Radical-Induced Oxidative Transformation of Quinoline

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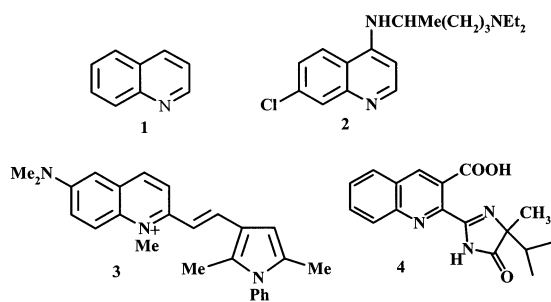
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The primary events of the oxidative transformation of quinoline, an environmental pollutant, by different radicals have been investigated using pulse radiolysis. The hydroxyl radical reacts by adding to both pyridine and benzene rings of quinoline to form the OH-adducts. On the other hand, $SO_4^{\bullet-}$ oxidizes the quinoline to its radical cation, which further undergoes hydrolysis to yield the OH-adducts. The possibility of the quinoline radical cation to undergo hydrolysis has been independently verified by generating the radical cation under laser induced photoionization conditions. The quinoline radical cation produced in acetonitrile shows high reactivity toward water. The rate for $^{\bullet}OH$ reaction is greater ($k = 1.0 \times 10^{10}$ M^{-1} s^{-1}) than that found for $SO_4^{\bullet-}$ reaction ($k = 3.5 \times 10^9$ M^{-1} s^{-1}). With oxidation potential at 1.87 V vs NHE, quinoline is nonreactive toward $^{\bullet}N_3$ radicals and less reactive toward $^{\bullet}O^-$ radicals ($k = 3.2 \times 10^8$ M^{-1} s^{-1}). The mechanistic understanding of the primary oxidation pathway of quinoline will aid in designing strategies for the abatement of pollutants containing nitrogen heterocycles.

Introduction

The contamination of surface and groundwater by N-heteroaromatics is a major environmental concern[1−3] since many of these compounds are considered toxic and/or mutagenic and carcinogenic.[4−9] Quinoline, **1**, is a simple heterocycle in which a benzene ring is fused to a pyridine ring. It occurs naturally and was originally isolated from coal tar. The quinoline derivatives are constituents of antiseptics, pharmaceuticals with a variety of medicinal purposes, chloroquine, **2**, being just one example of an antimalarial drug. Quinoline and its derivatives are also used as raw material and as solvent in the manufacture of dyes, paints, and herbicides.[10] Examples for commercially used quinolines include a mixed cyanine dye, the pyrvinium cation, **3**, and an herbicide, imazaquin, **4**. While the quinoline derivatives are constituents of antiseptics, herbicides, fungicides, insecticides, and pharmaceuticals, quinoline itself is a hepato-carcinogen in mice and rats.[4,9] It has been shown mutagene with the Ames assay[5,11] that quinoline (along with several derivatives), is indirect mutagene and "likely to be carcinogenic in humans".[12]

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Quinoline is, in concentrations of 10 mg/L, a major N-heterocyclic constituent of creosote (the distillate from coal tar), and a common contaminant of soil and groundwater in areas of wood preservation and fossil fuel facilities.[3,13,14] Consumption of wood preservatives in 1999 in the US totaled approximately 360 thousand metric tons with creosote being the primary wood preservative used in the United States.[15] According to an Environmental Protection Agency assessment[12] on the aquatic environmental fate of quinoline, this compound is biodegradable at a rate depending on different conditions, such as temperature and the microbial population. Complete biodegradation in water has been reported in as little as 4−5 days in natural water samples with the major metabolites expected to be 2-hydroxy-quinoline and 2,3-dihydroxyquinoline. Quinoline is also likely to be photolyzed with half-lives ranging from 21 days during the summer to 160 days during the winter. Hydrolysis, oxidation and volatilization are not considered to be significant for chemical transformation of quinoline under ambient conditions.

Advance oxidation processes (AOP) such as radiolysis, photo-Fenton oxidation, ozone/UV photolysis, photocatalysis, are radical-mediated processes that are effective for the removal of organic contaminants found in water.[16−21] However, recent reports have shown that in many instances, the end products can be more toxic than the parent compound or that the toxicity is not diminished after the treatment.[22,23] For example, Thomsen and co-workers used nitrifying bacteria to measure the inhibition from wet oxidative-treated quinoline samples under different reaction conditions (using air or pure O_2 in aqueous phase at elevated temperature and pressure).[20] In three out of four experiments, the products formed by wet oxidation were more toxic than quinoline itself and the samples using short oxidation times were less toxic than those using long times. There is still much debate about the mechanism and the main oxidative species involved in some of these processes.[24−26] The hydroxyl radical is thought to be the main reactive species in AOPs, but other possibilities include the oxidation by the hole produced by photoirradiation of TiO_2 or reaction with activated oxygen

species.[19] Cermenati and co-workers found different product distribution for the photo-Fenton degradation of quinoline (monohydroxylated quinolines dominant) and the TiO$_2$ photocatalysis (2-aminobenzaldehyde as the major product), suggesting the complexity in the oxidative degradation mechanism.[19]

