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Solvent-free Photooxidation of Alkanes by Dioxygen with 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone via Photoinduced Electron Transfer

Kei Ohkubo,*[a,b,c] Kensaku Hirose,[b] and Shunichi Fukuzumi *[c,d]

Abstract: Photooxidation of alkanes by dioxygen occurred under visible light irradiation of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) which acts as a super photooxidant. Solvent-free hydroxylation of cyclohexane and alkanes is initiated by electron transfer from alkanes to the singlet and triplet excited states of DDQ to afford the corresponding radical cations and $DDQ^{\bullet -}$ as revealed by femtosecond laser-induced transient absorption measurements, Alkane radical cations readily deprotonate to produce alkyl radicals, which react with dioxygen to afford alkylperoxyl radicals. Alkylperoxyl radicals abstract hydrogen atoms from alkanes to yield alkyl hydroperoxides, accompanied by regeneration of alkyl radicals to constitute the radical chain reactions, so called autoxidation. The termination of the radical chain is the bimolecular reactions of alkylperoxyl radicals to yield the corresponding alcohols and ketones. On the other hand, $DDQ^{\bullet -}$ produced by the photoinduced electron transfer from alkanes to the excited states of DDQ disproportionates with protons to yield $DDQH_2$.

Recently, photoredox catalysts have merited increasing attention, because they are well applied in photoinduced organic syntheses using inorganic[1-9] and organic photosensitizers.[10-13] The photoredox catalyst is initiated by photoinduced electron-transfer oxidation/reduction of substrates. Photoinduced electron-transfer reactions produce highly reactive radical cations and anions, leading to the finely tuned novel organic synthetic transformations.[1-13]

We have reported the hydroxylation of benzene to phenol under ambient conditions via photoinduced electron transfer from benzene to 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ).[14] The one-electron reduction potential of the triplet excited state of DDQ (^{3}DDQ*: * denote the excited state) is 3.18 V vs. SCE, which is high enough to oxidize benzene by electron transfer to produce benzene radical cation as a key intermediate.[14,15] Formation of radical cations of benzonitrile (PhCN), nitrobenzene ($PhNO_2$), and trifluoromethylbenzene ($PhCF_3$) for the hydroxylation also became possible by the singlet excited state of DDQ (^{1}DDQ*: * denote the excited state), which is 3.8 V vs. SCE.[16] The singlet excited state (^{1}DDQ*), which is rapidly relaxed to ^{3}DDQ* exhibited a short lifetime of a few picoseconds.[16,17] The lifetime of singlet excited state was too short to be able to oxidize PhCN at low concentrations.[16] Thus, neat PhCN was used as a solvent, when electron transfer from PhCN to ^{1}DDQ* occurred efficiently.[17] The ionization potentials of PhCN (9.72 eV) is somewhat lower than that of cyclohexane (9.88 eV).[18,19] Electron transfer from cyclohexane to $^1DDQ^*$ may be thermodynamically feasible to activate the C-H bond.[20] However, there has been no report on photoinduced electron-transfer oxidation of cycloalkanes or normal alkanes under the homogeneous conditions.[21]

We report herein solvent-free photooxidation of cyclohexane, hexane, 3-methylpentane and pentane by O_2 using the singlet excited state of DDQ as an effective photooxidant under visible light irradiation at ambient conditions. This is the first report for the direct photochemical hydroxylation of alkanes by O_2 via photoinduced electron transfer. The mechanism is discussed based on femtosecond and nanosecond laser-induced transient absorption measurements to directly monitor the photoinduced electron-transfer reactions.

Photooxidation of cyclohexane by O_2 occurred under visible light irradiation of DDQ (3.0 mM) in O_2-saturated cyclohexane with a xenon lamp (500 W) attached with a color glass filter (λ > 390 nm) to produce cyclohexane hydroperoxide, cyclohexanol and cyclohexanone. The yields were determined by GC analysis for cyclohexanol and cyclohexanone (see Figure S1 in the supporting information (SI)) and by iodometric titration for cyclohexane hydroperoxide. The reaction time profile is shown in Figure 1. It is known for long time that photooxidation of cyclohexane by O_2 occurs under UV light irradiation of the charge-transfer complex formed between cyclohexane and O_2.[22] It was confirmed, however, no photooxidation of cyclohexane by O_2 occurred without DDQ under visible light irradiation.

