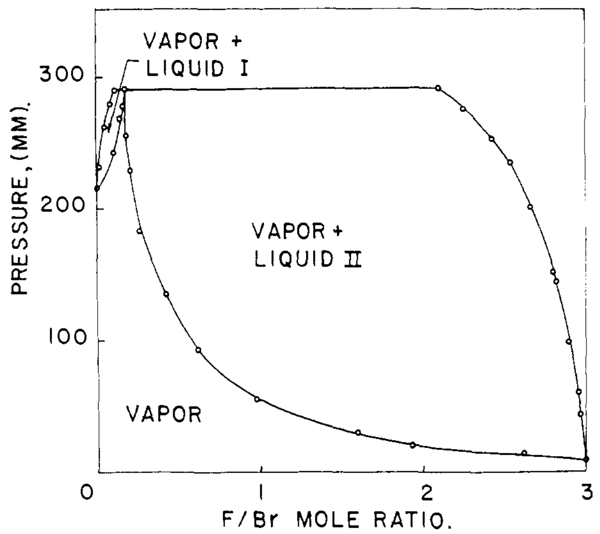

Fig. 3.—Vapor–liquid phase diagram of the system Br_2–BrF_3 at 25°.

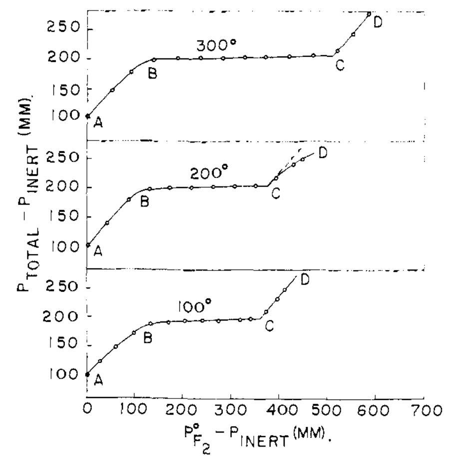

Fig. 4.—Pressure curves for the addition of F_2 to Br_2 at 100, 200 and 300°.

again as excess fluorine was added. At 100°, the reaction between fluorine and bromine trifluoride was still slow enough to allow the points between C and D to be determined, although the pressures were falling. At 200°, the excess fluorine reacted so rapidly with the trifluoride that the points between C and D could hardly be determined and no longer yielded a straight line. The relative amount of pentafluoride present at point C increased with temperature, as expected. At 300°, the plateau extended all the way to the bromine pentafluoride end-point, and the pressures measured between C and D were stable, since no higher fluoride than the pentafluoride was formed by the excess fluorine.

Acknowledgment.—The author wishes to thank Dr. Bernard M. Abraham, Mr. Howard E. Flotow and Mr. Roger D. Carlson for suggestions regarding the design of the differential pressure gauge and for the loan of a variable differential transformer; Mr. Irving Sheft for the provision of bromine trifluoride; and members of the Chemical Engineering Division for the distillation of the bromine trifluoride.

LEMONT, ILLINOIS

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY]

Infrared Studies of the Bromine Fluorides[1]

BY LAWRENCE STEIN

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The infrared absorption spectra of bromine monofluoride, trifluoride and pentafluoride were obtained in the vapor phase at approximately 25°. The reaction of bromine with bromine trifluoride was carried out in the infrared cell to produce the monofluoride, and it was found that small amounts of pentafluoride also were produced. A partial disproportionation of the trifluoride into monofluoride and pentafluoride was postulated. This was confirmed by the appearance of the pentafluoride in samples of the trifluoride which were heated to 150° or higher. The reactions of fluorine with bromine and fluorine with bromine trifluoride also were studied in the infrared cell.

