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Visible-Light-Induced Oxygenation of Benzene by the Triplet Excited State of 2,3-Dichloro-5,6-dicyano-*p*-benzoquinoneKei Ohkubo,[†] Atsushi Fujimoto,[†] and Shunichi Fukuzumi^{*,†,‡}[†]Department of Material and Life Science, Graduate School of Engineering, Osaka University, and ALCA, Japan Science and Technology (JST), Suita, Osaka 565-0871, Japan[‡]Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea

Supporting Information

ABSTRACT: Photocatalytic oxygenation of benzene to phenol occurs under visible-light irradiation of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in an oxygen-saturated acetonitrile solution of benzene and *tert*-butyl nitrite. The photocatalytic reaction is initiated by photoinduced electron transfer from benzene to the triplet excited state of DDQ.

Phenol is an important precursor for many chemicals and industrial products. The one-step oxygenation of benzene to phenol, which is one of the dream chemical reactions, has been extensively studied to develop new catalytic systems using heterogeneous inorganic catalysts.^{1–11} However, their synthetic utility has been limited because of low yield, poor selectivity, and the requirement of high temperature. Photochemical oxygenation of benzene to phenol in the gas and liquid phases has also been studied, but under high-energy UV irradiation conditions.^{2–13} Selective production of phenol from benzene is very difficult without further oxygenation of phenol to hydroquinone and CO_x because oxidation of phenol is much easier than that of benzene. Thus, there has been no report on the direct selective oxygenation of benzene to phenol under the conditions of low-energy visible-light irradiation.

Recently, metal-free transformations using organophotocatalysts have been widely investigated.^{14–16} 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) is a well-known and powerful organic oxidizing reagent for a number of organic transformations.¹⁷ However, electron-transfer oxidation of benzene by DDQ is impossible because the one-electron reduction potential of DDQ ($E_{\text{red}} = 0.51$ V vs SCE)¹⁸ is much lower than the one-electron oxidation potential of benzene (2.48 V).¹⁹ Visible-light-excited DDQ spontaneously relaxes to the long-lived $n-\pi^*$ triplet excited state by intersystem crossing.²⁰ Triplet-excited DDQ has a very strong oxidizing ability²⁰ and can oxidize benzene by electron transfer.

We report herein the direct oxygenation of benzene to phenol under visible-light irradiation of DDQ in an oxygen-saturated acetonitrile solution of benzene. The photooxygenation reaction is initiated by efficient photoinduced electron transfer from benzene to the triplet excited state of DDQ to give phenol and 2,3-dichloro-5,6-dicyanohydroquinone (DDQH₂), where DDQ acts a stoichiometric oxidant. *tert*-Butyl nitrite (TBN) can then be used as a recycle reagent to convert DDQH₂ to DDQ under aerobic conditions.²¹ The

photocatalytic oxygenation of benzene to phenol was also examined by adding TBN.

Photooxygenation of benzene occurs under visible-light irradiation of DDQ (40 mM) in oxygen-saturated MeCN containing benzene (30 mM) and H₂O (0.5 M) using a xenon lamp (500 W) with a color glass filter ($\lambda = 390$ –600 nm) to produce phenol and DDQH₂ (eq 1), as shown in Figure 1. The yield of phenol was 99%, with 99% conversion (>99% selectivity).

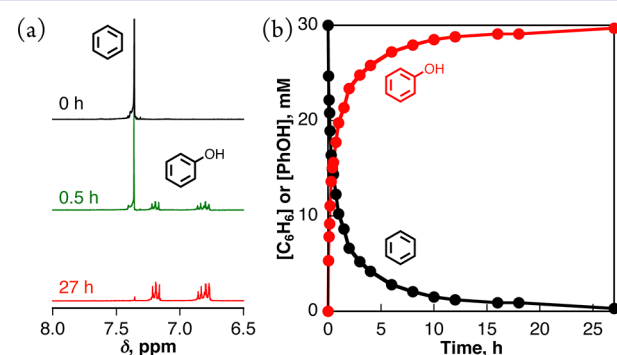
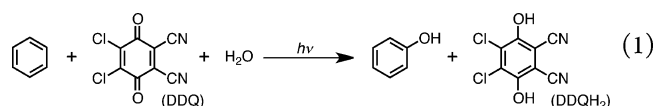


Figure 1. (a) ¹H NMR spectral changes in the photochemical oxygenation of benzene (30 mM) with DDQ (40 mM) and D₂O (0.5 M) in deaerated CD₃CN (0.6 mL) at 298 K. (b) Reaction time profiles of benzene and phenol.

