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Reduction of 10-Methylacridinium Ion with Fatty Acids by Photoinduced Electron-Transfer Reactions

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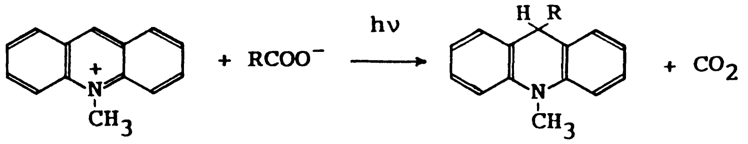
10-Methylacridinium ion ($AcrH^+$) is reduced efficiently by fatty acids (RCOOH) in the presence of a base in acetonitrile to yield 9-alkyl-10-methylacridan selectively under irradiation with visible light <u>via</u> photoinduced electron transfer from $RCOO^-$ to the singlet excited state of $AcrH^+$.

Nicotinamide adenine dinucleotide (NAD^+) is formally reduced with fatty acids used as electron sources through acetyl coenzyme A by the citric acid cycle to yield the corresponding 1,4-dihydropyridine derivative (NADH) which is provided for the oxidation by dioxygen in the respiratory chain.[1] Thus, there has been considerable interest in the reduction of NAD^+ analogues to the corresponding NADH analogues.[2] Although NAD^+ or its analogues cannot be reduced directly by fatty acids, it may be possible to reduce the excited state, which becomes much stronger oxidant than the ground state,[3] by fatty acids directly. However, there has so far been no report on the photoreduction of NAD^+ analogues by fatty acids, although photoinduced decarboxylation reactions have been studied extensively.[4] Unfortunately, the NAD^+ coenzyme is non-fluorescent.[5,6] Among NAD^+ analogues, however, the singlet excited state of 10-methylacridinium ion ($^1AcrH^{+*}$) has a relatively long lifetime (τ 31 ns),[3] and thus it may be used as a unique model of the excited state NAD^+, although $AcrH^+$ contains no amido group and the tricyclic structure of $AcrH^+$ makes it a stronger oxidant than NAD^+.[3] This work reports that $AcrH^+$ can be reduced efficiently by a series of fatty acids in the presence of a base under irradiation of visible light to yield 9-alkyl-10-methylacridan.

Irradiation of the absorption band (λ_{max} 358 nm) of $AcrH^+$ (1.0×10^{-4} mol dm^{-3}) in the presence of NaOH (3.0×10^{-2} mol dm^{-3}) in $MeCN/H_2O$ containing an excess amount of fatty acid (0.10 mol dm^{-3}) resulted in the increase in the absorbance at 285 nm, accompanied by the decrease in the absorbance due to $AcrH^+$ with a clean isosbestic point at 326 nm as shown in Fig. 1. The products from various fatty acids showed approximately the same absorption maxima at 285 nm. The isolated products were identified as 9-alkyl-10-methylacridan (AcrHR) by ^1H NMR as well as by the elemental analyses (Eq. 1).[7] The isolated yields of AcrHR are shown in



(1)

Table 1. Isolated Yields, the Rate Constants (k_{et}) of Photoinduced Electron Transfer from $RCOO^-$ to $AcrH^{+*}$, and the Limiting Quantum Yields (Φ_∞) for the Photoreduction of $AcrH^+$ by RCOOH in the Presence of NaOH in $MeCN/H_2O$ (1:1 v/v) at 298 K

RCOOH	Yield of AcrHR/%	k_{et} ^a)^ $dm^3\ mol^{-1}\ s^{-1}$	k_{obsd} ^b)^ $dm^{-3}\ mol^{-1}\ s^{-1}$	Φ_∞ ^b)^
R = H	84	2.9×10^8	2.6×10^8	0.033
CH_3	82	3.9×10^8	3.2×10^8	0.024
C_2H_5	90	6.5×10^8	5.8×10^8	0.10
$CH(CH_3)_2$	90	1.1×10^9	1.1×10^9	0.22
$C(CH_3)_3$	92	2.0×10^9	2.1×10^9	0.32
$C_{11}H_{23}$	85	3.0×10^9	3.0×10^9	0.14
$C_{15}H_{31}$	87	3.8×10^9	3.6×10^9	0.16

a) Obtained from the fluorescence quenching of $^1AcrH^{+*}$ by $RCOO^-$. b) Obtained from the dependence of the quantum yield on the concentration of $RCOO^-$ (Eq. 2).

