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ON THE PHOTOSYNTHESIS OF DIOXYGEN(1+) HEXAFLUOROARSENATE IN THE SYSTEMS O_2-F_2-AsF_5, OF_2-AsF_5 AND O_2-OF_2-AsF_5

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SUMMARY

The photochemical reactions in the systems O_2-F_2-AsF_5, OF_2-AsF_5 and O_2-OF_2-AsF_5, yielding O_2AsF_6 as the reaction product were investigated. The influence of the mole ratio of the reactants upon the rate of formation of O_2AsF_6 was studied and a reaction mechanism is suggested which is based on the formation of $O_2F\cdot$ radicals. Regarding the preparation of O_2AsF_6 the best results were obtained using the system O_2-F_2-AsF_5 with the mole ratio 1 : 1-1.5 : 1.

INTRODUCTION

The dioxygen(1+) compounds (or dioxygenyl compounds) are of great interest because of their high oxidizing power. The first dioxygen(1+) compound O_2PtF_6 was prepared by Bartlett and Lohmann [1]. Later on analogous compounds were prepared either by the reaction between dioxygen difluoride and the corresponding Lewis acid [2] [3], or thermally by the reaction of some pentafluorides with fluorine and oxygen [4] or with oxygen difluoride [5] under pressure.

The photosynthesis of dioxygen hexafluoroarsenate was first reported by Shamir and Binenboym [6]. They exposed a gaseous mixture of oxygen, fluorine and the corresponding pentafluoride to sunlight. The reaction mechanism they proposed is the following:

$$F_2 \xrightarrow{h\nu} F\cdot + F\cdot \quad (1)$$
$$O_2 + F\cdot \longrightarrow O_2F\cdot \quad (2)$$
$$O_2F\cdot + F_2 \longrightarrow O_2F_2 + F\cdot \quad (3)$$
$$O_2F_2 \longrightarrow O_2F\cdot + F\cdot \quad (4)$$
$$O_2F\cdot + MF_5 \longrightarrow O_2F.MF_5 \longrightarrow O_2^+MF_6^- \quad (5)$$

The relatively high rate of the reaction, in spite of the rather low absorption of fluorine in the visible region, is supposed to be caused by the formation of $O_2F\cdot$ radicals which can directly react with pentafluoride (5) or, alternatively, can take part in the chain reaction (3) and (4).

The $O_2F\cdot$ radical was found to exist in dioxygen difluoride at low temperatures and is considered to be formed during the thermal decomposition of O_2F_2 [7] [8]. It has also been found that the $O_2F\cdot$ radical is formed during the photolysis of oxygen difluoride as the product of the dark reaction between primarily formed $OF\cdot$ radicals and OF_2 molecules [7]:

$$OF_2 \xrightarrow{h\nu} OF\cdot + F\cdot$$
$$OF\cdot + OF_2 \longrightarrow O_2F\cdot + F_2$$

In our work we studied the photosynthesis of O_2AsF_6 in the systems O_2-F_2-AsF_5, OF_2-AsF_5 and O_2-OF_2-AsF_5. The influence of several factors (e.g. the mole ratio of the reactants and initial pressure of the reaction mixture) upon the reaction rate ($-dp_{AsF_5}/dt$) was investigated in order to find the optimal reaction conditions for preparative purposes. As Lewis acid, arsenic pentafluoride was chosen because of its easy handling and because it forms only one dioxygen compound - O_2AsF_6.

RESULTS AND DISCUSSION

The results obtained cannot be discussed quantitatively because of several factors which, although of minor extent, influence the reaction course and cannot be fully taken into account (e.g. a dead space of about 5% of total volume, and an increased absorption of light by the solid reaction product deposited on the walls of the reaction vessel). Furthermore, in many cases an irreproducible induction period was observed, which is most probably due to the formation of the radicals. In spite of these difficulties, the following conclusions can be drawn.

System O_2-F_2-AsF_5

The rate of the reaction

$$O_2 + 1/2\ F_2 + AsF_5 \xrightarrow{h\nu} O_2AsF_6$$

depends only on the mole fraction of fluorine and of the initial pressure of the reaction mixture (Fig. 1 and Fig. 2). An excess of the other reactants, or the addition of an inert gas (e.g. nitrogen) does not have any influence on the reaction rate.

