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Reaction between Fluorine and Alkali Metal Halides at Elevated Pressure and Temperature¹

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Reactions between fluorine and the chlorides of the alkali metals were carried out at temperatures up to 300° under pressures up to 4000 kg./sq. cm. The fluorides of lithium and sodium and the tetrafluorochlorate of potassium, is formed under these conditions. Analytical and X-ray data are given to substantiate the formation of the tetrafluorochlorate.

Introduction

The reaction of elementary fluorine with alkali metal chlorides, bromides and iodides to form solids which are powerful fluorinating agents, has been reported by Bode.^{2,3} The reaction products were assigned formulas of the type MF_x, where M is K, Rb or Cs and 1 < x < 3. In a recent communication, Asprey, *et al.*,⁴ disputed Bode's conclusions and reported that the products of the fluorination of alkali chlorides are metal tetrafluorochlorates, rather than polyfluorides.

In the present work we report additional data related to the above, obtained in attempting to prepare alkali metal polyfluorides. A study was made of the reaction between fluorine and alkali metal halides at elevated pressures.

Experimental

Equipment.—Experiments were conducted in a nickel Hoke tube reactor, Fig. 1, equipped with a bottom rupture assembly. The capacity of the reactor was approximately 9 cc. Copper gaskets were used in the rupture assembly with nickel rupture disks rated at 5000 kg./sq. cm. At lower temperatures monel metal was found to perform satisfactorily, but at the higher temperatures and pressures the nickel reactors were found to be more corrosion resistant, and nickel was therefore used for all parts exposed to fluorine at elevated pressures and temperatures. At 4000 kg./sq. cm. pressure and 300°, the nickel reactor suffered only a pink surface discoloration.

Procedure.—A sample, 1 g. to 2 g., of alkali metal chloride, vacuum dried at 120°, was weighed into the dried reactor tube in a drybox. The reactor was closed and connected to the fluorine and vacuum systems. After the reactor had been evacuated to less than 2 mm. pressure, it was reclosed and immersed in liquid N₂. Sufficient F₂ gas, in excess of the amount necessary to form KCIF₄ and to provide the pressure desired, was metered into and condensed in the reactor. The reactor was allowed to warm up to room temperature and was finally heated by means of a furnace to the desired temperature.

After being held at temperature until the pressure remained constant for 1 hour, the reactor was allowed to cool to room temperature. When the reactor reached room temperature, it was evacuated, closed and disassembled for transfer to the drybox. The reactor was opened in the dry-box and the product removed. Any surface discoloration of the product, which was usually fused, was removed by scraping. The cleaned product was ground to a fine powder in an agate mortar and pestle to obtain homogeneity. Portions of the product were then weighed into polyethylene capsules for analysis.

Analysis.—The total chloride and total fluoride were determined on the same sample by fusion with sodium peroxide in a Parr bomb. The alkali metal was determined on a separate sample by hydrolysis in distilled water and precipitation of K, Na, etc. X-Ray diffraction patterns of the powdered samples mounted in Halon plastic plates, were obtained using a Norelco diffractometer in conjunction with filtered CuK radiation. The sample was exposed to a stream of dry nitrogen to prevent hydrolysis during X-ray exposures.

Results

Potassium chloride was the first alkali metal chloride subjected to fluorination. A summary of the results is presented in Table I.

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(2) H. Bode, *Naturwiss.*, **37**, 377 (1950).

(3) H. Bode and E. Klesper, *Z. anorg. Chem.*, **267**, 97 (1951).

(4) L. B. Asprey, *et al.*, *J. Am. Chem. Soc.*, **83**, 2955 (1961).

In run 1, the X-ray pattern showed only KF and KCl. Taken together with the chemical analytical data, this meant that only part of the KCl reacted with the F₂ to form KF at room temperature, even when the pressure was 4000 kg./sq. cm. At 175° (run 2), new lines which could not be assigned to any known compound of K, F and Cl appeared in the pattern. For reasons which are discussed below, these lines were

TABLE I

RESULTS OF THE REACTION BETWEEN F₂ AND KCl UNDER PRESSURE AT ELEVATED TEMPERATURES

Run	Max. press., kg./sq. cm.	Max. temp., °C.	Analyses, %			Calcd. composition, %		
			K	F	Cl	KCl	KF	KCIF ₄
1	4000	25	56.8	9.8	33.4	70.0	30.0	..
2	3600	175	42.9	39.8	17.3	8.7	35.4	55.9
3	2800	300	30.2	47.9	21.9	1.9	9.0	89.1
4	3400	300	28.4	50.3	21.3	..	9.6	90.4

attributed to KCIF₄. X-Ray patterns of the products from runs 3 and 4 showed no KCl; KF was, however, present, plus the new phase which had appeared in run 2. From the analytical data the composition of the product from each run was calculated in terms of KCl, KF and KCIF₄ as

$$\% \text{KF} = \left(\frac{\% \text{K}}{\text{at. wt. K}} - \frac{\% \text{Cl}}{\text{at. wt. Cl}} \right) \text{mol. wt. KF}$$

$$\% \text{KCIF}_4 = \frac{1}{4} \left(\frac{\% \text{F}}{\text{at. wt. F}} - \frac{\% \text{KF}}{\text{mol. wt. KF}} \right) \text{mol. wt. KCIF}_4$$

$$\% \text{KCl} = \left(\frac{\% \text{Cl}}{\text{at. wt. Cl}} - \frac{\% \text{KCIF}_4}{\text{mol. wt. KCl}} \right) \text{mol. wt. KCl}$$

