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# ARTICLES

## Uranyl-Sensitized Photochemical Oxidation of Naphthalene by Molecular Oxygen. Role of Electron Transfer

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Naphthalene quenches the excited state $*UO_2^{2+}$ in two parallel pathways: oxidation to naphthalene radical cation, $C_{10}H_8^{\bullet+}$ ($\Phi = 0.3$), and exciplex formation. The overall rate constant in aqueous acetonitrile containing 0.1 M $H_3PO_4$ has a value $k_q = 2.20 \times 10^9$ $M^{-1}$ $s^{-1}$. In the presence of $O_2$, a portion of $C_{10}H_8^{\bullet+}$ is converted to 2-formylcinnamaldehyde and several other products, the rest reacting with $UO_2^+$ by back electron transfer.

### Introduction

$*UO_2^{2+}$ reacts with organic substrates by a variety of pathways: H atom abstraction, addition to multiple bonds, oxygen atom transfer, and exciplex formation.[1−4] Electron transfer has been observed only with easily oxidizable substrates, such as $ABTS^{2-}$,[5] amino acids,[6] and several others.[7]

H atom abstraction, eq 1, yields $UO_2^+$ and C-centered radicals, both of which react with molecular oxygen, eqs 2 and 3. Reaction 3 regenerates $UO_2^{2+}$, and the photooxidation of

$$*UO_2^{2+} + RH \rightarrow UO_2^{+} + R^{\bullet} + H^{+} \qquad (1)$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \rightarrow \text{products} \qquad (2)$$

$$2UO_2^{+} + O_2 + 2H^{+} \rightarrow 2UO_2^{2+} + H_2O_2 \qquad (3)$$

RH becomes catalytic. We have recently demonstrated this scheme for a number or organic compounds, including alkanes, alkenes, and side-chain aromatics.[5] Benzene, on the other hand, reacts with $*UO_2^{2+}$ exclusively by exciplex formation, and no oxidation took place when $O_2$ was used as oxidant. A different reaction scheme, in effect a photoinduced Fenton-like reaction, was devised to oxidize benzene to phenol with use of $H_2O_2$ as terminal oxidant.[8]

The obvious advantages of $O_2$ over $H_2O_2$ in catalytic oxidations have prompted us to return to $O_2$ in an attempt to oxidize polynuclear aromatics, many of which are potent carcinogens. We reasoned that the lower ionization potential of polycyclic aromatics, as compared to benzene, may open up one-electron oxidation as a feasible pathway. In the followup chemistry of radical cations, $O_2$ would once again become a competent terminal oxidant.

In this work we used the noncarcinogenic naphthalene as a model for polynuclear aromatics. This reaction provides the first example of electron transfer from a hydrocarbon to $*UO_2^{2+}$.

### Experimental Section

Naphthalene (Aldrich) was recrystallized from methanol. Naphthalene-$d_8$, 1-naphthol, and 2-naphthol (all Aldrich) were used as received. Stock solutions of uranyl perchlorate (0.10 M) were prepared by dissolving uranium trioxide (Strem Chemicals, 99.8%) in perchloric acid. All other chemicals were analytical grade or higher.

Absorption spectra were recorded with use of a Shimadzu 3101 PC spectrometer. A Waters' high-performance liquid chromatograph, equipped with a $C_{18}$ column (Alltech, Adsorbosphere) and a photodiode array detector (Waters 996), was used to monitor the accumulation of products. The eluent was aqueous acetonitrile. Mass spectra were measured by a GC−MS (Magnum, Finnigan MAT) equipped with a capillary column (DB5, 0.25 mm i.d. and 0.25 $\mu$m film), an EI/CI source, and an ion trap assembly operated by use of the ITS40 software package. $^1$H and $^{13}$C NMR spectra were recorded by use of Varian 300 and Bruker DRX-400 spectrometers. Time-resolved experiments used a laser photolysis system described elsewhere.[5]

