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Methylviologen-Accelerated Photoreduction of Tris(acetylacetonato)cobalt(III) with 1-Benzyl-1,4-dihydronicotinamide

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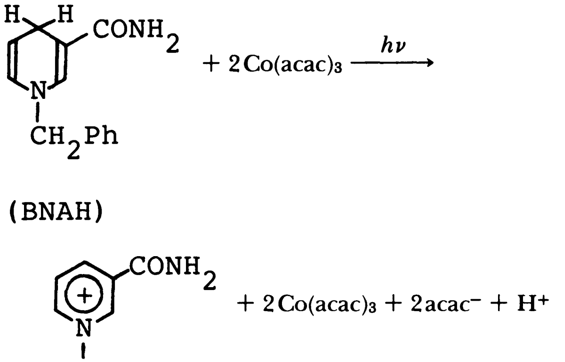
(Received May 13, 1988)

The photoreduction of tris(acetylacetonato)cobalt(III) ($Co(acac)_3$) by 1-benzyl-1,4-dihydronicotinamide (BNAH) was examined with or without methylviologen in the wavelength range of 340—410 nm. The reaction rate of electron transfer from BNAH to $Co(acac)_3$ was considerably enhanced by methylviologen, especially, in lower polar environments; The weaker the hydrophobic interaction between BNAH and the substrate become, the more effectively methylviologen acts as an electron mediator for the above photoreaction. The reaction mechanism is also discussed with particular reference to the participation of the electron mediator in the elementary steps of the present photoinduced reaction.

The photochemistry of organic or inorganic compounds including biological ones is of general interest because of their importance in relation to solar energy conversion, new methods of organic synthesis, biomimetic photoinduced reactions, etc.[1)] Recently, one of the biologically interesting compounds related to coenzyme NAD(P)H, 1,4-dihydropyridines (absorption maxima at 300—400 nm) have received considerable attention, since their reactivities as a reductant are enhanced remarkably by photoirradiation.[2—6)]

In our previous work,[3)] the photoactivated 1-benzyl-1,4-dihydronicotinamide (BNAH) was found to be very reactive for the reduction of cobalt(III) complexes such as tris(acetylacetonato)cobalt(III) ($Co(acac)_3$), especially in the presence of surfactant micelles which accelerate the reaction through the lengthening of the lifetime of the photoexcited BNAH and through the concentrating of BNAH and the substrates on the micellar surface.



(1)

BNAH has an absorption maxima of $\pi \rightarrow \pi^*$ excitation on the dihydropyridine ring at 360 nm and an oxidation potential of about −2 V (vs. SCE)[4,7)] in its photoexcitation state.

The electron transfer from photoactivated BNAH (BNAH*) to the substrate in the reaction expressed by Eq. 1 might be accelerated by using a good electron mediator such as methylviologen (MV^{2+}) (reduction potential of −0.69 V vs. SCE[6)]). This can effectively trap the activated electron from the short-living BNAH* (0.93 ns in methanol).[5,6)] The cationic radical of the methylviologen ($MV^{\dagger}$) formed by the reaction of MV^{2+} and BNAH* might donate the electron to the substrate directly or indirectly.[8)]

This report describes how methylviologen behaves as an electron mediator in the photoinduced reduction of $Co(acac)_3$ by BNAH, based on a kinetic analysis of the reaction.

Experimental

Materials. 1-Benzyl-1,4-dihydronicotinamide (BNAH) was prepared according to the previous method.[9)] The commercially available $Co(acac)_3$ was purified by recrystallization from petroleum ether-benzene. Satisfactory elemental analyses were obtained for both BNAH and $Co(acac)_3$. Methylviologen (MV^{2+}) was also commercially available as its chloride and was used without further purification. The solvents methanol and water were distilled and deoxygenated before use by purging with gaseous nitrogen.

