Micellar Effects on Photoinduced Electron Transfer from 1,4-Dihydronicotinamide **Derivatives to Tris(acetylacetonato)cobalt(III)**

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The photoreduction of tris(acetylacetonato)cobalt(III) ([Co(acac)₃]) by 1-benzyl-1,4-dihydronicotinamide (BNAH) and 1-dodecyl-1,4-dihydronicotinamide (DNAH) was performed with or without the surfactants anionic sodium dodecyl sulfate (SDS), anionic sodium decyl sulfate (SDeS), cationic dodecyltrimethylammonium chloride (DTAC), and cationic hexadecyltrimethylammonium bromide (HTAB). The quantum yields (Φ) of the present photoreduction were not appreciably changed by the cationic micelles but enhanced remarkably by the anionic micelles. The maximum enhancement by SDS was obtained in the reduction of [Co(acac)₃] by DNAH which possessed a long alkyl chain. Kinetic models, in which the reactants were distributed between a micellar phase and an aqueous phase, were used to explain the micellar effects. The anionic SDS micelles accelerated the electron transfer from photoexcited NADH model compounds (BNAH* and DNAH*) to [Co(acac)₃] in the micellar phase by concentrating them and by lengthening lifetimes of BNAH* and DNAH*. In the cationic DTAC micellar phase, however, the electron-transfer rate was retarded, despite the concentration of the reactants and the lengthening of lifetimes of BNAH* and DNAH*. Such a difference in the reaction rate between SDS and DTAC was explained by the difference in the micellar effect on the extent of heterolytic dissociation of the encounter complex of photoexcited NADH model compounds and [Co(acac)₃].

Introduction

The redox reactions involving 1,4-dihydropyridine derivatives capable of acting as excellent two-electron donors by transfer of a hydride equivalent^{1,2} have been extensively studied as model reactions of a reduced nicotinamide adenine dinucleotide (NAD(P)H).^{3,4} Since the reducing ability of NADH model compounds is substantially enhanced by photoirradiation⁵ on their absorption maxima at around 350 nm ($\pi \rightarrow \pi^*$ transition of dihydropyridine rings⁶), it is of interest to study the photoreaction of NADH model compounds by taking note of photoinduced electron transfer and subsequent reverse electron-transfer reaction between NADH model compounds and substrates.

In this respect, organized media like micelles are well documented as novel environments for photochemical conversion,⁷ because the micellar systems cannot only promote the electron transfer from photoexcited donors to acceptors by concentrating them^{8,9} but also affect lifetimes of the photoexcited states¹⁰ and efficiency of reverse electron transfer¹¹⁻¹⁸ by their intrinsic mi-

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croenvironments composed of a hydrophobic core, an aqueous phase, and a charged interface.

Among a number of studies of the photoreaction of NADH model compounds, 19-37 there has been only one report³² concerning

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Micellar Effects on Photoinduced Electron Transfer

the effects of micelles on the photochemical behavior of NADH model compounds. The detailed mechanisms of micellar effects such as concentration of reactants and microenvironmental influences on the photoreaction of NAD(P)H model compounds have not yet been unveiled.

In this paper, we describe the micellar effects on the photoreduction of tris(acetylacetonato)cobalt(III) ([Co(acac)₃]) by 1-benzyl-1,4-dihydronicotinamide (BNAH) and 1-dodecyl-1,4dihydronicotinamide (DNAH) in the presence of anionic and/or cationic surfactants. The effects of reactant concentration or dilution and those of microenvironments on the reaction are evaluated by the analysis of reactant distribution between the micellar phase and the aqueous phase. The results provide an example where the micellar system really enhances product formation.

Experimental Section

Materials and Equipment. 1-Benzyl-1,4-dihydronicotinamide (BNAH), 1-dodecyl-1,4-dihydronicotinamide (DNAH), and 1-benzyl[4- ${}^{2}H_{1}$]-1,4-dihydronicotinamide ([${}^{2}H_{1}$]BNAH) were prepared according to the literature.^{38,39} Commercially available tris(acetylacetonato)cobalt(III) ([Co(acac)₃]) was purified by recrystallization from petroleum ether-benzene. Sodium dodecyl sulfate (SDS), sodium decyl sulfate (SDeS), dodecyltrimethylammonium chloride (DTAC), and hexadecyltrimethylammonium bromide (HTAB) were also commercially available were used without further purification. The solvents methanol and water were distilled and deoxygenated before use by purging with N_2 .

Fluorescence intensity was measured by using Hitachi F-3010 fluorescence spectrophotometer with thermostated cell holder (30 \pm 0.1 °C), and HPLC was performed by using Merck LiChro-CART column (LiChrosphere 100 RP-18, 10 μ m, 250 × 4 mm).

