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# Photochemical Behavior of a Uranyl Bis(hexafluoroacetylacetonate)-Tetrahydrofuran Complex. 1

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Electronic excitation of solutions of the THF adduct of uranyl hexafluoroacetylacetonate results in production of a $U^{4+}$ product. Spectral and wet-chemical analyses suggest it is $U[(CF_3CO)_2CH]_4$. It is proposed that it occurs through the intermediacy of a hypothetical $U^{4+}$-peroxide complex, an isomer of $UO_2^{2+}$. The excited uranyl interacts with oxygen which acts as a fluorescence quenching agent.

## Introduction

The chelated uranyl salt $UO_2(CF_3COCHCOCF_3)_2{\cdot}THF$ (**1**), a bright yellow solid with a sharp melting point of 91.5 ± 1 °C that can be sublimed without dissociation, has recently been prepared.[1] The compound is particularly interesting because of its possible use in a gas-phase IR-laser-induced uranium isotope separation process. Its decomposition induced by IR radiation is described elsewhere;[2] this paper deals with its UV-visible photochemistry.

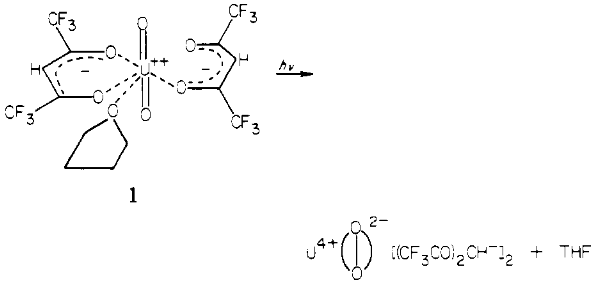
Photolyses have been carried out at wavelengths between 360 and 450 nm and with sunlight. As is well-known,[3] these frequencies correspond to absorption bands of the uranyl ion which are thought to excite the system to either one or a series of closely spaced electronic states. Intramolecular energy transfer very rapidly leads the system to the $v = 0$ level of the lowest electronically excited states, from which fluorescence and/or photochemical conversion occurs.

It should be noted that neither the hexafluoroacetylacetonate anion nor tetrahydrofuran absorbs photons at 450 nm. Also, **1** appears to have a charge-transfer band at 360 nm in addition to the uranyl ion absorption near 450 nm. One might expect different photochemistry to ensue, depending on which feature is irradiated since the initially excited electronic states are different. Product formation however is insensitive to the radiation wavelength in this range.

The literature indicates that $U^{IV}$ [4a-d] and sometimes $U^{V}$ [4e] compounds are formed during the photolyses of the uranyl ion. The reaction of **1** also leads to a $U^{IV}$ compound and other products which have been extensively characterized and which provide additional insight into the reactions occurring.

Irradiation in hydrocarbon media leads to the formation of products which precipitate as their concentration increases. Their formation is accompanied by changes in the visible, near-IR, IR, and NMR spectra of the solutions. The composition of some of the products can be deduced from spectral changes as well as from elemental analyses. The studies indicate that the photochemically excited uranyl compound converts to a $U^{4+}$ species and other products, in the course of which attack on the solvent also occurs. The excited species also appear to interact with molecular oxygen as evidenced by the consumption of oxygen during irradiation of the system. In addition the excited species fluoresce at low temperature, the fluorescence lifetime being influenced by self-quenching, the presence of oxygen, and the solvents or frozen matrices employed.

These observations are useful in considering the fate of **1** when electronically excited in the gas phase. In particular, IR examination of solutions immediately after excitation by a UV source show a loss of the asymmetric $UO_2^{2+}$ stretching vibration, followed by the slow regeneration of a uranyl compound. Furthermore, elemental analyses indicate that peroxides are photoproducts. These observations suggest that photoexcitation of **1** results in its isomerization to **2** (see eq 1), a novel $U^{4+}$-peroxide complex which may undergo a disproportionation reaction with more of the uranyl chelate. The peroxide anion is a typical ligand known to form a large number of complexes with the uranyl ion.[5a]



**1**

**2**

(1)

## Experimental Section

Photochemical experiments were typically conducted with 0.04 M solutions of $UO_2[(CF_3CO)_2CH]_2{\cdot}THF$ in aliphatic hydrocarbons like heptane, isopentane, and 2,3-dimethylbutane. Mercury lamps and an argon ion laser were used for studies at 360 and 450 nm. The experiments were normally done in either 1-cm glass cells or 0.7-cm NMR tubes. Many of the experiments using solar radiation were conducted with the cells connected to a water manometer, the sample being covered with $N_2$, $O_2$, or air. Normal solar radiation was sufficiently intense to provide visual evidence of reaction within 1 h or less.

The reaction products were subjected to standard spectral and elemental analyses. In addition, studies of the fluorescence lifetime of $UO_2^{2+}$ in a 20:80 isopentane/methylcyclohexane ($iC_5$/MCH) solution were made. The ion was excited by a conventional N-734 flash lamp, which provides an essentially uniform white emission (335->600 nm) lasting for about 5 μs. The light was filtered to allow irradiation from 300 to 500 nm. The output of the excited uranyl solution was passed through a Spex spectrophotometer which transmitted the signal at 524 nm to an oscilloscope. Photographs of the fluorescence curves were used to evaluate the decay kinetics. The 524-nm fluorescence is the most intense band emitted by the sample.