Reaction Procedure. The homogeneous 20—90% (v/v) methanol-0.02 mol dm^{-3} borate buffer (pH 9.0) solution, containing BNAH (1.25×10^{-3} mol dm^{-3}), $Co(acac)_3$ (1.25×10^{-3} mol dm^{-3}), and MV^{2+} ($0-3.13\times10^{-2}$ mol dm^{-3}), was irradiated in a Pyrex cell using a 400 W mercury lamp in the wavelength range $410>\lambda>340$ nm with Toshiba glass filter UV-35 and UV-D35. The reaction temperature was kept at 30 ± 0.5 °C by stirring with a thermostated cell holder. The reaction rates of the photoreduction of $Co(acac)_3$ with BNAH were followed by the spectrophotometric determination of the decreased amount of $Co(acac)_3$ at $\lambda_{max}=595$ nm and that of BNAH at $\lambda_{max}=360$ nm using a JASCO UVIDEC-430A spectrophotometer. The light intensities were determined by Reinecke's salt actinometry.[10)] The fluorescence spectrum of BNAH was measured by means of the JASCO FP-550A fluorescence spectrophotometer. The lifetime (τ) of photoexcited BNAH in the present reaction media was estimated from $\tau=0.93$ ns of BNAH* in methanol[5)] by measuring the fluorescence quantum yield relative to that obtained in methanol. Reduction potentials of MV^{2+} and $Co(acac)_3$ were determined by the cyclic voltammetry measurements which were performed on a Hokuto Denko Model HA-301 potentiostat/galvanostat at 298—313 K in 20—90% (v/v) methanol-borate buffer solution, using a standard calomel reference electrode (SCE).

Results and Discussion

When the reaction of BNAH and Co(acac)$_3$ was carried out in the 20—90% (v/v) methanol-0.02 mol dm^{-3} borate buffer solution (pH 9.0), in a nitrogen atmosphere at 30 °C, the photoirradiation of the reaction mixtures immediately caused the decrease in the absorbance of Co(acac)$_3$ at 595 nm, while such an absorption change of Co(acac)$_3$ was not observed during the thermal reaction in the dark for 6 h. Such an absorption decrease at 595 nm in the present photoreduction of Co(acac)$_3$ by BNAH was considerably accelerated by the presence of MV^{2+} (Fig. 2). All the reactions in Fig. 1 obeyed a pseudo-first-order rate law. The pseudo-first-order rate constants (k_{obs}) increased with increasing the concentration of MV^{2+}. In the case of the molar ratio of [MV^{2+}]/[BNAH]=25, the rate constant (k_{obs}) increased in value tenfold as compared with that in the absence of MV^{2+} (Fig. 3). The photoirradiation of the methanol-borate buffer solution containg BNAH and MV^{2+} caused electron transfer from the former to the latter with the formation of new absorption maxima of a reduced MV^{2+} (viz., MV$^{+\cdot}$) at 400 nm and 602 nm. These two peaks immediately disappeared by exposure to O$_2$ through the reaction of MV$^{+\cdot}$ and O$_2$; Such a MV$^{+\cdot}$ formation is also recognized in the photoreaction of NADH and MV^{2+}.[5] Therefore, the methylviologen cation radical, MV$^{+\cdot}$, formed by the photoirradiation of the reaction mixtures present (BNAH, MV^{2+}, and Co(acac)$_3$) participated in the reduction of Co(acac)$_3$.

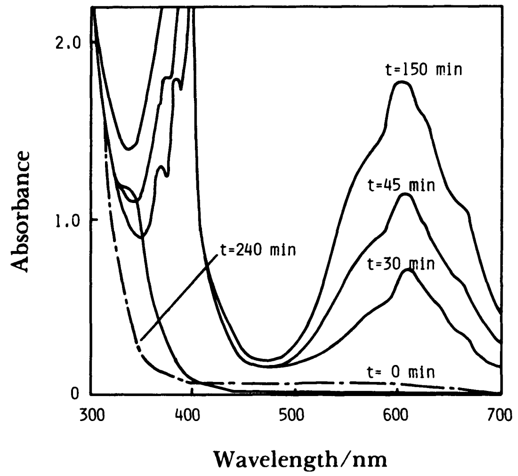


Fig. 1. Absorption spectral change during photoirradiation of BNAH and MV^{2+}. Broken line: O$_2$ bubling after t=240 min. [BNAH]=1.25×10^{-3} mol dm^{-3}, and [MV^{2+}]=1.25×10^{-3} mol dm^{-3} at 30 °C in 90% (v/v) methanol-borate buffer (pH 9.0) in a nitrogen atmosphere.

