# Mechanism of Hydride Transfer from an NADH Model Compound to *p*-Benzoquinone Derivatives

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*Received August 30, 1983*

Charge-transfer (CT) complexes formed between an NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH), and a series of *p*-benzoquinone derivatives Q were isolated from benzene solutions of these reactants. Some isolated CT complexes exhibited long-wavelength absorption maxima in the range 670–735 nm, depending on the electron-acceptor ability of the quinone derivatives. Transient CT bands equivalent to the CT bands of the isolated complexes were observed also in the course of the hydride-transfer reactions from BNAH to Q in acetonitrile, suggesting that the CT complexes are intermediates for the hydride-transfer reactions. The rate constants $k$ for the hydride-transfer reactions vary significantly with the redox potentials $E°(Q/Q^{-}·)$ of *p*-benzoquinone derivatives and span a range of more than $10^{11}$. The primary kinetic isotope effects $k_H/k_D$ also show a large variation in the range 1.5–6.2, and a bell-shaped dependence of the $k_H/k_D$ values on the $E°(Q/Q^{-}·)$ values has been obtained with a clear "Westheimer maximum". Quantitative analyses for these correlations of the rate constants and the isotope effects with the redox potentials of *p*-benzoquinone derivatives have been presented on the basis of a sequential electron–proton–electron transfer mechanism where the radical ion pair $[BNAH^{+}·Q^{-}·]$ formed by the first electron transfer from BNAH to Q in the CT complex [BNAH–Q] is considered to be closer to a "transition state" than an "intermediate" for most *p*-benzoquinone derivatives used in this study.

Although oxidation–reduction reactions of models for dihydronicotinamide coenzymes have generally been considered to involve one-step hydride transfer,[1] the presence of intermediates such as a charge-transfer (CT) complex and a radical ion pair formed by electron transfer from an NADH model compound to a substrate has often been suggested.[2,3] In general, CT complexes are formed when compounds which have low redox potentials, acting as electron donors, are combined with compounds with high reduction potentials as electron acceptors.[4] However, very little is known about transient CT complexes which may be intermediates in irreversible redox reactions, while a great deal is known about the reversible formation of stable CT complexes.[4] Thus, neither the isolation nor the properties of CT complexes in the course of NADH model reactions where irreversible hydride transfer occurs from an NADH model compound to a substrate has so far been reported despite the fact that NADH model compounds have low redox potentials.[5,6]

We report herein the isolation and properties of the CT complexes formed between an NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH), acting as an electron donor and various *p*-benzoquinone derivatives Q as electron acceptors, and also a systematic study on the mechanism of reduction of Q by BNAH in acetonitrile (MeCN), based on the products, stoichiometry, kinetics, and kinetic deuterium isotope effects with the aim of elucidating the role of the CT complexes in the NADH model reactions.[7] The BNAH–Q system is particularly suitable for such a systematic study since the electron-acceptor ability of the substrate can be systematically varied by introducing appropriate substituents on the 2, 3, 5, and 6 positions of *p*-benzoquinone to cover a wide range of the reactivity of the substrate.[8] For the sake of clarifying and better understanding of this study, we prefer to present the reaction mechanism of reduction of Q by BNAH in MeCN at the beginning and then show how the data lead to this mechanism, which will be shown to reconcile the controversy between one-step and multistep mechanisms for hydride-transfer reactions of NADH model compounds.[1-3]

## Results and Discussion

**Mechanism of Reduction of Q by BNAH.** The reactants BNAH and Q are rapid equilibrium with a CT complex [BNAH–Q] which also is in rapid equilibrium with the radical ion pair $[BNAH^{+}·Q^{-}·]$ formed by the reversible electron transfer from BNAH to Q in the CT complex (eq 1). The reversible electron transfer is fol-

$$BNAH + Q \overset{K_{CT}}{\rightleftharpoons} [BNAH\text{–}Q] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [BNAH^{+}·\text{–}Q^{-}·] \quad (1)$$

$$[BNAH^{+}·\text{–}Q^{-}·] \xrightarrow{k_H} [BNA·\text{–}QH·] \xrightarrow{fast} BNA^{+} + QH^{-} \quad (2)$$

$$QH^{-} + Q \xrightarrow{fast} QH· + Q^{-}· \quad (3)$$

$$2QH· \xrightarrow{fast} QH_2 + Q \quad (4)$$

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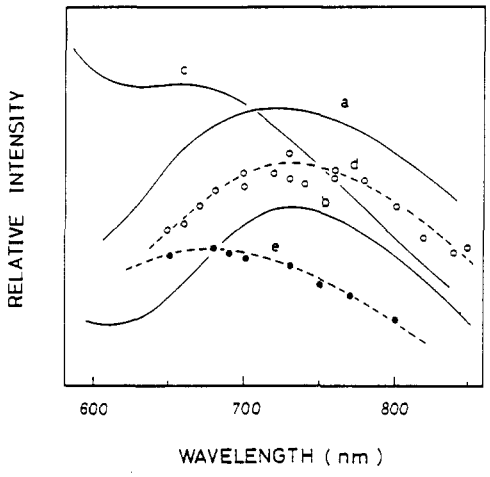


**Figure 1.** Reflectance spectra (—) of the 1:1 complexes of BNAH with (a) *p*-chloranil, (b) *p*-bromanil, and (c) 2,6-dichloro-*p*-benzoquinone, and the transient CT spectra (- - -) obtained by plotting the initial absorbances in the kinetic curves against the wavelengths in the reactions of (d) BNAH ($7.37 \times 10^{-2}$ M) with *p*-chloranil ($1.01 \times 10^{-1}$ M) and (e) BNAH ($1.45 \times 10^{-1}$ M) with 2,6-dichloro-*p*-benzoquinone ($2.22 \times 10^{-2}$ M) in MeCN at 298 K.

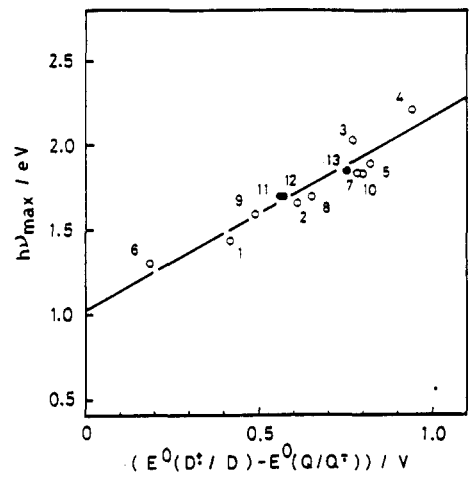


**Figure 2.** Correlation between the CT transition energies $h\nu_{CT}$ of BNAH–Q complexes (●) as well as other known CT complexes of Q (○)[16] and the free energy change of electron transfer $E^\circ(D/D^+\cdot) - E^\circ(Q/Q^-\cdot)$ (see eq 5); (1) *N,N,N′,N′*-tetramethylbenzidine–*p*-chloranil, (2) *N,N,N′,N′*-tetramethylbenzidine–2,5-dichloro-*p*-benzoquinone, (3) *N,N,N′,N′*-tetramethylbenzidine–chloro-*p*-benzoquinone, (4) *N,N,N′,N′*-tetramethylbenzidine–*p*-benzoquinone, (5) *N,N*-dimethylaniline–*p*-chloranil, (6) *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine–*p*-chloranil, (7) *N,N*-dimethyl-*m*-anisidine–*p*-chloranil, (8) *N,N*-dimethyl-*p*-anisidine–*p*-chloranil, (9) 3,4-dimethoxy-*N,N*-dimethylaniline–*p*-chloranil, (10) 3,5-dimethoxy-*N,N*-dimethylaniline–*p*-chloranil, (11) BNAH–*p*-chloranil, (12) BNAH–*p*-bromanil, (13) BNAH–2,6-dichloro-*p*-benzoquinone.

