Acid-Catalyzed Photoreduction of Dialkyl Sulfoxides by an Acid-Stable NADH Analogue

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Photoreduction of dialkyl sulfoxides (R_2SO) by an acid-stable NADH analogue, 10-methyl-9,10-dihydroacridine ($AcrH_2$), proceeds in the presence of perchloric acid in acetonitrile containing H_2O (0.50 M) to yield 10-methylacridinium ion ($AcrH^+$) and the corresponding dialkyl sulfides (R_2S). No photoreduction of R_2SO by $AcrH_2$ has occurred in the absence of perchloric acid. In the presence of perchloric acid the protonation of dialkyl sulfoxides occurs to increase the oxidizing ability of the sulfoxides significantly, when the singlet excited state ($^1AcrH_2^*$) is quenched efficiently by the protonated sulfoxides (R_2SOH^+). The $^1AcrH_2^*$ is also quenched by $HClO_4$. The dependence of quantum yields on [R_2SOH^+] indicates that the photoreduction of R_2SO by $AcrH_2$ proceeds via electron transfer from $^1AcrH_2^*$ to R_2SOH^+, followed by the hydrogen transfer from $AcrH_2^{\bullet+}$ to $R_2SOH^\bullet$, accompanied by the concomitant dehydration to yield $AcrH^+$ and R_2S.

Introduction

The use of the excited states of NADH analogues has been shown to be effective for the reduction of various substrates by NADH analogues.[1-3] A number of substrates can also be reduced readily by acid-stable NADH analogues such as 10-methyl-9,-10-dihydroacridine ($AcrH_2$) in the presence of $HClO_4$ in acetonitrile (MeCN).[3,4] However, neither thermal acid catalysis nor the use of the excited states of NADH analogues has been effective for the reduction of dimethyl sulfoxide (Me_2SO), which is commonly used as an inert aprotic solvent. In the biological system, the pathway of Me_2SO metabolism is known to involve the initial reduction of Me_2SO to dimethyl sulfide (Me_2S) by NADH being an electron donor.[5] On the other hand, there has been considerable interest in acid-catalyzed photochemical reactions in which the use of excited states and acid catalysis are combined to achieve high efficiencies for the reactions of interest.[6-8] However, few examples have so far been reported with regard to acid-catalyzed photoredox reactions.[9]

In this study we report that the use of the excited state of $AcrH_2$ combined with acid catalysis makes it possible for the first time to reduce Me_2SO and other dialkyl sulfoxides by an acid-stable NADH analogue, 10-methyl-9,10-dihydroacridine ($AcrH_2$) in the presence of perchloric acid ($HClO_4$) in MeCN to yield 10-methylacridinium ion ($AcrH^+$) and the corresponding dialkyl sulfides (R_2S).[10] The use of an acid-stable NADH analogue is essential to examine the acid-catalyzed reactions, since ordinary NADH analogues are known to decompose in the presence of acids.[11] The reaction mechanism of the acid-catalyzed photoreduction of R_2SO by $AcrH_2$ is revealed based on determination of the protonation equilibrium of R_2SO, the dependence of the quantum yields on the concentrations of R_2SO and $HClO_4$, and the fluorescence quenching of $AcrH_2$ by R_2SO as well as the lifetime measurements in the presence of $HClO_4$.

Experimental Section

Materials. 10-Methyl-9,10-dihydroacridine ($AcrH_2$) was prepared from 10-methylacridinium iodide ($AcrH^+I^-$) by the reduction with $NaBH_4$ in methanol and purified by recrystallization from ethanol.[12] 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.[13] The dideuterated compound, [9,9'-$^2H_2$]-10-methylacridine ($AcrD_2$) was prepared from 10-methylacridone by the reduction with $LiAlD_4$.[14] Dialkyl sulfoxides and dialkyl sulfides were obtained commercially. *For safety reasons* $HClO_4$ (70%) containing 30% water was used in this study. Acetonitrile used as a solvent was purified and dried by the standard procedure.[15]