Because of the low solubility of naphthalene (~0.2 mM) in $H_2O$, a cosolvent was required. We chose 15−50% aqueous acetonitrile, which does not quench $*UO_2^{2+}$ significantly.[5] The kinetic samples were prepared in 1-cm quartz cells with gastight septa and irradiated with light from a 250-W quartz tungsten halogen lamp (Oriel Corporation, 66181) or a solar lamp (GE, 250 W). To avoid direct excitation of naphthalene and the photoproducts, the irradiation wavelength was adjusted with an appropriate cutoff filter (Schott KV418) to $\lambda > 420$ nm. Most of the reactions were conducted in 0.10 M $H_3PO_4$, where the lifetime of the excited state[2,7] ($\tau_0 \approx 100$ $\mu$s) is much longer than in the absence of complexing anions ($\tau_0 \approx 2$ $\mu$s). The samples for GC−MS and $^1$H NMR analyses were obtained by extracting the reaction solutions with diethyl ether, evaporating the ether in a hood, and dissolving the residue in $CDCl_3$. All experiments were carried out at room temperature (23 ± 2 °C).

### Results

Spectral measurements showed no evidence for complex formation between $UO_2^{2+}$ (0.25 mM) and naphthalene (1 mM) in 0.1 M $H_3PO_4$. A new broad band did form, however, in the 340−550 nm range when 1 mM 1-naphthol and 0.25 mM $UO_2^{2+}$ were mixed. This result is consistent with the formation of a weak $UO_2^{2+}$−naphthol complex.[9]

**Products.** Figure 1 shows the HPLC chromatogram of an air-saturated solution of 10 mM naphthalene and 0.25 mM $UO_2^{2+}$ in 25% aqueous MeCN after 60 min of irradiation. The short retention times of all the products on a $C_{18}$ column are

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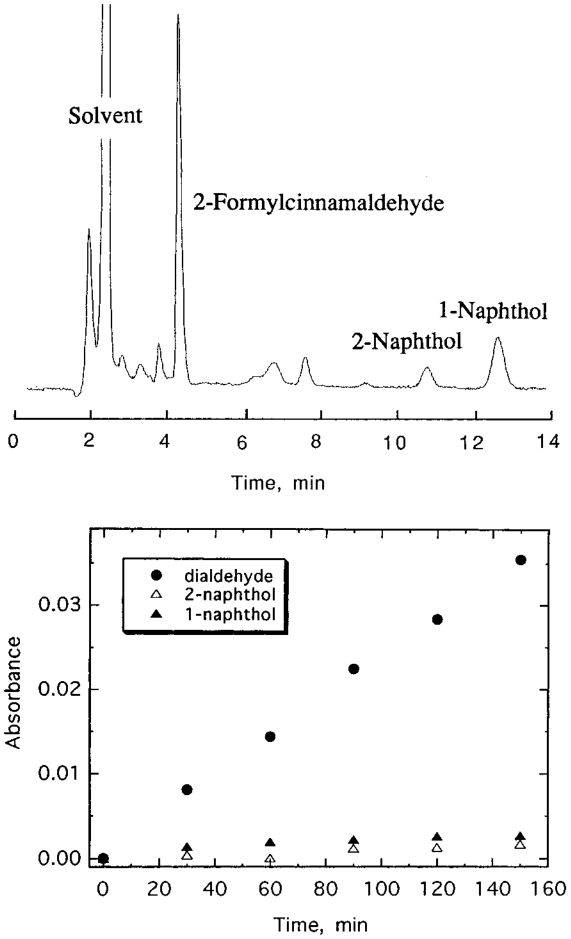


**Figure 1.** (top) HPLC chromatogram of 10 mM naphthalene and 0.25 mM $UO_2^{2+}$ in 25% aqueous $CH_3CN$ (0.1 M $H_3PO_4$) after 60 min of irradiation. Eluent was 40 vol % acetonitrile in water, $\lambda_{detection}$ 220 nm. (bottom) Growth of photochemical products with irradiation time (dialdehyde stands for 2-formylcinnamaldehyde).

consistent with the products being more polar than naphthalene. Only the peak at 4.1 min increased consistently with irradiation time.