lowed by the irreversible proton transfer from $BNAH^+\cdot$ to $Q^-\cdot$ in the radical ion pair and the subsequent electron transfer from BNA· to QH· in the radical pair [BNA·–QH·] (eq 2). The net reaction of eq 1 and 2 is hydride equivalent transfer from BNAH to Q to yield $BNA^+$ and $QH^-$, which is followed by the fast electron transfer reaction between $QH^-$ and Q (eq 3) and the subsequent disproportionation of the semiquinone radicals QH· (eq 4).[9-11]

A similar electron–proton–electron sequence for hydride equivalent transfer from an NADH model compound to a substrate has often been proposed in the literatures,[2,3] as opposed to a one-step hydride transfer.[1] It should be emphasized, however, that the present mechanism of hydride equivalent transfer (eq 1 and 2) involves the CT complex as an intermediate and the electron–proton–electron sequence occurs in the CT complex. Thus, the radical intermediates for the hydride equivalent transfer exist only as the radical pairs (eq 1 and 2) and thereby no free-radical species is involved.[12] In the following sections, the validity of the proposed mechanism (eq 1–4) is shown step by step and then a unified view of one-step and multistep mechanisms reported so far[1-3] is presented.

**Charge-Transfer Complexes Formed between BNAH and Q.** The existence of the CT complex (eq 1) is proved by the isolation and the observation of the CT band as follows. Upon mixing a benzene or toluene solution of BNAH with that of *p*-chloranil under nitrogen atmosphere, a green precipitate was separated and identified as a 1:1 complex of BNAH with *p*-chloranil (see Experimental Section). The reflectance spectrum of the BNAH–*p*-chloranil complex exhibits a broad absorption band at $\lambda_{max} = 725$ nm (Figure 1a) which may be assigned to an intermolecular charge-transfer (CT) transition between BNAH and *p*-chloranil, since neither BNAH nor *p*-chloranil shows any absorption at this wavelength. Similar 1:1 complexes of BNAH with other *p*-benzoquinone derivatives (*p*-bromanil, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, 2,6-dichloro-*p*-benzoquinone, chloro-*p*-benzoquinone, *p*-benzoquinone, methyl-*p*-benzoquinone, and tetramethyl-*p*-benzoquinone) also were isolated. The reflectance spectra of the BNAH–*p*-bromanil and BNAH–2,6-dichloro-*p*-benzoquinone complexes also are shown in Figure 1, b and c, respectively.[13]

Mixing of high concentrations of BNAH ($7.37 \times 10^{-2}$ M) with *p*-chloranil ($1.01 \times 10^{-2}$ M) in MeCN by using a stopped flow spectrophotometer displayed the instant rise of the CT band in the long-wavelength region. The plot of the absorbance against the wavelength shows essentially the same spectrum (Figure 1d) as that observed for the isolated CT complex (Figure 1a), indicating the presence of the CT complex formed between BNAH and a *p*-benzoquinone derivative (Q) in MeCN (eq 1). The CT complex in polar solvents such as MeCN is very unstable,[14] and the transient nature of the CT band suggests that the complex is a reaction intermediate for the reduction of Q by BNAH in MeCN as discussed in detail later. A transient long-wavelength absorption band has been detected also in the reaction of BNAH with 2,6-dichloro-*p*-benzoquinone in MeCN as shown in Figure 1e. The absorption maximum agrees with that of the isolated CT complex (compare Figure 1, c and e).[15] Thus, the CT interaction

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(12) For the formation of radical ion pairs via CT complexes without involvement of free radical species, see: (a) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2141, 7290. (b) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *Ibid.* **1980**, *102*, 2928. (c) Fukuzumi, S.; Kochi, J. K. *Ibid.* **1982**, *104*, 7599.
(13) The CT bands in the long-wavelength region have not been observed distinctly for BNAH complexes with other *p*-benzoquinone derivatives such as chloro-*p*-benzoquinone and *p*-benzoquinone having lower reduction potentials than 2,6-dichloro-*p*-benzoquinone, because of the overlap of the CT bands with the absorption bands due to the *p*-benzoquinone derivatives.
(14) For example, the color change due to the formation of the CT complex has not been visualized because of the facile reaction of the CT complex as well as the low absorbance of the system.

**Table I. Spin Concentrations and g Values of the ESR Spectra of the CT Complexes Formed between BNAH and p-Benzoquinone Derivatives Q**

| p-benzoquinone derivative | spin concn,[a] % | g value[b] |
|---|---|---|
| 2,3-dichloro-5,6-dicyano-p-benzoquinone | 6.2 | 2.0050 |
| p-chloranil | 26 | 2.0052 |
| p-bromanil | 20 | 2.0082 |
| 2,6-dichloro-p-benzoquinone | $3.7 \times 10^{-2}$ | 2.0050 |
| chloro-p-benzoquinone | $1.9 \times 10^{-2}$ | 2.0050 |
| p-benzoquinone | $4.3 \times 10^{-4}$ | 2.0045 |
| methyl-p-benzoquinone | $1.7 \times 10^{-3}$ | 2.0044 |
| tetramethyl-p-benzoquinone | $4.3 \times 10^{-5}$ | 2.0047 |

[a] Mol % of radical species in [BNAH–Q]. [b] The experimental error is ±0.0004.

between BNAH and p-benzoquinone derivatives (eq 1) does occur in solution as well as in the solid.

In order to compare the nature of these CT complexes with that of other known CT complexes of p-benzoquinone derivatives, the electronic transition energies $h\nu_{max}$ of the BNAH–Q complexes together with those of CT complexes formed between aromatic amines and quinones[16] are plotted against the difference between the redox potentials $E°(D^{+}\cdot/D)$ of BNAH[6] or the amines[17] and $E°(Q/Q^{-}\cdot)$ of the quinones,[18] which is related to the free energy change of electron transfer $\Delta G°_{et}$ from the donor (D) to the acceptor (Q) (eq 5, where $F$ is the Faraday constant),[19] as

$$\Delta G°_{et}/F = E°(D^{+}\cdot/D) - E°(Q/Q^{-}\cdot) \quad (5)$$

shown in Figure 2. The $h\nu_{max}$ values of the BNAH–Q complexes are consistent with those of other known CT complexes in the correlation with the $\Delta G°_{et}/F$ values. Thus, the BNAH–Q complexes are classified as donor–acceptor complexes of a quite general kind.[4]

Paramagnetism has often been observed in CT complexes prepared from organic donor molecules and acceptor p-benzoquinone derivatives.[20] In the present case as well, ESR signals were observed in all the isolated CT complexes. The g values and the spin concentrations of the BNAH–Q complexes are listed in Table I. The g values agree well with those of the radical anions of the corresponding p-benzoquinone derivatives.[20a,21] Thus, the semiquinone radical anions $Q^{-}\cdot$ may be formed through the CT interaction in the complexes. Although no ESR signal of the counter radical cation $BNAH^{+}\cdot$ has been observed owing to the broad one of $Q^{-}\cdot$,[22] the dependence of the spin concentrations on the electron-acceptor ability of p-benzoquinone derivatives (Table I) suggests that the semiquinone radical anions $Q^{-}\cdot$ are formed by electron transfer from BNAH to Q in the CT complexes (eq 1).[23] The partial charge transfer in the complexes is confirmed also from the infrared spectra of the BNAH-p-chloranil and BNAH–p-bromanil complexes in KBr disks, which exhibit strong bands at 1680 and 1670 $cm^{-1}$, respectively, assignable to $\nu$(C=O) of the p-chloranil and p-bromanil molecules, with weak bands of the red-shifted $\nu$(C=O) due to the radical anions of p-chloranil and p-bromanil.[24]

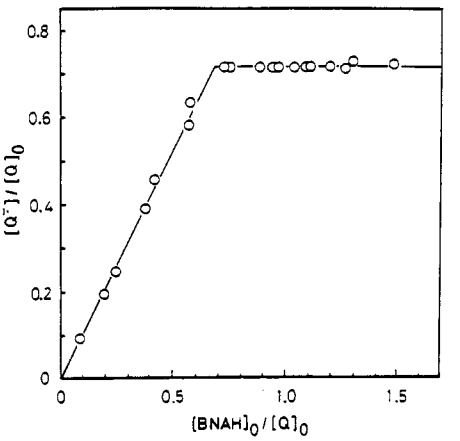


**Figure 3.** Ratio of the concentration of $QBr_4^{-}\cdot$ formed in the reaction of BNAH with $QBr_4$ in MeCN to the initial concentration of $QBr_4$ ($1.59 \times 10^{-4}$ M) plotted against the ratio of the BNAH concentration to the initial concentration of $QBr_4$.

