  Bull. Chem. Soc. Jpn., 65, 831—836 (1992)

Efficient Six-Electron Photoreduction of Nitrobenzene Derivatives by 10-Methyl-9,10-dihydroacridine in the Presence of Perchloric Acid

Shunichi FUKUZUMI* and Yoshihiro TOKUDA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka 565
(Received September 20, 1991)

Photoreduction of nitrobenzene derivatives by 10-methyl-9,10-dihydroacridine ($AcrH_2$) occurs efficiently in the presence of perchloric acid in acetonitrile containing H_2O (0.50 mol dm^{-3}) to yield the corresponding six-electron reduced products (aniline derivatives) and 10-methylacridinium ion efficiently. The initial two-electron reduction of $PhNO_2$ to PhNO by $AcrH_2$ in the six-electron reduction of nitrobenzene ($PhNO_2$) is started by electron transfer from $AcrH_2$ to the n,π^* triplet state ($^3PhNO_2^*$), followed by acid-catalyzed thermal reduction of PhNO to PhNHOH by $AcrH_2$ and the subsequent photoreduction of PhNHOH to $PhNH_2$ by $AcrH_2$.

Nitrobenzene and the para-substituted nitrobenzenes with electron-donating groups such as *p*-CH_3 are known to undergo photoreduction in 2-propanol to yield the four-electron reduced product (phenylhydroxylamine) and acetone.[1,2] On the other hand, the photoreduction of nitrobenzenes with electron-withdrawing groups such as *p*-CN in 2-propanol gives the corresponding six-electron reduced products (aniline derivatives).[2] Although the photoreduction of nitrobenzene by 2-propanol is rather inefficient, the addition of HCl to the nitrobenzene-2-propanol system enhances the efficiency significantly, when nitrobenzene is converted to chloroanilines.[3-5] As such the photoreduction of nitrobenzene derivatives is complex and the mechanisms remain to be solved. In this context we have recently reported that nitrobenzene derivatives can be reduced thermally by 10-methyl-9,10-dihydroacridine ($AcrH_2$) in the presence of perchloric acid ($HClO_4$) in acetonitrile via acid-catalyzed electron-transfer radical chain reactions.[6] In this case as well the reduction of nitrobenzene gives phenylhydroxylamine, while the reduction of the para-substituted nitrobenzenes gives the corresponding anilines.[6]

In this study we report that the photoreduction of nitrobenzene and the para-substituted derivatives with electron-donating or -withdrawing groups by $AcrH_2$ in the presence of $HClO_4$ in MeCN containing H_2O (0.50 mol dm^{-3}) gives exclusively the corresponding aniline derivatives (six-electron reduced products) irrespective of the substituent. The mechanism of the six-electron photoreduction of nitrobenzene derivatives is discussed based on the comparison of the photoreduction of nitrobenzene, nitrosobenzene (the two-electron reduced product of nitrobenzene), and phenylhydroxylamine (the four-electron reduced product of nitrobenzene).

Experimental

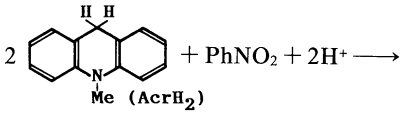
Materials. 10-Methyl-9,10-dihydroacridine ($AcrH_2$) was prepared from 10-methylacridinium iodide ($AcrH^+I^-$) by the reduction with $NaBH_4$ in methanol, and purified by recrystallization from ethanol.[7] Nitrosobenzene and nitrobenzene derivatives (nitrobenzene, *p*-nitrotoluene, *p*-ethylnitrobenzene, *p*-cyanonitrobenzene) and the corresponding aniline derivatives were also obtained commercially and purified by the standard methods.[8] Phenylhydroxylamine was prepared by the standard method of reduction of nitrobenzene with ammonium chloride and zinc dust.[9] *For safety reason*, perchloric acid containing 30% water, obtained from Wako Pure Chemicals, was used in this study. Acetonitrile or [$^2H_3$]acetonitrile (CD_3CN) used as a solvent was purified by the standard procedure.[8]

Reaction Procedure. Typically, $AcrH_2$ (36 μmol) was added to an NMR tube that contained a deaerated acetonitrile (CD_3CN) solution of nitrobenzene derivative (12 μmol), $HClO_4$ (36 μmol), and H_2O (300 μmol). After the reactant solution in the NMR tube had been deaerated again by bubbling through it with argon gas and sealed, the solution was irradiated with an Ushio Model UI-501C xenon lamp. The products were identified by comparing the ^1H NMR spectra of the products with those of authentic samples. The ^1H NMR measurements were carried out using a Japan Electron Optics JNM-GSX-400 NMR spectrometer (400 MHz). The product yields were determined by GLC.