The species with the retention times of 11.8 and 12.8 min were identified as 1-naphthol and 2-naphthol ($C_{10}H_7OH$), respectively, by comparison to the chromatograms of the commercial compounds. The greater yield of 1-naphthol is reasonable in view of the greater electron density at the C1 position of naphthalene.[10] The quantum yield of 1-naphthol was determined by comparison with the yield of benzaldehyde produced by oxidation of toluene in a similar system.[11] The concentrations of naphthalene (1 mM) and toluene (3.8 mM) in two separate experiments were chosen such that 98% of $*UO_2^{2+}$ was quenched by the substrates, the rest decaying spontaneously. The yield ratio of the respective products, 1-naphthol and benzaldehyde, was determined by HPLC, and led to $\Phi \approx 1 \times 10^{-4}$ for 1-naphthol.

The 4.1-min species was identified as 2-formylcinnamaldehyde on the basis of GC−MS, $^1$H NMR, and $^{13}$C NMR spectra. The $^1$H NMR spectrum, Figure 2, exhibits resonances at 10.16 ppm (singlet, −CHO bound to benzene), 9.74 ppm (doublet, $J = 8$ Hz, −CHO adjacent to α-CH), 6.61 ppm (doublet of doublets, α-CH), 8.55 ppm (doublet, $J = 15.6$ Hz, $\beta$-CH), and 7−8 ppm (aromatic resonances). A weak signal at ~7 ppm was not assigned. The areas under the two aldehydic hydrogens are comparable, suggesting that both −CHO groups belong to the same compound derived from naphthalene by ring cleavage and oxidation.[12−17] The large downfield shift of the $\beta$-hydrogen confirms the ortho arrangement of the two substituents, −CHO and −CH=CH−CHO.

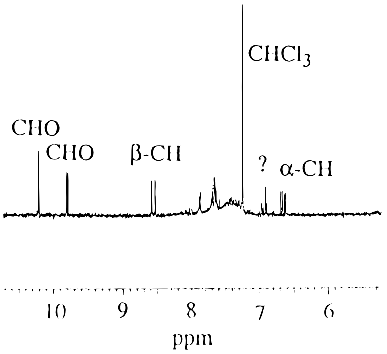
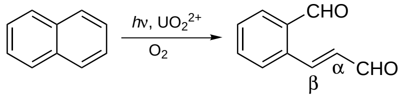


**Figure 2.** $^1$H NMR spectrum in $CDCl_3$ of the reaction products obtained by irradiating a solution of 0.25 mM $UO_2^{2+}$, 1.5 mM naphthalene, and 0.1 M $H_3PO_4$ for 60 min in 25% aqueous $CH_3CN$.

**TABLE 1: Effect of Experimental Conditions on the Yield of 2-Formylcinnamaldehyde[a]**

| conditions | relative yield |
|---|---|
| air | (1) |
| $O_2$ | 0.95 |
| Ar | ~0 |
| air/$H_2O_2$[b] | 1.5 |

[a] 1.5 mM naphthalene, 1.5 mM $UO_2^{2+}$, in 25% aqueous acetonitrile containing 0.1 M $H_3PO_4$ . [b] $[H_2O_2] = 0.1$ M.



(4)

In the $^{13}$C NMR spectrum, two prominent peaks in the carbonyl region (192.86 and 193.93 ppm) provide additional evidence for the two −CHO groups.

With an electron ionization source (EI), the main peak in the GC−MS chromatogram has a mass number 131, which we assign to cinnamaldehyde ($C_6H_5C_2H_2CHO - H = 131$), a fragment of 2-formylcinnamaldehyde. The main peak in the chemical ionization (CI) GC−MS chromatogram has a mass number 161, which matches that of 2-formylcinnamaldehyde [$C_6H_4(CHO)(C_2H_2CHO + H)$]. The two minor peaks with mass numbers 159 and 175/177 were not fully identified, but are consistent with naphthoquinone and 2-formylcinnamic acid, respectively.

The precise determination of the quantum yield of 2-formylcinnamaldehyde could not be carried out without an independent source of the compound for HPLC calibration. The yield was estimated from the absorbance at 220 nm, which was approximately 5 times greater than the absorbance of the 1-naphthol band at the same wavelength. Under the reasonable assumption that the molar absorptivities of the two compounds do not differ at this wavelength by more than a factor of 10, and taking $\Phi = 10^{-4}$ for 1-naphthol, we obtain $5 \times 10^{-5} < \Phi$(2-formylcinnamaldehyde) $< 5 \times 10^{-3}$.

