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Photochemistry of Chloro Complexes of Uranium(IV) and Dioxouranium(VI)

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The photochemistry of UCl_6^{2-} *and of* $UO_2Cl_4^{2-}$ *in acetonitrile solutions at 254 nm has been investigated under various experimental conditions. The main features of photochemical behaviour of* UCl_6^{2-} *are as follows: a) in non-deaerated solution the U(IV) undergoes an oxidation to* $UO_2Cl_4^{2-}$*, proceeding with a chain mechanism; b) in deaerated solution the* UCl_6^{2-} *is also transformed to the hexavalent state (*$UO_2Cl_4^{2-}$*), then photoreduced to the tetravalent; c) in the presence of dry HCl, the* UCl_6^- *compound is obtained.*

The photochemical process of $UO_2Cl_4^{2-}$ *can be summarized with the following points: a) in non-deaerated solution no photoreaction occurs; b) in deaerated solution the* $UO_2Cl_4^{2-}$ *undergoes a reduction to chloro complex of* UO^{2+} *and c) in the presence of HCl, the* UCl_6^- *is obtained.*

By analysis of the kinetic data, the quantum yields for all process are calculated and the photoreaction mechanisms are proposed in agreement with experimental observations.

Introduction

The photochemical studies dealing with transition metal coordination compounds constitute at present a rather developed area of photochemistry;[1] however, in the field of the actinide compounds only few scattered results on U(III) and U(IV) have been reported[2–5] and the most extensive investigations concern exclusively the photoreaction of the uranyl ion with organic substrate and iodine.[6] The numerous results are not devoid of contradictions and unresolved problems. Therefore we considered it interesting to renew systematic investigations in actinide photochemistry, in order to establish correlations or draw general conclusions.

In this research we turned our interest to simple systems, the tetra(ethyl)ammonium salts of UCl_6^{2-} and of $UO_2Cl_4^{2-}$ in acetonitrile solution. These complexes exhibit close correlations in their photochemical behaviour, as indicated by preliminary results reported in an earlier communication.[7]

The present investigation elucidates the kinetics and the mechanisms of these complex reactions, the nature and the fate of the probable intermediates and the role of the inorganic substrates. Moreover the results suggest the possibility of preparing, by photochemistry, compounds of uncommon valence uranium.

Experimental

Materials

$[(C_2H_5)_4N]_2UCl_6$ was prepared by adding tetraethylammonium chloride in 12*M* HCl to the U(IV) stock solutions adjusted to 8–12*M* HCl according to a reported method.[8] $[(C_2H_5)_4N]_2UO_2Cl_4$ was prepared by mixing solutions of uranyl(VI) chloride and tetraethylammonium chloride in 8–12*M* HCl.[9] $(C_2H_5)_4NUCl_6$ was prepared by heating a sealed chlorine saturated slurry of 0.3 g of $[(C_2H_5)_4N]_2UCl_6$ per ml of acetonitrile to 80–90° C as in a reported procedure.[10]

Acetonitrile was Merck spectrograde (H_2O = 0.03%). When used in dry form, the solvent was dried by reflux over anhydrous $CaSO_4$ for 24 hours followed by distillation in dry nitrogen current. All other common chemicals were reagent grade.

Apparatus

Radiation of 254 nm was obtained using the irradiation equipment previously described.[11] The intensity of the incident light measured by a ferric oxalate actinometer[12] was of the order of 10^{-7} Nhν/min.

Spectrophotometer measurements were carried out with an Optica CFN1 spectrophotometer with the cell compartment thermostated at 25° C.

Procedures

Samples (3 ml) of solutions containing the desidered uranium or uranyl compound concentration ($0.1–1 \times 10^{-4}M$) were introduced into standard spectrophotometric cells. The solutions were deaerated by bubbling a stream of very pure nitrogen through glass needles for a long time and sealing the cells.

When the HCl presence was required, the solution was saturated with a stream of dry HCl and then the cell was sealed.

Kinetics of the reaction were followed spectrophotometrically in the suitable region of absorption until photostationary state was attained.

