

nearly white, their O/P ratios are close to that of  $P_2O_5$  (O/P  $\leq 1.5$ ) and they appear to react similarly.<sup>15</sup> When they are deep yellow or orange-yellow, they are quite unreactive at room temperature.

When various finely divided reactive solids were spread across the surface of a small piece of ice cooled on Dry Ice, the solutions obtained by allowing this ice to melt were promptly analyzed by  $P^{31}$  n.m.r. It was found that  $P_4O_6$  gave 100% orthophosphorous acid and "PO<sub>2</sub>" gave approximately 50% orthophosphorous and 50% phosphoric acids, of which about one-third was pyro- with the remainder being ortho-. The solutions resulting from reaction of the white and yellow precipitates all contained about three-quarters of the phosphorus as orthophosphorous acid. The precipitates formed by allowing  $P_4O_6$  to react with  $PCl_3$  or  $P(OCH_3)_3$  showed the remainder of the soluble phosphorus to be orthophosphoric acid, with some (unreacted or precipitated) yellow material insoluble in water. As also found by Hossenlopp and Ebel,<sup>11</sup> the amount of  $H_3PO_4$  found after hydrolysis increased in parallel with the amount of unreactive yellow precipitate and with the yellowish coloration of the material prior to hydrolysis.

As noted above, continued heating of liquid  $P_4O_6$  yields a yellow precipitate, which may be structurally

(15) A similar substance was presumably prepared from  $O_2$  oxidation of P<sub>4</sub> in  $CCl_4$  by B. Blaser, *Ber.*, **64B**, 614 (1931).

similar (but with P-O-P linkages) to amorphous red phosphorus, as envisaged by Pauling and Simonetta.<sup>16</sup> Investigations<sup>17</sup> of amorphous red phosphorus produced by heating white phosphorus in the presence of various catalysts have been interpreted to mean that the catalyst furnishes terminal groups to the network polymer made up of triply-connected phosphorus atoms. It is apparent from the work reported above that there is a continuous range of network polymers extending from nearly pure  $P_2O_5$  to nearly pure phosphorus, with the color increasing from white through yellow, then orange, to red, as the phosphorus content increases. Presumably these polymers have highly complex structures involving P-P and P-O-P linkages as well as having some phosphorus atoms with unshared pairs of electrons and others of the phosphoryl variety. In addition, there are, of course, various structure-terminating groups, depending on the original composition and the thermal history. It is thought that the more reactive materials are those which have a predominance of P-O-P linkages and triply-connected phosphorus; *i.e.*, the precipitates first formed from  $P_4O_6$  exhibit a structure and reactivity most closely related to this starting material.

(16) I. Pauling and M. Simonetta, *J. Chem. Phys.*, **20**, 29 (1952); also see p. 117 of ref. 4.

(17) M. Ya. Kraft and V. P. Parini, *Dokl. Akad. Nauk SSSR*, **77**, 57 (1951); also see p. 114 of ref. 4.

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## Complexes of Xenon Oxide Tetrafluoride<sup>1</sup>

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Xenon oxide tetrafluoride bears a strong resemblance to the halogen fluorides both in physical properties and chemical behavior. A number of physical properties of  $XeOF_4$  have been measured. Xenon oxide tetrafluoride is a clear, colorless liquid freezing at  $-46.2^\circ$ . Its electrical conductivity at  $24^\circ$  is  $1.03 \times 10^{-5}$  ohm<sup>-1</sup> cm.<sup>-1</sup> and its dielectric constant is 24.6 at  $24^\circ$ . It is miscible with anhydrous HF, but its conductivity is not enhanced in such a solution. The addition of CsF or RbF to  $XeOF_4$  increases its conductivity markedly. Xenon oxide tetrafluoride forms a series of addition compounds with the heavier alkali fluorides. The following complexes have been isolated:  $CsF \cdot XeOF_4$ ,  $3RbF \cdot 2XeOF_4$ , and  $3KF \cdot XeOF_4$ . No reaction occurs with NaF. Thermogravimetric studies show that a number of intermediates are formed before final decomposition to the alkali fluorides. Xenon oxide tetrafluoride reacts with  $SbF_5$  to form a complex of composition  $XeOF_4 \cdot 2SbF_5$ . A reaction also occurs with  $AsF_5$  at  $-78^\circ$ , but the complex is unstable at room temperature.