Most of the fluorescence lifetime measurements were made at temperatures between 80 and 120 K. In addition, the photochemical conversion of $UO_2^{2+}$ to nonradiative products was studied by observing

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(1) G. M. Kramer, M. B. Dines, R. B. Hall, A. Kaldor, A. R. Jacobsen, and J. C. Scanlon, *Inorg. Chem.*, **19**, 1340 (1980).

(2) (a) A. Kaldor, R. B. Hall, D. M. Cox, J. B. Horsley, P. Rabinowitz, and G. M. Kramer, *J. Am. Chem. Soc.*, **101**, 4465 (1979); (b) D. M. Cox, R. B. Hall, J. A. Horsley, G. M. Kramer, P. Rabinowitz, and A. Kaldor, *Science* (*Washington, D.C.*), **205**, 390 (1979).

(3) H. D. Burrows and T. J. Kemp, *Chem. Soc. Rev.*, **3**, 139 (1974).

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(5) I. I. Chernyaev, Ed., "Complex Compounds of Uranium", Israel Program for Scientific Translations, Jerusalem, 1966: (a) Chapter 3; (b) p 419. (c) L. J. Heidt and K. A. Moor, *J. Am. Chem. Soc.*, **75**, 5803 (1953).

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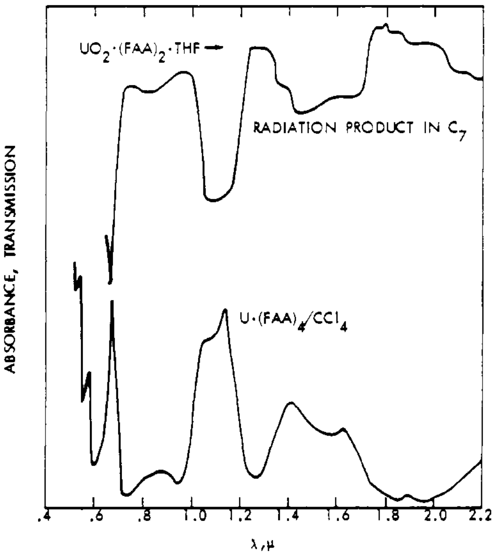


**Figure 1.** Visible–near-IR spectrum of the photoproduct.

the decay of fluorescence from mixtures being continually excited by Hg-lamp irradiation at 360 nm.

NMR measurements were made on a Varian A-60 instrument at ambient conditions. Approximately 0.1–1.0 M solutions of the uranyl compounds in chloroform, benzene, and other relatively nonpolar solvents were used, and studies were made during the course of irradiation.

## Observations and Discussion

**a. Formation of $U^{IV}$ Compounds and Peroxides.** Solar irradiation at ambient conditions causes the solutions to undergo a gradual color change from deep yellow-green, characteristic of the $UO_2^{2+}$ ion, to brown. Prolonged irradiation leads to the subsequent formation of precipitates.

The brown solution exhibits an absorption band near 650 nm and a series of bands in the visible and near-infrared region that are generally characteristic of $U^{4+}$ compounds. The 650-nm and near-IR bands are believed to be due to low-energy electronic transitions of 5f electrons to vacant 5f or available hybrid orbitals (two of the seven orbitals being singly populated in $U^{4+}$), but this is not firmly established.[5b,c] These bands are long lived and clearly indicate the formation of a stable $U^{4+}$ product. Compound **1** does not absorb in this region, and the 650-nm band can be used to quantitatively measure the formation of product.

The product spectrum coincides with that of $U[(CF_3CO)_2CH]_4$ which was synthesized independently (Figure 1). It is possible that this is a major component of the photochemical reaction, but the spectrum alone is not proof of structure since $U(HSO_4)_4$ in dilute $H_2SO_4$ exhibits a very similar spectrum. It is not clear to what extent the spectrum is influenced by the ligands, but it is reasonable that the correspondence of the $U(HSO_4)_4$ spectrum and that of the product indicates that the $U^{4+}$ ion is in a similarly symmetric environment. This supports the conjecture that $U[(CF_3CO)_2CH]_4$ is actually a photoproduct.

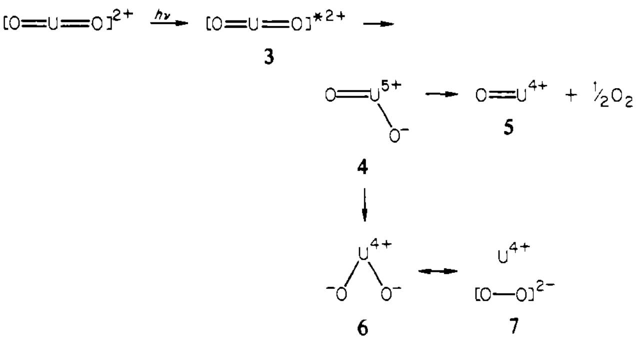
Compelling evidence that $U[(CR_3CO)_2CH]_4$ is a photoproduct stems from Fourier transform IR studies of the vapor after an analogous gas-phase reaction. These studies have clearly identified this compound as a reaction product in the vapor-phase decomposition; the spectra of the products after subtraction of the bands of residual **1** matching that of the tetrakis $U^{4+}$ compound.[6]

The photoproduct and $U[(CF_3CO)_2CH]_4$ also exhibit bands below 650 nm, some of these coinciding with the $UO_2^{2+}$ absorption. A strong band originating in the UV is believed to also involve a charge-transfer transition between $U^{4+}$ and the ligands as it is present in hydrocarbon media but not when $U[(CF_3CO)_2CH]_4$ is decomposed in $H_2SO_4$.

