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RADIATION SYNTHESIS OF XENON FLUORIDES

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Recently, chemical compounds of the noble gases—xenon and radon—with fluorine have become known ([1]). The first synthesis of xenon tetrafluoride was carried out by Claassen, Selig, and Malm ([2]), who obtained XeF_4 by heating a mixture of gaseous xenon and fluorine at 400° in a nickel vessel under pressure. In this process xenon difluoride is also formed ([3]). When xenon was heated under pressure with a large excess of fluorine to 300-400°, xenon hexafluoride was obtained (see review ([1])). In a number of studies xenon fluorides were obtained by the thermal method ([1, 3, 4]), and their physical and chemical properties were investigated ([1, 5-9]). In ([10-12]) a theoretical consideration was made of the possibility of formation of fluorides of inert gases, and their heats of formation were estimated ([12]). The reaction of xenon with fluorine was also achieved photochemically ([13]). It was shown that, upon irradiation of a mixture of fluorine with xenon by the light of a high-pressure mercury-quartz lamp ($\lambda = 2500$-3500 Å), xenon difluoride is formed. Since in this wavelength region there is continuous absorption by molecular fluorine, i.e., dissociation occurs, these data indicate that the xenon fluorination reaction is possibly caused by fluorine atoms. XeF_2 and XeF_4 were also obtained in a discharge in mixtures of fluorine with xenon ([14, 15]) and CF_4 with xenon ([16]). A conference held in the USA at Argonne National Laboratory in April 1963 was devoted to compounds of noble gases with fluorine ([17]).

The carrying out of the xenon fluorination reaction by the photochemical method, along with the thermal method, under conditions where fluorine dissociation already becomes appreciable, indicates that this reaction proceeds with participation of the fluorine atom. In light of these data, it was of interest to carry out the reaction of fluorine with xenon under the action of ionizing radiation. During radiolysis, fluorine atoms can be formed by direct dissociation. At the same time, the reaction may probably also be caused by metastably excited xenon atoms or ions that are formed.

The synthesis of xenon fluorides was carried out under the action of a beam of electrons with an energy of 1.6 MeV on a mixture of fluorine with xenon. The reactor was made of stainless steel and was a cylinder with a volume of 260 cm^3, closed by a lid on an annular Teflon seal. The lid was attached directly

to the flange of the electron accelerator and was electrically insulated from the reactor. The electron current to the reactor was 30-40 μA. The electron beam was introduced into the reactor through copper foil 0.2 mm thick and 2 cm in diameter, soldered into the center of the lid, the inner surface of which was coated with nickel. Gas was introduced into the reactor through a Kovar tube to which a glass tube with a vacuum stopcock and a standard ground joint was soldered. (The soldering of the metallic parts of the reactor was carried out with silver.)

Preparation of the gas mixture and measurement of the quantities of unreacted gases were carried out in a glass vacuum apparatus. Before experiments, the reactor was evacuated to a pressure below 10^{-3} mm Hg by a fore-vacuum pump through a trap with activated charcoal cooled by liquid nitrogen. The pressure was measured by thermocouple and glass membrane manometers. (The accuracy of measurements with the latter was 0.1 mm Hg.)

In the experiments, fluorine of 99.6% purity and spectroscopically pure xenon were used. To purify the fluorine from the impurity SiF_4, which forms during storage of fluorine in a glass cylinder, the fluorine was admitted into the reactor through a U-shaped trap cooled with liquid air. After xenon had been introduced into the reactor at a known pressure, the reactor was cooled with liquid air and fluorine was admitted to a specified pressure. The reactor was then connected to the flange of an electron accelerator (energy 1.6 MeV). During irradiation the reactor was blown with a stream of air to prevent heating. After irradiation the reactor was cooled with liquid nitrogen and the amount of unreacted fluorine was measured in a known volume. The fluorine was then slowly pumped off through a trap cooled with liquid nitrogen in order to capture xenon. After removal of the fluorine, the reactor was immersed in a Dewar vessel with a cooling mixture (acetone + solid CO_2) at a temperature of -78°C, and all the xenon was frozen into a U-shaped trap cooled with liquid nitrogen. The pressure of the remaining xenon was then measured, after which the xenon was pumped off. (In some experiments, the xenon remaining after the reaction was analyzed on a mass spectrometer. It was found to contain a small impurity of SiF_4.) After thorough evacuation of the apparatus, the pressure in the reactor was measured at room temperature. This pressure was approximately 3 mm Hg, which corresponds to the vapor pressure of xenon fluorides, XeF_4 and XeF_2 (1). However, if the reaction products were left in the reactor, then the next day a gas consisting of fluorine and xenon was found in it. The presence of xenon was demonstrated by mass-spectrometric analysis. In this case the amount of xenon was approximately equal to that consumed in the reaction.

