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Photochemical Reactions of Uranyl Complexes. Dipyridine Uranyl Nitrate

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The photochemical behavior of $UO_2(C_5H_5N)_2(NO_3)_2$ in absolute ethanol was investigated with radiation of 254 nm, corresponding to absorption band of the coordinated pyridine. Spectrophotometric measurements were used to establish the nature and the kinetics of the photoreaction. The results show that intraligand excitations cause, in the primary photochemical act, the formation of $UO_2(C_5H_5N)(C_2H_5OH)(NO_3)_2$ complex. In addition, pyridine photolysis in a secondary photoprocess occurs, with the formation of 5-amino-2,4-pentadienal. The reaction product between $UO_2(NO_3)_2$ and the compound formed in the photolysis of pyridine has been isolated and characterized as $UO_2(NO_3)_2(H_2N–CH=CH–CH=CH–CHO)$ by physico-chemical measurements.

Introduction

The photochemical studies dealing with uranium compounds concern the various reactions of uranyl ion, either complexed or as an aquo ion.[1]

While the nature of the excited states of uranyl ion is still an unresolved problem, it is thought that the transitions in the visible and near ultraviolet involve excitation of a bonding electron to a nonbonding orbital.[2] Since the photochemistry of uranyl ion is primarily of redox nature to give U(IV), the nonbonding orbital may then be one largely localized on the uranium atom.

From a comparison of the spectrum of the hydrated uranyl ion with those of the uranyl ion complexes, it seems that the presence of ligands does not cause the appearance of a new band, but only an enhancement of absorption or a little shift of the hydrated ion bands. This would indicate that the equatorial ligands only play a secondary role in determining the spectroscopic properties of uranyl complexes. Because of this lack of perturbation by the environment of the central metal ion, a trait critical to the photochemistry of transition metal complexes is thus impossible, namely interaction and mixing of states on the metal with those on the ligand. For these reasons in the photochemistry of uranyl complexes is very difficult to say whether there is any relation between type of excitation, type of reaction, and quantum yield.

The purpose of this paper is to report some recent results in which the uranyl complex, $UO_2(py)_2(NO_3)_2$, shows new spectral features principally associated with the pyridine ligand acting as a chromophoric center. In this case, using absolute ethanol as solvent, the primary photoreaction due to intraligand excitation is of a substitutional nature and gives the $UO_2(py)(C_2H_5OH)(NO_3)_2$ complex.

We also present the photolysis of released pyridine and discuss the properties of a complex of uranyl ion with 5-amino-2,4-pentadienal produced by U.V. photolysis of pyridine ligand.

Experimental

Materials

$UO_2(py)_2(NO_3)_2$ was prepared by the following method: 10 g $UO_2(NO_3)_2 \cdot 6H_2O$ were dissolved in 50 ml of amyl alcohol. The solution was evaporated to 25 ml, cooled in a nitrogen ambient and then 20 ml of a solution of 7 g pyridine in dry chloroform were added. The resulting yellow crystals were filtered off, and the non reacting pyridine was washed away with dry chloroform and dried in a dessiccator over H_2SO_4. All the chemicals used were of reagent grade.

Apparatus

The light sources used for irradiating and the general irradiation train were the same as previously described.[3]

The reaction cells were standard 1 cm spectrophotometric cells which could be thermostated in suitable metal cell holders. Spectrophotometric measurements were performed with a Perkin–Elmer 323 and an Optica (single beam) spectrophotometers. Infrared spectra were obtained on Bekman IR 10 spectrophotometer. Luminescence measurements were performed with a Perkin–Elmer MPF–2A spectrophotofluorimeter. Conductivity measurements were carried out with a LBR/B type instrument.

Procedures

The photochemical kinetic runs were always performed in a differential mode, using as the reference blank a dark solution identical to the irradiated one. During irradiation, the solutions were always stirred by a continuous stream of pure nitrogen coming from a glass capillary tube. Spectrophotometric kinetic measurements were carried out periodically by bringing the irradiated and dark reaction cells to the spectrophotometer for measuring.

The initial concentration of the reagent complex was always selected to ensure the maximum light absorption at the wavelength of excitation compatible with the type of measurements to be performed. In the kinetic measurements, the irradiation time was limited so as to decompose only a small percent of the initial complex concentration. In these conditions, experimental zero-order kinetics was always obeyed, and calculations were always based on two actinometric measurements performed on the reaction cell, before and after each photochemical run.

