December, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(12), 3585—3592 (1975) 3585

Presumptive Structures of Activated Complexes of Polarographic Redox Reactions of Unsaturated Organic Compounds. I.[1)] Polarographic Reductions of Aromatic Hydrocarbons, Aromatic Aldehydes, and Quinones

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(Received February 10, 1975)

Activated complexes of the polarographic reductions of unsaturated organic compounds were assumed to be formed by the interaction of the π-molecular orbital of each compound with a hypothetical atomic orbital of the electrode employed. Linear correlations were obtained between the mutual differences in the polarographic half-wave reduction potentials of a series of unsaturated organic compounds and the respective differences in the π-stabilization energies calculated on the basis of the presumed structures of activated complexes. These linear relationships were considered to lend experimental support to the propriety of the presumed structures of the activated complexes of the polarographic reductions of unsaturated organic compounds.

The electron-transfer phenomenon in electrochemical reactions has become rather clearer as a result of several theoretical investigations. However, the structures of the activated complexes in the electrochemical reaction are still ambiguous. For example, Marcus[2)] developed a unified theory of homogeneous and electrochemical electron-transfer rates; he also gave a basis for the quantitative correlations among the chemical and electrochemical rate constants. There have been several papers[3)] describing satisfactory results obtained by the application of Marcus's theory to each subject. Hush[4)] also developed a theory accounting for the activation process in electrochemical reactions.

With regard to the structures of activated complexes in electrochemical reactions, it may be said that no concrete figure of an activated complex has yet been presented. For example, Vlček[5)] reported that an initial activated complex ($*D \cdot E^-$) is formed by the contact of a depolarizer, $*D$, having an excited electronic state with the electrode, E^-, in the polarographic reduction reaction. However, this structure may not be considered to be concrete, because no definite explanation of either the mechanism of the contact of $*D$ with E^- or the mechanism of electronic excitation was given.

By the way, it is known that mutual reactivity differences in the chemical reactions of a homologous series of organic compounds with the same reagent and under the same reaction conditions must be explained in terms of the differences in the potential energy changes of their possible reaction paths calculated theoretically. However, this kind of calculation is almost impossible except for simple reactions of small molecules. Therefore, such differences are usually explained in terms of the differences in the activation energies of the reactions. If a profile of the potential energy surface of an electrochemical reaction is very similar to that of the homogeneous chemical reaction, as in Marcus's theory, the mutual differences in the electrode potentials required for polarographic reactions of organic compounds having analogous chemical structures with the same electrode in the same solvent to proceed may also have to be explained in terms of the differences in their activation energies.

It is known that the stabilization energy of an activated complex of a chemical reaction can be estimated by a simple quantum-chemical method.[6)] It has also been known that the mutual reactivity differences of a homologous series of organic compounds in the same kind of chemical reaction can be correlated rather roughly with the differences in their stabilization energies. This roughness may be assumed to be due to the complex reaction mechanisms involved and to the consequent difficulty of making presumptions as to the structures of the activated complexes.

However, in the case of polarographic reactions, many reactions proceed by means of rather simple reaction mechanisms. Moreover, the reagent in a usual chemical reaction is nothing else than the electron(s) on the electrode.[7)] Therefore, the presumption of the structures of activated complexes is expected to be rather easy. If this presumption can be made a mutual difference in the energies necessary for the reversible electrochemical oxidation-reduction reactions of two analogous compounds with the same electrode under the same condition to proceed, it may be expected to be correlated linearly with the difference in the stabilization energies of their activated complexes.

In this paper, the structures of activated complexes of the diffusion-controlled reversible polarographic reductions, employing a dropping mercury electrode, of unsaturated organic compounds are presumed. Moreover, an expected linear correlation between the mutual differences in the half-wave reduction potentials of a series of compounds and the differences in their stabilization energies calculated on the basis of the presumed structures of activated complexes is derived. Lastly, the proprieties of the presumed structures of activated complexes are examined on the basis of the experimental results.

Results and Discussion

Presumption of the Structure of Activated Complexes. The comparisons of the half-wave potentials ($E_{1/2}$) of a series of diffusion-controlled reversible polarographic one-electron reactions, employing a dropping mercury electrode, of a homologous series of unsaturated organic compounds (R) in the same solvent are considered. If these reactions are assumed to proceed *via* the respective activated complexes (Eq. (1)), the standard free-energy change (ΔG°) of the reaction of a compound, R, is equal to the difference in the free energies of the activation of its forward and reverse reactions ($\overrightarrow{\Delta G}^{\neq}-\overleftarrow{\Delta G}^{\neq}$):

$$\mathrm{R}+\mathrm{e}^-(\mathrm{Hg}) \rightleftharpoons [\text{activated complex}] \rightleftharpoons \mathrm{R}^- + (\mathrm{Hg}) \tag{1}$$

Moreover, the difference in the standard free-energy changes of two analogous compounds, $\mathrm{R_A}$ and $\mathrm{R_B}$, is expressed by Eq. (2). The polarographic half-wave reduction potential of a reversible reaction system such as Eq. (1) is known to be a linear function of the free-energy change (Eq. (3)).[8] Moreover, according to the law of linear free-energy relation, ($\Delta G^{\circ}_{\mathrm{A}}-\Delta G^{\circ}_{\mathrm{B}}$) can be considered to be proportional to ($\overrightarrow{\Delta G}^{\neq}_{\mathrm{A}}-\overrightarrow{\Delta G}^{\neq}_{\mathrm{B}}$) (Eq. (4)). Here, a is the proportional constant determined by the nature of the reaction. Therefore, the difference in the polarographic half-wave potentials of two compounds can be correlated with the difference in their free energies of activation (Eq. (5)).

$$\begin{aligned}\Delta G^{\circ}_{\mathrm{A}} - \Delta G^{\circ}_{\mathrm{B}} &= (\overrightarrow{\Delta G}^{\neq}_{\mathrm{A}}-\overleftarrow{\Delta G}^{\neq}_{\mathrm{A}}) - (\overrightarrow{\Delta G}^{\neq}_{\mathrm{B}}-\overleftarrow{\Delta G}^{\neq}_{\mathrm{B}})\\ &= (\overrightarrow{\Delta G}^{\neq}_{\mathrm{A}}-\overrightarrow{\Delta G}^{\neq}_{\mathrm{B}}) - (\overleftarrow{\Delta G}^{\neq}_{\mathrm{A}}-\overleftarrow{\Delta G}^{\neq}_{\mathrm{B}})\end{aligned} \tag{2}$$

$$E_{1/2} = -\frac{\Delta G^{\circ}}{F} + \frac{RT}{F}\ln\left(\frac{D_{\mathrm{R}^-}}{D_{\mathrm{R}}}\right)^{1/2}\left(\frac{f_{\mathrm{R}}}{f_{\mathrm{R}^-}}\right) \tag{3}$$

