J. Phys. Chem. **1992**, *96*, 8413–8416 **8413**

(30) (a) Baggott, J. E.; Pilling, M. J. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 221. (b) Eriksen, J.; Foote, C. S. *J. Phys. Chem.* **1978**, *82*, 2659. (c) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815.

(31) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(32) For recent reports on the experimental verification of the Marcus inverted region, see: (a) Fox, L. S.; Kozik, M.; Winkler, J. R.; Gray, H. B. *Science* **1990**, *247*, 1069. (b) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (c) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794. (d) DeCosta, D. P.; Pincock, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 8948. (e) Gould, I. R.; Moser, J. E.; Ege, D.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 1991.

(33) (a) Rehm, A.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834. (b) Rehm, A.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(34) In addition, the Marcus equation cannot be applied to the largely endergonic region ($\Delta G^0_{et} > 4\Delta G^{*}{}_0$) where eq 6 predicts the deviation from the linear dependence of ΔG^{*} on ΔG^0_{et} due to the contribution of the parabolic term $[(\Delta G^0_{et}/(4\Delta G^{*}{}_0)]^2$ but the experimental results show the linear dependence of log k_{et} on E^0_{red} with the slope of $1/2.3RT$ (Figure 5).

(35) The cyclic voltammogram of $(AcrH)_2$ showed an anodic wave with a current maximum at ca. 0.3 V (vs SCE) but the complementary cathodic peak was not seen even at a high scan rate (1 V s^{-1}) because of the instability of $(AcrH)_2{}^{\bullet+}$. The irreversibility together with the possible adsorption of the product on the electrode has precluded the detailed analysis of the cyclic voltammograms.

(36) The E^0_{ox} and $\Delta G^{*}{}_0$ values were obtained by the least-squares analysis as described previously.[5] The E^0_{ox} value agrees well with the E^0_{red} value at the point of intersection of the linear line with the slope of $1/2.3RT$ and the diffusion-limited line as shown by the broken line in Figure 5. On the other hand, the $\Delta G^{*}{}_0$ value (2.9 kcal mol^{-1}) may be less accurate than E^0_{ox}, including the experimental error of 2–3 kcal mol^{-1}, since it is derived mainly from the data of photoinduced electron-transfer reactions and the rate constants of thermal electron-transfer reactions being in the range of the linear dependence of log k_{et} on E^0_{red} with the slow of $1/2.3RT$ (Figure 5) are relatively insensitive to the $\Delta G^{*}{}_0$ value. This may be the reason why the $\Delta G^{*}{}_0$ value is smaller than the reported value of the self-exchange of ferrocene and ferrocenium ion (5.8 kcal mol^{-1} at 298 K), see: Yang, E. S.; Chen, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1980**, *84*, 3094.

Photoinduced Cleavage of the C–C Bond of 9-(1-Naphthylmethyl)-10-methyl-9,10-dihydroacridine by Perchloric Acid via Intramolecular Electron-Transfer Excitation

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The C(9)–C bond of 9-(1-naphthylmethyl)-10-methyl-9,10-dihydroacridine (AcrHR) is readily cleaved by $HClO_4$ in acetonitrile (MeCN) under irradiation of the absorption band of AcrHR to yield RH and $AcrH^+$. The dependence of the fluorescence maximum on solvent dielectric constant indicates a highly polar singlet excited state with the dipole moment of ca. 15.6 D, while the fluorescence maximum of 9,10-dihydro-10-methylacridine ($AcrH_2$) is insensitive to the solvent. The fluorescence of AcrHR is efficiently quenched by $HClO_4$ with the rate constant of 8.6×10^9 M^{-1} s^{-1} in MeCN at 298 K. The same quenching rate constant has been obtained from the dependence of the quantum yields on [$HClO_4$] for the photoinduced cleavage of the C–C bond of AcrHR by $HClO_4$ in MeCN at 298 K. Thus, the photoinduced intramolecular charge transfer from the acridine moiety to the naphthalene moiety in AcrHR results in the generation of the highly polarized C–C bond which is susceptible to the cleavage by $HClO_4$. The C(9)–C bond of AcrHR is also cleaved upon the intermolecular electron-transfer oxidation of AcrHR by $Fe(ClO_4)_3$ and $Fe(phen)_3{}^{3+}$ (phen = 1,10-phenanthroline) in MeCN to yield $AcrH^+$, while the C(9)–H bond is cleaved in the case of $AcrH_2$.

