Reports

Xenon Tetrafluoride: Reaction with Aqueous Solutions

Abstract. *Xenon tetrafluoride reacts with water to yield xenon, oxygen, hydrofluoric acid, and a very soluble species containing xenon. Evaporation of the solution yields a white, crystalline substance which has been identified as xenon (VI) oxide, XeO_3.*

In the original report on the preparation of XeF_4 (*1*), it was stated that after the initial hydrolysis of XeF_4 was complete, a compound with oxidizing properties remained in solution. We have observed that XeF_4 oxidizes water directly to O_2 with Xe and HF as byproducts and that it also reacts to give Xe and a xenon (VI) species by a mechanism not yet understood. Evaporation of the solution which contains the xenon (VI) species yields the white crystalline xenon (VI) oxide. The molecular and crystal structure of this compound have been reported elsewhere (*2*).

For the hydrolysis experiments, 3 to 20 mg samples of XeF_4 were sublimed into weighed, thin-walled Pyrex glass bulbs which had a typical volume of 0.07 ml. The XeF_4 was prepared by the method described by Templeton, Zalkin, Forrester, and Williamson (*3*). The thin-walled bulbs could easily be broken in the reaction vessel which contained the degassed reaction medium. A Toepler pumping system was used to measure directly the amounts of xenon and oxygen. For the accuracy required in these experiments it was necessary to use a trap at −210°C to collect the xenon quantitatively while the oxygen was being pumped into the measuring buret. By pumping on the liquid-N_2 trap, this lower temperature was attained. Another trap at −95°C held back any water.

Since the reaction of XeF_4 with an aqueous solution is heterogeneous, reproducible results were not obtained from identical samples. Hydrolysis in $6M$ NaOH gave nearly quantitative liberation of O_2 and Xe if the sample was assumed to be pure XeF_4. In $3M$ H_2SO_4 52 percent O_2 and 72 percent Xe (by moles) were liberated. The remaining Xe, but no additional oxygen, was liberated when solid KI was added to the acidic solution. When XeF_4 was added to distilled water, the O_2 recovered ranged from 40 to 50 percent; the remainder of the oxidizing power was recovered later as I_2. All hydrolyses tended to give a total recovery of Xe a few percent greater than 100 and of O_2 a few percent below 100. This observation suggests a small amount of contamination by XeF_2. The fact that the best yields of the aqueous xenon (VI) species were obtained in neutral or acidic solution or both, is contradictory to earlier observations (*1*). During hydrolysis at 0°C or lower the white XeF_4 turns yellow on the surface. On no occasion did the solution in contact with the yellow solid appear colored. At a few degrees below zero the yellow solid in $3M$ H_2SO_4 had a life time of the order of 20 minutes, whereas the life time of the yellow solid in $6M$ NaOH at a comparable temperature was approximately 10 seconds. A sample of the yellow solid, the composition of which is unknown to us, did not show an electron-spin resonance spectrum.

The solution which must result from the disproportionation of XeF_4 and which contains the new xenon species appears to be the most interesting part of the study. The aqueous species seems without doubt to be the same one that Dudley, Gard, and Cady (*4*) have described from the hydrolysis of XeF_6. We can add several observations to the description of its chemistry.

Table 1. Results of the determination of the ratio of oxygen to xenon.

Quantity (μmole)			O/Xe	H_2O/Xe
O_2	Xe	H_2*		
		Sample 1		
11.500	7.692	1.243	2.990	0.16
		Sample 2		
11.228	7.493	0.544	2.997	0.07

* The water was measured as H_2 gas after it had been passed over uranium turnings at 750°C.

The aqueous xenon (VI) species is very stable in acidic solution. The concentration of a solution that is $3.85 \times 10^{-3}M$ in xenon (VI) compound in $3M$ H_2SO_4 has not changed over a period of 40 days. The concentration of a sample was not affected by boiling for 5 minutes. The same solution, when made basic with NaOH, loses from 33 to 50 percent of its oxidizing power overnight. The hydrofluoric acid can be removed by passing the solution through a MgO column. A solution treated in this manner has given an I/Xe ratio for its oxidation number of 6.06 compared with the theoretical value of 6.00.

