Addition versus Oxygenation of Alkylbenzenes with 10-Methylacridinium Ion via Photoinduced Electron Transfer

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Abstract: Addition of alkylbenzenes with 10-methylacridinium ion ($AcrH^+$) occurs efficiently under visible light irradiation in deaerated acetonitrile containing H_2O to yield 9-alkyl-10-methyl-9,10-dihydroacridine selectively. On the other hand, the photochemical reaction of $AcrH^+$ with alkylbenzenes in the presence of perchloric acid in deaerated acetonitrile yields 10-methyl-9,10-dihydroacridine, accompanied by the oxygenation of alkylbenzenes to the corresponding benzyl alcohols. The photooxygenation of alkylbenzenes occurs also in the presence of oxygen, when $AcrH^+$ acts as an efficient photocatalyst. The studies on the quantum yields and fluorescence quenching of $AcrH^+$ by alkylbenzenes as well as the laser flash photolysis have revealed that the photochemical reactions of $AcrH^+$ with alkylbenzenes in both the absence and presence of oxygen proceed via photoinduced electron transfer from alkylbenzenes to the singlet excited state of $AcrH^+$ to produce alkylbenzene radical cations and 10-methylacridinyl radical ($AcrH^\bullet$). The competition between the deprotonation of alkylbenzene radical cations and the back electron transfer from $AcrH^\bullet$ to the radical cations determines the limiting quantum yields. In the absence of oxygen, the coupling of the deprotonated radicals with $AcrH^\bullet$ yields the adducts. The photoinduced hydride reduction of $AcrH^+$ in the presence of perchloric acid proceeds via the protonation of acridinyl radical produced by the photoinduced electron transfer from alkylbenzenes. In the presence of oxygen, however, the deprotonated radicals are trapped efficiently by oxygen to give the corresponding peroxyl radicals which are reduced by the back electron transfer from $AcrH^\bullet$ to regenerate $AcrH^+$, followed by the protonation to yield the corresponding hydroperoxide. The ratios of the deprotonation reactivity from different alkyl groups of alkylbenzene radical cations were determined from both the intra- and intermolecular competitions of the deprotonation from two alkyl groups of alkylbenzene radical cations. The reactivity of the deprotonation from alkylbenzene radical cations increases generally in the order methyl < ethyl < isopropyl. The strong stereoelectronic effects on the deprotonation from isopropyl group of alkylbenzene radical cations appear in the case of the *o*-methyl isomer.

Introduction

Recent advancement in photoinduced electron transfer chemistry has uncovered a large number of useful chemical and biological processes which involve electron transfer being a key step accompanied by the cleavage and formation of chemical bonds.[1,2] We have recently demonstrated that visible light irradiation of the absorption band of 10-methylacridinium ion ($AcrH^+$, green color) in the presence of organometallic compounds as well as alkenes results in efficient C−C bond formation between these electron donors and $AcrH^+$ via photoinduced electron transfer from the donors to the singlet excited state of $AcrH^+$ to yield the alkylated or allylated adducts selectively.[3−5] Mariano et al.[6,7] have shown that photoaddition reactions of alkylbenzenes to iminium salts occur under UV light irradiation via photoinduced electron transfer. Benzylation of aromatic nitriles can also be effected by UV irradiation in the presence of alkylbenzenes via photoinduced electron transfer.[8−10] In these cases alkybenzene radical cations formed by the photoinduced electron transfer oxidation of alkylbenzenes are believed to act as reactive and important intermediates. Since alkylbenzene radical cations are known as extremely strong carbon acids in solution,[11] they undergo proton loss from an α-carbon to yield benzyl radical and analogs.[12−15] Such

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deprotonation processes from alkylbenzenes have attracted considerable interest not only because of the mechanistic aspects but also in view of the practical utility.

In particular, the role of stereoelectronic effects (the rate of deprotonation could be influenced by the relative orientation of the C_α−H bond and the aromatic π systems)[16−18] has been one of the central issues of radical cation chemistry. Controversial results have so far been obtained on the role of stereoelectronic effects. Serious doubts have been raised on the actual role of stereoelectronic effects in the competitive deprotonation between methyl and isopropyl groups of the radical cation of *p*-cymene,[19] although convincing experimental evidence has recently been reported to support the existence of stereoelectronic effects in the deprotonation from 9-ethylanthracene radical cation.[20] Certainly more data on the deprotonation from alkylbenzene radical cations in definitive systems are required to gain a more comprehensive and confirmative understanding of the reality of stereoelectronic effects.

Since benzyl radicals and analogs produced by the deprotonation of alkylbenzenes are readily trapped by oxygen,[21] there have been extensive studies concerning the oxygenation of alkylbenzenes initiated by photoinduced electron transfer.[8,22−24] However, most of the photoinduced electron transfer reactions of alkylbenzenes have so far been limited to those with sensitizers having high-energy excited sates such as dicyanobenzenes and iminium ions, requiring irradiation with UV light. Such high-energy photochemistry has usually afforded a mixture of various products.

This study reports that 10-methylacridinium perchlorate which has an absorption maximum at 358 and 417 nm is highly effective for the selective photoaddition of various alkylbenzenes and that the oxygenation of alkylbenzenes occurs in the presence of oxygen when $AcrH^+$ acts as an efficient photocatalyst.[25] The oxygenation of alkylbenzenes has also been made possible without oxygen by the photoinduced hydride transfer from alkylbenzenes to $AcrH^+$ in the presence of perchloric acid.[26] The novel oxygenation mechanism without oxygen will be revealed in relation to the photoaddition mechanism. The clean and simple products formed by the photoreduction of $AcrH^+$ by alkylbenzenes together with the excellent stability of $AcrH^+$ as a photocatalyst for the photooxygenation reactions provide a nice opportunity to gain a more comprehensive and confirmative understanding of the photoinduced electron transfer reactions of alkylbenzenes as well as the reality of the stereoelectronic effects on the deprotonation from alkylbenzene radical cations.

Experimental Section

Materials. 10-Methylacridinium iodide was prepared by the reaction of acridine with methyl iodide in acetone, and it was converted to the perchlorate salt ($AcrH^+ClO_4^-$) by addition of magnesium perchlorate to the iodide salt, and purified by recrystallization from methanol.[27] Alkylbenzenes and perchloric acid ($HClO_4$; 70%) were obtained commercially. Acetonitrile and methanol used as solvents were purified and dried by the standard procedure.[28]

Reaction Procedure. Typically, a deaerated [$^2H_3$]acetonitrile (CD_3CN)/deuterium oxide (D_2O) (7:1 v/v) solution (0.8 mL) containing $AcrH^+$ (8.0×10^{-3} M) was added to an NMR tube sealed with a rubber septum under an atmospheric pressure of argon. After PhMe (4.0×10^{-2} M) was added to the solution by means of a microsyringe and mixed, the solution was irradiated with a high-pressure mercury lamp through an acetophenone−methanol filter transmitting $\lambda > 300$ nm at room temperature. After the reaction was complete, when the solution became colorless, the products were analyzed by ^1H NMR spectroscopy. The ^1H NMR measurements were performed using Japan Electron Optics JNM-PS-100 (100 MHz) and JNM-GSX-400 (400 MHz) NMR spectrometers. ^1H NMR (CD_3CN/D_2O (7:1 v/v): ($AcrHCH_2Ph$) δ 2.76 (d, 2H, $J = 7.3$ Hz), 3.27 (s, 3H), 4.16 (t, 1H, $J = 7.3$ Hz), 6.7−7.3 (m, 13H); (AcrHCH(Me)Ph) δ 1.10 (d, 3H, $J = 7.3$ Hz), 2.84 (quintet, 1H, $J = 7.3$ Hz), 3.14 (s, 3H), 3.99 (d, 1H, $J = 7.3$ Hz), 6.7−7.3 (m, 13H); ($AcrHCMe_2Ph$) δ 1.17 (s, 6H), 3.01 (s, 3H), 4.05 (s, 1H), 6.8−7.3 (m, 13H); (AcrHCH(OMe)Ph) δ 3.02 (d, 3H, $J = 4.9$ Hz), 3.46 (s, 3H), 4.11 (d, 1H, $J = 6.8$ Hz), 4.29 (d, 1H, $J = 6.8$ Hz), 6.7−7.4 (m, 13H); ($AcrHCHPh_2$) δ 3.45 (s, 3H), 4.06 (d, 1H, $J = 10.7$ Hz), 4.80 (d, 1H, $J = 10.7$ Hz), 6.6−7.4 (m, 18H); (AcrHCH(*c*-C_3H_5)Ph) δ 0.20−0.25 (m, 2H), 0.42−0.46 (m, 2H), 1.1−1.2 (m, 1H), 1.85 (dd, 1H, $J = 6.4$, 10.3 Hz), 3.00 (s, 3H), 4.26 (d, 1H, $J = 6.4$ Hz), 6.6−7.3 (m, 13H); ($AcrHCH_2CH{=}CHPh$) δ 2.41 (t, 2H, $J = 6.6$ Hz), 3.35 (s, 3H), 4.09 (t, 1H, $J = 6.6$ Hz), 5.9−6.1 (m, 2H), 6.9−7.4 (m, 13H); ($AcrHCH_2C_6H_4$-*p*-Me) δ 2.24 (s, 3H), 2.71 (d, 2H, $J = 7.3$ Hz), 3.27

