

DETECTION OF AN INTERMEDIATE TERNARY COMPLEX IN THE REDUCTION OF
p-BENZOQUINONE DERIVATIVES BY AN NADH MODEL COMPOUND IN THE PRESENCE
OF Mg²⁺ ION

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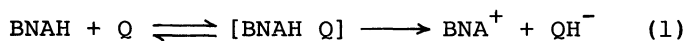
A transient charge-transfer (CT) band of a ternary complex due to the CT transition from an NADH model compound - Mg²⁺ ion complex to a *p*-benzoquinone derivative was observed in the reduction of a *p*-benzoquinone derivative by an NADH model compound in the presence of Mg²⁺ ion in acetonitrile. The role of the ternary complex in the reduction by an NADH model compound is reported.

There has been considerable interest in the effects of metal ions on the reduction of various substrates by NADH model compounds in connection with the involvement of metal ions in the oxidation-reduction reactions of nicotinamide coenzymes.¹⁾ The role of metal ions, however, still remains uncertain since some metal ions accelerate the reduction of various substrates,^{1,2)} whereas the same metal ions retard the reduction of other substrates by NADH model compounds.^{3,4)} Moreover, in some cases, both the accelerating and retarding effects have been observed depending upon the metal ion concentrations.⁵⁾ Although the presence of a ternary complex involving an NADH model compound, a substrate, and metal ions has often been suggested as an intermediate for the reduction by NADH model compounds,⁶⁾ no evidence for such a ternary complex has so far been reported in the reduction of a substrate by an NADH model compound in the presence of metal ions.

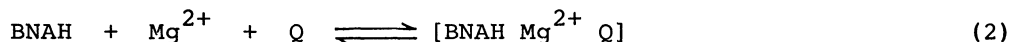
We wish to report here the first detection of an intermediate ternary complex in the reduction of a *p*-benzoquinone derivative by an NADH model compound in the presence of Mg²⁺ ion.

It has previously been reported that the hydride transfer from an NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH), to a *p*-benzoquinone derivative occurs *via* the CT complex formed between BNAH and *p*-benzoquinone derivatives Q

(Eq. 1).⁷⁾ When $\text{Mg}(\text{ClO}_4)_2$ was added to the



BNAH-2,6-dichloro-*p*-benzoquinone system, a transient CT band observed in the absence of Mg^{2+} ion ($\lambda_{\text{max}} = 680 \text{ nm}$; $h\nu_{\text{CT}} = 1.82 \text{ eV}$) by using a Union RA-103 stopped flow spectrophotometer was significantly blue-shifted in the presence of $0.10 \text{ mol dm}^{-3} \text{ Mg}^{2+}$ ion ($\lambda_{\text{max}} = 600 \text{ nm}$; $h\nu_{\text{CT}} = 2.07 \text{ eV}$) as shown in Fig. 1. Similar blue-shifts of the CT bands for other *p*-benzoquinone derivatives (*p*-chloranil, *p*-bromanil, and chloro-*p*-benzoquinone) were observed in the presence of $0.10 \text{ mol dm}^{-3} \text{ Mg}^{2+}$ ion.⁸⁾ The Mg^{2+} ion is known to form a 1 : 1 complex with BNAH in acetonitrile with the formation constant $1.2 \times 10^4 \text{ mol}^{-1} \text{ dm}^3$ at 298 K.⁴⁾ Thus, the change of the CT band in Fig. 1 may be explained by the formation of a ternary complex involving BNAH, Mg^{2+} ion, and a *p*-benzoquinone derivative (Eq. 2) since most BNAH molecules form the 1 : 1 complex



with Mg^{2+} ion at the Mg^{2+} concentration (0.10 mol dm^{-3}). The blue-shift of the CT band (+0.22 eV) in Fig. 1 is consistent with the positive shift in the oxidation peak potential (+0.2 V) of the cyclic voltammogram of BNAH in the presence of Mg^{2+} ion in acetonitrile.⁴⁾ No blue-shift of the CT band has been observed in the presence of $0.10 \text{ mol dm}^{-3} \text{ NaClO}_4$ which does not interact with BNAH.

