

100% Selective Oxygenation of *p*-Xylene to *p*-Tolualdehyde via Photoinduced Electron Transfer

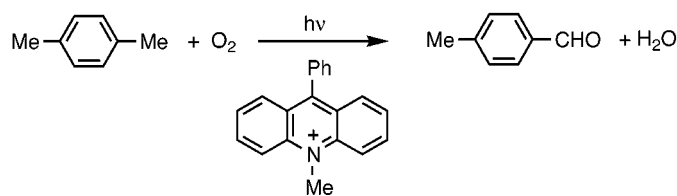
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ABSTRACT



The 100% selective oxygenation of *p*-xylene to *p*-tolualdehyde is initiated by photoinduced electron transfer from *p*-xylene to the singlet excited state of 10-methyl-9-phenylacridinium ion under visible light irradiation, yielding *p*-tolualdehyde exclusively as the final oxygenated product. The reason for the high selectivity in the photocatalytic oxygenation of *p*-xylene is discussed on the basis of the photoinduced electron transfer mechanism.

Selective oxygenation of ring-substituted toluenes to aromatic aldehydes has been one of the most important organic reactions in industrial chemistry because of useful applications of aromatic aldehydes as key chemical intermediates for production of a variety of fine or specialty chemicals such as pharmaceutical drugs, dyestuffs, pesticides, and perfume compositions.¹ A number of methods using inorganic oxidants such as chromium(IV),² cobalt(III),³ manganese(III),⁴ cerium(IV),⁵ benzeneseleninic anhydride,⁶ or peroxydisulfate/copper ion⁷ have so far been reported for

oxygenation of ring-substituted toluenes to aromatic aldehydes. However, their synthetic utility has been limited because of low yield and poor selectivity. In addition, the use of stoichiometric amounts of inorganic oxidants results in the generation of copious amounts of inorganic waste, which causes serious pollution of the environment. The electrochemical recycle of these oxidants has been reported to avoid the stoichiometric use of toxic inorganic oxidants.^{8,9} However, the development of catalytic alternatives employing clean oxidants such as O₂ is highly desired.¹⁰

This study reports that 10-methyl-9-phenylacridinium perchlorate (AcrPh⁺ClO₄⁻, green color) acts as an efficient photocatalyst for highly selective oxygenation of *p*-xylene to *p*-tolualdehyde under visible light irradiation via photo-

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

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induced electron transfer from *p*-xylene to the singlet excited state of AcrPh⁺ (¹AcrPh⁺*). In contrast to the oxidation by inorganic oxidants, the rate of photoinduced electron transfer is highly sensitive to the oxidation potentials of electron donors, and thus, no further oxidation of *p*-tolualdehyde has occurred via photoinduced electron transfer from *p*-tolualdehyde to ¹AcrPh⁺*, leading to formation of *p*-tolualdehyde as the sole oxygenated product of *p*-xylene.

Visible light irradiation of the absorption band ($\lambda_{\text{max}} = 358$ and 417 nm) of 10-methylacridinium perchlorate (AcrH⁺·ClO₄⁻; 10 mM) in oxygen-saturated acetonitrile containing *p*-xylene (30 mM) with a xenon lamp through a UV cutoff filter ($\lambda > 310$ nm) results in formation of *p*-tolualdehyde accompanied by the disappearance of *p*-xylene. After 24 h irradiation, the yield of *p*-tolualdehyde was 37%.¹¹ The product yield is improved to 66%, when the solvent, acetonitrile, is replaced by a less polar solvent, chloroform, under otherwise identical experimental conditions. The photocatalyst AcrH⁺ remained largely unchanged, but a small amount of the adduct, 9-*p*-xylenyl-10-methyl-9,10-dihydroacridine [AcrH(CH₂C₆H₄CH₃-*p*)], was produced after the photooxygenation reaction. The photooxygenated product yield is further improved to 100% when AcrH⁺ is replaced by AcrPh⁺ in chloroform as shown in Table 1. There was

