TABLE III

ELEMENTAL ANALYSES AND VAPOR PRESSURE DATA

	$CF_3C(O)NF_2$	$C_2F_5C(O)NF_2$	$C_3F_7C(O)NF_2$	$F_2N(O)C(CF_2)_3C(O)NF_2$
Log $P_{mm} = a - b/T$ a	7.80	7.96	7.91	7.95
b	1240	1418	1540	1865
Analysis	F, 64.6 (63.7)[a]	F, 66.8 (66.8)	F, 68.6 (68.7)	F, 61.3 (61.4) C, 19.4 (19.2) N, 9.0 (9.1)
Bp, °C	−21.1	6.2	33.1	94.8
ΔH_{vap}, kcal/mol	5.7	6.5	7.1	8.5
ΔS_{vap}, eu	22.5	23.2	23.0	23.2
Mol wt	150.8 (149.2)	203.8 (199.0)	248.6 (249.0)	312.9 (310)

[a] Calculated values in parentheses.

reaction mixture using −91, −131, and −196° traps resulted in an impure product in the −91° trap. Pumping on this sample at −78° gave essentially pure product (35% yield). Identification was made by ir analysis.[9]

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Studies on the Chemistry of Halogens and Polyhalides. XXXIII. Spectroscopic and Electrical Conductance Studies of the Bromine Trifluoride–Chlorine Trifluoride Systems[1,2]

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Raman, infrared, and electrical conductance studies were carried out on liquid mixtures of bromine trifluoride with chlorine trifluoride. The experimental data reveal the existence of a fluoride ion transfer equilibrium $ClF_3 + BrF_3 \rightleftharpoons ClF_2^+ + BrF_4^-$. The equilibrium constant for the above reaction was calculated to be $\sim 10^{-4}$.

Introduction

In connection with a detailed investigation of the chemistry of liquid halogen fluorides[3-6] carried out in this laboratory, it was decided to study the equilibria existing in the liquid mixtures of bromine trifluoride and chlorine trifluoride by spectroscopic and conductometric techniques. These techniques have been shown to be very useful in the identification and quantitative estimation of species present in halogen fluorides.[3]

The exchange of radioactive ^{18}F isotope between BrF_3 and ClF_3 in binary mixtures of these compounds was studied by Rogers and Katz.[7] They found that the exchange was complete in 10 min at 27° and concluded that this exchange was due to the existence of a fluoride ion transfer equilibrium, probably

$$BrF_3 + ClF_3 \rightleftharpoons ClF_2^+ + BrF_4^- \qquad (1)$$

This would imply that in these mixtures chlorine trifluoride behaves as a base (fluoride ion donor). It was of interest to us, therefore, to determine the magnitude of the interaction between the two halogen fluorides.

Experimental Section

Chemicals.—Bromine trifluoride, chlorine trifluoride, and arsenic pentafluoride were obtained from the Matheson Co. and were purified by previously described methods.[3]

Apparatus.—The vacuum line used for the handling of the halogen fluorides as well as the conductivity cells have also been described in previous publications.[3,4] The conductance measurements were made with an Industrial Model RC-18 conductivity bridge at 25°. The precision of the conductivity measurements was ±1%.

Raman spectra were obtained on a Cary Model 81 Raman spectrometer using previously described cells.[3] Infrared measurements were made on a Beckman IR-12 recording spectrophotometer with a specially constructed cell with diamond windows.[5] In general, Raman and infrared measurements were made in the 200–900-cm^{-1} spectral region, although some measurements were carried out to 2000 cm^{-1}. The spectra were resolved on a Du Pont Model 310 curve resolver.

Preparation of Solutions.—Bromine trifluoride–chlorine trifluoride solutions were prepared on a vacuum system using the same technique as was described for the hydrogen fluoride–bromine trifluoride mixtures.[6]

Results and Discussion

Chlorine Trifluoride Spectra.—The Raman spectrum of liquid chlorine trifluoride is shown in Figure 1 and the bands are listed in Table I. In general, the results

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Abstracted in part from the Ph.D. thesis of T. Surles, Michigan State University, 1970.

(3) T. Surles, H. H. Hyman, L. A. Quarterman, and A. I. Popov, submitted for publication.

(4) H. H. Hyman, T. Surles, L. A. Quarterman, and A. I. Popov, *J. Phys. Chem.*, **74**, 2038 (1970).

(5) H. H. Hyman, T. Surles, L. A. Quarterman, and A. I. Popov, *Appl. Spectrosc.*, **24**, 464 (1970).