The appearance of HPLC chromatograms and the yield of dialdehyde were unchanged when naphthalene was replaced by naphthalene-$d_8$. As shown in Table 1, no products were detected when the reaction was carried out under argon, but air-saturated and $O_2$-saturated samples had similar product yields.

The presence of $H_2O_2$ in the reaction system increases the dialdehyde yield, Table 1. The reaction scheme under these conditions may be similar to that in the benzene/$UO_2^{2+}$/$H_2O_2$ system, where $H_2O_2$ reacts with $UO_2^+$ and produces an oxidizing

**TABLE 2: Kinetic and Product Data on Photochemical Reactions between $UO_2^{2+}$ and Aromatic Compounds**

| quencher[a] | $k_q/M^{-1}\ s^{-1}$ [a,b] | products |
|---|---|---|
| naphthalene | $2.20(3) \times 10^9$ | 1-naphthol, 2-naphthol, 2-formylcinnamaldehyde |
| naphthalene-$d_8$ | $2.14(3) \times 10^9$ | 1-naphthol-$d_7$, 2-naphthol-$d_7$, 2-formylcinnamaldehyde-$d_6$ |
| 1-naphthol | $2.90(4) \times 10^9$ | |
| 2-naphthol | $2.38(4) \times 10^9$ | |
| 1,5-dihydroxynaphthalene | $3.81(7) \times 10^9$ | |
| 1,4-dimethoxybenzene[c] | $2.30(10) \times 10^9$ | $(CH_3O)_2C_6H_4^{\bullet+}$ |
| $ABTS^{2-}$ [d] | $1.33(2) \times 10^9$ | $ABTS^{\bullet+}$ |

[a] Rate constants for the quenching of $*UO_2^{2+}$. Conditions: 1.0 mM $UO_2^{2+}$, 0.1 M $H_3PO_4$, 23 ± 2 °C. The reaction with naphthalene was carried out in 50% aqueous acetonitrile. All other reactions used $H_2O$ as solvent. [b] Numbers in parantheses represent one standard deviation of the last significant figure. [c] Dimethoxybenzene radical cation was observed at 460 nm. [d] Reference 5.

**TABLE 3: Oxidation Products of Naphthalene**

| reaction system | reaction type | products |
|---|---|---|
| $C_{10}H_8$/air/$UO_2^{2+}$ [a] | photolysis | 1-naphthol, 2-naphthol, 2-formylcinnamaldehyde, others |
| $C_{10}H_8$/$Fe(CN)_6^{3-}$/$N_2O$[b] | $\gamma$-radiolysis | 1-naphthol (68%), 2-naphthol (32%) |
| $C_{10}H_8$/air/$Fe^{2+}$/$H_2O_2$[c] | thermal | 1-naphthol, 2-naphthol, salicylic acid, carboxyhydroxycinnamic acid, $CO_2$, others |
| $C_{10}H_8$/$PdCl_2$/HAc/$SiO_2$[d] | thermal | 1-naphthol, 1,4-naphthoquinone, 2-formylcinnamaldehyde |
| $C_{10}H_8$/Fe/mercaptobenzoate/$O_2$[e] | thermal | 1-naphthol, 2-naphthol, dihydroxydihydronaphthalene, 2-formylcinnamaldehyde, others |
| $C_{10}H_8$/air/$SiO_2(Al_2O_3)$[f] | photolysis | phthalic acid (49%) |

[a] This work. Conditions: air-saturated 0.1 M $H_3PO_4$ in 20% aqueous $CH_3CN$, 0.2 mM naphthalene, 0.5 mM $UO_2^{2+}$, $\lambda_{irr} > 420$ nm. [b] $\gamma$-Radiolysis in $N_2O$-saturated aqueous solution, 0.2 mM naphthalene, 1 mM $K_3Fe(CN)_6$, ref 10. [c] Aqueous solution, ref 27 . [d] In acetic acid, ref 16. [e] Udenfriend/Ullrich system, ref 28. [f] Solid state, naphthalene loading $2 \times 10^{-5}$ mol/g, $\lambda_{irr} > 300$ nm, ref 36.

intermediate, presumably $HO^\bullet$, which initiates further oxidation of substrate.[8]

