Inorg. Chem. **1995,** *34,* 6034−6039

Uranium(VI)-Catalyzed Photooxidation of Hydrocarbons with Molecular Oxygen

Wei-Dong Wang, Andreja Bakac,* and James H. Espenson

Ames Laboratory and Chemistry Department, Iowa State University, Ames, Iowa 50011

Received June 29, 1995[⊗]

Uranium(VI) catalyzes the photooxidation of alkanes, alkenes, alcohols, and aldehydes by molecular oxygen in aqueous solution. Despite the mechanistic complexities, each of the reactions investigated yielded a single organic product. On the basis of the quenching kinetics, the deuterium isotope effects, the nature of the products, and linear free energy relationships, all the reactions appear to take place by hydrogen atom abstraction from C−H bonds, followed by uranium-mediated product formation.

Introduction

Alkanes have a great potential as feedstocks in the chemical industry, but the low reactivity of alkanes requires that they be activated. Major research efforts are directed toward the discovery of novel chemical reactions, materials, and processes that would result in catalytic activation of hydrocarbons. The activation often consists of partial oxidation to a compound that is chemically more reactive, or occurs by oxidative addition to transition metal complexes to form metal alkyls and metal hydrides. Both chemical[1] and photochemical[2] activation of alkanes,[1,3−5] and specifically methane,[6−9] have been accomplished, but the bulk of the problem still remains to be solved.

Oxygen-centered radicals are among the rare species that react readily with alkanes. These reactions take place by hydrogen atom abstraction and yield carbon-centered radicals, which then react further with added reagents. For example, the rate constant for the reaction of cyclopentane with hydroxyl radicals is 4×10^9 M^{-1} s^{-1},[10] and that for reaction with *tert*-butoxyl radicals is 1×10^6 M^{-1} s^{-1}.[11,12] Thus any reaction producing $HO^\bullet$ or *tert*-$BuO^\bullet$ could be used to activate alkanes, but stoichiometric reactions are not useful from the practical point of view.

Visible light photolysis of UO_2^{2+} yields a long-lived, strongly luminescent excited state, which can be best described as an oxygen-centered radical bound to U(V).[13,14] The intense visible spectrum[15] of the excited state provides strong evidence for ligand-to-metal charge transfer (LMCT).

$^*UO_2^{2+}$ is a strong oxidant ($E° = 2.6$ V) and unreactive toward O_2.[13] Both of these factors are important for UO_2^{2+} to be useful as a photocatalyst for oxidations with molecular oxygen according to the mechanism of Scheme 1.

Scheme 1

$$UO_2^{2+} + h\nu \rightarrow {}^*UO_2^{2+} \tag{I-1}$$

$${}^*UO_2^{2+} + \text{substrate} \rightarrow UO_2^{+} + \text{substrate radical} + H^+ \tag{I-2}$$

$$\text{substrate radical} + O_2 \rightarrow \text{oxidized products} \tag{I-3}$$

$$2UO_2^{+} + O_2 + 2H^+ \rightarrow 2UO_2^{2+} + H_2O_2 \tag{I-4}$$

A large number of inorganic and organic materials quench the luminescence of $^*UO_2^{2+}$.[13,16] In the case of aliphatic alcohols,[15,17,18] carboxylic acids,[19−21] and several other substrates,[22−24] the quenching takes place in chemical reactions that include hydrogen atom abstraction, oxygen atom transfer, and electron transfer. The hydrogen atom abstraction of eq I-2 further demonstrates the free radical nature of $^*UO_2^{2+}$. The chemistry in eq I-3 is well documented,[25] and our recent work[26] on the autoxidation of UO_2^+ has shown that reaction I-4 is sufficiently rapid for Scheme 1 to work.

The reported rate constants for the oxidation of alcohols by $^*UO_2^{2+}$ vary widely,[15,17,27−29] although the lower values for each

---

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

(1) Shilov, A. E. D. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel Publishing Company: Dordrecht/Boston/Lancaster, 1984.

(2) Fox, M. A.; Dulay, M. T. *Chem. Rev.* **1993**, *93*, 341.

(3) Gai, P. L.; Kourtakis, K. *Science* **1995**, *267*, 661.

(4) Grinstaff, M. W.; Hill, M. G.; Labinger, J. A.; Gray, H. B. *Science* **1994**, *264*, 1311.

(5) Bergman, R. G. *Science* **1984**, *223*, 902.

(6) Bergens, S. H.; Gorman, C. B.; Palmore, G. T. R.; Whitesides, G. M. *Science* **1994**, *265*, 1418.

(7) Periana, R. A.; Taube, D. J.; Evitt, E. R.; Loffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. *Science* **1993**, *259*, 340.

(8) Hickman, D. A.; Schmidt, L. D. *Science* **1993**, *259*, 343.

(9) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305.

(10) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

(11) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.

(12) Baban, J. A.; Goddard, J. P.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1269.

(13) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.

(14) Wheeler, J.; Thomas, J. K. *J. Phys. Chem.* **1984**, *88*, 750.

(15) Hill, R. J.; Kemp, T. J.; Allen, D. M.; Cox, A. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 847.

(16) Hoffman, M. Z.; Bolletta, F.; Moggi, L.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1989**, *18*, 219.

(17) Azenha, M. E. D. G.; Burrows, H. D.; Formosinho, S. J.; Miguel, M. D. G. M. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2625.

(18) Ledwith, A.; Russell, P. J.; Sutcliffe, L. H. *Proc. R. Soc. London, A* **1973**, *332*, 151.

(19) Burrows, H. D.; Formosinho, S. J. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 201.

(20) Roundhill, D. M. *Photochemistry and Photophysics of Metal Complexes,* Plenum Press: New York and London, 1994; p 313.

