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Kinetic Studies on the Reduction of 1-Benzyl-3-cyanoquinolinium Cations by Sodium Borohydride and the Applicability of Marcus Theory

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The reduction of a series of 1-substituted benzyl-3-cyanoquinolinium ions (*p*-CH$_3$, H, *p*-Br, *m*-F, *p*-CN) by sodium borohydride has been investigated. In all cases the products from these reactions were found to be 1,2-dihydroquinolines over 82% yields. Rates of reduction were measured in basic condition and in solvent system consisting of 4 parts of isopropyl alcohol and 1 part of water by volume. Second order rate constants were obtained for these reactions. When the ratio of [OH$^-$] to [BH$_4^-$] becomes large the observed rate constants (k_{obs}) decrease by a small factor. Reaction scheme and rate law are discussed. Brønsted α ($= \frac{d \ln k}{d \ln K}$) obtained by using the value of equilibrium constant K, which was obtained previously, was not 0. Instead, a value of 0.36 was obtained which indicated that the reduction by borohydride was structure-dependent according to the Marcus formalism even though the reaction rate was close to the diffusion limit.

Introduction

Sodium borohydride (NaBH$_4$) has been commonly employed as a mild reducing agent for organic synthesis[1-3]. Yet the kinetic study of the reaction of NaBH$_4$ (BH$_4^-$) is rarely investigated. It seems that NaBH$_4$ is not a suitable substrate for kinetics because of its much hygroscopic property which makes it very difficult to weigh quantitatively. In addition, reactions with BH$_4^-$ usually take place too fast to be monitored by conventional methods. In present paper we report the reduction of 1-substituted benzyl-3-cyanoquinolinium ion (Q$^+$, 1) by BH$_4^-$ as shown in eq. (1), which was conducted in NaOH solution.

It is generally considered that the hydride transfer step is the rate determining for the hydride transfer reaction.

(1)
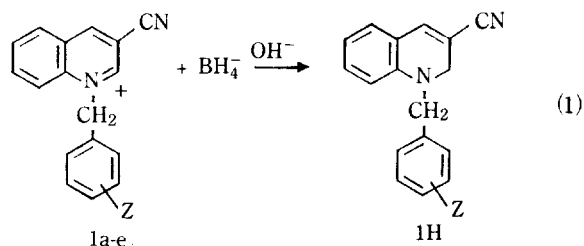
a, *p*-CH$_3$. b, H. c, *p*-Br. d, *m*-F. e, *p*-CN.

However, the rate determining step in the present system is in question according to the result of k_{obs} vs. [OH$^-$]/[BH$_4^-$] and it will be discussed in detail. Marcus theory[5-7] is applied to the present system in which two reactants have opposite charges.

Experimental

Compounds **1a-e** are known substances which were prepared by addition reaction of 3-cyanoquinoline with corresponding benzyl bromides at about 120°C and identified by their physical and spectroscopic properties[8]. In neutral or acidic solution both reactions of BH$_4^-$ with H$^+$ and with 1 are extremely rapid so it would be very difficult to measure the rate of the reaction of 1 with BH$_4^-$. For this reason 4.4 M-NaBH$_4$ dissolved in 14 N-NaOH solution (purchased from Alfa Chemical Co.) was used for the kinetic measurements and they were all made in basic solutions because such solutions are stable[9]. Thus, the BH$_4^-$ concentration was directly proportional to the OH$^-$ concentration in most of the reaction mixtures. However, some experiments were performed with added NaOH to deconvolute the effect due to the ratio of these two concentrations.

