Regular Articles

Relation between the First and the Second Nonaqueous Reduction Potentials of Substituted Stilbenes[1]

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The nonaqueous reduction polarograms of 4,4'-disubstituted stilbenes exhibited two waves, the half-wave reduction potentials, $E_{1/2 \cdot 1}^{red}$ and $E_{1/2 \cdot 2}^{red}$, of which are mainly controlled at the steps of monoanion and dianion formation, respectively. The physical meanings of $E_{1/2 \cdot 1}^{red}$ and $E_{1/2 \cdot 2}^{red}$ can be clearly seen by applying the Born–Haber type thermochemical cycle and molecular orbital (MO) calculation, and theoretical equations concerning $(E_{1/2 \cdot 1}^{red} + E_{1/2 \cdot 2}^{red})$ and $(E_{1/2 \cdot 1}^{red} - E_{1/2 \cdot 2}^{red})$ were formulated. The MO calculations of the PPP-SCFMO, LP-SCFMO, and CNDO/2 levels were used for checking the formulae. The results were quite reasonable on the assumption that the contribution from the solvation energy terms is almost constant or alters in parallel with the LUMO energy in a series of similar substances. In the case of NO_2 as a substituent, as in 4,4'-dinitrostilbene, the $E_{1/2 \cdot 2}^{red}$ value is markedly shifted in a negative direction from that expected from the other substituents, so that the NO_2 group does not fit well with the above theoretical treatment. High-speed cyclic voltammetric measurements were performed to investigate this phenomenon of nitro-substituted aromatics, and the results are discussed in detail.

Keywords——nonaqueous polarography; high-speed cyclic voltammetry; half-wave reduction potential; substituent effect on half-wave potential; Born–Haber thermochemical cycle; PPP-SCFMO; LP-SCFMO; CNDO/2; 4,4'-disubstituted stilbene

In the foregoing paper the nonaqueous oxidation and reduction potentials of substituted stilbenes were discussed in detail from the viewpoint of the correlation with their electronic spectra.[2] The first half-wave reduction $(E_{1/2 \cdot 1}^{red})$ and oxidation $(E_{1/2 \cdot 1}^{oxd})$ potentials are important in this connection.[2,3] However, it is well known that the reduction polarogram of usual organic compounds shows two well-resolved waves in nonaqueous solvents,[4-7] as we actually observed with the present stilbene derivatives. In this paper the physical meaning of the second reduction wave and the relation between the first and the second reduction potentials are discussed from a quantitative viewpoint using the stilbene derivatives as typical model substances.

Experimental

Polarographic and Cyclic Voltammetric (CV) Measurements——The direct current (DC) polarograms were

measured with a Yanagimoto polarograph, model P-1000 (three-electrode system), a saturated calomel electrode (SCE) being used as the reference electrode. The capillary constants used for the dropping mercury electrode are: $m =$ 1.355 mg s^{-1}, $t = 5.82$ s, and $h = 70$ cm in distilled water at open circuit. The CV measurement was made using a combination of a Yanagimoto polarograph (model P-1000), an NF-circuit function generator (model FG-121B), an Iwatsu digital memory (model DM-7100) with a resolution efficiency of 12 bit and 5 μs word^{-1}, and an Iwatsu synchroscope (model SS-5702). In the present study the CV curves were recorded at various sweep rates up to 500 V s^{-1} using the above CV measurement system. All the experiments were carried out at 25 ± 0.1 °C in N,N-dimethylformamide (DMF) containing 0.1 mol dm^{-3} tetrapropylammonium perchlorate (TPAP). The reduction CV measurement at low temperature (down to about -65 °C) was carried out by putting the cell in a dry ice-acetone bath.[8] A platinum electrode was employed as a working and counter electrodes,[8a] but the reference electrode was an SCE which was devised for low temperature measurement by using a long DMF bridge.[8b] Neutral alumina (ca. 3 g, ICN Pharmaceutical W-200, no water added) was added to a ca. 15 cm^3 sample solution according to the suggestion by Parker.[9,10] The purification methods of DMF and TPAP were the same as reported previously.[2]

Samples——The substances used in this study were 4,4'-disubstituted stilbenes as listed in Table I. These are in the $trans$-in-plane form, and the preparation methods and purities were as described in our foregoing paper.[2]

Results and Discussion

Nonaqueous Polarogram and Half-Wave Reduction Potentials

The reduction polarograms were recorded in DMF with a dropping mercury electrode. All the compounds exhibited two waves in DMF. As mentioned in the foregoing paper[2] the first wave is clearly due to anion radical formation by a reversible one-electron reduction process, except in the cases of 4,4'-Cl$_2$ and 4,4'-Br$_2$ substituents.[11] The second reduction wave, however, is irreversible for all substances except in the cases of 4,4'-(CN)$_2$, 4,4'-(COCH$_3$)$_2$, and 4,4'-(COOCH$_3$)$_2$ substituents, which exhibit a reversible wave even at slow (0.4 V s^{-1}) potential scanning speed in CV measurements. In the case of 4,4'-(NO$_2$)$_2$, however, the second reduction wave becomes reversible in faster CV measurement, as will be discussed later. Here, on the assumption that an electron transfer process plays an important role in the potential controlling step of the above reduction waves, the $E^{red}_{1/2 \cdot 1}$ and $E^{red}_{1/2 \cdot 2}$ values of the above compounds were employed as discussed in the later sections. All the experimental data pertinent to the $E^{red}_{1/2 \cdot 1}$ and $E^{red}_{1/2 \cdot 2}$ values of stilbenes are listed in Table I, typical reduction polarograms being illustrated in Fig. 1 for stilbene and the CN derivative. The nonaqueous $E^{red}_{1/2 \cdot 1}$ and $E^{red}_{1/2 \cdot 2}$ values of substituted stilbenes were reported in the literature,[4b,12] although