Introduction

The infrared spectra of bromine trifluoride[2,3] and bromine pentafluoride[2,4] previously have been reported in the literature. In the present article, several new vibrational bands of bromine pentafluoride and the fundamental and second harmonic of bromine monofluoride are reported. A comparison of the infrared absorption spectra of the three bromine fluorides shows that the strongest bands all occur in the region between 600 and 700 $cm.^{-1}$; fortunately they do not coincide, so each compound can be identified in the presence of the others. By infrared analysis, bromine pentafluoride is found as one of the products of the reaction between bromine and bromine trifluoride. The disproportionation of bromine trifluoride into monofluoride and pentafluoride must therefore occur to a small extent. In the reaction of fluorine with bromine, the pentafluoride also appears, confirming the results of the pressure studies.[5] The rate of reaction of fluorine with bromine trifluoride liquid is shown to be appreciable even at 25°.

Experimental

Reagents.—Bromine, fluorine and bromine trifluoride of the same purity as in previous experiments[5] were used. Bromine pentafluoride from Harshaw Chemical Company was distilled several times in Fluorothene test-tubes until

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. M. Haendler, G. W. Bukata, B. Millard, E. I. Goodman and J. Littman, *J. Chem. Phys.*, **22**, 1939 (1954).

(3) H. H. Claassen, B. Weinstock and J. G. Malm, *ibid.*, **28**, 285 (1958).

(4) J. G. Burke and E. A. Jones, *ibid.*, **19**, 1611 (1951).

(5) L. Stein, THIS JOURNAL, **81**, 1269 (1959).

a colorless middle fraction was obtained with a vapor pressure of 405 mm. at 25°. The infrared spectrum of this fraction was unchanged on further distillation.

Infrared Spectra.—A Model 21 Perkin-Elmer infrared spectrophotometer was used, with sodium chloride, potassium bromide and cesium bromide prisms. Although the cesium bromide region completely overlapped the potassium bromide region, better separation of bands in the interval 600 to 700 cm.$^{-1}$ was obtained with the potassium bromide prism in this instrument. The wave length scales were calibrated with known peaks of polystyrene and air.

Samples were contained in a nickel cell 8.5 cm. long and 2.5 cm. in diameter, which had a copper sidearm tube and an inlet valve which could be attached to a vacuum manifold. Samples either were condensed into the sidearm tube at low temperature and warmed to 25° or added to a known pressure at 25°.

From 4000 to 1000 cm.$^{-1}$, calcium fluoride windows and Teflon gaskets were used on the cell. These were not attacked by any of the fluorides and could be used continuously without replacement. From 1000 to 250 cm.$^{-1}$, polyethylene windows prefluorinated with fluorine or bromine pentafluoride were used, with an equivalent thickness of polyethylene in the reference beam of the instrument. The polyethylene was not very transparent from 1000 to 700 cm.$^{-1}$, but with a wide slit it could be used, and the transparency improved at longer wave lengths. The surprising ability of pretreated polyethylene to withstand attack by fluorides in the vapor phase was demonstrated by Claassen, Weinstock and Malm[3] and proved most helpful to this research. Although absorption bands gradually appeared in these windows due to reaction with bromine and the fluorides, the windows could be used for a number of hours before replacement became necessary.

Results and Discussion

The vapor phase absorption spectra were first obtained for bromine trifluoride and bromine pentafluoride, then for bromine monofluoride, which was made by mixing bromine and bromine trifluoride in the cell. The observed bands are given in Table I.

TABLE I

VAPOR PHASE INFRARED SPECTRA OF THE BROMINE FLUORIDES

Compound	Absorption frequency, cm.$^{-1}$	Relative intensity
BrF	1326	W
BrF	669	M
BrF_3	665	M
BrF_3	608	VS
BrF_5	1362	W
BrF_5	1328	S
BrF_5	1258	VW
BrF_5	1226	S
BrF_5	1192	S
BrF_5	644	VS
BrF_5	580	W
BrF_5	461	VW
BrF_5	411	S
BrF_5	378	S
BrF_5	366	S

The fundamental and second harmonic of bromine monofluoride are in good agreement with the vibrational frequencies computed by Broderson and Schumacher[6] and Durie[7] from band spectra in the visible region. The two bromine trifluoride bands agree moderately well with those of Claassen, Weinstock and Malm,[3] and a third band also was observed at 569 cm.$^{-1}$ but probably was due to droplets of liquid condensing on the cell windows.