Table 1

Experiment No.	Initial pressure, mm Hg	Initial pressure, mm Hg	Initial pressure, mm Hg	Q^*, $\mu A \cdot min$	Unreacted Xe	Unreacted Xe	Unreacted F_2	Unreacted F_2	Consumed, mm Hg	Consumed, mm Hg
	Xe	F_2	F/Xe		mm Hg	%	mm Hg	%	Xe	F_2
2	65	345	10.6	3953	39	59	274	82	26	74
3	67	252	7.6	2385	36	55	155	62	31	97
4	70	208	6	2835	46	66	150	72	24	58
6	71	218	6.1	3832	41	59	141	64	30	77
7	70	202	6	3246	41	50	142	70	29	60

* On average, for mixtures of this composition, 1 $\mu A \cdot min$ corresponds to an absorbed dose of ~0.73 Mrad.

The results of the experiments are presented in Table 1. It gives the initial amounts of fluorine and xenon in the reactor, the amounts remaining after the reaction, and the calculated amounts of fluorine and xenon that had reacted. Also given is the amount of fast electrons Q ($\mu A \cdot min$) that passed through the mixture.

On the basis of the data presented, it may be concluded that xenon does indeed enter into reaction with fluorine and is consumed by 30–50%. The ratio of consumed fluorine to xenon in these experiments was from 4 to 6. However, on this basis it is impossible to conclude which xenon fluorides are formed, since the fluorine could also have reacted partly with the reactor material. For example, it is possible that reaction with chromium, which is a component of stainless steel, produces volatile chromium fluorides.

Identification of the xenon fluorides was carried out from the infrared spectra. The spectrum of xenon fluoride vapors was recorded on an IKS-14 infrared spectrophotometer in a standard cell with potassium bromide windows (the windows were mounted on annular rubber gaskets). Measurements were made at wavelengths of 565 and 550 cm^{-1}, which correspo-

give an absorption maximum of the R and Q branches of XeF_2, and at a wavelength of 584 cm^{-1}, which corresponds to the maximum absorption of XeF_4 ([1]). When the vapors under study were admitted from the reactor into the cuvette, significant absorption was observed at wavelengths of 565 and 550 cm^{-1}, and to a lesser extent at a wavelength of 584 cm^{-1}. It should be noted that the absorption could be observed only at the first moment after the vapors were admitted into the cuvette; it then rapidly disappeared. This phenomenon may be associated with the decomposition of xenon fluorides as a result of their reaction with the rubber, leading to the formation of gaseous products that hinder the flow of the vapors under study from the reactor into the cuvette. However, ab-

sorption in this region of wavelengths could to some extent have been associated with the presence of volatile metal fluorides (for example, higher chromium fluorides, as noted above). To check this, control experiments were carried out in which fluorine without xenon was irradiated under the same conditions. When the infrared spectra of the vapors remaining in the reactor after removal of the fluorine were recorded, no absorption was observed at wavelengths of 565, 550, or 584 cm^{-1}. Consequently, the absorption at these wavelengths in the experiments with xenon was due to XeF_2 and XeF_4.

Thus, the results of the experiments show that xenon fluorides (XeF_2 and XeF_4) have been obtained by a radiation-chemical method.

In order to estimate the radiation yield of xenon fluorides, measurements were made of the radiation dose absorbed by the mixture. For this purpose methane was irradiated in the same reactor at a pressure of 160 mm Hg with a current of 30 μA for 14 minutes. Mass-spectrometric analysis of the radiolyzed methane showed that it contained 4.4% hydrogen. If it is assumed that the radiation yield of hydrogen is $C(H_2) = 5.6$ molecules/100 eV of absorbed energy ([18]), then calculation shows that in the experiments with the Xe and F_2 mixture the absorbed dose was approximately 3000 Mrad. An estimate of the radiation yield of xenon consumption $C(-Xe)$, calculated for the dose absorbed by both components of the mixture (Xe and F_2), gives $C(-Xe) = 0.4$-0.7. This value refers to large doses. The initial radiation yield may be greater. To determine the initial yield $C(-Xe)$, it is necessary to know the kinetics of xenon consumption during the radiolysis of a mixture of fluorine with xenon. The yield of products in this process is evidently also determined by the stability of xenon fluorides to the action of radiation.

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Note: Figure translations are in progress. See original paper for figures.