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Photochemistry of Actinide Complexes. III. The Photoproduction Mechanism of Uranium(V) Oxochloro-Complexes

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The photochemical preparation of oxochloro-complexes $UOCl_3$, $UOCl_5(C_5H_5NH)_2$, *and U(V) ethoxide,* $U(OC_2H_5)_5$, *is described. The absorption spectra of these U(V) complexes were measured and discussed. Irradiation of* $[UO_2Cl_2\cdot(C_5H_5N)_2]$ *complex in dry ethanol and in the presence of radical scavengers is considered to yield* UO_2Cl *as primary photoproduct which gives rise by thermal or secondary photochemical reaction to* $UOCl_3$. *Thermal reaction of* $UOCl_3$ *with pyridinium hydrochloride, formed in the photoreaction mixture, leads to* $UOCl_5(C_5H_5NH)_2$ *formation. Subsequent photoreaction of* $UOCl_5(C_5H_5NH)_2$ *produces* $U(OC_2H_5)_5$. *The photochemical pathway to U(V) complexes compatible with the experimental observations is proposed.*

Introduction

The photochemistry of the uranyl ion, UO_2^{2+}, either complexed or as an aquo ion, has attracted a great amount of interest over a long period of time[1,2] and even today it remains a widely studied field.[3]

The uranyl ion, which is very stable and difficult to reduce in the dark, generally undergoes a reduction reaction upon light excitation, yielding an unstable U(V) species with concomitant oxidation of the ligands or other species present in the solution.

The general features of the photoreaction types involving uranyl ions are: a) Photoredox reaction of UO_2^{2+} moiety as a consequence of a LMCT excitation. b) Electron transfer from some organic or inorganic substrates to UO_2^{2+}. Such photoreaction may originate from an encounter between the photoexcited uranyl ion and a molecule of the substrate. Thus, for UO_2^{2+}–aliphatic alcohol systems, the photoreaction involves the abstraction of an α-hydrogen atom, resulting in a transient alcohol radical together with the intermediate aquouranium(V) species.[4–6] c) In the UO_2^{2+} substrate system a sensitized auto-oxidation can be observed in the presence of oxygen. The photosensitized reaction may be considered as an oxidation of the substrate which is catalyzed by the excited UO_2^{2+} ion.[2]

In many of the reported uranyl ion photoreactions, a uranium(V) species was claimed to be a product of the primary photoprocess.[2,3] However, since the experimental conditions were such as to cause its rapid dismutation, no experimental evidence of its formation was ever reported.

Starting from the knowledge that the U(V) dismutation rate is greatly inhibited by the presence of U(VI)[7] and by ammonium salts[8], we recently carried out the photolysis of the $[UO_2Cl_2(C_5H_5N)_2]$ complex in dried ethanol under preparative conditions.[9] This permitted us to detect and also isolate some of the U(V) species from the photoreaction mixture.

As a result of our continuing research on the photochemistry[9] of U(VI) complexes, we are able now to report a photochemical route to $UOCl_3$, its infrared spectrum and the general features of the mechanism for the formation of U(V) oxochloro-complexes.

Experimental

All operations were carried out in an inert atmosphere dry box, using dried oxygen-free argon or helium.

Dipyridine uranyl chloride $[UO_2Cl_2(C_5H_5N)_2]$ (I) was prepared and purified with standard methods.[9]

2-Methyl-2-nitrosopropane was prepared using Emmons' method.[10] All the solvent used were degassed prior to use and distilled under argon from lithium aluminium hydride.

Apparatus

Photochemical reactions were carried out using a Hanau Q 400 mercury vapor lamp whose output was filtered through an Ealing TFP interference filter in order to obtain a 405 nm radiation.

Spectroscopic Measurements

Infrared spectra were recorded on a Beckman IR 10 or Perkin–Elmer 257 spectrophotometer, having an accuracy of ± 5 cm^{-1}, and calibrated with a polystyrene film. Samples were mulled in either nujol or hexachlorobutadiene, and they were also run in KBr pellets.

Electronic spectra were obtained from samples that were mulled in nujol and smeared onto KBr pellets, using a Perkin–Elmer 323 recording spectrophotometer.

