J. Am. Chem. Soc. **2001,** *123,* 8459−8467

Photoalkylation of 10-Alkylacridinium Ion via a Charge-Shift Type of Photoinduced Electron Transfer Controlled by Solvent Polarity

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Received December 20, 2000. Revised Manuscript Received June 14, 2001

Abstract: A charge-shift type of photoinduced electron-transfer reactions from various electron donors to the singlet excited state of 10-decylacridinium cation ($DeAcrH^+$) in a nonpolar solvent (benzene) is found to be as efficient as those of 10-methylacridinium cation ($MeAcrH^+$) and $DeAcrH^+$ in a polar solvent (acetonitrile). Irradiation of the absorption bands of $MeAcrH^+$ in acetonitrile solution containing tetraalkyltin compounds (R_4Sn) results in the efficient and selective reduction of $MeAcrH^+$ to yield the 10-methyl-9-alkyl-9,10-dihydroacridine (AcrHR). The same type of reaction proceeds in benzene when $MeAcrH^+$ is replaced by $DeAcrH^+$ which is soluble in benzene. The photoalkylation of $R'AcrH^+$ ($R' =$ Me and De) also proceeds in acetonitrile and benzene using 4-*tert*-butyl-1-benzyl-1,4-dihydronicotinamide (Bu^tBNAH) instead of R_4Sn, yielding $MeAcrHBu^t$. The quantum yield determinations, the fluorescence quenching of $R'AcrH^+$ by electron donors, and direct detection of the reaction intermediates by means of laser flash photolysis experiments indicate that the photoalkylation of $R'AcrH^+$ in benzene as well as in acetonitrile proceeds via photoinduced electron transfer from the alkylating agents (R_4Sn and Bu^tBNAH) to the singlet excited states of $R'AcrH^+$. The limiting quantum yields are determined by the competition between the back electron-transfer process and the bond-cleavage process in the radical pair produced by the photoinduced electron transfer. The rates of back electron transfer have been shown to be controlled by the solvent polarity which affects the solvent reorganization energy of the back electron transfer. When the free energy change of the back electron transfer (ΔG^0_{bet}) in a polar solvent is in the Marcus inverted region, the rate of back electron transfer decreases with decreasing the solvent polarity, leading to the larger limiting quantum yield for the photoalkylation reaction. In contrast, the opposite trend is obtained when the ΔG^0_{bet} value is in the normal region: the limiting quantum yield decreases with decreasing the solvent polarity.

Introduction

Electron transfer reactions are normally performed in polar solvents such as acetonitrile, in which the product ions of the electron transfer are stabilized by the strong solvation.[1−5] When a cationic electron acceptor (A^+) is employed in electron-transfer reactions with a neutral electron donor (D), the electron transfer from D to A^+ produces a radical cation ($D^{\bullet+}$) and a neutral radical ($A^\bullet$).[6,7] In such a case, the solvation before and after the electron transfer may be largely canceled out when the free energy change of electron transfer is expected to be rather independent of the solvent polarity.[8] On the other hand, the solvent reorganization energy for the electron-transfer reaction is expected to decrease with decreasing the solvent polarity.[9] It has been reported that a decrease in the solvent reorganization energy with decreasing the solvent polarity results in an increase in the quantum yield for formation of biphenyl radical cation produced in the photoinduced electron transfer from biphenyl to 10-methylacridinium cation ($MeAcrH^+$).[8] This result indicates that separation within the initially formed radical cation/radical pair can compete more effectively with the back electron transfer in nonpolar solvents as compared to that in polar solvents.[8] Although the utility of photoinduced electron transfer reactions is expected to be considerably extended if charge-shift type of electron-transfer reactions is developed in nonpolar solvents, there have so far been very few studies on photoinduced

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10.1021/ja004311l CCC: $20.00

electron-transfer reactions leading to the stable products in nonpolar solvents in comparison with those in polar solvents.[8,10]

We report herein the first systematic study on photoinduced electron-transfer reactions from a variety of neutral electron donors to the singlet excited states of organic cations, 10-methylacridinium cation ($MeAcrH^+$), and 10-decylacridinium cation ($DeAcrH^+$) in polar and nonpolar solvents, respectively. It is found that the photoinduced electron-transfer reactions in nonpolar solvents proceed as efficiently as those in polar solvents. It is also found that photoinduced electron-transfer reactions of $MeAcrH^+$ and $DeAcrH^+$ with organometallic alkylating agents such as tetraalkyltin compounds (R_4Sn) and 4-*tert*-butyl-1-benzyl-1,4-dihydronicotinamide (Bu^tBNAH) which are known as novel organic alkylating agents[11] lead to the reductive alkylation to yield the corresponding alkylated dihydroacridine (MeAcrHR or DeAcrHR) as a stable product. The efficiency for the product formation determined as the limiting quantum yield is highly dependent on the solvent polarity and the electron donor properties of the alkylating agents. The choice of a series of R_4Sn as electron donors is expected to benefit from an additional advantage other than the ability to act as alkylating reagents, that is the large inner-sphere reorganization energy ($\lambda = 41$ kcal mol^{-1}) associated with the electron-transfer oxidation.[12,13] The large reorganization energy for the electron-transfer oxidation of R_4Sn leads to extend the boundary of the Marcus inverted region to the highly exergonic region (−1.8 eV). Since the one-electron oxidation potentials (E^0_{ox}) of R_4Sn can be finely tuned by the choice of alkyl groups (R), the free energy change of back electron transfer can be so widely altered by changing R and the solvent polarity as to lie in the Marcus normal or inverted region. The reactivities of R_4Sn can also be compared with the organic electron donor (Bu^tBNAH) which has a much smaller reorganization energy ($\lambda = 22.0$ kcal mol^{-1})[14] Thus, the present study provides an excellent opportunity to clarify how the reactivity of charge-shift type of photoinduced electron transfer reactions which lead to stable products can be finely controlled by the solvent polarity.

Experimental Section

Materials. 10-Methylacridinium iodide was prepared by the reaction of acridine with methyl iodide in acetone, and it was converted to the perchlorate salt ($MeAcrH^+ClO_4^-$) by addition of $Mg(ClO_4)_2$ to the iodide salt, and purified by recrystallization from methanol.[15,16] Likewise, 10-decylacridinium hexafluorophosphate was prepared by the reaction of acridine with decyl iodide in acetone and the subsequent metathesis with sliver hexafluorophosphate, followed by recrystallization from methanol.[8] 9-Substituted 10-methylacridinium perchlorates ($MeAcrR^+ClO_4^-$: R = Pr^i, CH_2Ph, and Ph) were prepared by the reaction of 10-methylacridone in dichloromethane with the corresponding Grignard reagents (RMgX), then addition of sodium hydroxide for the hydrolysis and perchloric acid for the neutralization, and purified by recrystallization from ethanol-diethyl ether.[17]

Electron donors (benzene, toluene, ethylbenzene, cumene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, and 1,2,4,5-tetramethylbenzene, pentamethylbenzene, hexamethylbenzene, triphenylamine, *N*,*N*-dimethylaniline, ferrocene, decamethylferrocene) were obtained commercially and purified by the standard method.[18] Tetraalkyltin compounds [tetramethyltin (Me_4Sn), tetraethyltin (Et_4Sn), and tetra-*iso*-propyltin (Pr^i_4Sn)] were obtained commercially from Aldrich, and di-*tert*-butyldimethyltin ($Bu^t_2Me_2Sn$) was prepared by the literature procedure.[12] The *tert*-butylated BNAH (Bu^tBNAH) was prepared by the Grignard reaction with BNA^+Cl^-.[11,19] 9-Alkyl-9,10-dihydro-10-methylacridine (AcrHR) was prepared as reported previously.[20] Acetonitrile, dichloromethane, chloroform, and benzene used as solvents were purified and dried by the standard procedure.[18] [$^2H_3$]acetonitrile (CD_3CN) was obtained from EURI SO-TOP, France. Tetrabutylammonium perchlorate (TBAP), obtained from Fluka Fine Chemical, was recrystallized from ethanol and dried in vacuo prior to use. Tetrahexylammonium perchlorate (THAP) was prepared by the addition of $NaClO_4$ to the tetrahexylammonium bromide in acetone, followed by recrystallization from acetone.

