A Molecular Orbital Consideration on the Polarographic Reduction of Stilbene Derivatives

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The lowest vacant π-electronic energies, x_{lv}, of some stilbene derivatives were calculated by using the first order perturbation method on the basis of the LCAO MO theory. Between the obtained value of x_{lv} in units of β and the polarographic half-wave reduction potential $E_{1/2}$, of stilbene derivatives, was found to hold the following linear relationship :
$$E_{1/2}=2.27x_{lv}-1.05.$$
Discussions were made on the magnitudes of various energy parameters employed and on the relation between the positions of polarographic reductions of stilbene derivatives and their net π-electronic charge distributions.

INTRODUCTION

Considerable attention has been paid to the relation between polarographic reduction potentials of conjugated compounds and their π-electronic structures. Thus, Maccoll[1] first pointed out that the half-wave reduction potentials of unsaturated hydrocarbons can be linearly related to the lowest vacant π-electronic levels calculated with the aid of the molecular orbital theory, the potentials being less negative as the levels lie lower. The relationship has been further developed by Pullman et al.[2] and by Hoijtink and Schooten.[3~6] A similar relationship concerned with aromatic aldehydes has been reported by Schmid and Heilbronner.[7]

However, we have as yet very little information as to the quantum-mechanical discussion** on substituent effects upon the reduction potentials of conjugated molecules probably because of the uncertainty with regard to the integral parameters for various heteroatoms involved. According to the first order perturbation calculation, the lowest vacant π-electronic levels of substituted unsaturated hydrocarbons will be readily expressed as linear functions of the energy parameters.

In the present paper, the above-mentioned linear functions for stilbene derivatives were given in a tabular form with regard to teh relevant *reference* compounds (i. e., non-perturbed molecules) and it was shown that a linear relationship holds between polarographic half-wave reduction potentials of *actual* stilbene derivatives and their lowest vacant π-electronic energies obtained from the linear functions by assuming a reasonable set of values for Coulomb

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** On the basis of the molecular orbital theory, Koide and Tachi[8] studied of the effect of *p*-substituents (halogens and methyl group) on the reduction potentials of nitrobenzene and benzaldehyde.

integral parameters for substituents. Furthermore, the position of electro-chemical reduction of each stilbene derivative has been elucidated in terms of the negative net charge distribution in the molecule anion resulting from π-electron trapping of the parent compound.

METHOD OF CALCULATION

The lowest vacant π-electronic level, ε_{lv}, of a conjugated molecule may be represented as

$$\varepsilon_{lv} = \alpha + x_{lv}\beta, \tag{1}$$

where α and β are the Coulomb integral of a carbon atom and the resonance integral of a carbon-carbon π-bond in benzene, respectively, and accordingly x_{lv} may be referred to as the relative lowest vacant level of the molecule in question. The term x_{lv} was divided into three parts, i. e., the standard lowest vacant level, $x_{lv}{}^0$, the π-Coulombic effect perturbation term, I_π, and the σ-inductive effect perturbation term, I_σ, each of which was calculated in the following way:

The molecular orbital function, $\psi_{lv}{}^0$, of a reference (or non-perturbed) molecule corresponding to the lowest vacant level is given by such a linear combination of atomic orbitals, ϕ_r, as

$$\psi_{lv}{}^0 = \sum_r C_{lv}{}^0{}_{,r}\ \phi_r, \tag{2}$$

where $C_{lv}{}^0{}_{,r}$ is a linear combination coefficient. The term $x_{lv}{}^0$ is the eigenvalue of the equation:

$$H^0\psi_{lv}{}^0 = x_{lv}{}^0\psi_{lv}{}^0 \tag{3}$$

where H^0 is an effective one-electron Hamiltonian for the non-perturbed molecule. Practically, $x_{lv}{}^0$ was obtained by solving the molecular obital secular equation in which overlap integrals were completely neglected.

