

## Photocatalytic Oxidation of Aromatic Hydrocarbons

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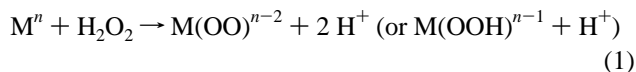
Received February 8, 1996<sup>⊗</sup>

In acidic aqueous solutions  $\text{UO}_2^{2+}$  serves as a photocatalyst ( $\lambda_{\text{irr}} \geq 425 \text{ nm}$ ) for the oxidation of benzene by  $\text{H}_2\text{O}_2$ . Under conditions where 50% of the excited state  $^*\text{UO}_2^{2+}$  is quenched by  $\text{H}_2\text{O}_2$  ( $k = 5.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) and 50% by benzene ( $k = 2.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), the quantum yield for the formation of phenol is 0.70. The yield does not change when benzene is replaced by benzene- $d_6$ , but decreases by a factor of  $\sim 4$  upon the change of solvent from  $\text{H}_2\text{O}$  to  $\text{D}_2\text{O}$ . Photocatalytic oxidation of toluene by  $\text{UO}_2^{2+}/\text{H}_2\text{O}_2$  produces PhCHO, PhCH<sub>2</sub>OH, and a mixture of cresols with a total quantum yield of 0.28 under conditions where 50% of  $^*\text{UO}_2^{2+}$  is quenched by  $\text{H}_2\text{O}_2$ . The quenching of  $^*\text{UO}_2^{2+}$  by benzene and substituted benzenes takes place with  $k > 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . The system  $\text{UO}_2^{2+}/t\text{-BuOOH}/\text{C}_6\text{H}_6/h\nu$  does not result in the oxidation of benzene, but instead yields methane and ethane.

## Introduction

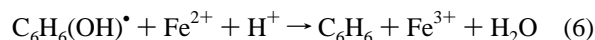
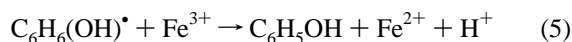
Catalytic oxidation of hydrocarbons has scientific and practical importance. Biological systems that utilize dioxygen or hydrogen peroxide as oxidants are catalyzed by oxygenases and peroxidases, respectively.<sup>1–3</sup> Laboratory and industrial oxidation of hydrocarbons utilize transition metal complexes as catalysts. Many of the reactive species involved are analogous to those encountered in the biological systems and include superoxo, peroxy, and oxo metal complexes, as well as metal-free intermediates such as  $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$  and  $\text{HO}^{\cdot}$ .<sup>3–7</sup>

Hydrogen peroxide has been explored extensively as a hydroxylating agent. Catalysts are needed because the reactivity of  $\text{H}_2\text{O}_2$  toward hydrocarbons is low. Transition metal complexes usually activate  $\text{H}_2\text{O}_2$  by converting it into reactive metal peroxy and hydroperoxy species,<sup>3,8–10</sup> or to hydroxyl radicals in Fenton-type reactions,<sup>11–14</sup> eqs 1–2. Photochemical cleavage of  $\text{H}_2\text{O}_2$  to hydroxyl radicals, eq 3, has also been explored.<sup>15</sup>



The reaction of  $\text{HO}^{\cdot}$  radicals with benzene produces cyclohexadienyl radicals, which undergo a number of reactions,

depending on the catalyst and reaction conditions. Both oxidation states of the catalyst usually react with cyclohexadienyl radicals, as shown in eqs 4–6 using  $\text{Fe}^{3+}/\text{Fe}^{2+}$  as example. The yield of phenol therefore depends on the redox properties of the catalyst and on the relative concentrations of the oxidized and reduced forms of the catalyst.



Much less is known about the mechanism of oxidation of  $\text{C}_6\text{H}_6$  by peroxy–metal species, but of those studied so far, peroxy–vanadium complexes appear to be the most efficient in hydroxylating aromatic hydrocarbons.<sup>8–10</sup> All the mechanistic studies agree that these processes involve radicals. Some workers proposed an intramolecular electron transfer resulting in a  $\text{V}^{\text{IV}}(\text{O}_2^{\cdot-})$  intermediate, which then inserts into a C–H bond.<sup>10</sup> Others<sup>8</sup> suggested the involvement of a one-electron reduced peroxovanadium complex.

We have recently used  $\text{UO}_2^{2+}$  as a photocatalyst for the oxidation of aliphatic hydrocarbons and toluene by molecular oxygen.<sup>16,17</sup> All of the reactions studied in that work involve a hydrogen atom abstraction by  $^*\text{UO}_2^{2+}$  from the substrate, as demonstrated by the kinetic isotope effects and the nature of the products. As expected, benzene was unreactive, owing to the strength of the C–H bonds and the ease with which benzene quenches  $^*\text{UO}_2^{2+}$  in a chemically unproductive reaction.

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We have now explored the use of  $\text{H}_2\text{O}_2$  as oxidant in the photochemical  $\text{UO}_2^{2+}$ /benzene system. Two fundamentally different mechanisms might be expected to operate.  $\text{U(VI)}$  is known to form complexes with  $\text{H}_2\text{O}_2$ ,<sup>18–21</sup> and chemistry similar to that reported for the peroxovanadium complexes is possible if photoexcitation is provided. (In the absence of light, the peroxouranium complexes are ineffective as oxidants.)<sup>22</sup> On the other hand,  $\text{H}_2\text{O}_2$  may reduce the photoexcited  $\text{UO}_2^{2+}$  to  $\text{UO}_2^+$ , which would then engage in Fenton-type chemistry.

The results of a kinetic and mechanistic study of the oxidation of benzene and several other aromatic hydrocarbons by  $\text{UO}_2^{2+}/\text{H}_2\text{O}_2/h\nu$  are reported herein. A brief study of the oxidation of  $\text{UO}_2^+$  by  $\text{H}_2\text{O}_2$  has also been conducted.