D: diffusion coefficient; R: gas const.;
F: Faradays const.; f: activity coefficient; T: K

$$\overrightarrow{\Delta G}^{\neq}_{\mathrm{A}} - \overrightarrow{\Delta G}^{\neq}_{\mathrm{B}} = a(\Delta G^{\circ}_{\mathrm{A}}-\Delta G^{\circ}_{\mathrm{B}}) \tag{4}$$

$$\begin{aligned}E^{\mathrm{A}}_{1/2} - E^{\mathrm{B}}_{1/2} &= -\frac{(\Delta G^{\circ}_{\mathrm{A}}-\Delta G^{\circ}_{\mathrm{B}})}{F}\\ &\quad + \frac{RT}{F}\ln\left(\frac{D_{\mathrm{R_A}^-}D_{\mathrm{R_B}}}{D_{\mathrm{R_A}}D_{\mathrm{R_B}^-}}\right)^{1/2}\left(\frac{f_{\mathrm{R_A}}f_{\mathrm{R_B}^-}}{f_{\mathrm{R_A}^-}f_{\mathrm{R_B}}}\right)\\ &= -\frac{(\overrightarrow{\Delta G}^{\neq}_{\mathrm{A}}-\overrightarrow{\Delta G}^{\neq}_{\mathrm{B}})}{aF}\\ &\quad + \frac{RT}{F}\ln\left(\frac{D_{\mathrm{R_A}^-}D_{\mathrm{R_B}}}{D_{\mathrm{R_A}}D_{\mathrm{R_B}^-}}\right)^{1/2}\left(\frac{f_{\mathrm{R_A}}f_{\mathrm{R_B}^-}}{f_{\mathrm{R_A}^-}f_{\mathrm{R_B}}}\right)\end{aligned} \tag{5}$$

$$E^{\mathrm{A}}_{1/2} - E^{\mathrm{B}}_{1/2} \simeq -\frac{(\overrightarrow{\Delta G}^{\neq}_{\mathrm{A}}-\overrightarrow{\Delta G}^{\neq}_{\mathrm{B}})}{aF} \tag{6}$$

Because $\mathrm{R_A}$ and $\mathrm{R_B}$ were supposed to have similar chemical structures, the contribution of the second term on the right-hand side of Eq. (5) to the left-hand side seems insignificant. Therefore, Eq. (5) is simplified to Eq. (6).

In order to estimate the free energy of activation of R, a presumption as to the structure of its activated complex is necessary. In the forward reaction of Eq. (1), the electron (e$^-$) on a dropping mercury electrode [(Hg)] may be considered to be supplied from the Fermi level of liquid mercury, whose energy is known to be −6.84 eV.[9] Since only one electron participates in the reaction, while innumerable electrons on (Hg) do not, it might be thought that the electron is the true reagent of the forward reaction, while (Hg) is its carrier. Therefore, the electron is assumed to occupy a hypothetical atomic orbital of liquid mercury $[\chi_{(\mathrm{Hg})}]$[10] with the orbital energy of −6.84 eV. The magnitude of the energy of this hypothetical atomic orbital is not much different from that of the Coulomb integral (α) of a carbon atom forming part of a π-electronic system of organic compounds, because the Coulomb integral is generally considered to be about −7 to −9 eV. Therefore, the hypothetical atomic orbital of the electrode is considered to be able to interact with the π-molecular orbital of a compound, R. Therefore, when the compound is going to collide with the electrode, the hypothetical atomic orbital of the electrode and the π-molecular orbital of R may begin to overlap each other; at the moment of collision, this overlap may become complete. In this state, of course, it cannot be considered that the electron and R are bound rigidly, but it may be considered that the π-electronic cloud of R spreads not only over the molecule, but also over the hypothetical atom of the electrode. In other words, the electron localized initially on the hypothetical atomic orbital of the electrode is considered to be delocalized on the π-electronic system newly formed. Therefore, the transference of an electron from the electrode to R may occur. This state may be presumed to be the activated complex, and its structure may be expressed by $[\mathrm{R}\cdots\mathrm{e}^-\cdots(\mathrm{Hg})]^{\neq}$. Just after the collision, the electron may be localized on the original π-electronic system of R, and an activated complex of the reaction may begin to decompose. This decomposition may produce the products (an anion radical and the electrode with a vacant hypothetical atomic orbital).

In the reverse reaction of Eq. (1), a vacant hypothetical atomic orbital of the electrode of the same kind as that of the forward reaction may be assumed. Much as in the case of the forward reaction, the formation of an activated complex, $[\mathrm{R}\cdots\mathrm{e}^-\cdots(\mathrm{Hg})]^{\neq}$, may be considered.

Therefore, the process of the reversible one-electron polarographic reductions of a series of unsaturated organic compounds may be assumed to be as follows (Eq. (7)):

$$\mathrm{R} + \mathrm{e}^-(\mathrm{Hg}) \rightleftharpoons [\mathrm{R}\cdots\mathrm{e}^-\cdots(\mathrm{Hg})]^{\neq} \rightleftharpoons \mathrm{R}^- + (\mathrm{Hg}) \tag{7}$$

The presumed structure of the activated complexes of one-electron reactions may be applicable, with a slight modification, to the structure of the activated complexes of two-electron reactions. That is, in a reversible reaction of an unsaturated organic compound, R(Eq. (8)), a hypothetical atomic orbital of the electrode occupied by two electrons may be assumed. These two electrons may then be assumed to be transferred to the π-molecular orbital of R. The formation of an activated complex, $[\mathrm{R}\cdots 2\mathrm{e}^-\cdots(\mathrm{Hg})]^{\neq}$, may also be assumed:

$$\mathrm{R} + 2\mathrm{e}^-(\mathrm{Hg}) \rightleftharpoons [\mathrm{R}\cdots 2\mathrm{e}^-\cdots(\mathrm{Hg})]^{\neq} \rightleftharpoons \mathrm{R}^{2-} + (\mathrm{Hg}) \tag{8}$$

π-Stabilization Energy of the Presumed Activated Complex. According to the transition-state theory, the $\overrightarrow{\Delta G}^{\neq}$ of a forward reaction of Eq. (7) can be correlated with its equilibrium constant $K^{\neq}$ (Eq. (9)), and $K^{\neq}$ can be expressed by Eq. (10). Here, Q is the parti-

tion function, and $\vec{E}_0$ is the activation energy, defined by the difference between the zero-point energy of the reactant and that of the activated complex.

$$\overrightarrow{\varDelta G}^{\ddagger} = -RT\ln K^{\ddagger} \tag{9}$$

$$K^{\ddagger} = \frac{Q_{[\mathrm{R}\cdots \mathrm{e}^-\cdots(\mathrm{Hg})]^{\ddagger}}}{Q_{\mathrm{R}}Q_{\mathrm{e}^-(\mathrm{Hg})}}\exp\left(-\frac{\vec{E}_0}{RT}\right) \tag{10}$$

$$\overrightarrow{\varDelta G}^{\ddagger} = -RT\ln\left(\frac{Q_{[\mathrm{R}\cdots \mathrm{e}^-\cdots(\mathrm{Hg})]^{\ddagger}}}{Q_{\mathrm{R}}Q_{\mathrm{e}^-(\mathrm{Hg})}}\right) + \vec{E}_0 \tag{11}$$

$$\overrightarrow{\varDelta G}^{\ddagger}_{\mathrm{A}} - \overrightarrow{\varDelta G}^{\ddagger}_{\mathrm{B}} = -RT\ln\left(\frac{Q_{\mathrm{R_B}}}{Q_{\mathrm{R_A}}}\right) + (\vec{E}_0^{\mathrm{A}} - \vec{E}_0^{\mathrm{B}}) \tag{12}$$

$$\overrightarrow{\varDelta G}^{\ddagger}_{\mathrm{A}} - \overrightarrow{\varDelta G}^{\ddagger}_{\mathrm{B}} \simeq (\vec{E}_0^{\mathrm{A}} - \vec{E}_0^{\mathrm{B}}) \tag{13}$$

$$E^{\mathrm{A}}_{1/2} - E^{\mathrm{B}}_{1/2} \simeq -\frac{(\vec{E}_0^{\mathrm{A}} - \vec{E}_0^{\mathrm{B}})}{aF} \tag{14}$$

