

Photochemical Water Oxidation and Origin of Nonaqueous Uranyl Peroxide Complexes

Brendan T. McGrail,[†] Laura S. Pianowski,[†] and Peter C. Burns^{†,‡,*}

[†]Department of Civil & Environmental Engineering & Earth Sciences and [‡]Department of Chemistry & Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States

S Supporting Information

ABSTRACT: Sunlight photolysis of uranyl nitrate and uranyl acetate solutions in pyridine produces uranyl peroxide complexes. To answer longstanding questions about the origin of these complexes, we conducted a series of mechanistic studies and demonstrate that these complexes arise from photochemical oxidation of water. The peroxy ligands are easily removed by protonolysis, allowing regeneration of the initial uranyl complexes for potential use in catalysis.

Metal/peroxy complexes are key intermediates in many biological¹ and industrial catalytic oxidation processes.² These complexes are usually short-lived and are consumed to give metal (hydr)oxo or oxidized organic products. Actinyl peroxide complexes, however, are remarkably stable, both with respect to cleavage of the peroxy ligand³ and to dissociation into their constituent oxides and molecular oxygen.⁴ This stability is exemplified by the mineral studtite, [UO₂(O₂)(H₂O)₂](H₂O)₂, which is known to form on the surfaces of irradiated nuclear fuel,⁵ and a large family of actinyl peroxide cage clusters containing from 20 to 124 actinyl ions with peroxide bridges.⁶ There are also several reports⁷ of uranyl peroxide complexes generated without the addition of hydrogen peroxide, some of which may be relevant to the PUREX process used for nuclear fuel recycling. We have prepared two such complexes and demonstrated that they form by base-assisted photochemical water oxidation by the uranyl ion followed by capture of the liberated dioxygen.

The photochemical oxidation reactivity of the uranyl ion has been studied in nonaqueous solvents for decades,⁸ with the preponderance of evidence supporting the formation of U^V products⁹ at high UO₂²⁺ concentrations, whereas U^{IV} forms below a (solvent-dependent) critical UO₂²⁺ concentration.^{9c,10} Bakac and Espenson¹¹ studied the photochemical reduction of uranyl in water and aqueous alcohols using fluorescence quenching methods and demonstrated that the photoexcited uranyl ion oxidizes n-alkanes. The fluorescence quenching was interpreted as being due to the one electron oxidation of organic substrates by the excited state of the uranyl(VI) ion, UO₂^{2+*}, with the resulting U^V species being reoxidized by molecular oxygen to regenerate UO₂²⁺ and give H₂O₂. Similar H-atom abstraction reactions have been reported toward a number of aliphatic, but not aromatic, substrates by other groups.^{10–12}

In aqueous acidic solutions peroxide competes with strong donors such as H₂O to complex uranyl, with the formation of H₂O₂ or the hydroxyl radical favored over the formation of uranyl peroxide complexes.¹⁰ The photolysis of the uranyl ion in basic solutions is not well understood, but no photochemical redox processes have been observed.¹³

In organic solvents with low water content, hydrolysis of uranyl is not a concern. Zubieta et al. prepared a uranyl peroxide complex from ethanol/triethylamine solutions, although in low yields.^{7d} A later attempt^{7e} to understand the reaction mechanism proposed that the aryl thiolate ligands employed provided the reducing equivalents required to capture atmospheric dioxygen as peroxide, but the mechanism proposed U^V species that, despite their purported longevity, were not observed. Other uranyl peroxide complexes, some with relevance to speciation in the PUREX process and its waste streams, have been isolated in recent years, but their origin remains unclear.^{7a,c,e,g} Of particular interest is the diuranyl- μ - η^2 : η^2 -peroxide complex prepared by Arnold et al.¹⁴ by exposure of a uranyl(V) “pacman” complex to dioxygen, which suggests a possible origin of the complexes consistent with the known formation of uranyl(V) photolysis products.^{9b}

We have found that exposure of a solution of uranyl nitrate hexahydrate (UO₂(NO₃)₂·6H₂O) in pyridine (0.350 g/6 mL) to direct sunlight for 6 h under ambient conditions, followed by layering with one volume of diethyl ether and cooling to –20 °C for 3–5 days, gives large diffraction quality single crystals of the uranyl nitrate peroxide complex [UO₂(py)₂(NO₃)₂]₂O₂·py, **1** (Figure 1), with a yield of 48% based on U.

