Photoinduced Hydride Reduction of 10-Methylacridinium Ion by Alkylbenzenes in the Presence of Perchloric Acid

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Photoinduced hydride reduction of 10-methylacridinium ion ($AcrH^+$) by alkylbenzene occurs to yield 10-methyl-9,10-dihydroacridine in the presence of perchloric acid, while photoaddition occurs to yield 9-alkyl-10-methyl-9,10-dihydroacridine in the absence of perchloric acid. The hydride reduction of $AcrH^+$ in the presence of perchloric acid proceeds *via* protonation of acridinyl radical produced by photoinduced electron transfer from alkylbenzene.

In anodic or chemical oxidation of alkylbenzene (RH), two-electron oxidation of RH occurs to yield arylmethyl cation (R^+) followed by the nucleophilic addition as shown in Eq. 1,[1,2] since

$$RH \xrightarrow{-e^-} RH^{+\bullet} \xrightarrow{-H^+} R^\bullet \xrightarrow{-e^-} R^+ \xrightarrow{Nu^-} R\text{-}Nu \qquad (1)$$

arylmethyl radical ($R^\bullet$) is more easily oxidized than the starting RH.[3] In the case of photochemical oxidation of RH *via* photoinduced electron transfer from RH to cationic electron acceptor (A^+), however, $R^\bullet$ is not furthermore oxidized to R^+ but is coupled with $R^\bullet$ (homo coupling) or with $A^\bullet$ (hetero coupling) as shown in Eq. 2.[4] Photochemical two-electron oxidation of

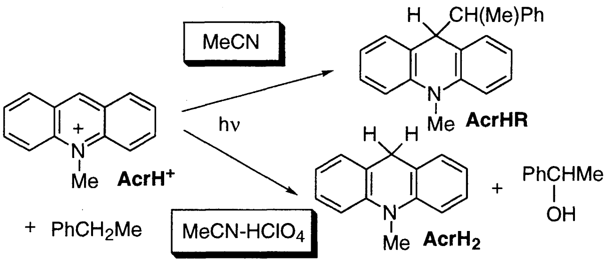
$$RH + A^+ \xrightarrow{h\nu} RH^{+\bullet} + A^\bullet \xrightarrow{-H^+} R^\bullet + A^\bullet \begin{array}{l} \nearrow R\text{-}R,\ A\text{-}A \\ \searrow R\text{-}A \end{array} \qquad (2)$$

RH would be made possible if $A^\bullet$ is protonated by an acid to yield radical cation ($AH^{+\bullet}$) which can oxidize $R^\bullet$ to R^+. In such a case net hydride transfer from RH to A^+ would occur to yield R^+ and AH (Eq. 3). However, there has so far been no report on

$$R^\bullet + A^\bullet \xrightarrow{H^+} R^\bullet + AH^{+\bullet} \longrightarrow R^+ + AH \qquad (3)$$

photoinduced hydride reduction of A^+ *via* protonation of $A^\bullet$.[5] This study reports that photoinduced hydride reduction of 10-methylacridinium ion ($AcrH^+$) by alkylbenzene proceeds efficiently in the presence of perchloric acid ($HClO_4$), while photoaddition of alkylbenzene with $AcrH^+$ occurs in the absence of $HClO_4$.[6]

Visible light irradiation of the absorption band (λ_{max} 358 nm) of 10-methylacridinium perchlorate ($AcrH^+ClO_4^-$; 1.5×10^{-3} mol dm^{-3}) in deaerated acetonitrile (MeCN) containing water (5.5 mol dm^{-3}) and ethylbenzene (4.0×10^{-2} mol dm^{-3}) results in the formation of a hetero coupling product, i. e. 9-(1-phenyl-1-ethyl)-10-methyl-9,10-dihydroacridine (AcrHR). In contrast, the photochemical reaction of $AcrH^+$ with ethylbenzene in the presence of $HClO_4$ (1.2 mol dm^{-3}) containing H_2O (2.9 mol dm^{-3}) under otherwise the same conditions results in the formation of 10-methyl-9,10-dihydroacridine ($AcrH_2$) exclusively, accompanied by the oxidation of ethylbenzene to 1-phenyl-1-ethanol, as shown in Scheme 1. These products were identified by ^1H NMR spectra.[7] Such photoinduced hydride reduction of $AcrH^+$ to $AcrH_2$ also takes place when ethylbenzene is replaced by other alkylbenzenes such as cumene and diphenylmethane, which are oxidized to the corresponding arylmethy alcohol together with the hydride reduction of $AcrH^+$ in the presence of $HClO_4$ in deaerated MeCN.