Conversion of **1** to a $U^{4+}$ ion raises two immediate questions; namely, what was oxidized and what is the fate of the oxygen atoms originally on the uranyl ion? This is an old unsettled question in uranyl chemistry which we wish to discuss further.[4]

There are a number of possibilities for the reducing species. Foremost are the $O^{2-}$ oxide ions and the $(CF_3CO)_2CH^-$ anions. If $O^{2-}$ is the reducing agent, it could be oxidized either to $O^-$ or to an oxygen atom. These transformations are shown in Chart I.

**Chart I.** Possible Intramolecular Conversion of Photoexcited $UO_2^{2+}$



The reduction of uranium is depicted as starting with an electron transfer out of a uranium–oxygen bonding orbital into an empty 5f orbital of electronically excited uranium. This yields **4** which either cleaves heterolytically to yield $O{=}U^{4+}$ and oxygen or an oxygenated product or undergoes a second intramolecular electron shift to **6**, a $U^{4+}–O_2^{2-}$ species. Species **6** and **7** may be resonance structures of a $U^{4+}$–peroxide compound which is an isomer of $UO_2^{2+}$.

These transformations appear more plausible than reductions initiated by electron transfer from the $(CF_3CO)_2CH$ anion when excitation is at 450 nm because this is on the red side of the characteristic uranyl adsorption band of the compound (**1**). There is, however, a small contribution to this adsorption feature arising from what is believed to be an anion-to-metal charge-transfer band at 360 nm which could be responsible for some of the photochemistry. In any event, when higher energy bands are excited, ligand excitation becomes more reasonable,[7] but the chemistry appears to be the same. Thus, it appears that rapid relaxation processes lead the system from what may be a mixture of excited states to a common one which ultimately yields observable products. This view is supported by low-temperature fluorescence studies (77 K) which indicate that emission comes from a common state independent of the excitation wavelength between 360 and 450 nm. However, these experiments do not unequivocally rule out chemistry from a distribution of excited states because quantum yield determinations as a function of wavelength have not been made.

The possible formation of peroxides, oxygen, and other oxidation products was studied by wet-chemical and spectral techniques. Peroxide formation has been deduced by the following procedure. Approximately 0.04 M solutions of **1** are irradiated for varying times, and then either the total product mixture or its isolated components are contacted with 20% $H_2SO_4$. This solubilizes both $U^{4+}$ and $UO_2^{2+}$ compounds and dissolves peroxides as $H_2O_2$. The $U^{4+}$ and $UO_2^{2+}$ con-

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(6) R. G. Bray and R. B. Hall, unpublished work.

(7) R. T. Lintvedt in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Eds., Wiley, New York, 1975.

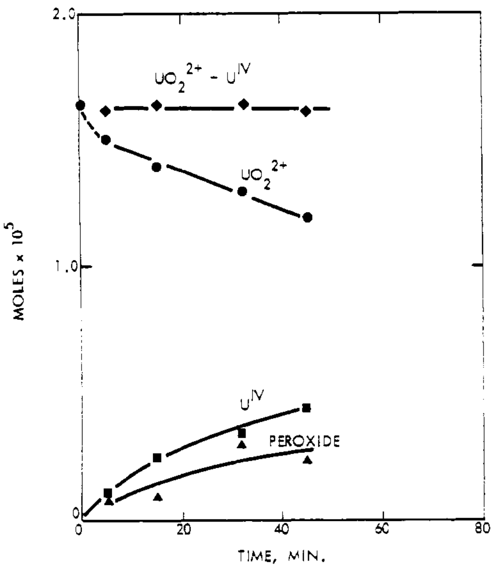

**Figure 2.** Product formation during irradiation of $UO_2[(CF_3CO)_2CH]_2 \cdot THF$ ($N_2$ atmosphere, room temperature).

**Table I.** Solar Radiation of $UO_2[(CF_3CO)_2CH]_2 \cdot THF$ in $nC_7$[a]

| | run | | |
|---|---|---|---|
| | A ($N_2$) | B (air) | C (air) |
| radiatn time, min | 157 | 157 | 420 |
| mol of $O_2$ (ads) ($\times 10^6$) | 0 | 18.8 | 62.4 |
| product | | | |
| liquid, mL | 0.65 | 0.65 | not analyzed |
| $U^{4+}$, mol $\times 10^6$ | 7.77 | 3.67 | |
| $UO_2^{2+}$, mol $\times 10^6$ (diff) | 15.93 | 15.53 | |
| solid, g | 0.0047 | 0.0078 | 0.0526 |
| $U^{4+}$, mol $\times 10^6$ | 2.78 | 5.47 | 16.3 |
| $UO_2^{2+}$, mol $\times 10^6$ | 2.82 | 4.13 | 4.1 |
| amt of peroxide, mol $\times 10^6$ | 3.7 | 3.6 | 16.2 |
| material balance, % uranium | 102 | 100 | not determined |

[a] Reactants: 0.0443 M $UO_2[(CF_3CO)_2CH]_2 \cdot THF$; vol = 0.65 mL; mol of $UO_2^{2+} = 28.8 \times 10^{-6}$.