(21) Greatorex, D.; Hill, R. J.; Kemp, T. J.; Stone, T. J. *J. Chem.Soc., Faraday Trans. 1* **1972**, 2059.

(22) Miyake, C.; Yamana, Y.; Imoto, S.; Ohya-Nishiguchi, H. *Inorg. Chim. Acta* **1984**, *95*, 17.

(23) Sandhu, S. S.; Kohli, K. B.; Brar, A. S. *Inorg. Chem.* **1984**, *23*, 3609.

(24) Bhatt, R.; Shrimali, P. S.; Ameta, S. C.; Chowdhry, H. C. *Z. Phys. Chem. (Leipzig)* **1986**, *267*, 817.

(25) Batt, L. *Int. Rev. Phys. Chem.* **1987**, *6*, 53.

(26) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1995**, *34*, 1730.

(27) Sergeeva, G.; Chibisov, A.; Levshin, L.; Karyakin, A. *J. Chem. Soc., Chem. Commun.* **1974**, 159.

(28) Sergeeva, G. I.; Chibisov, A. K.; Levshin, L. V.; Karyakin, A. V. *J. Photochem.* **1976**, *5*, 253.

(29) Burrows, H. D.; Formosinho, S. J. *J. Chem. Educ.* **1978**, *55*, 125.

0020-1669/95/1334-6034$09.00/0

alcohol (MeOH, $k \sim 10^6\ M^{-1}\ s^{1}$, 2-PrOH, $k \sim 10^7\ M^{-1}\ s^{1}$) appear to be more realistic. Thus $*UO_2^{2+}$ is 2–3 orders of magnitude less reactive than $HO^{\bullet}$ toward aliphatic alcohols. This result has probably discouraged any serious attempts to use $*UO_2^{2+}$ as oxidant for the more challenging substrates, such as straight chain hydrocarbons, given that the C–H bond energies are larger and the expected reactivities lower for hydrocarbons than for alcohols. The poor solubility of hydrocarbons in water makes the problem even more difficult in that the combination of the expected small rate constants and low concentrations would make the bimolecular reactions of these substrates with $*UO_2^{2+}$ too slow to compete with the spontaneous decay of $*UO_2^{2+}$.

The solubility problem can be circumvented by use of "innocent" cosolvents, i.e. those that do not engage in chemical reactions with $*UO_2^{2+}$, although the benefit of increased solubility is partly offset by the reduced lifetimes of $*UO_2^{2+}$ in such solvents.[16] The bottom line is that Scheme 1 can work for alkanes only if the rate constant for reaction I-2 is $\gg 10^4\ M^{-1}\ s^{-1}$. We now report that this is indeed true for all the alkanes examined, with the likely exception of CH_4.

Experimental Section

Materials. Solutions of UO_2^{2+} were prepared by dissolving UO_3 (Strem) in dilute $HClO_4$. The commercial products 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt, $(NH_4)_2ABTS$ (Aldrich), alkanes (Aldrich and Air Products), and alkenes (Aldrich) were used as received. Chloride-free solutions of methyl viologen (MV^{2+} = 4,4′-dimethyl-4,4′-bipyridinium ion) were prepared by ion exchange of $(MV)Cl_2$ (Aldrich) on Sephadex C-25. The dication was eluted with 1 M lithium trifluoromethanesulfonate.

The Kinetics of the reactions of $*UO_2^{2+}$ with the desired substrates were studied by laser flash photolysis using either a Phasar dye laser[30] (λ_{exc} = 490, 460, or 423 nm; pulse width = 0.5 μs) or an Applied Photophysics Nd:Yag laser (λ_{exc} = 355 nm; pulse width = 10 ns).[31] In the dye laser experiments, the excited state was generated by laser-flashing an acidic aqueous or semiaqueous solution of 0.25–2.5 mM UO_2^{2+} containing the substrate and 0.6 M H_3PO_4. In such solutions the lifetime of $*UO_2^{2+}$ is ~100 μs, much longer than in the absence of H_3PO_4 (~3 μs),[13,16] but the reactivities toward oxidizable substrates are comparable in the two media.[16] The 10 ns pulse width of the Nd:Yag laser allowed experiments to be carried out in both the presence and absence of H_3PO_4.

The concentration of the excited state was kept in the 0.5–5 μM range. Owing to the strong luminescence and intense absorption spectrum ($\epsilon_{*580} = 4.5 \times 10^3\ M^{-1}\ cm^{-1}$, see later), even such low concentrations were sufficient to produce good signals for the kinetics determinations.

Most of the reactions were monitored by observing the decay of the $*UO_2^{2+}$ luminescence at 495 nm. Occasionally, a decrease in the 580 nm absorbance of $*UO_2^{2+}$ was monitored. The two kinds of experiments yielded identical results.

Product Analysis. Reaction mixtures were photolyzed by use of a Rayonet UV reactor, a 300 W sunlamp, or an Oriel quartz tungsten halogen source equipped with a cold mirror and a 250 W lamp. Because of the low molar absorptivity of UO_2^{2+} in the visible part of the spectrum and the low energy output of the tungsten lamp, the samples had to be photolyzed for a long time (2 h) to yield the amounts of products comparable to those obtained by 30 min photolyses in the Rayonet reactor. The uranium product, UO_2^{+}, was identified by its UV spectrum in air-free experiments.[32] For this purpose, the photolysis times were cut to 2–20 min, because the disproportionation of UO_2^{+} becomes significant at longer times.