The degree of hydration in solution is not known, but hydrolysis of the XeF_4 in Teflon vessels open to the air has yielded the anhydrous xenon (VI) oxide after evaporation at room temperature in a desiccator over Drierite or barium oxide. *This anhydrous material has exploded violently on several occasions in our laboratory* (*5*). Several hundred milligrams is more than sufficient to blow a hole through Teflon 3/4-inch thick. It seems to us that the explosive material reported by Bartlett and Rao (*6*) could have been the xenon (VI) oxide. This tendency to detonate violently made direct determination of the ratio of xenon to oxygen difficult. A sample as small as 0.7 mg ruptured the quartz tubing used as the decomposition vessel.

Because of the extreme hygroscopic nature of the oxide, the sample weights were not useful for obtaining data on percentage composition. Our Toepler pumping system made it possible to measure the oxygen to xenon ratio on a sample of arbitrary weight, if the evacuated quartz tube could withstand the shock of the thermal decomposition. Before the sample was added the quartz tube and quartz wool were heated to 950°C in an O_2 stream to insure removal of any organic material. The sample was then placed directly in the 10-mm quartz tube on quartz wool and covered with additional quartz wool in order to absorb the shock when the sample detonated. The tube was constricted, evacuated under high-vacuum conditions for 45 minutes, sealed, and heated in an iron container at 500°C for 15 minutes. Sample tubes heated at a lower temperature had no greater chance of surviving the detonation.

Many tubes were broken by the shock of decomposition but from two that remained intact the data in Table 1 were obtained. It can be seen that not all the water was removed even with extensive pumping.

To confirm the quantitative recovery of O_2 from the Toepler pumping system, $KClO_3$ was used as a standard. It gave 2.994 oxygen atoms per mole of $KClO_3$.

The stability of the xenon (VI) oxide seems to be greatly increased with respect to detonation if the oxide is originally prepared from distilled water with a trace of added sulfuric acid, for example, 10 ml of $H_2O + 4\mu l$ of 1*M* H_2SO_4 (*7*).

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References and Notes

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7. We thank Professors R. E. Connick and D. H. Templeton for interest and encouragement.

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Krypton Tetrafluoride: Preparation and Some Properties

After the discovery of xenon and radon fluorides at Argonne National Laboratory (*1, 2*), the obvious question was: Does krypton, the lower analog of these two inert gases, form similar compounds? The answer is yes.

It was first found that gaseous krypton (Kr) and fluorine (F_2) do not form noticeable amounts of krypton fluorides when they are heated at 400° to 500°C in a nickel vessel. A mixture of Kr (1 part) and F_2 (5 parts) was heated for 1 hour, with negative results. Under the same conditions xenon tetrafluoride is formed from xenon and fluorine, practically quantitatively (*1*). Similarly negative results were obtained (*3*) when a mixture of Kr and F_2 was irradiated with ultraviolet light at −60°C. Furthermore, when Bartlett (*4*) who initiated the recent work on noble-gas compounds by his discovery of $XePtF_6$, tried the same experiment with Kr and PtF_6 or RhF_6, no oxidation took place at temperatures up to 50°C.

However, by taking advantage of the experience of workers at the Research Institute of Temple University in the preparation of the thermally very unstable O_3F_2 (*5*) and O_4F_2 (*6*), we were able to produce krypton fluoride. Recently, we showed that xenon tetrafluoride can be produced quantitatively by electric discharge (see *7*). By using the same method, we have now been successful in producing krypton tetrafluoride (*8*).

