10-Methylacridine Derivatives Acting as Efficient and Stable Photocatalysts in Reductive Dehalogenation of Halogenated Compounds with Sodium Borohydride via Photoinduced **Electron Transfer**

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Abstract: 10-Methylacridine derivatives, 9,10-dihydro-10-methylacridine (AcrH₂) and acriflavine (AFH⁺), act as efficient and stable photocatalysts in reductive dechlorination of p-chlorobiphenyl (CIBP) as well as dehalogenation of other halogenated compounds with sodium borohydride (NaBH₄) in a mixture of acetonitrile and H_2O (9:1 v/v) at 298 K. The reductive dechlorination proceeds via the reduction of ClBP by the singlet excited state ($^{1}AcrH_{2}^{*}$) to yield dechlorinated product (biphenyl) and 10-methylacridinium ion (AcrH⁺), followed by the facile reduction of AcrH⁺ with NaBH₄ to regenerate AcrH₂. The absence of the primary kinetic isotope effect as well as the comparison of the observed rate constants with those predicted by using the Marcus theory of electron transfer indicates that the reduction of halogenated compounds (RX) by the singlet excited state (¹AcrH₂*) proceeds via photoinduced electron transfer from ¹AcrH₂* to RX, which results in the cleavage of C-X bonds. In the photocatalytic reductive dehalogenation of o-, m-, and p-bromochlorobenzenes, cleavage of the C-Br bond predominates over that of the C-Cl bond in each case. In the case of halobenzyl halide $(X-C_6H_4CH_2X; X = Cl, Br)$ only the CH₂-X bond is cleaved to yield halotoluene $(X-C_6H_4CH_2)$ selectively.

Photochemical reductive dehalogenation of halogenated compounds, especially polychlorinated biphenyls (PCBs) has been studied extensively, in part due to their role as environmental pollutants.²⁻⁸ Since direct irradiation of most halogenated compounds requires UV irradiation,³⁻⁶ it is desired to use an appropriate photocatalyst which has sufficient spectral overlap with solar spectrum. Although several photocatalytic systems for reductive dehalogenation have been reported,^{7,8} no photocatalyst has so far satisfied high efficiency and stability at the same time.

On the other hand, the carbon-halogen bond of halogenated compounds is known to be cleaved readily upon the one-electron reduction. Such dissociative electron transfer processes of halogenated compounds have been studied extensively by means of electrochemical techniques,9-11 electron spin resonance (ESR),12-14

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and pulse radiolysis¹⁵ for the detection of radical species formed upon the one-electron reduction of halogenated compounds. As such, the mechanisms of dissociative electron transfer have been well established,9-15 and important parameters describing the energetics, such as the one-electron reduction potentials (E°_{red}) and the intrinsic barrier of electron transfer (the activation Gibbs energy at zero driving force) of both aliphatic and aromatic halides, are now available.⁹⁻¹¹ However, few applications of such dissociative electron transfer processes to appropriate photocatalytic systems have so far been reported. The mechanistic aspects of photocatalytic reductive dehalogenation also remain to be resolved.

This study reports efficient and stable photocatalytic systems for reductive dechlorination of p-chlorobiphenyl (ClBP), which is known to be one of the most difficult to be reduced among PCBs, 3f,5b as well as dehalogenation of other halogenated compounds using sodium borohydride (NaBH₄) and 10-methylacridine derivatives [9,10-dihydro-10-methylacridine (AcrH₂) and acriflavine (AFH⁺)] as a reductant and photocatalysts, respectively.



Mechanisms of the photocatalytic systems are discussed on the basis of the quantum yield determinations of both the photocatalytic reactions and the photoreduction of ClBP and other halogenated compounds by AcrH₂ (or AFH₂ which is the reduced

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form of AFH⁺), the fluorescence quenching by halogenated compounds, the primary kinetic isotope effects, and the comparison of the observed rate constants with those predicted by using the Marcus theory of electron transfer. We report also the selectivities of cleavage of carbon-halogen bonds of halogenated compounds containing different types of carbon-halogen bonds in the present photocatalytic system.

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.¹⁶ The dideuteriated compound, [9,9'-2H2]-9,10-dihydro-10-methylacridine $(AcrD_2)$, was prepared from 10-methylacridone by reduction with Li-AlD₄,¹⁷ which was obtained from Aldrich Chemical Co. Acriflavine (AFH⁺), p-chlorobiphenyl (ClBP), o-, m-, and p-bromochlorobenzene, o-, m-, and p-chlorobenzyl chloride, p-bromobenzyl bromide, and other halogenated compounds were obtained commercially and purified by standard methods.¹⁸ Sodium borohydride (NaBH₄) was obtained from Wako Pure Chemicals. Potassium ferrioxalate used as an actinometer was prepared according to the literature¹⁹ and purified by recrystallization from hot water. Acetonitrile (MeCN) as well as acetonitrile d_3 (CD₃CN) used as a solvent was purified by a standard procedure.¹⁸

Reaction Procedure. Typically, after a mixture of MeCN and H₂O (9:1 v/v, 0.5 mL) containing AcrH₂ (2.0×10^{-3} M), ClBP (1.0×10^{-1} M), and NaBH₄ (0.10-1.0 M)²⁰ in a square quartz cuvette (1 mm i.d.) was deaerated with a stream of argon, it was irradiated with the light from an Ushio Model U1-501 xenon lamp. All the resulting products were analyzed by GLC. The change of concentrations of $AcrH_2$ (λ_{max} = 285 nm) during the reaction was measured by using a Union SM-401 spectrophotometer.

The photoreduction of halogenated compounds by AcrH₂ was also carried out in the absence of NaBH₄. Typically, AcrH₂ (60 μ mol) was added to an NMR tube that contained a CD₃CN solution (0.6 mL) of halogenated compounds (30 μ mol). After the reactant solution in the NMR tube was deaerated, it was irradiated for about 10 h with light from a xenon lamp. The products were identified by comparison of their ¹H NMR spectra with those of authentic samples of AcrH⁺ and dehalogenated compounds. The deuterium incorporation into products was also determined from the ¹H NMR spectra. The ¹H NMR measurements were carried out using a Japan Electron Optics JNM-PS-100 (100 MHz) or JNM-GSX-400 (400 MHz) NMR spectrometer.