Because the partition functions of two activated complexes, $[\mathrm{R_A}\cdots \mathrm{e}^-\cdots(\mathrm{Hg})]^{\ddagger}$ and $[\mathrm{R_B}\cdots \mathrm{e}^-\cdots(\mathrm{Hg})]^{\ddagger}$, formed from two compounds, $\mathrm{R_A}$ and $\mathrm{R_B}$, with analogous chemical structures and the same electrode can be assumed to be very similar, the difference in their free energies of activation, $\overrightarrow{\varDelta G}^{\ddagger}_{\mathrm{A}} - \overrightarrow{\varDelta G}^{\ddagger}_{\mathrm{B}}$, can be correlated with the difference in their activation energies, $\vec{E}_0^{\mathrm{A}} - \vec{E}_0^{\mathrm{B}}$ (Eq. (12)). Moreover, $Q_{\mathrm{R_A}}$ and $Q_{\mathrm{R_B}}$ may also be regarded as very similar. Equations (13) and (14) can thus be obtained.

The activation energy of a molecule is considered to be contributed by five energy changes[11]: the vibrational energy change $(\varDelta\varepsilon^{\ddagger}_{v})$, the energy change of localized bonds $(\varDelta\varepsilon^{\ddagger}_{l})$, the energy change of delocalized system $(\varDelta\varepsilon^{\ddagger}_{d})$, the energy change of interaction between nonbonded atoms $(\varDelta\varepsilon^{\ddagger}_{n,l})$ and the energy change of solvation $(\varDelta\varepsilon^{\ddagger}_{s}(T))$ (Eq. (15)). When the differences $(\vec{E}_0^{\mathrm{A}} - \vec{E}_0^{\mathrm{B}})$ between two unsaturated organic

$$\vec{E}_0 = \varDelta\varepsilon^{\ddagger}_{v} + \varDelta\varepsilon^{\ddagger}_{l} + \varDelta\varepsilon^{\ddagger}_{d} + \varDelta\varepsilon^{\ddagger}_{n,l} + \varDelta\varepsilon^{\ddagger}_{s}(T) \tag{15}$$

compounds with analogous chemical structures in the same solvent is considered, the following approximations may be considered to be reasonable. The vibrational energies of their activated complexes may not be much different each other. Not only the magnitude of $\varDelta\varepsilon^{\ddagger}_{l}$ itself, but also the difference in $\varDelta\varepsilon^{\ddagger}_{l}$ between two compounds may be insignificant, because the formation of an activated complex is presumed to be based on the interaction of the π-electronic system of a compound and a hypothetical atomic orbital of the electrode. For the same reason, both $\varDelta\varepsilon^{\ddagger}_{n,l}$, and its difference between two compounds may also be insignificant. Because the overlap of two orbitals is considered to occur very rapidly, the value of $\varDelta\varepsilon^{\ddagger}_{s}(T)$ may be rather small and its difference between two compounds may be insignificant. If these approximations are made, the difference $(\vec{E}_0^{\mathrm{A}} - \vec{E}_0^{\mathrm{B}})$ may become a function of the difference in $(\varDelta\varepsilon^{\ddagger}_{d})_{\mathrm{A}}$ and $(\varDelta\varepsilon^{\ddagger}_{d})_{\mathrm{B}}$ (Eq. (16)).

In the activated complex, the original π-electronic system of R is considered to be perturbed slightly by the interaction with a hypothetical atomic orbital of the electrode. The energy change of the π-electronic system of R due to this kind of perturbation is called the π-stabilization energy $(\varDelta E_{\mathrm{rs}})$. Here, r and s denote the atoms of the two reactants where the interaction occurs. In the present case, one of the reactants is the electron on the electrode, so it may be expressed as $\varDelta E_{\mathrm{r(Hg)}}$. It is known that the larger the $\varDelta E_{\mathrm{rs}}$, the smaller the π-activation energy. Therefore, it may be said that the larger the $\varDelta E_{\mathrm{r(Hg)}}$, the smaller the $(\varDelta\varepsilon^{\ddagger}_{d})$ (Eq. (17)).

$$(\vec{E}_0^{\mathrm{A}} - \vec{E}_0^{\mathrm{B}}) \simeq (\varDelta\varepsilon^{\ddagger}_{d})_{\mathrm{A}} - (\varDelta\varepsilon^{\ddagger}_{d})_{\mathrm{B}} \tag{16}$$

$$\varDelta\varepsilon^{\ddagger}_{d} = b - c\cdot\varDelta E_{\mathrm{r(Hg)}} \tag{17}$$

Equation (17) is known to be useful not only in predicting the specific position, *r*, of a molecule where a reaction is expected to occur preferentially, but also in predicting the difference in the reactivities of the molecules of a series of compounds with analogous chemical structures in the same kind of chemical reaction. Therefore, both *b* and *c* can be assumed to keep nearly constant throughout a series of reactions employing analogous compounds. Therefore, it might be possible to expect that the difference in the activation energies of the reversible polarographic reactions of $\mathrm{R_A}$ and $\mathrm{R_B}$ can be correlated linearly with the difference in their maximum π-stabilization energies (Eq. (18)):

$$\begin{aligned}\vec{E}_0^{\mathrm{A}} - \vec{E}_0^{\mathrm{B}} &\simeq (\varDelta\varepsilon^{\ddagger}_{d})^{\mathrm{A}}_{\mathrm{min}} - (\varepsilon^{\ddagger}_{d})^{\mathrm{B}}_{\mathrm{min}} \\ &\simeq -c[(\varDelta E_{\mathrm{r(Hg)}})^{\mathrm{A}}_{\mathrm{max}} - (\varDelta E_{\mathrm{r(Hg)}})^{\mathrm{B}}_{\mathrm{max}}]\end{aligned} \tag{18}$$