Scheme 1.

The quantum yields (Φ) of the photoaddition reaction of alkylbenzenes with $AcrH^+$ in deaerated MeCN containing water (1.9 mol dm^{-3}) and those of the photoinduced hydride reduction of $AcrH^+$ by alkylbenzenes in the presence of $HClO_4$ (0.4 mol dm^{-3}) in MeCN containing water (1.0 mol dm^{-3}) were calculated from the decrease of the absorption bands due to $AcrH^+$ (λ_{max} 358 nm) and the increase of 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. 4, where k_{obs} is the observed rate

$$\Phi^{-1} = \Phi_\infty^{-1}(1 + (k_{obs}\,\tau[RH])^{-1}) \qquad (4)$$

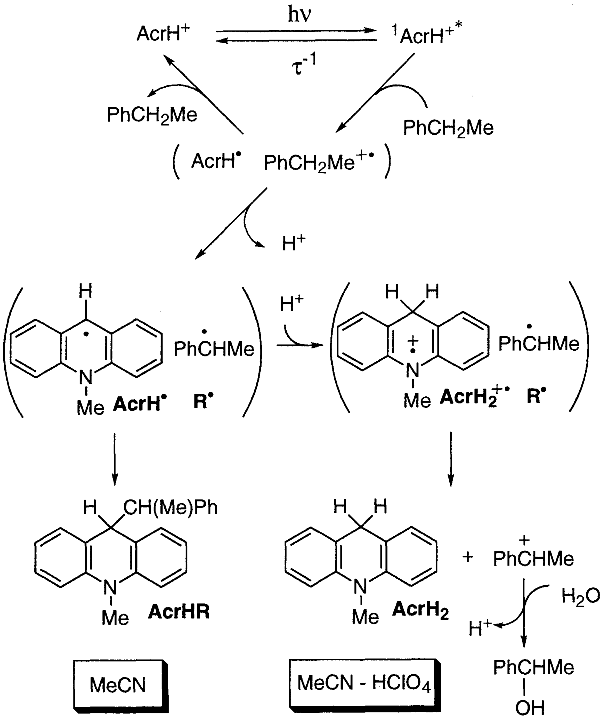
constant of photoreduction of $AcrH^+$ by alkylbenzene, and τ is the lifetime of the singlet excited state ($^1AcrH^{+*}$) of $AcrH^+$ (τ = 37 ns).[6,8] From the slopes and intercepts of the linear plots of Φ^{-1} *vs.* $[RH]^{-1}$, the Φ_∞ and k_{obs} values are obtained as summarized in Table 1.[9] On the other hand, the fluorescence of $^1AcrH^{+*}$ is quenched efficiently by electron transfer from alkylbenzene to $^1AcrH^{+*}$.[6] The quenching rate constants (k_q) are also listed in Table 1, where the k_q values agree well with the

Table 1. Comparison of Φ_∞, k_{obs}, and k_q for the Photoreduction of $AcrH^+$ by Alkylbenzenes in the Presence and Absence of $HClO_4$ in Deaerated MeCN

Alkylbenzene	Φ_∞	k_{obs} / dm^3 mol^{-1} s^{-1}	k_q / dm^3 mol^{-1} s^{-1}
$PhCH_2Me$[a]	0.10	3.3×10^8	3.5×10^8
$PhCH_2Me$[b]	0.25	4.3×10^8	3.5×10^8
$PhCHMe_2$[a]	0.12	2.8×10^8	1.6×10^8
$PhCHMe_2$[b]	0.22	3.4×10^8	1.6×10^8
$PhCH_2Ph$[a]	0.11	8.7×10^8	8.4×10^8
$PhCH_2Ph$[b]	0.25	1.0×10^9	8.4×10^8