The crystallographic analysis of **1** revealed two symmetrically distinct and nearly linear (UO₂)²⁺ uranyl ions with U≡O bond lengths in the range of 1.75(1)–1.76(1) Å. These uranyl ions are bridged by a μ - η^2 : η^2 peroxide ligand that has an O–O bond length of 1.46(2) Å. The U–O₂–U dihedral angle is 125°, consistent with those found in a variety of uranyl peroxides. Each uranyl ion is further coordinated by a bidentate nitrate group, and two N atoms of pyridine ligands that are arranged in a *trans* configuration, together resulting in a hexagonal bipyramidal coordination geometry about the U^{VI} cation.

Strikingly, and in contrast to earlier reports,^{7f} carrying out the analogous photolysis reaction under argon using Schlenk and glovebox techniques, but without drying the uranyl nitrate or pyridine, afforded **1** as well in similar yields. The Raman spectrum collected for the reaction mixture under argon is very

Received: September 4, 2013

Published: March 17, 2014

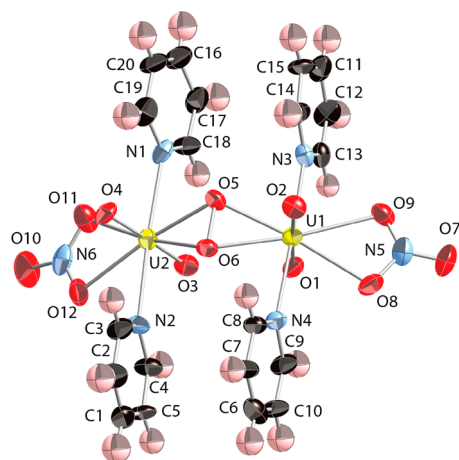


Figure 1. Thermal ellipsoid representations of **1** with ellipsoids drawn at the 30% probability level.

similar to that collected for the mixture photolyzed under air (Figure 2). Formation of **1** under oxygen-free conditions

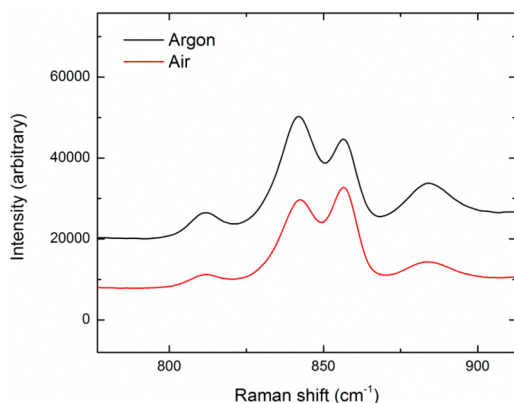


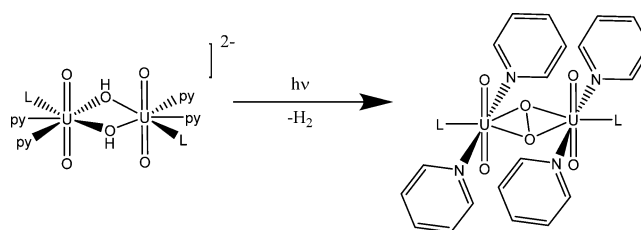
Figure 2. Raman spectra of photolyzed uranyl nitrate solutions in pyridine after 2 h of irradiation under air (red trace) and argon (black trace). The spectra have been shifted vertically to facilitate viewing.

indicates that the peroxide ligand was generated in situ without action of atmospheric oxygen. Headspace analysis of reaction mixtures prepared under argon with undried uranyl nitrate in pyridine (stored under ambient conditions and degassed by three freeze–pump–thaw cycles before use) by isotope ratio mass spectrometry (IR-MS) revealed evolution of dihydrogen.