With the addition of TBN, which oxidizes DDQH₂ to DDQ in the presence of O₂ (Figure S1 in the Supporting Information),²¹ catalytic oxygenation occurred, affording phenol in 93% yield with 98% conversion of benzene (30 mM) in the presence of DDQ (9.0 mM), TBN (1.5 mM), and water (0.5 M) after photoirradiation for 30 h (eq 2).²² The reaction time course monitored by ¹H NMR spectroscopy is shown in Figure 2. After the reaction, DDQ was completely recovered as a result of the addition of a catalytic amount of TBN under O₂ atmosphere.²³

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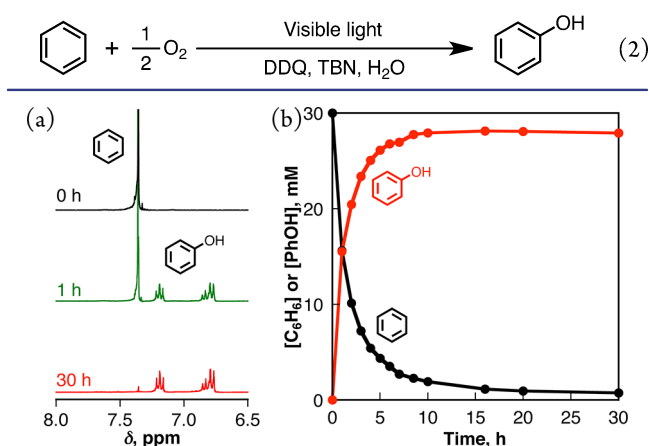


Figure 2. (a) ^1H NMR spectral changes in the photochemical oxygenation of benzene (30 mM) with DDQ (9.0 mM), D_2O (0.5 M), and TBN (1.5 mM) in O_2 -saturated CD_3CN (0.6 mL) at 298 K. (b) Reaction time profiles of benzene and phenol.

Phenol was also detected by GC–MS. A mass peak was observed at $m/z = 94$ in the crude solution after photoirradiation of an MeCN solution containing benzene, H_2O , and DDQ. When H_2^{16}O was replaced by H_2^{18}O to clarify the oxygen source, the peak location increased to $m/z = 96$ (Figure S2). Thus, the origin of the phenol oxygen was confirmed to be water.

The mechanism of oxygenation of benzene was examined by time-resolved transient absorption experiments. The triplet–triplet absorption spectrum of DDQ was observed at 630 nm in deaerated MeCN by nanosecond laser flash photolysis ($\lambda_{\text{ex}} = 430 \text{ nm}$) (Figure 3a). The lifetime of the triplet excited state of

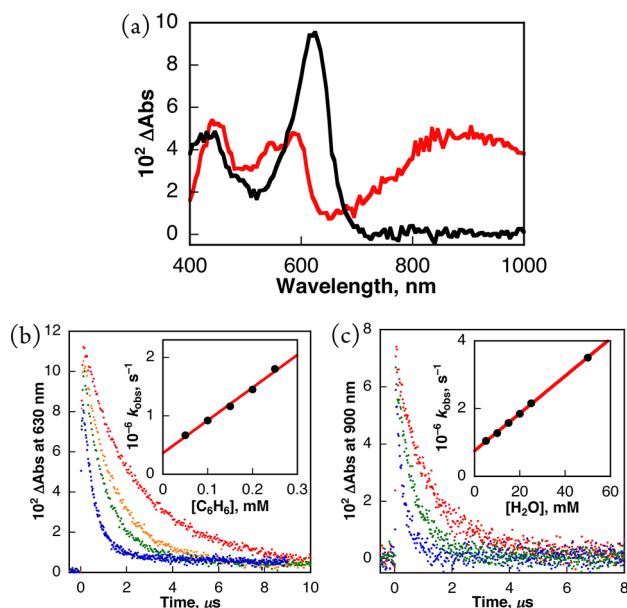


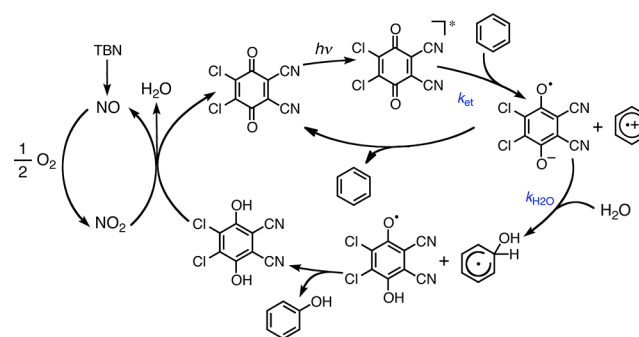
Figure 3. (a) Transient absorption spectra of DDQ (1.2 mM) in the absence (black) and presence (red) of benzene (1.0 M) in deaerated MeCN taken $0.4 \mu\text{s}$ after nanosecond laser excitation ($\lambda = 355 \text{ nm}$). (b) Decay time profiles at 630 nm due to $^3\text{DDQ}^*$ at various concentrations of benzene. Inset: Plot of k_{obs} vs $[\text{C}_6\text{H}_6]$. (c) Decay time profiles at 900 nm due to benzene π -dimer radical cation generated by photoinduced electron transfer from benzene to DDQ at various concentrations of H_2O . Inset: Plot of k_{obs} vs $[\text{H}_2\text{O}]$.