The major reaction product (82%) was 1,2-dihydroquinoline (**1H**) which has an absorption at 415 nm, the longest wavelength observed among dihydroquinolines. The remain-

Table 1. Rate Constants for the Reaction of NaBH₄ with 1b in NaOH Solution

[BH₄⁻], M	[OH⁻], M	k_{obs}, s⁻¹	k_2, M⁻¹s⁻¹[a]
3.69×10^{-2}	1.27×10^{-1}	6.85×10^{-5}	1.36×10^{7}
1.19×10^{-2}	3.89×10^{-2}	6.83×10^{-5}	1.37×10^{7}
3.96×10^{-3}	1.37×10^{-2}	6.64×10^{-5}	1.41×10^{7}
3.96×10^{-3}	2.66×10^{-2}	4.41×10^{-5}	1.82×10^{7}
3.96×10^{-3}	8.33×10^{-2}	2.00×10^{-5}	2.58×10^{7}
3.96×10^{-3}	1.28×10^{-1}	1.23×10^{-5}	2.44×10^{7}

[a] Obtained from eq. (6).

$$1 + R'OH \underset{}{\overset{K_a^*}{\rightleftharpoons}} 2 + H^+ \tag{2}$$

R' = iPr or H (major)

2
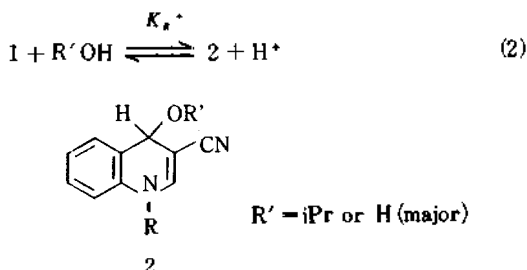
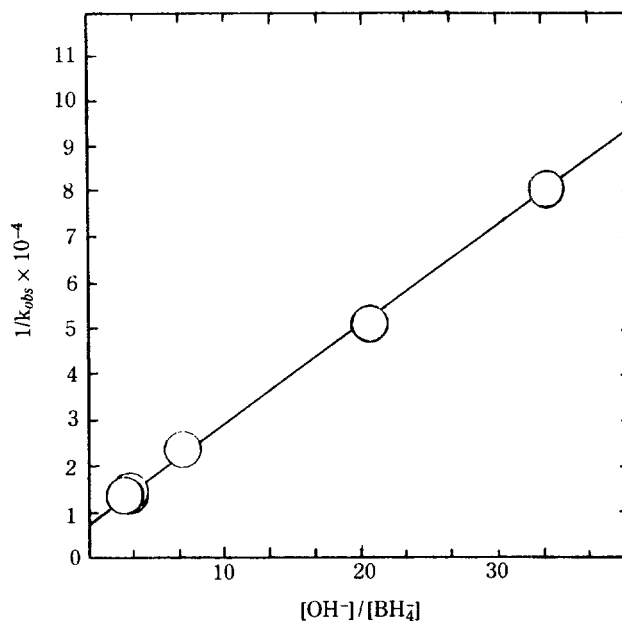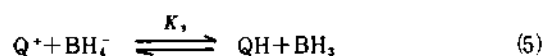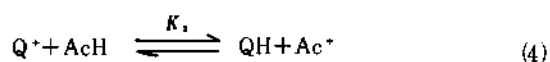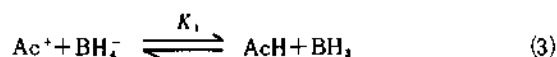ing product appeared to be the 1,4-dihydroquinolines as judged by the product spectra.

The observed rate constants (k_{obs}) were measured spectrophotometrically in a solvent containing 4 parts of isopropyl alcohol (iPrOH) and 1 part of water by volume at 25°C. The values of k_{obs}, pseudo-first-order rate constants, were obtained by the conventional way where the concentration of BH₄⁻ was always in excess by at least a factor of 20.

Results

The value of k_{obs} was obtained by monitoring the concentration of the 1,2-dihydroquinoline products. The observed reaction rates for 1b at various NaBH₄ and NaOH concentrations are shown in Table 1. The plot of $1/k_{obs}$ vs. $[OH^-]/[BH_4^-]$ is shown in Fugure 1. The rate constants k_2 for other variants of 1 obtained according to eq. (6) are shown in Table II. Equilibrium constants for the reaction of 1 with BH₄⁻ are needed in order to get the Brønsted α $(= \dfrac{d \ln k}{d \ln K})$ in Marcus formalism[7]. Since the reverse reaction of the present system is hard to measure the equilibrium constant (K_2) for the reaction of 1 with 10-methylacridan (AcH) can be used for the substitution by the following reason.