These issues demand a better understanding of free-radical-induced reactions of quinoline and its derivatives so that effective strategies for environmental remediation could be developed. Compared to other AOPs, radiolysis has the advantage of generating oxidizing radicals selectively and of providing mechanistic and kinetic information of the primary processes responsible for chemical transformations. Quinoline also serves as a model compound to establish the mechanism of oxidative transformation of a larger class of N-heterocyclic compounds (e.g., imazaquin) that are commonly used as herbicides or fungicides. Here, we report the reaction of quinoline with different oxidative radicals—hydroxyl radicals/oxide radical anions, azide radicals, and sulfate radicals—generated by pulse radiolysis.

Experimental Section

Materials and Methods. Quinoline was purchased from Lancaster (98% purity) and it was distilled before using. All other chemicals were purchased from Aldrich, Fluka, or Sigma and were used without further purification. The pHs of the phosphate buffers and other solutions were adjusted with HClO$_4$ (70%) and NaOH. The oxidation potential of quinoline in acetonitrile was determined using cyclic voltammetry method. A BAS-100 Electrochemical Analyzer was used for these measurements.

Pulse Radiolysis. Pulse radiolysis experiments were carried out using the Notre Dame 8-MeV Titan Beta model TBS-8/16-1S linear accelerator with a pulse length of 2.5–10 ns. A typical experiment consisted of a series of 6–10 replicate shots, which were averaged for a single measurement. Dosimetry was carried out with N$_2$O-saturated solutions of 10 mM KSCN assuming $\epsilon_{472\,nm}((SCN)_2^-) = 7580$ M^{-1} cm^{-1} and $G = 6.13$. The G-value is defined as the number of species formed/100 eV, and $G = 1$ corresponds to 0.1036 μM J^{-1} in SI units. Experiments were performed using continuous solution flow mode. Analysis of optical absorption versus time was done using ORIGIN (Microcal) software.

When dilute aqueous solutions are irradiated with high-energy radiation, the energy is absorbed mainly by the solvent water, giving rise to the production of •OH radicals, hydrated electrons and •H atoms as reactive free radicals and to some to some H$_2$O$_2$, H$_2$, and H$_3$O$^+$:

$$H_2O \leadsto ^\bullet OH(2.7) + e^-_{aq}(2.7) + {}^\bullet H(0.55) + H_2(0.45) +$$
$$H_2O_2(0.71) + H^+(2.7) \quad (1)$$
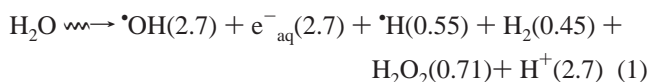
where the values in parentheses indicate the G values. The concentration of •OH was in the 3–5 μM range.

The •OH radical is a very strong oxidant ($E° = 1.9$ V vs NHE).[27] The reaction of •OH radicals with quinoline was carried out in N$_2$O-saturated solutions. Solvated electrons e$^-_{aq}$ were converted to •OH radicals (reaction 2).

$$e^-_{aq} + N_2O \rightarrow {}^\bullet OH + OH^- + N_2 \quad (2)$$

and a system consisting of 90% •OH radicals and 10% H atoms was achieved under these conditions with $G(^\bullet OH) = 5.4$ and $G(^\bullet H) = 0.55$.[28]

Reaction with •O$^-$ was studied in N$_2$O-saturated basic solutions (pH > 13). At this pH most of the •OH radicals are converted into •O$^-$ as pK_a(•OH) = 11.9; the rate constants of the forward and reverse reactions are 1.2×10^{10} M^{-1} s^{-1} and 1×10^8 s^{-1}, respectively.[29] This species can behave as an oxidant with $E^0 = 1.77$ V vs NHE.[30]

The azide radical •N$_3$ was formed by pulse radiolysis of sodium azide solutions (0.01 M) using phosphate buffer (50 mM) at two pH values (pH ∼ 7 and pH ∼ 4) and N$_2$O-saturated:

$$^\bullet OH + N_3^- \rightarrow OH^- + {}^\bullet N_3 \quad (3)$$
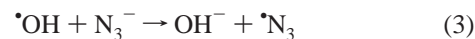
Azide radical is a mild oxidant ($E^0 = 1.33$ V vs NHE),[31] more selective than hydroxyl radical and participates in one-electron oxidation via primary formation of radical cations. The azide radical has a very sharp absorption band at ∼274 nm and very little absorption above 300 nm. The sulfate radical SO$_4^{\bullet-}$ is a very strong oxidant ($E^0 = 2.43$ V vs NHE) and reacts with organic substrates by electron transfer.[32,33] It was prepared by the reaction of persulfate dianion (5 mM) with solvated electron in N$_2$-saturated solutions:

$$e_{aq}^- + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{\bullet-} \quad (4)$$
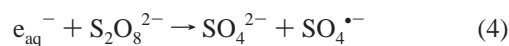
The hydroxyl radical was scavenged by adding t-BuOH (0.05 M), and the yield of SO$_4^{\bullet-}$ was $G(SO_4^{\bullet-}) = 2.7$.