Procedure. Aliquots (3 cm^3) of the homogeneous 4% (v/v)methanol-0.02 mol dm⁻³ H₃BO₃-NaOH buffer (pH 9.0, $\mu = 0.02$ mol dm⁻³ with KCl) solution containing NADH model compounds $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$, [Co(acac)₃] ($(0.4-2.0) \times 10^{-3} \text{ mol dm}^{-3}$), and surfactants ($(0-7.5) \times 10^{-2} \text{ mol dm}^{-3}$) were introduced into 1-cm Pyrex cells under N₂ atmosphere and were bubbled for 30 min with nitrogen. The solutions were then placed in a thermostated $(30 \pm 0.2 \text{ °C})$ cell holder with a magnetic stirring device and were irradiated by using a 400-W mercury lamp in the wavelength range of $410 > \lambda > 340$ nm with Toshiba UV-35 and UV-D35 glass filters. The reaction rate was followed by spectroscopic determination of the decreased amount of [Co(acac)₃] at 595 nm. Analyses of the starting materials (BNAH and [Co(acac)₃]) were performed at 350 nm with methanol-water (55/45) as an eluent. The production of bis(acetylacetonato)-



Figure 1. Micellar effects on quantum yields for photoreduction of $[Co(acac)_3]$ by BNAH with SDS (0), BNAH with SDeS (Δ), BNAH with DTAC (\bullet), BNAH with HTAB (\blacktriangle), DNAH with SDS (\Box), and DNAH with DTAC (\blacksquare). [BNAH] = [DNAH] = 5.0 × 10⁻⁴ mol dm⁻³; $[[Co(acac)_3]] = 1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ under } N_2 \text{ at } 30 \text{ °C}.$

cobalt(II) ([Co(acac)₂]) and 1-benzylnicotinamide (BNA⁺) was determined at 265 nm by using methanol-water (40/60) and methanol-water (55/45) with 0.005 mol dm⁻³ sodium decyl sulfate, respectively.

The quantum yields of the reduction were determined for the solution with sufficiently high absorbance (absorbance (abs) \gg 2.0) at $\lambda = 340-410$ nm to ensure complete absorption of light entering the samples during the experiments. The light intensity was determined by Reinecke's salt actinometry,⁴⁰ and the amounts (1) of photons absorbed by NADH model compounds were corrected by the equation

$$I = \frac{\int_{\lambda_2}^{\lambda_1} T(\lambda) \frac{abs_{NADH}(\lambda)}{abs_{NADH}(\lambda) + abs_{Co}(\lambda)} d\lambda}{\int_{\lambda_2}^{\lambda_1} T(\lambda) d\lambda} I_t \qquad (2)$$

where T is the transmittance of the cutoff filters, abs_{NADH} and abs_{Co} are absorbances of NADH model compounds and [Co- $(acac)_{1}$, respectively, I_{t} is the light intensity determined by Reinecke's salt actinometry, $\lambda_1 = 340$ nm, and $\lambda_2 = 410$ nm.

The lifetimes (τ) of the photoexcited BNAH and DNAH were estimated on the basis of $\tau = 0.93$ ns for both NADH model compounds in methanol^{19,32} by estimating the ratio of theoretical lifetimes calculated from Strickler and Berg equation⁴¹ vs fluorescence intensity relative to that obtained in methanol. The relative emission intensity was measured for 4% (v/v) methanol-0.02 mol dm⁻³ borate buffer (pH 9.0) solution containing BNAH or DNAH (1.0 \times 10⁻⁵ mol dm⁻³) and the surfactants $((0-7.5) \times 10^{-2} \text{ mol dm}^{-3})$. The excitation and monitoring wavelengths were 360 and 370-700 nm, respectively.

Results and Discussion

The photoreduction of [Co(acac)₃] by BNAH was carried out in 4% (v/v) methanol-borate buffer (pH 9.0) solution with or without surfactants at 30 °C under N_2 . Although the amount of $[Co(acac)_3]$ in the solution decreased gradually in the dark, the reduction of [Co(acac)₃] by BNAH was accelerated remarkably by photoirradiation. The HPLC analysis at 350 nm showed that both the concentrations of BNAH and $[Co(acac)_3]$ decreased during photoirradiation. The productions of 1benzylnicotinamide (BNA⁺) and bis(acetylacetonato)cobalt(II) $([Co(acac)_2])$ were confirmed by comparing retention times with their authentic samples on reversed-phase HPLC analysis at 265 nm.

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TABLE I: Quantum Yield and Molar Ratio of [Co(acac)₃] Reduced by 1 mol of BNAH for Photoreduction of [Co(acac)₃] by BNAH under N2 at 30 °C

10 ⁴ [BNAH], mol dm ⁻³	10 ³ [[Co(acac) ₃]], mol dm ⁻³	pН	10² Φ_{BNAH} ″	$10^2 \Phi_{\rm CO}^{b}$	n
0	1.00	9.0		0	
5.00	0	9.0	0.077		
5.00	1.00	9.0	0.72	1.37	2.1
5.00	1.15	9.0	0.81	1.52	2.1
5.00	1.33	9.0	0.95	1.84	2.1
5.00	1.60	9.0	1.12	2.22	2.1
5.00	2.00	9.0	1.44	2.78	2.0
2.00	1.00	9.0	0.63	1.18	2.1
4.00	1.00	9.0	0.71	1.34	2.1
6.00	1.00	9.0	0.68	1.36	2.3
8.00	1.00	9.0	0.64	1.32	2.3
5.00	1.00	8.5	0.66	1.32	2.3
5.00	1.00	9.5	0.66	1.32	2.3
5.00	1.00	10.0	0.70	1.40	2.3
5.00	1.00	9.0	0.67	1.32	2.2

"Quantum yield evaluated on the basis of the amount of BNAH consumed by the photoreaction. ^bQuantum yield evaluated on the basis of the amount of $[Co(acac)_3]$ consumed by the photoreaction. ^c [²H₁]BNAH was used.

