SYNTHESIS OF XENON DIFLUORIDE IN A GLOW DISCHARGE

S. M. Sinel'nikov, I. V. Nikitin, and V. Ya. Rosolovskii

UDC 542.944+546.16+546.295

Xenon difluoride can be obtained from mixtures of fluorine and zenon in a discharge maintained with a spark inductor [1, 2]. The reaction of fluorine with zenon in a glow discharge at low pressures was studied in this work.

EXPERIMENTAL

A mixture of equal volumes of fluorine and xenon was passed through a quartz discharge tube having an internal diameter of 15 mm. The source of high voltage was a NOM-10 transformer. Copper electrodes were cooled with running water; the distance between the electrodes was 7 cm. The reaction product settled on the walls of the discharge tube cooled to a temperature of 195°K. The unreacted xenon coming out of the tube was condensed in a trap at a temperature of 77°K, and the unreacted fluorine was absorbed in a column of lime absorbent. At the end of the reaction the amount of unreacted xenon was determined and the reaction product was recovered and weighed. In each experiment, the product was analyzed for fluorine content by the reaction of a weighed sample with an acidified solution of potassium iodide. In isolated cases, the sample was subjected to hydrolysis and the fluorine ion content in the obtained solution was determined by titration with thorium nitrate. The results of the analyses did not change noticeably from experiment to experiment. Analytical results are given for one of the experiments. Found F, 22.3% (iodometrically); 22.7% (thorimetrically). XeF_2. Calculated F, 22.45%.

The degree of transformation of xenon called α was expressed as a percent of the ratio of the amount of xenon reacted in forming the difluoride to the xenon contained in the gas mixture passed through the discharge. The accuracy in the determination of the values of the degree of transformation in our experiments amounted to 4%. Gas volumes were recalculated to normal conditions in the calculations.

Results of experiments having different pressures in the discharge apparatus at a constant current intensity (60 mA) and a rate of introduction of the gas mixture into the discharge of 1.50 liters/h are given in Table 1. In the investigated interval of pressure, the degree of transformation does not depend on pressure.

The degree of transformation in a dependence on the rate of introduction of the mixture into the discharge ν at a pressure of 10 mm Hg in the apparatus was found in three series of experiments. The current intensity i in each series of experiments was held constant. The calculated values of the specific energy U/ν [3] are presented below. The degree of transformation exceeded 90% in all experiments. In the apparatus used at a gas introduction rate of 1 liter/h, after 1 h of glowing of the discharge 3.4-3.7 g of xenon difluoride was obtained.

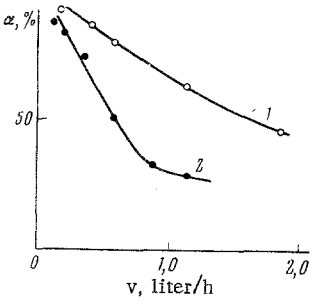

Fig. 1. Dependence of the degree of transformation on the rate of introduction of the gas mixture: 1) 10 mA; 2) 5 mA.

$i = 90$ mA

v, liter/h	0.19	0.31	0.50	0.52	0.77	1.08	1.27
U/v, w·h/liter	790	500	298	273	204	146	124
α, %	96	94	92	93	95	94	93

$i = 60$ mA

v, liter/h	0.13	0.26	0.36	0.45	0.55	0.90
U/v, w·h/liter	740	370	268	210	173	105
α, %	94	92	92	93	93	93

$i = 30$ mA

v, liter/h	0.15	0.59	0.99	1.01	1.08
U/v, w·h/liter	312	77	45	44	41
α, %	93	94	93	94	93

Institute of New Chemical Problems, Academy of sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2806-2807, December, 1968. Original article submitted June 4, 1968.

TABLE 1. Dependence of the Degree of Transformation on Pressure

Pressure, mm Hg	10	20	30	50
α, %	93	96	95	94

Several experiments were carred out under mild conditions at a pressure of about 1 mm of Hg in the apparatus and a current intensity of 5 and 10 mA (Fig. 1). A noticeable decrease of α with increasing rate ν, in particular, at a discharge current intensity of 5 mA, was observed in these experiments. This is evidently a result of a decrease of the power input into the discharge in comparison with the input in experiments at current intensities of 30, 60, or 90 mA. However, in experiments with a current intensity of 5 or 10 mA, the degree of transformation is also close to 90% at a rate of introduction of the mixture of 0.1-0.2 liter/h (see Fig. 1).

Since the degree of transformation of xenon exceeded 90% with relatively low energetic losses, it could be proposed that the main process requiring activation in the discharge was dissociation of fluorine. Participation of xenon in the reaction is evidently not associated with significant consumption of energy for its activation. In this case, the reaction of fluorine activated in the discharge with nonactivated zenon seemed possible. To confirm this hypothesis, syntheses were carried out with cooling of the discharge tube to 77°K with liquid nitrogen. A known amount of xenon was condensed in the tube before an experiment, and then the discharge was connected and fluorine was introduced. In one of these experiments, after 75 min of glowing of the discharge at a fluorine flow rate of 0.50 liter/h, 45% of the xenon condensed in the discharge tube had reacted and 0.46 g of xenon difluoride was obtained. It was also shown that the fluorine leaving the discharge reacts with xenon frozen at 77°K on the walls of a trap located 15 cm from the discharge zone.

CONCLUSIONS

1. Synthesis of xenon difluoride in a glow discharge from a mixture of equal volumes of fluorine and xenon was investigated. Upon changing the pressure in the apparatus from 10 to 50 mm Hg, the current intensity from 30 to 90 mA, and the rate of introduction of the mixture into the discharge from 0.13 to 1.27 liters/h, the degree of transformation of xenon exceeds 90%.

2. Fluorine passed through the discharge reacts with xenon cooled to 77°K.

LITERATURE CITED

1. R. Hoppe, W. Dähne, H. Mattauch, and K. M. Rödder, Angew. Chem., 74, 903 (1962).
2. R. Hoppe, H. Mattauch, K. M. Rödder, and W. Dähne, Z. Anorg. Allg. Chem., 324, 214 (1963).
3. S. S. Vasil'ev, N. I. Kobozev, and E. N. Eremin, Zh. Fiz. Khim., 7, 619 (1936).