Theoretical Estimation of the Redox Potentials Involving Organic and Inorganic Free Radicals

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A simple theoretical expression for the redox potential of a redox couple ($X/X^{-\bullet}$ or $X^{\bullet}/X^{-}$) has been presented by using a modified Born equation and has been successfully applied to the organic and inorganic redox couples the reliable standard redox potentials of which are directly measured electrochemically, and to polarographic half-wave redox potentials of organic compounds. The expression has also been applied to inorganic redox couples the provisional standard redox potentials of which are estimated indirectly by using thermodynamic cycles, to examine the validity of the provisional potentials. At least, the provisional redox potentials, with which the potentials calculated approximately agree, seem to be reliable.

The reduction potentials of organic and inorganic molecules involving free radicals have recently been used in mechanistic studies on electron transfer reactions. All the reduction potentials of these free radicals have not always been measured electrochemically. Especially, most of the potentials of the inorganic free radicals have been obtained indirectly by using thermodynamic cycles, because the radicals are usualy transient species. According to Stanbury,[1] the difficulty in measuring thermochemical parameters for transient free radicals is considerably greater than for more persistent species and thus the literature contains several reports for free radicals that are far from correct. It is, therefore, desirable to compare the provisional reduction potentials estimated thermochemically with those estimated theoretically to examine the validity of the provisional potentials. For the first time, 58 years ago, Makishima[2] succeeded in calculating the standard reduction potentials of monoatomic ions and halogenes theoretically. He obtained excellent results. However, no theoretical attempt has been made to estimate the redox potentials of the redox couples of $X/X^{-\bullet}$ and $X^{\bullet}/X^{-}$, although it has been known that there are good correlations between the polarographic half-wave redox potentials ($E_{1/2}$) and the electron affinities calculated.[3] The polarographic reversible $E^{r}_{1/2}$ value is approximately equal to the standard potential of the metal-amalgam electrode.[6]

For the reduction of an aromatic hydrocarbon (R) by a reversible one-electron transfer, i.e., $R+e^{-}(Hg)\rightleftharpoons R^{-\bullet}$, Dewar et al.[4] gave the following approximate expression for $E^{r}_{1/2}$, neglecting entropy effects:

$$E^{r}_{1/2} = -\frac{\Delta G^{\circ}}{F}, \tag{1}$$

where $e^{-}(Hg)$ is an electron involved in mercury and

$$\Delta G^{\circ} = -A + G^{\circ}_{e^{-}(Hg)} + \Delta G^{\circ}_{solv}. \tag{2}$$

Here F is the Faraday constant, A the electron affinity of R in the gas phase, $G^{\circ}_{e^{-}(Hg)}$ the standard free energy of the electon involved in mercury, and ΔG°_{solv} the difference in the standard free energies between R and $R^{-\bullet}$ in solution. Next, Dewar et al. reduced Eq. 1 to

$$E^{r}_{1/2} = \frac{A}{F} + \text{constant}, \tag{3}$$

because the last two terms in Eq. 2 should be constant for the polarographic reduction of a series of similar compounds under similar experimental conditions. According to Eq. 3, a plot of $E^{r}_{1/2}$ vs. A should be linear, as confirmed by them.

In this paper, an attempt has been made to derive a simple equation for the standard redox potential of the redox couple of $X/X^{-\bullet}$ or $X^{\bullet}/X^{-}$ by writing the terms of $G^{\circ}_{e^{-}(Hg)}$ and ΔG°_{solv} explicitly by using a modified Born equation.[7]

Theory

One considers the following reduction of an organic or inorganic species (R) by an electron transfer in a solvent (S);

$$R(S) + e^{-}(Pt) \rightleftharpoons R^{-\bullet}(S), \tag{4}$$

where R is a neutral compound or a free radical (involving an atomic radical) and $e^{-}(Pt)$ the electron involved in a platinum electrode. Therefore, $R^{-\bullet}(S)$ is always an anion but not necessarily a radical. For example, R(S) means that R is in the phase of S.

For convenience, the free energy changes for transfers of a solute X from the solvent (S) to the gas phase and vice versa in the standard state are denoted by ΔG°_{tr} (X; S→g) and ΔG°_{tr} (X; g→S), respectively. The standard state for all solutes is the unit molar solution at 25°C.