centrations of the acid are determined from its visible absorption spectrum, and then the acid is titrated with $KMnO_4$. Titration oxidizes all the $U^{4+}$ to $UO_2^{2+}$ and any $H_2O_2$ to oxygen. The difference between the total number of equivalents of oxidizable species per unit volume and the number of equivalents of $U^{4+}$ per unit volume determined spectrally is assumed to be the number of equivalents of peroxide, the titration following the oxidation stoichiometry shown in eq 2.

$$2MnO_4 + 5H_2O_2 + 6H^+ \rightleftharpoons 2Mn^{2+} + 8H_2O + 5O_2 \quad (2a)$$

$$2MnO_4^- + 5U^{4+} + 2H_2O \rightleftharpoons 2Mn^{2+} + 5UO_2 + 4H^+ \quad (2b)$$

(The existence of peroxides is not proved by the titration, but the presence of excess oxidizable species over the amount of $U^{4+}$ is consistent with their proposed presence.)

Figure 2 shows the formation of $U^{4+}$ and peroxide as a result of irradiation of heptane solutions at 450 nm at 23 °C in a nitrogen atmosphere. The shape of the formation curves suggests that both are primary irradiation products. It is not clear because of experimental uncertainty if the peroxide concentration reaches a maximum value or even declines, but this would not be unreasonable as any peroxide would be expected to be photochemically reactive.

These procedures were applied to experiments shown in Table I. The first two columns of data refer to two heptane solutions which were irradiated with sunlight for about 3 h. One was kept under $N_2$ and the other in the presence of air. (Preliminary studies had shown that irradiation under air or $O_2$ results in the adsorption of $O_2$ by the system.) These experiments resulted in the formation of precipitates which were separated and analyzed for $U^{4+}$, $UO_2^{2+}$, and peroxide content. The remaining heptane solutions were analyzed for $U^{4+}$, and residual $UO_2^{2+}$ was estimated by a difference calculation.

**Table II.** Quantum Yield for $O_2$ Adsorption During 450-nm Irradiation of $UO_2[(CF_3CO)_2CH]_2 \cdot THF$ in $nC_7$ (0.0446 M, 23 °C)

| power, mW | $\phi_{O_2}$ |
|---|---|
| 200 | 0.008 |
| 18 | 0.096 |
| 2 | 0.555 (0–4 min)<br>0.33 (2–15 min)<br>0.14 (>20 min) |

These experiments indicate that the same amount of $U^{4+}$ formed and that the solid contained an approximately 1:1:1 mixture of $U^{4+}$, $UO_2^{2+}$, and peroxides in both cases. In a prolonged irradiation experiment under air, the solid products contained more $U^{4+}$ and peroxide in a 1:1 ratio, but the $UO_2^{2+}$ content was substantially reduced.

The data in Table I indicate that oxygen is adsorbed by the system during irradiation in air. This might indicate that electronically excited $[UO_2^{2+}]^*$ is being trapped, but oxygen consumption could be due to other factors. For example, oxygen could react with a radical formed after the attack of $[UO_2^{2+}]^*$ on solvent or its ligands, or the excited uranyl ion could be sensitizing oxygen, perhaps by inducing its conversion to a reactive singlet or triplet. In any case, manometric measurements show that $O_2$ is absorbed when $UO_2^{2+}$ is photoexcited in heptane solutions and further show no evidence of gas absorption or generation when the irradiation is done in an $N_2$ environment. Thus there is no indication of the elimination of gaseous $O_2$ in this reaction.

On the contrary, water has been found to be a reaction product of irradiations under air or $N_2$. In the presence of air and paraffins, the photochemical reaction appears to be catalytic with respect to uranium, and much more than 1 mol of $O_2$/mol of uranyl can be consumed. The use of fluorinated solvents and deuterated tetrahydrofuran in **1** has shown that water is primiarily formed by attack of a reactive intermediate on the hydrocarbon solvent, not the bound THF molecule.

Several experiments have been conducted in order to estimate the quantum yield for oxygen consumption. In these studies light from an argon ion laser at 450 nm was passed through a cylindrical reactor containing a 0.0446 M solution of **1** in $nC_7$. The power absorbed was estimated by the difference between the amount of power passing through the empty reactor and that containing the sample. The measurements were performed with a Model 201 coherent radiation power meter. The solution was saturated with air, and pressure changes were measured with a manometer. The power of the incident CW laser beam was varied from 2 to 200 mW, and the light was confined to about a $^1/_8$ in. diameter area in the reactor.

Solids formed in the region being irradiated and slowly precipitated from solution. From the initial rate of oxygen uptake, quantum yields were estimated as varying from 0.008 to 0.55 as the rate of introducing energy was decreased as shown in Table II. The increase in efficiency at low power suggests that reaction of $O_2$ with the "trappable" intermediate may be a diffusion-controlled process limited by the oxygen solubility. The 55% conversion of photons to oxygenated products indicates that $O_2$ is a good trapping reagent and might be reacting with the primary photoexcited species. For further information concerning this matter, a study of fluorescence quenching of $[UO_2^{2+}]^*$ was undertaken. This is discussed later.