Reaction Procedure. Typically, an [$^2H_3$]acetonitrile (CD_3CN) solution (0.8 cm^3) containing $MeAcrH^+$ (1.0×10^{-2} M) in an NMR tube sealed with a rubber septum was deaerated by bubbling with argon gas through a stainless steel needle for 5 min. After an alkylating agent [R_4Sn (2 μL) or Bu^tBNAH (2.4 mg)] was added to the solution, the solution was irradiated with a xenon lamp through a UV-cut filter ($\lambda < 310$ nm) at room temperature. After the reaction was complete, when the solution became colorless, the reaction solution was analyzed by ^1H NMR spectroscopy. The ^1H NMR measurements were performed using a Japan Electron Optics JNM-GSX-400 (400 MHz) NMR spectrometer. The products for the photochemical reaction of $MeAcrH^+$ with R_4Sn were identified as MeAcrHR by comparing the ^1H NMR spectra with those of the authentic samples.[20]

Fluorescence Quenching. Quenching experiments of the fluorescence of $MeAcrH^+$ and $DeAcrH^+$ by electron donors were performed using a Shimadzu RF-5000 fluorescence spectrophotometer. The excitation wavelength was 398 nm for $MeAcrH^+$ and $DeAcrH^+$. The monitoring wavelengths were those corresponding to the maxima of the emission bands at $\lambda = 488$ and 498 nm, respectively. The solutions were deoxygenated by argon purging for 10 min prior to the measurements. Relative emission intensities were measured for acetonitrile (MeCN) solution containing $MeAcrH^+$ or $DeAcrH^+$ (5.0×10^{-5} M) with electron donors at various concentrations ($3.0 \times 10^{-3} - 2.5$ M). There was no change in the shape but there was a change in the intensity of the fluorescence spectrum by the addition of an electron donor. The Stern−Volmer relationship (eq 1)

$$I_0/I = 1 + K_{SV}[D] \tag{1}$$

was obtained for the ratio of the emission intensities in the absence and presence of quenchers (I_0/I) and the concentrations of quenchers [D]. The fluorescence lifetimes τ of $MeAcrH^+$ and $DeAcrH^+$ were determined as 31 ns in MeCN, 30 ns in $CHCl_3$ and 29 ns in benzene by single photon counting using a Horiba NAES-1100 time-resolved spectrofluorophotometer. The observed quenching rate constants k_q (= $K_{SV}\tau^{-1}$) were obtained from the Stern−Volmer constants K_{SV} and the emission lifetimes τ.

Electrochemical Measurements. Cyclic voltammetry measurements were performed at 298 K on a BAS 100W electrochemical analyzer in deaerated solvent containing 0.1 M tetrabutylammonium perchlorate (TBAP) or tetrahexylammonium perchlorate (THAP) as supporting electrolyte. A conventional three-electrode cell was used with a gold working electrode (surface area of 0.3 mm^2) and a platinum wire as the counter electrode. The Pt working electrode (BAS) was routinely

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(10) Although the radical/radical cation pair was observed in benzene in competition with return electron transfer in photoinduced charge-shift reaction from biphenyl to 10-decylacridinium cation ($DeAcrH^+$), products in such nonpolar solvent have yet to be reported in ref 8.

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Table 1. Fluorescence Quenching Rate Constants (k_q) of $MeAcrH^+$ and $DeAcrH^+$ by Electron Donors in Various Solvents, Oxidation Potential of Electron Donors, and the Free Energy Change of Photoinduced Electron Transfer (ΔG^0_{et})

no.	electron donor	E^0_{ox} vs SCE[a] in MeCN, V	ΔG^0_{et},[b] eV	k_q,[c] $M^{-1}\ s^{-1}$		
				MeCN $MeAcrH^+$	$CHCl_3$ $MeAcrH^+$	C_6H_6 $DeAcrH^+$
1	benzene	2.35	0.03	1.3×10^7	7.6×10^6	–
2	toluene	2.20	−0.12	2.4×10^{8}[d]	6.6×10^7	3.5×10^7
3	ethylbenzene	2.14	−0.18	4.5×10^8	1.0×10^8	4.5×10^7
4	cumene	2.14	−0.18	2.4×10^8	4.4×10^8	5.7×10^7
5	*m*-xylene	2.02	−0.30	7.7×10^{9}[d]	3.5×10^{9}[d]	1.8×10^9
6	*o*-xylene	1.98	−0.34	7.9×10^{9}[d]	5.5×10^{9}[d]	2.0×10^9
7	1,3,5-trimethylbenzene	1.98	−0.34	1.2×10^{10}	5.0×10^9	2.7×10^9
8	*p*-xylene	1.93	−0.39	8.6×10^{9}[d]	4.2×10^{9}[d]	–
9	1,2,3-trimethylbenzene	1.88 (1.98)	−0.44	1.3×10^{10}	8.1×10^9	3.9×10^9
10	1,2,4-trimethylbenzene	1.79 (1.89)	−0.53	1.3×10^{10}	7.2×10^9	6.2×10^9
11	1,2,3,4-tetramethylbenzene	1.71 (1.81)	−0.61	1.5×10^{10}	7.1×10^9	7.9×10^9
12	1,2,3,5-tetramethylbenzene	1.71 (1.77)	−0.61	1.6×10^{10}	1.3×10^{10}	7.2×10^9
13	1,2,4,5-tetramethylbenzene	1.63 (1.75)	−0.69	1.9×10^{10}	6.7×10^9	9.1×10^9
14	pentamethylbenzene	1.58 (1.68)	−0.74	1.9×10^{10}	9.9×10^9	1.1×10^{10}
15	hexamethylbenzene	1.49 (1.60)	−0.83	2.1×10^{10}	8.4×10^9	1.1×10^{10}
16	triphenylamine	0.84	−1.48	2.2×10^{10}	–	–
17	*N*,*N*-dimethylaniline	0.71	−1.61	2.6×10^{10}	1.7×10^{10}	1.3×10^{10}
18	ferrocene	0.37	−1.95	–	2.1×10^{10}	–
19	decamethylferrocene	−0.20	−2.52	–	1.6×10^{10}	1.9×10^{10}

[a] Values in parentheses are determined in CH_2Cl_2. [b] Determined from the E^0_{red} value of $^1MeAcrH^{+*}$ (= 2.32 V vs SCE in MeCN)[22] and eq 2. [c] The experimental error is ±5%. [d] Taken from ref 23.

cleaned by soaking it in concentrated nitric acid, followed by repeating rinsing with water and acetone, drying at 353 K prior to use to avoid possible fouling of the electrode surface. The reference electrode was an Ag/0.01 M $AgNO_3$. The cyclic voltammograms were measured with various sweep rates in a deaerated solvent containing TBAP (0.10 M) or THAP (0.50 M) used as a supporting electrolyte at 298 K.

The second harmonic ac voltammetry (SHACV) measurements were performed on a BAS 100B electrochemical analyzer in deaerated MeCN containing 0.10 M TBAP as a supporting electrolyte at 298 K to determine the one-electron oxidation potentials of alkylbenzenes and triphenylamine. The platinum working electrode (BAS) was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire (BAS). The E^0_{ox} values (vs Ag/Ag^+) are converted to those vs SCE by adding 0.29 V.

ESR Measurements. The $MeAcrPh^\bullet$ was generated by the electron-transfer reduction of $MeAcrPh^+ClO_4^-$ ($1.7 \times 10^{-4} - 5.0 \times 10^{-3}$ M) with tetramethylsemiquinone radical anion (2.0×10^{-5} M) generated by comproportionation of tetramethyl-*p*-benzoquinone and tetramethylhydroquinone with tetrabutylammonium hydroxide. The solution containing the radical was transferred to an ESR tube under an atmospheric pressure of Ar. The ESR spectra were measured at various temperatures with a JEOL X-band spectrometer (JES-RE1XE). 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 ESR measurements were also carried out to detect the radical intermediates produced in the photochemical reaction of $MeAcrH^+ClO_4^-$ (1.0×10^{-2} M) with $Bu^t_2Me_2Sn$ (4.5×10^{-2} M) in frozen MeCN at 77 K under irradiation of light with a high-pressure mercury lamp (USH-1005D) focusing at the sample cell in the ESR cavity. The *g* values were calibrated with an Mn^{2+} marker and the hyperfine coupling constants (hfc) were determined by computer simulation using a Calleo ESR Version 1.2 program coded by Calleo Scientific on an Apple Macintosh personal computer.

