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Outer-Sphere Electron-Transfer Oxidation of 10.10'-Dimethyl-9,9',10,10'-tetrahydro-9,9'-biacridine

Shunichi Fukuzumi* and Yoshihiro Tokuda

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan (Received: April 28, 1992; In Final Form: July 14, 1992)

10,10'-Dimethyl-9,9',10,10'-tetrahydro-9,9'-biacridine [(AcrH)₂] acts as a unique two-electron donor in the electron-transfer oxidation with various organic oxidants. The rate-determining step is electron transfer from (AcrH)2 to oxidants, followed by facile cleavage of the C(9)-C bond of (AcrH)2⁺⁺ to yield the acridinyl radical (AcrH⁺) and 10-methylacridinium ion (AcrH⁺). The second electron transfer from AcrH⁺ to oxidants is much faster than the initial electron transfer from (AcrH)₂ to oxidants. On the other hand, the corresponding monomer, 10-methyl-9,10-dihydroacridine (AcrH₂), acts as a normal hydride (two electrons and proton) donor in the reactions with oxidants. Rates of electron-transfer reactions from (AcrH), to various inorganic and organic one-electron oxidants depend solely on the one-electron-reduction potentials of the oxidants irrespective of the size of the oxidants, indicating that (AcrH)₂ acts as a novel two-electron outer-sphere electron-transfer reagent. The one-electron-oxidation potential of (AcrH)₂ (vs SCE) has been evaluated as 0.62 V, which is less positive than that of the corresponding monomer (0.80 V).

Introduction

The outer-sphere mechanism for electron-transfer reactions has been extremely useful and successful in predicting the electrontransfer rates of a number of inorganic redox reagents in terms of the Marcus simple and classical theory.1 This concept requires no specific knowledge of the transition-state structure, since rates of the outer-sphere electron-transfer reactions having nonbonded transition states can be described only in terms of the thermodynamic parameters of each independent reductant and oxidant. In contrast, transition-state structures play important roles in mechanistic thinking in organic redox chemistry, since bonding is so important in transition states of organic redox reactions. In addition, electron-transfer oxidation of organic reductants usually involve the cleavage of C-H bonds, since radical cations are much stronger acids than the neutral parent molecules. Thus, welldocumented cases of outer-sphere electron-transfer reactions involving organic redox reagents are rare as Eberson and Shaik have recently pointed out.2,3

We report herein that 10,10'-dimethyl-9,9',10,10'-tetrahydro-9,9'-biacridine [(AcrH)₂] acts as a two-electron donor accompanied by the cleavage of the C(9)-C bond instead of the C(9)-H bond in the outer-sphere electron-transfer reactions with various inorganic and organic one-electron oxidants.⁴ The donor properties of the dimer are compared with those of the corresponding monomer, 10-methyl-9,10-dihydroacridine (AcrH₂).⁵ The second electron transfer from AcrH[•], formed by the C-C bond cleavage upon the initial electron-transfer oxidation, to oxidants to yield 10-methylacridinium ion (AcrH⁺) may be much faster than the initial electron transfer, judging from the low one-electron oxidation potential of AcrH[•] (E_{ox}^0 vs SCE = -0.43 V).^{5,6} In such a case, initial electron-transfer oxidation of (AcrH)₂ may be the

rate-determining step for the over-all two-electron oxidation of $(AcrH)_2$ to two AcrH⁺. Thus, $(AcrH)_2$ is suitable to investigate the electron-transfer reactions with a variety of oxidants which can cover wide range of steric and electronic effects. To the best of our knowledge, such a unique donor property of (AcrH), may be the first example of an organic reductant acting as a pure two-electron donor in the outer-sphere electron-transfer oxidation.