Quantum-Yield Determinations. A standard actinometer (potassium ferrioxalate)¹⁹ was used for the quantum yield determinations. The actinometry experiments were carried out under the same conditions as those of the photoreduction of halogenated compounds. Typically, after an McCN/H₂O (9:1 v/v) solution (2.0 mL) containing AcrH₂ (2.0 × 10^{-3} M) and a halogenated compound in the absence or presence of NaBH₄ ((1.0-2.0) × 10⁻¹ M)²⁰ in a square quartz cuvette (10 mm i.d.) was deaerated thoroughly with a stream of argon, it was irradiated with monochromatized light from a Ushio Model UXL-157 xenon lamp of a Hitachi 650-10S fluorescence spectrophotometer. The monochromatized wavelengths for the photochemical reactions of AcrH2 and AFH2 were selected normally as 320 nm and 350 nm, which are beyond the absorption due to halogenated compounds, respectively. The intensities of monochromatized light of λ = 320 nm (20-mm slit width) and λ = 350 nm (20-mm slit width) were determined as 2.2×10^{-6} and 2.4×10^{-6} einstein dm⁻³ s⁻¹, respectively. The quantum yields were determined from the rates of product formation (dehalogenated compounds and AcrH⁺) by comparing with the incident light intensity absorbed by AcrH₂ and AFH2. In most cases the concentrations of AcrH2 were chosen such that approximately all the incident light was absorbed by $AcrH_2$. In the presence of $NaBH_4$, the absorption by $AcrH^+$ or AFH^+ was negligible, since the facile reduction of AcrH⁺ or AFH⁺ by NaBH₄ occurred during the photocatalytic reactions. In the case of photoreduction of halogenated compounds by AcrH₂ in the absence of NaBH₄, the quantum yields were



Figure 1. Photodechlorination of CIBP (0.10 M) with NaBH₄ (1.0 M) (a) in the absence of catalyst (Δ), (b) in the presence of AcrH₂ (2.0 × 10^{-2} M) (O), and (c) AFH⁺ (2.0 × 10^{-2} M) (\bullet) in a mixture of MeCN and H₂O (9:1 v/v) at 298 K under irradiation of light from a xenon lamp. Plots of ratio of the product concentration [Ph-Ph] to the initial ClBP concentration [ClBP]₀ vs irradiation time.

determined from the initial rate of formation of AcrH⁺ under the conditions that the light absorption by AcrH⁺ can be neglected as compared to that by AcrH₂. The light absorption of chlorinated compounds was negligible at the irradiation wavelength of $\lambda > 320$ nm. At high concentrations of halogenated compounds such as alkyl iodides, however, the absorption by the halogenated compounds were taken into account in determining the quantum yields of the photoreduction by AcrH₂. The concentrations of products were determined by GLC as well as the electronic spectra.

Fluorescence Quenching. Fluorescence measurements were carried out on a Hitachi 650-10S fluorescence spectrophotometer. In the fluorescence quenching experiments, the excitation wavelengths beyond the quencher absorption were selected normally as 320 nm and 350 nm for $AcrH_2$ and AFH_2 , respectively. Relative fluorescence intensities were measured for deaerated MeCN/H₂O (9:1 v/v) solutions of AcrH₂ (or AFH⁺) with a quencher at various concentrations in the presence of $NaBH_4$ (1.0 × 10⁻¹ M).²⁰ Relative fluorescence intensities were measured also for deaerated MeCN solutions of AcrH₂ (1.0×10^{-5} M) with a quencher at various concentrations in the absence of NaBH4. 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 fluorescence inten-

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

sities in the absence and presence of a quencher (I_0/I) and the concentrations of halogenated compounds used as quenchers [RX]. The fluorescence lifetime τ of AcrH₂ was determined as 7.0 ns in MeCN by single photon counting by using a Horiba fluorescence lifetime apparatus (NAES-1100). The τ value in the presence of H₂O [MeCN/H₂O (9:1 v/v] was the same as that in its absence. The observed quenching rate constants k_q (= $K_{SV}\tau^{-1}$) was obtained from the Stern-Volmer constant $K_{\rm SV}$ and the fluorescence lifetime τ .

Results and Discussion

Photoreduction of CIBP by NaBH₄ Catalyzed by Acridine Derivatives. No appreciable photoreduction of CIBP by NaBH₄ occurs in the absence of photocatalyst in a mixture of acetonitrile and H_2O (MeCN/H₂O, 9:1 v/v) under irradiation of light from a xenon lamp as shown in Figure 1 (part a).²¹ When 9,10-dihydro-10-methylacridine (AcrH₂) or acriflavine (AFH⁺) is added to this system at 298 K, each species acts as an efficient photocatalyst for reductive dechlorination of CIBP with NaBH4 to yield biphenyl as shown in Figure 1 (parts b and c, respectively). The formation of biphenyl was identified by GLC (see Experimental Section). When AcrH₂ was replaced by the oxidized form, 10methylacridinium perchlorate (AcrH⁺ClO₄⁻), essentially the same result was obtained, since AcrH+ was immediately reduced by NaBH₄ to yield AcrH₂ selectively.¹⁶ Similarly AFH⁺ was readily converted to the reduced form (AFH₂) by the reduction by

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⁽²⁰⁾ In the presence of high concentrations of NaBH₄ (e.g., 1.0 M), a mixture of MeCN and H₂O (9:1 v/v) separates into two phases. Thus, the quantum yield as well as the fluorescence measurments in the presence of NaBH₄ were performed at the lower concentrations.

