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Photoinduced Cleavage of the C-C Bonds of 9-Alkyl-10-methyl-9,10-dihydroacridines by Perchloric Acid

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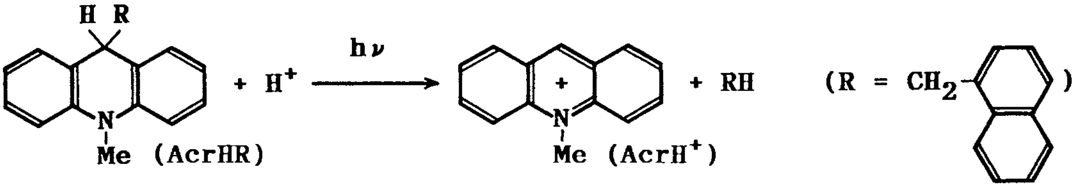
The C-C single bonds of 9-alkyl-10-methyl-9,10-dihydroacridines [AcrHR: R = 1-naphthylmethyl, diphenylmethyl, and AcrH (dimer)] are readily cleaved by perchloric acid in acetonitrile under irradiation of the absorption band of AcrHR to yield the corresponding alkane (RH) and 10-methylacridinium ion ($AcrH^+$).

Since the carbon-carbon bonds are normally stable toward acids, super acids have been required to cleave the C-C bonds.1) Thus, no electrophilic cleavage of the C-C bonds of neutral organic compounds has so far been reported, although cleavage of C-C bonds in organic radical cations has recently attracted considerable attention.2,3) We report herein the first example of photoinduced cleavage of the C-C single bonds of neutral organic compounds, 9-alkyl-10-methyl-9,10-dihydroacridines [AcrHR: R = 1-naphthylmethyl, diphenylmethyl, and AcrH (dimer)], by perchloric acid ($HClO_4$) in acetonitrile (MeCN).

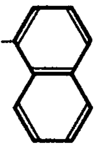
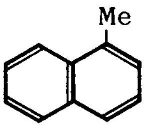
9-(1-Naphtylmethyl)-9,10-dihydroacridine (AcrHR: R = 1-naphthylmethyl)4) shows no reactivity toward $HClO_4$ in deaerated MeCN in the dark. When a deaerated MeCN solution of AcrHR containing $HClO_4$5) and H_2O is irradiated with an xenon lamp, however, the C-C bond of AcrHR is readily cleaved to yield RH and 10-methylacridinium ion ($AcrH^+$), Eq. 1. The photoinduced cleavage of the C-C bond also takes place for 10,10'-dimethyl-9,9'-biacridine [$(AcrH)_2$]6) and AcrHR5) (R = $CHPh_2$). The product yields are listed in Table 1.



(1)

The excitation of the absorption band (λ_{max} = 283 nm) of an deaerated

Table 1. The products and limiting quantum yields for the photoinduced cleavage of the C-C bonds of AcrHR by $HClO_4$ (0.30 mol dm^{-3}) in deaerated MeCN containing H_2O (0.50 mol dm^{-3}) at 298 K under irradiation with a xenon lamp

AcrHR (mol dm^{-3})	Irradiation time / h	RH (yield/%)$^{a)}$	Φ_∞ $^{b)}$
R = CH_2-  (4.0×10^{-2})	40	 (86)	0.059
AcrH (2.0×10^{-2})	40	$AcrH_2$ (80)	0.090
$CHPh_2$ (4.0×10^{-2})	20	Ph_2CH_2 (42)	0.030

a) The same amount of $AcrH^+$ as that of RH is also formed. b) Limiting quantum yield determined by the iron(III) oxalate actinometry.