TABLE I.   Nonaqueous Reduction Polarographic Data of Substituted Stilbenes in Dimethyl Formamide

Substituent	$E^{red}_{1/2 \cdot 1}$ (V)[a]	I_1[b]	$E^{red}_{1/2 \cdot 2}$ (V)[a]	I_2[b]	$E^{red}_{1/2 \cdot 1} - E^{red}_{1/2 \cdot 2}$ (V)	$E^{red}_{1/2 \cdot 1} + E^{red}_{1/2 \cdot 2}$ (V)
4,4'-[N(CH$_3$)$_2$]$_2$	-2.530	1.92	-2.745	0.78	0.215	-5.275
4,4'-(NH$_2$)$_2$	-2.635	1.97	-2.878	1.00	0.243	-5.513
4,4'-(OCH$_3$)$_2$	-2.408	2.09	-2.726	1.40	0.318	-5.134
4,4'-(CH$_3$)$_2$	-2.315	1.92	-2.695	1.47	0.380	-5.010
H (Stilbene)	-2.200	1.59	-2.554	1.16	0.354	-4.754
4,4'-Cl$_2$	-1.933	5.40	—[c]	—[c]	—	—
4,4'-Br$_2$	-1.818	6.09	—[c]	—[c]	—	—
4,4'-(COOCH$_3$)$_2$	-1.583	1.73	-1.783	1.43	0.200	-3.366
4,4'-(COCH$_3$)$_2$	-1.517	1.44	-1.648	1.19	0.131	-3.165
4,4'-(CN)$_2$	-1.495	1.44	-1.795	1.54	0.300	-3.290
4,4'-(NO$_2$)$_2$	-0.971	3.29	-1.900	9.45	0.929	-2.871

$a)$ First and second half-wave reduction potentials $vs.$ SCE are given by $E^{red}_{1/2 \cdot 1}$ and $E^{red}_{1/2 \cdot 2}$, respectively.

$b)$ I_1 and I_2 are equal to $i_d / C \cdot m^{2/3} \cdot t^{1/6}$, where i_d, C and $m \cdot t$ are diffusion current (μA), concentration (mol m^{-3}), and capillary constants (see the text) at the diffusion current near the half-wave potential, respectively.
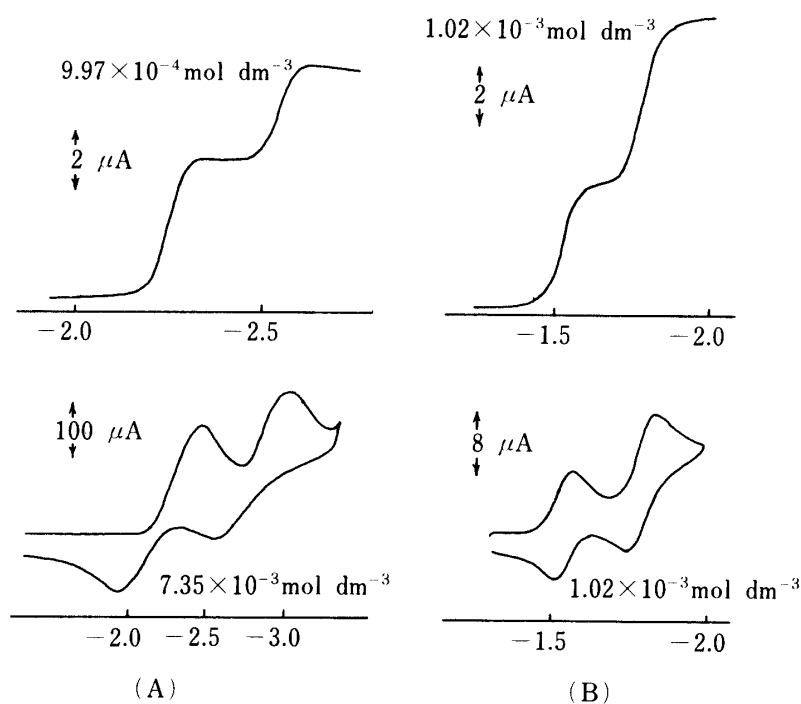
$c)$ See refs. 11 and 28.

Fig. 1.   Nonaqueous Polarograms and Cyclic Voltammograms of Stilbene (A) and
4,4'-Dicyanostilbene (B)

The cyclic voltammogram of the former was obtained at a sweep rate of $4.24\,\mathrm{V\,s^{-1}}$ and
$-64\,^{\circ}\mathrm{C}$, and at $0.5\,\mathrm{V\,s^{-1}}$ and room temperature for the latter. See the text for details.

no detailed discussion was given regarding the second reduction potentials. Our $E^{\mathrm{red}}_{1/2 \cdot 2}$ value for the 4,4'-$(\mathrm{NO_2})_2$ substituent is in quite good agreement with that of Shapiro et al.[4b] We will pay particular attention to this value in the later sections.

