

Direct Oxygenation of Benzene to Phenol Using Quinolinium Ions as Homogeneous Photocatalysts**

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Phenol, which is currently produced from benzene by a three-step cumene process, is one of the most important chemicals in industry. Because the cumene process affords very low yields (around 5%) with byproducts such as acetone and α -methylstyrene under severe conditions,^[1–4] extensive efforts have been made to develop a one-step oxygenation process of benzene to phenol using heterogeneous inorganic catalysts.^[5–15] However, only low yields of phenol have so far been obtained under high-temperature conditions. Thus, direct oxygenation of benzene to phenol with oxygen in homogeneous media remains a formidable challenge.

We report herein that the 3-cyano-1-methylquinolinium ion (QuCN^+) acts as an efficient photocatalyst for selective oxygenation of benzene to phenol using oxygen and water under homogeneous and ambient conditions. The QuCN^+ ion has a strong oxidizing ability at the singlet excited state (E_{red} vs. SCE = 2.72 V),^[16,17] which is capable of oxidizing benzene (E_{ox} vs. SCE = 2.32 V)^[18,19] through photoinduced electron transfer. Such a photocatalytic transformation through photoinduced electron transfer has recently gained increased attention, because it provides a valuable means for metal-free and environmentally benign synthesis.^[20]

Photocatalytic oxygenation of benzene with oxygen occurs under photoirradiation of $\text{QuCN}^+\text{ClO}_4^-$ (λ_{max} = 330 nm, 5.0 mM) in an oxygen-saturated acetonitrile (MeCN) solution containing benzene (30 mM) and H_2O (3.0 M) by a xenon lamp (500 W, λ = 290–600 nm), to which a color-cut glass filter was attached. Phenol and hydrogen peroxide were selectively produced [Eq. (1)] after photoirradiation, which were identified by ^1H NMR spectroscopy and iodometry (see Figure S1 in the Supporting Information). The selectivity of formation of phenol was 98% with a quantum yield of 16% after 1 h of irradiation and 51% after

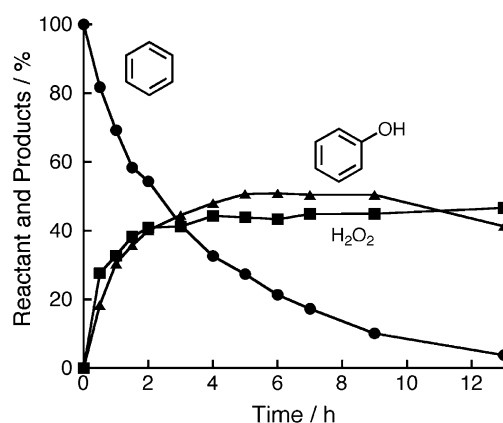
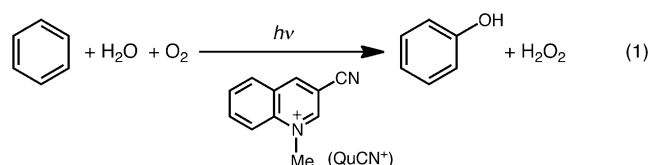


Figure 1. Irradiation time profile of benzene (circles), phenol (triangles), and H_2O_2 (squares) for the photocatalytic oxygenation of benzene by oxygen and water with QuCN^+ in oxygen-saturated MeCN (1.0 mL) at 298 K: [benzene] = 30 mM, [QuCN^+] = 2.0 mM, and [H_2O] = 2.0 M.

5 h of irradiation (Figure 1). The photocatalytic turnover number (TON) was 7.5. This is the first example of photocatalytic oxygenation of benzene to phenol in a homogeneous system. A preparative gram-scale photocatalytic reaction with benzene (2.3 g, 29 mmol) and QuCN^+ (210 mg, 0.8 mmol) in MeCN (200 mL) for 48 h was also examined to afford phenol (1.1 g, 12 mmol) in 41% yield.

Phenol was also detected by GC–MS. A mass peak was observed at m/z = 94 in a crude solution after photoirradiation of a MeCN solution containing benzene, QuCN^+ , and H_2^{16}O (see Figure S2 in the Supporting Information). When H_2^{16}O was replaced by H_2^{18}O to clarify the oxygen source, the mass number increased to m/z = 96. Thus, the origin of the phenol oxygen was confirmed to be water.

When QuCN^+ was replaced by 1-methylquinolinium (QuH^+) and 1,2-dimethylquinolinium (QuMe^+), the oxygenation of benzene to phenol by oxygen and water yielded 5.7 and 18% of phenol, respectively (Table 1). In the case of chlorobenzene and QuCN^+ , selective formation of phenol was also observed to afford *p*- and *o*-chlorophenol in 27 and 3% yield at 31% conversion, respectively.