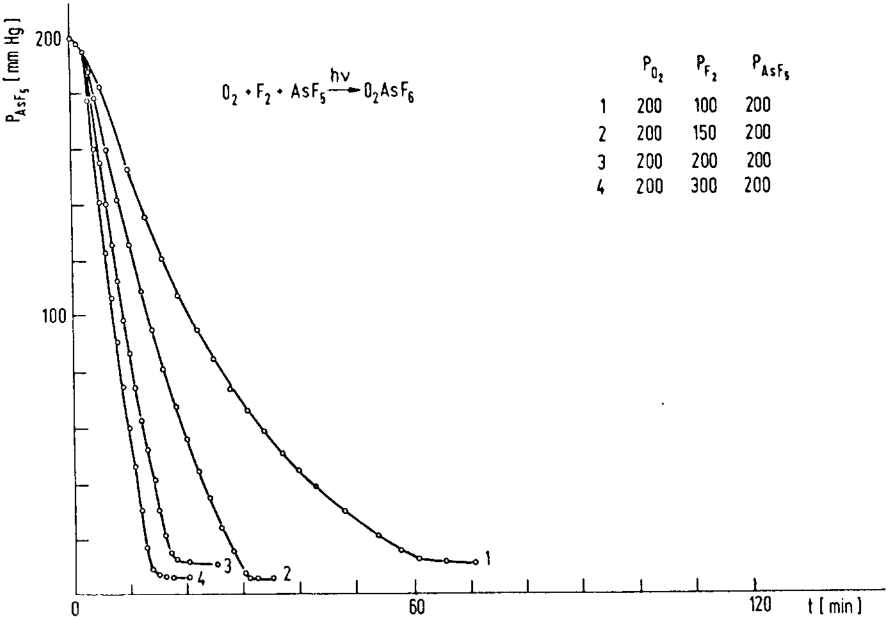

Fig. 1. The influence of the initial pressure of fluorine upon the rate of formation of O_2AsF_6 in the system O_2-F_2-AsF_5

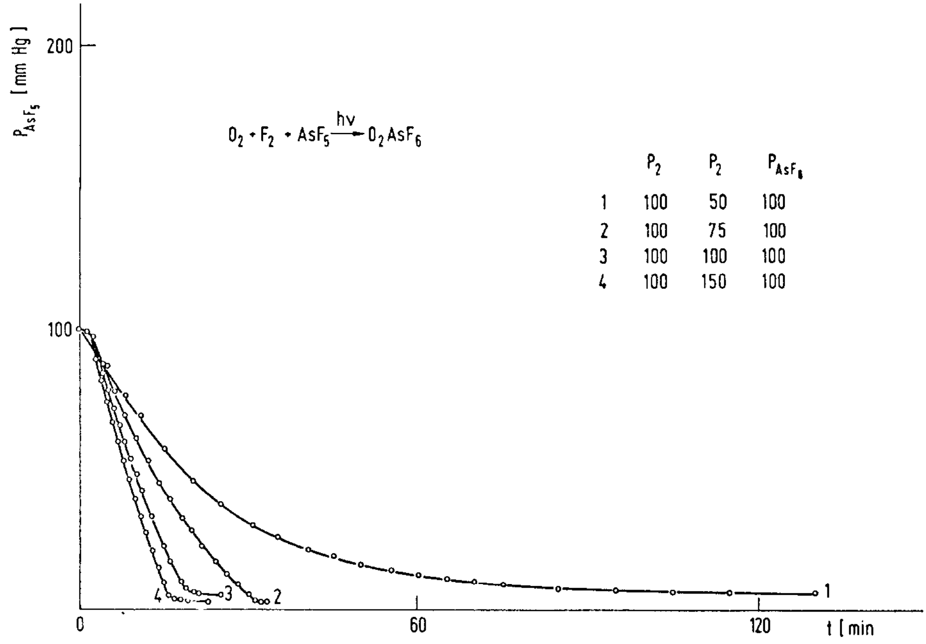

Fig. 2. The influence of the initial pressure of fluorine upon the rate of formation of O_2AsF_6 in the system O_2-F_2-AsF_5