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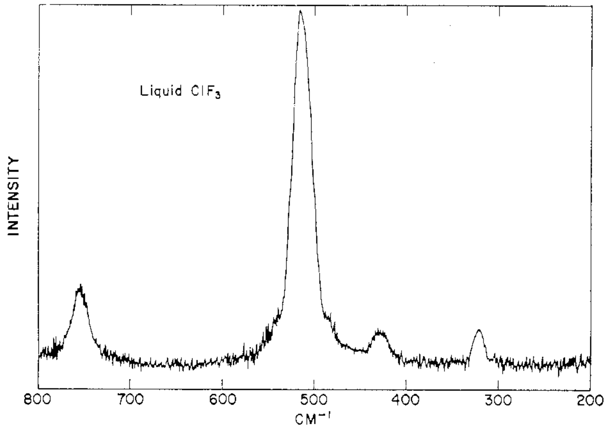

Figure 1.—Raman spectrum of liquid ClF_3.

TABLE I

VIBRATION SPECTRUM OF LIQUID CHLORINE TRIFLUORIDE

Liquid ClF_3		Gaseous ClF_3[a]		
Raman	Infrared	Raman	Infrared	Assignment
324 (8)	328 m	321, 337 p, w	328 s	ν_3 (a_1)
n.o.[b]	334 m	n.o.	328 s	ν_6 (b_2)
426 (6)	416 w	431 w	442 w	ν_5 (b_1)
518 (100)	519 m	529 p, vs	522, 538 m	ν_2 (a_1)
n.o.	703 vs	n.o.	702 vs	ν_4 (b_1)
756 (22)	758 s	752 p, s	742, 760 s	ν_1 (a_1)

[a] Reference 9. [b] Not observed.

agree with those of Jones, *et al.*,[8] with the exception of a strong band at 502 cm^{-1} which we do not observe. The infrared spectrum of liquid chlorine trifluoride, which does not appear to have been observed previously, is shown in Figure 2. The Raman and infrared spectra are in essential agreement with the recently published results for gaseous chlorine trifluoride.[9] No extraneous bands have been found in the liquid which could be attributed to ionic or polymeric species. The absence of ionic species in any appreciable concentrations is consistent with the low specific conductance of the liquid.[10]

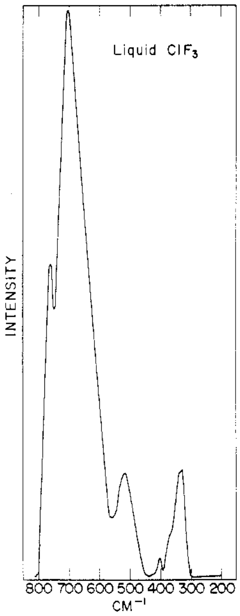

Figure 2.—Infrared spectrum of liquid ClF_3.

Figure 3 shows the Raman spectrum of a 3.1 *M* solution of arsenic pentafluoride in chlorine trifluoride. The elimination of bands attributable to the solvent and to the AsF_6^- anion leaves only one band at 782 cm^{-1} which cannot be attributed to the two above species. There is little doubt that this band is due to the ν_1 symmetric stretching vibration of the difluorochlorinium(III) cation, ClF_2^+, formed in the reaction $ClF_3 + AsF_5 \rightleftharpoons ClF_2^+ + AsF_6^-$. It is interesting to note that the band is observed at a lower frequency in solution than in the solid complex ClF_2AsF_6 (806 cm^{-1}).[11] The same behavior has been recently observed by us for the BrF_2^+ cation.[3] The decrease in the frequency of the ν_1 band in solution of the two cations may well be associated with interaction with the solvent. In the solvated ion, the Cl–F and Br–F force constants might well be less than in the crystal, and related stretching vibrations occur at somewhat lower frequencies. This shift, however, is rather less in chlorine trifluoride than in bromine trifluoride. Much of the comparative behavior of the two liquids can be described in terms of weaker interaction between chlorine trifluoride molecules and their derivative ions than between bromine trifluoride molecules and their derivative ions.