Analytical data of the complexes (the calculated values are reported in parentheses): $UO_2(py)(C_2H_5OH)(NO_3)_2$: U, 46.00(45.86); O, 27.60(27.74); C, 15.95(16.19); N, 8.20(8.09); H, 2.20(2.13). $UO_2(NO_3)_2 \cdot L$ ($L = H_2N{-}CH{=}CH{-}CH{=}CH{-}CHO$): U, 48.80(48.47); O, 29.15(29.32); C, 12.10(12.22); N, 8.60(8.55); H, 1.60(1.44).

Uranium was weighed as U_3O_8 after treatment of the complexes with nitric acid, followed by ignition.

I.R. spectra were recorded on nujol mulls between CsI plates or on KBr pellets.

Results

The spectra of $UO_2(py)_2(NO_3)_2$ and pyridine in dry ethanol solutions are shown in Figure 1.

The inner sphere of uranyl pyridinate $UO_2(py)_2(NO_3)_2$ at 25° C was very stable in alcoholic solutions within the time range of our photochemical experiments.

When ethanolic solutions of uranyl pyridinate were irradiated with 254 nm radiations, the appearance of an intense absorption band was observed which had a maximum at 340 nm. These spectral variations were essentially the same as those previously observed for the photolysis of pyridine in aqueous solutions.[4]

The kinetics of the pyridine decomposition products were measured, in order to establish whether the decomposition of pyridine observed during $UO_2(py)_2(NO_3)_2$ irradiation was a primary or a secondary photoprocess. It was found that the product formation rate increased with the irradiation time and was the higher the lower the initial complex concentration. Both these results indicated that the pyridine photolysis was actually a secondary photoprocess due to the light absorption by the free pyridine, released in a primary photochemical reaction.

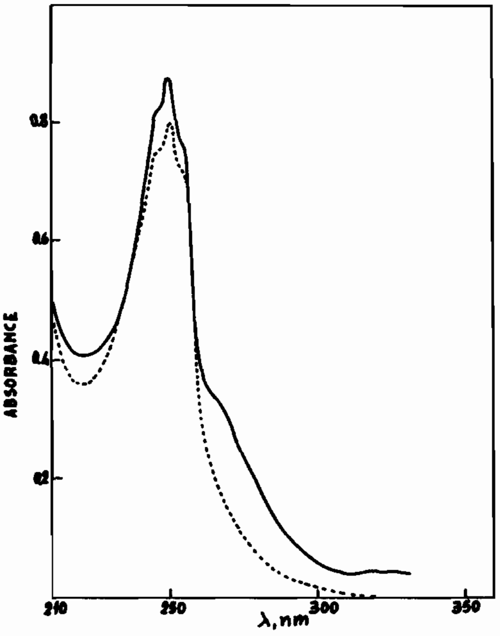

Figure 1. UV spectra of $UO_2(py)_2(NO_3)_2$ (——) and pyridine (----) in absolute ethanol ($1.2 \times 10^{-4} M$).

The spectral variations, even when recorded for the very initial irradiation periods, did not allow the identification of the primary pyridine releasing photoprocess. However, evidence for the stepwise sequence of the photoreaction was derived from a study of the irradiation of $UO_2(py)_2(NO_3)_2$ complex in concentrated ($10^{-2} M$) ethanolic solutions. After irradiating for some hours, bright yellow crystals began to form and their analytic composition corresponded to the formula $UO_2(py)(C_2H_5OH)(NO_3)_2$ (I). Their i.r. spectrum presented the following absorption frequencies: 3585, 3010, 2990, 1530, 1280, 910, and 810 cm^{-1}.

The obtained photoproduct dissolved well in pure dry pyridine. Evaporating the pyridine solution *in vacuo* over H_2SO_4, the formation of $UO_2(py)_2(NO_3)_2$ was again observed. These results are consistent with the primary formation of (I). On the other hand, the intermediate formation of $UO_2(py)(C_2H_5OH)(NO_3)_2$ as a primary photochemical product permits the understanding of the u.v. spectral profile in the first stages of the photoreaction. In fact, an u.v. profile of the