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(s, 3H), 4.13 (t, 1H, J = 7.3 Hz), 6.6−7.2 (m, 12H); (AcrHCH$_2$C$_6$H$_3$-3,5-Me$_2$) δ 2.13 (s, 6H), 2.66 (d, 2H, J = 6.8 Hz), 3.27 (s, 3H), 4.11 (t, 1H, J = 6.8 Hz), 6.3−7.2 (m, 11H); (AcrHCH$_2$C$_6$H$_4$-*p*-Et) δ 1.16 (t, 3H, J = 7.3 Hz), 2.54 (q, 2H, J = 7.3 Hz), 2.72 (d, 2H, J = 6.8 Hz), 3.24 (s, 3H), 4.14 (t, 1H, J = 6.8 Hz), 6.6−7.3 (m, 12H); (AcrHCH$_2$C$_6$H$_4$-*m*-Et) δ 1.07 (t, 3H, J = 7.3 Hz), 2.45 (q, 2H, J = 7.3 Hz), 2.73 (d, 2H, J = 6.8 Hz), 3.23 (s, 3H), 4.14 (t, 1H, J = 6.8 Hz), 6.5−7.3 (m, 12H); (AcrHCH$_2$C$_6$H$_4$-*o*-Et) δ 0.97 (t, 3H, J = 7.8 Hz), 2.26 (q, 2H, J = 7.8 Hz), 2.79 (d, 2H, J = 7.3 Hz), 3.37 (s, 3H), 4.11 (t, 1H, J = 7.3 Hz), 6.5−7.3 (m, 12H); (AcrHCH(Me)C$_6$H$_4$-*p*-Me) δ 1.07 (d, 3H, J = 6.8 Hz), 2.22 (s, 3H), 2.81 (quint, 1H, J = 7.3 Hz), 3.14 (s, 3H), 3.97 (d, 1H, J = 7.3 Hz), 6.6−7.3 (m, 12H); (AcrHCH(Me)C$_6$H$_4$-*m*-Me) δ 1.08 (d, 3H, J = 7.3 Hz), 2.15 (s, 3H), 2.80 (quint, 1H, J = 6.8 Hz), 3.12 (s, 3H), 3.98 (d, 1H, J = 6.8 Hz), 6.5−7.3 (m, 12H); (AcrHCH(Me)C$_6$H$_4$-*o*-Me) δ 1.02 (d, 3H, J = 7.3 Hz), 1.66 (s, 3H), 3.21 (quint, 1H, J = 7.3 Hz), 3.28 (s, 3H), 3.96 (d, 1H, J = 7.8 Hz), 6.5−7.3 (m, 12H); (AcrHCH$_2$C$_6$H$_4$-*p*-Pr^i) δ 1.17 (d, 6H, J = 6.8 Hz), 2.73 (d, 2H, J = 6.8 Hz), 2.81 (sept, 1H, J = 6.8 Hz), 3.20 (s, 3H), 4.16 (t, 1H, J = 6.8 Hz), 6.7−7.2 (m, 12H); (AcrHCH$_2$C$_6$H$_4$-*m*-Pr^i) δ 1.08 (d, 6H, J = 6.8 Hz), 2.69 (sept, 1H, J = 6.8 Hz), 2.73 (d, 2H, J = 6.8 Hz), 3.22 (s, 3H), 4.14 (t, 1H, J = 6.8 Hz), 6.4−7.3 (m, 12H); (AcrHCH$_2$C$_6$H$_4$-*o*-Pr^i) δ 0.96 (d, 6H, J = 6.8 Hz), 2.82 (d, 2H, J = 7.3 Hz), 2.84 (sept, 1H, J = 6.8 Hz), 3.38 (s, 3H), 4.10 (t, 1H, J = 7.7 Hz), 6.7−7.3 (m, 12H); (AcrHCMe$_2$C$_6$H$_4$-*p*-Me) δ 1.15 (s, 6H), 2.25 (s, 3H), 2.99 (s, 3H), 4.01 (s, 1H), 6.7−7.2 (m, 12H); (AcrHCMe$_2$C$_6$H$_4$-*m*-Me) δ 1.16 (s, 6H), 2.18 (s, 3H), 2.98 (s, 3H), 4.01 (s, 1H), 6.4−7.3 (m, 12H); (Ph$_2$CHCHPh$_2$) δ 5.08 (s, 2H). ^{1}H NMR (CD$_3$OD): (AcrHCH$_2$C$_6$H$_4$-*p*-Et) δ 1.19 (t, 3H, J = 7.8 Hz), 2.57 (q, 2H, J = 7.8 Hz), 2.71 (d, 2H, J = 6.8 Hz), 3.20 (s, 3H), 4.06 (t, 1H, J = 6.8 Hz), 6.5−7.2 (m, 12H); (AcrHCH$_2$C$_6$H$_4$-*m*-Et) δ 1.07 (t, 3H, J = 7.8 Hz), 2.58 (q, 2H, J = 7.8 Hz), 2.72 (d, 2H, J = 6.4 Hz), 3.19 (s, 3H), 4.07 (t, 1H, J = 6.4 Hz), 6.3−7.3 (m, 12H); (AcrHCH$_2$C$_6$H$_4$-*o*-Et) δ 0.97 (t, 3H, J = 7.8 Hz), 2.21 (q, 2H, J = 7.8 Hz), 2.79 (d, 2H, J = 7.3 Hz), 3.35 (s, 3H), 4.04 (t, 1H, J = 7.3 Hz), 6.5−7.3 (m, 12H); (AcrHCH(Me)C$_6$H$_4$-*p*-Me) δ 1.10 (d, 3H, J = 7.3 Hz), 2.22 (s, 3H), 2.79 (quint, 1H, J = 7.1 Hz), 3.09 (s, 3H), 3.90 (d, 1H, J = 6.8 Hz), 6.5−7.2 (m, 12H); (AcrHCH(Me)C$_6$H$_4$-*m*-Me) δ 1.12 (d, 3H, J = 6.8 Hz), 2.13 (s, 3H), 2.79 (quint, 1H, J = 6.8 Hz), 3.08 (s, 3H), 3.90 (d, 1H, J = 6.8 Hz), 6.3−7.3 (m, 12H); (AcrHCH(Me)-C$_6$H$_4$-*o*-Me) δ 1.05 (d, 3H, J = 7.3 Hz), 1.61 (s, 3H), 3.2 (m, 1H), 3.25 (s, 3H), 3.89 (d, 1H, J = 8.3 Hz), 6.5−7.3 (m, 12H); (AcrHCH$_2$C$_6$H$_4$-*p*-Pr^i) δ 1.21 (d, 6H, J = 6.8 Hz), 2.72 (d, 2H, J = 6.8 Hz), 2.83 (sept, 1H, J = 6.8 Hz), 3.16 (s, 3H), 4.07 (t, 1H, J = 6.8 Hz), 6.5−7.2 (m, 12H); (AcrHCH$_2$C$_6$H$_4$-*m*-Pr^i) δ 1.07 (d, 6H, J = 6.8 Hz), 2.65 (sept, 1H, J = 6.8 Hz), 2.73 (d, 2H, J = 6.8 Hz), 3.17 (s, 3H), 4.08 (t, 1H, J = 6.8 Hz), 6.5−7.2 (m, 12H); (AcrHCH$_2$C$_6$H$_4$-*o*-Pr^i) δ 0.96 (d, 6H, J = 6.8 Hz), 2.78 (sept, 1H, J = 6.8 Hz), 2.82 (d, 2H, J = 7.3 Hz), 3.36 (s, 3H), 4.04 (t, 1H, J = 7.3 Hz), 6.7−7.3 (m, 12H); (AcrHCMe$_2$C$_6$H$_4$-*p*-Me) δ 1.17 (s, 6H), 2.25 (s, 3H), 2.96 (s, 3H), 3.93 (s, 1H), 6.5−7.2 (m, 12H); (AcrHCMe$_2$C$_6$H$_4$-*m*-Me) δ 1.19 (s, 6H), 2.16 (s, 3H), 2.94 (s, 3H), 3.93 (s, 1H), 6.5−7.3 (m, 12H).

