

PHOTOLYSIS OF URANIUM HEXAFLUORIDE AND SOME REACTION VARIABLES AFFECTING THE APPARENT QUANTUM YIELD*

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Summary

Photolysis of UF_6 in the spectral range 275.0 - 404.7 nm leads to the production of β - UF_5 and fluorine atoms with an apparent quantum yield which varies greatly with light intensity, UF_6 pressure and the nature of the inner absorption cell surface. No correlation of the apparent quantum yield with wavelength of the light source is observed. Reduction of the apparent quantum yield from unity is attributed to the recombination reaction $UF_5 + F \rightarrow UF_6$. Competitive processes which reduce the fluorine atom concentration or the UF_5 monomer concentration prevent the yield from approaching zero. These are formation of molecular F_2 , direct reaction of fluorine atoms with the wall material, flow of fluorine atoms out of the cell and polymerization of UF_5 monomer. The addition of the fluorine atom scavenger H_2 increases the yield to 1.75.

1. Introduction

In the near ultraviolet absorption spectrum of uranium hexafluoride at wavelengths greater than 250 nm there are two relatively weak bands for which the photon energy is great enough to dissociate one, but not more than one, U—F bond. The published thermodynamic [1 - 3], spectroscopic [4 - 6] and chemical literature [3] indicate that β - UF_5 and F_2 are probably the only stable products of this decomposition and that the primary photolytic process is



Recent X-ray diffraction analyses of the solid product confirm that it is indeed β - UF_5 [7]. Some obvious secondary processes are therefore



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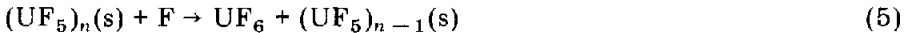
and



where M is a third body. Only the rate of the latter reaction has been determined. However, β -UF₅ is readily converted to UF₆ by fluorine atoms, *e.g.* by F₂ gas in the presence of UV radiation, suggesting that the recombination reactions



and



must also be considered as secondary processes. Depending upon the relative rates of each of these secondary reactions, the apparent quantum yield for the photolysis of UF₆ may be substantially less than unity. In fact, the yield should vary according to the conditions of the photolysis, *i.e.* pressure of UF₆ and light intensity, even though the primary yield may be unity at all wavelengths in the absorption bands.

The present experiments were undertaken in an effort to determine the relative importance of the above reactions and the degree to which they influence the apparent quantum yield, and at least to infer the primary quantum yield at several wavelengths in the absorption spectrum.

2. Experimental

Although we have the option of using either a continuous working (CW) arc lamp and monochromator or tunable UV lasers as light sources for decomposing UF₆, we have chosen the arc lamp and monochromator source since interpretation of the quantum yields through computer modelling of the kinetics is much less complex. Particularly with the use of pulsed lasers, the temperature and pressure profiles across the reaction zone as a function of time are not easily determined. Even though CW UV ion lasers could be substituted for an arc lamp-monochromator source, kinetic modelling would also be exceedingly difficult unless the laser beam were expanded to fill a substantial fraction of the cavity, and ion lasers have useful output levels at fewer frequencies in the UF₆ absorption bands.

In the experiments described later the apparent quantum yield is defined as the ratio of the number of molecules of product UF₅ collected as aerosol on an impactor to the number of photons absorbed by the UF₆. With the exception of reaction (3), reactions (1) - (5) are exceedingly fast, so that the quantum yield defined in this way represents an effective yield unless reactions (3) - (5) are suppressed by adding a fluorine atom scavenger to remove them much more rapidly than does UF₅. A variety of such scavengers have been reported in the literature [8] but only H₂ was included in this investigation.

The light source consisted of a 1 kW xenon-mercury arc lamp whose output was passed through a 0.25 m monochromator with a predispersion prism to remove higher order radiation. The bandwidth was typically 10 nm full width at half maximum or less, and the corresponding power output was 15 mW at the front cell window. Power levels were measured with a carbon disc calorimeter whose calibration was verified with a ferrioxalate actinometer.

Mixtures of UF_6 in helium carrier gas were photolyzed by flowing them from a storage cylinder through a reaction cell with quartz or CaF_2 windows and irradiating them in transit at room temperature with an arc lamp-monochromator source. The UF_5 product was collected on a single hole impactor at slightly subsonic velocities and analyzed for uranium content colorimetrically with a Cary-14 spectrophotometer. The impactor collection efficiency was determined to be at least 95%, both by calculation [9] and calibration. The collected UF_5 particles consist of agglomerates of smaller primary particles, the agglomerate size being in the range of 0.1 - 0.2 μm or more than ten times that of the primary particles [10].