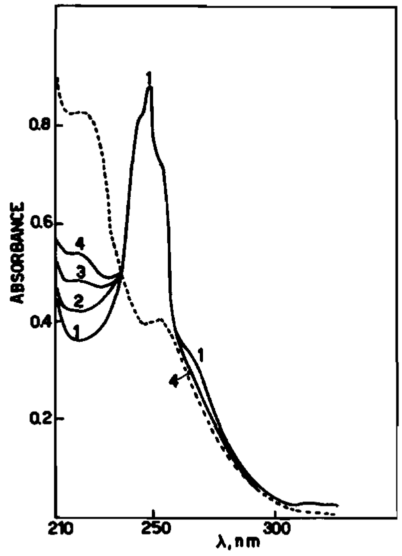

Figure 2. Spectral changes on irradiation of $UO_2(py)_2(NO_3)_2$ in absolute ethanol with 254 nm light : 1, initial; 2–4, after 10, 20, and 30 min. (----) UV spectrum of $UO_2(py)(C_2H_5OH)(NO_3)_2$ complex ($1.2 \times 10^{-4} M$).

photoreaction (Figure 2) indicated that a gradual increase of the absorption took place in the 200–230 nm region, simultaneously with the appearance of an isosbestic point at 238 nm.* These results indicate that the following photochemical process occurred:

$$UO_2(py)_2(NO_3)_2 \xrightarrow[C_2H_5OH]{h\nu} UO_2(py)(C_2H_5OH)(NO_3)_2 + py$$

Moreover, it was possible to verify the photosensitivity of the intermediate compound (I) to the 254 nm light. An u.v. profile in the 230–350 nm range of the intermediate (I) photoreaction revealed u.v. changes analogous to those described for $UO_2(py)_2(NO_3)_2$, the pyridine photorelease being finally supplanted by its photolysis.

The u.v. reaction profile for the secondary pyridine photolysis (Figure 3) was essentially the same as that observed by J. Joussot–Dubien for the photodecomposition of pyridine in aqueous solution.** However, there appeared two significantly new features in the u.v. pattern of the latest stages of photoreaction, one consisting in a slow decrease of the 340 nm band and the other, in a new strong absorption band at 220 nm (Figure 3). Moreover, when the irradiation was completed, the 220 nm absorption band continued to increase but finally stopped at the same point, where no further decrease in the 340 nm band was observed. It had been suspected that these spectral changes were due to thermal reactions of the free uranyl ion with the photodecomposition product of the pyridine. Hence, further attempts to investigate this secondary thermal reaction were made. It was thus isolated a yellow residue after $10^{-2} M$ $UO_2(py)_2(NO_3)_2$ was irradiated. Elemental analysis of the product supports the following formulation: $UO_2(NO_3)_2 \cdot L$ (L = $H_2N{-}CH{=}CH{-}CH{=}CH{-}CHO$).

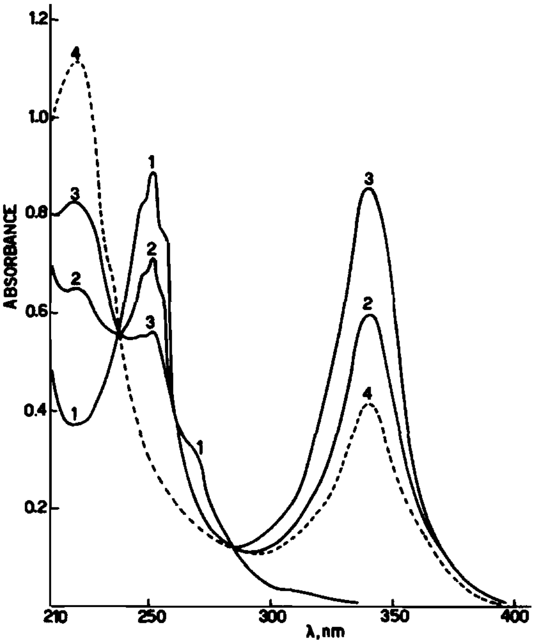

Figure 3. Photolysis of $UO_2(py)_2(NO_3)_2$ at 254 nm ($1.2 \times 10^{-4} M$) in absolute ethanol : 1, initial spectrum; 2–3, spectra following successively longer irradiations; 4, spectrum taken after the thermal reaction was completed.

The infrared spectrum showed that absorption took place at 3220 m, 3110 m, 2905 m, 1710 b,m, 1618 s, 1382 s, 910 s, 820 w, 375 s, and 355 s, cm^{-1}.

Discussion

The electronic spectrum of $UO_2(py)_2(NO_3)_2$ is shown in Figure 1. It consists of two different though partially overlapping absorption zones.