According to Marcus,[8] one constructs a galvanic cell from the special standard hydrogen electrode (immersed in the solvent S) (SHE≡$Pt|H_2(g)|H^{+}$ ($S, a_{H^{+}}=1$)) on the left and the measuring half-cell of Eq. 4 on the right, using two platinum electrodes. One can obtain formally the standard redox potential E°_{S} vs. SHE for the process of Eq. 4, because it is possible to measure the electromotive force of the cell. On the extrathermodynamic assumption, Marcus[8] shows that this E°_{S} value is transformed into one vs. the nor-

mal hydrogen electrode (NHE) by adding algebraically the term of ΔG°_{tr} (H^+; water→S)/F for the Gibbs free energy change of transfer of H^+ involed in the SHE reaction (in the solvent S) to the aqueous normal hydrogen electrode. Marcus calculated small values of ΔG°_{tr} (H^+; water→S)/F for various solvents.[8] As described below, small values for ΔG°_{tr} (H^+; water→S)/F were also calculated in this work. Therefore, the E°_S values vs. SHE may be regarded to be approximately equal to those vs. NHE.

The free energy change for the process of Eq. 4 is written as

$$\Delta G^{\circ}_S = \mu^{\ominus}_{R^{-\bullet}(S)} - \mu^{\ominus}_{R(S)} - F\phi^S, \tag{5}$$

where $\mu^{\ominus}$ denotes the standard chemical potential and ϕ^S is the inner potential of the platinum electrode of the measuring half-cell. One assumes that the surface potentials of the same two platinum electrodes of the galvanic cell approximately cancel out, i.e., that the Galvani potential difference of the galvanic cell may be equal to the Volta potential difference. The work corresponding to the outer potential (ψ^S) of the measuring half-cell is equal to the amount of work necessary to bring the electron from infinity to its position (in the solvent) near the surface of the electrode.[9] This work given by $F\psi^S$ corresponds to the free energy of e^- in the solvent S, because the solvent is polarized by e^- and this polarization leads to a non-zero potential at the position of e^-. Therefore, e^-(Pt) and $F\phi^S$ both corresponding to ϕ^S may be replaced by e^-(S) and $G^{\circ}_{e^-(S)}$ both corresponding to ψ^S in Eqs. 4 and 5, respectively. Here E°_S vs. SHE is written as

$$E^{\circ}_S = -\frac{\Delta G^{\circ}_S}{F}. \tag{6}$$

To obtain the value for ΔG°_S, one considers the following stepwise process based on the thermodynamic Born–Haber cycle for the reaction of R(S) + e^-(S)⇌$R^{-\bullet}$(S):

$$\begin{aligned} &R(S) \rightarrow R(g),\\ &e^-(S) \rightarrow e^-(g),\\ &R(g) + e^-(g) \rightarrow R^{-\bullet}(g),\\ &R^{-\bullet}(g) \rightarrow R^{-\bullet}(S). \end{aligned}$$

If one neglects entropy effects as done by Dewar et al.,[4] one obtains the following equation from the above process:

$$\begin{aligned} \Delta G^{\circ}_S = {} & \Delta G^{\circ}_{tr}(R; S \rightarrow g) + \Delta G^{\circ}_{tr}(e^-; S \rightarrow g)\\ & - A + \Delta G^{\circ}_{tr}(R^{-\bullet}; g \rightarrow S), \end{aligned} \tag{7}$$

where A is the electron affinity of R in the gas phase. Equation 7 corresponds to Eq. 2.

One assumes that interactions among all the solutes can be neglected. In Eq. 7, the sum of ΔG°_{tr} (R; S→g) and ΔG°_{tr} ($R^{-\bullet}$; g→S) may be calculated as follows:

$$\begin{aligned} &\Delta G^{\circ}_{tr}(R; S \rightarrow g) + \Delta G^{\circ}_{tr}(R^{-\bullet}; g \rightarrow S)\\ &\quad = \Delta G^{\circ}_{tr}(R^{-\bullet}; g \rightarrow S) - \Delta G^{\circ}_{tr}(R; g \rightarrow S). \end{aligned} \tag{8}$$