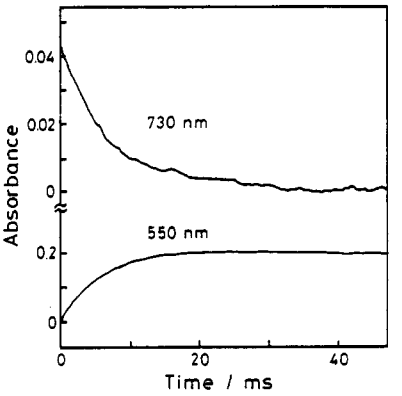


**Figure 4.** Decay and the rise of absorbances at 730 and 550 nm due to the BNAH–p-chloranil complex and the p-chloranil radical anion, respectively, in the reaction of BNAH ($7.37 \times 10^{-2}$ M) with p-chloranil ($1.01 \times 10^{-2}$ M) in MeCN at 298 K.

**Hydride Transfer from BNAH to Q.** When the BNAH–p-bromanil or BNAH–p-chloranil complex was dissolved in MeCN, the CT band disappeared instantly and instead a strong absorption band due to the radical

(15) The absorption maxima of the transient CT bands for other p-benzoquinone derivatives such as chloro-p-benzoquinone and p-benzoquinone in MeCN have not been determined because of the overlap of the CT bands with the absorption band due to the respective semiquinone radical anion formed as a product (see eq 6).

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(19) The standard free energy change of electron transfer $\Delta G°_{et}$ ($D + Q \rightarrow D^{+}\cdot + Q^{-}\cdot$) derives from the sum of the two half reactions involving the free oxidized and reduced species. The relation between the free energy change for the formation of the radical ion pair $\Delta G_{et}$ ($D + Q \rightarrow [D^{+}\cdot\ Q^{-}\cdot]$) and $\Delta G°_{et}$ is given in eq 21.

(20) (a) Eastman, J. W.; Engelsma, G.; Calvin, M. *J. Am. Chem. Soc.* **1962**, *84*, 1339. (b) Hove, M. J.; Hoffman, B. M.; Loyd, R. J. *J. Phys. Chem.* **1972**, *76*, 1849. (c) Bijl, D.; Kainer, H.; Rose-Innes, A. C. *J. Chem. Phys.* **1959**, *30*, 765. (d) Matsunaga, Y.; McDowell, C. A. *Nature (London)* **1960**, *185*, 916. (e) Browne, M. E.; Ottenberg, A.; Brandon, R. L. *J. Chem. Phys.* **1964**, *41*, 3265.

(21) (a) Venkataraman, B.; Segal, B. G.; Fraenkel, G. K. *J. Chem. Phys.* **1959**, *30*, 1006. (b) Hove, M. J.; Hoffman, B. M.; Loyd, R. J. *J. Phys. Chem.* **1972**, *76*, 1849. (c) Fukuzumi, S.; Ono, Y.; Keii, T. *Int. J. Chem. Kinet.* **1975**, *7*, 535.

(22) The counter radical cations have rarely been detected in CT complexes formed between organic donors and $\pi$ acceptors (ref 20).

(23) The spin concentration of the CT complex generally increases with the positive shift of the redox potential of Q (Table II), although there are a few exceptions (e.g., in the case of 2,3-dichloro-5,6-dicyano-p-benzoquinone), probably because of the partial decomposition of the radical ion pair.

(24) Matsunaga, Y. *J. Chem. Phys.* **1964**, *41*, 1609.

anion[25] appeared at $\lambda_{max}$ = 452 nm ($\epsilon$ = 8.38 × $10^3$ $M^{-1}$ $cm^{-1}$) for *p*-bromanil or $\lambda_{max}$ = 449 nm ($\epsilon$ = 9.00 × $10^3$ $M^{-1}$ $cm^{-1}$) for *p*-chloranil. The amount of the semiquinone radical anion $Q^{-}\cdot$ determined from the electronic spectrum was equal to about $^2/_3$ of the CT complex. Mixing of BNAH with *p*-bromanil in MeCN also was accompanied by the formation of the semiquinone radical anion $Q^{-}\cdot$. The ratio of the radical concentration to the initial concentration of the quinone $[Q^{-}\cdot]/[Q]_0$ is plotted against the ratio of the initial concentration of BNAH to Q $[BNAH]_0/[Q]_0$ in Figure 3, where the $[Q^{-}\cdot]/[Q]_0$ value increases linearly with the slope of unity in the region $[BNAH]_0/[Q]_0 < ^2/_3$ and becomes a constant in the region $[BNAH]_0/[Q]_0 > ^2/_3$. Thus, the stoichiometries of the reaction of the CT complex and the reduction of Q by BNAH in MeCN may be given by eq 6 and 7, respectively. Both stoichiometries

$$[BNAH\text{–}Q] \xrightarrow[MeCN]{} \frac{2}{3}Q^{-}\cdot + \frac{1}{3}QH_2 + \frac{2}{3}BNA^{+} + \frac{1}{3}BNAH \quad (6)$$

$$2BNAH + 3Q \rightarrow 2BNA^{+} + 2Q^{-}\cdot + QH_2 \quad (7)$$

are consistent with the reaction mechanism (eq 1–4), where the CT complex is an intermediate for the reduction of Q by BNAH in MeCN. Indeed, the decay of the transient CT band of the BNAH–*p*-chloranil complex in MeCN coincides with the rise of the absorption band due to the semiquinone radical anion as shown in Figure 4.

The radical anion $Q^{-}\cdot$ was stable in the presence of excess amount of quinone.[26] When acids such as HCl were introduced into the BNAH–*p*-bromanil system, the radical anion disappeared instantly and the stoichiometry changed to that in eq 8.[8] In the presence of acid, the semiquinone

$$BNAH + Q + H^{+} \rightarrow BNA^{+} + QH_2 \quad (8)$$

$$Q^{-}\cdot + H^{+} \rightarrow QH\cdot \quad (9)$$

radical anion $Q^{-}\cdot$ is converted to the neutral radical QH· (eq 9). Then, the stoichiometry of eq 8 also agrees with that of the net reaction of eq 1–4 and 9.