Results

Photochemistry of UCl_6^{2-}

Undried acetonitrile solution of UCl_6^{2-} exposed at radiations of 313 and 333 nm (corresponding to the 5f→6d transition bands), 405 and 436 nm (corresponding to the internal 5f transition bands) did not show any spectral change even after prolonged irradiation. Irradiation with light of 254 nm (corresponding to the $\pi \rightarrow 5f$ electron tranfer bands)[13] resulted in photochemical changes which were followed spectrophotometrically. The photoreaction path was different in the presence or absence of air.

In *non-deaerated solutions,* the excitation caused a complete oxidation of UCl_6^{2-} to a U(VI) compound, identified as $UO_2Cl_4^{2-}$ by comparison with the absorption spectra of this compound prepared independently. From spectral data of the irradiated solutions, it was found that at all times only the two species UCl_6^{2-} and $UO_2Cl_4^{2-}$ were present (Figure 1). The apparent quantum yields were calculated by the differential equation

$$-\frac{d[UCl_6^{2-}]}{dt} = \Phi\frac{I}{V}\cdot\frac{1-10^{-D}}{D}\cdot\varepsilon_{UCl_6^{2-}}[UCl_6^{2-}] \quad (1)$$

where:

Φ quantum yield for the $[UCl_6^{2-}]$ decrease;
V volume in liters;
ε molar extinction coefficient at 254 nm;
I the light intensity (einsteins/min);
D total optical density at the wave length of irradiation;

$\frac{1-10^{-D}}{D}\cdot\varepsilon_{UCl_6^{2-}}[UCl_6^{2-}]$ = fraction of absorbed light by the UCl_6^{2-}; $\frac{d|UCl_6^{2-}|}{dt}$ was determined graphically from the slope of the experimental curve, $[UCl_6^{2-}]$ *vs.* time, at appropriate time intervals.

It was found that the Φ values increased with time. This suggested that the photochemical excitation leads to events initiating a chain reaction which results in the $UO_2Cl_4^{2-}$ formation. This supposition was strengthened by observation that, upon interrupted excitation, the $UO_2Cl_4^{2-}$ formation proceeded to completion in the dark.

In *deaerated solutions* the UCl_6^{2-} irradiation led to spectral variations (Figure 2) which could be fitted, assuming again oxidation of U(IV) to $UO_2Cl_4^{2-}$;

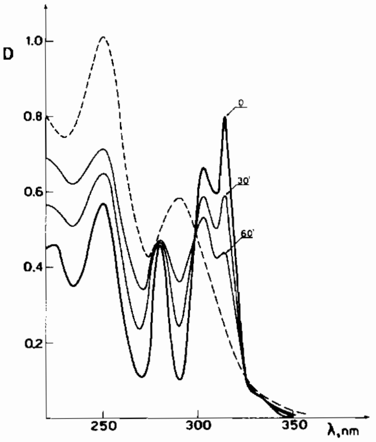

Figure 1. (——) Spectral changes of the non-deaerated acetonitrile solution of UCl_6^{2-}. Numbers refer to the irradiation time in minutes. (----) Absorption spectrum of $UO_2Cl_4^{2-}$.

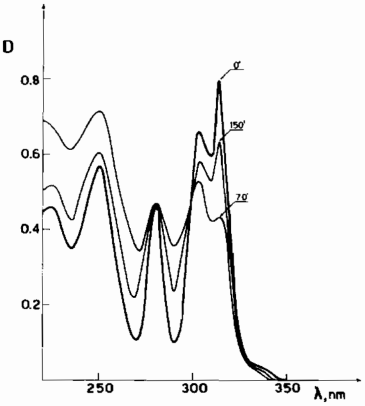

Figure 2. Spectral changes of the deaerated acetonitrile solution of UCl_6^{2-} with irradiation time.