Hydrogen peroxide was determined by adding an excess of NaI to a spent reaction solution and monitoring the formation of I_3^- at 350 nm. The concentration of I_3^- was calculated from the absorbance change, and the kinetics confirmed that H_2O_2 was the oxidant. Such experiments were conducted for cyclopentane, cyclohexane, and 2-propanol.

The organic products were determined for several reactions that were run in air- or O_2-saturated solutions. In a typical experiment, 0.1 mL of substrate (cyclopentane or cyclohexene) was added to an aqueous solution containing 25 mL of 1.5 mM UO_2^{2+} and 0.6 M H_3PO_4 in a quartz tube. The tube was sealed, and the solution was stirred and photolyzed. The solution was then purged for 30 min with a stream of argon to remove most of the volatile organic materials and deposit them in a liquid nitrogen/ethanol trap. This organic material contained both the unchanged reactants as well as products and some water. The analysis of the products was carried out by GC-MS (cyclopentanone) or HPLC (2-cyclohexen-1-one).

The reaction of acetaldehyde (1 M) was run in air-saturated D_2O at 0.6 M H_3PO_4 and 1.5 mM UO_2^{2+}. After 60 min, the NMR spectrum was run directly on the reaction solution.

GC-MS analyses employed a Magnum GC-MS instrument equipped with a DB-5 capillary column. HPLC chromatograms were obtained by use of a Waters instrument equipped with a model 996 photodiode array detector and a Waters Nova-Pak C_{18} reverse phase column. The NMR spectra were run on a Nicolet 300 spectrometer.

Results

Molar Absorptivity of $*UO_2^{2+}$. The spectrum of $*UO_2^{2+}$ in 0.6 M H_3PO_4 exhibits a maximum at 580 nm. The molar absorptivity (ϵ_{*580}) was determined by use of two different reactions involving the strongly colored species $ABTS^{\bullet-}$ and $MV^{\bullet+}$, as described below.

$*UO_2^{2+}$ was generated in a laser flash (λ_{exc} = 423 nm), and the absorbance at 580 nm was recorded. The colorless $ABTS^{2-}$ was then injected in small increments, and each time the solution was flashed. The formation and subsequent disappearance of $ABTS^{\bullet-}$, reactions 1 and 2, were monitored at 650 nm. This process was repeated until additional amounts of $ABTS^{2-}$ caused no further increase in $[ABTS^{\bullet-}]$ produced, i.e. when the quenching by $ABTS^{2-}$ became much faster than the self-decay of $*UO_2^{2+}$. It was assumed that all the $*UO_2^{2+}$ had reacted by the electron transfer of eq 1. Using $\epsilon_{650}(ABTS^{\bullet-}) = 1.35 \times 10^4\ M^{-1}\ cm^{-1}$,[33] we obtain $\epsilon_{*580} = 4.4 \times 10^3\ M^{-1}\ cm^{-1}$. In these experiments, the kinetics of absorbance increase and the subsequent decrease at 650 nm yielded $k_1 = (1.33 \pm 0.02) \times 10^9\ M^{-1}\ s^{-1}$ and $k_2 = (4.6 \pm 0.5) \times 10^7\ M^{-1}\ s^{-1}$.

$$*UO_2^{2+} + ABTS^{2-} \rightarrow UO_2^{+} + ABTS^{\bullet-} \qquad (1)$$

$$UO_2^{+} + ABTS^{\bullet-} \rightarrow UO_2^{2+} + ABTS^{2-} \qquad (2)$$

The second method for the determination of ϵ_{*580} was based on the known chemistry of eqs 3–5.[15,32,34,35] The concentrations

$$*UO_2^{2+} + (CH_3)_2CHOH \rightarrow UO_2^{+} + (CH_3)_2C^{\bullet}OH + H^{+} \qquad (3)$$

$$(CH_3)_2C^{\bullet}OH + MV^{2+} \rightarrow (CH_3)_2CO + MV^{\bullet+} \qquad (4)$$

$$UO_2^{2+} + MV^{\bullet+} \rightarrow UO_2^{+} + MV^{2+} \qquad (5)$$

of 2-PrOH (0.26 M) and MV^{2+} (2×10^{-4} M) were chosen such that reaction 3 was the sole pathway for the disappearance of

---

(30) Melton, J. D.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986**, *25*, 4104.

(31) Huston, P.; Espenson, J. H.; Bakac, A. *J. Am. Chem. Soc.* **1992**, *114*, 9510.

(32) Howes, K. R.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1988**, *27*, 791.

(33) Scott, S. L.; Chen, W.-J.; Bakac, A.; Espenson, J. H. *J. Phys. Chem.* **1993**, *97*, 6710.

(34) Venturi, M.; Mulazzani, Q. G.; Hoffman, M. Z. *J. Phys. Chem.* **1984**, *88*, 912.

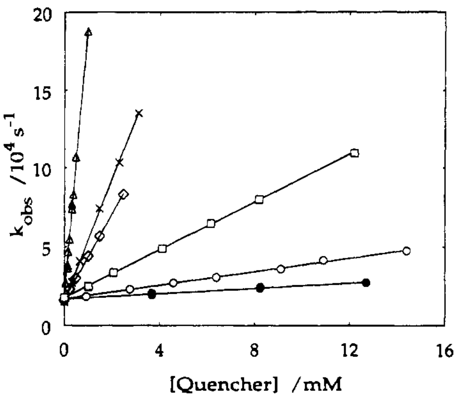

Figure 1. Plot of k_{obs} against the concentration of excess reagent for the reactions of $*UO_2^{2+}$ with cyclohexene (triangles), acetaldehyde (crosses), 3,3-dimethyl-1-butene (diamonds), 2-propanol (squares), cyclohexane (open circles), and cyclohexane-d_{12} (filled circles) in 0.6 M aqueous H_3PO_4 at 25 °C.