The isolation of products was carried out with about 100 times as large a scale as compared to that of the procedure described above. Typically, a deaerated MeCN (50 mL)/H$_2$O (15 mL) solution containing AcrH$^+$ClO$_4^-$ (100 mg) and PhMe (2.0 mL) was irradiated with a high-pressure mercury lamp through an acetophenone−methanol filter transmitting $\lambda > 300$ nm at room temperature. After the reaction was complete, water was added to the resulting solution. The vacuum concentration resulted in precipitation of the products. The isolated products were analyzed by ^{1}H NMR spectroscopy in CDCl$_3$. The product was identified as 9-benzyl-10-methyl-9,10-dihydroacridine (AcrHCH$_2$Ph). The isolation yield was 93%. The elemental analysis of the isolated products gave satisfactory results. Anal. Calcd for C$_{21}$H$_{19}$N (AcrHCH$_2$Ph): C, 88.38; H, 6.71; N, 4.91. Found: C, 88.38; H, 6.62; N, 5.02. Anal. Calcd for C$_{28}$H$_{23}$N(AcrHC$_{14}$H$_{11}$): C, 90.04; H, 6.21; N, 3.75. Found: C, 90.27; H, 6.10; N, 3.77.

The AcrH$^+$-catalyzed photooxidation of alkylbenzenes with oxygen was carried out in an oxygen-saturated CD$_3$CN solution (0.80 mL) containing AcrH$^+$ (8.0×10^{-3} M). After PhMe (3.0×10^{-2} M) was added to the solution by means of a microsyringe and mixed, the solution was irradiated with a high-pressure mercury lamp through an acetophenone−methanol filter transmitting $\lambda > 300$ nm at room temperature. The oxidized products were identified by comparing the ^{1}H NMR spectra of the products with those of the authentic samples.

The photochemical reactions of AcrH$^+$ with alkylbenzenes were also carried out in the presence of HClO$_4$ (70%) in acetonitrile. The products were identified by comparison with authentic sample by using HPLC and ^{1}H NMR. The increase of photoreduction products of AcrH$^+$ and the decrease of AcrH$^+$ were monitored by using HPLC and UV−vis, respectively.

Quantum Yield Determinations. A standard actinometer (potassium ferrioxalate)[29] was used for the quantum yield determination of the photoaddition of alkylbenzenes with AcrH$^+$ and the AcrH$^+$-catalyzed photooxygenation of alkylbenzenes. Typically a square quartz cuvette (10 mm i.d.) containing an MeCN−H$_2$O or MeOH solution (3.0 cm^3) of AcrH$^+$ (3.0×10^{-4} M) and alkylbenzenes (3.0×10^{-3} to 8.0×10^{-2} M) was irradiated with monochromatized light of $\lambda = 358$ nm from a Shimadzu RF-5000 fluorescence spectrophotometer. Under the conditions of actinometry experiments, both the actinometer and AcrH$^+$ absorbed essentially all the incident light of $\lambda = 358$ nm. The light intensities of monochromatized light of $\lambda = 358$ nm were determined as 1.83×10^{-8} and 5.35×10^{-8} einstein s^{-1} with slit widths of 10 and 20 nm, respectively. The photochemical reaction was monitored using a Shimadzu UV-160A spectrophotometer. The quantum yields of the photoreduction of AcrH$^+$ by alkylbenzenes were determined from the decrease in absorbance due to AcrH$^+$ ($\lambda = 396$ nm, $\epsilon = 3.5 \times 10^3$ M^{-1} cm^{-1}) and those of the photooxygenation with oxygen were determined from the rate of formation of the oxygenated products.

Fluorescence Quenching. Fluorescence measurements were carried out on a Shimadzu RF-5000 spectrofluorophotometer. The excitation wavelength of AcrH$^+$ was 360 nm in MeCN or MeOH. The monitoring wavelength was that corresponding to the maxima of the emission band at 488 nm. The solution was deoxygenated by argon purging for 10 min or saturated with oxygen prior to the measurements. Relative emission intensities were measured for an MeCN or MeOH solution containing AcrH$^+$ (3.0×10^{-5} M) and alkylbenzene at various concentrations (3.0×10^{-3} to 8.0×10^{-2} M). There was no change in the shape, but there was a change in the intensity of the fluorescence spectrum by the addition of an alkylbenzene. The Stern−Volmer relationship (eq 1) was obtained for the ratio of the emission intensities

$$I_0/I = 1 + K_q[\mathrm{RH}] \tag{1}$$

in the absence and presence of alkylbenzene (I_0/I) and the concentrations of alkylbenzene ([RH]). The fluorescence lifetime τ of AcrH$^+$ was determined as 37 ns in MeCN by single photon counting using a Horiba NAES-1100 time-resolved spectrofluorophotometer. The quenching rate constants k_q ($=K_q\tau^{-1}$) in MeCN and MeOH were obtained from the quenching constants K_q and the fluorescence lifetime; $\tau = 37$ and 31 ns in MeCN and MeOH, respectively.[30]

Laser-Flash Photolysis. A sample is contained in a 10 × 10 mm^2 quartz cell. Deaerated MeCN containing AcrH$^+$ (5.0×10^{-5} M) and alkylbenzene was excited by third harmonic light (355 nm) of a Nd:YAG laser (4-ns pulses; 180 mJ/pulse). The excitation light was parallel to the analyzing light from a 450-W Xe lamp (Osram, XBO-450). The analyzing light passing through a sample cell was focused on a computer-controlled monochromator (CVI Digikrom-240) by two lenses and four mirrors. The output light of the monochromator was monitored by a photomultiplier tube (PMT; Hamamatsu Photonix, R1417). The signal from a PMT was recorded on a transient digitizer (Tektronix, 7912AD with plug-ins, 7A19 and 7B92A). Total system control and date processing were carried out with a microcomputer (Sharp, X-6800) which was connected to the measurement components with a GP−IB interface.

Theoretical Calculations. The theoretical studies were performed using the PM3 molecular orbital method.[31,32] The MOPAC program (QCPE No. 455), which was revised as OS/2 Version 5.01 to adapt

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(30) Poulos, A. T.; Hammond, G. S.; Burton, M. E. *Photochem. Photobiol.* **1981**, *34*, 169.

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Table 1. Photoaddition of Alkylbenzenes (4×10^{-2} to 2×10^{-2} M) with $AcrH^+$ (8.5×10^{-3} M) in Deaerated CD_3CN Containing D_2O at 298 K

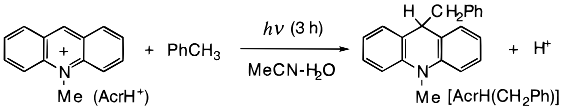
no.	alkylbenzene	time (h)	product (yield, %)[a]
1	PhMe[b]	3	$AcrHCH_2Ph$ (100) [93]
2	PhEt[b]	3	AcrHCH(Me)Ph (100)
3	$PhPr^i$ [b]	3	$AcrHCMe_2Ph$ (100) [92]
4	*p*-$Me_2C_6H_4$[c]	6	$AcrHCH_2C_6H_4$-*p*-Me (100) [88]
5	1,3,5-$Me_3C_6H_3$[c]	17	$AcrHCH_2C_6H_3$-3,5-Me_2 (100)
6	$PhCH_2OMe$[b]	3	AcrHCH(OMe)Ph (100)
7	PhCH2(*c*-C_3H_5)[b]	3	AcrHCH(*c*-C_3H_5)Ph (100)
8	$PhCH_2CH{=}CH_2$[b]	3	$AcrHCH_2CH{=}CHPh$ (100)
9	$PhCH_2Ph$[b]	3	$AcrHCHPh_2$ (77), $(PhCH_2)_2$ (12), $(AcrH)_2$ (12)
10	9,10-dihydroanthracene[b]	3	$AcrHC_{14}H_{11}$ (84), $(AcrH)_2$ (8)

[a] The values in brackets refer to the isolated product yields (%). [b] CD_3CN/D_2O (7:1 v/v). [c] CD_3CN/D_2O (3:1 v/v).

for the use on a NEC PC computer, was obtained through the Japan Chemistry Program Exchange (JCPE).[33] The calculations were also performed by using the MOL-GRAPH program, Version 2.8, by Daikin Industries, Ltd. The structural output was recorded by using the MOPC program (JCPE No. P038). The final geometry and energetics were obtained by optimizing the total molecular energy with respect to all structural variables. The geometries of alkylbenzene benzyl radicals were optimized using the unrestricted Hartree–Fock (UHF) formalism.

