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Photocatalytic Oxidation of Toluene to Benzaldehyde by Molecular Oxygen

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The visible light irradiation of aqueous solutions containing toluene, uranyl(VI) ions, and O_2 results in the formation of benzaldehyde as a major product. Small amounts of $PhCH_2OH$ are also formed. The yields of benzaldehyde are 3 times greater for toluene-h_8 than for toluene-d_8, but the kinetic isotope effect for the quenching of the excited state $*UO_2^{2+}$ by toluene is negligible ($k_{\text{toluene-}h_8}/k_{\text{toluene-}d_8} = 1.2$). This and other evidence indicate that the quenching takes place in two parallel pathways. The major one involves the aromatic portion of toluene and leads to the recovery of the reactants. The minor, productive path takes place by hydrogen atom abstraction from the methyl group, followed by the oxidation of $PhCH_2^{\bullet}$. Cumene, benzyl alcohol, and benzaldehyde react similarly.

Introduction

Selective oxidation of hydrocarbons by O_2 is an important goal for economic, environmental, and scientific reasons.[1−6] The problem is twofold in that the spontaneous autoxidation of hydrocarbons is not only slow, but also nonselective, yielding a number of products. A desirable catalyst should therefore improve both the rates and selectivity of such reactions.

A photocatalytic system using solar energy and molecular oxygen would seem ideal, because both sunlight and O_2 are readily available and practically inexhaustible, and no harmful oxidant-derived products are formed. Because of its unique properties, the uranyl ion, UO_2^{2+}, appeared to us[7] to have a potential as a photocatalyst for the oxidation of organic materials by O_2. The UO_2^{2+} absorbs visible light (λ_{max} 414 nm, $\epsilon = 7.70$ M^{-1} cm^{-1} in 0.1 M $HClO_4$)[7,8] to produce a long-lived, strongly oxidizing excited state, $*UO_2^{2+}$ ($E^0 = 2.6$ V),[9,10] which is unreactive towards O_2. Also, $*UO_2^{2+}$ has been shown to react with alcohols and several other substrates by hydrogen atom abstraction. We have recently proposed[7] and then demonstrated[11] that (a) such reactions can be made catalytic and (b) even low molecular weight alkanes and alkenes react with $*UO_2^{2+}$ according to Scheme 1, using cyclopentane as an example. Significantly, only a single organic product was detected in each of the reactions studied, demonstrating that UO_2^{2+} serves as a selective catalyst for the oxidation of organic substrates by molecular oxygen.

SCHEME 1

$$UO_2^{\ 2+} + h\nu \rightarrow *UO_2^{\ 2+} \qquad \text{(I-1)}$$

$$*UO_2^{\ 2+} + c\text{-}C_5H_{10} \rightarrow UO_2^{\ +} + c\text{-}C_5H_9^{\bullet} + H^+ \qquad \text{(I-2)}$$

$$c\text{-}C_5H_9^{\bullet} + O_2 \rightarrow c\text{-}C_5H_9O_2^{\bullet} \qquad \text{(I-3)}$$

$$c\text{-}C_5H_9O_2^{\bullet} \xrightarrow{UO_2^{+}/UO_2^{2+}} c\text{-}C_5H_8O + 0.5H_2O_2 \qquad \text{(I-4)}$$

$$2UO_2^{\ +} + O_2 + 2H^+ \rightarrow UO_2^{\ 2+} + H_2O_2 \qquad \text{(I-5)}$$

In the context of selective oxidation, toluene holds a special place among hydrocarbons. The great industrial importance of toluene-derived products has made this topic a subject of much research.[12] Several recent papers report some success in the catalytic oxidation on vanadium oxide and other oxide surfaces[13−15] and on zeolites.[16,17] Some polyoxometalates catalyze the photocatalytic oxidation of side-chain aromatics in solution using $\lambda_{irr} \geq 320$ nm [18] or ≥ 270 nm.[19] On the basis of our recent success with UO_2^{2+} as a photocatalyst for the oxidation of alkanes and alkenes in aqueous solution using visible light,[11] one might expect that toluene would also be oxidized under these conditions. However, the rapid ($k_q > 10^8$ M^{-1} s^{-1}) quenching of $*UO_2^{2+}$ by aromatic and side-chain-aromatic compounds has been reported to take place by the formation of an exciplex which then decays back to the reactants and results in no net chemical change.[20]

