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One-electron Oxidation Potentials of an NADH Model Compound and a Dimeric Rhodium(I) Complex in Irreversible Systems. A Convenient Determination from the Fluorescence Quenching by Electron Acceptors

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A new methodology for experimental determinations of redox potentials of oxidants or reductants in both reversible and irreversible systems is presented. The Rehm-Weller free energy relationship between the activation free energy ΔG^{-} and the free energy change ΔG for the electron transfer quenching of the excited states of oxidants or reductants by a series of reductants or oxidants is converted to a linear correlation between $\Delta G^{\neq}-\Delta G$ and $(\Delta G^{\neq})^{-1}$, which can be utilized in convenient determinations of redox potentials of oxidants or reductants. This methodology is established in various reversible systems where the redox potentials of oxidants or reductants determined based on the Rehm-Weller free energy relationship agree well with those determined independently by electrochemical methods. By using this method, one-electron oxidation potentials of two quite different compounds, one is an NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH), and the other $[Rh_2(dicp)_4]^{2+}$ (dicp=1,3-diisocyanopropane), in MeCN have been determined as 0.60±0.10 and 0.38±0.10 V *vs.* SCE, respectively. The relation between the oxidation potential and the oxidation peak potential of BNAH measured by the cyclic voltammetry is discussed in the context of free energy relationships.

Electron transfer processes are receiving increased attention in oxidation-reduction reactions especially in those related to biological redox systems which play a dominant role in energy conversion and substrate metabolism in living systems.[1] Electrons are transferred in the direction of increasing redox potentials. Therefore, redox potentials of oxidants and reductants are of great importance for an understanding of electron transfer processes from reductants to oxidants. Redox potentials of a number of oxidants or reductants, however, have not been determined precisely by electrochemical methods because of the irreversible nature of these one-electron oxidation or reduction on the time scale of electrochemical measurements. In such irreversible systems, there have been no established methodology for experimental determinations of redox potentials of oxidants or reductants. In principle, however, redox potentials of oxidants or reductants in irreversible systems as well as reversible systems can be determined from the activation free energy $\Delta G^{\neq}$ for one-electron transfer reactions between oxidants and reductants, since $\Delta G^{\neq}$ is known to be expressed as a monotonous function of the redox potentials of the oxidants and reductants.[2–5] Thus, if the other parameters in the relation between $\Delta G^{\neq}$ and the redox potential of an oxidant (or a reductant) are somehow obtained, the redox potential can be determined from $\Delta G^{\neq}$. When the excited states of oxidants (or reductants) show the emissions, the $\Delta G^{\neq}$ values for electron transfer reactions of the excited states of the oxidants (or reductants) are readily determined experimentally from the electron transfer quenching of the excited states by a series of appropriate reductants (or oxidants).[3,6–9]

In the present study, we wish to show how free energy relationships between $\Delta G^{\neq}$ and ΔG obtained from the emission quenching by electron transfer reactions can be utilized in convenient determinations of redox potentials of oxidants or reductants in both reversible and irreversible systems. First, the methodology of experimental determinations of redox potentials will be established in various reversible systems reported in the literatures,[3,6–9] where the redox potentials of oxidants or reductants determined by the method based on the free energy relationships for electron transfer quenching of the excited states are compared with those obtained independently by conventional electrochemical methods. Next, the methodology thus established is applied to irreversible systems of current interest to determine one-electron oxidation potentials of 1-benzyl-1,4-dihydronicotinamide (BNAH), a model compound of NADH, which is one of the principal coenzymes for biochemical oxidation-reduction reactions[10] and also of a dimeric rhodium(I) complex $[Rh_2(dicp)_4]^{2+}$ (dicp=1,3-diisocyanopropane) which has recently merited a special attention as offering a possibility for photochemical energy storage.[11,12] The one-electron oxidation potential of BNAH in the irreversible system will be compared with the oxidation peak potential measured by the cyclic voltammetry in the context of free energy relationships for electron transfer reactions.

Experimental

Materials. 1-Benzyl-1,4-dihydronicotinamide (BNAH) and the 4-deuterio compound (BNAH-4-d_1) were prepared according to the literature,[13] and purified by recrystallization from ethanol. Preparation of $[Rh_2(dicp)_4]^{2+}$ was described previously.[14] Electron acceptors used in this study are commercially available and were purified by the standard methods.[15] Acetonitrile was purified and dehydrated with calcium hydride by the standard procedure.[15]

Fluorescence Quenching Experiments. Fluorescence measurements were performed using a Hitachi 650-10S fluorescence spectrophotometer. The excitation wavelengths of BNAH, BNAH-4-d_1, and $[Rh_2(dicp)_4]^{2+}$ were chosen so that the absorption by quenchers may be neglected (normally 360 nm for BNAH and BNAH-4-d_1 but 400 nm when acetophenone derivatives are used as quenchers, and 553 nm for $[Rh_2(dicp)_4]^{2+}$). The monitoring wavelengths were those corresponding to the maxima of the respective emission bands (BNAH and BNAH-4-d_1, 443 nm; $[Rh_2(dicp)_4]^{2+}$, 656 nm). Relative fluorescence intensities were measured for an MeCN solution of BNAH, BNAH-4-d_1, or $[Rh_2(dicp)_4]^{2+}$ with a quencher at various concentrations. There has been no change in the shape but intensity of the fluorescence spectrum by the addition of a quencher. The Stern-Volmer relationship (Eq. 1) was obtained

$$I_f^0/I_f = 1 + K_{SV}[Q] \qquad (1)$$

between the ratio of the fluorescence intensities in the absence and presence of a quencher I_f^0/I_f and the quencher concentration [Q]. The quenching rate constant k_q was determined from the Stern-Volmer constant K_{SV} and the fluorescence lifetime τ (BNAH, 0.76 ns;[16] $[Rh_2(dicp)_4]^{2+}$, 1.3 ns[17]) by using

$$k_q = K_{SV}\tau^{-1} \qquad (2)$$

Eq. 2. Degassing of an MeCN solution of BNAH, BNAH-4-d_1, or $[Rh_2(dicp)_4]^{2+}$ with a quencher has been found to cause no effect on the fluorescence intensity in accordance with the quenching of the singlet excited state.