Results and Discussion

Photoaddition of Alkylbenzenes with 10-Methylacridinium Ion. Visible light irradiation of the absorption band of 10-methylacridinium perchlorate ($AcrH^+ClO_4^-$) in deaerated acetonitrile (MeCN)/H_2O (7:1 vol %) solution containing toluene for 3 h gave 9-benzyl-10-methyl-9,10-dihydroacridine ($AcrHCH_2Ph$), as shown in eq 2. The products are well identified by the ^1H NMR spectra and elemental analysis (see the Experimental Section). The yield of $AcrHCH_2Ph$ determined by ^1H NMR was 100%, and $AcrHCH_2Ph$ was isolated as the sole product (the isolated yield was 93%; see the Experimental Section). The $AcrH^+$ is also photoreduced by other alkylbenzenes to yield the corresponding 9-substituted 10-methyl-9,10-dihydroacridine (AcrHR) as shown in Table 1. The presence of a sufficient amount of H_2O is essential to obtain high yields of AcrHR. In most cases the alkyl group which is deprotonated from the benzyl position is introduced selectively at the C-9 position of the acridine moiety (nos. 1–8 in Table 1). α-Cyclopropyltoluene was introduced at the C-9 position without opening the cyclopropyl ring (no. 7). The photoaddition of allylbenzene yields the cinnamyl adduct (no. 8). In the case of photoreduction of $AcrH^+$ by diphenylmethane (no. 9) and 9,10-dihydroanthracene (no. 10), however, 10,10′-dimethyl-9,9′,10,10′-tetrahydro-9,9′-biacridine [$(AcrH)_2$] is also obtained as a minor product in the photoreduction of $AcrH^+$. In this case, the same amounts of the other homocoupling products, i.e., 1,1,2,2-tetraphenylethane and 9,9′-bis(9,10-dihydroanthracene), as that of $(AcrH)_2$ are also obtained.



(2)

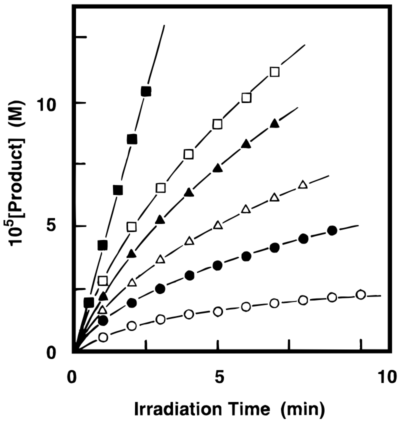
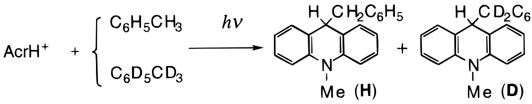


Figure 1. Photoaddition of *p*-xylene (1.4×10^{-2} M) with $AcrH^+$ (3.0×10^{-4} M) in deaerated MeCN containing H_2O: 0 M (○), 9.3×10^{-2} M (●), 1.9×10^{-1} M (△), 3.7×10^{-1} M (▲), 5.6×10^{-1} M (□), 5.6 M (■) at 298 K; irradiation with monochromatized light of $\lambda = 358$ nm, slit width 20 nm from a xenon lamp of a Shimadzu RF-5000 fluorescence spectrophotometer.

Irradiation of the absorption band of $AcrH^+$ ($\lambda_{max} = 358$ nm) in deaerated MeCN containing alkylbenzene results in the decrease in the absorption band of $AcrH^+$ and the concomitant increase in the absorption band ($\lambda_{max} = 285$ nm) due to the adduct. The rate of formation of the adduct decreases gradually with a progress of the photoaddition as shown in Figure 1. The addition of H_2O to the MeCN solution results in a remarkable acceleration of the rate to approach a constant rate with an increase in [H_2O]. As shown in eq 2, the photoaddition of alkylbenzenes with $AcrH^+$ is accompanied by the liberation of H^+ from the benzyl position of alkylbenzenes. The liberation of H^+ is observed as the low-field shift of H_2O protons in the ^1H NMR spectra as the reaction proceeds. Thus, the acceleration of the rate with an increase in [H_2O] may be ascribed to that of the deprotonation step, which may be involved as a rate-determining step for the photoaddition reaction, because of the strong solvation of H^+ with H_2O as discussed later.

The presence of a rate-determining deprotonation step is confirmed by the deuterium isotope effects on the photoaddition reactions (eq 2). The deuterium isotope effects (Y_H/Y_D) on the deprotonation process are determined from intermolecular competition between toluene-h_8 and toluene-d_8 as shown in eq 3, where Y_H and Y_D are the product yields of the toluene-h_8 adduct (**H**) and toluene-d_8 (**D**), respectively. The Y_H/Y_D values of toluene and ethylbenzene are determined as 3.7 and 2.5, respectively.



(3)

Photoinduced Electron Transfer. Irradiation of the absorption bands of $AcrH^+$ causes fluorescence at 488 nm in MeCN. The fluorescence of $^1AcrH^{+*}$ is quenched efficiently by alkylbenzenes. The quenching rate constants k_q are determined

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Table 2. Gibbs Energy Change (ΔG_{et}) of Photoinduced Electron Transfer from Alkylbenzenes to $^1AcrH^{+*}$, Fluorescence Quenching Rate Constants (k_q) of $^1AcrH^{+*}$ by Alkylbenzenes, and Rate Constants (k_{obs}) and Limiting Quantum Yields Φ_∞ in the Photoaddition of Alkylbenzenes with $AcrH^+$ in Deaerated MeCN Containing H_2O or in Deaerated MeOH[a] at 298 K

alkylbenzene	ΔG_{et}[b] (kcal mol^{-1})	k_q ($M^{-1}\ s^{-1}$)	k_{obs} ($M^{-1}\ s^{-1}$)	Φ_∞
PhMe[c]	+0.7	3.4×10^8 (6.0×10^8)	3.8×10^8 (5.2×10^8)	0.13 (0.13)
p-MeC_6H_4Me[d]	−6.0	1.4×10^{10} (1.2×10^{10})	1.1×10^{10} (1.1×10^{10})	0.04 (0.050)
p-Me(Et)C_6H_4		(1.3×10^{10})	(1.2×10^{10})	(0.057)
p-Me(Pr^i)C_6H_4		(1.1×10^{10})	(7.5×10^9)	(0.051)
p-$Et_2C_6H_4$		(1.1×10^{10})	(1.1×10^{10})	(0.078)
m-$Me_2C_6H_4$		(1.2×10^{10})	(1.0×10^{10})	(0.068)
m-Me(Et)C_6H_4		(1.0×10^{10})	(9.7×10^9)	(0.079)
1,3,5-$Me_2C_6H_4Me$[d]	−4.8	1.3×10^{10} (1.3×10^{10})	*e* (1.1×10^{10})	$\sim 10^{-3}$ (0.033)
p-$MeOC_6H_4Me$[d]		1.8×10^{10}	*e*	*e*
$PhCH_2Me$[f]	−1.2	3.5×10^8 (5.7×10^8)	4.3×10^8 (5.2×10^8)	0.16 (0.17)
$PhCHMe_2$[f]	−0.7	1.6×10^8 (3.2×10^8)	3.2×10^8 (4.2×10^8)	0.20 (0.18)
$PhCH_2Ph$[f]		8.5×10^8	9.2×10^8	0.22
$PhCH_2CH{=}CH_2$[f]		2.5×10^8	2.7×10^8	0.04
$PhCH_2OH$		(6.5×10^8)	(7.1×10^8)	(0.43)
p-$MeC_6H_4CH_2OH$		(9.0×10^9)	(1.1×10^{10})	(0.30)

[a] The values in parentheses are those obtained in MeOH. [b] The E°_{ox} values of alkylbenzenes are taken from ref 34. [c] $[H_2O] = 0.55$ M. [d] $[H_2O] = 5.5$ M. [e] Too slow to be determined accurately or no reaction. [f] $[H_2O] = 0$ M.

from the slopes of the Stern−Volmer plots and lifetime of the singlet excited state $^1AcrH^{+*}$ ($\tau = 37$ ns in MeCN and $\tau = 31$ ns in MeOH). The k_q values thus determined are listed in Table 2. The Gibbs energy change of photoinduced electron transfer from alkylbenzenes to $^1AcrH^{+*}$ (ΔG°_{et}) is given by eq 4, where

$$\Delta G^\circ_{et} = F(E^\circ_{ox} - E^\circ_{red}) \qquad (4)$$

E°_{ox} and E°_{red} are the one-electron oxidation potentials of alkylbenzenes and the one-electron reduction potential of $^1AcrH^{+*}$ (2.32 V).[4] Since the one-electron oxidation potentials of various alkylbenzenes have previously been reported,[34] the ΔG°_{et} values are determined by using eq 4 as listed in Table 2 for comparison. The k_q value increases with a decrease in the ΔG°_{et} value to reach a diffusion limit value in MeCN ($2.0 \times 10^{10}\ M^{-1}\ s^{-1}$) as the photoinduced electron transfer becomes energetically more favorable (i.e., more exergonic). Thus, the fluorescence quenching of $^1AcrH^{+*}$ by alkylbenzenes may occur via photoinduced electron transfer from alkylbenzenes (RH) acting as electron donors to the singlet excited state $^1AcrH^{+*}$ (eq 5).