The reaction rates for the quenching of $*UO_2^{2+}$ by aliphatic compounds respond to the energy of the weakest C−H bond(s) in these molecules.[11] The bond dissociation energy (BDE) of the PhC(H_2)−H bond (368 kJ/mol) is lower than BDE of the C−H bonds in several reactive aliphatic compounds studied so far,[11] and we reasoned that a portion of the $*UO_2^{2+}-PhCH_3$ reaction ought to take place by hydrogen atom abstraction. We were encouraged in this belief by a recent report on the reaction between $*UO_2^{2+}$ and azulene which yields a complex mixture of products.[21]

We now report that $*UO_2^{2+}$ indeed reacts with $PhCH_3$ in part by hydrogen atom abstraction. In the presence of O_2 and visible light, the oxidation of toluene is catalytic and yields benzaldehyde and benzyl alcohol as products.

Experimental Section

Stock solutions of uranium(VI) perchlorate were prepared by dissolving uranium trioxide (Strem Chemicals, 99.8%) in aqueous perchloric acid. Toluene (Fisher) was purified by distillation. Toluene-d_8, benzaldehyde, benzyl alcohol, and benzoic acid (all Aldrich) were used without further purification.

Absorption spectra were recorded by use of a Shimadzu 3101PC spectrophotometer. Most of the product analyses were carried out by use of a Waters high performance liquid chromatograph (HPLC), equipped with a C_{18} column and a photodiode array detector (Waters 996), and operated by the Millennium 2010 software package. A 40% (v/v) acetonitrile/water solution was used as eluent. For each compound determined, a commercial sample was used to ascertain the retention time and to construct a calibration line for quantitative determinations. The GC−MS spectra were obtained by use of

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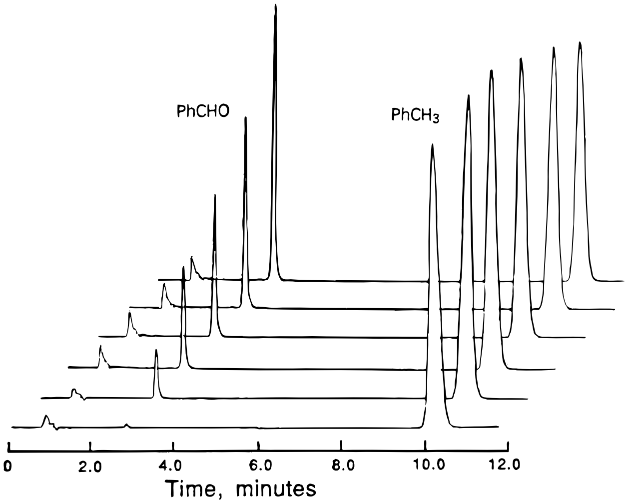


Figure 1. HPLC chromatograms of air-saturated solutions of 0.5 mM UO_2^{2+} and 5 mM $PhCH_3$ in 0.01 M H_3PO_4 after irradiation with visible light in 15 min intervals. The monitoring wavelength was 254 nm.

a Magnum (Finnigan-MAT) instrument equipped with a capillary column (DB5, 0.25mm i.d. and 0.25 μm film) and operated by use of ITS40 software package. ^{1}H NMR spectra were recorded on a Varian 300 NMR spectrometer. Formaldehyde was determined by the chromotropic acid method.[22]

Time-resolved experiments were performed by use of a dye-laser flash photolysis system.[23] Steady-state photolyses utilized a 275-W sun lamp or a 250-W quartz−tungsten−halogen lamp (Oriel Corporation, Model 66181) with appropriate cutoff filters. Unless stated otherwise, the samples were prepared in 1-cm quartz cells. The pH was adjusted with $HClO_4$ or H_3PO_4, as appropriate. The cells were sealed with gastight septa, and the appropriate gas (O_2, air, or argon) was bubbled through the solution for 15 min. In some experiments the desired concentrations of O_2 were obtained by mixing O_2-and Ar-saturated solutions. A measured amount of freshly distilled toluene was then injected to give $[PhCH_3] \sim 5$ mM. In experiments using the sun lamp, the temperature was maintained at ~20 °C by use of circulating tap water. The Oriel lamp was equipped with a beam turning assembly with a dichroic reflecting mirror.

All the experiments utilized low concentrations of UO_2^{2+} (0.25−1 mM) to prevent significant depletion of O_2. Under these conditions all the reaction solutions remained clear indefinitely. At higher concentrations of UO_2^{2+}, reaction solutions had to be repeatedly resaturated with O_2 to avoid the formation of insoluble precipitates.