Figure 1 indicates the micellar effects on the quantum yields (Φ_{Co}) evaluated on the basis of the amount of $[Co(acac)_3]$ consumed by photoexcited BNAH and/or DNAH. The quantum yields were increased remarkably by the anionic SDS; the SDS concentration of about 1.5×10^{-2} mol dm⁻³ maximized the Φ_{Co} value, and the Φ_{Co} value showed a gradual decrease under [SDS] $\geq 2.5 \times 10^{-2}$ mol dm⁻³. On the other hand, both the cationic surfactants DTAC and HTAB did not influence the quantum yields appreciably. The extent of the micellar effects by SDS was larger than that of SDeS, and remarkably enhanced quantum yields in the presence of SDS were observed for the photoreduction of $[Co(acac)_3]$ by DNAH possessing a long hydrophobic chain. From these facts, both incorporation of the reactants to the micelles and the charge of the micellar surface seem to play important roles in acceleration of the present reaction.

Table I summarizes the quantum yields (Φ) and the molar ratio (n) of $[Co(acac)_3]$ reduced by 1 mol of BNAH for the photoreduction of [Co(acac)₃] by BNAH under various conditions. The quantum yields (Φ_{BNAH} and Φ_{Co}) were evaluated on the basis of amounts of BNAH and $[Co(acac)_3]$ consumed by photoreaction in unit time, respectively. Since BNAH was hydrated to 1benzyl-6-hydroxy-1,4,5,6-tetrahydronicotinamide, 39,42 the *n* values of the photoreduction of [Co(acac)₃] by BNAH were calculated by $n = \Phi_{Co}/(\Phi_{BNAH} - \Phi_{dec})$, where Φ_{dec} is the quantum yield for hydration of BNAH ($\Phi_{dec} = 7.7 \times 10^{-4}$).

The quantum yields obtained increased appreciably with increasing the [Co(acac)₃] concentration but was independent of the BNAH concentration. The almost constant n values of 2.0-2.3 obtained at various concentrations of BNAH and [Co(acac)₃] indicate that 2 mol of $[Co(acac)_3]$ were consumed by 1 mol of BNAH under the present reaction conditions.

The quantum yields and the n value for the photoreaction between $[{}^{2}H_{1}]BNAH$ and $[Co(acac)_{3}]$ were exactly the same as

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those for the photoreaction between BNAH and $[Co(acac)_3]$. Accordingly, a direct hydride transfer from the photoexcited BNAH to [Co(acac)₁] was excluded from the reaction mechanism of the present reaction.

From above-mentioned results, the reaction mechanism shown in Scheme I can be proposed for the present photoreaction.^{32,33} SCHEME I

$$BNAH \xrightarrow{i} BNAH^*$$
 (3a)

$$BNAH^* \xrightarrow{k_k} BNAH \tag{3b}$$

$$BNAH^* \xrightarrow{\kappa_l} BNAH + h\nu \qquad (3c)$$

BNAH* +
$$[Co(acac)_3] \xrightarrow{\kappa_1} [BNAH^+Co(acac)_3^-]$$
 (3d)

$$[BNAH^+Co(acac)_3^-] \xrightarrow{k_2} BNAH^{*+} + [Co(acac)_2] + acac^-$$
(3e)

$$[BNAH^+Co(acac)_3^-] \xrightarrow{\kappa_3} BNAH + [Co(acac)_3]$$
 (3f)

$$BNAH^{*+} \xrightarrow{\kappa_{H^+}} BNA^* + H^+$$
(3g)

$$BNA^{\bullet} + [Co(acac)_3] \xrightarrow{\sim_4} [BNA^+Co(acac)_3^-] \qquad (3h)$$

$$[BNA^+Co(acac)_3^-] \xrightarrow{s_3} BNA^+ + [Co(acac)_2] + acac^- (3i)$$

$$[BNA^+Co(acac)_3^-] \xrightarrow{k_6} BNA^* + [Co(acac)_3] \qquad (3j)$$

According to Scheme I, the rate constants (k_{el}) of the first electron transfer from BNAH* to [Co(acac)₃] is given by eq 4.

$$k_{\rm el} = k_1 \frac{k_2}{k_2 + k_3} = k_{\rm diff} \frac{k_2}{k_2 + k_3} \tag{4}$$

Since the reduction potential $(E_{red} = ca. -0.3 \text{ V vs SCE})^{35}$ of $[Co(acac)_3]$ is more positive than the oxidation potential ($E_{ox} =$ -2.6 V vs SCE)⁵ of BNAH^{*} and more negative than that (E_{ox}) = $0.57 \text{ V vs SCE}^{1}$ of BNAH, the following assumptions can be made: (a) the encounter complex formation corresponds to a diffusion process, i.e., $k_1 = k_{\text{diff}}$; (b) the production of BNAH^{•+}, $[Co(acac)_2]$, and $acac^-$ from the encounter complex (eq 3e) competes with the reproduction of BNAH and $[Co(acac)_3]$ (eq 3f). Thus, the electron-transfer rate from BNAH* to $[Co(acac)_3]$ is affected by both the diffusion process of the reactants and the dissociation process of the encounter complex.