Preparation of U(V) Compounds

$UOCl_3$ (II)

$[UO_2Cl_2(C_5H_5N)_2]$ (6.3 gr) was added to 30 ml of dried ethanol in a quartz reaction tube that contained 2-methyl-2-nitrosopropane as a radical trapping agent. The presence of 2-methyl-2-nitrosopropane did not affect the stability of $UO_2Cl_2(C_5H_5N)_2$ solutions in the dark. Nitrogen was then bubbled into the mixture for 30 minutes. The reaction mixture was then degassed by alternatively freezing and thawing it while under vacuum to ensure oxygen removal. After the third thawing, the system was filled with pure nitrogen. The reaction vessel was then placed within a pyrex jacket cooled by a rapid flow of air and irradiation started. The mixture, after some irradiation time, turned green and a yellow precipitate began to form within a few hours. The photoreaction was then stopped in order to prevent the production of a large amount of possible secondary thermal and/or photochemical products. The resulting yellow amorphous precipitate was recovered under vacuum and dried at room temperature. This precipitate was identified as UO_3 from its infrared spectrum and elemental analysis. The UO_3 obtained contained 83.31% of Uranium (UO_3 requires 83.22%). The dark green solution was also evaporated under vacuum and the crude residue, which consisted of a mixture of $UOCl_3$, $C_5H_5N \cdot HCl$ and unreacted starting materials, was crystallized from a chloroform–ethanol mixture and then from acetone–nitromethane, to give pure $UOCl_3$ (II) in the form of extremely hygroscopic crystals that are soluble in absolute ethanol and almost insoluble in acetone. No formation of II was observed upon irradiation of I for reasonable periods in the absence of 2-methyl-2-nitrosopropane. The electronic spectrum of these irradiated solutions showed an increasing U(IV) concentration with irradiation time but little or no U(V).

Compound II gave elemental analysis that was consistent with its proposed formula. *Anal.* Calcd. for $UOCl_3$: U, 66.05; Cl, 29.51. Found: U, 66.52; Cl, 29.04. The characteristic infrared absorption frequencies are: 450, 615, 750, 855 and 950 cm^{-1}. These results are similar to those found for U(V) oxide trichloride that was prepared heating UO_3 and $MoCl_5$ together[11], according to the reaction:

$$MoCl_5 + UO_3 \rightarrow UOCl_3 + MoO_2Cl_2$$

TABLE I. Analytical Results and Infrared Spectrum of $(C_5H_5NH)_2UOCl_5$.

Element	Analytical Results	
	Calcd. for $(C_5H_5NH)_2UOCl_5$	Found
U	40.24	40.20
Cl	29.97	29.65
C	20.31	20.35
N	4.74	4.70
H	2.04	2.40

Infrared Spectrum

Infrared bands, not directly attributable to the organic cation, are found at 5055, 5030, 1550, 935, and 830 cm^{-1}

$(C_5H_5NH)_2UOCl_5$ (III)

A sample of $UOCl_3$ (0.1 gr) was dissolved in dried ethanol. Reagent grade $C_5H_5N \cdot HCl$ (0.84 gr) was then dissolved in this solution. The mixture was allowed to react slowly with thorough agitation for some hours. The solvent was then removed under vacuum at room temperature and the residue was then treated with nitromethane and filtered. An excess of dried acetone was added to the solution. The resulting crystals were filtered and washed with acetone and then dried in argon. The electronic spectrum of the product showed that it contained no more than 2% of U(IV) and U(VI) species. The product was characterized by means of its elemental analysis and infrared and electronic spectra (Table I and Figure 1).

Compound III can also be obtained from the photoreaction mixture when photolysis of I is carried out for long periods.[9]

$U(OC_2H_5)_5$ (IV)

Complex III is photosensitive under conditions of its formation. The irradiation of III in dried ethanol, with the same light source used to promote photoreaction of I and III led to production of a dark brown solution after a long irradiation time. The solvent was then evaporated under vacuum, and the uranium(V) ethoxide was recovered from the residue by distillation with a diffusion pump vacuum. IV was identified by comparing its elemental analysis and infrared and electronic spectra with those of an authentic sample.[9, 12]

Results and Discussion

The photolysis of $[UO_2Cl_2(C_5H_5N)_2]$ in ethanol solutions in the presence of a radical scavenger gave known compounds which were identified by comparing their physical and chemical properties with those of authentic samples.