When cyclohexane was replaced by *n*-hexane, the photooxidation of neat *n*-hexane by O_2 occurred under visible light irradiation of DDQ (3.0 mM) in O_2-saturated *n*-hexane to produce the corresponding hydroperoxides, alcohols and ketones (Figure 2).[23] Similarly 3-methylpentane and pentane were oxidized under visible light irradiation of O_2-saturated neat solvents containing DDQ (Figures S3 and S4 in SI). The product yields are summarized in Table 1.

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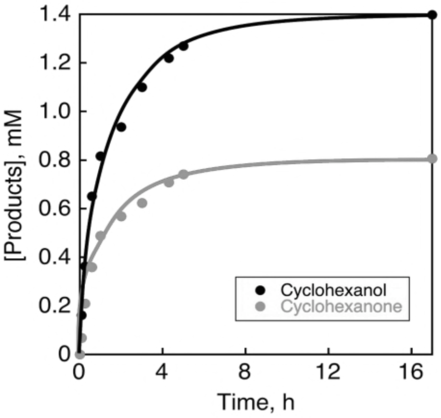


Figure 1 Reaction time profiles for formation of cyclohexanol (black) and cyclohexanone (gray) in the photooxidation of cyclohexane by O_2 with DDQ (3.0 mM) under visible light irradiation of an O_2-saturated cyclohexane solution by use of a xenon lamp (500 W; λ > 390 nm) at 298 K. The GC charts are shown in Figure S1 (SI).

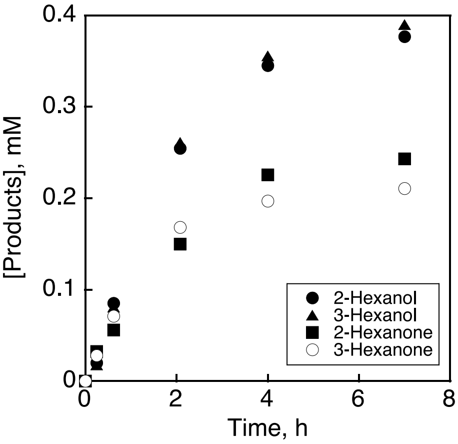
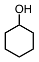
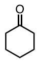
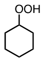
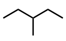
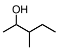
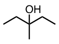
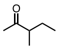
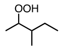
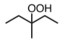
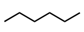
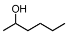
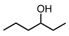
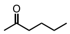
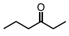
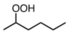
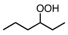
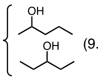
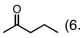
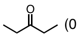
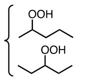


Figure 2 Reaction time profiles for formation of 2-hexanol (black) and 3-hexanol (red), 2-hexanone (blue) and 3-hexanone (green) in the photooxidation of *n*-hexane by O_2 with DDQ (5.0 mM) under visible light irradiation of an O_2-saturated *n*-hexane by use of a xenon lamp (500 W; λ > 390 nm) at 298 K. The GC charts are shown in Figure S2 (SI).

Table 1 Product yields and quantum yields (Φ) for the photooxidation of alkanes by O_2 with DDQ in O_2-saturated alkanes under visible light irradiation[a]

substrate	products (yields vs $[DDQ]_0$)			time, h	Φ,[b] %
	 (70%)	 (40%)	 (200%)	17	280
	 (7%)  (55%)	 (8%)	 (37%)  (350%)	20	300
	 (19%)  (20%)	 (12%)  (11%)	 (59%)  (86%)	7	34
	 (9.1%)	 (6.3%)  (0.8%)	 (88%)	4.8	18

[a] $[DDQ]_0$ = 2.0 mM, *T* = 298 K. [b] Total quantum yield for formation of oxygenated products.