Experimental Section

Materials. 10,10'-Dimethyl-9,9'-biacridine [(AcrH)₂] was prepared by the one-electron reduction of 10-methylacridinium perchlorate by hexamethylditin.7 10-Methylacridinium iodide was prepared by the reaction of acridine with methyl iodide in acetone, and it was converted to the perchlorate salt (AcrH⁺ClO₄⁻) by the addition of magnesium perchlorate to the iodide salt, and purified by recrystallization from methanol.⁶ Triphenylmethyl perchlorate $(Ph_3C^+ClO_4^-)$ was prepared according to the literature.⁸ (Triphenylmethyl)methanol was obtained commercially. Cobalt(II) tetraphenylporphyrin (CoTPP) was prepared as given in the literature.⁹ The CoTPP was oxidized by dioxygen in the presence of HCl in methanol to obtain (tetraphenylporphinato)cobalt(III) chloride (CoTPPCl),10 which was purified by recrystallization from methanol. The perchlorate salt of CoTPP⁺ was obtained by the metathesis of the chloride salt with AgClO₄ and recrystallized from toluene.¹¹ Quinones, ferrocene derivatives, 7,7,8,8-tetracyano-p-quinodimethane were obtained commercially. Tris-(2,2'-bipyridine)ruthenium(II) dichloride hexahydrate, [Ru-(bpy)₃]Cl₂·6H₂O was prepared and purified by the literature procedure.¹² 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 .¹³ Ferrocenium ions, $([Fe(C_5H_5)_2]^+, [Fe(BuC_5H_4)_2]^+, [Fe(MeC_5H_4)_2]^+, [Fe(C_5H_5)(BuC_5H_4)]^+, [Fe(C_5H_5)(t-amylC_5H_4)]^+, [Fe(C_5H_5)(HgClC_5H_4)]^+)$ were prepared by the oxidation of the corresponding ferrocene derivatives with $[Fe(phen)_3]^{3+}$. Since ferrocenium ions are rather unstable in MeCN, the MeCN solutions of ferrocenium ions were prepared just before the examination of the reactions with (AcrH)₂; they were stable enough to examine the reactions for a few hours. Reagent grade acetonitrile was purified by the successive distillation (four times) over P_2O_5 before use.

Spectral and Kinetic Measurements. The reactions of (AcrH)₂ with various inorganic and organic oxidants in deaerated MeCN were monitored using a Shimadzu UV-2200 or 160A spectrophotometer. The disappearance of the absorbance due to (AcrH), $(\lambda_{max} = 285 \text{ nm})$ was accompanied by the appearance of the absorbance due to the oxidized product (AcrH⁺: $\lambda_{max} = 358$ nm, absorbance due to the obtained product (refer : $\lambda_{max} = 3.50$ mm, $\epsilon_{max} = 1.80 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and the reduced products, semi-quinone radical anions (e.g., $Cl_4Q^{\bullet-}$: $\lambda_{max} = 446 \text{ nm}$, $\epsilon_{max} = 9.0$ $\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), $^{14} \text{ TCNQ}^{\bullet-}$ ($\lambda_{max} = 842 \text{ nm}$, $\epsilon_{max} = 4.33 \times 10^4$ $\text{M}^{-1} \text{ cm}^{-1}$), $^{15} \text{ TCNE}^{\bullet-}$ ($\lambda_{max} = 457 \text{ nm}$, $\epsilon_{max} = 5.67 \times 10^3 \text{ M}^{-1}$ $\epsilon_{max} = 5.67 \times 10^3 \text{ M}^{-1}$ cm⁻¹).¹⁶ Rates of the oxidation of (AcrH)₂ were monitored by the rise of the absorption band due to AcrH⁺ in MeCN at 298 K. Rates of the reduction of CoTPP⁺ by (AcrH)₂ were monitored by the rise and decay of the absorption bands at 412 and 434 nm due to CoTPP and CoTPP+,17 respectively. Kinetic measurements were performed by using a conventional spectrophotometer or by using a Union RA-103 stopped-flow spectrophotometer for the fast reactions with half-lives <10 s. All the kinetic measurements were carried out under pseudo-first-order conditions where the concentrations of oxidants were maintained at greater than 10-fold excess of the concentration of $(AcrH)_2$ (2.0 × 10⁻⁵ to 5.0 × 10⁻⁵ M). Pseudo-first-order rate constants were determined by least-squares curve fit by use of a Union System 77 micro computer. The pseudo-first-order plots were linear for three or more half-lives with the correlation coefficient $\rho > 0.999$.