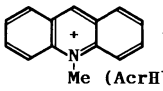
Kinetic Measurements. The rates of the photoreduction of nitrobenzene derivatives (e.g., 1.4×10^{-2} mol dm^{-3}) by $AcrH_2$ (e.g., 2.0×10^{-3} mol dm^{-3}) were determined from the rise of the absorbance due to $AcrH^+$ ($\lambda_{max} = 358$ nm, $\varepsilon = 1.8 \times 10^4$ dm^3 mol^{-1} cm^{-1}) under irradiation with a xenon lamp by using a Union SM-401 spectrophotometer. The initial rates were determined from the linear increase of the absorbance at low conversions (<10%) under the conditions that the rates are independent of the irradiation time. The wavelength dependence of the initial rate was determined by changing the irradiation wavelength of monochromatized light from an Ushio Model UXL-157 xenon lamp of a Hitachi 650-10S fluorescence spectrophotometer by taking account of the change in the light intensity with the wavelength. The reference light intensity was taken at 390 and 320 nm for the reduction of $PhNO_2$ and PhNHOH by $AcrH_2$, respectively. A standard actinometer (potassium trioxalatoferrate (III))[10] was used for the quantum yield determination for the photoreduction of $PhNO_2$ by $AcrH_2$.

Results and Discussion

Nitrobenzene can be reduced by $AcrH_2$ in the presence of $HClO_4$ in MeCN to yield the four-electron reduction product, phenylhydroxylamine (Eq. 1).[6] Addition of H_2O to the $AcrH_2$–$PhNO_2$ system in the presence of



$$+ PhNO_2 + 2H^+ \longrightarrow$$



$$+ PhNHOH + H_2O \quad (1)$$

$HClO_4$ in MeCN, however, results in a significant decrease in the reaction rate. Thus, no appreciable reduction of nitrobenzene by $AcrH_2$ occurs thermally in the presence of $HClO_4$ (2.0×10^{-2} mol dm^{-3}) in MeCN containing 0.50 mol dm^{-3} H_2O at 298 K. When the reactant solution is irradiated with a xenon lamp, however, the reduction of $PhNO_2$ by $AcrH_2$ takes place efficiently at 298 K. In contrast with the case of acid-catalyzed thermal reduction of $PhNO_2$ by the $AcrH_2$ (Eq. 1), The photoreduction of $PhNO_2$ by $AcrH_2$ gives exclusively the six-electron reduced species, aniline. The product yields are shown in Table 1 where three $AcrH_2$ and H^+ react with one $PhNO_2$ to yield three $AcrH^+$ and one $PhNH_2$ (Eq. 2). The photoreduction of

$$3AcrH_2 + PhNO_2 + 3H^+ \xrightarrow{h\nu} 3AcrH^+ + PhNH_2 + 2H_2O \quad (2)$$

nitrosobenzene (the two-electron reduced product of nitrobenzene) by $AcrH_2$ also takes place to yield the same product as that obtained from nitrobenzene (Eq. 3). We have previously reported that PhNO is readily reduced by

$$2AcrH_2 + PhNO + 2H^+ \xrightarrow{h\nu} 2AcrH^+ + PhNH_2 + H_2O \quad (3)$$

$AcrH_2$ in the presence of $HClO_4$ and H_2O in the dark to yield $AcrH^+$ and PhNHOH.[6] The rate constant for the thermal reduction of PhNO by $AcrH_2$ is 2.4×10^3 dm^3 mol^{-1} s^{-1} at 298 K.[6] Thus, the four-electron photoreduction of PhNO may proceed by the two-electron photoreduction of PhNHOH following the thermal reduction of PhNO to PhNHOH. In fact, the two-electron photoreduction of PhNHOH by $AcrH_2$ also occurs to yield $AcrH^+$ and $PhNH_2$ (Eq. 4) as shown in Table 1. Thus, the overall six-electron photoreduction

