Simultaneous production of *p*-tolualdehyde and hydrogen peroxide in photocatalytic oxygenation of *p*-xylene and reduction of oxygen with 9-mesityl-10-methylacridinium ion derivatives†

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Photooxygenation of *p*-xylene by oxygen occurs efficiently under photoirradiation of 9-mesityl-2,7,10-trimethylacridinium ion (Me_2Acr^+–Mes) to yield *p*-tolualdehyde and hydrogen peroxide, which is initiated *via* photoinduced electron transfer of Me_2Acr^+–Mes to produce the electron-transfer state.

Oxygenation of aromatic compounds to produce aromatic aldehydes is key chemical reaction for production of precursors of a variety of fine or specialty chemicals such as pharmaceutical drugs, dyestuffs, pesticides and perfume compositions. A number of methods using inorganic heavy metal oxidants have so far been reported for oxygenation of aromatic compounds to produce the corresponding aromatic aldehyde.[1–4] However, their synthetic utility has been limited because of low yield and poor selectivity. Moreover, the use of stoichiometric amounts of inorganic oxidants should be avoided because of environmental problems.[5] For this reason, catalytic oxygenation processes with molecular oxygen or hydrogen peroxide (H_2O_2), have merited increasing attention.[6] H_2O_2 is desirable as a clean and mild oxidant because the by-product in oxygenation of substrates is only H_2O.[6,7]

There have been extensive studies on photocatalytic formation of H_2O_2,[8] or photocatalytic oxygenation of aromatic substrates.[9–11] If valuable aromatic aldehydes can be produced together with H_2O_2 in the photocatalytic oxygenation of alkyl aromatic compounds by O_2, such a process would be superior as compared to the conventional methods to produce either or both H_2O_2 and aromatic aldehydes. However, no photocatalytic reaction to produce both aromatic aldehydes and H_2O_2 together has ever been reported.

We report herein that 9-mesityl-10-methylacridinium ion (Acr^+–Mes)[12–14] and its derivative act as efficient photocatalysts for simultaneous production of aromatic aldehydes and H_2O_2 in the photocatalytic reduction of O_2 by alkyl aromatic compounds under visible light irradiation. The electron-transfer state ($Acr^\bullet$–$Mes^{\bullet+}$), produced upon photoexcitation of Acr^+–Mes, has both strong oxidizing and reducing ability, and this enables not only to oxidize alkyl aromatic compounds but also to reduce O_2.[12,14]

Visible light irradiation of $[Acr^+–Mes]ClO_4^-$ (λ_{max} = 430 nm, 0.20 mM) in oxygen-saturated acetonitrile (MeCN) containing *p*-xylene (4.0 mM) with a xenon lamp attached with a colour glass filter (λ = 380–500 nm) for 80 min resulted in formation of an oxygenated product, *p*-tolualdehyde (34%), *p*-methylbenzyl alcohol (10%) and H_2O_2 (30%). The products and quantum yields in the photocatalytic oxygenation were determined by ^1H NMR, GC-MS and iodometry.[15] The photooxygenation of mesitylene and durene also occur to afford the corresponding benzaldehyde and H_2O_2 with a slight amount of benzyl alcohol, as listed in Table 1. It is important to note that 9-phenyl-10-methylacridnium ion (Acr^+–Ph), which contains no electron donor moiety, is not effective as a photocatalyst for the simultaneous formation of *p*-tolualdehyde and H_2O_2 (Table 1).

