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Laser photolysis reactions in liquid fluorine

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Abstract

The photolysis by laser radiation (488 nm) of Kr, Xe, O_2 and UF_5 dissolved in liquid fluorine affords KrF_2, XeF_2, O_4F_2 or O_2F_2, and UF_6, respectively. No reaction product was observed on laser photolysis of liquid fluorine with Ar, N_2, IF_5, RuF_5 or OsF_6.

Introduction

The only previous report on the use of laser photolysis reactions in noble-gas chemistry is that by Howard and Andrews [1] who photolysed fluorine in krypton and xenon matrices at 14 K to yield matrix-isolated KrF_2 and XeF_2, respectively. Following the observation that UV photolysis reactions of noble gases in liquid fluorine at 77 K readily afforded the same noble-gas fluorides [2, 3], we were interested to see if the range of reactions in liquid fluorine could be extended by the use of the laser radiation and our results are presented in this paper.

Results

Scheme 1 summarizes the laser-photolysed reactions in liquid fluorine studied. Raman spectra of the products from the photolysis of krypton or xenon-fluorine mixtures, either dissolved in liquid fluorine or as solids at 77 K, gave only one Raman-active stretch (466 cm^{-1} and 515 cm^{-1}, respectively) characteristic of KrF_2 [3] and XeF_2 [4]. In both cases, high yields [28% (0.45 mmol) and 100% (1.6 mmol), respectively] of the difluorides were obtained after only 30 min photolysis. This may be compared with the 28% yield of α-KrF_2 after 8h of UV photolysis [3]. We therefore recommend laser photolysis of krypton–fluorine mixtures as a convenient, high-yield, small-scale synthesis of KrF_2. However, we could not oxidise KrF_2 or XeF_2 either by the prolonged laser photolysis (up to 8 h) of noble gas–fluorine mixtures or by the laser photolysis of solid samples of KrF_2 or XeF_2 in liquid fluorine.

Following these initial successes, we have investigated the general applicability of this type of reaction. Argon–fluorine and nitrogen–fluorine

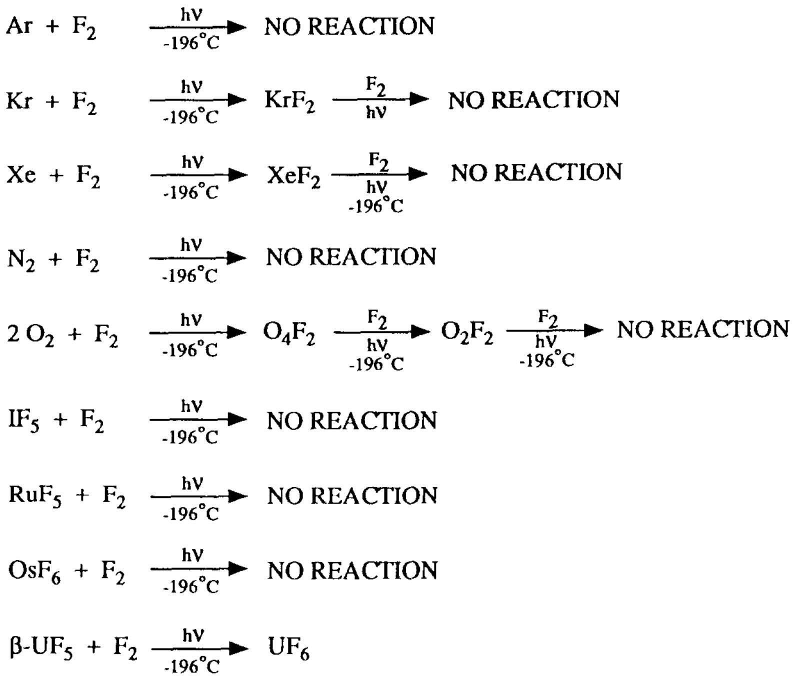

Fig. 1. Laser–induced photolysis reactions in liquid fluorine.

mixtures showed no evidence of reaction, even after prolonged laser photolysis. Oxygen–fluorine mixtures, however, gave a sequence of reaction products. Oxygen–fluorine mixtures readily afforded a deep red product after 30 min which was partially soluble in liquid fluorine. The colour prohibited its characterisation by Raman spectroscopy, but the ESR spectra on samples dissolved in CF_4 at 90 K gave a doublet ($g_{iso} = 2.0059$) characteristic of the FOO· radical [5] which, on cooling to 77 K, collapsed to a broad signal as has been observed previously for O_4F_2 [6]. The addition of more fluorine to a sample of O_4F_2, followed by laser photolysis for 8 h, gave a yellow solid insoluble in liquid fluorine which gave a Raman spectrum at 77 K characteristic of O_2F_2 [7]. Prolonged laser photolysis of O_2F_2: F_2 mixtures gave no evidence of further reaction.