The efficient and selective photocatalytic oxygenation of benzene to phenol is made possible by the difference in the

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Table 1: Rate constants of photoinduced electron transfer (k_{et}), conversions of benzene, selectivities, and quantum yields of phenol after photocatalytic oxygenation of benzene by oxygen and water in the presence of quinolinium ions.^[a]

Catalyst	Substrate	k_{et} [$\text{M}^{-1} \text{s}^{-1}$]	Irradiation time [h]	Conversion [%]	Yield [%]	Selectivity [%]	Quantum yield ^[b] [%]
QuCN ⁺	C ₆ H ₆	1.1×10^{10}	1.0	31	30	98	16
QuCN ⁺	C ₆ H ₆		5.0	73	51	70	
QuH ⁺	C ₆ H ₆	5.8×10^9	5.0	88	5.7	6.5	26
QuMe ⁺	C ₆ H ₆	6.7×10^8	5.0	21	18	87	3.0
QuCN ⁺	C ₆ H ₅ Cl	1.3×10^{10}	0.5	31	27 (p-), 3 (o-)	88 (p-), 11 (o-)	3.4
QuCN ⁺	C ₆ H ₅ OH	1.1×10^{10}	1.0	7	—		3.7 ^[c]

[a] Conditions for photocatalytic reactions: [QuCN⁺] = 2.0 mM, [substrate] = 30 mM, [H₂O] = 3.0 M. [b] Determined from the initial rate for the yield of the corresponding phenol derivative(s). [c] Based on the consumption of phenol.

reactivity of benzene and phenol. When benzene was replaced by phenol as a starting material, the reactivity significantly decreased relative to that obtained by benzene. Prolonged photoirradiation of phenol with QuCN⁺ afforded only small amounts of further oxygenated products such as quinones and diphenol derivatives.^[21]

The mechanism of oxygenation of benzene was examined by fluorescence quenching and transient absorption experiments. The fluorescence lifetime (τ) of QuCN⁺ ($\lambda_{\text{em}} = 430 \text{ nm}$) in the absence and presence of benzene or phenol were determined by femtosecond laser flash photolysis. A transient absorption spectrum of QuCN⁺ was observed in deaerated MeCN after femtosecond laser excitation at 355 nm. The spectrum is assigned to the singlet–singlet absorption because of the singlet excited state of ¹QuCN⁺* detectable at 450 nm (Figure 2a). Photoinduced electron transfer from benzene or phenol to ¹QuCN⁺* is energetically feasible, because the one-electron reduction potential of ¹QuCN⁺* (E_{red} vs. SCE = 2.72 V)^[17] is higher than the one-electron oxidation potential of benzene (E_{ox} vs. SCE = 2.32 V).^[18,19] In the case of QuH⁺ and QuMe⁺ photocatalysts the rates of photoinduced electron transfer were slower than that of QuCN⁺, because the E_{red} values of ¹QuH⁺* (2.46 V) and ¹QuMe⁺* (2.54 V) are lower than that of ¹QuCN⁺* (2.72 eV).^[17,22] The lower yields of phenol with QuH⁺ and QuMe⁺ photocatalysts (Table 1) are ascribed to the lower oxidizing ability of ¹QuH⁺* and QuMe⁺* as compared with that of ¹QuCN⁺*.

The addition of benzene to QuCN⁺ in MeCN solution followed by laser photoexcitation results in formation of electron-transfer products, that is, the quinolinyl radical (QuCN[•]) detectable at 520 nm and the π -dimer benzene radical cation detectable in the near-IR region (Figure 2a). The π -dimer benzene radical cation is generated by π – π association of the radical cation of benzene with a large excess of benzene (1.5 M).^[18] The rate constant of formation of the π -dimer benzene radical cation increased with increasing concentration of benzene (inset of Figure 2a). The second-order rate constant of formation of the π -dimer benzene radical cation is determined from the linear plot shown in Figure 2b to be $2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is close to the diffusion-limited value in MeCN as expected from the exergonic electron transfer. The rate constant (k_{et}) of electron transfer from benzene to ¹QuCN⁺* was determined by fluorescence quenching of ¹QuCN⁺* with benzene and by a Stern–Volmer plot to be $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (see Figure S3 in the Supporting Information). Because the E_{ox} value of phenol