### Introduction

Similarities between xenon fluorides and the halogen fluorides in their chemical bonding have been pointed out on a number of occasions.<sup>2-4</sup> It is to be expected that these analogies should be reflected in the chemical behavior of the xenon fluorides, and this has already

been verified to some extent. It has been shown, for instance, that certain substances form complexes with xenon hexafluoride. Although it has not yet been unequivocally demonstrated, there are indications that these complexes are formed *via* acid-base type reactions and both basic salts<sup>5</sup> and acid salts<sup>6,7</sup> of xenon hexafluoride have been isolated. This similarity in chemi-

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

(2) D. F. Smith, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 295.

(3) R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).

(4) K. S. Pitzer, *Science*, **139**, 414 (1963).

(5) R. D. Peacock, H. Selig, and I. Sheft, *Proc. Chem. Soc.*, 285 (1964).

(6) G. L. Gard and G. H. Cady, *Inorg. Chem.*, **3**, 1745 (1964).

(7) H. Selig, *Science*, **144**, 537 (1964).

cal behavior of xenon hexafluoride to halogen fluorides apparently extends also to xenon oxide tetrafluoride. Indeed, it has been shown recently that bonding in this compound is remarkably similar to that in the series of compounds  $\text{IF}_5$ ,  $\text{BrF}_5$ ,  $\text{ClF}_5$ .<sup>8</sup>

In this paper, these analogies are extended further in an investigation of the chemical reactions of xenon oxide tetrafluoride with alkali fluorides and with antimony pentafluoride. These studies have resulted in the isolation of a series of complexes analogous to those obtained in the  $\text{XeF}_6$  system.

### Experimental Section

**Materials.**—Cesium and rubidium fluorides were prepared by repeated treatment of the hydroxides (obtained from A. D. Mackay, Inc., 99.0% minimum purity) with 48% HF and final dehydration and dehydrofluorination by heating to the melting point. The salts were subjected to chemical and spectrochemical analysis and showed only minor impurities (RbF: 0.2% K, 0.1% Si, 0.05% Cs; CsF: 0.2% K, 0.1% Si, ~1% Rb). Potassium and sodium fluorides were ACS reagent grade materials. The alkali fluorides were additionally pretreated with HF-free fluorine before use.

Antimony pentafluoride was obtained from the Harshaw Chemical Co. and was purified by repeated vacuum sublimations in an all-Kel-F system until it assumed the high viscosity characteristic of pure  $\text{SbF}_5$ . Xenon oxide tetrafluoride was prepared by partial hydrolysis of  $\text{XeF}_6$ .<sup>9</sup> Infrared spectra were obtained to attest to the absence of HF and the characteristic 520  $\text{cm}^{-1}$  band of  $\text{XeF}_6$ .

**Melting Point.**—The melting point of  $\text{XeOF}_4$  was measured by the thermal-arrest method. Three-gram samples were condensed into a welded nickel tube, 1 cm. o.d. A concentric thermocouple well, 2 mm. o.d., extended nearly to the bottom of the tube so that the end of the thermocouple dipped at least 1 cm. into the surrounding compound. Temperatures were measured with a copper-constantan thermocouple which had been calibrated against an NBS platinum resistance thermometer. The sample had a marked tendency to supercool up to about 10° below the freezing point. Melting points of two separately prepared samples agreed within 0.2°.