$$AcrH_2 + PhNHOH + H^+ \xrightarrow{h\nu} AcrH^+ + PhNH_2 + H_2O \quad (4)$$

of $PhNO_2$ by $AcrH_2$ may proceed consecutively via the photoreduction of $PhNO_2$ to PhNO, the acid-catalyzed thermal reduction of PhNO to PhNHOH, and the photoreduction of PhNHOH to $PhNH_2$. The photoreduction of the para-substituted nitrobenzenes with electron-donating groups (*p*-Me, *p*-Et) and an electron-withdrawing group (*p*-CN) by $AcrH_2$ also takes place to yield the corresponding anilines exclusively (Table 1). Such efficient six-electron photoreduction of nitrobenzene derivatives by $AcrH_2$ is in contrast with the photoreduction by 2-propanol in which the four- or six-electron reduction takes place depending upon the substituents of nitrobenzene derivatives.[2]

The singlet excited state of $AcrH_2$ ($^1AcrH_2$*, * denotes the excited state) is known to be a strong one-electron reductant, judging from the largely negative one-electron oxidation potential (E^0_{ox}=−3.1 V vs. SCE).[11] On the other hand, the triplet excited state of nitrobenzene ($^3PhNO_2$*) is known to be a strong one-electron oxidant; the singlet excited states of simple aromatic nitro compounds have not been described presumably owing to the short lifetimes.[1] Thus, both $^1AcrH_2$* and $^3PhNO_2$* are possible candidates of the photoreactive species for the photoreduction of $PhNO_2$ by $AcrH_2$. In order to determine which is the photoreactive species involved in

Table 1. Photoreduction of Nitrobenzene Derivatives by $AcrH_2$ in the Presence of $HClO_4$ in MeCN Containing H_2O (0.50 mol dm^{-3}) at 298 K

Substrate	$AcrH_2$	$HClO_4$	Time	Product yield
mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	h	(%)
$PhNO_2$ (0.02)	0.06	0.06	28	$AcrH^+$ (98) $PhNH_2$ (98)
PhNO (0.022)	0.04	0.04	16	$AcrH^+$ (84) $PhNH_2$ (84)
PhNHOH (0.02)	0.05	0.04	24	$AcrH^+$ (100) $PhNH_2$ (100)
p-$MeC_6H_4NO_2$ (0.04)	0.06	0.06	70	$AcrH^+$ (83) *p*-$MeC_6H_4NH_2$ (82)
p-$EtC_6H_4NO_2$ (0.0032)	0.01	0.01	3	$AcrH^+$ (97) *p*-$EtC_6H_4NH_2$ (91)
p-$CNC_6H_4NO_2$ (0.06)	0.06	0.06	28	$AcrH^+$ (71) *p*-$CNC_6H_4NH_2$ (70)

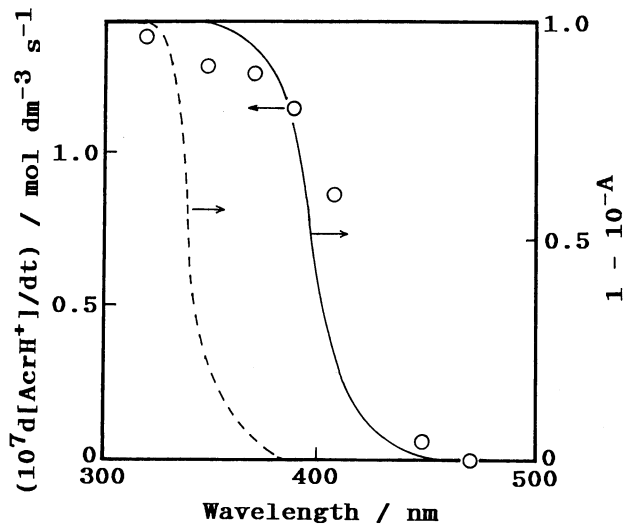


Fig. 1. Plots of the initial rate ($d[AcrH^+]/dt$) for the photoreduction of $PhNO_2$ (1.4×10^{-2} mol dm^{-3}) by $AcrH_2$ (2.0×10^{-3} mol dm^{-3}) in the presence of $HClO_4$ (0.10 mol dm^{-3}) in MeCN containing H_2O (0.50 mol dm^{-3}) and the fraction of light ($1-10^{-A}$) absorbed by $PhNO_2$ (—) and $AcrH_2$ (----) vs. the irradiation wavelength. The change of light intensity with the wavelength is taken into account with reference to that at 390 nm.