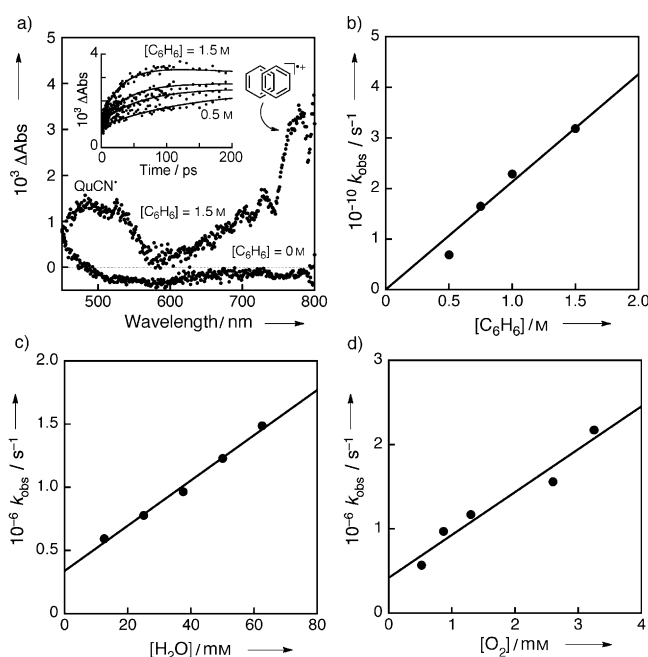


Figure 2. a) Transient absorption spectra of QuCN⁺ with benzene (1.5 M) and without benzene in deaerated MeCN taken at 200 ps after femtosecond laser excitation ($\lambda_{\text{ex}} = 355 \text{ nm}$). Inset: The rise time profiles at 760 nm and at various concentrations of benzene (0–1.5 M). b) Plot of the observed rate constant (k_{obs}) versus [C₆H₆]. c) Plot of k_{obs} versus [H₂O] determined from the decay of absorbance at 760 nm because of the reaction of the π -dimer benzene radical cation with H₂O (0, 25, 50 mM) in MeCN. d) Plot of k_{obs} versus [O₂] determined from the decay of absorbance because of QuCN[•] at various concentrations of O₂ by nanosecond laser flash photolysis at 355 nm of an MeCN solution containing QuCN⁺ (0.40 mM) and benzene (100 mM).

(1.60 V)^[23] is smaller than that of benzene, electron transfer from phenol to ¹QuCN⁺* is also highly exergonic. As a result the electron-transfer rate constant ($k_{\text{et}} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) is close to the diffusion-limited value in MeCN. The k_{et} values obtained are summarized in Table 1.

The near-IR absorption band of the π -dimer benzene radical cation was also observed by nanosecond laser flash photolysis (see Figure S4 in the Supporting Information). The association constant (K_{dimer}) of benzene to the radical cation of benzene was determined to be 11 M^{-1} , which was obtained from the transient absorption intensities at 800 nm and at various concentrations of benzene. The K_{dimer} value agrees well with the reported value of 12 M^{-1} .^[18] The transient species

of QuCN[•] and the π -dimer benzene radical cation is the solvent-separated radical ion pair generated by photoinduced electron transfer.

The rates of decay of QuCN[•] and the π -dimer benzene radical cation obeyed second-order kinetics because of the bimolecular back electron transfer (see Figure S4b in the Supporting Information). The rate constant (k_{bet}) was determined using the molar absorption coefficient of QuCN[•] ($\epsilon_{520} = 2000 \text{ M}^{-1} \text{ cm}^{-1}$)^[24] of $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is close to the diffusion-limited rate constant in MeCN ($2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). The decay of absorbance at 800 nm because of the π -dimer benzene radical cation was accelerated by addition of H₂O. The decay time profile obeys first-order kinetics in the presence of H₂O (see Figure S6 in the Supporting Information). The decay rate constant (k_{obs}) increased linearly with increasing concentration of H₂O as shown in Figure 2c. The rate constant for the reaction of the benzene radical cation or π -dimer benzene radical cation with H₂O was determined from the slope of k_{obs} versus [H₂O] to be $k_{\text{H}_2\text{O}} = 1.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. On the other hand, QuCN[•] was efficiently quenched by O₂ (see Figure S7 in the Supporting Information). The decay rate constant of the transient absorption band at 500 nm for QuCN[•] increased linearly with increasing concentration of O₂ as shown in Figure 2d. The rate constant for the electron-transfer reduction of O₂ with QuCN[•] was determined to be $k_{\text{O}_2} = 5.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