Table 1. Photooxygenation of Xylenes and Toluene (3.0×10^{-2} M), Catalyzed by AcrPh⁺ (1.0×10^{-2} M) with O₂ in O₂-Saturated Chloroform at 298 K^a

	conversion	selectivity	
			
<i>p</i> -xylene	100 %	100 %	0 %
<i>m</i> -xylene	67 %	99 %	1 %
<i>o</i> -xylene	70 %	94 %	6 %
toluene	3 % ^b	100 % ^b	

^a Irradiation time is 10 h. ^b Benzaldehyde.

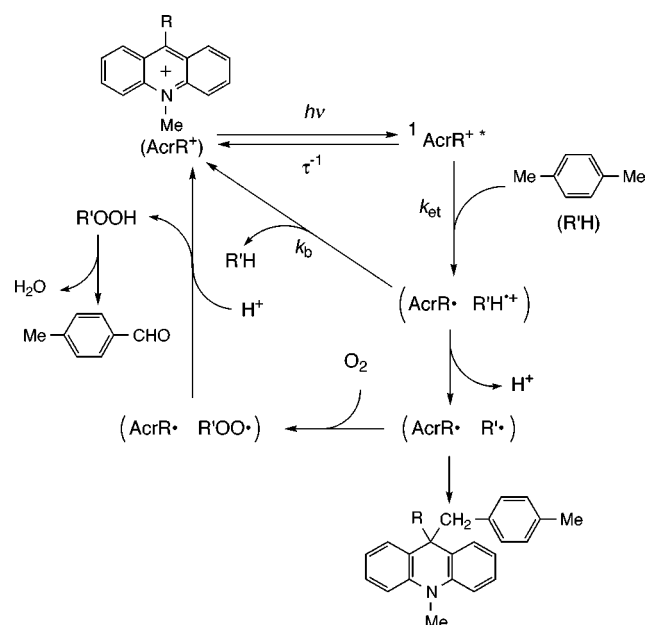
no dioxygenated product following prolonged photoirradiation. It was confirmed that there was no adduct formation between the photocatalyst, AcrPh⁺, and *p*-xylene. Thus, the 100% selective photooxygenation of *p*-xylene to *p*-tolualdehyde has been accomplished by using AcrPh⁺ as a photocatalyst in chloroform. The photoirradiation time to obtain a 100% yield of *p*-tolualdehyde (3.0×10^{-2} M) was reduced from 24 to 10 h when the xenon lamp was replaced by a high-pressure Hg lamp and an acetophenone–methanol filter ($\lambda > 300$ nm).

Other isomers, *o*- and *m*-xylene, are also converted to *o*- and *m*-tolualdehyde, respectively (Table 1). The product yields of *o*-, *m*-, and *p*-tolualdehyde and benzaldehyde after 10 h of photoirradiation of an oxygen-saturated chloroform

solution of xylenes and toluene (3.0×10^{-2} M) containing AcrPh⁺ (1.0×10^{-2} M) with a high-pressure Hg lamp ($\lambda > 300$ nm) decreases in the following order: *p*- → *o*- → *m*-xylene > toluene. The selectivity for tolualdehyde decreases in the following order: *p*- (100%) > *m*- (99%) > *o*-xylene (94%). The further oxygenation of *m*- and *o*-xylene occurs to yield small amounts of the corresponding phthalaldehyde. In the case of *p*-xylene, it was confirmed that no photooxygenation of *p*-tolualdehyde occurs when *p*-tolualdehyde was used as a starting material.