## Experimental Section

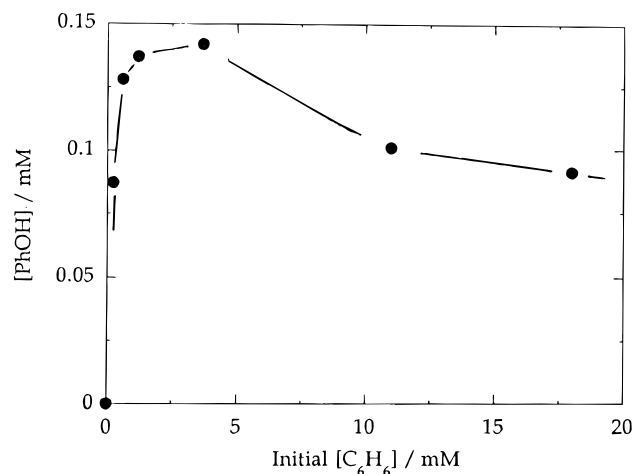
**Chemicals.** Benzene, toluene and *p*-xylene (Aldrich) were distilled prior to use. Phenol, benzaldehyde, *p*-benzoquinone, *p*-tolualdehyde, 4-methylbenzyl alcohol, phthalic dicarboxaldehyde, *p*-toluic acid, 1,3,5-mesitylene (all Aldrich), and 3,5-dimethylbenzaldehyde (Lancaster) were used without further purification. Stock solutions of uranyl perchlorate were prepared by dissolving uranium trioxide (Strem Chemicals, 99.8%) in aqueous perchloric acid. Hydrogen peroxide (Fisher) and *tert*-butyl hydroperoxide (Aldrich) were used as received.

**Instrumentation.** Product analyses were carried out by use of a Waters high performance liquid chromatograph, equipped with a  $\text{C}_{18}$  column and a photodiode array detector (Waters 996), which simultaneously records the chromatogram and the absorption spectrum. The eluent was usually the 40% aqueous acetonitrile. In some experiments the proportion of acetonitrile was changed for better separation of products. The GC-MS spectrometer (Magnum, Finnigan MAT) was equipped with a capillary column (DB5, 0.25 mm i.d. and 0.25  $\mu\text{m}$  film), EI source, and an ion trap assembly and operated by use of ITS40 software package. Methane and ethane were detected by use of a gas chromatograph (Hewlett-Packard, Model 5790) equipped with a flame ionization detector and a VZ-10 column.  $^1\text{H}$  NMR and UV absorption spectra were recorded by use of Varian 300 NMR and Shimadzu 3101 PC spectrometers, respectively. Molecular oxygen was quantitated by use of a YSI biological oxygen monitor (Model 5300) with a DAQ-data acquisition software package.

Time-resolved experiments were performed with use of a flash-lamp pumped dye-laser photolysis system described earlier.<sup>16</sup> The dyes used were LD 423 and LD 490. Most of the reactions were monitored by observing the luminescence of  $^*\text{UO}_2^{2+}$  at 515 nm. In some experiments the concentration of  $^*\text{UO}_2^{2+}$  was obtained from the absorbance at 580 nm ( $\epsilon = 4500 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>16,23</sup> Steady-state irradiations used a 250-W quartz tungsten halogen lamp (Oriental Corporation), equipped with a beam turning assembly. The irradiation wavelength was adjusted to  $>425$  nm by use of a Corning 3-67 filter.

**Sample Preparation.** Aqueous solutions of  $\text{UO}_2^{2+}$  at the desired pH (adjusted with  $\text{H}_3\text{PO}_4$ ) were placed in a 1 cm quartz cell and sealed with a gastight septum. The appropriate gas (argon, oxygen, or air) was bubbled through the solution for 20 min, followed by injection and dissolution of the substrate. After photolysis, the reaction solution was introduced directly into the HPLC chromatograph. For GC-MS and  $^1\text{H}$  NMR spectra, several samples were combined and concentrated by extraction with diethyl ether. All experiments were carried out at room temperature.

Solutions of  $\text{UO}_2^+$  were prepared by the reduction<sup>24</sup> of  $\text{UO}_2^{2+}$  (0.25 mM) by substoichiometric amounts of  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  (0.1 mM) in 5 mM



**Figure 1.** Effect of the initial concentration of  $\text{C}_6\text{H}_6$  on the yield of phenol. Conditions:  $[\text{UO}_2^{2+}] = 0.25 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 0.2 \text{ M}$ ,  $[\text{H}_3\text{PO}_4] = 0.1 \text{ M}$ , and irradiation time 60 min.

$\text{HClO}_4$ . The kinetics of the  $\text{UO}_2^+/\text{H}_2\text{O}_2$  reaction were monitored at the 255 nm maximum of  $\text{UO}_2^+$ .<sup>25</sup>

## Results

**Identification of the Photochemical Product.** A 60-min steady-state photolysis of a solution containing 0.25 mM  $\text{UO}_2^{2+}$ , 0.2 M  $\text{H}_2\text{O}_2$ , and 3.7 mM  $\text{C}_6\text{H}_6$  produced a single new peak in the HPLC chromatogram. The intensity of the peak increased linearly with irradiation time. The retention time and the UV spectrum of the product coincided with those of phenol.

The GC-MS and  $^1\text{H}$  NMR spectra confirmed this assignment. The new component in the GC-MS chromatogram yielded a mass spectrum identical to that of phenol. The  $^1\text{H}$  NMR spectrum exhibits multiplets at  $\delta$  6.85 and 7.25 ppm (phenol), in addition to a singlet at 7.26 ppm corresponding to unreacted benzene.

The quantum yield of phenol ( $\Phi_{\text{PhOH}}$ ) was determined indirectly by comparison with the known quantum yield of benzaldehyde ( $\Phi_{\text{PhCHO}} = 0.01$ )<sup>17</sup> produced under identical experimental conditions in the system toluene/ $\text{UO}_2^{2+}/\text{O}_2$ . The experiments were conducted under "standard" reactions conditions, see later, such that 50% of  $^*\text{UO}_2^{2+}$  was quenched by  $\text{H}_2\text{O}_2$ , and the rest by benzene. Similar experiments in the toluene/ $\text{UO}_2^{2+}/\text{H}_2\text{O}_2$  system yielded  $\Phi_{\text{PhCHO}} = 0.11$ , approximately 10 times greater than that obtained with  $\text{O}_2$  as oxidant.