Luminescence Quenching. Quenching experiments of the fluorescence of 9,10-dicyanoanthracene and pyrene and the $[Ru(bpy)_3]^{2+}$ luminescence were performed using a Hitachi 650-10S fluorescence spectrophotometer. The excitation wavelengths were 430, 350, and 452 nm for 9,10-dicyanoanthracene, pyrene, and $[Ru(bpy)_3]^{2+}$ in MeCN, respectively. The monitoring wavelengths were those corresponding to the maxima of the respective emission bands at 460, 395, and 608 nm, respectively. The solutions were deoxygenated by argon purging for 10 min prior to the measurements. Relative emission intensities were measured for MeCN solutions of each sensitizer with (AcrH)₂ at various concentrations. There was no change in the shape but there was a change in the intensity of the fluorescence spectrum by the addition of a quencher. The Stern-Volmer relationship (eq 1) was obtained for the ratio of the emission intensities in the

$$I_0/I = 1 + K_{\rm SV}[({\rm Acr}{\rm H})_2]$$
 (1)

absence and presence of $(AcrH)_2(I_0/I)$ and the $(AcrH)_2$ concentrations. The observed quenching rate constants by electron transfer k_{et} (= $K_{SV}\tau^{-1}$) was obtained from the Stern-Volmer constant K_{SV} and the emission lifetime τ .

ESR Measurements. The ESR measurements were performed on a JEOL X-band spectrometer (JES-ME-LX). Deaerated MeCN solutions of (AcrH)₂ (1.5×10^{-3} M) and Ph₃C⁺ClO₄⁻ (1.5×10^{-3} M) were mixed in an ESR capillary cell under degassed conditions. A JEOL JES-SM-1 rapid mixing flow apparatus was used for the ESR measurements of the electron-transfer oxidation of (AcrH)₂ by Fe(ClO₄)₃. The flow rate was 1–2 cm³ s⁻¹. The ESR spectra were recorded under nonsaturating microwave power conditions. The magnitude of modulation was chosen to optimize the resolution and the signal to noise (S/N) ratio of the observed spectra. The g values were calibrated by using an Mn²⁺ marker.

Theoretical Calculations. The theoretical studies were performed using the PM3 molecular orbital method.^{18,19} The MO-PAC 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



Figure 1. Electronic spectra observed in the reactions of $(AcrH)_2$ with TCNQ in MeCN at 298 K.



Figure 2. Plot of the ratio of the TCNQ⁻⁻ concentration to the initial concentration of $(AcrH)_2$ (1.3 × 10⁻⁵ M), $[TCNQ^{--}]/[(AcrH)_2]_0$ vs the ratio of the initial concentration of TCNQ to $(AcrH)_2$, $[TCNQ]/[(AcrH)_2]_0$.

(JCPE).²⁰ 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. The geometries of the radical cations were optimized using the unrestricted Hartree-Fock (UHF) formalism.

Results and Discussion

Two-Electron Oxidation of (AcrH)₂. Upon mixing of (AcrH)₂ with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) in deaerated MeCN at 298 K, TCNQ is readily reduced to the corresponding radical anion (TCNQ^{•-}, $\lambda_{max} = 842$ nm), accompanied by the formation of 10-methylacridinium ion (AcrH⁺, $\lambda_{max} = 358$ nm) as shown in Figure 1. The stoichiometry is established by the spectral titration shown in Figure 2, where one (AcrH)₂ reduces two TCNQ to yield two TCNQ^{•-} (eq 2). The same stoichiometry



as eq 2 has been established for the reactions with other organic neutral oxidants [tetracyanoethylene (TCNE), p-chloranil, and p-bromanil] as well as inorganic oxidants (ferrocenium ions and CoTPP⁺).