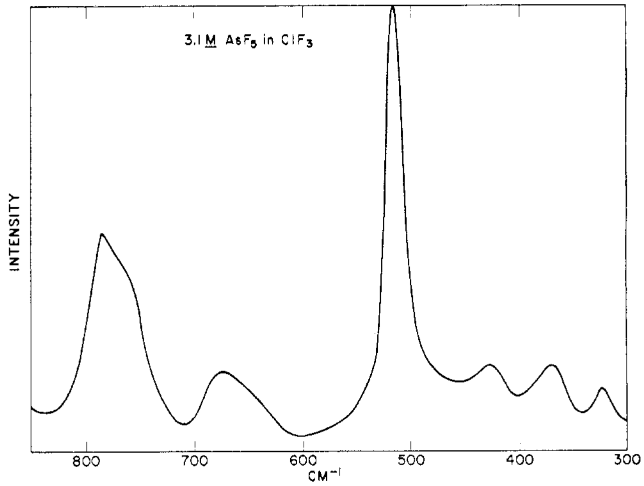

Figure 3.—Raman spectrum of 3.1 *M* AsF_5 in ClF_3.

Spectra of BrF_3–ClF_3 Mixtures—A typical Raman spectrum of a bromine trifluoride–chlorine trifluoride mixture is shown in Figure 4. In essence, the addition of chlorine trifluoride to bromine trifluoride does not produce any substantial change in the spectrum. When the spectra were resolved, however, it became evident that the decrease in the intensity of the BrF_4^- bands was definitely *smaller than that predicted on the basis of simple dilution*. This observation is consistent with the postulated existence of equilibrium 1. It should be noted, however, that no band was observed at 782 cm^{-1} which would correspond to the ClF_2^+ cation and, therefore, the equilibrium lies largely to the left. The quantitative aspects are discussed below.

Chlorine trifluoride is probably a much weaker fluoride ion acceptor (Lewis acid) than bromine trifluoride.

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(9) H. Selig, H. H. Claassen, and J. H. Holloway, *ibid.*, **52**, 2517 (1970).

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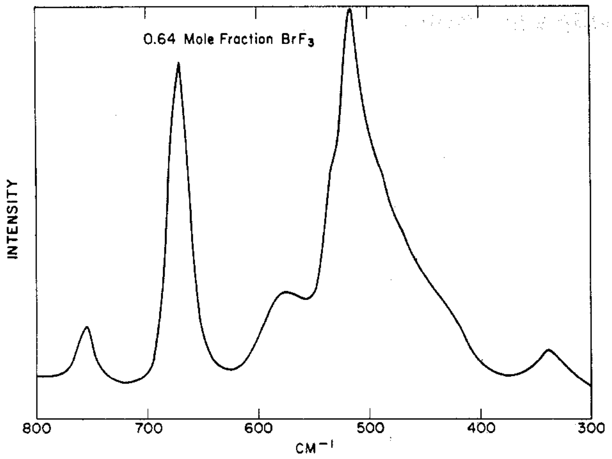

Figure 4.—Raman spectrum of a BrF_3–ClF_3 mixture containing 0.64 mole fraction of BrF_3.

Many bases are known in bromine trifluoride while the ClF_4^- anion has been detected only when stabilized in a few specific lattices. While this is the only quantitative evidence for their relative acid strength, there is no evidence as to their comparative strengths as fluoride ion donors (bases). A very superficial approach based on their comparative bond strengths[12] would suggest that chlorine trifluoride is a stronger base (weaker average bond energy, better donor) than bromine trifluoride, but the slight extent to which the equilibrium is demonstrated in solution indicates that the overall difference is small.

The concentration of the BrF_4^- and BrF_2^+ ions in the liquid mixtures was calculated from the values of the integrated areas of the Raman bands. The concentration of the ClF_2^+ cation was calculated by subtracting the concentration of the BrF_2^+ ion from that of the BrF_4^- ion. Since the initial concentrations of chlorine trifluoride and bromine trifluoride were known, the value of the equilibrium constant

$$K = \frac{(ClF_2^+)(BrF_4^-)}{(ClF_3)(BrF_3)}$$

could be calculated. The results of these calculations are shown in Tables II and III. These values are only approximate since a small error in the determination of the integrated areas of the BrF_2^+ and BrF_4^- bands is compounded in the calculations of the equilibrium constant. Nevertheless, the values indicate the correct order of magnitude of the constant and show that chlorine trifluoride behaves as a weak base in bromine trifluoride solutions. The calculations also show that the maximum concentration of the ClF_2^+ cation in the mixtures is <0.1 *M* and, therefore, too low to observe the band at 782 cm^{-1} due to this species.