Laser Flash Photolysis. The quinoline solutions in acetonitrile were prepared using a fresh bottle of acetonitrile HPLC grade. All solutions were prepared so that the optical density at 308 nm was ∼1.5. All solutions were irradiated using an Applied Physics Excimer laser system (308 nm, output 10−20 mJ/pulse, pulse width ∼10 ns). A typical experiment consisted of a series of five replicate shots, which were averaged for single measurement.

Computational Methods. Theoretical results were obtained using the Gaussian 98 at the B3LYP/6-31G* level.[34] This level of the theory has been shown to adequately predict reaction energies and transition-state energies for radical pathways.[35,36] All single-point energies were corrected for zero-point energies from harmonic frequency analysis of the optimized structures. Solvent effects evaluated using the CPCM model for water with $\epsilon = 78.39$ and the energies from these calculations were also corrected by adding zero-point energies corrections from the gas-phase frequency calculations.

Results and Discussion

Reaction with •OH Radicals. The hydroxyl radical is highly reactive toward aromatic and heterocyclic compounds and it usually adds to the aromatic ring to form the hydroxycyclohexadienyl radical with a characteristic absorption in the 310−350 nm range.[37−39] The time-resolved transient absorption spectra of quinoline (0.85 mM, pH ∼ 6) recorded following pulse radiolysis of a N$_2$O-saturated aqueous solution are shown in Figure 1. Both the uncorrected (the difference) and the spectra corrected for the quinoline ground-state absorption show a characteristic peak at 320 nm, which we attribute to the OH-adduct of quinoline by analogy with previous studies done on pyridine and benzene.[37,40] On the basis of the dosimetry and maximum absorbance values, we obtain an extinction coefficient of 6400 M^{-1} cm^{-1} at 320 nm for the OH-adduct of quinoline.

The absorption−time profile at 320 nm (Figure 2A) allows the determination of the rate at which the primary OH-adduct is formed during the radiolysis of a quinoline solution (0.8 mM,
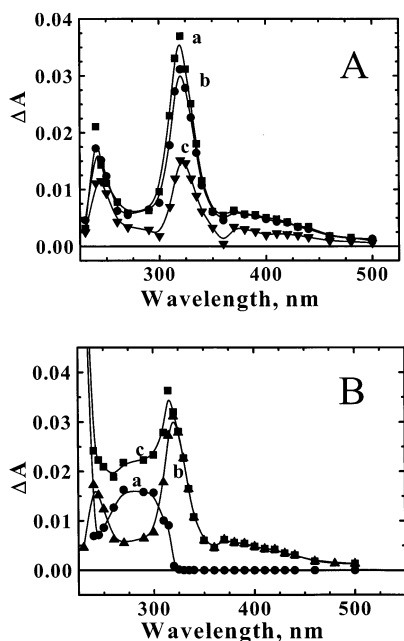
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Figure 1. (A) Time-resolved absorption spectrum of the transient(s) formed after the pulse radiolysis of an aqueous N_2O-saturated solution of quinoline (0.85 mM) at pH $\sim$ 6, at (a) 1, (b) 10, and (c) 160 μs. (B) (a) Absorption spectrum of ground-state quinoline, (b) difference absorption spectrum of the transient at 10 μs and (c) transient absorption spectrum corrected for the ground-state absorption of quinoline
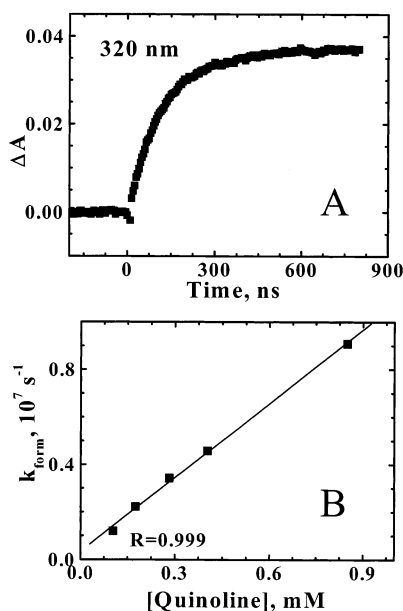

Figure 2. (A) The buildup of the intermediate(s) at 320 nm in a pulse-irradiated solution of quinoline (0.85 mM, pH $\sim$ 6, N_2O-saturated). (B) Plot of the first-order transient formation rate constant at 320 nm vs different quinoline concentrations (N_2O purged solutions).