System OF_2-AsF_5

Analogous to the former system, the rate of the reaction

$$2\ OF_2 + AsF_5 \xrightarrow{h\nu} O_2AsF_6 + 1.5\ F_2$$

depends only on the mole fraction of oxygen difluoride and on initial pressure of the reaction mixture. However, the reaction rate is much lower than the reaction rate in the analogous system with fluorine and oxygen instead of oxygen difluoride (Fig. 3, curves 1 and 2), but significantly higher than would be expected if it were controlled only by the rate of photochemical decomposition of OF_2 into molecular oxygen and fluorine (Fig. 3, curves 1a and 2a). The increased reaction rate can be most plausibly explained by the following proposed reaction mechanism which includes the formation of $O_2F\cdot$ radicals

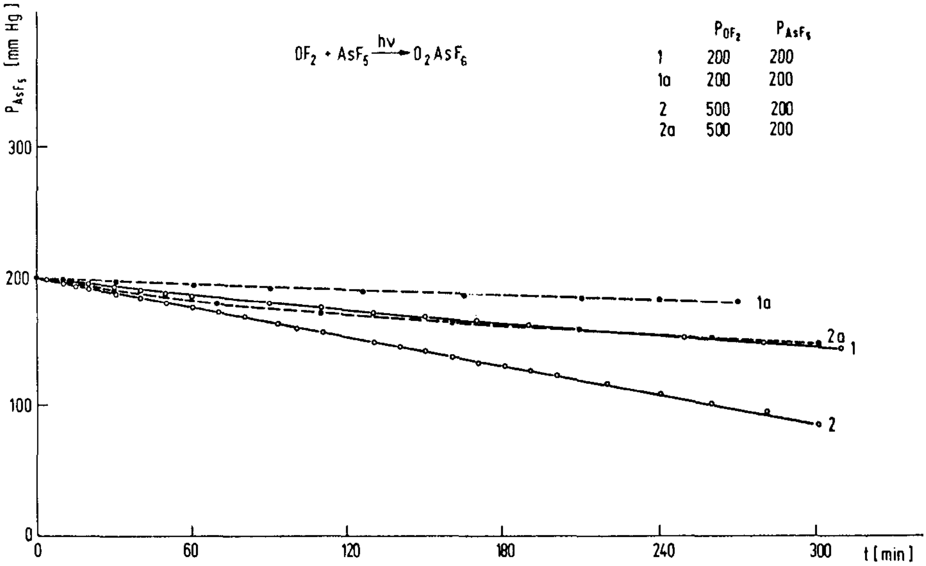

Fig. 3. The influence of the initial pressure and mole fraction of oxygen difluoride upon the rate of formation of O_2AsF_6 in the system OF_2-AsF_5.

by the dark reaction between the molecules of oxygen difluoride and the OF• radical:

$$OF_2 \xrightarrow{h\nu} OF\cdot + F\cdot$$

$$OF\cdot + OF_2 \longrightarrow O_2F\cdot + F_2$$

$$F\cdot + F\cdot \longrightarrow F_2$$

$$O_2F\cdot + AsF_5 \longrightarrow O_2F.AsF_5 \longrightarrow O_2{}^+AsF_6{}^-$$

$$\frac{dp_{O_2F\cdot}}{dt} > \frac{\frac{1}{2}\, dp_{OF_2}(\text{photolysis})}{dt}$$

In order to confirm this assumption, the reaction between xenon and oxygen difluoride was carried out in which oxygen takes no part. As expected, the rate of this reaction was practically the same as the rate of photochemical decomposition of OF_2. The only difference was the relatively long induction period of the reaction with xenon (Fig. 4).