Most of the product analyses were conducted after 1–2 h of irradiation at  $<1$  turnover and  $<10\%$  conversion to products. To confirm the catalytic nature of the reaction, a solution containing 0.67 M  $\text{H}_2\text{O}_2$ , 0.01 M benzene and 10  $\mu\text{M}$   $\text{UO}_2^{2+}$  was photolyzed for 6 h. The reaction produced 0.22 mM PhOH, yielding a turnover number  $[\text{PhOH}]/[\text{UO}_2^{2+}] = 22$ , and turnover/h = 3.6.

**The yield of PhOH first increases, and then decreases with increasing benzene concentration.** The maximum is reached at  $[\text{C}_6\text{H}_6] = 2\text{--}4 \text{ mM}$ , Figure 1. The decrease at high  $[\text{C}_6\text{H}_6]$  is caused by the unproductive quenching of  $^*\text{UO}_2^{2+}$  by benzene, which reduces the amount of  $^*\text{UO}_2^{2+}$  available for the reaction with  $\text{H}_2\text{O}_2$ , as discussed later.

As shown in Figure 2 the yield of phenol increases with  $[\text{UO}_2^{2+}]$  in a nonlinear fashion. A rapid increase at low  $[\text{UO}_2^{2+}]$  ( $<0.1 \text{ mM}$ ) is followed by a more moderate and approximately linear increase up to the highest concentration investigated (1

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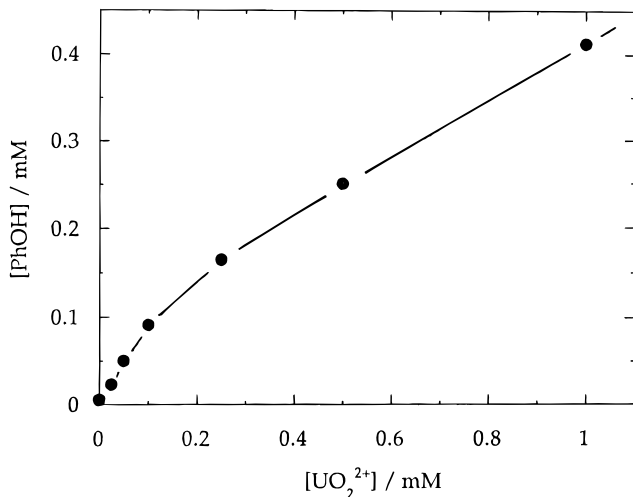
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**Figure 2.** Effect of  $[\text{UO}_2^{2+}]$  on the yield of phenol. Conditions:  $[\text{C}_6\text{H}_6] = 3.7 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 0.2 \text{ M}$ , and  $[\text{H}_3\text{PO}_4] = 0.1 \text{ M}$ .

mM). The yield also increases with  $[\text{H}_2\text{O}_2]$ , reaches a maximum at  $\sim 0.5 \text{ M H}_2\text{O}_2$ , and then decreases slightly, Figure 3. No product was observed if any of the three ingredients ( $\text{UO}_2^{2+}$ ,  $\text{H}_2\text{O}_2$ , or benzene) was absent.

To ascertain that the catalytic decomposition of  $\text{H}_2\text{O}_2$  is not a serious side reaction, the concentration of  $\text{H}_2\text{O}_2$  was determined before and after a 60-min irradiation of a solution containing  $0.25 \text{ mM UO}_2^{2+}$ ,  $0.10 \text{ M H}_2\text{O}_2$ , and  $3 \text{ mM C}_6\text{H}_6$  at pH 1. After the irradiation the concentration of  $\text{H}_2\text{O}_2$  was  $0.097 \text{ M}$ , which is reasonably close to the initial concentration, and shows that the unproductive loss of  $\text{H}_2\text{O}_2$  is minimal under the experimental conditions. At the typical 10% conversion, the consumption of  $\text{H}_2\text{O}_2$  was expected to be  $6 \times 10^{-4} \text{ M}$ .

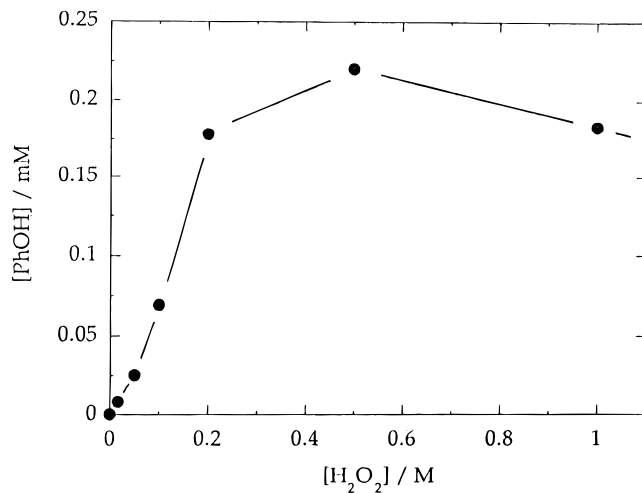
**Deuterium Isotope Effects.** There was no significant decrease in the yield of phenol when  $\text{C}_6\text{H}_6$  was replaced by  $\text{C}_6\text{D}_6$ ,  $\Phi_{\text{Ph-d}_5\text{OH}}/\Phi_{\text{PhOH}} \sim 0.94$ . However, when the reaction was conducted in  $\text{D}_2\text{O}$  (93% D), the yield of phenol was only 25% of that observed in  $\text{H}_2\text{O}$ , yielding a product isotope effect  $\Phi_{\text{H}_2\text{O}}/\Phi_{\text{D}_2\text{O}} = 4$ .