Burke and Jones[4] reported infrared bands for bromine pentafluoride vapor at 690, 645, 583 and 418 cm.$^{-1}$, and Stephenson and Jones[8] reported a number of Raman bands for the liquid. Although no band at 690 cm.$^{-1}$ was found in the present research, it may have been missed due to the low transmission of the polyethylene in this region. A weak band at approximately 678 cm.$^{-1}$ was sometimes found as a shoulder of the very strong 644 cm.$^{-1}$ band and was attributed to bromine monofluoride impurity.

The spectrum of bromine pentafluoride at various pressures is shown in Fig. 1, with the dotted line indicating the background curve of the empty cell. Curve 1 of Fig. 2 shows the appearance of bromine trifluoride vapor at 8 mm. pressure in equilibrium with liquid in the sidearm of the cell, and curves 2, 3 and 4 show the effect of successive additions of bromine to the cell. It was found that in addition to the peak for bromine monofluoride at 669 cm.$^{-1}$, a peak for bromine pentafluoride also appeared at 644 cm.$^{-1}$. After the third bromine addition, when the intensity of the major peaks had increased to the point shown in curve 4, a weaker peak was also found at approximately 366 cm.$^{-1}$. Since this is the frequency of the second strongest band of bromine pentafluoride, it was considered to be verification of the presence of this compound. The partial pressure of bromine pentafluoride in curve 4 was estimated to be approximately 2 mm., whereas that of the monofluoride was much higher, probably 20 to 40 mm. When similar mixtures of bromine trifluoride and bromine were examined at shorter wave lengths, only the second harmonic of bromine monofluoride at 1326 cm.$^{-1}$ appeared as the bromine was added.

Several other experiments were tried to check the possibility that the bromine pentafluoride was present as an impurity in the bromine trifluoride liquid and was driven into the vapor phase by a decrease in solubility on the addition of bromine. Bromine and bromine trifluoride were mixed to form the two immiscible phases,[5] liquid I and liquid II, and the vapor in equilibrium with these phases was examined; it appeared similar to curve 4 of Fig. 2, except that the bromine trifluoride peak at 608 cm.$^{-1}$ was weaker. The vapor above the immiscible liquids then was pumped off for about 30 minutes until only bromine trifluoride liquid remained, as determined by the color, the vapor pressure and the infrared spectrum. On the addition of bromine to this liquid to form the two immiscible phases again, the infrared peaks of both the monofluoride and the pentafluoride reappeared. Also, when the reaction was carried out with only the vapor phase in the cell, similar results were obtained. Figure 3a shows the appearance of bromine trifluoride at 6 mm. pressure, curve 1, to which was added 15 mm. of bromine, curve 2, and another 17 mm. of bromine, curve 3. The bromine trifluoride was largely converted to the monofluoride plus a small amount of the pentafluoride.

The growth of the pentafluoride peak with the monofluoride peak was puzzling, since these compounds should bear an inverse ratio to one another

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(6) P. H. Broderson and H. J. Schumacher, *Z. Naturforsch.*, **2a**, 358 (1947).

(7) R. A. Durie, *Proc. Roy. Soc.* (*London*), **A207**, 388 (1951).

(8) C. V. Stephenson and E. A. Jones, *J. Chem. Phys.* **20**, 1830 (1952).

