Letter

Micellar-accelerated Electron Transfer from Photoactivated 1-Benzyl-1,4dihydronicotinamide to a Hydrophilic Metal Complex of Potassium Ethylenediaminetetraacetatocobaltate(III)

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Although growing interest in electron transfer reactions of NADH models has recently centered around the reduction of metal complexes by 1,4-dihydronicotinamide derivatives via a multi-step electron transfer (e^{-} , H^{\dagger} , e⁻) [1, 2], the photoaccelerated electron transfer reactions between NADH model and metal complexes have hitherto been the subject of limited investigation. Only three reports dealing with the above subject have appeared in the literature; the photocleavage of organo-thallium(III) and -mercury(II) by 1-benzyl-1,4-dihydronicotinamide [3] and the photoreduction of tris(acetylacetonato)cobalt(III) by 1,4-dihydronicotinamide derivatives [4]. Since it is of significant interest to investigate the micellarpromoted photoreduction of hydrophilic transition metal complexes by photoactivated NADH models in aqueous solution, this paper describes the micellar-accelerated electron transfer from photoexcited 1-benzyl-1,4dihydronicotinamide (BNAH; λ_{max} (ϵ) = 359 nm (7600 mol⁻¹ dm²)) to ethylenediaminetetraacetatocobaltate(III), KCo(edta), with potassium cationic and anionic surfactants of dodecyltrimethylammonium chloride (DTAC) and sodium dodecylsulfate (SDS).

$$\stackrel{H}{\longrightarrow} \stackrel{H}{\longrightarrow} CONH_{2} + 2Co(edta)^{-} \stackrel{h_{v} (>310 \text{ nm})}{\longrightarrow} \stackrel{OONH_{2}}{\bigoplus} + 2Co(edta)^{2-} + H^{+}$$

The homogeneous H_3BO_3 (0.02 mol dm⁻³) buffer solution (containing 4 vol.% MeOH) of BNAH (5.0 × 10⁻⁴ mol dm⁻³), Co(edta)⁻ (1.0 × 10⁻³ mol dm⁻³), and/or the surfactant ((0 - 7.0) × 10⁻² mol dm⁻³) was irradiated at 30 °C (pH 9.0) by Pyrex-filtered light (500 W xenon lamp) with a merry-go-

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round apparatus, and the reaction rate which obeyed a pseudo-first-order rate law up to conversion $\simeq 75\%$ was followed by monitoring the reacted amount of BNAH at 359 nm. The acid-catalyzed decomposition of BNAH into inactive 1-benzyl-6-hydroxy-1,4,5,6-tetrahydronicotinamide was negligible during the present short photoreaction time (within 1.5 h), even in the presence of the anionic SDS micelles, and the reaction between photoexcited $Co(edta)^-$ (λ_{max} (ϵ) = 385 (229) and 538 nm (324 mol⁻¹ dm²)) and BNAH (or photoactivated BNAH) can be neglected in the evaluation of pseudo-firstorder rate constant (k) from the amount of BNAH consumed.



Fig. 1. Concentration effects of DTAC and SDS on the pseudo-first-order rate constant k (cmc = 2.0×10^{-2} (DTAC) and 8.0×10^{-3} mol dm⁻³ (SDS)).

As indicated in Fig. 1, the present photoinduced electron transfer from BNAH to Co(edta)⁻ proceeded more rapidly than the thermal transfer, and was considerably accelerated by the DTAC micelles. The condensation of BNAH (through hydrophobic forces) and the anionic Co(edta)⁻ substrate (through ionic forces) by the cationic DTAC micelles seems to play an important role in the acceleration of the present photoreaction, and the micellar-promoted reaction rate was well reflected in the quantum yield (ϕ_{BNAH} evaluated by the amount of BNAH consumed) of the present reaction (see Table 1).

The reaction mechanism of the present photoreduction may be expressed by the following simplified reaction:

BNAH $\xrightarrow{h\nu}$ BNAH* (photoactivated state) BNAH* $\xrightarrow{k_{ic}}$ BNAH BNAH* $\xrightarrow{k_t}$ BNAH + $h\nu$

TABLE 1

Kinetic parameters

Surfactant (conc.)	$\frac{10^5 k}{(s^{-1})}$	$10^3 \phi_{BNAH}$	$\frac{k_1 \tau}{(\mathrm{mol}^{-1} \mathrm{dm}^3)}$	I' / I ^a
DTAC $(4.0 \times 10^{-2} \text{ mol dm}^{-3})$	19.9	38.5	35.97	1.0
SDS $(1.2 \times 10^{-2} \text{ mol dm}^{-3})$	5.42	10.2	10.03	2.3
none	4.62	7.58	7.86	1.8

^a Ratio of fluorescence intensity.

BNAH* + Co(edta)⁻ $\xrightarrow{k_1}$ BNAH[‡] + Co(edta)²⁻ BNAH[‡] $\xrightarrow{k_2}$ BNA^{*} + H[‡] BNA^{*} + Co(edta)⁻ $\xrightarrow{k_3}$ BNA^{*} + Co(edta)²⁻

where the photoactivated BNAH^{*} takes the singlet state, because the reaction rate observed in an oxygen atmosphere was not different from that in a nitrogen atmosphere, and where the two-electron transfer from BNAH^{*} to $Co(edta)^-$ via a multi-step electron transfer (e^- , H⁺, e^-) process was supported by the fact that more than 50% of the initial amount of $Co(edta)^-$ was reduced when $[Co(edta)^-]/[BNAH] = 2$. The steady-state assumption of the concentration of BNAH^{*}, BNAH⁺ and BNA^{*} resulted in the following Stern-Volmer relation:

$$\frac{1}{\phi_{\text{BNAH}}} = \frac{k_{\text{ic}} + k_{\text{f}}}{k_{1}} \frac{1}{[\text{Co(edta)}^{-}]} + 1 = \frac{1}{k_{1}\tau} \frac{1}{[\text{Co(edta)}^{-}]} + 1$$

 τ = lifetime of BNAH*

This Stern-Volmer relationship was well established in the present reactions, as is indicated in Fig. 2; the order of $k_1\tau \pmod{10}$ dm³) values, $k_1\tau = 35.97$ (DTAC) $\gg 10.03$ (SDS) > 7.86 (none), was in accord with that of the reaction rate (see Table 1). However, the fluorescence intensity ratios (I'/I), I'/I = 2.3 (DTAC), 1.8 (SDS) and 1.0 (none), suggest that the lifetime (τ) of BNAH^{*} is lengthened by both the DTAC and SDS micelles to approximately the same extent, probably through the depression of vibrational relaxation of BNAH^{*} incorporated into the micelles. Therefore, the remarkable difference in the $k_1\tau$ values obtained with DTAC and SDS is caused by the difference in the k_1 values of the reactions with the cationic and anionic micelles; that is, the reaction of BNAH^{*} with Co(edta)⁻ was facilitated by the cationic DTAC micelles capable of condensing Co(edta)⁻ but retarded by the anionic SDS micelles repelling Co(edta)⁻.



Fig. 2. Stern-Volmer plots of $1/\phi_{BNAH}$ vs $1/[Co(edta)^{-}]$.

The photoaccelerated electron transfer from BNAH to $Co(edta)^-$ was thus realized through the concentration of both the species and by increasing the lifetime of BNAH^{*}. However, a more detailed investigation of the kinetics of the present reaction is now in progress.

References

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