**Quenching Kinetics.** The quenching of  $^*\text{UO}_2^{2+}$  by benzene and several derivatives was studied by laser flash photolysis in  $0.1 \text{ M H}_3\text{PO}_4$ . The bimolecular rate constants  $k_q$  were obtained as a slope of the plot of  $k_{\text{obs}}$  against the concentration of the substrate according to eq 7. The value of  $k_0$  for the self-decay

$$k_{\text{obs}} = k_0 + k_q[\text{Q}] \quad (7)$$

of  $^*\text{UO}_2^{2+}$  in  $0.1 \text{ M H}_3\text{PO}_4$  is  $(1.45 \pm 0.07) \times 10^4 \text{ s}^{-1}$ . The rate constants  $k_q$  exceed  $10^8 \text{ M}^{-1} \text{ s}^{-1}$  for all the compounds studied, Table 1. There is no kinetic isotope effect upon substituting  $\text{C}_6\text{D}_6$  for  $\text{C}_6\text{H}_6$ , as expected if the quenching takes place by exciplex formation.<sup>26</sup> The kinetic data in Table 1 allow one to calculate that at low conversions ( $< 10\%$ )  $^*\text{UO}_2^{2+}$  reacts mainly with  $\text{H}_2\text{O}_2$  and benzene and that the quenching by the product phenol is minor.

The quenching of  $^*\text{UO}_2^{2+}$  by  $\text{C}_6\text{H}_6$  was also examined in the presence of  $5.0 \text{ mM H}_2\text{O}_2$ . The intercept of the plot of  $k_{\text{obs}}$  vs  $[\text{C}_6\text{H}_6]$  was larger than in the absence of  $\text{H}_2\text{O}_2$  ( $4.0 \times 10^4$  vs  $1.5 \times 10^4 \text{ s}^{-1}$ ), Figure 4, because two processes, the self-decay and the reaction with  $\text{H}_2\text{O}_2$  (see below) contribute. The slope of the line was, however, practically unchanged ( $2.86 \times 10^8$  vs  $3.18 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), indicating that either peroxouranium complexes are not formed under these conditions or their excited states do not react with  $\text{C}_6\text{H}_6$  significantly faster than the

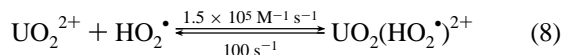


**Figure 3.** Effect of  $[\text{H}_2\text{O}_2]$  on the yield of phenol. Conditions:  $[\text{C}_6\text{H}_6] = 3.7 \text{ mM}$ ,  $[\text{UO}_2^{2+}] = 0.25 \text{ mM}$ ,  $[\text{H}_3\text{PO}_4] = 0.1 \text{ M}$ , and irradiation time 30 min.

uncomplexed  $^*\text{UO}_2^{2+}$  does. Careful spectral measurements on solutions of  $\text{UO}_2^{2+}$  containing  $0.1 \text{ M H}_2\text{O}_2$  in  $0.1 \text{ M H}_3\text{PO}_4$  showed no evidence for peroxouranium species. Similarly, there was no indication that a benzene–uranium complex formed in a solution containing  $0.25 \text{ mM UO}_2^{2+}$ ,  $0.1 \text{ M H}_3\text{PO}_4$ , and  $3 \text{ mM C}_6\text{H}_6$ .

The quenching of  $^*\text{UO}_2^{2+}$  emission by  $\text{H}_2\text{O}_2$  obeyed the general rate law of eq 7 and yielded  $k_q = 5.45 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  in  $\text{H}_2\text{O}$  and  $8.28 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  in  $\text{D}_2\text{O}$ . This kinetic isotope effect of 6.5 is undoubtedly caused by the rapid hydrogen exchange between hydrogen peroxide and water, such that the reactive species changes from  $\text{H}_2\text{O}_2$  in  $\text{H}_2\text{O}$  to  $\text{D}_2\text{O}_2$  in  $\text{D}_2\text{O}$ .

Time-resolved absorbance measurements on  $\text{UO}_2^{2+}/\text{H}_2\text{O}_2/h\nu$  reaction detected an intermediate after the quenching was complete. The kinetics of the formation and decay of the intermediate were monitored at  $320 \text{ nm}$ . At  $5 \text{ mM UO}_2^{2+}$ ,  $0.1 \text{ M H}_2\text{O}_2$ , and  $0.1 \text{ M H}_3\text{PO}_4$ , the formation stage obeyed first-order kinetics with  $k = (1.8 \pm 0.5) \times 10^3 \text{ s}^{-1}$ . The large standard deviation is the result of the small signal to noise ratio. This rate constant is somewhat larger than expected if the intermediate is the known complex  $\text{UO}_2(\text{HO}_2^*)^{2+}$ , eq 8.<sup>27</sup>



From the rate constants in eq 8, one would expect  $k = 850 \text{ s}^{-1}$  for the absorbance increase under our conditions. This kinetic discrepancy may be the result of different reaction conditions in the two studies ( $0.1 \text{ M HClO}_4$  vs  $0.1 \text{ M H}_3\text{PO}_4$ ). A recent report<sup>28</sup> also concluded that  $\text{UO}_2(\text{HO}_2^*)^{2+}$  is produced in the  $\text{UO}_2^{2+}/\text{H}_2\text{O}_2/h\nu$  system, although the yield has not been quantitated.

The point by point spectrum of the intermediate was recorded. The absorbance rises from  $\sim 400 \text{ nm}$  into the UV and has no prominent features, similar to the published spectrum of  $\text{UO}_2(\text{HO}_2^*)^{2+}$ .<sup>27</sup> From the measured initial concentration of  $^*\text{UO}_2^{2+}$  in these experiments, we calculate that  $\geq 80\%$  of  $^*\text{UO}_2^{2+}$  is converted to  $\text{UO}_2(\text{HO}_2^*)^{2+}$  ( $\epsilon_{305} = 725 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>27</sup> From the equilibrium constant  $K_8 = 1.5 \times 10^3 \text{ M}^{-1}$ , the maximum amount of  $\text{UO}_2(\text{HO}_2^*)^{2+}$  that could be observed under our experimental conditions is 88%. The chemistry observed is thus fully accounted for by eqs 8–10.

