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SHORT COMMUNICATION

Photosynthesis of xenon tetrafluoride

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Xenon tetrafluoride is usually prepared by heating gaseous mixture of xenon and fluorine either under moderate pressure [1,2] or in flow [3]. It has been demonstrated also that the thermal methods in principle cannot yield pure xenon tetrafluoride [4,5]. Pure xenon tetrafluoride can be best prepared by subsequent chemical purification of the crude product with arsenic pentafluoride [6] or by thermal dissociation of xenon hexafluoride [7]. Some other methods for the preparation of xenon tetrafluoride are described as well, e.g. the electric discharge method [8] and irradiation of xenon-fluorine mixtures with Co γ-rays or with 1,5 MeV electrons [9].

In contrast to the above mentioned methods, the photochemical reaction between xenon and fluorine is known so far to give only xenon difluoride as the reaction product and is used as a convenient method for the preparation of this compound [10,11,12]. We have, however, found that the photochemical reaction between xenon and excessive fluorine (mole ratio $Xe/F_2 = 1:6-4$) at room temperature takes course in two steps:

$$Xe + F_2 = XeF_2 \tag{1}$$

$$XeF_2 + F_2 = XeF_4 \tag{2}$$

The second reaction is about 20 times slower than the first one.

The reaction is carried in a 1,5 l Pyrex glass photochemical reactor. As the light source a 400 W medium pressure mercury lamp (Applied Photophysics Ltd., Model 400 LQ) radiating predominantly 365 - 366 nm light is used. The lamp is placed in a water-cooled well in the middle of the reactor. A Helicoid gauge (Type 460 K, 0 - 760 mm Hg absolute) is connected to the reactor. Xenon was supplied by L'Air Liquide, Paris (99,95 % Xe), fluorine, however, was prepared in our laboratory and additionally photochemically purified [13].

In a typical experiment gaseous mixture of xenon (9,0 mmoles) and fluorine (54,0 mmoles) with total pressure 700 mm Hg was irradiated at constant temperature 12°C. The pressure was followed throughout the reaction. As shown in the diagram, the first step of the reaction i.e. the formation of xenon difluoride is under conditions used complete in less than 2 hours and in about 36 hours all xenon is quantitatively transformed to xenon tetrafluoride.

The purity of xenon tetrafluoride obtained was checked through the triple point determination and in addition i.r. spectra of the product were recorded. Triple point determinations were carried out in sealed thick wall quartz capillaries. The obtained value of 117,1°C (± 0,05°C) agrees within the experimental error with the value cited in the literature for pure XeF_4 [14]. Infrared spectroscopy 10 cm path gas cell made of nickel equipped with AgCl windows was used. In the

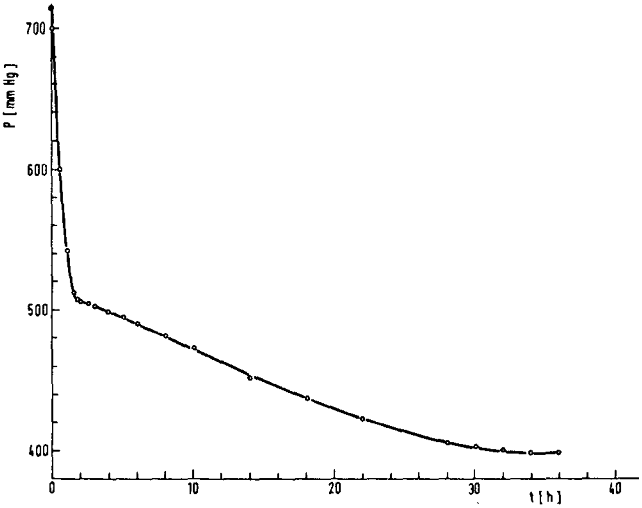

Fig. 1. Pressure vs. time diagram for the photochemical reaction between xenon and fluorine (p^{o}_{Xe} = 100 mm Hg, $p^{o}_{F_2}$ = 600 mm Hg, λ = 365 - 366 nm, T = 12°C)

spectra obtained at the vapour pressure of the product at room temperature the only bands observed were those of xenon tetrafluoride.

The method described above lends itself for preparation of gram lots of pure xenon tetrafluoride. In comparison with other methods for preparation of xenon tetrafluoride the described method has some advantages: there is no need for the supervision of the reaction during the irradiation and in addition, since the method yields pure xenon tetrafluoride no additional purification of the reaction product is necessary.

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