⁽²¹⁾ The photolysis with a Ushio model U1-501 xenon lamp results in no appreciable reaction under our experimental conditions although photolysis of CIBP and NaBH₄ with a low-pressure mercury lamp is reported to result in the dechlorination of CIBP.^{5b}



Figure 2. Plots of Φ^{-1} vs $[C1BP]^{-1}$ for photodechlorination of CIBP (a) in the presence of AcrH₂ (2.0 × 10⁻³ M) and NaBH₄ (2.0 × 10⁻¹ M) (O), in the presence of AcrH⁺ (2.0 × 10⁻³ M) and NaBH₄ (1.0 × 10⁻¹ M) (\bullet) under irradiation of light of λ 320 nm, (b) in the presence of AFH⁺ (2.0 × 10⁻² M) and NaBH₄ (1.0 × 10⁻¹ M) under irradiation of light λ 350 nm (Δ), and (c) in the presence of AcrH₂ (2.0 × 10⁻³ M) without NaBH₄ under irradiation of light λ 320 nm (\bullet) in MeCN/H₂O (9:1 v/v) at 298 K.

NaBH₄. No appreciable photodegradation of the catalysts has been observed during the photocatalytic reaction, since the concentration of AcrH₂ or AFH₂ remains unchanged during the photocatalytic reactions. Thus, both AcrH₂/AcrH⁺ and AFH₂/AFH⁺ redox pairs act as not only efficient but also stable photocatalysts for dechlorination of ClBP with NaBH₄.

The quantum yields (Φ) of the photocatalytic dechlorination of CIBP were determined by using a ferrioxalate actinometer (see Experimental Section). The Φ values in the presence of AcrH₂ under irradiation of light of $\lambda = 320$ nm were constant with the change of both AcrH₂ and NaBH₄ concentrations. On the other hand, the quantum yield increased with an increase in the concentration of CIBP to approach a limiting value (Φ_{∞}) in the high concentrations in accordance with eq 2, where K_{obs} is the observed quenching constant of the excited state involved in the photocatalytic reaction. Equation 2 can be rewritten as eq 3, which

$$\Phi = \Phi_{\infty} K_{\text{obs}} [\text{CIBP}] / (1 + K_{\text{obs}} [\text{CIBP}])$$
(2)

$$\Phi^{-1} = \Phi_{\infty}^{-1} [1 + (K_{obs}[ClBP])^{-1}]$$
(3)

predicts a linear correlation between Φ^{-1} and [ClBP]. Such a linear correlation is confirmed for the photocatalytic reduction of CIBP by NaBH₄ in the presence of AcrH₂ as shown in Figure 2 (part a). From the linear plot are obtained the Φ_{∞} and K_{obs} values as listed in Table I. When AcrH₂ is replaced by AcrH⁺ClO₄⁻, essentially the same Φ value is obtained as shown in Figure 2 (part a), since AcrH⁺ is readily converted to AcrH₂ by the reduction with NaBH₄ (vide supra). A linear correlation between Φ^{-1} and [ClBP]⁻¹ is also obtained for the photocatalytic reduction of ClBP by NaBH₄ in the presence of AFH⁺ under irradiation of light of $\lambda = 350$ nm as shown in Figure 2 (part b). The Φ_{∞} value determined for the AFH₂/AFH⁺ catalytic system $(\Phi_{\infty} = 0.63)$ from the plot in Figure 2 (part b) is larger than the Φ_{∞} value of the AcrH₂/AcrH⁺ system (0.42), but the K_{obs} value $(3.3 \times 10^1 \text{ M}^{-1})$ is smaller than that of the latter system (1.6 × 10^2 M⁻¹) as shown in Table I.

In the absence of NaBH₄, the stoichiometric reduction of ClBP by AcrH₂ in MeCN/H₂O (9:1 v/v) under irradiation of light of $\lambda = 320$ nm occurs to yield biphenyl and AcrH⁺ (eq 4). The

$$AcrH_2 + Cl - + Cl - +$$

(4)

 Φ value in the absence of NaBH₄ shows a similar dependence on

Table I. Limiting Quantum Yields (Φ_m) and the Observed
Quenching Constants K_{obs} of the Excited States Involved in the
Photoreduction of ClBP in the Presence of AcrH ₂ (2.0×10^{-3} M) or
AFH ⁺ (2.0 × 10 ⁻² M) in MeCN/H ₂ O (9:1 v/v) at 298 K, and the
Stern-Volmer Constants (K_{SV}) for the Fluorescence Quenching of
¹ AcrH ₂ * and ¹ AFH ₂ * by CIBP in MeCN/H ₂ O (9:1 v/v) at 298 K

actidine	in th of	ne presence `NaBH₄	in ti of	he absence NaBH ₄	in the presence of NaBH ₄	
derivative	Φ <i>a</i> , <i>b</i>	K_{obs} , ^{<i>a,b</i>} M ⁻¹	$\Phi_{\infty}^{a,b}$	K_{obs} , ^{<i>a,b</i>} M ⁻¹	$\overline{K_{SV}}^{b,c}$ M ⁻¹	
AcrH ₂ ^d	0.42	1.6×10^{2}	0.61	1.2×10^{2}	1.2×10^{2}	
AFH [∓] ″	0.63	3.3×10^{1}	-	-	3.6×10^{1}	

^a Determined from the plots in Figure 2. ^b Determined from the Stern-Volmer plots for the fluorescence quenching. ^cThe experimental errors are within $\pm 10\%$. ^dThe irradiation wavelength is 320 nm; [Na-BH₄] = 2.0 × 10⁻¹ M. ^cThe irradiation wavelength is 350 nm; [NaB-H₄] = 1.0 × 10⁻¹ M.