Carrying out the analogous reaction with a saturated uranyl acetate dihydrate ($\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$) solution in 2:1 pyridine:acetone affords $[\text{UO}_2(\text{py})_2(\text{OAc})]_2\text{O}_2 \cdot \text{py}$, **2**, the acetate analog of **1**, in 23% yield based on U. In this case U(VI) is also confirmed by $\text{U}=\text{O}$ bond lengths in the range of 1.771(6)–1.789(6) Å, the peroxide O–O bond length is 1.479(8) Å, and the U–O₂–U dihedral angle is 137°.

Based on earlier studies showing a minimum critical concentration of $(\text{UO}_2)^{2+}$ for forming U^{V} over U^{IV} as photolysis products in tri-*n*-butyl phosphate,^{9c} we propose that the nonaqueous uranyl peroxides **1** and **2** form from a precursor containing a water or hydroxo-bridged diuranyl complex according to the overall reaction shown in Scheme 1. This reaction mechanism is supported by experiments we conducted with uranyl chloride, UO_2Cl_2 , and uranyl triflate, $\text{UO}_2(\text{OTf})_2$, which do not form peroxo-bridged dimers of uranyl ions as in **1** and **2** under analogous conditions. In other work, uranyl

Scheme 1. Proposed Overall Reaction for Uranyl Peroxide Formation in Pyridine^a



^aL = [−]OAc, NO₃[−].

chloride has been shown to form a dinuclear, di- μ_2 -chloride complex, $(\text{UO}_2)_2\text{Cl}_4(\text{THF})_4$ (THF = tetrahydrofuran) in THF solution and in the solid state,¹⁵ and uranyl triflate has been shown to form a diuranyl- μ -oxo complex in pyridine with adventitious water.¹⁶ We posit that the speciation of uranyl chloride in pyridine is similar to its speciation in THF, precluding the formation of the di- μ_2 -hydroxo/water complex that we propose is an essential intermediate in the formation of **1** and **2**. Support for this intermediate is provided by the behavior of uranylbis(acetylacetonate), which forms only a simple pyridine adduct in pyridine and pyridine/methanol solution and gives no peroxy complex even after 5 days of photolysis. Additionally, the ¹H NMR spectrum of unphotolyzed uranyl nitrate in pyridine-*d*₅ shows a broad resonance at 2.48 ppm¹⁷ that is comparable to the resonance of HO[−] coordinated to uranyl and a larger, broader resonance at 8.22 ppm that is identical to the resonance of nitric acid in C₅D₅N. The well-established acidity of uranyl/water complexes, the abundance of base, and the observation of a pyridine/“HNO₃” complex suggest that the uranyl/water complex exists in some state of deprotonation.

Residual nitrate and acetate ligands are easily isolated in 70–80% yield as large, colorless needles of the pyridinium salts by layering the mother liquors with toluene after **1** or **2** have been removed and mechanically separating the large needle crystals from the small amount of **1** or **2** that coprecipitate.

Isolated pyridinium acetate and nitrate were identified by their FT-IR spectra and by single crystal X-ray diffraction. Spectroscopic monitoring of the photolysis of uranyl nitrate in pyridine shows that the reaction proceeds to completion rapidly, with no further growth of the 856 cm^{−1} Raman peak after 60 min in direct sunlight (Figure 3, left). UV–vis spectra (Figure 3, right) indicate that the reaction requires 2–3 h to go

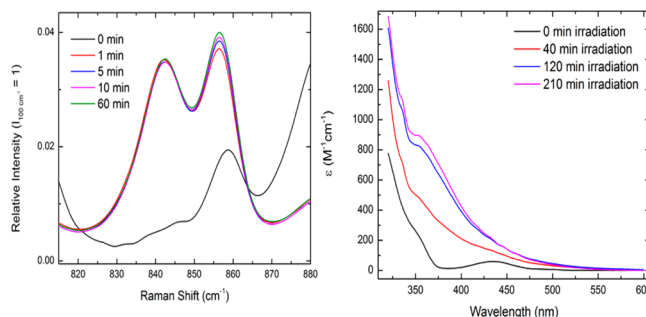


Figure 3. Time resolved Raman (left) and UV–vis (right) spectroscopic monitoring of the photolysis of a uranyl nitrate solution in pyridine. Extinction coefficient is based on initial $\text{UO}_2(\text{NO}_3)_2$ concentration.