$$RH + {}^1AcrH^{+*} \rightarrow RH^{\bullet +} + AcrH^\bullet \qquad (5)$$

Laser flash irradiation (355 nm from a Nd:YAG laser) of 10-methylacridinium ion (5.0×10^{-5} M) in deaerated MeCN solution containing diphenylmethane (1.3×10^{-2} M) gave transient absorption of 10-methylacridinyl radical ($AcrH^\bullet$; a broad absorption band between 450 and 540 nm)[35] as shown in Figure 2. When ethylbenzene is used instead of diphenylmethane, the transient absorption of $AcrH^\bullet$ is observed as well. The concomitant formation of alkylbenzene radical cations could not be confirmed because of the overlap of the absorption bands (e.g., 445 nm for ethylbenzene radical cation)[36] with the depletion of $AcrH^+$. However, the direct observation of $AcrH^\bullet$ in Figure 2 confirms the occurrence of photoinduced electron transfer from alkylbenzenes to the singlet excited state $^1AcrH^{+*}$ to yield $AcrH^\bullet$ and alkylbenzene radical cation.

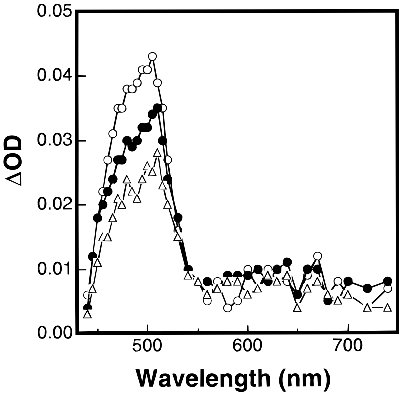
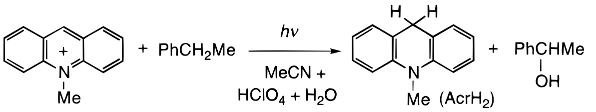


Figure 2. Transient absorption spectra observed in laser flash photolysis of $AcrH^+$ (5×10^{-5} M) in deaerated MeCN containing diphenylmethane (5×10^{-2} M). Spectra were recorded 1 μs (○), 7 μs (●), and 17 μs (△) after the laser pulse.

Photooxygenation of Alkylbenzenes with $AcrH^+$ in the Presence of $HClO_4$. In contrast with the photoaddition of alkylbenzenes with $AcrH^+$ (eq 2), the photooxygenation of ethylbenzene to 1-phenyl-1-ethanol occurs in the photochemical reaction of $AcrH^+$ with ethylbenzene in the presence of perchloric acid [$HClO_4$ (70%); 1.2 M, containing 2.9 M H_2O] in deaerated MeCN as shown in eq 6, where $AcrH^+$ is reduced to 10-methyl-9,10-dihydroacridine ($AcrH_2$) instead of the adduct.



(6)

In the case of the other alkylbenzenes such as cumene and diphenylmethane, the photoinduced hydride reduction of $AcrH^+$ to $AcrH_2$ occurs in the presence of $HClO_4$, accompanied by the oxygenation of alkylbenzenes to the corresponding benzyl alcohol as shown in Table 3. When the $HClO_4$ concentration is reduced from 1.2 to 0.10 M in the photochemical reaction of $AcrH^+$ with diphenylmethane, both $AcrH_2$ and $AcrHCHPh_2$ are obtained in the ratio 59:41. In the case of the photoinduced hydride reduction of $AcrH^+$ by diphenylmethane, the corresponding dimer, i.e., 1,1,2,2-tetraphenylethane was also obtained in addition to benzhydrol. The yield of 1,1,2,2-tetraphenylethane in the presence of $HClO_4$ corresponds to that of 1,1,2,2-tetraphenylethane and 10,10′-dimethyl-9,9′-biacridine [$(AcrH)_2$] in the absence of $HClO_4$. Figure 3 shows that the formation of

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(34) (a) Fukuzumi, S.; Kochi, J. K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 969. (b) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968. (c) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916.

(35) (a) Peters, K. S.; Pang, E.; Rudzki, J. *J. Am. Chem. Soc.* **1982**, *104*, 5535. (b) Poulos, A. T.; Hammond, G. S.; Burton, M. E. *Photochem. Photobiol.* **1981**, *34*, 169.

(36) Bockman, T. M.; Karpinski, Z. J.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 1970.

Table 3. Photochemical Reaction of $AcrH^+$ (1.5×10^{-3} M) with Alkylbenzenes (4.0×10^{-2} M) in the Presence of $HClO_4$ (1.2 M) in Deaerated CD_3CN

	yield (%)		
alkylbenzene	$AcrH_2$	alcohol	dimer
$PhCH_2Me$	88	53 (PhCH(Me)OH)	
$PhCHMe_2$	92	46 ($PhCMe_2OH$)	
$PhCH_2Ph$	78	44 (Ph_2CHOH)	13 ($(PhCH_2)_2$)

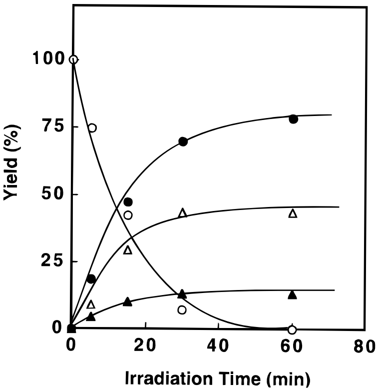


Figure 3. Photochemical reaction of $AcrH^+$ (○, 2.4×10^{-2} M) with diphenylmethane (6.0×10^{-2} M) in the presence of $HClO_4$ (1.2 M) in deaerated CD_3CN under irradiation with $\lambda > 366$ nm light from a high-pressure mercury lamp, monitored by ^1H NMR: $AcrH_2$ (●), Ph_2CHOH (△), and $(Ph_2CH)_2$ (▲).

$AcrH_2$ is concomitant with the decrease of $AcrH^+$, indicating that $AcrH_2$ is formed directly from $AcrH^+$ rather than a subsequent photochemical reaction of AcrHR which could be initially formed.

Quantum Yields. The quantum yields (Φ) of the photoaddition of alkylbenzenes with $AcrH^+$ in deaerated MeCN containing H_2O (0−5.5 M) or in MeOH and those of the photoinduced hydride reduction of $AcrH^+$ by alkylbenzenes in the presence of $HClO_4$ (0.40 M) in MeCN containing H_2O (1.0 M) were determined from the decrease in the absorption band due to $AcrH^+$ ($\lambda_{max} = 358$ nm) and the increase in the concentration of $AcrH_2$ determined by HPLC, respectively. The Φ values in the absence and presence of $HClO_4$ increase with an increase in the concentration of alkylbenzene ([RH]), to approach a limiting value (Φ_∞) according to eq 7 as shown in Figure 4. Equation 7 is rewritten by eq 8, and the linear plots

$$\Phi = \Phi_\infty K_{obs}[RH]/(1 + K_{obs}[RH]) \qquad (7)$$

$$\Phi^{-1} = \Phi_\infty^{-1}[1 + (K_{obs}[RH])^{-1}] \qquad (8)$$

of Φ^{-1} vs $[RH]^{-1}$ are shown in Figure 5. From the slopes and intercepts are obtained the Φ_∞ and K_{obs} values. The K_{obs} values can be converted to the corresponding rate constants (k_{obs}) provided that the excited state of $AcrH^+$ involved in the photochemical reaction is singlet ($^1AcrH^{+*}$; $k_{obs} = K_{obs}\tau^{-1}$, $\tau = 37$ ns in MeCN, $\tau = 31$ ns in MeOH). The Φ_∞ and k_{obs} values of photoaddition of alkylbenzene to $AcrH^+$ in MeCN containing H_2O and in MeOH are listed in Table 2. The Φ_∞ and k_{obs} values of the photoinduced hydride reduction of $AcrH^+$ by alkylbenzene in the presence of $HClO_4$ are given in Table 4. As shown in both Tables 2 and 4, the k_{obs} values agree well with the k_q values determined independently by the fluorescence quenching of $^1AcrH^{+*}$, indicating that both the photoaddition of alkylbenzenes to $AcrH^+$ and the photoinduced hydride reduction of $AcrH^+$ proceed via photoinduced electron transfer from alkylbenzenes to the singlet excited state, $^1AcrH^{+*}$.

