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SHORT COMMUNICATION

A New Method for the Preparation of Krypton Difluoride

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In spite of the rather early discovery of krypton difluoride in 1963 [1], the research of its chemistry was significantly hindered in the past since KrF_2 is rather difficult to prepare. The commonly used method for the preparation of krypton difluoride described so far is the electric discharge in gaseous mixture of krypton and fluorine at low temperatures and pressures [2]. The method is claimed to yield about 250 mg KrF_2 per hour. The experimental conditions of this method were studied into great detail in order to optimize the yields [3]. High frequency discharge in the mixture of krypton and CF_2Cl_2 is a patented method for the preparation of KrF_2 [4]. Other methods known are either expensive (e.g. irradiation of fluorine-krypton mixture with 1.5 MeV electrons [5] or with 10 MeV protons [6]) or less efficient (e.g. exposure of gaseous mixture of fluorine and krypton to sunlight [7]).

The method for preparation of krypton difluoride we have developed is based on the irradiation of a liquefied mixture of fluorine and krypton with the near UV light at -196°C. The reaction is carried out in a 100 ml photochemical reactor made of pyrex glass (patent pending). As a light source a 400 W medium pressure mercury lamp (Applied Photophysics Ltd., 400 LQ) radiating predominantly 365-366 nm light is used. The lamp is positioned in the middle of the reactor. The pressure is controlled by a Helicoid gauge (type 460 R, range O-1500 mm Hg absolute) attached to the reactor.

In a typical experiment 2 moles of fluorine (99,5%, produced in our laboratory [8]) and 1 mole of krypton (99,95%, L´Air Liquide, Paris) were condensed into the reactor and irradiated in liquid phase for 48 hours. The reactor was then warmed up to liquid oxygen temperature and unreacted gases were condensed into a 800 ml nickel container cooled by liquid nitrogen. This container is used as a storage vessel for the mixture of the reactants. The reactor was subsequently warmed up to the dry ice-acetone slush temperature and the remaining krypton was condensed into the nickel container. The reaction product was then thoroughly pumped on at -78°C. After that the reactor was connected to a KelF apparatus and slowly warmed up to room temperature. The reaction product was collected in dynamic vacuum in a KelF U-tube at -78°C and finally sublimed into a 3/4 in. KelF container fitted with a KelF valve. The purity of the reaction product which forms colourless crystals was checked by IR spectrum. The yield of the reaction was 4.7 g KrF_2.

As compared with the electric discharge method, the method described above is much simpler - the only control needed is a maintenance of the level of liquid nitrogen in which the reactor is immersed during the reaction. The relatively large quantities of the reactants used allove the preparation of gram-quantities of KrF_2 in a single run. The unreacted fluorine-krypton mixture can be used for further preparations of KrF_2.

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