After the catalytic nature of the reaction was established, the subsequent product analyses were carried out after less than one turnover.

Results

Products. The steady state photolysis of acidic, air-saturated solutions of $PhCH_3$ ($\leq$5 mM) and UO_2^{2+} ($\leq$1 mM) resulted in an increase in absorbance at <260 nm, indicating the formation of a product that is more strongly absorbing than toluene. No spectral changes were seen if any of the three components (UO_2^{2+}, $PhCH_3$, or air) were omitted. Also, careful spectral measurements showed no evidence for complex formation between UO_2^{2+} and toluene in aqueous solutions.

The product analysis was conducted on solutions that had been irradiated for up to 90 min and had undergone <1% conversion to products. HPLC chromatograms showed a new peak, which increased steadily with the irradiation time, Figure 1. The UV spectrum and the retention time (2.9 min) of the new species were identical to those of commercial benzaldehyde. The broad peak at ~1 min is that of phosphoric acid.

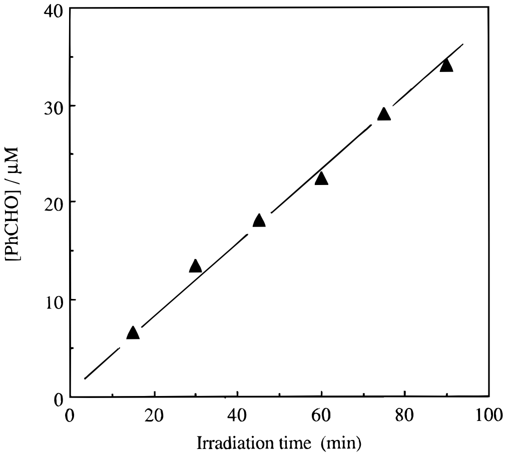


Figure 2. Plot showing increase in [PhCHO] with irradiation time. Data from Figure 1.

At much longer irradiation times (20 h), a second, small peak appeared in HPLC chromatograms. The retention time (2.7 min, using 25% CH_3CN/75% H_2O as eluent) coincided with that of benzyl alcohol. The low molar absorptivity in the UV and low yields of $PhCH_2OH$ made its detection difficult. From the size of the HPLC signal, we estimate that the yield of $PhCH_2OH$ is $\leq$30% of the total product. In all the subsequent experiments the progress of the reaction was monitored by observing PhCHO and assuming that $PhCH_2OH$ was consistently produced in $\leq$30% yield.

The GC−MS and ^{1}H NMR spectra were run on ethereal extracts of spent reaction solutions. The gas chromatograms showed a single new peak, with a mass spectrum identical to that of PhCHO ($m/e = 106$ for the parent peak). The aldehydic hydrogen appeared in the ^{1}H NMR spectrum at 10.02 ppm.

When toluene was replaced by toluene-d_8, the observations were qualitatively the same, but the yield of aldehyde (by HPLC) was ~3 times lower for the deuterated sample.

As shown in Figure 2, the yield of PhCHO increases linearly with irradiation time. This is to be expected, because the concentrations of both O_2 (0.25 mM) and $PhCH_3$ (5 mM) remain practically unchanged during the course of the reaction. The concentration of the photocatalyst, UO_2^{2+}, was 0.5 mM in these experiments.

A spent reaction solution that had produced 10 μM PhCHO was analyzed for H_2O_2 iodometrically. The yield of H_2O_2 was 4 μM, i.e., 0.4[PhCHO]. Under the conditions employed the oxidation of UO_2^{+} by H_2O_2 is much slower than the oxidation with O_2, such that H_2O_2 accumulates in solution.

The effect of UO_2^{2+}, $PhCH_3$, and O_2 on the yield of PhCHO is shown in Figure 3. The yield increases linearly with increasing concentrations of UO_2^{2+}, and only the point at the highest concentration of UO_2^{2+} (0.5 mM) appears to deviate somewhat from the line. Owing to the small molar absorptivity of UO_2^{2+} in the visible region, the absorbance of these solutions was <0.01, which explains the approximate linearity of the plot.