The deprotonation step (eq 3g) does not participate in the rate-determining step of the reaction, since the present reaction was not affected by changing pH of the solution in the range of 8.5 < pH < 10.0 and any kinetic isotope effect was not observed as shown in Table I.

Since the oxidation potential (-1.08 V vs SCE)¹ of BNA[•] is considerably negative than the reduction potential (ca. -0.3 V)³⁵ of $[Co(acac)_3]$, the formation of the encounter complex (eq 3h) and the dissociation of the complex (eq 3i) might proceed very quickly. Accordingly, the rate constant, k_{e2} , for the second electron-transfer reaction is expressed by eq 5. Thus, the second

$$k_{\rm e2} = k_4 = k_{\rm diff} \tag{5}$$

electron-transfer reaction is not a rate-determining step but a diffusion-controlled process.

Consequently, the initial electron transfer from BNAH* to $[Co(acac)_3]$ is the rate-determining step in a stepwise $e^-H^+-e^$ sequence. Therefore, the stationary-state assumption of the concentrations of intermediates results in the following equation.

$$\frac{1}{\Phi_{\rm Co}} = \frac{1}{2\Phi_{\rm BNAH}} = \frac{1}{2k_{\rm el}\tau} \frac{1}{[[\rm Co(acac)_3]]} + \frac{k_2 + k_3}{2k_2} \quad (6)$$

where τ is the lifetime of BNAH* in the absence of [Co(acac)₃]. According to eq 6, the quantum yields of the present reaction can be affected by the reaction rate constants of the electron transfer

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Figure 2. Effects of surfactant concentration on lifetimes of photoexcited BNAH and DNAH: BNAH with SDS (O), BNAH with DTAC (Δ), DNAH with SDS (\bullet), and DNAH with DTAC (\blacktriangle).

TABLE II: Effects of D₂O on Relative Fluorescence Intensity of BNAH with or without 8.0×10^{-3} mol dm⁻³ SDS in 4% (v/v) Methanol-0.02 mol dm⁻³ H₃BO₃-NaOH Buffer (pH 9.0) Solution

	surfactant	rel fluorescence intensity		
		in H ₂ O	in D ₂ O	
	none	1.00	1.45	
	SDS	2.05	2.51	

from BNAH* to $[Co(acac)_3]$ and the lifetime of BNAH*.

The lifetimes (τ) of BNAH^{*} and DNAH^{*} were estimated from the fluorescence intensity.^{19,31} Figure 2 shows the lifetimes of BNAH* and DNAH* estimated at various surfactant concentrations. The lifetime of BNAH* was lengthened by the concentration increase of SDS and DTAC to approach a constant value in the high concentration. The lifetime of DNAH* in the presence of micelles (0.78 and 0.93 ns in SDS and DTAC, respectively) was fairly longer than that (0.38 ns) of BNAH* in the absence of the micelles.

The fluorescence measurements with or without the surfactant were performed in water and heavy water (D_2O) to account for enhancement of the lifetimes of BNAH* and DNAH* by the micelles. As shown in Table II, the fluorescence intensity of BNAH was increased by changing the solvent from water to heavy water, and the solvent effect was more appreciably reduced in the micellar solution as compared with the case in the nonmicellar solution. These facts suggest that the photoexcited BNAH* molecule would be quenched by the high-frequency O-H vibration of water molecules in a bulk aqueous phase,45 and the incorporation of BNAH into the micelles might suppress the interaction of BNAH* with water molecules,⁴⁶ so that the lifetime of BNAH* is lengthened by the micelles.

The rate constant (k_{ei}) of the electron transfer from photoexcited NADH model compounds (BNAH* and DNAH*) to [Co(acac)₃] was evaluated from the slopes of the linear plots of Φ^{-1} vs [[Co(acac)₃]]⁻¹ according to eq 6 by using the lifetime (τ). The micellar effects on the k_{el} values were indicated in Figure 3. Both the k_{el} values obtained for BNAH* and DNAH* were extremely increased by negatively charged SDS micelles up to $[SDS] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$, and in the case of [SDS] > 2.0 \times 10⁻² mol dm⁻³, the rate constant decreased monotonously on



Figure 3. Micellar effects on rate constants (k_{el}) for photoinduced electron transfer to [Co(acac)₃] from BNAH with SDS (O), BNAH with DTAC (Δ), DNAH with SDS (\oplus), and DNAH with DTAC (Δ). Curves are k_{el} values calculated by eq 13.



the addition of SDS. These features were well correlated with the micellar effects of SDS on the Φ values (Figure 1). On the other hand, the cationic DTAC micelles remarkably retarded the electron transfer from BNAH* or DNAH* to [Co(acac)₃]. Such a retardation effect of DTAC was compensated by the lengthened lifetime of BNAH* or DNAH* in the micellar solution, so that no appreciable changes of Φ (Figure 1) were observed in the presence of DTAC.