The experimental setup (a reaction vessel of volume approximately 650 cm^3, with copper electrodes 2.0 cm in diameter and 7 cm apart) and the experimental conditions (current of 24 to 37 ma, 700 to 2200 volts) were the same as in the earlier investigations (*5*). The mixture of Kr and F_2 (1 and 2 volumes, respectively, to within ±0.1 percent) was admitted, at a pressure of 7 to 12 mm-Hg, into the discharge vessel, which had been cooled to 84° to 86°K by mixtures of liquid O_2 and N_2. In a successful experiment 500 cm^3 of the mixture of Kr and F_2 (at normal temperature and pressure) was *completely* converted to 1.15 g of KrF_4 in 4.0 hours. The rate of conversion depends on the surface condition of the copper-electrodes; in the course of time the electrodes become covered with a white layer of typical CuF_2. With less efficient electrodes the production rate may go down to a tenth of the rate just indicated.

The KrF_4 is deposited on the glass walls of the discharge vessel, primarily in the region between the electrodes, in the form of a white solid. Any unreacted Kr and F_2, as well as SiF_4 or O_2 are pumped, off, as impurities, at a temperature of −78°C. Then the KrF_4 can be sublimed, at −30° to −40° or even 0°C, into a glass storage vessel containing some dry potassium fluoride powder (as a getter for hydrogen fluoride). The composition of the deposit is known from its synthesis and also from analysis on heating (as mentioned below). Like XeF_4, KrF_4 forms beautiful, transparent, colorless crystals, as shown in Fig. 1.

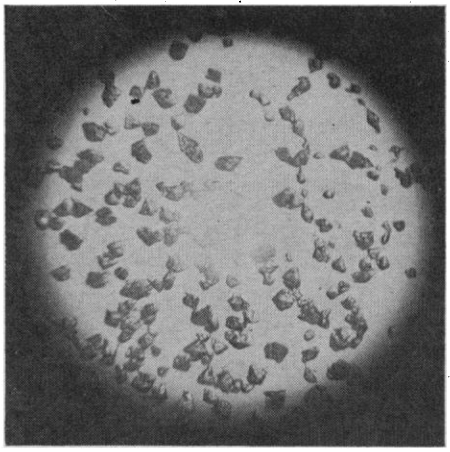

Fig. 1. Crystals of krypton tetrafluoride. [About × 31]

Krypton tetrafluoride is thermally much less stable than XeF_4. However, at −78°C it can be stored for weeks without decomposing. In a polychlorotrifluoroethylene (Kel-F) tube with copper valves, at about 20°C, about one-tenth of the amount present decomposes per hour (*9*). At 60°C the decomposition is rapid; KrF_4 decomposes into its elements—that is

$$KrF_4 \longrightarrow Kr + 2F_2$$

—as determined by analysis (the F_2 is determined by mercury burette; afterwards the krypton gas is determined by volumetric analysis). This rapid decomposition at higher temperatures explains why previous attempts to prepare krypton tetrafluoride had been unsuccessful.

The vapor pressure of the solid KrF_4 was determined (see Fig. 2) by determining and subtracting from the total pressure the amounts attributable to decomposition. For comparison, the

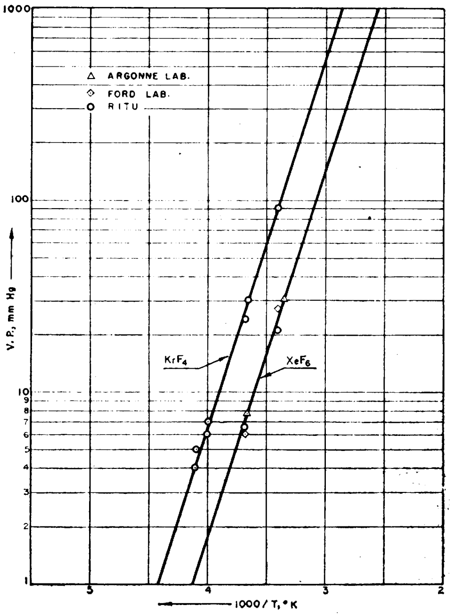

Fig. 2. Vapor pressure of KrF_4 and XeF_6.