We have previously reported that oxygenation of ring-substituted toluenes to aromatic aldehydes proceeds via photoinduced electron transfer from toluenes to the singlet excited state of 10-methylacridinium ion (¹AcrH⁺*) as shown in Scheme 1 for the case of *p*-xylene.¹² The photoinduced

Scheme 1



electron transfer from *p*-xylene to ¹AcrH⁺* (k_{et}) is followed by the deprotonation of the *p*-xylene radical cation in competition with the back electron transfer (k_{b}) to the reactant pair to produce the *p*-xylenyl radical which couples with AcrH⁺ in the absence of oxygen to yield the adduct [AcrH(CH₂C₆H₄CH₃-*p*)].¹² In the presence of oxygen, the *p*-xylenyl radical is readily trapped by oxygen to give a *p*-xylenylperoxy radical that is reduced by back electron transfer from AcrH⁺ to yield *p*-xylenyl hydroperoxide, accompanied by regeneration of AcrH⁺ (Scheme 1). The hydroperoxide decomposes to yield *p*-tolualdehyde selectively.¹²


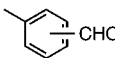
The 100% selective photocatalytic oxygenation of *p*-xylene is made possible by the difference in the reactivity of *p*-xylene and the oxygenated product, *p*-tolualdehyde, as indicated by the following fluorescence quenching experiments. The fluorescence lifetimes (τ) of AcrH⁺ ($\lambda_{\text{em}} = 488$

(11) The products were analyzed by ¹H NMR spectroscopy.

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nm) in the absence and presence of xylenes, toluene, or the corresponding aldehydes were determined by using a time-resolved fluorescence spectrofluorophotometer. The rate constants of fluorescence quenching k_q ($= K_q\tau^{-1}$) by photoinduced electron transfer are determined from the slopes of the linear Stern–Volmer plots of τ_0/τ ($\tau_0 = 37$ ns in MeCN¹³) vs the quencher concentration. The k_q values thus determined are listed in Table 2.

Table 2. Fluorescence Quenching Rate Constants of AcrH⁺ with Xylenes, Toluene, and Aldehydes in Deaerated MeCN at 298 K

	$k_q, \text{M}^{-1}\text{s}^{-1}$	
	 Me	 CHO
<i>p</i> -xylene	8.6×10^9	a
<i>m</i> -xylene	7.7×10^9	5.2×10^7
<i>o</i> -xylene	7.9×10^9	3.8×10^8
toluene	2.4×10^8	a

^a Too slow to be determined accurately.

The ¹AcrH⁺ fluorescence was quenched efficiently by electron transfer from xylenes to ¹AcrH⁺, whereas no quenching was observed by *p*-tolualdehyde ($k_q \ll 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). The k_q value decreases in the following order: *p*-xylene > *o*-xylene > *m*-xylene > *o*-tolualdehyde > toluene > *m*-tolualdehyde \gg *p*-tolualdehyde (not observed). This order is consistent with the order of the monoxygenated and dioxygenated product yields in Table 1. Thus, the faster the photoinduced electron transfer, the larger is the product yield. However, the k_q value for *p*-xylene determined in chloroform ($4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) is smaller than the value in acetonitrile in Table 2, in contrast to the improved product yield in chloroform as compared to that in the more polar solvent acetonitrile (vide supra). The improved product yield in chloroform may result from a decrease in the reorganization energy of the electron transfer with a decrease in the solvent polarity, which results in a slower back electron transfer from AcrH^{*} to the *p*-xylene radical cation in Scheme 1 (vide infra). Since the deprotonation of the *p*-xylene radical cation, which leads to the oxygenated product, competes with the back electron transfer, the slower back electron transfer results in the larger product yield.