Analytical Procedure. Typically, $AcrH_2$ (3.6×10^{-5} mol) was added to an NMR tube which contained deaerated [$^2H_3$]acetonitrile (CD_3CN) solution (0.60 cm^3) of R_2SO (0.10 M), $HClO_4$ (0.20 M), and H_2O (0.50 M) under an atmospheric pressure of argon. The reactant solution was then irradiated with light from a Ushio Model UI-501C xenon lamp for 20 h. The products were identified as 10-methylacridinium ion ($AcrH^+$) and R_2S by the ^1H NMR spectra by comparing with those of the authentic samples. The ^1H NMR measurements were performed using Japan Electron Optics JNM-PS-100 (100 MHz) and JNM-GSX-400 (400 MHz) NMR spectrometers. ^1H NMR (CD_3CN): $AcrH^+ClO_4^-$ δ 4.76 (s, 3H), 7.9–8.8 (m, 8H), 9.87 (s, 1H). The yields of R_2S were also determined by using a Shimadzu GC-7A gas–liquid chromatograph equipped with a SE-30 column.

The protonation equilibrium constants (K) of R_2SO were determined from the change in the absorbance ($\Delta A/\Delta A_0$) at λ = 220 nm due to the protonation of R_2SO as given by eq 1, where $[R_2SO]_0$ and $[H^+]_0$ are the initial concentrations of R_2SO and $HClO_4$, respectively. The best fit values were obtained by the computer simulation; the experimental errors are $<\pm 10\%$.

$$\Delta A/\Delta A_0 = (2[R_2SO]_0)^{-1}([R_2SO]_0 - [H^+]_0 - K^{-1} + \{([R_2SO]_0 + [H^+]_0 + K^{-1})^2 + 4[H^+]_0[R_2SO]_0\}^{1/2}) \quad (1)$$

Quantum Yield Determinations. A standard actinometer (potassium ferrioxalate)[16] was used for the quantum yield determination of the acid-catalyzed photoreduction of R_2SO by $AcrH_2$. A square quartz cuvette (10 mm i.d.) which contained an MeCN solution (2.0 cm^3) of $AcrH_2$ (2.0×10^{-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 = 320 nm from a Hitachi 650-10S fluorescence spectrophotometer. Under the conditions of actinometry experiments, both the actinometer and $AcrH_2$ absorbed essentially all the incident light of λ = 320 nm. The light intensity of monochromatized light of λ = 320 nm was determined as 1.12×10^{-6} einstein dm^{-3} s^{-1} with the slit width of 10 nm. The photochemical reaction was monitored using a Union SM-401 spectrophotometer. The quantum yields were

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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 $AcrH_2$ were measured in the presence of various concentrations of $HClO_4$ in MeCN containing H_2O (0.50 M) at 298 K. Fluorescence lifetimes were measured using a Horiba NAES-1100 time-resolved spectrofluorophotometer. In the quenching experiments, the excitation wavelength of $AcrH_2$ was 320 nm, which excites $AcrH_2$ selectively. Relative fluorescence lifetimes were measured for MeCN solution containing $AcrH_2$ (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 2) was obtained between the ratio of the lifetime in the absence and presence of $HClO_4$ (τ_0/τ) and [$HClO_4$].

$$\tau_0/\tau = 1 + k_q\tau_0[HClO_4] \quad (2)$$

Theoretical Calculations. Theoretical studies were performed using the PM3 molecular orbital method.[17,18] 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).[19] The calculations were also performed by using the MOL-GRAPH program, version 2.8, by Daikin Industries, Ltd. The structural output was recorded by using the MOPC program (JCPE No. P038). Final geometry and energetics were obtained by optimizing the total molecular energy with respect to all structural variables. The geometry of the radical cation ($AcrH_2^{\bullet+}$) was optimized using the unrestricted Hartree–Fock (UHF) formalism. The value of heat of formation (ΔH_f) of $AcrH_2^{\bullet+}$ was calculated with the UHF-optimized structures using the half-electron (HE) method with the restricted Hartree–Fock (RHF) formalism.[20] The ΔH_f values of $Me_2SO^{\bullet-}$ and $Me_2SOH^{\bullet}$ were calculated with the RHF-optimized structures. The ΔH_f value of the singlet excited state ($^1AcrH_2^*$) was calculated with the key word "EXCITED" by optimizing the total molecular energy with respect to all structural variables.