Table 1. Typically, irradiation of a deaerated $MeCN/H_2O$ (1:1 v/v) solution (50 cm^3) containing $AcrH^+$ (6.8×10^{-3} mol dm^{-3}), fatty acid (0.20 mol dm^{-3}), and NaOH (6.8×10^{-2} mol dm^{-3}) was carried out with a Xenon lamp through a filter cutting off < 360 nm for 3 h. The concentrations of fatty acids were maintained at excess of the concentration of NaOH, since $AcrH^+$ would react with excess OH^- to yield 9-hydroxy-10-methylacridan.[8] The product was isolated by filtration after evaporating MeCN, and recrystallized from ethanol/water. No acridan dimer has been detected under the present experimental conditions.

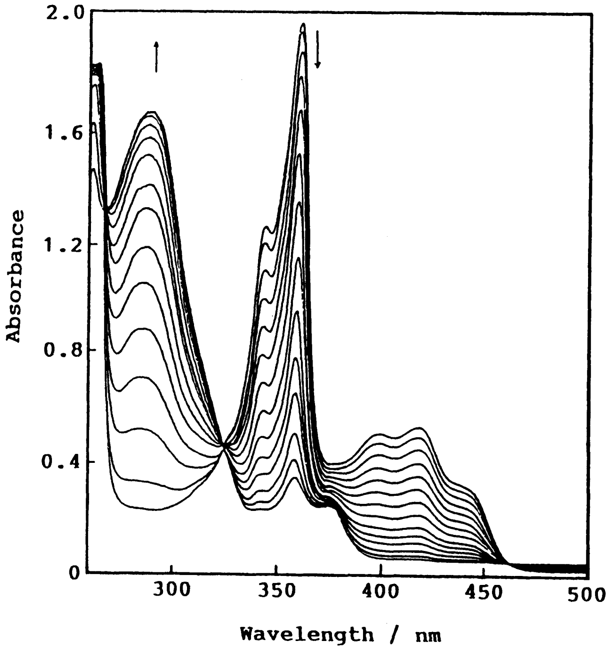


Fig. 1. Electronic spectra observed in photoreduction of $AcrH^+$ (1.0×10^{-4} mol dm^{-3}) by $(CH_3)_2CHCOOH$ (0.10 mol dm^{-3}) in the presence of NaOH (3.0×10^{-2} mol dm^{-3}) in deaerated $MeCN/H_2O$ (1:1 v/v) at 298 K.

The anodic oxidation of $RCOO^-$ at about 2 V (vs. SCE), known as the Kolbe reaction, produces the radical coupling products of the alkyl groups of $RCOO^-$, R-R, and CO_2.[9] The one-electron reduction potential of the singlet excited state $^1AcrH^{+*}$ is 2.3 V (vs. SCE),[3] which is positive enough to oxidize $RCOO^-$. In fact, the fluorescence of $^1AcrH^{+*}$ (λ_{max} 490 nm) is readily quenched by photoinduced electron transfer from $RCOO^-$ to $^1AcrH^{+*}$. The rate constants (k_{et}) of the photoinduced electron transfer were determined from the slopes of the Stern-Volmer plots and the lifetime of the singlet excited state $^1AcrH^{+*}$ (τ 31 ns).[3] The k_{et} values are also listed in Table 1.

The quantum yields (Φ) of the photoreduction of $AcrH^+$ (1.0×10^{-4} mol dm^{-3}) by $RCOO^-$ in $MeCN/H_2O$ (1:1 v/v) at 298 K were determined using a ferrioxalate actinometer[10] with 358 nm irradiation. The quantum yield increased with an increase in the NaOH concentration in the presence of excess fatty acid (0.10 mol dm^{-3}), which corresponds to the concentration of $RCOO^-$, to approach a limiting value (Φ_∞) in accordance with Eq. 2. The linear

$$\Phi^{-1} = \Phi_\infty^{-1}[1 + (K_{obsd}[RCOO^-])^{-1}] \qquad (2)$$

plots of Φ^{-1} vs. $[RCOO^-]^{-1}$ are shown in Fig. 2. The rate constants (k_{obsd} = $K_{obsd}\tau^{-1}$; τ 31 ns)[3] of the quenching of $^1AcrH^{+*}$ in the photoreduction of $AcrH^+$ by $RCOO^-$ as well as the Φ_∞ values were obtained from the dependence of Φ on the $RCOO^-$ concentration (Eq. 2). The k_{obsd} and Φ_∞ values are also listed in Table 1, where k_{obsd} value increases with increasing donor ability of the alkyl group of $RCOO^-$. The largest and smallest Φ_∞ values are 0.32 and 0.024 for R = $C(CH_3)_3$ and CH_3, respectively (Table 1).