As shown in eqs. (3)-(5) equilibrium constant K_3 for the reaction of 1 with BH₄⁻ is directly proportional to K_2 for the reaction of 1 with 10-methylacridan (AcH, eq. (4)), which was reported previously[a], because K_3 can be obtained by multiplying K_1 by K_2.

$$Ac^+ + BH_4^- \underset{}{\overset{K_1}{\rightleftharpoons}} AcH + BH_3 \tag{3}$$

$$Q^+ + AcH \underset{}{\overset{K_2}{\rightleftharpoons}} QH + Ac^+ \tag{4}$$

$$Q^+ + BH_4^- \underset{}{\overset{K_3}{\rightleftharpoons}} QH + BH_3 \tag{5}$$

Figure 1. $1/k_{obs}$ vs. $[OH^-]/[BH_4^-]$ for the reaction of 1b.

Table 2. Rate Constants (k_2) for the Reaction between NaBH₄ and 1

Q⁺	k_{obs}, s⁻¹	k_2, M⁻¹s⁻¹[a]	$\ln k_2$
1a	$7.73(\pm 0.12) \times 10^{-5}$	$1.22(\pm 0.07) \times 10^{7}$	16.31
1b	$6.64(\pm 0.10) \times 10^{-5}$	$1.41(\pm 0.08) \times 10^{7}$	16.46
1c	$5.39(\pm 0.02) \times 10^{-5}$	$2.32(\pm 0.03) \times 10^{7}$	16.96
1d	$3.53(\pm 0.03) \times 10^{-5}$	$1.70(\pm 0.05) \times 10^{7}$	16.65
1e	$2.49(\pm 0.05) \times 10^{-5}$	$2.57(\pm 0.19) \times 10^{7}$	17.06

[a] Obtained from eq. (6).

Table 3. Equilibrium Constants for Eq. (4) and Eq. (2)

Q⁺	$K_2^{a,b}$ ($\ln K_2$)		$10^4 K_F +^b$ ($pK_R +$)	
1a	15.8	(2.76)	3.63	(5.44)
1b	22.2	(3.10)	4.90	(5.31)
1c	40.5	(3.70)	10.00	(5.00)
1d	45.9	(3.83)	11.20	(4.95)
1e	83.3	(4.42)	24.00	(4.62)

[a] Dimensionless. [b] Taken from ref. 8.

Equilibrium constants K_2 and K_R+ for 1 are shown in Table 3. Noting that the step for the reduction of 1 by BH₄⁻ may not be completely rate determining, eq. (8) was obtained using a steady-state approximation ($dQ^*/dt \approx 0$). In order to get k_2, k_{-1} should be known. These values were estimated from the data of Bunting, et al.[10] which were related to the present work. They are shown in Table 4 and in Figure 2. The rate constants (k_2) obtained according to eq. (8) are shown in Table 5 and the correlation with $\ln k$ taken from Table 3 is shown in Figure 2. The slope is 0.36. Comparison of the values in Table 5 with those in Table 2 as well as the effect of NaOH on k_2 (Table 2) shows that the reduction of 1 by BH₄⁻ is not, in fact, completely rate limiting.