The dependence on $[PhCH_3]$ is linear at low concentrations, but levels off at ~5 mM $PhCH_3$. At this concentration, ~98% of $^*UO_2^{2+}$ is quenched by toluene, so that the further increase in $[PhCH_3]$ does not affect the rate. Similarly, the reaction rate depends on $[O_2]$ only at the lowest O_2 concentrations used. The rate saturation is reached at ~0.1 mM O_2, showing that O_2 is essential for the product formation, but under most conditions the actual concentration is irrelevant. When the reaction was conducted in an argon atmosphere, only a trace amount of

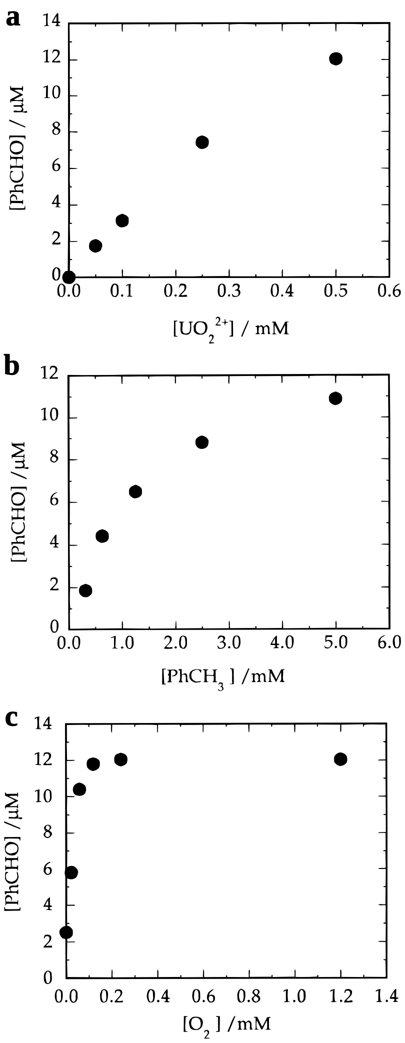


Figure 3. Dependence of yield of PhCHO on concentrations of (a) UO_2^{2+}, (b) toluene, and (c) O_2 after 30 min of irradiation. Conditions as in Figure 1.

PhCHO was produced. The oxidant in this experiment was probably air that slowly diffused through the septum.

On the basis of these data, the rate law for the oxidation of $PhCH_3$ at high concentrations of substrate (>5 mM) and O_2 (>0.1 mM) is given in eq 1, where I_0 stands for light intensity, and Φ is the quantum yield for the reaction.

$$-d[PhCH_3]/dt \sim d[PhCHO]/dt = \Phi I_0[UO_2^{2+}] \qquad (1)$$

The quantum yield of benzaldehyde was determined relative to the yield of acetone produced by the oxidation of 2-propanol. Earlier we have presented evidence[11] that the latter reaction has a quantum yield of ~1.

In two separate experiments all the conditions and concentrations were held constant (0.010 M H_3PO_4, 0.5 mM UO_2^{2+}, air saturated), except that one solution contained 180 mM 2-PrOH, and the other 5 mM $PhCH_3$. On the basis of the kinetic data in Table 1, we calculate that at these concentrations ~98% of $^*UO_2^{2+}$ is quenched by each substrate, and only 2% of $^*UO_2^{2+}$ undergoes self-decay ($k_0 = 5.4 \times 10^4\ s^{-1}$ in 0.01 M H_3PO_4). The yields of the respective products, acetone and benzaldehyde, were determined by HPLC. The yield of PhCHO was ~1% of the yield of acetone.

When an alcohol, such as methanol, was present in solutions of $PhCH_3$, the yield of PhCHO decreased, as expected if methanol and $PhCH_3$ compete for $^*UO_2^{2+}$. For example, 5 mM solutions of $PhCH_3$ yielded ~30% less PhCHO when 1 M CH_3OH was present during the photolysis, in excellent agreement with the theoretical 33% decrease calculated from the rate constants in Table 1 and concentrations of CH_3OH and toluene used in these experiments.