Scheme I



[ClBP] to the Φ value in the presence of NaBH₄. Thus, a linear correlation between Φ^{-1} and [ClBP]⁻¹ (eq 3) is also obtained for the stoichiometric photoreduction of ClBP by AcrH₂ as shown in Figure 2 (part c). The Φ_{∞} and K_{obs} values, determined from the plot in Figure 2 (part c), agree reasonably well with those obtained for the catalytic reaction in the presence of NaBH₄ (Table I).²²

Since the one-electron oxidation potential (E°_{ox}) of the singlet excited state $^{1}AcrH_{2}^{*}$ is known to be largely negative (E°_{ox} = -3.1 V vs SCE), ²³ ¹AcrH₂* may act as a very strong reductant. In fact, the fluorescence of ¹AcrH₂* as well as ¹AFH₂* is readily quenched by ClBP. The fluorescence quenching may be a dynamic process, since no complex formation is observed between CIBP and AcrH₂ as well as AFH₂. From the Stern-Volmer plots are obtained the Stern-Volmer constants (K_{SV}) of ${}^{1}AcrH_{2}^{*}$ and ${}^{1}AFH_{2}^{*}$ as listed in Table I $(1.2 \times 10^{2} \text{ M}^{-1} \text{ and } 3.6 \times 10^{1} \text{ M}^{-1}$, respectively). The K_{SV} values of ${}^{1}AcrH_{2}^{*}$ and ${}^{1}AFH_{2}^{*}$ agree well with the K_{obs} values determined from the plots of Φ^{-1} vs [ClBP]⁻¹ (eq 3) for the photoreduction of ClBP with $AcrH_2$ and AFH_2 in the presence and absence of NaBH₄ (Table I). Such agreements of K_{SV} and K_{obs} values indicate that the photocatalytic dechlorination of CIBP by NaBH₄ proceeds via the reductive dechlorination of CIBP by the singlet excited states ¹AcrH₂* (or $^{1}AFH_{2}^{*}$), followed by the facile thermal reduction of AcrH⁺ (or AFH⁺) with NaBH₄ to regenerate AcrH₂ (or AFH₂) as shown in Scheme I.

Photoreduction of Halogenated Compounds by AcrH₂ via Photoinduced Electron Transfer. In the absence of NaBH₄, the stoichiometric reduction of various halogenated compound (RX; X = I, Br, and Cl) by AcrH₂ occurs also in MeCN under irradiation of light of $\lambda = 320$ nm to yield RH and AcrH⁺. When AcrH₂ is replaced by the 9,9'-dideuteriated analogue (AcrD₂), the deuterium is incorporated into the dehalogenated product (see Experimental Section, eq 5).²⁴ As the case of ClBP (eq 3), the

$$\operatorname{Acr} D_2 + \mathrm{RX} \xrightarrow{n\nu} \operatorname{Acr} D^+ + \mathrm{RD} + \mathrm{X}^-$$
 (5)

$$\Phi^{-1} = \Phi_{\infty}^{-1} [1 + (K_{obs}[RX])^{-1}]$$
(6)

⁽²²⁾ The limiting quantum yields in the presence of NaBH₄ may be larger than the observed value 0.42, since the photolysis in the presence of NaBH₄ results in the formation of H₂ which bubbles up from the reactant solution, causing the slight decrease in the light absorption, which is not taken account in determining the Φ values. (23) Fukuzumi, S.; Tanaka, T. Photoinduced Electron Transfer; Fox, M.

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Table II.	Observed Rate	e Constants	(k_a) for the	Reactions of	¹ AcrH ₂ * and	$^{1}AcrD_{2}^{*}$	with RX in	MeCN at	298 K,	Calculated Rate	Constants of
Electron	Transfer from ¹	AcrH ₂ * to	RX, and the	Gibbs Energ	y Change ($\Delta 0$	G° _{et}) and	Intrinsic Ba	arrier (ΔG_0^*) of the	Electron Transfe	r

RX	ΔG°_{et} , ^{<i>a</i>} kcal mol ⁻¹	$\Delta G_0^{*,b}$ kcal mol ⁻¹	$k_{q}(\operatorname{Acr} H_{2}), c$ $M^{-1} s^{-1}$	$k_q(\operatorname{Acr} D_2), c$ $M^{-1} s^{-1}$	k_{et} , ^d M ⁻¹ s ⁻¹
PhCl	-7.4°	5.8°	6.0×10^{8}	6.2×10^{8}	5×10^{8}
p-CNC ₆ H ₄ Cl	-21.2 ^e	5.88	2.2×10^{10}	2.2×10^{10}	2×10^{10}
PhBr	-15.2 ^e	6.3e	1.2×10^{9}	_	7×10^{9}
PhI	_	-	2.6×10^{10}	2.7×10^{10}	-
PhCH ₂ Cl	-50.9	18.3*	3.0×10^{9}	2.7×10^{9}	4×10^{9}
CCl	-52.5	11.7'	3.2×10^{10}	-	2×10^{10}
CHCh	-	-	2.0×10^{10}	-	-
CH ₂ Cl ₂	-	-	3.8×10^{8}	3.3×10^{8}	-
C ₃ H ₃ Br	-44.5	17.7	4.6×10^{8}	4.6×10^{8}	1×10^{9}
C ₂ H ₄ Br	-45.2	17.7	7.0×10^{8}	6.4×10^{8}	1×10^{9}
PhCH ₃ Br	-55.34	17.7	2.6×10^{10}	-	1×10^{10}
C ₄ H ₆ I	-43.6	14.5 ^k	1.7×10^{10}	_	9×10^{9}
CH	-41.2^{f}	14.5/	1.8×10^{10}	-	7×10^{9}
C ₃ H ₄ I	-44.75	14.5/	1.8×10^{10}	-	1×10^{10}

^a Obtained from the E_{ox}° and E_{red}° values of ¹AcrH₂* (refs 23 and 26) and RX by using eq 8, respectively. ^bAssumed to be the same as those reported for electron transfer from aromatic radical anions to RX. ^cThe experimental errors are ±10%. ^dCalculated by using eqs 7-9 (see text). The $\mathcal{E}^{\circ}_{red}$ values are taken from ref 9. ^fThe $\mathcal{E}^{\circ}_{red}$ values are taken from ref 27. ^gAssumed to the same as that of PhCl. ^hTaken from ref 11b. ⁱObtained from the data reported in ref 11c by using eq 7. ^jAssumed to be the same as that of C₄H₉Br (ref 10), since the simple alkyl halides are known to have similar ΔG_0^{\dagger} values (ref 11a). ^kTaken from ref 10. ^lAssumed to be the same as that of C₄H₉I.