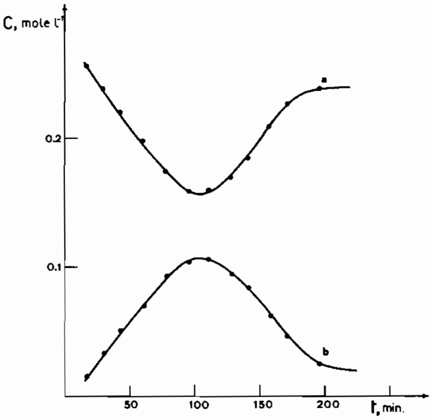

Figure 3. Change of composition in the deaerated UCl_6^{2-} solution with irradiation time; a = 10^3 $[UCl_6^{2-}]$; b = 10^3 $[UO_2Cl_4^{2-}]$.

moreover the process did not go to completion, the U(VI) underwent a back reduction to UCl_6^{2-} and a photochemical stationary state was attained (Figure 3).

Upon interrupted excitation, interesting post effects were observed. In the dark the photochemically attained state was stable in the absence of air; if the reaction cell was unsealed, fast and complete oxidation to $UO_2Cl_4^{2-}$ occurred. This suggests the presence in irradiated solution of a species initiating a chain reaction with oxygen. By bubbling dry HCl before back reduction, a small amount of UCl_6^- (of the order of $10^{-6}M$) was immediately detectable by the absorbance at 390 nm. On the basis of our experimental observations of the reversibility of equilibrium U(V) $\rightleftarrows$ U(IV) + U(VI) in function of dry HCl, we ascribed the U(V) formation to deoxygenation of an intermediate, probably $UOCl_5^{2-}$ rather than to change of the indicated equilibrium. At photostationary state attained, by nitrogen bubbling and subsequent irradiation, the UCl_6^{2-} again underwent the oxidation and back reduction until a new stationary state was obtained. Therefore a species which was removed by nitrogen has to take part in the final equilibrium.

Further experiments were carried out in order to elucidate the partecipation of free radicals and the role of inorganic substrate (H_2O and HCl) in the reaction path.

In samples saturated with propylene, a radical trapping agent, the oxidation rate of U(IV) to U(VI), was slowed down, but the back reduction did not occur. Thus it is reasonable to believe that the reaction mechanism involves free radicals, like Cl· and H·.

When dried acetonitrile was used, the irradiation caused small spectral changes and a stationary state was quickly attained. This elucidates the importance of inorganic substrate, as H_2O, in the reaction.

In solutions saturated with dry HCl, the UCl_6^{2-} was converted photochemically to UCl_6^-, identified by comparing the absorption spectra with those of this compound independently prepared (Figure 4). The oxidation did not go to completion and small hydrolysis side-reactions, revealable by the appearance of $UO_2Cl_4^{2-}$, were observed.

The analysis of the photoxidation kinetics revealed interesting features.

In the experimental conditions, after a short induction period, the rate of U(IV) disappearance and of U(VI) or U(V) formation were equal; moreover the isosbestic points were almost constant. These observations suggested that the intermediates are unstable and their concentrations much smaller than those of U(IV) and U(VI) or U(V). Therefore the Bodenstein state approximation is applicable and the rate determining step in the kinetics of overall reaction $UCl_6^{2-} \xrightarrow{h\nu} UO_2Cl_4^{2-}$ or $UCl_6^{2-} \xrightarrow{h\nu} UCl_6^-$ is the photochemical primary reaction. The rate of the photoreaction is given by the equation (1) which can be rearranged as

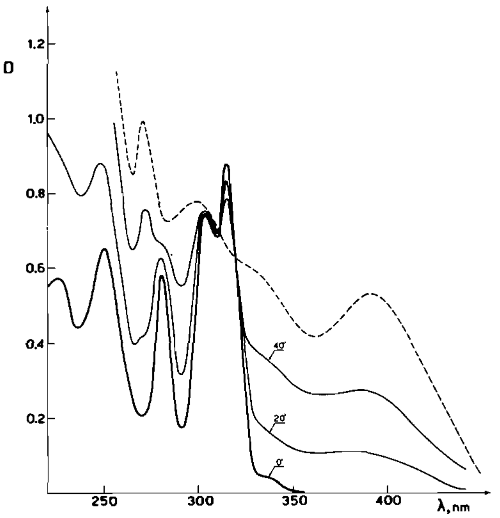

Figure 4. (——) Spectral changes of the UCl_6^{2-} acetonitrile solution, satured with dry HCl. Numbers refer to the irradiation time in minutes. (----) Absorption spectrum of UCl_6^-.

