Photoreduction of Phenacyl Halides by NADH Analogues. Origins of Different Mechanistic Pathways

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Photoreduction of phenacyl halides ($PhCOCH_2X$) by an NADH analogue, 10-methyl-9-acridone ($AcrH_2$) in acetonitrile (MeCN) under irradiation of light ($\lambda > 320$ nm) proceeds *via* the rate-determining photoinduced electron transfer from the singlet excited state of $AcrH_2$ to $PhCOCH_2X$ to give the radical ion pair ($AcrH_2^{+\bullet}$ $PhCOCH_2X^{-\bullet}$). The subsequent fast reaction is completed within the complex by proton transfer from $AcrH_2^{+\bullet}$ to $PhCOCH_2X^{-\bullet}$, followed by electron transfer from $AcrH^\bullet$ to $Ph\dot{C}(OH)CH_2X$, yielding 10-methylacridinium ion ($AcrH^+$) and acetophenone ($PhCOCH_3$). However, photoreduction of $PhCOCH_2X$ by another NADH analogue, 1-benzyl-1,4-dihydronicotinamide (BNAH), in MeCN under irradiation with visible light of $\lambda > 360$ nm proceeds by a different reaction pathway; electron-transfer radical chain reactions, in which the chain carrier radicals are produced by photoinduced electron transfer from the singlet excited state of BNAH to $PhCOCH_2X$. The origins of these different mechanistic pathways dependent on the NADH analogues are discussed.

Reduced nicotinamide adenine dinucleotide (NADH) is known to play a vital role as an electron source in biological redox reactions.[1] Although NADH is a rather mild reducing agent, it can reduce a variety of substrates in the presence of an appropriate enzyme, termed a dehydrogenase, which activates the substrates by the action of acid catalysis.[1,2] In the absence of the enzyme (or appropriate catalysts) which can activate the substrates, NADH and NADH analogues can only reduce substrates which are rather strong oxidants.[3,4] However, the excited states of NADH or its analogues become much stronger reductants than the ground states, since the one-electron oxidation potentials of the excited states are shifted to the positive direction by excitation.[5] For example, the one-electron oxidation potential of a typical NADH analogue, 1-benzyl-1,4-dihydronicotinamide (BNAH), which has been reported to be 0.57 V (*vs.* SCE),[5–7] is changed to -2.6 V (*vs.* SCE) in the singlet excited state.[5–7] Thus, the use of the excited states of NADH analogues can expand the number of reducible substrates which would otherwise be very difficult to reduce. In fact, it has been reported that the singlet excited state of BNAH can reduce alkyl halides to yield the corresponding alkane by electron-transfer radical chain reactions in which alkyl radicals, produced by photoinduced electron transfer from the singlet excited state of BNAH to alkyl halides, act as the chain carrier of the radical chain reactions.[8,9] On the other hand, some direct photoreduction of substrates by NADH analogues not associated with radical chain reactions have also been reported.[10] Thus, mechanisms of photoreduction of substrates by NADH analogues may be different depending on the reaction systems. The origins of such mechanistic differences are difficult to understand without a systematic comparison of different mechanisms under comparable conditions.

In this study, we report the photoreduction of phenacyl halides by two different types of NADH analogues—one is BNAH and the other is 10-methyl-9-acridone ($AcrH_2$)—in acetonitrile (MeCN). The reactions proceed *via* different mechanistic pathways; the direct photoreduction and the radical chain reaction.[11] Thus, this study offers an excellent opportunity to provide an understanding of the origins of the mechanistic difference in photoreductions by NADH analogues.

Experimental

Materials.—$AcrH_2$ was prepared from 10-methylacridinium iodide ($AcrH^+I^-$) by reduction with $NaBH_4$ in methanol, and purified by recrystallization from ethanol.[12] The dideuteriated compound, [9,9′-$^2H_2$]-10-methyl-9-acridone ($AcrD_2$), was prepared from 10-methyl-9-acridone by reduction with $LiAlD_4$ which was obtained from the Aldrich Chemical Co.[13] 10-[$^2H_3$]Methyl-9-acridone ($AcrH_2$–CD_3) was prepared by $NaBH_4$ reduction of 10-[$^2H_3$]methylacridinium iodide which was obtained by reaction of acridine with CD_3I in methanol.[14] The preparation and purification of 1-benzyl-1,4-dihydronicotinamide (BNAH) and [4-^{2}H]-1-benzyl-1,4-dihydronicotinamide ([^{2}H]BNAH) were described previously.[15] Phenacyl bromide, *p*-bromophenacyl bromide, and phenacyl chloride were obtained commercially and purified by standard methods.[16] *p*-Methylphenacyl bromide, *p*-methoxyphenacyl bromide, and *p*-cyanophenacyl bromide were prepared by bromination of the corresponding acetophenone derivatives in methanol.[17] Potassium ferrioxalate used as an actinometer was prepared according to the literature,[18] and purified by recrystallization from hot water. Acetonitrile and [$^2H_3$]acetonitrile used as solvents were purified and thoroughly dried with calcium hydride by a standard procedure.[16]