The reorganization energies are evaluated by determining the rate constants of electron-transfer self-exchange reactions between 9-phenyl-10-methylacridinium ion (AcrPh⁺) and the corresponding one-electron reduced radical (AcrPh^{*}) in acetonitrile and chloroform. The AcrPh^{*} radical was produced by the electron-transfer reduction of AcrPh⁺ by tetrameth-

ylsemiquinone radical anion. The ESR spectrum of AcrPh^{*} was persistent for several hours in deaerated acetonitrile. The hyperfine splitting constants and the maximum slope line widths (ΔH_{msl}) were determined from a computer simulation of the ESR spectra. The ΔH_{msl} value thus determined increases linearly with an increase in the concentration of AcrPh⁺ in MeCN. Such line width variations of the ESR spectra can be used to investigate the rate processes involving the radical species. The rate constants (k_{ex}) of the electron-transfer exchange reactions between AcrPh⁺ and AcrPh^{*} were determined using eq 1, where ΔH_{msl}^0 is the maximum slope line width of the ESR spectra in the absence of AcrPh⁺, respectively, and P_i is a

$$k_{\text{ex}} = \frac{1.57 \times 10^7 (\Delta H_{\text{msl}} - \Delta H_{\text{msl}}^0)}{(1 - P_i)[\text{AcrPh}^+]} \quad (1)$$

statistical factor which can be taken as nearly zero (see Supporting Information).¹⁴ The reorganization energies (λ) of the electron-transfer reactions are obtained from the k_{ex} values using eq 2 ($Z = 10^{11} \text{ M}^{-1} \text{ s}^{-1}$), where the effect of

$$[(k_{\text{ex}})^{-1} - (k_{\text{diff}})^{-1}] = Z^{-1} \exp(\lambda/4k_{\text{B}}T) \quad (2)$$

diffusion ($k_{\text{diff}} = 2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in MeCN and $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in chloroform, respectively) is taken into account and k_{B} is the Boltzmann constant. The λ value in chloroform is determined as 0.27 eV which is smaller than the value in MeCN (0.34 eV).

Since the λ values (0.27, 0.34 eV) are much smaller than the driving force of the back electron transfer ($-\Delta G_{\text{et}}^0 = 2.36$ eV) from AcrH^{*} (E_{ox}^0 vs SCE = -0.43 V)¹⁵ to the *p*-xylene radical cation ($E_{\text{red}}^0 = 1.93$ V),¹⁶ the back electron transfer is deeply in the Marcus inverted region, where the back electron transfer rate is expected to slow as the λ value decreases.¹⁷ The slower back electron transfer rate with decreasing the solvent polarity leads to an increase in the product yield as observed experimentally.

The further improvement of the product yield by employing AcrPh⁺ instead of AcrH⁺ can also be ascribed to the slower back electron transfer rate for the former than the latter. In the Marcus inverted region, the back electron transfer becomes slower as the driving force increases. Since the E_{ox}^0 value of AcrPh^{*} (E_{ox}^0 vs SCE = -0.55 V)¹⁸ is more negative than the value of AcrH^{*} (E_{ox}^0 vs SCE = -0.43 V),¹⁵ the driving force of the back electron transfer from AcrPh^{*}

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(2.48 eV) is larger than that from AcrH[•] (2.36 eV). The larger driving force results in the slower back electron transfer, leading to the improved product yield.

The enhanced stability of AcrPh⁺ as a photocatalyst as compared to AcrH⁺ is ascribed to the steric effect of the phenyl group of AcrPh[•] which hampers the radical coupling with the deprotonated radicals, that is, the deactivation process of the photocatalyst in Scheme 1.

In conclusion, the use of AcrPh⁺ as a photocatalyst in chloroform has enabled us to accomplish the 100% selective photooxygenation of *p*-xylene to *p*-tolualdehyde as well as

(18) The E_{ox}^0 value of AcrPh[•], which corresponds to the E_{red}^0 value of AcrPh⁺, was determined by the CV measurements in acetonitrile: Fukuzumi, S.; Ohkubo, K.; Tokuda, Y.; Suenobu, T. *J. Am. Chem. Soc.* **2000**, *122*, 4286.

highly selective photooxygenation of other isomers to the corresponding aromatic aldehydes.

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Supporting Information Available: ESR spectra of AcrPh[•] in chloroform (S1) and plot of ΔH_{msl} vs [AcrPh⁺] (S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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