Micellar-accelerated Photoreduction of Tris(acetylacetonato)cobalt(III) by 1,4-Dihydronicotinamide Derivatives

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The photo-accelerated reduction of tris(acetylacetonato)cobalt(III) by 1,4-dihydronicotinamide derivatives (BNAH and DNAH) was considerably promoted by anionic micelles of sodium dodecylsulphate through the condensation (or incorporation) of the reductant and the substrate and through the stabilization of cationic species (such as $BNAH^{\cdot +}$ and BNA^+), generated during the reaction.

The biomimetic chemistry of biologically important co-enzymes of NADH has recently received considerable attention, and one investigation in this field has centred around the reduction of metal complexes by 1,4-dihydronicotinamide derivatives as NADH models.[1] Although the photoreduction of organo-thallium(III) and -mercury(II) with *N*-benzyl-1,4-dihydronicotinamide has recently been reported,[2] there are no reports dealing with the micellar-promoted photoreduction of transition-metal complexes by efficient NADH models with a particular view to the micellar effects on the reaction between the photo-excited NADH models and the substrate. In this paper, we describe a micellar-accelerated photoreduction of tris(acetylacetonato)cobalt(III) (**2**) by 1,4-dihydronicotinamide derivatives (**1a,b**) with the ionic or nonionic surfactants sodium dodecylsulphate (**3a**), dodecyltrimethylammonium chloride (**3b**), and the tricosa(oxyethylene) compound (**3c**).

Table 1. Surfactant effects on the photoreduction of (**2**) by (**1a**).[a]

Surfactant (conc.)	Maximum rate enhancement	% Decomp.[b]	$10^3 \Phi$
None	1.0	3.5	6.47
(**3a**) (30 mM)	2.1	7.0	20.9
	(2.3[c])		(25.8[c])
(**3b**) (10 mM)	1.2	3.2	6.36
(**3a**) (2 mM)	1.4	6.8	6.32

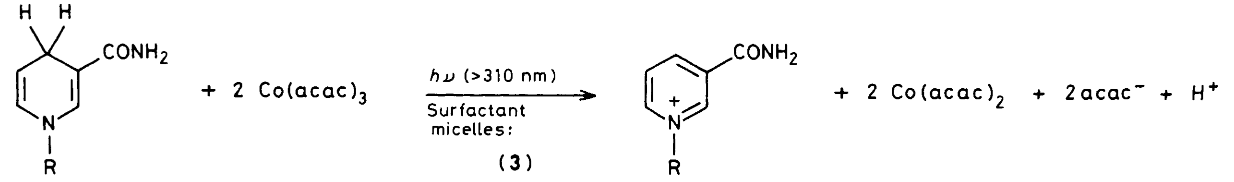
[a] 4% (v/v) MeOH–0.02 M borate buffer under N_2 at 30 °C (pH 9.0); [(**1a**)] = 5.0×10^{-4}, [(**2**)] = 5.0×10^{-4} M. [b] The amount of decomposition of (**1a**) during the reaction for 1 h. [c] Photoreduction of (**2**) by (**1b**) under identical conditions.

The homogeneous 4% (v/v) $MeOH–H_2O$ solution (5 ml) of 0.02 M H_3BO_3 buffer (pH 9.0), containing (**1a,b**) (5.0×10^{-4} M), (**2**) (5.0×10^{-4} M), and (**3a—c**) (0—5.0×10^{-2} M), was irradiated (without stirring, in a nitrogen atmosphere at 30 °C) with Pyrex-filtered light (500 W Xenone lamp) in a 10 ml test tube with a merry-go-round apparatus, and the amount of photoreduced (**2**) was determined spectrophotometrically in chloroform at 520 nm and 595 nm after separation of (**2**) and $Co(acac)_2$ from the reaction mixtures with toluene. The conversion of (**2**) into $Co(acac)_2$ in the reaction was linear with time up to 50% conversion, and the amount of (**2**) reduced by (**1a**) ($\lambda_{max.}$ = 357 nm) in the photo-reaction for 1 h was considerably larger than that in the thermal reaction for 24 h (Figure 1). Figure 1 also indicates that this photoreduction of (**2**) was apparently accelerated by the surfactant micelles. Since the photoreduced amount of (**2**) for the photo-irradiation time of 1 h in the absence of (**1a,b**) was negligibly small within experimental error, the present photoreduction of (**2**) must proceed *via* electron transfer from the photo-excited (**1a,b**) to (**2**), and the photoreduction rate was affected by changes in the surfactants and the NADH models. The extent of the rate enhancement by the micelles, which followed the order of anionic (**3a**) > neutral (**3c**) > cationic (**3b**), was not related to the acid-catalysed decomposition of (**1a,b**) into 1-benzyl- (or dodecyl-)6-hydroxy-1,4,5,6-tetrahydronicotinamide but was directly reflected in the quantum yield (Φ) of the reaction (Table 1). The rate enhancement through the condensation (or incorporation) of hydrophobic (**1a,b**) and (**2**) by the micelles contributed to the increase in the quantum yield, and the importance of the concentration of the NADH model and/or (**2**) by the micelles for the acceleration of the present reaction was deduced from