Reaction Procedure.—Typically, $AcrH_2$ (60 μmol) was added to an n.m.r. tube that contained a CD_3CN solution (0.6 cm^3) of phenacyl halide (180 μmol). After the reactant solution in the n.m.r. tube had been de-aerated by bubbling argon gas through it, it was irradiated with monochromatized light from a Ushio Model UXL-157 Xenon lamp of a Hitachi 650-10S fluorescence spectrophotometer. The wavelength of monochromatized light was normally 320 nm, which is beyond the absorption maximum of phenacyl halide when the absorption band due to $AcrH_2$ (λ_{max} 285 nm) was mainly irradiated. In the case of photoreduction of phenacyl bromide by BNAH, the selective excitation of the absorption band due to BNAH (λ_{max}

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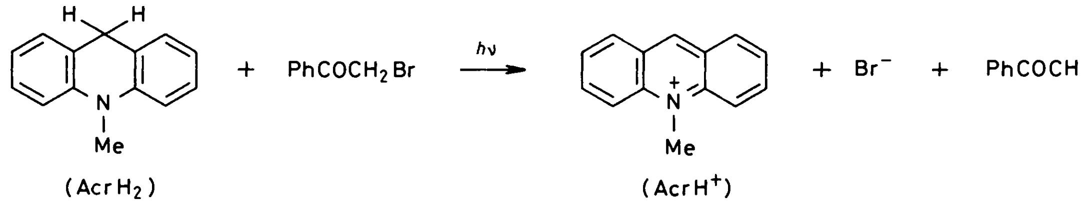

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Table 1. Photoreduction of phenacyl halides (0.30 mol dm^{-3}) by NADH model compounds (0.10 mol dm^{-3}) in acetonitrile at 298 K.

NADH Model compound[a]	Substrate	Time/h	Product yield/%	
$AcrH_2$	$PhCOCH_2Br$	20	$AcrH^+$ (86)	$PhCOCH_3$ (84)
$AcrD_2$	$PhCOCH_2Br$	15	$AcrD^+$ (60)	$PhCOCH_2D$ (60)
$AcrD_2$[b]	$PhCOCH_2Br$	12	$AcrD^+$ (53)	$PhCOCH_3$ (53)
$AcrH_2$	$PhCOCH_2Cl$	29	$AcrH^+$ (86)	$PhCOCH_3$ (86)
$AcrH_2$–CD_3	$PhCOCH_2Cl$	29	$AcrH^+$–CD_3 (85)	$PhCOCH_3$ (85)
$AcrH_2$	p-$MeOC_6H_4CH_2Br$	19	$AcrH^+$ (100)	p-$MeOC_6H_4COCH_3$ (100)
$AcrH_2$	p-$BrC_6H_4CH_2Br$	13	$AcrH^+$ (56)	p-$BrC_6H_4COCH_3$ (56)
BNAH[c]	$PhCOCH_2Br$	0.5	BNA^+ (50)	$PhCOCH_3$ (47)

[a] The irradiation wavelength is 320 nm unless otherwise noted. [b] In the presence of H_2O (0.10 mol dm^{-3}). [c] The irradiation wavelength is 370 nm.

350 nm) was achieved by using visible light from a Ushio model UI-501 Xenon lamp through a Toshiba glass filter L-39 transmitting light of λ >360 nm.

The products were identified by comparison of their ^1H n.m.r. spectra with those of authentic samples of $AcrH^+$, BNA^+, and acetophenone derivatives. The deuterium incorporation into products was also determined from the ^1H n.m.r. spectra. The ^1H n.m.r. measurements were carried out using a Japan Electron Optics JNM-PS-100 ^1H n.m.r. spectrometer (100 MHz).

Quantum-yield Determinations.—A standard actinometer (potassium ferrioxalate)[16] was used for the quantum yield determinations. The actinometry experiments were carried out under the same conditions as those of the photoreduction of phenacyl halides by NADH analogues ($AcrH_2$ and BNAH). The intensities of monochromatized light of λ 320, 330, 340, and 370 nm with a 10 nm slit width were determined to be 1.1, 1.5, 1.2, and 2.3 × 10^6 einstein dm^{-3} s^{-1}, respectively. The incident light intensity at a fixed wavelength was varied by changing the slit width. The quantum yields were determined from the rates of the rise of the absorption band due to $AcrH^+$ (λ_{max} 358 nm, ε 1.8 × 10^4 dm^3 mol^{-1} cm^{-1}) or the disappearance of the absorption band due to BNAH (λ_{max} 350 nm, ε 6.0 × 10^3 dm^3 mol^{-1} cm^{-1}) by comparing with the incident light intensity absorbed by the reactants ($AcrH_2$ and BNAH). At high concentrations of phenacyl halides, the absorption by phenacyl halides at λ 320 nm was taken into account in determining the quantum yields.