Here ΔG°_{tr} ($R^{-\bullet}$; g→S) is due to both the electrostatic and nonelectrostatic contributions resulting from the interactions of $R^{-\bullet}$ with the solvent. On the other hand, ΔG°_{tr} (R; g→S) is due to only the nonelectrostatic contribution of interactions between R and the solvent. The nonelectrostatic contribution for $R^{-\bullet}$ may be approximately equal to that for R. One, therefore, assumes that the nonelectrostatic contributions for both $R^{-\bullet}$ and R approximately cancel out in Eq. 8. The remaining electrostatic contribution for $R^{-\bullet}$ is the free energy of solvation of the negative charge of $R^{-\bullet}$ and may be given by the modified Born equation of Abe,[7] because Abe's equation can be successfully applied to the estimation of the free energies[7] and entropies[10] of solvation of ions and to that of the solubilities of sparingly soluble lanthanoid iodates.[11] According to Abe's equation,[7] therefore, Eq. 8 may be written as

$$\begin{aligned} &\Delta G^{\circ}_{tr}(R; S \rightarrow g) + \Delta G^{\circ}_{tr}(R^{-\bullet}; g \rightarrow S)\\ &\quad = \frac{e^2 L}{8\pi\varepsilon_0 a}\left(\frac{1}{\ln \epsilon_r} - \frac{1}{\epsilon_r \ln \epsilon_r} - 1\right), \end{aligned} \tag{9}$$

where ε_0 is the permittivity of a vacuum, e the charge of a proton, L the Avogadro constant, ϵ_r the bulk relative permittivity of the solvent, and a the radius of a spherical cavity at whose center the negative charge of $R^{-\bullet}$ is placed. The term of ΔG°_{tr} (e^-; S→g) in Eq. 7 is the negative value of solvation energy of e^- and may be similarly written by Abe's equation as

$$\begin{aligned} \Delta G^{\circ}_{tr}(e^-; S \rightarrow g) &= -\Delta G^{\circ}_{tr}(e^-; g \rightarrow S)\\ &= -\frac{e^2 L}{8\pi\varepsilon_0 r_e}\left(\frac{1}{\ln \epsilon_r} - \frac{1}{\epsilon_r \ln \epsilon_r} - 1\right), \end{aligned} \tag{10}$$

where r_e is the radius of a spherical cavity at whose center e^- is placed.

Thus, from Eqs. 6, 7, 9, and 10, one obtains the theoretical expression for E°_S vs. SHE as

$$E^{\circ}_{S,calcd} = \frac{A}{F} - \frac{e^2 L}{8\pi\varepsilon_0 F} \times \left(\frac{1}{\ln \epsilon_r} - \frac{1}{\epsilon_r \ln \epsilon_r} - 1\right) \times \left(\frac{1}{a} - \frac{1}{r_e}\right), \tag{11}$$

where $e^2 L/8\pi\varepsilon_0 F = 0.720$ nm V.

As described above, the value for ΔG°_{tr} (H^+; water→S)/F must be added to the $E^{\circ}_{S,calcd}$ value calculated by Eq. 11, to transform the $E^{\circ}_{S,calcd}$ value vs. SHE into the value vs. NHE. By using Abe's equation,[7] ΔG°_{tr} (H^+; water→S)/F may be approximately written as

$$\begin{aligned} &\frac{\Delta G^{\circ}_{tr}(H^+; \text{water} \rightarrow S)}{F}\\ &\quad = \frac{e^2 L}{8\pi\varepsilon_0 F a_{H^+}} \times \left\{\left(\frac{1}{\ln \epsilon_r} - \frac{1}{\epsilon_r \ln \epsilon_r} - 1\right)_S\right.\\ &\quad \left. - \left(\frac{1}{\ln \epsilon_r} - \frac{1}{\epsilon_r \ln \epsilon_r} - 1\right)_{water}\right\} \end{aligned}$$

$$= \frac{0.720\text{nmV}}{a_{H+}} \times \{(\frac{1}{\ln \epsilon_r} - \frac{1}{\epsilon_r \ln \epsilon_r} - 1)_S + 0.774\}, \quad (12)$$

where a_{H+} is the radius of H^+ (oxonium ion). Marcus[12] calculated the ionic radius of H_3O^+ to be 0.141 nm. By using $a_{H+}=0.141$ nm in Eq. 12, several values for $\Delta G^\circ_{tr}(H^+;\text{ water}\rightarrow S)/F$ were calculated to be 0.15 (−0.20), 0.05 (0.52), 0.22 (−0.19), 0.22 (0.48) and 1.07 (—) V for dimethyl sulfoxide, propylene carbonate, *N*,*N*-dimethylformamide, acetonitrile, and 1,2-dimethoxyethane, respectively. The values in parentheses are those given by Marcus.[8] These values except for 1,2-dimethoxyethane are very small. In this paper, for convenience, it is assumed that the values for E°_S vs. SHE are approximately equal to those vs. NHE. Accordingly, values calculated for the E°_S values vs. SHE according to Eq. 11 will be directly compared with those observed for the E°_S values vs NHE without any correction in the next section.