**Conductivity Measurements.**—Measurements were carried out with a Model 216B Industrial Instruments Co. conductivity bridge. The cell and procedure were identical with ones described previously.<sup>10</sup>

**Dielectric Constant Measurements.**—The dielectric constant of  $\text{XeOF}_4$  was measured by the substitution method at 1 Mc. using a General Radio 716-CS1 Schering bridge, a 1214-M 1-Mc. oscillator, a 722-D Precision condenser, and a Tektronix 513-C oscilloscope as null detector. Interference of extraneous frequencies was minimized by also using the oscillator output as an external sweep. The dielectric constant cell was of all polychlorotrifluoroethylene (Kel-F) construction and the plates consisted of concentric Pt cylinders held rigidly in place with Teflon pins. The plate capacitance was 8.1  $\mu\text{f}$ . The cell was calibrated by measuring its capacitance with purified samples of benzene, chlorobenzene, benzonitrile, and nitrobenzene.

**Procedure.**—Reactions were carried out in Kel-F containers sealed with Kel-F valves. The alkali fluorides were ground in a drybox and transferred to the empty preweighed container. After evacuation and pretreatment with fluorine, the tube was reweighed and the amount of material obtained by difference. A large excess of  $\text{XeOF}_4$  was then distilled onto the salts and the

valve was closed. The mixture was then warmed intermittently to 50° and generally allowed to remain in contact overnight. The volume of solid increased markedly in the case of CsF and RbF and to a lesser extent with KF. The unreacted  $\text{XeOF}_4$  was then distilled off under reduced pressure until constant weight was obtained. The extent of conversion of the alkali fluoride to  $\text{XeOF}_4$  adduct was determined from the increase in weight of the starting material. On occasion, samples of the salt were dissolved in water in a Teflon bottle and aliquots were analyzed for xenon by iodometric titration.

Thermogravimetric analyses of the Cs, Rb, and K salts were run on a thermobalance previously described.<sup>11</sup>

### Results and Discussion

A number of the physical constants of  $\text{XeOF}_4$  which are important in characterizing its solvent properties were measured. These are summarized in Table I.

TABLE I  
PHYSICAL PROPERTIES OF  $\text{XeOF}_4$

Appearance	Clear, colorless liquid
Melting point, °C.	-46.2 to 0.2
Electrical conductivity, ohm <sup>-1</sup> cm. <sup>-1</sup>	$1.03 \times 10^{-3}$ at 24°
Dielectric constant	24.6 at 24° 28.0 at 0°
Density, g. cm. <sup>-3</sup>	$3.11 \pm 0.03$ at 22.5°
Solubility in anhydrous HF	Miscible
Electrical conductivity in HF, ohm <sup>-1</sup> cm. <sup>-1</sup>	$3 \times 10^{-3}$ at 0° for 0.78 M soln.

Two previous determinations of the melting point have been reported: -28°<sup>9</sup> and -41°.<sup>12</sup> These were obtained by visual observations of the melting point in quartz tubes. Xenon oxide tetrafluoride is known to react with quartz<sup>9</sup>; and, although the melting point is relatively low, this could account for discrepancies in previously reported values. The present value of -46.2° lies fairly close to one of these.

The extent of self-ionization in pure liquid  $\text{XeOF}_4$  is indicated by the electrical conductivity given in Table I. The two substances most likely to be present as impurities, HF and  $\text{XeF}_6$ , do not affect this result. The electrical conductivity of  $\text{XeOF}_4$  containing approximately 15%  $\text{XeF}_6$  was essentially the same as that of pure  $\text{XeOF}_4$ . Moreover, the specific conductance of  $\text{XeOF}_4$  is changed only slightly by HF. However, solutions of CsF or RbF in  $\text{XeOF}_4$  increase markedly in conductivity. Cesium fluoride dissolves in  $\text{XeOF}_4$  to give a clear, colorless solution. A 0.29 M solution possessed a specific conductance of  $8.5 \times 10^{-3}$  ohm<sup>-1</sup> cm.<sup>-1</sup> at 24°. Rubidium fluoride is less soluble in  $\text{XeOF}_4$ . Conductivity measurements made on a saturated solution of RbF in  $\text{XeOF}_4$  yielded a specific conductance of  $6.5 \times 10^{-3}$  ohm<sup>-1</sup> cm.<sup>-1</sup> at 24°.