The UF_6 was carefully separated from HF by condensation from the gas phase at -23°C and the helium carrier gas was dried by passage through a trap filled with copper turnings and cooled by liquid nitrogen. Blanks were run on each mixture in duplicate before and after photolysis runs by repeating the experiment with the light source off. They averaged 2 μg of uranium or 2 - 10% of the photolysis yields. The storage cylinder, which was always filled to a total pressure of helium of 25 lbf in $^{-2}$, was discharged until the final pressure was 5 lbf in $^{-2}$, the elapsed time for this operation being in the range 55 - 106 s, depending upon the composition of the gas mixture.

The irradiated volume in the cell was roughly shaped like a truncated pyramid and occupied about one-third of the total cell volume. The cell dimensions were 4 in long \times 1.5 in diameter and the flow rate was sufficient to give a particular UF_6 molecule a half-time of 1 - 2 s in the cell.

Materials used in construction of the photolysis system consisted of stainless steel storage cylinders and photolysis cell, brass and Teflon in valves and fittings, and copper tubing. The system as a whole was treated by exposure to fluorine overnight but the irradiation cell required more drastic procedures to keep blanks low. Owing to the extraordinary reactivity of fluorine atoms, it was necessary to expose the cell interior to fluorine atoms by irradiating fluorine inside the cell for periods of 1 - 2 h, and keeping the cell and photolysis system filled with a small amount of WF_6 until experiments commenced.

3. Results

Photolysis quantum yields in pure UF_6 proved to be extremely variable even with the same cell in spite of extensive efforts to find a treatment for the cell wall which would render it inert to fluorine atoms. The problem is partly one of surface condition. For example, polished quartz windows

appear to have no effect, but a quartz cell fabricated by fusing tubing and plates destroys nearly all of the fluorine atoms released. The problem is also partly due to deposition of UF_5 on the walls which results in an increasing yield in a series of repeated experiments. Since the loss of UF_5 in the impactor is only a few per cent, we believe the lowest yields for a given set of conditions represent the best values. The variations in yield for a given set of conditions did not occur at random but occurred slowly over a period of more than a year. The yields in the earlier experiments gradually decreased as the method of cell passivation improved but eventually the trend reversed. Consequently, loss of fluorine atoms at the wall is the most reasonable source of error in the higher yields.

The results for mixtures of UF_6 in helium carrier gas are collected in Fig. 1. The UF_6 content of the mixtures varied over the range 0.3 - 90 Torr, depending upon the light intensity and absorption coefficient. The quantity I_{abs} represents the initial number of photons absorbed by UF_6 in einsteins per second. Actual yields were calculated by integrating this quantity for the duration of each experiment. The apparent quantum yield Φ was obtained through the expression

$$\Phi = N_{\text{U}} \left(\int_0^{t_0} I_{\text{abs}} [1 - \exp\{-2.303 C_0 \epsilon l \exp(-kt)\}] dt \right)^{-1} \quad (8)$$

where C_0 is the initial UF_6 concentration in mol cm^{-3} , ϵ the molar absorptivity in $\text{cm}^3 \text{mol}^{-1} \text{cm}^{-1}$, l the cell length, k the discharge rate constant in s^{-1} , t_0 the duration of flow and N_{U} the uranium content of the product in moles (assumed to be UF_5). It is evident that the minimum yields are around 0.10 at both 366 and 275 nm.

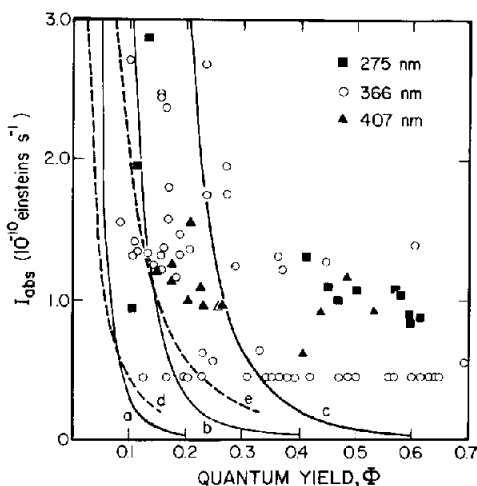
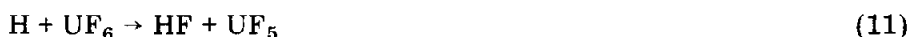


Fig. 1. Photolysis quantum yield of irradiated UF_6 in helium mixtures as a function of photon absorption rate. E_a for curves a, b and c is $5.0 \text{ kcal mol}^{-1}$ and E_a for curves d and e is $1.4 \text{ kcal mol}^{-1}$. Sticking coefficients are: $a = 1.0$, $b = 0.3$, $c = 0.1$, $d = 0.1$ and $e = 0.03$.