TABLE II
CONCENTRATION OF SPECIES PRESENT IN BROMINE TRIFLUORIDE–CHLORINE TRIFLUORIDE MIXTURES

Initial concn			Ionic concn, *M*		
Mole fraction	$[BrF_3]$, *M*	$[ClF_3]$, *M*	BrF_2^+	BrF_4^-	ClF_2^+
0.849	17.2	3.1	0.71	0.72	0.01
0.825	16.7	3.5	0.71	0.72	0.01
0.648	13.0	7.0	0.60	0.62	0.02
0.606	12.1	7.9	0.55	0.56	0.01
0.426	8.4	11.3	0.36	0.39	0.03
0.414	8.1	11.5	0.34	0.37	0.03
0.218	4.2	15.2	0.22	0.25	0.03
0.151	2.9	16.4	0.20	0.22	0.02

TABLE III
EQUILIBRIUM CONSTANTS FOR
$BrF_3 + ClF_3 \rightleftharpoons BrF_4^- + ClF_2^+$

Mole fraction of BrF_3	10^4K^a	Mole fraction of BrF_3	10^4K^a
0.849	1.43	0.426	1.30
0.825	1.28	0.414	1.24
0.648	1.43	0.218	1.23
0.606	0.62	0.151	0.96

[a] These are the numbers as actually calculated. The precision of these measurements is such that there is no significant difference between them. The actual equilibrium constant may be taken as $(1 \pm 0.4) \times 10^{-4}$.

The infrared data confirm the absence of any significant additional interactions as the change in the bromine trifluoride spectrum can be accounted for largely as the diluting effect of chlorine trifluoride. As in the case of the hydrogen fluoride–bromine trifluoride mixtures, more quantitative data could not be obtained due to the limitations inherent in such measurements.

A plot of the molar conductance of bromine trifluoride *vs.* the mole fraction of bromine trifluoride in the mixture is shown in Figure 5.

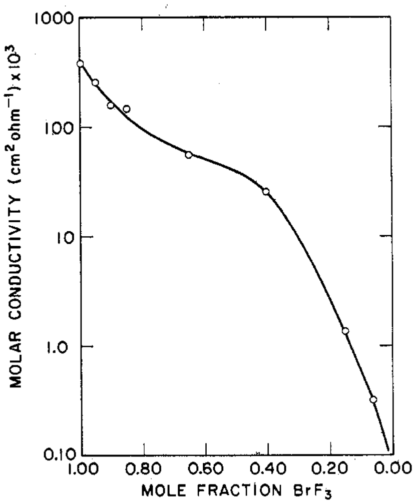

Figure 5.—Molar conductivity for the BrF_3–ClF_3 system.

Toy and Cannon[13] have previously measured the conductivity of BrF_3–ClF_3 mixtures. They reported no data for concentrations below 32 mol % ClF_3 and drew a rather smooth curve for specific conductivity decreasing with decreasing bromine trifluoride content.

Our measurements, which, in the high chlorine trifluoride concentration range, are in fair agreement with those reported by Toy and Cannon, also include the conductivity in the high bromine trifluoride concentration range and are in substantial disagreement with their extrapolated curve. The specific conductivity shown by Toy and Cannon at 32 mol % ClF_3, the single measurement they reported in the BrF_3 richer region, is above 2×10^{-3} ohm^{-1} cm^{-1} as compared with an interpolated value of 10^{-3} ohm^{-1} cm^{-1} from

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[12] L. Stein, "Halogen Chemistry," Vol. 1, V. Gutman, Ed., Academic Press, New York, N. Y., 1967, p 183.

[13] M. S. Toy and W. A. Cannon, *J. Phys. Chem.*, **70**, 2241 (1966).

TABLE IV

CONDUCTIVITY OF BROMINE TRIFLUORIDE IN CHLORINE TRIFLUORIDE AT 25°

Concn, *M*	Specific conductivity × 10^3, ohm^{-1} cm^{-1}	Molar conductivity × 10^3, ohm^{-1} cm^2	Concn, *M*	Specific conductivity × 10^3, ohm^{-1} cm^{-1}	Molar conductivity × 10^3, ohm^{-1} cm^2
20.5^a	8.01	391	12.95	0.717	55.4
19.39	5.09	263	8.13	0.209	25.7
18.29	2.88	157	2.92	0.00403	1.28
17.19	2.52	147	1.32	0.000412	0.312

^{a} Pure BrF_3.

our measurements. As seen from Figure 5, initial addition of chlorine trifluoride produces a sharp drop in the conductance which becomes more gradual in solutions containing ~85 mol % bromine trifluoride. It appears, therefore, that our conductance data support the postulate that the high electrical conductivity of pure bromine trifluoride is due to a chain-conducting mechanism.[6] (See also Table IV.)