N_2O-saturated, pH $\sim$ 6). The bimolecular rate constant for the reaction of quinoline with $^\bullet$OH radicals, determined from the linear dependence of the first-order growth rate constant on the quinoline concentration (Figure 2B), is 1.0 ($\pm$0.05) $\times$ 10^{10} M^{-1} s^{-1}. This shows that the $^\bullet$OH radical attack on the quinoline occurs with a diffusion controlled rate. These results are in agreement with previous studies[37,41] which showed that $^\bullet$OH radicals are highly reactive toward arenes and react with nearly diffusion controlled rates ($k >$ 10^9 M^{-1} s^{-1}).

Although the strong absorption above 300 nm confirms the formation of hydroxycyclohexadienyl-type radicals, it does not
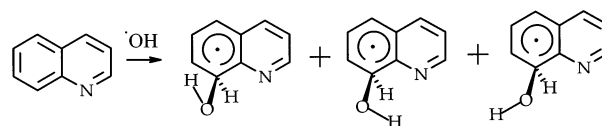
SCHEME 1
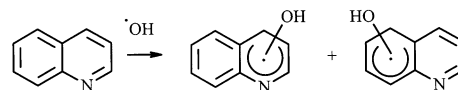
SCHEME 2

TABLE 1: The Reaction Energies for the Formation of the Isomeric OH-Adducts in Gas Phase and in Water

isomers	ΔE_{ave} (gas phase) [kcal/mol]	ΔE_{ave} (water) [kcal/mol]
Q$-$2OH[a]	-18.9	-19.5
Q$-$3OH	-16.8	-18.9
Q$-$4OH	-19.9	-21.2
Q$-$5OH	-21.5	-23.5
Q$-$6OH	-16.8	-18.6
Q$-$7OH	-16.3	-17.8
Q$-$8OH	-21.8	-23.9

[a] Only two rotamers were averaged for this isomer.

indicate if there is specificity of $^\bullet$OH addition. Possibility exists for $^\bullet$OH addition at different positions of the aromatic rings (Scheme 1).

Whereas $^\bullet$OH is a very reactive species, it has been shown in the past to be very selective in both the addition and H abstraction reactions with six-membered heterocyclic compounds.[42,43] We employed computational analysis to calculate the energies of the reactants and of various hydroxylated radical products (OH-adducts) in the gas phase and in a cavity model representing the aqueous solution. The attack of $^\bullet$OH on quinoline could produce three rotamers for each position, as is illustrated in Scheme 2.

Table 1 summarizes the computed reaction energies, i.e., the differences between the energies of the product and reactant, averaged for each isomer in gas phase and in water. The computations suggest that the addition reactions of $^\bullet$OH to both rings are energetically favorable. The reaction energy values range from -18.6 to -23.9 kcal/mol for the formation of the OH-adducts in water and from -16.3 to -21.8 kcal/mol for the formation of the OH-adducts in gas phase. Since these values are spread across an interval of only $\sim$5 kcal/mol, there seems to be no overwhelming energetic preference for any isomer adduct as compared to the others. On the basis of these results, it is likely that the observed absorption spectra in Figure 1 represent the weighted average of the isomeric OH-adducts formed from the addition of $^\bullet$OH to both rings of quinoline.

Reaction with $^\bullet$O$^-$. Although the reactions of $^\bullet$O$^-$ have not been extensively studied, there has been an increased interest in its chemistry. Its contribution can be significant in the radiolytic chemistry of highly alkaline solutions. In strongly alkaline solutions, $^\bullet$OH radical is rapidly converted to its conjugated base $^\bullet$O$^-$.[44] The time-resolved transient absorption spectra of quinoline (0.61 mM, pH $\sim$ 13.2) recorded following pulse radiolysis of a N_2O-saturated aqueous solution are shown in Figure 3.

The difference absorption spectra of the transient(s) recorded following the attack of $^\bullet$O$^-$ on the quinoline are very similar to the transient(s) formed by the attack of $^\bullet$OH. This similarity between the spectra was observed in other studies as well.[45-47] For example, Dey and co-workers[45] suggested that in the
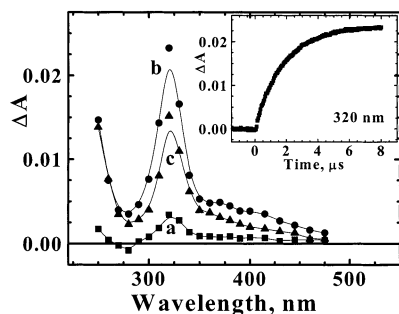
Figure 3. Time-resolved absorption spectrum of the transient(s) formed after the pulse radiolysis of an aqueous N$_2$O-saturated solution of quinoline (0.61 mM) at pH $\sim$ 13.2 at (a) 0.75, (b) 10, and (c) 160 μs. The inset shows the build-up trace of the intermediate(s) at 320 nm.

reaction of $^\bullet$O$^-$ with 2-aminopyridine, an OH-adduct is ultimately formed in the presence of water. However, no explanation on the reaction pathway was given in their study. Simic and co-workers[48] reported that $^\bullet$O$^-$ addition to benzoate at pH 14 produces a transient species with identical absorption spectrum to that of the OH-adduct and suggested that the pK_a of the hydroxyl group on the resultant hydroxycyclohexadienylcarboxylate radical is greater than 14.

