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Presumptive Structures of Activated Complexes in Polarographic Redox Reactions of Unsaturated Organic Compounds. II. Polarographic Oxidations of Aromatic Hydrocarbons, Aromatic Amines, Aromatic Bromides and Benzaldehyde Derivatives, and Polarographic Reductions of Several Kinds of Disubstituted Compounds

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The theoretically proposed structures of activated complexes in polarographic redox reactions of unsaturated organic compounds were shown to be valid without exception in the cases of the oxidation reactions examined. Additional data supporting the validity of the assumption for reduction reactions were also obtained. The MASP-HMO method was very useful for the calculation of π-stabilization energies of *para-* and *meta-*disubstituted aromatic compounds.

Keywords——activated complex; π-stabilization energy; HMO calculation; polarographic redox potentials; aromatic compounds

In the preceding paper of this series,[2] the activated complexes in the diffusion-controlled reversible polarographic reductions of unsaturated organic compounds were presumed to be formed by the interaction of the π-molecular orbital of each molecule with a hypothetical atomic orbital of the electrode employed, liquid mercury, having an energy close to the energy of its Fermi level. It was shown theoretically that if this assumption is correct, the difference in the half-wave reduction potentials of every two compounds of a group of compounds having analogous chemical structures should be proportional to the difference in the maximum π-stabilization energies of the two compounds calculated from the presumed structures of their activated complexes. In all cases of polarographic reductions of aromatic hydrocarbons, aromatic aldehydes and quinones studied in the previous paper, this proportionality was found to hold. It was concluded that the presumed structures of the activated complexes are correct.

In this paper the presumed structures of activated complexes are extended to the case of diffusion-controlled reversible polarographic oxidation reactions of unsaturated organic compounds employing a platinum electrode. Supplemental data supporting the correctness of the presumed structures of activated complexes in polarographic reductions are also given. The most likely mechanism of the potential-determining step in the polarographic reductions of chloro- and bromobenzene derivatives is discussed.

Experimental

The polarographic half-wave redox potentials employed in this paper were limited to those which have been reported in the literature for diffusion-controlled reversible polarographic redox reactions in aprotic solvents.

In the HMO calculation of all compounds, the hetero-atomic parameters proposed in our previous paper[3] were employed. In the cases of compounds having two substituents in the molecule the mutual

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additive substituent parameters (MASP) proposed in our previous paper[3] were also employed. The molecular orbital calculations were carried out on FACOM 230-75 and FACOM M-190 computers at the Computation Center of Kyushu University.

Results and Discussion

Polarographic Oxidation Reactions of Aromatic Compounds

In the polarographic oxidation reactions of unsaturated organic compounds employing a platinum anode the π electron(s) is considered to be transferred from the molecule to the Fermi level of the electrode metal. The magnitude of the energy of the Fermi level of platinum is known to be about -8.9 eV[4] and it is not much different from that of the Coulomb integral of a carbon atom forming part of a π-electronic system in an organic compound. Therefore, by analogy with the polarographic reduction reactions of unsaturated organic compounds mentioned in the previous paper, the hypothetical atomic orbital of the platinum electrode can be presumed to interact with the π-molecular orbital of a molecule (R) to form an activated complex ($[\mathrm{R}\ldots ne^{-}\ldots(\mathrm{Pt})]^{\ddagger}$) for the oxidation reaction (Eq. (1)). The transference of electron(s) from R to the electrode can be considered to occur at this stage of the reaction. In addition, the difference in the polarographic half-wave oxidation potentials of two compounds of a group of compounds having analogous chemical structures, $\mathrm{R_A}$ and $\mathrm{R_B}$, should be correlated linearly with the difference in their activation energies. If the basic assumption is correct, the difference in the maximum π-stabilization energies calculated for the presumed structures of the activated complexes of $\mathrm{R_A}$ and $\mathrm{R_B}$, $[\varDelta E_{\mathrm{r(Pt)}}]^{\mathrm{A}}_{\mathrm{max}}$ and $[\varDelta E_{\mathrm{r(Pt)}}]^{\mathrm{B}}_{\mathrm{max}}$, is expected to correlate linearly with the difference in their activation energies. Therefore, Eq. (2) is derived. Here, F and r denote the Faraday constant and the atom of a molecule where the interaction with the hypothetical atomic orbital of the platinum electrode occurs, respectively. Both a and c are constants having the same physical significance as the corresponding constants of the polarographic reductions described in the previous paper; their values can be considered to be nearly constant for a series of reactions of analogous compounds.