Table 4. Rate Constants for Pseudo Base (2) Fromation from 1

Q^+	k_{OH^-}, $M^{-1}s^{-1a}$	log k_{OH^-}
1a	3.02×10^7	7.48
1b	3.47×10^7	7.54
1c	4.90×10^7	7.69
1d	5.13×10^7	7.71
1e	7.41×10^7	7.89

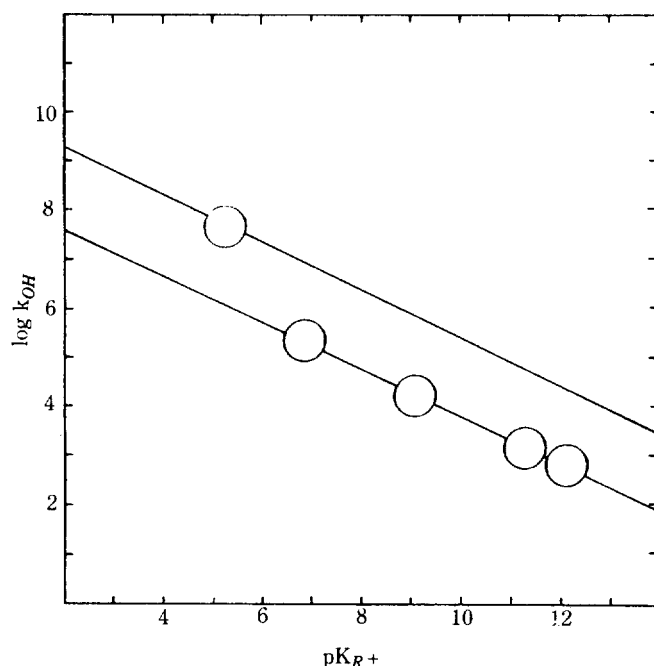[a] Taken by the extrapolation of plot ($pK_R +$ vs.k_{OH^-}) from Table 3 in ref. 10.

Figure 2. Correlation of log k_{OH^-} with $pK_R +$ for the reactions of OH⁻ with 3-substituted-1-methylquinolinium ions (lower line) and with **1b** (upper line). The upper line was made under assumption that variants of **1** have the same trend.
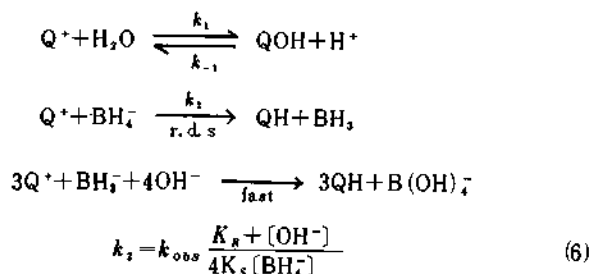
Discussion

The reaction between $NaBH_4$ and **1** in basic solution results in the reduction of **1** to mostly 1-substituted benzyl-3-cyano-1,2-dihydroquinoline (**1H**) as shown in eq. (1). **1H** has an absorption maximum at longer wavelength (415 nm) than its isomer, 1,4-dihydroquinoline (329 nm). It is of interest to note that the reduction of varients of **1** by 10-methylacridan[9] or 5-deazaflavin[11] gave 1,4-dihydroquinolines, while 1,2-isomers (**1H**) were produced by BH_4^-. When the reaction was conducted in the basic solution solvent played a role as a nucleophile giving the adduct **2**. Although the concentration of **1** maintained at equilibrium (Scheme 1) was very small because the pH is far above the $pK_R +$, the reduction of it by BH_4^- took place anyway. However, the reaction rate was reduced greatly and was easily monitored. As soon as BH_3 is liberated, it reacts immediately with solvent (OH⁻ here) to generate BH_3OH^-, followed by consecutive reduction of Q^+ (**1**) until the three hydrides in BH_3OH^- are consumed[12]. A possible kinetic scheme is shown in Scheme 1.