**The Kinetics** of the quenching of $*UO_2^{2+}$ with naphthalene and several other compounds were measured by monitoring the luminescence of $*UO_2^{2+}$. The data for all the compounds obeyed the rate law of eq 5, where $k_0$ represents the rate constant for the spontaneous decay of $*UO_2^{2+}$, $k_q$ is the quenching constant, and [Q] is the concentration of the quencher.

$$-d[*UO_2^{2+}]/dt = k_{obs}[*UO_2^{2+}] = (k_0 + k_q[Q])[*UO_2^{2+}] \tag{5}$$

From a linear plot of $k_{obs}$ *vs* [naphthalene], we obtain $k_q = 2.20 \times 10^9\ M^{-1}\ s^{-1}$. The phenolic derivatives have similar rate constants. For example, $k_q = 2.9 \times 10^9\ M^{-1}\ s^{-1}$ for 1-naphthol. The adherence of all the data to eq 5 shows that either the $UO_2^{2+}$−naphthol complex does not form in appreciable amounts at the low concentrations of 1-naphthol (<0.1 mM) used in the kinetics experiments or that the complex is kinetically insignificant.

The value for naphthalene-$d_8$, $k_q = 2.14 \times 10^9\ M^{-1}\ s^{-1}$, is comparable to that for naphthalene. The negligible kinetic isotope effect, combined with the lack of deuterium isotope effect on product yields, is consistent with the reaction taking place by electron transfer and/or exciplex formation, i.e. a reaction that does not involve a C−H bond breaking in a kinetically significant step. The kinetic data for all the reactions studied are summarized in Table 2.

A point-by-point UV−visible spectrum of the intermediate produced by quenching of $*UO_2^{2+}$ by naphthalene, Figure 3, shows the characteristic broad absorption of $C_{10}H_8^{\bullet+}$ [18,19] in the 600−750-nm range. Transient absorption also was observed in the 300−500-nm range, as expected for $C_{10}H_8^{\bullet+}$, although these measurements were complicated by high background absorbance. Thus at least part of the quenching reaction takes place by electron transfer. The concentration of naphthalene radical cations ($\epsilon_{690} = 1350\ M^{-1}\ cm^{-1}$),[18] produced from $*UO_2^{2+}$ and naphthalene (1.5 mM) was determined in laser flash experiments. The concentration of $*UO_2^{2+}$ ($\epsilon_{570} = 4500\ M^{-1}\ cm^{-1}$)[5,20] was determined under identical conditions in the absence of naphthalene. The data were combined to give $\Phi(C_{10}H_8^{\bullet+}) = [C_{10}H_8^{\bullet+}]/[*UO_2^{2+}] = 0.3 \pm 0.1$. As expected, this yield was the same irrespective of whether the reaction was conducted under $O_2$ or Ar.

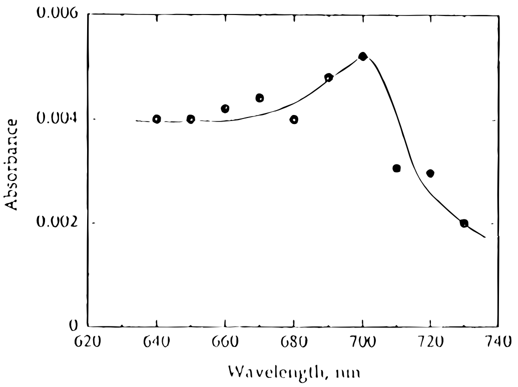


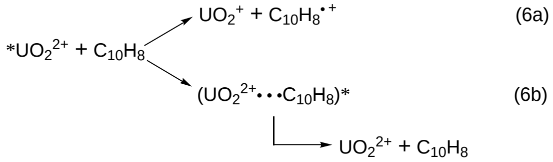
**Figure 3.** Transient absorption spectrum obtained 3.5 $\mu$s after the laser flash. Conditions: 4.0 mM $UO_2^{2+}$, 1.5 mM naphthalene, 0.1 M $H_3PO_4$, 25% aqueous $CH_3CN$, $\lambda_{exc}$ 423 nm.

The lifetime of $C_{10}H_8^{\bullet+}$ was ~10 $\mu$s in 50% aqueous acetonitrile at 0.1 M $H_3PO_4$. As discussed later, most of $C_{10}H_8^{\bullet+}$ disappears in back electron transfer with $UO_2^+$.