$$\mathrm{R} + (\mathrm{Pt}) \rightleftharpoons [\mathrm{R}\cdots ne^{-}\cdots(\mathrm{Pt})]^{\ddagger} \rightleftharpoons \mathrm{R}^{n+} + ne^{-}(\mathrm{Pt}) \qquad (1)$$

$$F(E^{\mathrm{A}}_{1/2}-E^{\mathrm{B}}_{1/2}) = \frac{c}{a}\left[(\varDelta E_{\mathrm{r(Pt)}})^{\mathrm{A}}_{\mathrm{max}}-(\varDelta E_{\mathrm{r(Pt)}})^{\mathrm{B}}_{\mathrm{max}}\right] \qquad (2)$$

From the viewpoint of chemical reactions, the formation of an activated complex having the presumed structure mentioned above may be considered to fall in the category of addition reactions. The π-stabilization energy for the addition reaction of a neutral molecule with a cation can be calculated by means of Eq. (3), irrespective of the number of electrons involved in the electrode reaction. Here, $C_r{}^m$ and η_m denote the coefficients of the rth atomic orbital and the coefficients of the resonance energy part of the mth molecular orbital of a molecule to be oxidized, respectively, as calculated by the HMO method. $\gamma\beta$ denotes the resonance integral of the π-electronic structure newly formed between the molecule to be oxidized and the platinum electrode.

$$\varDelta E_{\mathrm{r(Pt)}} = 2\sum_{m}^{occ}\frac{(C_r{}^m)^2}{\eta_m}(-\gamma^2\beta) \qquad (3)$$

If the proportionality expressed by Eq. (2) actually holds between the differences in the observed polarographic half-wave oxidation potentials ($\varDelta E_{1/2}$) and the differences in the calculated maximum π-stabilization energies ($\varDelta(\varDelta E_{\mathrm{r(Pt)}})_{\mathrm{max}}$), it can be concluded that

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3) Y. Ono and Y. Ueda, *Chem. Pharm. Bull.*, **22**, 390 (1974).

4) J.B. Ketterson, F.M. Muller and L.R. Windmillar, *Phys. Rev.*, **186**, 657 (1969); O.K. Anderson, *Phys. Rev. B*, **2**, 883 (1970).

the assumption expressed in Eq. (1) is reasonable. Therefore, this proportionality was examined, employing the half-wave potentials of aromatic hydrocarbons,[5] methyl-substituted aromatic hydrocarbons,[6] aromatic amines,[7] aromatic bromides,[7] and benzaldehydre derivatives.[8]

The results are shown in Fig. 1. Maccoll's relationships[9] were also examined, and the results are shown in Fig. 2. Fig. 1 clearly shows that the linear relationship expressed by Eq. (2) holds satisfactorily in all of the cases examined. Maccoll's relationship does not hold in the case of benzaldehyde derivatives. This clearly suggests that the presumed structure of the activated complex for polarographic oxidation reactions is correct.