The second-order rate constants k for the hydride transfer from BNAH ($1.1 \times 10^{-4} - 4.7 \times 10^{-4} \text{ mol dm}^{-3}$) to some *p*-benzoquinone derivatives (more than 10 fold excess of BNAH) in the absence and presence of $0.10 \text{ mol dm}^{-3} \text{ Mg}^{2+}$ ion have been determined by measuring the decay of the absorbance due to BNAH using a stopped flow spectrophotometer. Retarding effects of the Mg^{2+} ion on the rate constant k for the hydride transfer from BNAH to *p*-chloranil, *p*-bromanil, 2,6-dichloro-*p*-benzoquinone, and chloro-*p*-benzoquinone were observed in the presence of $0.10 \text{ mol dm}^{-3} \text{ Mg}^{2+}$ ion in the BNAH-*p*-benzoquinone derivative systems. The

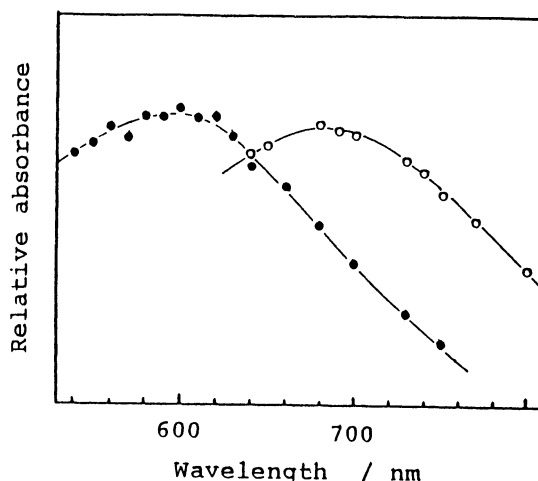


Fig. 1. Transient CT spectra observed in the reduction of 2,6-dichloro-*p*-benzoquinone ($0.043 \text{ mol dm}^{-3}$) by BNAH ($0.097 \text{ mol dm}^{-3}$) in the absence of Mg^{2+} ion (O) and the presence of $0.10 \text{ mol dm}^{-3} \text{ Mg}^{2+}$ ion (●) in acetonitrile at 298 K.

logarithms of the rate constants are plotted against the CT transition energies $h\nu_{CT}$ in the absence and presence of $0.10 \text{ mol dm}^{-3} \text{ Mg}^{2+}$ ion as shown in Fig. 2, where the $\log k$ value decreases linearly with increasing the $h\nu_{CT}$ value. Since $h\nu_{CT}$ corresponds to the energy required for the electron transfer from BNAH to *p*-benzoquinone derivatives in the CT complexes, a correlation in Fig. 2 suggests that the electron transfer from BNAH to *p*-benzoquinone derivatives in the CT complexes in the absence and presence of Mg^{2+} ion plays an important role in the activation process of the hydride transfer from BNAH to *p*-benzoquinone derivatives. As such, the presence of the ternary complex (Eq. 2) may be responsible for the retarding effect of Mg^{2+} ion by decreasing the donor ability of BNAH toward *p*-benzoquinone derivatives in the ternary complex. Thus, the accelerating effects of metal ions^{1,2)} must require the activation of a substrate by forming a metal ion-substrate complex other than a metal ion-NADH model compound complex.

In the present case, the accelerating effect of Mg^{2+} ion was observed in the higher concentrations of Mg^{2+} ion ($> 0.10 \text{ mol dm}^{-3}$); the rate constant for the hydride transfer from BNAH ($1.23 \times 10^{-4} - 2.18 \times 10^{-4} \text{ mol dm}^{-3}$) to 2,6-dichloro-*p*-benzoquinone (more than 10 fold excess of BNAH) increased parabolically with increasing the Mg^{2+} concentration following the decrease of the rate constant in the lower concentrations of Mg^{2+} ion as shown in Fig. 3. The change of the

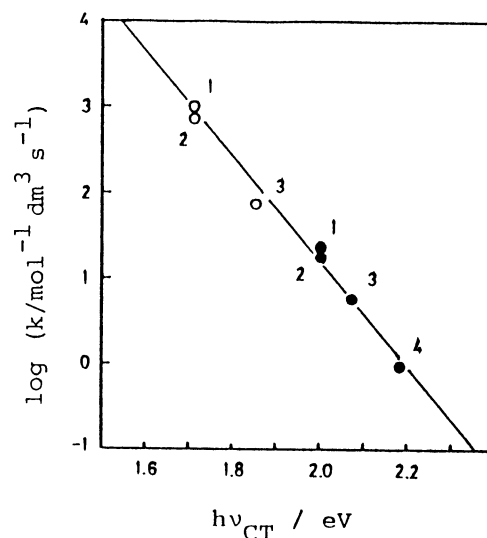


Fig. 2. A correlation between $\log k$ and $h\nu_{CT}$ in the absence of Mg^{2+} ion (O) and the presence of $0.10 \text{ mol dm}^{-3} \text{ Mg}^{2+}$ ion (●) in acetonitrile at 298 K. Numbers refer to *p*-benzoquinone derivatives; 1) *p*-chloranil, 2) *p*-bromanil, 3) 2,6-dichloro-*p*-benzoquinone, 4) chloro-*p*-benzoquinone.