Physical Meaning of $E^{\mathrm{red}}_{1/2 \cdot 1}$ and $E^{\mathrm{red}}_{1/2 \cdot 2}$ Values

In our previous paper the physical meaning of the first reduction and oxidation potentials due to a redox couple written as $R + e \rightleftarrows R^-$ or $R - e \rightleftarrows R^+$ was discussed by applying the Born–Haber type thermochemical cycle.[3] In the case of reduction potential, the $E^{\mathrm{red}}_{1/2 \cdot 1}$ value is given by Eq. (1) in eV unit, where the energy zero level is placed in vacuo.

$$F \cdot E^{\mathrm{red}}_{1/2 \cdot 1} \, (\mathrm{R^-/R}) = \varDelta G^\circ - \varepsilon_{\mathrm{lu}} - \varDelta E^-_{\mathrm{solv}} \tag{1}$$

where $\varDelta E^-_{\mathrm{solv}}$ is the solvation energy difference of the monoanion (anion radical) and the neutral species: $\varDelta E^-_{\mathrm{solv}} = E^-_{\mathrm{solv}} - E_{\mathrm{solv}}$. The absolute potential of the reference electrode is expressed by $\varDelta G^\circ$, which is $-4.70\,\mathrm{eV}$ in the case of the $(\mathrm{Ag/Ag^+})$ electrode in acetonitrile.[13] The LUMO energy of the samples is given by $\varepsilon_{\mathrm{lu}}$. Let us now consider the Born–Haber type energy cycle for dianion formation from the monoanion radical. Referring to Chart 1 and
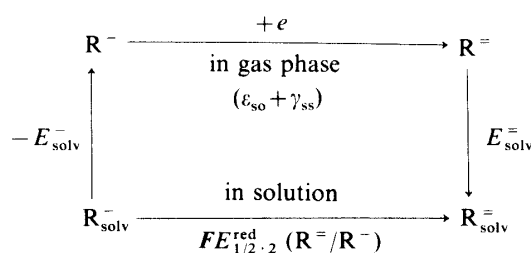

Chart 1

assuming Koopmans' theorem[14] we can easily derive Eq. (2), which is rewritten as Eq. (3).

$$\Delta G^\circ - F \cdot E^{red}_{1/2 \cdot 2} = \varepsilon_{so} + \gamma_{ss} + E^=_{solv} - E^-_{solv} \tag{2}$$

$$F \cdot E^{red}_{1/2 \cdot 2} (R^=/R^-) = \Delta G^\circ - \varepsilon_{so} - \gamma_{ss} - \Delta E^=_{solv} \tag{3}^{[15,16]}$$

where $\Delta E^=_{solv} = E^=_{solv} - E^-_{solv}$, and γ_{ss} is the coulomb repulsion integral between the two electrons existing in the singly occupied MO (SOMO : ψ_s) of the monoanion radical (R^-),[17,18] ε_{so} being the SOMO energy. If differential overlaps are neglected, γ_{ss} is given by Eq. (4),[18] where $\gamma_{\mu\nu} = \langle \mu(1)\nu(2) | G | \mu^*(1)\nu^*(2)\rangle$, which represents the two-electron repulsion integral in the atomic orbitals χ_μ and χ_ν.

$$\gamma_{ss} = \langle \psi_s(1)\psi_s(2) | G | \psi_s^*(1)\psi_s^*(2)\rangle = \sum_\mu \sum_\nu c^2_{s\mu} c^2_{s\nu} \gamma_{\mu\nu} \tag{4}$$

Now, the difference and the sum of Eqs. (1) and (3) lead to Eqs. (5) and (6), respectively.

$$F(E^{red}_{1/2 \cdot 1} - E^{red}_{1/2 \cdot 2}) = \varepsilon_{so} - \varepsilon_{lu} + \gamma_{ss} + (\Delta E^=_{solv} - \Delta E^-_{solv}) \tag{5}$$

$$F(E^{red}_{1/2 \cdot 1} + E^{red}_{1/2 \cdot 2}) = 2\Delta G^\circ - (\varepsilon_{lu} + \varepsilon_{so} + \gamma_{ss}) - (\Delta E^-_{solv} + \Delta E^=_{solv}) \tag{6}$$

Here, $(\Delta E^=_{solv} - \Delta E^-_{solv})$ and $(\Delta E^=_{solv} + \Delta E^-_{solv})$ are respectively given by Eqs. (7) and (8).

$$(\Delta E^=_{solv} - \Delta E^-_{solv}) = E^=_{solv} + E_{solv} - 2E^-_{solv} \tag{7}$$

$$(\Delta E^=_{solv} + \Delta E^-_{solv}) = E^=_{solv} - E_{solv} \tag{8}$$

Molecular Orbital (MO) Calculation for Neutral, Monoanion, and Dianion Species of Substituted Stilbenes

In order to interpret Eqs. (5) and (6), MO calculation for the neutral (R) and dianion $(R^=)$ species of stilbenes was carried out by the π-electron approximation at the PPP-SCFMO level and also by the standard CNDO/2 method.[19,20] For the monoanion (R^-), which is the anion free radical, a restricted Longuet-Higgins–Pople type open shell SCFMO (LP-SCFMO) calculation was performed with π-electron approximation.[21,22] Two-center repulsion integrals appearing in the SCFMO calculations were evaluated by using Nishimoto–Mataga's approximation.[23] The details of the MO calculations and the parameters necessary for them were the same as reported in the foregoing papers.[24] Although the molecular dimensions seem to be somewhat different among the neutral, monoanion, and dianion species,[25] this kind of difference was neglected in the actual MO calculation for the sake of convenience, since the effect may not be too great for the present rigid molecule.