**Kinetics.** According to the reaction mechanism (eq 1–4), the rate of formation of $Q^{-}\cdot$ in the presence of large excess Q or BNAH is given by eq 10 or 11, where $K_{et}$ (=

(i) Q in excess:

$$\frac{d[Q^{-}\cdot]}{dt} = \frac{k_H K_{et}[Q]}{1 + K_{et}[Q]}([Q^{-}\cdot]_\infty - [Q^{-}\cdot]) \quad (10)$$

(ii) BNAH in excess:

$$\frac{d[Q^{-}\cdot]}{dt} = \frac{3}{2}\left(\frac{k_H K_{et}[BNAH]}{1 + K_{et}[BNAH]}\right)([Q^{-}\cdot]_\infty - [Q^{-}\cdot]) \quad (11)$$

$K_{CT}k_1/k_{-1}$) corresponds to the formation constant of the radical ion pair $[BNAH^{+}\cdot\text{–}Q^{-}\cdot]$ (eq 1) and $[Q^{-}\cdot]_\infty$ is the final concentration of $Q^{-}\cdot$. From eq 10 or 11, the pseudo-first-order rate contant $k_{obsd}$ in the presence of large excess Q or BNAH is given by eq 12 or 13 under the conditions

$$\text{(i) } k_{obsd} = k_H K_{et}[Q] \quad (12)$$

$$\text{(ii) } k_{obsd} = (3/2)k_H K_{et}[BNAH] \quad (13)$$

$K_{et}[Q]$ or $K_{et}[BNAH] \ll 1$. Indeed, the pseudo-first-order rate constant $k_{obsd}$ for the formation of the semiquinone radical anion of *p*-chloranil $QCl_4$ is proportional to the $QCl_4$ or BNAH concentration used in a large excess, and the

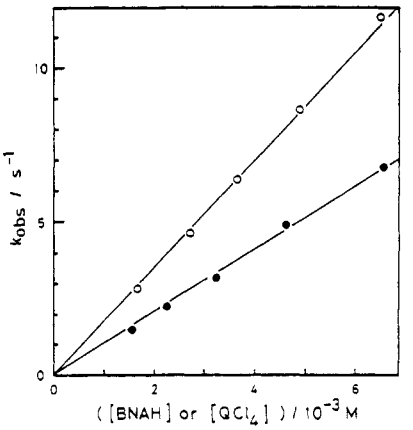


**Figure 5.** Pseudo-first-order rate constant $k_{obsd}$ for the formation of the *p*-chloranil radical anion in the reaction of BNAH with *p*-chloranil in MeCN at 298 K plotted against the BNAH (○) or *p*-chloranil (●) concentration used in a large excess.

slope of the plot of $k_{obsd}$ vs. [BNAH] is approximately 1.5 times larger than that of $k_{obsd}$ vs. $[QCl_4]$, agreeing with eq 12 and 13, as shown in Figure 5. Then, the $k_H K_{et}$ value can be obtained from $k_{obsd}$ by using eq 12 or 13. It should be noted that under the conditions $K_{et}[Q]$ or $K_{et}[BNAH] \ll 1$, $k_H K_{et}$ corresponds to the rate constant *k* for hydride equivalent transfer from BNAH to Q (eq 14), which is the

$$BNAH + Q \xrightarrow{k} BNA^{+} + QH^{-} \quad (14)$$

overall reaction of eq 1 and 2 in the reaction mechanism. Thus, according to the reaction mechanism (eq 1 and 2), *k* in eq 14 consists of the formation constant and the rate constants of the elementary reactions, i.e., the formation constant $K_{CT}$ of the CT complex, the rate constants $k_1$ and $k^{-1}$ for the electron transfer from BNAH to Q in the CT complex and the back reaction, respectively, and the proton-transfer rate constant $k_H$, as given by eq 15, where

$$k = K_{CT}k_H k_1/k_{-1} \; (= k_H K_{et}) \quad (15)$$

the rate constant for the electron transfer from BNA· to QH· following the proton transfer is not included since the electron transfer being highly exothermic (the redox potential of BNA· (–1.2 V vs. SCE)[27] is much more negative than the redox potentials of QH·[28]) may be very rapid.

From the temperature dependence of *k* in the case of *p*-chloranil measured at 298, 308, and 318 K, the observed activation enthalpy and entropy were determined as $\Delta H^{\ddagger}_{obsd}$ = 2.6 ± 0.4 kcal $mol^{-1}$ and $\Delta S^{\ddagger}_{obsd}$ = –(30 ± 3) cal $mol^{-1}$ $K^{-1}$, respectively. According to eq 15, $\Delta H^{\ddagger}_{obsd}$ and $\Delta S^{\ddagger}_{obsd}$ are given by eq 16 and 17, respectively, where $\Delta H_{CT}$

$$\Delta H^{\ddagger}_{obsd} = \Delta H_{CT} + \Delta H^{\ddagger}_{H^-} \quad (16)$$

$$\Delta S^{\ddagger}_{obsd} = \Delta S_{CT} + \Delta S^{\ddagger}_{H^-} \quad (17)$$

and $\Delta S_{CT}$ are the enthalpy and entropy of formation of the CT complex, respectively, and $\Delta H^{\ddagger}_{H^-}$ and $\Delta S^{\ddagger}_{H^-}$ are the activation parameters of the hydride equivalent transfer ($k_H k_1/k_{-1}$) in the CT complex. Then, the small $\Delta H^{\ddagger}_{obsd}$ and $\Delta S^{\ddagger}_{obsd}$ values described above are more consistent with the presence of the CT complex as an intermediate (eq 1 and 2) than a nonproductive complex lying off the

(25) (a) Iida, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2772. (b) Iida, Y. *Ibid.* **1971**, *44*, 1777.

(26) In the presence of excess BNAH, however, the radical anion $Q^{-}\cdot$ disappeared slowly.

(27) (a) Anderson, R. F. *Biochim. Biophys. Acta* **1980**, *590*, 277. (b) Farrington, J. A.; Land, E. J.; Swallow, A. J. *Ibid.* **1980**, *590*, 273. (c) Cunningham, A. J.; Underwood, A. L. *Biochemistry* **1967**, *6*, 266. (d) Hermolin, J.; Eisner, E. K.; Kosower, E. M. *J. Am. Chem. Soc.* **1981**, *103*, 1591.

(28) Dryhurst, G.; Kadish, K. M.; Scheller, F.; Renneberg, R. "Biological Electrochemistry"; Academic Press: New York, 1982, and references cited therein.

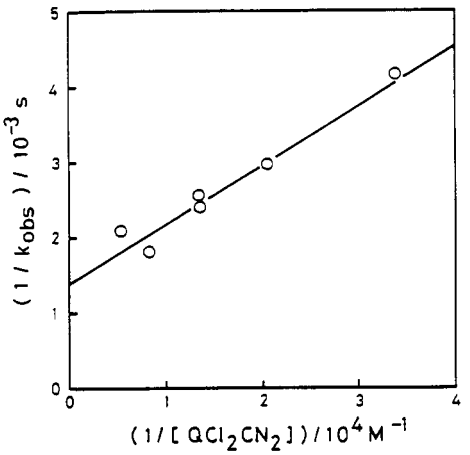


**Figure 6.** Plot of $1/k_{obsd}$ against $1/[QCl_2CN_2]$ for the reaction of BNAH with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone ($QCl_2CN_2$) in MeCN at 298 K. See eq 19 in text.