Results and Discussion

Photoreduction of Dialkyl Sulfoxides by $AcrH_2$. The $AcrH_2$ shows no reactivity toward Me_2SO in the presence of $HClO_4$ in MeCN in the dark. No photoreduction of Me_2SO by $AcrH_2$ has occurred in the absence of $HClO_4$ in MeCN, either. When $HClO_4$ and photoirradiation are combined together, however, Me_2SO can be reduced efficiently by $AcrH_2$ to yield 10-methylacridinium ion ($AcrH^+$) and dimethyl sulfide as shown in eq 3 (see Experimental Section). Other dialkyl sulfoxides [Bu_2SO, $(PhCH_2)_2SO$] are also reduced by $AcrH_2$ in the presence of $HClO_4$ in MeCN under photoirradiation as shown in Table I. In the presence of $HClO_4$ (70%, 0.20 M) both $AcrH_2$ and R_2SO are readily protonated in MeCN judging from the change in their electronic absorption and ^1H NMR spectra in the presence of $HClO_4$.[21,22] When H_2O (0.50 M) is added to the MeCN solution, however, only R_2SO is protonated (eq 4) while essentially no protonation of $AcrH_2$ takes place. Figure 1 shows the change in

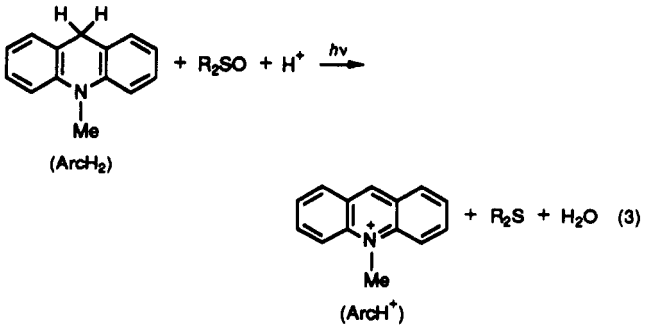


TABLE I: Photoreduction of Dialkyl Sulfoxides (0.10 M) by $AcrH_2$ (5.7 × 10^{-2} M) in the Presence of $HClO_4$ and H_2O (0.50 M) in MeCN at 298 K under Irradiation with a Xenon Lamp

substrate	[$HClO_4$]/M	product (yield/%)[a]
Me_2SO	0	No reaction
Me_2SO	0.20	$AcrH^+$ (90) Me_2S (87)
Bu_2SO	0	No reaction
Bu_2SO	0.20	$AcrH^+$ (92) Bu_2S (92)
$(PhCH_2)_2SO$	0	No reaction
$(PhCH_2)_2SO$	0.20	$AcrH^+$ (92) $(PhCH_2)_2S$ (92)

[a] Irradiation time: 20 h.

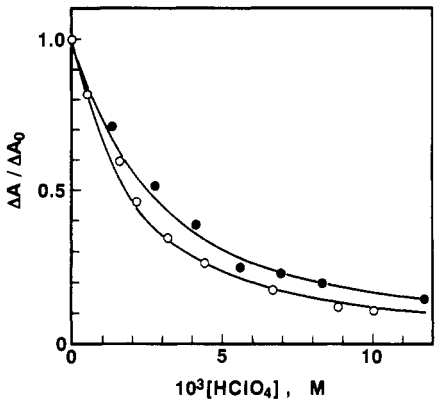


Figure 1. Change in absorbance at λ = 220 nm due to the protonation of Me_2SO (○) and Bu_2SO (●) with an increase in [$HClO_4$] in MeCN containing H_2O (0.50 M) at 298 K. The solid lines are drawn with K = 8.0 × 10^2 and 5.0 × 10^2 M^{-1} for the protonation of Me_2SO and Bu_2SO by using eq 1, respectively.

$$R_2SO + H^+ \overset{K}{\rightleftarrows} R_2SOH^+ \quad (4)$$

the absorbance due to R_2SO (λ = 220 nm, R = Me and Bu) in the presence of $HClO_4$ in MeCN containing H_2O (0.50 M). The protonation equilibrium constants (K) are obtained by computer simulation based on eq 1 as 8.0 × 10^2 and 5.0 × 10^3 M^{-1} for Me_2SO and Bu_2SO, respectively (see Experimental Section). The solid lines in Figure 1 are drawn by using the K values based on eq 1, demonstrating good agreement with the experimental values.[23] The protonation of R_2SO may enhance the oxidizing ability significantly as reported for the case of flavin analogues.[3,24]