Introduction

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] On the other hand, the photophysics of intramolecular photoinduced electron transfer in many molecules where the donor and acceptor are linked together has been studied extensively.[4–6] However, no photochemistry on the C–C bond cleavage accompanied by intramolecular electron transfer has so far been reported. We wish to report herein the photoinduced cleavage of the C–C single bond of 9-(1-naphthylmethy)-10-methyl-9,10-dihydroacridine (AcrHR) by perchloric acid ($HClO_4$) in acetonitrile (MeCN) via intramolecular electron-transfer excitation.[7] The C–C bond cleavage upon the intermolecular electron-transfer oxidation by $Fe(ClO_4)_3$ and $Fe(phen)_3{}^{3+}$ is also examined in comparison with the C–H bond cleavage upon the electron-transfer oxidation of 9,10-dihydro-10-methylacridine ($AcrH_2$). The mechanism of the photoinduced cleavage of the C–C bond by $HClO_4$ is discussed in relation with that of the cleavage by the intermolecular electron-transfer oxidation.

Experimental Section

Materials. 9,10-Dihydro-10-methylacridine ($AcrH_2$) was prepared from 10-methylacridinium iodide ($AcrH^+I^-$) by reduction with $NaBH_4$ in methanol and purified by recrystallization from ethanol.[8] 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 the addition of magnesium perchlorate to the iodide salt, and purified by recrystallization from methanol.[9] 9-(1-Naphthylmethyl)-10-methyl-9,10-dihydroacridine (AcrHR) was prepared by the photoreduction of $AcrH^+ClO_4^-$ with RCOOH in the presence of NaOH in H_2O–MeCN as reported previously.[10] The purity of AcrHR thus obtained was checked by elemental analysis and ^1H NMR spectra. Anal. Calcd for $C_{25}H_{21}N$ [$AcrH(1\text{-}CH_2C_{10}H_7)$]: C, 89.5; H, 6.3; N, 4.2. Found: C, 89.2; H, 6.3; N, 4.2. ^1H NMR (CD_3CN) δ 3.30 (d, 2 H), 3.42 (s, 3 H), 4.36 (t, 1 H), 6.8–8.0 (m, 15 H). Tris(1,10-phenanthroline(iron)(III) hexafluorophosphate, $[Fe(phen)_3](PF_6)_3$, was prepared by oxidizing a solution of the iron(II) complex with ceric sulfate in an aqueous solution containing H_2SO_4.[11] Iron perchlorate [$Fe(ClO_4)_3 \cdot 9H_2O$] and perchloric acid ($HClO_4$, 70%) were obtained commercially. Acetonitrile used as a solvent was purified and dried by the standard procedure.[12]

Reaction Procedure. The photoinduced cleavage of the C–C bond of AcrHR by $HClO_4$ was monitored using a ^1H NMR spectrometer. Typically, AcrHR (2.4×10^{-5} mol) was added to an NMR tube which contained deaerated CD_3CN solution (0.60 cm^3) of $HClO_4$ (0.30 M) and H_2O (1.2 M). After the reactant solution in the NMR tube was thoroughly degassed by repeated freeze–pump–thaw cycles, the NMR tube was sealed under vacuum and then irradiated with light from a Ushio Model UI-501C xenon lamp for 40 h. In the case of the electron-transfer oxidation of AcrHR, $Fe(ClO_4)_3$ or $Fe(phen)_3{}^{3+}$ (4.0×10^{-2} M)

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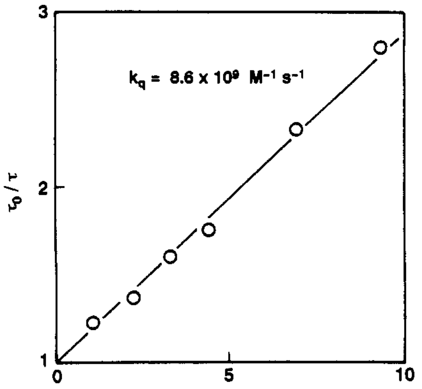