According to Hentz et al.,[13] the cavity volume of a solvated electron in water is about 10 $cm^3\,mol^{-1}$ at 1×10^5 Pa and 29 °C. From this value, r_e is calculated to be 0.158 nm according to $10\ cm^3\,mol^{-1}/L=(4/3)\pi r_e^3$. According to a semi-continuum approach,[14] the different r_e radii of 0.193, 0.228, and 0.254 nm for e^- were given for the water, methanol, and ethanol matrices, respectively, at 25 °C. In this paper, for convenience, the same r_e value of 0.158 nm for e^- was used as an approximation for all solvents. When the density (d) of a neutral solute (R) is known, the a value for $R^{-\bullet}$ may be approximated by[15]

$$a = (\frac{3M_r}{4\pi Ld})^{1/3}, \quad (13)$$

where M_r is the relative molecular mass of the solute. When the d value for a solid was used, for example, for a solute of an aromatic hydrocarbon such as naphthalene and 1,4-dinitrobenzene, the van der Waals radius of 0.120 nm for a hydrogen atom[16] was added to the a value calculated by Eq. 13 in this paper.

Applications and Discussion

Comparison of $E^\circ_{S,calcd}$ Values with the Reliable Potentials. To justify Eq. 11, it was applied to one-electron redox couples the standared redox potentials of which were directly determined electrochemically. These reliable redox potentials[16—18] for the couples in which the electron affinities of species reduced are available, are shown in Table 1. The redox potentials ($E^\circ_{S,calcd}$) calculated according to Eq. 11 are also listed in Table 1 together with the A and a values used. The a value for O_2^- was calculated from a=(the bond length of O–O)/2+(the van der Waals radius of O) by using data[16] for them. The a values for $(PhCH_2)^-$, $(Ph_2CH)^-$, (9-fluorene)$^-$ and $SO_2^{-\bullet}$ were calculated by using the d values for toluene, diphenylmethane ($d=1.001$ g cm^{-3} at 26°C),[22] 9-fluorene ($d=1.203$ g cm^{-3} at 0°C),[22] and SO_2 ($d=1.40$ g cm^{-3} for liquid at −10°C),[16] according to Eq. 13. In the case of (9-fluorene)$^-$, 0.120 nm was added to the a value so calculated above. The a value for (tetracyanoethylene)$^{-\bullet}$ was assumed to be equal to that calculated by Eq. 13 for tetrachloroethylene ($d=1.6230$ g cm^{-3} at 20°C).[23] Based on the a value (0.319 nm) for 1,4-benzoquinone ($d=1.318$ g cm^{-3}),[24] the a values for (tetracyanoquinodimethane)$^{-\bullet}$ and (tetrachloro-1,4-benzoquinone)$^{-\bullet}$ were estimated to be a=0.319 nm + 0.144 nm (the bond length of C–C)[16]+0.116 nm (the C–N length)[16]= 0.579 nm and a=0.319 nm + 0.172 nm (the C–Cl length)[16]−0.108 nm (the C–H length)[16]+0.175 nm (the van der Waals radius of Cl)[16]=0.558 nm, respectively. In the case of (tetracyanoquinodimethane)$^{-\bullet}$, the van der Waals radius of N was not considered particularly, since it was nearly equal ot that of O, which was already considered in the a value (0.319 nm) for 1, 4-benzoquinone.