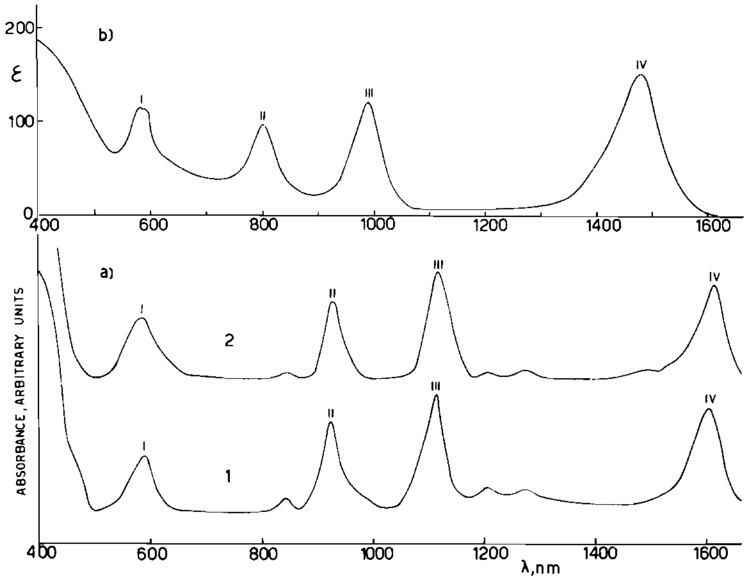

Figure 1. Electronic spectra of the Uranium(V) complexes: a) 1, solid $UOCl_3$; 2, solid $UOCl_5(C_5H_5NH)_2$
b) $U(OC_2H_5)_5$ in CCl_4.

When $UOCl_3$ (II) was added to water or moist ethanol, dismutation to U(IV) and U(VI) occurred, as was determined spectrophotometrically.

The infrared and electronic spectra of II showed features which are only characteristic of U(V) oxochloro complexes.[7,8] Above all, there are two very strong and narrow infrared bands at 950 and 855 cm^{-1}, as is found for $UOCl_5(C_5H_5NH)_2$[9]. Since there is theoretical and experimental evidence[13–15] that there is only one M=O stretching frequency for oxometal(V) complexes, it is improbable that they are both due to uranium–oxygen vibrations. At present, only the 950 cm^{-1} infrared band can be assigned to a U=O stretching frequency. Pertinent evidence for this attribution can be: i) the UO_3 infrared spectrum presents a band at 930 cm^{-1} which is assignable to the same stretching mode; ii) the metal–oxygen multiple bond stretching frequencies for several oxometal complexes are all much closer to the 950 cm^{-1} value[13,14]; iii) in the electronic spectrum of U(V) oxochloro-complexes there are vibronic transitions with a separation of ±820 cm^{-1} from the 0–0 pure electronic band.[8] On the basis of these observations, it is more likely that the 950 cm^{-1} infrared absorption is due to the metal–oxygen stretch in the ground state than 855 cm^{-1} absorption.

The electronic spectra of uranium(V) oxochloro complexes and those of $U(OC_2H_5)_5$ are shown in Fig. 1. It appears that all the compounds present four transition groups as are found in hexahalide complexes.[16] These bands, as foreseen theoretically by Selbin and others[7,8], are mainly the result of different vibronic transitions but they also could arise from further removal of the non-Kramer degeneracies from both Γ_8 and Γ_8' levels of the 5f manifold. This degeneracy removal can arise form the lowering of the O_h symmetry of the complexes to the C_{4v} symmetry. These considerations receive support from the splitting diminution presented by the absorptions going from the oxochloro-complexes to lower symmetric $U(OC_2H_5)_5$ (Fig. 1 and Table II). In connection with this result, a particular importance also assumes the shift towards higher energies of all $U(OC_2H_5)_5$ absorptions in comparison to the oxochloro-complexes. The energy level shifts between the compounds almost surely reflect the increased crystal field in $U(OC_2H_5)_5$.[7]

TABLE II. Electronic Absorptions Found for U(V) Complexes.