Quantum Yield Determinations. A standard actinometer (potassium ferrioxalate)[21] was used for the quantum yield determination of the photochemical reactions of $MeAcrH^+$ and $DeAcrH^+$ with R_4Sn and Bu^tBNAH. A square quartz cuvette (10 mm i.d.) which contained a deaerated MeCN solution (3.0 cm^3) of $MeAcrH^+$ or $DeAcrH^+$ ($5.0 \times 10^{-5} - 1.0 \times 10^{-4}$ M) and R_4Sn ($1.0 \times 10^{-3} - 2.5$ M) or Bu^tBNAH ($5.0 \times 10^{-4} - 1.0 \times 10^{-3}$ M) was irradiated with monochromatized light of $\lambda = 398$ nm from a Shimadzu RF-5000 fluorescence spectrophotometer. Under the conditions of actinometry experiments, both the actinometer and $MeAcrH^+$ or $DeAcrH^+$ absorbed essentially all the incident light. The light intensity of monochromatized light of $\lambda = 398$ nm was determined as 1.8×10^{-8} einstein s^{-1} with the slit width of 20 nm. The photochemical reaction was monitored by using Hewlett-Packard 8452A and 8453 diode-array spectrophotometers. The quantum yields were determined from the decrease in absorbance due to $MeAcrH^+$ ($\lambda = 358$ nm, $\epsilon = 1.8 \times 10^4\ M^{-1}\ cm^{-1}$)[22] and $DeAcrH^+$ ($\lambda = 362$ nm, $\epsilon = 2.0 \times 10^4\ M^{-1}\ cm^{-1}$).

Laser Flash Photolysis. The measurements of transient absorption spectra in the photochemical reactions of $DeAcrH^+$ with R_4Sn in benzene were performed according to the following procedures. The benzene solution was deoxygenated by argon purging for 10 min prior to the measurement. The deaerated benzene solution containing $DeAcrH^+$ (5.0×10^{-5} M) and R_4Sn ($1.0 \times 10^{-3} - 2.5$ M) was excited by a Nd:YAG laser (Quanta-Ray, GCR-130, 6 ns fwhm) at 355 nm with the power of 30 mJ. A pulsed xenon flash lamp (Tokyo Instruments, XF80-60, 15 J, 60 ms fwhm) was used for the probe beam, which was detected with a Si-PIN module (Hamamatsu, C5331-SPL) after passing through the photochemical quartz vessel (10 mm × 10 mm) and a monochromator. The output from Si-PIN module was recorded with a digitizing oscilloscope (HP 54510B, 300 MHz). The transient spectra were recorded using fresh solutions in each laser excitation. All experiments were performed at 298 K.

Results and Discussion

Photoinduced Electron Transfer from Electron Donors to $MeAcrH^+$ and $DeAcrH^+$. Irradiation of the absorption band of $MeAcrH^+$ results in fluorescence at $\lambda = 488$ nm in MeCN and $CHCl_3$. The fluorescence lifetimes were determined by single photon counting, as 31 and 30 ns in MeCN and $CHCl_3$, respectively. Due to its limited solubility of $MeAcrH^+ClO_4^-$, it cannot be used in nonpolar solvents such as benzene. To overcome the solubility problem, 10-decylacridinium hexafluorophosphate ($DeAcrH^+PF_6^-$) instead of $MeAcrH^+ClO_4^-$ was dissolved in benzene. The fluorescence maximum of $DeAcrH^+$ (498 nm) in benzene is nearly the same as that of $MeAcrH^+$ in MeCN (488 nm). The fluorescence lifetime of $DeAcrH^+$ in

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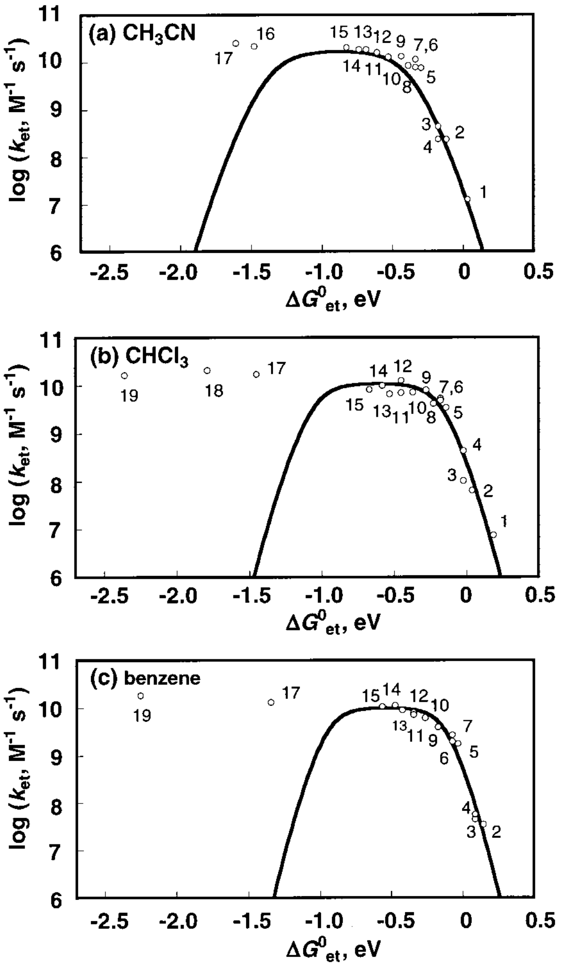


Figure 1. Plots of log k_q vs ΔG^0_{et} for the fluorescence quenching of MeAcrH$^+$ (2.0 × 10^{-4} M) by various electron donors in (a) MeCN and (b) in CHCl$_3$ and that of DeAcrH$^+$ (2.0 × 10^{-4} M) (c) in benzene at 298 K.

benzene (30 ns) is also nearly the same as that of MeAcrH$^+$ in MeCN (31 ns) (see Supporting Information, S1).

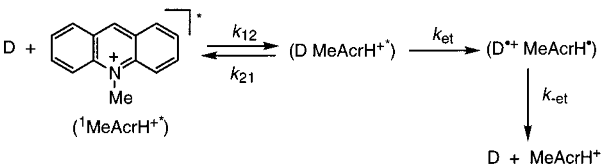
The fluorescence of the singlet excited state (^{1}MeAcrH^{+*}) is quenched efficiently by a variety of electron donors in MeCN and CHCl$_3$.[22,23] The quenching rate constants k_q are determined from the slopes of the Stern–Volmer plots and lifetime of the singlet excited state ^{1}MeAcrH^{+*}. The fluorescence of ^{1}DeAcrH^{+*} is also quenched efficiently by the same series of electron donors in benzene and the k_q values thus obtained are summarized in Table 1.

The free energy change of photoinduced electron transfer from electron donors to ^{1}MeAcrH^{+*} (ΔG^0_{et} in eV) is given by eq 2,

$$\Delta G^0_{\ et} = e(E^0_{\ ox} - E^0_{\ red}) \tag{2}$$

where e is elementary charge, E^0_{ox} and E^0_{red} are the one-electron oxidation potentials of electron donors and the one-electron reduction potential of ^{1}MeAcrH^{+*} (2.32 V), respectively.[7,22] Since the E^0_{ox} values of electron donors in MeCN have been determined in this study (see Experimental Section), the ΔG^0_{et} values are determined by using eq 2 as listed in Table 1 for comparison. Figure 1a shows a plot of log k_{et} vs ΔG^0_{et} in MeCN, which exhibits a typical feature of an electron-transfer process; the log k_{et} value increases with a decrease in the ΔG^0_{et} value to reach a plateau value corresponding to the diffusion rate constant (2.0 × 10^{10} M^{-1} s^{-1}) as the photoinduced electron transfer becomes energetically more favorable (i.e., more exergonic).[24]

Scheme 1



Photoinduced electron transfer from an electron donor (D) to ^{1}MeAcrH^{+*} may occur as shown in Scheme 1, where k_{12} and k_{21} are diffusion and dissociation rate constants in the encounter complex (D MeAcrH^{+*}), k_{et} and k_{-et} are the rate constants of the forward electron transfer from D to MeAcrH^{+*} and the back electron transfer to the ground state.[22,26] The observed quenching rate constant (k_q) of photoinduced electron transfer is given by eq 3.

$$k_q = \frac{k_{et}k_{12}}{k_{21} + k_{et}} \tag{3}$$

The dependence of k_{et} on ΔG^0_{et} for adiabatic outer-sphere electron transfer has well been established by Marcus as given by eq 4,

$$k_{et} = \left(\frac{kT}{h}\right)\exp\left[-\left(\frac{\lambda}{4}\right)\frac{\left(1 + \frac{\Delta G^0_{\ et}}{\lambda}\right)^2}{kT}\right] \tag{4}$$

where k is the Boltzmann constant, h is the Planck constant, and λ is the reorganization energy of electron transfer.[9] From eqs 3 and 4 is derived eq 5

$$k_q = k_{12}\,Z\exp\left[-\left(\frac{\lambda}{4}\right)\frac{\left(1 + \frac{\Delta G^0_{\ et}}{\lambda}\right)^2}{kT}\right] \Bigg/ \left(k_{12} + Z\exp\left[-\left(\frac{\lambda}{4}\right)\frac{\left(1 + \frac{\Delta G^0_{\ et}}{\lambda}\right)^2}{kT}\right]\right) \tag{5}$$

where $Z = [(kT/h)(k_{12}/k_{21})]$ is the collision frequency which is taken as 1 × 10^{11} M^{-1} s^{-1}.[9] The k_{12} values in MeCN, CHCl$_3$, and benzene are taken as 2.0 × 10^{10}, 1.2 × 10^{10}, and 1.1 × 10^{10} M^{-1} s^{-1}, respectively.[26]

The dependence of k_q on ΔG^0_{et} for electron-transfer quenching of ^{1}MeAcrH^{+*} by electron donors in MeCN is calculated on the basis of eq 5 using the best fit value of λ value (0.88 eV) as shown by the solid line in Figure 1a. The k_q values agree well with the calculated values except for the k_q values in the highly exergonic region, $\Delta G^0_{et} \ll -1$ eV, which are significantly larger than the calculated values (Figure 1a). The calculated dependence of k_q on ΔG^0_{et} (eq 5) predicts a decrease in the k_q value from a diffusion-limited value with increasing the driving force of electron transfer ($-\Delta G^0_{et}$) when the k_{et} values become smaller than the diffusion-limited value in the Marcus inverted region ($\Delta G^0_{et} < \lambda$), provided that the λ value is constant in a

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[23] Ohkubo, K.; Fukuzumi, S. *Org. Lett.* **2000**, *2*, 3647.