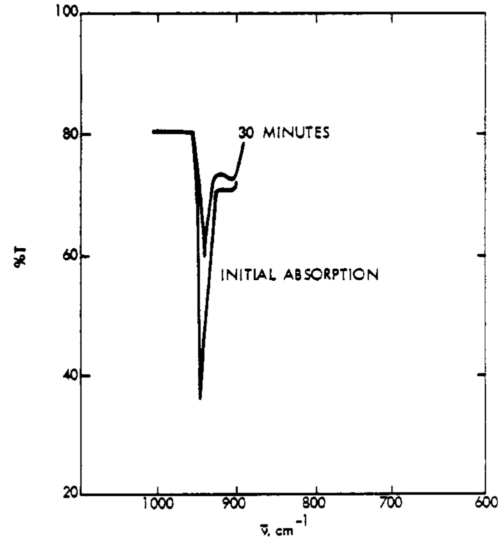

**Figure 3.** 450-nm radiation depletion of $UO_2^{2+}$ in $iC_5$.

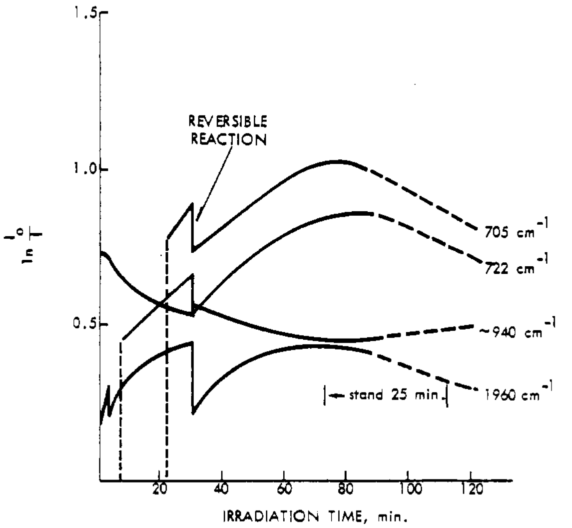

**Figure 4.** Some reversible photochemical changes of $UO_2[(CF_3CO)_2CH]_2{\cdot}THF$ in $iC_5$ (450-nm radiation).

**b. IR and Raman Spectral Changes upon Electronic Excitation.** With respect to the identification of the photoproduct, a pertinent series of observations was made of the infrared spectrum of **1** in isopentane shortly after irradiation at 450 nm. The photoreaction initially leads to the disappearance of the 950-cm$^{-1}$ absorption that characterizes the $\nu_3$ asymmetric stretch of $UO_2^{2+}$. On standing, however, the 950-cm$^{-1}$ band rapidly reappears. Clearly, photoexcitation has led to an intermediate product in which the $[O{=}U{=}O]^{2+}$ bonding system is disrupted, but which thermally reverts in good part to a uranyl compound. In addition to this change there are others in the IR spectrum which appear to revert on the same time scale as the regeneration of the uranyl band (Figures 3 and 4). These spectra were obtained in a cell permitting simultaneous irradiation with an argon ion laser and sample interrogation with an infrared spectrometer.

Figure 4 shows that there is a slow production of product peaks at 705, 722, and 1960 cm$^{-1}$ while the uranyl band at 950 cm$^{-1}$ is depleted during continuous exposure to the argon ion laser. When the laser was turned off (at 30 min), there was a very rapid regeneration of some of the uranyl absorption accompanied by simultaneous loss of the three product peaks.

This facile regeneration of the uranyl absorption makes it unlikely that the participating oxygen atoms of the photoexcited $UO_2^{2+}$ group moved outside the bonding radius of the parent uranium atom or that they were immediately assimilated into a stable oxygenated organic compound. A simple hypothesis that is in accord with all the data is that compound **7**, a $U^{4+}$ peroxide, is initially formed by an intramolecular isomerization. Subsequently, this species might undergo anion-exchange or condensation reactions with other uranyl complexes or reaction with the solvent.

Table III. Raman Bands of Uranyl Compounds

| $UO_2[(CF_3CO)_2CH]_2{\cdot}THF^a$ | | $UO_4 2H_2O^{b,c}$ | | photoproduct$^b$ | |
|---|---|---|---|---|---|
| Δν, cm$^{-1}$ | intensity$^d$ | Δν, cm$^{-1}$ | intensity | Δν, cm$^{-1}$ | intensity |
| 250 | 10 | 831 | 10 | | |
| 744 | 7 | 867 | 7 | 308 | 8 |
| 848 | 5 | 1648 | 1 | | |
| 871 | 10 | 1736 | 0.7 | 393 | 2.5 |
| 953 | 4 | | | 402 | 2.5 |
| 1115 | 4 | | | 841 | 5 |
| 1360 | 10 | | | 855 | 5 |
| | | | | 888 | 2.5 |
| | | | | 900 | 7.5 |
| | | | | 1044 | 2.5 |
| | | | | 1081 | 3 |
| | | | | 1139 | 3 |
| | | | | 1302 | 7 |
| | | | | 1439 | 9 |
| | | | | 1454 | 10 |

[a] Incident λ = 6328 nm. [b] Incident λ = 5145 nm. [c] Not purified. [d] On a scale of 1–10 from weak to strong.

The peroxide unit, $O_2^{2-}$, is not observable by infrared spectroscopy because of the absence of a dipole moment but might be detected by Raman spectroscopy. Accordingly, the Raman spectra of samples of the precipitated photoproduct, of $UO_2[(CF_3CO)_2CH]_2{\cdot}THF$, and of $UO_2O_2(H_2O)_x$, a uranyl peroxide, were examined. The results are consistent with the formation of $U^{4+}O_2^{2-}$ as a Raman band was observed at 900 cm$^{-1}$ in the photoproduct. This is at a slightly higher frequency than found for $UO_2O_2(H_2O)_x$ which exhibited bands at 831 and 867 cm$^{-1}$. Compound **1** has no interfering absorption in the 900-cm$^{-1}$ region. The Raman bands are tabulated in Table III.