The $(AcrH)_2$ also acts as a two-electron donor in the reaction with a typical hydride acceptor, trityl cation (Ph_3C^+) , eq 3. Upon

$$(AcrH)_2 + 2Ph_3C^* \rightarrow 2AcrH^+ + 2Ph_3C^*$$
(3)

mixing $(AcrH)_2$ with Ph_3C^+ in deaerated acetonitrile (MeCN)



Figure 3. ESR spectrum observed in the reaction of $(AcrH)_2 (1.5 \times 10^{-3} M)$ with $Ph_3C^+ (1.5 \times 10^{-3} M)$ in deaerated MeCN.

SCHEME I



SCHEME II

$$\operatorname{AcrH}_{2} \xrightarrow{\operatorname{Fe}^{3^{+}}} \operatorname{Fe}^{2^{+}} \xrightarrow{\operatorname{AcrH}^{2^{+}}} \xrightarrow{\operatorname{AcrH}^{+}} \operatorname{AcrH}^{+} \xrightarrow{\operatorname{Fe}^{3^{+}}} \operatorname{Fe}^{2^{+}} \operatorname{AcrH}^{+}$$

at 298 K, (AcrH)₂ is readily oxidized to AcrH⁺ ($\lambda_{max} = 358$ nm), accompanied by the formation of new absorption band at λ_{max} = 320 nm, which disappears on introducing dioxygen to the deaerated solution. The electron spin resonance (ESR) measurement of the deaerated product solution reveals the formation of triphenylmethyl radical (g = 2.0024) as shown in Figure 3.²¹ The triphenylmethyl radical is stable in MeCN at 298 K²² but disappears on introducing dioxygen to the deaerated solution to yield triphenylmethyl peroxide.²³ Thus, (AcrH)₂ acts as a twoelectron donor in the one-electron reduction of Ph₃C⁺ (eq 3).²⁴ In contrast, the corresponding monomer (AcrH₂) is known to act as a hydride donor in the two-electron reduction Ph₃C⁺ (eq 4),

$$H + H + Ph_{3}C^{*} - AcrH^{*} + Ph_{3}CH \qquad (4)$$

$$H + Ph_{3}C^{*} - AcrH^{*} + Ph_{3}CH = (4)$$

when no Ph_3C^{\bullet} has been detected.²⁵ Thus, $(AcrH)_2$ acts as a unique two-electron donor in the one-electron reduction of organic and inorganic oxidants.

The rates of oxidation of $(AcrH)_2$ obey second-order kinetics, showing the first-order dependence on each reactant concentration, indicating that the initial electron transfer from $(AcrH)_2$ to oxidants (Ox) is the rate-determining step, followed by facile cleavage of the C-C bond of $(AcrH)_2^{*+}$ to yield $AcrH^+$ and $AcrH^*$ (Scheme I). The second electron transfer from $AcrH^*$ to Ox may be much faster than the initial electron transfer, since the one-electronoxidation potential of $AcrH^*$ is largely negative ($E_{ox}^0 = -0.43$ V vs SCE).^{5,6} In such a case the observed second-order rate constant (k_{obs}) corresponds to $2k_{ct}$.

We have previously reported that the transient electronic spectrum of $AcrH_2^{*+}$ formed by the electron-transfer oxidation with Fe³⁺ decays via the cleavage of the C(9)-H bond, i.e., the deprotonation to yield AcrH^{*} which can transfer electron to Fe³⁺ (Scheme II).^{26,27} Thus, AcrH₂ can act as an overall hydride (two electrons and a proton) donor. Unfortunately, the lifetime of the dimer radical cation (AcrH)₂^{*+} was too short to be detected by using a stopped-flow spectrophotometer, indicating the facile cleavage of the C(9)-C bond of (AcrH)₂^{*+}. Recently we have also reported the ESR spectra of AcrH₂^{*+} and the deuterated analogues, since the decay lifetime of AcrH₂^{*+} was suitable for