[24] (a) Rehm, A.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834. (b) Rehm, A.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

[25] In Scheme 1, the back electron transfer to the excited state is neglected when the back electron transfer to the ground state is much faster than the back electron transfer to the excited state.

[26] Kavarnos, G. J. *Fundamentals of Photoinduced Electron Transfer*; Wiley-VCH: New York, 1993.

Table 2. One-Electron Reduction Potentials E^0(MeAcrR$^+$/MeAcrR$^\bullet$) of MeAcrR$^+$ClO$_4^-$ Determined by the Cyclic Voltammograms in Deaerated Various Solvents at 298 K

		E^0(MeAcrR$^+$/MeAcrR$^\bullet$), V vs SCE		
solvent	ϵ	R = PhCH$_2$	R = Ph	R = Pr^i
MeCN^a	37.5	−0.50^c	−0.55^c	−0.63^c
CH$_2$Cl$_2$^{a}	7.8	−0.44^c	−0.49^c	−0.54^c
CHCl$_3$^{a}	4.8	−0.44^c	−0.47^c	−0.52^c
C$_6$H$_6$^{b}	2.3	−0.42^d	−0.45^d	−0.42^d

[a] Containing 0.1 M TBAP. [b] Containing 0.5 M THAP. [c] Sweep rate is 50 mV s^{-1}. [d] Sweep rate is 10 mV s^{-1}. See Supporting Information, Figure S2.

series of electron-transfer reactions.[9] The absence of a Marcus inverted region has well been recognized in forward photoinduced electron-transfer reactions.[24] In the case of back electron-transfer reactions, however, the observation of the Marcus-inverted region has been well established.[27−30] The absence of an inverted region in forward photoinduced electron transfer reactions in the highly exergonic region ($\Delta G^0_{et} < -\lambda$) can be explained by an increase in the λ value from the value for a contact radical ion pair (CRIP) to the value for a solvent separated radical ion pair (SSRIP) which has a larger distance between the radical ions in the highly exergonic region.[30] The existence of low-energy excited states of radical cations may also contribute to the nonexistence of an inverted region.[31]

The solvent independent ΔG^0_{et} value is confirmed by determination of the E^0_{ox} values of electron donors and the E^0_{red} values of acridinium ions in solvents with different polarity. The E^0_{ox} values of alkylbenzene derivatives have been determined in MeCN and CH$_2$Cl$_2$ as listed in Table 1 (see the values in parentheses). The E^0_{red} values of 10-methyl-9-substituted acridinium ions instead of MeAcrH$^+$ have also been determined in MeCN, CH$_2$Cl$_2$, CHCl$_3$ and benzene, since the reversible redox couples can be obtained for the 9-substituted derivatives in contrast to the case of MeAcrH$^+$ (see Supporting Information, S2). The E^0_{red} values are also listed in Table 2. The E^0_{ox} values in a less polar solvent (CH$_2$Cl$_2$) are shifted to the positive direction by about 0.1 V due to the less solvation of the radical cations as compared to that in MeCN (Table 1). Similar positive shifts are observed for the E^0_{red} values of acridinium ions in CH$_2$Cl$_2$ as compared to the E^0_{red} values in MeCN, and the larger shifts are observed in CHCl$_3$ and benzene (Table 2). Thus, the ΔG^0_{et} values obtained as the difference between the E^0_{ox} and E^0_{red} values (eq 2) become rather solvent-independent because of the cancellation of the solvation. However, the cancellation is not complete, since the positive shifts in the E^0_{ox} values are slightly larger than the shifts in the E^0_{red} values.

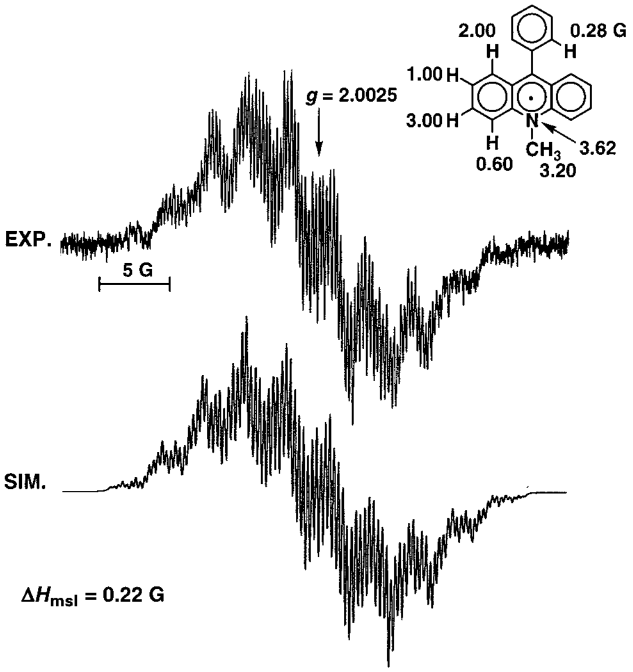

Figure 2. ESR spectrum of MeAcrPh$^\bullet$ in deaerated MeCN at 298 K and the computer simulation spectrum.

The dependence of k_q on ΔG^0_{et} for electron-transfer quenching of ^{1}R′AcrH^{+*} by aromatic electron donors in CHCl$_3$ and benzene is also calculated on the basis of eq 5 as shown in Figure 1b and Figure 1c, respectively. The ΔG^0_{et} values CHCl$_3$ and benzene are evaluated from the values in MeCN [ΔG^0_{et} (MeCN)] by using eq 6,

$$\Delta G^0_{et} = \Delta G^0_{et}\,(\text{MeCN}) + C \tag{6}$$

where the constant value C, which is dependent on the solvent, is determined by fitting the data to eq 5. The best fit values of λ and C are determined as $\lambda = 0.62$ eV, $C = 0.16$ eV in CHCl$_3$ and $\lambda = 0.53$ eV, $C = 0.27$ eV in benzene (see Supporting Information, S3).[32,33] The λ value decreases from the value in MeCN (0.88 eV) with decreasing the solvent polarity due to the smaller solvent reorganization energy, whereas the ΔG^0_{et} value increases, since the difference in solvation between aromatic donor radical cations and acridinium ion decreases with decreasing the solvent polarity.

Electron-Transfer Self-Exchange Reactions between MeAcrPh$^\bullet$ and MeAcrPh$^+$ in Different Solvents. The decrease in the solvent reorganization energy of electron transfer with decreasing the solvent polarity is examined by determining the rate constants of electron-transfer self-exchange reactions

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(27) (a) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (b) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047. (c) Asahi, T.; Mataga, N. *J. Phys. Chem.* **1989**, *93*, 6575. (d) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290. (e) Gould, I. R.; Farid, S. *Acc. Chem. Res.* **1996**, *29*, 522.

(28) (a) McLendon, G. *Acc. Chem. Res.* **1988**, *21*, 160. (b) Winkler, J. R.; Gray, H. B. *Chem. Rev.* **1992**, *92*, 369. (c) McLendon, G.; Hake, R. *Chem. Rev.* **1992**, *92*, 481.

(29) (a) Rau, H.; Frank, R.; Greiner, G. *J. Phys. Chem.* **1986**, *90*, 2476. (b) Stevens, B.; Biver, C. J., III; McKeithan, D. N. *Chem. Phys. Lett.* **1991**, *187*, 590. (c) Kikuchi, K.; Takahashi, Y.; Katagiri, T.; Niwa, T.; Hoshi, M.; Miyashi, T. *Chem. Phys. Lett.* **1991**, *180*, 403.