Substituent Effect on $E^{red}_{1/2 \cdot 1}$ and $E^{red}_{1/2 \cdot 2}$ Values

It has been well verified that the $E^{red}_{1/2 \cdot 1}$ and $E^{oxd}_{1/2 \cdot 1}$ values are in good linear relation to the Hammett type substituent constants.[24] For the case of stilbene derivatives we have reported this kind of relation in an earlier paper.[2] Now we can see in Fig. 2 that a good linearity of the $E^{red}_{1/2 \cdot 2}$ vs. substituent constant plot also holds for the substituted stilbenes in a nonaqueous solvent,[26] the slope being quite similar to that in the case of $E^{red}_{1/2 \cdot 1}$ values. This means that the $(E^{red}_{1/2 \cdot 1} - E^{red}_{1/2 \cdot 2})$ value takes a similar order of magnitude for all substituents, except for the NO_2 group, which shows a large deviation from the regression line (the $(E^{red}_{1/2 \cdot 1} - E^{red}_{1/2 \cdot 2})$ value is very large).

Correlation between the Half-Wave Reduction Potentials and the MO Calculation Results

In this section, we will discuss the correlation of $E^{red}_{1/2 \cdot 1}$ and $E^{red}_{1/2 \cdot 2}$ values to the MO calculation results. The PPP-SCFMO calculation results necessary for the present discussion of 4,4'-disubstituted stilbenes are listed in Table II. According to Eqs. (1) and (3), $E^{red}_{1/2 \cdot 1}$ and $E^{red}_{1/2 \cdot 2}$ may be linearly related to ε_{lu} and $(\varepsilon_{so} + \gamma_{ss})$, respectively, on the assumption that the solvation energy terms are almost constant or alter in parallel to the change of ε_{lu} in a series of similar substances. Many studies have reported linear $E^{red}_{1/2 \cdot 1}$ vs. ε_{lu} plots based on Eq. (1).[27]

TABLE II.   Orbital Energies, Two-Center Repulsion Integral Values (γ_{ll} and γ_{ss}), and
Total Energy Difference between R$^=$ and R Species Necessary to Interpret
$E_{1/2 \cdot 1}^{red}$ and $E_{1/2 \cdot 2}^{red}$ Values of Substituted Stilbenes[a]

Substituent	ε_{lu}[b,h]	ε_{so}[c,h]	$\varepsilon_{so} - \varepsilon_{lu}$	$\varepsilon_{ho}^{=}$[d]	γ_{ll}[e]	γ_{ss}[f]	$E_t(R^=)$[g]$ - E_t(R)$[g]
4,4'-[N(CH$_3$)$_2$]$_2$	−1.7753	−0.0491	1.7262	1.6245	4.0293	3.9518	—
4,4'-(NH$_2$)$_2$	−2.0828	−0.3480	1.7348	1.3387	4.0464	3.9751	8.3254
4,4'-(OCH$_3$)$_2$	−2.3639	−0.6036	1.7603	1.1090	4.0736	4.0049	8.0332
4,4'-(CH$_3$)$_2$	−2.3662	−0.6089	1.7572	1.0918	4.0807	3.9971	7.3598
H (Stilbene)	−2.4846	−0.7080	1.7767	1.0182	4.0908	4.0205	7.7391
4,4'-Cl$_2$	−2.4383	−0.6665	1.7718	1.0557	4.0889	4.0180	—
4,4'-(COCH$_3$)$_2$	−3.1187	−1.5940	1.5247	−0.1310	3.4763	3.4285	4.9487
4,4'-(CN)$_2$	−2.9049	−1.3622	1.5427	−0.1061	3.6060	3.5235	5.7008
4,4'-(NO$_2$)$_2$	−3.8605[i]	−2.3305	1.5301	−0.8868	3.3306	3.2525	3.8344

a) All the values are in eV unit. The calculations except for $E_t(R^=)$ and $E_t(R)$ were carried out by the PPP-SCFMO method.

b) LUMO energy of neutral species.

c) SOMO energy of anion radicals.

d) HOMO energy of dianion species.

e) Values at LUMO of neutral species.

f) Values at SOMO of anion radicals.

g) CNDO/2 total energy for dianion (R$^=$) and neutral (R) species.

h) The orbital symmetry in all cases is b_g.

i) Here it should be noted that the penultimate LUMO (a$_u$) for 4,4'-dinitro-substituents is especially stabilized to a position close to ε_{lu}.
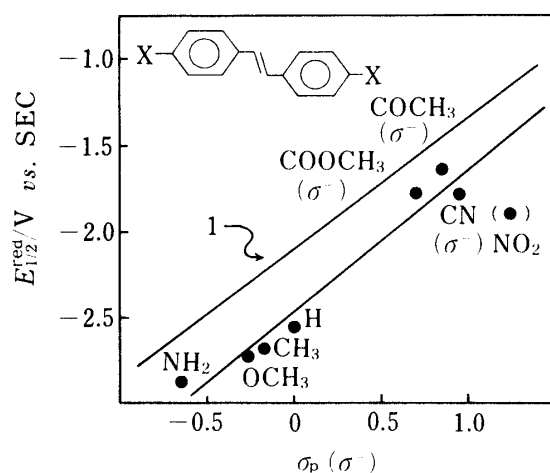

Fig. 2.   Linear Relation between the $E_{1/2 \cdot 2}^{red}$ Values and σ_p (σ^-) Values for 4,4'-Disubstituted Stilbenes