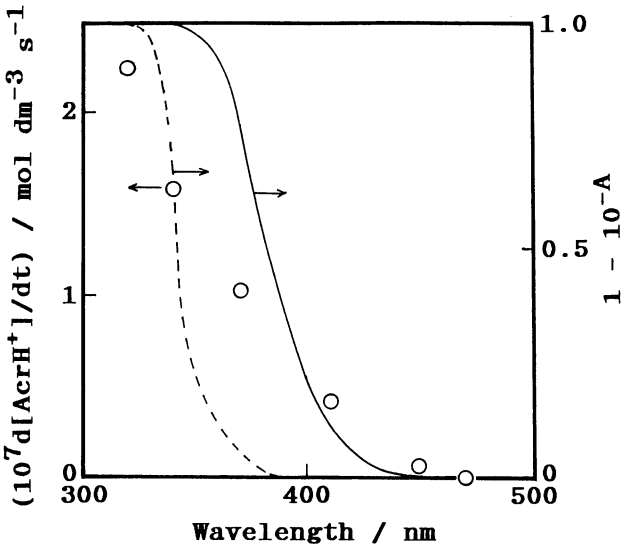


Fig. 2. Plots of the initial rate ($d[AcrH^+]/dt$) for the photoreduction of PhNHOH (2.6×10^{-3} mol dm^{-3}) by $AcrH_2$ (2.0×10^{-3} mol dm^{-3}) in the presence of $HClO_4$ (0.10 mol dm^{-3}) in MeCN containing H_2O (0.50 mol dm^{-3}) and the fraction of light ($1-10^{-A}$) absorbed by PhNHOH (—) and $AcrH_2$ (----) vs. the irradiation wavelength. The change of light intensity with the wavelength is taken into account with reference to that at 320 nm.

the photoreduction, the dependence of the rate on the irradiation wavelength was examined by measuring the photochemical rate by changing the irradiation wavelength. The initial rate ($d[AcrH^+]/dt$) of formation of $AcrH^+$ in the photoreduction of $PhNO_2$ by $AcrH_2$ in the presence of $HClO_4$ (0.10 mol dm^{-3}) in MeCN containing H_2O (0.50 mol dm^{-3}) is plotted against the irradiation wavelength in Fig. 1, where the change of light intensity with the wavelength was taken into account (see Experimental). As seen in Fig. 1, where the fraction of light absorbed by $AcrH_2$ and $PhNO_2$ ($1-10^{-A}$, A is the absorbance) is also shown for comparison, the rate starts to increase from zero as light begins to be absorbed by $PhNO_2$ at the wavelengths shorter than ca.450 nm. This indicates that the excitation of $PhNO_2$ causes the reduction and that the photoreactive species is not $^1AcrH_2$* but most likely $^3PhNO_2$*. The apparent quantum efficiency of the formation of $AcrH^+$ in the photoreduction of $PhNO_2$ by $AcrH_2$ at 320 nm is 0.10, that is significantly larger than the value of the photoreduction of $PhNO_2$ by 2-propanol (0.011).[1] In Fig. 2 the $d[AcrH^+]/dt$ values in the photoreduction of PhNHOH by $AcrH_2$ are plotted against the irradiation wavelength together with the fraction of light absorbed by $AcrH_2$ and PhNHOH. The rate starts to increase from zero as light begins to be absorbed by PhNHOH at the wavelengths shorter than 450 nm, but it continues to increases in the region where the fraction of light absorbed by PhNHOH reaches zero, but that by $AcrH_2$ starts to increase (Fig. 2). Thus, both $^1AcrH_2$* and ^3PhNHOH* may be involved in the photoreduction of PhNHOH by $AcrH_2$ under the irradiation conditions.

Addition of an acid (HCl) to the 2-propanol–$PhNO_2$ system has been reported to cause a significant increase of the efficiency of nitrobenzene photoreduction.[3-5] The enhancement of the efficiency was initially attributed to protonation of n,π* triplet nitrobenzene leading to a more reactive or longer lived nitrobenzene.[3] Later electron transfer from Cl^- to $^3PhNO_2$* in the presence of proton was shown to be responsible for the enhancement of efficiency of nitrobenzene photoreduction in the presence of HCl.[4,5] In order to know the effect of $HClO_4$ on our system, we examined the dependence of the rate for the photoreduction of nitrobenzene derivatives by $AcrH_2$ on $[HClO_4]$. The results are shown in Fig. 3, where the rates are rather independent of $[HClO_4]$. Thus, $HClO_4$ acts only as a reactant to provide the stoichiometric amount of protons, but not as a catalyst to accelerate the rate of photoreduction of nitrobenzene derivatives by $AcrH_2$. The slight decrease in the rate at the large $[HClO_4]$ value ($[HClO_4]$ = ca.1×10^{-1} mol dm^{-3}) observed in Fig. 3 may be attributed to the protonation of $AcrH_2$ (Eq. 5), which is known to result in the decrease of

$$AcrH_2 + H^+ \rightleftharpoons (AcrH_2)H^+ \quad (5)$$

the reducing ability of $AcrH_2$.[12]