The quantum yield (Φ_{BNAH}) was evaluated on the basis of the amount of BNAH consumed by Co(acac)$_3$ or MV^{2+}. The Φ_{BNAH} value obtained in the present electron transfer reaction with MV^{2+} was characterized as the sum of the Φ_{BNAH} values evaluated in the reaction between BNAH* and MV^{2+} and in the reaction between BNAH* and Co(acac)$_3$. For instance, the presence of MV^{2+} in amounts equimolar with BNAH resulted in Φ_{BNAH}=7.31×10^{-3}, which was equal to the sum of the quantum yield for the reduction MV^{2+} by BNAH (Φ_{BNAH}=3.01×10^{-3}) and for the reduction of Co(acac)$_3$ by BNAH without MV^{2+} (Φ_{BNAH}=4.13×10^{-3}). Therefore, it is obvious that the photoinduced reduction of Co(acac)$_3$ by BNAH with MV^{2+} proceeds through the direct electron transfer from BNAH* to Co(acac)$_3$ and through the electron transfer from MV$^{+\cdot}$

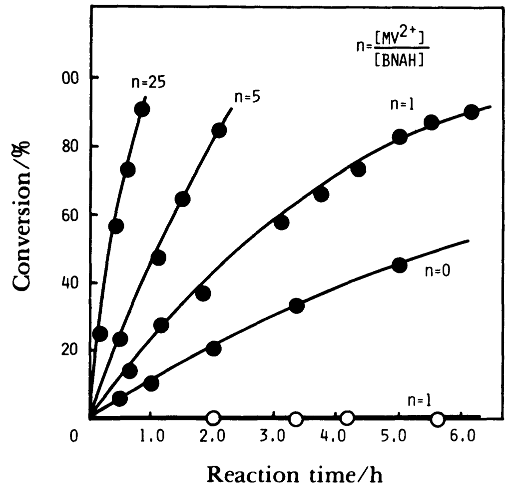


Fig. 2. Reduction of Co(acac)$_3$ with BNAH. Filled circle: Photoreduction, Empty circle: Thermal reduction. n=[MV^{2+}]/[BNAH]. [BNAH]=1.25×10^{-3} mol dm^{-3}, [Co(acac)$_3$]=1.25×10^{-3} mol dm^{-3}, at 30 °C in 90% (v/v) methanol-borate buffer (pH 9.0) in a nitrogen atmosphere.

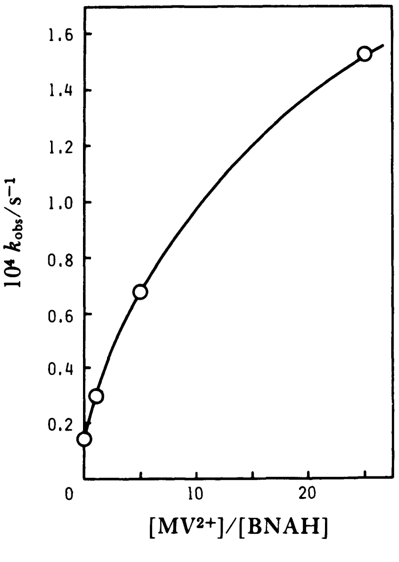


Fig. 3. The concentration effects of MV^{2+} on the pseudo-first-order rate constants in the photoreduction of Co(acac)$_3$ with BNAH. Reaction conditions are the same as Fig. 2.

(formed by the reaction of BNAH* and MV^{2+}) to Co(acac)$_3$. In this sense, the inactivation of BNAH* without the direct electron transfer to Co(acac)$_3$ is suppressed by the efficient electron mediator action of MV^{2+}.

In regard to the reaction mechanism of the present photoreduction of Co(acac)$_3$ by BNAH with MV^{2+}, the following multi-step electron transfer (1e$^-$, H$^+$, 1e$^-$) mechanism (see Scheme) can be suggested as the most

$$\mathrm{BNAH} \xrightarrow{h\nu} \mathrm{BNAH}^* \qquad (2a)$$

$$\mathrm{BNAH}^* \xrightarrow{k_{1c}} \mathrm{BNAH} \qquad (2b)$$

$$\mathrm{BNAH}^* \xrightarrow{k_f} \mathrm{BNAH} + h\nu \qquad (2c)$$

$$\mathrm{BNAH}^* + \mathrm{MV}^{2+} \xrightarrow{k_1} \mathrm{BNAH}^{+\cdot} + \mathrm{MV}^{+\cdot} \qquad (2d)$$

$$\mathrm{BNAH}^* + \mathrm{Co(acac)_3} \xrightarrow{k_1'} \mathrm{BNAH}^{+\cdot} + \mathrm{Co(acac)_2} + \mathrm{acac}^- \qquad (2e)$$