TABLE 1: Summary of the Kinetics and Product Data for the Reactions of $^*UO_2^{2+}$ with Organic Substrates in the Presence of Molecular Oxygen[a]

compound	$k_q{}^b/(M^{-1}\ s^{-1})$	product	Φ^c
$C_6H_5CH_3$	$5.84(9) \times 10^8$	C_6H_5CHO	0.01
		$C_6H_5CH_2OH$	≤0.004
$C_6D_5CD_3$	$4.94(4) \times 10^8$	C_6D_5CDO	0.003
		$C_6D_5CD_2OH$	*d*
$C_6H_5CH(CH_3)_2$	$4.11(8) \times 10^8$	$C_6H_5COCH_3$	0.003
		HCHO	0.002
$C_6H_5CH_2OH$	$4.31(17) \times 10^8$	C_6H_5CHO	0.034
C_6H_5CHO	$2.08(9) \times 10^8$	C_6H_5COOH	0.04
CH_3OH	$1.54(3) \times 10^{6\,e}$	CH_2O	*d*
$CH(CH_3)_2OH$	$1.36(1) \times 10^{7\,e}$	$(CH_3)_2CO$	(1.0)
0.1 M H_3PO_4	$1.60(5) \times 10^{4\,f}$		
0.01 M H_3PO_4	$5.40(5) \times 10^{4\,f}$		

[a] $[UO_2^{2+}] = 1.0$ mM, $[H_3PO_4] = 0.1$ M, $T = 24 \pm 1$°C. [b] Numbers in parantheses represent one standard deviation of the last significant figure. [c] Quantum yield for product formation. [d] Not determined. [e] In 0.6 M H_3PO_4, ref 11. [f] First-order rate constant for the self-decay of $^*UO_2^{2+}$.

The yield of PhCHO decreased somewhat when a 425-nm cutoff filter (Corning 3-67) was used in place of a Pyrex filter ($\lambda > 350$ nm). However, the fact that benzaldehyde was still produced at $\lambda_{irr} \geq 425$ nm shows unequivocally that the photoreaction is initiated by UO_2^{2+}, which is the only absorbing species in the visible part of the spectrum. The diminished amount of light available to the system explains the decreased yield of PhCHO.

In order to prove that the reaction is indeed catalytic, an air-saturated solution containing 0.25 mM UO_2^{2+}, 5 mM toluene, and 0.01 M H_3PO_4 was photolyzed continuously for 30 h. Occasionally the solution was resaturated with air. The increase in [PhCHO] was linear with time and showed no indication of slowing down even after the concentration of PhCHO produced (0.3 mM) exceeded the concentration of UO_2^{2+}. The results show that the concentration of the catalyst, UO_2^{2+}, remained unchanged after one catalytic cycle.

Kinetics. The quenching of $^*UO_2^{2+}$ in 0.1 M H_3PO_4 by all the compounds examined followed the rate law of eq 2. The

$$-d[^*UO_2^{2+}]/dt = k_{obs}[^*UO_2^{2+}] = (k_0 + k_q[\text{substrate}])[^*UO_2^{2+}] \qquad (2)$$

self-decay has $k_0 = 1.6 \times 10^4\ s^{-1}$ in 0.1 M H_3PO_4. From the slope of the line obtained by plotting k_{obs} against the concentration of toluene, Figure 4, one obtains $k_q = (5.84 \pm 0.09) \times 10^8$, which agrees qualitatively with an earlier estimate placing it close to the diffusion-controlled limit.[20] A summary of all the rate constants is given in Table 1.

Other Substrates. The photochemical reaction of benzyl alcohol with UO_2^{2+}/O_2 yielded benzaldehyde as the only product. However, benzyl alcohol is not an intermediate in the oxidation of toluene to benzaldehyde, as discussed later.

The photooxidation of benzaldehyde by UO_2^{2+}/O_2 yields benzoic acid as the only product by HPLC. Cumene was oxidized to acetophenone and CH_2O in a ~1.5:1 ratio, Table 1.

Discussion

The data show unequivocally that UO_2^{2+} oxidizes $PhCH_3$ under visible light irradiation in the presence of O_2, eq 3. This

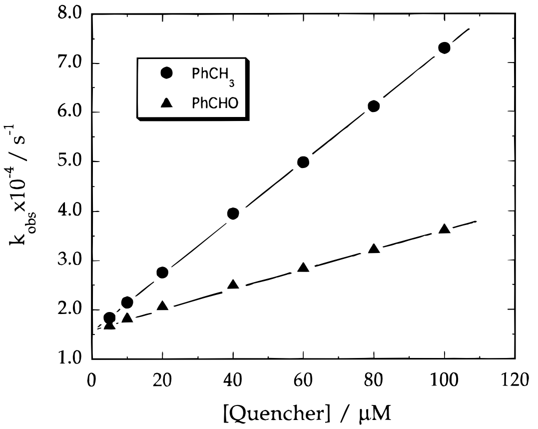


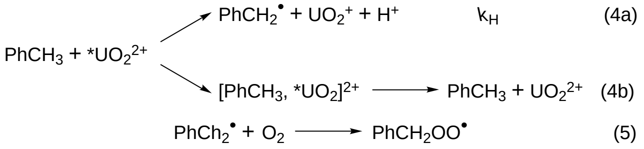
Figure 4. Plots of pseudo-first-order rate constants for quenching of $*UO_2^{2+}$ luminescence as a function of substrate concentrations. Conditions: 0.1 M H_3PO_4, 1 mM UO_2^{2+}, room temperature (24 ± 1 °C).