(30) Mataga, N.; Miyasaka, H., In *Electron Transfer from Isolated Molecules to Biomolecules, Part 2*; Jortner, J., Bixon, M., Eds.; Wiley: New York, 1999; p 431.

(31) Mataga, N.; Konda, Y.; Asahi, T.; Miyasaka, H.; Okada, T.; Kakitani, T. *Chem. Phys.* **1988**, *127*, 239.

(32) Since the redox potentials have been determined in the presence of the high concentration of electrolyte (Tables 1 and 3), the positive shifts of the redox potentials in less polar solvents may be larger in the absence of electrolyte as compared to those in its absence. This may be the reason the estimated C value is larger than that expected from the difference in the redox potentials determined in the presence of the high concentration of electrolyte.

(33) The best fit is obtained by linear plots between $(\Delta G^{\ddagger})^{1/2}$ vs ΔG^0_{et} (see Supporting Information, S3) which is derived from eq 5 as given by $(\Delta G^{\ddagger})^{1/2} = \lambda^{1/2}/2 + \Delta G^0_{et}/(2\lambda^{1/2})$, where $\Delta G^{\ddagger} = kT\ln[Z(k_q^{-1} - k_{12}^{-1})$ and $\Delta G^0_{et} = \Delta G^0_{et}(\text{MeCN}) + C$. The λ and C values were determined from the slope and the intercept of the least-squares linear plot. The correlation coefficients ρ of the linear plots for the fluorescence quenching in MeCN, CHCl$_3$, and benzene are 0.97, 0.96, and 0.97, respectively. The experimental errors in the λ and C values in MeCN, CHCl$_3$, and benzene are estimated using a standard graphical method as ±2, ±12, and ±11%, respectively. For a standard graphical method of determining the limit of error in an intercept and slope of a linear plot, see: Shoemaker, D. P.; Garland, C. W.; Steinfeld, J. I.; Nibler, J. W. *Experiments in Physical Chemsitry*; McGraw-Hill Book Company: New York, 1981; p 51.

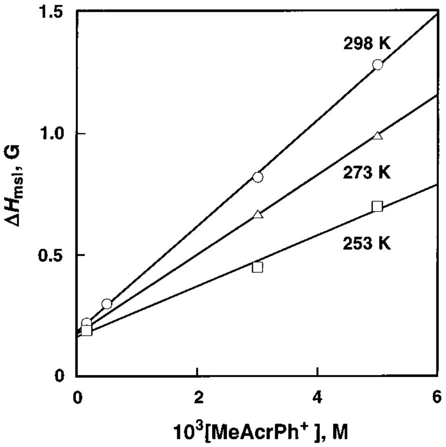


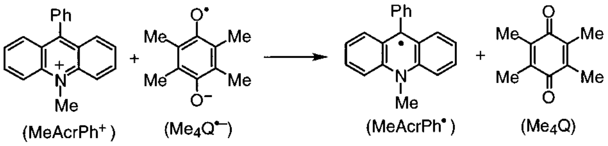
Figure 3. Plots of ΔH_{msl} vs [MeAcrPh$^+$] for the ESR spectra of MeAcrPh$^•$ in deaerated MeCN at various temperatures.

Table 3. Electron-Transfer Self-Exchange Rate Constants (k_{ex}), the Reorganization Energies (λ), and the Activation Parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the MeAcrPh$^•$/MeAcrPh$^+$ System

solvent	k_{ex},[a] $\mathrm{M^{-1}\,s^{-1}}$	λ, eV	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
MeCN	3.1×10^9	0.34	2.2	3.7
CH_2Cl_2	4.1×10^9	0.28	1.0	1.3
$CHCl_3$	4.2×10^9	0.27	1.1	1.3
C_6H_6	5.9×10^9	0.21	1.9	0.5

[a] The experimental error is ± 5%.

between 9-phenyl-10-methylacridinium ion (MeAcrPh$^+$) and the corresponding one-electron reduced radical (MeAcrPh$^•$) in solvents with different polarity. The MeAcrPh$^•$ radical was produced by the electron-transfer reduction of MeAcrPh$^+$ by tetramethylsemiquinone radical anion (eq 7). ESR spectra for



(7)

MeAcrPh$^•$ were persistent for several hours in deaerated MeCN. The hyperfine splitting constants and the maximum slope line widths (ΔH_{msl}) were determined from a computer simulation of the ESR spectra as shown in Figure 2. The ΔH_{msl} value thus determined increases linearly with an increase in the concentration of MeAcrPh$^+$ in MeCN as shown in Figure 3. Such line width variations of the ESR spectra can be used to investigate the rate processes involving the radical species.[34] The rate constants (k_{ex}) of the electron-transfer self-exchange reactions between MeAcrPh$^+$ and MeAcrPh$^•$ were determined using eq 8,

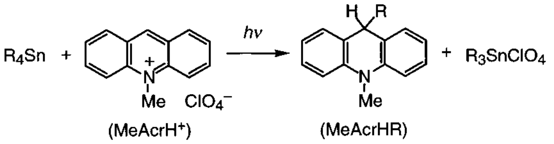
$$k_{\mathrm{ex}} = \frac{1.57 \times 10^7(\Delta H_{\mathrm{msl}} - \Delta H^0{}_{\mathrm{msl}})}{(1 - P_{\mathrm{i}})[\mathrm{MeAcrPh^+}]} \tag{8}$$

where ΔH_{msl} and $\Delta H^0{}_{\mathrm{msl}}$ are the maximum slope line width of the ESR spectra in the presence and absence of MeAcrPh$^+$, respectively, and P_{i} is a statistical factor which can be taken as nearly zero.[34,35] The k_{ex} values are determined from the slope of the linear correlations between ΔH_{msl} and [MeAcrPh$^+$] within experimental error of ±5% (Figure 3). The k_{ex} values in other solvents were determined in a similar manner and are listed in Table 3. The activation parameters were also determined by the Arrhenius plots (see Supporting Information, S4) as listed in Table 3. The small $\Delta S^{\ddagger}$ values in Table 3 are consistent with the outer-sphere electron-transfer reactions. The reorganization energies (λ) of the electron-transfer reactions are obtained from the k_{ex} values using eq 9

$$[(k_{\mathrm{ex}})^{-1} - (k_{\mathrm{diff}})^{-1}] = Z^{-1}\exp\left(\frac{\lambda}{4kT}\right) \tag{9}$$

where k_{diff} is the diffusion rate constant which corresponds to k_{12} in Scheme 1 ($k_{\mathrm{diff}} = 2.0 \times 10^{10}$ M^{-1} s^{-1} in MeCN, 2.0×10^{10} M^{-1} s^{-1} in CH_2Cl_2, 1.2×10^{10} M^{-1} s^{-1} in $CHCl_3$ and 1.1×10^{10} M^{-1} s^{-1} in benzene, respectively).[26] The λ values thus determined are also listed in Table 3. It is clearly shown that the λ value decreases with decreasing the solvent polarity.[36]

Photoalkylation of MeAcrH$^+$ and DeAcrH$^+$ with R$_4$Sn. Irradiation of the absorption band of MeAcrH$^+$ClO$_4^-$ in a deaerated MeCN solution containing R$_4$Sn with a xenon lamp for 1 h gave the alkyl adduct (MeAcrHR) as shown in eq 10 (see Experimental Section).[37] The quantum yields (Φ) of the



(10)

photoalkylation of MeAcrH$^+$ and DeAcrH$^+$ with R$_4$Sn were determined from the spectral change under irradiation of monochromatized light of $\lambda_{\mathrm{max}} = 398$ nm (see Experimental Section). The Φ value increases with an increase in the concentration of R$_4$Sn [R$_4$Sn] to approach a limiting value (Φ_∞) in accordance with eq 11

$$\Phi = \frac{\Phi_\infty K_{\mathrm{obs}}[\mathrm{R_4Sn}]}{1 + K_{\mathrm{obs}}[\mathrm{R_4Sn}]} \tag{11}$$

(see Supporting Information, S5). Equation 11 is rewritten by eq 12 which predicts a linear correlation between Φ^{-1} and [R$_4$Sn]$^{-1}$.

$$\Phi^{-1} = \Phi_\infty{}^{-1}[1 + (K_{\mathrm{obs}}[\mathrm{R_4Sn}])^{-1}] \tag{12}$$

From the slopes and intercepts of linear plots are obtained the Φ_∞ and K_{obs} values (see Supporting Information, S6). The K_{obs} values can be converted to the corresponding rate constants (k_{obs}) using the relation $K_{\mathrm{obs}} = k_{\mathrm{obs}}\tau$ provided that the excited state of MeAcrH$^+$ or DeAcrH$^+$ involved in the photochemical reaction is singlet. The k_{obs} and Φ_∞ values thus determined are listed in Table 4.