Table 5. k_2 for Hydride Transfer between $NaBH_4$ and 1

Q^+	k_2, $M^{-1}s^{-1a}$	ln k_2
1a	2.28×10^7	16.94
1b	2.65×10^7	17.09
1c	5.12×10^7	17.75
1d	2.75×10^7	17.13
1e	4.30×10^7	17.58

[a] Obtained from eq. (8) using k_{-1} in Table 4.

$$Q^+ + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} QOH + H^+$$

$$Q^+ + BH_4^- \xrightarrow[r.d.s]{k_2} QH + BH_3$$

$$3Q^+ + BH_3^- + 4OH^- \xrightarrow[fast]{} 3QH + B(OH)_4^-$$

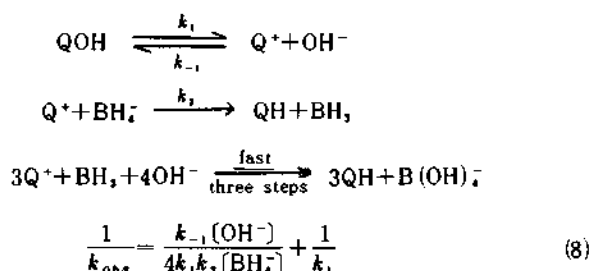$$k_2 = k_{obs} \frac{K_R + [OH^-]}{4K_s [BH_4^-]} \tag{6}$$

Scheme 1

If the first step is in a fast equilibrium ($K_R +$) and the second step is the rate determining step and the third is fast, the second-order rate constant is given by eq. (6). In eq. (6), K_s is the autoprotolysis constant of the mixed solvent as shown in eq. (7). K_s has not been measured, but it was assumed equal to the autoprotolysis constant (2×10^{-17}) for pure methanol[13] which is a similar hydroxylic solvent of nearly equal dielectric constant. ϵ is 33 for methanol and for $iPrOH-H_2O$ (4:1)[13].

$$Solvent \overset{K_s}{\rightleftharpoons} OH^- + H^+$$

$$K_s = [OH^-][H^+] \tag{7}$$
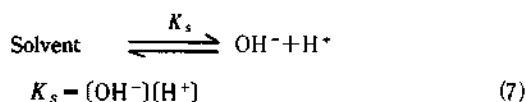
The derivation of eq. (6) and its symbols are shown in Appendix 1. The observed values of k_{obs} for **1b** are shown in Table 1 as a function of the ratio, $[OH^-]/[BH_4^-]$. The plot of $1/k_{obs}$ vs. $[OH^-]/[BH_4^-]$ from eq. (6) is shown in Figure 1. According to eq. (6) the slope in Figure 1 should pass the zero point, but in fact, it does not. As a result, the apparent values of k_2 given by eq. (6) increase with the ratios. These results show that Scheme 1 is invalid as it stands. They suggest that, the [Q^+] is below that required by Scheme 1. Therefore, the simplest modification is to remove the assumption that the first step is fast compared to the second. A similar conclusion has been reached by Bunton and coworkers[4]. With this notion Scheme 2 can be written.

$$QOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Q^+ + OH^-$$

$$Q^+ + BH_4^- \xrightarrow{k_2} QH + BH_3$$

$$3Q^+ + BH_3^- + 4OH^- \underset{three\ steps}{\overset{fast}{\rightleftharpoons}} 3QH + B(OH)_4^-$$

$$\frac{1}{k_{obs}} = \frac{k_{-1}[OH^-]}{4k_1 k_2 [BH_4^-]} + \frac{1}{k_1} \tag{8}$$
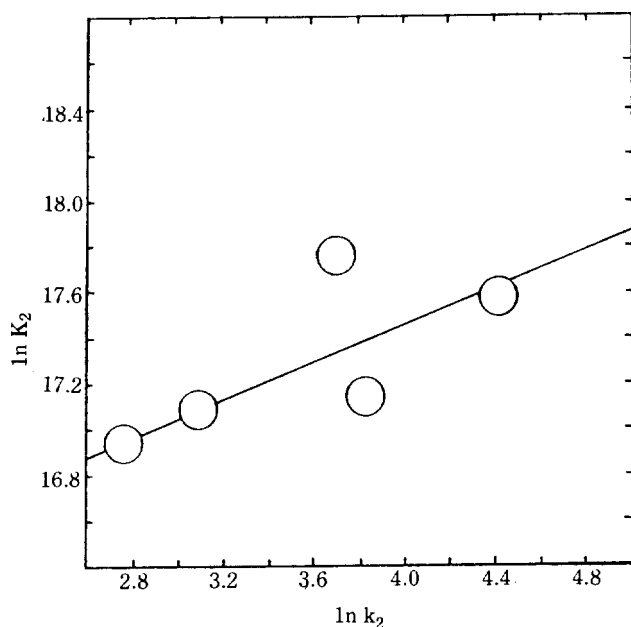
Scheme 2

Figure 3. Correlation of $\ln k_2$ with $\ln K_2$. k_2 was obtained by eq. (8) with aid of ref. 10.