**Table II. Rate Constants $k$ (= $k_HK_{et}$) and the Primary Kinetic Isotope Effects $k_H/k_D$ for Hydride-Transfer Reactions from BNAH to *p*-Benzoquinone Derivatives Q in MeCN at 298 K and the Redox Potentials of Q, $E°(Q/Q^{-}·)$**

| no. | *p*-benzoquinone derivative | $E°(Q/Q^{-}·)$,[a] V | $k$,[b] $M^{-1}$ $s^{-1}$ | $k_H/k_D$[b] |
|---|---|---|---|---|
| 1 | 2,3-dichloro-5,6-dicyano-*p*-benzoquinone | 0.51 | $8.4 \times 10^6$ | 1.5 |
| 2 | 2,3-dicyano-*p*-benzoquinone | 0.28 | $7.2 \times 10^5$ | 2.6 |
| 3 | *p*-chloranil | 0.01 | $1.0 \times 10^3$ | 5.3 |
| 4 | *p*-bromanil | 0 | $7.3 \times 10^2$ | 5.2 |
| 5 | 2,6-dichloro-*p*-benzoquinone | −0.18 | $7.5 \times 10$ | 5.6 |
| 6 | 2,5-dichloro-*p*-benzoquinone | −0.18 | $5.0 \times 10$ | 5.5 |
| 7 | chloro-*p*-benzoquinone | −0.34 | 7.6 | 6.1 |
| 8 | *p*-benzoquinone | −0.50 | $1.3 \times 10^{-2}$ | 6.2 |
| 9 | methyl-*p*-benzoquinone | −0.58 | $2.3 \times 10^{-3}$ | 5.9 |
| 10 | 2,6-dimethyl-*p*-benzoquinone | −0.67 | $8.4 \times 10^{-5}$ | 5.6 |
| 11 | trimethyl-*p*-benzoquinone | −0.75 | $1.3 \times 10^{-5}$ | 5.6 |
| 12 | tetramethyl-*p*-benzoquinone | −0.84 | *c* | *c* |

[a] vs. SCE, taken from ref 18. [b] The experimental errors are within ±5%. [c] Too slow to be determined accurately.

reaction pathway, since both $\Delta H_{CT}$ and $\Delta S_{CT}$ in eq 16 and 17 would have negative values, resulting in lowering the $\Delta H^{\ddagger}_{obsd}$ and $\Delta S^{\ddagger}_{obsd}$ values, respectively.[29]

The $k$ (= $k_HK_{et}$) values for other *p*-benzoquinone derivatives in MeCN at 298 K have been determined under the conditions $K_{et}[Q] \ll 1$ in the presence of large excess Q. When a strong electron acceptor, i.e., 2,3-dichloro-5,6-dicyano-*p*-benzoquinone ($QCl_2CN_2$) is used as a substrate, however, $K_{et}$ has been too large to satisfy the conditions $K_{et}[QCl_2CN_2] \ll 1$. In such a case, from eq 10 the pseudo-first-order rate constant $k_{obsd}$ in the presence of large excess $QCl_2CN_2$ may be expressed by eq 18, which

$$k_{obsd} = \frac{k_HK_{et}[QCl_2CN_2]}{1 + K_{et}[QCl_2CN_2]} \quad (18)$$

$$\frac{1}{k_{obsd}} = \frac{1}{k_H} + \frac{1}{k_HK_{et}[QCl_2CN_2]} \quad (19)$$

is rearranged as eq 19. The validity of eq 19 is shown by the plot of $1/k_{obsd}$ against $1/[QCl_2CN_2]$, which gives a linear correlation between them (Figure 6). Then, the

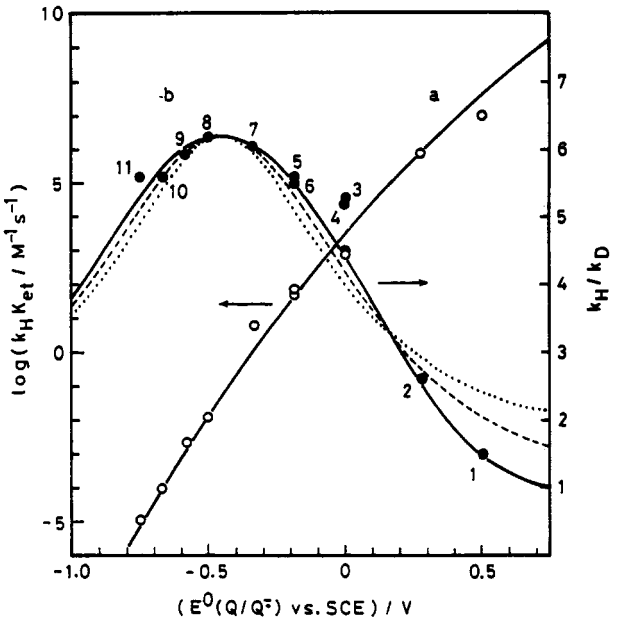


**Figure 7.** (a) Correlation between log $k_HK_{et}$ for the hydride equivalent transfer reactions from BNAH to a series of *p*-benzoquinone derivatives Q and the redox potential $E°(Q/Q^{-}·)$. The solid line is drawn by the simulation based on the reaction mechanism (eq 1 and 2) by using the free energy relationships for the electron transfer (eq 22) and the proton transfer (eq 23–26), see text. (b) Bell-shaped dependence of the primary kinetic isotope effect $k_H/k_D$ on the redox potential $E°(Q/Q^{-}·)$. The solid, dotted, and broken lines correspond to the simulations by the Marcus (eq 23–25), the Rehm–Weller (eq 28), and the Marcus–Levine (eq 29) formalism, respectively; see text. The numbers refer to *p*-benzoquinone derivatives in Table II.

$k_HK_{et}$ value in the case of $QCl_2CN_2$ can be obtained from the slope in Figure 6. The $k$ (= $k_HK_{et}$) values for the hydride equivalent transfer from BNAH to a series of *p*-benzoquinone derivatives Q in MeCN at 298 K are listed in Table II together with the redox potentials $E°(Q/Q^{-}·)$.[18] The values of $k_HK_{et}$ vary significantly with the redox potentials $E°(Q/Q^{-}·)$ and span more than $10^{11}$ from 2,3-dichloro-5,6-dicyano-*p*-benzoquinone which is the most reactive to tetramethyl-*p*-benzoquinone being the least reactive.[30]

The primary kinetic isotope effects for the hydride equivalent transfer have also been determined from the ratio of the rate constants $k$ of BNAH to BNAH-*4,4-d*$_2$,[31] which corresponds to the primary kinetic isotope effect $k_H/k_D$ for the proton transfer from $BNAH^{+}·$ to $Q^{-}·$ since there may be no isotope effect for the formation constant $K_{et}$ of the radical ion pair.[6] The $k_H/k_D$ values also are listed in Table II. The most significant result of the primary kinetic isotope effects is the wide variation of the $k_H/k_D$ values in the range from the smallest ($k_H/k_D$ = 1.5) with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone to the largest ($k_H/k_D$ = 6.2) with *p*-benzoquinone, the latter of which is close to the largest kinetic isotope effect reported so far for the reduction by NADH model compounds.[32]

**Simulation of the Dependences of $k$ and $k_H/k_D$ on $E°(Q/Q^{-}·)$ by the Marcus Formalism.** The logarithm

(29) Even negative values of the observed activation enthalpy in the range −1.6 to −3.1 kcal $mol^{-1}$ together with highly negative values of the observed activation entropy in the range −41 to −45 cal $mol^{-1}$ $K^{-1}$ have been reported for the Diels–Alder addition of tetracyanoethylene to 9,10-dimethylanthracene in various solvents, where a strong CT complex is formed between tetracyanoethylene and 9,10-dimethylanthracene as a reaction intermediate; Kiselev, V. D.; Miller, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 4036.

(30) The rate of the reaction of BNAH with tetramethyl-*p*-benzoquinone has been too slow to be determined accurately.

(31) The secondary α-deuterium isotope effects are assumed to be unity. Indeed, the secondary isotope effects determined from the rate constants $k_{HH}$ of BNAH, $k_{HD}$ of BNAH-*4-d*$_1$, and $k_{DD}$ of BNAH-*4,4-d*$_2$ for the reactions with *p*-chloranil, *p*-bromanil, and 2,6-dichloro-*p*-benzoquinone were 1.0 ± 0.1.

