## Letter

## The Micellar-promoted Photoreduction of Cobalt(III) Tris-acetylacetonate by 1-Benzyl-1,4-dihydronicotinamide

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Although the reduction of metal complexes by NADH models via a multi-step electron transfer ( $e^-$ ,  $H^+$ ,  $e^-$ ) has recently been documented in several papers [1 - 4], there is no report dealing with micellar-promoted photoinduced electron transfer reactions between NADH models and transition metal complexes. In this paper, we describe a micellar-accelerated photo-irradiated reduction of cobalt(III) tris-acetylacetonate (Co(acac)<sub>3</sub>) by 1-benzyl-1,4-dihydronicotinamide (BNAH) with ionic or neutral surfactants of sodium dodecylsulfate (SDS), dodecyltrimethylammonium chloride (DTAC), and polyoxyethylene(23) dodecyl ether (Brij 35).

$$\begin{array}{c} H \\ H \\ H \\ H \\ C H_2 \end{array} + 2Co(acac)_3 \xrightarrow{h\nu > 310 \text{ nm}} BNA^+ + 2Co(acac)_2 + 2acac^- + H^+ \\ + 2acac^- + H^+ \end{array}$$

(BNAH)

When homogeneous 10% (v/v) MeOH-H<sub>2</sub>O solutions (5 ml) of  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup> Co(acac)<sub>3</sub>, (2.5 - 5.0) × 10<sup>-3</sup> mol dm<sup>-3</sup> BNAH, and/or (2.0 - 100) × 10<sup>-3</sup> mol dm<sup>-3</sup> surfactant were irradiated (without stirring in a nitrogen atmosphere at room temperature) by Pyrex-filtered light (500 W xenon lamp) in a 10 ml test tube with a merry-go-round apparatus, the amount of unreacted Co(acac)<sub>3</sub> and/or Co(acac)<sub>2</sub> produced, which was separated from the reaction mixtures with toluene, was determined spectrophotometrically in chloroform at 520 and 595 nm.

The micellar-promoted reduction of  $Co(acac)_3$  by BNAH was first recognized in both the thermal and photoirradiated reaction systems (Fig. 1).

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Fig. 1. Micellar-promoted reduction of Co(acac)<sub>3</sub> by BNAH; (a) thermal reaction for 1 day and (b) photoirradiated reaction for 1 h; [BNAH] = [SDS] =  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>; cmc: SDS =  $8 \times 10^{-3}$  mol dm<sup>-3</sup>, DTAC =  $2 \times 10^{-2}$  mol dm<sup>-3</sup>, and Brij  $35 = 3.6 \times 10^{-3}$  mol dm<sup>-3</sup>.

Probably, the incorporation of BNAH into the ionic or neutral micelles through the hydrophobic benzyl group and the condensation of neutral  $Co(acac)_3$  possessing hydrophobicity on the micellar surface accelerated the reaction between BNAH and  $Co(acac)_3$ , and the high concentration of the surfactant with respect to that of BNAH diminished the amount of incorporated BNAH per micelle unit so as to decrease the reduction rate.

The reaction between BNAH and Co(acac)<sub>3</sub> occurred considerably faster in the photoreduction system than in the thermal one, and the rate enhancement by the micelles was the most remarkable in the case of anionic SDS micelles. The rate increase by photoirradiation is directly related to the photoactivation of BNAH ( $\lambda_{max} = 359$  nm), and the anionic SDS micelles facilitate the electron transfer from BNAH to Co(acac)<sub>3</sub> through the stabilization of BNA<sup>+</sup> formed on the anionic micellar surface. However, the SDS micelles capable of condensing protons result in the acid-catalyzed decomposition of BNAH into inactive 1-benzyl-6-hydroxy-1,4,5,6-tetrahydronicotinamide ( $\lambda_{max} = 292$  nm) [5], as is indicated in Fig. 2. The decomposition rate constants obtained from Fig. 2 were 7.76 × 10<sup>-6</sup> s<sup>-1</sup> and 2.20 × 10<sup>-5</sup> s<sup>-1</sup> in the absence and presence of SDS, respectively\*. In this sense, the

<sup>\*</sup>The rate constants were calculated from linear plots of  $\ln(A\delta^{55}/A^{355})$  (where  $A\delta^{55}$  = initial absorbance of BNAH at 355 nm) vs. time (correlation coefficients >0.995).



Fig. 2. Decomposition of BNAH in the photoirradiated system (excluding Co(acac)<sub>3</sub>); (a) in the absence of SDS ([BNAH]<sub>0</sub> =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>); (b) in the presence of SDS ([BNAH]<sub>0</sub> =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> and [SDS] =  $6.0 \times 10^{-4}$  mol dm<sup>-3</sup>); reaction time: curve 1, 0 h; curve 2, 1 h; curve 3, 2 h; curve 4, 3 h.

anionic SDS surfactant cannot show efficient micellar effects on the thermal reduction of  $Co(acac)_3$  by BNAH over long periods of time (See Fig. 1).

At any rate, the electron transfer from the photoactivated BNAH to  $Co(acac)_3$  is accelerated by the anionic micelles, and the nitrogen nonbonding orbital in the heterocyclic ring of BNAH might play an important role in the initial rate-determining electron-transfer step. In regard to the participation of the deprotonation of BNAH in the rate-determining step, the increase of basicity in the pH range 8.50 - 9.96 did not change the reaction rate within experimental error, even though the thermal reduction of hexacyanoferrate(III) by 1-propyl-1,4-dihydronicotinamide was accelerated by the basicity increase from pH 10.70 to pH 11.0 [3]. Therefore, the deprotonation of BNAH, which is promoted in basic conditions through the interaction between a hydroxide anion and BNAH, might not take part directly in the rate-limiting step in the present photoactivated system.

The final electron transfer leads easily to the transfer of a proton, and two molecules of  $Co(acac)_3$  can be reduced by one molecule of BNAH via

the two electron-transfer steps. In fact, more than 50% of the initial amount of Co(acac)<sub>3</sub> was reduced when the ratio  $[Co(acac)_3]/[BNAH] = 2$ . For example, 76% of the initial quantity  $(5.0 \times 10^{-3} \text{ mol dm}^{-3})$  of Co(acac)<sub>3</sub> was reduced to Co(acac)<sub>2</sub> by  $2.5 \times 10^{-3} \text{ mol dm}^{-3}$  BNAH for the irradiation time of 6 h.

Finally, it should be stressed that the contribution of photoexcited  $Co(acac)_3$  and/or  $Co(acac)_2$  to the acceleration of the present reaction was negligible, because the photoreduced amount of  $Co(acac)_3$  during the photoirradiation time of 1 h was less than 1% in the absence of BNAH.

## References

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