From the viewpoint of chemical reactions, a polarographic reduction may be considered to fall in the category of addition reactions. Also, it is known that the π-stabilization energy of the addition reaction of a neutral molecule (R_m) with a radical molecule (R_n) or with an ionic molecule (R_i) at their *r*th and *s*th atom can be calculated by means of Eq. (19) or Eq. (20) respectively:

$$\begin{aligned}\varDelta E_{\mathrm{rs}} = {} & 2\Big(\sum_{m}^{occ}\sum_{n}^{unocc} - \sum_{n}^{occ\text{-}N}\sum_{m}^{unocc}\Big)\frac{(C_r^m)^2(d_s^n)^2}{\lambda_n - \eta_m}(\gamma^2\beta) \\ & + \Big(\sum_{m}^{occ} - \sum_{m}^{unocc}\Big)\frac{(C_r^m)^2(d_s^N)^2}{\lambda_N - \eta_m}(\gamma^2\beta)\end{aligned} \tag{19}$$

$$\varDelta E_{\mathrm{rs}} = 2\Big(\sum_{m}^{occ}\sum_{i}^{unocc} - \sum_{m}^{unocc}\sum_{i}^{occ}\Big)\frac{(C_r^m)^2(d_s^i)^2}{\lambda_i - \eta_m}(\gamma^2\beta) \tag{20}$$

Here, C_r^m, d_s^n, and d_s^i denote the coefficient of the *r*th atomic orbital of the *m*th molecular orbital of R_m and the coefficient of the *s*th atomic orbital of *n*th (or *i*th) molecular orbital of R_n (or R_i) as calculated by the HMO method, respectively. γ_n, γ_i, and η_m denote the coefficients of the resonance-energy parts of the energy levels of R_n, R_i, and R_m respectively. *N* denotes the half-occupied orbital of R_n. $\gamma\beta$ denotes the resonance integral of the π-electronic system newly formed between R_m and R_n (or R_i).

In the case of the calculation of the $\varDelta E_{r(\mathrm{Hg})}$ of a one-electron reduction, R_n has only one half-occupied orbital and d_s^N is unity. Moreover, λ_n has already been assumed to be approximately equal to 0. Equation (19) is, therefore, simplified to Eq. (21),* and, in the case of two-electron reductions, Eq. (22)* is derived:

$$\Delta E_{\mathrm{rs}} = \Big(\sum_{m}^{occ} - \sum_{m}^{unocc}\Big)\frac{(C_r^m)^2}{-\eta_m}(\gamma^2\beta) \tag{21}$$

$$\Delta E_{\mathrm{rs}} = \sum_{m}^{unocc}\frac{(C_r^m)^2}{\eta_m}(\gamma^2\beta) \tag{22}$$

Now, the difference in the half-wave reduction potentials of two analogous compounds, R_A and R_B, can be correlated with the difference in their π-stabilization energies (Eq. (23)):

$$F(E^{\mathrm{A}}_{1/2}-E^{\mathrm{B}}_{1/2}) \simeq \frac{c}{a}[(\Delta E_{\mathrm{r(Hg)}})^{\mathrm{A}}_{\mathrm{max}}-(\Delta E_{\mathrm{r(Hg)}})^{\mathrm{B}}_{\mathrm{max}}] \tag{23}$$

If the presumption of the structures of activated complexes is proper, the linear relationship expressed by Eq. (23) can be expected to hold. Therefore, the validity of this equation was examined by using the values of both the diffusion-controlled reversible polarographic half-wave reduction potentials and the calculated π-stabilization energies of several types of organic compounds.

Examination of the Validity of Eq. (23). Maccoll[8] indicated that the polarographic half-wave potentials of the reversible one-electron reductions of eight unsaturated hydrocarbons can be linearly correlated with the magnitudes of the energies of the lowest vacant π-molecular orbitals (E^{π}_{LVMO}) of these compounds, as calculated by the HMO method. This indication has also been recognized to hold in many hydrocarbons by several groups of researchers, such as Hoijtink *et al.*[12] and Pullman *et al.*[13] Since this kind of quantum chemical approach to the interpretation of the $E_{1/2}$'s of organic compounds has been widely accepted as relevant, parallel examinations of the validity of Maccoll's indication and that of Eq. (23) by means of the same experimental results were thought to be significant.

a) Aromatic Hydrocarbons: According to the conclusion of Wawzonek *et al.*,[14] the first reduction waves of these compounds, determined in 75% dioxane–water, correspond to the addition of either one or two electrons to the compounds. Later, Hoijtink *et al.*[15] clarified the reduction mechanism of unsaturated hydrocarbons in a protic solvent (75% and 96% dioxane–water) as follows: (i) At first, an anion radical (R^-) is formed by the reversible addition of one electron to the compound, regardless of the solvent employed, and (ii) the number of electrons corresponding to the first wave is decided according to whether the rate of the proton addition to R^- is lower or higher than the rate of the diffusion of R^- from the electrode surface layer to the bulk of the solution. The latter mechanism means that, if the former rate is lower than the latter one, as it is so in many unsaturated hydrocarbons, the first wave corresponds to the addition of one electron.

The first wave of the polarographic reduction of unsaturated hydrocarbons, such as stilbene, styrene, and 1,1-diphenylethylene, as determined in an aprotic solvent, has also been reported[16] to correspond to the addition of either one or two electrons to the compounds. However, Bergman[17] concluded that the first reduction wave of many aromatic hydrocarbons, as determined in ethylene glycol monomethyl ether, corresponds to the addition of one electron. Bergman's investigation not only included seventy-two aromatic polynuclear hydrocarbons of a variety of chemical structures, but also all of the $E_{1/2}$ of these compounds were determined in the same solvent. Therefore, the $E_{1/2}$ values of the present study were taken from this literature. He classified these compounds into several classes with respect to the similarities in their chemical structures. In this study, at first sixty-nine compounds were classified into four classes (a, b, c, and d) in accordance with Bergman's classification, as is shown below. However, the three compounds which form the class e in Bergman's report were omitted, because one of them, diindeno[1,2,3-*fg*: 1′,2′,3′-*op*]naphthacene, has a nonbonding orbital which makes the calculation of $\Delta E_{\mathrm{r(Hg)}}$ impossible. Consequently, the remainder was insufficient for the investigation. Also, it was considered that four compounds (No. 42, 43, 57, and 58) should be classified into a new class, c′, because they are related not only to both perylene and pyrene, but also to *p*-terphenyl.

a) the *cata*-condensed aromatic hydrocarbons (No. 1—31)

b) the *peri*-condensed aromatic hydrocarbons related to perylene (No. 32—41)

c) the *peri*-condensed aromatic hydrocarbons related to pyrene (No. 44—61(except 57 and 58))

c′) the *peri*-condensed aromatic hydrocarbons related to perylene, pyrene, and *p*-terphenyl(No. 42, 43, 57, and 58)

d) the non-alternant hydrocarbons related to fluoranthene (No. 62—69)

Unlike the case of the aromatic carbonyl compounds to be discussed later, each aromatic hydrocarbon can be expected to be reduced simply at the position bearing the maximum π-stabilization energy. Then, the π-stabilization energies at all positions of all compounds were calculated.