Figure 1. Plot of τ_0/τ vs [$HClO_4$] for the quenching of ^{1}AcrHR* by $HClO_4$ in deaerated MeCN containing H_2O (0.50 M) at 298 K.

was added to an NMR tube which contained CD_3CN solution (0.60 cm^3) of AcrHR (4.0 × 10^{-2} M) under an atmospheric pressure of argon. The oxidized products of AcrHR were identified as 10-methylacridinium ion ($AcrH^+$) and alcohols (ROH) or 9-(1-naphthylmethyl)-10-methylacridinium ion ($AcrR^+$) and H^+ by comparing the ^{1}H NMR spectra with those of the authentic samples. The ^{1}H NMR measurements were performed using a Japan Electron Optics JNM-PS-100 (100 MHz) and JNM-GSX-400 (400 MHz) NMR spectrometers. ^{1}H NMR (CD_3CN): $AcrH^+ClO_4^-$ δ 4.76 (s, 3 H), 7.9–8.8 (m, 8 H), 9.87 (s, 1 H). $Acr(1\text{-}CH_2C_{10}H_7)^+ClO_4^-$: δ 4.80 (s, 3 H), 5.72 (s, 2 H).

Quantum Yield Determinations. A standard actinometer (potassium ferrioxalate)[13] was used for the quantum yield determination of the photochemical reaction of AcrHR with $HClO_4$. A square quartz cuvette (10 mm i.d.) which contained an MeCN solution (2.0 cm^3) of AcrHR (5.0 × 10^{-3} M), $HClO_4$ (5.0 × 10^{-3} to 1.0 × 10^{-1} M), and H_2O (0.50 M) was irradiated with monochromatized light of λ = 300 nm from a Hitachi 650–10S fluorescence spectrophotometer. Under the conditions of actinometry experiments, both the actinometer and AcrHR absorbed essentially all the incident light of λ = 300 nm. The light intensity of monochromatized light of λ = 300 nm was determined as 3.5 × 10^{-6} einstein dm^{-3} s^{-1} with the slit width of 20 nm. The photochemical reaction was monitored using a Shimadzu UV-160 A spectrophotometer. The quantum yields were determined from the increase in absorbance due to $AcrH^+$ (λ_{max} = 358 nm, ϵ_{max} = 1.8 × 10^4 M^{-1} cm^{-1}).

Fluorescence Measurements. Fluorescence measurements were carried out on a Shimadzu RF-5000 spectrofluorophotometer. The fluorescence spectra of AcrHR were measured in various solvents. Fluorescence lifetimes were measured using a Horiba NAES-1100 time-resolved spectrofluorophotometer. In the quenching experiments, the excitation wavelength of AcrHR was 300 nm which excites AcrHR selectively. Relative fluorescence lifetimes were measured for MeCN solution containing AcrHR (5.0 × 10^{-5} M), H_2O (0.50 M) and various concentrations of $HClO_4$ (1.0 × 10^{-3} to 1.0 × 10^{-2} M). The Stern–Volmer relation (eq 1) was obtained between the ratio of the lifetime in the absence and presence of $HClO_4$ (τ_0/τ) and [$HClO_4$].

$$\tau_0/\tau = 1 + k_q\tau_0[\mathrm{HClO_4}] \qquad (1)$$

Kinetic Measurements. Kinetic measurements were performed on a Union RA-103 stopped-flow spectrophotometer at 298 K. Decay of transient radical cations ($AcrH_2^{\bullet+}$ and $AcrHR^{\bullet+}$) formed in electron transfer from $AcrH_2$ and AcrHR (1.0 × 10^{-4} M) to $Fe(phen)_3^{3+}$ (5.0 × 10^{-4} M) or $Fe(ClO_4)_3$ (1.5 × 10^{-3} M) in deaerated MeCN was followed by measuring the disappearance of the absorbance at λ_{max} = 640 and 690 nm due to $AcrH_2^{\bullet+}$ and $AcrHR^{\bullet+}$, respectively. The first-order decay kinetics was analyzed using a Union System 77 computer.

