	2.74
0.429	3.60	0.109	2.62

[a] $K = [HF_2^-][BrF_2^+]/[HF][BrF_3]$.

The infrared data were less helpful than the Raman. In the region we investigated (800–200 cm^{-1}) the main feature was a slight increase in the intensity of the 635-cm^{-1} band (attributed to solvated BrF_2^+) on addition of HF to the BrF_3. The poorer correlation of observed spectra with concentration inherent in the infrared spectra and the chemical interactions involving the window material prevented quantitative studies.

Conductometric Measurements.—A plot of the specific conductance of the BrF_3–HF mixtures as a function of composition is shown in Figure 2. It is interesting to note that initial addition of HF to BrF_3 causes a decrease in conductance. The minimum is reached at ~70 mol % BrF_3 after which the conductance increases to a maximum at 30 mol % BrF_3 after which it decreases rapidly to the specific conductance of pure hydrogen fluoride (Table IV).

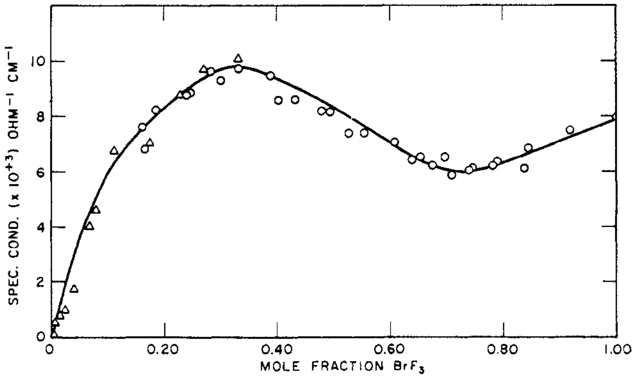

Figure 2.—Specific conductance for the bromine trifluoride–hydrogen fluoride system.

TABLE IV

CONDUCTIVITY OF BROMINE TRIFLUORIDE IN HYDROGEN FLUORIDE

Mole fraction BrF_3	$[BrF_3]$, *M*	Specific conductivity × 10^3, ohm^{-1} cm^{-1}	Molar conductivity, cm^2 ohm^{-1} M^{-1}
1.00	20.5	8.02	0.391
0.844	19.0	6.91	0.363
0.711	17.5	5.94	0.339
0.611	16.2	7.05	0.435
0.496	14.3	8.22	0.576
0.389	12.4	9.52	0.770
0.332	11.2	9.80	0.879
0.226	8.89	8.89	1.000
0.171	6.60	6.87	1.041
0.078	3.06	4.04	1.32
0.042	1.96	1.86	0.949
0.041	1.92	1.72	0.896
0.025	1.17	0.98	0.84
0.016	0.79	0.75	0.96
0.009	0.44	0.47	1.09

The molar conductance of bromine trifluoride also falls from the value for pure material to a minimum at 70 mol % BrF_3. From this point it increases steadily to a maximum at ~5 mol % BrF_3, goes through a minimum at ~2.5 mol % BrF_3, and again increases with dilution (Table IV).

It seems reasonable to postulate that the initial addition of hydrogen fluoride to bromine trifluoride disrupts the chain-conducting mechanism operating in BrF_3. Therefore, although the ionic concentration in the solution increases, both the specific and the molar conductances decrease until ionic concentrations of BrF_2^+ and HF_2^- ions are sufficiently large to contribute significantly to the conductance. In the region from 70 to 30 mol % BrF_3 the equilibrium favors increased formation of ionic species. The mixture appears somewhat less viscous and an increase in the mobilities of the ions might be expected. In solutions containing less than 30 mol % BrF_3 the total concentration of ions decreases with increasing concentration of hydrogen fluoride and the conductivity also decreases. The peculiar behavior of the molar conductance in the 5–2.5 mol % BrF_3 solution may be due to the formation of a new and possibly less mobile species as indicated by the appearance of the 662-cm^{-1} Raman band.

As we approach pure HF, BrF_3 becomes a simple base and, as expected, its molar conductance increases with increased dilution.

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