$$-\frac{d[UCl_6^{2-}]}{[UCl_6^{2-}]}\frac{D}{1-10^{-D}} = \Phi\frac{I}{V}\varepsilon_{UCl_6^{2-}}\,dt \qquad (2)$$

If we let $A = \Phi\frac{I}{V}\varepsilon_{UCl_6^{2-}}$ and $F([UCl_6^{2-}]) = \int\frac{d[UCl_6^{2-}]}{[UCl_6^{2-}]}\frac{D}{1-10^{-D}}$, then we can write $F(|UCl_6^{2-}|) = -A\ t + \text{const.}$; a plot of $F([UCl_6^{2-}])$ *vs.* time gives the constant A and hence Φ. In order to find $F([UCl_6^{2-}])$, the function $D/1-10^{-D}$ can be represented as the power series[14]

$$\frac{D}{1-10^{-D}} = \frac{1}{2.3} + \frac{D}{2} + \frac{D^2\times 2.3}{12}\ \ldots\ldots$$

Figure 5 shows various plots obtained using the experimental data. In all cases good straight lines were obtained omitting the first and the last points close to the back reaction beginning. The found value of the quantum yield is the same in the presence or absence of dry HCl: $\Phi = 0.037 \pm 0.002$.

The analysis of the kinetics of the inverse reaction $UO_2Cl_4^{2-} \rightarrow UCl_6^{2-}$ shows that, over a range far from the initial and final points of the reaction, the experimental data fit the differential equation

$$-\frac{d[UO_2Cl_4^{2-}]}{[UO_2Cl_4^{2-}]}\frac{D}{1-10^{-D}} = \Phi\frac{I}{V}\varepsilon_{UO_2Cl_4^{2-}}\,dt \qquad (3)$$

where each symbol has its usual meaning and Φ is the quantum yield for the $[UO_2Cl_4^{2-}]$ decrease.

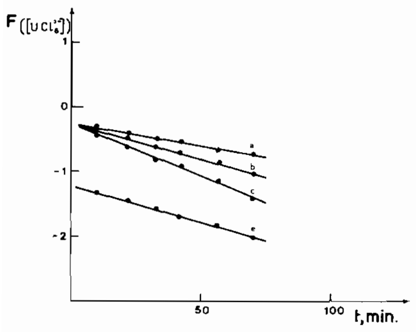

Figure 5. Plots of F([UCl$_6$$^{2-}$]) *vs.* time: a, b and c are for the same concentration (0.16 × 10^{-3}M), and for I = 1.7 × 10^{-7}, 2.8 × 10^{-7} and 4 × 10^{-7} Nhν/min respectively; b and e are for the same light intensity, and for [UCl$_6$$^{2-}$] = 0.16 × 10^{-3} and 0.41 × 10^{-3}M respectively.

Making the same assumptions as above, the plots of F([UO$_2$Cl$_4$$^{2-}$]) *vs.* time are good straight lines and by the slope the quantum yield is calculated: Φ = 0.05 ± 0.002.

Photochemistry of $UO_2Cl_4{}^{2-}$

The photosensibility of deaerated acetonitrile solutions, 10^{-3}–10^{-4}M in UO$_2$Cl$_4$$^{2-}$, was explored at 333, 313 and 254 nm. We found that only the irradiation with light of 254 nm was active and led to regular variations of absorptions spectra with a constant isosbestic point (Figure 6). At the photostationary state, in the dark the photoprodukt a) underwent a very slow oxidation to U(VI), b) returned rapidly to UO$_2$Cl$_4$$^{2-}$, if the reaction cell was unsealed, c) by bubbling of dry HCl was converted immediately to UCl$_6$$^{2-}$ of concentration equal to that of initial U(VI), d) did not react when N(C$_2$H$_5$)$_4$Cl was added. On the basis of these observations, we suggest that the photoreaction was a complete U(VI) reduction to a halogenated complex of UO^{2+}.