$*UO_2^{2+}$, and all of $(CH_3)_2C^{\bullet}OH$ was oxidized by MV^{2+} in reaction 4. The formation and disappearance of $MV^{\bullet+}$ were monitored at 600 nm, where $\epsilon(MV^{\bullet+}) = 1.37 \times 10^4\ M^{-1}\ cm^{-1}$.[36] Except for the sign, the absorbance changes in reactions 4 and 5 were identical and yielded values for $\Delta[MV^{\bullet+}] = [*UO_2^{2+}]_0$ which led to $\epsilon_{*580} = 4.6 \times 10^4\ M^{-1}\ cm^{-1}$. These experiments also yielded the rate constants $k_4 = (3.34 \pm 0.10) \times 10^9\ M^{-1}\ s^{-1}$ and $k_5 = (3.80 \pm 0.10) \times 10^7\ M^{-1}\ s^{-1}$, both in good agreement with the published values.[34,35,37]

The close agreement between the two values of ϵ_{*580} strongly supports the notion that reactions 1 and 3 are the only important pathways for the quenching of $*UO_2^{2+}$ by $ABTS^{2-}$ and $(CH_3)_2CHOH$, respectively. If other pathways were operative, then their relative importance, and therefore the values of ϵ_{*580}, would be expected to differ significantly for species so chemically different as $ABTS^{2-}$ and 2-PrOH. The average value of ϵ_{*580} obtained here, $(4.5 \pm 0.1) \times 10^3\ M^{-1}\ cm^{-1}$, is almost twice as large as that reported earlier ($2.5 \times 10^3\ M^{-1}\ cm^{-1}$) in 1 M H_3PO_4.[28]

The reactions of $*UO_2^{2+}$ with organic substrates took place according to the rate law of eq 6. These experiments were

$$-d[*UO_2^{2+}]/dt = k_{obs}[*UO_2^{2+}] = (k_0 + k_Q[RH])[*UO_2^{2+}] \quad (6)$$

conducted under pseudo-first-order conditions with [RH] much greater than $[*UO_2^{2+}]$. A plot of the pseudo-first order rate constants against the concentration of excess reagent is shown for several substrates in Figure 1. Table 1 summarizes the results.

In addition to alkanes, several alkenes and an aldehyde were also studied. Because of the discrepancies among the reported rate constants for the oxidation of aliphatic alcohols by $*UO_2^{2+}$, we have remeasured the kinetics for several alcohols under the conditions used for other substrates in this work. The results agree with some of the literature reports.[15,17,29]

Some of the measurements were conducted in purely aqueous solutions, but in most cases a cosolvent was required. The oxidation of cyclopentane and the alcohols was conducted in both H_2O and 1:1 H_2O/CH_3CN. Once the difference in the lifetimes of $*UO_2^{2+}$ in the two media is taken into account ($k_0 = 1.0 \times 10^4\ s^{-1}$ in H_2O, $1.7 \times 10^4\ s^{-1}$ in 1:1 H_2O/MeCN), the rate constants differ by less than a factor of two. We assume that the solvent effect for other substrates in Table 1 is similarly small.

Table 1. Kinetic Data ($M^{-1}\ s^{-1}$) for the Quenching of $*UO_2^{2+}$ by Organic Substrates[a]

substrate	$k_Q(H_2O)$[b]	k_Q(1:1 $MeCN/H_2O$)[c]
	Alkanes	
methane[d]	$<2 \times 10^5$	
ethane[d]	1.4×10^6	
butane[d]	2.6×10^6	
2,2,3,3-tetramethylbutane		$(3.21 \pm 0.29) \times 10^5$
n-pentane		$(5.90 \pm 0.47) \times 10^5$
n-hexane		$(7.43 \pm 0.23) \times 10^5$
cyclopentane	$(2.41 \pm 0.25) \times 10^6$	$(1.43 \pm 0.10) \times 10^6$
cyclohexane		$(2.16 \pm 0.07) \times 10^6$
cyclohexane-d_{12}		$(8.20 \pm 0.47) \times 10^5$
	Alkenes	
3,3-dimethyl-1-butene		$(2.69 \pm 0.01) \times 10^7$
1-hexene		$(3.28 \pm 0.04) \times 10^7$
trans-3-hexene		$(7.75 \pm 0.07) \times 10^7$
c-hexene		$(1.76 \pm 0.03) \times 10^8$
2,3-dimethyl-2-butene		$(4.10 \pm 0.40) \times 10^8$
	Alcohols	
methanol	$(1.54 \pm 0.03) \times 10^6$ $(6.23 \pm 0.14) \times 10^6$[e]	$(9.49 \pm 0.04) \times 10^5$
ethanol	$(6.65 \pm 0.08) \times 10^6$	$(4.14 \pm 0.07) \times 10^6$
c-pentanol		$(1.04 \pm 0.01) \times 10^7$
2-propanol	$(1.36 \pm 0.01) \times 10^7$	$(7.56 \pm 0.04) \times 10^6$
t-butanol	$(1.42 \pm 0.02) \times 10^5$	$(7.48 \pm 1.26) \times 10^4$
$(CD_3)_3COH$	$(6.29 \pm 0.05) \times 10^4$	
$(CD_3)_3COD$	$(6.72 \pm 0.03) \times 10^4$[f]	
	Aldehydes	
acetaldehyde	$(3.83 \pm 0.03) \times 10^7$	
CD_3CDO	$(1.60 \pm 0.01) \times 10^7$ $(1.44 \pm 0.01) \times 10^7$[f]	
CH_3CDO	$(1.49 \pm 0.01) \times 10^7$ $(1.34 \pm 0.01) \times 10^7$[f]	

[a] Temperature 25 °C, $[UO_2^{2+}] = 0.25-2.5$ mM, $\lambda_{excitation} = 490$, 460, 423, or 355 nm. [b] In H_2O containing 0.6 M H_3PO_4. [c] In 1:1 CH_3CN/H_2O (v/v) containing 0.6 M H_3PO_4. [d] Single experiment. [e] In 0.1 M aqueous CF_3SO_3H, no phosphate present. [f] In D_2O containing 0.6 M H_3PO_4.