**c. NMR Observations.** Nuclear magnetic resonance is particularly useful in studying compound **1** and in assessing the results of photolysis. $^1H$, $^{13}C$, and $^{19}F$ NMR data provide additional information about both the reagent and its derivatives. $^1H$ NMR studies show the $(CF_3CO)_2CH$ proton at δ 6.72 and indicate that the THF molecule is complexed sufficiently to the $UO_2^{2+}$ ion to cause substantial deshielding of its α- and β-$CH_2$ groups. In $HCCl_3$ they appear at δ 5.08 and 2.48, being shifted 1.43 and 0.89 ppm from the corresponding values in neat THF. When small amounts of THF are added to solutions of excess $UO_2[(CF_3CO)_2CH]_2$,[8] which has been independently synthesized and is dimeric in $HCCl_3$, the resonances of the complexed THF molecule are the same as for the 1:1 uranyl–THF complex. This indicates that the complex is relatively stable and equilibrium 3 lies far to the

$$UO_2[(CF_3CO)_2CH]_2{\cdot}THF \rightleftharpoons UO_2[(CF_3CO)_2CH]_2 + THF \quad (3)$$

left. Otherwise the chemical shifts of the $CH_2$ groups would have shifted for the stoichiometric compound **1**.

When **1** is irradiated with UV or visible light, the $^1H$ NMR of the $FAA^-$ proton is unchanged while the α and β methylene groups on THF move upfield. The shift is accompanied by some broadening of the lines in the group multiplets. This

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[8] A. Ekstrom, H. Loeh, C. H. Randall, L. Szego, and J. C. Taylor, *Inorg. Nucl. Chem. Lett.*, **14**, 301 (1978).

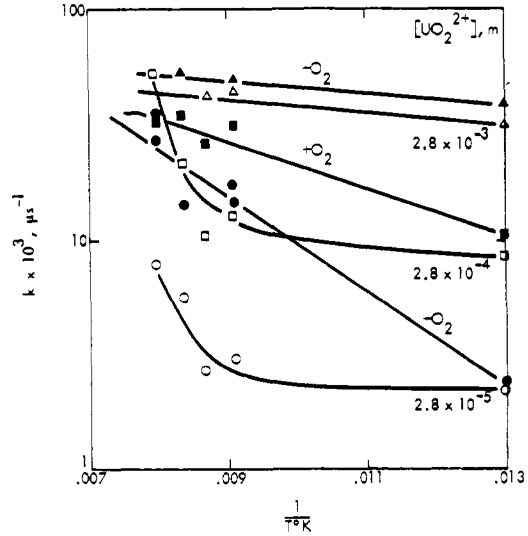

**Figure 5.** Competitive trap in $iC_5$ (oxygen).

change is probably due to two effects. It could be partly the result of an intermolecular exchange process, wherein THF molecules which have been released by photochemical excitation and are now present in slight excess over $UO_2^{2+}(FAA)_2$ act as nucleophilic displacing agents on other $UO_2^{2+}$-$(FAA)_2$·THF molecules (see eq 4). This exchange can be

$$\text{THF} + UO_2[(CF_3CO)_2CH]_2\cdot\text{THF} \rightleftharpoons \text{THF}\cdot UO_2\,[(CF_3CO)_2CH]_2 + \text{THF} \quad (4)$$

observed by adding THF to solutions of **1** in chloroform or benzene. However, another exchange reaction involving THF transfer to $U[(CF_3CO)_2CH]_4$ also is believed to be partly responsible for the shift. Thus, it has been found that the addition of $U[(CF_3CO)_2CH]_4$ to **1** also causes a fast reversible migration of THF and a consequent strong increase in shielding of the methylene protons, as well as broadening.

The radiation-induced THF shifts may therefore be related either to the formation of free THF as **1** is converted to products or to the formation of a $U^{4+}$ product.

Further consideration of the exchange induced by THF alone raises several questions about the structure of $UO_2[(CF_3CO)_2CH]_2$·THF in solution. Low-temperature $^{13}C$ and $^{19}F$ studies indicate that the compound is not static but rather is undergoing an equilibrating process until it is cooled to −90 °C. The nature of this process will be reported separately.[9]

**d. Reaction with Solvent.** Visible photoexcitation of **1** in heptane leads to apparently random attack on the solvent. After reaction, several solutions were analyzed by gas chromatography and mass spectrometry. The analyses were done after 0.04 M solutions of **1** were subjected to sunlight under both $N_2$ and air environments. The uranium compounds were first removed by extraction with 20% $H_2SO_4$ and the remaining products examined on a GC containing an SE-30 column. The separated components were sampled by a mass spectrometer as they exited the GC.