The micellar effects on the rate constants (k_{el}) of the electron-transfer reaction of BNAH* with [Co(acac)₃] were analyzed according to a simple model (Scheme II).^{8,47} In Scheme II, the subscript and superscript letters w and m stand for an aqueous phase and micellar phase, respectively. In Scheme II, BNAH* is assumed not to move between the two phases during the reaction by the following reason. The micellar entry and exit rate constants for neutral organic species have been reported to be $(5-12) \times 10^9$ mol⁻¹ dm³ s⁻¹ and (4-83) \times 10⁵ s⁻¹, respectively,⁴³ and the pseudo-first-order rate constants for the entry of BNAH into the micelles are calculated to be $(3-12) \times 10^5 \text{ s}^{-1}$ under the present reaction conditions. Since the decay rate constant of (1.3-2.6) $\times 10^9$ s⁻¹ for BNAH^{*} is given as the reciprocal lifetime (1/ τ) of BNAH*, the deactivation rate of photoexcited state seems to be much faster than their micellar entry and exit rate.

The distributions of the reactants between the micellar phase and the aqueous phase were evaluated as their binding constants and partition coefficients. The binding constants (K_{BNAH} and K_{Co}) of BNAH and [Co(acac)₃] were previously determined by fluorescence measurement of BNAH and by kinetic treatments for the thermal reaction between BNAH and [Co(acac)₃], respectively,⁴⁸ while the molar ratio (P_{BNAH^*}) of BNAH* in the

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Figure 4. Plots of $(\tau_w^{-1} - \tau^{-1})^{-1}$ vs C_m^{-1} for lifetimes of BNAH^{*} in the presence of SDS (\dot{O}) and DTAC (Δ).

micellar phase to that in the aqueous phase is evaluated from the micellar effects on the lifetime of BNAH*. In the case of the photoirradiation on BNAH without $[Co(acac)_3]$, the following equation is obtained from Scheme II by stationary-state assumption of the BNAH* concentrations ([BNAH*,] and [BNAH*_m]) in the aqueous phase and the micellar phase.

$$I_{t} = I_{m} + I_{w}$$

= $(k_{ic}^{m} + k_{f}^{m})[BNAH^{*}_{m}]C_{m}v + (k_{ic}^{w} + k_{f}^{w})[BNAH^{*}_{w}](1 - C_{m}v)$ (8)

where I is the number of photons absorbed by BNAH in a unit time, v is the partial molar volume of the micelles, and C_m is the concentration of micelles ($C_m = [surfactant] - cmc$). On the other hand, the apparent lifetime of BNAH* in the micellar solution is obtained as an average lifetime of BNAH* in the micellar phase and the aqueous phase. In this respect, the stationary-state assumption of [BNAH*] leads to the alternative expression (eq 9) of eq 8. Since the total concentration of BNAH* ([BNAH*])

$$I_{\rm t} = (k_{\rm ic} + k_{\rm f})[{\rm BNAH}^*]$$
(9)

in the solution and the ratio (P_{BNAH^*}) of the BNAH^{*} concentration in the micellar phase to that in the aqueous phase are given by eqs 10 and 11, respectively, eq 12 is derived from eqs 8 and 9 with $1 \gg C_{\rm m} v$ and $P_{\rm BNAH^{\bullet}} \gg 1$.

$$[BNAH^*] = [BNAH^*_m]C_mv + [BNAH^*_w](1 - C_mv)$$
(10)

$$P_{\mathsf{BNAH}^*} = [\mathsf{BNAH}^*_{\mathsf{m}}] / [\mathsf{BNAH}^*_{\mathsf{w}}]$$
(11)

$$\frac{1}{1/\tau_{\rm w} - 1/\tau} = \frac{1}{1/\tau_{\rm w} - 1/\tau_{\rm m}} \left(\frac{1}{P_{\rm BNAH^{*U}}} \frac{1}{C_{\rm m}} + 1\right) (12)$$

where the lifetime (τ) is defined by $\tau = 1/(k_{ic} + k_f)$.

Figure 4 shows the linear relationships between $(1/\tau_w - 1/\tau)^{-1}$ vs $C_{\rm m}^{-1}$ for SDS and DTAC solutions. Since the partial molar volume (v) of SDS and DTAC micelles were respectively estimated to be 0.251 and 0.256 mol⁻¹ dm³ from their partial specific volume,⁴⁴ the P_{BNAH^*} and τ_m values were evaluated to be 1780 and 0.78 ns for SDS, and 949 and 0.88 ns for DTAC, respectively. Since the lifetime of BNAH* in the micellar phase were fairly longer than the τ_w value in the aqueous phase, the apparent lifetime of BNAH* in the micellar solution was increased with increasing the surfactant concentration by distribution of BNAH* to the micellar phase. In Table III, P_{BNAH} , values are summarized in addition to the binding constants of BNAH and [Co(acac)₃] $(K_{BNAH} \text{ and } K_{Co})$ and the cmc values of SDS and DTAC.