The dielectric constant of  $\text{XeOF}_4$  lies between those of  $\text{IF}_5$  and  $\text{BrF}_5$ .

Other properties of interest with respect to its value as a solvent are the density which is listed in Table I and the viscosity. No quantitative measurements were made of the viscosity, but qualitative observations show

(8) G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

(9) C. L. Chernick, H. H. Claassen, J. G. Malm, and P. L. Plurien, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 106.

(10) H. Selig and J. Shamir, *Inorg. Chem.*, **3**, 294 (1964).

(11) C. E. Johnson and J. Fischer, *J. Phys. Chem.*, **65**, 1849 (1961).

(12) D. F. Smith, *Science*, **140**, 899 (1963).

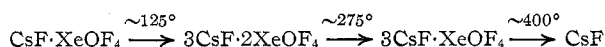
TABLE II  
COMPLEXES OF ALKALI FLUORIDES WITH XeOF<sub>4</sub>

Starting matl.	Initial wt. of MF, g.	Final wt. of XeOF <sub>4</sub> , g.	Mole ratio MF/XeOF <sub>4</sub>	Remarks
CsF	0.0637	0.0890	1.05	Excess XeOF <sub>4</sub> removed at 0°
	0.499	0.753	0.97	
	0.6275	0.9204	1.00	
RbF	0.6177	0.9343	1.41	Excess XeOF <sub>4</sub> removed at room temp. Same results at 0°
	1.0159	1.4824	1.46	
	0.8645	1.1162	1.65	
KF	0.0319	0.0420	2.90	Excess pumped off at room temp.
	0.6031	0.7574	3.06	
	0.6912	0.9030	2.95	
NaF	0.4186	0.0459	50	No reaction. Possible small impurity
	0.5006	0.0186	144	

it to be fairly mobile, although perhaps slightly more viscous than water.

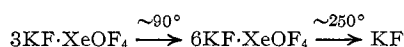
The reactions of alkali fluorides with XeOF<sub>4</sub> are summarized in Table II. Although adducts are easily formed in the case of CsF, RbF, and KF, no NaF adduct was isolated at room temperature. The relative stabilities of the adducts appear to exhibit a trend similar to that observed with the XeF<sub>6</sub> adducts<sup>5</sup> and that of the analogous alkali fluoride complexes of BrF<sub>3</sub> and ClF<sub>3</sub>,<sup>13</sup> namely, CsF > RbF > KF.

Several samples of each adduct were subjected to thermogravimetric analyses, the results of which are shown in Figures 1 and 2. Although CsF·XeOF<sub>4</sub> loses XeOF<sub>4</sub> slowly at room temperature under vacuum, in a nitrogen stream at 1 atm. weight loss begins only at about 60°. The initial weight loss to 100° could be due to desorption of occluded XeOF<sub>4</sub>. Two further inflection points are observed for which the weight loss indicates roughly the intermediate compounds noted in Figure 1. This may be summarized by the equations



It should be emphasized that these decomposition temperatures are strongly dependent on reaction conditions such as atmosphere above the sample and heating rate. The gas evolved in the first step is XeOF<sub>4</sub> as shown by infrared spectra. However, above 300° the evolved gas consists of mostly xenon, fluorine, and oxygen.

Thermogravimetric decomposition of the KF adduct shows that an intermediate is formed corresponding approximately to the stoichiometry 6KF·XeOF<sub>4</sub> (found 23.4% Xe, calculated 23.0% Xe). This may be summarized by the sequence



The final weight loss in all cases is somewhat less than that expected from the amount of starting material. This is due to slight attack on the nickel weighing pan at high temperatures as evidenced by a small

(13) E. D. Whitney, R. O. MacLaren, C. E. Fogle, and T. J. Hurley, *J. Am. Chem. Soc.*, **86**, 2583 (1964).