The product distributions were virtually identical from runs with or without oxygen. They consisted of small amounts of about 30 product components, most being heavier than heptane and unidentifiable from the MS cracking patterns. The light components included $CF_3COCH_3$, $CF_3COCH_2COCF_3$, and THF. The major conclusion to be drawn from the large number of relatively small peaks and the similarity of samples obtained under $O_2$ and $N_2$ is that there appears to have been an energetic free-radical process, initiated most likely by $[UO_2^{2+}]^*$ attacking either solvent or coordinated THF. The initial distribution of "hydrocarbon" radicals was the same under both gases and not subject to selective reaction with oxygen. Consequently similar product distributions were observed. No attempts have been made to evaluate the quantum yields of the solvent derived products, but these are believed to be small.

The picture of the photochemical process that emerges from these observations is that activated $UO_2[(CF_3CO)_2CH]_2$·THF yields products containing $U^{4+}$, peroxides, THF, and $UO_2^{2+}$ compounds. It is suggested that an important early product is $U^{4+}O_2^{2-}[(CF_3CO)_2CH]_2\cdot x$THF, an isomer of **1**. Through subsequent ligand exchange with other reactants this is probably converted to a complex mixture of $U[(CF_3CO)_2CH]_4$, $UO_4$, $UO_2^{2+}$, and THF which precipitates from solution. Sections a–d lead to the photochemistry summarized in Chart II.

**Chart II.** Photochemical Conversion of $UO_2[(CF_3CO)_2CH]_2$·THF

$$\underset{\mathbf{1}}{UO_2[(CF_3CO)_2CH]_2\cdot\text{THF}} \xrightarrow{h\nu} \underset{\mathbf{2}}{U^{4+}O_2^{2-}[(CF_3CO)_2CH]_2} + \text{THF}$$

$$\mathbf{1} + \mathbf{2} \rightleftharpoons \text{adduct } \mathbf{8}$$

$$\mathbf{8} \rightarrow \underset{\mathbf{9}}{U[(CF_3CO)_2CH]_4} + \underset{\mathbf{10}}{UO_4}$$

$$\mathbf{2} + \text{solvent} \rightarrow \text{H-}\mathbf{2} + \text{solvent}$$

The reversible formation of the $U^{4+}$–peroxide complex **2** is inferred from the time dependence of the IR spectra immediately after excitation with a visible or UV laser. Whether or not THF is bound to **2** is unknown, but the formation of adduct **8** is indicated by the elemental analysis of the solid precipitates formed in either the presence or absence of molecular oxygen and is supported by the Raman observations. The eventual formation of **9** is evident from the visible–near-IR spectral studies of the initial product solutions and the vapor-phase FTIR detection of the compound by Hall and Bray.[6] Finally, the attack on solvent is inferred by the detection of water as a photoproduct.

The reactions in Chart II occur in the absence of molecular oxygen. It has been noted that photoexcitation in the presence of $O_2$ leads to its eventual incorporation into $H_2O$, but no indication was found of a change in the distribution of the organic reaction products which might have indicated the formation of a special oxidizing intermediate. Whether or not $O_2$ interacts with the excited uranyl or only perhaps with free radicals subsequent to their formation can be studied by observing its effect upon the fluorescence behavior of the ion. This is considered in the next section.

**e. Fluorescence Studies in Solution.** The activated $UO_2^{2+}$ ion interacts with $O_2$ and results in its incorporation into products as indicated above. For a further probe of this interaction, the fluorescence and quenching of **1** was studied.

Although many uranyl compounds fluoresce readily at room temperature, **1** does not. Its fluorescence can, however, be observed when it is cooled or frozen in a glassy matrix at 77 K. In hydrocarbon matrices like isopentane or a 20:80 isopentane/methylcyclohexane mixture the fluorescence lifetime is about 300 μs. ($\tau$ is the reciprocal of the rate constant for the first-order decay process.)

Fluorescence lifetime measurements were made as described above, and the rate constants are plotted in Figure 5 as a function of temperature and concentration in isopentane. Also shown is the effect of oxygen on the quenching rate. The data indicate that the fluorescence quenching rate is constant until the matrices are warmed to about 100 K and then accelerates.

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[9] G. M. Kramer, M. B. Dines, R. Kastrup, M. T. Melchior, and E. T. Maas, Jr., *Inorg. Chem.*, **20**, 3 (1981).

This increase has an activation energy of about 3–4 kcal/mol and begins slightly below isopentane's melting point of 113 K.

Of considerable interest is the effect of varying the concentration of **1**. The data again indicate that there is a substantial interaction or self-quenching between the small fraction of $UO_2^{2+}$ ions which are excited and the remaining molecules, even though they are isolated in the frozen matrix. In addition, the graph shows $O_2$ to be an effective fluorescence quenching agent. Oxygen was added to the reactor cells at 1 atm at 23 °C for these experiments.

In a series of related studies the conversion of $UO_2^{2+}$ to nonradiative products was observed between 91 and 117 K. A mercury lamp was used to produce a steady-state excitation of a solution of **1** in an 80:20 MCH/iC$_5$ mixture. The slow conversion of **1** to some product was followed by measuring the fluorescence intensity being emitted. This decreased either because of the conversion of **1** to a nonfluorescing compound or because of the formation of quenching agents.

The apparent loss of **1** is orders of magnitude slower than the rate of fluorescence of $[UO_2^{2+}]^*$ at these temperatures. The rate constant, $k_{nr} = 3.4 \times 10^3 e^{-2900}/RT$, shows both a very low preexponential factor and a low temperature coefficient similar to that for the radiative process. If extrapolation of the rate constants for both processes to ambient temperatures were meaningful, one would conclude that, in the absence of a trapping reagent, fluorescence emission from $[UO_2^{2+}]^*$ proceeds preferentially. This means that inefficient photochemical conversion of **1** to product is to be expected unless a good trap is available for the excited ion.