Since the equilibrium between $^\bullet$OH and $^\bullet$O$^-$ (equilibrium 5)

$$^\bullet\text{OH} \overset{K_a}{\rightleftharpoons} {}^\bullet\text{O}^- + \text{H}^+ \tag{5}$$

is achieved well before the reaction with the solute, some studies[49] assume that the reactivity at high pHs is due mainly to the oxide radical anion, with a negligible contribution from the hydroxyl radical. However, since the reactivity of hydroxyl radical is significantly higher than that of $^\bullet$O$^-$, we can expect contribution from both these oxidative species at high alkaline pH. Thus, it is necessary to evaluate the individual contributions from these radicals at high pH.

The bimolecular rate constant k_{exp} was determined by measuring the transient absorption growth constant (320 nm) at different quinoline concentrations. From the slope of the linear plot of growth rate constant versus quinoline concentration we obtain k_{exp} as 8 $\times$ 10^8 M^{-1} s^{-1}. Since both $^\bullet$OH and $^\bullet$O$^-$ collectively contribute to this value, one can express k_{exp} in the form of eq 6.

$$k_{exp} = k_{OH}[{}^\bullet\text{OH}]/([{}^\bullet\text{OH}] + [{}^\bullet\text{O}^-]) + k_{O^-}[{}^\bullet\text{O}^-]]/ \\ ([{}^\bullet\text{OH}] + [{}^\bullet\text{O}^-]) \tag{6}$$

Expressing the [$^\bullet$OH] and [$^\bullet$O$^-$] concentrations as a function of the dissociation constant K_a of hydroxyl radical, eq 6 can be summarized as follows,[44]

$$k_{exp} = \frac{k_{OH} + k_{O^-}(K_a/[\text{H}^+])}{1 + K_a/[\text{H}^+]} \tag{7}$$

where K_a = 1.26 $\times$ 10^{-12} M, k_{exp} = 8 $\times$ 10^8 M^{-1} s^{-1}, and $k_{^\bullet OH}$ = 1 $\times$ 10^{10} M^{-1} s^{-1}. By substituting the values of K_a, $k_{^\bullet OH}$, and k_{exp} in eq 7, we obtain the bimolecular rate constant for the reaction of quinoline with $^\bullet$O$^-$ as $k_{^\bullet O^-}$ = 3.2 $\times$ 10^8 M^{-1} s^{-1}. Although the rate constant of $^\bullet$O$^-$ reaction ($k_{^\bullet O^-}$) is nearly 30 times lower than that for OH radical reaction, high concentration of $^\bullet$O$^-$ at pH 13.2 drives the $^\bullet$O$^-$ reaction with $\sim$40% probability. (Note that the ratio between the concentration of the two species was calculated to be [$^\bullet$O$^-$]/[$^\bullet$OH] = 20/1 at pH 13.2, using the Henderson$-$Hasselbalch equation.[50])

SCHEME 3
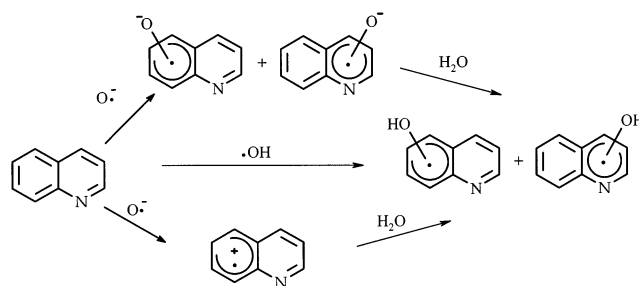
The lower rate constant for the oxide radical ion as observed in this study is an indication of a different type of reactivity with quinoline than that of the OH radical. $^\bullet$O$^-$ is a nucleophilic species with a preference for H abstraction and has a low tendency to undergo addition reactions (2$-$3 orders of magnitude less than $^\bullet$OH).[44,46,51,52] Since quinoline has no alkyl side chains and the formation of an aryl radical is energetically unfavorable, hydrogen abstraction is not a feasible pathway in this reaction. The addition pathway has been suggested previously for reactions of $^\bullet$O$^-$ with aromatics.[53] Neta and Schuler[54] reported the rate constant for the addition reaction of $^\bullet$O$^-$ with p-phenoxybenzoic acid to be 1.6 $\times$ 10^8 M^{-1} s^{-1} or a partial rate constant of 8 $\times$ 10^7 M^{-1} s^{-1} per aromatic ring. Simic and co-workers[48] reported the rate constants for the reaction of $^\bullet$O$^-$ with 1- and 2-naphthoic acids in the range of 1.2$-$4.8 ($\pm$30%) $\times$ 10^8 M^{-1} s^{-1}. For quinoline, such an addition reaction would involve a nucleophilic attack predominantly on the heteroaromatic ring, which is deactivated by the electronegativity of the nitrogen atom. Should such an addition reaction occur, we would expect the [quinoline-$^\bullet$O$^-$]-adduct to protonate immediately via the reaction with the solvent and the observed spectrum should be that of on OH-adduct.