The least-squares equation is $E_{1/2 \cdot 2}^{red} = 0.820\sigma_p (\sigma^-) + 0.276$ with $n = 7$, $r = 0.979$, $s = 0.120$. The solid straight line (1) is for the $E_{1/2 \cdot 1}^{red}$ vs. σ_p (σ^-) plot, the details of which have already been reported in ref. 2. For the NO$_2$ group, which shows a quite large deviation from linearity, see the text.
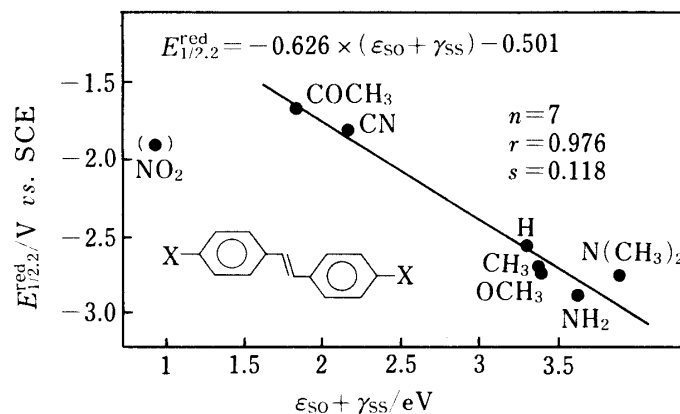

Fig. 3.   Linear Relation between $E_{1/2 \cdot 2}^{red}$ and ($\varepsilon_{so} + \gamma_{ss}$) Values for the 4,4'-Disubstituted Stilbenes

The NO$_2$ group shows a large deviation from the linearity (see the text).

Our result on 4,4′-disubstituted stilbenes is also quite good:[12] $E_{1/2 \cdot 1}^{\text{red}} = -0.869\varepsilon_{\text{lu}} - 4.260$ with $n=9$ (all substituents in Table I), $r=0.952$, $s=0.185$, where ε_{lu}'s are taken from Table II. The fact that the absolute slope is less than the theoretical value of 1 indicates that the above-mentioned assumption does not hold strictly, and also the ε_{lu} values do not exactly correspond to the true orbital energies.

Figure 3 shows the linear relation between $E_{1/2 \cdot 2}^{\text{red}}$ and $(\varepsilon_{\text{so}} + \gamma_{\text{ss}})$; it is clear that Eq. (3) is well satisfied.[28] However, the NO_2 group is exceptional, deviating markedly from the linear relation. This is similar to the behavior in Fig. 2. The reason will be discussed later. The absolute slope of the regression line in Fig. 3 is also less than 1, possibly for the reasons mentioned above. As has been stated already (see ref. 17), $(\varepsilon_{\text{so}} + \gamma_{\text{ss}})$ is a good approximation for $\varepsilon_{\text{ho}}^{=}$ (HOMO energy of dianion $R^{=}$), and thus we expect good linearity in the $E_{1/2 \cdot 2}^{\text{red}}$ vs. $\varepsilon_{\text{ho}}^{=}$ plot. The result is: $E_{1/2 \cdot 2}^{\text{red}} = -0.745\varepsilon_{\text{ho}}^{=} - 1.779$ with $n=7$, $r=0.966$, $s=0.142$. Again, the NO_2 group deviates from the linear relation, as will be discussed later.

Next, let us focus our attention on Eq. (5), which indicates a linear relation between $(E_{1/2 \cdot 1}^{\text{red}} - E_{1/2 \cdot 2}^{\text{red}})$ and $(\varepsilon_{\text{so}} - \varepsilon_{\text{lu}} + \gamma_{\text{ss}})$ under the same conditions as above regarding the contribution of the solvation energy terms to Eqs. (2) and (3) (vide ante). Now, plotting of the above relationship led to the result shown in Fig. 4, where we see apparently two straight lines, one of which is mainly for electron-donating groups and the other is for electron-accepting ones except for the NO_2 group, which again deviates markedly from the linear relation. This behavior of the NO_2 group is the same as seen in Fig. 2. However, it should be noted here that the values of $(E_{1/2 \cdot 1}^{\text{red}} - E_{1/2 \cdot 2}^{\text{red}})$ are very small and in almost the same order throughout all the substituents except for the NO_2 group as can be seen from Figs. (2) and (4) and Table I. Accordingly the change of the solvation energy term (Eq. (7)) values in Eq. (5) with the substituents may play a more important role compared to its contribution to the other equations. If the solvation energy terms could be estimated accurately, we believe that the results for all the substituents would be expressed by Eq. (5) as one straight line.[29] The result in Fig. 4 is for the case where the solvation energy terms are assumed to be constant as was mentioned hitherto, so that it reflects the change in the MO calculation results with the substituents. Now Table II shows that the change of γ_{ss} (also γ_{ll}) is in the range of 3.952 (4.029) to 4.021 (4.091) eV for electron-donating substituents including stilbene itself, but for the case of electron-accepting substituents this change is smaller and is in the range of 3.252 (3.331) to 3.524 (3.606) eV. The same tendency as with the γ_{ss} values is also found with the $(\varepsilon_{\text{so}} - \varepsilon_{\text{lu}})$ values, that is, the values for electron-donating substituents are 1.726—1.777 eV, but those for
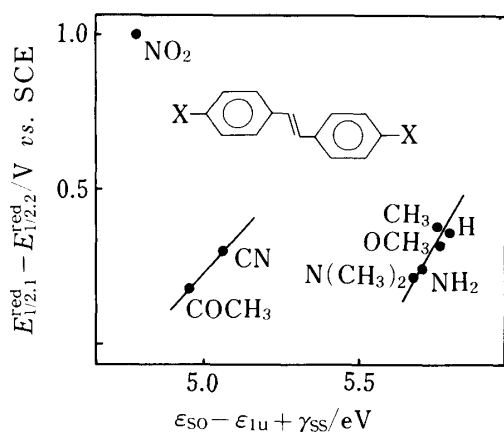

Fig. 4. The Correlation of $(E_{1/2 \cdot 1}^{\text{red}} - E_{1/2 \cdot 2}^{\text{red}})$ and $(\varepsilon_{\text{so}} - \varepsilon_{\text{lu}} + \gamma_{\text{ss}})$ Values

See the text for a detailed explanation.

