

Photophysical Studies of Uranyl Complexes.

3. Photodecomposition of the Uranyl Complexes of Ethylenediaminetetraacetic Acid and Diethylenetriaminepentaacetic Acid

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The photodecomposition of the two title compounds has been carried out at 254 nm, and a single decarboxylation of the ligand was observed in each case. The decarboxylated complexes that resulted were characterized by visible and infrared spectroscopy, and it was concluded that uranium(IV) products were produced as a result of the reaction. The quantum yield of the ethylenediaminetetraacetic acid (EDTA) complex was found to be 0.84 ± 0.02 , and the quantum yield of the diethylenetriaminepentaacetic acid (DTPA) was $0.50 + 0.01$. The photoproducts could be isolated free from starting material or secondary photoproducts, since these other materials were not water-soluble. When the photoproduct was obtained in solid form, however, it formed as a plastic-like material, and this observation suggested polymerization of the uranium(IV) complexes due to radical reactions that occurred during the photolysis process.

Introduction

The photochemistry associated with the uranyl ion is perhaps the best known and least understood of inorganic photochemistry [1, 2]. Photoreactions of uranyl complexes of carboxylic acids lead to the decarboxylation of the acids, and in the absence of dissolved oxygen, one can isolate the uranium(IV) photoreduction products [3]. The basic photochemical process is thought to proceed in two steps: a) oxidation of ligands or other solution species at

the same time as a reduction of uranium(VI) to uranium(IV) occurs, and b) oxidation of the uranium(IV) by dissolved oxygen to regenerate uranium(VI) [2]. A variety of processes can take place within this scheme, and Burrows and Kemp have classified the photoreactions as to being an excitation of complex, intermolecular abstraction of a hydrogen atom, intermolecular energy transfer, or intermolecular electron transfer [2].

While the use of uranyl oxalate as an actinometer has led to a very detailed investigation of the photochemistry associated with this system [1, 2], reactions with other aliphatic carboxylic, dicarboxylic, and hydroxycarboxylic acids have also been documented. Little work, however, has been done regarding the possible photoreactions of amino acid complexes, and no photochemistry involving aminopolycarboxylic acids has been reported.

In the present study, the photochemistry associated with the uranyl complexes of two aminopolycarboxylic acids, ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), is described. These two systems were chosen for the first studies, since the starting materials were found to be insoluble in water; the primary photoproducts were water-soluble.

Experimental

$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was obtained from Alfa Inorganics, while the EDTA and DTPA ligands were obtained from Aldrich; all materials were used as received. The uranyl complexes were prepared by mixing equimolar amounts of uranyl nitrate hexahydrate and the appropriate aminopolycarboxylic acid in water. When the pH was in the 2–4 range, a yellow 1:1 uranyl:ligand precipitated in an essentially quantitative yield. This synthesis is almost the same as has been reported before [4]. Elemental

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analyses of the isolated complexes confirmed the stoichiometry and revealed that the complexes precipitated as hydrates. The EDTA complex was obtained as the dihydrate [4], while the DTPA complex was found to be a monohydrate. The found and calculated analytical results (with the calculated values in parentheses) were as follows: for $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$, % U = 39.86 (39.92), % C = 20.05 (20.14), % H = 3.02 (3.02), and % N = 4.77 (4.70), while for $\text{UO}_2\text{DTPA}\cdot \text{H}_2\text{O}$, % U = 35.33 (35.04), % C = 24.80 (24.86), % H = 3.05 (3.68), and % N = 6.15 (6.18).

Photochemical studies were conducted in a reaction system that was manufactured by Ultra-Violet Products. Carefully weighed samples of $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ and $\text{UO}_2\text{DTPA}\cdot \text{H}_2\text{O}$ were suspended in 50 ml H_2O (the suspension was maintained with constant mechanical stirring), the excitation energy being provided by immersing a mercury lamp into the suspension. The principal output of this lamp was at 254 nm, and the intensity of the light was measured using ferrioxalate actinometry [5]. It was found that photolysis of the suspended solid resulted in the dissolution of this material, and the time required to fully dissolve the complex was measured. Initial quantities of the complexes were systematically varied from 0.3 g to 2.0 g, and runs were repeated until consistency in elapsed times was obtained. It was not possible to obtain more detailed kinetics, since the starting materials were insoluble, but it was possible to characterize the photoproducts after the reaction was over.