Since $^\bullet$O$^-$ is also a strong oxidant,[30,55] possibility exists for the direct electron transfer between $^\bullet$O$^-$ and quinoline. The oxidation potential of quinoline in acetonitrile was determined to be 1.63 V vs SCE (or $E°$ =1.87 V vs NHE). The small difference (0.1 V) between the two redox couples shows that the electron transfer between the $^\bullet$O$^-$ and quinoline is still possible. The lower rate constant determined from our analysis (3.2 $\times$ 10^8 M^{-1} s^{-1}) is in the range of electron-transfer rate that one would expect on the basis of electron-transfer theory.[56-59] Single-electron-transfer processes with $^\bullet$O$^-$ have been described by several researchers. For example, Neta and Schuler suggested that $^\bullet$O$^-$ reacts with the phenoxide anion by electron transfer with the formation of the phenoxyl radical (k = 6.5 $\times$ 10^8 M^{-1} s^{-1}).[51,54] Ioele and co-workers[60] suggested that $^\bullet$O$^-$ reacts with uracil, cytosine, adenine, and guanine by one-electron oxidations with rate constants in the range of (2.8$-$7.8) $\times$ 10^8 M^{-1} s^{-1}. If such an electron-transfer process should proceed with quinoline, the formation of a radical cation in the radiolysis at alkaline pH is expected. However, direct observation of radical cation under these experimental conditions poses additional problems. In the absence of strong acidic media as well as in the absence of any stabilizing electron donating groups, the radical cations are very short lived and are likely to undergo hydrolysis to form OH-adducts.[40,61,62] Thus, both addition of $^\bullet$O$^-$ and single-electron transfer are probable pathways of quinoline oxidation at pH 13.2. Since the observable transient species is the OH-adduct in both these types of mechanisms (Scheme 3), it is not possible to distinguish between these two mechanisms. Moreover, the similarity of the reported rate constants of both the addition and single-electron-transfer
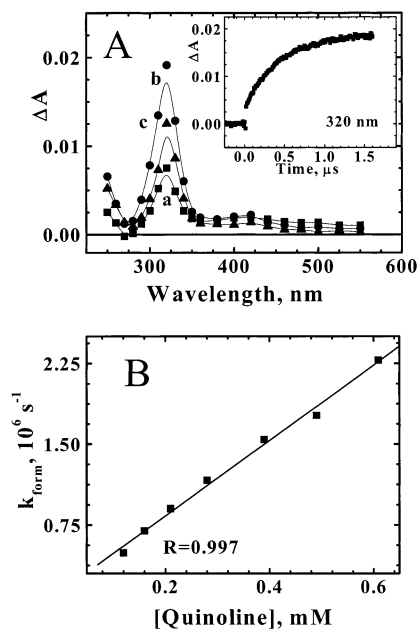
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Figure 4. (A) Time-resolved absorption spectra following oxidation of quinoline with $SO_4^{\bullet-}$ at pH $\sim$ 7 (N_2-purged 0.6 mM quinoline solutions containing 0.05 M t-BuOH, 5 mM $K_2S_2O_8$, 50mM phosphate buffer; reaction 4) (a) 0.75, (b) 5.75, and (c) 80 μs after the pulse (Inset shows the formation of the transient(s) at 320 nm). (B) Plot of the first-order transient formation rate constant at 320 nm vs different quinoline concentrations in the reaction of quinoline with sulfate radical.

reactions poses further challenge toward estimating the contribution of individual processes.

Reaction with Sulfate and Azide Radicals. To obtain further insight into a possible electron-transfer mechanism, we investigated reactions of quinoline with other oxidizing radicals. As described in the Experimental Section, it is possible to generate secondary oxidizing radicals such as $N_3^{\bullet}$ and $SO_4^{\bullet-}$ by using appropriate primary radical scavengers (see reactions 5 and 6) in a pulse radiolysis experiment. It has been shown that $SO_4^{\bullet-}$ reacts with aromatic compounds and DNA-nucleobases via direct electron transfer to form a radical cation.[62-64]

The reaction of quinoline with these oxidizing radicals provides us a means to compare the oxidation process with that of $^{\bullet}$OH radicals. The azide radical is a selective oxidant which reacts exclusively by single-electron-transfer with the primary formation of radical cations.[65,66] The transient absorption spectrum recorded following the reaction with $N_3^{\bullet}$ radicals does not show any significant absorption in the 300–350 nm region. The weak absorption change (ΔA < 0.001 at 320 nm) observed in the radiolysis experiment (not shown) was indicative of low reactivity of quinoline toward $N_3^{\bullet}$ radicals. This low reactivity arises from the lower oxidation potential of $N_3^{\bullet}$ radicals ($E^0 =$ 1.33 V vs NHE)[31] as compared to the oxidation potential of quinoline (1.87 V vs NHE).