Compound	Transitions (cm^{-1})			
	I	II	III	IV
$UOCl_3$	16,949	10,810	8,849	6,250
$UOCl_5(C_5H_5NH)_2$	17,064	10,928	8,850	6,300
$U(OC_2H_5)_5$	17,255	12,500	10,152	6,735

Several previous studies on the U(VI) photooxidation of aliphatic alcohols, including e.s.r. experiments[5] and laser flash photolysis results,[17] have indicated the mechanism reported in the equation

$$UO_2Cl_2 + CH_3CH_2OH \rightarrow UO_2Cl + HCl + CH_3\dot{C}HOH \quad (1)$$

followed by a rapid dismutation of the UO_2Cl compound. We believe our system has the same primary photoreaction, where UO_2Cl is formed but does not dismutate:

$$[UO_2Cl_2(C_5H_5N)_2] \xrightarrow{h\nu} [UO_2Cl_2(C_5H_5N)_2]^* \quad (2)$$

$$[UO_2Cl_2(C_5H_5N)_2]^* + CH_3CH_2OH \rightarrow UO_2Cl + C_5H_5N \cdot HCl + CH_3\dot{C}HOH + C_5H_5N \quad (3)$$

$$\text{Radical scavenger} + CH_3\dot{C}HOH \rightarrow \text{Products} \quad (4)$$

This view is supported by our experimental results: i) The radical is trapped by the 2-methyl-2-nitrosopropane. This avoids a possible action of the same radical on the UO_2Cl species. ii) The formation in the primary process of $C_5H_5N \cdot HCl$, whose presence for the arguments above cited[8] avoids UO_2Cl dismutation.

Under the conditions of the photochemical preparation, compound II must arise from a thermal or secondary photochemical reaction of a primary photoproduct UO_2Cl which is indicated by the failure to isolate II when the photoreaction was carried out in the absence of a radical scavenger.

The chemical mechanism of the reaction leading to $UOCl_3$ and UO_3 could take place as follows: the primary photoproduct, UO_2Cl, interacts with the UO_2Cl_2 moiety of the excess of the starting complex, with the following thermal reaction:

$$UO_2Cl + [UO_2Cl_2\,(C_5H_5N)_2] \rightarrow UO_3 + UOCl_3 + 2C_5H_5N$$

This reaction is in agreement with earlier chemical experiments on the basis of which the formation of $UOCl_3$ was found in the thermal rearrangement of UO_2Cl, in the presence of UO_2Cl_2[11]. The analogy is not a perfect one since our mechanism postulates a UO_2Cl_2 coordinated reaction with UO_2Cl instead of free UO_2Cl_2. However, we would expect the UO_2Cl to be even more reactive in our photoreactive mixture.

The role that $UOCl_3$ plays in the formation of $UOCl_5^{2-}$ is seen from the experiments performed with dry pyridinium hydrochloride and uranium oxide trichloride. The reaction of $UOCl_3$ with $C_5H_5N \cdot HCl$ imparts a blue color to the $UOCl_3$ nitromethane solution, and the absorption spectra in the visible and near infrared region of the resulting compound accord with the spectra obtained from the $UOCl_5^{2-}$ oxochloride complex obtained photochemically. Finally, a comment on the photoproduction of $U(OC_2H_5)_5$ complex is necessary. It seems quite clear that a photochemical reaction is taking place since no $U(OC_2H_5)_5$ formation occurs under similar conditions in the absence of light. We suggest tentatively that the following photoreaction may occur:

$$[UOCl_5\,(C_5H_5NH)_2] \xrightarrow{h\nu} [UOCl_5\,(C_5H_5NH)_2]^* \quad (5)$$

$$[UOCl_5\,(C_5H_5NH)_2]^* + 3C_2H_5OH \rightarrow UO(OC_2H_5)_3 + 3HCl + 2C_5H_5N\ HCl \quad (6)$$

apparently producing the uranium oxide–alkoxide. However, under the conditions of the reaction, the oxide–alkoxide was converted by thermal and/or photochemical rearrangement without valency change into the uranium pentaalkoxide (eq. 7).

$$nUO(OC_2H_5)_3 \rightarrow U(OC_2H_5)_5 + U_{n-1}O_n(OC_2H_5)_{3n-5} \quad (7)$$

This behavior has a formal analogy to the thermal rearrangement that is proposed for the preparation of similar pentavalent alkoxide complexes of chromium, molybdenum and tungsten.[18]

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