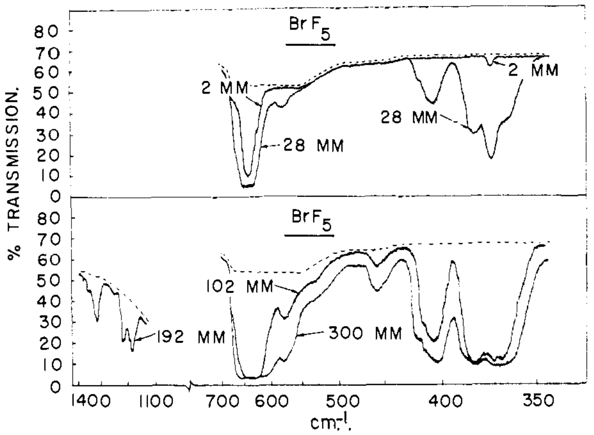

Fig. 1.—Infrared spectrum of BrF_5.

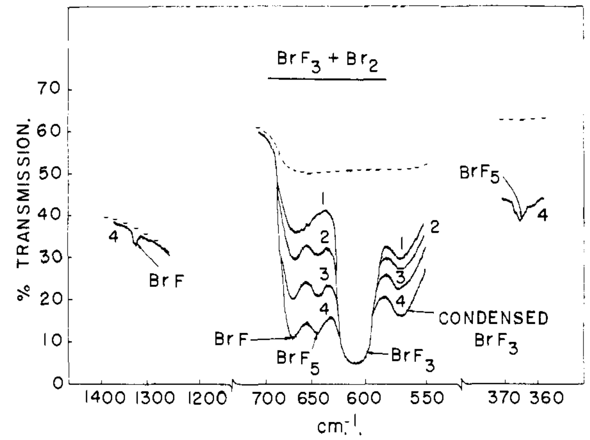

Fig. 2.—Infrared bands appearing on addition of Br_2 to BrF_3, with the liquid phase present.

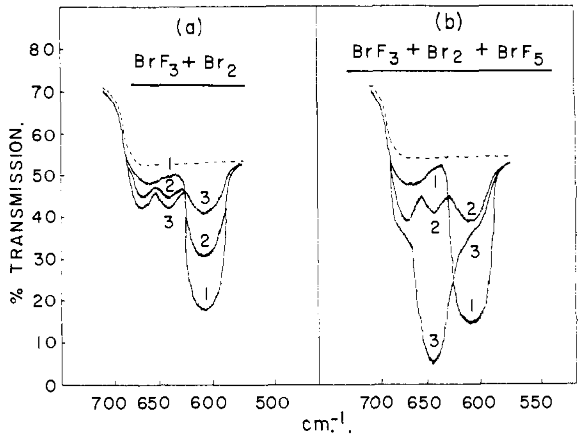

Fig. 3.—Infrared bands appearing on addition of (a) Br_2 to BrF_3, and (b) Br_2 and BrF_5 to BrF_3, in the vapor phase.

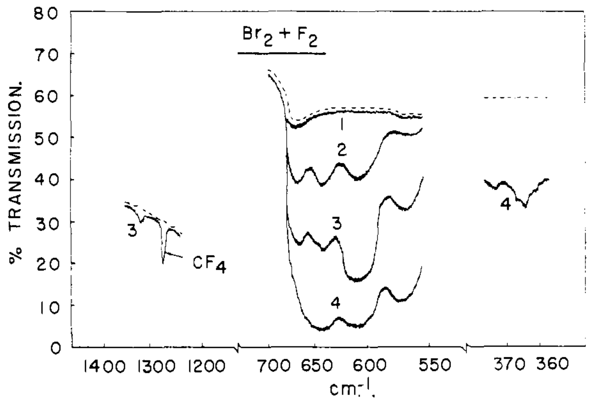

Fig. 4.—Infrared bands produced by the reaction of F_2 with Br_2.

if present together in equilibrium. In Fig. 3b, the effect of added bromine pentafluoride upon the spectra is shown. To 7 mm. of bromine trifluoride vapor, curve 1, was added 75 mm. of bromine, curve 2, then 5 mm. of bromine pentafluoride, curve 3. No reaction of the excess pentafluoride was detected; the 644 cm.$^{-1}$ peak increased by the requisite amount for 5 mm. of pentafluoride, and the small monofluoride and trifluoride peaks seemed to be unchanged. In other experiments, the cell was filled with bromine pentafluoride, and bromine was added; no change in the pentafluoride spectrum was observed within 1 hr. It was therefore concluded that bromine pentafluoride, although produced in the various mixtures, was not in equilibrium with the other compounds at 25°.