MeCN solution of AcrHR (R = 1-naphthylmethyl) results in fluorescence (λ_{max} = 455 nm). The large Stokes shift of the fluorescence emission, compared to $AcrH_2$ (λ_{max} = 285, 385 nm for the absorption and emission, respectively), suggests that the singlet excited state ($^1AcrHR^*$) is highly polarized, probably because of the contribution of intramolecular charge-transfer transition from the acridine moiety to 1-naphthylmethyl group. The fluorescence lifetime (τ_0 = 21.5 ns) of $^1AcrHR^*$ in the absence of $HClO_4$ in deaerated MeCN containing H_2O (0.50 mol dm^{-3}), determined by a single photon counting technique, is much longer than that of 9,10-dihydro-10-methylacridine ($^1AcrH_2{}^*$: τ_0 = 7.0 ns).[7)] The τ value at 298 K decreases with an increase in [$HClO_4$]. The Stern-Volmer plot (τ_0/τ vs. [$HClO_4$]) gives a linear correlation as shown in Fig. 1, indicating that a dynamic quenching of the singlet excited state ($^1AcrHR^*$) by $HClO_4$ occurs

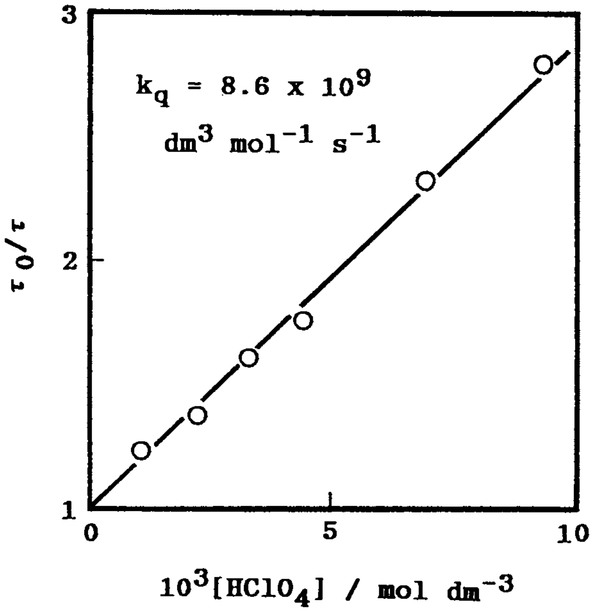


Fig. 1. Plot of τ_0/τ vs. [$HClO_4$] for the quenching of $^1AcrHR^*$ (R = 1-naphthylmethyl) by $HClO_4$ in deaerated MeCN containing H_2O (0.50 mol dm^{-3}) at 298 K.

efficiently.

It was confirmed that no protonation of AcrHR occurred in the ground state in the presence of $HClO_4$ in MeCN containing H_2O (0.50 mol dm^{-3}).[8] From the slope in Fig. 1 is obtained the quenching rate constant as 8.6×10^9 dm^3 mol^{-1} s^{-1} at 298 K.