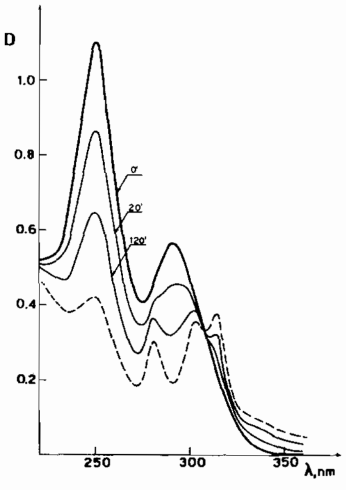

Figure 6. (——) Spectral changes of the deaerated acetonitrile solution of UO$_2$Cl$_4$$^{2-}$ with irradiation time. (----) Absorption spectrum of UO^{2+} chloro complex.

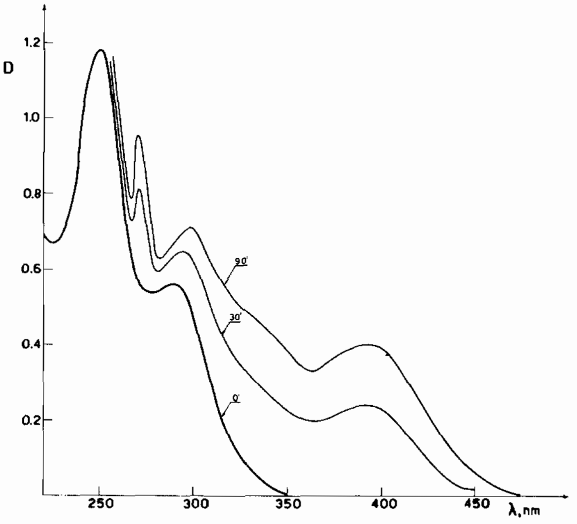

Figure 7. Spectral changes of the UO$_2$Cl$_4$$^{2-}$ acetonitrile solution, satured with dry HCl. Numbers refer to the irradiation time in minutes.

In the presence of dry HCl the irradiation of UO$_2$Cl$_4$$^{2-}$ resulted in a reduction to UCl$_6$$^{-}$ (Figure 7), but the reaction did not go to completion.

By analysis of kinetic data, it was found that the rate of the UO$_2$Cl$_4$$^{2-}$ photoreduction was the same in the presence or absence of HCl and was equal to the UO^{2+} or UCl$_6$$^{-}$ formation. Making the usual steady state, the rate determining step for overall reaction is the

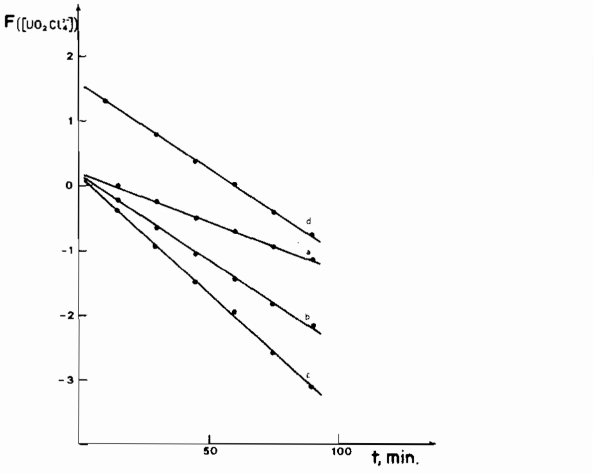

Figure 8. Plots of F([UO$_2$Cl$_4$$^{2-}$]) *vs.* time: a, b and c are for the same concentration (0.22 × 10^{-3}M) and for I = 1.7 × 10^{-7}, 2.8 × 10^{-7} and 4 × 10^{-7} Nhν/min respectively; b and d are for the same light intensity, and for [UO$_2$Cl$_4$$^{2-}$] = 0.22 × 10^{-3} and 0.42 × 10^{-3}M respectively.

photochemical primary reaction and the kinetics could be expressed by the differential equation (3). The experimental data were in agreement with the proposed rate law, as shown by the observation that the plots (Figure 8) of $F([UO_2Cl_4^{2-}])$ *vs.* time are straight lines. By the slope, the value of quantum yield, independent of the presence or absence of HCl, was calculated: $\Phi = 0.05$. This value was equal to that calculated in the back reaction of the photochemistry of UCl_6^{2-}.