When H_2 is added to remove fluorine atoms more rapidly than reactions (4) or (5), the additional reactions



must also occur. These reactions have been extensively investigated in the development of the chemical laser systems H_2-F_2 and H_2-UF_6 [11, 8]. Since we have defined the quantum yield in terms of UF_5 collected, it is evident that reactions (9) and (11) together will increase the yield beyond 1.0 with sufficient H_2 present. Reaction (10) never becomes important because the rate of reaction (3) is too slow to accumulate significant amounts of F_2 . As the results in Fig. 2 show, only a trace of H_2 (about 2 mTorr) is necessary to give a quantum yield close to 2.0, while the initial UF_6 pressure for these experiments was 18 Torr. The remainder of the mixture was helium to give a total pressure of 25 lbf in⁻². The fraction of UF_6 photolyzed was typically about 1 part in 10^4 of the total UF_6 . The fact that the yield is not quite 2.0, even with a large amount of H_2 present, is not indicative of loss of UF_5 in the impactor but only that reaction (11) has a rate constant less than about $1 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Values of this constant lower than $1 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ reduce the quantum yield even further by making it impossible for all of the hydrogen atoms to react with UF_6 before being swept out through the impactor.

The large number of reactions involved in the post-photolysis of UF_6 and mixtures with H_2 made it essential to develop a computer model to account for the behaviour of the quantum yield as a function of composition and light intensity. The model uses a hard sphere plus attractive potential to estimate polymerization rate constants for UF_5 . The recombination rate of UF_5 (monomer) + $F \rightarrow UF_6$ was assumed to be given by the product of the hard sphere collision rate and a sticking coefficient. For UF_5 polymer recombination an activation energy term $\exp(-E_a/RT)$ was also added. Further details on the calculation are given in the Appendix. The lowest yields of about 0.10 in Fig. 1 are consistent with a sticking coefficient of 0.6 or greater and an activation energy of about 3 kcal or greater. The same model has been applied to the results of Lewis *et al.* [12], in which the recovery of UF_6 after partial photolysis by a KrF laser pulse was followed by observing the UF_6 fluorescence induced by a tunable dye probe laser. Their data were fitted using an activation energy E_a of 2.37 kcal with a sticking coefficient of 1.00. The solid curves in Fig. 2 show the variation of quantum yield with H_2 densities when the sticking coefficient is assumed to be 1.00 and $E_a = 5.0 \text{ kcal mol}^{-1}$. It should be noted that the model accounts for the limiting effect of the rate constant of reaction (11) on the maximum yield when a substantial

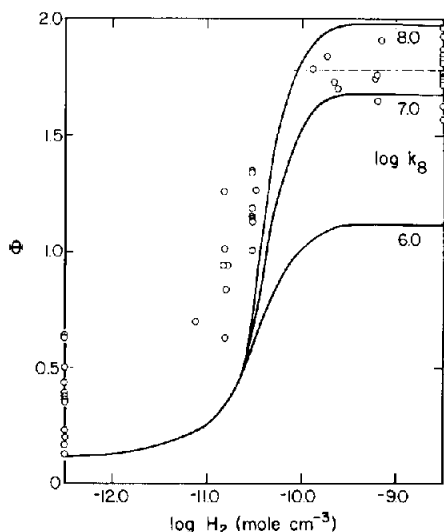


Fig. 2. Photolysis quantum yield of irradiated UF_6 , helium and H_2 mixtures at a photon absorption rate of 4.5×10^{-11} photons s^{-1} . Solid curves are computed for a recombination sticking coefficient of 1.00 and $E_a = 5.0$ kcal mol^{-1} .

amount of H_2 is present and suggests a value of $k_8 \approx 1 \times 10^7$ cm^3 mol^{-1} s^{-1} . It is evident that the model underestimates the quantum yield in the region of the inflection. We believe this is largely due to a mixing rate that is too slow relative to the reaction rate of F with H_2 in addition to the usual variable loss of fluorine atoms at the wall. The model assumes an instantaneous mixing rate. If the rate of mixing is too slow, however, some fluorine atoms react with H_2 at a high concentration of H_2 while others react with an H_2 concentration that is too low, the net result in Φ being in the vicinity of 1.0. At the experimental inflection point there is only half as much H_2 as the model predicts to be necessary to give $\Phi = 1.0$. Other possible explanations are that the H_2 concentration is too high by a factor of 2 or that the measured light intensity is too high by the same factor. These explanations are rejected as extremely unlikely. An error in light intensity of this amount, for example, would also lower the quantum yields by the same factor.

4. Conclusions

Photodissociation of UF_6 beyond 250 nm initially produces UF_5 molecules and fluorine atoms with essentially unit quantum yield. The primary products are extremely reactive, however, and if the container walls are sufficiently inert only a small fraction fails to recombine. The variation of the apparent quantum yield based on the mole ratio of UF_5 collected to photons absorbed can be predicted with the aid of a computer model which assumes that UF_5 polymerization is much faster than gas kinetic, recombina-

tion of UF_5 monomer with fluorine atoms is equal to the gas kinetic rate, and recombination of polymer with fluorine atoms involves an activation energy of about 3 kcal or greater.