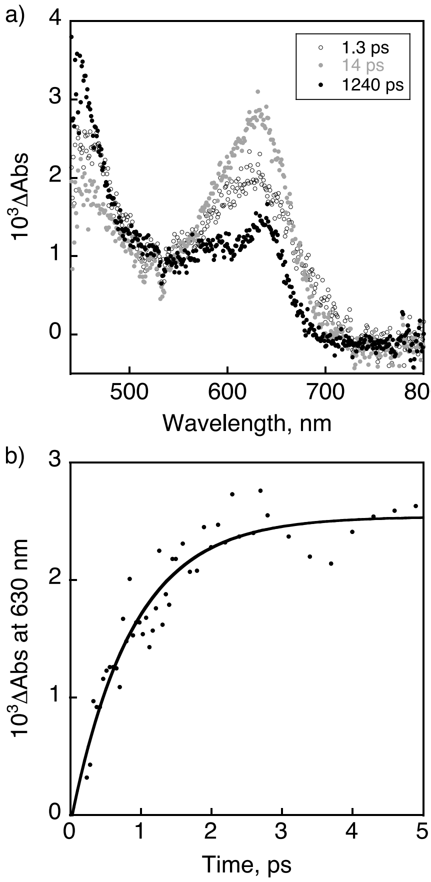
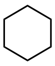
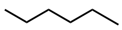
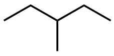
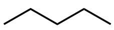


Figure 3 a) Transient absorption spectra of DDQ (3.0 mM) in deaerated cyclohexane after femtosecond laser excitation at 420 nm; b) Time profile of absorbance at 630 nm.

Table 2 Ionization potentials of alkanes and the rate constant of electron transfer from alkanes to $^1DDQ^*$

Substrate	IP,[a] eV	k_{et}, s^{-1}
	9.79	9.2×10^{11} (9.2×10^{11}) [b]
	10.18	9.0×10^{10}
	10.08	1.4×10^{11}
	10.34	3.8×10^{11}

[a] Taken from refs. 18, 19. [b] Value in parenthesis is determined in cyclohexane-d_{12}.

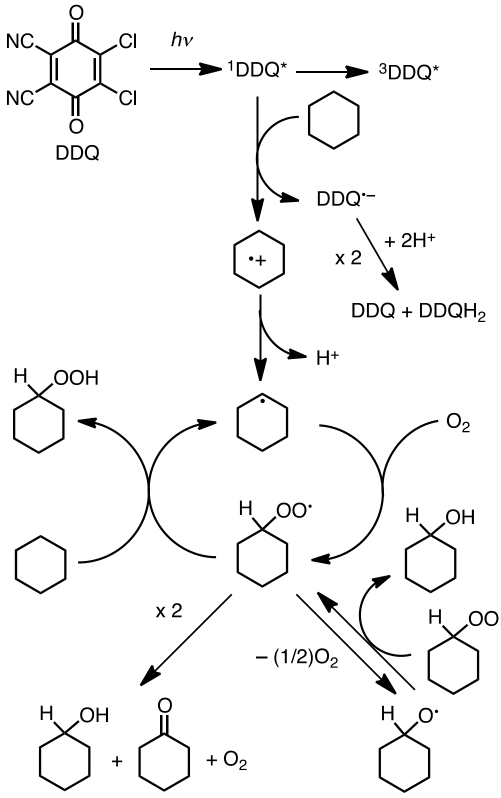
The quantum yields (Φ) of the formation of oxygenated products were determined by use of a standard actinometer, potassium ferrioxalate (see the experimental section in SI).[24] The Φ value of the photooxidation of cyclohexane by O_2 with DDQ increased with increasing concentration of O_2 to reach a constant value. The Φ values of cyclohexane and 3-methylpentane are significantly larger than 100 %, 280% for cyclohexane and 300% for 3-methylpentane (Table 1). This indicates that the photochemical step induces radical chain processes (vide infra).