According to Scheme II, the rate constant (k_{el}) of electron transfer is expressed by eq 13.^{8,47} A linear relationship between $k_{el}(1 + P_{BNAH*}vC_m)(1 + K_{Co}C_m)$ and C_m is then derived from eq 13.

TABLE III: Critical Micelle Concentration (cmc), Binding Constants of BNAH and [Co(acac)₃] to Micelles, and Apparent Partition Coefficient of BNAH* between a Micellar Phase and an Aqueous Phase at 30 °C



0.2 0 ō.0 2.0 4.0 6.0 $10^2 C_m / mol dm^{-3}$

Figure 5. Plots of $k_{el}(1 + P_{BNAH*}vC_m)(1 + K_{Co}C_m)$ vs C_m for electron-transfer reaction between BNAH* and [Co(acac)₃] in the presence of SDS (0) or DTAC (Δ).

$$k_{\rm e1} = \frac{k_{\rm e1}{}^{\rm m} P_{\rm BNAH^{\bullet}} K_{\rm Co} C_{\rm m} + k_{\rm e1}{}^{\rm w}}{(1 + P_{\rm BNAH^{\bullet}} v C_{\rm m})(1 + K_{\rm Co} C_{\rm m})}$$
(13)

$$k_{e1}(1 + P_{BNAH^{\bullet}}UC_{m})(1 + K_{Co}C_{m}) = k_{e1}^{m}P_{BNAH^{\bullet}}K_{Co}C_{m} + k_{e1}^{w}$$
(14)

From the linear plots of $k_{el}(1 + P_{BNAH*}vC_m)(1 + K_{Co}C_m)$ vs C_m in Figure 5, the rate constants were calculated to be $k_{e1}^{m} = 8.9$ × 10⁸ (SDS) and 1.7 × 10⁸ mol⁻¹ dm³ s⁻¹ (DTAC). The rate constant of $k_{el}^{w} = 1.8 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ was given as the rate constant obtained for the reaction without the surfactants. Since similar k_{ei}^{m} values (1.1 × 10⁹ and 3.0 × 10⁸ mol⁻¹ dm³ s⁻¹ for SDS and DTAC, respectively) were obtained for the photoreduction of [Co(acac)₃] by DNAH in a manner similar to the photoreaction of BNAH, it seems reliable that the rates of the electron transfer from photoexcited NADH model compounds to Co(acac)₃ were retarded in the micellar phase.

Figure 6 indicates the apparent rate constants (k^{m} and k^{w} in the micellar phase and the aqueous phase, respectively) calculated at various surfactant concentrations by using eqs 15a and 15b.

$$k^{\mathrm{m}} = \frac{k_{\mathrm{el}}^{\mathrm{m}} P_{\mathrm{BNAH}*} K_{\mathrm{Co}} C_{\mathrm{m}}}{(1 + P_{\mathrm{BNAH}*} v C_{\mathrm{m}})(1 + K_{\mathrm{Co}} C_{\mathrm{m}})}$$
(15a)

$$k^{w} = \frac{k_{e1}^{w}}{(1 + P_{BNAH^{*}}vC_{m})(1 + K_{Co}C_{m})}$$
 (15b)

The k^w values decreased drastically with increasing the surfactant concentration due to diminution of the reactant concentrations in the aqueous phase. On the other hand, the k^m values were maximized at [SDS] = 1.5×10^{-2} and [DTAC] = 3.0×10^{-2} mol dm⁻³. Since the apparent rate constant (k_{el}) of the electron transfer is expressed by the sum of the k^{m} and k_{w} values (eq 13), the characteristic curves in Figures 3 are attributable to variation of the reaction rates in the micellar phase and the aqueous phase. Thus, the SDS micelles promoted the electron transfer from BNAH* to [Co(acac)₃] by concentrating them through the hydrophobic interaction, while the retardation of the electron transfer



Figure 6. Calculated rate constants for electron transfer from BNAH^{*} to $[Co(acac)_3]$ in the micellar phase (---) and in the aqueous phase (---).

by DTAC is due to the smaller k_{e1}^{m} value (1.7 × 10⁸ mol⁻¹ dm³ s⁻¹) in the DTAC micellar phase when compared with that (8.9 × 10⁸ mol⁻¹ dm³ s⁻¹) in the SDS micellar phase.