$$\mathrm{BNAH}^{+\cdot} \xrightarrow{k_2} \mathrm{BNA}\cdot + \mathrm{H}^+ \qquad (2f)$$

$$\mathrm{BNA}\cdot + \mathrm{MV}^{2+} \xrightarrow{k_3} \mathrm{BNA}^+ + \mathrm{MV}^{+\cdot} \qquad (2g)$$

$$\mathrm{BNA}\cdot + \mathrm{Co(acac)_3} \xrightarrow{k_3'} \mathrm{BNA}^+ + \mathrm{Co(acac)_2} + \mathrm{acac}^- \qquad (2h)$$

$$\mathrm{MV}^{+\cdot} + \mathrm{Co(acac)_3} \xrightarrow{k_4} \mathrm{MV}^{2+} + \mathrm{Co(acac)_2} + \mathrm{acac}^- \qquad (2i)$$

plausible mechanism.[6,11] In this mechanism, BNAH is activated to its singlet excited state, BNAH*, by photoirradiation (Reaction 2a), and the BNAH* once formed turns into a cationic radical (BNAH$^{+\cdot}$) by releasing one electron toward MV^{2+} or Co(acac)$_3$ via Reactions 2d, e, otherwise it is deactivated via Reactions 2b, c. A proton-releasing Reaction 2f is followed by the second electron-transfer step of the reaction between BNA· and the electron acceptor (Co(acac)$_3$ or MV^{2+}), as shown in Reaction 2g or 2h. The cationic radical (MV$^{+\cdot}$) formed by Reaction 2d and 2g donate the electron to Co(acac)$_3$ directly (Reaction 2i). These proton elimination and electron transfers might proceed very quickly because the pK_a value of BNAH$^{+\cdot}$ was 3.6 and the oxidation and reduction potentials (vs. SCE) of BNA·, MV^{2+}, and Co(acac)$_3$ were estimated to be −1.08, −0.47, and about −0.3 V respectively.[12,13] In practice, the accumulation of MV$^{+\cdot}$ ($\varepsilon_{max}\cong$12000 mol^{-1} dm^3 cm^{-1} at 602 nm)[6] was not observed spectrophotometrically in the present photoreaction with MV^{2+}. It should be stressed that the amount of BNAH consumed by the thermal or photoinduced decomposition is negligibly small in comparison with that of BNAH reacted for the reduction of Co(acac)$_3$ and MV^{2+} in the present conditions (pH 9.0 at 30 °C), although 1,4-dihydropyridines such as BNAH undergo acid-catalyzed decomposition.[14]

From the reaction scheme (2a—i) the following Stern-Volmer equation (Eq. 3) was derived by a stationary state assumption of the concentration of BNAH*, BNAH$^{+\cdot}$, BNA·, and MV$^{+\cdot}$:

$$\frac{1}{\dfrac{1}{\Phi_{\mathrm{BNAH}}}-1} = \tau(k_1\mathrm{MV}^{2+} + k_1'\mathrm{Co(acac)_3}) \qquad (3)$$

where Φ_{BNAH}=quantum yield evaluated from the BNAH consumption and τ=lifetime of BNAH* in the absence of Co(acac)$_3$ and MV^{2+}. The Stern-Volmer equation (Eq. 3) can be rewritten as Eq. 4 or 5 for the present reaction without Co(acac)$_3$ and MV^{2+}, respectively.

$$\frac{1}{\Phi_{\mathrm{BNAH}}} = \frac{1}{k_1\tau}\,\frac{1}{[\mathrm{MV}^{2+}]} + 1 \qquad (4)$$

$$\frac{1}{\Phi_{\mathrm{BNAH}}} = \frac{1}{k_1'\tau}\,\frac{1}{[\mathrm{Co(acac)_3}]} + 1 \qquad (5)$$