The photocatalytic reaction is initiated by photoinduced electron transfer from benzene to ¹QuCN⁺⁺ as shown in Scheme 1. The benzene radical cation, which is in equilibrium with the π -dimer benzene radical cation, formed by photoinduced electron transfer reacts with H₂O to yield the OH-adduct radical. On the other hand, O₂ can be reduced by QuCN[•] to O₂^{•-} followed by protonation of O₂^{•-} to afford HO₂[•]. The hydrogen abstraction of HO₂[•] from the OH-adduct radical affords phenol and H₂O₂ (Scheme 1). When benzene was replaced by phenol, the transient absorption spectrum of

the radical ion pair was not observed by nano- and femto-second laser flash photolysis (see Figures S8 and S9 in the Supporting Information), although the fluorescence of ¹QuCN⁺⁺ was efficiently quenched by phenol. This indicates that the back electron transfer is much faster than the electron transfer from phenol to QuCN[•]. The back electron transfer in the case of the benzene radical cation is highly exergonic and thereby the process is located deep in the Marcus inverted region, where the rate of the back electron transfer becomes faster with decreasing driving force.^[19,25] The back electron transfer of the phenol radical cation may be much faster because of the much smaller driving force of the back electron transfer ($-\Delta G_{\text{bet}} = 3.29 \text{ eV}$) relative to the driving force of the back electron transfer of the benzene radical cation ($-\Delta G_{\text{bet}} = 3.08 \text{ eV}$). This difference may be the reason why benzene was oxidized but phenol was not oxidized in the photocatalytic oxygenation catalyzed by QuCN[•]. Thus, benzene was selectively and photocatalytically oxidized to phenol by oxygen and water and no further oxygenation of phenol was observed.

In summary, the efficient and selective photooxygenation of benzene to phenol has been accomplished in the presence of oxygen and H₂O through photoinduced electron-transfer oxidation of benzene under homogeneous conditions using QuCN[•] as photocatalyst. The quantum yield for the formation of phenol (26% for QuH⁺) is the highest value ever reported for the direct photocatalytic oxygenation of benzene to phenol.^[26]

Experimental Section

Reaction procedures: A quinolinium ion derivative (1.0–5.0 mM) and D₂O (1.0–3.0 M) were added to a CD₃CN solution (1.0 cm³). The solution was sealed in a sample tube and saturated with oxygen. Then, benzene (30–50 μmol) was added to the solution. The mixture was irradiated with a 500 W xenon lamp through a color glass filter of transmittance at $\lambda > 290 \text{ nm}$. After photoirradiation, the oxygenated products were identified and quantified by comparison of the ¹H NMR spectra with those of identical samples using cyclohexane as internal standard. The spectra confirmed that the reaction of cyclohexane did not occur in this photocatalytic system. The yield of H₂O₂ was determined by titration with excess NaI (100 mM). The amount of I₃⁻ formed was determined from the UV/Vis spectrum ($\epsilon_{361 \text{ nm}} = 25000 \text{ M}^{-1} \text{ cm}^{-1}$).^[27]

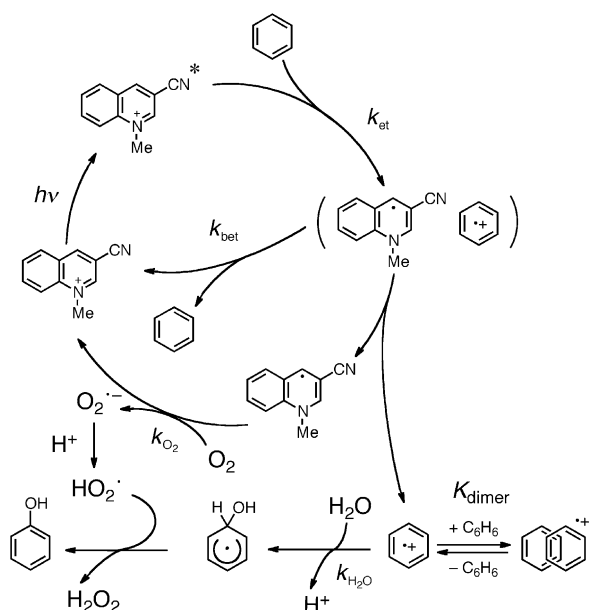
Preparative synthesis of phenol: QuCN[•]ClO₄⁻ (210 mg, 0.80 mmol) and benzene (2.3 g, 29 mmol) were dissolved in an O₂-saturated MeCN solution (200 mL) containing H₂O (3.6 mL, 0.2 mol). The solution was stirred and saturated with oxygen under photoirradiation using a 300 W mercury lamp for 48 h. The temperature of the solution was held constant at 20 °C by cooling with water. The isolated yield of phenol was 41% (1.1 g, 12 mmol).

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Scheme 1.

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