On the other hand, the sulfate radical is a stronger oxidant ($E^{\circ} = 2.43$ vs NHE)[32,33] and capable of undergoing single-electron transfer with quinoline. The transient absorption spectra obtained following the reaction of $SO_4^{\bullet-}$ with quinoline are shown in Figure 4A. The difference absorption spectrum, uncorrected for the ground-state absorption of quinoline, shows a strong absorption band at 320–330 nm and a very weak and broad absorption in the region 370–450 nm. It is important to note the point that the overall spectral features of the electron-transfer product are similar to that of OH-adduct.

The pseudo-first-order rate constant for the formation of the intermediate k_{form} was monitored at the absorption maximum 320 nm using different quinoline concentrations. The bimolecular rate constant for the reaction of quinoline with sulfate radical was found to be 3.5×10^9 $M^{-1}s^{-1}$. The dependence of the pseudo-first-order rate constant for the formation of the intermediate on the quinoline concentration is shown in Figure 4B. This follows the trend that the rate constants for $SO_4^{\bullet-}$ reaction are generally lower than those found for the $^{\bullet}$OH reaction.[39]

While discussing the reaction of $^{\bullet}O^-$ with quinoline, we pointed out the possibility that the radical cations, in the absence of strong acidic media as well as in the absence of any stabilizing electron-donating groups, are very short-lived and undergo fast hydrolysis to form OH-adducts.[40,61,62] If this argument holds true, the stable form (microsecond scale) of the transient following the oxidation of quinoline with oxidizing radicals would be the OH-adduct form. Indeed, the similarities of the spectral characteristics of those obtained in the reaction with sulfate and hydroxyl radical (Figures 1A and 4A) support the hydrolysis of quinoline cation radical in aqueous solutions (reaction 8).

$$Q + SO_4^{\bullet-} \rightarrow Q^{\bullet+} + SO_4^{2-}$$
$$\downarrow H_2O$$
$$[Q\text{-}OH]^{\bullet} \qquad (8)$$
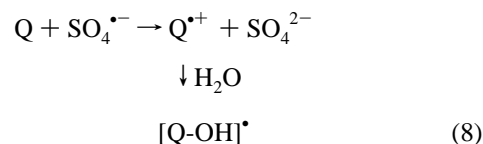
Photoionization of Quinoline. To assess the stability of quinoline radical cation, we employed pulsed UV laser to induce photoionization. This alternate way to oxidize quinoline involves subjecting the acetonitrile solution of quinoline to high energy laser excitation (308 nm, 20 mJ/pulse).

$$Q + h\nu \rightarrow {}^1Q^* \rightarrow {}^3Q^* \qquad (9a)$$
$$Q + nh\nu \rightarrow Q^{\bullet+} + e_{aq}^- \qquad (9b)$$
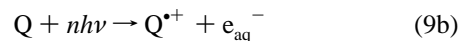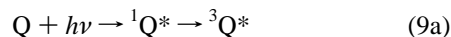
Both triplet excited state and the radical cation formed during the laser pulse excitation were characterized using nanosecond laser flash photolysis apparatus. The radical cation of the quinoline formed following laser excitation is quite stable on the monitoring time scale, since typical unimolecular decay reactions such as deprotonation and carbon–carbon bond fragmentation are not favored in this case. The transient absorption spectra recorded 1 and 40 μs after laser pulse excitation of quinoline in N_2-saturated acetonitrile are shown in Figure 5 A.

The absorption maximum at 400 nm in the spectrum recorded at early times corresponds to the triplet excited state. The spectral characteristics of $^3Q^*$ have been independently confirmed from a triplet–triplet energy-transfer process.[67] This triplet quinoline decays with a lifetime of 1.4 μs while the 330 nm absorption peak remains undisturbed during this time period (Figure 5A). In aerated solutions, only the absorption peak at 330 nm is observed, as the triplet excited state (absorption at 400 nm) is quenched by dissolved oxygen (Figure 5B). On the basis of these observations we assign the absorption peak at 330 nm to the quinoline radical cation.