The dependence of the rate of formation of $AcrH^+$ for

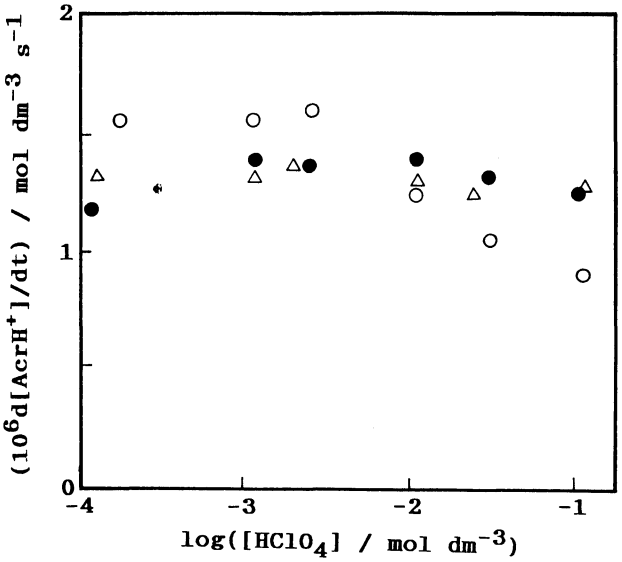


Fig. 3. Plots of the initial rate ($d[AcrH^+]/dt$) vs. $\log[HClO_4]$ for the photoreduction of $PhNO_2$ (○, 9.4×10^{-4} mol dm^{-3}), p-$MeC_6H_4NO_2$ (●, 8.0×10^{-4} mol dm^{-3}), and p-$EtC_6H_4NO_2$ (△, 7.2×10^{-4} mol dm^{-3}) by $AcrH_2$ (2.0×10^{-3} mol dm^{-3}) in the presence of $HClO_4$ in MeCN containing H_2O (0.50 mol dm^{-3}) at 298 K.