Figure 3. Stern-Volmer plots for fluorescence quenching of ¹AcrH₂*(O) and $^{1}AcrD_{2}^{*}(\bullet)$ with *p*-CNC₆H₄Cl and C₂H₅Br in MeCN at 298 K.

linear correlation between Φ^{-1} and $[RX]^{-1}$ are also obtained (eq 6). The fluorescence of $AcrH_2$ is also quenched efficiently with RX. From the Stern-Volmer plots are obtained the Stern-Volmer constants (K_{SV}) which agree well with the K_{obs} values obtained from the plots of Φ^{-1} and $[RX]^{-1}$ as observed in the case of CIBP (Table I). Thus, the observed quenching rate constants (k_q) are obtained from the fluorescence lifetime τ and K_{SV} (or K_{obs}) by using the relation, $k_q = K_{SV}\tau^{-1}$ (or $K_{obs}\tau^{-1}$). Typical Stern-Volmer plots for both AcrH₂ and the 9,9'-dideuteriated analogue (AcrD₂) are shown in Figure 3, where no appreciable primary kinetic isotope effects are observed. The k_q and Φ_{∞} values of both AcrH₂ and AcrD₂, thus obtained are summarized in Table II and Table III, respectively.

The absence of primary kinetic isotope effects on both k_q and Φ_{∞} (Tables II and III) suggests that the quenching of ¹AcrH₂* with RX may be electron transfer from ${}^{1}AcrH_{2}^{*}$ to RX. The activation Gibbs energy (ΔG_{et}^*) of such electron transfer may be calculated by using the Marcus equation (eq 7),²⁵ where ΔG°_{et}

$$\Delta G_{\rm et}^{*} = \Delta G_{0}^{*} [1 + (\Delta G_{\rm et}^{\circ} / 4 \Delta G_{0}^{*})]^{2}$$
(7)

is the standard Gibbs energy change of electron transfer and ΔG_0^* is ΔG_{et}^* at zero driving force ($\Delta G_{et}^\circ = 0$). The ΔG_{et}° values of

Table III. Limiting Quantum Yields (Φ_{∞}) of the Photoreduction of Halogenated Compounds (RX) by AcrH₂ and AcrD₂ in MeCN at 298 K and the Gibbs Energy Change (ΔG°_{be}) of Back Electron Transfer from RX* to AcrH₂

PY	AG9 # koal mal-	Φ (AcrH)b	Φ (AcrD) ^b
<u> </u>	<u>ao be, Kear mor</u>	$\Psi_{\omega}(Acm_2)$	$\Psi_{\infty}(ACD_2)$
PhCI	-83	0.12	0.12
p-CNC ₆ H ₄ Cl	-69	0.17	0.17
PhBr	-76	0.20	-
PhI	-	0.21	0.20
PhCH ₂ Cl	-39	0.21	0.21
CCl₄ ¯	-37	0.34	-
CHCl ₃	-	0.27	0.27
CH ₂ Cl ₂	-	0.17	0.17
C ₃ H ₇ Br	-45	0.20	-
C ₂ H ₅ Br	-45	0.15	0.13
C₄H₀I	-46	0.32	-
PhCH ₂ Br	-35	0.31	-
CH ₃ I	49	0.12	-
C ₂ H ₅ I	-45	0.15	-

^a Obtained from the E°_{ox} and E°_{red} values of AcrH₂ (ref 26) and RX (refs 9 and 27) by using eq 8. ^b The experimental errors are $\pm 10\%$.

electron transfer from ${}^{1}AcrH_{2}^{*}$ to RX are obtained from the oxidation potential of the singlet excited state ${}^{1}AcrH_{2}^{*}$ (E°_{ox} = -3.1 V vs SCE)^{23,26} and the one-electron reduction potentials of RX $(E^{\circ}_{red})^{9-11,27}$ by using eq 8, where F is the Faraday constant.

$$\Delta G^{\circ}_{\text{et}} = F(E^{\circ}_{\text{ox}} - E^{\circ}_{\text{red}}) \tag{8}$$

With regard to the intrinsic barrier for the one-electron reduction of RX, the ΔG_0^* values of electron transfer from electrogenerated aromatic radical anions to various halogenated compounds have been reported.⁹⁻¹¹ The reported ΔG_0^* values may be applied directly to the present case, since the intrinsic barrier for the one-electron oxidation of various aromatic radical anions being constant are similar to that of AcrH₂.^{23,26} The ΔG°_{et} and ΔG^{\ddagger}_{0} values thus obtained are listed in Table II.28 On the other hand, the rate constant of photoinduced electron transfer $(k_{\rm el})$ is known to be given as a function of $\Delta G^{*}_{\rm et}$ and $\Delta G^{\circ}_{\rm et}$ (eq 9).²⁹ The $k_{\rm et}$ $k_{et} =$

$$\frac{(2.0 \times 10^{10})}{[1 + 0.25[\exp(\Delta G_{\rm et}^*/RT) + \exp(\Delta G_{\rm et}^\circ/RT)]]}$$
(9)

⁽²⁴⁾ In the case of CHCl₃, the dechlorinated product was obtained as CDHCl₂ (see Experimental Section). (25) (a) Marcus, R. A. J. Chem. Phys. **1965**, 43, 679. (b) Marcus, R. A.

Ann. Rev. Phys. Chem. 1964, 15, 155.

⁽²⁶⁾ Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. J. Am. Chem. Soc. 1987, 109, 305.