[a] in the presence of $HClO_4$ (0.4 mol dm^{-3}) in deaerated MeCN containing H_2O (1.0 mol dm^{-3}). [b] in the absence of $HClO_4$ in deaerated MeCN containing H_2O (1.9 mol dm^{-3}).

k_{obs} values in both presence and absence of $HClO_4$. Such agreements indicate that the photoreaction of $AcrH^+$ with alkylbenzene in both presence and absence of $HClO_4$ is initiated by photoinduced electron transfer from alkylbenzene to $^1AcrH^{+*}$ as shown in Scheme 2.



Scheme 2.

10-Methylacridinyl radical (AcrH•) produced by photoinduced electron transfer from the alkylbenzene to $^1AcrH^{+*}$ was detected as a transient spectrum (λ_{max} 520 nm)[10] by using laser flash photolysis of $AcrH^+$ in MeCN containing alkylbenzene in this study. In the absence of $HClO_4$, the radical (AcrH•) may be coupled with arylmethyl radical (R•) produced by the deprotonation of alkylbenzene radical cation ($RH^{+\bullet}$) to yield the hetero coupling product (AcrHR). On the other hand, addition of $HClO_4$ in MeCN solution resulted in a decrease in the amount of AcrH• to one-half, which was detected by the laser flash photolysis. Such a decrease in the amount of AcrH• may be ascribed to the protonation of AcrH• by $HClO_4$, followed by fast electron transfer from R• to 10-methyl-9,10-dihydroacridine radical cation ($AcrH_2^{+\bullet}$). The semiempirical molecular orbital calculation[11] also indicates that the protonation of AcrH• occurs at the C-9 position to give $AcrH_2^{+\bullet}$.[12] Judging from the one-electron oxidation potentials of R• reported by Wayner et al.[2] being more negative ($E_{1/2}^{ox}$ = 0.37, 0.16, and 0.35 V *vs.* SCE for PhCHMe•, $PhCMe_2$•, and Ph_2CH•, respectively) than the reduction potential of $AcrH_2^{+\bullet}$ (E^0_{red} = 0.81 V *vs.* SCE),[13] the electron transfer from R• to $AcrH_2^{+\bullet}$ is highly exergonic and thereby proceeds efficiently to yield $AcrH_2^{+\bullet}$ and arylmethyl cation (R^+). The arylmethyl cation (R^+) may undergo the nucleophilic addition of H_2O to yield the corresponding arylmethy alcohol (ROH). In conclusion, photoinduced hydride reduction of $AcrH^+$ by alkylbenzene proceeds in the presence of $HClO_4$ *via* protonation of AcrH• generated by the photoinduced electron transfer from alkylbenzene to $^1AcrH^{+*}$ followed by the subsequent electron transfer from R• to $AcrH_2^{+\bullet}$.

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7 The NMR measurements were performed using a JNM-EX270 (270MHz) NMR spectrophotometer. AcrHR: ^1H NMR (CD_3CN) 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), 6.7-6.3 (m, 13H). The other products were determined by the comparison with authentic samples. The yields of AcrHR, $AcrH_2$ and 1-phenyl-1-ethanol were 100, 88 and 53 % respectively.

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9 The Φ values determined from the increase of the concentration of $AcrH_2$ were essentially same as those determined from the decrease of the absorption bands due to $AcrH^+$. The Φ_∞ values of hydride reduction in the presence of $HClO_4$ are smaller than those of photoaddition in the absence of $HClO_4$ because the deprotonation from alkylbenzene radical cations may be slower in the presence of $HClO_4$ than in the absence of $HClO_4$.

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12 The heat of formation values calculated by the PM3 method indicate that the radical cation protonated at the C-9 position of AcrH• is more stable by 9 kcal mol^{-1} than that at the N-10 position. In addition, those calculated by the MNDO method also indicate that the former is more stable by 8 kcal mol^{-1} than the latter.

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