Table 2. Kinetic parameters for the photoreduction of (**2**) by (**1a**).

Medium	I'/I	$k_{r1}\tau$/mol^{-1} dm^3	τ/ns[a]	$10^{10}k_{r1}$/ mol^{-1} dm^3 s^{-1}
MeOH	1.0	—	0.93[b]	—
4% (v/v) $MeOH–H_2O$ in the absence of (**3a**)	0.44	5.75	0.41	1.40
4% (v/v) $MeOH–H_2O$ in the presence of (**3a**)	0.75	14.6	0.71	2.08

[a] Obtained from the I'/I value. [b] From ref. 3.



(**1**) (**2**) (**3**)

a; R = $PhCH_2$ (BNAH)
b; R = $C_{12}H_{25}$ (DNAH)

a; $C_{12}H_{25}OSO_3Na$
b; $C_{12}H_{25}NMe_3Cl$
c; $C_{12}H_{25}[OCH_2CH_2]_{23}OH$

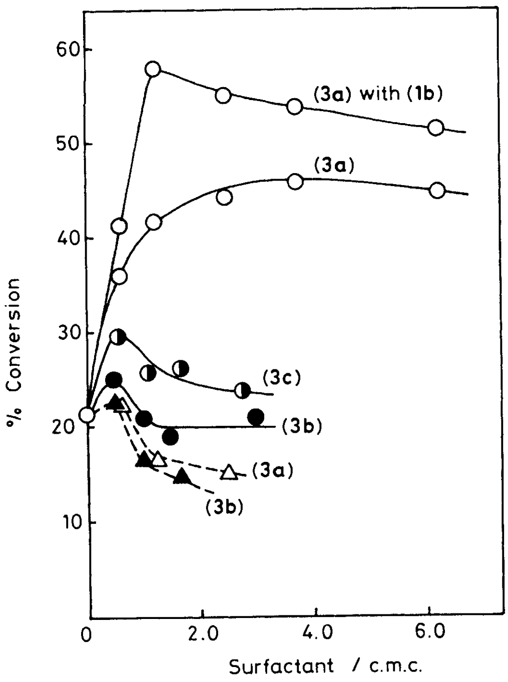


Figure 1. Micellar-promoted photoreduction of (**2**) with (**1a**). (Solid line: photoreduction for 1 h. Dotted line: thermal reduction for 24 h). [(**1a**,**b**)] = [(**2**)] = 5.0 × 10^{-4} M; critical micelle concentration (c.m.c.): (**3a**) = 8.0 × 10^{-3}, (**3b**) = 2.0 × 10^{-2}, (**3c**) = 3.6 × 10^{-3} M.

the remarkable rate enhancement in the micellar-promoted photoreduction of (**2**) by (**1b**) ($\lambda_{max.}$ = 359 nm) possessing a long hydrophobic chain ($R = C_{12}H_{25}$).

With regard to the high efficiency of the anionic surfactant (**3a**) for increasing the photoreduction rate, the contribution of the anionic nature of this micelle to the reaction between the photo-excited (**1a**,**b**) and (**2**) should be taken into consideration along with the condensation (or incorporation) effect of (**3a**). In the simplified reaction steps (1a—f) of the photoreduction of (**2**) by (**1a**) (BNAH), the stationary-state assumption of the concentrations of BNAH*, BNAH$^{\cdot+}$, and BNA$^{\cdot}$ resulted in the Stern–Volmer equation of 1/Φ *vs.* 1/[(**2**)], equation (2), where τ = lifetime of BNAH*. Reaction (1d) is the rate-determining step in the multi-step electron transfer (e^-, H^+, e^-) reactions (1d—f), and the two-electron transfer from BNAH* to (**2**) was supported by the fact that more than 50% of the initial amount of (**2**) was reduced when [(**2**)]/[(**1a**)] = 2.