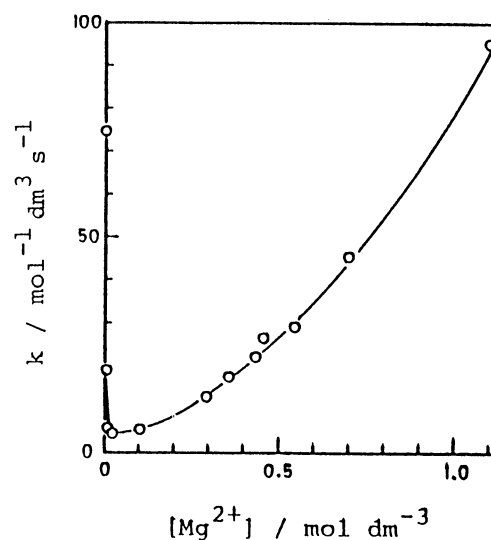


Fig. 3. Variation of the rate constant k for the hydride transfer from BNAH to 2,6-dichloro-*p*-benzoquinone with the Mg^{2+} concentration in acetonitrile at 298 K.

electronic spectrum of BNAH in the presence of Mg^{2+} ion at various concentrations showed that BNAH forms only a 1 : 1 complex with Mg^{2+} ion even in the high concentrations of Mg^{2+} ion ($\gg 0.10 \text{ mol dm}^{-3}$). On the other hand, there was observed a change of the electronic spectrum of 2,6-dichloro-*p*-benzoquinone only in the high concentrations of Mg^{2+} ion ($> 0.10 \text{ mol dm}^{-3}$) and the absorbance of the quinone at 290 nm showed a parabolic dependence on the Mg^{2+} ion concentration, which is similar to that of the rate constant k in Fig. 3. Thus, the presence of a ternary complex involving two or more Mg^{2+} ions to activate the substrate other than the ternary complex in Eq. 2 may be responsible for the accelerating effect of Mg^{2+} ion in the higher concentrations (Fig. 3). The detailed study on the accelerating effect of Mg^{2+} ion in the higher concentrations in the reduction of various *p*-benzoquinone derivatives by BNAH is now under progress.

References

- 1) D. S. Sigman, J. Hajdu, and D. J. Creighton, "Bioorganic Chemistry," ed by E. E. van Tamelen, Academic Press, New York (1978), Vol. IV, p. 385 and references therein.
- 2) R. A. Hood and R. H. Prince, *J. Chem. Soc., Chem. Commun.*, 1979, 163; R. A. Gase and U. K. Pandit, *J. Am. Chem. Soc.*, 101, 7059 (1979); A. Ohno, H. Yamamoto, and S. Oka, *ibid.*, 103, 2041 (1981).
- 3) S. Shinkai, T. Ide, H. Hamada, O. Manabe, and T. Kunitake, *J. Chem. Soc., Chem. Commun.*, 1977, 848; A. Ohno, H. Yamamoto, and S. Oka, *Tetrahedron Lett.*, 1979, 4061.
- 4) S. Fukuzumi, Y. Kondo, and T. Tanaka, *Chem. Lett.*, 1983, 485.
- 5) R. A. Gase, G. Boxhoorn, and U. K. Pandit, *Tetrahedron Lett.*, 1976, 2889; M. Hughes and R. H. Prince, *J. Inorg. Nucl. Chem.*, 40, 703 (1978); A. Ohno, H. Yamamoto, T. Okamoto, S. Oka, and Y. Ohnishi, *Bull. Chem. Soc. Jpn.*, 50, 2385 (1977); Y. Murakami, A. Aoyama, and J. Kikuchi, *ibid.*, 55, 2898 (1982).
- 6) N. Nishiyama, N. Baba, J. Oda, and Y. Inoue, *J. Chem. Soc., Chem. Commun.*, 1976, 101; J.-P. Behr and J.-M. Lehn, *ibid.*, 1978, 143; K. Watanabe, R. Kawaguchi, and H. Kato, *Chem. Lett.*, 1978, 255; A. Kitani and K. Sasaki, *J. Electroanal. Chem.*, 94, 201 (1978).
- 7) Observations of the transient CT bands were limited to the *p*-benzoquinone derivatives with electron-withdrawing substituents used in this study owing to the overlap of the CT bands for other *p*-benzoquinone derivatives with electron-donating substituents such as methyl-substituted *p*-benzoquinone derivatives with the absorption bands due to the *p*-benzoquinone derivatives.

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