Fig. 5. The Relationship between $(E_{1/2 \cdot 1}^{\text{red}} + E_{1/2 \cdot 2}^{\text{red}})$ and $(\varepsilon_{\text{lu}} + \varepsilon_{\text{so}} + \gamma_{\text{ss}})$ Values
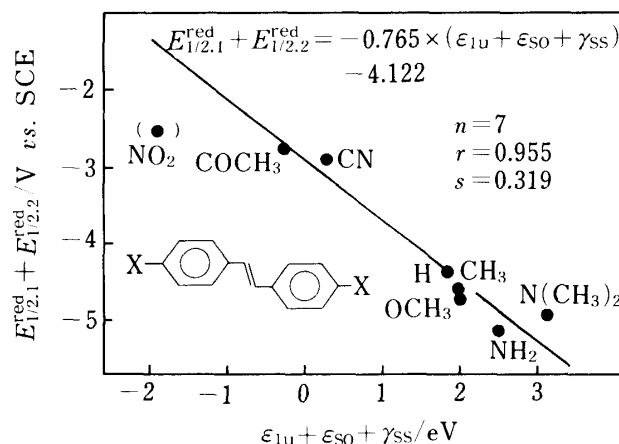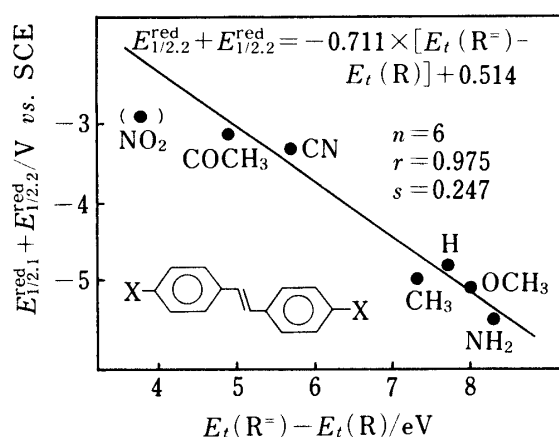
See the text for a detailed explanation.

Fig. 6. The Relationship between $(E^{red}_{1/2 \cdot 1} + E^{red}_{1/2 \cdot 2})$ and $(E_t(R^=) - E_t(R))$ Values
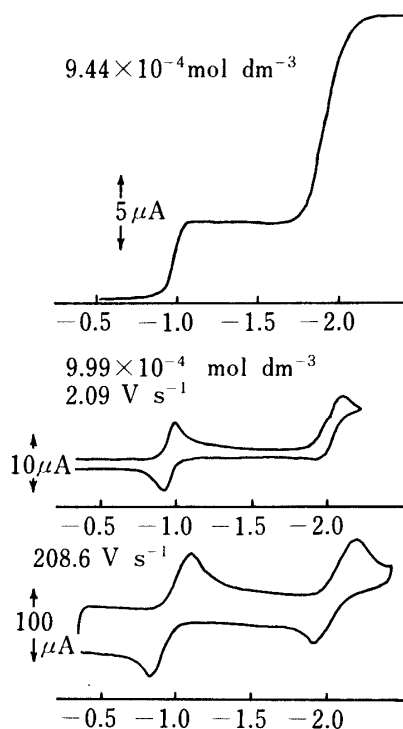
See the text for a detailed explanation.

Fig. 7. Nonaqueous (DMF) Polarogram and Cyclic Voltammograms of 4,4'-Dinitrostilbene at Room Temperature under the Conditions Given in the Figure

See the text for details.

electron-accepting groups are 1.525—1.543 eV, being smaller than the former. We may thus expect that the linear relation based on Eq. (5) is divided into two cases, as is actually seen in Fig. 4.[19,20,30] Finally the physical meaning of the relation given by Eq. (6) will be discussed. Under the same conditions as given hitherto regarding the solvation energy terms, Eq. (6) shows $(E^{red}_{1/2 \cdot 1} + E^{red}_{1/2 \cdot 2})$ to be linearly related to $(\varepsilon_{1u} + \varepsilon_{so} + \gamma_{ss})$. As is clear from the Born–Haber type energy cycle (see Chart 1)[3] ε_{1u} and $(\varepsilon_{so} + \gamma_{ss})$ correspond to the total energy difference written as $(E_t(R^-) - E_t(R))$ and $(E_t(R^=) - E_t(R^-))$, respectively, so that the $(\varepsilon_{1u} + \varepsilon_{so} + \gamma_{ss})$ value also corresponds to the $(E_t(R^=) - E_t(R))$ value, which is the total energy difference between the dianion and the neutral species.[31] Figure 5 shows the relation of $(E^{red}_{1/2 \cdot 1} + E^{red}_{1/2 \cdot 2})$ to $(\varepsilon_{1u} + \varepsilon_{so} + \gamma_{ss})$; the linearity seems to be quite good. However, the NO_2 group is also an exceptional substituent (vide ante). The relation of $(E^{red}_{1/2 \cdot 1} + E^{red}_{1/2 \cdot 2})$ to the total energy difference of R and $R^=$ has also been studied, the latter values being calculated by the standard CNDO/2 method[32] (see Table II). The results are depicted in Fig. 6, and a good linear relation was again obtained. Note here that the NO_2 group has been brought into the linear relation. This is presumably because[33] the calculated total energies at the CNDO/2 level are appropriate to make up for the large negative shift of $E^{red}_{1/2 \cdot 2}$ value of the NO_2-substituted stilbene.