During the course of the irradiation, gas was continually evolved at the surface of the immersion lamp. This gas was proved to be carbon dioxide by venting it into a saturated solution of $\text{Ba}(\text{OH})_2$, then collecting and analyzing the BaCO_3 precipitate. The evolved CO_2 was also collected in a manometer, thus determining quantitatively how much gas was liberated. Within experimental error, it was found that complete dissolution of the initial amount of $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ or $\text{UO}_2\text{DTPA}\cdot \text{H}_2\text{O}$ yielded an equimolar amount of CO_2 gas. It could therefore be concluded that the photochemical reaction leading to dissolution of the uranyl complexes was accompanied by a single decarboxylation of the attached ligand.

The solution produced after the photolysis was concluded was distinctly green in color and was also totally stable. The absorption of the photoproduct in the visible region was obtained on a Cary 11 spectrometer, the spectrum showing no degradation of features over a 24 hour period. The product was isolated by slow evaporation of the reaction solution, obtaining a green product in both cases which formed as a plastic film over the surface of the solution. Analysis of this material confirmed that only a single decarboxylation had occurred in both

cases, producing ethylenediaminetriacetic acid and diethylenetriaminetetraacetic acid complexes of mixed uranium species. The analyses indicated that the solids were isolated as hydrates, but reproducible results proved difficult to obtain. The percentages of uranium, carbon, nitrogen, and hydrogen appeared to depend critically on the amount of starting material, on the length of irradiation time, on the stirring rate of the reaction mixture, and on the presence of oxygen in the solution. Reproducible deaeration was also difficult to achieve due to the tendency of the solid material to retain dissolved oxygen.

Further characterization of the starting EDTA uranyl complex and its photoproduct was obtained by measuring the infrared spectra of these materials. The spectra were obtained both as Nujol mulls between KBr plates and as KBr pellets; in both cases, the recorded spectra were identical, and it could be assumed that pressure-induced reactions did not occur while the sample was being pressed with KBr. All results were obtained on a Perkin-Elmer Model 283 infrared spectrometer.

Results

Irradiation of $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ or $\text{UO}_2\text{DTPA}\cdot \text{H}_2\text{O}$ at 254 nm produced a relatively rapid photo-reaction. Photochemical studies of the analogous cobalt(II) complexes have established the presence of charge transfer bands in this region (of the ligand-to-metal type) [6], and there is no reason to assume a different identity for the absorption of the uranyl complexes in this same region. The photoreaction was accompanied by the production of CO_2 gas at the surface of the immersion lamp, and it was established that one mole of CO_2 was produced per mole of aminocarboxylate ligand.

The reaction was quite unusual, because the primary photoproduct could be isolated in solution form merely by filtering the reaction medium. Both the starting materials, $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ and $\text{UO}_2\text{DTPA}\cdot \text{H}_2\text{O}$, were insoluble in aqueous solution, and a preliminary crystal structure of $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ indicates that it exists as a polymeric material (which would account for its solubility) [7]. Due to its equal insolubility, one can conclude that the DTPA complex also probably exists as a polymeric species. Photolyzing an aqueous suspension of these complexes resulted in their dissolution and subsequent formation of a clear, green solution. Continued photolysis of the green solutions eventually resulted in the formation of a new insoluble material that analyzed as a mixture of various uranium oxides. Thus one could simply filter the reaction solution to recover the primary photoproduct, free from any starting material or secondary photolysis products.

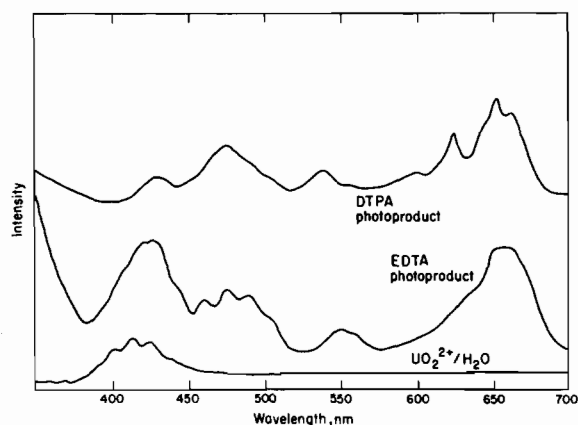


Fig. 1. Absorption spectra of 0.035 *M* uranyl nitrate hexahydrate in water and the absorption spectra of the photodecomposition products of the $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ and $\text{UO}_2\text{DTPA}\cdot \text{H}_2\text{O}$ complexes.