The data in Figure 5 indicate that $O_2$ may be such a trap. It should also be noted however that the extrapolation from 100 to 300 K is a long one, and it may well be that additional photochemical decomposition paths open up at the elevated temperatures. These would naturally tend to enhance the changes of capturing the photoexcited ion by a intramolecular process.

The quenching processes can be considered in a Stern–Volmer kinetic framework. With respect to quenching rates such a treatment is described by eq 5–10. In these equations,

$$UO_2^{2+} \xrightarrow{h\nu} [UO_2^{2+}]^* \tag{5}$$

$$[UO_2^{2+}]^* \rightarrow UO_2^{2+} + h\nu \tag{6}$$

$$[UO_2^{2+}]^* \xrightarrow[L,\,S]{} UO_2^{2+} \text{ or product} \tag{7}$$

$$[UO_2^{2+}]^* \xrightarrow[UO_2^{2+},\,Q]{} UO_2^{2+} \text{ or product} \tag{8}$$

$$k = k_6 + k_7 + k_8[Q] \tag{9}$$

$$\frac{k}{k_0} = 1 + \frac{k_8[Q]}{k_6 + k_7} = 1 + k_8\tau[Q] = 1 + k_{SV}[Q] \tag{10}$$

L and S denote ligands or solvent, Q is a quenching agent which may be $UO_2^{2+}$ when self-quenching occurs, $\tau$ is the measured fluorescence lifetime in the absence of quenching agent, and $k_{SV}$ is the Stern–Volmer quenching constant.

Equation 9 expresses the rate constant for the overall depletion of activated $UO_2^{2+}$. It is composed of three terms, $k_6$ being the fluorescence rate constant measured in the flash photolysis experiments, $k_7$ being the nonradiative decay constant in the absence of added quenching agents, which is what is measured in the steady-state Hg-lamp studies, and $k_8[Q]$ being the quenching or self-quenching contribution. The last contribution is expected to be a negligible at low concentrations of Q or $UO_2^{2+}$.

**Table IV.** Fluorescence Quenching Constants ($k/k_0 = 1 + K_{SV}[Q]$)

| | | $K_2$, atm$^{-1}$ $O_2$ | | |
|---|---|---|---|---|
| *T*, K | $K_1$,[a] M$^{-1}$ | $3 \times 10^{-5}$ | $3 \times 10^{-4}$ | $3 \times 10^{-3}$ [b] |
| 77 | 4790 | 0.9 | 0.9 | 1 |
| 110 | 4920 | 11 | 4 | 0.4 |
| 115 | 5200 | 88 | 4 | 2 |

[a] $K_1$ is the Stern-Volmer constant for self-quenching and $K_2$ for quenching by oxygen. [b] Concentration of $UO_2[(CF_3CO)_2 \cdot THF$, M.

**Table V.** Fluorescence Lifetimes in Frozen Matrices ($UO_2[(CF_3CO)_2CH]_2 \cdot THF$, $1.7 \times 10^{-4}$ M, 110 K)

| solvent | $\tau$, $\mu$s | solvent | $\tau$, $\mu$s |
|---|---|---|---|
| cyclohexane | 221 | tetrahydrofuran | 28 |
| benzene | 147 | perfluoromethylcyclohexane | <28 |
| $CCl_4$ | 216 | benzaldehyde | <28 |
| isopentane | 61 | heptane | <28 |
| ethanol | 37 | | |

In Table IV the apparent $K_{SV}$ constants for self-quenching and for reaction with oxygen are listed for the experiments in isopentane. From the data it can be shown that $O_2$ at 110–115 K will compete very effectively with the other uranyl compounds in quenching $[UO_2^{2+}]^*$. The fact that oxygen is a good reagent is also seen in Figure 5.

As indicated above, the lifetime of excited **1** depends on the matrix in which it is frozen. The variation may be related to viscosity or vibrations of the frozen lattice but may also be related to chemical reaction with the solvent. A comparison of lifetimes in solvent matrices at 110 K is shown in Table V. We do not have a good explanation for the observed order of stability, particularly for the cyclohexane:isopentane:heptane series in which it is 221 and 61 s and *then too short to measure.* Ethanol, tetrahydrofuran, and benzaldehyde all contain potentially labile hydrogen atoms and might be expected to be reasonable trapping reagents. The role of perfluoromethylcyclohexane is also unclear although it could be acting as an effective electron acceptor or oxidizing agent. The series does clearly indicate that there are many potential trapping reagents for photoexcited **1**.

## Summary

Electronic excitation of $UO_2[(CF_3CO)_2CH]_2 \cdot THF$ in hydrocarbon media has been found to yield a $U^{4+}$ product, probably $U[(CF_3CO)_2CH]_4$. Its formation is proposed as occurring via the intermediacy of a "$U^{4+}$–peroxide" or isouranyl species, an isomer of $UO_2^{2+}$. Formation of these compounds are deduced from IR, UV, NMR, Raman, and wet-chemical studies.

The excited uranyl compound has further been found to interact with oxygen which acts both as a fluorescence quenching agent and as a reagent in the reactions of organic solvents.

Both the isouranyl and the possible uranyl–oxygen adduct are potentially important intermediates in the chemistry of electronically excited uranyls.

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