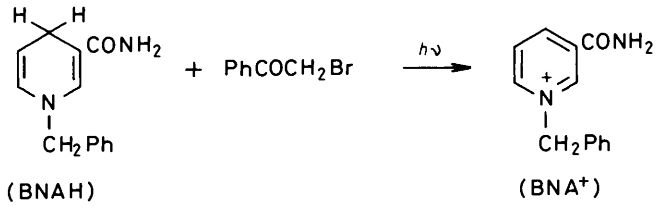
Fluorescence Quenching.—Fluorescence measurements were carried out on a Hitachi 650-10S fluorescence spectrophotometer. In the quenching experiments for the photoinduced electron-transfer reactions, excitation wavelengths beyond the quencher absorption were selected normally as 330 and 380 nm for $AcrH_2$ and BNAH, respectively. Relative emission intensities were measured for acetonitrile (MeCN) solutions of $AcrH_2$ (5.0 × 10^{-5} mol dm^{-3}) and BNAH (1.0 × 10^{-4} mol dm^{-3}) with a quencher at various concentrations. There was no change in the shape but there was a change in the intensity of the emission spectrum by the addition of a quencher. The Stern–Volmer relationship [equation (1)] was obtained for the ratio of the emission intensities in the absence and presence of a quencher (I_0/I) and the quencher concentration [Q]. The electron-transfer rate constants k_{et} ($=K_{et}\tau^{-1}$) was obtained from the quenching constant K_{et} and the emission lifetime τ ($AcrH_2$ 16 ± 2, BNAH, 0.76 ± 0.03 ns[19]). The τ value of $^1AcrH_2^*$ was evaluated from the K_{et} value of fumaronitrile which is assumed to accept an electron from $^1AcrH_2^*$ with the diffusion rate constant; 2.0 × 10^{10} dm^3 mol^{-1} s^{-1}. In the case of fluorescence quenching of $^1AcrH_2^*$ by phenacyl bromide, the Stern–Volmer plot showed a deviation from a linear correlation between I_0/I and [$PhCOCH_2Br$] for high concentrations of phenacyl bromide which absorbs light at the excitation wavelength. In such a case, the longer excitation wavelength (*e.g.* λ 340 nm) was selected and the quenching constant was determined from the initial slope of the Stern–Volmer plot.

$$I_0/I = 1 + K_{et}[Q] \qquad (1)$$

Results

Photoreduction of Phenacyl Halides by NADH *Model Compounds.*—Irradiation of a de-aerated MeCN solution containing ($AcrH_2$) and phenacyl halide ($PhCOCH_2X$; X = Br and Cl) with monochromatized light of λ 320 nm results in the conversion of $AcrH_2$ and $PhCOCH_2X$ into $AcrH^+$ and $PhCOCH_3$, respectively [equation (2)]. Similarly, the direct excitation of the absorption band due to $AcrH_2$ in the presence of phenacyl chloride, *p*-methylphenacyl bromide, and *p*-bromophenacyl bromide gives the corresponding acetophenone derivatives. The product yields are shown in Table 1. No reduction of phenacyl halides by $AcrH_2$ has been observed in the dark under the present experimental conditions.

When $AcrH_2$ is replaced by the 9,9′-dideuteriated compound ($AcrD_2$) in the photochemical reaction with phenacyl bromide in thoroughly dried MeCN, phenacyl bromide is converted to monodeuteriated acetophenone ($PhCOCH_2D$) quantitatively as shown in Table 1. However, no deuterium was incorporated into the reduced product when H_2O (0.10 mol dm^{-3}) was added to the $AcrD_2$–phenacyl bromide system (Table 1). The use of 10-[$^2H_3$]methyl-9-acridone ($AcrH_2$–CD_3) instead of $AcrD_2$ does not result in incorporation of deuterium into the reduced product either (Table 1). Thus, the photoreduction of phenacyl bromide by $AcrH_2$ involves the transfer of a hydrogen from the C-9 position of $AcrH_2$ to phenacyl bromide, although it has been reported that a hydrogen of the 10-methyl position is



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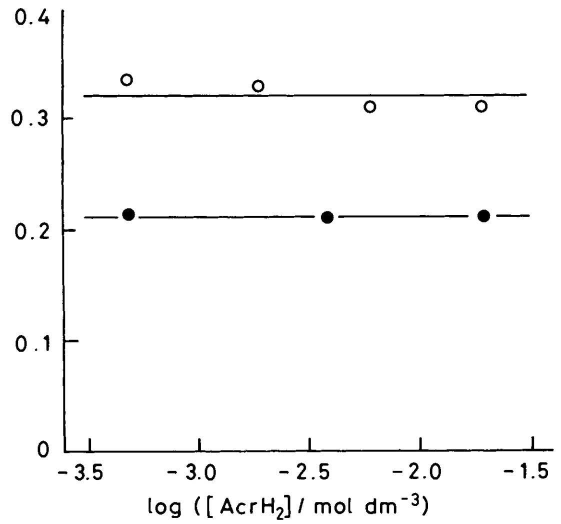


Figure 1. Dependence of the quantum yields φ on the $AcrH_2$ concentration for the photoreduction of phenacyl bromide (○) and phenacyl chloride (●) by $AcrH_2$ in MeCN under irradiation of light λ 340 nm; $[PhCOCH_2X] = 1.0 \times 10^{-3}$ mol dm^{-3}, the light intensity $I_n = 1.2 \times 10^{-6}$ einstein dm^{-3} s^{-1}.