$$\text{BNAH} \xrightarrow{h\nu} \text{BNAH}^* \quad (1a)$$

$$\text{BNAH}^* \xrightarrow{k_{ic}} \text{BNAH} \quad (1b)$$

$$\text{BNAH}^* \xrightarrow{k_f} \text{BNAH} + h\nu \quad (1c)$$

$$\text{BNAH}^* + \text{Co(acac)}_3 \xrightarrow{k_{r1}} \text{BNAH}^{\cdot+} + \text{Co(acac)}_2 + \text{acac}^- \quad (1d)$$

$$\text{BNAH}^{\cdot+} \xrightarrow{k_{r2}} \text{BNA}^{\cdot} + \text{H}^+ \quad (1e)$$

$$\text{BNA}^{\cdot} + \text{Co(acac)}_3 \xrightarrow{k_{r3}} \text{BNA}^+ + \text{Co(acac)}_2 + \text{acac}^- \quad (1f)$$

$$1/\Phi = \frac{k_{ic} + k_f}{k_{r1}} \frac{1}{[\text{Co(acac)}_3]} + \frac{1}{2} = \frac{1}{2k_{r1}\tau[\text{Co(acac)}_3]} + \frac{1}{2} \quad (2)$$

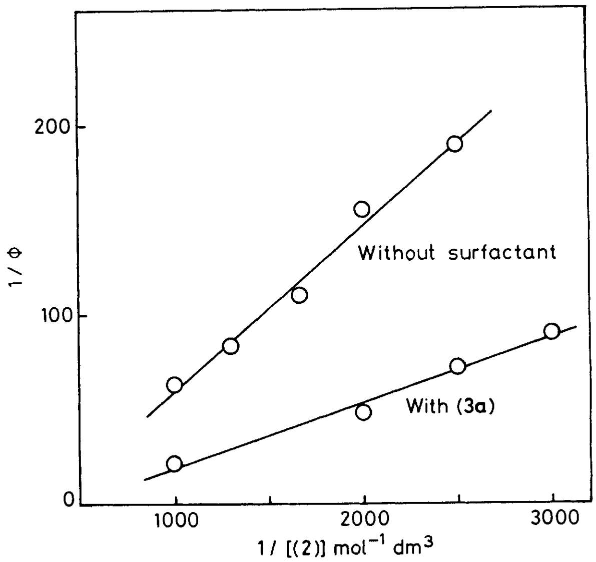


Figure 2. Stern–Volmer plots for the photoreduction of (**2**) by (**1a**). [(**1a**)] = 5.0 × 10^{-4}, [(**2**)] = 3.3 × 10^{-4}—1.0 × 10^{-3}, and [(**3a**)] = 3.0 × 10^{-2} M.

Although the straight line Stern–Volmer plots did not pass through the (0, 1/2) point (Figure 2), probably because of the association or aggregation of the hydrophobic substrate, the $k_{r1}\tau$ value (14.6 mol^{-1} dm^3) obtained in the presence of (**3a**) was considerably larger than that (5.75 mol^{-1} dm^3) in the absence of (**3a**), and this suggests that the reaction between BNAH* and (**2**) was facilitated by the anionic surfactant (**3a**). The k_{r1} and τ values estimated from the ratio of fluorescence intensity (I'/I) were appreciably larger in the presence of (**3a**) than those in the absence of (**3a**) (Table 2). Hence the anionic micelles of (**3a**) encourage the reaction of BNAH* and (**2**) partly through the stabilization of the cationic species, BNAH$^{\cdot+}$ and BNA$^+$, and partly through lengthening the lifetime of BNAH* *via* the depression of vibrational relaxation of BNAH* incorporated by the micelles.

Finally, it should be stressed that the reaction rate of the photoreduction of (**2**) by (**1a**,**b**) with or without (**3a**) was independent of the pH change of the reaction system in the range of pH 8.5—10.0. The deprotonation step (1e), which is promoted in basic conditions in the thermal reaction probably through the interaction between a hydroxide anion and an NADH model,[1c] does not participate in the rate-determining step, probably because the electron excitation from π (HOMO) to π* (LUMO) orbitals on the heterocyclic ring weakens the C–H bond strength of the dihydro-part of the NADH models (**1a**,**b**).

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