The quantum yields (Φ) of the photoreduction of R_2SO by $AcrH_2$ and the 9,9′-dideuterated compound ($AcrD_2$) in the presence of $HClO_4$ in MeCN containing H_2O (0.50 M) were determined by using an iron(III) oxalate actinometer (see Experimental Section).[16] The increase in the H_2O concentration from 0.50 to 2.0 M in the presence of $HClO_4$ (0.10 M) resulted in little effect on the Φ value (0.045 at [H_2O] = 0.50 M, 0.043 at [H_2O] = 2.0 M). The Φ value increases with an increase in the $HClO_4$ concentration to reach a maximum value and then decreases in the high $HClO_4$ concentrations as shown in Figure 2. The increase in the Φ value corresponds to the increase in [Me_2SOH^+] which reaches a constant value when all Me_2SO molecules are protonated. It should be noted that no primary kinetic isotope effect is observed when $AcrH_2$ is replaced by $AcrD_2$; Φ_H/Φ_D = 1.0 ± 0.1 (Figure 2). The retarding effect of $HClO_4$ in high [$HClO_4$] in Figure 2 may be ascribed to the quenching of $^1AcrH_2^*$ by the protonation with $HClO_4$ (eq 5). In fact, the

$$^1AcrH_2^* + H^+ \overset{k_H}{\rightarrow} {}^1AcrH_3^{+*} \quad (5)$$

fluorescence lifetime of $AcrH_2$ (5.0 × 10^{-5} M) in MeCN containing H_2O (0.50 M) is reduced by addition of $HClO_4$ as

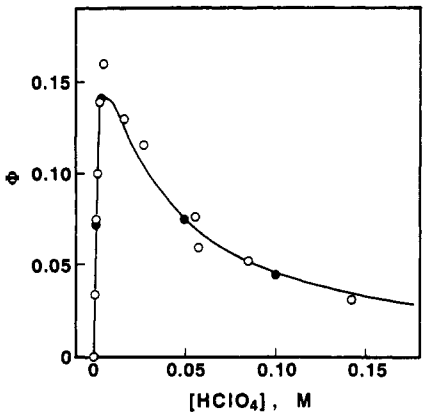


Figure 2. Dependence of the quantum yield Φ on $[HClO_4]$ for the photoreduction of Me_2SO (3.4×10^{-3} M) by $AcrH_2$ (○) and $AcrD_2$ (●) in the presence of $HClO_4$ and H_2O (0.50 M) in MeCN at 298 K. The solid line is drawn with the rate constants (k_{et} and k_H), the fluorescence lifetime (τ_0), and the protonation equilibrium constant (K) by using eq 10.

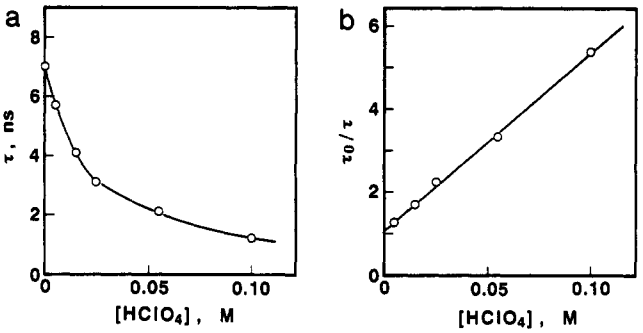


Figure 3. (a) Dependence of the fluorescence lifetime τ of $^1AcrH_2^*$ on $[HClO_4]$ for the fluorescence quenching by $HClO_4$ in MeCN containing H_2O (0.50 M) at 298 K. (b) Plot of τ_0/τ vs $[HClO_4]$.

shown in Figure 3a. From the slope of the Stern–Volmer plot in Figure 3b is obtained the rate constant of the protonation (k_H) as 6.1×10^9 M^{-1} s^{-1}.

Fluorescence Quenching by R_2SOH^+. The fluorescence of $AcrH_2$ is further quenched by addition of R_2SO in the presence of $HClO_4$ in MeCN containing H_2O (0.50 M). In the absence of $HClO_4$, however, no fluorescence quenching has occurred by R_2SO. The ratio of the fluorescence intensities in the absence and presence of Me_2SO (I_0/I) is plotted against the Me_2SO concentration at various concentrations of $HClO_4$ as shown in Figure 4, where the I_0/I values increase with an increase in $[Me_2SO]$ to reach a constant value. The saturated I_0/I values increase with an increase in $[HClO_4]$. Thus, the fluorescence quenching may occur by the protonated species, i.e., Me_2SOH^+, the concentration of which varies depending on $[HClO_4]$ according to the protonation equilibrium in eq 4.