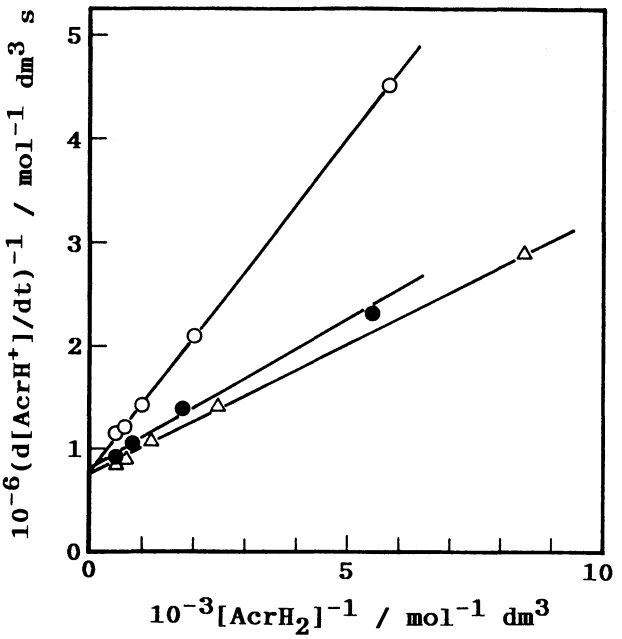


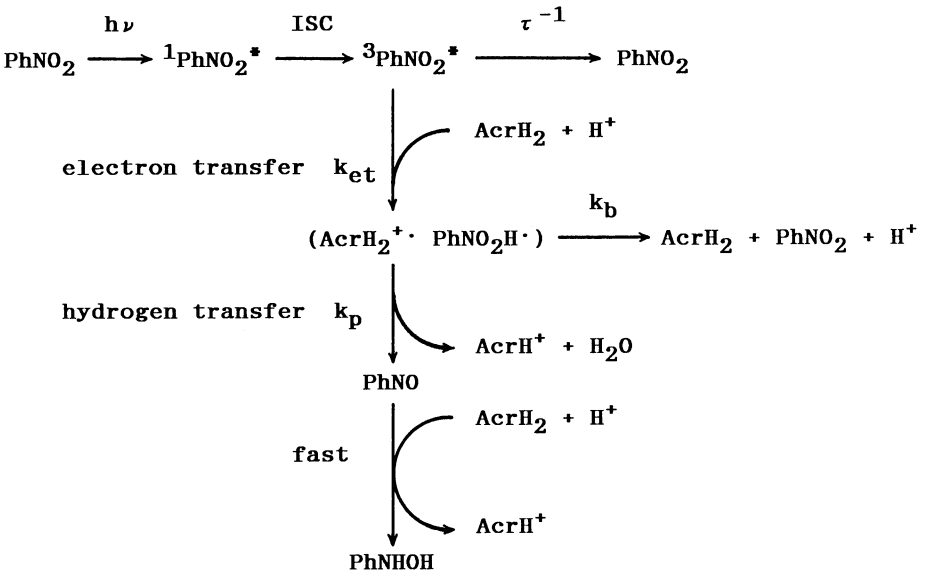
Fig. 4. Plots of $(d[AcrH^+]/dt)^{-1}$ vs. $[AcrH_2]^{-1}$ for the photoreduction of $PhNO_2$ (○, 9.4×10^{-4} mol dm^{-3}), p-$MeC_6H_4NO_2$ (●, 8.0×10^{-4} mol dm^{-3}), and p-$EtC_6H_4NO_2$ (△, 7.2×10^{-4} mol dm^{-3}) by $AcrH_2$ in the presence of $HClO_4$ (0.10 mol dm^{-3}) in MeCN containing H_2O (0.50 mol dm^{-3}) at 298 K.

the photoreduction of nitrobenzene derivatives ($PhNO_2$, p-$MeC_6H_4NO_2$, and p-$EtC_6H_4NO_2$) by $AcrH_2$ in the presence of $HClO_4$ (0.10 mol dm^{-3}) in MeCN containing H_2O (0.50 mol dm^{-3}) is shown in Fig. 4, where each plot of $(d[AcrH^+]/dt)^{-1}$ vs. $[AcrH_2]^{-1}$ gives a straight line with an intercept. Thus, the rate is given by Eq. 6, where

$$(d[AcrH^+]/dt)^{-1}=(d[AcrH^+]/dt)_0^{-1}\,(1+K_{obs}^{-1}[AcrH_2]^{-1}) \quad (6)$$

K_{obs} is the quenching constant of the excited state of X-$C_6H_4NO_2$ by $AcrH_2$ and $(d[AcrH^+]/dt)_0$ is the limiting rate. From the slope and intercept are obtained the K_{obs} values as 1.2×10^3, 2.9×10^3, and 1.6×10^3 dm^3 mol^{-1} for $PhNO_2$, p-$MeC_6H_4NO_2$, and p-$EtC_6H_4NO_2$, respectively. The K_{obs} values for the photoreduction of nitrobenzene derivatives by $AcrH_2$ are significantly larger than those reported for the photoreduction of $PhNO_2$ by 2-propanol and tributylstannane (8.3×10^{-4} and 0.44 dm^3 mol^{-1}, respectively).[13] In the latter case, the photoreduction of $PhNO_2$ is believed to proceed via hydrogen abstraction by the n, π* triplet excited state of $PhNO_2$. The small K_{obs} values are ascribed to the existence of the activation barrier for the hydrogen abstraction process and the rapid deactivation of the n, π* triplet excited state of $PhNO_2$. The rapid triplet deactivation for $PhNO_2$ has been demonstrated as the small quenching constant (1.4 dm^3 mol^{-1}) for the energy transfer to *cis*-1,3-pentadiene despite of their comparable triplet energies (56.9 and 60 kcal mol^{-1} for *cis*-1,3-pentadiene and $PhNO_2$, respectively).[14] In addition, dioxygen (1×10^{-3} mol dm^{-3}), a typical triplet quencher, has been reported to quench $^3PhNO_2$* only partially (ca. 30%).[1] Such a rapid radiationless decay of $^3PhNO_2$* has precluded the observation of the phosphorescence, making it difficult to observe its triplet-triplet absorption.[14-16] Thus, the large K_{obs} values observed in this study (Fig. 4) suggest that the photoreduction of nitrobenzene derivatives by $AcrH_2$ proceeds via electron transfer which is expected to be much faster than hydrogen abstraction.[17] In fact, the Gibbs energy change of electron transfer from $AcrH_2$ to the triplet excited states of nitrobenzene derivatives are largely negative, judging from the one-electron oxidation potential of $AcrH_2$ (0.80 V vs. SCE)[18] and the one-electron reduction potentials of $^3PhNO_2$* [1.50 V, obtained by adding the triplet energy (2.6 eV)[19] to the E°_{red} value of the ground state (−1.1 V vs. SCE)[20]].