Figure 4. Optimized structures of (a) $(AcrH)_2^{*+}$ and (b) $AcrH_2^{*+}$, calculated by the PM3 method. The values show the C(9)-C and C-(9)-H bond distances (the values in parentheses are those of the corresponding neutral species).

reasonably accurate measurements of the transient ESR spectra by applying a rapid-mixing flow technique.²⁷ The observed hyperfine coupling constants agree reasonably well with those estimated by the PM3 molecular orbital calculations.^{18-20,28} Thus, we performed the molecular orbital calculations by using the PM3 method (see Experimental Section) in order to know the origin of such difference in the reactivities between (AcrH)2.+ and AcrH2*+.18-20 The optimized structures of (AcrH)2*+ and AcrH2*+, obtained by the PM3 calculations, are shown in Figure 4 (parts a and b, respectively). The C(9)-C bond of $(AcrH)_2^{*+}$ is in a boat-axial conformation with respect to the central acridine ring. In addition, the C-C bond of the radical cation $(AcrH)_2^{*+}$ (1.569 Å) lengthens as compared to that of the neutral species $(AcrH)_2$ (1.559 Å) as shown in Figure 4a.²⁹ On the other hand, the C(9)–H bond of $(AcrH)_2^{*+}$ (1.118 Å) is little changed from that of $(AcrH)_2^{*+}$ (1.119 Å). In contrast, the acridine ring of $AcrH_2^{*+}$ is close to be planar and the C(9)-H bond of $AcrH_2^{*+}$ (1.113 Å) lengthens as compared to that of $AcrH_2$ (1.098 Å) as shown in Figure 4b. Thus, AcrH2⁺⁺ is susceptible to cleavage of the C-H bond, while the C-C bond instead of the C-H bond is cleaved in $(AcrH)_2^{+}$.

Outer-Sphere Electron Transfer. The $(AcrH)_2$ can quench the fluorescence of 9,10-dicyanoanthracene and pyrene as well as the emission of $[Ru(bpy)_3]^{2+*}$ (* denotes the excited state) by electron transfer (eq 5 in the case of $[Ru(bpy)_3]^{2+*}$). The rate constants

$$(AcrH)_2 + [Ru(bpy)_3]^{2+*} \xrightarrow{k_{at}} (AcrH)_2^{*+} + [Ru(bpy)_3]^+$$
(5)

 (k_{et}) for the photoinduced electron-transfer reactions of $(AcrH)_2$ were determined by quenching experiments of the fluorescence of the aromatic compounds and luminescence of $[Ru(bpy)_3]^{2+*}$ by $(AcrH)_2$ in MeCN at 298 K (see Experimental Section). The k_{et} values for both thermal and photoinduced electron transfer reactions are listed in Table I, together with the one-electronreduction potentials (E_{red}^0) of the oxidants.^{6,17,30}

reduction potentials (E_{red}^0) of the oxidants.^{6,17,30} The plot of log k_{et} vs E_{red}^0 in Figure 5 demonstrates a typical dependence of the rate constant on E_{red}^0 for outer-sphere electron-transfer reactions; the log k_{et} value increases linearly with an increase in the E_{red}^0 value with a slope of 1/(2.3RT) (=16.9 at 298 K) to reach a diffusion-limited value ($k_{et} = 2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). The k_{et} values for both photoinduced and thermal electron-transfer reactions of (AcrH)₂ depend solely on the E_{red}^0 values, irrespective of the very different size (bulkiness) or type of oxidants including organic and inorganic compounds (Table I). Thus, the dimer [(AcrH)₂] acts as not only a unique two-electron donor