When the bromine-fluorine reaction was carried out in the infrared cell, bromine pentafluoride appeared as one of the products, as expected. In Fig. 4, curve 1 was obtained with 100 mm. of bromine in the cell, and curves 2, 3 and 4 were obtained after separate additions of 58, 67 and 570 mm. of fluorine. Curve 4 shows the appearance of the spectrum approximately five minutes after the last fluorine addition; the pentafluoride bands at 644 and 366 cm.$^{-1}$ slowly grew stronger after this as the excess fluorine reacted with the trifluoride. At shorter wave lengths, the growth and disappearance of bromine monofluoride was observed in the band at 1326 cm.$^{-1}$. Carbon tetrafluoride impurity in the fluorine produced a sharp band at 1280 cm.$^{-1}$.

Further evidence that the reaction of fluorine with bromine trifluoride is not negligible at 25° is shown in Fig. 5. Curve 1 was obtained with bromine trifluoride vapor in the cell, in equilibrium with liquid in the sidearm, and curves 2, 3 and 4 were obtained after separate additions of 33, 40 and 97 mm. of fluorine at about ten minute intervals. With each increase in fluorine pressure, the 644 cm.$^{-1}$ band increased in intensity, rapidly at first, then more slowly; the final rate of increase seemed roughly proportional to the fluorine pressure. Curve 4 shows the appearance of the spectrum several minutes after the last fluorine addition, with the 366 cm.$^{-1}$ band discernible. About 15 minutes later, the very broad 644 cm.$^{-1}$ band was completely merged with the 608 cm.$^{-1}$ trifluoride band. In a similar experiment at shorter wave lengths, the strongest harmonic and combination bands of bromine pentafluoride at 1328, 1226 and 1192 cm.$^{-1}$ appeared 15 minutes after the last fluorine addition, as shown in curve 5.

Steunenberg, Vogel and Fischer[9] have shown that equilibrium (1) is established rapidly when bromine is added to bromine trifluoride

$$Br_2 + BrF_3 \rightleftarrows 3BrF \qquad (1)$$

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(9) R. K. Steuenberg, R. C. Vogel and J. Fischer, THIS JOURNAL, **79**, 1320 (1957).

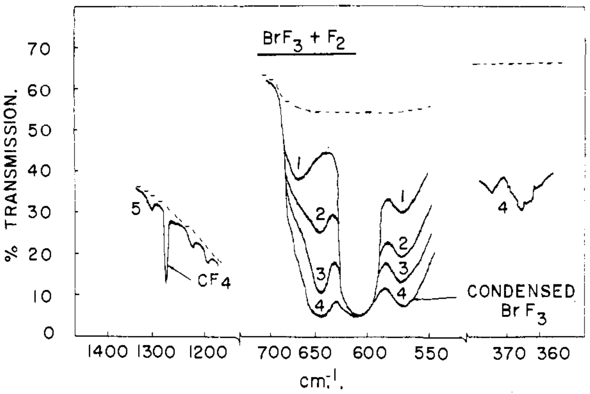

Fig. 5.—Infrared bands of BrF_5 produced by the reaction of F_2 with BrF_3.