The mechanism of photooxidation of alkanes was examined by laser-induced time-resolved transient absorption experiments. A singlet-singlet absorption spectrum of DDQ was observed at 470 nm in cyclohexane at 1.3 ps after femtosecond laser excitation of λ_{ex} = 420 nm (see Figure 3). The singlet-singlet absorption due to $^1DDQ^*$ decayed, accompanied by an increase in absorption at 630 nm due to the triplet-triplet absorption band of DDQ. The absorption at λ_{max} = 605 nm is assigned to the semiquinone radical anion of DDQ ($DDQ^{\bullet-}$).[25] This absorption band agrees with that observed in the electron-transfer reduction of DDQ by decamethylferrocene in 1,2-dichloroethane (λ_{max} = 605 nm) (Figure S5 in SI).[16,25] We also confirmed the formation of $DDQ^{\bullet-}$ by the ESR measurements (Figure S6 in SI). Thus, efficient electron transfer from cyclohexane to $^1DDQ^*$ occurs to produce the radical ion pair ($CyH^{\bullet+}$ and $DDQ^{\bullet-}$), in which only $DDQ^{\bullet-}$ has the absorption in the visible region (Figure 3a).

The rate constant of formation radical ion pair (k_{et}) was determined from the first-order rate constant of the rise in absorbance at 605 nm (k_{obs} = 1.1 × 10^{12} s^{-1} in Figure 3b) using Equation (1), to be 9.2 × 10^{11} s^{-1}. Similarly the k_{et} values were

$$k_{et} = k_{obs} - k_{ISC} \qquad (1)$$

determined for electron transfer from other alkanes to $^1DDQ^*$ as listed in Table 2 (data are shown in Figure S7-S9 in SI). The k_{et} value of *n*-hexane (9.0 × 10^{10} s^{-1}) is one-order of magnitude smaller than the value of cyclohexane in accordance with the higher ionization potential of *n*-hexane (10.13 eV) as compared with the value of cyclohexane (9.88 eV).[19] No kinetic isotope effect was observed in the case of deuterated cyclohexane (C_6D_{12}) (see Table 1 and Figure S10 in SI), indicating that the observed behavior is an electron-transfer process rather than a hydrogen abstraction from the substrate. It has been well known that triplet excited ketones are quenched by hydrogen abstraction from substrates.[26-32] In the case of DDQ, $^1DDQ^*$ is quenched by electron transfer from alkanes prior to the rapid intersystem crossing to the triplet excited state.[33,34]



Scheme 1 Proposed reaction mechanism for the photooxidation of cyclohexane by O_2 with DDQ via photoinduced electron transfer

The photooxidation of cyclohexane (CyH) by O_2 with DDQ is initiated by electron transfer from CyH to $^1DDQ^*$ form the radical ion pair of cyclohexene radical cation ($CyH^{\bullet+}$) and $DDQ^{\bullet-}$ (Scheme 1). $CyH^{\bullet+}$ is deprotonated rapidly to produce cyclohexyl radical ($Cy^{\bullet}$) and 2,3-dichloro-5,6-dicyano-1,4-hydroquinone ($DDQH_2$). The addition of O_2 to $Cy^{\bullet}$ is known to occur rapidly to afford cyclohexylperoxyl radical ($CyOO^{\bullet}$), which abstracts a hydrogen atom from cyclohexane to produce cyclohexyl hydroperoxide (CyOOH), accompanied by regeneration of cyclohexyl radical ($Cy^{\bullet}$) to constitute the radial chain reactions. Because the quantum yield became constant with increasing concentration of O_2 (Figure 3) , the O_2 addition process is not the rate-determining process in O_2-saturated cyclohexane. The chain reactions are terminated by the disproportionation of $CyOO^{\bullet}$ to yield cyclohexanol (CyOH) and cyclohexanone (Cy=O).[35-38] The reason why the yield of cyclohexanol is larger than that of cyclohexanone may result from the radical chain decomposition of CyOOH to CyOH via cyclohexanoxyl radical ($CyO^{\bullet}$) as shown in Scheme 2.