Cyclic Voltammetry. Reduction potentials of some electron acceptors were determined by the cyclic voltammetry (CV) measurements which were performed on a Hokuto Denko Model HA-301 potentiostat/galvanostat at 298 K in MeCN containing 0.1 mol dm^{-3} n-Bu_4NClO_4 as a supporting electrolyte, using a standard NaCl calomel reference electrode (SCE) or a Ag/Ag$^+$ reference electrode ($Ag/AgNO_3$ 0.1 mol dm^{-3}); the reduction potential *vs.* Ag/Ag$^+$ is 0.34 V lower than that *vs.* SCE.[18] The oxidation peak potentials of BNAH and BNAH-4-d_1 were measured by changing the sweep rate in the range 10—1000 mV s^{-1}.

Results and Discussion

Determination of Redox Potentials of Oxidants or Reductants from the Electron Transfer Quenching of the Excited States. The increase of the donor or acceptor abilities of electron donors or acceptors by the electronic excitation often results in electron transfer quenching of the excited states by the ground states of acceptors or donors.[3,6—9] Rehm and Weller[3] have formulated the following reaction scheme for the fluorescence quenching by electron transfer reactions in polar solvents such as MeCN,

$$D^* + A \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} (D^*A) \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} (D^+A^-) \xrightarrow{k_{30}} D + A, \qquad (3)$$

where asterisk stands for the excited state which can be either the donor (D*) or the acceptor (A*) molecule, k_{12} and k_{21} are the diffusion and the dissociation rate constants, k_{23} and k_{32} are the rate constants of forward electron transfer for the actual electron transfer process and the back electron transfer to the excited state, respectively, and k_{30} is the rate constant of back electron transfer to the ground state. The over-all rate constant k_q of fluorescence quenching is given by Eq. 4,

$$k_q = \frac{k_{12}k_{23}}{k_{23}+k_{21}(1+k_{32}/k_{30})}, \qquad (4)$$

which is reduced to Eq. 5 under the condition that the

$$k_q = \frac{k_{12}k_{23}}{k_{23}+k_{21}} \qquad (5)$$

back electron transfer to the ground state is much faster than that to the excited state, *i.e.*, $k_{30} \gg k_{32}$. Then, the activation free energy $\Delta G^{\neq}$ for the actual electron transfer process k_{23}, encounter complex (D* A)→ion pair (D$^+$ A$^-$), is obtained from the quenching rate constant k_q by using Eq. 6 derived from Eq. 5,

$$\Delta G^{\neq} = \frac{RT}{F}\ln\left[Z\left(\frac{1}{k_q}-\frac{1}{k_{12}}\right)\right], \qquad (6)$$

where $\Delta G^{\neq}$ is given in the unit of V, Z is the collision frequency which is generally taken as 1×10^{11} mol^{-1} dm^3 s^{-1},[1,2,16] F is the Faraday constant, the k_{12} value has been reported as 2×10^{10} mol^{-1} dm^3 s^{-1} for neutral organic molecules,[3,8,9,16] and the other notations are conventional. The Rehm-Weller free energy relationship for the quenching of excited states of oxidants or reductants by electron transfer reactions (Eq. 3) has well been established as represented by Eq. 7,[3,6—9]

$$\Delta G^{\neq} = \frac{\Delta G}{2} + \left[\left(\frac{\Delta G}{2}\right)^2 + (\Delta G_0^{\neq})^2\right]^{1/2}, \qquad (7)$$

where $\Delta G_0^{\neq}$ is the intrinsic barrier representing the activation free energy for electron transfer when the driving force is zero, *i.e.*, $\Delta G^{\neq}=\Delta G_0^{\neq}$ at $\Delta G=0$. According to the thermochemical cycle in Scheme 1, the free energy change ΔG of the actual electron transfer process, (D* A)→(D$^+$ A$^-$), is expressed in terms of the redox potentials of electron donors (E_{ox}^0) and acceptors (E_{red}^0) as shown in Eq. 8,

$$\begin{tikzcd} D^* + A \arrow[r, "w_r"] \arrow[d, "E_{ox}^0 - E_{red}^0 - \Delta E_{0,0}"'] & (D^*\ A) \arrow[d, "\Delta G"] \\ D^+ + A^- \arrow[r, "w_p"] & (D^+\ A^-) \end{tikzcd}$$

Scheme 1.

$$\Delta G = E_{ox}^0 - E_{red}^0 + w_p - \Delta E_{0,0}, \qquad (8)$$

where w_p is the work term required to bring the products D$^+$ and A$^-$ together, w_r which is the corresponding term for the reactants has been neglected in Eq. 8,[19] and $\Delta E_{0,0}$ is the zero-zero transition energy which is obtained from the frequencies of the absorption (ν) and fluorescence (ν_f) maxima by using Eq. 9.[3,20]

$$\Delta E_{0,0} = (h\nu + h\nu_f)/2 \qquad (9)$$

A simple mathematical consideration of Eq. 7 yields a linear formulation between $\Delta G^{\neq}-\Delta G$ and $(\Delta G^{\neq})^{-1}$ (Eq. 10),

$$\Delta G^{\neq} - \Delta G = (\Delta G_0^{\neq})^2/\Delta G^{\neq}, \qquad (10)$$

which is rewritten by Eq. 11, using Eq. 8. Thus, the $E_{red}^0 - w_p$ value of the acceptor can be evaluated from

$$\Delta G^{\neq} - E_{ox}^0 + \Delta E_{0,0} = \frac{(\Delta G_0^{\neq})^2}{\Delta G^{\neq}} - (E_{red}^0 - w_p) \qquad (11)$$

the intercept of the linear correlation between $\Delta G^{\neq} - E_{ox}^0 + \Delta E_{0,0}$ and $(\Delta G^{\neq})^{-1}$ based on Eq. 11. This methodology for determining reduction potentials of electron acceptors (oxidants) is tested for reductive quenching of fluorescent aromatic hydrocarbons Ar* (acceptors) by a series of electron donors (amines and methoxybenzenes) having various known oxidation potentials (Eq. 12).[3]

$$Ar^* + D \xrightarrow{k_q} Ar^{\cdot-} + D^{\cdot+} \qquad (12)$$

The plots of $\Delta G^{\neq} - E_{ox}^0 + \Delta E_{0,0}$ *vs.* $(\Delta G^{\neq})^{-1}$ for the