The present experiments indicate that a disproportionation of bromine trifluoride also occurs

$$2BrF_3 \rightleftarrows BrF + BrF_5 \qquad (2)$$

A complete thermodynamic treatment of the system must therefore include reaction 2 as well as reaction 1. If the data of Steunenberg, Vogel and Fischer[9] are corrected for the presence of 0.5 to 2.0 mm. of bromine pentafluoride, their equilibrium constants for reaction 1 are increased by approximately 10 to 30%. The correction is therefore comparable to the experimental error in the original constants, and the change in the temperature dependence of the constants may be small. From the free energies of formation of the monofluoride[10] and trifluoride[9] and the estimated free energy of formation of the pentafluoride,[10] the standard free energy change for reaction 2 at 25° can be estimated, with all compounds in the gaseous state at one atm. pressure

$$\begin{aligned}\Delta F^0 &= \Delta F^0{}_{f\cdot BrF(g)} + \Delta F^0{}_{f\cdot BrF_5(g)} - 2\Delta F^0{}_{f\cdot BrF_3(g)} \qquad (3)\\ &= -18.7 - 101.9 - 2(-54.9)\\ &= -10.8 \text{ kcal. per mole of } BrF_5\end{aligned}$$

Although this calculation is not precise, chiefly because of the uncertainty in the free energy of formation of the pentafluoride, it shows that the disproportionation of the trifluoride is to be expected from thermodynamic considerations.

When bromine is mixed with bromine trifluoride at 25°, reaction 1 occurs rapidly and reaches a state of equilibrium within several minutes. It is postulated that reaction 2 also occurs but that the products are not in equilibrium with the bromine trifluoride at 25°. It has been observed that both bromine monofluoride and bromine pentafluoride appear in purified bromine trifluoride after long storage in nickel vessels at room temperature, so the spontaneous disproportionation of the trifluoride takes place, but apparently very slowly. The mechanism by which bromine or an intermediate product causes the pentafluoride to appear rapidly in bromine trifluoride is not understood.

At higher temperatures, the equilibria for reactions 1 and 2 are both established in short periods of time. Bromine pentafluoride reacts with bromine at a moderate rate at 150° and very rapidly at 300°, forming bromine monofluoride and trifluoride. In several experiments at 150°, it was found that the disproportionation of bromine trifluoride produced detectable amounts of pentafluoride within five minutes. When bromine trifluoride vapor at 100 to 300 mm. pressure was kept at 200° for 20 minutes or longer in a Monel vessel, then flashed into an infrared cell at room temperature, bromine pentafluoride was found to the extent of about 2% of the initial trifluoride, and bromine monofluoride was presumably present to the same extent, although it was not detected in such small amount. The order of magnitude of the equilibrium constant for reaction 2 computed from this was 10^{-4} at 200°, assuming no recombination of the products on rapid cooling.

At the higher temperatures, the relative amounts of bromine monofluoride and bromine pentafluoride were also found to bear the inverse relation to each other required by the equilibrium constant for reaction 2. When fluorine was added to bromine in a Monel vessel at 200° and the products flashed into the infrared cell for analysis, the concentration of pentafluoride was very low in the region where bromine and bromine monofluoride were present in large amounts. The concentration of pentafluoride increased gradually as that of the monofluoride decreased, and at the "titration end-point," the amount of pentafluoride rose rapidly as the last of the monofluoride disappeared. Although the "quenching" technique yielded only approximate results due to rapid shifts in equilibrium 1, it allowed these qualitative observations of equilibrium 2 to be made, since the pentafluoride and monofluoride did not recombine rapidly after being cooled to room temperature.

It is interesting to note that at the elevated temperatures bromine monofluoride was found considerably beyond the point where three equivalents of fluorine had been added to bromine, *i.e.*, in the composition region of a fluorine-to-bromine mole ratio between three and five. This is in accord with the results of Broderson and Schumacher,[6] who obtained the visible spectrum of the monofluoride with a mixture of 101 mm. of bromine and 344 mm. of fluorine.

Acknowledgment.—The author wishes to thank Dr. Howard H. Claassen for advice regarding infrared techniques and Mr. Herbert H. Hyman for stimulating discussions of the chemical properties of the bromine fluorides.

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(10) W. H. Evans, T. R. Munson and D. D. Wagman, *J. Research Natl. Bur. Standards*, **55**, 147 (1955).