When the Born equation[25] is used instead of Abe's equaiton,[7] one obtains the following expression in the same way as in the derivation of Eq. 11:

$$E^\circ_{S,calcd} = \frac{A}{F} - \frac{e^2L}{8\pi\varepsilon_0 F} \times (\frac{1}{\epsilon_r} - 1) \times (\frac{1}{a} - \frac{1}{r_e}). \quad (14)$$

The results of calculations by Eqs. 11 and 14 were compared with the reliable experimental values, as shown in Fig. 1. The figure shows that Eq. 11 reproduces the $E^\circ_{S,obsd}$ values much better than does Eq. 14 and that Eq. 14 overestimates the $|E^\circ_S|$ values as a whole. The correlation coefficient between the $E^\circ_{S,obsd}$ (Eq. 11) and $E^\circ_{S,obsd}$ values in Table 1 is 0.980. In Fig. 1, only the Eq. 11 plot of benzene in 1,2-dimethoxyethane deviates

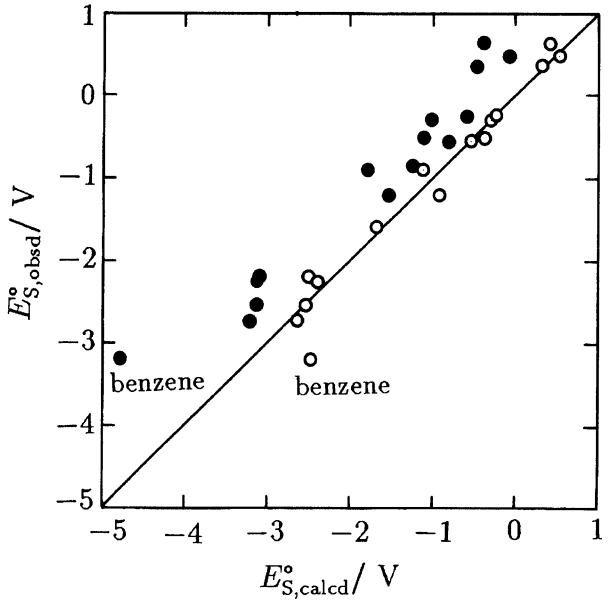

Fig. 1. Plots of observed redox potentials (Table 1) vs. theoretical redox potentials calculated by Eq. 11 (○) and by Eq. 14 (●).

Table 1. Reliable Redox Potentials (vs. NHE) of Redox Couples and Their Calculated Values

Reduced form of redox couple	Solvent[a)]	A/eV[b)]	$E^\circ_{S,obsd}$/V	$E^\circ_{S,calcd}$/V	a/nm
$(Benzene)^{-\cdot}$	DME	−1.15[c)]	−3.2[d)]	−2.48	0.328
$(Tetracyanoethylene)^{-\cdot}$	AN	2.3[c)]	0.48[d)]	0.50	0.343
$(Bromobenzene)^{-\cdot}$	DMF	−0.70[c)]	−2.20[d)]	−2.51	0.347
$(Naphthalene)^{-\cdot}$	AN	−0.19[c)]	−2.26[d)]	−2.41	0.474
$(Chlorobenzene)^{-\cdot}$	DMF	−0.75[c)]	−2.54[d)]	−2.55	0.344
$(Fluorobenzene)^{-\cdot}$	DMF	−0.89[c)]	−2.73[d)]	−2.65	0.335
$(Tetracyanoquinodimethane)^{-\cdot}$	AN	2.8[c)]	0.64[d)]	0.38	0.579
$SO_2^{-\cdot}$	Water	1.14[c)]	−0.26[d)]	−0.24	0.259
O_2^-	Water	0.44[c)]	−0.563[d)]	−0.55	0.220
$(1,4\text{-Dinitrobenzene})^{-\cdot}$	DMF	1.89[e)]	−0.30[d)]	−0.31	0.465
$(Nitrobenzene)^{-\cdot}$	DMF	0.97[e)]	−0.84[d)]	−0.69	0.316
$(Tetrachloro\text{-}1,4\text{-}benzoquinone)^{-\cdot}$	AN	2.68[e)]	0.35[d)]	0.29	0.558
$(PhCH_2)^-$	AN	0.88[f)]	−1.21[g)]	−0.94	0.349
$(Ph_2CH)^-$	AN	0.9[h)]	−0.90[g)]	−1.13	0.405
$(9\text{-Fluorene})^-$	AN	1.9[h)]	−0.52[g)]	−0.38	0.500

a) DME, AN, and DMF represent 1,2-dimethoxyethane, acetonitrile, and *N*,*N*-dimethylformamide, respectively. b) 1 eV=96.48 kJ mol^{-1}. c) Ref. 16. d) Ref. 17. e) Ref. 19. f) Ref. 20. g) Ref. 18. h) Ref. 21.

greatly from the line. This deviation seems to be due to selective solvation, because the solvent of 1,2-dimethoxyethane is a mixture of rotational isomers having different dipole moments.