The fluorescence quenching of $AcrH_2$ by R_2SOH^+ may occur by electron transfer from $^1AcrH_2^*$ to R_2SOH^+ as indicated by the energy diagram in Scheme I, where the energies required for electron transfer from $AcrH_2$ and $^1AcrH_2^*$ to Me_2SO and Me_2SOH^+ (shown in parentheses) are compared. The ΔH values are estimated as the calculated difference in the ΔH_f (heat of formation) values by using the PM3 semiempirical molecular orbital method (see Experimental Section).[17-20] Although the reliability for the calculated ΔH_f values which do not include the solvation energies precludes the quantitative comparison, the solvation energies in the charge shift reaction such that the total charge is unchanged ($^1AcrH_2^* + Me_2SOH^+ \rightarrow AcrH_2^{\bullet+} + Me_2SOH^*$) may be largely canceled out. Thus, the large exothermicity for the electron transfer from the singlet excited state ($^1AcrH_2^*$)[25] to the protonated species, Me_2SOH^+ (−64.8 kcal mol^{-1}), as compared to the endothermic electron transfer from the ground state ($AcrH_2$) to Me_2SOH^+ (+16.6 kcal mol^{-1})

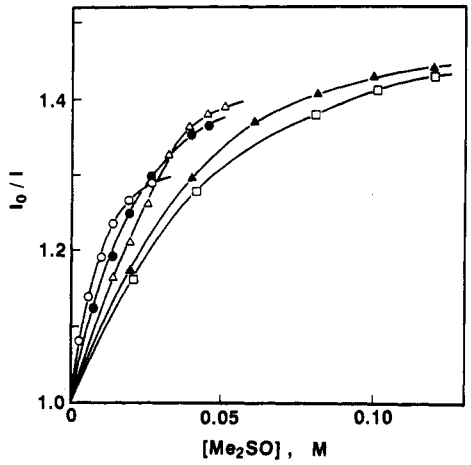


Figure 4. Stern–Volmer plots (I_0/I vs $[Me_2SO]$) for the fluorescence quenching of $^1AcrH_2^*$ by Me_2SO and $HClO_4$ in MeCN containing H_2O (0.50 M) at 298 K. $[HClO_4] = 1.4 \times 10^{-2}$ M (○), 2.7×10^{-2} M (●), 4.0×10^{-2} M (△), 5.7×10^{-2} M (▲), and 8.4×10^{-2} M (□).

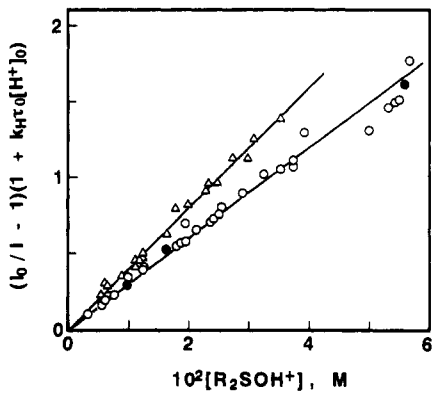
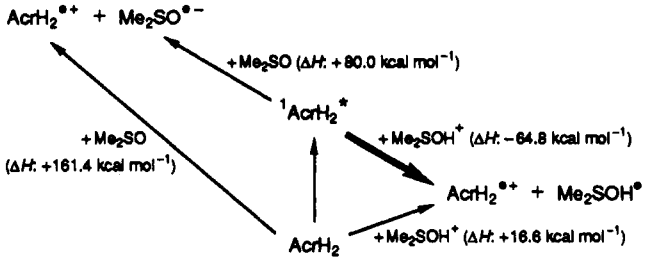


Figure 5. Plots of $(I_0/I - 1)(1 + k_H\tau_0[HClO_4])$ vs $[R_2SOH^+]$ for the fluorescence quenching of $AcrH_2$ by R_2SO, R = Me (○) and Bu (△) in the presence of $HClO_4$ in MeCN containing H_2O (0.50 M) at 298 K. The values of τ_0/τ (●) are also plotted according to eq 7, where I_0/I is replaced by τ_0/τ.