The quenching of $*UO_2^{2+}$ by 1,4-dimethoxybenzene takes place with a rate constant $k = 2.3 \times 10^9\ M^{-1}\ s^{-1}$. The reaction produces a radical cation, 1,4-$C_6H_4(OCH_3)_2^{\bullet+}$, which was identified by its UV−visible spectrum.[21]

## Discussion

A significant fraction (~30%) of the $*UO_2^{2+}$−naphthalene reaction produces naphthalene radical cations, $C_{10}H_8^{\bullet+}$, clearly demonstrating the electron-transfer nature of the process, eq 6a. The 70% of $*UO_2^{2+}$ that does not yield any observable intermediates presumably takes place by exciplex formation, eq 6b, as suggested previously for other unsaturated compounds.[3,22] The experiments were carried out in 0.1 M $H_3PO_4$, a medium where phosphate complexes of $UO_2^{2+}$ and $*UO_2^{2+}$ predominate[2] and almost certainly take part in reaction 6 and beyond. For the sake of simplicity, the coordinated phosphate ions are not shown.



Even though the oxidation of organic substrates by $^*UO_2^{2+}$ is fairly common,[1,2,5,7,23–25] such reactions typically take place by hydrogen atom abstraction or initial addition to multiple bonds. To our knowledge, an outer-sphere electron transfer between $^*UO_2^{2+}$ and a hydrocarbon has not been reported previously. As expected, the rate constant $k_{6a}$ ($\sim 0.3 \times k_6 \sim 7 \times 10^8\ M^{-1}\ s^{-1}$) is somewhat smaller than those for the more easily oxidizable $ABTS^{2-}$ ($1.3 \times 10^9\ M^{-1}\ s^{-1}$) and 1,4-dimethoxybenzene ($2.3 \times 10^9\ M^{-1}\ s^{-1}$). A more quantitative comparison would be difficult to make, because all three reactions approach the diffusion-controlled limit. The data do suggest, however, that the proportion of electron transfer to exciplex formation would become even greater for the larger, more strongly reducing[26] polynuclear aromatics.

Naphthols are typical products of oxidation of naphthalene in aqueous solvents.[10,16,27,28] In the commonly accepted mechanism of eqs 7–9, the OH adduct is produced either directly by addition of $HO^\bullet$ to naphthalene or by hydrolysis of $C_{10}H_8^{\bullet +}$. The intermediates produced by one-electron oxidation ($C_{10}H_8^{\bullet +}$) and in Fenton-type reactions ($C_{10}H_8(OH^\bullet)$) are thus related by acid–base chemistry of eq 8. Further oxidation of $C_{10}H_8(OH)^\bullet$ then yields a mixture of naphthols.[29,30] In the $^*UO_2^{2+}$-initiated oxidation, the oxidant in eq 9 is either $O_2$ or $UO_2^{2+}$. No products were observed in the absence of $O_2$, which may mean that it plays a role in eq 9. Another possibility is that $O_2$ helps the reaction only indirectly by keeping the concentration of $UO_2^+$ low,[31] eq 3, thus slowing down the back electron transfer of eq 10. In this scenario, the oxidant in eq 9 is $UO_2^{2+}$.

$$C_{10}H_8 + HO^\bullet \rightarrow C_{10}H_8(OH)^\bullet \qquad (7)$$

$$C_{10}H_8^{\bullet +} + H_2O \rightleftarrows C_{10}H_8(OH)^\bullet + H^+ \qquad (8)$$

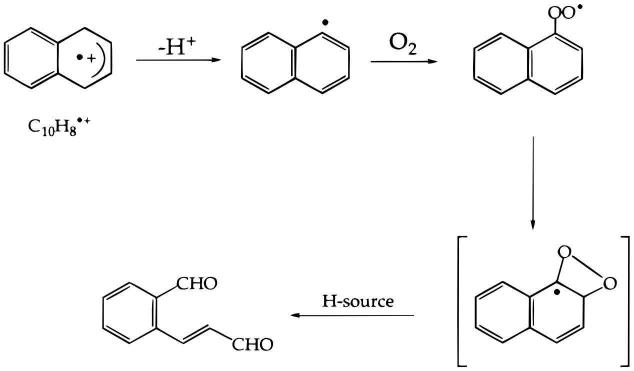
$$C_{10}H_8(OH)^\bullet \xrightarrow{Ox} C_{10}H_7(OH) \qquad (9)$$

$$UO_2^{+} + C_{10}H_8^{\bullet +} \rightarrow UO_2^{2+} + C_{10}H_8 \qquad (10)$$