⁽²⁷⁾ Eberson, L. Acta Chem. Scand. 1982, B36, 533. (28) The E°_{red} values in DMF^{9,10,27} are used to obtain the G°_{el} values, since the most reported ΔG°_{0} values have been determined in DMF.⁹⁻¹¹ The use of the E°_{red} and ΔG°_{el} values in DMF instead of those in MeCN may be justified, since no significant difference in the rate constants of electron transfer from aromatic radical anions to RX in MeCN and DMF has been observed.^{11a}

Scheme II



values calculated from the ΔG°_{et} and ΔG^{*}_{0} values in Table II by using eqs 7 and 9 are also listed in Table II.

If uncertainties in the ΔG°_{et} and ΔG^{*}_{0} values are taken into account, reasonable agreement between k_{et} and k_{q} combined with the absence of the primary kinetic isotope effects on k_q (Table II) strongly indicates that the photoreduction of RX by $AcrH_2$ proceeds via photoinduced electron transfer from ${}^{1}AcrH_{2}^{*}$ to RX as shown in Scheme II. It is well known that the one-electron reduction of RX results in the cleavage of C-X bond to give R* and X^{-,9-15} Thus, the photoinduced electron transfer from ¹AcrH₂* to RX may be followed by the fast hydrogen transfer from Acr H_2^{*+} to R^{*}, yielding Acr H^+ and RH (Scheme II).³⁰ In the case of aromatic halides the radical anions (RX^{*-}) are generally believed to have a finite lifetime.^{10,12,14} In such a case the bond-breaking process of $RX^{-}(k_{br})$ yielding the dehalogenated products may compete with the back-electron-transfer process (k_{be}) from ArX^{*-} to $AcrH_2^{*+}$ (Scheme II). By applying the steady-state approximation to the reactive intermediates, ¹AcrH₂* and $(AcrH_2^{+}RX^{-})$ in Scheme II, the dependence of Φ on [RX] can be derived as given by eq 10, which agrees with the experimental results in eq 6 (or eq 2). By comparing eqs 6 and 10 the limiting quantum yield (Φ_{∞}) may be given by eq 11. The absence of

$$\Phi = k_{\rm et}\tau k_{\rm br}[{\rm RX}]/(1+k_{\rm et}\tau[{\rm RX}])(k_{\rm br}+k_{\rm be}) \qquad (10)$$

$$\Phi_{\infty} = k_{\rm br} / (k_{\rm br} + k_{\rm be}) \tag{11}$$

primary kinetic isotope effects on Φ_{∞} values in Table III also supports eq 11, where no hydrogen transfer process is involved. According to eq 11, the Φ_{∞} value may be determined by the competition between the bond-breaking process (k_{br}) and the back-electron-transfer process (k_{be}) . The Gibbs energy change of the back electron transfer from RX^{•-} to AcrH₂^{•+} (ΔG°_{be}) is obtained from the one-electron oxidation potential of AcrH2++ $(E^{\circ}_{ox} = 0.80 \text{ V vs SCE})^{26.31}$ and the one-electron reduction potentials of RX $(E^{\circ}_{red})^{.9.27}$ The ΔG°_{be} values thus obtained are also listed in Table III.

It has been reported that the lifetime of radical anions of aromatic halides (k_{br}^{-1}) increases generally with the positive shift of the one-electron-reduction potentials of aromatic halides.^{10b} Unlike the case of aromatic halides, radical anions of alkyl halides are generally believed to have no detectable lifetime.^{10,32-34} In this case as well, the lifetime may increase with the positive shift of the one-electron-reduction potentials of alkyl halides, since the discreet radical anions of alkyl halides with electron withdrawing



Nuclear Configuration

Figure 4. Qualitative potential energy curves for photoinduced electron transfer from $^{1}AcrH_{2}^{*}$ to RX emphasizing the similarity of the energetic barrier of back electron transfer from RX⁺ to AcrH₂⁺⁺ and that of C-X bond breaking of RX*-.

Scheme III



substituents such as CCl4 - and CF3X - are known to exist.35,36 Thus, the k_{br} values of radical anions of halogenated compounds in Table III, where the Gibbs energy change of back electron transfer from RX^{•-} to AcrH₂^{•+} (ΔG°_{be}) spanning a wide range are expected to vary significantly. In this context, the rather constant Φ_{∞} values in Table III (0.12–0.32) may at first sight seem surprising. However, the k_{be} value may also vary in parallel with the $k_{\rm hr}$ value. This possibility is indicated in Figure 4, which displays the plausible energy surface profiles of photoinduced electron transfer from ¹AcrH₂* to RX schematically.³⁷ Initially, excitation of AcrH₂ brings the reactant system to an excited-state energy surface where thermal equilibration into a lower vibration state is rapidly established. Following electron transfer, nuclear relaxation rapidly established the thermally equilibrated radical ion pair (AcrH2*+ RX*-). The stretching of R-X bond of RX*by surmounting the bond breaking barrier (ΔG_{br}^*) yields the products (Acr $H_2^{\bullet+}$, R[•], and X⁻). When the back electron transfer from RX^{•-} to AcrH₂^{•+} is highly exergonic ($\Delta G^{\circ}_{be} \ll 0$) as shown in Table III, the activation Gibbs energy of back electron transfer (ΔG_{bc}^*) may be close to that of bond-breaking process (ΔG_{br}^*) as shown in Figure 4.38-40 Thus, irrespective of the magnitude of

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Wang, J. T.; Williams, F. J. Am. Chem. Soc. 1970, 95, 4000. (b) Wang, J. T.; Williams, F. J. Am. Chem. Soc. 1980, 102, 2860. (37) Electron transfer from $^{1}AcrH_{2}^{*}$ to RX may be adiabatic, although no splitting at the crossing point between the reaction and product potential surfaces is shown in the simplified figure.