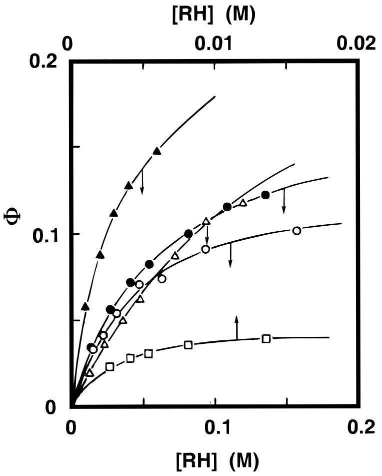


Figure 4. Dependence of the quantum yields (Φ) on [RH] for the photoaddition of RH [PhMe (○), PhEt (●), $PhPr^i$ (△), $PhCH_2Ph$ (▲), p-$Me_2C_6H_4$ (□)] with $AcrH^+$ (3.0×10^{-4} M) in deaerated MeCN at 298 K.

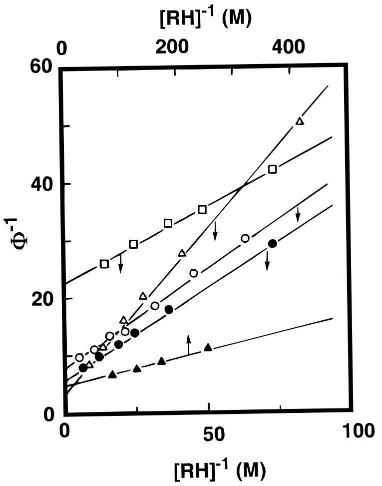


Figure 5. Φ^{-1} vs $[RH]^{-1}$ for the photoaddition of RH [PhMe (○), PhEt (●), $PhPr^i$ (△), $PhCH_2Ph$ (▲), p-$Me_2C_6H_4$ (□)] with $AcrH^+$ (3.0×10^{-4} M) in deaerated MeCN at 298 K.

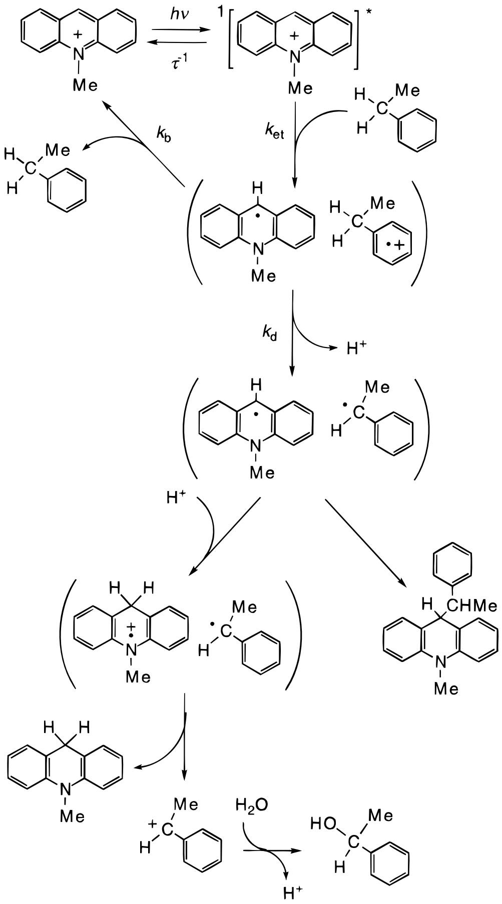
Table 4. Limiting Quantum Yields Φ_∞, Observed Quenching Constants K_{obs}, and Rate Constants k_{obs} in the Photochemical Reaction of $AcrH^+$ with Alkylbenzenes and Fluorescence Quenching Rate Constants k_q of $^1AcrH^{+*}$ by Alkylbenzenes in the Presence of $HClO_4$ (0.40 M) in MeCN at 298 K

alkylbenzene	Φ_∞	K_{obs} (M^{-1})	k_{obs} (M^{-1} s^{-1})	k_q (M^{-1} s^{-1})
$PhCH_2Me$	0.10	1.2×10	3.3×10^8	3.5×10^8
$PhCHMe_2$	0.12	1.0×10	2.8×10^8	1.6×10^8
$PhCH_2Ph$	0.11	3.2×10	8.7×10^8	8.4×10^8
p-$MeOC_6H_4Me$	*a*	*a*	*a*	1.8×10^{10}

[a] No reaction.

Addition vs Oxygenation of Alkylbenzenes via Photoinduced Electron Transfer. On the basis of the above results, the reaction mechanism for both the photoaddition of alkylbenzenes to $AcrH^+$ and the photooxygenation of alkylbenzenes with $AcrH^+$ in the presence of $HClO_4$ may be summarized as shown representatively for the reaction with ethylbenzene in Scheme 1. Both reactions are initiated by photoinduced electron transfer from the alkylbenzene to the singlet excited state ($^1AcrH^{+*}$) to give the alkylbenzene radical cation−acridinyl radical pair. The deprotonation from the alkylbenzene radical cation gives the corresponding benzyl radical ($R^\bullet$). The acceleration of the photoaddition rate by the presence of H_2O (Figure 1) may be ascribed to that of the deprotonation rate of

Scheme 1



the alkylbenzene radical cation because of the strong solvation of H^+ with H_2O. The observed deuterium isotope effects (*vide supra*) may correspond to those on the deprotonation from the alkylbenzene radical cation. In the absence of $HClO_4$, the two radical species ($AcrH^{\bullet}$ and $R^{\bullet}$) may couple efficiently to yield the adduct (AcrHR) selectively. In the case of diphenylmethane, however, the radical coupling process in the cage may in part compete with escape of the radicals from the cage because of the steric effects of two phenyl groups. The escaped radicals may couple with each other to yield 1,1,2,2-tetraphenylethane and 10,10′-dimethyl-9,9′,10,10′-tetrahydro-9,9′-biacridine [$(AcrH)_2$] as shown in Table 1.

On the other hand, the addition of $HClO_4$ in MeCN solution may result in the protonation of $AcrH^{\bullet}$ to produce $AcrH_2^{\bullet+}$. The semiempirical molecular orbital calculation indicates that the protonation of acridinyl radical occurs at the C-9 position to give 10-methyl-9,10-dihydroacridine radical cation ($AcrH_2^{\bullet+}$).[37] The transient absorption of $AcrH^{\bullet}$ in Figure 2 became significantly weaker in the presence of $HClO_4$ (0.40 M) as compared to that in its absence because of the protonation of $AcrH^{\bullet}$. However, the concomitant formation of $AcrH_2^{\bullet+}$ ($\lambda_{max} = 640$ nm)[39] was not observed probably because of the rapid electron transfer from benzyl radical and analogs ($R^{\bullet}$) to $AcrH_2^{\bullet+}$. Judging from the one-electron oxidation potential of benzyl radical and analogs ($R^{\bullet}$), being more negative ($E^{\circ}_{ox} = 0.73$, 0.37, 0.16, and 0.35 V vs SCE for $PhCH_2^{\bullet}$, $PhCHMe^{\bullet}$, $PhMe_2^{\bullet}$, and $Ph_2CH^{\bullet}$, respectively)[38] than the reduction potential of $AcrH_2^{\bullet+}$ ($E^{\circ}_{red} = 0.81$ V vs SCE),[39] the electron transfer from $R^{\bullet}$ to $AcrH_2^{\bullet+}$ is highly exergonic, and thereby it may proceed efficiently to yield $AcrH_2$ and R^+. The benzyl cation and analogs (R^+) may undergo the nucleophilic addition of H_2O to yield the oxygenated product, i.e., the corresponding benzyl alcohol derivatives (ROH). In the case of diphenylmethane, the oxidation of diphenylmethyl radical by $AcrH_2^{\bullet+}$ in the cage leads to formation of benzhydrol, while some diphenylmethyl radicals escape from the cage to undergo the radical coupling to yield the corresponding dimer, i.e., 1,1,2,2-tetraphenylethane (Table 3), the yield of which agrees with that obtained in the absence of $HClO_4$ (Table 1).

