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AN INHIBITORY EFFECT OF Mg^{2+} ION BY THE COMPLEX FORMATION WITH 1-BENZYL-1,4-DIHYDRONICOTINAMIDE ON THE REDUCTION OF 7,7,8,8-TETRACYANO-*p*-QUINODIMETHAN

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A 1 : 1 complex formed between 1-benzyl-1,4-dihydronicotinamide (BNAH) and Mg^{2+} ion with the formation constant (1.2 ± 0.1) x 10^4 $mol^{-1}dm^3$ at 298 K causes the 23 fold decrease in the rate constant for the reduction of 7,7,8,8-tetracyano-*p*-quinodimethan by BNAH.

The effects of metal ions such as Mg^{2+} and Zn^{2+} on the reduction of various substrates by NADH model compounds in acetonitrile (MeCN) have extensively been studied in connection with the involvement of metal ions in the oxidation-reduction reactions of nicotinamide coenzymes.[1-4] However, there still remains uncertainty as to the function of metal ions; some metal ions have been reported to catalyze the reduction of various substrates,[3] whereas the same metal ions reported to retard the reduction of other substrates by an NADH model compound.[4] Some metal ions are known to form complexes with NADH model compounds although the stoichiometry and the formation constant have scarecely been reported.[2-4] As far as the role of such NADH model-metal ion complexes is concerned, there have been contradictory proposals as to whether the reduction of substrates by an NADH model compound is enhanced[3] or retarded[4] by the complex formation.

In this report, we wish to clarify the role of the complex formed between Mg^{2+} ion and an NADH model compound 1-benzyl-1,4-dihydronicotinamide (BNAH) as being whether to enhance or retard the reduction of a substrate. 7,7,8,8-Tetracyano-*p*-quinodimethan (TCNQ) is chosen as a substrate since TCNQ does not interact with Mg^{2+} ion.

The absorption spectrum of BNAH in anhydrous MeCN under nitrogen atmosphere was significantly affected by the addition of $Mg(ClO_4)_2$, whereas that of TCNQ was not. The addition of Mg^{2+} ion to an MeCN solution of BNAH caused not only a red-

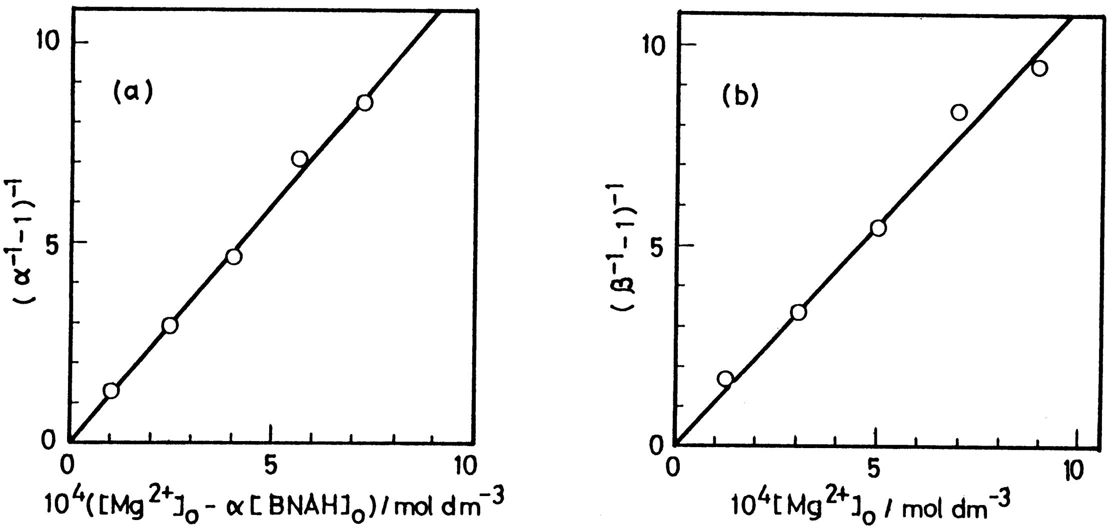

Fig. 1. Determination of the formation constant K of the Mg^{2+}- BNAH complex; (a) from the change of the absorption spectrum of BNAH (see Eq. 2) and (b) from the kinetics for the reduction of TCNQ by BNAH (see Eq. 7).

