Photocatalysis

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

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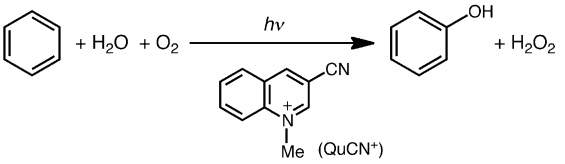
Phenol, which is currently produced from benzene by a three-step cumene process, is one of the most important chemicals in industry. Because the cumene process affords very low yields (around 5%) with byproducts such as acetone and α-methylstyrene under severe conditions,[1–4] extensive efforts have 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 $QuCN^+ClO_4^-$ (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 ^{1}H 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 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.



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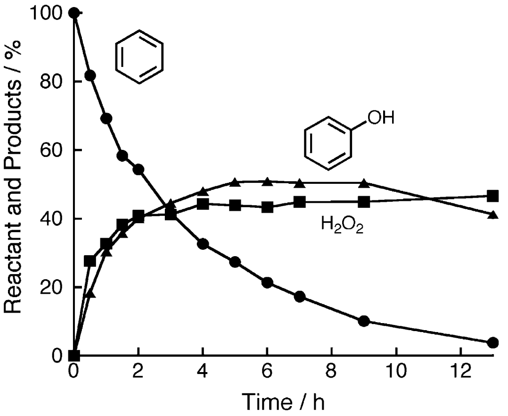

Figure 1. Irradiation time profile of benzene (circles), phenol (triangles), and H_2O_2 (squares) for the photocatalytic oxygenation of benzene by oxygen and water with $QuCN^+$ in oxygen-saturated MeCN (1.0 mL) at 298 K: [benzene] = 30 mM, [$QuCN^+$] = 2.0 mM, and [H_2O] = 2.0 M.

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} [$M^{-1}s^{-1}$]	Irradiation time [h]	Conversion [%]	Yield [%]	Selectivity [%]	Quantum yield[b] [%]
$QuCN^+$	C_6H_6	1.1×10^{10}	1.0	31	30	98	16
$QuCN^+$	C_6H_6		5.0	73	51	70	
QuH^+	C_6H_6	5.8×10^{9}	5.0	88	5.7	6.5	26
$QuMe^+$	C_6H_6	6.7×10^{8}	5.0	21	18	87	3.0
$QuCN^+$	C_6H_5Cl	1.3×10^{10}	0.5	31	27 (*p*-), 3 (*o*-)	88 (*p*-), 11 (*o*-)	3.4
$QuCN^+$	C_6H_5OH	1.1×10^{10}	1.0	7	–		3.7[c]

[a] Conditions for photocatalytic reactions: [$QuCN^+$] = 2.0 mM, [substrate] = 30 mM, [H_2O] = 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 $QuCN^+$ ($\lambda_{em} = 430$ 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 $2.1\times10^{10}\,M^{-1}s^{-1}$, 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 $1.1\times10^{10}\,M^{-1}s^{-1}$ (see Figure S3 in the Supporting Information). Because the E_{ox} value of phenol (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 ($k_{et} = 1.1\times10^{10}\,M^{-1}s^{-1}$) is close to the diffusion-limited value in MeCN. The k_{et} values obtained are summarized in Table 1.

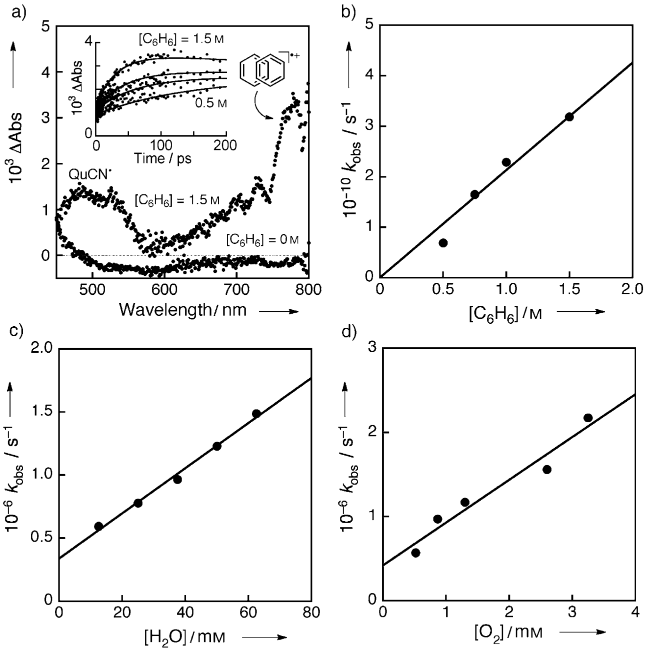
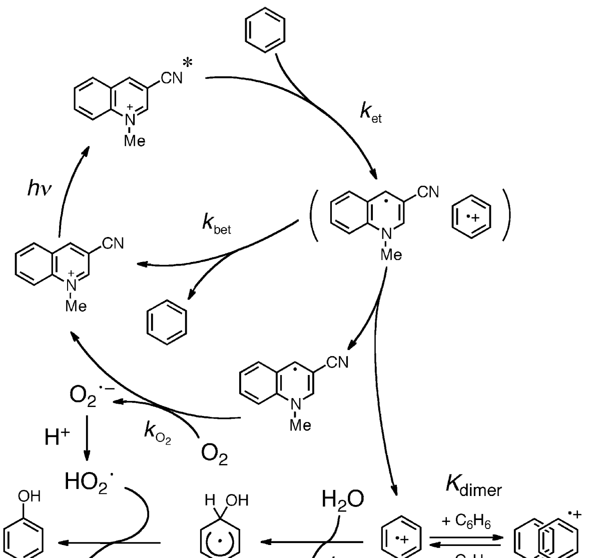