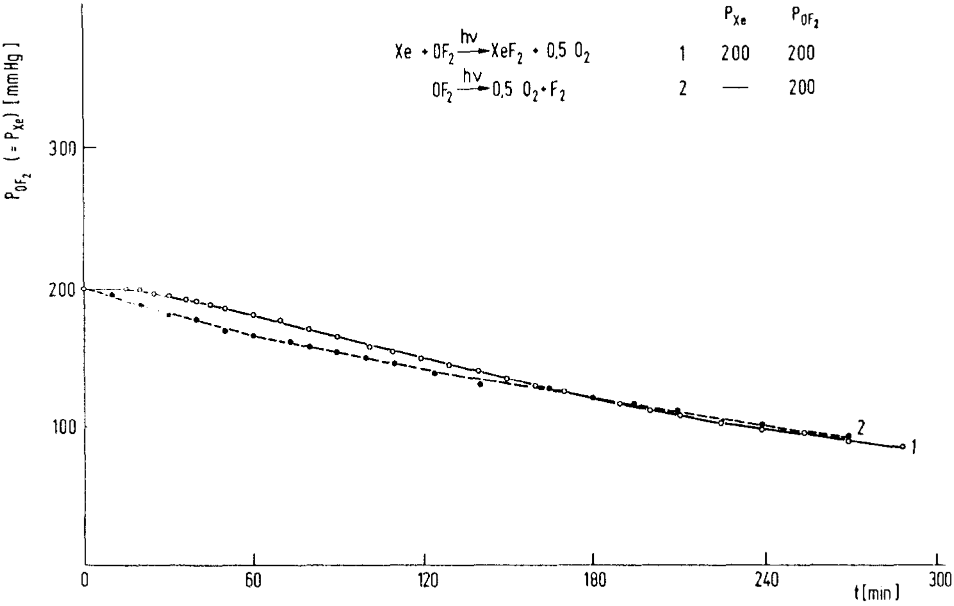

Fig. 4. The rate of the photochemical reaction between xenon and oxygen difluoride compared with the rate of photochemical decomposition of oxygen difluoride.

System O_2-OF_2-AsF_5

Since in the system OF_2-AsF_5 free fluorine is formed during the reaction, the formation of $O_2F\cdot$ radicals and thus the rate of the formation of O_2AsF_6 can be increased by the addition of a stoichiometric amount of oxygen to the reaction mixture. The rate of the reaction

$$3\ O_2 + 2\ OF_2 + 4\ AsF_5 \xrightarrow{h\nu} 4\ O_2AsF_6$$

is influenced only by the mole fraction of OF_2 and the initial pressure of the reaction mixture (Fig. 5, curves 1, 2 and 3). It is, however, about 5 times higher than that in the same system without oxygen. An excess of oxygen does not influence the reaction rate. If a substoichiometric amount of oxygen is added, the reaction rate is lowered at once when all the oxy-

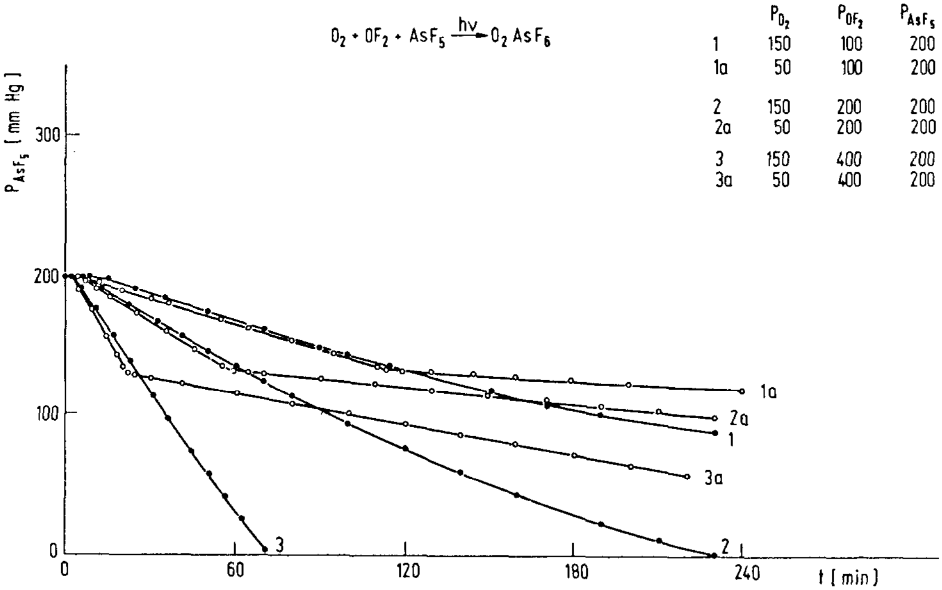

Fig. 5. The influence of the mole fraction of OF_2 and the initial pressure of the reaction mixture upon the rate of formation of O_2AsF_6 in the system O_2-OF_2-AsF_5.

gen is consumed. From this point the reaction proceeds with a rate which corresponds to that in the system OF_2-AsF_5 (Fig. 5, curves 1a, 2a and 3a).