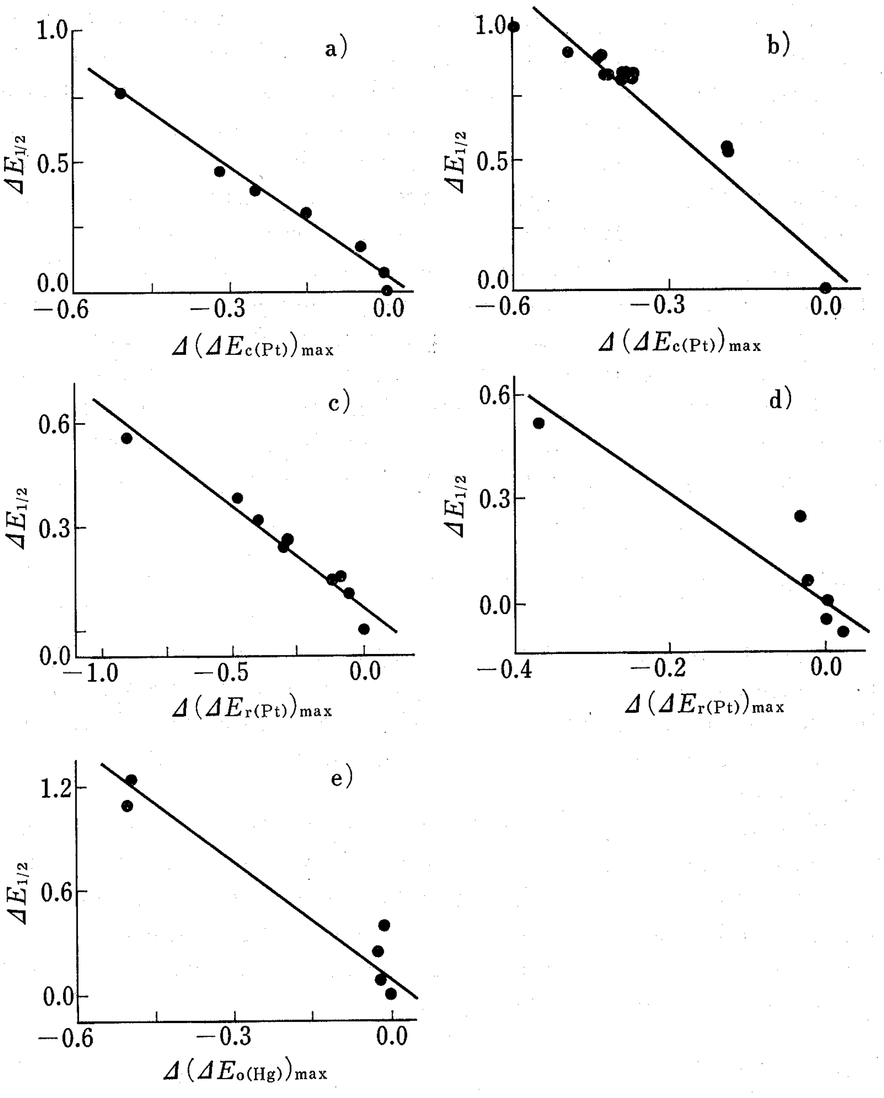

Fig. 1. Correlation between Differences of $E_{1/2}$ (V) and the Corresponding Differences of $(\Delta E_{r(pt)})_{\max}(-\gamma^2\beta)$*: a) Aromatic Hydrocarbons; b) Methyl-substituted Aromatic Hydrocabons; c) Aromatic Amines; d) Aromatic Bromides; e) Benzaldehyde Derivatives

*: $(\Delta E_{r(Pt)})_{\max}$ values were calculated by the Pauling-Wheland method in cases a), b), c) and d) and by the HMO-MASP method in the case of e).

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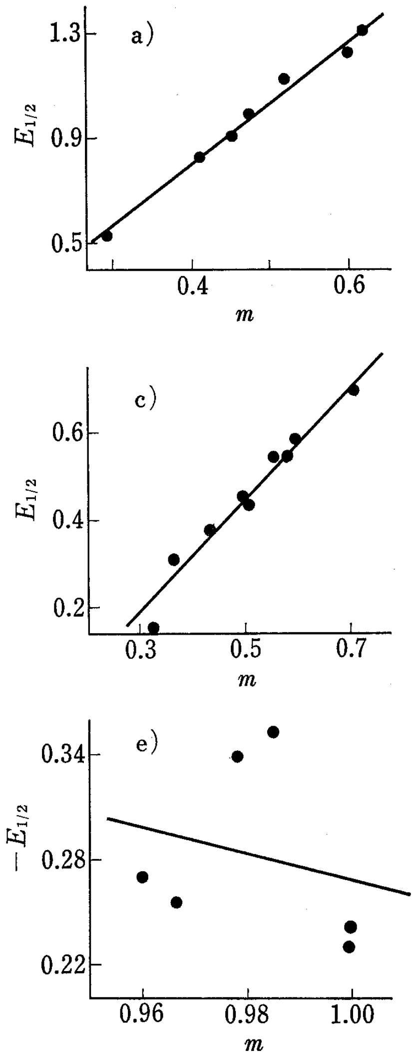

Fig. 2. Correlation between $E_{1/2}$ (V) and E^{π}_{HOMO} $(\alpha+m\beta)$*: a) Aromatic Hydrocarbons; b) Methyl-substituted Aromatic Hydrocarbons; c) Aromatic Amines; d) Aromatic Bromides; e) Benzaldehyde Derivatives

*: E^{π}_{HOMO} values were calculated by the Pauling–Wheland method in cases a), b), c) and d) and by the HMO-MASP method in the case of e).