The quantum yields of the reactions were measured by determining the time required for a given amount of $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ or $\text{UO}_2\text{DTPA}\cdot \text{H}_2\text{O}$ to completely dissolve. Attempts to follow the reaction kinetics via absorption spectroscopy did not prove fruitful because of a lack of reproducibility and were not pursued further. It was found that by controlling the experimental conditions as fully as possible, reproducible values for the quantum yield of complex decomposition could be obtained. For $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$, the quantum yield was found to be 0.84 ± 0.02 , and for $\text{UO}_2\text{DTPA}\cdot \text{H}_2\text{O}$, the quantum yield was determined to be 0.50 ± 0.01 .

The absorption spectra of the green photoproducts resulting from the photoreactions of the uranyl EDTA and DTPA complexes were obtained over the visible region, and these spectra were contrasted with the absorption spectrum of the uranyl ion at the same concentration. The spectrum of the uranyl ion has been extensively studied [1, 2] and consists merely of a few weak bands centered about 420 nm. Alternately, the spectra of the photoproducts contained a number of very strong absorption bands, and these were found in the near-infrared region of the spectrum. The wavelength positions and band-shapes of these new bands were extremely similar to those obtained for uranium(IV) in phosphate glass and phosphoric acid [8] and clearly demonstrate that the photoreaction of the uranyl aminopolycarboxylate complexes was accompanied by a reduction of uranium(VI) in the uranyl ion to uranium(IV).

In order to demonstrate that the new bands could not be due to any new uranyl absorption promoted by formation of the aminopolycarboxylic complex, the absorption spectra of a number of soluble uranyl

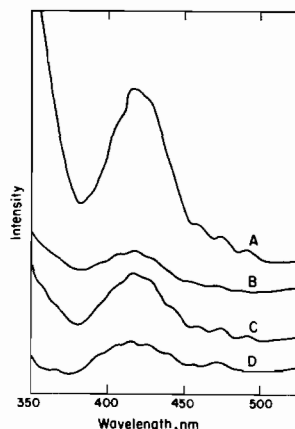


Fig. 2. Absorption spectra of the solution 1:1 uranyl complexes with (A) iminodiacetic acid, (B) *N*-(2-hydroxyethyl)-ethylenediaminetetraacetic acid, (C) (1,2-cyclohexylenedinitrilo)-tetraacetic acid, and (D) ethylenebis(oxyethylenenitrilo)-tetraacetic acid. The uranyl ion concentration in each case was 0.035 *M*.

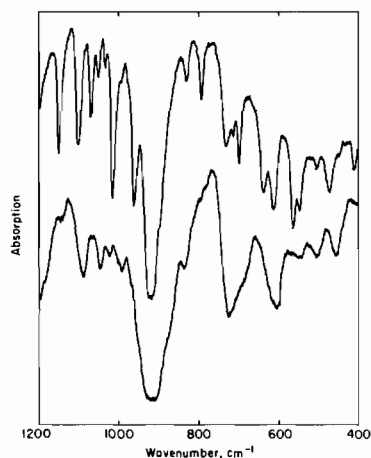


Fig. 3. Infrared absorption of $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ (upper spectrum) and its photodecomposition product (lower spectrum) over the 400–1200 cm^{-1} region. These spectra were taken as KBr pellets.

complexes were also obtained. In Fig. 2, one can examine the spectra of the uranyl complexes of iminodiacetic acid, *N*-(2-hydroxyethyl)-ethylenediaminetetraacetic acid, (1,2-cyclohexylenedinitrilo)-tetraacetic acid, and ethylenebis(oxyethylenenitrilo)-tetraacetic acid. All complexes were prepared by the addition of one mole of ligand to one mole of uranyl ion and raising the pH of the solution to approximately neutral [9]. No absorptions were noted between 550 and 700 nm, which therefore made it highly unlikely that a uranyl complex of any aminopolycarboxylic acid would absorb in this region. One can thus be fairly confident that the new absorption bands of Fig. 1 are indeed due to the presence of uranium(IV) in the primary photoproduct.