(32) The largest $k_H/k_D$ value reported so far for the reduction by an NADH model compound is 7.0: Ohno, A.; Yamamoto, H.; Oka, S. *Tetrahedron Lett.* **1979**, 4061.

of the rate constant $k$ (= $k_H K_{et}$) in Table II is plotted against the redox potential $E°(Q/Q^{-}·)$ in Figure 7a, where a smooth but somehow curved correlation between log $k_H K_{et}$ and $E°(Q/Q^{-}·)$ is observed. The primary kinetic isotope effect $k_H/k_D$ in Table II is also plotted against $E°(Q/Q^{-}·)$ in Figure 7b, where a bell-shaped dependence of $k_H/k_D$ on $E°(Q/Q^{-}·)$ is observed with a maximum value at $E°(Q/Q^{-}·) \simeq -0.45$ V vs. SCE. According to the reaction mechanism for the hydride equivalent transfer from BNAH to Q (eq 1 and 2), both dependences of log $k_H K_{et}$ and $k_H/k_D$ on $E°(Q/Q^{-}·)$ in Figure 7 can be simulated quantitatively as follows. We first analyze the dependence of log $K_{et}$ on $E°(Q/Q^{-}·)$, then the dependences of $k_H$ and $k_H/k_D$ on $E°(Q/Q^{-}·)$, and finally combine them to simulate both plots in Figure 7.

The log $K_{et}$ value is related to the free energy change for the formation of the radical ion pair $\Delta G_{et}$ (BNAH + Q → [$BNAH^{+}·$–$Q^{-}·$]) by eq 20, and $\Delta G_{et}$ is expressed in

$$\log K_{et} = -\Delta G_{et}/(2.3RT) \quad (20)$$

terms of the standard free energy change of the electron transfer $\Delta G°_{et}$ (BNAH + Q → $BNAH^{+}·$ + $Q^{-}·$) determined from eq 5 and the work term required to bring the products ($BNAH^{+}·$ and $Q^{-}·$) to their mean separation in the activated complex as shown by eq 21.[33,34] Then, by com-

$$\Delta G_{et} = \Delta G°_{et} + w_p \quad (21)$$

bining eq 5, 20, and 21, log $K_{et}$ is expressed as a linear function of $E°(Q/Q^{-}·)$ with the slope of $F/(2.3RT)$ which is equal to 16.9 at 298 K (eq 22), where $C_1$ is equal to

$$\log K_{et} = FE°(Q/Q^{-}·)/(2.3RT) + C_1 \quad (22)$$

$(-FE°(BNAH^{+}·/BNAH) - w_p)/(2.3RT)$, which is considered as a constant for the reaction of BNAH with each $p$-benzoquinone derivative. Since the log $K_{et}$ value in the case of 2,3-dichloro-5,6-dicyano-$p$-benzoquinone has been obtained as 4.3 from the plot in Figure 6 (eq 19) and the $E°(Q/Q^{-}·)$ value is 0.51 V,[18] the $C_1$ value in eq 22 is determined as −4.3.

On the other hand, the activation free energy for the proton transfer from $BNAH^{+}·$ to $Q^{-}·$ in the radical ion pair, $\Delta G^{‡}_H$, can be expressed as a function of the free energy change of the proton transfer in the radical ion pair $\Delta G$ by using the Marcus formalism (eq 23–25),[33,35] where $\Delta G^{‡}_{H0}$

$$\Delta G^{‡}_H = \Delta G^{‡}_{H0}[1 + (\Delta G/4\Delta G^{‡}_{H0})]^2$$

$$\text{when } -4\Delta G^{‡}_{H0} < \Delta G < 4\Delta G^{‡}_{H0} \quad (23)$$

$$\Delta G^{‡}_H \simeq 0$$

$$\text{when } \Delta G < -4\Delta G^{‡}_{H0} \quad (24)$$

$$\Delta G^{‡}_H \simeq \Delta G$$

$$\text{when } \Delta G > 4\Delta G^{‡}_{H0} \quad (25)$$

is the intrinsic barrier for the proton transfer which corresponds to the activation free energy within the radical ion pair [$BNZH^{+}·$–$Q^{-}·$] when $\Delta G = 0$. Since $\Delta G$ is equal to $2.3RT\Delta pK_a + w_{p'} - w_{r'}$ where $w_{p'}$ and $w_{r'}$ are the work terms required to bring the products and reactants to their mean separation in the activated complex, respectively,[33,35] and $\Delta pK_a = pK_a(BNAH^{+}·/BNA·) - pK_a(QH·/Q^{-}·)$, the $\Delta G$ value can be obtained from the $pK_a$ values of $BNAH^{+}·$ and semiquinone radicals QH·, if the $w_{p'} - w_{r'}$ value can be neglected. The $pK_a$ values of semiquinone radicals QH·[36] are linearly related to the $E°(Q/Q^{-}·)$ values of the corresponding quinones,[18] as shown in Figure 8. Then, $\Delta G$ ($\simeq 2.3RT\Delta pK_a$) may be linearly related to $E°(Q/Q^{-}·)$ with a proportional constant $\alpha$ as given by eq 26, where the

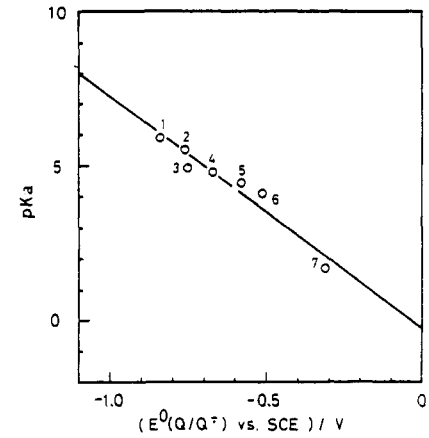


**Figure 8.** Correlation between $pK_a$ of semiquinone radicals[36] and the redox potentials $E°(Q/Q^{-}·)$ of the corresponding quinones;[18] (1) ubiquinone, (2) vitamin K, (3) trimethyl-$p$-benzoquinone, (4) 2,6-dimethyl-$p$-benzoquinone, (5) methyl-$p$-benzoquinone, (6) $p$-benzoquinone, (7) $o$-benzoquinone.

$$\Delta G = \alpha FE°(Q/Q^{-}·) + C_2 \quad (26)$$

constant $C_2$ can be determined, provided that the $\alpha$ value is given, since the $pK_a$ values of $BNAH^{+}·$ and semiquinone radical QH· are known as 3.6[10] and 4.1,[36] respectively, and the $E°(Q/Q^{-}·)$ value of $p$-benzoquinone is −0.50 V (Table II). Thus, the proton-transfer rate constant $k_H$ can be calculated as a function of $E°(Q/Q^{-}·)$ by using eq 23–26 if the $\Delta G^{‡}_{H0}$ and $\alpha$ values are given.[37]

Taken altogether, the $k_H K_{et}$ values have been calculated from eq 22–26 as a function of $E°(Q/Q^{-}·)$ by using the values of $\Delta G^{‡}_{H0}$ = 3.0 kcal $mol^{-1}$ and $\alpha$ = 0.58 as the best fit parameters. The result is shown by the solid line in Figure 7a, where the reasonable agreement of the caclulated curve with the experimental results shows the success of the present simulation by the Marcus formalism in predicting the curved dependence of log $k_H K_{et}$ on $E°$-$(Q/Q^{-}·)$. Although the choice of the parameters $\Delta G^{‡}_{H0}$ and $\alpha$ is somehow arbitrary, the $\Delta G^{‡}_{H0}$ value used in this study (3.0 kcal $mol^{-1}$) is typical in proton transfer reactions,[35,38] and the $\alpha$ value (0.58) shows a reasonable agreement with that found as the slope in Figure 8, which corresponds to $\alpha = 0.5 \pm 0.1$.