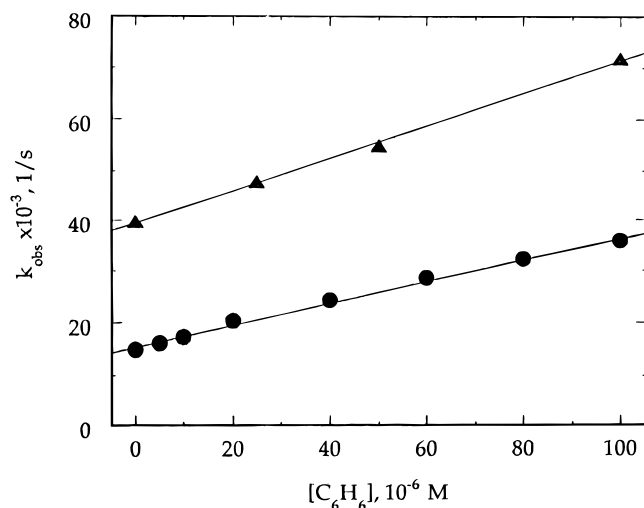
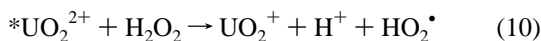
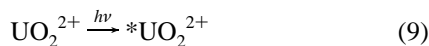
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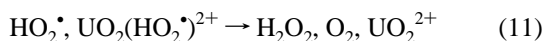
**Table 1.** Summary of the Kinetic Data (25 °C) for Quenching of  $^*\text{UO}_2^{2+}$  by Aromatic Hydrocarbons and Peroxides and Product Analysis Under Photocatalytic Conditions Using  $\text{H}_2\text{O}_2$  as Oxidant

compound	$k_q, \text{M}^{-1} \text{s}^{-1}{}^a$	photochemical product	quantum yield $\Phi^b$
benzene	$2.86(9) \times 10^8$	phenol	0.70 (<0.002)
benzene- $d_6$	$2.85(12) \times 10^8$	phenol- $d_5$	0.67 (<0.002)
phenol	$1.66(4) \times 10^9$	<i>p</i> -benzoquinone	0.005 (<0.0002)
toluene	$5.84(9) \times 10^8$	benzaldehyde	0.11 (0.01)
		benzyl alcohol	0.06 (<0.004)
		<i>p</i> -cresol	0.05 (<0.003)
		<i>o</i> -cresol	0.035 (<0.003)
		<i>m</i> -cresol	0.03 (<0.003)
<i>p</i> -xylene	$8.50(9) \times 10^8$	<i>p</i> -tolualdehyde	0.24 (0.02)
<i>p</i> -methylbenzyl alcohol	$7.51(45) \times 10^8$	<i>p</i> -methylbenzyl alcohol	0.02 (<0.002)
<i>p</i> -tolualdehyde	$3.80(22) \times 10^8$	<i>p</i> -tolualdehyde <sup>d</sup>	0.70 (0.07)
		<i>p</i> -toluic acid	0.10 (0.02)
1,3,5-mesitylene	$8.37(8) \times 10^8$	phthalic dicarboxaldehyde	
		3,5-dimethyl benzaldehyde	0.10 (0.016)
		3,5-dimethyl benzyl alcohol	0.028 (<0.003)
$\text{H}_2\text{O}_2$	$5.45(4) \times 10^6$		
$\text{D}_2\text{O}_2$	$8.28(19) \times 10^5$		
$\text{Me}_3\text{COOH}$	$7.61(30) \times 10^6$		

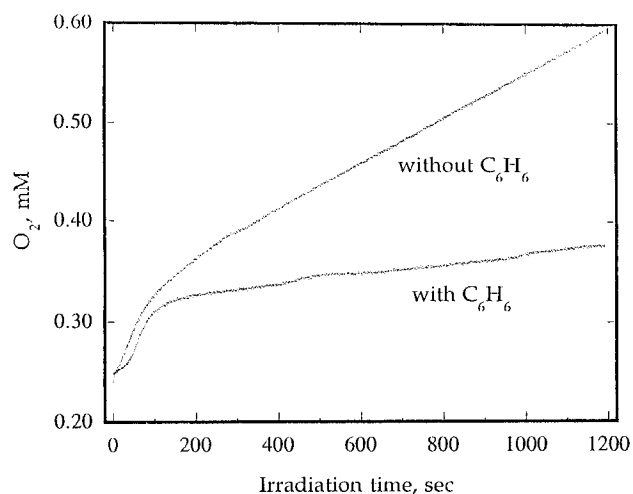
<sup>a</sup>  $[\text{UO}_2^{2+}] = 1.0 \text{ mM}$ ,  $[\text{H}_3\text{PO}_4] = 0.1 \text{ M}$ , 25 °C. Numbers in parantheses represent 1 standard deviation of the last significant figure. Product analyses were carried out at <1 turnover and <10% conversion to products. <sup>b</sup> Numbers in parentheses refer to  $\text{O}_2$  as oxidant.<sup>17</sup> <sup>c</sup> Reference 17.<sup>d</sup> An unidentified product was also formed; see text.

**Figure 4.** Plot of the observed rate constants for the quenching of  $^*\text{UO}_2^{2+}$  with benzene against the concentration of benzene in the presence (top line) and absence (bottom line) of  $\text{H}_2\text{O}_2$ . Conditions:  $[\text{UO}_2^{2+}] = 1 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 5 \text{ mM}$ , and  $[\text{H}_3\text{PO}_4] = 0.1 \text{ M}$ .

The subsequent slow decrease in absorbance in the 320–400 nm range is caused by the disappearance of  $\text{UO}_2(\text{HO}_2^\bullet)^{2+}$  in self- and cross-disproportionation reactions of eq 11. The



production of  $\text{O}_2$  was confirmed by use of an oxygen electrode. Figure 5 shows an increase in  $\text{O}_2$  concentration under steady state irradiation of a solution containing 5 mM  $\text{UO}_2^{2+}$  and 0.1 M  $\text{H}_2\text{O}_2$  in 0.1 M  $\text{H}_3\text{PO}_4$ . The addition of 3 mM benzene to this solution slowed down the  $\text{O}_2$  production significantly, owing to the competing quenching of  $^*\text{UO}_2^{2+}$  by  $\text{C}_6\text{H}_6$  and the consumption of  $\text{O}_2$  in the reaction(s) with intermediates; see Discussion. The rapid initial increase in both traces in Figure 5 is the result of the equilibration of the oxygen electrode after the injection of the last reagent.

