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SHORT COMMUNICATION

On the Photosynthesis of Uranium Hexafluoride (PART 2)

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The photosynthesis of krypton difluoride in liquefied fluorine at -196°C [1] offered a number of advantages as compared to methods of syntheses published elsewhere. Consequently, we have applied the same method to some similar systems such as dioxygen difluoride [2] and the synthesis of uranium hexafluoride [3]. The latter can be obtained by irradiation of a suspension of solid uranium tetrafluoride in liquefied fluorine but the observed yield was rather low. Therefore, this photochemical reaction was investigated at higher temperature with fluorine in the gaseous phase. Our primary intention was to find the optimal reaction conditions for the photochemical synthesis of uranium hexafluoride starting either from uranium tetrafluoride or uranium pentafluoride and gaseous fluorine on a preparative laboratory scale.

The reactions were carried out in a cylindrical photochemical reactor made of pyrex glass (volume 1300 ml, diameter 110 mm). A 400 W medium pressure mercury lamp (Applied Photophysichs LtD., Model 400 LQ) radiating predominantly 365 - 366 nm light is placed in a water cooled well in the middle of the reactor. During the reaction the reactor was immersed in a bath of constant temperature. Uranium tetrafluoride was prepared by hydrofluorination of uranium dioxide and uranium pentafluoride was made by low temperature pressure fluorination of uranium tetrafluoride [4]. Fluorine was prepared in this laboratory and in addition photochemically purified [5,2].

Uranium tetrafluoride to be used in an experiment was thoroughly dried by pumping on it at 100°C for 72 hours. The reactor containing the tetrafluoride was, prior to the experiment, treated with vapours of uranium hexafluoride to remove traces of moisture. Uranium pentafluoride was, however, put into the pretreated photochemical reactor in a dry box. The reactor was then filled with elemental fluorine and irradiated for two hours. The excess fluorine was removed after the reaction by pumping at - 183°C and other volatiles which were possibly present were removed by pumping at Dry-Ice temperature. Uranium hexafluoride was subsequently transferred in a dynamic vacuum into a Kel-F U-tube held at -78°C and finally sublimed into a Kel-F container and weighed. The purity of the reaction product was examined by IR spectroscopy and chemical analysis while the solids remaining were identified by X-ray powder diffraction patterns.

TABLE 1

Yield of uranium hexafluoride in dependence on temperature

Starting material (7,5 millimoles)	Temperature (°C)	Yield (%)
UF_4	- 60	80 - 85
UF_4	- 20	80 - 85
UF_4	0	50 - 55
UF_4	+ 60	25 - 30
UF_5	- 20	80 - 90

Table 1 shows the influence of temperature on the yield of the reaction. It is obvious that the reaction takes place on the surface of the solid fluoride. The diffusion of uranium hexafluoride from the surface of uranium pentafluoride appears to be the slowest part of the reaction. This is confirmed by our observations and results published elsewhere [3]. The yield appears to be best when the temperature is high enough for the hexafluoride to distil from the surface of the pentafluoride onto the cooler wall of the reactor. Since the yield of the reaction is practically the same for either of the starting materials used the fluorination of the solid appears not to be rate determining factor.

Our observations confirm that the exposed surface of solid lower uranium fluoride is the critical factor influencing the yield of the reaction. The reactor was normally shaken every thirty minutes in order to redistribute the solid uranium tetrafluoride on to the walls of the reactor where the irradiation is most efficient. If this periodical shaking was omitted the yield dropped significantly.

As shown in Table 2 a higher excess of fluorine does not influence the yield of the reaction.

TABLE 2

Influence of the mole ratio of the reactants on the rate of the reaction

Mole ratio UF_4/F_2	Yield (%)
1 : 2	80
1 : 7	80-85
1 : 15	80

time of irradiation: 2 hours
reactor temperature: - 20°C
amount of UF_4 used: 7,5 millimoles

If larger initial quantity of uranium tetrafluoride was employed e.g. 30 millimoles instead of 7,5 millimoles, the absolute amount of uranium hexafluoride after two hours of irradiation at - 20°C was of course higher but the yield decreased.

It is possible by the method described here to obtain several grams of uranium hexafluoride per hour per one liter of volume of the reactor space if the outer wall of the reactor is kept within the temperature range from -20°C to - 60°C, and a mole ratio $UF_4 : F_2 = 1 : 2$ is employed. The yield of reaction is drastically lowered if the surface of the reacting lower fluoride is not kept exposed either by periodical redistribution of the solid or by controlling the transport of uranium hexafluoride from the surface.

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