$$PhCH_3 + O_2 \xrightarrow{h\nu, UO_2^{2+}} \{PhCHO + PhCH_2OH\} + H_2O/H_2O_2 \quad (3)$$

finding is contrary to the generally accepted view that aromatic and side-chain aromatic compounds quench $*UO_2^{2+}$ by a mechanism(s) that yields no permanent products.[20,24]

On the basis of the bond-dissociation energy for $PhC(H)_2{-}H$ (368 kJ/mol),[25] we expected $*UO_2^{2+}$ to abstract a hydrogen atom from the methyl group of toluene with $k_H \sim 10^7$ M^{-1} s^{-1}. In that case the photochemical reaction between UO_2^{2+} and $PhCH_3$ in the presence of O_2 should lead to the formation of oxidation products with a quantum yield that measures directly the fraction of the quenching reaction taking place by hydrogen atom abstraction.

The kinetic data (Table 1), deuterium isotope effects, and the product yields together form a clear picture of the $*UO_2^{2+}/PhCH_3$ reaction, eqs 4, 5, and I-4: a small portion of $*UO_2^{2+}$



$$PhCH_3 + *UO_2^{2+} \rightarrow PhCH_2^{\bullet} + UO_2^{+} + H^{+} \qquad k_H \quad (4a)$$

$$PhCH_3 + *UO_2^{2+} \rightarrow [PhCH_3, *UO_2]^{2+} \longrightarrow PhCH_3 + UO_2^{2+} \quad (4b)$$

$$PhCh_2^{\bullet} + O_2 \longrightarrow PhCH_2OO^{\bullet} \quad (5)$$

(1%) abstracts a hydrogen atom from $PhCH_3$, and the majority of the quenching process results in no observable products and probably takes place by exciplex formation.

The rate constant for the chemical reaction, $k_H \sim 6 \times 10^6$ M^{-1} s^{-1} (i.e., $k_H = \Phi k_q = 0.01 \times 5.84 \times 10^8$), is in good agreement with the value expected for hydrogen abstraction, especially in view of the large uncertainties in the reported values of BDE's for compounds used in the correlation.[11] This result underscores the consistency of all the data and provides additional evidence for the mechanism in eq 4. Moreover, the values of k_H for $PhCH_2OH$ and PhCHO, calculated from the data in Table 1, agree with this model. As illustrated in Figure 5, all three new data points fall close to the line obtained in our previous work for compounds that react exclusively by hydrogen atom abstraction.

The negligible kinetic isotope effect for k_q (1.2) is consistent with the fact that only a small portion of the quenching occurs in a chemical reaction. The isotopic substitution is not expected to have a substantial effect on the large part of the reaction that takes place by exciplex formation. On the other hand, the yield of benzaldehyde, which measures only the contribution from the chemical reaction, has an isotope effect of 3, similar to the

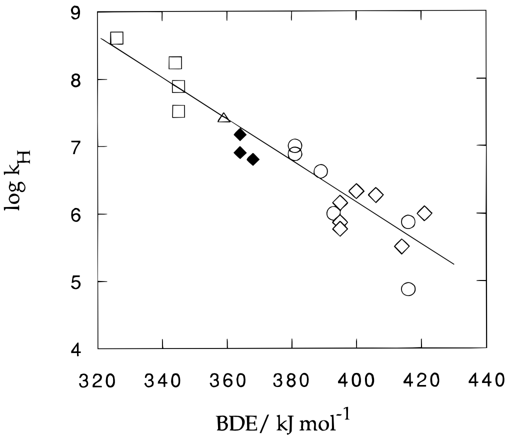


Figure 5. Plot of rate constants for hydrogen atom abstraction by $*UO_2^{2+}$ against bond dissociation energy (BDE) of quenchers. Open symbols are from previous work (ref 11) and represent rate constants k_q for the quenching of alcohols (circles), alkanes (diamonds), an aldehyde (triangle), and alkenes (squares). The filled diamonds are (from left to right) for $PhCH_2OH$, PhCHO, and $PhCH_3$, and represent the calculated rate constants for H-atom abstraction, $k_H = \Phi k_q$. BDE's are from ref 25.