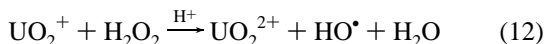
**Figure 5.** Increase in the concentration of  $\text{O}_2$  during photoirradiation of an air-saturated solution of 0.5 mM  $\text{UO}_2^{2+}$ , 0.1 M  $\text{H}_2\text{O}_2$ , and 0.1 M  $\text{H}_3\text{PO}_4$  in the absence and presence of 3 mM  $\text{C}_6\text{H}_6$ .

**Other Oxidations.** Toluene yielded benzaldehyde, benzyl alcohol and cresols. *p*-Xylene was oxidized to tolualdehyde and methylbenzyl alcohol. 1,3,5-Mesitylene yielded 3,5-dimethylbenzaldehyde and 3,5-dimethylbenzyl alcohol. Dimethylphenol and trimethylphenol were not observed, indicating a lower probability of attack at phenyl ring in the case of *p*-xylene and 1,3,5-mesitylene, respectively. The overall quantum yields for these oxidations by  $\text{H}_2\text{O}_2$ , Table 1, are significantly higher than those obtained in oxidations by  $\text{O}_2$ .<sup>17</sup>

The phenol, produced by the oxidation of benzene, was oxidized further to *p*-benzoquinone, although the yields were low. Methylbenzyl alcohol was oxidized to *p*-tolualdehyde. Another product, possibly *p*-hydroxymethyl benzaldehyde, was also observed, but it was not identified unequivocally. *p*-Tolualdehyde was oxidized further to phthalic dicarboxaldehyde and *p*-toluic acid. All the results are summarized in Table 1.

**tert-Butyl hydroperoxide** was found to quench  $^*\text{UO}_2^{2+}$  with  $k_q = 7.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . Under steady-state photolysis, the  $\text{UO}_2^{2+}/t\text{-BuOOH}/\text{C}_6\text{H}_6/h\nu$  reaction yielded no products detectable by HPLC. When the reaction was carried out under strictly air-free conditions, gas chromatography showed large amounts of methane and some ethane.

The kinetics of the reaction of  $\text{H}_2\text{O}_2$  with  $\text{UO}_2^{2+}$  were measured briefly. The bimolecular rate constant  $k = 3.4 \pm 0.7 \text{ M}^{-1} \text{ s}^{-1}$  was determined at  $[\text{HClO}_4] = 5 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 0.5\text{--}1.0 \text{ mM}$ , and  $[\text{UO}_2^{2+}] = 0.1 \text{ mM}$ . After correction for the stoichiometric factor,  $[\text{UO}_2^{2+}]/[\text{H}_2\text{O}_2] = 2$ , one obtains  $k_{12} = 1.7 \pm 0.4 \text{ M}^{-1} \text{ s}^{-1}$  for the rate-determining step, which we presume takes place as shown in eq 12.



### Discussion

Both  $\text{C}_6\text{H}_6$  and  $\text{H}_2\text{O}_2$  quench  $^*\text{UO}_2^{2+}$ . The quenching by  $\text{C}_6\text{H}_6$  alone yields no products when the reaction is carried out under either  $\text{Ar}$  or  $\text{O}_2$ , consistent with the previously proposed mechanism involving the formation and decay of an exciplex.<sup>26</sup>

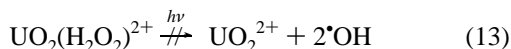
The findings for the reaction of  $^*\text{UO}_2^{2+}$  with  $\text{H}_2\text{O}_2$ , eq 10, suggest hydrogen atom abstraction. The kinetic isotope effect  $k_{\text{H}}/k_{\text{D}} = 6.6$ , and quantitative formation of  $\text{UO}_2(\text{HO}_2^\bullet)^{2+}$  strongly support this mechanism.

The quenching by a mixture of  $\text{C}_6\text{H}_6$  and  $\text{H}_2\text{O}_2$  takes place with a rate constant that is, within experimental error, identical with the sum of rate constants for the quenching by individual components. This result establishes the irrelevancy of the quenching of any uranium peroxy complexes by benzene or uranium–benzene complexes by  $\text{H}_2\text{O}_2$ . No spectroscopic evidence for such complexes was found at the high  $[\text{H}^+]$  (0.1 M) and low  $[\text{C}_6\text{H}_6]$  ( $\leq 5 \text{ mM}$ ) used. Peroxouranium complexes are known to exist at  $\text{pH} \geq 5$ .<sup>18–21</sup>

Because of the simultaneous quenching of the excited state by  $\text{H}_2\text{O}_2$  and  $\text{C}_6\text{H}_6$ , the product yield is a function of the concentration ratio of the two quenchers. The quenching by benzene reduces the amount of the excited state available for product formation, which requires that  $[\text{C}_6\text{H}_6]$  be kept low. On the other hand, benzene is the substrate, and its concentration determines the amount of the product formed; ergo  $[\text{C}_6\text{H}_6]$  should be high. Our “standard” conditions,  $[\text{H}_2\text{O}_2]/[\text{C}_6\text{H}_6] = 52$ , for the catalytic oxidation are a compromise which allows 50% of  $^*\text{UO}_2^{2+}$  to be quenched by  $\text{C}_6\text{H}_6$  and 50% by  $\text{H}_2\text{O}_2$ . This ratio is obtained from the rate constants in Table 1.

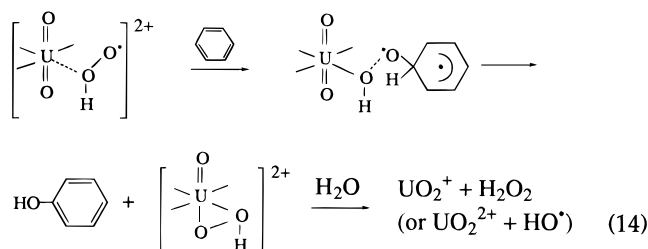
The overall quantum yield for the formation of  $\text{PhOH}$  ( $\Phi = 0.7$ ) was obtained under these conditions. Thus for each mol of the excited state that had reacted with  $\text{H}_2\text{O}_2$ , 1.4 mol of  $\text{PhOH}$  was produced. This value is a result of several different determinations (quantum yield of acetone in the  $\text{UO}_2^{2+}/\text{H}_2\text{O}_2/2\text{-PrOH}/h\nu$  reaction,<sup>16</sup> kinetics of quenching of  $^*\text{UO}_2^{2+}$  by  $\text{C}_6\text{H}_6$  and by  $\text{H}_2\text{O}_2$ , and finally the yield of  $\text{PhOH}$  in the  $\text{UO}_2^{2+}/\text{H}_2\text{O}_2/\text{C}_6\text{H}_6/h\nu$  reaction). As a result, the accumulated error is large, and we are not confident that the quantum yield indeed exceeds unity, but only that it is close to it.