Theoretical Calculations. The theoretical studies were performed using the PM3 molecular orbital method.[14,15] The MOPAC program (QCPE No. 455), which was revised as OS/2 Version 5.01 to adapt for the use on a NEC PC computer, was obtained through the Japan Chemistry Program Exchange (JCPE).[16] The structural output was recorded by using the MOPC program (JCPE No. P038). Final geometries and energetics were obtained by optimizing the total molecular energy with respect to all structural variables.

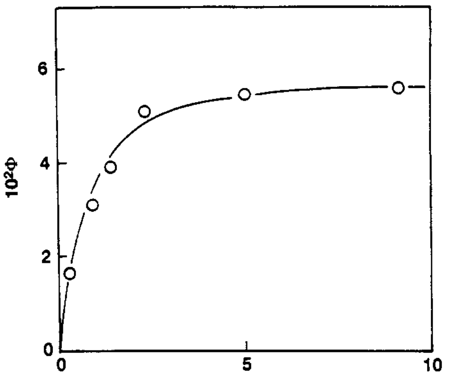
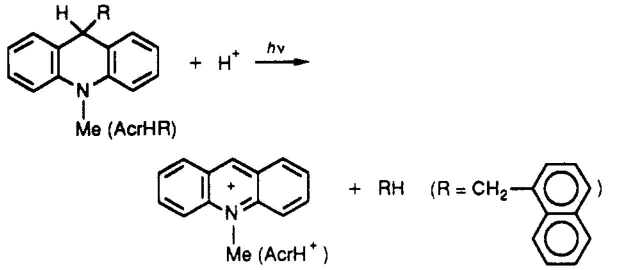


Figure 2. Dependence of Φ on [$HClO_4$] for the photoinduced C–C bond cleavage of AcrHR (5.0 × 10^{-3} M) by $HClO_4$ in deaerated MeCN containing H_2O (0.50 M) at 298 K. The solid line is drawn by using eq 3 in which k_q = 8.6 × 10^9 M^{-1} s^{-1}, τ_0 = 21.5 ns, and Φ_∞ = 0.059.

Results and Discussion

Photoinduced Cleavage of the C–C Bond of AcrHR by $HClO_4$. 9-(1-Naphthylmethyl)-9,10-dihydroacridine (AcrHR) shows no reactivity toward $HClO_4$ in deaerated MeCN in the dark. When a deaerated MeCN solution of AcrHR containing $HClO_4$ and H_2O is irradiated with a xenon lamp, however, the C–C bond of AcrHR is readily cleaved to yield 1-methylnaphthalene (RH) and $AcrH^+$ (eq 2).[17] The yield of $AcrH^+$ was the same as that of RH (86%) in 40 h irradiation with a xenon lamp at 298 K.



(2)

The excitation in the absorption band (λ_{max} = 283 nm) of a deaerated MeCN solution of AcrHR results in fluorescence (λ_{max} = 452 nm). The fluorescence lifetime (τ_0 = 21.5 ns) of ^{1}AcrHR* in the absence of $HClO_4$ in deaerated MeCN containing H_2O (0.50 M), 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).[18] 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 Figure 1, indicating that a dynamic quenching of the singlet excited state (^{1}AcrHR*) by $HClO_4$ occurs 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 M).[19] From the slope in Figure 1, the quenching rate constant is obtained as 8.6 × 10^9 M^{-1} s^{-1} at 298 K.

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). The Φ value increases with an increase in [$HClO_4$] to reach a limiting value (Φ_∞) as shown in Figure 2. Such saturated dependence of Φ on [$HClO_4$] is expressed by eq 3, where k_q is the

$$\Phi = \frac{\Phi_\infty k_q\tau_0[\mathrm{HClO_4}]}{1 + k_q\tau_0[\mathrm{HClO_4}]} \qquad (3)$$

quenching rate constant of ^{1}AcrHR* and τ_0 is the fluorescence lifetime in the absence of $HClO_4$. The solid line in Figure 2, drawn

TABLE I: Fluorescence Maxima (λ_{max}) of $AcrH_2$ and AcrHR in Various Solvents with the Solvent Parameter Δf

solvent	Δf[a]	$\lambda_{max}(AcrH_2)$, nm	$\lambda_{max}(AcrHR)$, nm
C_6H_6	0.120	350	380
$CH_3CO_2C_2H_5$	0.292	354	410
CH_2Cl_2	0.307	357	432
C_2H_5OH	0.379	359	447
CH_3CN	0.392	362	452

[a] $\Delta f = [(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2)]$.