Figure 2. a) Transient absorption spectra of $QuCN^+$ with benzene (1.5 M) and without benzene in deaerated MeCN taken at 200 ps after femtosecond laser excitation ($\lambda_{ex} = 355$ nm). Inset: The rise time profiles at 760 nm and at various concentrations of benzene (0–1.5 M). b) Plot of the observed rate constant (k_{obs}) versus [C_6H_6]. c) Plot of k_{obs} versus [H_2O] determined from the decay of absorbance at 760 nm because of the reaction of the π-dimer benzene radical cation with H_2O (0, 25, 50 mM) in MeCN. d) Plot of k_{obs} versus [O_2] determined from the decay of absorbance because of $QuCN^•$ at various concentrations of O_2 by nanosecond laser flash photolysis at 355 nm of an MeCN solution containing $QuCN^+$ (0.40 mM) and benzene (100 mM).

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$^\bullet$ 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$^\bullet$ 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$^\bullet$ ($\varepsilon_{520} = 2000\,\text{M}^{-1}\text{cm}^{-1}$)[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 H_2O. The decay time profile obeys first-order kinetics in the presence of H_2O (see Figure S6 in the Supporting Information). The decay rate constant (k_{obs}) increased linearly with increasing concentration of H_2O as shown in Figure 2c. The rate constant for the reaction of the benzene radical cation or π-dimer benzene radical cation with H_2O was determined from the slope of k_{obs} versus $[H_2O]$ to be $k_{H_2O} = 1.8 \times 10^7\,\text{M}^{-1}\text{s}^{-1}$. On the other hand, QuCN$^\bullet$ was efficiently quenched by O_2 (see Figure S7 in the Supporting Information). The decay rate constant of the transient absorption band at 500 nm for QuCN$^\bullet$ increased linearly with increasing concentration of O_2 as shown in Figure 2d. The rate constant for the electron-transfer reduction of O_2 with QuCN$^\bullet$ was determined to be $k_{O_2} = 5.1 \times 10^8\,\text{M}^{-1}\text{s}^{-1}$.

The photocatalytic reaction is initiated by photoinduced electron transfer from benzene to ^{1}QuCN^{+*} 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 H_2O to yield the OH-adduct radical. On the other hand, O_2 can be reduced by QuCN$^\bullet$ to $O_2^{\bullet-}$ followed by protonation of $O_2^{\bullet-}$ to afford $HO_2^\bullet$. The hydrogen abstraction of $HO_2^\bullet$ from the OH-adduct radical affords phenol and H_2O_2 (Scheme 1). When benzene was replaced by phenol, the transient absorption spectrum of the radical ion pair was not observed by nano- and femtosecond laser flash photolysis (see Figures S8 and S9 in the Supporting Information), although the fluorescence of ^{1}QuCN^{+*} was efficiently quenched by phenol. This indicates that the back electron transfer is much faster than the electron transfer from phenol to QuCN$^\bullet$. 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 ($-\Delta G_{\text{bet}} = 3.29$ eV) relative to the driving force of the back electron transfer of the benzene radial cation ($-\Delta G_{\text{bet}} = 3.08$ 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.



Scheme 1.

In summary, the efficient and selective photooxygenation of benzene to phenol has been accomplished in the presence of oxygen and H_2O 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 D_2O (1.0–3.0 M) were added to a CD_3CN solution (1.0 cm^3). 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 $\lambda > 290$ nm. After photoirradiation, the oxygenated products were identified and quantified by comparison of the ^{1}H NMR spectra with those of identical samples using cyclohexane as internal standard. The spectra confirmed that the reaction of cyclohexane did not occurred in this photocataytic system. The yield of H_2O_2 was determined by titration with excess NaI (100 mM). The amount of I_3^- formed was determined from the UV/Vis spectrum ($\varepsilon_{361\,\text{nm}} = 25\,000\,\text{M}^{-1}\text{cm}^{-1}$).[27]

Preparative synthesis of phenol: QuCN$^+$ClO$_4^-$ (210 mg, 0.80 mmol) and benzene (2.3 g, 29 mmol) were dissolved in an O_2-saturated MeCN solution (200 mL) containing H_2O (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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[1] R. A. Sheldon, R. A. van Santen, *Catalytic Oxidation, Principles and Applications*, World Scientific, Singapore, **1995**.