The deuterium kinetic isotope effects were determined for cyclohexane ($k_H/k_D = 2.6$), *tert*-BuOH (2.2), and acetaldehyde (2.4) (Table 1). These values are similar to those measured for the oxidation of alcohols by $*UO_2^{2+}$,[15,17] and of alcohols and other substrates by the oxygen-centered radicals $Me_3CO^{\bullet}$,[11] $SO_4^{\bullet-}$,[38] and $NO_3^{\bullet}$.[39] The solvent isotope effect on k_Q (Table 1) is negligible in all cases.

Only a single kinetic measurement on an alkane-saturated aqueous solution was made for each of the gaseous alkanes (methane, ethane, and *n*-butane). The solubilities of alkanes in 0.6 M H_3PO_4 were assumed to be the same as those in pure H_2O (methane, 1.31 mM; ethane, 1.78 mM; butane, 1.25 mM).[40,41]

Products. The irradiation of 0.1 mM UO_2^{2+} and an excess of substrate under argon in a Rayonet UV reactor ($\lambda_{irradiation} = 254$ nm) for 1–2 min yielded measurable amounts of UO_2^{+} in all the cases examined (methanol, 2-propanol, *tert*-butanol, ethane, butane, cyclopentane, and 3,3-dimethyl-1-butene), confirming the redox nature of the quenching processes. With alcohols as reductants, the conversion of UO_2^{2+} to UO_2^{+} was

---

(35) Meisel, D.; Mulac, W. A.; Matheson, M. S. *J. Phys. Chem.* **1981**, *85*, 179.

(36) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

(37) Howes, K. R.; Pippin, C. G.; Sullivan, J. C.; Meisel, D.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1988**, *27*, 2932.

(38) Clifton, C. L.; Huie, R. E. *Int. J. Chem. Kinet.* **1989**, *21*, 677.

(39) Ito, O.; Akiho, S.; Iino, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1606.

(40) Fogg, P. G. T.; Gerrard, W. *Solubility of Gases in Liquids: a critical evaluation of gas/liquid systems in theory and practice*; Wiley: New York, 1991.

(41) Dean, J. A. *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, 1985; Section 10.

quantitative, as expected.[26] In the case of alkanes and CH_2CHCMe_3, the reduction to UO_2^+ was ~50% complete.

The photolysis with visible light yielded a well defined spectrum of UO_2^+ ($\lambda_{max} = 250$ nm) only in the case of alcohols (0.4 M). After 20 min of irradiation, alkanes and alkenes produced a shoulder at 250 nm, corresponding to ~20% reduction of UO_2^{2+} to UO_2^+. The low molar absorptivity of UO_2^{2+} at $\lambda > 350$ nm, and the reoxidation of UO_2^+ by the alkyl radicals formed are responsible for the low yields of UO_2^+.

Significant amounts of H_2O_2 (~1 mM) were produced in the reactions of cyclopentane, cyclohexane, and 2-propanol in the presence of O_2. A direct comparison with the yields of organic products cannot be made, however, because the sample preparation was different for the two types of analyses, as described in the Experimental Section.

The organic products were determined for representative compounds in the presence of O_2 for three classes of substrates: alkanes, alkenes, and aldehydes. Previous work has already established that $*UO_2^{2+}$ oxidizes alcohols to aldehydes/ketones.

The reaction of $*UO_2^{2+}$ with acetaldehyde yielded acetic acid, which was identified by NMR. Cyclopentane yielded cyclopentanone as the only observable product by GC-MS, and cyclohexene produced 2-cyclohexen-1-one (HPLC). In all three cases, $*UO_2^{2+}$ was generated by photolysis with visible light (sun lamp or quartz tungsten halogen lamp). Small amounts of other products might have been formed, but their yields would have to be <10% to escape detection. The reactions of UO_2^{2+} with cyclopentane and with cyclohexene were also conducted under UV irradiation (Rayonet). Again, the products were cyclopentanone and 2-cyclohexen-1-one, respectively, confirming that the chemistry is independent of irradiation wavelength.

Discussion

Alkanes quench $*UO_2^{2+}$ with rate constants that are comparable to those for primary alcohols. Significantly, the reactions with alkanes are also redox processes, as demonstrated by the reduction of UO_2^{2+} to UO_2^+ in all cases and by the oxidation of cyclopentane to cyclopentanone. These results, in combination with a kinetic isotope effect of 2.6 (for cyclohexane), support the general mechanism in Scheme 2.