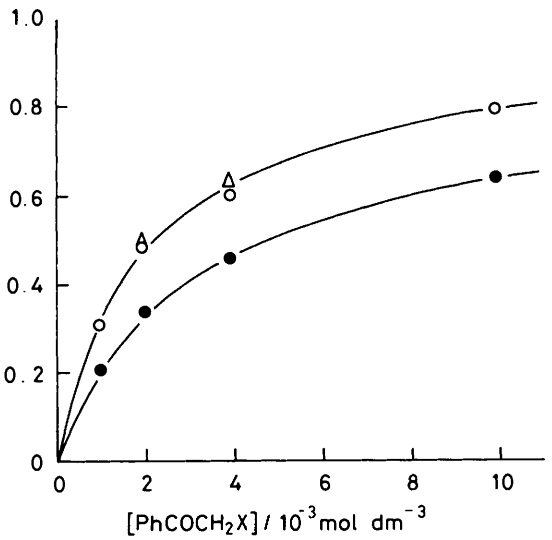


Figure 2. Dependence of the quantum yields φ on the phenacyl halide concentration for the photoreduction of phenacyl bromide (○) and phenacyl chloride (●) by $AcrH_2$ or $AcrD_2$ (△) in MeCN under irradiation of light λ 340 nm; $[AcrH_2] = 2.0 \times 10^{-2}$ mol dm^{-3}, light intensity $I_n = 1.2 \times 10^{-6}$ einstein dm^{-3} s^{-1}.

transferred to benzophenone in the photoreduction by $AcrH_2$.[20] The transferred hydrogen can be readily exchanged with H_2O (Table 1). These facts should be accommodated in any mechanistic consideration of the photoreduction of phenacyl bromide by $AcrH_2$.

Another NADH analogue, 1-benzyl-1,4-dihydronicotinamide (BNAH) which is a stronger reductant than $AcrH_2$,[5,7] can reduce phenacyl bromide thermally.[21] Although the thermal reaction is sluggish, the facile photoreduction of phenacyl bromide in dry MeCN occurs under irradiation of visible light of λ >360 nm to yield 1-benzylnicotinamidium (BNA^+) and acetophenone, equation (3) (Table 1). The addition of water to the BNAH–$PhCOCH_2Br$ system resulted in a decrease in the yields of BNA^+ and acetophenone, accompanied by the hydration of BNAH.[22]

Quantum Yield.—The quantum yields (φ) for the photoreduction of $PhCOCH_2X$ by $AcrH_2$ and $AcrD_2$ were determined under irradiation at λ 320 or 340 nm (see the Experimental section). Comparison of the φ values between $PhCOCH_2Br$ and $PhCOCH_2Cl$ is shown in Figure 1, where the φ values are plotted as a function of the $AcrH_2$ concentration at a fixed concentration of $PhCOCH_2X$ (1.0×10^{-3} mol dm^{-3}). The φ values of $PhCOCH_2Br$ are larger than those of $PhCOCH_2Cl$, and both the φ values are constant with a change in the $AcrH_2$ concentration. On the other hand, the φ value increases with an increase in the $PhCOCH_2X$ concentration to approach a constant value at high concentrations as shown in Figure 2. The φ values for the photoreduction of $PhCOCH_2Br$ by $AcrD_2$ were also determined under the same conditions as those of $AcrH_2$ (Figure 2). The φ values of $AcrD_2$ are essentially the same as those of $AcrH_2$ and thus, no kinetic isotope effect is observed in the photoreduction of phenacyl bromide.

In contrast with the φ dependence on the $AcrH_2$ concentration in Figure 1, the φ value for the photoreduction of $PhCOCH_2Br$ by BNAH increases linearly with an increase in the BNAH concentration to exceed unity (Figure 3). When BNAH was replaced by the 4-monodeuteriated compound ([$^2H_1$]BNAH), the quantum yield was reduced by a factor of 1.6, *i.e.*, $\varphi(\mathrm{BNAH})/\varphi([^2H_1]\mathrm{BNAH}) = 1.61 \pm 0.05$. This value corresponds to the kinetic isotope effect, $\varphi_H/\varphi_D = 4.1 \pm 0.6$, which is obtained from equation (4), where the secondary

$$\varphi_H/\varphi_D = [2\varphi([^2H_1]\mathrm{BNAH})/\varphi(\mathrm{BNAH}) - 1]^{-1} \quad (4)$$

isotope effect is assumed to be unity.[23] The φ value also rises with an increase in the $PhCOCH_2Br$ concentration, but approaches a constant value at high concentrations as shown in Figure 4. When the light intensity absorbed by BNAH is changed, the different φ values are obtained (Figure 4). The dependence of φ^{-2} on the light intensity (I_n) is shown in Figure 5, which demonstrates that φ^2 is proportional to In_n^{-1}.

Photoinduced Electron Transfer.—The excitation of the absorption band (λ_{max} 285 nm) of an MeCN solution of $AcrH_2$ results in fluorescence (λ_{max} 385 nm).[5] The $AcrH_2$ fluorescence is known to be quenched with various electron acceptors (A) by electron transfer from the singlet excited state $^1AcrH_2^*$ to A in MeCN, equation (5).[5] The rate constant of photoinduced