The fluorescence of ^{1}MeAcrH^{+*} and ^{1}DeAcrH^{+*} is quenched efficiently by electron transfer from R$_4$Sn in MeCN and benzene, respectively. The quenching rate constants k_{q} are also listed in Table 4, where the k_{obs} values derived from the dependence of

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(34) (a) Chang, R. *J. Chem. Educ.* **1970**, *47*, 563. (b) Cheng, K. S.; Hirota, N. In *Investigation of Rates and Mechanisms of Reactions*; Hammes, G. G., Ed.; Wiley-Interscience: New York, 1974; Vol. VI, p 565.

(35) Fukuzumi, S.; Nakanishi, I.; Suenobu, T.; Kadish, K. M. *J. Am. Chem. Soc.* **1999**, *121*, 3468.

(36) The difference in the λ values for the electron-transfer self-exchange of MeAcrPh$^+$/MeAcrPh$^•$ between MeCN and benzene (0.13 eV) is smaller than the corresponding difference for the electron-transfer reactions from aromatic electron donors to the singlet excited state of acridinium ion (0.27 eV). This is consistent with the smaller solvation of acridinium ion as compared to aromatic donor radical cations due to the more delocalized charge.

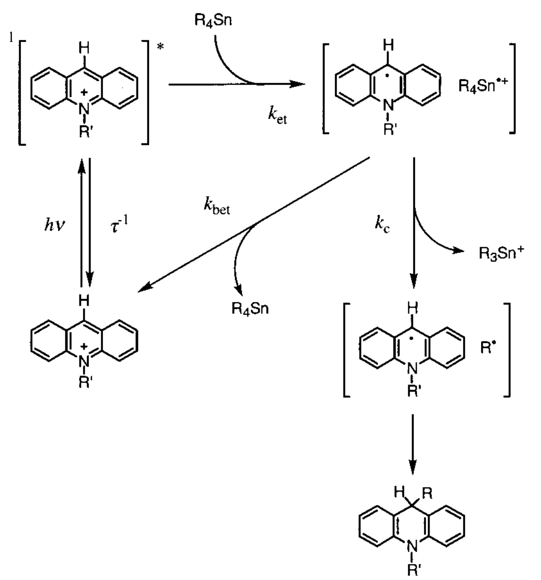
(37) Fukuzumi, S.; Kuroda, S.; Tanaka, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1553.

Table 4. Rate Constants (k_q) for the Fluorescence Quenching of $R'AcrH^+$ by R_4Sn, the Observed Rate Constants (k_{obs}) Derived from the Dependence of the Quantum Yields on [R_4Sn] in the Photoalkylation of $R'AcrH^+$ with R_4Sn in MeCN and Benzene at 298 K, and the Driving Force of Back Electron Transfer ($-\Delta G^0_{bet}$) from $R'AcrH^\bullet$ to $R_4Sn^{\bullet+}$ in MeCN

R_4Sn	solvent	k_q,[a] $M^{-1}\,s^{-1}$	k_{obs},[b] $M^{-1}\,s^{-1}$	Φ_∞[b]	$-\Delta G^0_{bet}$, eV[c]
Me_4Sn	benzene	1.1×10^8	1.1×10^8	0.0088	
	MeCN	3.3×10^8	4.2×10^8	0.00042	2.11
Et_4Sn	benzene	2.4×10^9	2.1×10^9	0.028	
	MeCN	2.0×10^{10}	2.4×10^9	0.007	1.67
$Pr^i{}_4Sn$	benzene	5.3×10^9	5.0×10^9	0.027	
	MeCN	7.7×10^9	8.0×10^9	0.0028	1.43
$Bu^t{}_2Me_2Sn$	benzene	1.1×10^{10}	1.7×10^{10}	0.0055	
	MeCN	1.1×10^{10}	1.4×10^{10}	0.021	1.29

[a] The experimental error is ±5%. [b] The experimental error is ±10%. [c] The $-\Delta G^0_{bet}$ values are obtained using eq 2 where ΔG^0_{et} is replaced by ΔG^0_{bet}.

Scheme 2



Φ on [R_4Sn] in both MeCN and benzene agree well with the corresponding k_q values of the fluorescence quenching. Such an agreement indicates that the photochemical reaction proceeds via photoinduced electron transfer from R_4Sn to the singlet excited states ($^1MeAcrH^{+*}$ and $^1DeAcrH^{+*}$).

The formation of $DeAcrH^\bullet$ in photoinduced electron transfer from Et_4Sn to $^1DeAcrH^{+*}$ in MeCN is confirmed by the laser flash photolysis of the $DeAcrH^+$-Et_4Sn system as shown in Figure 4a. The laser excitation (355 nm from a Nd:YAG laser) of $DeAcrH^+$ (8.0×10^{-5} M) in deaerated MeCN and benzene solutions containing Et_4Sn (8.2×10^{-3} M) gives transient absorption of $DeAcrH^\bullet$ which is essentially the same as that of $MeAcrH^\bullet$ (a broad absorption band between 450 and 540 nm).[22,38] The formation of $DeAcrH^\bullet$ in photoinduced electron transfer from the weakest electron donor employed in this study, that is Me_4Sn to $DeAcrH^+$ has also been confirmed in benzene as shown in Figure 4b. Thus, the photoalkylation of $R'AcrH^+$ (R = Me and De) with R_4Sn proceeds via photoinduced electron transfer from R_4Sn to $^1R'AcrH^{+*}$ as shown in Scheme 2.

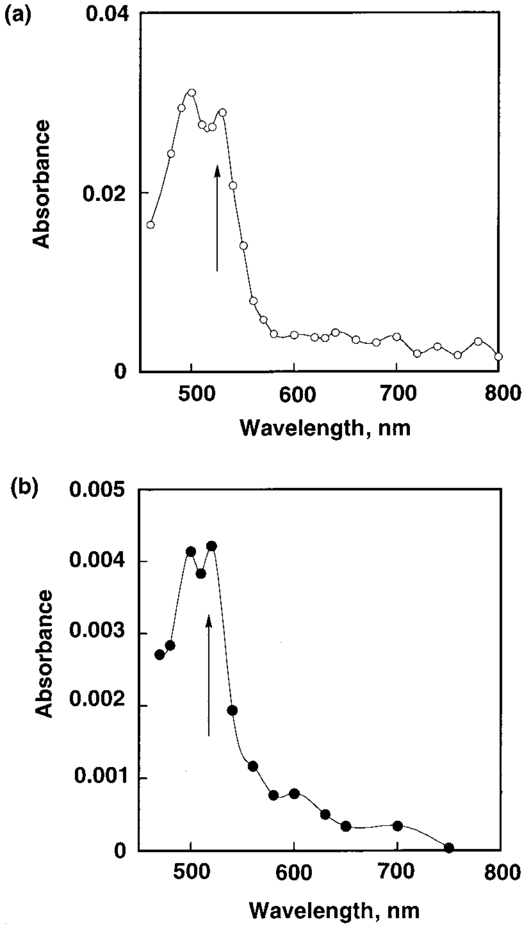


Figure 4. (a) Transient absorption spectra of $DeAcrH^\bullet$ generated in electron transfer from Et_4Sn (8.2×10^{-3} M) to $DeAcrH^+$ (8.0×10^{-5} M) in MeCN at 150 μs after laser excitation (355 nm) at 298 K. (b) Transient absorption spectra of $DeAcrH^\bullet$ generated in electron transfer from Me_4Sn (1.0×10^{-1} M) to $DeAcrH^+$ (5.0×10^{-4} M) in benzene at 150 μs after laser excitation (355 nm) at 298 K.

The photoalkylation is initiated by photoinduced electron transfer (k_{et}) from R_4Sn to $^1R'AcrH^{+*}$ to give the radical cation−acridinyl radical pair ($R_4Sn^{\bullet+}$ $R'AcrH^\bullet$). The Sn−C bond of $R_4Sn^{\bullet+}$ is known to be cleaved to give the alkyl radical,[39−42] which is coupled within the cage to yield the adduct selectively without dimerization of free $R'AcrH^\bullet$ radicals escaped from the cage,[43] in competition with the back electron transfer to the ground state (k_{bet}). In such a case, the limiting quantum yield Φ_∞ is determined by the competition between the cleavage of Sn−C bond of $R_4Sn^{\bullet+}$ in the radical cation/radical pair (k_c) and the back electron transfer from $R'AcrH^\bullet$ to $R_4Sn^{\bullet+}$ (k_{bet}) as given by eq 13.

$$\Phi_\infty = \frac{k_c}{k_{bet} + k_c} \tag{13}$$

In the case of $Bu^t{}_2Me_2Sn$, the Sn−Bu^t bond of $Bu^t{}_2Me_2Sn^{\bullet+}$ is cleaved selectively as compared to the Sn−Me bond,[40] to

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(38) (a) Peters, K. S.; Pang, E.; Rudzki, J. *J. Am. Chem. Soc.* **1982**, *104*, 5535. (b) Poulos, A. T.; Hammond, G. S.; Burton, M. E. *Photochem. Photobiol.* **1981**, *34*, 169.