The diffraction lines which could not be attributed to KF were readily indexed on the basis of a tetragonal unit cell with *a* = 6.18 and *c* = 10.94 Å. A survey of the structures of possibly related compounds indicated that the new phase is isostructural with KBrF₄; the latter is also tetragonal, with *a* = 6.162 and *c* = 11.081 Å. Its structure has been determined by Siegel⁵; the space group is D_{4h}¹⁸-I4/m. cm. and there are four

TABLE II

PARTIAL X-RAY POWDER PATTERNS OF KBrF₄ AND NEW COMPOUND

<i>hkl</i>	KBrF ₄		New compound <i>d</i> , Å.
	<i>d</i> , Å.	<i>l/l</i> ₀	
002	5.54	30	5.51
110	4.37	50	4.39
112	3.43	100	3.42
200	3.08	45	3.09
004	2.77	15	..
202 } 211 }	2.67	50	2.70
114	2.35	10	2.31
220	2.18	35	2.17
204	2.07	55	..
222	2.04	17	2.03

(5) S. Siegel, *Acta Cryst.*, **9**, 493 (1956).

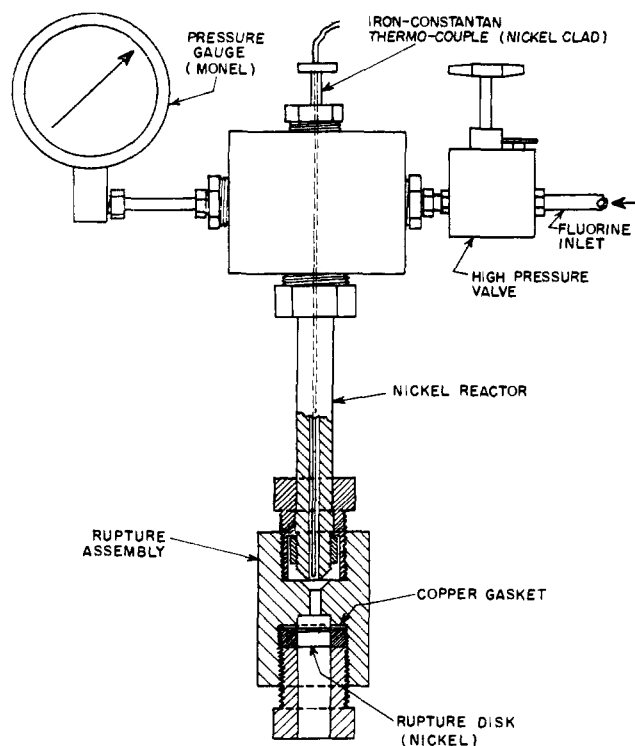


Fig. 1.—Pressure reactor.

molecules per unit cell. The close similarity between the X-ray patterns of the new phase and KBrF_4 (Table II) indicates not only that the composition of the former is KClF_4 but also that the arrangements of atoms must be very similar in both crystals.

It appears likely that this new phase is identical with that mentioned by Asprey, *et al.*⁴ The latter did not interpret their X-ray powder diffraction data, but did mention that it resembled "closely, but not exactly" the pattern of potassium perchlorate. Incidentally, our X-ray pattern of KClF_4 also resembles that of KClO_4 .

Similar fluorination reactions were also carried out with RbCl and CsCl . The product of the RbCl-F_2

reaction, carried out at 300° and at 1500 kg./sq. cm., was a white powder with the chemical composition: Rb, 56.7%; F, 30.9%; Cl, 11.3%.

The X-ray powder diffractometer pattern of this product indicated that it contained RbF plus an additional phase whose lines could be indexed on the basis of a primitive cubic unit cell with $a = 4.36 \text{ \AA}$. It is interesting to note that the high temperature form of RbNO_3 is also cubic, with $a = 4.38 \text{ \AA}$.⁶ The similarity between the two patterns goes beyond a mere similarity in lattice constants. In both cases the (100) reflection is absent, (110) is very strong, and all reflections—up to and including (300)—are observed.

The high temperature form of RbNO_3 is of the CsCl type; the NO_3^- ion is presumably randomly oriented at the center of the cubic unit cell. It appears likely therefore—on the basis of this admittedly sketchy evidence—that the new Rb phase is also of the CsCl type and that, as in RbNO_3 , the absence of the (100) reflection results from the near equivalence of the scattering powers of the Rb^+ ion and the anion at the unit cell center. The composition of the latter is not known but it is worth noting that both the chemical analysis and the limited X-ray data may be "explained" on the basis of a product containing approximately 62.5% RbClF_4 and 36.2% RbF .

The product of the reaction of CsCl and F_2 at 1250 kg./sq. cm. and 300° had the composition: Cs, 61.3%; F, 28.3%; Cl, 10.0%. A diffuse X-ray powder diffraction pattern of this product was obtained, indicating the absence of crystalline phases.

Attempts to form NaClF_4 and LiClF_4 by the interaction of F_2 and the corresponding chloride at elevated pressures and temperatures were unsuccessful. The corresponding fluorides (NaF and LiF) were formed in each instance.

An attempt to form KF_3 (or anything with a fluorine content higher than KF) by the interaction of F_2 and KF at 3000 kg./sq. cm. and 300° was unsuccessful.

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(6) C. Finbak and O. Hassel, *Z. Phys. Chem.*, **35**, 25 (1937).