Several mechanisms for the oxidation of benzene and its derivatives by  $\text{UO}_2^{2+}/\text{H}_2\text{O}_2/h\nu$  can be put forward. The homolysis of coordinated  $\text{H}_2\text{O}_2$  in an intermediate/transition state of the form  $[\text{UO}_2(\text{H}_2\text{O}_2)^{2+}]$  to yield hydroxyl radicals, eq 13, would eventually produce phenol. In the absence of substrates, hydroxyl radicals would react with  $\text{H}_2\text{O}_2$  to yield  $\text{HO}_2^\bullet$ , and finally the observed  $\text{UO}_2(\text{HO}_2^\bullet)^{2+}$ . This mechanism will not be considered further, however, because it cannot explain the deuterium isotope effect of hydrogen peroxide on the yield of phenol,  $\Phi_{\text{H}_2\text{O}_2}/\Phi_{\text{D}_2\text{O}_2} = 4$ .

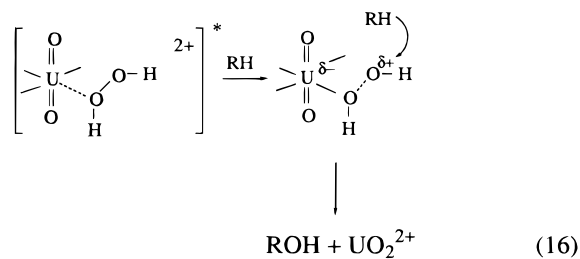
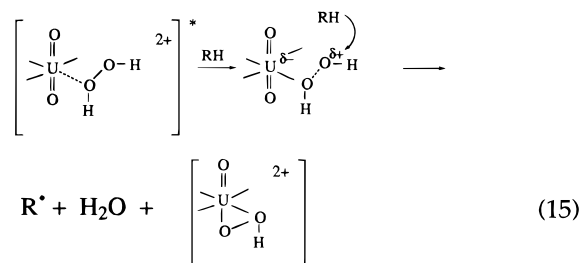


Next we consider a mechanism similar to that proposed for the hydroxylation of benzene by complexes of vanadium, iron, and cobalt.<sup>29</sup> The addition of  $\text{UO}_2(\text{HO}_2^\bullet)^{2+}$  to the aromatic ring,

eq 14, produces a transient cyclohexadienyl radical, which is then oxidized to phenol with the concomitant formation of a peroxouranium(V) complex or uranium(VI) and hydroxyl radicals. This mechanism is consistent with the strong isotope effect associated with  $\text{H}_2\text{O}_2$  and the lack of substrate isotope effect, but does not explain the facile oxidation of the methyl group in toluene, Table 1.

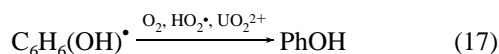
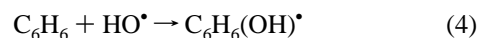
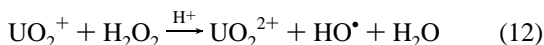
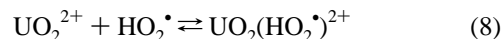
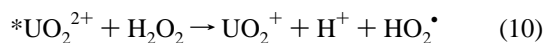


Similarly, hydrogen atom abstraction by coordinated<sup>30</sup> hydrogen peroxide in the transient complex  $^*\text{U}^{\text{VI}}\text{O}_2(\text{H}_2\text{O}_2)^{2+}$  (eq 15) leading to the formation of carbon-centered radicals is inconsistent with the lack of substrate isotope effect. Moreover, this mechanism would require that the quenching of  $^*\text{UO}_2^{2+}$  by a mixture of  $\text{H}_2\text{O}_2$  and benzene be faster than quenching by the individual components, contrary to the experimental observation. The same would be true for a mechanism involving a nucleophilic attack at coordinated  $\text{H}_2\text{O}_2$  in eq 16.



The best mechanistic candidate seems to be the photochemically induced Fenton reaction in Scheme 1.

### Scheme 1



A number of observations support this mechanism. The quenching of  $^*\text{UO}_2^{2+}$  by  $\text{H}_2\text{O}_2$  produces  $\text{UO}_2^{2+}$  (in addition to

HO<sub>2</sub><sup>•</sup>). The oxidation of UO<sub>2</sub><sup>+</sup> by H<sub>2</sub>O<sub>2</sub> ( $k[\text{H}_2\text{O}_2] \sim 0.3 \text{ s}^{-1}$ ), is much faster than the competing oxidation with molecular oxygen ( $k[\text{O}_2] < 0.04 \text{ s}^{-1}$ )<sup>25</sup> at the concentrations used. UO<sub>2</sub><sup>+</sup> can undergo only one-electron oxidation, and an odd-electron intermediate has to be involved in the reaction with H<sub>2</sub>O<sub>2</sub>. We propose that this intermediate is the HO<sup>•</sup> radical as shown in eq 12, although we cannot rule out the possibility that some closely related species,<sup>12</sup> such as a short-lived U<sup>V</sup>-H<sub>2</sub>O<sub>2</sub> complex, is the active oxidant for aromatic hydrocarbons.