SCHEME I



and that from $AcrH_2$ and $^1AcrH_2^*$ to Me_2SO (+161.4 and +80.0 kcal mol^{-1}, respectively), is unmistakable. In such a case the significant enhancement of the electron acceptor ability by the protonation of Me_2SO results in the efficient fluorescence quenching via exothermic electron transfer from the singlet excited state ($^1AcrH_2^*$) to Me_2SOH^+ (eq 6). In the presence of both

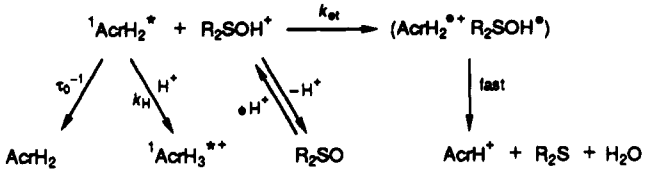
$$^1AcrH_2^* + R_2SOH^+ \xrightarrow{k_{et}} AcrH_2^{\bullet+} + R_2SOH^+ \quad (6)$$

$HClO_4$ and Me_2SO, the fluorescence of $AcrH_2$ is quenched by H^+ (eq 5) as well as Me_2SOH^+ (Scheme I). Then, the dependence of I_0/I on $[H^+]$ and $[Me_2SOH^+]$ is derived as given by eq 7, where τ_0 is the fluorescence lifetime of $^1AcrH_2^*$ in the absence

$$(I_0/I - 1)(1 + k_H\tau_0[H^+]) = (k_{et} - k_H)\tau_0[Me_2SOH^+] \quad (7)$$

of $HClO_4$ and Me_2SO. The data in the curved Stern–Volmer

SCHEME II



plots in Figure 4 are plotted by using the relation in eq 7 as shown in Figure 5, where the $[Me_2SOH^+]$ and $[H^+]$ values in eq 7 are obtained from the K value ($8.0 \times 10^2\ M^{-1}$) in eq 4 by using eqs 8 and 9 respectively). The fluorescence lifetime measurements

$$[Me_2SOH^+] = ([Me_2SO]_0 + [H^+]_0 + K^{-1})/2 - \{([Me_2SO]_0 + [H^+]_0 + K^{-1})^2 - 4[Me_2SO]_0[H^+]_0\}^{1/2}/2 \quad (8)$$

$$[H^+] = [H^+]_0 - [Me_2SOH^+] \quad (9)$$

in the presence of $HClO_4$ and Me_2SO should give essentially the same dependence on $[H^+]$ and $[Me_2SOH^+]$ as eq 7, provided that the fluorescence quenching by Me_2SOH^+ is a dynamic process (eq 6). In fact, the dependence of τ_0/τ values on $[H^+]$ and $[Me_2SO]$ agrees well with eq 7 in which I_0/I is replaced by τ_0/τ as also shown in Figure 5. From the slopes of the linear plots in Figure 5 are obtained the k_{et} value of electron transfer from $^1AcrH_2^*$ to Me_2SOH^+ and Bu_2SOH^+ as 1.0×10^{10} and $1.1 \times 10^{10}\ M^{-1}\ s^{-1}$, respectively. Thus, electron transfer from $^1AcrH_2^*$ to Me_2SOH^+ and Bu_2SOH^+ occurs efficiently with the rates being close to diffusion-controlled.

Mechanism of Acid-Catalyzed Photoreduction of R_2SO by $AcrH_2$. Based on the above results, the reaction mechanism of the acid-catalyzed photoreduction of R_2SO by $AcrH_2$ may be summarized as shown in Scheme II. The protonation of R_2SO enhances the electron acceptor ability, resulting in efficient electron transfer from $^1AcrH_2^*$ to R_2SOH^+ (k_{et}) to give the radical pair ($AcrH_2^{\bullet+}$ $R_2SOH^\bullet$). At the same time, however, the quenching of $^1AcrH_2^*$ by H^+ (k_H) reduces the lifetime of $^1AcrH_2^*$. In order to know the feasible subsequent reaction process, the ΔH_f values of $AcrH_2^{\bullet+}$, $AcrH^+$, $Me_2SOH^\bullet$, $Me_2SH(OH)$, Me_2S, and H_2O are calculated by using the PM3 method (see Experimental Section).[17-20] The calculated difference in the ΔH_f values for the hydrogen transfer from $AcrH_2^{\bullet+}$ to $Me_2SOH^\bullet$ to yield $AcrH^+$ and $Me_2SH(OH)$ is largely positive, +27.4 kcal mol^{-1}, while that for the hydrogen transfer accompanied by the dehydration of $Me_2SH(OH)$ to yield $AcrH^+$, Me_2S, and H_2O is largely negative, −26.3 kcal mol^{-1}. Thus, the hydrogen transfer from $AcrH_2^{\bullet+}$ to Me_2SOH may be accompanied by the concomitant dehydration to yield the final product, $AcrH^+$, R_2S, and H_2O (Scheme II). The hydrogen transfer process may not be the rate-determining step, since no primary kinetic isotope effects have been observed in the overall quantum yields (Figure 2).[25]