Scheme 2

$$*UO_2^{2+} + c\text{-}C_5H_{10} \rightarrow c\text{-}C_5H_9^{\bullet} + UO_2H^{2+} (\rightarrow UO_2^+ + H^+) \quad \text{(II-1)}$$

$$c\text{-}C_5H_9^{\bullet} + O_2 \rightarrow c\text{-}C_5H_9O_2^{\bullet} \quad \text{(II-2)}$$

$$c\text{-}C_5H_9O_2^{\bullet} \rightarrow c\text{-}C_5H_8O + H_2O/H_2O_2 \quad \text{(II-3)}$$

$$2UO_2^+ + O_2 + 2H^+ \rightarrow UO_2^{2+} + H_2O_2 \quad \text{(II-4)}$$

The hydrogen atom abstraction of eq II-1 is followed by the rapid formation of alkylperoxyl radicals, which eventually yield cyclopentanone (eq II-3), as discussed below. The autoxidation of UO_2^+ (eq II-4) replenishes the catalyst UO_2^{2+}.[26]

The formation of cyclopentanone as the only organic product observed even at low conversions (<1%) rules out the intermediacy of cyclopentanol. The rate constant for the quenching of $*UO_2^{2+}$ by the alcohol is only ~10 times larger than that for the quenching by the alkane (Table 1). Had the alcohol been formed, a significant oxidation to ketone would ensue only after >10% of the alkane had been oxidized to the alcohol.

The failure to observe cyclopentanol shows that the main product-forming step is not an unassisted self reaction of $c\text{-}C_5H_9O_2^{\bullet}$, because this reaction is known[42] to yield cyclopentanone and cyclopentanol in a 2:1 ratio, in addition to several ring-opened products. We also dismiss the reaction of $c\text{-}C_5H_9O_2^{\bullet}$ with cyclopentane (eq 7) as a major path, because both the rate constant k_7 (~1 M^{-1} s^{-1})[43,44] and the concentration of cyclopentane (0.01 M) are low. This situation is different from the autoxidation of neat hydrocarbons, where the hydrogen abstraction reaction of eq 7 represents a chain-propagating step.

$$c\text{-}C_5H_9O_2^{\bullet} + c\text{-}C_5H_{10} \rightarrow c\text{-}C_5H_9OOH + c\text{-}C_5H_9^{\bullet} \quad (7)$$

Consistent with the above argument, no cyclopentyl hydroperoxide was found in the present work. As pointed out recently,[42] the hydroperoxide may escape detection by GC-MS, because of the decomposition in the injector ($c\text{-}C_5H_9OOH \rightarrow C_5H_8O + H_2O$), resulting in an apparently high yield of the ketone. However, results strictly analogous to those for cyclopentane were obtained in the oxidation of cyclohexene (see below) and toluene.[45] In the latter cases, the products were analyzed by HPLC at room temperature, where the decomposition of the hydroperoxides can be ruled out. We therefore believe that the clean four-electron oxidation is a general feature in the chemistry of all three substrates.

Having ruled out the self-reaction of $c\text{-}C_5H_9O_2^{\bullet}$ and the hydrogen atom abstraction of eq 7, we are left with a limited number of possibilities to rationalize the formation of cyclopentanone and hydrogen peroxide as the only observed products. Clearly, either UO_2^{2+} or UO_2^+ (or both) plays a special role in product formation. We present several possibilities below.

One option is the reaction of $c\text{-}C_5H_9O_2^{\bullet}$ with UO_2^+ to yield an alkylperoxouranium(VI) complex, which decomposes to cyclopentanone and UO_2^{2+} (eqs 8 and 9). In this scenario, H_2O_2 is produced only in the autoxidation of UO_2^+ (eq II-4).

$$c\text{-}C_5H_9O_2^{\bullet} + UO_2^+ \rightarrow c\text{-}C_5H_9OOUO_2^+ \quad (8)$$

$$c\text{-}C_5H_9OOUO_2^+ + H^+ \rightarrow c\text{-}C_5H_8O + H_2O + UO_2^{2+} \quad (9)$$

Treating $c\text{-}C_5H_9OO^{\bullet}$ and UO_2^+ as steady-state intermediates and using the available kinetic data for the self-reaction of $c\text{-}C_5H_9OO^{\bullet}$ ($k_{self} = 1.5 \times 10^7$ M^{-1} s^{-1})[46] and for the autoxidation of UO_2^+ ($k = 31.4$ M^{-1} s^{-1}),[26] we calculate that $c\text{-}C_5H_9OO^{\bullet}$ will react predominantly with UO_2^+ if $k_8 > 1 \times 10^6$ M^{-1} s^{-1}. This limit appears reasonable in view of the facts that the reaction of UO_2^+ with $HO_2^{\bullet}$ has $5 \times 10^5 < k < 5 \times 10^7$ M^{-1} s^{-1} [26] and that $RO_2^{\bullet}$ and $HO_2^{\bullet}$ have comparable reactivities towards metal ions.[46,47]

It is also possible that the decay of $c\text{-}C_5H_9OOUO_2^+$ yields U(IV) and H_2O_2 as initial products, followed by oxidation of U(IV) by H_2O_2 to regenerate UO_2^{2+}.

Another possibility is the formation of a complex between UO_2^{2+} and $c\text{-}C_5H_9OO^{\bullet}$, in analogy to the known complex $U^{VI}(HO_2^{\bullet})$.[48] The reaction of free and complexed $c\text{-}C_5H_9OO^{\bullet}$ then

---

(42) Zegota, H.; Schuchmann, M. N.; von Sonntag, C. *J. Phys. Chem.* **1984**, *88*, 5589.

(43) The value given is the rate constant for the reaction of $PhCH_2O_2^{\bullet}$ with $PhCH_3$.[44]

(44) Vasvari, G.; Gal, D. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 22.

(45) Mao, Y.; Bakac, A. Manuscript in preparation.

(46) Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1990**, *19*, 413.

(47) Bielski, B. H. J.; Cabelli, D. E.; Arudi, R. L.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1985**, *14*, 1041.