As shown in Fig. 4, the linear relationship between $1/(1/\Phi_{\mathrm{BNAH}}-1)$ and [Co(acac)$_3$] was realized by the straight line of plots of $1/(1/\Phi_{\mathrm{BNAH}}-1)$ vs. [Co(acac)$_3$] for the photoreduction of Co(acac)$_3$ (0.80—3.75×10^{-3} mol dm^{-3}) with BNAH (1.25×10^{-3} mol dm^{-3}) in the presence of MV^{2+} (1.25×10^{-3} mol dm^{-3}); that is, the reaction sequences shown in scheme seems reliable for the present photoreactions. The k_1 and k_1' values in Eq. 3 were respectively estimated to be (2.8±0.2)×10^9 and (3.3±0.2)×10^9 mol^{-1} dm^3 s^{-1} from the above linear relationship by using the reported lifetime (τ=0.93 ns) value of BNAH*.[5] The relationship expressed by Eq. 4 or 5 was also satisfied in the photoreduction of Co(acac)$_3$ with BNAH or of MV^{2+} with BNAH (Fig. 5),

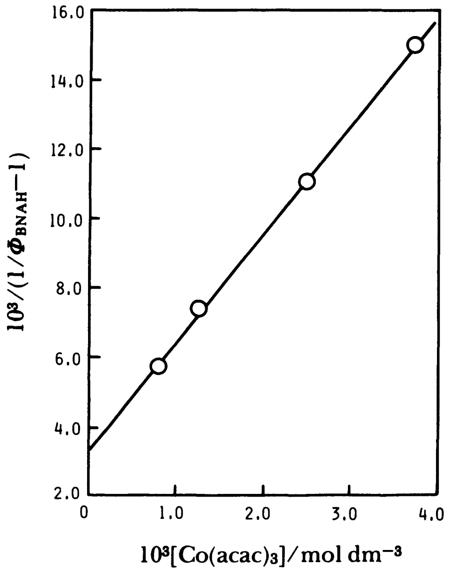


Fig. 4. Stern-Volmer plots for the photoreduction of Co(acac)$_3$ with BNAH in the presence of MV^{2+}. [BNAH]=1.25×10^{-3} mol dm^{-3}, and [MV^{2+}]=1.25×10^{-3} mol dm^{-3} at 30 °C in 90% (v/v) methanol-borate buffer (pH 9.0) in a nitrogen atmosphere.

and the straight lines in Fig. 5 resulted in $(3.0\pm0.2)\times10^9$ and $(3.4\pm0.2)\times10^9$ mol dm^{-3} s^{-1} for the k_1 and k_1' values, respectively. Notably, these two k_1 and k_1' values are approximately the same as those obtained from Eq. 3. This implies that both the electron-transfer reactions between BNAH and MV^{2+} and between BNAH and Co(acac)$_3$ are induced by the photoirradiation without interaction of Co(acac)$_3$ and MV^{2+} themselves.

The above-mentioned reaction mechanism suggests that the present photoreaction proceeds via the following photoactivation of such charge-transfer (CT) complexes as BNAH-MV^{2+}, if one takes account of the fact that 1,4-dihydropyridine compounds form CT-complexes with MV^{2+} in homogeneous or micellar solutions.[5]

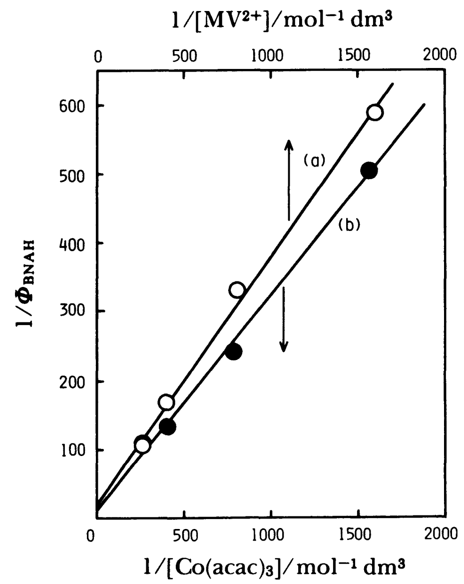


Fig. 5. Stern–Volmer plots for the photoreduction of (a) MV^{2+} and (b) Co(acac)$_3$ with BNAH. [BNAH]= 1.25×10^{-3} mol dm^{-3} at 30 °C in 90% (v/v) methanol-borate buffer (pH 9.0) in a nitrogen atmosphere.

$$\text{BNAH} + \text{MV}^{2+} \longrightarrow \text{BNAH-MV}^{2+} \tag{6}$$

$$\text{BNAH-MV}^{2+} \xrightarrow{h\nu} \text{BNAH-MV}^{2+*} \xrightarrow{\text{Co(acac)}_3} \text{BNAH}^{\ddagger} + \text{Co(acac)}_2 + \text{MV}^{2+} + \text{acac}^- \tag{7}$$

However, such a CT-complex formation between BNAH and MV^{2+} can be negligible in the present reaction, because the present reaction did not generate the CT spectra of BNAH-MV^{2+} and the appreciable deviations of the observed data from the linear lines of the Stern–Volmer relationship by the CT-complex formation.