Cyclic Voltammetry of Nitro-Substituted Aromatics Including 4,4'-Dinitrostilbene

As was mentioned heretofore, the $E^{red}_{1/2 \cdot 2}$ value of 4,4'-dinitrostilbene (DNS) shows an exceptionally large negative shift, so that a quite large deviation is observed from the linear relation between $E^{red}_{1/2 \cdot 2}$ vs. Hammett's σ, or $E^{red}_{1/2 \cdot 2}$ vs. MO energies (vide ante). A possible reason for this phenomenon is that the reduction potential $E^{red}_{1/2 \cdot 2}$ is not mainly controlled at the step of the dianion $(R^=)$ formation. In order to check this possibility, highspeed CV

measurements were tried on DNS as well as nitro-substituted aromatics such as 4-nitropyridine N-oxide (4NPO) and 4-nitroquinoline N-oxide (4NQO), the $E^{red}_{1/2 \cdot 2}$ values of which are well known to be strongly negatively shifted. Figure 7 illustrates the polarogram and the CV curves at two different sweep rates of DNS. At the rate of 2.09 V s^{-1} it is clear that the CV curve corresponding to the second wave is irreversible and no backward sweep wave appears, although the first reduction wave is completely reversible. However, the second wave turns out to be reversible at the sweep rate 208.6 V s^{-1}, as is clearly seen in Fig. 7. These results may indicate that the dianion is formed as the first process in the second reduction wave, and $E^{red}_{1/2 \cdot 2}$ would be mainly controlled at this dianion formation process. Thus, the large negative shift of the $E^{red}_{1/2 \cdot 2}$ value of DNS, compared to those of the other substituents, may be due to some reason other than the aforementioned possibility. The same conclusion has also been obtained in the cases of 4NPO and 4NQO, the dianions of these compounds being much more stable than that of DNS. The analysis of the CV curve by the method developed by Nicholson and Shain[34] led to the result that the life-times of the dianions of DNS, 4NPO, and 4NQO are of the order of $ca.$ 10^{-4}, $ca.$ 1.2, and $ca.$ 3.3 s.[35] Thus, the origin of the large negative shift of $E^{red}_{1/2 \cdot 2}$ value of DNS, $etc.$ is still not clear at present. Nevertheless the following possibility may be considered. Since the NO_2 group has a strongly electron-withdrawing nature, an intramolecular charge transfer occurs from the stilbene moiety to the two NO_2 groups in the molecule of DNS, as was discussed formerly. As a result, the orbital electron densities (frontier densities) in SOMO (or HOMO of the dianion $R^=$) are largely localized in the nitro group, so that we may expect significant short-range solute-solvent interactions, which cannot be well described by the Born type formulae.[18,36] Such interactions may well be one of the reasons for the exceptional behaviour of $E^{red}_{1/2 \cdot 2}$ of the NO_2 substituent. More rigorous consideration of this possibility must await a further study.

References and Notes

1) Presented at the 102nd (Osaka, April 1982) Annual Meeting of the Pharmaceutical Society of Japan (Abstract, p. 345), and the 28th Symposium of Polarography and Electrochemical Analysis (Sapporo, Novermber 1982) (*Abstr., Rev. Polarogr.* (Kyoto), **28**, 54 (1982)).

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11) See Note 47 in ref. 2. As a final result, dehalogenation may occur at the reduction wave.

12) This kind of linear relation pertinent to stilbene derivatives was also formerly reported by T. Fueno *et al.*, who used the Hückel naive MO. T. Fueno, K. Morokuma, and J. Hurukawa, *J. Chem. Soc. Jpn., Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 116 (1958).

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14) See, for example, R. G. Pearson, "Symmetry Rules for Chemical Reactions," Wiley-Interscience, New York, 1976, p. 240.

15) This equation corresponds well with the treatment by Hush and Blackledge.[16] However, the dianion $R^=$ is produced from the monoanion radical R^- in the equilibrium state, so that the ε_{so} value obtained from the LP-SCFMO (see the text) calculation of R^- should be used instead of the ε_{1u} value of the neutral species R.

16) N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

17) When an electron enters the SOMO orbital, electron repulsion interaction occurs between the two electrons in SOMO. This type of interaction also seems to play an important role in the energy change from R^- to $R^=$ in the gas phase, and is given by γ_{ss}.[18] Ultimately the electron affinity of R^- becomes $-(\varepsilon_{so} + \gamma_{ss})$, which is a good approximation for the HOMO energy $(\varepsilon_{ho}^=)$ of the dianion $R^=$. Our actual SCFMO calculation for $R^=$ of various 4,4'-disubstituted stilbenes ($N(CH_3)_2$, NH_2, OCH_3, CH_3, Cl, H, CN, $COCH_3$, NO_2) led to a very good linear relation of $(\varepsilon_{so} + \gamma_{ss})$ to $\varepsilon_{ho}^=$ with a positive correlation coefficient of $r = 0.999$ (see the text): $\varepsilon_{ho}^= = 0.819 \cdot (\varepsilon_{so} + \gamma_{ss}) - 1.655$.

18) N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel Dekker, New York, 1970, p. 235, 281.