The usefulness of laser photolysis for oxidative fluorine chemistry was tested by the photolysis of IF_5–, RuF_5–, β-UF_5– and OsF_6–fluorine mixtures. IF_5, RuF_5 and OsF_6 gave no evidence of reaction, and the reagents could be recovered even after extended photolysis at 77 K. Solid β-UF_5 is slightly soluble in liquid fluorine and dissolves to give a light green solution over a green solid. On laser photolysis at 77 K, the solution rapidly decolourises and a white precipitate is formed. The Raman spectrum at 77 K and a mass spectrum confirmed the white solid as UF_6 which may be obtained in 100% (1.6 mmol) yield after only 30 min laser photolysis.

Discussion

The absorption spectrum of fluorine indicates that photolysis at 488 nm will readily cleave the F—F bond, and so it is expected that all the reactions described in this paper involve fluorine radicals. However, the reactions only occur when the substrate is dissolved in the liquid fluorine. The compounds IF_5, RuF_5, OsF_6 and O_2F_2 apparently have virtually no solubility in liquid fluorine at 77 K and we have observed no evidence for the occurrence of fluorination. On the other hand, O_2, O_4F_2, Kr, Xe and β-UF_5 are all soluble in liquid fluorine and undergo oxidative fluorination reactions very rapidly under laser photolysis. Substrate solubility is clearly not the only significant criterion for reaction since KrF_2, XeF_2, N_2 and Ar are all partially soluble in liquid fluorine but do not undergo oxidative fluorination on laser photolysis at 77 K. In the case of KrF_2, XeF_2 and N_2 this may be due to a kinetic effect resulting from the very low reaction temperature. The stability of XeF_4, XeF_6, N_2F_2 and N_2F_4 at room temperature certainly supports this. For argon, we observed a small amount of turbidity during photolysis which may be due to the formation of transient ArF_2, but the predicted limited thermodynamic stability of ArF_2 [8] may preclude its isolation at 77 K.

Experimental

All reactions were carried out in pre-fluorinated 6-mm Teflon F.E.P. reactors with a 0.5 mm wall (6 cm^3 total volume) which were connected to an all-metal vacuum manifold via PTFE valves [Chemcon STD/VC-4P; Production Techniques, Fleet, Hampshire, UK]. Solid reagents were weighed and loaded into these reactors in an inert atmosphere dry box [Dri-Lab HE Series; Vacuum Atmospheres, CA, USA], while volatile reagents and fluorine were charged into the reactors at 77 K via a nickel and stainless-steel vacuum manifold [Autoclave Engineers, PA, USA].

In typical preparations, Kr (36 cm^3, 1.6 mmol), Xe (36 cm^3, 1.6 mmol), O_2 (36 cm^3, 1.6 mmol) or UF_5 (0.7 g, 1.6 mmol) were combined with excess F_2 (98% purity). After charging the reactor, the mixture was photolysed at 77 K in an unsilvered Pyrex Dewar vessel (3 cm i.d.) for between 30 min and 8 h, using the blue 488 nm line of a Coherent Radiation Laboratories model 52 argon ion laser. After photolysis, Raman spectra were recorded at 77 K on a Coderg T800 Raman spectrometer for the products dissolved in liquid fluorine (when the product had sufficient solubility) or on the solid product at 77 K after the removal of unreacted fluorine.

WARNING: Great care should be exercised in manipulating liquid fluorine. Apparatus must be free from dust and fully fluorinated. Every precaution to ensure that the liquid fluorine container is maintained at 77 K throughout must be taken.

Conclusions

Laser photolysis gives rise to the oxidative fluorination of some reagents dissolved in liquid fluorine. The technique as described has little applicability for reagents insoluble in liquid fluorine at 77 K.

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