$$^1AcrH_2^* + A \longrightarrow AcrH_2^{+\bullet} + A^- \quad (5)$$

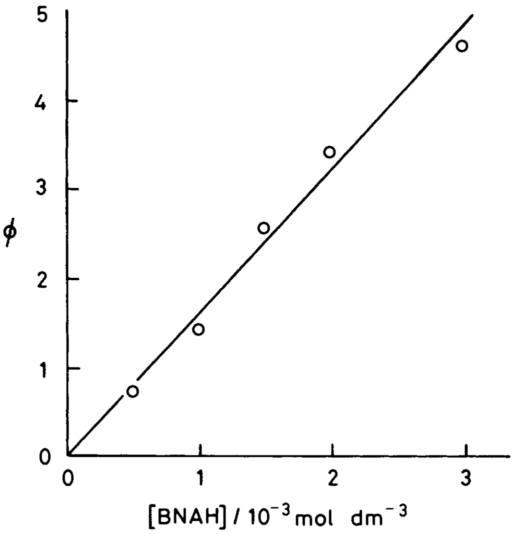


Figure 3. Dependence of the quantum yields φ on the BNAH concentration for the photoreduction of phenacyl bromide by BNAH in MeCN under irradiation of light λ 370 nm; $[PhCOCH_2Br] = 5.0 \times 10^{-2}$ mol dm^{-3}, light intensity $I_n = 2.3 \times 10^{-6}$ einstein dm^{-3} s^{-1}.

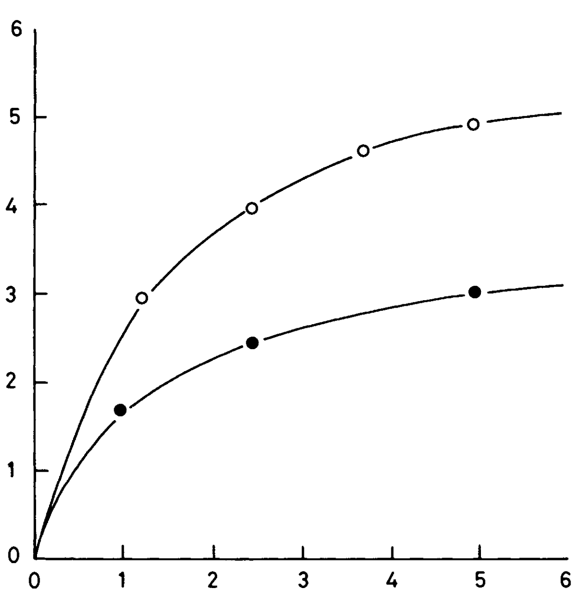


Figure 4. Dependence of the quantum yields φ on the phenacyl bromide concentration for the photoreduction of phenacyl bromide by BNAH (2.0×10^{-3} mol dm^{-3}) in MeCN under irradiation of light λ 370 nm; light intensity $I_n = 1.2 \times 10^{-6}$ (○), 3.9×10^{-6} (●) einstein dm^{-3} s^{-1}.

electron transfer (k_{et}) from $^1AcrH_2{}^*$ to various phenacyl halides were determined from the fluorescence quenching (see the Experimental section). The k_{et} values are listed in Table 2, together with the quenching constants ($K_{et} = k_{et}\tau^{-1}$). The excitation of the absorption band (λ_{max} 350 nm) of an MeCN solution of BNAH also results in fluorescence (λ_{max} 443 nm),[6,19] which is quenched by electron transfer from the singlet excited state $^1BNAH^*$ to phenacyl bromide in MeCN, equation (6).

$$^1BNAH^* + PhCOCH_2Br \longrightarrow BNAH^{+\cdot} + PhCOCH_2Br^{-\cdot} \quad (6)$$

The quenching constant (K_{et}) and the rate constant of electron transfer (k_{et}) are also listed in Table 2.

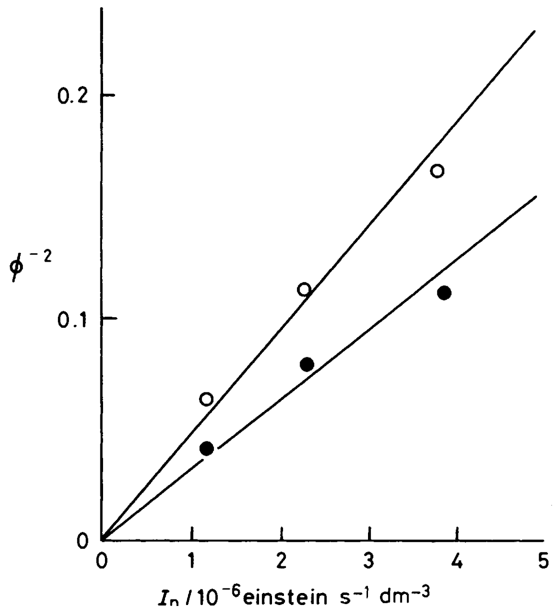


Figure 5. Plots of φ^{-2} *vs.* light intensity for the photoreduction of phenacyl bromide by BNAH (2.0×10^{-2} mol dm^{-3}) in MeCN under irradiation of light λ 370 nm; $[PhCOCH_2Br] = 2.5 \times 10^{-2}$ (○), 5.0×10^{-2} (●) mol dm^{-3}.