When the values for ΔG°_{tr} (H^+; water→S)/F (0.22 V for both *N*,*N*-dimethylformamide and acetonitrile) are added to the corresponding $E^\circ_{S,calcd}$ values listed in Table 1, one can obtain the corrected potentials vs. NHE. The correlation coefficient between the $E^\circ_{S,obsd}$ values and the corrected potentials vs. NHE for the 14 redox couples except for the benzene/benzene$^{-\cdot}$ couple in Table 1 was 0.988.

Thus, Eq. 11 may be applied to estimate the approximate values for the redox potentials involving organic and inorganic free radicals, although data points for only two inorganic species could be used for this purpose.

Comparison of $E^\circ_{S,calcd}$ Values with the Provisional Potentials. The provisional redox potentials[1)] indirectly measured by using thermodynamic cycles for inorganic redox couples, in which the electron affinities of species reduced in aqueous solution are available, are shown in Table 2 together with the $E^\circ_{S,calcd}$ values calculated according to Eq. 11. In this case, Eq. 11 is simply reduced to

$$E^\circ_{S,calcd} = (A/\text{eV})\text{V} + \frac{0.5571\ \text{V}}{a/\text{nm}} - 3.526\ \text{V}, \qquad (15)$$

where A is in the unit of eV and a is in the unit of nm. In Table 2, the A and a values used are also listed. As in the case of the O_2/O_2^- couple, the a values for Cl_2^-, Br_2^-, and I_2^- were calculated from a=(the bond length)/2+(the van der Waals radius) by using data[16)] for the bond lengths of these halogens and the van der Waals radii of the halogen atoms. The a value for O^- was assumed to be equal to the van der Waals radius[16)] of O.

Table 2. Provisional Redox Potentials (vs. NHE) of Redox Couples in Aqueous Solution and Their Calculated Values

Redox couple	A/eV	E°_S/V[a)]	$E^\circ_{S,calcd}$/V	a/nm
F/F^-	3.399[b)]	3.6	3.97	0.136[c)]
Cl/Cl^-	3.615[b)]	2.41	3.17	0.181[c)]
Br/Br^-	3.364[b)]	1.92	2.69	0.195[c)]
I/I^-	3.061[b)]	1.33	2.11	0.216[c)]
Cl_2/Cl_2^-	2.38[b)]	0.70	0.89	0.274
Br_2/Br_2^-	2.55[b)]	0.58	0.89	0.299
I_2/I_2^-	2.55[b)]	0.21	0.71	0.331
OH/OH^-	1.83[b)]	1.90	2.28	0.140[c)]
SH/SH^-	2.19[d)]	1.08	1.52	0.195[c)]
CN/CN^-	3.17[d)]	2.59	2.56	0.191[c)]
O/O^-	1.462[b)]	1.63	1.60	0.152
O_3/O_3^-	2.14[b)]	1.01	0.93	0.241
NO_2/NO_2^-	2.28[b)]	1.04	1.14	0.233
NO/NO^-	0.46[b)]	−0.35	−0.43	0.211
SCN/SCN^-	2.17[d)]	1.63	1.50	0.195[c)]
SO_3/SO_3^-	1.70[b)]	0.25	0.36	0.255
HSe/HSe^-	2.21[b)]	0.62	1.13	0.228
SO_2/SO_2^-	1.097[b)]	−0.26	−0.29	0.261

a) Ref. 1. b) Ref. 16. c) Ref. 8. d) Ref. 24.

The a values for O_3^-, NO_2^-, SO_3^-, and SO_2^- were taken to be equal to those calculated by Eq. 13 for O_3 (d=1.352 g cm^{-3} for liquid at −111°C),[16)] NO_2 (d=1.448 g cm^{-3} at 20°C),[22)] SO_3 (d=1.923 g cm^{-3} for liquid),[22)] and SO_2 (d=1.434 g cm^{-3} for liquid at 0°C),[22)] respectively. The a values for NO^- and HSe^- were assumed to be those for NO and HSe, respectively. The latter a values were estimated to be a={(the bond length)+(the sum of van der Waals radii)}/2 by using data[16)] of the bond lengths and van der Waals radii concerning NO and HSe.