Further experiments showed that the effect of H_2O percentage in the solvent was negligible and that in aerated solutions the reduction process did not occur and the solution was photochemically almost stable.

Discussion

The main feature of photochemical behaviour of the UCl_6^{2-} and the $UO_2Cl_4^{2-}$ complexes is the close dependence of photoreactivity on the type of excited state reached upon irradiation. In accordance with recent assignments,[13–15] in both complexes irradiation with 254 nm light generates charge transfer excited states, involving promotion of an electron from an orbital localized on the Cl^- to the metal. We can then predict that predominant primary photoreaction should be oxidation of Cl^- and reduction to a lower oxidation state of uranium.

At first we can try to elucidate the mechanism of $UO_2Cl_4^{2-}$ reduction because this reaction is a part of the overall photochemistry of UCl_6^{2-}.

A mechanism which agrees with the observed rate law (3) and allows us to interpret the experimental results involves a charge transfer species of U(V) and may be schematized as follows:

$$[UO_2^{2+}(Cl^{1-})_4]^{2-} \xrightarrow[\text{rate determining step}]{h\nu} [UO_2^{+}(Cl^{1-})_3Cl^{0}]^{2-} \tag{4}$$

$$[UO_2^{+}(Cl^{1-})_3Cl^{0}]^{2-} \xrightarrow[\text{fast}]{} [UO_2^{2+}(Cl^{1-})_4]^{2-} \tag{5}$$

$$[UO_2^{+}(Cl^{1-})_3Cl^{0}]^{2-} \xrightarrow[\text{fast}]{} UO^{2+} + 3Cl^- + ClO^- \tag{6}$$

The chloride can react rapidly with Cl(I) formed in (6), to give dissolved chlorine which has been shown to oxidize U(IV) only slowly.[16]

If oxygen is present, the fast reoxidation of UO^{2+} species by the reaction $UO^{2+} + {}^1/_2O_2 \rightarrow UO_2^{2+}$ prevents the experimental observation of reduction U(VI)→U(IV).

In the presence of dry HCl, the UO_2^+ species is rapidly deoxygenated and a U(V) complex is stabilized:

$$[UO_2^{+}(Cl^{1-})_3Cl^{0}]^{2-} + 2HCl \xrightarrow[\text{fast}]{} UOCl_5^{2-} + Cl\cdot + H_2O \tag{7}$$

$$UOCl_5^{2-} + 2HCl \xrightarrow[\text{fast}]{} UCl_6^{-} + Cl^- + H_2O \tag{8}$$

The fact that the reaction did not go to completion can be attributed to side-reaction of hydrolysis and to the reaction

$$UCl_6^{-} + Cl^- \xrightarrow[\text{very slow}]{} UCl_6^{2-} + Cl \tag{9}$$

For UCl_6^{2-} irradiation, no net reduction of the metal is detected. In this case, it is reasonable to postulate that the instantaneous charge transfer species formed (10) reacts via heterolytic bond breaking to give radical Cl· and a U(III) species kinetically labile (12). This has reducing properties so strong that the hydrogen is evolved from the water present[17] and back reoxidation to U(IV) occurs (13). The ligand photolabilized as Cl· radical can again oxidize the U(IV) as the reactions (14) and (15). A scheme of the mechanism consistent with the observed rate law (2) may be written as follows:

$$[U^{4+}(Cl^{1-})_6]^{2-} \xrightarrow[\text{rate determining step}]{h\nu} [U^{3+}(Cl^{1-})_5Cl^{0}]^{2-} \tag{10}$$

$$[U^{3+}(Cl^{1-})_5Cl^{0}]^{2-} \xrightarrow[\text{fast}]{} [U^{4+}(Cl^{1-})_6]^{2-} \tag{11}$$

$$[U^{3+}(Cl^{1-})_5Cl^{0}]^{2-} + H_2O \xrightarrow[\text{fast}]{} [U^{3+}(Cl^{1-})_5H_2O]^{2-} + Cl\cdot \tag{12}$$