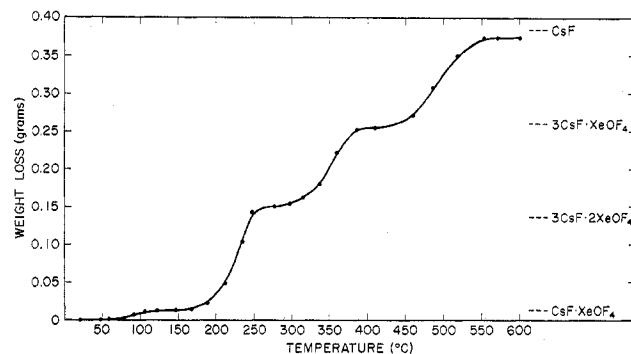


Figure 1.—Thermal decomposition of CsF·XeOF<sub>4</sub> in nitrogen flow of 200 cc./min. at 1 atm.; heating rate ~4°/min.

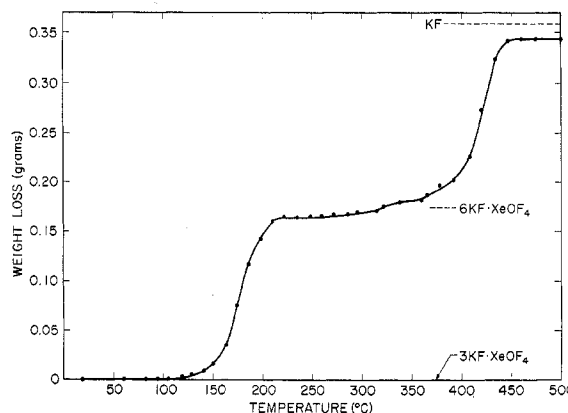


Figure 2.—Thermal decomposition of 3KF·XeOF<sub>4</sub> in nitrogen flow of 200 cc./min. at 1 atm.; heating rate ~2.5°/min.

purple deposit with strong oxidizing power, presumably M<sub>2</sub>NiF<sub>6</sub> (M = Cs, Rb, K).<sup>14</sup>

In the case of the RbF adducts the situation is much less clear-cut. Thus far no consistent results have been obtained, and experiments had to be suspended because of limited access to the thermobalance. Two runs terminated in explosions of the samples. The RbF adduct isolated at room temperature has the approximate composition 3RbF·2XeOF<sub>4</sub>. It begins to lose weight at about 50°, and the final decomposition occurs at about 400°. There is evidence for two intermediate compositions of as yet indeterminate stoichiometry.

A striking analogy thus exists in the stoichiometries of the RbF and KF adducts obtained at room temperature to those observed as intermediates in the decomposition of the CsF adduct. This analogy and the fact that NaF does not appear to form an adduct suggests that the size of the alkali cation plays an important role in the formation of these complexes.

All the alkali fluoride adducts are white solids which are nearly amorphous. It was not possible to obtain good X-ray powder photographs, and no lines due to the starting materials were observed. X-Ray analyses of the final decomposition products of all samples showed them to be alkali fluorides. Tests with KI showed that no oxidizing power was retained in the final product.

The XeOF<sub>4</sub> adducts are chemically very reactive and in bulk tend to react violently with water. No xenon

(14) H. Bode and E. Voss, *Z. anorg. allgem. Chem.*, **286**, 136 (1956).

TABLE III  
 SLOW HYDROLYSIS OF CsF·XeOF<sub>4</sub>

Initial wt. of CsF·XeOF <sub>4</sub> , g.	Final wt., g.	Final mol. wt.
0.1734	0.1526	330.2
0.2928	0.2624	332.8