Introduction of a heteroatom into a position of X in the reference compound will cause the change in H, say H'. The corresponding change in the energy, δx_{lv}, of the lowest vacant level will be expressed according to the usual first order perturbation theory as

$$\delta x_{lv} = \int \psi_{lv}{}^0 H' \psi_{lv}{}^0 d\tau = (C_{lv}{}^0{}_{,x})^2 \int \phi_X H' \phi_X d\tau + \sum_r{}' (C_{lv}{}^0{}_{,r})^2 \int \phi_r H' \phi_r d\tau, \tag{4}$$

where the summation in the second term of the right-hand side covers all the atoms but X. Since the perturbation integrals will lead to the Coulomb integral increments, $\delta\alpha$, for the corresponding atoms, Equation (4) will be written as

$$\delta x_{lv} = (C_{lv}{}^0{}_X)^2 \delta\alpha_X + \sum_r{}' (C_{lv}{}^0{}_{,r})^2 \delta\alpha_r. \tag{5}$$

It will be reasonable to consider that the perturbation will be more significant in the vicinity of the heteroatom introduced. Assuming that the Coulomb integral increment, $\delta\alpha_r$, would decrease with increasing number of bonds, n, intervening between atoms X and r in the manners where $\delta\alpha = \frac{1}{3}\delta\alpha_X$, $\delta\alpha = \frac{1}{10}\delta\alpha_X$ and $\delta\alpha = 0$ for $n = 1, 2$ and more, respectively, one will obtain

$$\delta x_{lv} = (C_{lv}{}^0{}_{,x})^2 \delta\alpha_X + \left(\frac{1}{3} \sum_{r_1}{}' (C_{lv}{}^0{}_{r_1})^2 + \frac{1}{10} \sum_{r_2}{}' (C_{lv}{}^0{}_{,r_2})^2 \right) \delta\alpha_X, \tag{6}$$

where r_1 and r_2 refer to the atoms with $n=1$ and $n=2$, respectively. In the right-hand side of Equation (6), we define the first and the second terms as I_π and I_σ, respectively. It need hardly be mentioned that, when two heteroatoms or more are introduced into a non-perturbed molecule, δx_{lv} in Equation (6) should be summed up over all of them.

Thus, the lowest vacant level, ε_{lv}, may be given by

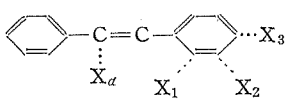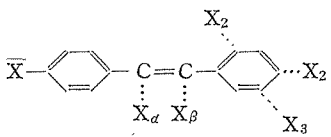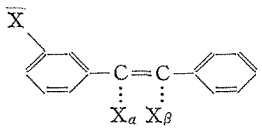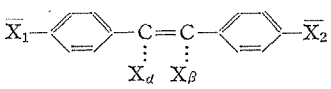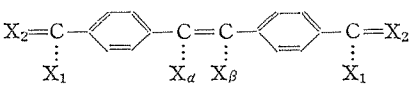$$\varepsilon_{lv} = a + (x_{lv}^0 + I_\pi + I_\sigma)\beta. \tag{7}$$

The structures of reference compounds for stilbene derivatives are illustrated in the Appendix.

RESULTS AND DISCUSSION

1. Relationship between the Half-Wave Reduction Potentials and the Lowest Vacant π-Electronic Levels

The calculation results of x_{lv}^0, I_π and I_σ for the reference compounds of some stilbene derivatives are collected in Table 1, where k_X denotes $\delta a_X/\beta$ and all the energy quantities are given in units of β. The substituents linked

Table 1. Separation of x_{lv} of stilbene derivatives[a].