Table 3. Polarographic Half-Wave Redox Potentials (vs. NHE) and the Redox Potentials Calculated

Substance	Solvent[a)]	A/eV	$E^{r}_{1/2,obsd}$/V	$E^{\circ}_{S,calcd}$/V	a/nm
1,4-Benzoquinone	AN	1.89[b)]	−0.30[c)]	−0.24	0.439
Benzaldehyde	DMF	≥0[b)]	−1.43[c)]	−1.79	0.343
Anthracene	DMF	0.556[d)]	−1.69[c)]	−1.73	0.504
	AN	0.556[d)]	−1.83[c)]	−1.73	0.504
Azulene	DMF	0.656[d)]	−0.86[c)]	−0.96	0.308[e)]
Benzophenone	DMF	0.62[f)]	−1.48[c)]	−1.41	0.406
Acetone	DMF	−1.51[b)]	−2.60[c)]	−3.13	0.308
				(−2.76)[g)]	0.308

a) AN and DMF represent acetonitrile and *N*,*N*-dimethylformamide, respectively. b) Ref. 16. c) Ref. 27. d) Ref. 28. e) Ref. 29. f) Ref. 30. g) See text.

In a previous paper,[26)] the solvation free energies of OH^-, SH^-, and CN^- were calculated by considering the shifts of the point charges from the centers of the spherical cavities for these ions. The Δ factors which indicate the degrees of contributions due to the shifts of the charges from the centers of cavities for the solvation free energies, were approximately unity for these ions: The Δ values for OH^-, SH^-, and CN^- were 1.09, 1.09, and 1.07, respectively.[26)] In this case, therefore, the effect of the Δ values of these ions on the redox potentials was ignored for simplicity.

As is known from Eq. 11, the $E^{\circ}_{S,calcd}$ value depends considerably on the a value used. The choice of the a values is important. Therefore, Eq. 11 does not necessarily give a good redox potential acccording to the choice of the a value. The amount of scatter in measured values[16)] of electron affinities is generally within 0.2 eV and does not lead to serious scattering in the $E^{\circ}_{S,calcd}$ values calculated by Eq. 11. In Table 2, the $E^{\circ}_{S,calcd}$ values of the redox couples of O_3/O_3^-, NO_2/NO_2^-, SO_3/SO_3^-, and SO_2/SO_2^-, for which the a values were calculated by using Eq. 13, agree approximately with the provisional potentials. Among the provisional redox potentials in Table 2, at least those with which the corresponding $E^{\circ}_{S,calcd}$ values approximately agree, seem to be reliable, although the problem pointed out by Stanbury[1)] is involed in these provisional potentials as mentioned above.

Comparison of $E^{\circ}_{S,calcd}$ Values with the Polarographic Half-Wave Redox Potentials. As shown in Table 3, the polarographic half-wave redox potentials[27)] of organic compounds whose electron affinities were available, were compared with the $E^{\circ}_{S,calcd}$ values calculated from Eq. 11. The a values for the reduced anions of the substances listed in Table 3 except for azulene, were estimated by putting the d values[22,24)] into Eq. 13. Moreover, in the case of 1,4-benzoquinone and anthracene, the van der Waals radius of 0.120 nm for the hydrogen atom was added to the a values calculated above. The a value for azulene is the same one used in a previous paper.[29)] As the A value for benzaldehyde, 0 eV was used.

In the case of acetone, the negative charge is probably located mainly at the oxygen atom in the reduced anion radical ($(CH_3)_2C^{\bullet}-O^-$) of the acetone molecule. From the consideration of the atomic arrangement of the molecule, the oxygen atom may be apart from the cavity surface by the van der Waals radius of 0.152 nm[16)] for the oxygen atom. Therefore, the oxygen atom may shift from the center of the cavity by $r_0 =$ 0.308 nm − 0.152 nm = 0.156 nm. From the r_0/a value of 0.506, the Δ factor of 1.22 was calculated according to a previous paper.[26)] When this Δ factor is considered in this case, the term of $1/a$ in Eq. 11 should be replaced with Δ/a. The calculation considering the Δ factor gave the $E^{\circ}_{S,calcd}$ value of −2.76 V. This value is shown in the parentheses for acetone in Table 3 and better agrees with the $E^{r}_{1/2}$ value of −2.60 V than does the value (−3.13 V) simply calculated by Eq. 11.

It is known from Table 3 that the agreement between the $E^{r}_{1/2}$ and $E^{\circ}_{S,calcd}$ values is good. Thus, the polarographic reversible half-wave redox potentials of organic compounds may be approximately calculated according to Eq. 11.

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