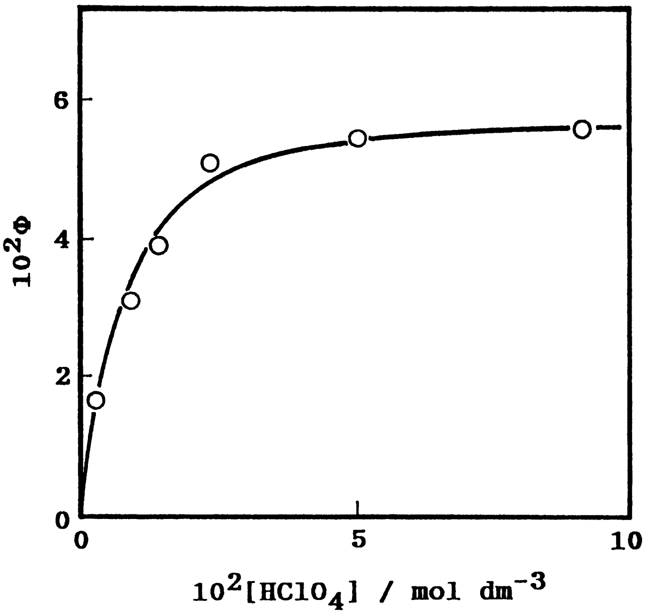


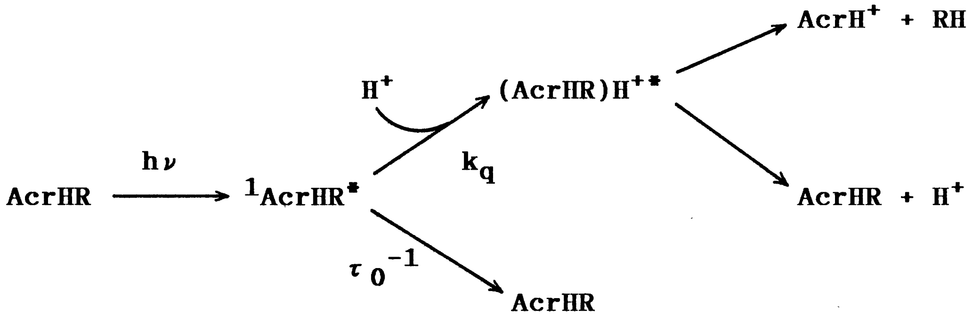
Fig. 2. Dependence of Φ on $[HClO_4]$ for the photoinduced C-C bond cleavage of AcrHR (R = 1-naphthylmethyl: 5.0×10^{-3} mol dm^{-3}) by $HClO_4$ in deaerated MeCN containing H_2O (0.50 mol dm^{-3}) at 298 K. The solid line is drawn by using Eq. 2 in which $k_q = 8.6 \times 10^9$ dm^3 mol^{-1} s^{-1} and τ_0 = 21.5 ns.

The quantum yields (Φ) of the photoinduced cleavage of the C-C bond of AcrHR by $HClO_4$ in MeCN were determined from the increase in the absorbance due to $AcrH^+$ (λ_{max} = 358 nm) by using an iron(III) oxalate actinometer.[9] The Φ value increases with an increase in $[HClO_4]$ to reach a limiting value (Φ_∞) as shown in Fig. 2. The Φ_∞ values of AcrHR used in this study are also listed in Table 1. Such a saturated dependence of Φ on $[HClO_4]$ is expressed by Eq. 2,

$$\Phi = \frac{\Phi_\infty k_q \tau_0 [HClO_4]}{(1 + k_q \tau_0 [HClO_4])} \qquad (2)$$

where k_q is the quenching rate constant of $^1AcrHR^*$ and τ_0 is the fluorescence lifetime in the absence of $HClO_4$. The solid line in Fig. 2, drawn by using Eq. 2, agrees well with the experimental results. Thus, the reaction mechanism may be summarized as shown in Scheme 1.

The singlet excited state ($^1AcrHR^*$) may be polarized as expressed by



Scheme 1.

$AcrH^{\delta+}R^{\delta-}$, judging from the large Stokes shift in the emission spectrum (vide supra).[10] Such a polarized C-C bond of $^1AcrHR^*$ may be susceptible to cleavage by acids following the protonation. Thus, the protonation of $^1AcrHR^*$ may occur efficiently in competition with the decay to the ground state, followed by the cleavage of the C-C bond to yield $AcrH^+$ and RH (Scheme 1). In such a case the limiting quantum yield (Φ_∞) may be determined by the competition between the cleavage of the C-C bond and the decay to the ground state accompanied by the deprotonation (Scheme 1).

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4) The AcrHR was prepared by the photoreduction of $AcrH^+$ with the corresponding RCOOH in the presence of NaOH in $MeCN/H_2O$; S. Fukuzumi, T. Kitano, and T. Tanaka, Chem. Lett., **1989**, 1231.
5) For safety reason $HClO_4$ (70%) was used in this study.
6) The dimer $(AcrH)_2$ was prepared by the one-electron reduction of $AcrH^+$ by hexamethylditin; S. Fukuzumi, T. Kitano, and K. Mochida, J. Am. Chem. Soc., **112**, 3246 (1990).
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8) Without the addition of H_2O, AcrHR was partially protonated by $HClO_4$ in MeCN, when the absorbance due to AcrHR at λ_{max} = 283 nm decreased with an increase in $[HClO_4]$.
9) C. G. Hatchard and C. A. Parker, Proc. R. Soc. London, Ser. A, 235, 518 (1956).
10) In the case of dimer $[(AcrH)_2]$, however, a different mechanism should be considered, since the Stokes shift of the fluorescence was comparable with that of $AcrH_2$.

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