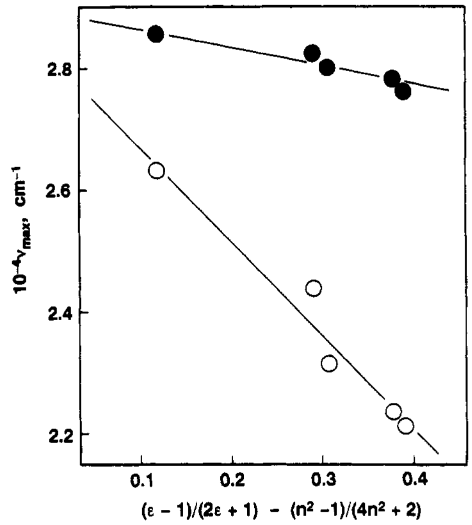


Figure 3. Plots of the fluorescence maxima (ν_{max}) of AcrHR (○) and $AcrH_2$ (●) in various solvents in Table I (C_6H_6, MeCOOEt, CH_2Cl_2, EtOH, MeCN) vs $\Delta f = [(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2)]$.

by using eq 3, agrees well with the experimental results. Thus, the photoinduced cleavage of the C–C bond of AcrHR by $HClO_4$ proceeds via the singlet excited state $^1AcrHR^*$.

Intramolecular Charge-Transfer Excitation. The fluorescence from $^1AcrHR^*$ is highly solvatochromic as compared to $AcrH_2$. The strong red shifts are observed for λ_{max} of $^1AcrHR^*$ in going from a nonpolar solvent (benzene) to a highly polar solvent (acetonitrile), while small shifts are observed for $^1AcrH_2^*$ as shown in Table I. The dipole moment of the excited state can be estimated by eqs 4 and 5, where *h* is the Planck's constant, *c* is

$$\nu_{max} = \nu_{max}(0) - 2\mu_e^2\Delta f/hca^3 \qquad (4)$$

$$\Delta f = [(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2)] \qquad (5)$$

the speed of light, ν_{max} is the fluorescence maximum in a solvent of dielectric constant ϵ and refractive index *n*, $\nu_{max}(0)$ is the fluorescence maximum in the gas phase, and μ_e is the excited-state dipole moment.[20] The slope of a plot of ν_{max} vs Δf gives the value of $2\mu_e^2/a^3$ in which *a* is the effective radius of the solvent shell around the molecule that is usually taken as 40% of the major axis for an approximately ellipsoidal solvent cavity. The highly polar nature of $^1AcrHR^*$ is demonstrated by the plots of ν_{max} vs Δf in Figure 3, where the slope for $^1AcrHR^*$ is much larger than that for $^1AcrH_2^*$. By using the reported a value of 9-(*p*-*N*,*N*-diethylanilino)anthracene (5.4×10^{-10} m) which has a similar molecular size to AcrHR, the excited-state dipole moment of 15.6 D for $^1AcrHR^*$ is derived from the large slope in Figure 3. The large magnitude of the excited-state dipole moment is consistent with an intramolecular charge-transfer (ICT) state from the acridine to the naphthalene moiety in $^1AcrHR^*$.[21-23] In fact, the position of the ICT fluorescence maximum in MeCN (λ_{max} = 452 nm, $h\nu_{max}$ = 2.74 eV) agrees well with the predicted value derived from the redox potentials of each component in MeCN (vide infra).