The following reaction mechanism is proposed:

$$OF_2 \xrightarrow{h\nu} OF\cdot + F\cdot$$
$$OF\cdot + OF_2 \longrightarrow O_2F\cdot + F_2$$
$$O_2 + F\cdot \longrightarrow O_2F\cdot$$
$$O_2F\cdot + F_2 \longrightarrow O_2F_2 + F\cdot$$
$$O_2F_2 \longrightarrow O_2F\cdot + F\cdot$$
$$O_2F\cdot + AsF_5 \longrightarrow O_2F.AsF_5 \longrightarrow O_2^+AsF_6^-$$

Generally, the rate of the reaction in the system O_2-OF_2-AsF_5 is about 10 times lower than in the analogous system with fluorine instead of oxygen difluoride (Fig. 6).

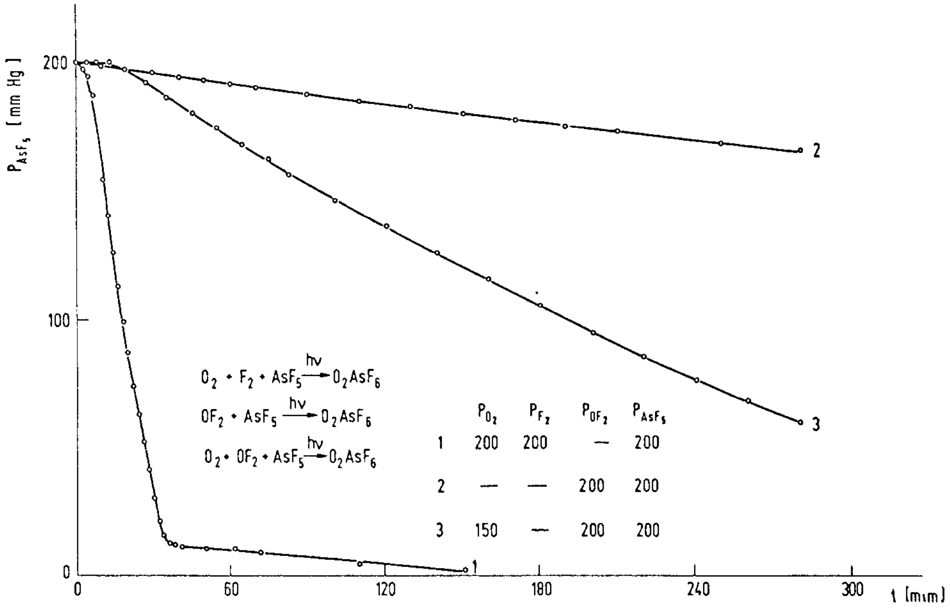

Fig. 6. The rate of formation of O_2AsF_6 in the systems O_2-F_2-AsF_5, OF_2-AsF_5 and O_2-OF_2-AsF_5.

This can be explained by the low rate of formation of the OF• radicals and fluorine atoms in the first step of photolysis of oxygen difluoride and, consequently, by the lower rate of formation of O_2F• radicals.

Regarding the photochemical preparation of O_2AsF_6, the best yield was obtained by irradiation of a reaction mixture of O_2-F_2-AsF_5 with the mole ratio 1 : 1-1.5 : 1.

EXPERIMENTAL

Apparatus

The reactions were carried out in a 1500 ml Pyrex reaction vessel, equipped with a Rotaflo valve and water cooled well for the light source. The reaction vessel was connected to a pressure gauge (Helicoid gauge 0-1500 mm Hg absolute). The light source was a 400 W medium pressure mercury lamp (Type 400 LQ, Applied Photophysics Ltd.).

During the irradiation the reaction vessel was cooled with tap water to a practically constant temperature within the particular experiment.

Reagents

Fluorine (99 ± 0.5%) was produced in our laboratory in a 120 A medium temperature electrolytic cell. After the usual purification, it contains about 1% oxygen as the main impurity besides smaller amounts of HF, SiF_4 and CF_4.

Arsenic pentafluoride was synthesized from the elements using 99.999% arsenic metal (Koch & Light). The product was purified from AsF_3 by fractional condensation *in vacuo* (-78°C, -196°C).

Oxygen from a cylinder was dried over P_2O_5 and subsequently purified by trap-to-trap distillation.

Oxygen difluoride (99 ± 0.5%) was obtained by electrolysis of an electrolyte containing 85-90% HF and 10% NaF. The crude product was purified first by pumping off oxygen at -196°C. Subsequently it was condensed in a dynamic vacuum into a trap cooled with liquid nitrogen.

ACKNOWLEDGEMENT

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