Polarographic Reduction Reactions of Benzaldehyde Derivatives, Acetophenone Derivatives, Benzophenone Derivatives, Nitrobenzene Derivatives, Chlorobenzene Derivatives, Bromobenzene Derivatives, Aromatic Hydrocarbons and Aromatic Mono-nitro Compounds

Examination of the validity of the presumed structures for the activated complexes of diffusion-controlled polarographic reductions of unsaturated compounds using Eq. (4) derived in the previous paper was extended to the cases of disubstituted benzene derivatives (benzaldehyde derivatives,10) acetophenone derivatives,11) benzophenone derivatives,12) and nitrobenzene derivatives,13)). Seven aromatic hydrocarbons14) which were not included in the previous paper, as well as aromatic mono-nitro compounds15) were included in this supplemental examination.

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10) L. Holleck and H. Marsen, *Z. Elektrochem.*, **57**, 301, 944 (1953).
11) R.O. Loutfy and R.O. Loutfy, *Tetrahedron*, **29**, 2251 (1973).
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$$F(E^{A}_{1/2}-E^{B}_{1/2}) = \frac{c}{a}\left[(\Delta E_{r(Hg)})^{A}_{max}-(\Delta E_{r(Hg)})^{B}_{max}\right] \qquad (4)$$

(The physical significances of F, r, a and c were given in the previous paper.)

All of the potential-determining steps for benzaldehyde derivatives, acetophenone derivatives, benzophenone derivatives, nitrobenzene derivatives and aromatic mono-nitro compounds have been shown to correspond to the stage of addition of one electron to the oxygen atom of a molecule. Next, the π-stabilization energies ($\Delta E_{O(Hg)}$) calculated by means of Eq. (5) were employed to examine the validity of the assumption. In the case of aromatic hydrocarbons the maximum π-stabilization energies ($\Delta E^{max}_{r(Hg)}$) calculated with the same equation were employed. Here, $C_r{}^m$, η_m

$$\Delta E_{r(Hg)} = \left(\sum_{m}^{occ} - \sum_{m}^{unocc}\right) \frac{(C_r{}^m)^2}{-\eta_m}(-\gamma^2\beta) \qquad (5)$$

and $\gamma\beta$ have the same meanings as in Eq. (3).