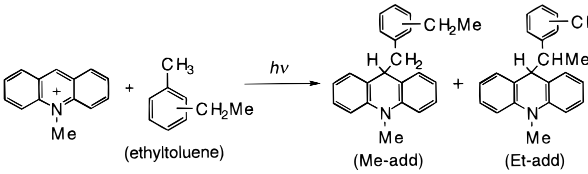
According to Scheme 1, the quantum yield is expressed by eq 9, which agrees well with the experimental result (eq 7). The limiting quantum yield Φ_∞ is then expressed by eq 10,

$$\Phi = [k_d k_{et}\tau/(k_d + k_b)][RH]/(1 + k_{et}\tau[RH]) \qquad (9)$$

$$\Phi_\infty = k_d/(k_d + k_b) \qquad (10)$$

where the competition between the rate of deprotonation from the alkylbenzene radical cation (k_d) and the back electron transfer (k_b) from $AcrH^{\bullet}$ to the alkylbenzene radical cation determines the limiting quantum yield. The deprotonation reactivity from the radical cation decreases with increasing electron donor property of alkylbenzenes, because of the stabilization of the cationic charge. Thus, the strongly electron donating alkylbenzenes have the low Φ_∞ values despite the diffusion-limited values of k_{obs} and k_q as shown in Table 2. In addition, the Φ_∞ values in MeOH are generally larger than those in MeCN, since the deprotonation from alkylbenzene radical cation may be facilitated in MeOH because of the high solvating ability of MeOH to H^+ as compared to that of MeCN. Thus, the deprotonation from alkylbenzene radical cations is an important step in determining the limiting quantum yields. The decrease in the Φ_∞ values with an increase in the electron-donor ability of alkylbenzenes (Table 2) may be ascribed to the decrease in the deprotonation rate constant (k_d) as the acidity decreases.[3,4a,10] Thus, no photoaddition of p-$MeOC_6H_4Me$, the strongest electron donor employed in this study, with $AcrH^+$ occurs because of the slow deprotonation rate as compared with the fast back electron transfer despite the efficient fluorescence quenching of $AcrH^+$ by p-$MeOC_6H_4Me$ (Table 2).

Stereoelectronic Effects on Intra- and Intermolecular Competition in Deprotonation from Alkylbenzene Radical Cations. The photoaddition of *p*-ethyltoluene yields two different adducts, 9-(4-ethylbenzyl)-10-methyl-9,10-dihydroacridine (Me-add) and 9-(4-methyl-α-methylbenzyl)-10-methyl-9,10-dihydroacridine (Et-add) as shown in eq 11. In such a case



(11)

the product ratio (Me-add/Et-add) directly gives the ratio of the deprotonation rate constant from *p*-ethyltoluene radical cation, since the other terms such as the forward and back electron transfers are common. The results of such intramolecular competition of *p*-, *m*-, and *o*-ethyltoluenes and *p*-, *m*-, and

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[37] The heat of formation values calculated by the PM3 method indicate that the radical cation protonated at the C-9 position of $AcrH^{\bullet}$ is more stable by 9 kcal mol^{-1} than that at the N-10 position. The values calculated by the MNDO method also indicate that the former is more stable by 8 kcal mol^{-1} than the latter.

[38] (a) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132. (b) Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635.

[39] (a) Fukuzumi, S.; Tokuda, Y.; Kitano, T.; Okamoto, T.; Otera, J. *J. Am. Chem. Soc.* **1993**, *115*, 8960. (b) Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305.

Table 5. Intramolecular Competition of Deprotonation from Ethyltoluenes (2.7×10^{-2} M) and Cymenes (2.4×10^{-2} M) in the Photoaddition Reactions with $AcrH^+$ (8.5×10^{-3} M) in Deaerated CD_3CN/D_2O (3:1 v/v)

	product (yield, %)[a]		
alkylbenzene	Me-add	Et-add	Pr^i-add
p-ethyltoluene	16 (20) [21]	84 (80) [79]	
m-ethyltoluene	17 (20)	83 (80)	
o-ethyltoluene	23 (24)	77 (76)	
p-cymene	45 (48) [45]		55 (52) [55]
m-cymene	50 (50)		50 (50)
o-cymene	100 (100)		0 (0)

[a] The values in parentheses refer to product yields obtained in the photoaddition of ethyltoluenes (2.7×10^{-2} M) or cymenes (2.4×10^{-2} M) with $AcrH^+$ (6.4×10^{-3} M) in deaerated CD_3OD. The values in brackets refer to product yields obtained in the intermolecular competition of ethylbenzene (1.02×10^{-1} M) and cumene (9.0×10^{-2} M) vs toluene (1.18×10^{-1} M) in the photoaddition with $AcrH^+$ (8.0×10^{-3} M) in deaerated CD_3CN/D_2O (3:1 v/v).

o-cymenes in MeCN containing H_2O and in MeOH are summarized in Table 5. The yields of the adducts are about the same for the photoaddition reactions in MeCN and MeOH.

The intermolecular competition was also performed between toluene (1.18×10^{-1} M) and ethylbenzene (1.02×10^{-1} M) as well as between toluene (1.18×10^{-1} M) and cumene (9.00×10^{-2} M) for the photoaddition with $AcrH^+$ (8.0×10^{-3} M). The difference in the quenching efficiency between two alkylbenzenes, **1** and **2**, was corrected on the basis of the dependence on the quencher concentration using the fluorescence quenching constants of the two alkylbenzenes (K_1 and K_2, respectively). Thus, the ratio of the deprotonation reactivity from two alkylbenzene radical cations, $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$, was determined from the product ratio of **1**-add/**2**-add times $K_2[\mathbf{2}](1 + K_1[\mathbf{1}])/[K_1[\mathbf{1}](1 + K_2[\mathbf{2}])]$. The deprotonation reactivity ratios derived from such intermolecular competition are also listed in Table 5, where the values of the intermolecular competition agree well with those of the intramolecular competition. Such agreement indicates that there is no significant difference in the rate of the back electron transfer process in the intermolecular competition between two monoalkylbenzenes. This is consistent with a recent report on the rate constants of back electron transfer from 1,2,4,5-tetracyanobenzene radical anion to alkylbenzene radical cations, which increase only slightly with a significant decrease in the oxidation potentials of alkylbenzenes.[40]

In Table 5, the significant amount of product via the deprotonation from the isopropyl group is observed, in sharp contrast to the pervious results,[16] indicating the absence of stereoelectronic effects of the isopropyl group. The relative reactivity of isopropyl to ethyl to methyl is 3.7:7.9:1 after correction for the statistical factor. The heat of formation values of toluene, ethylbenzene, cumene, and the corresponding radical cations with various dihedral angles between the benzylic ring and the plane of the benzene ring were calculated by the PM3 method.[31] The calculation indicates that the rotation barriers of the isopropyl group are only 1.7 and 1.6 kcal mol^{-1} for cumene and the radical cation, respectively, which are not significantly larger than those of the methyl group (0.1 kcal mol^{-1} for toluene and the radical cation).[41] The EPR work by Symons[42] has demonstrated that free rotation of the isopropyl group is possible even at 130 K although the rotation is hindered at 77 K. Thus, there may be no preferred conformation of the isopropyl group with respect to the benzene ring at 298 K, in agreement with the absence of the stereoelectronic effects.

Table 6. Photooxygenation of Alkylbenzenes with O_2, Catalyzed by $AcrH^+$ (1.0×10^{-2} M) in O_2-Saturated CD_3CN at 298 K[a]

alkylbenzene (concentration, M)	time (h)	product (yield, %)
PhMe (3.1×10^{-2})	6	PhCHO (69)
PhMe (3.1×10^{-2})[b]	18	PhCHO (74)
PhEt (3.3×10^{-2})	6	PhCOMe (52), PhCH(OH)Me (46)
PhEt (3.3×10^{-2})[b]	18	PhCOMe (34), PhCH(OH)Me (29)
$PhPr^i$ (3.1×10^{-2})	6	$PhCMe_2OH$ (49), PhCOMe (25) $PhCMe_2OOH$ (6), Me_2CO (6) $PhCMe_2OOCMe_2Ph$ (4)
$PhPr^i$ (3.1×10^{-2})[b]	18	Me_2CO (76)
p-$Me_2C_6H_4$ (3.3×10^{-2})	6	*p*-MeC_6H_4CHO (66)

[a] Irradiated with a high-pressure mercury lamp through an acetophenone−methanol filter transmitting $\lambda > 300$ nm. [b] $[HClO_4] = 0.19$ M.

It should be noted, however, that no adduct via the deprotonation from the isopropyl group is obtained in the case of *o*-cymene (see Table 5). The heat of formation values calculated by the PM3 method[31] indicate that the adduct derived from the deprotonation from the isopropyl group of *o*-cymene radical cation is less stable by 14 kcal mol^{-1} than that from the methyl group. Thus, the diminished deprotonation reactivity of the isopropyl group of *o*-cymene radical cation may be ascribed to the pronounced steric effects operating in the C−C bond formation step between the sterically hindered tertiary radical and the acridinyl radical.

However, we cannot discard the possibility that such decreased reactivity of the isopropyl group is due, at least in part, to the stereoelectronic effects in the case of *o*-cymene. In order to evaluate the stereoelectronic effects in such a case, we examined the $AcrH^+$-catalyzed photooxygenation of alkylbenzenes with oxygen, since there is no C−C bond formation step in the photooxygenation reaction (*vide infra*).