Further characterization of the photoproducts was obtained by measuring the infrared absorption spectra of $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ and its decarboxylation product. The spectra of the parent compound and the decarboxylated complex in the 1200–400 cm^{-1} region are shown in Fig. 3. The most marked change in the spectrum of the decarboxylation product from the spectrum of the parent complex was that of the increase in bandwidths in the spectrum of the former compound. This increased bandwidth was most likely due to extensive polymerization and hydrogen bonding involving the carboxylate, water, and uranyl oxygen atoms; association such as this has been observed in other uranyl complexes [10–12] in which hydrogen bonding was operable.

Although the infrared spectrum of the $\text{H}_2\text{UO}_2\text{-EDTA}\cdot 2\text{H}_2\text{O}$ complex was quite sharp in the entire 4000–200 cm^{-1} region, this was not true of the spectrum of the decarboxylation product. Much of the 4000–1200 cm^{-1} spectral region of this compound consisted of broad, featureless bands that made the spectrum useless for the purpose of comparing it to the spectrum of the parent compound. This lack of well-defined bands was especially true of the O–H stretching region centered at 3500 cm^{-1} , even in the parent complex. The problem of obtaining good, reproducible spectra in this region for this complex has been addressed by other investigators [4].

Several changes occurred in the spectrum of $\text{H}_2\text{-UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ upon decarboxylation. Two strong bands at 1150 and 795 cm^{-1} almost disappeared on photolysis, while bands at 1070, 1015, 560, and 405 cm^{-1} disappeared entirely. A triplet set of bands at 700, 715, and 730 cm^{-1} in the spectrum of the parent compound coalesced into a broad band centered at 725 cm^{-1} in the spectrum of the photolysis product; also, two bands at 960 and 915 cm^{-1} fused with a band at 875 cm^{-1} to form one single, broad peak.

The band at 915 cm^{-1} could be assigned unequivocally as the asymmetric ν_3 uranyl stretch, while the 875 cm^{-1} band was attributable to the symmetric ν_1 stretch [13, 14]. Bands at 470 and 455 cm^{-1} in the spectra were uranium–oxygen stretching frequencies and compared quite favorably to those found in uranyl monothiocarboxylic-like derivatives [15].

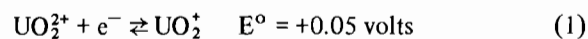
Discussion

Much earlier work on the uranyl sensitized photodecomposition of carboxylic acids has been summarized in the text of Rabinowitch and Belford [1], and several generalizations can be made. The photoreaction is invariably accompanied by the

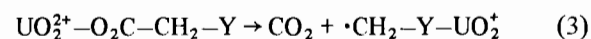
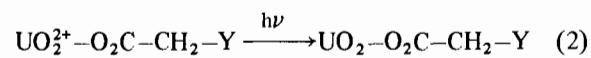
production of CO_2 as a result of the decarboxylation of the acid. In the presence of excess carboxylic acid and in the absence of dissolved oxygen, one is often able to isolate uranium(IV) complexes of the carboxylic acid. It has also been found that these complexes, once isolated in solid form, cannot be redissolved in water. Quantum yields for the reactions range from 0.1 to 1.0, with the best studied system, uranyl oxalate, having its quantum yield most accurately determined [16].

Many of the reaction features found in the studies of simple mono- and dicarboxylic acids were present in the study here involving the aminopolycarboxylate ligands. One mole of CO_2 was evolved per mol of ligand, evidence was presented for the existence of uranium(IV) in the products, and the attempted isolation of the uranium(IV) photoproduct yielded a plastic material which was insoluble in all common solvents. These features indicated that the mechanisms proposed in these studies can be applied to the present situation.

Since the redox potential for the reduction of the uranyl ion is

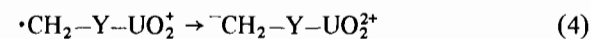


so low [1], it would seem reasonable that the first step in the photochemical is a photoreduction of the uranyl ion. Since one knows for certain that the UO_2^{2+} must be bound to the aminopolycarboxylic acid (the EDTA ligand shall be used for the rest of the discussion), this photoreduction must be accompanied by a transfer of that electron to one of the carboxylic acid groups attached to the uranyl ion. This transfer creates an unstable species, which then loses a molecule of CO_2 and forms an EDTA radical.