[2] G. I. Panov, *CATTECH* **2000**, *4*, 18.
[3] R. J. Schmidt, *Appl. Catal. A* **2005**, *208*, 89.
[4] R. Molinari, T. Poerio, *Asia-Pac. J. Chem. Eng.* **2010**, *5*, 191.
[5] S. Niwa, M. Eswaramoorthy, J. Nair, A. Raj, N. Ito, H. Shoji, T. Namba, F. Mizukami, *Science* **2002**, *295*, 105.
[6] S. Santra, H. Stoll, G. Rauhut, *Phys. Chem. Chem. Phys.* **2010**, *12*, 6345.
[7] Y. Ide, M. Matsuoka, M. Ogawa, *J. Am. Chem. Soc.* **2010**, *132*, 16762.
[8] Y. Shiraishi, N. Saito, T. Hirai, *J. Am. Chem. Soc.* **2005**, *127*, 12820.
[9] H. Yoshida, H. Yuzawa, M. Aoki, K. Otake, H. Itoh, T. Hattori, *Chem. Commun.* **2008**, 4634.
[10] K. Shimizu, H. Akahane, T. Kodama, Y. Kitayama, *Appl. Catal. A* **2004**, *269*, 75.
[11] T. D. Bui, A. Kimura, S. Ikeda, M. Matsumura, *J. Am. Chem. Soc.* **2010**, *132*, 8453.
[12] R. Bal, M. Tada, T. Sasaki, Y. Iwasawa, *Angew. Chem.* **2006**, *118*, 462; *Angew. Chem. Int. Ed.* **2006**, *45*, 448.
[13] T. Kusakari, T. Sasaki, Y. Iwasawa, *Chem. Commun.* **2004**, 992.
[14] M. Tani, T. Sakamoto, S. Mita, S. Sakaguchi, Y. Ishii, *Angew. Chem.* **2005**, *117*, 2642; *Angew. Chem. Int. Ed.* **2005**, *44*, 2586.
[15] T. Dong, J. Li, F. Huang, L. Wang, J. Tu, Y. Torimoto, M. Sadakata, Q. Li, *Chem. Commun.* **2005**, 2724.
[16] K. Ohkubo, K. Suga, K. Morikawa, S. Fukuzumi, *J. Am. Chem. Soc.* **2003**, *125*, 12850.
[17] H. Kitaguchi, K. Ohkubo, S. Ogo, S. Fukuzumi, *J. Phys. Chem. A* **2006**, *110*, 1718.
[18] P. B. Merkel, P. Luo, J. P. Dinnocenzo, S. Farid, *J. Org. Chem.* **2009**, *74*, 5163.
[19] S. Fukuzumi, K. Ohkubo, T. Suenobu, K. Kato, M. Fujitsuka, O. Ito, *J. Am. Chem. Soc.* **2001**, *123*, 8459.
[20] M. Neumann, S. Füldner, B. König, K. Zitler, *Angew. Chem.* **2011**, *123*, 981; *Angew. Chem. Int. Ed.* **2011**, *50*, 951.
[21] In the case of QuH^+, the main products were the further oxygenated phenol such as quinones and diphenol. When phenol was used as a substrate with QuH^+, the conversion of phenol was 35% and the oxygenated products were similar.
[22] S. Fukuzumi, M. Fujita, S. Noura, K. Ohkubo, T. Suenobu, Y. Araki, O. Ito, *J. Phys. Chem. A* **2001**, *105*, 1857.
[23] T. Osako, K. Ohkubo, M. Taki, Y. Tachi, S. Fukuzumi, S. Itoh, *J. Am. Chem. Soc.* **2003**, *125*, 11027.
[24] E. Baciocchi, T. D. Giacco, O. Lanzalunga, P. Mencarelli, B. Procacci, *J. Org. Chem.* **2008**, *73*, 5675.
[25] a) R. A. Marcus, *Annu. Rev. Phys. Chem.* **1964**, *15*, 155; b) R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265; c) R. A. Marcus, *Angew. Chem.* **1993**, *105*, 1161; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1111.
[26] A comparison of yields and selectivities of state-of-the-art systems based on homogeneous metal catalysts with the system of Shiraishi et al. has been reported in Ref. [8].
[27] a) R. D. Mair, A. J. Graupner, *Anal. Chem.* **1964**, *36*, 194; b) S. Fukuzumi, S. Kuroda, T. Tanaka, *J. Am. Chem. Soc.* **1985**, *107*, 3020; c) S. Fukuzumi, M. Ishikawa, T. Tanaka, *J. Chem. Soc. Perkin Trans. 2* **1989**, 1037.