Discussion

Direct Photoreduction of Phenacyl Halides by $AcrH_2$.—The singlet excited state of $AcrH_2$ has a very low oxidation potential, -3.1 *vs.* SCE.[5] Thus, electron transfer from $^1AcrH_2{}^*$ to phenacyl halides may be highly exothermic. In fact, the rates of electron transfer from $^1AcrH_2{}^*$ to phenacyl halides are diffusion limited (Table 2). The absence of kinetic isotope effect (Figure 2) indicates that electron transfer from $^1AcrH_2{}^*$ to phenacyl bromide is the rate-determining step in the photoreduction of phenacyl bromide by $AcrH_2$. This is also confirmed by the kinetic analysis as follows. When the electron transfer from $^1AcrH_2{}^*$ to phenacyl halides is the rate-determining step, the quantum yield of the photoreduction of phenacyl halides ($PhCOCH_2X$) by $AcrH_2$ may be independent of the $AcrH_2$ concentration as observed in Figure 1 and given by equation (7), where φ_∞ is the limiting quantum yield at high

$$\varphi = \varphi_\infty K_{et}[PhCOCH_2X]/(1 + K_{et}[PhCOCH_2X]) \quad (7)$$

concentrations of phenacyl halides, and $K_{et} = k_{et}\tau$ (τ is the lifetime of $^1AcrH_2{}^*$). Equation (7) can be rewritten as equation (8), which predicts a linear correlation between φ^{-1} and

$$\varphi^{-1} = \varphi_\infty{}^{-1}[1 + (K_{et}[PhCOCH_2X])^{-1}] \quad (8)$$

$[PhCOCH_2X]^{-1}$. Such correlations are confirmed for the photoreduction of $PhCOCH_2X$ by $AcrH_2$ as shown in Figure 6 where the data in Figure 2 are replotted. Moreover, the K_{et} values of $PhCOCH_2Br$ and $PhCOCH_2Cl$, obtained from the slopes and intercepts in Figure 6 as 4.4 and 3.3×10^{-2} dm^3 mol^{-1}, respectively, agree well with those obtained directly from the fluorescence quenching of $^1AcrH_2{}^*$ by phenacyl bromide and phenacyl chloride (3.9 and 3.3×10^{-2} dm^3 mol^{-1}, respectively).

Based on the above results, the mechanism of the photoreduction of $PhCOCH_2X$ by $AcrH_2$ may be represented by Scheme 1. First, the photoinduced electron transfer from $^1AcrD_2{}^*$ to $PhCOCH_2X$ may occur to yield the radical ion pair ($AcrD_2{}^{+\cdot}$ $PhCOCH_2X^{-\cdot}$). Radical anions of phenacyl halides are known to undergo an intramolecular electron

Table 2. Quenching constants K_{et} and the electron-transfer rate constants k_{et} for the fluorescence quenching of NADH model compounds by phenacyl halides in acetonitrile at 298 K.

NADH Model compound	Quencher[a]	K_{et}/ $dm^3\ mol^{-1}$ [b]	k_{et}/ $dm^3\ mol^{-1}\ s^{-1}$ [c]
$AcrH_2$	$PhCOCH_2Br$	3.9×10^2	2.3×10^{10}
$AcrH_2$	$PhCOCH_2Cl$	3.3×10^2	2.0×10^{10}
$AcrH_2$	p-$MeC_6H_4COCH_2Br$	3.9×10^2	2.6×10^{10}
$AcrH_2$	p-$BrC_6H_4COCH_2Br$	3.9×10^2	2.6×10^{10}
BNAH[d]	$PhCOCH_2Br$	1.6×10	2.1×10^{10}

[a] The excitation wavelength is 330 nm unless otherwise noted. [b] The experimental errors are within ±10%. [c] Obtained from the relation $k_{et} = K_{et}\tau^{-1}$. [d] The excitation wavelength is 380 nm.

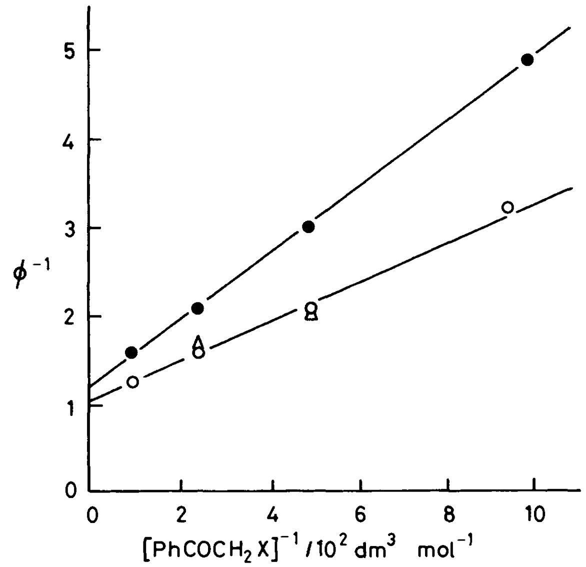
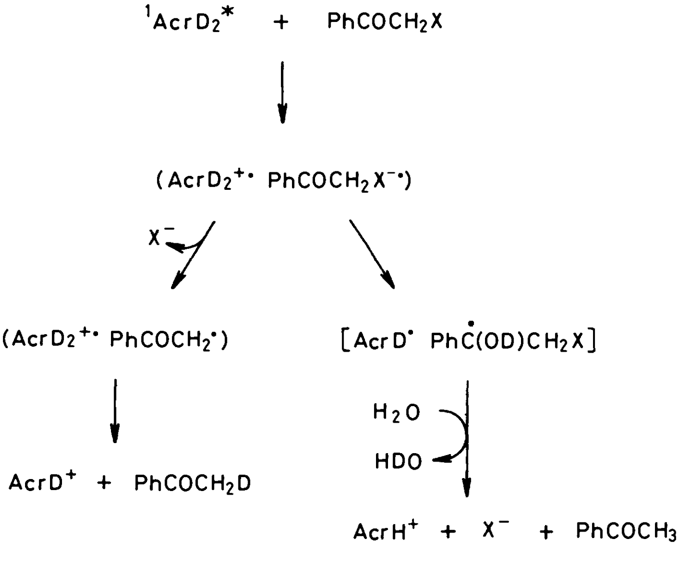


