under contract with the Atomic Energy Commission. One of us (D. F. E.) acknowledges support from the National Science Foundation.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

High Temperature Fluorination Reactions of Inorganic Substances with Bromine Trifluoride Addition Compounds[1a,1b]

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RECEIVED JUNE 29, 1955

The addition compounds of BrF_3 with KF or SbF_5 are found to be excellent high temperature fluorinating agents. Dissociation pressures of $KBrF_4$ and BrF_2SbF_6 to 350° have been measured and are of such a magnitude that these reagents can be used even at 500° in closed reaction vessels without developing high pressures. Many inorganic compounds, including refractory oxides, feldspars and oxygen-containing salts which resist fluorination by BrF_3 itself are readily converted to fluorides and elemental oxygen by $KBrF_4$ and BrF_2SbF_6 at elevated temperatures. Apparatus and techniques for carrying out these unusual high temperature fluorination reactions are described and the relative merits of these two reagents compared on the basis of their acid–base relationship.

Introduction

Although numerous oxides or oxygen-containing compounds can be fluorinated smoothly with bromine trifluoride (b.p. 127°) in the liquid phase near room temperature,[2,3] there are many compounds which fail to react quantitatively or indeed to react at all with BrF_3 even at its boiling point. Certain of these, it is true, can be completely fluorinated with BrF_3 at temperatures of 200–300° and at pressures which are so high as to present formidable and at present intractable apparatus problems. Emeléus and co-workers[4,5] have described a number of addition compounds of BrF_3, in particular with KF and SbF_5, which appeared to present the possibility of utilizing the fluorinating capacity of BrF_3 at high temperature without the attendant disadvantages of high pressure. To this end the dissociation pressures of these two addition compounds have been measured and their capacity to function as fluorinating agents studied. We find that these compounds can be readily employed to temperatures of at least 500°, that they are exceedingly powerful and versatile reagents at elevated temperatures, and that in many respects $KBrF_4$ and BrF_2SbF_6 are by far the most convenient form in which fluorine can be utilized in the laboratory.

Experimental

Materials.—Bromine trifluoride (Harshaw Chemical Company) was purified from the main impurities which are bromine, bromine pentafluoride, hydrogen fluoride and nonvolatile metal fluorides by vacuum distillation; the fraction, b.p. 95–95.5° (250 mm.), was collected as a very pale yellow liquid and stored in a nickel vessel. The bromine trifluoride was again purified by distillation in the vacuum line just prior to use. Antimony pentafluoride was a commercial product obtained from the Harshaw Chemical Company and was used as received. The other chemicals in this work were of reagent grade and the standard feldspar sample was obtained from the National Bureau of Standards.

Preparation of BrF_2SbF_6 and $KBrF_4$.—The BrF_3–SbF_5 addition compound was prepared readily in quantity by dissolving SbF_5 in a 10% excess of BrF_3 in a nickel vessel. The excess BrF_3 was then removed from the solution by heating *in vacuo* at 130°. The identity of the product was established from the stoichiometry of the reaction. When pure, BrF_2SbF_6 is canary-colored; when prepared from commercial reagents, it is usually brick-red. BrF_2SbF_6 prepared as above is obtained as a free-flowing crystalline solid which is stable in dry air. Although the compound reacts vigorously with water, and will char or inflame moist cellulose, these reactions are very much more moderate than with liquid BrF_3 itself.

$KBrF_4$ can be prepared in exactly similar fashion by dissolving KF in a 10% excess of BrF_3 and removing the excess BrF_3 *in vacuo* at 130°. The addition compound is obtained as a free-flowing white crystalline powder, stable in dry air. In its reactions with water and various organic compounds it is distinctly less vigorous than BrF_2SbF_6.

The crystal structure of $KBrF_4$ was examined by Dr. Stanley Siegel. The symmetry of $KBrF_4$ is tetragonal with $a = 6.162$ kX. and $c = 11.081$ kX. The observed density leads to 4 molecules per unit cell with a calculated density $\rho = 3.06$ g./cm.³. The space group is I4/mcm. The fluorine atoms are distributed in tetrahedral configurations about each bromine atom at a distance Br–F = 1.81 Å., which is close to the value (1.78 Å.) found in BrF_3 itself. The F–F distances within the BrF_4 group are 2.81 and 3.03 Å. Each potassium is bonded to 8 fluorine atoms with K–8F = 2.84 Å.