(48) Meisel, D.; Czapski, G.; Samuni, A. *J. Am. Chem. Soc.* **1973**, *95*, 4148.

yields cyclopentanone and the known[49] U(VI)/H_2O_2 complex (eqs 10 and 11). The formation of the U(VI)/H_2O_2 complex may favor the self-reaction of eq 11 rather than the more common Russell reaction (eq 12). Even in the absence of uranium, there is a pathway in the self-reaction that yields H_2O_2 and cyclopentanone.[42]

$$\text{c-C}_5\text{H}_9\text{OO}^{\bullet} + \text{UO}_2^{2+} \rightleftharpoons \text{U}^{\text{VI}}(\text{c-C}_5\text{H}_9\text{OO}^{\bullet}) \qquad (10)$$

$$\text{U}^{\text{VI}}(\text{c-C}_5\text{H}_9\text{OO}^{\bullet}) + \text{c-C}_5\text{H}_9\text{OO}^{\bullet} \rightarrow \text{U}^{\text{VI}}(\text{H}_2\text{O}_2) + 2\text{c-C}_5\text{H}_8\text{O} \qquad (11)$$

$$2\text{c-C}_5\text{H}_9\text{OO}^{\bullet} \rightarrow \text{c-C}_5\text{H}_8\text{O} + \text{c-C}_5\text{H}_9\text{OH} + \text{O}_2 \qquad (12)$$

Alkenes. The results support a mechanism analogous to that for alkanes. The formation of UO_2^+ under air-free conditions clearly shows that the quenching takes place in a one-electron process (probably hydrogen atom abstraction), and the oxidation of cyclohexene to 2-cyclohexen-1-one (eq 13) in oxygenated solutions is exactly as expected for the mechanism of Scheme 2.

$$\text{c-C}_6\text{H}_{10} + \text{O}_2 \rightarrow \text{c-C}_6\text{H}_8\text{O} + \text{H}_2\text{O}_2 \qquad (13)$$

This mechanism and the nature of the organic product differ from those reported previously. Some authors[50] proposed that cyclohexene reacts with $^*UO_2^{2+}$ in aqueous acetone by forming an exciplex, which then decays to the reactants, resulting in no net chemical change. Others[51,52] found that UO_2^{2+} in oxygenated pyridine sensitizes the photooxidation of alkenes to β-hydroxy hydroperoxides. It was also reported that the quenching of $^*UO_2^{2+}$ in air-free aqueous acetone yields U(IV),[53] clearly showing that at least some of the quenching takes place in a redox reaction.

The formation of β-hydroxy hydroperoxides in pyridine was explained[51] by the involvement of HO• and peroxy radicals and the reduction by an unidentified H atom source (eqs 14-16).

$$\text{UO}_2^{2+} + \text{H}_2\text{O} \rightarrow \text{HO}^{\bullet} + \text{UO}_2^{+} + \text{H}^{+} \qquad (14)$$

$$\text{R}_2\text{C}{=}\text{CR}_2 \xrightarrow{\text{HO}^{\bullet},\ \text{O}_2} \text{R}_2\text{C}(\text{OO}^{\bullet}){-}\text{C}(\text{OH})\text{R}_2 \qquad (15)$$

$$\text{R}_2\text{C}(\text{OO}^{\bullet}){-}\text{C}(\text{OH})\text{R}_2 + \text{H}^{\bullet} \rightarrow \text{R}_2\text{C}(\text{OOH}){-}\text{C}(\text{OH})\text{R}_2 \qquad (16)$$

This mechanism was later replaced by one where several steps take place concertedly.[52] Details aside, the olefinic double bond is clearly involved at some point. In our hands, however, the double bond remains intact.

The most obvious difference between our work and that in refs 51 and 52 is the solvent. The first coordination spheres of U(VI), *U(VI), and U(V) in pyridine are almost certainly different from those in acidic water. The reduction potentials of various couples and the steric effects will also differ in the two solvents. More importantly, pyridine may take an active part in the reaction. Given the high reactivity of $^*UO_2^{2+}$ toward essentially all organic compounds and especially aromatics, one would expect pyridine to be a good quencher. An intermediate may form that eventually leads to the observed products. Alternatively, pyridine may mediate the reaction in a more subtle way, for example by providing a loose "electron bridge" between *U(VI) and the olefin. In such a case, the addition reactions involving the olefinic double bond may indeed become the preferred mechanistic option.

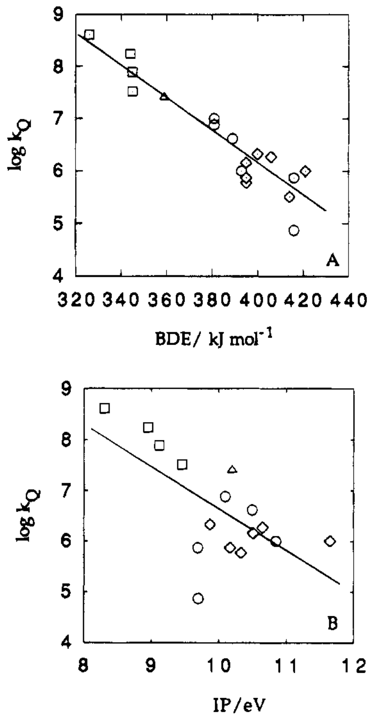

Figure 2. Plot of log k_Q in 1:1 H_2O/MeCN against (A) C−H bond dissociation energy (BDE) and (B) ionization potentials (IP's) for alcohols (circles), alkanes (diamonds), acetaldehyde (triangle), and alkenes (squares) The rate constants for the purely aqueous solutions of gaseous alkanes and acetaldehyde were multiplied by a factor of 1.5 to bring them on the MeCN/H_2O scale. The BDE and IP data are from ref 57.

Aldehydes and Alcohols. The kinetic isotope effects (Table 1) for the reaction of acetaldehyde with $^*UO_2^{2+}$ clearly establish that the reaction takes place by abstraction of the aldehydic hydrogen atom (Scheme 3).