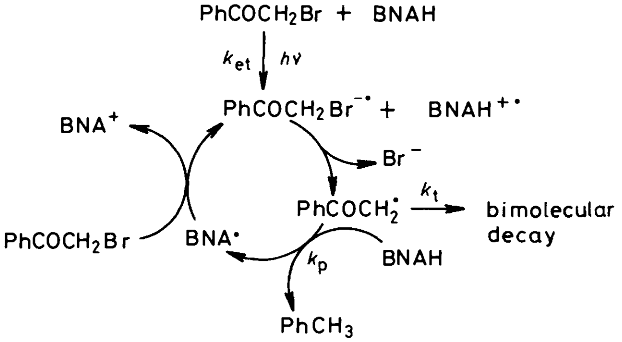
Figure 6. Plots of φ^{-1} vs. $[PhCOCH_2Br]^{-1}$ (○) and $[PhCOCH_2Cl]^{-1}$ (●) for the photoreduction of phenacyl halides by $AcrH_2$ or $AcrD_2$ (△) (2.0×10^{-2} mol dm^{-3}) in MeCN.



Scheme 1.

transfer and to release halide ions.[24] At the same time, the radical anions are readily protonated, and the resulting neutral radicals do not release the halide ions.[25] Thus, there may be competition between the proton transfer from $AcrD_2^{+\bullet}$ to $PhCOCH_2X^{-\bullet}$ and the intramolecular electron transfer to release the halide ion (Scheme 1). If the proton transfer is much faster than the dehalogenation the deuterium of the resulting $Ph\dot{C}(OD)CH_2X$ radical may be readily exchanged with H_2O to give $Ph\dot{C}(OH)CH_2X$ which yields the final product $PhCOCH_3$ by the subsequent electron transfer from $AcrH^\bullet$ (Scheme 1). This may be the reason why no deuterium has been incorporated into acetophenone in the presence of water (Table 1). Alternatively, if the dehalogenation is much faster than the proton transfer, a hydrogen transfer from $AcrH_2^{+\bullet}$ to the dehalogenated radical $PhCOCH_2^\bullet$ yields $PhCOCH_2D$. In such a case, however, no deuterium exchange with H_2O would be expected.

Electron-transfer Radical Chain Reaction.—The singlet excited state of BNAH can also act as an excellent electron donor, judging from the largely negative one-electron oxidation potential (−2.6 V *vs.* SCE).[5,6] In fact, the rate constant of electron transfer from $^1BNAH^*$ to phenacyl bromide [equation (6)] in Table 2 is about the same as the diffusion rate constant[26] in MeCN, 2.0×10^{10} dm^3 mol^{-1} s^{-1}. A linear correlation between φ and the BNAH concentration as well as the φ values exceeding unity indicate that the photoreduction of phenacyl bromide by BNAH proceeds by radical chain reactions which are initiated by photoinduced electron transfer [equation (6)]. The observation of a large kinetic isotope effect ($\varphi_H/\varphi_D = 4.1$) suggests that the rate-determining step of chain propagation involves the abstraction of a hydrogen atom from BNAH. The chain termination step may be a bimolecular reaction of chain-carrier radicals, judging from the dependence of φ on the light intensity (Figure 6). Thus, a radical chain mechanism initiated by photoinduced electron transfer, which can explain all the experimental results, may be summarized as shown in Scheme 2.



Scheme 2.

In the initiation step, electron transfer from $^1BNAH^*$ to $PhCOCH_2Br$ may occur with the diffusion rate constant. The proton transfer from $BNAH^{+\bullet}$ to $PhCOCH_2Br^{-\bullet}$ may follow the photoinduced electron transfer as in the case of $AcrH_2$ (Scheme 1). However, the proton transfer step from $BNAH^{+\bullet}$ to $PhCOCH_2Br^{-\bullet}$ may be much slower than for the case of $AcrH_2$ since the $pK^{7,27}$ value of $BNAH^{+\bullet}$ (3.6) is larger than that of $AcrH_2^{+\bullet}$ (2.0). In such a case, the fission of the carbon–halogen bond of $PhCOCH_2Br^{-\bullet}$ caused by an intramolecular electron transfer from the carbonyl oxygen to Br of $PhCOCH_2Br^{-\bullet}$ may well compete with the proton transfer, yielding the carbon centre radical, $PhCOCH_2^\bullet$. Such alkyl radicals are known to abstract a hydrogen atom from BNAH (with the rate constant of 1.6×10^4 dm^3 mol^{-1} s^{-1} for the benzyl radical).[8] Thus, $PhCOCH_2^\bullet$ may also abstract a hydrogen atom from BNAH to yield $PhCOCH_3$ and $BNA^\bullet$. This may be the rate-determining step responsible for the observation of the kinetic isotope