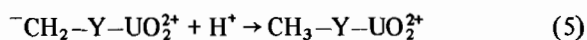


where $\text{Y} = \text{O}_2\text{CCH}_2\overset{|}{\text{N}}\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)_2$

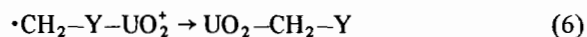
It is not likely that the UO_2^+ species produced will be free from the EDTA radical, since it is initially bound to the uranium in at least three other sites. The presence of radicals has been demonstrated during the photolysis of uranyl complexes of simple carboxylic acids, since an electron paramagnetic resonance signal of these can be recorded during photolysis [17]. The radical might then possibly back-react with the uranium(IV) species



which could easily abstract a proton from the solvent.



A process of this sort would regenerate the uranyl ion. Some regeneration must take place during the photolysis of the EDTA complex, since the spectrum shown in Fig. 1 appears to consist of a superimposition of the spectra of UO_2^{2+} and uranium(IV) compounds. Another possibility might involve a further reduction of the UO_2^{2+} species by the radical, producing some type of uranium(IV) compound which would then undergo other possible reactions.



The type of reaction depicted in eqn. 6 is not at all unlikely when one considers that the radical will already be bound to the UO_2^+ species and is thus ideally situated for such an electron transfer. Of course, the observation of uranium(IV) absorption bands in the spectrum of the $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ photolysis product effectively argues for such a reaction.

The absorption spectrum of the $\text{UO}_2\text{DTPA}\cdot\text{H}_2\text{O}$ photolysis product also contains absorption bands attributable to uranium(IV), but it does not appear to contain any peaks which would be unique to uranium(IV). This might imply that reactions 4 and 5 do not occur significantly, thus indicating that reaction 6 might be the major step for the radical reaction. The mode of attachment existing between the DTPA ligand and the uranyl ion is not known, but one would not anticipate that all five carboxylic groups could bind to the uranyl ion around the equatorial positions of that ion. If only four were bound and one of these were decarboxylated, the previously unattached group might immediately bind to the metal ion and eliminate the reaction pathway corresponding to eqns. 4 and 5*.

The authors believe that the intractable materials isolated from the photoreaction mixture represent polymerizations of materials produced during the course of the radical reactions. The broadening of the infrared spectral features is strongly suggestive

*It is not known at the present time if both the carboxylic and amino groups bond to the central uranium atom in this complex. Bonding in the uranyl-iminodiacetic acid complex [11] has been shown to occur through the carboxylic groups exclusively; the nitrogen atom is protonated and thus not coordinated. Recently reported infrared and X-ray photoelectron data [D. L. Perry, 179th National Meeting of the American Chemical Society, Houston, 1980] are consistent with carboxylate-only bonding in the $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ compound that forms at low pH. The data are ambiguous, however, and unequivocal corroboration of this mode of bonding must await a completed single-crystal structural study.

of such polymerization, and the loss of several vibrational bands argues that the fundamental bending and stretching modes associated with the ligand have changed in nature. This can only occur as a result in a change in bonding in going from the parent uranyl complexes to the photolysis products.

It is illuminating to compare the magnitude of the quantum yield obtained during irradiation of the $\text{H}_2\text{UO}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ complex with values obtained for other cations. During photolysis of $\text{Co}(\text{EDTA})\cdot\text{X}^-$, Natarajan and Endicott [8] found that the quantum yield for complex decomposition depended on the identity of the halide ion, and they reported quantum yield values ranging from 0.12 to 0.18. Wallo and Brittain examined the photolysis of $\text{Nd}(\text{III})$ and $\text{Ho}(\text{III})$ complexes of EDTA, and they found that the quantum yields were quite pH dependent [18]; quantum yields ranging from 0.1 to 0.5 mol/Einstein were observed. The results of these studies have shown that aminopolycarboxylate complexes do possess interesting photochemistry; however, the photoreactions are similar in nature to those of simpler ligands.

Acknowledgement

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