19) The reason why the values of γ_{ss} (or γ_{11}) and $(\varepsilon_{so} - \varepsilon_{lu})$ are somewhat different between electron-donating substituents and electron-accepting ones may be as follows. Let us apply the treatment of the so-called "composite-system method"[20] to the substituted stilbenes by dividing them into stilbene itself and the substituent. Though the electron-donating substituents such as NH_2 *etc.* do not have vacant π-orbitals, the electron accepting ones such as $>C=O$, $-C\equiv N$ *etc.* do have them, so that the mutual interaction of the vacant π-orbitals of stilbene itself with the vacant orbitals of electron-accepting substituents is rather large, though this kind of interaction is small for the case of electron-donating ones. Consequently, the LUMO of the whole molecule is a little different in nature for the two types of substituent groups. In other words, the charge transfer contribution from stilbene itself to the electron-accepting substituent is reflected in the LUMO.

20) S. Nagakura, *Pure Appl. Chem.*, **7**, 79 (1963).

21) The ground state of LP-SCFMO calculation is not completely in so-called SCF state,[22] so excited configurations are slightly mixed in the ground state. Neglecting this effect the MO's were employed in the interpretation of Eqs. (5) and (6).

22) *a)* H. C. Longuet-Higgins, J. A. Pople, *Proc. Phys. Soc., London, Sec. A*, **68**, 591 (1955); *b)* A. Ishitani and S. Nagakura, *Theor. Chim. Acta* (Berlin), **4**, 236 (1966); *c)* R. Zahradnik and P. Cársky, *J. Phys. Chem.*, **74**, 1235, 1240, 1249 (1970); *d)* K. Ezumi, T. Kubota, H. Miyazaki, and M. Yamakawa, *J. Phys. Chem.*, **80**, 980 (1976).

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24) See ref. 2 and other papers cited therein.

25) *a)* K. Ezumi, H. Miyazaki, and T. Kubota, *J. Phys. Chem.*, **74**, 2397 (1970); *b)* H. Suzuki, K. Koyano, T. Shida, and A. Kira, *Bull. Chem. Soc. Jpn.*, **55**, 3690 (1982).

26) Similar results have also been observed for the $E_{1/2 \cdot 2}^{red}$ values of *p*-substituted azobenzenes. To be published later.

27) *a)* A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York 1961, p. 173; *b)* S. Koide, *Kagaku No Ryoiki*, **8**, 287 (1954); **11**, 572 (1957) (Review, in Japanese); *c)* T. Kubota, K. Nishikida, H. Miyazaki, K. Iwatani, and Y. Ōishi, *J. Am. Chem. Soc.*, **90**, 5080 (1968).

28) In the case of the Cl substituent there is a possibility that dechlorination may occur at the first reduction wave,[11] so the second wave of 4,4'-dichlorostilbene may be due to stilbene itself produced by the dechlorination reaction. This seemed likely from CV and polarographic measurements, so that the Cl substituent was omitted from the plot in Fig. 3.

29) Loutfy[36] discussed theoretically the substituent dependence of the solvation energies, derived from the $E_{1/2 \cdot 1}^{oxd}$ or $E_{1/2 \cdot 1}^{red}$ values of substituted pyridine *N*-oxides, on the basis of Born type equations. The results indicate that the solvation energy difference among the substituents is not large, but there is some systematic relationship with the substituent properties. This approach bears some relation to the treatment of Eq. (5).

30) As described in the text the largest contribution to $(\varepsilon_{so} - \varepsilon_{lu} + \gamma_{ss})$ is, of course, γ_{ss}. Moreover, if we discuss the present problem by using only the MO pertaining to the neutral species, $(\varepsilon_{so} - \varepsilon_{lu})$ becomes zero. These circumstances make it possible to obtain a figure very similar to Fig. 4 when $(E_{1/2 \cdot 1}^{red} - E_{1/2 \cdot 2}^{red})$ *vs.* γ_{11} is plotted, as actually observed.

31) This conclusion can also be derived as follows. For the equilibria of $R + e \rightleftarrows R^-$ and $R^- + e \rightleftarrows R^=$ the following equations can be written for the $E_{1/2 \cdot 1}^{red}$ and $E_{1/2 \cdot 2}^{red}$ under the conditions of equal diffusion constants and equal activity coefficients between R and R^-, and also between R^- and $R^=$.

$$E_{1/2 \cdot 1}^{red} \simeq E_1 + (RT/nF) \ln(R^-/R), \text{ and } E_{1/2 \cdot 2}^{red} \simeq E_2 + (RT/nF) \ln(R^=/R^-)$$

Thus, $(E_{1/2 \cdot 1}^{red} + E_{1/2 \cdot 2}^{red}) = (E_1 + E_2) + (RT/nF) \ln(R^=/R)$, which indicates that $nF(E_{1/2 \cdot 1}^{red} + E_{1/2 \cdot 2}^{red})$ is combined with the free energy change between R and $R^=$.

32) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, Inc., New York, 1970.

33) The total energy difference between R and $R^=$ is obtained as the difference of very large quantities, so that concomitant error is unavoidable. Nevertheless, the mutual relation between $(\varepsilon_{lu} + \varepsilon_{so} + \gamma_{ss})$ and $(E_t (R^=) - E_t(R))$ is quite good, as $(E_t(R^=) - E_t(R)) = 1.049 (\varepsilon_{lu} + \varepsilon_{so} + \gamma_{ss}) + 6.643$ with $n = 7$, $r = 0.986$, $s = 0.315$ in eV unit.

34) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

35) In this experiment at 20 °C we did not add the neutral alumina to the measuring sample solution in order to remove trace water (see Experimental). If this had been done, the life time given in the text might have been longer. This kind of result was reported for the dianion of nitrobenzene.[10]

36) R. O. Loutfy, *J. Chem. Phys.*, **66**, 4781 (1977).