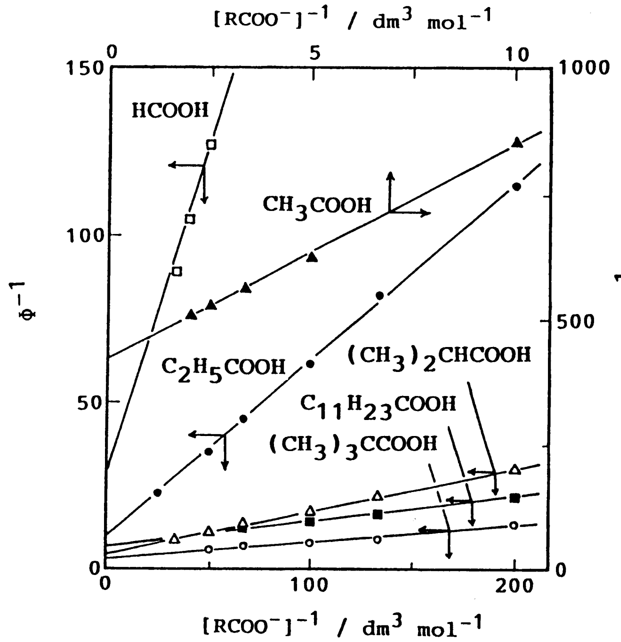
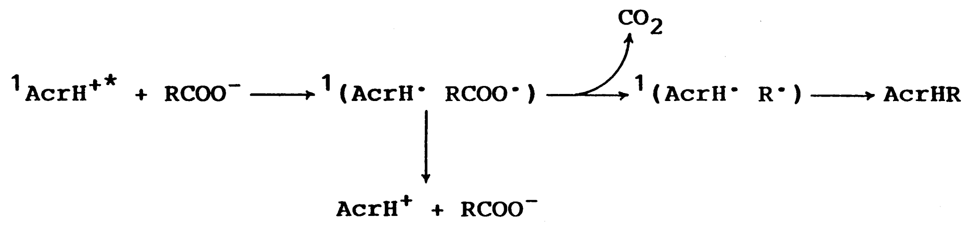


Fig. 2. Plots of Φ^{-1} vs. $[RCOO^-]^{-1}$ for the photoreduction of $AcrH^+$ by $RCOO^-$ in deaerated $MeCN/H_2O$ (1:1 v/v) at 298 K (Eq. 2).

The k_{obsd} values obtained from the dependence of Φ on the $RCOO^-$ concentration agree well with the k_{et} values obtained independently by the fluorescence quenching of $^1AcrH^{+*}$ by $RCOO^-$. Such agreements suggest that the photoreduction of $AcrH^+$ by fatty acids is initiated by the photoinduced electron transfer from $RCOO^-$ to $^1AcrH^{+*}$ as shown in Scheme 1. The photoinduced electron transfer to the singlet



Scheme 1.

excited state may generate a singlet radical pair $^1(AcrH^\cdot\ RCOO^\cdot)$ in which $RCOO^\cdot$ is known to undergo facile decarboxylation,[3,9] followed by the radical coupling in the singlet radical pair ^{1}(AcrH$^\bullet$ R$^\bullet$) to yield 9-alkyl-10-methylacridan (AcrHR) selectively. This may be the reason why no acridan dimer has been detected. According to Scheme 1, the limiting quantum yield (Φ_∞) may be determined by the competition between the decarboxylation of RCOO$^\bullet$ and the back electron transfer from AcrH$^\bullet$ to RCOO$^\bullet$ in the radical pair. The decarboxylation rate may be the fastest for R = $C(CH_3)_3$ because of the stability of the resulting $(CH_3)_3C^\bullet$ radical. This may be the reason why the largest Φ_∞ value is obtained for R = $(CH_3)_3C$ (Table 1).

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