shift of the absorption maximum of BNAH from 350 to 363 nm but also an increase in the extinction coefficient from 6.0×10^4 to 8.4×10^4 mol^{-1}dm^2. If the Mg^{2+} ion forms the 1 : 1 complex with BNAH (Eq. 1), such a change of the

$$\mathrm{BNAH} + \mathrm{Mg}^{2+} \overset{K}{\rightleftharpoons} [\mathrm{BNAH\ Mg}^{2+}] \qquad (1)$$

absorption spectrum by the addition of Mg^{2+} is expressed by Eq. 2,

$$(\alpha^{-1} - 1)^{-1} = K([\mathrm{Mg}^{2+}]_0 - \alpha[\mathrm{BNAH}]_0) \qquad (2)$$

where $\alpha = (A - A_0)/(A_\infty - A_0)$; A is the absorbance at 363 nm in the presence of a certain concentration of Mg^{2+}, A_0 and A_∞ are the initial and the final absorbances at the same wavelength in the absence of Mg^{2+} and in the presence of large excess Mg^{2+}, respectively. The linear plot between $(\alpha^{-1} - 1)^{-1}$ *vs.* $([Mg^{2+}]_0 - \alpha[BNAH]_0)$ shown in Fig. 1a indicates the formation of the 1 : 1 complex (Eq. 1). The formation constant K is obtained as 1.2×10^4 mol^{-1}dm^3 from the slope in Fig. 1a. The K value decreases by the addition of H_2O to an

Table 1. Effect of H_2O on the formation constant K of the Mg^{2+} complex with BNAH in MeCN.[a]

$[H_2O]$ mol dm^{-3}	K mol^{-1}dm^3
Dehydrated	1.21×10^4
1.67×10^{-3}	1.04×10^4
1.83×10^{-2}	4.48×10^3
1.83×10^{-1}	8.08×10^2
1.77	4.31×10

[a] T = 298 K, $[BNAH]_0 = 1.0 \times 10^{-4}$ mol dm^{-3}.

anhydrous MeCN solution of BNAH as shown in Table 1, probably because of the hydration of Mg^{2+} ion.[5)]

The hydride transfer from BNAH to TCNQ (Eq. 3) occurs upon mixing BNAH and

$$\text{BNAH} + \text{TCNQ} \xrightarrow{k_1} \text{BNA}^+ + \text{TCNQH}^- \qquad (3)$$

TCNQ in MeCN. The reaction rate was measured by the rise of the absorption band due to $TCNQ^{\overline{\cdot}}$ (λ_{max} = 842 nm, $\varepsilon = 4.33 \times 10^5$ $mol^{-1}dm^2$)[6)] formed by the subsequent reaction of $TCNQH^-$ with TCNQ (Eq. 4),[7)] using a Union RA-103 stopped flow spectrophotometer.

$$\text{TCNQH}^- + \text{TCNQ} \longrightarrow \text{TCNQH}\cdot + \text{TCNQ}^{\overline{\cdot}} \qquad (4)$$

The second-order rate constant k_1 has been determined as (1.64 ± 0.06) x 10^3 $mol^{-1}dm^3s^{-1}$ at 298 K. The addition of Mg^{2+} ion to the BNAH-TCNQ system in anhydrous MeCN caused a decrease in the reaction rate. The rate constant decreased with increasing the Mg^{2+} concentration and gradually reached a constant value which is 23 times smaller than that in the absence of Mg^{2+}. This result is well interpreted by the presence of the 1 : 1 complex formed between BNAH and Mg^{2+} (Eq. 1), which reacts with TCNQ at a much slower rate than free BNAH (Eq. 5).

$$[\text{BNAH Mg}^{2+}] + \text{TCNQ} \xrightarrow[\text{slow}]{k_2} \text{BNA}^+ + \text{Mg}^{2+} + \text{TCNQH}^- \qquad (5)$$

Thus, the observed rate constant k_{obsd} in the presence of excess Mg^{2+} relative to BNAH is given by Eq. 6, which is rewritten by Eq. 7,

$$k_{obsd} = \frac{k_1 + k_2K[\text{Mg}^{2+}]_0}{1 + K[\text{Mg}^{2+}]_0} \quad (6) \qquad (\beta^{-1} - 1)^{-1} = K[\text{Mg}^{2+}]_0 \quad (7)$$

where $\beta = (k_{obsd} - k_1)/(k_2 - k_1)$. The linear plot of $(\beta^{-1} - 1)^{-1}$ *vs.* $[Mg^{2+}]_0$ is shown in Fig. 1b, which confirms the validity of Eq. 6. The slope in Fig. 1b gives the K value for the complex formation as 1.1 x 10^4 $mol^{-1}dm^3$ at 298 K, which agrees well with the K value (1.2 x 10^4 $mol^{-1}dm^3$) determined independently from the slope in Fig. 1a. The decrease in the reducing ability of BNAH upon complex formation with Mg^{2+} is indicated also by the increase of the oxidation peak potential (+0.2 V) in the cyclic voltammogram of BNAH in the presence of large excess Mg^{2+} (0.5 mol dm^{-3}).[8)]

Thus, it is concluded that the complex formation between BNAH and Mg^{2+} causes the decrease in the reactivity to reduce TCNQ as opposed to the postulated enhancement of the reactivity by the complex formation.3) The catalyzing effect of Mg^{2+} ion in the reduction of substrates by NADH model compounds3) may be ascribed to the formation of the Mg^{2+} complex with a substrate which enhances the reactivity towards an NADH model compound to exceed the retarding effect of the Mg^{2+} complex with an NADH model compound.

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