Dissociation Pressure Measurements.—Dissociation pressures were measured in an all-nickel apparatus which was placed in an air-thermostat. The temperature of the thermostat was maintained at 130° to prevent sublimation and condensation since it was found that no distillation of BrF_2SbF_6 occurred from the reaction zone when the cooler portions of the apparatus are maintained above 130°. The probable explanation for this behavior is that the vapor of BrF_2SbF_6 may be completely dissociated and recombination cannot occur in the absence of a liquid phase; the vapor pressures of the BrF_3 and SbF_5 themselves are such as to preclude their condensation. Pressures were measured through a Booth–Cromer[6] nickel diaphragm gage which was balanced by a precision mercury manometer.

Apparatus.—Nickel is usable with pure BrF_2SbF_6 and $KBrF_4$ up to a temperature of 500° and is therefore a suitable material of construction for high temperature fluorination apparatus. The dimensions of the nickel reaction tubes were $^3/_4$″ × 6″ with an SAE $^3/_4$″ female flare at the top. The reaction tubes were attached by means of a $^3/_4$″ flare nut to a nickel block containing a Teflon-gasketed addition port through which the sample could be introduced; also attached to the nickel block (by means of silver solder) was a nickel diaphragm Hoke valve. The lower four-inch section of the reaction vessel was heated by an electric furnace; inserted into the furnace was a resistance thermometer which served as the sensing element for an electronic controller. The temperature cycle was followed

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[1] (a) Based on work performed under the auspices of the U. S. Atomic Energy Commission; (b) presented in part before the Division of Physical and Inorganic Chemistry at the 127th meeting of the American Chemical Society, Cincinnati, Ohio, April, 1955.

[2] H. J. Emeléus and A. A. Woolf, *J. Chem. Soc.*, 164 (1950).

[3] H. R. Hoekstra and J. J. Katz, *Anal. Chem.*, **25**, 1609 (1953).

[4] A. G. Sharpe and H. J. Emeléus, *J. Chem. Soc.*, 2135 (1948).

[5] A. A. Woolf and H. J. Emeléus, *ibid.*, 2865 (1949).

[6] S. Cromer, "The Electronic Pressure Transmitter and Self Balancing Relay," MDDC-803, 1949.

on a Brown potentiometer recorder. The entire reaction vessel including the valve and the addition port were surrounded by an aluminum hood containing an electrical strip heater. Since nickel is a relatively poor conductor of heat, the temperature of the addition port remained low enough to prevent leakage through the Teflon gasket even when the reaction tube was heated as high as 500°. Nevertheless thermal conditions were such as to require a new Teflon gasket usually after six heating cycles.

The reactor was connected through the valve to a vacuum line similar to that described by Hoekstra and Katz.[3] In order to follow the course of the reaction, gaseous reaction products could be removed from the reaction vessel and examined; where one of the gaseous products was a non-condensable gas such as oxygen, it could be transferred by an automatic Toepler pump to the appropriate measuring system.

Procedure.—Approximately 20 g. of crystalline fluorinating reagent was poured into a clean, dry, nickel reaction tube, the tube was attached with a $^3/_4''$ flare nut to the nickel block, and the whole system was evacuated to less than 2×10^{-5} mm. The nickel diaphragm valve was closed to isolate the reaction tube, and the air temperature in the aluminum hood was raised to 120°. When the temperature in the hood reached 80°, the furnace surrounding the reaction tube was turned on. The furnace was maintained at 500 ± 15° for 5 hours to complete the prefluorination. Prefluorination is essential in order to eliminate from the reaction system impurities and contaminants which would be certain to confuse the interpretation of subsequent reaction. After the reaction tube was cooled and again evacuated, the system was filled with dry nitrogen at 800–1000 mm. pressure. The cap covering the addition port was removed; the flow of nitrogen out through the port serves to prevent, very effectively, the entry of water vapor into the system. The dried sample, weighed into a small cup made from 0.2 mil. gold foil, was dropped through the addition port, the cap was replaced, the system evacuated, the valve closed and the reactor heated just as in the prefluorination. When the tube had again cooled, the gaseous reaction products were transferred by means of a Toepler pump into the calibrated glass bulb. Another heating cycle may then be carried out to ensure complete reaction. The stoichiometry and course of the reaction can then be deduced from the amount and nature of the reaction products collected.