Based on the above discussion the reaction sequence for the reduction of $PhNO_2$ to PhNHOH by $AcrH_2$ is summarized in Scheme 1. The primary step for the photoreduction of $PhNO_2$ by $AcrH_2$ may be started by electron transfer (k_{et}) from $AcrH_2$ to $^3PhNO_2$*, which arises from an intersystem crossing (ISC) from an n,π* singlet, in the presence of $HClO_4$ to give $AcrH_2^{+\bullet}$ and $PhNO_2H^\bullet$ (Scheme 1). The electron transfer may be diffusion-limited, since the intrinsic barriers for both the one-electron oxidation of $AcrH_2$ and the one-electron reduction of $PhNO_2$ are known to be small.[18,21] The subsequent hydrogen transfer (k_p) to yield the products ($AcrH^+$ and PhNO) after dehydration may compete with the back electron transfer (k_b) to regenerate the reactants



Scheme 1.

(Scheme 1). The initial photoproduct (PhNO) is known to be reduced to PhNHOH by the facile thermal reduction by $AcrH_2$ (Scheme 1).[6] According to Scheme 1, the initial rate of formation of $AcrH^+$ is given by Eq. 7, where In is the initial rate of formation of $^3PhNO_2$* and

$$d[AcrH^+]/dt=2In[k_p/(k_p+k_b)]k_{et}\tau[AcrH_2]/(1+k_{et}\tau[AcrH_2]) \quad (7)$$

τ is the lifetime of $^3PhNO_2$* (note that two $AcrH^+$ is produced by the primary photochemical reaction and the subsequent thermal reaction at the initial stage). From Eq. 7 is derived Eq. 6, where $(d[AcrH^+]/dt)_0$ corresponds to $2In\,k_p/(k_p+k_b)$ and $K_{obs}=k_{et}\tau$.

The radical chain processes as reported in the acid-catalyzed thermal reduction of nitrobenzene derivatives by $AcrH_2$[6] may not be involved in the photoreduction, since the rate derived from such radical chain processes in which the hydrogen abstraction from $AcrH_2$ is the rate-determining step would increase with an increase in $[AcrH_2]$ without showing saturation as opposed to the experimental observation in Fig. 4.

With prolonged irradiation time PhNHOH is accumulated and the next photochemical reduction of PhNHOH to $PhNH_2$ by $AcrH_2$ may take place. Such a step was examined independently and compared to the overall reaction. As shown in Fig. 5, the rate of photoreduction of PhNHOH by $AcrH_2$ in the presence of $HClO_4$ (0.10 mol dm^{-3}) in MeCN containing H_2O (0.50 mol dm^{-3}) at 298 K is about three times faster than the rate of overall photoreduction of $PhNO_2$ by $AcrH_2$ at the identical concentrations of PhNHOH and $PhNO_2$. It should be noted that no thermal reduction of PhNHOH to $PhNH_2$ by $AcrH_2$ takes place in the dark under