$$[U^{3+}(Cl^{1-})_5H_2O]^{2-} \xrightarrow[\text{fast}]{} UO^{2+} + HCl + H\cdot + 4Cl^- \tag{13}$$

$$UCl_6^{2-} + Cl\cdot + H_2O \xrightarrow[\text{fast}]{} UOCl_5^{2-} + 2HCl \tag{14}$$

$$UO^{2+} + Cl\cdot + 4Cl^- \xrightarrow[\text{fast}]{} UOCl_5^{2-} \tag{15}$$

$$2UOCl_5^{2-} \xrightarrow[\text{fast}]{} UO_2Cl_4^{2-} + UCl_6^{2-} \tag{16}$$

The radicals formed can disappear by the fast reactions:

$$2H\cdot \rightarrow H_2 \tag{17}$$

$$2Cl\cdot \rightarrow Cl_2 \tag{18}$$

$$Cl\cdot + H_2 \rightarrow HCl + H\cdot \tag{19}$$

The $UO_2Cl_4^{2-}$ formation (16) proceeds until the H_2 concentration becomes important; at this point the molecular hydrogen reacts with chlorine radicals (19) and inhibits further U(IV) oxidation. The $UO_2Cl_4^{2-}$ back photoreduction by the previously described mechanism (4)–(6) becomes the sole detectable reaction; it is noted that the species UO^{2+} is deoxygenated by the stoicheiometric amount of HCl, formed in the overall reaction, and UCl_6^{2-} is obtained. At the final photostationary state, the rate of the reaction (10) and (13) are the same. The concentration of UCl_6^{2-}

should be very close to the initial one; in effect a less concentration (about 90% of that initial) experimentally is observed, probably owing to undetected side-reaction.

Our assumption is supported by the experimental observations: a) the back reduction begins always at constant value of $[UO_2Cl_4^{2-}]$ and therefore of $[H_2]$ independently of the initial concentration of the complex; b) in the presence of propene, the radicals $H\cdot$ are trapped and the reduction does not occur; c) by removing the hydrogen with nitrogen, the photoreaction occurs again.

In the presence of dry HCl, the acid plays the role of the H_2O according to the reactions (20)–(22).

$$[U^{3+}(Cl^{1-})_5Cl^0]^{2-} + HCl \xrightarrow[\text{fast}]{} [U^{3+}(Cl^{1-})_5HCl]^{2-} + Cl\cdot \quad (20)$$

$$[U^{3+}(Cl^{1-})_5HCl]^{2-} \xrightarrow[\text{fast}]{} [U^{4+}(Cl^{1-})_6]^{2-} + H\cdot \quad (21)$$

$$UCl_6^{2-} + Cl\cdot \underset{\text{very slow}}{\overset{\text{fast}}{\rightleftharpoons}} UCl_6^{-} + Cl^{-} \quad (22)$$

For the photochemistry of UCl_6^{2-} in non-deaerated solutions, the effect of oxygen on reaction pathways can be ascribed to ready formation of $HO_2\cdot$ radicals by hydrogen atoms and to a chain initiation. This accounts for the observed rate increasing and for oxidation in the dark after irradiation. A suitable mechanism can be written as

$$H\cdot + O_2 \rightarrow HO_2\cdot \quad (23)$$

$$HO_2\cdot + UCl_6^{2-} \xrightarrow{H_2O} UOCl_5^{2-} + H_2O_2 + HCl \quad (24)$$

$$UCl_6^{2-} + H_2O_2 \rightarrow UOCl_5^{2-} + OH\cdot + HCl \quad (25)$$

$$UCl_6^{2-} + OH\cdot \rightarrow UOCl_5^{2-} + HCl \quad (26)$$

$$UOCl_5^{2-} + H_2O_2 \rightarrow UO_2Cl_4^{2-} + OH\cdot + HCl \quad (27)$$

$$H_2O_2 + OH\cdot \rightarrow HO_2\cdot + H_2O \quad (28)$$

This scheme is in agreement with those proposed for oxidation of U(IV) by H_2O_2 and O_2 in different conditions.[18]

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