In Scheme 2, $Q^*(1)$ is an intermediate. Using a steady state approximation for the concentration of Q^* and an assumption that the third step is fast as described in Scheme 1, eq. (8) is obtained. The detailed calculations are shown in Appendix 2. In eq. (8) the slope of the plot ($1/k_{obs}$ vs. $[OH^-]/[BH_4^-]$) is k_{-1}/k_1k_2 and the intercept is $1/k_1$. And k_{-1}/k_1 can be replaced by $K_R + /K_s$ as shown in eqs. (9), (10) and (7).

From Scheme 2

$$\frac{k_{-1}}{k_1} = \frac{[QOH]}{[Q^+][OH^-]} \tag{9}$$

From eq. (2)

$$K_R^+ = \frac{[QOH][H^+]}{[Q^+]} \tag{10}$$

Using the points from Figure 1 one can obtain the slope and from it k_2, k_1, and k_{-1}. The values are 2.65×10^7, 1.42×10^{-4}, and 3.47×10^7, respectively.

Bunting and Fitzgerald have investigated the kinetics of pseudo-base formation for 3-substituted-1-methylquinolinium cations[10]. The correlation of the second order rate constants (k_{-1}) for the OH^- addition to quinolinium ions with $pK_R +$ showed a good linear relation with a slope of 0.47 as shown in Figure 2. The other values of k_{-1} for the addition of OH^- to variants of **1** have been obtained by assuming that they have the same trend as 3-substituted-1-methylquinolinium ions. When the assumed values (k_{-1}) obtained by the extrapolation, as shown in Table 4, were used in eq. (8), the value of k_2 could be calculated, and these are listed in Table 5. These values (k_2) are larger than the values in Table 2 by a factor of 2 and are correlated with $\ln K_2$, taken from Table 3, to give a Brønsted α of 0.36.

In Marcus formalism the Brønsted α can be expressed in eq. (11).

$$\alpha = -\frac{1}{RT}\left(\frac{d\,W^r}{d\,\ln K}\right) + \frac{1}{2}(\tau - 1) + b - \frac{RT}{2\lambda}\ln K \tag{11}$$

where $b = \frac{1}{2} + \frac{W^p - W^r}{2\lambda}$

Each term in the eq. (11) can be defined as follows: the first term is due to the structure-sensitivity of W^r; the second is the perpendicular effect[8]; the third and the fourth terms together give the Leffer-Hammond effect since χ is $b - \frac{kT}{2\lambda}$ $\ln K$ when the simplifying assumption ($W^r = W^p$) is removed[8]. The derivation of eq. (11) and its symbols are shown in Appendix 3.

The most important outcome from the present system is that the Brønsted α is not close to 0 but is a significant number. This indicates that the reduction by BH_4^- is structure-dependent. In eq. (11) the value of the second term is reported previously as -0.12 and the value of χ is expected to be very small because the reaction rate (k_2) is close to the diffusion limit. It also strongly suggests that the terms in eq. (11) related to W^r and their variation with structure are significant. At the present time α can not be dissected into its structure-related terms (eq. (11)). However, it may be possible to do so by studying complex formation with analogue of BH_4^- such as I^-.