TABLE I: Rate Constants (ket) for Electron Transfer from (AcrH)2 to Various Organic and Inorganic Oxidants in MeCN at 298 K

oxidant ^e	$E_{\rm red}^{\rm U}$ vs SCE, ^b V	$k_{a}, M^{-1} s^{-1}$
1. <i>p</i> -bromanil	0.00	2.3
2. <i>p</i> -chloranil	0.01	2.4
3. Ph ₂ C ⁺	0.21	1.8×10^{3}
4. TCNO	0.19	3.8×10^{3}
5. TCNE	0.22	3.8×10^{3}
6. 2,3-dicyano-p-benzoquinone	0.28	1.1×10^{4}
7. $[Fe(BuC_{4})_{2}]^{+}$	0.25	2.0×10^{4}
8. $[Fe(MeC_{4}H_{4})_{2}]^{+}$	0.26	2.1×10^{4}
9. $[Fe(C_4H_4)(BuC_4H_4)]^+$	0.31	8.1 × 10 ⁴
10. $[Fe(C,H_{s})(t-amy C,H_{4})]^+$	0.32	1.1 × 10 ⁵
11. CoTPP+	0.35	1.8×10^{5}
12. $[Fe(C_{1}H_{1})_{2}]^{+}$	0.37	2.3×10^{5}
13. $[Fe(C_{4}H_{4})(HgClC_{4}H_{4})]^{+}$	0.36	2.8×10^{5}
14. [Ru(bpy)] ^{2+*}	0.78	5.3×10^{9}
15. pyrene*	1.23	1.6×10^{10}
16. 9,10-dicyanoanthracene*	1.91	2.0×10^{10}

^a The asterisk denotes the excited state. ^b Taken from refs 6, 17, and 30. The E_{red}^0 values of the excited states of $[Ru(bpy)_3]^{2+}$, pyrene, and 9,10-dicyanoanthracene are obtained by adding the zero-zero excitation energies to the E_{red}^0 values of the ground states.⁵



Figure 5. Plot of log k_{et} vs E_{red}^0 for the electron-transfer reactions of (AcrH)₂ in MeCN at 298 K. The numbers refer to oxidants in Table I. The solid line is drawn based on eqs 7-9.

without release of a proton (eq 2) but also a novel outer-sphere electron-transfer organic reagent. The outer-sphere mechanism may be only the choice left for the electron-transfer reactions of (AcrH)₂, since the steric hindrance of the dimer as shown in Figure 4a, together with the facile cleavage of the C-C bond upon the one-electron oxidation (Scheme I) may prevent any specific orbital interaction with oxidants.

The Marcus-Gibbs energy relation (eq 6) has been used to

$$\Delta G^{*} = \Delta G^{*}_{0} [1 + \Delta G^{0}_{et} / (4 \Delta G^{*}_{0})]^{2}$$
(6)

analyze outer-sphere electron-transfer reactions (ΔG^*_0 is the intrinsic barrier which represents the activation represents the activation Gibbs energy when the driving force of electron transfer is zero, i.e., $\Delta G^* = \Delta G^*_0$ at $\Delta G^0_{\text{et}} = 0$.^{1,31} It is well-known, that eq 6 cannot be applied to forward electron transfer in the largely exothermic region [eq 6 predicts the increase in the ΔG^* value as $\Delta G_{\rm et}^0$ decreases in the region $\Delta G_{\rm et}^0 < -4\Delta G_0^*$ (inverted region)]. No such behavior has been reported for forward electron-transfer processes, although the inverted region has been found for the back-electron-transfer processes.³² Thus, from an empirical point of view the use of the Rehm-Weller relation $(eq 7)^{33}$ is preferable

$$\Delta G^* = (\Delta G_{\rm et}^0/2) + [(\Delta G_{\rm et}^0/2)^2 + (\Delta G^*_0)^2]^{1/2}$$
(7)

to analyze the outer-sphere electron-transfer reactions for the wide range of Gibbs energy change of electron transfer.³⁴ The activation Gibbs energy of electron transfer (ΔG^*) is obtained from the observed rate constants (k_{et}) by using eq 8, where the effect of