No.	Reference Compound	# of the π-electrons	x_{lv}^0	I_π^b	I_σ^b
I		14	-0.5043	0	$0.2716k_a'$ $0.0928k_1'$ $0.0641k_2'$ $0.1026k_3'$
II		16	-0.6180	$0.1045k$	$0.0153k$ $0.2798k_a'$ $0.2317k_\beta'$ $0.0945k_1'$ $0.0676k_2'$ $0.1112k_3'$
III		16	-0.5107	$0.0066k$	$0.0190k$ $0.2773k_a'$ $0.2746k_\beta'$
IV		18	-0.7244	$0.0885k_1$ $0.0885k_2$	$0.0165k_1$ $0.0165k_2$ $0.2686k_a'$ $0.2686k_\beta'$
V		18	-0.4540	$0.1090k_2$	$0.0748k_1'$ $0.0214k_2$ $0.2277k_a'$ $0.2277k_\beta'$

a. All the energy quantities are given in units of β.
b. $k_X = \delta a_X/\beta$.

with the conjugated systems by dotted lines mean that they do not enter the π-conjugation, the Coulomb integral parameter k' being the one for the carbon atom bearing an unconjugating (*i. e.*, inductive) substituent. In order to compute x_{lv} of each stilbene derivative from the results collected in Table 1, it is required to estimate a set of numerical values for the Coulomb integral parameters. Unfortunately, however, we have no means to do this *a priori*; the parameters should be chosen empirically so that they might illustrate the substituent effects upon a possible variety of chemical phenomena.

In the light of the linear relationship between the polarographic half-wave reduction potentials, $E_{1/2}$, and the relative lowest vacant π-electronic energy level, x_{lv}, of unsaturated hydrocarbons,[1-6] it may never be unreasonable to make a preliminary assumption that a similar linearity would also hold in the case of stilbene derivatives. The values for k are thus to be reduced from the expected linear correlation of $E_{1/2}$'s for stilbene derivatives which were determined by Goulden and Warren,[9] with their x_{lv}-values.

First, provided that both methyl and ethyl groups are regarded as equivalent inductive substituents, the values of x_{lv} for α-ethylstilbene and 2, 4, 6, 2', 4', 6'-hexamethylstilbene are to depend merely on a common value of k' for these two substitueuts. The lowest vacant levels of stilbene itself and of the above two alkyl-substituted derivatives can be linearly correlated to their experimental data on half-wave potentials when k' is estimated as -0.2 in complete agreement with our previous assumption.[10]

Next, on the bases of the results in Table 1 and of $k' = -0.2$ for alkyl groups, x_{lv}'s of a variety of stilbenes with dimetylamino-, methoxy- or hydroxy-group substituted on their benzene nuclei were computed with the k-values for these newly introduced substituents varying from zero to unity at a regular numerical interval of 0.1. If the plots of x_{lv}'s for these substituted stilbenes *versus* their experimentally determined reduction potentials are to fall in the vicinity of the straight line obtained above, the most reasonable set of k-values for the three substituents ought to give a maximum value of the over-all correlation coefficient for the plots. The values for the unknown parameters k were thus evaluated as 0.5, 0.6 and 0.8 for dimethylamino-, hydroxy- and methoxy-groups, respectively, and the maximum correlation coefficient was found to be 0.953.

Since the parameter k is regarded as an index for the electronegativity of the heteroatom in the relevant substituent, it may be rather probable that both of the k-values for hydroxy- and methoxy-groups proved larger than that for dimethylamino-group. In Table 2 are collected the computed results of x_{lv}'s for stilbene derivatives together with the experimental data[9] on their $E_{1/2}$'s.

Inspection of Table 2 shows that the value of $-E_{1/2}$ increases with the increasing magnitude of $-x_{lv}$ or, in other words, that a stilbene derivative is electrochemically reduced more easily as its lowest vacant π-electronic level lies lower. It may be due to the relatively higher lying property of the lowest vacant level that 4-methoxy-α,β-diethylstilbene and 4, 4'-dihydroxy-α,β-diethyl-

Table 2.   Relation between $E_{1/2}$ and x_{lv} of stilbene derivatives and the derived β-values.