kinetic isotope effects measured in other hydrogen atom abstractions by $*UO_2^{2+}$.[11,26,27]

Having established that benzylperoxyl radicals are involved in reaction 3, we next consider the chemistry leading to PhCHO. At the low conversions used in this work, $PhCH_2OH$ can be safely ruled out as an intermediate, because the quenching constants k_q (Table 1) are comparable for $PhCH_3$ and $PhCH_2OH$, but the concentration of toluene is always at least 100 times greater than the maximum possible concentration of $PhCH_2OH$.

The bimolecular self-reaction of $PhCH_2OO^{\bullet}$ in aqueous solution takes place in several parallel pathways (Scheme 2).[28]

SCHEME 2

$$2PhCH_2OO^{\bullet} \rightarrow PhCH_2OH + PhCHO + O_2 \qquad 1 \times 10^8\ M^{-1}\ s^{-1} \quad (II\text{-}1)$$

$$\rightarrow 2PhCHO + H_2O_2 \qquad 4 \times 10^7\ M^{-1}\ s^{-1} \quad (II\text{-}2)$$

$$\rightarrow 2PhCH_2O^{\bullet} + O_2 \qquad 3.4 \times 10^7 \quad (II\text{-}3)$$

$$\rightarrow 2PhC^{\bullet}HOOH \qquad 4.2 \times 10^7 \quad (II\text{-}4)$$

$$PhCH_2O^{\bullet} \xrightarrow{fast} PhC^{\bullet}HOH \xrightarrow{O_2} PhCHO + HO_2^{\bullet} \quad (II\text{-}5)$$

$$PhC^{\bullet}HOOH \rightarrow PhCHO + HO^{\bullet} \quad (II\text{-}6)$$

The rate constants are given at 75 °C, but we presume that the relative contributions from the four pathways do not differ greatly from those at 25 °C.

The radicals produced in reactions II-3 and II-4 are rapidly converted to benzaldehyde, eqs II-5 and II-6.[28,29] Thus, according to Scheme 2, more than 75% of benzylperoxyl radicals should be oxidized to PhCHO, the balance yielding $PhCH_2OH$, in agreeement with our findings.

Another path may involve the abstraction of a hydrogen atom from toluene to yield the hydroperoxide and initiate a chain reaction, eqs 5 and 6. The low concentration of toluene (5 mM)

$$PhCH_2OO^{\bullet} + PhCH_3 \rightarrow PhCH_2OOH + PhCH_2^{\bullet} \quad (6)$$

and the small value of k_6 ($<1\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$)[28] make this path slow, but possibly still competitive with the bimolecular self-reactions of the low concentrations of the radicals. The failure to observe the hydroperoxide suggests either that reaction 6 is unimportant or that the hydroperoxide is converted rapidly to PhCHO. The latter process may be catalyzed by the uranium species present in solution. In any case, the chain reaction is not very efficient, as judged by the derived value of k_H, which assumes that only one equivalent of PhCHO is produced for each H-abstraction event.

We also consider a reaction of $PhCH_2OO^\bullet$ with UO_2^+, as we proposed recently[11] for several alkylperoxy radicals. The peroxouranium complex then decomposes to the aldehyde and regenerates UO_2^{2+}.

$$PhCH_2OO^\bullet + UO_2^+ \rightarrow PhCH_2OOUO_2^+ \xrightarrow{H^+} PhCHO + H_2O + UO_2^{2+} \quad (7)$$

At the present time the data are insufficient to select any one mechanism with confidence, and it is possible that several are involved. However, we rule out any mechanism involving a charge-transfer $PhCH_3/O_2$ complex,[30] which is known to form in O_2-saturated solutions of neat toluene and to absorb light at $\lambda < 350$ nm. There is no evidence for this complex in dilute aqueous solutions, but even if trace amounts are present, they do not play a productive role. This is clearly shown by the independence of reaction rates on [O_2], and by the fact that the chemistry is triggered by visible light irradiation.

The results of a cursory study of the oxidation of other substrates in Table 1 are also consistent with the chemistry of alkylperoxy radicals.[31]

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