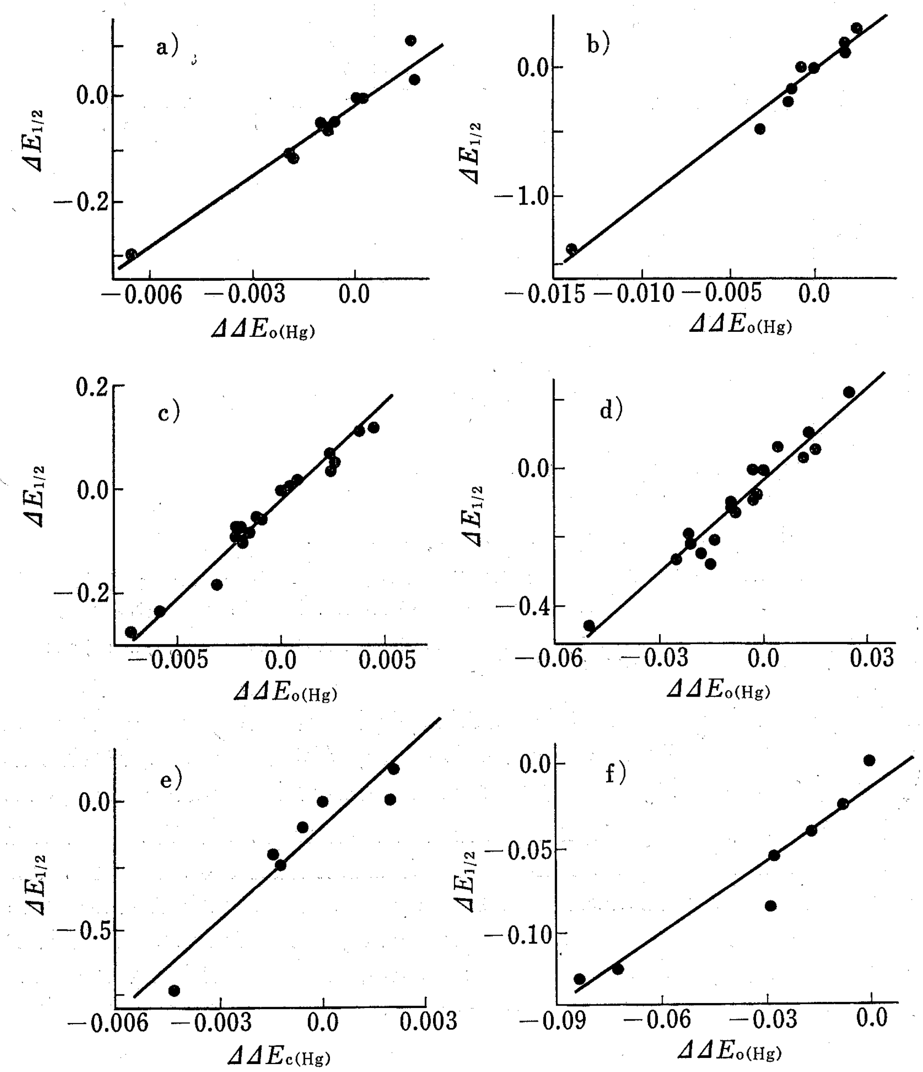

Fig. 3. Correlation between Differences of $E_{1/2}$ (V) and the Corresponding Differences of $\Delta E_{r(Hg)}(-\gamma^2\beta)$*: a) Benzaldehyde Derivatives; b) Acetophenone derivatives; c) Benzophenone Derivatives; d) Nitrobenzene Derivatives; e) Aromatic Hydrocarbons; f) Aromatic Mono-nitro Compounds

*: $\Delta E_{r(Hg)}$ values were calculated by the Pauling–Wheland method in cases e) and f) and by the HMO-MASP method in cases a), b), c) and d).