to completion based on the disappearance of the band at 434 nm, although carrying out these experiments at several uranyl concentrations suggests that this is likely a concentration effect. This band cannot be found in the photolyzed mixtures by derivative or second derivative peak searches, and its absence is consistent with the nonfluorescence of compound **1** in the solid state.

The 838 cm^{-1} band is consistent with the position of the symmetric stretching mode of the uranyl ion, and the 860 cm^{-1} band is consistent with the symmetric stretching mode of the peroxide ion coordinated to uranyl in other uranyl peroxide complexes.¹⁸ When the reaction is carried out in the presence of ^{18}O -labeled H_2O , additional Raman bands appear at 810 and 827 cm^{-1} , with smaller bands at 838 and 860 cm^{-1} , resulting from the unlabeled waters in the hydrated starting material (Figure 4) and confirming that the peroxo ligand results from

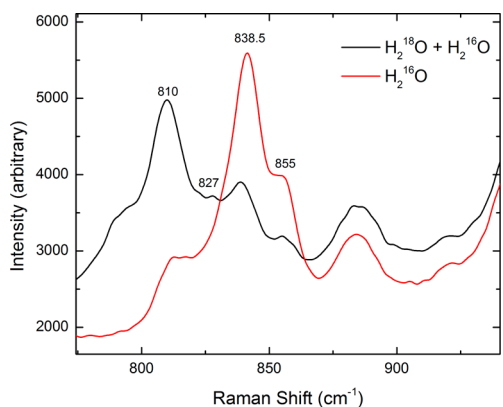


Figure 4. Raman spectra of a uranyl nitrate solution in pyridine/water (4 mL/0.110 mL) with H_2^{18}O (black trace) and isotopically normal water (red trace) after 4 h photolysis. Numbers indicate peak frequencies.

the oxidative coupling of two water or hydroxide ligands. Incorporation of isotopic labels into both the “yl” and peroxo oxygens is consistent with the base-promoted exchange between axial (“yl”) and equatorial (hydro)oxo ligands within the uranyl moiety observed by Clark,¹³ Grenthe,¹⁹ and Tsushima.²⁰

Both **1** and **2** are air-stable, hygroscopic solids that smell strongly of pyridine even when dried under vacuum overnight. Microanalyses for **1** and **2** consistently give high H analyses accompanied by low C and N analyses, and the FT-IR spectra of both **1** and **2** show strong water bands after exposure to air for 2 h (Figure S3), suggesting that both the uncoordinated and coordinated pyridines exchange readily with atmospheric water. **1** is sparingly soluble in acetone, pyridine, and dimethylformamide (DMF), while **2** is very sparingly soluble in DMF and pyridine. The peroxo ligands are easily removed as H_2O_2 in nearly quantitative (76–101%) yield (as determined by starch/iodine assay)²¹ by treatment of **1** or **2** with 2 equiv of trifluoroacetic acid (TFA) or triflic acid, which rapidly and quantitatively returns the uranyl ion to a coordination environment similar to its environment prior to irradiation based on the position of the symmetric stretching mode of the uranyl ion in the Raman spectrum (Figure 5). The solutions may be photolyzed again up to water contents of 25% v/v to regenerate the peroxo complexes, although a significant inhibitory effect of water on peroxo formation is observed

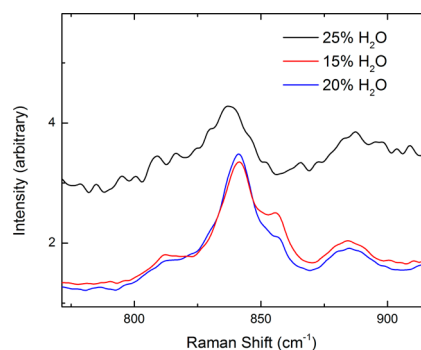


Figure 5. Raman spectra of photolyses of uranyl nitrate solutions in pyridine–water at 15, 20, and 25% H_2O (v/v) after 60 min photolysis. The poor signal-to-noise ratio in the 25% H_2O spectrum is due to the low solubility of uranyl nitrate in this solvent mixture.