(39) The transient absorption spectrum of $Et_4Sn^{\bullet+}$ is not observed because of the facile Sn−C bond cleavage of $Et_4Sn^{\bullet+}$; see: ref 40.

(40) Fukuzumi, S.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5961.

(41) (a) Walther, B. W.; Williams, F.; Lau, W.; Kochi, J. K. *Organometallics* **1983**, *2*, 688. (b) Symons, M. C. R. *Chem. Soc. Rev.* **1984**, *13*, 393.

(42) Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* **1980**, *45*, 2654.

(43) No significant amount of the dimer was observed in the present case, indicating that the radical coupling in the cage is highly efficient as compared to the escape of radicals from the cage. In the case of the photochemical reaction of diphenylmethane with $MeAcrH^+$, however, the dimers, $(MeAcrH)_2$ and $(Ph_2CH)_2$ have been obtained in addition to the adduct; see: ref 22.

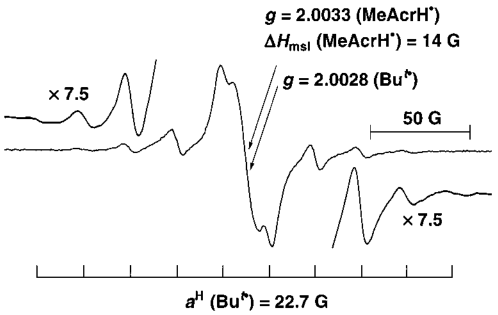

Figure 5. ESR spectrum of acridinyl radical ($MeAcrH^•$) and *tert*-butyl radical ($Bu^{t•}$) generated in photoinduced electron transfer from $Bu^t_2Me_2Sn$ (4.5×10^{-2} M) to the singlet excited state of $MeAcrH^+$ (1.0×10^{-2} M) observed in frozen MeCN at 77 K under irradiation of UV light by using high-pressure mercury lamp.

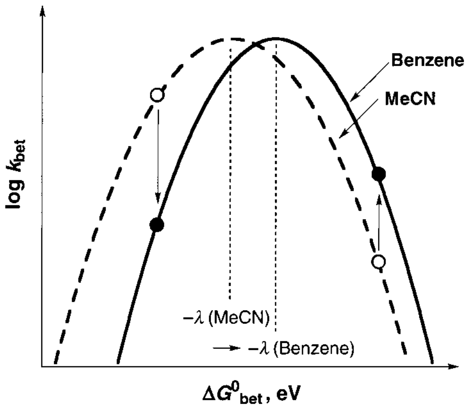

Figure 6. Dependence of log k_{bet} on $\Delta G^0{}_{bet}$ in MeCN (solid line) and benzene (broken line). The lines are drawn schematically based on eq 4. The $\Delta G^0{}_{bet}$ value at which k_{bet} is maximum corresponds to $-\lambda$ (eq 4).

give $MeAcrHBu^t$ rather than MeAcrHMe (see Experimental Section). This is confirmed by the ESR spectrum observed in photoinduced electron transfer from $Bu^t_2Me_2Sn$ to the singlet excited state of $MeAcrH^+$ observed in frozen MeCN at 77 K under photoirradiation with a high-pressure mercury lamp as shown in Figure 5. The 10-line isotropic spectrum is ascribed to the hyperfine coupling of an unpaired electron with the 9 equivalent protons of $Bu^{t•}$.[42,44] The broad signal at the center can be assigned due to $MeAcrH^•$.[45]

Solvent Dependence of the Limiting Quantum Yield. The Φ_∞ value varies drastically depending on the alkyl group (R) of R_4Sn and solvents from the smallest value (4.2×10^{-4}) for Me_4Sn in MeCN to the largest value (2.8×10^{-2}) for Pr^i_4Sn in MeCN as shown in Table 4. It is interesting to note that the Φ_∞ value of Me_4Sn in benzene is 21 times larger than the corresponding value in MeCN. However, this is reversed for $Bu^t_2Me_2Sn$; the Φ_∞ value in a polar solvent (MeCN) is 38 times larger than the corresponding value in a nonpolar solvent (benzene). The ratio of the Φ_∞ value in benzene to that in MeCN changes systematically from Me_4Sn to $Bu^t_2Me_2Sn$ with decreasing the driving force ($-\Delta G^0{}_{bet}$) of back electron transfer from $R'AcrH^•$ to $R_4Sn^{•+}$. The driving force is obtained from the difference between the $E^0{}_{ox}$ value of R_4Sn and $E^0{}_{red}$ value of $R'AcrH^+$ (eq 2),[46] and the $-\Delta G^0{}_{bet}$ values are listed in Table 4. According to eq 13, the Φ_∞ value is determined by the competition between the cleavage of Sn−C bond of $R_4Sn^{•+}$ in the radical cation/radical pair (k_c) and the back electron transfer from $R'AcrH^•$ to $R_4Sn^{•+}$ (k_{bet}). The solvent effects on the cleavage rates of Sn−C bond of $R_4Sn^{•+}$ have been studied previously, and it has been shown that the k_c values are rather independent of solvent polarity.[42,47] Thus, the Φ_∞ value is mainly determined by the back electron-transfer rate from $R'AcrH^•$ to $R_4Sn^{•+}$ (k_{bet}); the smaller the k_{bet} value, the larger is the Φ_∞ value. The k_{bet} value varies depending on $\Delta G^0{}_{bet}$ of back electron-transfer according to the Marcus equation (eq 4) as shown in Figure 6 where the dependence of log k_{bet} vs $\Delta G^0{}_{bet}$ in MeCN and benzene is drawn schematically.[9]

Table 5. Rate Constants (k_q) for the Fluorescence Quenching of $R'AcrH^+$ by Bu^tBNAH, the Observed Rate Constants (k_{obs}), and the Limiting Quantum Yields (Φ_∞) Derived from the Dependence of the Quantum Yields on [Bu^tBNAH] in the Photoalkylation of $R'AcrH^+$ with Bu^tBNAH

solvent	k_q, M^{-1} s^{-1}	k_{obs}, M^{-1} s^{-1}	Φ_∞
MeCN	2.1×10^{10}	2.3×10^{10}	0.04
$CHCl_3$	2.0×10^{10}	1.9×10^{10}	0.12
C_6H_6	2.3×10^{10}	2.1×10^{10}	0.81

The $-\Delta G^0{}_{bet}$ value at which the maximum k_{bet} value is obtained corresponds to the reorganization energy (λ) for the back electron transfer. The λ value for the electron-transfer oxidation of R_4Sn is known to be large ($\lambda = 41$ kcal mol^{-1} = 1.78 eV).[12,13] This is confirmed by analyzing the k_q values of photoinduced electron transfer from R_4Sn to $^1MeAcrH^{+*}$ in Table 4. The λ value can be obtained from the k_q and $\Delta G^0{}_{et}$ values using eq 5. The λ values thus evaluated are $\lambda = 1.95$ and 1.82 eV for Me_4Sn and Et_4Sn in MeCN, respectively.[48] These values agree with the reported large value.[12,13] In such a case, the $-\Delta G^0{}_{et}$ value is changed from the value in the Marcus inverted region in the case of Me_4Sn to the normal region up to 1.2 eV which is significantly smaller than the λ value in the case of $Bu^t_2Me_2Sn$. According to the Marcus equation (eq 4), the k_{bet} value decreases with decreasing the λ value in the inverted region, whereas the k_{bet} value increases in the normal region (Figure 6). The λ value is expected to decrease with decreasing the solvent polarity (Table 3). In fact, the λ values evaluated from the k_q and $\Delta G^0{}_{et}$ values in benzene using eq 5 ($\lambda = 1.52$ and 1.30 eV for Me_4Sn and Et_4Sn, respectively) are significantly smaller than those in MeCN (vide supra).[49] This is the reason the Φ_∞ value of Me_4Sn in benzene is much larger than the corresponding value in MeCN, whereas this is reversed for $Bu^t_2Me_2Sn$, the Φ_∞ value of which in MeCN is 38 times larger than the corresponding value in benzene (Table 4). Thus, whether the back electron transfer is in the Marcus inverted region or in the normal region determines whether the Φ_∞ value increases or decreases with decreasing the solvent polarity. In such a case, the solvent dependence of Φ_∞ would be reversed if the photoinduced electron-transfer system with the much smaller λ value than the $R_4Sn-R'AcrH^+$ system is chosen (*vide infra*).