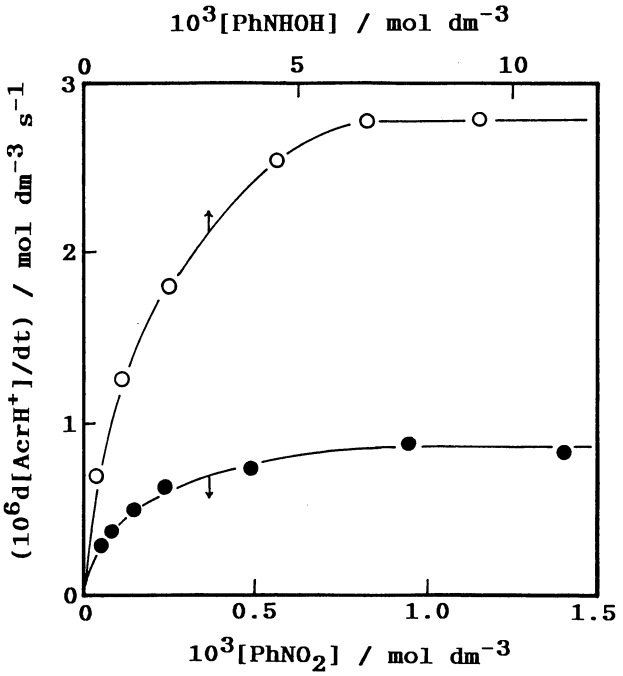


Fig. 5. Plots of $d[AcrH^+]/dt$ vs. $[PhNO_2]$ and [PhNHOH] for the photoreduction of $PhNO_2$ (○) and PhNHOH (●) by $AcrH_2$ in the presence of $HClO_4$ (0.10 mol dm^{-3}) in MeCN containing H_2O (0.50 mol dm^{-3}) at 298 K, respectively.

the present experimental conditions. Although the detailed mechanism of the photoreduction of PhNHOH to $PhNH_2$ by $AcrH_2$ is not clear at present, the enhanced efficiency for the photoreduction of PhNHOH as compared to that of $PhNO_2$ is certainly the origin for the efficient six-electron photoreduction of $PhNO_2$ by $AcrH_2$ at prolonged irradiation time (Table 1).

The present work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1) R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, **88**, 4330 (1966); **89**, 6917 (1967).

2) S. Hashimoto and K. Kano, *Bull. Chem. Soc. Jpn.*, **45**, 549 (1972); *Tetrahedron Lett.*, **1970**, 3509.

3) A. Chu and A. C. Testa, *J. Phys. Chem.*, **77**, 1487 (1973).

4) G. G. Wubbels, J. W. Jordan, and N. S. Mills, *J. Am. Chem. Soc.*, **95**, 1281 (1973).

5) A. Cu and A. C. Testa, *J. Am. Chem. Soc.*, **96**, 1963 (1974).

6) S. Fukuzumi, M. Chiba, and T. Tanaka, *J. Chem. Soc., Chem. Commun.*, **1989**, 941; *J. Chem. Soc., Perkin Trans. 2*, **1991**, 1393.

7) A. K. Colter, G. Saito, and F. Sharom, *Can. J. Chem.*, **55**, 2741 (1977).

8) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, New York (1966).

9) A. I. Vogel, " Practical Organic Chemistry," 2nd ed, Longman, London (1954), p. 602.

10) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **275**, 518 (1956).

11) S. Fukuzumi and T. Tanaka, "Photoinduced Electron Transfer," ed by M. A. Fox and M. Chanon, Elsevier, Amsterdam (1988), Chap. 10.

12) S. Fukuzumi, M. Ishikawa, and T. Tanaka, *Tetrahedron*, **42**, 1021 (1986); S. Fukuzumi, S. Kuroda, T. Goto, K. Ishikawa, and T. Tanaka, *J. Chem. Soc., Perkin Trans. 2*, **1989**, 1047.

13) W. Trotter and A. C. Testa, *J. Am. Chem. Soc.*, **90**, 7044 (1968).

14) R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, **90**, 1949 (1968).

15) J. Wolleben and A. C. Testa, *J. Phys. Chem.*, **81**, 429 (1977).

16) The earlier report on the long-lived phosphorescence from the π, π^* triplet at 77 K (J. A. Barltrop and N. J. Bunce, *J. Chem. Soc. C*, **1968**, 1467) has been shown to be incorrect, since the extensively purified nitrobenzene does not give the long-lived emision.[13]

17) Unfortunately, the exact lifetime of $^3PhNO_2^*$ is not known, although it is estimated as shorter than 1 μs and longer than 1 ns based on the triplet quenching by dioxygen[1] and *cis*-1,3-pentadiene,[14] respectively. If one assumes that electron transfer from $AcrH_2$ to $^3PhNO_2^*$ is diffusion-controlled (2.0×10^{10} dm^3 mol^{-1} s^{-1}), from the K_{obs} value is obtained the lifetime of $^3PhNO_2^*$ as 60 ns, which is consistent with the estimation mentioned above.

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

19) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

20) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

21) S. Fukuzumi, K. Ishikawa, K. Hironaka, and T. Tanaka, *J. Chem. Soc., Perkin Trans. 2*, **1987**, 751.