$AcrH^+$-Catalyzed Photooxygenation of Alkylbenzenes with Oxygen. The oxygenation of the alkyl group of alkylbenzenes occurs when the photochemical reaction of $AcrH^+$ with alkylbenzenes is carried out in the presence of oxygen. The yields of the oxygenated products are shown in Table 6. In the case of the photooxygenation of cumene, cumene hydroperoxide is detected as the initial photooxygenated product which decomposes to yield the other oxygenated products (Table 6). In the presence of $HClO_4$, the acid-catalyzed decomposition of cumene hydroperoxide gives acetone and phenol. The rate constants of fluorescence quenching of $AcrH^+$ by alkylbenzenes as well as the quantum yields were also determined in oxygen-saturated MeCN.[43] Figure 6 shows the comparison of the quantum yields for the photochemical reactions of toluene with $AcrH^+$ in the absence and presence of oxygen as a function of the toluene concentration, demonstrating the similar dependence in the absence and presence of oxygen. The quantum yields obeyed the same kinetic formulation as employed for the photochemical reactions of $AcrH^+$ with alkylbenzenes in the absence of oxygen (i.e., eq 7). The Φ_∞ and k_{obs} values of the photooxygenation reactions were obtained as 0.19 and 4.8×10^8 M^{-1} s^{-1} for toluene, and 0.06 and 1.2×10^{10} M^{-1} s^{-1} for *p*-xylene. These values agree well with those obtained in the photoaddition reaction in the absence of oxygen (0.13 and 3.8×10^8 M^{-1} s^{-1} for toluene and 0.04 and 1.1×10^{10} M^{-1} s^{-1} for *p*-xylene).

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(40) Arnold, B. R.; Noukakis, D.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1995**, *117*, 4399.

(41) There are two energy minima for cumene radical cation: one is the conformation with hydrogen being perpendicular to the plane of the benzene ring and the other is that with the methyl group perpendicular to the plane of the benzene ring. The energy of the former is 1 kcal lower than that of the latter.

(42) Rao, D. N. R.; Chanda, H.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1201.

(43) The singlet excited state of $AcrH^+$ has been reported to be quenched slightly by triplet oxygen: Kikuchi, K.; Sato, C.; Watanabe, M.; Ikeda, H.; Takahashi, Y.; Miyashi, T. *J. Am. Chem. Soc.* **1993**, *115*, 5180.

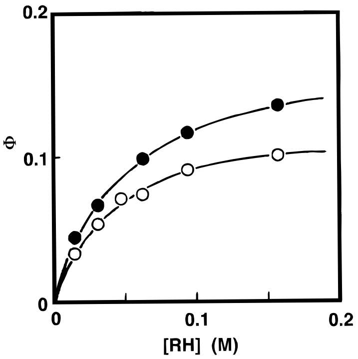
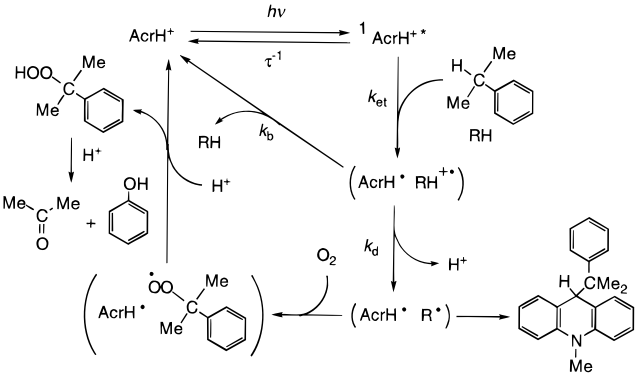


Figure 6. Dependence of the quantum yields (Φ) on [RH] for the photochemical reaction of $AcrH^+$ (3.0×10^{-4} M) with toluene in deaerated MeCN containing H_2O (0.55 M) (○) and in O_2-saturated MeCN containing $HClO_4$ (5.8×10^{-2} M) (●) at 298 K.

Scheme 2



Such agreement indicates that the rate-determining step is common in both cases, i.e., photoinduced electron transfer from alkylbenzenes to $^1AcrH^{+*}$ as shown representatively for the $AcrH^+$-catalyzed photooxygenation of cumene in Scheme 2. The photoinduced electron transfer may be followed by the deprotonation of cumene radical cation to produce cumyl radical in competition with the back electron transfer to the reactant pair. In the absence of oxygen, the coupling of cumyl radical with $AcrH^•$ gives the adduct, while in the presence of oxygen cumyl radical may be trapped efficiently by oxygen to give cumylperoxyl radical which is reduced to yield cumene hydroperoxide by the back electron transfer from $AcrH^•$, accompanied by regeneration of $AcrH^+$.[44] The cumene hydroperoxide decomposes to the other oxygenated products as shown in Table 6. Although the comparable Φ_∞ and k_{obs} values in the absence and presence of oxygen indicate that there is no significant contribution of autoxidation (radical chain reactions) of alkylbenzenes in the photooxygenation reactions, the formation of small amounts of peroxides in the case of photooxygenation of cumene suggests some minor participation of the autoxidation in this particular case.

According to Scheme 2, the limiting quantum yields Φ_∞ are determined by the competition between the deprotonation of alkylbenzene radical cations and the back electron transfer from $AcrH^•$. Thus, the difference in the deprotonation reactivity from alkyl groups of alkylbenzene radical cations can also be evaluated from intramolecular competition of the $AcrH^+$-catalyzed photooxygenation of ethyltoluene and cymene with oxygen. The photooxygenation of *p*-ethyltoluene gave *p*-ethylbenzaldehyde (18% yield on the basis of the conversion), *p*-methylacetophenone (43%), and 1-(4-methylphenyl)-1-ethanol (39%) at 38% conversion.

From the product distribution, the relative reactivity of ethyl to methyl after correction for the statistical factor is determined as 6.8:1, agreeing with that determined from intramolecular competition of the photoaddition reaction (7.9:1, *vide supra*). This indicates that the C−C bond formation step in the photoaddition of ethyltoluene is not affected by the steric effects between the deprotonated radicals and $AcrH^•$.

The photooxygenation of *p*-cymene gave *p*-isopropylbenzaldehyde (12% yield on the basis of the conversion), *p*-methylacetophenone (55%), and acetone (33%) at 41% conversion. From the product distribution, the relative deprotonation reactivity of isopropyl to methyl after correction for the statistical factor is determined as 22:1, which is much larger than that determined from intramolecular competition in the photoaddition reaction of *p*-cymene in the absence of oxygen (3.7:1, *vide supra*). The heat of formation values calculated by the PM3 method[31] indicate that the adduct derived from the deprotonation from the isopropyl group of *p*- and *m*-cymene radical cation is less stable by 8.6 kcal mol^{-1} than that from the methyl group. This indicates that the C−C bond formation between $AcrH^•$ and the hindered radicals deprotonated from the isopropyl group of the radical cations is affected by the steric effects. In contrast to the C−C bond formation, there may be fewer steric effects in the C−O bond formation of the deprotonated radicals with oxygen. Thus, the relative deprotonation reactivity of isopropyl to methyl (22:1) may be regarded as the actual value without the influence of the steric effects in the bond formation step. The same relative reactivity of isopropyl to methyl (22:1) is derived from the photooxygenation of *m*-cymene.

In the case of the photooxygenation of *o*-cymene, only *o*-isopropylbenzaldehyde was obtained at 100% yield on the basis of the conversion (20%). Despite the fewer steric effects on the C−O bond formation of the deprotonated radicals with oxygen, no oxygenated products were derived from the deprotonation of the isopropyl group. The heat of formation values calculated by the PM3 method[31] indicate that the deprotonated radical from the isopropyl group of *o*-cymene radical cation is more stable by 6 kcal mol^{-1} than that from the methyl group. Thus, the absence of oxygenated products via the deprotonation from the isopropyl group of *o*-cymene radical cation despite the favorable thermodynamic stability of the deprotonated tertiary radical may be ascribed to the stereoelectronic effects in this particular case. The methyl group at the *ortho* position may prevent the orientation where the $C-H_\alpha$ bond of the isopropyl group is collinear with the aromatic π-system, resulting in the significant decrease in the deprotonation reactivity of the isopropyl group.

In conclusion, the reactivity ratio of the deprotonation from alkylbenzene radical cations increases in the order methyl < ethyl < isopropyl for the *p*- and *m*-isomers, and the strong stereoelectronic effects appear in the case of the deprotonation from the isopropyl group of *o*-cymene radical cation.

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(44) The transient absorption of $AcrH^•$ in Figure 2 was decreased significantly in the presence of oxygen, suggesting that $AcrH^•$ is also trapped efficiently by oxygen. In such a case $AcrHOO^•$ may be combined with cumyl radical to give the peroxide which decomposes with H^+ to yield the final products. At present, however, it cannot be distinguished whether cumyl radical and/or $AcrH^•$ is trapped by oxygen.