The one-electron-oxidation potential (E^0_{ox} vs SCE) of $AcrH_2$[9] and the one-electron-reduction potential (E^0_{red} vs SCE) of naphthalene[24] are reported to be 0.80 and −2.58 V, respectively. Thus, the energy required for electron transfer from $AcrH_2$ to naphthalene is 3.38 eV in MeCN. In the ICT state of $^1AcrHR^*$ the acridine moiety and naphthalene moiety are connected by the CH_2 group. In such a case the electrostatic interaction in the radical cation/radical anion pair in $^1AcrHR^*$ should be taken into account. Suppan[25] has derived the electrostatic interaction for a contact ion pair in a highly polar solvent such as MeCN expressed by $-e^2/4r$, in which *r* is the distance between the charge centers.[26,27] The *r* value can be taken from the center of the acridine ring to the center of naphthalene ring, which is obtained as 5.5 Å from the optimized structure of AcrHR calculated by the PM3 method. From the *r* value is estimated the electrostatic interaction energy between the charge centers of the ICT as 0.65 eV in MeCN. Thus, the energy required for electron transfer between the acridine and naphthalene moieties in MeCN is estimated as 3.38 − 0.65 = 2.73 eV, which is compatible with the observed emission energy from the ICT state (2.74 eV). Taking the ground-state Franck–Condon energy into account, however, the electrostatic interaction energy mentioned above (0.65 eV) may be somewhat overestimated. The PM3 molecular orbital calculation also supports such a complete ICT state as follows. The coefficients of the atomic orbitals in the HOMO of AcrHR are located mainly in the acridine moiety and essentially none in the naphthalene moiety as shown in Figure 4. This is completely reversed in the LUMO which is located in the naphthalene moiety.

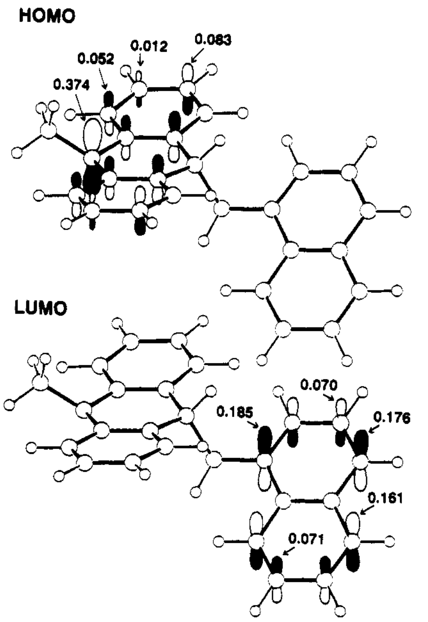
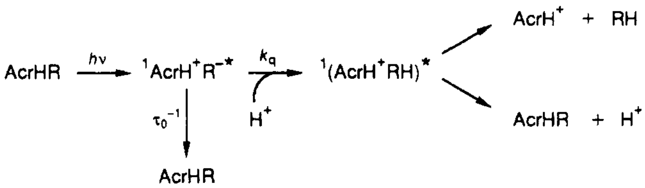
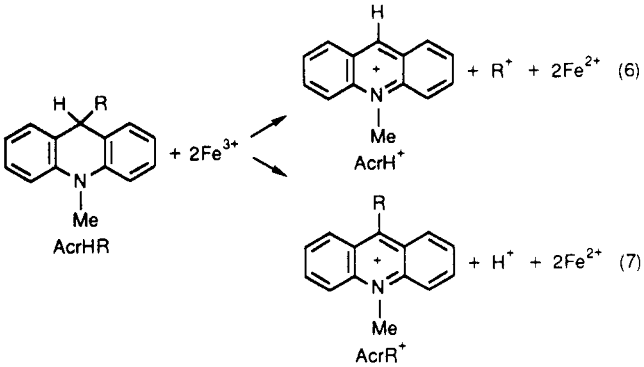


Figure 4. Atomic orbital coefficients in the HOMO and LUMO orbitals of AcrHR, calculated by the PM3 method.

SCHEME I



Cleavage of the C–C Bond of AcrHR Accompanied by the Electron-Transfer Oxidation. When AcrHR is oxidized by $Fe(ClO_4)_3$ in deaerated MeCN, the C(9)–C bond of AcrHR is cleaved to yield 10-methylacridinium ion ($AcrH^+$; 83% yield) and R^+ (eq 6). The carbonium ions R^+ formed primarily may react with H_2O contained in MeCN to yield mainly the corresponding alcohol (see Experimental Section). The C(9)–H bond is also cleaved in the electron-transfer oxidation to yield 9-(1-naphthylmethy)-10-methylacridinium ion ($AcrR^+$; 17% yield), eq 7. The electron-transfer oxidation of AcrHR by $Fe(phen)_3^{3+}$ also results in the cleavage of the C(9)–C bond (65%) and C(9)–H bond (35%). In the case of $AcrH_2$, the electron-transfer oxidation



results in the cleavage of the C(9)–H bond to yield $AcrH^+$.