Since the rate constant $k$ corresponds to $k_H K_{et}$ under the conditions $K_{et}[Q]$ or $K_{et}[BNAH] \ll 1$ (eq 15), and no primary kinetic isotope effect is expected for the formation of the radical ion pair ($K_{et}$), the primary kinetic isotope effects $k_H/k_D$ observed for the hydride-transfer reactions from BNAH to Q may be ascribed to those for the proton transfer from $BNAH^{+}·$ to $Q^{-}·$ in the radical ion pair. In

(33) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.
(34) It should be noted that the work term $w_r$ required to bring the reactants to their mean separation in the activated complex is not involved in eq 21 since $\Delta G_{et} = \Delta G°_{et}' + w_{r'}$ where $\Delta G°_{et}'$ is the free energy change of electron transfer in the complex ([BNAH–Q] → [$BNAH^{+}$–$Q^{-}·$]) which is equal to $\Delta G°_{et} + w_p - w_r$ (ref 33).
(35) Kreevoy, M. M.; Oh, S. *J. Am. Chem. Soc.* **1973**, *95*, 4805.
(36) Patel, K. B.; Willson, R. L. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 814.
(37) The proton transfer in eq 2 ([$BNAH^{+}$–$Q^{-}·$] → [BNA–QH·]) is a unimolecular reaction and thereby the calculated value of $k_H$ [= $(\kappa T/h)\exp(-\Delta G^{‡}_H/RT)$] has a unit $s^{-1}$.
(38) (a) Bell, R. P. "The Proton in Chemistry"; Cornell University: Ithaca, New York, 1959; p 172. (b) Albery, W. J.; Campbell-Crawford, A. N.; Curran, J. S. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2206. (c) Ahrens, M. L.; Eigen, M.; Kruse, W.; Maass, G. *Chem. Ber.* **1970**, *74*, 380.

such a case, $k_H/k_D$ may be expressed as a function of the free energy change of the proton transfer $\Delta G$, using the Marcus formalism (eq 23–25), where $\Delta G^{\ddagger}_D$ can be calculated by substituting $\Delta G^{\ddagger}_{H0}$ by $\Delta G^{\ddagger}_{D0}$. Then, the maximum $k_H/k_D$ values may be given by eq 27 when $\Delta G = 0$.[39]

$$\left(\log \frac{k_H}{k_D}\right)_{max} = \frac{1}{2.3RT}(\Delta G^{\ddagger}_{D0} - \Delta G^{\ddagger}_{H0}) \quad (27)$$

It should be emphasized that indeed, the $k_H/k_D$ value reaches the maximum when $\Delta G$ ($\simeq 2.3RT\Delta pK_a$) = 0, since the $pK_a$(BNAH$^+$·/BNA·) value 3.6[10] corresponds to $E°$-(Q/Q$^-$·) = −0.49 ± 0.05 V in the plot (Figure 6), showing a reasonable agreement with the $E°$(Q/Q$^-$·) value −0.45 ± 0.05 V where the $k_H/k_D$ value reaches the maximum (Figure 7b). Thus, the maximum $k_H/k_D$ value (6.2) corresponds to exp[$(\Delta G^{\ddagger}_{D0} - \Delta G^{\ddagger}_{H0})/RT$] from eq 27 and thereby the $\Delta G^{\ddagger}_{D0} - \Delta G^{\ddagger}_{H0}$ value is obtained as 1.1 kcal mol$^{-1}$. By using the $\Delta G^{\ddagger}_{H0}$ and $\Delta G^{\ddagger}_{D0}$ values, the dependence of $k_H/k_D$ on $E°$(Q/Q$^-$·) has been calculated as shown by the solid line in Figure 7b, which agrees well with the experimental plot. It should be noted that this is the first clear "Westheimer maximum" observed for the hydride equivalent transfer reactions of NADH model compounds.[40]

The use of other free energy relationships such as the Rehm–Weller (eq 28)[41] and the Marcus–Levine (eq 29)[33,42]

$$\Delta G^{\ddagger}_H = (\Delta G/2) + [(\Delta G/2)^2 + (\Delta G^{\ddagger}_{H0})^2]^{1/2} \quad (28)$$

$$\Delta G^{\ddagger}_H = \Delta G + \frac{\Delta G^{\ddagger}_{H0}}{\ln 2} \ln[1 + \exp(-\Delta G \ln 2/\Delta G^{\ddagger}_{H0})] \quad (29)$$

formalisms gives essentially the same results for the log $k_HK_{et}$ dependence on $E°$(Q/Q$^-$·) by using the same parameters as those used for the Marcus formalism. The $k_H/k_D$ dependence on $E°$(Q/Q$^-$·) calculated from the Rehm–Weller (eq 28) and the Marcus–Levine (eq 29) formalisms also are shown by the dotted and broken lines, respectively, in Figure 7b. The Marcus formalism (solid line in Figure 7b) seems to give the best fit to simulate the $k_H/k_D$ dependence on $E°$(Q/Q$^-$·).

Thus, the simulation to the dependences of both log $k_HK_{et}$ and $k_H/k_D$ on $E°$(Q/Q$^-$·) for the hydride equivalent transfer from BNAH to Q based on the sequential electron–proton–electron transfer via the CT complex (eq 1 and 2) has been successful by utilizing the Marcus formalism for the proton-transfer step. Nonetheless, one-step hydride-transfer mechanism without any intermediate except for the CT complex for the reduction by NADH and its model compounds seem to be well established.[1,43] In the next section, we clarify the confusion concerning one-step vs. multistep mechanisms for the hydride-transfer reactions.

**One-Step vs. Multistep Mechanisms for the Hydride Transfer.** For most p-benzoquinone derivatives used as substrates in this study except for the strong electron acceptors 2,3-dichloro-5,6-dicyano-p-benzoquinone ($QCl_2CN_2$) and 2,3-dicyano-p-benzoquinone ($QCN_2$), the formation constants of the radical ion pair $K_{et}$ are much smaller than 0.1 M$^{-1}$ (eq 22). The equilibrium constant $K_{diff}$ for the formation of the encounter complex with a distance $a = 5 \times 10^{-8}$ cm has been estimated to be 0.32 M$^{-1}$.[44] Thus, the radical ion pair with much smaller formation constants than the encounter complex may have little chance, if any, to be detected by physical or chemical methods. As such, the hydride equivalent transfer from BNAH to the p-benzoquinone derivatives used in this study except for $QCl_2CN_2$ and $QCN_2$ may well be regarded as one-step process from the CT complexes. By the same token, it may well be understood that a number of efforts to trap the reaction intermediates in hydride-transfer reactions from NADH and its model compounds to substrates which have low reactivities has been unsuccessful.[1,43] In these cases, the radical ion pair may be better described as a continuous spectrum between an "intermediate" and a "transition state", depending on the lifetime of the radical ion pair. In one extreme case when a strong electron acceptor $QCl_2CN_2$ is used as a substrate, however, the radical ion pair [BNAH$^+$·–$QCl_2CN_2^-$·] becomes a distinctive "intermediate", since the formation constant log $K_{et}$ (4.3) of the radical ion pair is large enough to be determined as shown by the plot of eq 19 in Figure 6.