$$\Delta G^* = (2.3RT) \log \left[Z(k_{\rm et}^{-1} - k_{12}^{-1}) \right]$$
(8)

diffusion is taken into account (Z is the collision frequency which is taken as 1×10^{11} M⁻¹ s⁻¹; the diffusion rate constant (k_{12}) in MeCN is $2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). On the other hand, the ΔG_{et}^{0} values are obtained from the one-electron-oxidation potential of the donor (E_{ox}^0) and the one-electron-reduction potential of the excited state of the acceptor (E_{red}^0) by using eq 9. The solid line in Figure 5

$$\Delta G_{\rm et}^0 = F(E_{\rm ox}^0 - E_{\rm red}^0) \tag{9}$$

is drawn based on eqs 7–9 using the E_{ox}^0 value of 0.62 V (vs SCE) and the ΔG^*_0 value of 2.9 kcal mol^{-1,35,36} The E_{ox}^0 value of (AcrH)₂ is less positive than that of AcrH₂ ($E_{ox}^0 = 0.80$ V),^{5,6} indicating that the dimer $[(AcrH)_2]$ is a stronger electron donor than the corresponding monomer ($AcrH_2$).

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(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". 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_{ox}^{0} and ΔG_{0}^{*} values were obtained by the least-squares analysis as described previously.⁵ The E_{ox}^{0} value agrees well with the E_{bot}^{0} value at the point of intersection of the linear line with the slope of 1/2.3RT and the both of interval of the most interval into the broken line in Figure 5. On the other hand, the ΔG^*_0 value (2.9 kcal mol⁻¹) may be less accurate than $E^0_{\alpha\alpha}$, 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_{red}^0 with the slow of 1/2.3RT (Figure 5) are relatively insensitive to the ΔG^*_0 value. This may be the reason why the ΔG^*_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

Shunichi Fukuzumi,* Yoshihiro Tokuda, and Morifumi Fujita

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan (Received: April 27, 1992; In Final Form: July 14, 1992)

The C(9)-C bond of 9-(1-naphthylmethyl)-10-methyl-9,10-dihydroacridine (AcrHR) is readily cleaved by HClO4 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 (AcrH₂) is insensitive to the solvent. The fluorescence of AcrHR is efficiently quenched by HClO₄ with the rate constant of $8.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in MeCN at 298 K. The same quenching rate constant has been obtained from the dependence of the quantum yields on [HClO₄] for the photoinduced cleavage of the C-C bond of AcrHR by HClO4 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 HClO4. 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 AcrH₂.

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 (HClO₄) 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 (AcrH₂). The mechanism of the photoinduced cleavage of the C-C bond by HClO₄ is discussed in relation with that of the cleavage by the intermolecular electron-transfer oxidation.

Experimental Section

Materials. 9,10-Dihydro-10-methylacridine (AcrH₂) was prepared from 10-methylacridinium iodide (AcrH+I-) by reduction with NaBH₄ 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⁺ClO₄⁻) by the addition of magnesium perchlorate to the iodide salt, and purified by recrystallization from methanol.⁹ 9-(1-Naphthylmethyl)-10methyl-9,10-dihydroacridine (AcrHR) was prepared by the photoreduction of AcrH⁺ClO₄⁻ with RCOOH in the presence of NaOH in H₂O-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-CH₂C₁₀H₇)]: C, 89.5; H, 6.3; N, 4.2. Found: C, 89.2; H, 6.3; N, 4.2. ¹H NMR (CD₃CN) § 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 H₂SO₄.¹¹ Iron perchlorate [Fe(ClO₄)₃·9H₂O] and perchloric acid (HClO₄, 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 HClO₄ was monitored using a ¹H NMR spectrometer. Typically, AcrHR (2.4×10^{-5} mol) was added to an NMR tube which contained deaerated CD₃CN solution (0.60 cm^3) of HClO₄ (0.30 M) and H₂O (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)