(Figure 6), likely due to the formation of photochemically inert and poorly soluble hydrolysis products.

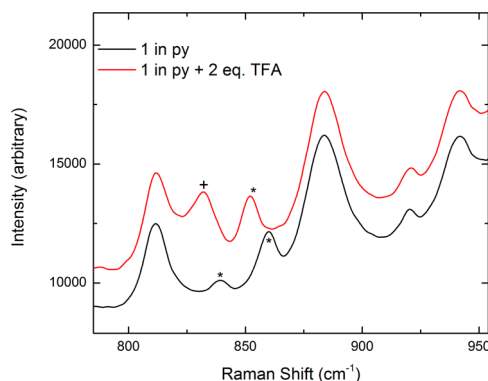


Figure 6. Raman spectra of uranyl peroxide complex **1** in pyridine solution before (black trace) and after (red trace) treatment with trifluoroacetic acid. Asterisks indicate uranyl and uranyl peroxide modes. The cross indicates a C–F stretching or bending mode of the trifluoroacetate ion.

In summary, we have described the formation mechanism of uranyl peroxides by photochemical water oxidation and conducted preliminary studies on the reactivity of the uranyl peroxide moiety.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details, characterization data, and crystallographic parameters (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

pburns@nd.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, grant no. DE-FG02-07ER15880.