We have previously reported that mixing an MeCN solution of $Fe(ClO_4)_3$ with $AcrH_2$ in a stopped-flow spectrophotometer results in an instant appearance of a new absorption band at $\lambda_{max} = 640$ nm due to $AcrH_2{}^{•+}$.[28,29] The decay time of $AcrH_2{}^{•+}$ is suitable for reasonably accurate measurements of the absorbances obtained immediately after mixing the reagents. The transient ESR spectrum of $AcrH_2{}^{•+}$ formed by the electron-transfer oxidation of $AcrH_2$ has also been detected by applying a rapid-mixing ESR technique.[29] When $AcrH_2$ is replaced by AcrHR, the absorption spectrum of $AcrHR^{•+}$ ($\lambda_{max} = 690$ nm) is red-shifted as compared with that of $AcrH_2{}^{•+}$. The $AcrHR^{•+}$ decays obeying the first-order kinetics. The first-order decay rate constant of $AcrHR^{•+}$ is determined as 1.7×10^2 s^{-1}, which is significantly larger than that of $AcrH_2{}^{•+}$ (3.8 s^{-1}).[30] The facile cleavage of the C(9)–C bond of $AcrHR^{•+}$ to yield $AcrH^•$ and R^+ (eq 8) may be responsible for the faster decay of $AcrHR^{•+}$ than $AcrH_2{}^{•+}$ in which the C(9)–H bond is cleaved (eq 9). In each case $AcrH^•$ is further oxidized by Fe^{3+} to yield $AcrH^+$ (eqs 6 and 7).

$$AcrHR^{•+} \rightarrow AcrH^• + R^+ \qquad (8)$$

$$AcrH_2{}^{•+} \rightarrow AcrH^• + H^+ \qquad (9)$$

Mechanism of Photoinduced Cleavage of the C–C Bond of AcrHR by $HClO_4$. Based on the above discussion, the reaction mechanism for the photoinduced cleavage of the C–C bond of AcrHR may be summarized as shown in Scheme I. The excitation of AcrHR results in the formation of the highly polarized singlet excited state ($^1AcrH^+R^{-*}$). The C(9)–C bond is significantly weakened by the intermolecular electron-transfer oxidation and thus, readily cleaved to yield $AcrH^•$ and R^+ (eq 8). Thus, in the intramolecular electron-transfer state as well the C(9)–C bond may be weakened significantly. In addition, the naphthalene moiety which accept an electron from the acridine moiety by the intramolecular electron-transfer excitation may be readily protonated and, thus, the C(9)–C bond is susceptible to cleavage by $HClO_4$ (Scheme I). 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 I).

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References and Notes

(1) (a) Olah, G. A.; Klopman, G.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 3261. (b) Olah, G. A.; Halpern, Y.; Shen, J.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 1251. (c) Hogeveen, H.; Bickel, A. F. *Chem. Commun.* **1967**, 635. (d) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1980**, *102*, 3257.

(2) For recent reviews see: (a) Chanon, M.; Rajzmann, M.; Chanon, F. *Tetrahedron* **1990**, *46*, 6193. (b) Bally, T. In *Radical Ionic Systems*; Lund, A., Shiotani, M., Ed.; Kluwer: Amsterdam, 1991; p 3.

(3) (a) Trahanovsky, W. S.; Brixius, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 6778. (b) Snook, M. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 860. (c) Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931. (d) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80–86. (e) Davis, H. F.; Das, P. K.; Reichel, L. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 6968. (f) Ci, X.; Whitten, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 7215. (g) Maslak, P.; Asel, S. L. *J. Am. Chem. Soc.* **1988**, *110*, 8260. (h) Sankararaman, S.; Perrier, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 6448. (i) Popitlarz, R.; Arnold, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 3068. (j) Bergmark, W. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1990**, *112*, 4042. (k) Fukuzumi, S.; Kitano, T.; Mochida, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1236. (l) Maslak, P.; Chapman, W. H., Jr. *Tetrahedron* **1990**, *46*, 2715. (m) Penn, J. H.; Lin, Z.; Deng, D. L. *J. Am. Chem. Soc.* **1991**, *113*, 1001.