The differences in both $E_{1/2}$ and $(\Delta E_{\mathrm{r(Hg)}})_{\mathrm{max}}$, and the values of both $E_{1/2}$ and E^{π}_{LVMO}, are shown in Tables 1—4. The standard deviations and correlation coefficients are also shown in these tables. The correlation between the differences in the values of $(\Delta E_{\mathrm{r(Hg)}})_{\mathrm{max}}$ and the differences in the $E_{1/2}$ values of compounds of Group a is shown in Fig. 1. This figure indicates that the linear relationship given by Eq. (23) is satisfactorily fullfilled.

b) Aromatic Aldehydes: Schmidt *et al.*[18] described how, in a strong alkaline solution, the polarographic half-wave reduction potential of aromatic aldehydes is independent of the pH value of the solution employed, and how the diffusion current corresponds to the addition of one electron to the oxygen atom of a molecule (Eq. (24)). They also showed that the $E_{1/2}$ of six aromatic aldehydes determined in a strong alkaline solution are linearly correlated with the E^{π}_{LVMO}'s expressed by the unit of γ. Streitwieser[19] confirmed the

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* These equations are also known to be equations giving the superdelocalizabilities of a radical substitution and a nucleophilic substitution reaction respectively.

TABLE 1. VALUES OF $E_{1/2}(V)$, $\Delta E_{1/2}(V)$, $\Delta(\Delta E_{r(Hg)})_{max}$-$(-\gamma^2\beta)$ AND $E^{\pi}_{LVMO}(\alpha-m\beta)$ OF a GROUP AROMATIC HYDROCARBONNS

Compound	$-\Delta E_{1/2}$ [a]	$-\Delta(\Delta E_{r(Hg)})_{max}$ [b]	$-E_{1/2}$	m
1	0.0	0.0	1.98	0.6180
2	0.52	0.3192	1.46	0.4142
3	0.845	0.5108	1.135	0.2950
4	1.12	0.8006	0.86	0.2197
5	0.045	0.0034	1.935	0.6052
6	0.45	0.2574	1.53	0.4523
7	0.79	0.4515	1.19	0.3271
8	1.035	0.7006	0.945	0.2436
9	0.01	−0.0656	1.97	0.6840
10	0.44	0.1592	1.54	0.4991
11	0.775	0.3920	1.205	0.3557
12	1.05	0.6124	0.93	0.2621
13	0.435	0.1518	1.545	0.4735
14	0.73	0.3385	1.25	0.3584
15	1.13	0.5849	0.85	0.2691
16	0.175	0.0497	1.805	0.5201
17	0.545	0.2949	1.435	0.4048
18	0.65	0.3144	1.33	0.3482
19	0.235	0.0046	1.745	0.5676
20	0.41	0.2061	1.57	0.4918
21	0.335	0.0378	1.645	0.5319
22	0.41	0.1226	1.57	0.5224
23	0.39	−0.0288	1.59	0.5115
24	0.25	0.0343	1.73	0.5498
25	0.58	0.2771	1.40	0.4186
26	0.19	0.0491	1.79	0.5019
27	0.455	0.2517	0.525	0.4372
28	0.76	0.4363	1.22	0.3358
29	0.485	0.2603	1.495	0.4287
30	0.465	0.1558	1.515	0.4321
31	0.515	0.2655	1.465	0.3940
Standard Deviation		0.0901		0.0764
Correlation Coefficient		0.9553		0.9681

a) $\Delta E_{1/2}=(E_{1/2})^{\text{Naphthalene}}-(E_{1/2})^{\text{Compound}}$

b) $\Delta(\Delta E_{r(Hg)})_{max}=(\Delta E_{r(Hg)})^{\text{Naphthalene}}_{max}-(\Delta E_{r(Hg)})^{\text{Compound}}_{max}$

$(\Delta E_{r(Hg)})^{\text{Naphthalene}}_{max}=0.9940$

TABLE 2. VALUES OF $E_{1/2}(V)$, $\Delta E_{1/2}(V)$, $\Delta(\Delta E_{r(Hg)})_{max}$-$(-\gamma^2\beta)$ AND $E^{\pi}_{LVMO}(\alpha-m\beta)$ OF b GROUP AROMATIC HYDROCARBONS

Compound	$-\Delta E_{1/2}$ [a]	$-\Delta(\Delta E_{r(Hg)})_{max}$ [b]	$-E_{1/2}$	m
32	0.0	0.0	1.25	0.3473
33	0.285	0.4592	0.965	0.2648
34	0.37	0.6015	0.88	0.2135
35	0.25	0.4531	1.00	0.2673
36	−0.235	−0.1000	1.485	0.4392
37	−0.265	−0.1111	1.515	0.4631
38	−0.10	0.0843	1.35	0.4114
39	−0.39	−0.2036	1.64	0.5392
40	−0.03	0.1227	1.28	0.3557
41	0.335	0.4241	0.915	0.2539
Standard deviation		0.0593		0.0378
Correlation coeffieient		0.9737		0.9894

a) $\Delta E_{1/2}=(E_{1/2})^{\text{Perylene}}-(E_{1/2})^{\text{Compound}}$

b) $\Delta(\Delta E_{r(Hg)})_{max}=(\Delta E_{r(Hg)})^{\text{Perylene}}_{max}-(\Delta E_{r(Hg)})^{\text{Compound}}_{max}$

$(\Delta E_{r(Hg)})^{\text{Perylene}}_{max}=1.1949$

TABLE 3. VALUES OF $E_{1/2}(V)$, $\Delta E_{1/2}(V)$, $\Delta(\Delta E_{r(Hg)})_{max}$-$(-\gamma^2\beta)$ AND $E^{\pi}_{LVMO}(\alpha-m\beta)$ OF c GROUP AROMATIC HYDROCARBONS

Compound	$-\Delta E_{1/2}$ [a]	$-\Delta(\Delta E_{r(Hg)})_{max}$ [b]	$-E_{1/2}$	m
44	0.0	0.0	1.61	0.4450
45	−0.06	−0.0508	1.67	0.4970
46	0.25	0.2930	1.36	0.3711
47	0.53	0.2416	1.08	0.3983
48	0.165	0.1476	1.445	0.4216
49	−0.075	−0.1177	1.685	0.5550
50	0.45	0.4214	1.16	0.3027
51	0.295	0.3234	1.315	0.3420
52	0.105	0.0420	1.505	0.5053
53	0.46	0.4182	1.15	0.3026
54	0.83	0.7111	0.78	0.2130
55	0.46	0.4752	1.15	0.2734
56	0.27	0.1594	1.34	0.3957
59	0.42	0.3896	1.19	0.2910
60	0.55	0.5282	1.06	0.2580
61	0.81	0.8832	0.80	0.1891
Standard Deviation		0.0805		0.1034
Correlation Coefficient		0.9533		0.9212

a) $\Delta E_{1/2}=(E_{1/2})^{\text{Pyrene}}-(E_{1/2})^{\text{Compound}}$

b) $\Delta(\Delta E_{r(Hg)})_{max}=(\Delta E_{r(Hg)})^{\text{Pyrene}}_{max}-(\Delta E_{r(Hg)})^{\text{Compound}}_{max}$

$(\Delta E_{r(Hg)})^{\text{Pyrene}}_{max}=1.1149$

TABLE 4. VALUES OF $E_{1/2}(V)$, $\Delta E_{1/2}(V)$, $\Delta(\Delta E_{r(Hg)})_{max}$-$(-\gamma^2\beta)$ AND $E^{\pi}_{LVMO}(\alpha-m\beta)$ OF c′ AND d GROUPS AROMATIC HYDROCARBONS