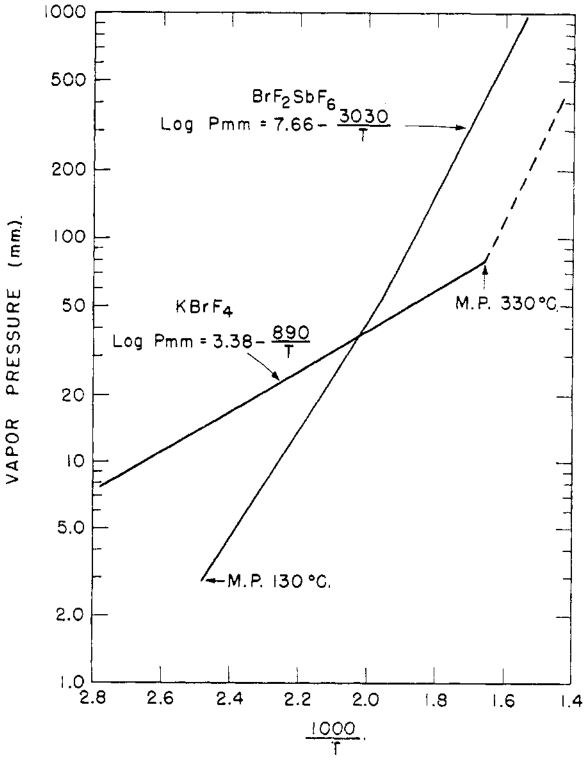

Fig. 1.—Vapor pressure of BrF_2SbF_6 and $KBrF_4$.

Results and Discussion

Dissociation Pressures.—$KBrF_4$ is found to have a vapor pressure of 20 mm. at 158° and 90 mm. at 356°; the dissociation pressure in this temperature range is given by

$$\log p_{\text{mm}} = 3.38 - (890/T)$$

The melting point of the compound is approximately 330° and there are indications that the pressure due to BrF_3 from the thermal decomposition of $KBrF_4$ rises rapidly above this temperature (Fig. 1).

The dissociation pressure of BrF_2SbF_6 is found to be 40 mm. at 225° and 650 mm. at 350° and between these temperatures obeys the equation

$$\log p_{\text{mm}} = 7.66 - (3030/T)$$

The vapor pressure data are shown in Fig. 1. The melting point of BrF_2SbF_6 is observed to be approximately 130°, very considerably lower than that of $KBrF_4$. It is thus possible to achieve a considerable liquid range without producing high pressures in a closed system. As mentioned above, BrF_2SbF_6 will not distil from a heated region to a cold zone if the temperature of the coolest portion of the reaction system is above 130°. This fortunate circumstance coupled with the long liquid range makes BrF_2SbF_6 a particularly convenient reagent for fluorination reactions. $KBrF_4$ (m.p. approximately 330°) is thus most useful at temperatures above 350° where it exists as a liquid.

Fluorination Reactions.—In Table I are listed a number of compounds all of which resist fluorination by BrF_3 itself even under very vigorous experimental conditions.[7] Conditions which lead to complete reaction are given in the table. These are not minimum experimental conditions but rather those which are found to be convenient. All of the oxides (except MgO) listed in the table can be completely fluorinated by either $KBrF_4$ or BrF_2SbF_6. Compounds which can yield gaseous oxide or oxyfluoride intermediate products however may undergo only partial reaction. Thus, sodium carbonate, which forms carbonyl fluoride, and barium sulfate, where sulfuryl fluoride is an intermediate, fail to undergo complete reaction in the sense that their oxygen content ends up completely as molecular oxygen. After a 5-hour heating period at 500° with either BrF_2SbF_6 or $KBrF_4$, barium sulfate yielded only 50% of its oxygen as molecular oxygen. A similar treatment of sodium carbonate with $KBrF_4$ yielded 67% of the oxygen; with BrF_2SbF_6, the yield of oxygen was 70–80%. A 60-hour heating of sodium carbonate gave 74% oxygen with $KBrF_4$ and 100% oxygen with BrF_2SbF_6. This circumstance is very probably the re-

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(7) High temperature fluorination reactions with liquid BrF_3 have been carried out in nickel bomb tubes sealed with a plug, copper gasket and screw cap. The bombs were heated to 315° for as long as 15 hours. Under these conditions a number of compounds which react only incompletely with BrF_3 at its boiling point (127°) are quantitatively converted to the corresponding highest fluoride: BeO, HgO, CeO_2, ZrO_2, MnO_2, Bi_2O_3, Ta_2O_5, Co_2O_3, NiO and PbO. However, Cr_2O_3, Al_2O_3, La_2O_3, MgO, CuO, ZnO, CdO and Fe_2O_3 do not react quantitatively even after prolonged heating at 300°. It is estimated that the pressure developed in these bombs by BrF_3 at 315° is well over 180 atmospheres. These pressures coupled with the high chemical reactivity of the halogen fluoride has made it very difficult to devise equipment in which the gaseous reaction products can be collected.

sult of poor contact of the gaseous intermediate reaction product with the molten fluorinating reagent. This conclusion is rendered plausible by the observation that in the case of sodium carbonate complete fluorination with a quantitative yield of molecular oxygen is achieved by prolonged heating with BrF_2SbF_6.