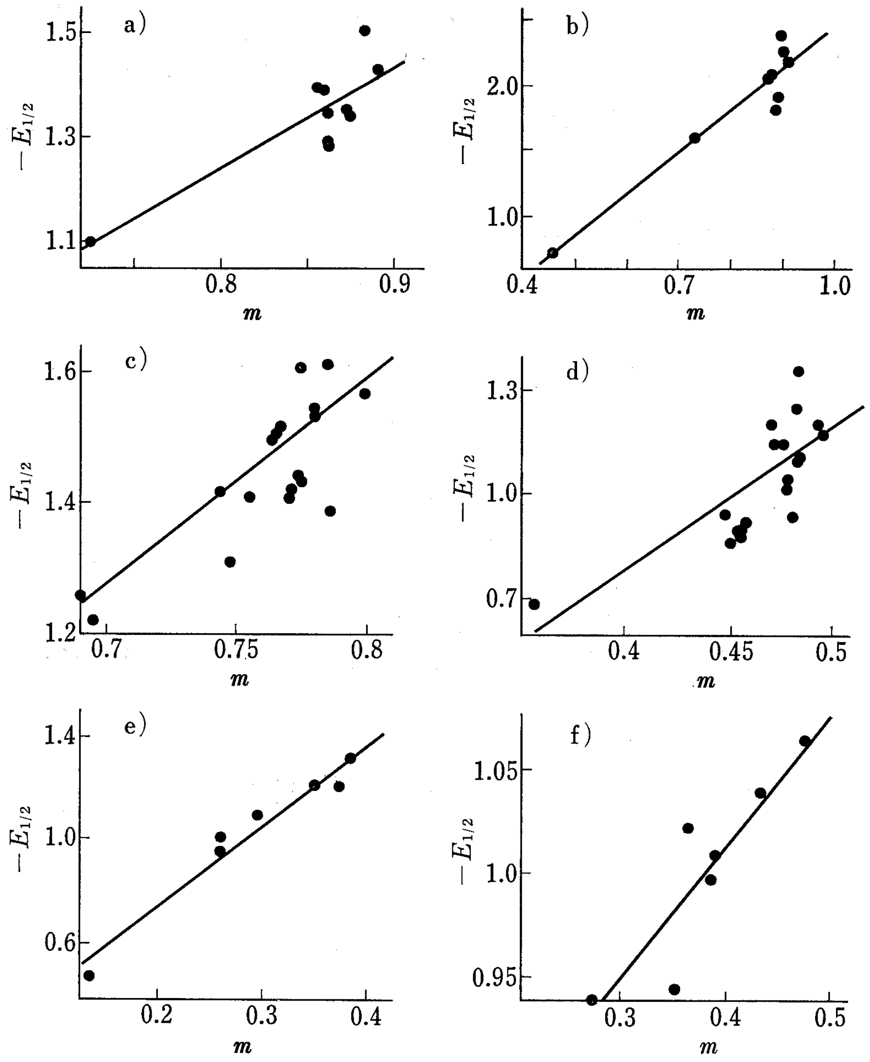

Fig. 4. Correlation between $E_{1/2}(V)$ and $E^{\pi}_{\mathrm{LVMO}}(\alpha - m\beta)$*: a) Benzaldehyde Derivatives; b) Acetophenone Derivatives; c) Benzophenone Derivatives; d) Nitrobenzene Derivatives; e) Aromatic Hydrocarbons; f) Aromatic Mono-nitro Compounds

*: E^{π}_{LVMO} values were calculated by the Pauling–Wheland method in cases e) and f) and by the HMO-MASP method in cases a), b), c) and d).

Seven aromatic hydrocarbons employed in this paper can be classified as class *b* compounds according to the previous paper.[2] Thus, Eq. (4) was applied not only in the case of these seven compounds but also in the case of all compounds belonging to the same class. In the latter examination the correlation coefficient was found to be 0.9171.

The results are shown in Fig. 3. Maccoll's relationships were also examined, and the results are shown in Fig. 4. Fig. 3 shows clearly that the linear relationship expressed by Eq. (4) holds satisfactorily in all of the cases examined. Therefore, these results provide strong additional support for the validity of the presumed structures of the activated complexes in polarographic reductions. Maccoll's relationship was found to be less well satisfied.

An S_N2-type mechanism has been proposed for the polarographic reductions of chloro- and bromobenzene derivatives.[16] However, both the number of electrons taken up and the atom to which the electron is transferred have not yet been clarified. The reduction reaction can be considered to fall either in the category of a radical reaction (in the case of one-electron

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[16] J.W. Sease, F.G. Burton and S.E. Nickol, *J. Am. Chem. Soc.*, **90**, 2595 (1968).

uptake) or a nucleophilic reaction (in the case of two-electron uptake). Thus, π-stabilization energies were calculated by means of either Eq. (5) or Eq. (6). The maximum π-stabilization energies ($[\varDelta E_{r(Hg)}]_{max}$) and π-stabilization energies ($[\varDelta E_{X(Hg)}]$; X is the halogen atom) were also calculated. The relationships between the differences in the observed half-wave potentials and

$$\varDelta E_{r(Hg)} = 2\sum_{m}^{unocc} \frac{(C_r{}^m)^2}{-\eta_m}(-\gamma^2\beta) \qquad (6)$$

four kinds of mutual differences in the π-stabilization energies were compared. The cases of two-electrons uptake at halogen atoms give the most satisfactory results (Fig. 5). Therefore, it may be concluded that the potential-determining step of the polarographic reductions of chloro- and bromobenzene derivatives is the transfer of two electrons from the electrode to the halogen atom of a molecule. Maccoll's relationship (Fig. 6) has no mechanistic significance.

The half-wave potentials employed in the previous paper and in the present paper were taken from many available literature reports on systematic investigations of diffusion-controlled reversible polarographic redox reactions of unsaturated organic compounds. Therefore, it may be concluded that the presumed structures of the activated complexes in the reversible polarographic redox reactions are generally valid.

Correlation coefficients of the relationships between $\varDelta E_{1/2}$ and $\varDelta(\varDelta E_{r(Pt)})$ (or $\varDelta(\varDelta E_{r(Hg)})$) and of Maccoll's relationships obtained from values calculated by the Pauling-Wheland method

