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Abstract

Full Text

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Reactivity of Noble Gases. A New Method for Obtaining XeF₂

(Presented by Academician I. L. Knunyants, XII 2, 1963)

The publication of the first works ^(1,2) devoted to the preparation of compounds of the "inert" gases aroused great interest. Under rather severe conditions, a whole series of xenon fluorides has been synthesized. Thus, xenon octafluoride was obtained by heating a mixture Xe : F₂ = 1 : 10 under a pressure of 81 atm to a temperature of 620° ⁽³⁾. To obtain the hexafluoride, it is likewise necessary to heat xenon with a large excess of fluorine under pressure to temperatures not below 300° ⁽⁴⁻⁷⁾. The tetrafluoride is obtained by heating a mixture of fluorine with xenon in the ratio Xe : F₂ = 1 : 5 under pressure at 400° ⁽²⁾. The difluoride was obtained by ultraviolet irradiation of a mixture of xenon with fluorine circulating through a vessel with a synthetic-sapphire window ⁽⁸⁾. The synthesis of XeF₂ can also be carried out by the action of an electric discharge on a mixture of the starting elements ⁽⁹⁾; by circulating this mixture through a zone heated to 400° with removal of the products from the reaction sphere ⁽¹⁰⁾; and by irradiating a mixture of xenon with CF₄ or SiF₄ with vacuum ultraviolet light, or by passing high-voltage electrical or powerful microwave pulses through this mixture ⁽¹¹⁾.

All these methods for obtaining xenon fluorides are associated with great experimental difficulties. We believed that the use of such severe conditions is not necessary. Confirmation of this is provided by the formation of XePtF₆ at ordinary temperature by direct combination of xenon with platinum hexafluoride ⁽¹⁾. A recently published work ⁽¹²⁾ reports a significantly lower ionization potential of xenon (~ 8 eV instead of 12.1) and krypton (~ 10 eV instead of 14) than had previously been accepted.

Indeed, in the present work it is shown that XeF₂ is formed from the elements at ordinary temperature and under pressure, with evolution of heat (approximately 40-60 kcal/mole), and sometimes with explosion. The highest reaction rate was observed at a volume ratio of the elements close to 1 : 1. By using an excess of one of the components (not more than 1.5-fold), an almost quantitative yield with respect to the other component can be achieved. This method for obtaining xenon difluoride is extremely simple and does not require the use of special apparatus. At the same time, such high reactivity of xenon makes it possible to hope for success in attempts to synthesize XeCl₂, XeO, KrF₂, etc., under conditions considerably milder than those used up to now, since under severe conditions these substances might prove to be unstable.

Experimental Part

The experiments were carried out in vessels made of nickel, stainless steel, or Monel metal. The manometers were brass.

Fluorine was introduced into an 80-ml vessel to a pressure of 18 atm (2.17 g), and then the pressure was brought to 35 atm (6.81 g) with xenon. At the indicated pressure and vessel volume an instantaneous increase in pressure occurred; then it spontaneously fell to 8 atm. After removal of the unreacted gases, 6.79 g of solid substance remained.

In vessels of 30 ml volume, at the same pressures, the reaction proceeds gradually. During the first day the pressure decreases by approximately a factor of two. At a pressure of 8–12 atm the reaction rate becomes negligible.

A weighed sample of the substance was hydrolyzed with an excess amount of 0.1 *N* alkali solution and titrated.

Found, %: F 22.5; 21.15; calculated, %: F 22.4.

On treating the weighed sample with a 1% potassium iodide solution, iodine was liberated quantitatively.

Found, %: F 22.0, 21.75; calculated, %: F 22.4.

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