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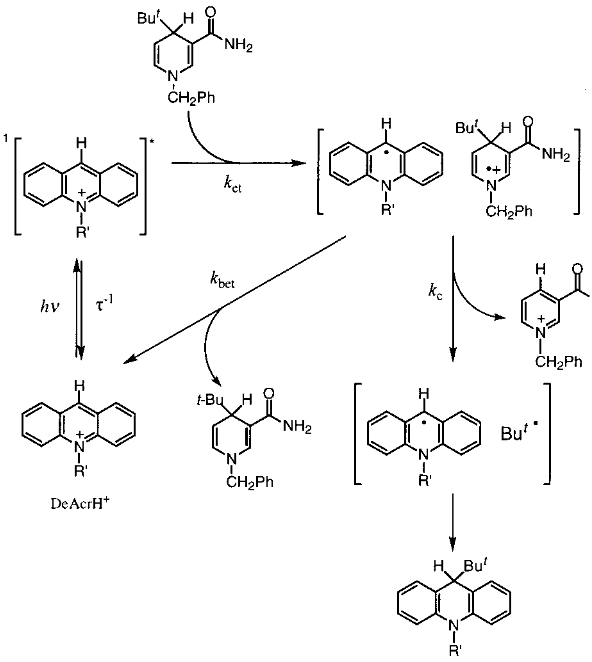
[46] The $E^0{}_{red}$ value of $DeAcrH^+$ is assumed to be the same as that of $MeAcrH^+$. See ref 8.

[47] The counterion may also affect the cleavage rates of Sn−C bond of $R_4Sn^{•+}$. In this study, however, the counterion remains the same (ClO_4^-). The selectivities of the cleavage of Sn−C bond of $R_xR'_{4-x}Sn^{•+}$ ($x = 1-3$) are known to be the same irrespective of the difference in the counterion between I^- and $IrCl_6^{3-}$.[42] The selectivities are also unaffected by changes in the solvent.[42]

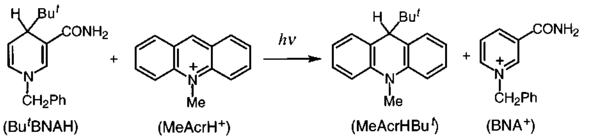
[48] The λ value of Pr^i_4Sn is also determined as 1.82 eV. However, the evaluation of the λ value from the k_q value which is close to the diffusion-limit involves a large experimental error.

[49] The $\Delta G^0{}_{et}$ values in benzene are evaluated from those in MeCN by using eq 6.

Scheme 3



Photoalkylation of Bu^{t}BNAH with MeAcrH$^+$ and DeAcrH$^+$. Irradiation of the absorption band of MeAcrH$^+$ClO$_4^-$ in a deaerated MeCN solution containing Bu^{t}BNAH with a xenon lamp for 1 h gave an adduct (MeAcrHBu^t) as shown in eq 14 (see Experimental Section). The same type of reaction



(14)

occurs when MeAcrH$^+$ is replaced by DeAcrH$^+$ in benzene. Thus, the product derived from R′AcrH$^+$ is the same as obtained in the photoalkylation with Bu$^t_2$Me$_2$Sn. The quantum yields (Φ) of the photoalkylation of R′AcrH$^+$ with Bu^{t}BNAH were determined from the spectral change under irradiation of monochromatized light of $\lambda_{max} = 398$ nm (see Experimental Section). The Φ_∞ and k_{obs} values are determined as the case of the photoalkylation with R$_4$Sn, and they are listed in Table 5 (see Supporting Information, S7). In contrast with the case of Bu$^t_2$Me$_2$Sn (Table 4), the Φ_∞ value increases with decreasing the solvent polarity and the Φ_∞ value in benzene is *20 times larger* than that in MeCN.

The k_q values are also determined independently by the fluorescence quenching via electron transfer from Bu^{t}BNAH to ^{1}MeAcrH^{+*} and ^{1}DeAcrH^{+*}, and they are also listed in Table 5 in which the k_q values agree with the k_{obs} values. Such an agreement indicates that the photoalkylation of R′AcrH$^+$ with Bu^{t}BNAH proceeds via photoinduced electron transfer from Bu^{t}BNAH to ^{1}R′AcrH^{+*} as shown in Scheme 3. The photoinduced electron transfer from Bu^{t}BNAH to ^{1}R′AcrH^{+*} produces the radical cation/radical pair (Bu^{t}BNAH$^{\bullet+}$ R′AcrH$^\bullet$). Savéant et al. have reported that the electrochemical oxidation of Bu^{t}BNAH results in the selective C(4)−C bond cleavage of Bu^{t}BNAH$^{\bullet+}$.[50] Although there are two possible modes of the carbon−carbon bond cleavage in such reactions to generate (a) Bu$^{t\bullet}$ and BNA$^+$ or (b) Bu^{t+} and BNA$^\bullet$, the formation of Bu$^{t\bullet}$ in the one-electron oxidation of Bu^{t}BNAH has been confirmed by applying a rapid mixing flow electron spin resonance (ESR) technique.[51] Thus, cleavage of Bu^{t}BNAH$^{\bullet+}$ gives Bu$^{t\bullet}$ that is coupled immediately with MeAcrH$^\bullet$ to yield the adduct (MeAcrHBu^t) in competition with the back electron transfer from MeAcrH$^\bullet$ to Bu^{t}BNAH$^{\bullet+}$ (Scheme 3).

By applying the steady-state approximation to the reactive species in Scheme 2, the dependence of Φ on [Bu^{t}BNAH] can be derived as given by eq 15, which agrees with the observed dependence of Φ on [Bu^{t}BNAH].

$$\Phi = \frac{\left[\dfrac{k_c}{k_c + k_{bet}}\right] k_{et}\tau[\mathrm{Bu}^t\mathrm{BNAH}]}{1 + k_{et}\tau[\mathrm{Bu}^t\mathrm{BNAH}]} \qquad (15)$$

The limiting quantum yields Φ_∞ corresponds to $k_c/(k_c + k_{bet})$. In such a case the Φ_∞ value is determined by the competition between the C(4)−C bond cleavage (k_c) and the back electron transfer (k_{bet}). Since the reorganization energy (λ) of photoinduced electron transfer reactions of BNAH and derivatives in MeCN is relatively small ($\lambda = 0.5$ eV),[16] the back electron transfer from MeAcrH$^\bullet$ to Bu^{t}BNAH$^{\bullet+}$ should be in the Marcus inverted region ($-\Delta G^0_{bet} = 1.1$ eV $\gg 0.5$ eV) in contrast with the case of Bu$^t_2$Me$_2$Sn ($-\Delta G^0_{bet} = 1.1$ eV $\ll 1.8$ eV). Thus, the solvent reorganization energy should decrease with decreasing the solvent polarity, leading to the decrease in the back electron-transfer rate in the Marcus inverted region as shown in Figure 6 and thereby an increase in the Φ_∞ value (Table 5).

Summary and Conclusions

The present study has shown that the reactivity of charge-shift type of photoinduced electron transfer reactions which lead to stable products can be finely controlled by the solvent polarity. The photoinduced electron transfer from electron donors to ^{1}R′AcrH^{+*} occurs efficiently even in a nonpolar solvent as well as in a polar solvent to yield the stable adducts between R′AcrH$^\bullet$ and radicals produced by the bond-cleavage of the radical cations to yield the stable adducts. The limiting quantum yield increases with decreasing the solvent polarity when the back electron transfer from R′AcrH$^\bullet$ to the radical cations is in the Marcus inverted region, whereas the yield decreases when the back electron transfer is in the Marcus normal region.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research Priority Area (No. 11228205) from the Ministry of Education, Science, Culture and Sports, Japan.

Supporting Information Available: Fluorescence decay curves of R′AcrH$^+$ (Figure S1), cyclic voltammograms of MeAcrPr^{i+}ClO$_4^-$ in various solvents (Figure S2), plots of $(\Delta G^\ddagger)^{1/2}$ vs ΔG^0_{et} for the fluorescence quenching of R′AcrH$^+$ by various electron donors in different solvents (Figure S3), Arrhenius plots of k_{ex} for the electron-transfer self-exchange reaction of MeAcrPh$^\bullet$/MeAcrPh$^+$ system (Figure S4), dependence of the quantum yields for photoalkylation of R′AcrH$^+$ with R$_4$Sn (Figure S5), plots of Φ^{-1} vs [R$_4$Sn]$^{-1}$ (Figure S6), plots of Φ^{-1} vs [Bu^{t}BNAH]$^{-1}$ (Figure S7) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA004311L

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