The rate constants (k_{el}) of the electron transfer from BNAH* to [Co(acac)₃] were strongly affected by changing the reaction medium from the aqueous phase to the micellar phase. As can been seen from eq 4, the k_{ei} values depend on the diffusion of the reactants and the efficiency of the dissociation of the encounter complex. The estimation of a bimolecular rate constant (k_{diff}) for a diffusion-controlled reaction under the present reaction conditions needs to include the so-called unimolecular lifetime effect. That is, consumption of the photoexcited NADH model compounds through a deactivation process cannot be excluded from estimation of the k_{diff} value, since the lifetime of BNAH* is of the order of nanoseconds. Recently, Kizer proposed the diffusion-controlled reaction theory based on statistical nonequilibrium thermodynamics.^{49,50} According to Kizer's theory, the k_{diff} value in the aqueous phase was calculated to be 2.7 \times 10¹⁰ mol⁻¹ dm³ s⁻¹ by using the diffusion coefficients of BNAH* and $[Co(acac)_3]$ $(D_{BNAH} = D_{Co} = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ taken from

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(50) According to Kizer's theory, the k_1 value in the aqueous phase was calculated by following equation⁴⁹

 $k_1/$

$$N_{\rm A} = k_{\rm diff} / N_{\rm A} = 4\pi DRC(R)$$

where

$$C(R) = \left[\frac{(D_{Co} - D_{BNAH})}{2D_{Co}} \exp(-R\alpha^{1/2}) + \frac{(D_{Co} + D_{BNAH})}{2D_{Co}} \exp(-R\beta^{1/2})\right]^{-1}$$

$$\alpha = \left[(\tau^{-1} + k_1[[Co(acac)_3]]) / D_{BNAH}\right]$$

$$\beta = \left[(\tau^{-1} + k_1[[Co(acac)_3]]) / (D_{BNAH} + D_{Co})\right]$$

where N_A is Avogadoro's number, D is the sum of the diffusion coefficients of reactants, R is the fictitious encounter radius, and k^0 is the intrinsic bimolecular rate constant. While, the k_1 value in the miceliar phase was estimated by following equations⁴⁹

$$k_{1}/N_{A} = Ck_{1}^{(2)}N_{A} = C\frac{4\pi D_{BNAH}k^{0}/K_{0}(R\alpha^{1/2})}{k^{0} + 4\pi D_{BNAH}/K_{0}(R\alpha^{1/2})}$$

$$\alpha = (\tau_{m}^{-1} + k_{1}[[Co(acac)_{3}]_{m}])/D_{BNAH}$$

typical D values of small molecules in aqueous solution) and the reaction radii of BNAH^{*} and [Co(acac)₃] ($R_{BNAH} = 0.2$ nm and $R_{Co} = 0.5$ nm estimated from molecular models). This value is very close to $k_{e1}^{w} = 1.8 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ obtained experimentally, suggesting that the encounter complex of [BNAH⁺ Co(acac)₃⁻] efficiently dissociates to BNAH^{*+}, [Co(acac)₂], and acac⁻ (eq 3e) in the aqueous phase.

On the other hand, the diffusion of reactants in the micellar phase may be restricted by the characteristic microenvironments of the micelles. In this respect, both BNAH and [Co(acac)₃] were substantially associated with the micelles at the micelle-water interface: (1) the ¹H NMR chemical shifts of BNAH suggested incorporation of BNAH by the micelles except for a part of the dihydropyridine ring moiety which was exposed to the aqueous phase; (2) although the ¹H NMR chemical shifts of $[Co(acac)_3]$ were reported to be identical in water and in SDS solution, association of [Co(acac)₃] with the micelles was indicated by the binding constant of K_{Co} (11 and 27 mol⁻¹ dm³ with SDS and DTAC, respectively). Therefore, the reaction between BNAH* and [Co(acac)₃] might proceed in a spherical shell at the surface of the micelle, so that the diffusion process needs to be treated by two-dimensional motions. The values for D_{BNAH} and D_{Co} of $2.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ were used to estimate the diffusion rate constants in the micellar phase since microviscosity in the micelle is about 25 times as high as in the aqueous solution.⁵⁴ Consequently, the k_1 values for a two-dimensional system calculated by using Kizer's theory were coincident with the intrinsic bimolecular rate constants.⁵⁰ The fact suggests that the photoexcited species (BNAH* and DNAH*) generated in the micellar phase form the encounter complex immediately only with neighboring $[Co(acac)_3]$. That is, the encounter complex of BNAH* and DNAH* with [Co-(acac)₃] is produced in the micellar phase without any effect of diffusion.

Accordingly, the smaller k_{el}^{m} values, as compared with the k_{el}^{w} value, are attributable to the smaller $k_2/(k_2 + k_3)$ values in eq 4. That is, dissociation of the encounter complex in SDS and DTAC micellar phases is considerably less than that in the aqueous phase. Since the heterolytic dissociation of the encounter complex (eq 3e) produces ionic species (BNAH^{*+} and acac⁻) and hydrophilic species ([Co(acac)₂]), the rates of the heterolytic dissociation (eq 3e) might be decreased by lower polar environments in the micellar phase, so that the k_{el}^{m} value becomes small.