Compound	$-\Delta E_{1/2}$ [a]	$-\Delta(\Delta E_{r(Hg)max})$ [b]	$-E_{1/2}$	m
42	0.0	0.0	0.675	0.1826
43	−0.020	−0.0368	0.695	0.1916
57	−0.500	−0.2516	1.175	0.2847
58	−0.475	−0.3885	1.15	0.3445
Standard deviation		0.0821		0.0836
Correlation coefficient		0.9391		0.9368
62	0.0	0.0	1.345	0.3709
63	0.370	0.4525	0.975	0.2521
64	0.695	0.8777	0.65	0.1604
65	−0.030	0.0957	1.375	0.3770
66	0.180	0.0661	1.165	0.3116
67	−0.045	0.0095	1.39	0.4007
68	0.290	0.2036	1.055	0.2666
69	−0.030	0.2229	1.375	0.3966
Standard deviation		0.1051		0.0287
Correlation coefficient		0.9042		0.9932

a) $\Delta E_{1/2}=(E_{1/2})^{X}-(E_{1/2})^{\text{Compound}}$

b) $\Delta(\Delta E_{r(Hg)})_{max}=(\Delta E_{r(Hg)})^{X}_{max}-(E_{r(Hg)})^{\text{Compound}}_{max}$

c′ group: X=Tetrabenzo[*de,h,kl,rst*]pentaphene (42)

d group: X=Fluoranthene (62)

$(\Delta E_{r(Hg)})_{max}$ of (42)=1.5117 and that of (62)=1.1370.

TABLE 5. VALUES OF $\Delta E_{1/2}(V)$ AND $\Delta(\Delta E_{o(Hg)})(-\gamma^2\beta)$ OF AROMATIC ALDEHYDES

Parameter		1[c]	2[d]	3[e]
Compound	$-\Delta E_{1/2}$[a]	$-\Delta(\Delta E_{o(Hg)})$[b]	$-\Delta(\Delta E_{o(Hg)})$[b]	$-\Delta(\Delta E_{o(Hg)})$[b]
70	0.0	0.0	0.0	0.0
71	0.257	0.0394	0.0746	0.1517
72	0.116	0.0163	0.0366	0.0728
73	0.087	0.0043	0.0108	0.0213
74	0.385	0.0498	0.1090	0.2182
75	0.143	0.0167	0.0377	0.0750
Standard deviation		0.0251	0.0185	0.0188
Correlation coefficient		0.9795	0.9889	0.9885

a) $\Delta E_{1/2} = (E_{1/2})^{\text{Benzaldehyde}} - (E_{1/2})^{\text{Compound}}$. b) $\Delta(\Delta E_{o(Hg)}) = (\Delta E_{o(Hg)})^{\text{Benzaldehyde}} - (\Delta E_{o(Hg)})^{\text{Compound}}$.
c) Ref. 20. d) Ref. 18. e) Ref. 19.
$(\Delta E_{o(Hg)})^{\text{Benzaldehyde}}$ values are 0.5260 (parameter 1), 0.6753 (parameter 2), and 1.0783 (parameter 3).

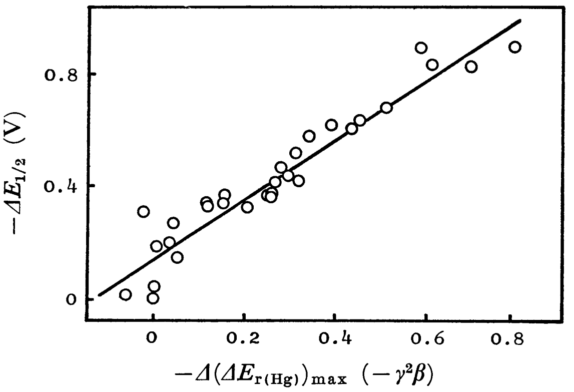


Fig. 1. Correlation between mutual differences of $E_{1/2}$ values and the respective differences of $(\Delta E_{r(Hg)})_{\max}$ values of a group aromatic hydrocarbons.

same linear relationship between the very same value of every one of the $E_{1/2}$ values determined by Schmidt *et al.* and the E^{π}_{LVMO} value expressed by the unit of β.

$$\text{R-CHO} + e^- \rightleftharpoons \text{R-}\dot{\text{C}}\text{HO}^- \qquad (24)$$

In this case, the activated complex $[(\text{R–C(H)=O}\cdots e^-\cdots(\text{Hg}))^{\ddagger}]$ is assumed to be formed by the interaction of a hypothetical atomic orbital occupied by one electron of the electrode with the π-molecular orbital of a molecule at the oxygen atom of the carbonyl group. Then the linear relationship between the differences in $E_{1/2}$ values and the differences in the π-stabilization energies $(\Delta E_{O(Hg)})$ of the same series of six aromatic aldehydes was investigated.

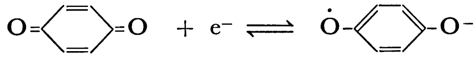
Although neither Schmidt *et al.* nor Streitwieser described anything about the influence of the change in the hetero-atomic parameters of the carbonyl group on the linearity between $E_{1/2}$ and E^{π}_{LVMO}, this influence ought not to be ignored. Also, the $\Delta E_{O(Hg)}$ values should be dependent on the same change. Therefore, the $\Delta E_{O(Hg)}$ values were calculated repeatedly by the HMO method with the employment of three sets of parameters proposed in the literature.[18–20] The results, the differences in the two $E_{1/2}$ values determined by Schmidt *et al.*, and the $\Delta E_{O(Hg)}$ values calculated by three kinds of parameters are listed in Table 5. The $E_{1/2}$ values and three kinds of E^{π}_{LVMO} values are shown in Table 6. The standard deviations and correlation coefficients of each set of parameters are also listed in these tables. These tables indicate that all three sets of hetero-atomic parameters gave the comparable linear relationships expected by Eq. (23).

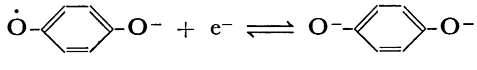
TABLE 6. VALUES OF $E_{1/2}(V)$ AND $E^{\pi}_{\text{LVMO}}(\alpha - m\beta)$ OF AROMATIC ALDEHYDES

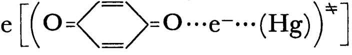
Parameter		1[a]	2[b]	3[c]
Compound	$-E_{1/2}$	*m*	*m*	*m*
70	1.553	0.8561	0.4251	0.3859
71	1.296	0.5656	0.2776	0.2602
72	1.437	0.5654	0.3245	0.3028
73	1.466	0.5946	0.3789	0.3500
74	1.168	0.3720	0.2081	0.1993
75	1.410	0.5553	0.3211	0.3000
Standard Deviation		0.0607	0.0254	0.0237
Correlation Coefficient		0.8733	0.9789	0.9818

a) Ref. 20. b) Ref. 18. c) Ref. 19.

c) Quinones: With regard to the polarographic reduction of quinones in an aprotic solvent, Wawzonek *et al.*[21] made it clear that the first wave corresponds to the formation of semiquinone anion radicals (Eq. (25)), while the succeeding reduction of these anions to dianions (Eq. (26)) is the second step:

 (25)

 (26)

Then the linear relationship between the differences between the $E_{1/2}$ values taken from the literature[22] and the differences between the $\Delta E_{O(Hg)}$ values corresponding to the structure  of the four *p*-quinones was investigated. *p*-Quinones with substituents in their molecule and *o*-quinones were omitted from this investigation, because it was considered that the usefulness of the hetero-atomic parameters employed in this work has not yet been examined for the calculation of compounds with an *ortho* di-substituted structure.