It is evident from the above results that the fluoride ion transfer in bromine trifluoride–chlorine trifluoride mixtures does take place and leads to the formation of BrF_4^- and ClF_2^+ ions, but, at room temperature, the extent of the reaction is quite limited.

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The Interaction of Chromium(III) Ion with Bromide Ion in Hydrobromic Acid Solution[1]

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The inner-sphere association of chromium(III) ion and bromide ion has been studied in aqueous hydrobromic acid solution (~0.5–9.0 *M*) at 45, 60, and 75° and in aqueous hydrobromic acid–perchloric acid solution ($I = 7.14$ *M*, 45°). Outer-sphere interactions of oppositely charged ions also occur in the concentrated electrolyte solutions studied, thereby complicating greatly the interpretation of the data. The association reaction to form pentaaquobromochromium(III) ion occurs to a greater extent at high electrolyte concentration; this is due, in part, to the low activity of water in these solutions. The association reaction is endothermic ($\Delta H = +7.5$ kcal mol^{-1} at 0.50–2.0 *M* hydrobromic acid; $\Delta H = +5.9$ kcal mol^{-1} at 8.0 *M* hydrobromic acid). The rate of formation of pentaaquobromochromium(III) ion has been studied at 45°.

The interaction of a metal ion and an anionic ligand in solution may produce two (or more) definable types of species: inner-sphere species with direct bonding of the ligand to the metal ion and outer-sphere species (ion pairs) with one (or more) solvent molecules separating the metal ion and the ligand. In addition, there are ion atmosphere effects in electrolyte solution; it is unnecessary and inappropriate to describe such interaction in terms of the formation of new species.[3] Distinguishing inner-sphere and outer-sphere interaction is facilitated for chromium(III) ion by the large difference in rates of establishment of equilibrium in the two types of interaction. Distinguishing outer-sphere interaction from ion atmosphere effects is aided by no such experimental criterion; the basis for establishing the extent of outer-sphere interaction is usually an assumption which cannot be proved (*e.g.*, the validity of the ionic strength principle).

The present paper deals with studies on chromium(III) bromide in aqueous solutions of hydrobromic acid or perchloric acid–hydrobromic acid mixtures. The interactions investigated are *the inner-sphere interactions*[4]

$$Cr(OH_2)_{7-n}Br_{n-1}{}^{4-n} + Br^- = Cr(OH_2)_{6-n}Br_n{}^{3-n} + H_2O \qquad (n = 1, 2, 3(?))$$

with equilibrium quotients Q_n and *the outer-sphere interactions*

$$Cr(OH_2)_{6-n}Br_n{}^{3-n} + Br^- = Cr(OH_2)_{6-n}Br_n{}^{3-n}\cdot Br^- \qquad (n = 0, 1)$$

with equilibrium quotients q_{n1} and

$$Cr(OH_2)_{6-n}Br_n{}^{3-n} + ClO_4^- = Cr(OH_2)_{6-n}Br^{3-n}\cdot ClO_4^- \qquad (n = 0, 1)$$

with equilibrium quotients q_{n2}. In addition, the presence of outer-sphere species containing more than one ion-paired anionic ligand (*e.g.*, $Cr(OH_2)_6{}^{3+}\cdot(Br^-)_2$) is possible in media of high electrolyte concentration. These several equilibria must be considered simultaneously, resulting in difficulties which will be explored in the interpretation of the data.

The following system of notation will be used in concentration terms in equilibrium quotients and rate laws: C_{Cr}, total stoichiometric concentration of chromium(III); $[Cr(OH_2)_6{}^{3+}]$, molarity of hexaaquochromium(III) ion; $[Cr^{3+}] = [Cr(OH_2)_6{}^{3+}] + [Cr(OH_2)_6{}^{3+}\cdot Br^-] + \ldots$; $[Cr(OH_2)_5Br^{2+}]$, molarity of

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[1] Based on the Ph.D. thesis of L. O. Spreer, University of Colorado, 1969; work supported by grants from the National Science Foundation (Grants GP-680 and GP-7185X).

[2] National Science Foundation Predoctoral Trainee, 1968–1969.

[3] T. F. Young and A. C. Jones, *Ann. Rev. Phys. Chem.*, **3**, 275 (1952); O. Redlich and G. C. Hood, *Discuss. Faraday Soc.*, **24**, 87 (1957).

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