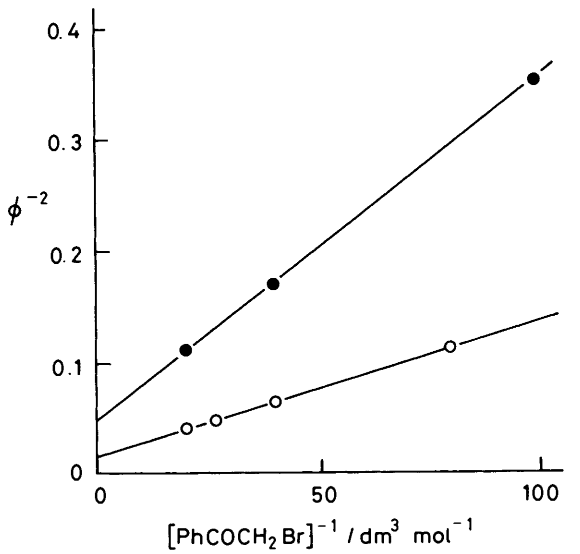


Figure 7. Plots of φ^{-2} *vs.* $[PhCOCH_2Br]^{-1}$ for the photoreduction of phenacyl bromide by BNAH in MeCN; light intensity = 1.2×10^{-6} (○), 3.9×10^{-6} (●) einstein dm^{-3} s^{-1}.

effect. Since the BNA$^{\bullet}$ radical is known to be a strong one-electron reductant,[8,28] electron transfer from BNA$^{\bullet}$ to phenacyl bromide may occur readily to yield BNA^{+}, accompanied by regeneration of $PhCOCH_2Br^{-\bullet}$. Thus, the chain-carrier radical is $PhCOCH_2^{\bullet}$ which may decay by the bimolecular reaction.

By applying the steady-state approximation to the radical species in Scheme 2, the quantum yield may be expressed by equation (10), where k_p is the rate constant of the rate-

$$\varphi = k_p(\varphi_i/2k_tI_n)^{\frac{1}{2}}[BNAH] \qquad (10)$$

determining propagation step, φ_i is the quantum yield for the initiation, k_t is the rate constant of the termination step, and I_n is the light intensity absorbed by BNAH. The initiation quantum yield φ_i may be given by equation (11), where φ_{∞} is the limiting

$$\varphi_i = \varphi_{\infty}K_{et}[PhCOCH_2Br]/(1 + K_{et}[PhCOCH_2Br]) \qquad (11)$$

quantum yield for quenching of all the singlet excited states by $PhCOCH_2Br$ and $K_{et} = k_{et}\tau^{-1}$ (k_{et} is the rate constant of electron transfer from ^{1}BNAH* to phenacyl bromide and τ is the lifetime of ^{1}BNAH*). Equation (11) agrees well with the dependence of φ on the BNAH concentration in Figure 4 as well as on the light intensity (I_n) in Figure 6. From equations (10) and (11) is derived equation (12), where $C = 2k_tI_n/$

$$\varphi^{-2} = C\{1 + (K_{et}[PhCOCH_2Br])^{-1}\} \qquad (12)$$

$(\varphi_{\infty}k_p[BNAH]^2)$. Plots of φ^{-2} *vs.* $[PhCOCH_2Br]^{-1}$ for different light intensities are shown in Figure 7 using the data in Figure 4. Linear correlations in Figure 7 agree well with equation (12). From the intercepts and slopes in Figure 7, essentially the same K_{et} values are obtained for different light intensities (K_{et} = 14 and 16 for $I_n = 1.2 \times 10^{-6}$ and 3.9×10^{-6} einstein dm^{-3} s^{-1}, respectively). More importantly, the K_{et} values obtained from Figure 7 agree well with that obtained from the fluorescence quenching of ^{1}BNAH* by phenacyl bromide (K_{et} = 16 dm^3 mol^{-1} in Table 2). Such agreements clearly demonstrate that the electron transfer from ^{1}BNAH* to phenacyl bromide is solely responsible for the photoinitiation of the radical chain reaction (Scheme 2).

The mechanistic difference between the NADH analogues, $AcrH_2$ and BNAH, may be ascribed to the difference in pK of the corresponding radical cations between $AcrH_2^{+\bullet}$ and BNAH$^{+\bullet}$ as well as the difference in the one-electron oxidation potentials between AcrH$^{\bullet}$ and BNA$^{\bullet}$. The smaller pK[7,27] value of $AcrH_2^{+\bullet}$ (2.0) than BNAH$^{+\bullet}$ (3.6) may be less favourable for the formation of free radicals $PhCOCH_2^{\bullet}$, which can initiate the chain reactions (Scheme 2), by the facile proton transfer from $AcrH_2^{+\bullet}$ to $PhCOCH_2Br^{-\bullet}$. In addition, the more positive E^0_{ox} value of AcrH$^{\bullet}$ (−0.43 V *vs.* SCE)[7] than BNA$^{\bullet}$ (−1.1 V *vs.* SCE)[7] may be less favourable for electron transfer from AcrH$^{\bullet}$ to $PhCOCH_2Br$, which is essential to constitute the radical-chain process (Scheme 2). Thus, we may conclude that an NADH analogue with a smaller pK value of the radical cation and a more positive E^0_{ox} value of the deprotonated radical becomes more favoured for the direct photoreduction pathway (Scheme 1), and that the opposite one favours the electron-transfer radical chain pathway (Scheme 2).

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