## Summary and Conclusions

The reaction mechanism (eq 1–4) for the reduction of a series of p-benzoquinone derivatives Q by an NADH model compound BNAH has been verified by various experimental results, i.e., the isolation of the CT complexes formed between BNAH and Q as reaction intermediates, the product analysis, the stoichiometry of the reaction, the kinetics, and the kinetic deuterium isotope effect. Especially, the dependence of both the rate constant $k$ ($= k_HK_{et}$) and the kinetic isotope effect $k_H/k_D$ for the hydride equivalent transfer from BNAH to Q (eq 14) on $E°$(Q/Q$^-$·) has successfully been simulated quantitatively for the first time on the basis of the reaction mechanism (eq 1 and 2) by using the free energy relationships for the electron transfer (eq 22) and the proton transfer (eq 23–27). With regard to the controversy concerning hydride-transfer reactions from NADH and its model compounds to substrates being whether one-step or multistep,[1-3,43] such a distinction may simply depend on the lifetime of the radical ion pair in the reaction mechanism (eq 1 and 2) and thus a continuous spectrum between one-step and multistep may be most probable for the hydride equivalent transfer from the NADH model compound to a series of substrates, in agreement with the theoretical prediction based on the orbital interactions for many NADH–substrate systems.[45]

## Experimental Section

**Materials.** 1-Benzyl-1,4-dihydronicotinamide (BNAH) and the monodeuteriated compound (BNAH-4-$d_1$) were prepared according to the literatures.[46] Dideuteriated BNAH (BNAH-4,4-$d_2$) was prepared from BNAH-4-$d_1$ by three cycles of oxidation with p-chloranil in dimethylformamide and reduction with di-

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thionite in deuterium oxide.[47] The deuterium content of BNAH-*4,4*-$d_2$ was determined as 96% by using a Japan Electron Optics JNM-PS-100 $^1$H NMR spectrometer (100 MHz). Most *p*-benzoquinone derivatives (*p*-chloranil, *p*-bromanil, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, 2,6-dichloro-*p*-benzoquinone, 2,5-dichloro-*p*-benzoquinone, *p*-benzoquinone, methyl-*p*-benzoquinone, 2,6-dimethyl-*p*-benzoquinone, and tetramethyl-*p*-benzoquinone) were obtained commercially and purified by the standard methods.[48] Chloro-*p*-benzoquinone, 2,3-dicyano-*p*-benzoquinone, and trimethyl-*p*-benzoquinone were prepared from the corresponding hydroquinones according to the literatures.[49] Acetonitrile was purified and dried with calcium hydride by the standard procedure.[48]

**BNAH–Q Complexes.** Upon mixing a benzene or toluene solution of BNAH (0.28 mmol in 30 mL) with that of *p*-bromanil (0.41 mmol in 30 mL) under nitrogen atmosphere, a green precipitate appeared immediately. After being collected by filtration, it was identified as a 1:1 complex of BNAH with *p*-bromanil. Anal. Calcd for $C_{19}H_{14}N_2O_3Br_4$: C, 35.77; H, 2.21; N, 4.39. Found: C, 35.87; H, 2.28; N, 4.40. Other BNAH–Q complexes also were isolated similarly. Representative results for the elemental analyses are given as follows. BNAH–*p*-chloranil: Anal. Calcd for $C_{19}H_{14}N_2O_3Cl_4$: C, 49.60; H, 3.07; N, 6.09. Found: C, 49.30; H, 3.01; N, 5.81. BNAH–2,3-dichloro-5,6-dicyano-*p*-benzoquinone: Anal. Calcd for $C_{21}H_{14}N_4O_3Cl_2$: C, 57.16; H, 3.20; N, 12.70. Found: C, 57.42; H, 3.43; N, 12.01. BNAH–2,6-dichloro-*p*-benzoquinone: Anal. Calcd for $C_{19}H_{16}N_2O_3Cl_2$: C, 58.33; H, 4.12; N, 7.16. Found: C, 58.36; H, 4.09; N, 6.67. BNAH–chloro-*p*-benzoquinone: Anal. Calcd for $C_{19}H_{17}N_2O_3Cl$: C, 63.96; H, 4.80; N, 7.85. Found: C, 63.00; H, 4.62; N, 8.42. These BNAH–Q complexes are hygroscopic and the samples were kept under deaerated conditions. They have not been subject to recrystallization since they are sparingly soluble in most nonpolar or less polar solvents (carbon tetrachloride, benzene, toluene, chloroform, and methylene chloride). In addition, they are unstable in polar solvents such as acetonitrile (MeCN) and methanol (MeOH). Electronic reflectance spectra of the BNAH–Q complexes were measured with a Hitachi 340 spectrophotometer equipped with a Hitachi NIR (near IR) or R-10A (UV and visible) integrating sphere unit. Infrared spectra (KBr pellet) were recorded on a Hitachi 215 spectrophotometer.

**ESR Measurements.** ESR spectra were measured with a JEOL *X*-band spectrometer (JES-ME-2X). Spin concentrations in the BNAH–Q complexes were determined by comparing the doubly integrated area of the ESR spectra with that of a standard 1,1-diphenyl-2-picrylhydrazyl (DPPH) in benzene.[50] Experimental error in the determination of spin concentrations by this method is about ±20%. The *g* values of the ESR spectra were calibrated by using an $Mn^{2+}$ ESR marker. The formation of *p*-benzosemiquinone radical anions during the reactions of BNAH with some *p*-benzoquinone, derivatives (2,3-dichloro-5,6-dicyano-*p*-benzoquinone, 2,6-dichloro-*p*-benzoquinone, 2,5-dichloro-*p*-benzoquinone) in MeCN were confirmed from the ESR measurements by using a JEOL JES-SM-1 sample mixing apparatus. The minimum dead time for the measurements was 15 ms.

**Kinetic Measurements.** Kinetic measurements were carried out by using a Union RA-103 stopped flow spectrophotometer for the fast reactions of BNAH, BNAH-*4*-$d_1$, and BNAH-*4,4*-$d_2$ with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, 2,3-dicyano-*p*-benzoquinone, *p*-chloranil, *p*-bromanil, 2,6-dichloro-*p*-benzoquinone, 2,5-dichloro-*p*-benzoquinone, and chloro-*p*-benzoquinone in MeCN at 298 K under deaerated conditions. Reaction rates were followed by the rise of absorbances at the absorption maxima of the respective radical anions[25] under the pseudo-first-order condition by using more than 10-fold excess BNAH or Q. Pseudo-first-order rate constants were determined by the least-squares curve fit, using a microcomputer Union System 77.

Kinetic measurements for the slower reactions of BNAH, BNAH-*4*-$d_1$, and BNAH-*4,4*-$d_2$ with *p*-benzoquinone, methyl-*p*-benzoquinone, 2,6-dimethyl-*p*-benzoquinone, and trimethyl-*p*-benzoquinone were performed by using a Schlenk tube equipped with two side arms, one of which is fused to a square quartz cuvette (1 cm i.d.). After the reactant solutions in the separate arms of a Schlenk tube were thoroughly degassed in vacuum by the successive freeze–pump–thaw cycles, the solutions were mixed and transferred into the quartz cuvette which was placed in the thermostated compartment of a Union SM-401 spectrophotometer. Initial rates of the formation of the respective radical anions of *p*-benzoquinone derivatives were determined by monitoring the rise of absorbances at the absorption maxima of the radical anions[36] in order to avoid the effect of the decay of the radical anions. In the presence of 0.10 mol dm$^{-3}$ *n*-$Bu_4NClO_4$, the radical anions disappeared and the hydride transfer from BNAH to *p*-benzoquinone derivatives was irreversible.

**Registry No.** 1, 84-58-2; 1·BNAH complex, 91238-36-7; 2, 4622-04-2; 3, 118-75-2; 3·BNAH complex, 83824-39-9; 4, 488-48-2; 4·BNAH complex, 91238-37-8; 5, 697-91-6; 5·BNAH complex, 91238-38-9; 6, 615-93-0; 7, 695-99-8; 7·BNAH complex, 91238-39-0; 8, 106-51-4; 8·BNAH complex, 91238-40-3; 9, 553-97-9; 9·BNAH complex, 91238-41-4; 10, 527-61-7; 11, 935-92-2; 12, 527-17-3; 12·BNAH complex, 91238-42-5; BNAH, 952-92-1; deuterium, 7782-39-0.

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