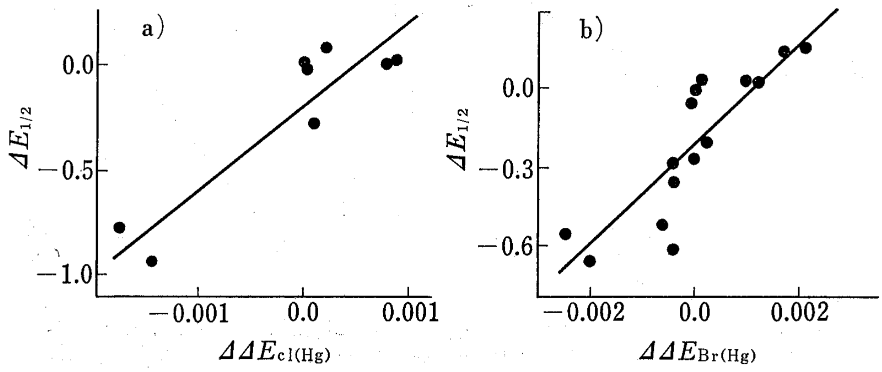

Fig. 5. Correlation between Differences of $E_{1/2}(V)$ and the Corresponding Differences of $\varDelta E_{X(Hg)}(-\gamma^2\beta)$*: a) Chlorobenzene Derivatives; b) Bromobenzene Derivatives

*: $\varDelta E_{X(Hg)}$ values were calculated by the HMO-MASP method.

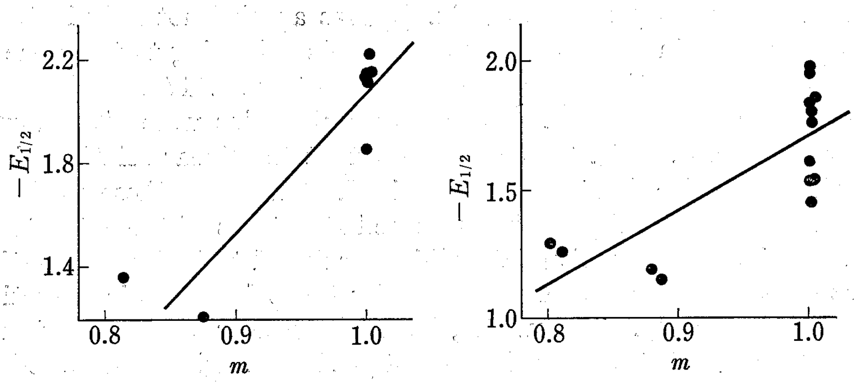

Fig. 6. Correlation between $E_{1/2}(V)$ and $E^{\pi}_{LVMO}(\alpha-m\beta)$*: a) Chlorobenzene Derivatives; b) Bromobenzene Derivatives

*: E^{π}_{LVMO} values were calculated by the HMO-MASP method.

were compared with those obtained from the values calculated by the MASP method, and the results are shown in Table I. This table indicates that the MASP method is very useful for the HMO calculation of π-stabilization energy (namely, superdelocalizability) of aromatic compounds having two kinds of substituents.

Table I. Comparison of Correlation Coefficients

Groups of compounds	n*	Oxidation			
		$\Delta E_{1/2}-\Delta(\Delta E_{r(Pt)})_{max}$		$E_{1/2}-E^{\pi}_{HOMO}$	
		HMO–MASP	Pauling–Wheland	HMO–MASP	Pauling–Wheland
Aromatic hydrocarbons	7		−0.9881		0.9928
Methyl-substituted aromatic hydrocarbons	16		−0.9549		0.9923
Aromatic amines	9		−0.9712		0.9781
Aromatic bromides	6		−0.9047		0.9828
Benzaldehyde derivatives	6	−0.9647	−0.9584	0.2036	0.1079

Groups of compounds	n*	Reduction			
		$\Delta E_{1/2}-\Delta\Delta E_{r(Hg)}$		$E_{1/2}-E^{\pi}_{LVMO}$	
		HMO–MASP	Pauling–Wheland	HMO–MASP	Pauling–Wheland
Benzaldehyde derivatives	10	0.9771	0.5446	0.8468	0.7572
Acetophenone derivatives	9	0.9856	0.9298	0.9492	0.9460
Benzophenone derivatives	18	0.9821	0.4789	0.7941	0.7948
Nitrobenzene derivatives	19	0.9605	0.7194	0.7388	0.7747
Aromatic hydrocarbons	7		0.9366		0.9775
Aromatic mono-nitro compounds	7		0.9521		0.8737
Chlorobenzene derivatives	8	0.8984	0.7985	0.9129	0.9144
Bromobenzene derivatives	15	0.8468	0.5997	0.7670	0.8646

*: Number of compounds.