Scheme IV

$$(AcrH_{2}^{*}CIC_{6}H_{4}^{*}-Br^{-}) \longrightarrow AcrH^{*} + PhBr + Ci^{-}$$

$$^{1}AcrH_{2}^{*} + CIC_{6}H_{4}Br$$

$$(AcrH_{2}^{*}BrC_{6}H_{4}^{*}-Ci^{-}) \longrightarrow AcrH^{*} + PhCi + Br^{-}$$

Table IV. Selectivity (%) of Photocatalytic Reductive Dehalogenation of Halogenated Compounds $(2.0 \times 10^{-1} \text{ M})$ by NaBH₄ $(2.0 \times 10^{-1} \text{ M})$ in the Presence of AcrH₂ $(2.0 \times 10^{-3} \text{ M})$ under Irradiation of Light $\lambda = 320$ nm in MeCN/H₂O (9:1 v/v) at 298 K

halogenated compound	product,ª %	
o-BrC ₆ H ₄ Cl	PhCl (89), PhBr (11)	_
m-BrC ₆ H ₄ Cl	PhCl (94), PhBr (6)	
P-BrC ₆ H₄Cl	PhCl (87), PhBr (13)	
o-CIC6H4CH2CI	$o-ClC_{6}H_{4}CH_{1}(100)$	
m-ClC ₆ H ₄ CH ₂ Cl	$m - ClC_6H_4CH_3$ (100)	
p-CIC ₆ H ₄ CH ₂ CI	$p-ClC_{6}H_{4}CH_{3}$ (100)	
<i>p</i> -BrC ₆ H ₄ CH ₂ Br	$p-BrC_{6}H_{4}CH_{3}$ (100)	
4D to a line of C to the	(<1007) 43	

⁹ Determined by GLC at low conversions (<10%).⁴³

 ΔG_{br}^* (or lifetime of RX^{*-}) the approximate relation $\Delta G_{br}^* \simeq \Delta G_{be}^*$ $(k_{\rm br} \simeq k_{\rm be})$ may always hold, when the Φ_{∞} value $[k_{\rm br}/(k_{\rm br} + k_{\rm be})]$ is approximately constant being close to 0.5 as observed in Tables I and III (0.12-0.63).41

Selectivities of Reductive Dehalogenation. With regard to radical anions of aromatic halides both the π^* and σ^* radicals which differ in the orbital occupied by the unpaired electron (π^* and σ^* denote that the unpaired electron lies in the π^* and σ^* type orbitals, respectively) are known to exist.¹² If electron is transferred initially to the π^* orbital of ArX, the σ bond breaking may occur via intramolecular electron transfer from the π^* to σ^* orbital, the energy barrier of which may correspond to that of the bondbreaking process.^{10b} Alternatively, an electron may be transferred directly to the σ^* orbitals to yield the σ^* radicals.⁴² The distinction whether the π^* radicals are intermediates for the formation of σ^* radicals or not may be achieved by examining the selectivities in the reductive dehalogenation of aromatic halides containing different C-X bonds (vide infra). In the former case photoinduced electron transfer from ¹AcrH₂* to ClC₆H₄Br gives the corresponding π^* radical anions which are converted to different σ^* radical anions, $ClC_6H_4^{\bullet}-Br^{-}$ and $BrC_6H_4^{\bullet}-Cl^{-}$ to yield chlorobenzene and bromobenzene, respectively (Scheme III). In this case the selectivities of the reductive dehalogenation may be determined by the competition of intramolecular electron transfer from the π^* to σ^* orbitals of the C-Cl and C-Br bonds. In the latter case the selectivities may be determined by the competition of initial electron transfer from ¹AcrH₂* to the C-Br and C-Cl σ^* orbitals of ClC₆H₄Br (Scheme IV).

The selectivities of reductive dehalogenation of bromochlorobenzenes (o-, m-, and $p-ClC_6H_4Br$) were determined by the product ratio of PhBr and PhCl in the AcrH₂/AcrH⁺-catalyzed photoreduction of ClC_6H_4Br with NaBH₄ in MeCN/H₂O (9:1



Figure 5. Calculated heat of formation $[\Delta(\Delta H_f)]$ for radical anions of PhCl(O) and p-CNC₆H₄Cl(\bullet) relative to ΔH_{f} at the same C-Cl bond distance as the corresponding neutral molecules and the energies (E) of the respective $\pi^*(\Delta, \blacktriangle)$ and $\sigma^*(\Box, \blacksquare)$ orbitals plotted against the bond-stretching distance (ΔC -Cl). The MNDO^{45,46} calculations of the ΔH_f and E values were carried out by taking the C-Cl bond distance as an independent variable with the rest of geometrical parameters being optimized.

v/v) under irradiation of light of $\lambda = 320 \text{ nm.}^{43}$ The concentrations of ClC_6H_4Br (0.20 M) were chosen such that the quantum yields are close to the limiting values (Φ_{∞}) . The results of the selectivities of reductive dehalogenation of o-, m-, and p-ClC₆H₄Br are summarized in Table IV, where PhCl is obtained as a major product in each case.⁴⁴ If the reductive dehalogenation of Cl- C_6H_4Br proceeds by direct formation of the σ^* radical anions (Scheme IV), the rates of reductive debromination of ClC₆H₄Br would be comparable to those of reductive dechlorination, judging from the similar Φ_{∞} values of reductive debromination of PhBr and dechlorination of PhCl (Table III). Thus, selective debromination of ClC₆H₄Br as compared to the dechlorination (Table IV) may indicate that the reductive dehalogenation proceeds via initial formation of the π^* radical anions (Scheme III), which should be more stable than the corresponding σ^* radical anions. Our quantum chemical calculations by using the semiempirical MNDO methodology^{45,46} also support this conclusion. The ΔH_f (heat of formation) values of radical anions of PhCl and p-CNC₆H₄Cl were calculated by taking the C-Cl bond distance as an independent variable with the rest of geometrical parameters being optimized. The relative energies $[\Delta(\Delta H_f)]$ as compared to those of the standard radical anions at the same C-Cl bond distance as the corresponding neutral molecules are plotted against the bond-stretching distance (Δ C-Cl) as shown in Figure 5, where the energy changes in the π^* and σ^* orbitals with ΔC -Cl are also given. As is clearly seen in the figure there is a sharp energetic barrier in the transition from the π^* to σ^* radicals at the crossing points between the π^* and σ^* orbitals.⁴⁷ The higher barrier for

⁽³⁸⁾ In such a highly exergonic reaction the crossing point between the product and ground-state reactant potential surfaces in the reaction coordinate may appear after the energy minimum of the product potential surface as known as the Marcus inverted region.^{39,40} In fact, the relation $\Delta G^{\circ}_{bc} < -4\Delta G^{\circ}_{0}$ holds in the case of aromatic halides (Tables II and III).