The micellar cage effects also affect the efficiency of dissociation of the encounter complex, [BNAH⁺ Co(acac)₃⁻]. As can be seen from significantly high viscosity in the micellar phase,⁵⁴ the mobility of solutes in the micelles decreased considerably as compared with the homogeneous aqueous phase. This restriction might depress the dissociation of the encounter complex (eq 3e) to promote the back electron transfer (eq 3f) within the complex in the micelles because of weak electron-donating ability ($E_{ox} =$ 0.57 V vs SCE)³⁶ of BNAH in a ground state; the encounter complex in the aqueous phase dissociates immediately to BNAH⁺⁺, [Co(acac)₂], and acac⁻ because of their rapid diffusion. Anyhow, the efficiency of the dissociation of the encounter complex is a dominant factor in the promotion of the electron-transfer reaction between photoexcited NADH model compounds and [Co(acac)₃] in the micellar phase.

In this regard, it may be significant that the k_{el}^{m} value was remarkably enhanced by SDS micelles despite a viscosity value comparable to that in the DTAC micellar phase. Since the identical hydrophobic alkyl chain length of SDS and DTAC seems to result in the same extent of hydrophobic interaction with

where superscript (2) refer to two dimensions, the coefficient C is the ratio of the surface area to the volume of a micellar particle, and K_0 is the McDonald function of zero order. The C value was estimated to be 5.2×10^{-7} m⁻² dm³ by using the partial molar volume (v = 0.251-0.256 mol⁻¹ dm³), the aggregation number (AN = 62),^{52,53} and the radius (2 nm) of a micellar particle. Thus, the α value calculated was large under the present reaction conditions, so that $K_0(R\alpha^{1/2})$ was exponentially small ($K_0(x) \sim (\pi/2x)^{1/2}e^{-x}$) under the present reaction conditions.

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NADH model compounds and $[Co(acac)_3]$, the charge of the micellar surface might play an important role in the heterolytic dissociation of the encounter complex. The anionic charge of SDS micelles accelerates the heterolytic dissociation of the encounter complex of $[BNAH^+ Co(acac)_3^-]$ not only through stabilization of the positive charge of $BNAH^{++}$ generated but also through the charge separation of acac⁻ from the micellar surface. Thus, it is concluded that anionic SDS and SDeS promoted the photoreduction of [Co(acac)₃] with BNAH and/or DNAH by concentrating them through the hydrophobic interaction and by lengthening the lifetime of the photoexcited NADH model compounds, while cationic DTAC and HTAB retarded the photoreaction by suppressing the heterolytic dissociation of the encounter complex between BNAH* (or DNAH*) and [Co(acac)₃].

Bimetallic CuPt Particles Supported in Y Zeolite: Structural Characterization by EXAFS

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The structures of bimetallic CuPt particles in freshly reduced and outgassed CuPt/NaY zeolites were characterized by extended X-ray absorption fine structure (EXAFS) at the Cu K-edge and Pt L₃-edge. In order to understand the effect of copper on the coordinative environment of platinum, reduced Cu/NaY and Pt/NaY were also studied. It is found that the structure of CuPt bimetallic particles is dependent on the atomic ratio of Cu and Pt in the zeolites. At room temperature, some of the Cu atoms are oxidized, presumably by reacting with protons on the zeolite surface. By outgassing in helium at 500 °C, additional Cu atoms were leached from the surface of the CuPt particles to expose more Pt atoms on the surface. Thus, an enhancement in the activity of toluene hydrogenation was observed. Due to the leaching of Cu atoms upon outgassing in helium or under vacuum, hydrogen chemisorption is not an appropriate method to estimate the number of surface Pt atoms in bimetallic CuPt particles supported in NaY.

Introduction

Bimetallic catalysts have been widely used in heterogeneous catalysis.^{1,2} One of the major applications is in the catalytic reforming of refinery naphtha. The main reason for their remarkable stability and selectivity compared to monometallic catalysts is due to the altered surface structure and composition. One of the major challenges in bimetallic catalyst research is obtaining particles with homogeneous composition. Most bimetallic catalysts are prepared by impregnation of metal salts into a support followed by activation in hydrogen. It is merely by chance that the two metallic components come together to form bimetallic particles on the support.³ It was found by EXAFS analysis of a number of supported bimetallic catalysts (e.g., Cu-Ru,⁴-Os,⁵-Rh;⁶ Ir-Pt,⁷-Rh;⁸ Rh-Co;^{9,10} Cu-Ni¹¹) that the bulk composition often differed from that of the surface. An in situ EXAFS study by Esteban et al. also indicated that pure Pt and Ru particles as well as PtRu alloy aggregates were formed on alumina.¹² Anisotropy was also observed by transmission electron microscopy coupled with energy dispersive X-ray spectroscopy and electron diffraction to obtain morphological, analytical, and structural data on individual metal clusters in the catalysts. It was found that the composition of copper on ruthenium particles is not uniform in $CuRu/SiO_2$ catalyts prepared from $Cu(NO_3)_2$

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and RuCl₃.¹³ One route to bimetallic catalysts is to use heterometallic molecular clusters as precursors.¹⁴ This provides an opportunity to control the composition of the catalyst particles produced. However, this method is limited because of the availability of bimetallic clusters and possible segregation of the

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