(4) (a) Grabowski, Z. R.; Dobkowski, J. *Pure Appl. Chem.* **1983**, *55*, 245. (b) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. (c) Wasielewski, M. R. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Ed.; Elsevier: Amsterdam, 1988; Part A, p 161. (d) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971.

(5) (a) Kosower, E. M.; Dodiuk, H. *J. Am. Chem. Soc.* **1978**, *100*, 4173. (b) Van der Auweraer, M.; Gilbert, A.; De Schryver, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 4007. (c) Hagopian, S.; Singer, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 1874. (d) Van der Auweraer, M.; Grabowski, Z. R.; Rettig, W. *J. Phys. Chem.* **1991**, *95*, 2083.

(6) (a) Weller, A.; Staerk, H.; Treichel, R. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 271. (b) Staerk, H.; Busmann, H.-G.; Kühnle, W.; Treichel, R. *J. Phys. Chem.* **1991**, *95*, 1906. (c) Tanimoto, Y.; Hasegawa, K.; Okada, N.; Itoh, M.; Iwai, K.; Sugioka, K.; Takemura, F.; Nakagaki, R.; Nagakura, S. *J. Phys. Chem.* **1989**, *93*, 3586.

(7) A preliminary report has appeared: Fukuzumi, S.; Tokuda, S.; Fujita, M. *Chem. Lett.* **1991**, 1905.

(8) Roberts, R. M. G.; Ostović, D.; Kreevoy, M. M. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 257.

(9) Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305.

(10) Fukuzumi, S.; Kitano, T.; Tanaka, T. *Chem. Lett.* **1989**, 1231.

(11) (a) Ford-Smith, M. H.; Sutin, N. *J. Am. Chem. Soc.* **1961**, *83*, 1830. (b) Fukuzumi, S.; Nishizawa, N.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3482.

(12) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Elmsford, 1966.

(13) (a) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser, A* **1956**, *235*, 518. (b) Calvert, J. C.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966; p 783.

(14) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221.

(15) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

(16) Toyoda, J. *JCPE News Lett.* **1990**, *2*, 37.

(17) For safety reasons $HClO_4$ (70%) was used in this study.

(18) Fukuzumi, S.; Tokuda, S. *Chem. Lett.* **1991**, 897.

(19) Without the addition of H_2O, AcrHR was partially protonated by $HClO_4$ in MeCN, when the absorbance due to AcrHR at $\lambda_{max} = 283$ nm decreased with an increase in $[HClO_4]$.

(20) Mataga, N. In *The Exciplex*; Gordon, M., Ware, W., Eds.; Academic Press: New York, 1975.

(21) Tseng, J. C.-C.; Singer, L. A. *J. Phys. Chem.* **1989**, *93*, 7092.

(22) Hagopian, S.; Singer, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 1874.

(23) (a) Siemiarczuk, A.; Koput, J.; Pohorille, A. *Z. Naturforsch.* **1982**, *37A*, 598. (b) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971. (c) Detzer, N. N.; Baumann, W.; Schwager, B.; Frohling, J.-C.; Brittinger, C. *Z. Naturforsch.* **1987**, *42A*, 395.

(24) Rieke, R. D.; Rich, W. E.; Ridgway, T. H. *Tetrahedron Lett.* **1969**, 4381.

(25) Suppan, P. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 509.

(26) The electrostatic interaction between two ions in the contact ion pair is much larger than estimated by the usual Coulomb term $-e^2/\epsilon r$, because the space between the charge centers is not filled with the solvent of static dielectric constant ϵ.

(27) For the intermolecular electrostatic interaction in the radical ion pair formed by electron transfer from neutral donor to acceptor molecules; see: Fukuzumi, S. In *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: Greenwich, CT, Vol. 2; pp 67–175.

(28) Fukuzumi, S.; Mochizuki, S.; Tanaka, T. *J. Chem. Soc., Dalton Trans.* **1990**, 695.

(29) Fukuzumi, S.; Kitano, T. *Chem. Lett.* **1990**, 1275.

(30) The detailed kinetic study on the decay of $AcrHR^{•+}$ with various substituents R is to be reported elsewhere.