is evolved in either rapid or slow hydrolyses. When allowed to stand in air, samples of CsF·XeOF<sub>4</sub> slowly evolved HF and eventually came to constant weight. Two such experiments are summarized in Table III. This suggests that the final composition corresponds to CsF·XeO<sub>3</sub> (calculated molecular weight 331.2). X-Ray powder photographs of this material are identical with those obtained from the slow hydrolysis of CsXeF<sub>7</sub>.<sup>15</sup> No lines could be identified with CsF and XeO<sub>3</sub>. A chemical analysis of one of the samples gave the following results: 40.9% Xe, 6.1% Fe, 39.4% Cs (calculated for CsF·XeO<sub>3</sub>: 39.6% Xe, 5.7% F, 40.1% Cs). An infrared spectrum showed absorptions at 750 and 800 cm.<sup>-1</sup>. These may possibly be identified with the  $\nu_1$  and  $\nu_3$  frequencies of XeO<sub>3</sub>.<sup>2</sup> No absorptions were found in the Xe-F bond stretching region. Although both CsF and XeO<sub>3</sub> are very hygroscopic, the CsF·XeO<sub>3</sub> product does not take up water. Moreover, in this case the CsF appears to have lost its normal tendency to absorb HF. These facts suggest that the hydrolysis product is not merely an equimolar mixture of CsF and XeO<sub>3</sub> but may consist of a loosely bound 1:1 molecular addition compound. CsF·XeO<sub>3</sub> decomposes explosively at about 160°.

As in the case of XeF<sub>6</sub>, antimony pentafluoride forms a complex with XeOF<sub>4</sub>. When XeOF<sub>4</sub> is warmed with an excess of SbF<sub>5</sub>, a white precipitate is formed. After pumping off the excess SbF<sub>5</sub> to constant weight, the remaining solid has the composition XeOF<sub>4</sub>·2SbF<sub>5</sub>. Results of two experiments are given in Table IV. Chemical analysis of the second sample gave the following results: 39.0% F, 33.9% Sb (calculated for XeOF<sub>4</sub>·2SbF<sub>5</sub>: 40.5% F, 37.1% Sb). XeOF<sub>4</sub>·2SbF<sub>5</sub> is a nonvolatile white solid melting at approximately 70°. In contact with excess SbF<sub>5</sub> it has a strong tend-

(15) R. D. Peacock, H. Selig, and I. Sheft, to be published.

 TABLE IV  
 REACTION OF XeOF<sub>4</sub> WITH EXCESS SbF<sub>5</sub>

Initial wt. of XeOF <sub>4</sub> , g.	Final wt. of SbF <sub>5</sub> , g.	Mole ratio, SbF <sub>5</sub> /XeOF <sub>4</sub>	Remarks
0.6928	1.3411	2.00	Reaction carried out in Ni vessel
0.6583	1.1506	1.80 (1.97)	Reaction carried out in Kel-F. Small amt. of gas evolution. When corrected for Xe and O <sub>2</sub> SbF <sub>5</sub> /XeOF <sub>4</sub> = 1.97

ency to attack and rupture Kel-F. It reacts violently with water and organic materials.

Experiments with AsF<sub>5</sub> indicate that it forms an addition product with XeOF<sub>4</sub> at -78°. The adduct is unstable at room temperature. No reaction was observed between XeOF<sub>4</sub> and BF<sub>3</sub> up to 200°.

The foregoing results show that the chemistry of XeOF<sub>4</sub> bears a marked similarity to that observed with XeF<sub>6</sub> and the halogen fluorides. A number of halogen fluorides, notably BrF<sub>3</sub> and ClF<sub>3</sub>, have been shown to undergo self-ionization, and the existence of ionic salts of both acidic and basic types has been demonstrated. Analogs of these have been isolated in the XeF<sub>6</sub> and XeOF<sub>4</sub> systems.

Although the enhancement of conductivity of XeOF<sub>4</sub> by CsF and RbF points to a similar mechanism, it is possible that this merely reflects enhanced ionization and mobility of fluoride ion in a solvent of high dielectric constant. Conductometric titration studies would be desirable. These are difficult to carry out on a small scale. Unfortunately, large scale experiments are attended by the possibility of inadvertent leaks and the resulting formation of large amounts of the explosive XeO<sub>3</sub>.

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