By comparing with the spectrum of free pyridine (Figure 1) the characteristic absorption seen at wavelengths longer than 240 nm can be confidently assigned

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* The characteristic absorption at 220 nm in the spectrum of the $UO_2(py)(C_2H_5OH)(NO_3)_2$ complex can be tentatively attributed to solvation of uranyl ion by alcohol. Even though this interpretation appears speculative, it is quite similar to that suggested independently by other observers for the explanation of the spectra of other nitrates in mixed solvents (Ref. 2).

** The absorbing product noted in the photolysis of pyridine in ethanol was similar to that found in aqueous solution (Ref. 4).

to $\pi\rightarrow\pi^*$ transitions of the pyridine ligands. This absorption is only slightly displaced from that of free pyridine after its coordination. The absorption at 270 nm, which is not observed for the free pyridine can probably be due to electronic transition from the equatorial ligands to UO_2^{2+}, similar to the one shown by other uranyl complexes.[1]

The excitation wavelength used corresponds to the absorption band of the coordinated pyridine ligand. The fact that this excitation gives rise to ligand photorelease rather than to pyridine decomposition implies that $\pi\rightarrow\pi^*$ excited states of the coordinated pyridine deactivate to lower excited states before reacting. Thus, interaction and mixing of states on the metal with those of the ligand appear to be involved. Further, it should be noticed that the proposed mechanism for pyridine photoreaction in water involves hydrogen abstraction from the water by the pyridinic nitrogen atom.[4]* Since in the complex the lone pair of the nitrogen atom is engaged in bonding to the metal, a marked decrease in the reactivity of the intraligand excited states, relative to those of free pyridine, is to be expected.

Following irradiation of a $UO_2(py)_2(NO_3)_2$ complex the observed pattern of u.v. changes indicates that in the primary photoreaction a substitution of a pyridine molecule with an alcohol one took place.

The consideration that the photorelease of the pyridine ligand is the likely mechanism of the primary photoreaction is supported by the kinetic data and its validity was also established by the spectral changes, which took place following the formation of the isolated product (I) (Figure 2).

The presence of ethanol in the coordination sphere of the complex $UO_2(py)(C_2H_5OH)(NO_3)_2$ is rather evident from the i.r. spectra and it was however confirmed by an observed pyridine release mechanism. Moreover, the fluorescence maximum of the photoproduct (I) exibits a shift to higher energy (19,200 from 18,900 cm^{-1}) as is expected for the decrease of basicity of the molecules in the coordination sphere.[2]

As far as (I) is concerned, the study of its i.r. spectrum shows that the antisymmetric ν_3 stretching band of the uranyl group at 910 cm^{-1} is lower than that for the corresponding $UO_2(py)_2(NO_3)_2$ complex (925 cm^{-1}). This result, which indicates that the vibration in the uranyl group is somewhat affected by the nature of the coordinated molecule, supports the $UO_2(py)(C_2H_5OH)(NO_3)_2$ formulation, the energy shift direction in this case being similar to that observed in other cases examined.[5]

From the thermal reaction between uranyl nitrate and 5-amino-2,4-pentadienal, produced from pyridine photolysis, it was possible to isolate a complex formulated as $UO_2(NO_3)_2 \cdot L$. The i.r. spectrum exibits both a C=O and $-NH_2$ stretching frequency of the parent 5-amino-2,4-pentadienal. The fact that the vibration of the C=O group is lowered from 1680 cm^{-1} (the value of the free L compound) to 1618 cm^{-1} in the uranyl complex indicates that the coordination of the 5-amino-2,4-pentadienal takes place through the carbonyl oxygen atom. On the other hand, it appears that $-NH_2$ absorptions are not shifted in agreement with analogous observations from the literature.[5] This is consistent with the general behaviour of the uranyl ion, which is known to be a typical "hard" Lewis acid.

The low molar conductance in ethanol (Λ = 0.4 ohm^{-1}) and the analysis of the infrared spectrum of the complex in the 1500–1700 cm^{-1} range, suggest that the complex is correctly formulated as $[UO_2(L)(NO_3)_2]$. The i.r. spectrum of the complex described here exibits also the expected asymmetric uranyl stretching frequency at 910 cm^{-1}. Absence of the corresponding symmetric vibrations implies that the linearity of the O–U–O group in the complex is maintained.

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* See footnote ** on page *229*.

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