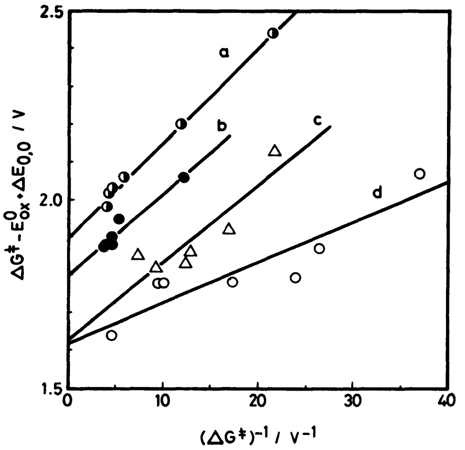

Fig. 1. Plots of Eq. 11 ($\Delta G^{\neq}-E^0_{ox}+\Delta E_{0,0}$ *vs.* $(\Delta G^{\neq})^{-1}$) for the reductive quenching of the excited states of electron acceptors ((a) benz[*a*]anthracene, (b) 4-pyrencarboxylic acid, (c) benz[*c*]acridine, and (d) 3-pyrenecarboxylic acid) by a series of electron donors (amines and methoxybenzenes) in MeCN (Eq. 12); the data of the quenching rate constants k_q from which the $\Delta G^{\neq}$ values are obtained by using Eq. 6, E^0_{ox} of the donors, and $\Delta E_{0,0}$ were taken from Ref. 3. Note that the intercepts correspond to the $-(E^0_{red}-w_p)$ values of the acceptors, see Eq. 11 in text.

TABLE 1. COMPARISON OF THE $E^0_{red}-w_p$ OR $E^0_{ox}+w_p$ VALUES OF OXIDANTS OR REDUCTANTS DETERMINED BY THE PLOTS OF Eq. 11 OR 14, RESPECTIVELY, WITH THE CORRESPONDING ELECTROCHEMICAL VALUES OF E^0_{red} OR E^0_{ox}

Oxidant	$E^0_{red}-w_p$ / V	E^0_{red} / V	w_p / V
Organic[a]			
3-Pyrenecarboxylic acid	−1.62	−1.67	−0.05
Benz[*c*]acridine	−1.63	−1.75	−0.12
4-Pyrenecarboxylic acid	−1.80	−1.92	−0.12
Benz[*a*]anthracene	−1.90	−2.02	−0.12
Inorganic[b]			
$[Ru(bpy)_3]^{2+}$	−1.47	−1.35	0.12
$[Cr(bpy)_3]^{3+}$	−0.28	−0.26	0.02
$[Ir(Me_2phen)_2Cl_2]^+$	−1.22	−1.16	0.06
Inorganic reductants[c]	$E^0_{ox}+w_p$	E^0_{ox}	w_p
$[Ru(bpy)_3]^{2+}$	1.45[d]	1.32[e]	0.13[f]
$[Ru(phen)_2(CN)]$	0.79	0.84	−0.05
$[Ru(bpy)_2(CN)]$	0.80	0.83	−0.03
$[Ru(bpy)_3]^{2+}$	1.31	1.32	−0.01

a) Used in reactions (Eq. 12) taken from Ref. 3. b) Used in reactions (Eq. 13) taken from Ref. 7. c) Used in reactions (Eqs. 15—17) taken from Refs. 8,9,6. d) This value corresponds to $E^0_{ox}+w_p-w_r$ (Ref. 25). e) N. E. Tokel-Takvoryan, R. E. Hemingway, and A. J. Bard, *J. Am. Chem. Soc.*, **95**, 6582 (1973). f) This value corresponds to w_p-w_r.

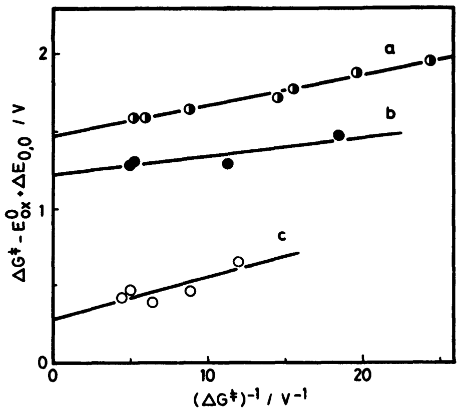

Fig. 2. Plots of Eq. 11 ($\Delta G^{\neq}-E^0_{ox}+E_{0,0}$ *vs.* $(\Delta G^{\neq})^{-1}$) for the reductive quenching of the excited states of electron acceptors ((a) $[Ru(bpy)_3]^{2+}$, (b) $[Ir(Me_2phen)_2Cl_2]^+$, and (c) $[Cr(bpy)_3]^{3+}$) by a series of electron donors (aromatic amines and methoxybenzenes) in MeCN (Eq. 13); the data of the quenching rate constants k_q from which the $\Delta G^{\neq}$ values are obtained by using Eq. 6, E^0_{ox} of the donors, and $\Delta E_{0,0}$ were taken from Ref. 7. The intercepts correspond to the $-(E^0_{red}-w_p)$ values of the acceptors, see Eq. 11 in text.

fluorescence quenching of some aromatic acceptors (benz[*a*]anthracene, 4-pyrenecarboxylic acid, benz[*c*]-acridine, and 3-pyrenecarboxylic acid) by a series of electron donors in MeCN are shown in Fig. 1.[21] The $E^0_{red}-w_p$ values for the acceptors obtained from the intercepts in Fig. 1 by the least squares analysis are listed in Table 1 together with the E^0_{red} values determined independently by electrochemical methods.[3] Although the linear correlations in Fig. 1 are not very impressive,[22] the $E^0_{red}-w_p$ values obtained from the intercepts in Fig. 1 agree well with the electrochemical values of E^0_{red} (Table 1) by taking into account the work terms w_p which are considered as being small negative values for the product ions of opposite charge in outer-sphere electron transfer reactions.[23]