The formation of 2-formylcinnamaldehyde as a major product shows that the ring cleavage is an important process. As shown in Scheme 1, this pathway probably starts with deprotonation of the strongly acidic[32] radical cation followed by the reaction with $O_2$ and formation of the peroxyl radicals. The radical center may couple with the neighboring ring carbon to produce a transient cyclic peroxide,[13,15] although there is no direct evidence for such intermediates.[28] Irrespective of whether the cyclic peroxide is involved or not, further reaction requires a hydrogen source (possibly solvent) or one-electron reduction (possibly by $UO_2^+$) followed by protonation to yield the dialdehyde. A similar mechanism has been proposed in some other oxidations of naphthalene.[28,33] The $UO_2^+$, produced in reaction 6a, reacts either with $O_2$ to regenerate $UO_2^{2+}$ (eq 3) or in a back electron transfer of eq 10.

**SCHEME 1**

$$^*UO_2^{2+} + C_{10}H_8 \rightarrow UO_2^{+} + C_{10}H_8^{\bullet +} \qquad (6a)$$



Despite the fact that ~30% of quenching in eq 6 takes place by electron transfer, the total quantum yield of all the products is less than 1%. The most apparent reason is the back electron transfer of eq 10, which restores the reactants in their ground states. On the basis of the known precedents, the rate constant $k_{10}$ is expected to be large and probably close to diffusion control. For example, ferrocene reduces pyrene radical cations ($C_{16}H_{10}^{\bullet +}$) with $k = 1.0 \times 10^{10}\ M^{-1}\ s^{-1}$,[34] and $Eu_{aq}^{2+}$ reacts with $C_{10}H_8^{\bullet +}$ with $k = 3.9 \times 10^9\ M^{-1}\ s^{-1}$.[35] The driving force[26] for reaction 10 is smaller than that for the reaction of $C_{10}H_8^{\bullet +}$ with $Eu^{2+}$, and the rate constant $k_{10}$ on the order of $10^8$–$10^9$ $M^{-1}\ s^{-1}$ appears reasonable.

Table 3 compares the products of oxidation of naphthalene in several systems. Naphthols are produced in most of the reactions, but the yield and distribution of all the products vary widely, presumably because of the high reactivity of intermediates involved. The Fenton reaction,[27] which involves $HO^\bullet$ radicals, and Udenfriend's system,[28] which is believed to utilize iron-oxo and -peroxo species, yield a large number of products. $\gamma$-Radiolysis in the presence of $Fe(CN)_6^{3-}$ produces naphthols in a scheme[6] that involves rapid oxidation of $C_{10}H_8(HO^\bullet)$ adducts by $Fe(CN)_6^{3-}$. A $PdCl_2$-based system[16] produces 2-formylcinnamaldehyde and 1-naphthol. The latter is oxidized further to 1,4-naphthoquinone. In the photochemical $UO_2^{2+}$/$O_2$ system described here, 2-formylcinnamaldehyde is the major product, Scheme 1. The yields are low, but the results are encouraging in that electron transfer is a significant pathway in the quenching process. We expect the yields of products, especially naphthols, to increase in the presence of sacrificial oxidants, which would rapidly remove $UO_2^+$ and thus prevent the back electron transfer of eq 10.

## Conclusions

The photochemical oxidation of naphthalene by $UO_2^{2+}/O_2$ yields 2-formylcinnamaldehyde as a major product. Minor amounts of 1- and 2-naphthols were also found. The reaction takes place by one-electron oxidation of naphthalene, followed by further reactions of $C_{10}H_8^{\bullet +}$. The quantum yield for the formation of $C_{10}H_8^{\bullet +}$ in the quenching process is 0.3, but the overall quantum yield for the formation of products is <0.01, suggesting that most of $C_{10}H_8^{\bullet +}$ is re-reduced to naphthalene by back electron transfer with $UO_2^+$.

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