Since the lifetime (τ) of BNAH* and the reaction rate (k_1 or k_1') of BNAH* consumption by MV^{2+} or Co(acac)$_3$ might be affected by the reaction conditions, it is of interest to note how the present photoreduction of Co(acac)$_3$ by BNAH is dependent on the water content in the methanol-borate buffer solvent. As shown in Table 1, increasing the water content in the range of 10—80 vol.% accelerated Reaction 2e but retarded Reaction 2d. The reduction potentials of MV^{2+} and Co(acac)$_3$ seem not to be affected essentially by the increased water content. In a polar solvent the hydrophobic BNAH* can interact more easily with the hydrophobic Co(acac)$_3$ rather than with the hydrophilic MV^{2+}, so as to augment the k_1' value con-

Table 1. Solvent Effects on the Overall and Electron-Transfer Reaction Rates

Content of water	$10^{-9}\,k_1$[b]	$10^{-9}\,k_1'$[b]	τ[c]	$10^4\,k_{\text{obs}}$[d]
vol.%	mol^{-1} dm^3 s^{-1}	mol^{-1} dm^3 s^{-1}	ns	s^{-1}
10	3.0±0.2	3.4±0.2	0.93±0.04	2.9±0.2
50	1.3±0.1	5.6±0.3	0.85±0.03	2.9±0.2
80	1.4±0.1	12.6±0.9	0.52±0.02	3.2±0.2

a) [BNAH]=1.25×10^{-3} mol dm^{-3}, [Co(acac)$_3$]=1.25×10^{-3} mol dm^{-3}, and [MV^{2+}]=1.25×10^{-3} mol dm^{-3} at 30 °C in 90% (v/v) methanol-borate buffer (pH 9.0) in a nitrogen atmosphere. b) Respective rate constants (k_1 and k_1') for Reactions 2d and 2e. c) Lifetime of BNAH*. d) The pseudo-first-order rate constant for the overall reaction.

Table 2. Temperature Dependence of the k_1 and k_1' Values for the Elementary Electron-Transfer Processes of Reactions 2d and 2e

Temperature	τ[b]	$10^{-9}\,k_1$	$10^{-9}\,k_1'$	$10^3\Phi_{\text{BNAH}}$
K	ns	mol^{-1} dm^3 s^{-1}	mol^{-1} dm^3 s^{-1}	
293	1.16±0.05	2.9±0.2	2.9±0.2	8.9±0.4
298	1.04±0.05	3.1±0.3	3.1±0.3	8.1±0.4
303	0.93±0.04	3.0±0.2	3.4±0.2	7.3±0.4
313	0.71±0.02	3.3±0.2	4.4±0.2	7.0±0.4

a) [BNAH]=1.25×10^{-3} mol dm^{-3}, [Co(acac)$_3$]=1.25×10^{-3} mol dm^{-3}, and [MV^{2+}]=1.25×10^{-3} mol dm^{-3} in 90% (v/v) methanol-borate buffer (pH 9.0) in a nitrogen atmosphere. b) Lifetime of BNAH*.

Table 3. Estimated Values of the Activation Parameters ($\Delta G^{\neq}$, $\Delta H^{\neq}$, $\Delta S^{\neq}$) for the Reaction of BNAH* and MV^{2+} (Reaction 2d) and of BNAH* and $Co(acac)_3$ (Reaction 2e)

Elementary reaction	$\Delta G^{\neq}/\text{kJ mol}^{-1}$ a)	$\Delta H^{\neq}/\text{kJ mol}^{-1}$	$T\Delta S^{\neq}/\text{kJ mol}^{-1}$ a)
2d	19	2.3	−17
2e	19	15	−4.3

a) Calculated at 303 K.

siderably. However, the increased water content in the solvents shortened the lifetime of BNAH* (see Table 1), because BNAH* is inactivated by vibrational relaxation with water. Nevertheless, the increase of the water content in the solvents resulted in the slightly increased value of the pseudo-first-order rate constant (k_{obs}) of the overall reaction. This is probably because of the considerable acceleration of the elementary reaction between BNAH* and $Co(acac)_3$ at the higher water content in the solvents. In this sense, the extent of the contribution of MV^{2+} to the present photoreaction as an electron mediator via Reaction 2d is apparently large at low water contents of the solvents.