■ REFERENCES

- (1) (a) Jacobson, R. R.; Tyeklar, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 3690. (b) Park, G. Y.; Qayyum, M. F.; Woertink, J.; Hodgson, K. O.; Hedman, B.; Sarjeant, A. A. N.; Solomon, E. I.; Karlin, K. D. *J. Am. Chem. Soc.* **2012**, *134*, 8513. (c) Tahsini, L.; Kotani, H.; Lee, Y. M.; Cho, J.; Nam, W.; Karlin, K. D.; Fukuzumi, S. *Chem.—Eur. J.* **2012**, *18*, 1084. (d) Verma, P.; Pratt, R. C.; Storr, T.; Wasinger, E. C.; Stack, T. D. P. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 18600.
- (2) (a) Ellis, W. C.; Tran, C. T.; Roy, R.; Rusten, M.; Fischer, A.; Ryabov, A. D.; Blumberg, B.; Collins, T. J. *J. Am. Chem. Soc.* **2010**, *132*, 9774. (b) Munakata, H.; Oumi, Y.; Miyamoto, A. *J. Phys. Chem. B* **2001**, *105*, 3493. (c) Polshin, V.; Popescu, D. L.; Fischer, A.; Chanda, A.; Horner, D. C.; Beach, E. S.; Henry, J.; Qian, Y. L.; Horwitz, C. P.; Lente, G.; Fabian, I.; Munck, E.; Bominaar, E. L.; Ryabov, A. D.; Collins, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 4497.
- (3) Gil, A.; Karhanek, D.; Miro, P.; Antonio, M. R.; Nyman, M.; Bo, C. *Chem.—Eur. J.* **2012**, *18*, 8340.
- (4) (a) Armstrong, C. R.; Nyman, M.; Shvareva, T.; Sigmon, G. E.; Burns, P. C.; Navrotsky, A. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 1874. (b) Kubatko, K. A. H.; Helean, K. B.; Navrotsky, A.; Burns, P. C. *Science* **2003**, *302*, 1191.
- (5) (a) Burns, P. C.; Ewing, R. C.; Navrotsky, A. *Science* **2012**, *335*, 1184. (b) Burns, P. C.; Hughes, K. A. *Am. Mineral.* **2003**, *88*, 1165.
- (6) (a) Nyman, M.; Burns, P. C. *Chem. Soc. Rev.* **2012**, *41*, 7354. (b) Qiu, J.; Burns, P. C. *Chem. Rev.* **2013**, *113*, 1097.
- (7) (a) Aladzheva, I. M.; Bykhovskaya, O. V.; Nelyubina, Y. V.; Klemenkova, Z. S.; Petrovskii, P. V.; Odinets, I. L. *Inorg. Chim. Acta* **2011**, *373*, 130. (b) John, G. H.; May, I.; Sarsfield, M. J.; Steele, H. M.; Collison, D.; Helliwell, M.; McKinney, J. D. *Dalton Trans.* **2004**, 734. (c) Masci, B.; Thuery, P. *Polyhedron* **2005**, *24*, 229. (d) Rose, D.; Chang, Y. D.; Chen, Q.; Zubieta, J. *Inorg. Chem.* **1994**, *33*, 5167. (e) Rose, D. J.; Chen, Q.; Zubieta, J. *Inorg. Chim. Acta* **1998**, *268*, 163. (f) Thuery, P.; Masci, B. *Supramol. Chem.* **2003**, *15*, 95. (g) Thuery, P.; Nierlich, M.; Baldwin, B. W.; Komatsuzaki, N.; Hirose, T. *J. Chem. Soc., Dalton Trans.* **1999**, 1047.
- (8) (a) Mao, Y.; Bakac, A. *Inorg. Chem.* **1996**, *35*, 3925. (b) McCleskey, T. M.; Burns, C. J.; Tumas, W. *Inorg. Chem.* **1999**, *38*, 5924. (c) Nagaishi, R.; Katsumura, Y.; Ishigure, K.; Aoyagi, H.; Yoshida, Z.; Kimura, T.; Kato, Y. *J. Photochem. Photobiol., A* **2002**, *146*, 157.
- (9) (a) Kramer, G. M.; Dines, M. B.; Kaldor, A.; Hall, R.; McClure, D. *Inorg. Chem.* **1981**, *20*, 1421. (b) Miyake, C.; Yamana, Y.; Imoto, S.; Ohyanishiguchi, H. *Inorg. Chim. Acta* **1984**, *95*, 17. (c) Roferdepoorter, C. K.; Depoorter, G. L. *J. Inorg. Nucl. Chem.* **1977**, *39*, 631.
- (10) Burrows, H. D.; Kemp, T. J. *Chem. Soc. Rev.* **1974**, *3*, 139.
- (11) (a) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1995**, *34*, 1730. (b) Howes, K. R.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1988**, *27*, 791. (c) Wang, W. D.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1995**, *34*, 6034.
- (12) Matsushi, R. *J. Am. Chem. Soc.* **1972**, *94*, 6010.
- (13) Clark, D. L.; Conradson, S. D.; Donohoe, R. J.; Keogh, D. W.; Morris, D. E.; Palmer, P. D.; Rogers, R. D.; Tait, C. D. *Inorg. Chem.* **1999**, *38*, 1456.
- (14) Jones, G. M.; Arnold, P. L.; Love, J. B. *Angew. Chem., Int. Ed.* **2012**, *51*, 12584.
- (15) Wilkerson, M. P.; Burns, C. J.; Paine, R. T.; Scott, B. L. *Inorg. Chem.* **1999**, *38*, 4156.
- (16) Berthet, J. C.; Lance, M.; Nierlich, M.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2000**, 1969.
- (17) Pasilis, S. P.; Blumenfeld, A. *Inorg. Chem.* **2011**, *50*, 8302.
- (18) McGrail, B. T.; Sigmon, G. E.; Jouffret, L. J.; Andrews, C. R.; Burns, P. C. *Inorg. Chem.* **2014**, *53*, 1562.
- (19) Szabo, Z.; Grenthe, I. *Inorg. Chem.* **2010**, *49*, 4928.
- (20) Tsushima, S. *Inorg. Chem.* **2012**, *51*, 1434.
- (21) Repka, V. *Biol. Plant.* **1999**, *42*, 599.