Transition metal complexes containing bpy (2,2′-bipyridine) or phen (1,10-phenanthroline) as ligands have recently been shown to act excellent donors or acceptors in the excited state electron transfer reactions and thus the rate data for both reductive[7] and oxidative[6,8,9] quenching of excited states by electron transfer reactions are now available. The linear plots of Eq. 11 for the reductive quenching of excited states of transition metal complexes M^{n+} ($[Ru(bpy)_3]^{2+}$, $[Ir(Me_2phen)_2Cl_2]^+$, and $[Cr(bpy)_3]^{3+}$) by a series of electron donors D (aromatic amines and methoxybenzenes) in MeCN (Eq. 13)[7] are shown in Fig. 2. The $E^0_{red}-w_p$ values of

$$M^{n+*} + D \longrightarrow M^{(n-1)+} + D^+ \qquad (13)$$

M^{n+} determined from the intercepts in Fig. 2 are slightly more negative than the corresponding electrochemical values of E^0_{red} (Table 1). Therefore, the work terms w_p obtained by subtracting $E^0_{red}-w_p$ from E^0_{red} are small positive values, which agree with those expected for the product ions of the same charge type (Eq. 13)[24] in contrast with those of opposite charge (Eq. 12).

The oxidation potentials of electron donors (reductants) can also be determined from oxidative quenching of excited donors by appropriate electron acceptors (oxidants) having various reduction potentials, based on the plots of Eq. 14 ($\Delta G^{\neq}+E^0_{red}+\Delta E_{0,0}$ *vs.* $(\Delta G^{\neq})^{-1}$) which is obtained by rearranging Eq. 11. Figure 3 depicts the plots of $\Delta G^{\neq}+E^0_{red}+\Delta E_{0,0}$ *vs.*

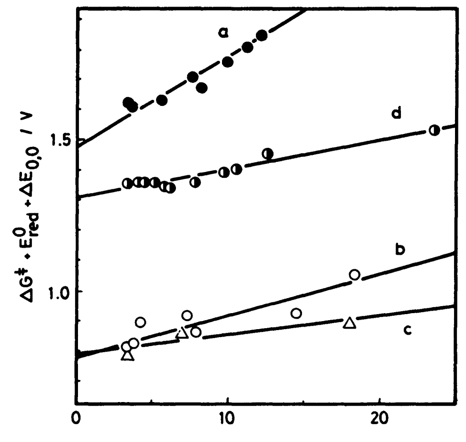

Fig. 3. Plots of Eq. 14 ($\Delta G^{\ddagger}+E^0_{red}+\Delta E_{0,0}$ *vs.* $(\Delta G^{\ddagger})^{-1}$) for the oxidative quenching of the excited stated of electron donors ((a) $[Ru(bpy)_3]^{2+}$, (b) $[Ru(phen)_2(CN)]$, and (c) $[Ru(bpy)_2(CN)]$) by pyridinium ions (Eqs. 15 and 16; the data were taken from Refs. 8 and 9 and of (d) $[Ru(bpy)_3]^{2+}$ by nitrobenzene derivatives (Eq. 17); the data were taken from Ref. 6. Note that the intercepts correspond to the $E^0_{ox}+w_p$ values of the donors, see Eq. 14 in text.

$$\Delta G^{\ddagger} + E^0_{red} + \Delta E_{0,0} = \frac{(\Delta G^{\ddagger}_0)^2}{\Delta G^{\ddagger}} + E^0_{ox} + w_p, \tag{14}$$

$(\Delta G^{\ddagger})^{-1}$ for the oxidative quenching of $[Ru(bpy)_3]^{2+*}$ by bipyridinium ions BP^{2+} as electron acceptors (Eq. 15),[8] that of $[RuL_2(CN)]^*$ (L=bpy and phen) by pyridinium ions P^+ (Eq. 16)[9] and also that of $[Ru(bpy)_3]^{2+*}$ by nitrobenzene derivatives (Eq. 17).[6]

$$[Ru(bpy)_3]^{2+*} + BP^{2+} \longrightarrow [Ru(bpy)_3]^{3+} + BP^{+} \tag{15}$$

$$[RuL_2(CN)]^* + P^+ \longrightarrow [RuL_2(CN)]^+ + P^0 \tag{16}$$

$$[Ru(bpy)_3]^{2+*} + Ar\text{–}NO_2 \longrightarrow [Ru(bpy)_3]^{3+} + Ar\text{–}NO_2^{\bar{\cdot}} \tag{17}$$

The $E^0_{ox}+w_p-w_r$ value of $[Ru(bpy)_3]^{2+}$, the E^0_{ox} values of $[RuL_2(CN)]$, and the $E^0_{ox}+w_p$ value of $[Ru(bpy)_3]^{2+}$ determined from the respective intercepts in Fig. 3 by using Eq. 14[25] show reasonable agreement with the corresponding E^0_{ox} values determined electrochemically by taking into account the small work terms.[23]

Thus, the methodology of experimental determinations of both reduction and oxidation potentials based on the Rehm-Weller free energy relationship (Eqs. 11 and 14) for electron transfer quenching of excited states of oxidants and reductants, respectively, has well been established. The experimental errors in the determinations of redox potentials by this method are considered to be comparable with those by electrochemical methods.[26] Of course, as far as the determinations of the redox potentials in reversible systems are concerned, electrochemical methods are more suitable and convenient than the present method. It should be emphasized, however, that the method based on Eq. 11 or 14 does not depend on the systems whether oxidation of reductants (or reduction of oxidants) is reversible or irreversible, since with regard to reductants or oxidants of interest, only the kinetic data (k_q or $\Delta G^{\ddagger}$) are required in Eq. 11 or 14.