DDQ ($^3\text{DDQ}^*$) was determined from the decay of the T–T absorption band (Figure 3b) to be $2.4 \mu\text{s}$. The transient absorption spectrum of an MeCN solution containing benzene and DDQ exhibited the formation of benzene π -dimer radical cation ($\lambda_{\text{max}} = 900 \text{ nm}$)^{13,24} and $\text{DDQ}^{\bullet-}$ ($\lambda_{\text{max}} = 595 \text{ nm}$),¹⁸ where benzene π -dimer radical cation was formed by the reaction of benzene radical cation with the large excess of neutral benzene (Figure 3a, red line). Thus, the photo-oxygenation of benzene to phenol is initiated by intermolecular photoinduced electron transfer from benzene to $^3\text{DDQ}^*$, because the free energy change for electron transfer is negative ($\Delta G_{\text{et}} = -0.70 \text{ eV}$), as determined from the one-electron oxidation potential of benzene ($E_{\text{ox}} = 2.48 \text{ V}$ vs SCE)¹⁹ and the one-electron reduction potential of $^3\text{DDQ}^*$ ($E_{\text{red}} = 3.18 \text{ V}$ vs SCE).²⁵ The decay rate constant (k_{obs}) of $^3\text{DDQ}^*$ increased with increasing concentration of benzene (Figure 3b). The electron-transfer rate constant of $^3\text{DDQ}^*$ with benzene (k_{et}) was determined from the slope of the plot of k_{obs} versus $[\text{C}_6\text{H}_6]$ (Figure 3b inset) to be $(5.3 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

$\text{DDQ}^{\bullet-}$ and the benzene π -dimer radical cation disappeared via back electron transfer to the ground state in dry MeCN. The decay of the absorbance at 900 nm due to the benzene π -dimer radical cation was accelerated by the addition of H_2O . The decay time profile obeyed first-order kinetics in the presence of H_2O (Figure 3c). The decay rate constant (k_{obs}) increased linearly with increasing concentration of H_2O . The rate constant for the reaction of benzene radical cation or the π -dimer radical cation with H_2O was determined from the slope of k_{obs} versus $[\text{H}_2\text{O}]$ to be $k_{\text{H}_2\text{O}} = (5.5 \pm 0.3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

On the basis of above-mentioned results, the catalytic mechanism is summarized in Scheme 1. Benzene radical cation

Scheme 1



formed by photoinduced electron transfer reacts with water to yield the OH-adduct radical.¹³ On the other hand, $\text{DDQ}^{\bullet-}$ can react with the OH-adduct radical to form phenol and DDQH_2 . DDQH_2 is known to be oxidized by reaction with TBN and O_2 via NO_2 to regenerate DDQ.²¹

The quantum yields (Φ) for formation of phenol under photoirradiation with monochromatized light ($\lambda = 420 \text{ nm}$) were determined by GC–MS from the phenol peak using an actinometer. The dependence of Φ on the concentration of H_2O is shown in Figure 4. The value of Φ increases with increasing concentration of H_2O until it reaches a constant value of 0.45, which is the highest value ever reported for direct photooxygenation of benzene to phenol.

No further oxygenation of phenol as a product to form diphenol, hydroquinone, or CO_x occurred under the present catalytic conditions. Electron-transfer oxidation of phenol is

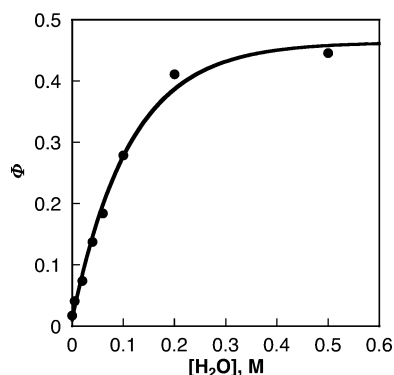


Figure 4. Plot of the quantum yield for formation of phenol (Φ) vs $[\text{H}_2\text{O}]$.

much easier than that of benzene, because the one-electron oxidation potential of phenol ($E_{\text{ox}} = 1.60 \text{ V vs SCE}$)²⁶ is smaller than that for benzene. Furthermore, as evidenced by nano-second and femtosecond laser flash photolysis measurements (Figures S3 and S4), photoinduced electron transfer from phenol to $^3\text{DDQ}^*$ occurred efficiently with a rate constant of $(1.2 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, as determined from the slopes in the insets of Figures S3 and S4. This value is larger than k_{et} for benzene [$(5.3 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$]. In such a case, the fact that no photocatalytic oxygenation of phenol to hydroquinone occurred may result from the much slower reaction with H_2O compared with fast back electron transfer (vide infra).