The **product** isotope effect demonstrates clearly that the UO<sub>2</sub><sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> reaction is the main (and probably only) productive reaction of the excited state. The measured **kinetic** isotope effect for \*UO<sub>2</sub><sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> reaction is 6.6. Under the conditions employed, only 50% of \*UO<sub>2</sub><sup>2+</sup> reacts with H<sub>2</sub>O<sub>2</sub>. Upon substitution of H<sub>2</sub>O<sub>2</sub> by D<sub>2</sub>O<sub>2</sub> the quantum yield of phenol decreased by a factor of ~4, in reasonable agreement with the expected factor of ~3.3, calculated from eq 18, where  $k_b$  represents the rate constant for the quenching of \*UO<sub>2</sub><sup>2+</sup> by benzene.

$$\frac{[\text{PhOH}]}{[\text{PhOD}]} = \frac{\frac{k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]}{k_b[\text{C}_6\text{H}_6] + k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]}}{\frac{k_{\text{D}_2\text{O}_2}[\text{D}_2\text{O}_2]}{k_b[\text{C}_6\text{H}_6] + k_{\text{D}_2\text{O}_2}[\text{D}_2\text{O}_2]}} \quad (18)$$

A thorough analysis of the available literature data has led to the conclusion<sup>31</sup> that there is no "fingerprint" product distribution in Fenton-type oxidations of aromatic hydrocarbons. The ratio of the three isomeric cresols depends on acidity and on the nature and concentration of the metal ions involved. Also, the presence of O<sub>2</sub> has a dramatic effect on this ratio. The formation of PhCHO, PhCH<sub>2</sub>OH and cresols in the UO<sub>2</sub><sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/hν system, and the cresol ratio (*o*:*m*:*p* = 1.2:1:1.8) suggest that both benzyl and cyclohexadienyl radicals are produced, the final products being derived mostly from the reactions of the radicals with O<sub>2</sub>. This conclusion is consistent with the decreased accumulation of O<sub>2</sub> in the \*UO<sub>2</sub><sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> reaction in the presence of aromatic hydrocarbons, Figure 5. A typical<sup>31</sup> ratio of cresols derived from the reaction of cyclohexadienyl radicals with O<sub>2</sub> is 1:1.2:1. The smaller fraction of *m*-cresol in the present system is probably the result of the low pH used. Such conditions favor the formation of toluene radical cations,<sup>32</sup> which yield only *m*- and *p*-cresols. Scheme 2 summarizes the proposed mechanism.

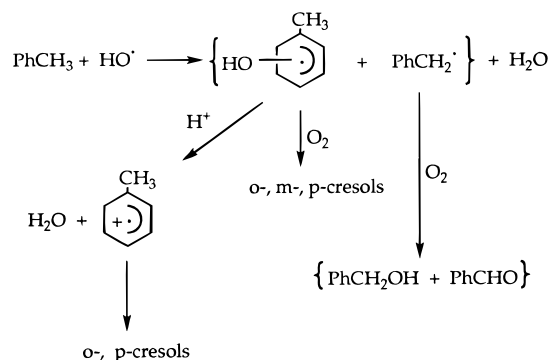
The oxidation of cyclohexadienyl radicals with UO<sub>2</sub><sup>2+</sup> appears to be insignificant. If this were not the case, reaction 19 would regenerate UO<sub>2</sub><sup>+</sup> and initiate a chain reaction, resulting in Φ > 0.5 for the formation of phenol.



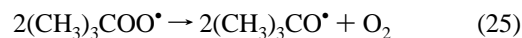
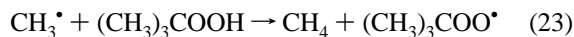
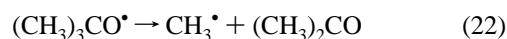
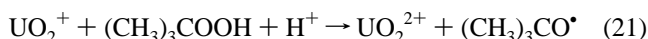
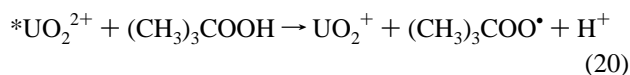
Even if the observed Φ = 0.7 is outside the experimental error of 0.5, expected on the basis of Scheme 1 at 50% quenching by H<sub>2</sub>O<sub>2</sub>, the chain length is still short and demonstrates that reaction 19 is a minor path at best.

Additional support for a Fenton-type mechanism of Scheme 1 comes from the experiments with *t*-BuOOH. The failure to

Scheme 2



oxidize benzene, and the formation of (mostly) methane and (some) ethane under air-free conditions are indicative of a one-electron process yielding *t*-BuO<sup>•</sup> radicals, followed by rapid β-scission,<sup>33</sup> hydrogen atom abstraction from *t*-BuOOH, and self-reactions<sup>34</sup> of *t*-BuOO<sup>•</sup> radicals, eqs 20–25.



**Conclusions.** UO<sub>2</sub><sup>2+</sup> catalyzes the photochemical oxidation of benzene and substituted benzenes by H<sub>2</sub>O<sub>2</sub>. The following evidence suggests that these are photochemically driven Fenton-type reactions. (1) \*UO<sub>2</sub><sup>2+</sup> reacts with H<sub>2</sub>O<sub>2</sub> to yield UO<sub>2</sub><sup>+</sup> and HO<sup>•</sup>. The reaction has a kinetic isotope effect,  $k_{\text{H}_2\text{O}_2}/k_{\text{D}_2\text{O}_2}$ , of 6.6, consistent with hydrogen-atom abstraction as rate determining step. (2) UO<sub>2</sub><sup>+</sup> reacts with H<sub>2</sub>O<sub>2</sub> ( $k = 1.7 \text{ M}^{-1} \text{ s}^{-1}$ ) in a presumably Fenton-type reaction. (3) The yield of PhOH derived from H<sub>2</sub>O<sub>2</sub> is ~4 times greater than the yield of PhOD derived from D<sub>2</sub>O<sub>2</sub>. Combined with the kinetic isotope effect of 6.6 for the reaction of \*UO<sub>2</sub><sup>2+</sup> with H<sub>2</sub>O<sub>2</sub>, this product isotope effect clearly identifies the \*UO<sub>2</sub><sup>2+</sup>-H<sub>2</sub>O<sub>2</sub> (or D<sub>2</sub>O<sub>2</sub>) reaction as the only productive reaction of the excited state. (4) When H<sub>2</sub>O<sub>2</sub> is replaced by *t*-BuOOH, the reaction produces large amounts of methane and some ethane, as expected if *tert*-butoxyl radicals are involved.

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