TABLE I

FLUORINATION REACTIONS WITH $KBrF_4$ AND BrF_2SbF_6

Substance	Time for complete reaction at 500° (hr.) $KBrF_4$	BrF_2SbF_6	Av. fluorination rate $k_{400°}$, hr.$^{-1}$ $KBrF_4$	BrF_2SbF_6
Nd_2O_3	1 (350°)	2 (300°)	30.6[a]	67.2[a]
CeO_2	1 (350°)	1 (350°)	15.3[a]	9.8
ThO_2	2 (400°)	1 (450°)	12.0	11.3
ZrO_2	1 (350°)	5	11.6[a]	0.06
MnO_2	1	1 (450°)	7.6	0.89
Al_2O_3	1 (400°)	5	2.3[a]	0.15
NiO	2	5	0.62	0.05[a]
MgO	20 (550°)(85%)	4	0.38	9.9
Fe_2O_3	5	5	0.06[a]	0.05[a]
CaO	16	2	0.04[a]	11.2
Feldspar	5	4	0.04[a]	0.06[a]

[a] Minimum value.

Fluorination reactions were carried out under conditions where only partial reaction occurred and the rate of the reaction followed by the rate at which oxygen was produced. First-order rate constants were calculated for the reactions in order to provide a semi-quantitative basis for comparing the reactivity of $KBrF_4$ and BrF_2SbF_6. From the observed rate at various temperatures, activation energies could be calculated; these varied from 17 to 23 kcal. with the average about 20 kcal. For comparative purposes, the apparent rate constants were calculated for a single temperature, 400°, and these are shown in Table I. The constants marked with a letter "a" are minimum values, complete reaction having occurred under the imposed reaction conditions. Although no great accuracy can be claimed for the rate constants, the order of reactivities is probably correct if the minimum values are excluded. Obviously, particle size and the previous history of the compound may be expected to have a marked effect in the observed rate of reaction.

The observed reaction behavior of various oxides with $KBrF_4$ and BrF_2SbF_6 can be related quite well with the acid–base properties of these reagents. In BrF_3 solution, KF functions as a base, while SbF_5 shows acid properties

$$2BrF_3 \rightleftarrows BrF_2^+ + BrF_4^-$$

$$KF + BrF_3 \rightleftarrows K^+ + BrF_4^-$$

$$SbF_5 + BrF_3 \rightleftarrows BrF_2^+ + SbF_6^-$$

We can consider molten $KBrF_4$ as a basic flux and BrF_2SbF_6 as an acidic flux in the sense used by Audrieth.[8] The rate of fluorination with these reagents would then depend strongly on the acid–base properties of the reactant. Strongly basic oxides such as CaO and MgO react much more readily with BrF_2SbF_6 than with $KBrF_4$. With amphoteric oxides, those without pronounced acidic or basic properties, both reagents are equally effective as evidenced by the behavior of ThO_2 and Fe_2O_3. Zirconium oxide and aluminum oxide, which form stable anion fluoride complexes, are considerably more reactive with $KBrF_4$. It is interesting to note that feldspar (a complex sodium potassium aluminum silicate) can be completely fluorinated and the oxygen recovered quantitatively as molecular oxygen. This observation is of interest to isotope geologists who are faced with the problem of oxygen recovery from minerals. Preliminary experiments with these fluorinating reagents have also indicated complete argon recovery from feldspars in connection with the A^{40}-K^{40} dating technique.[9]

The results described here indicate that the addition compounds of BrF_3 are particularly useful fluorinating reagents for many inorganic compounds. The apparatus requirements are minimal as compared to that involved in handling pure BrF_3 at elevated temperatures near its critical temperature. The fact that the reactions described here can be made to yield a quantitative recovery of oxygen as molecular oxygen makes it clear that these reactions can be made by further work the basis for analytical procedures for oxygen in a wide variety of inorganic (and probably organic[10]) compounds. We are of the opinion that the physical and chemical properties of $KBrF_4$ and BrF_2SbF_6 are such as to make them particularly useful for laboratory studies and manipulations involving fluorination.

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(8) L. F. Audrieth, "Acids, Bases, and Non-Aqueous Systems," Pennsylvania State College, State College, Pennsylvania, 1949, p. 57.

(9) G. J. Wasserburg and R. J. Hayden, *Geochim. et Cosmochim. Acta*, **7**, 51 (1955).

(10) Preliminary experiments indicate that oxygen can be quantitatively recovered from certain organic oxygen-containing compounds such as pentaerythritol and benzoic acid by high temperature fluorination with BrF_2SbF_6. The applicability of these reagents to other oxygen-containing organic compounds is presently under investigation.