A Comparison between the Rehm-Weller and the Marcus Free Energy Relationships. The Marcus free energy relationship (Eq. 18) also has frequently been used for electron transfer reactions.[2,5,8] From Eqs. 8 and 18 is obtained Eq. 19. According to Eq. 19, the intercept

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}_0 \left(1+\frac{\Delta G}{4\Delta G^{\ddagger}_0}\right)^2 \tag{18}$$

$$(\Delta G^{\ddagger})^{1/2} = (\Delta G^{\ddagger}_0)^{1/2} + (16\Delta G^{\ddagger}_0)^{-1/2}(E^0_{ox}-E^0_{red}+w_p-\Delta E_{0,0}) \tag{19}$$

to the abscissa of the linear plot between $(\Delta G^{\ddagger})^{1/2}$ and E^0_{ox} or $-E^0_{red}$ gives the relation of Eq. 20. Then, the

$$E^0_{ox} - E^0_{red} + w_p - \Delta E_{0,0} + 4\Delta G^{\ddagger}_0 = 0 \tag{20}$$

$E^0_{red}-w_p$ or $E^0_{ox}+w_p$ value can be evaluated from Eq. 20 by using the $\Delta G^{\ddagger}$ value obtained from the slope $(16\Delta G^{\ddagger})^{-1/2}$ of the plot between $(\Delta G^{\ddagger})^{1/2}$ and E^0_{ox} or $-E^0_{red}$ (Eq. 19).

As pointed out by Indelli and Scandola,[27] however, the Marcus equation (Eq. 18) cannot be applied to electron transfer quenching of excited states because of the serious disagreement with experimental results especially in the largely exothermic region (Eq. 18 predicts the increase of $\Delta G^{\ddagger}$ as ΔG decreases in the region $\Delta G < -4\Delta G^{\ddagger}_0$, although most experimental results have shown that $\Delta G^{\ddagger} \rightarrow 0$ in the largely exothermic region).[6–9] Thus, the application of the Marcus equation is restricted to the region $\Delta G > -4\Delta G^{\ddagger}_0$.[28] In order to compare the Marcus free energy relationship (Eq. 18 or 19) with the Rehm-Weller's (Eq. 7 or 11), the data for the fluorescence quenching of 1,2-benzanthracene by electron donors (Fig. 1a) are replotted according to Eq. 19, *i.e.*, $(\Delta G^{\ddagger})^{1/2}$ *vs.* E^0_{ox}, as shown by open circles in Fig. 4, where the solid line represents the plot corresponding to the Rehm-Weller equation (Eq. 7). A significant deviation from the linear relation between $(\Delta G^{\ddagger})^{1/2}$ and E^0_{ox} is observed in the region $E^0_{ox} < 1.3$ V. However, the extrapolation of the linear

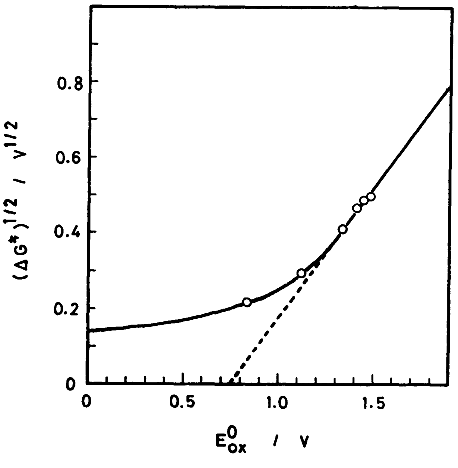

Fig. 4. A plot of $(\Delta G^{\ddagger})^{1/2}$ *vs.* E^0_{ox} (Eq. 19) for the reductive quenching of 1,2-benzanthracene by electron donors; the solid line represents the plot corresponding to the Rehm-Weller equation (Eq. 7 or 11) for the data shown in Fig. 1a. For the deviation of the solid line from the linear correlation between $(\Delta G^{\ddagger})^{1/2}$ and E^0_{ox} in the region $E^0_{ox} < 1.3$ V, see the discussion in text.

TABLE 2. QUENCHING RATE CONSTANTS k^h_q AND k^d_q OF THE BNAH AND BNAH-4-d_1 FLUORESCENCE, RESPECTIVELY, BY ELECTRON ACCEPTORS HAVING VARIOUS REDUCTION POTENTIALS E^0_{red}, AND THE KINETIC ISOTOPE EFFECT k_H/k_D.

Acceptor	E^0_{red} a) / V	k^h_q / mol^{-1} dm^3 s^{-1}	k^d_q / mol^{-1} dm^3 s^{-1}	k_H/k_D b)
Diethyl fumarate	−1.50	1.4×10^{10} c)	1.4×10^{10}	1.0
Acetophenone	−2.10	9.1×10^{9} c)	8.5×10^{9}	1.1
Propiophenone	−2.15	9.1×10^{9}	8.6×10^{9}	1.1
trans-Stilbene	−2.20	5.8×10^{9} c)		
4-Methoxyacetophenone	−2.29	5.9×10^{9}	5.8×10^{9}	1.0
Cyanobenzene	−2.35	4.9×10^{9} c)	4.6×10^{9}	1.1
Methyl benzoate	−2.37	4.4×10^{9} c)	4.6×10^{9}	0.9
Ethyl benzoate	−2.40	3.6×10^{9}	3.6×10^{9}	1.0

a) Relative to a standard NaCl calomel reference electrode (SCE), measured by cyclic voltammetry. b) Determined from k^h_q and k^d_q by using Eq. 21. c) Similar values are reported in Ref. 16.

part in the region $E^0_{ox}>1.3$ V to the abscissa gives the intercept value $E^0_{ox}=0.74$ V with the slope of 0.69, which yields essentially the same $E^0_{red}-w_p$ value (−1.92 V) of benz[*a*]anthracene using Eq. 20 as the value (−1.90 V in Table 1) obtained from the intercept to the ordinate in the plot of Eq. 11 (Fig. 1a).

In conclusion, from a purely empirical point of view, the use of the Rehm-Weller free energy relationship (Eq. 11 or 14) is preferable to that of the Marcus free energy relationship (Eq. 19), since the method based on the plot of Eq. 11 or 14 directly gives the $E^0_{red}-w_p$ or $E^0_{ox}+w_p$ value from the intercept, respectively, while that of Eq. 19 is restricted to the region $\Delta G>-4\Delta G^{\neq}_0$ (Fig. 4) and also requires both the slope and intercept in determining the $E^0_{red}-w_p$ or $E^0_{ox}+w_p$ value.