The photocatalytic reactivity was enhanced by the presence of H_2O (0.9 M) and sulfuric acid (1.0 mM) to yield *p*-tolualdehyde (75%), *p*-methylbenzyl alcohol (15%) and H_2O_2 (74%) with a high quantum yield (0.25). The 100% yields of tolualdehyde and H_2O_2 with a higher quantum yield (0.37) were achieved by using 9-mesityl-2,7,10-trimethylacridinium ion (Me_2Acr^+–Mes), where the hydrogens at 2 and 7 positions of the acridinium ring are replaced by methyl groups (Table 1). The synthetic procedures for Me_2Acr^+–Mes are described in ESI S2.†

No further oxygenated product, *p*-toluic acid or *p*-phthaladehyde, was produced as shown in ^1H NMR spectra (ESI S3†).[17] The photocatalytic turnover number (TON) was 20 under the experimental conditions. When the concentration of Me_2Acr^+–Mes (1.0×10^{-4} M) was decreased, TON was increased to 200. A preparative scale photocatalytic reaction with *p*-xylene (0.5 g, 4.7 mmol) and Me_2Acr^+–Mes (60 mg, 0.14 mmol) in MeCN (150 mL) under irradiation with a xenon lamp for 48 h was also examined to afford *p*-toluadehyde (59%), *p*-benzyl alcohol (28%) and H_2O_2 (51%) with 87% conversion of substrate determined by ^1H NMR.[18] The catalyst can be recycled because no decomposition of photocatalyst occurred under the present experimental conditions.[19] Fig. 1 shows the time profiles of the reactant and products in the photocatalytic reactions. *p*-Methylbenzyl alcohol was formed as a reaction intermediate and this was readily oxygenated to form *p*-benzaldehyde under the present reaction conditions.

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Table 1 Products and quantum yields (Φ) for photocatalytic oxygenation of methyl-substituted benzenes with 10-methylacridinium derivatives

Photocatalyst	Substrate	$E_{ox}{}^{a}$/V (*vs.* SCE)	Yield^{b} (%) RCHO : RCH_2OH : H_2O_2	$\Phi^{c,d}$
Acr^+–Mes	*p*-Xylene	1.93	75 : 15 : 74 (34 : 3 : 30)	0.25 (0.13)
	Mesitylene	1.71	77 : 19 : 75 (47 : 3 : 44)	0.30 (0.078)
	Durene	1.63	75 : 15 : 70 (35 : 1 : 33)	0.30 (0.065)
Me_2Acr^+–Mes	*p*-Xylene	1.93	100 : 0 : 100 (54 : 5 : 52)	0.37 (0.13)
	Mesitylene	1.71	66 : 2 : 65 (40 : 1 : 39)	0.26 (0.14)
	Durene	1.63	64 : 10 : 62 (37 : 2 : 36)	0.25 (0.15)
Acr^+–Ph	*p*-Xylene	1.93	12 : 18 : 10 (5 : 2 : 4)	0.042 (0.019)

[a] Taken from ref. 16. [b] After photoirradiation for 80 min. *Conditions*: [photocatalyst] = 0.2 mM, [substrate] = 4.0 mM, $[H_2O]$ = 0.9 M, $[H_2SO_4]$ = 1.0 mM. Values in parentheses are determined. [c] Values in parenthesis are determined without H_2O and H_2SO_4. [d] Based on formation of the corresponding aldehyde.

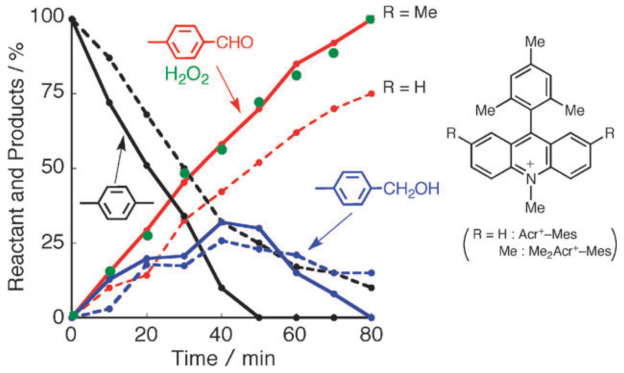
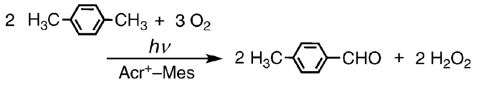


Fig. 1 Irradiation time profiles of the Acr^+–Mes (---) and Me_2Acr^+–Mes (—) catalyzed photooxygenation of *p*-xylene (4.0×10^{-3} M) in oxygen-saturated MeCN (0.6 mL) at 298 K; [photocatalyst] = 2.0×10^{-4} M; $[H_2O]$ = 0.9 M; $[H_2SO_4]$ = 1.0×10^{-3} M.