The presence of H_2 during photolysis of UF_6 causes the apparent quantum yield to reach values somewhat less than 2.0 owing to rapid removal of fluorine atoms by H_2 and the slower reaction of hydrogen atoms with UF_6 .

Acknowledgment

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Appendix

The major part of the kinetics which follows the photolysis of UF_6 deals with particle growth of UF_5 . Electron photomicrographs of UF_5 produced by arc lamp or KrF laser photolysis show that the UF_5 condenses initially into spheres of about 100 Å diameter or greater and that these agglomerate later to produce irregular chains or clumps of particles [10]. For chemical properties we assume that the particles are spherical and uniform in size, the maximum size being determined by the number density of critical nuclei and the amount of UF_5 photolyzed.

The polymerization rate constants are estimated by a method similar to that of Bauer and Frurip [A1]. We use, however, bimolecular rate constants

since UF_5 is polyatomic, calculating the constants according to expressions given by Amdur and Hammes [A2] for a hard sphere plus attractive potential but adding additional factors for polymer size [A1]. From their eqn. (2 - 15) we can obtain the rate constant expression

$$k_{12} = \pi d_{12}^2 \left(\frac{8RT}{\pi M^*} \right)^{1/2} \left(1 - \frac{U(d_{12})}{RT} \right) \quad (14)$$

by replacing πd_{12}^2 for the hard sphere potential by

$$S(u_r) = \pi d_{12}^2 \left(1 - \frac{U(d_{12})}{RT} \right) \quad (15)$$

In these equations k_{12} is the rate constant for the reaction between species 1 and 2, d_{12} the distance of closest approach if they are hard spheres, $U(d_{12})$ the potential minimum at d_{12} , which we assume to be the heat of vaporization of $\beta\text{-UF}_5$ or $+34.2 \text{ kcal mol}^{-1}$ [1], $S(u_r)$ the scattering factor for the potential $U(d_{12})$ and M^* the reduced mass of the pair of species 1,2. In addition, $U(d_{12})$ is multiplied by a factor similar to that used by Bauer and Frurip [A1] to adjust $U(d_{12})$ for different size polymers. This factor is completely empirical, but it results in a dimerization rate constant of $7 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The model considers all UF_5 polymer collisions up to $n = 30$. All UF_5 which exceeds that size is considered to have a uniform particle size which grows in time, being determined by the number density of nuclei and rate of production of UF_5 polymer with $n > 30$. The resulting particles are about 60 Å in diameter for the conditions reported here, or within a factor of 2 of actual particle size. Processes leading to reevaporation of UF_5 were considered but are negligible for UF_5 since Hildenbrand [A3] has found that ΔG for dissociation of the dimer is too large and positive and is comparable with ΔG for vaporization.

Recombination of fluorine atoms with UF_5 monomers has been assumed to be gas kinetic, *i.e.* that given by eqn. (14) when $U(d_{12}) = 0$. The data of Lewis *et al.* [12] indicate that the UF_5 monomer recombination rate constant must be roughly equal to or greater than the gas kinetic value; otherwise, a distinctly non-linear rate would have been observed. The recombination rate constants for the UF_5 polymers were further assumed to be equal to their respective gas kinetic values multiplied by the factor $\exp(-E_a/RT)$, where the activation energy $E_a \geq 3 \text{ kcal mol}^{-1}$ gives the best fit to the data in Fig. 1. Other reactions such as (3) and (9) - (13) were included using selected constants from the literature which are given in Table A1.

The flow system characteristics were simulated by adding appropriate terms to the differential equations describing the kinetics. The gas components coming into the cell contribute both positive and negative terms to their respective differential equations, since they flow both into and out of the cell. The products formed in the cell, however, contribute only negative terms due to their being swept from the cell. The differential equations were integrated by a modified Gear method, and the apparent quantum yield Φ calculated for each set of conditions.

TABLE A1

Reaction rate constants at 298 K

Reaction	Rate constant		Reference
$2F + M \rightarrow F_2 + M$	3×10^{13}	$\text{cm}^6 \text{mol}^{-2} \text{s}^{-1}$	A4
$F + H_2 \rightarrow HF + H$	1.5×10^{13}	$\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	A5
$H + H + M \rightarrow H_2 + M$	4.2×10^{15}	$\text{cm}^6 \text{mol}^{-2} \text{s}^{-1}$	A6
$H + F_2 \rightarrow HF + F$	2.1×10^{12}	$\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	A7
$H + F + M \rightarrow HF + M$	1×10^{16}	$\text{cm}^6 \text{mol}^{-2} \text{s}^{-1}$	A8

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