One-electron Oxidation Potentials of an NADH Model Compound and [Rh$_2$(dicp)$_4$]$^{2+}$ in Irreversible Systems. The excitation of the absorption band (350 nm) of an MeCN solution of BNAH or the 4-deuterio compound BNAH-4-d_1 results in fluorescence ($\lambda_{max}=443$ nm, $h\nu_f=2.80$ eV, and $\tau=0.76$ ns).[16] The BNAH or BNAH-4-d_1 fluorescence was quenched by electron acceptors which have various reduction potentials. The quenching rate constants k_q determined by the Stern-Volmer plots (see Experimental, Eq. 1) are listed in Table 2 together with the reduction potentials of the acceptors. The kinetic isotope effect k_H/k_D has also been determined from the ratio of the quenching rate constants of BNAH (k^h_q) and BNAH-4-d_1 (k^d_q) by using Eq. 21.[29] No isotope

$$k_H/k_D = (2k^d_q/k^h_q-1)^{-1} \qquad (21)$$

effect for the fluorescence quenching of BNAH by the electron acceptors is observed (Table 2), indicating that the quenching process is one-electron transfer from BNAH* to an acceptor (Eq. 22). One-electron transfer from BNAH is known to be irreversible since BNAH$^{+\cdot}$

$$\mathrm{BNAH}^* + \mathrm{A} \xrightarrow{k_q} \mathrm{BNAH}^{+\cdot} + \mathrm{A}^{-\cdot} \qquad (22)$$

formed by the electron transfer reaction (Eq. 22) is unstable to undergo the disproportionation reaction (Eq. 23).[30] The $\Delta G^{\neq}$ values for the actual electron

$$2\mathrm{BNAH}^{+\cdot} \longrightarrow \mathrm{BNA}^+ + (\mathrm{BNAH})\mathrm{H}^+ \qquad (23)$$

transfer process k_{23} (Eq. 3) are obtained from the k_q values in Table 2 by using Eq. 6. The zero-zero transition energy $\Delta E_{0,0}$ of BNAH and BNAH-4-d_1 is obtained as 3.17 eV from the $h\nu$ and $h\nu_f$ values (3.54 and 2.80 eV, respectively) by using Eq. 9. In order to determine the one-electron oxidation potential E^0_{ox} of BNAH and BNAH-4-d_1, the values of $\Delta G^{\neq}+E^0_{red}+\Delta E_{0,0}$ are plotted against the $(\Delta G^{\neq})^{-1}$ values in Fig. 5a which shows the same linear correlation for BNAH and BNAH-4-d_1. Thus, the intercept in Fig. 5a gives the $E^0_{ox}+w_p$ value of BNAH and BNAH-4-d_1 as 0.50 V.

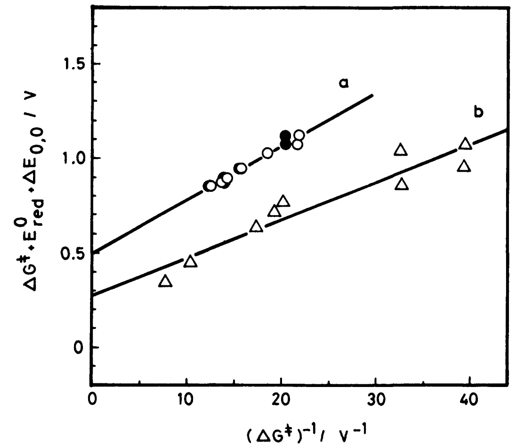

Fig. 5. Plots of $\Delta G^{\neq}+E^0_{red}+\Delta E_{0,0}$ *vs.* $(\Delta G^{\neq})^{-1}$ (Eq. 14) for the fluorescence quenching of (a) ○ BNAH and ● BNAH-4-d_1 by the electron acceptors in Table 2 (Eq. 22) and that of (b) ◑ [Rh$_2$(dicp)$_4$]$^{2+}$ by the acceptors in Table 3 (Eq. 24). The intercepts 0.50 and 0.28 V give the $E^0_{ox}+w_p$ values of BNAH (or BNAH-4-d_1) and [Rh$_2$(dicp)$_4$]$^{2+}$, respectively, according to Eq. 14.

Similarly, the one-electron oxidation potential of [Rh$_2$(dicp)$_4$]$^{2+}$ whose one-electron oxidation also is irreversible[14] has been determined from the fluorescence quenching of [Rh$_2$(dicp)$_4$]$^{2+}$ by a series of electron acceptors A (Eq. 24). The k_q values of [Rh$_2$(dicp)$_4$]$^{2+*}$

$$[\mathrm{Rh_2(dicp)_4}]^{2+*} + \mathrm{A} \xrightarrow{k_q} [\mathrm{Rh_2(dicp)_4}]^{3+} + \mathrm{A}^{-\cdot} \qquad (24)$$

as well as the reduction potentials of the acceptors are listed in Table 3. The $E^0_{ox}+w_p$ value of [Rh$_2$(dicp)$_4$]$^{2+}$ is obtained as 0.28 V from the intercept of the linear plot between $\Delta G^{\neq}+E^0_{red}+\Delta E_{0,0}$[31] and $(\Delta G^{\neq})^{-1}$, as shown in Fig. 5b. Thus, the one-electron oxidation

Table 3. Quenching rate constants k_q of the $[Rh_2(dicp)_4]^{2+}$ fluorescence by electron acceptors having various reduction potentials E^0_{red}