To study the reactivity of quinoline cation radical toward water, we recorded the transient spectrum in the presence of small amount ($\sim$1%) of water, which was added to the acetonitrile solution prior to laser excitation. In the presence of water, the cation radical was short-lived as indicated by the faster decay of the absorption at 330 nm, (Figure 6A). These
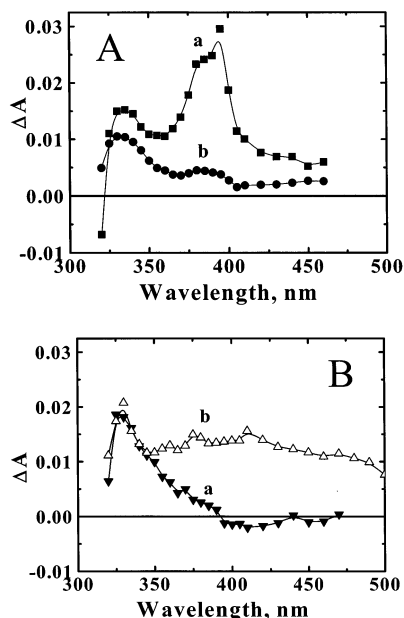
Figure 5. Time-resolved absorption spectra of the transients formed after the laser pulse (308 nm) excitation of a solution containing 0.1 mM quinoline in acetonitrile under different experimental conditions: (A) Deaerated solution: spectra were recorded at (a) 1 μs and (b) 40 μs after laser pulse excitation. (B) Aerated solution: spectra were recorded in the (a) absence of water and (b) presence of ~1% of water, 2.7 μs after laser pulse excitation.
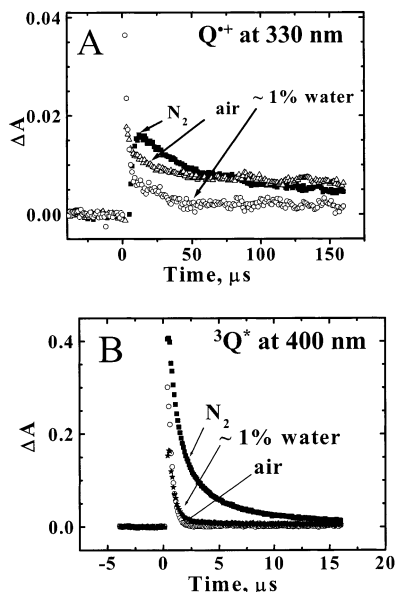

Figure 6. Absorption-time profiles of the transients at (A) 330 nm and (B) 400 nm, recorded after the laser pulse (308 nm) excitation of a solution of 0.1 mM quinoline in acetonitrile under different conditions: in deaerated solutions and in aerated solutions, in the absence and in the presence of 1% water.

observations further support our argument that the quinoline radical cation is susceptible to rapid hydrolysis.

Sehested and co-workers[68] have investigated the stability of radical cations and the OH-adducts of methylated benzenes in acidic solutions. The radical cation, if formed, should have an extremely short lifetime in the absence of electron donating substituents. For example, the lifetime of the benzene radical cation was estimated to be ~20 ns in the photoionization studies of benzene. Mohan et al.[40] obtained the spectrum of the benzene radical cation working in strongly acidic conditions, i.e., 7.8 M HClO$_4$ and compared it to the spectrum of OH-adduct. While

SCHEME 4
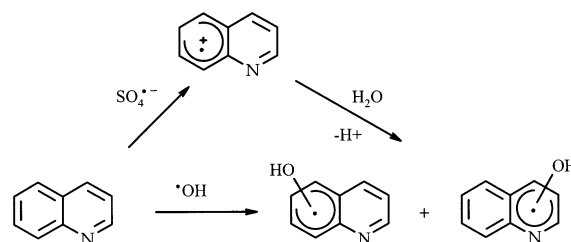
the strong absorption band at 310 nm was characteristic for both species (viz., cation radical and OH-adduct of quinoline), the decay kinetics and molar absorptivity at longer wavelengths were different for these two transients. The strong reactivity of cation radicals toward water is the major reason for observing OH-adduct in the direct electron-transfer reactions involving SO$_4^{\bullet-}$ radicals (Scheme 4).

The pulse radiolysis experiments presented here provide an insight into the oxidative transformation of quinoline. These results also aid in establishing the oxidative pathways in different advanced oxidation processes. For example, the present study can elaborate on the electron-transfer mechanism proposed in TiO$_2$ photocatalysis of quinoline.[19] To explain the predominant formation of 2-aminobenzaldehyde, Cermenati at al. invoked the oxidation mechanism involving quinoline radical cation. As demonstrated in the present study, the cation radical formed at the TiO$_2$ interface will undergo rapid hydrolysis and thus the fate of the final transformation will depend on the decay pathway of the hydroxyl adduct.

Conclusions

The free-radical-induced reactions of organic pollutants are of immense interest as they provide strategies to abate the chemical pollution for minimizing their impact on the environment. Quinoline is considered to be a major pollutant in areas of creosote contamination and is part of the structures of herbicides and dyes. Quinoline is very reactive toward strong oxidizing species such as hydroxyl radicals and sulfate radicals. OH-adducts are the primary intermediates formed during the oxidation process and survive on the microsecond−millisecond time scale. The photoionization experiments conducted in acetonitrile medium confirm the ability of the radical cation to undergo fast hydrolysis. Thus, even if the quinoline participates in a single-electron-transfer reaction, the cation radical is quickly hydrolyzed to form OH-adduct in the aqueous medium (Schemes 3 and 4).

The final products in the reaction of quinoline with hydroxyl radicals are mostly monohydroxylated quinolines. Preliminary experiments involving product analysis have confirmed the attack of hydroxyl radicals on both rings of quinoline and experiments are underway to elucidate the selectivity of the attack and to establish the ultimate fate of the OH-adducts.

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