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⁽⁴¹⁾ In the case of alkyl halides without electron-withdrawing substituents no appreciable energy minimum may exist in the product potential surface, when $\Delta G_{br}^* \simeq \Delta G_{be}^* \simeq 0$. (42) Moreno, M.; Gallardo, I.; Bertran, J. J. Chem. Soc., Perkin Trans.

^{2 1989, 2017.}

⁽⁴³⁾ The product ratio was determined under a low conversion condition such that further dehalogenation of primary dehalogenated products can be neglected

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

⁽⁴⁶⁾ The personal computer version of a QCPE program by Prof. K. Kitaura (Osaka City University) was used for the calculations. (47) The energy barrier of the C-Cl bond cleavage in solution may be

significantly lower than the calculated value due to the solvation.



Figure 6. Calculated heat of formation $[\Delta(\Delta H_f)]$ for radical anions of o-(0, \bullet), m-(Δ , \blacktriangle), and p-ClC₆H₄CH₂Cl(\Box , \blacksquare) relative to ΔH_f at the same C-Cl bond distance as the corresponding neutral molecules plotted against the bond-stretching distance (Δ C-Cl) of the Cl-C₆H₄ and CH₂-Cl bonds, respectively. The MNDO^{45,46} calculations were carried out by taking each C-Cl bond distance as an independent variable with the rest of geometrical parameters being optimized. The geometrical change of the CH₂Cl group with stretching of the CH₂-Cl bond is shown as the plot of the dihedral angle (θ) between the aromatic ring and the CH₂ planes vs Δ C-Cl.

p-CNC₆H₄Cl⁻⁻ as compared to PhCl⁻⁻ (Figure 5) agrees with the reported longer lifetime of the former radical anion.^{9b}

The more enhanced selectivities are observed in the AcrH₂/ AcrH⁺-catalyzed reductive dehalogenation of halobenzyl halides

 $(X-C_6H_4CH_2X; X = Cl, Br)$ with NaBH₄ as shown in Table IV, where $X-C_6H_4CH_3$ is obtained selectively with no detectable formation of PhCH₂X in each case. Such highly selective cleavage of the CH_2 -X bond as compared to that of the X-C₆H₄ bond may also indicate that the reductive dehalogenation proceeds via initial formation of the π^* radical anions, since the rate of reductive cleavage of the CH₂-X bond would otherwise be comparable with that of the X-C₆H₄ bond, judging from the similar Φ_{∞} values of PhX and PhCH₂X (Table III). Figure 6 depicts the energy profiles of the reductive cleavage of both the CH₂-Cl and Cl-C₆H₄ bonds calculated by a similar manner to those in Figure 5, by taking each C-Cl bond distance as an independent variable. As is clearly seen in Figure 6, the energetic barrier in the cleavage of the $Cl-C_6H_4$ bond is significantly larger than that of the CH2-Cl bond, in agreement with the observed highly selective cleavage of the CH₂-Cl bond (Table IV). As the CH₂-Cl bond of ClC₆H₄CH₂Cl⁻⁻ begins to stretch, continuous flattering of $ClC_6H_4CH_2^-$ group occurs to yield $ClC_6H_4CH_2^+$ and Cl^- (Figure 6).

In conclusion, the photocatalytic dehalogenation of aromatic and alkyl halides in the present system may proceed via photoinduced electron transfer from the singlet excited state of 10methylacridine derivatives used as catalysts to the halogenated compounds, when the bond-breaking process upon the electron transfer can compete well with the back-electron-transfer process to yield the dehalogenated products efficiently. The facile reduction of the oxidized form of 10-methylacridine derivatives with NaBH₄ regenerates the catalysts, constituting not only efficient but also stable photocatalytic systems.

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Specific Asymmetric Fusion between Artificial and Biological Model Membranes

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Abstract: Experimental conditions are delineated for specific asymmetric fusion, induced by Ca^{2+} ions, of vesicles formed from di-*n*-dodecyl phosphate (DDP) with phosphatidylserine (PS) and dioleoylphosphatidylcholine (DOPC) liposomes as well as with erythrocyte ghost (EG) membranes. Initial rates and extents of fusion were obtained with the resonance energy transfer assay. The merging of the bilayers rather than vesicle aggregation represents the rate-determining step in the overall fusion event. Unexpectedly, asymmetric PS-DDP and DOPC-DDP vesicle fusion does occur below the main phase-transition temperature of the DDP bilayer. At 25 °C and pH 7.4, DDP vesicles fuse with EG membranes more rapidly and efficiently than PS vesicles. The possible relevance of these findings for cell biological and drug-targetting experiments is pointed out.

Fusion of lipid bilayer membranes is a crucial biological event and occurs, for example, in processes like endo- and exocytosis, cell division, and the infectious entry of viruses into cells.^{2,3} Because of the complexities involved in using natural cell membranes, liposomal model systems have been frequently employed to study mechanistic aspects of membrane fusion. Recently we have shown that artificial membrane vesicles formed from simple synthetic surfactants also fuse upon addition of appropriate fusogenic agents and that their fusogenic activity mimics important features of phospholipid membrane fusion.⁴ This previous work concerned the occurrence of *symmetric* vesicle fusion, i.e., merging between like vesicle bilayers. Mechanistic studies of the Ca^{2+} -

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