In the preceding example it was clarified that all three sets of hetero-atomic parameters gave comparable

TABLE 7. VALUES OF $E_{1/2}(V)$, $\Delta E_{1/2}(V)$, $\Delta(\Delta E_{o(Hg)})$-$(-\gamma^2\beta)$ AND $E^{\pi}_{LVMO}(\alpha-m\beta)$ OF QUINONES

Compound	$-\Delta E_{1/2}$[a)]	$-\Delta(\Delta E_{o(Hg)})$[b)]	$-E_{1/2}$	m
76	0.0	0.0	0.51	0.4827
77	−0.20	−0.0388	0.71	0.5570
78	−0.24	−0.0400	0.75	0.5772
79	−0.43	−0.0685	0.94	0.6452
Standard deviation		0.0178		0.0050
Correlation coefficient		0.9932		0.9995

a) $\Delta E_{1/2}=(E_{1/2})^{\text{1,4-Benzoquinone}}-(E_{1/2})^{\text{Compound}}$.

b) $\Delta(\Delta E_{o(Hg)})=\Delta(\Delta E_{o(Hg)})^{\text{1,4-Benzoquinone}}-(\Delta E_{o(Hg)})^{\text{Compound}}$.
$(\Delta E_{o(Hg)})^{\text{1,4-Benzoquinone}}=0.6524$.

results. Therefore, only one set of the hetero-atomic parameters, one which had previously been proposed by us,[20)] was employed.

The differences between the two $E_{1/2}$ values taken from the literature[22)] and $\Delta E_{o(Hg)}$, and the values of both $E_{1/2}$ and E^{π}_{LVMO} are shown in Table 7. The standard deviations and correlation coefficients obtained are also listed in the same table.

The standard deviations and correlation coefficients shown in Tables 1—7 indicate that, in all the cases examined, the differences in the $E_{1/2}$'s can be correlated linearly with the differences in the π-stabilization energies as satisfactorily as the linear relationship observed between $E_{1/2}$'s and E^{π}_{LVMO}'s. Since no investigation of the systematic polarographic reduction reaction of unsaturated organic compounds with no substituent other than that of these three groups of compounds has yet been reported in the literature, this examination can be considered to include all of the cases. Therefore, the results of these examinations may be considered to be experimental support to the presumed structures of the activated complexes of the reversible polarographic reductions of unsaturated organic compounds are proper.

Experimental

The molecular orbital calculations were carried out on a FACOM 230-60 computer at the Computation Center of Kyushu University.

The names of all the compounds employed in this study are listed below. The basic structures of many aromatic polynuclear hydrocarbons are shown in Chart 1.

1. Naphthalene
2. Anthracene
3. Naphthacene
4. Pentacene
5. Phenanthrene
6. Benzo[*a*]anthracene
7. Benzo[*a*]naphthacene
8. Benzo[*a*]pentacene
9. Triphenylene
10. Benzo[*b*]triphenylene
11. Dibenzo[*a*, *c*]naphthacene
12. Dibenzo[*a*, *c*]pentacene
13. Dibenzo[*a*, *h*]anthracene
14. Dibenzo[*a*, *j*]naphthacene

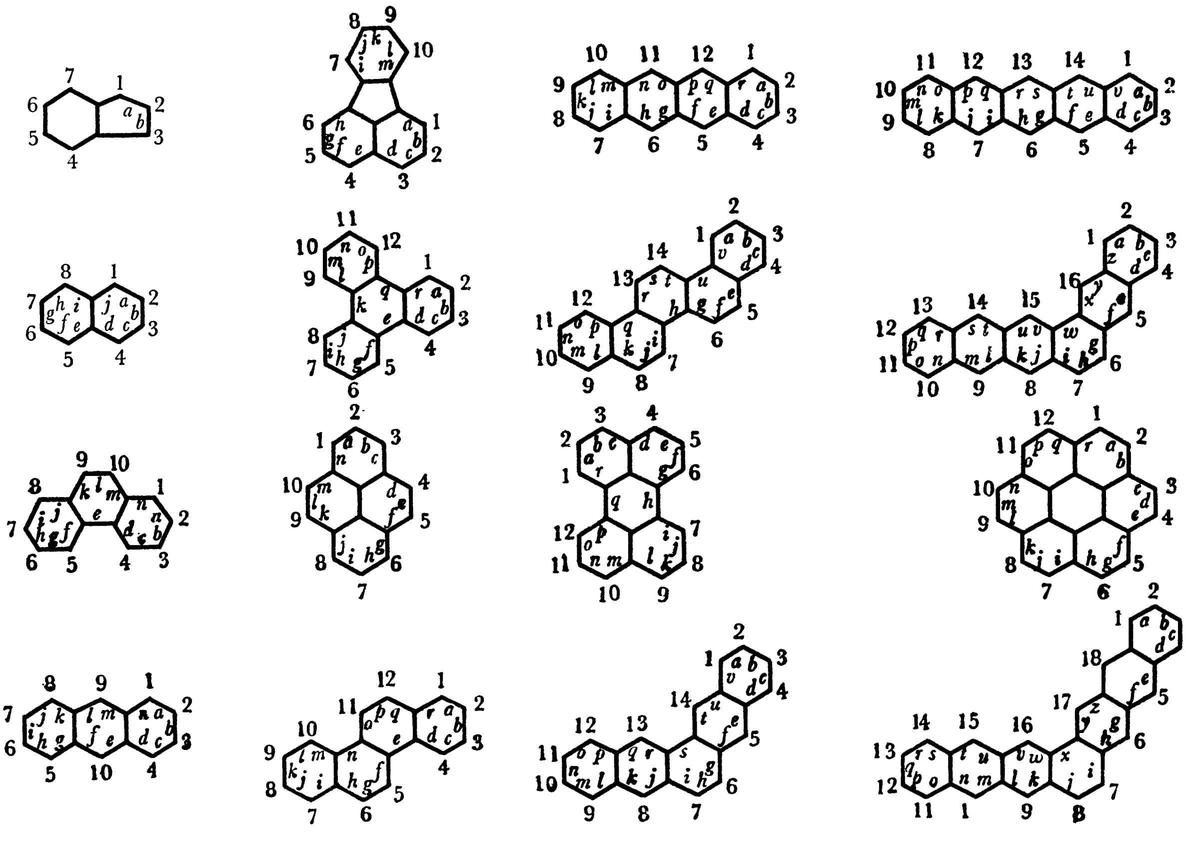


Chart 1.