In conclusion, efficient photooxidation of alkanes by O_2 are initiated by photoinduced electron transfer from alkanes used as neat solvents to the singlet excited state of DDQ ($^1DDQ^*$) to produce the radical ion pair (alkane radical cation and $DDQ^{\bullet-}$). Deprotonation of alkane radical cation produces the alkyl radical to which O_2 is added rapidly to give the alkylperoxyl radical. Then, the well-known chain propagation proceeds via the hydrogen abstraction from the alkane by the alkylperoxyl radical to yield the alkyl hydroperoxide. The corresponding alcohols and ketones are produced by the termination step, that is the disproportionation of the alkylperoxyl radicals. Such radical chain autoxidation processes with high concentrations of substrates (neat solvent) have enabled to obtain the high quantum yields. Thus, the present study provides an environmentally benign way for photooxidation of alkanes by O_2 initiated by photoinduced electron transfer.

Experimental Section

Materials. Chemicals were purchased from commercial source and used without purification, unless otherwise noted. DDQ was recrystallized from hot ethanol. Potassium ferrioxalate used as an actinometer to determine the quantum yield was prepared according to the literature and purified by recrystallization from hot water.[24]

Reaction procedures. The photooxygenation of saturated hydrocarbons with DDQ was carried out by the following procedure. Typically, a cyclohexane solution (3.0 cm^3) containing DDQ (2.0 mM) with acetonitrile as a co-solvent (2%) in a square quartz cuvette (10 mm x 10 mm) with a silicon septum was saturated with oxygen by bubbling oxygen through a stainless tube for 5 min. The solution was then irradiated with a 500 W xenon lamp (Ushio Optical Module X SX-UID 500XAMQ) through a color filter glass (Asahi Techno Glass Y43) transmitting λ > 390 nm at room temperature. After photoirradiation, the corresponding oxygenated products were identified and quantified by comparison of the GC retention time and the MS spectra (Shimadzu QP-5000) in comparison with those of authentic samples.

The amounts of hydroperoxides were determined by titration by iodide ion as follows. The photoirradiated solution was titrated with excess amount of NaI (0.1 M). The amount of I_3^- formed was then determined from the UV-vis spectrum (λ_{max} = 361 nm, ε_{361} = 2.5 x 10^4 M^{-1} cm^{-1}).[39]

Quantum yield determination. A standard actinometer (potassium ferrioxalate) was used for the quantum yield determination of the photooxygenation of cyclohexane with DDQ. Typically, a square quartz cuvette (10 mm i.d.), which contained an O_2-saturated cyclohexane solution (3.0 cm^3) of DDQ (2.0 mM) was irradiated with monochromatized light (λ = 420 nm) from a Shimadzu RF-5300PC fluorescence spectrophotometer. Under the conditions of actinometric experiments, DDQ absorbed essentially 35% incident light of λ = 420 nm. The light intensity of monochromatized light of λ = 420 nm was determined as 1.5×10^{-9} einstein s^{-1}. The progress of photochemical reaction was monitored using a Shimadzu GC-17A gas chromatograph and Shimadzu MS-QP5000 mass spectrometer. The quantum yields were determined from increase of total amount of products.

Laser flash photolysis measurements. The measurements of femtosecond transient absorption spectra in the photochemical reactions of DDQ with saturated hydrocarbons were performed according to the following procedures. Typically, a nitrogen-saturated cyclohexane solution containing DDQ (10 mM) was excited by a femtosecond laser pulse. Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.) and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The instrumental details are described in SI.

Acknowledgements

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Keywords: photoredox catalysis • quinone • radical • oxygenation • electron transfer

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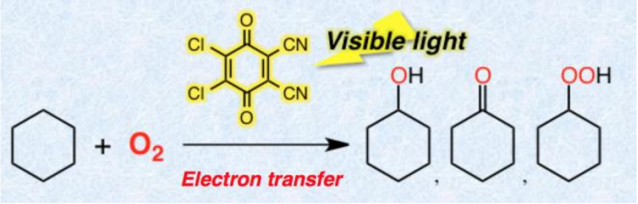
COMMUNICATION



Aerobic photooxidation of alkanes occurred under visible light irradiation of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone via the photoinduced electron-transfer process.

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Solvent-free Photooxidation of Alkanes by Dioxygen with 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone via Photoinduced Electron Transfer