By applying the steady-state approximation to the reactive species $^1AcrH_2^*$ and ($AcrH_2^{\bullet+}$ $R_2SOH^\bullet$) in Scheme II, the overall quantum yield can be derived as given by eq 10. Since the $k_{et}\tau_0$

$$\Phi = k_{et}\tau_0K[R_2SO][H^+]/(1 + k_H\tau_0[H^+] + k_{et}\tau_0K[R_2SO][H^+]) \quad (10)$$

and $k_H\tau_0$ values are already determined by the fluorescence quenching by H^+ and Me_2SOH^+ (Figure 3 and Figure 5), the dependence of the quantum yield on $[H^+]$ and $[Me_2SOH^+]$ (the concentrations are obtained from the protonation equilibrium constant K by using eqs 8 and 9) can be calculated by using eq 10. The calculated dependence of the quantum yield Φ on $[HClO_4]$ at a fixed concentration of Me_2SO (3.4×10^{-3} M) shown by the solid line in Figure 2 agrees well with the

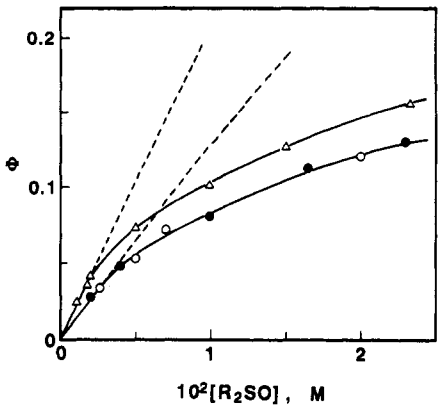


Figure 6. Dependence of Φ on $[R_2SO]$ for the photoreduction of R_2SO [R = Me (○) and Bu (△) by $AcrH_2$ (○, △) and $AcrD_2$ (●)] in the presence of $HClO_4$ (0.10 M) and H_2O (0.50 M) in MeCN at 298 K. The broken lines are drawn with the rate constants (k_{et} and k_H), the fluorescence lifetime (τ_0), and the protonation equilibrium constant (K) by using eq 10.

experimental results. Such agreement strongly indicates the validity of the reaction mechanism in Scheme II.

The dependence of the quantum yield on $[R_2SO]$ for the photoreduction of R_2SO by $AcrH_2$ and $AcrD_2$ at a fixed concentration of $HClO_4$ (0.10 M) was also examined as shown in Figure 6.[27] It is confirmed that no appreciable primary kinetic isotope effect is observed at different concentrations of Me_2SO. The broken lines in Figure 6 show the calculated dependence based on eq 10. At low concentrations of Me_2SO and Bu_2SO the calculated Φ values agree well with the experimental values. With an increase in $[R_2SO]$, however, the experimental values become smaller than the calculated values based on eq 10. Such a retarding effect of R_2SO in the presence of $HClO_4$ may be caused by the electron exchange between $R_2SOH^\bullet$ and R_2SOH^+, which interrupts the hydrogen transfer leading to the final products, resulting in the back electron transfer from $R_2SOH^\bullet$ to $AcrH_2^{\bullet+}$ to regenerate the reactant pair (eq 11).[28]

$$(AcrH_2^{\bullet+}\ R_2SOH^\bullet) + R_2SOH^+ \rightarrow AcrH_2 + 2R_2SOH^+ \quad (11)$$

In conclusion, the catalytic function of acid in the photoreduction of R_2SO by $AcrH_2$ is attributed to the protonation of the ground-state substrate, which enhances the electron transfer from the singlet excited state $^1AcrH_2^*$ significantly. In order to achieve the high efficiency of the acid-catalyzed photoreduction, the concentration of acid should be optimized, since the acid can also retard the reaction through the quenching of $^1AcrH_2^*$ (Scheme II) and also by facilitating the back electron transfer (eq 11).

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References and Notes

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