The present reaction also changes with the reaction temperature, as is shown in Table 2. The temperature elevation does not benefit the reaction in terms of the shortening of the lifetime of photoexcited BNAH* by increased vibrational relaxation of BNAH* in the solution.[15] However it does promote the electron transfer reactions expressed by Eqs. 2d and 2e , as reflected in the increased rate constants (k_1 and k_1') at higher temperatures. At any rate, the quantum yield (Φ_{BNAH}) given for the overall reaction in the presence of MV^{2+} decreased with increasing temperature, because the enhanced rate of BNAH* consumption by MV^{2+} or $Co(acac)_3$ did not affect the elevation of the Φ_{BNAH} value by overcoming the shortened lifetime of BNAH*. As reflected in the different extent of the rate change by the temperature difference between Reactions 2d and 2e, the magnitude of the contribution of MV^{2+} to the present reaction through the reaction with BNAH* suffers with the reaction temperature: the k_1 value (at 293 K) for the reaction between BNAH* and MV^{2+}, which was almost equal to the k_1' value (at 293 K) for the reaction between BNAH* and $Co(acac)_3$, was enhanced by the temperature elevation to a smaller extent as compared with the k_1' value in Reaction 2e; that is, the participation of MV^{2+} in the present reaction via Reaction 2d becomes less important at a temperature higher than 293 K.

Since linear Eyring relationships are obtainable from both the rate constants (k_1 and k_1') estimated at the temperature range of 293—313 K (Fig. 6), it is of interest to note the thermodynamic parameters (free energy of activation $\Delta G^{\neq}$, enthalpy of activation $\Delta H^{\neq}$, and entropy of activation $\Delta S^{\neq}$) for Reactions 2d and 2e.[16] Although the same $\Delta G^{\neq}$ values were obtained for Reactions 2d and 2e at 303 K, $T\Delta S^{\neq}$ value for Reaction 2e was less than that for Reaction 2e. This suggests that BNAH and $Co(acac)_3$ react each other through a hydrophobic interaction as mentioned above.

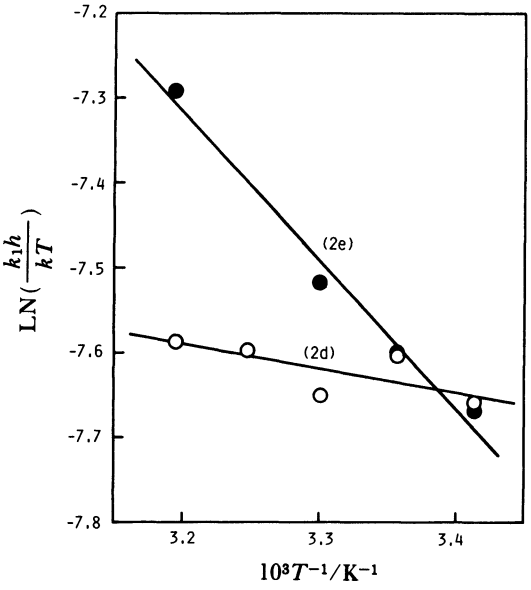


Fig. 6. Eyring relationships for the elementary reactions of 2d and 2e. Empty circle: Reaction 2d. Filled circle: Reaction 2e. $[BNAH]=1.25\times10^{-3}$ mol dm^{-3}, $[MV^{2+}]=1.25\times10^{-3}$ mol dm^{-3}, $[Co(acac)_3]=1.25\times10^{-3}$ mol dm^{-3} in 90% (v/v) methanol-borate buffer (pH 9.0) in a nitrogen atmosphere.

Thus, it is concluded from the present study that the presence of hydrophilic MV^{2+} as an electron mediator in the photoreduction of hydrophobic $Co(acac)_3$ with hydrophobic BNAH accelerates the reaction considerably through the efficient acceptance of the electrons from the photoactivated BNAH*, especially in the lower polarity of the reaction conditions (viz., in the smaller content of water in the solvents in the present reaction) and, of course, through the smooth electron transfer from the electron mediator itself to $Co(acac)_3$.

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