The fast back electron transfer in the case of phenol was confirmed by femtosecond laser flash photolysis measurements. In contrast to the case of benzene, where the transient absorption band at 900 nm due to benzene π -dimer radical cation and that at 595 nm due to $\text{DDQ}^{\bullet-}$ were clearly observed (Figure 3a), no transient absorption due to phenol π -dimer radical cation or $\text{DDQ}^{\bullet-}$ was observed in the case of phenol because of fast back electron transfer (Figure 5). Such

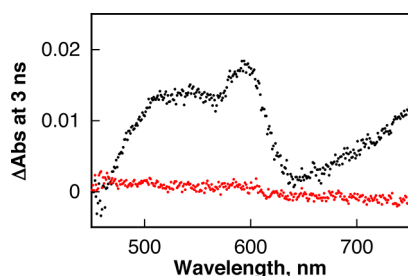


Figure 5. Transient absorption spectra of DDQ with benzene (1.0 M, black) and phenol (1.0 M, red) in deaerated MeCN taken 3.0 ns after femtosecond laser excitation at 393 nm.

contrasting results are well-rationalized by the difference in the driving forces for back electron transfer. The driving force of back electron transfer from $\text{DDQ}^{\bullet-}$ to benzene radical cation (1.97 eV) is much larger than that from $\text{DDQ}^{\bullet-}$ to phenol radical cation (1.09 eV). Because the driving force in the case of benzene radical cation is so large, the back electron transfer may occur in the Marcus inverted region,²⁷ where the back electron transfer in the radical ion pair is much slower than the dissociation of radical ions. On the contrary, the back electron transfer from $\text{DDQ}^{\bullet-}$ to phenol radical cation may occur in the Marcus top region, where the back electron transfer is much faster than the dissociation of radical ions. In such a case, no net

reaction would occur despite the diffusion-controlled photo-induced transfer.

When benzene was replaced by halogenated benzenes (fluoro-, chloro-, and bromobenzene), photooxygenation also occurred with DDQ under similar reaction conditions to yield the corresponding phenols (the GC data are shown in Figure S5). The substrate conversions and product selectivities are summarized in Table 1.

Table 1. Reactant Conversions and Product Selectivities in Photooxygenation of Halogenated Benzene Derivatives

substrate (conversion, %)	product: yield, % (selectivity, %)
fluorobenzene (44)	phenol: 14 (32) <i>p</i> -fluorophenol: 24 (55) <i>o</i> -fluorophenol: 5.7 (13)
chlorobenzene (34)	phenol: 0 (0) <i>p</i> -chlorophenol: 28 (82) <i>o</i> -chlorophenol: 6.1 (18)
bromobenzene (14)	phenol: 0 (0) <i>p</i> -bromophenol: 11 (80) <i>o</i> -bromophenol: 2.8 (20)

Selective photooxygenation was observed for chloro- and bromobenzene. In contrast, photooxygenation of fluorobenzene gave phenol together with the fluorophenols. The product selectivity depends on the electronic charge of the radical cation species (Figure 6). The positive charge in fluorobenzene radical

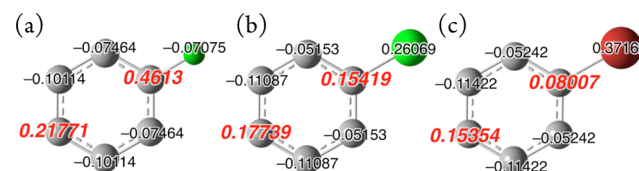


Figure 6. Electronic charges on the carbon atoms in (a) fluoro-, (b) chloro-, and (c) bromobenzene radical cations calculated at the density functional theory at the B3LYP/6-31+G(d,p) level with natural population analysis.

cation is localized on C1 (+0.46) and C4 (+0.22). A water molecule can be added at C1 to form phenol via dehalogenation. In the case of chloro- and bromobenzene radical cation, the positive charges on C1 are significantly smaller than in fluorobenzene radical cation. Thus, addition of OH^- at the para position results in the formation of *p*-halophenol selectively.

In conclusion, DDQ has been shown to act as an efficient photocatalyst for the one-step oxygenation of benzene to phenol under visible-light irradiation with a highest quantum yield of 45%. The radical intermediates in the photocatalytic oxygenation of benzene with H_2O were successfully detected by laser flash photolysis to clarify the photocatalytic mechanism.

■ ASSOCIATED CONTENT

● Supporting Information

UV-vis and GC-MS data and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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