Acceptor[a]	E^0_{red} / V	k_q / mol^{-1} dm^3 s^{-1}
1,4-Dinitrobenzene	−0.69	1.8×10^{10}
1,3-Dinitrobenzene	−0.90	1.5×10^{10}
Methyl 4-nitrobenzoate	−0.95	1.4×10^{10}
3-Nitrobenzaldehyde	−1.02	1.3×10^{10}
1-Chloro-4-nitrobenzene	−1.06	1.2×10^{10}
Nitrobenzene	−1.15	1.3×10^{10}
2-Nitroaniline	−1.27	1.2×10^{10}
4-Nitroaniline	−1.36	8.3×10^{9}
1-Methoxy-2-nitrobenzene	−1.40	7.7×10^{9}
Diethyl fumarate	−1.50	6.8×10^{9}
1,4-Dicyanobenzene	−1.72	1.9×10^{9}
Benzophenone	−1.86	5.9×10^{8}

a) Taken from Ref. 31 unless otherwise noted. b) This study.

potentials E^0_{ox} of BNAH (or BNAH-4-d_1) and $[Rh_2(dicp)_4]^{2+}$ are determined as 0.60±0.1 and 0.38±0.1 V, respectively, by taking into account the value −0.1 V as the work term w_p.[32]

Thus, the oxidation potentials in irreversible systems can be determined based on the Rehm-Weller free energy relationship (Eq. 14) for the electron transfer quenching of the excited states of reductants by a series of oxidants. Although this method requires the knowledge of the emission lifetime τ of the excited states to determine the electron transfer rate constants k_q from the quenching constants K_{SV} (Eq. 2), the k_q values can be estimated from the K_{SV} values without the direct measurement of τ by assuming that the K_{SV} value which reaches a constant value with increasing E^0_{red} of oxidants is equivalent to the diffusion rate constant k_{12}.

A Comparison between the Oxidation Potential E^0_{ox} and the Oxidation Peak Potential E^p_{ox} in an Irreversible System. In the foregoing sections, we have shown that how free energy relationships between $\Delta G^{\ne}$ and ΔG obtained from the electron transfer quenching of the excited states of oxidants or reductants can be successfully used in determining the redox potentials of the oxidants or reductants in irreversible systems as well as reversible systems. In this section, such free energy relationships are shown to be utilized also for the irreversible electrochemical oxidation of BNAH to determine the oxidation potential E^0_{ox} of BNAH from the cyclic voltammetry (CV) measurements, which is compared with the E^0_{ox} value determined from the electron transfer quenching study of the BNAH fluorescence.

The cyclic voltammogram of BNAH is illustrated in Fig. 6, which shows an anodic wave with a current maximum but no cathodic wave on the reverse scan as confirmed by changing the sweep rates in the range 10 to 1000 mV s^{-1}. The anodic oxidation of BNAH is thus irreversible, indicating that the follow-up chemical reaction (Eq. 23)[30] is fast on the time scale of the CV measurements. The width of the anodic wave $E^p_{ox}-E^{p/2}_{ox}$ in such an irreversible system has been shown to depend only on the transfer coefficient β according to Eq. 25.[33,34] Then, the transfer coefficient β defined by

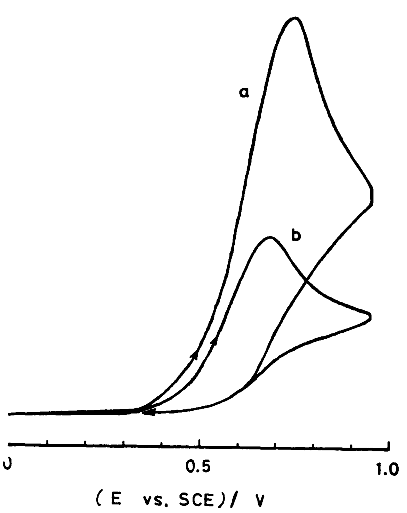

Fig. 6. Cyclic voltammograms of BNAH in MeCN containing 0.1 mol dm^{-3} n-Bu_4NClO_4 at the sweep rates of (a) 0.5 V s^{-1} and (b) 0.1 V s^{-1}.

$$E^p_{ox} - E^{p/2}_{ox} = 1.857\,(RT/\beta F) \tag{25}$$

the tangent of the free energy relationship $\partial\Delta G^{\ne}/\partial\Delta G$ at the oxidation peak potential E^p_{ox} is obtained from the width of the anodic wave $E^p_{ox}-E^{p/2}_{ox}$ by using Eq. 26,

$$\beta = \frac{1.857\,RT}{F(E^p_{ox}-E^{p/2}_{ox})}, \tag{26}$$

which is derived from Eq. 25. The β value can be determined also from the dependence of the oxidation peak potential E^p_{ox} on the sweep rate v (V s^{-1}) by using Eq. 27,[33,34]

$$E^p_{ox} = \frac{2.3\,RT}{2\beta F}\log v + \text{Const}, \tag{27}$$

in which the constant is given by Eq. 28,

$$\text{Const} = E^0_{ox} + \frac{2.3\,RT}{\beta F}\log\frac{2.18\,D\beta F}{k(E^0_{ox})RT}, \tag{28}$$

where $k(E^0_{ox})$ (cm s^{-1}) is the electron transfer rate constant at the oxidation potential E^0_{ox}. On the other hand, the transfer coefficient β is expressed as a function of $\Delta G(=E^0_{ox}-E)$ (Eq. 29) by differentiating the Rehm-Weller free energy relationship (Eq. 7) with respect to ΔG.

$$\beta = \frac{1}{2} + \frac{\Delta G}{4[(\Delta G/2)^2+(\Delta G^{\ne}_0)^2]^{1/2}} \tag{29}$$

From Eq. 29 is derived a relation between the oxidation potential E^0_{ox} and the oxidation peak potential E^p_{ox} (Eq. 30) when $\Delta G=E^0_{ox}-E^p_{ox}$. According to Eq. 30,

$$E^p_{ox}=E^0_{ox} + \frac{(1-2\beta)}{[\beta(1-\beta)]^{1/2}}\Delta G^{\ne}_0 \tag{30}$$

the oxidation potential E^0_{ox} can be evaluated from the intercept of the linear plot between E^p_{ox} and $(1-2\beta)/[\beta(1-\beta)]^{1/2}$. The E^p_{ox} values of BNAH obtained from the cyclic voltammograms of BNAH measured at various sweep rates are plotted against the corresponding values of $(1-2\beta)/[\beta(1-\beta)]^{1/2}$ in which β is determined by Eq. 26, as shown in Fig. 7a. The intercept of the linear correlation in Fig. 7a gives the E^0_{ox} value of BNAH as 0.57 V which agrees well with the E^0_{ox} value 0.60±