Scheme 3

$$^*\text{UO}_2^{2+} + \text{CH}_3\text{CHO} \rightarrow \text{UO}_2^{+} + \text{H}^{+} + \text{CH}_3\text{CO}^{\bullet} \qquad (\text{III-1})$$

$$\text{CH}_3\text{CO}^{\bullet} + \text{O}_2 \rightarrow \text{CH}_3\text{C(O)OO}^{\bullet} \qquad (\text{III-2})$$

$$\text{CH}_3\text{C(O)OO}^{\bullet} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{C(O)OOH} + \text{CH}_3\text{CO}^{\bullet} \qquad (\text{III-3})$$

$$\text{CH}_3\text{C(O)OOH} + \text{CH}_3\text{CHO} \rightarrow 2\text{CH}_3\text{COOH} \qquad (\text{III-4})$$

$$\text{CH}_3\text{C(O)OO}^{\bullet} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2^{\bullet} \qquad (\text{III-5})$$

$$2\text{HO}_2^{\bullet} \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \qquad (\text{III-6})$$

Both acetaldehyde and acetyl radicals exist in equilibrium with their hydrated forms, $CH_3CH(OH)_2$ and $CH_3C^{\bullet}(OH)_2$, respectively.[54] To simplify the equations, the hydrated forms are not shown, although they do take part in reactions III-2 to III-5[54] and most probably in reaction III-1 as well.

---

(49) Nash, K. L.; Sullivan, J. C. *Adv. Inorg. Bioinorg. Mech.* **1986**, *4*, 185.
(50) Ahmad, M.; Cox, A.; Kemp, T. J.; Sultana, Q. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1867.
(51) Murayama, E.; Sato, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3022.
(52) Murayama, E.; Kohda, A.; Sato, T. *J. Chem. Soc., Perkin Trans. 1* **1980**, 947.
(53) Park, Y.-Y.; Tomiyasu, H. *J. Photochem. Photobiol., A* **1992**, *64*, 25.
(54) Schuchmann, M. N.; von Sonntag, C. *J. Am. Chem. Soc.* **1988**, *110*, 5698.

The large concentrations of acetaldehyde (≥1 M) in product analysis experiments and the small bond dissociation energy of the aldehydic C−H bond favor the hydrogen abstraction reaction of eq III-3. Reactions III-2 and III-3 represent a chain, leading to the formation of peroxyacetic acid, which reacts with acetaldehyde to produce 2 equiv of acetic acid in eq III-4.[55] The reaction of eq III-5 has also been established.[55]

Low concentrations of primary and secondary alcohols react with $*UO_2^{2+}$ by hydrogen atom abstraction from the α-carbon atoms.[15,17,18,29] Analogs of eqs III-2, III-3, III-5, and III-6 explain the reaction in the presence of O_2.

On the basis of both thermodynamics and statistics, *tert*-butanol is expected to react by H atom abstraction from a C−H bond. Still, the unexpectedly low rate constant has moved some authors[19] to suggest the O−H bond as the site of primary attack. The kinetic isotope effects in Table 1 now show unequivocally that a C−H bond is cleaved in the reaction with $*UO_2^{2+}$.

Linear Free Energy Relationships. The rate constants for the quenching of $*UO_2^{2+}$ have been previously correlated with the bond dissociation energies (BDE's) of the weakest C−H bond and the ionization potentials (IP's) of the quenchers. Owing to the limited number of data points used and the relatively large errors associated with the published values of BDE's, different authors[13,19,29,56] found one or the other correlation to be more successful.

The quenchers used in this work fall in several distinctly different chemical classes (alkanes, alkenes, alcohols, and an aldehyde), and their BDE's span a range of ~100 kJ/mol, allowing one to assess the general reactivity pattern with some confidence. Figure 2 shows the plots of k_Q against BDE and IP for the quenchers listed in Table 1.[57-59] The rate constants respond qualitatively to both parameters, but the correlation with the BDE's is clearly the better of the two. In fact, the plot of k_Q against IP strongly resembles the one relating BDE and IP to each other.

If the rate constants in Figure 2 are corrected by the appropriate statistical factors, the deviations from the line are somewhat greater, although the correlation is still satisfactory. This may indicate that steric effects play a role in the reactions of the bulky $*UO_2^{2+}$ and that all the C−H bonds may not be equally accessible in some substrates.

The correlation in Figure 2 further supports our conclusions, based on the products and kinetics, that all four groups of compounds react by hydrogen abstraction to yield UO_2^+ and carbon-centered radicals in the rate-determining step.

Acknowledgment. We thank Professor G. A. Russell for helpful comments and suggestions. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under Contract W-7405-Eng-82. A.B. gratefully acknowledges an Ames Laboratory Directed Research and Development Grant.

IC950816E

---

(55) Allan, J. T. *J. Phys. Chem.* **1964**, *68*, 2714.

(56) Sykora, J.; Sima, J. *Coord. Chem. Rev.* **1990**, *107*, 1.

(57) The BDE and IP data are from: (a) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (b) Cohen, N.; Benson, S. W. In *The Chemistry of Alkanes and Cycloalkanes*; Patai, S., Rappoport, Z., Eds.; Wiley: 1992. (c) *CRC Handbook of Chemistry and Physics*, 58th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, p E-74.

(58) The BDE's have been recalculated recently[59] for several compounds in Figure 2. The new recommended values are higher and would result in diminished deviations of these data points from the line in Figure 2. We have not used these new BDE's, however, because only a few are available, and the use of a consistent (old) set probably provides a more accurate qualitative picture.

(59) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.