The photocatalytic oxygenation also occurred for durene and mesitylene. The one-electron oxidation potentials (E_{ox}) of the toluene derivatives in MeCN are listed in Table 1. The E_{ox} values are lower than the one-electron reduction potential (E_{red}) of the electron-transfer state of Acr^+–Mes ($Acr^•$–$Mes^{•+}$: 2.06 V *vs.* SCE in MeCN). Thus, electron transfer from toluene derivatives such as *p*-xylene to $Acr^•$–$Mes^{•+}$ is energetically feasible, whereas electron transfer from toluene itself (E_{ox} = 2.20 V)[16] to the $Mes^{•+}$ moiety is energetically unfavourable and so no photocatalytic oxidation of toluene occurred under the same experimental conditions.

The E_{ox} values of 3,5-dimethylbenzaldehyde and 1,3,4-trimethylbenzaldehyde were determined by cyclic voltammetry (CV) and second harmonic alternative current voltammetry (SHACV)[20] to be 2.30 and 2.07 V, respectively. No CV and SHACV wave for the oxidation of *p*-tolualdehyde was observed before the solvent oxidation. The E_{ox} value of *p*-tolualdehyde is higher than 2.4 V due to an electron withdrawing formyl group of *p*-tolualdehyde. The E_{ox} values of the alkylbenzenes, the oxygenated products of the corresponding benzaldehyde, are also higher than the E_{red} value of $Acr^•$–$Mes^{•+}$ (2.06 V). This is the reason why the oxygenated product of *p*-xylene was only *p*-tolualdehyde and no further oxygenated product such as *p*-phthalaldehyde was formed. On the other hand, the one-electron reduction of O_2 by $Acr^•$–$Mes^{•+}$ is energetically feasible to produce $O_2^{•-}$.[12,14]

The photocatalytic reaction is initiated by intramolecular photoinduced electron transfer from the mesitylene moiety to the singlet excited state of the Acr^+ moiety of Acr^+–Mes, which affords $Acr^•$–$Mes^{•+}$, as shown in Scheme 1.[12–14] The $Mes^{•+}$ moiety can oxidize *p*-xylene to produce the radical cation, whereas the $Acr^•$ moiety can reduce O_2 to $O_2^{•-}$.[14] The produced *p*-xylene radical cation gives the corresponding benzyl type radical *via* deprotonation. This is followed by rapid O_2 addition to afford the peroxyl radical, leading to the final oxygenated product, *p*-tolualdehyde.[11] The radical intermediates were detected by ESR ($g_{\parallel}$ = 2.101, $g_{\perp}$ = 2.009 for $O_2^{•-}$ and $g_{\parallel}$ = 2.033, $g_{\perp}$ = 2.006 for *p*-methylbenzyl peroxyl radical) in frozen MeCN: see ESI S4†).[11b,14,21,22] The disproportionation of the peroxyl radical affords *p*-tolualdehyde, *p*-methylbenzyl alcohol and O_2. *p*-Methylbenzyl alcohol is readily oxygenated to yield *p*-tolualdehyde with $Acr^•$–$Mes^{•+}$.[23] On the other hand, $O_2^{•-}$ disproportionates in the presence of protons to yield H_2O_2 and O_2 (Scheme 1).[24] H_2O and H_2SO_4 enhance the deprotonation of *p*-xylene radical cation and the disproportionation process of $O_2^{•-}$, respectively,[25] leading to a remarkable enhancement of photocatalytic reactivity by addition of aqueous sulfuric acid. The reaction pathway of photooxygenation is not the radical chain process because there was no dependence of the product quantum yield on concentration of *p*-xylene (ESI S5†) and no induction period, typical for an autoxidation process was observed (Fig. 1).[11] The overall stoichiometry of the photocatalytic reaction is given by eqn (1).