It is worth noting that the symmetrical complex of BH_4^- with BH_3 ($B_2H_7^-$) has been considered to be more stable than its fragments[14]. This complex is the analogue of the transition state for symmetrical transfer of H^- between BH_3 units. As a result, intrinsic barrier, λ_{22} for borohydride may be negative and λ_{12} for the present system will be much smaller than λ_{11} for quinolinium ions (1). As far as W^r is concerned, it would negative because of oppositely charged reactants leading to ion pair formation[4]. Both of these factors probably contribute to the very high reactivity of BH_4^- with quinolinium ions.

Appendix I

From Scheme 1,

$$K_R^+ = \frac{[QOH][H^+]}{[Q^+]} \tag{1-1}$$

where $[QOH] \cong [Q^+]_{st}$ because $pH \gg pK_R +$; $[OH^-] \geqslant 1 \times 10^{-2}$ M. Then,

$$[Q^+] = \frac{[Q^+]_{st}[H^+]}{K_R^+}$$

Here, $[H^+]$ is for the solvent studied.
Eq. (1-1) can be rewritten as eq. (1-2).

$$[Q^+] = \frac{[Q^+]_{st}K_s}{K_R^+[OH^-]} \tag{1-2}$$

$$\frac{d\,[QH]}{dt} = 4k_2[Q^+][BH_4^-] \tag{1-3}$$

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Substitution of eq. (1-2) into eq. (1-3) yields eq. (6).

Appendix 2

From Scheme II,

$$\frac{d [Q^+]}{dt} = 0 = k_1 [QOH] - k_{-1} [Q^+][OH^-] - 4k_2 [BH_1^-][Q^+]$$
(2-1)

$$[Q^+] = \frac{k_1 [QOH]}{k_{-1}[OH^-] + 4k_2 [BH^-]}$$
(2-2)

where $[QOH] \cong [Q^+]_{sr}$.

$$\frac{d [QH]}{dt} = 4k_2 [Q^+][BH_1^-]$$
(2-3)

Substitution of eq. (2-2) into eq. (2-3) yields eq. (8).

Appendix 3

$$\Delta G^* = W^r + (1 + \frac{\Delta G^\circ + C}{\lambda})^2 \frac{\lambda}{4}$$
(3-1)

where $C = W^p - W^r$

$$\Delta G^* = RT (\ln \frac{kT}{h} - \ln k)$$
(3-2)

and $\quad \Delta G^\circ = - RT \ln K$
(3-3)

With substitution of eqs. (3-2) and (3-3) into eq. (3-1) ΔG^* is converted to ln k.

$$\ln k = - \frac{1}{RT} (W^r + \frac{\lambda}{4} + \frac{C}{2} + \frac{C^2}{4\lambda}) + \ln \frac{kT}{h}$$
$$+ (\frac{1}{2} + \frac{C}{2\lambda}) \ln K - \frac{RT}{4\lambda} (\ln K)^2$$
(3-4)

$$\ln k = a + b (\ln K) + c (\ln K)^2$$
(3-5)

Coefficients a, b, and c in eq. (3-5) can be obtained from eq. (3-4).

Differentiation of ln k, from eq. (3-5) and coefficients a, b, and c by ln K gives eq. (11), where

$$\frac{d \lambda}{d \ln K} = - 2RT (\tau - 1)$$

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Study of Diffusion-Controlled Processes. Potential Shape Dependence in One-dimension

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The Smoluchowski equations with a linear and a parabolic potentials in one-dimensional case are solved for the reflecting boundary condition. Analytic expressions for the long-time behaviors of the remaining probabilities are obtained. These results, together with the previous result for a step potential, show the dependence of the desorption process on the form of potential. The effect of the radiation boundary condition is also investigated for three types of potentials.

Introduction

The study of diffusion-controlled processes is very important to understand the various chemical phenomena occurring in solution[1,2,3]. The dynamics of these processes is usually described by the Smoluchowski equation in the presence of an external force field[4].

The kind of process treated here is the desorption process which is important in the study of surface catalysis[5,6] and the investigation of charge transfer at interfaces[7]. We are primarily interested in the solution of the Smoluchowski equation with a model potential. In the previous work[8], we solved the