15. Dibenzo[*a, l*]pentacene
16. Chrysene
17. Benzo[*b*]chrysene
18. Dibenzo[*b, k*]chrysene
19. Benzo[*c*]phenanthrene
20. Dibenzo[*a,j*]anthracene
21. Benzo[*g*]chrysene
22. Tribenzo[*a, c, h*]anthracene
23. Dibenzo[*g, p*]chrysene
24. Benzo[*c*]chrysene
25. Dibenzo[*b, g*]phenanthrene
26. Picene
27. Pentaphene
28. Hexaphene
29. Benzo[*c*]pentaphene
30. Dibenzo[*c, m*]pentaphene
31. Naphtho[2,3-*c*]pentaphene
32. Perylene
33. Benzo[*a*]perylene
34. Dibenzo[*a, j*]perylene
35. Dibenzo[*a, n*]perylene
36. Benzo[*ghi*]perylene
37. Dibenzo[*b, pqr*]perylene
38. Tribenzo[*b,ghi,k*]perylene
39. Coronene
40. Dibenzo[*fg, qr*]pentacene
41. Dibenzo[*bc, ef*]coronene
42. Tetrabenzo[*de, h, kl, rst*]pentaphene
43. Tetrabenzo[*de, hi, op, st*]pentacene
44. Pyrene
45. Benzo[*e*]pyrene
46. Benzo[*a*]pyrene
47. Bibenzo[*a, l*]pyrene
48. Dibenzo[*a, e*]pyrene
49. Dibenzo[*fg, op*]naphthacene
50. Dibenzo[*a, h*]pyrene
51. Benzo[*rst*]pentaphene
52. Dibenzo[*de, qr*]naphthacene
53. Naphtho[2,3-*a*]pyrene
54. Dinaphtho[2,3-*a*,2′,3′-*h*]pyrene
55. Benzo[*xyz*]heptaphene
56. Dibenzo[*h,rst*]pentaphene
57. Dibenzo[*cd,lm*]perylene
58. Tetrabenzo[*a,cd,j,lm*]perylene
59. Dibenzo[*def,mno*]chrysene
60. Tribenzo[*ghi,m,pqr*]picene
61. Tetrabenzo[*b,def,k,mno*]chrysene
62. Fluoranthene
63. Benzo[*a*]fluoranthene
64. Dibenzo[*b,g*]fluoranthene
65. Benzo[*b*]fluoranthene
66. Benzo[*j*]fluoranthene
67. Benzo[*k*]fluoranthene
68. Naphtho[2,3-*j*]fluoranthene
69. Naphtho[2,3-*k*]fluoranthene
70. Benzaldehyde
71. Cinnamaldehyde
72. 1-Naphthalenealdehyde
73. 2-Naphthalenealdehyde
74. 9-Anthracenealdehyde
75. 9-Phenanthrenealdehyde
76. 1,4-Benzoquinone
77. 1,4-Naphthoquinone
78. 1,4-Anthraquinone
79. 9,10-Anthraquinone

References

1) This paper forms Part V of "The Application of Molecular Orbital Method," Part IV: Y. Ueda, Y. Ono, K. Ogawa, Y. Ohkura, and K. Kohashi, *Yakugaku Zasshi*, **95**, 470 (1975), "X-Ray Photoelectron Spectra of σ Complexes of 1,3,5-Trinitrobenzene and Picric Acid." A part of this paper was presented at the Meeting of the Kyushu Branch of the Pharmaceutical Society of Japan, Fukuoka, February, 1973.

2) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964); R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1965).

3) *e.g.*, H. Bartelt, *J. Electroanal. Chem.*, **27**, 447 (1970); F. C. Anson, N. Rathjen, and R. D. Frisbee, *J. Electrochem. Soc.*, **117**, 477 (1970); J. L. Huntington and D. G. Davis, *ibid.*, **118**, 57 (1971).

4) N. S. Hush, *J. Chem. Phys.*, **28**, 962 (1958).

5) A. A. Vlček, "Progress in Polarography," Vol. I, ed. by P. Zuman and I. M. Kolthoff, Interscience Publishers, New York (1962); A. A. Vlček, "Progress in Inorganic Complexes," Vol. V, ed. by F. A. Cotton, Interscience Publishers, New York (1963), p. 211.

6) T. Yonezawa, K. Hayashi, C. Nagata, S. Okamura, and K. Fukui, *J. Polymer Sci.*, **14**, 312 (1954); K. Hayashi, T. Yonezawa, C. Nagata, S. Okamura, and K. Fukui, *ibid.*, **20**, 537 (1956); K. Fukui, T. Yonezawa, and C. Nagata, This Bulletin, **27**, 423 (1954); K. Fukui, K. Morokuma, T. Yonezawa, and C. Nagata, *ibid.*, **33**, 963 (1960).

7) P. Zuman, *Rev. Polarography* (Kyoto), **11**, 102 (1963).

8) A. Maccoll, *Nature*, **163**, 178 (1949).

9) E. G. Wilson and S. A. Rice, "Optical Properties and Electronic Structure of Metals and Alloys," ed. by F. Abeles, North-Holland, Amsterdam (1966), p. 271.

10) E. Heilbronner, "Hückel Bunshi Kido Ho 1 (Translated edition of "Das HMO-Model und seine Anwendung" by H. Sakurai and T. Takeuchi)," Hirokawa Publ. Co., Tokyo (1973), p. 335.

11) R. Daudel, "Kagaku Hanno no Ryoshiron (Translated edition of "Theorie Quantique de la Reactivite Chimique" by J. Souma, K. Hayashi, and M. Shiotani)," Baifukan, Tokyo (1972), p. 102.

12) G. J. Hoijtink and J. Van Schooten, *Rec. Trav. Chim.*, **71**, 1089 (1952).

13) A. Pullman, B. Pullman, and G. Berthier, *Bull. Soc. Chim. Fr.*, **17**, 591 (1950).

14) H. A. Laitinen and S. Wawzonek, *J. Amer. Chem. Soc.*, **64**, 1765 (1942); S. Wawzonek and H. A. Laitinen, *ibid.*, **64**, 2365 (1942).

15) G. J. Hoijtink, J. Van Schooten, E. De Boer, and W. I. Aalbersberg, *Rec. Trav. Chim.*, **73**, 355 (1954).

16) S. Wawzonek and E. W. Blaha, *J. Electrochem. Soc.*, **102**, 235 (1956); S. Wawzonek and D. Wearring, *J. Amer. Chem. Soc.*, **81**, 2067 (1959).

17) I. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954).

18) R. W. Schmidt and E. Heilbronner, *Helv. Chim. Acta*, **37**, 1453 (1954).

19) A. Streitwieser Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York (1961).

20) Y. Ono and Y. Ueda, *Chem. Pharm. Bull.* (Tokyo), **18**, 2013 (1970).

21) S. Wawzonek, R. Berkey, E. W. Blaha, and M. E. Runner, *J. Electrochem. Soc.*, **103**, 456 (1956).

22) M. E. Peover, *J. Chem. Soc.*, **1962**, 4540.