(1)

In contrast to the case of Acr^+–Mes, the photocatalytic oxygenation of *p*-xylene with O_2 in the presence of Acr^+–Ph proceeds *via* electron transfer from *p*-xylene to Acr^+–Ph. However, the lifetime of the singlet excited state of Acr^+–Ph (τ = 1.5 ns in MeCN)[11a] is much shorter than that of the electron-transfer state of Acr^+–Mes. A high concentration of substrate is needed to quench the short-lived singlet excited state of Acr^+–Ph.

The reducing ability of the electron-transfer state of Acr^+–Mes is improved by the electron-donating methyl substitution of the acridinium ring of Acr^+–Mes. Cyclic voltammograms of Acr^+–Mes and Me_2Acr^+–Mes in deaerated MeCN are shown in Fig. 2 to compare the reducing abilities of the

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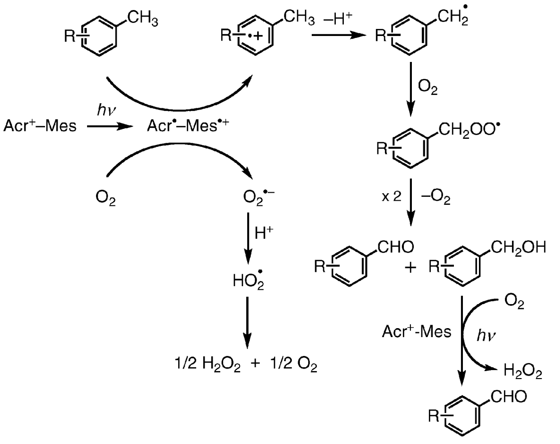

Scheme 1

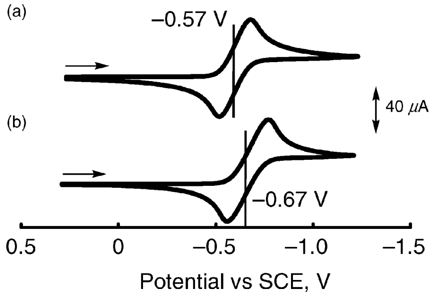

Fig. 2 Cyclic voltammograms of (a) Acr^+–Mes and (b) Me_2Acr^+–Mes (10 mM) in deaerated MeCN containing $TBAPF_6$ (0.1 M) at 298 K.

electron-transfer states of Acr^+–Mes and Me_2Acr^+–Mes. The E_{red} value of Me_2Acr^+–Mes (−0.67 V *vs.* SCE) is 0.1 eV more negative than that of Acr^+–Mes (−0.57 V).

Dynamics of the electron-transfer reduction of O_2 by the electron-transfer states of Acr^+–Mes and Me_2Acr^+–Mes were examined by nanosecond laser flash photolysis. The rates of the electron-transfer reduction were determined from the quenching of the transient absorption due to the electron-transfer state by O_2 to be 6.8×10^8 M^{-1} s^{-1} for $Acr^•$–$Mes^{•+}$,[14] and 2.0×10^{10} M^{-1} s^{-1} for $Me_2Acr^•$–$Mes^{•+}$ (see ESI S6†). Thus, the reducing ability of $Me_2Acr^•$–$Mes^{•+}$ is significantly enhanced by the methyl substitution. This may be the reason why a 100% yield of tolualdehyde and H_2O_2 with a higher quantum yield (0.37) was achieved by using Me_2Acr^+–Mes.

In conclusion, the electron-transfer states of Acr^+–Mes and Me_2Acr^+–Mes, which have both high oxidizing and reducing ability, make it possible to produce both aromatic aldehydes and H_2O_2 selectively in the photocatalytic oxygenation of alkyl aromatic compounds with oxygen for the first time. After aromatic aldehydes were formed, no further oxidation takes place because electron transfer from aromatic aldehydes to the $Mes^{•+}$ moiety is thermodynamically unfavorable. Thus, the use of charge-separation dyads as photocatalysts paves a new way for the selective oxygenation of alkyl aromatic compounds with simultaneous formation of H_2O_2.

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