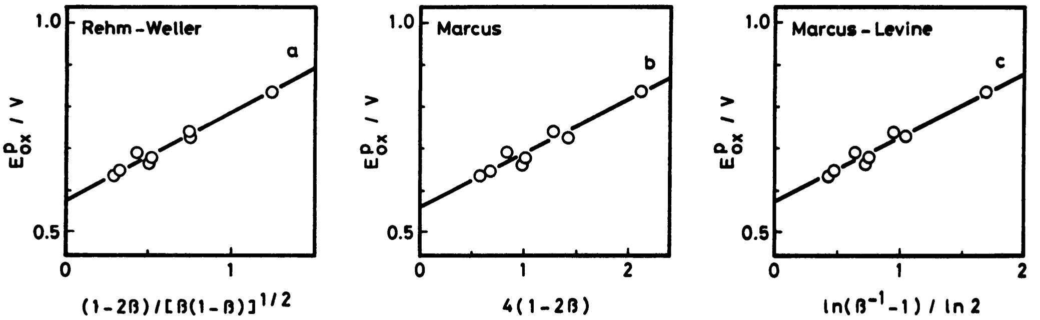

Fig. 7. The oxidation peak potential E^{p}_{ox} of BNAH plotted as a function of the transfer coefficient β based on (a) the Rehm-Weller (Eq. 7), (b) the Marcus (Eq. 18), and (c) the Marcus-Levine (Eq. 30) free energy relationships. See Eqs. 28, 29, and 31 in text, respectively. Note that the intercept corresponds to the E^{0}_{ox} value of BNAH.

0.10 V determined by the fluorescence quenching study described above. The same E^{0}_{ox} value of BNAH-4-d_1 was obtained from the cyclic voltammograms of BNAH-4-d_1 at various sweep rates by the plot of Eq. 30.

The other free energy relationships which are currently used also are applied to the determination of the E^{0}_{ox} value of BNAH from the CV measurements. One is the Marcus free energy relationship being already given by Eq. 18, from which Eq. 31 is derived. The other is

$$E^{p}_{ox} = E^{0}_{ox} + 4(1-2\beta)\Delta G^{\neq}_{0} \qquad (31)$$

the Levine free energy relationship (Eq. 32)[4] which has the equivalent formulation to that derived by

$$\Delta G^{\neq} = \Delta G + \frac{\Delta G^{\neq}_{0}}{\ln 2}\ln\left[1+\exp\left(-\frac{\Delta G \ln 2}{\Delta G^{\neq}_{0}}\right)\right] \qquad (32)$$

Marcus.[35] From Eq. 32 is derived a relation between E^{p}_{ox} and E^{0}_{ox} as well (Eq. 33). The plots according to Eqs. 31 and 33 are shown in Figs. 7b and 7c, respectively. The intercept values in Figs. 7a—c are essentially the

$$E^{p}_{ox} = E^{0}_{ox} + \frac{\Delta G^{\neq}_{0}}{\ln 2}\ln(\beta^{-1}-1) \qquad (33)$$

same, and thereby the same E^{0}_{ox} value of BNAH is obtained irrespective of the use of different free energy relationships for electron transfer reactions (Eqs. 7, 18, and 32).

In conclusion, reliable values of redox potentials of oxidants or reductants in irreversible systems can be determined based on the free energy relationships for the electron transfer quenching of the excited states of oxidants or reductants (Eq. 11 or 14) as well as for the electrochemical electron transfer measured by cyclic voltammetry (Eqs. 30, 31, and 33).

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19) The work term w_r for the neutral reactants is known to be negligible (see Ref. 3).

20) The energy difference $\Delta E_{0,0}$ between the thermally equilibrated excited and ground states of the donor D or the

acceptor A is larger than the energy corresponding to the emission maximum $h\nu_f$ and smaller than the energy corresponding to the absorption maximum $h\nu$ since the absorption and emission are vertical processes.

21) The ΔG^{*} values are evaluated for the quenching rate constant k_q smaller than 1.3×10^{10} mol^{-1} dm^3 s^{-1} since the experimental errors in determining ΔG^{*} by using Eq. 6 become large when the k_q values are close to the diffusion rate constant $k_{12}=2\times10^{10}$ mol^{-1} dm^3 s^{-1}.

22) The correlation coefficients ρ of the plots in Fig. 1 are 0.995 for benz[*a*]anthracene, 0.97 for 4-pyrenecarboxylic acid, 0.87 for benz[*c*]acridine, and 0.90 for 3-pyrenecarboxylic acid.

23) The work term w_r or w_p can be estimated from Debye-Hückell theory by using the equation w (in V)$=(0.395z_Az_B/d)/(1+0.48d\mu^{1/2})$, in which z_A and z_B are the ion charges, μ is the ionic strength, and d is the distance (in Å) between the ion centers (Ref. 8). The w_p values of the product ions of opposite charge have been evaluated as -0.01—-0.08 V depending on the systems (Refs. 3, 6—8), which are the same order of magnitude as those in Table 1.

24) In the case of $[Ir(Me_2phen)_2Cl_2]^+$, however, the work term w_p is expected to be negligiblly small since the product $[Ir(Me_2phen)_2Cl_2]$ is an uncharged species.

25) In the case of the oxidative quenching of $[Ru(bpy)_3]^{2+*}$ by BP^{2+} (Eq. 15), the intercept corresponds to $E^0_{ox}+w_p-w_r$, since the work term w_r of the reactants which are charged species cannot be neglected. The work terms w_r and w_p for the reactions of $[RuL_2(CN)]^*$ (Eq. 16) may be negligibly small since both reactants and products contain uncharged species.

26) The experimental errors in the $E^0_{red}-w_p$ or $E^0_{ox}+w_p$ values determined by the present method (Table 1) are considered to be less than ±0.1 V by taking into account the small w_p values (Ref. 23).

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