No.	Substituents	$-E_{1/2}$ (V. *vs.* S.C.E.)[a]	$-x_{lv}$[b]	$-\beta$[c]	Δ
1	None	2.17	0.5043	2.22	+0.05
2	3-N(CH₃)₂	2.19	0.4979	2.29	−0.02
3	4-OCH₃	2.24	0.5222	2.28	−0.01
4	4-N(CH₃)₂	2.29	0.5581	2.22	+0.05
5	α-C₂H₅	2.30	0.5450	2.29	−0.02
6	4-N(CH₃)₂-2′-CH₃	2.31	0.5770	2.18	+0.09
7	4, 4′-*di*OCH₃	2.32	0.5564	2.28	−0.01
8	4-N(CH₃)₂-3′-CH₃	2.33	0.5716	2.24	+0.03
9	4-OH	3.34	0.5461	2.36	−0.09
10	4-N(CH₃)₂-4′-CH₃	2.35	0.5803	2.24	+0.03
11	4-N(CH₃)₂-2′, 5′-*di*CH₃	2.37	0.5905	2.24	+0.03
12	4-NH₂-4′-OH	2.45	0.6089	2.30	−0.03
13	2, 4, 6, 2′, 4′, 6′-*hexa*CH₃	2.48	0.6196	2.31	−0.04
14	4-OCH₃-α,β-*di*C₂H₅	NW[d]	0.6522	—	—
15	4, 4′-*di*OH-α,β-*di*C₂H₅	NW[d]	0.7058	—	—

mean : $\beta = -2.27 \pm 0.014 \mathrm{eV}$[e]

a.   In 75% dioxane containing 0.1M *tetra-n*-butylammonium iodide ; ref. 9.
b.   In units of β. Coulomb integral parameters : N(CH₃)₂, 0.5 ; OH, 0.6 ; OCH₃, 0.8 ; CH₃, −0.2 ; C₂H₅, −0.2.
c.   Derived from the equation : $E_{1/2} = -x_{lv}\beta - 1.05$.
d.   No reduction wave.
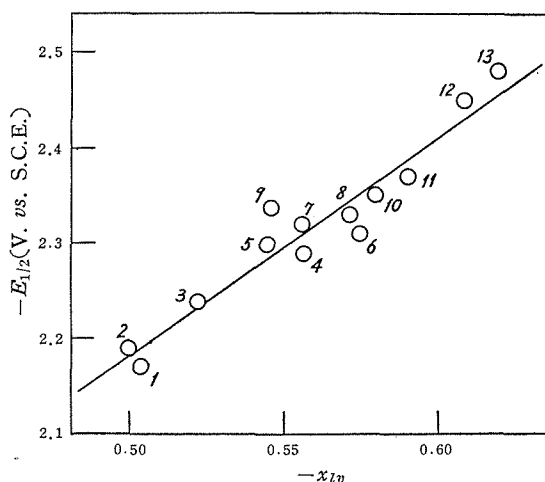e.   Standard error, $\sqrt{\dfrac{\sum \Delta^2}{13 \times 12}}$.

Fig. 1.   Linear relationship between x_{lv} and $E_{1/2}$ of stilbene derivatives.   As to the numbering, see Table 2.

stilbene do not give any reduction wave.

Fig. 1 illustrates graphically the correlation between x_{lv} and $E_{1/2}$ of stilbene

derivatives collected in Table 2. By use of the method of least squares, the regression line of $E_{1/2}$ against x_{lv} was determined as

$$E_{1/2} = 2.27x_{lv} - 1.05. \tag{8}$$

Here the standard deviation of $E_{1/2}$ from this line was 0.029 V.

Hoijtink and Schooten suggested[3] that $E_{1/2}$ for unsaturated hydrocarbons, which was determined under essentially the same conditions as adopted by Goulden and Warren for stilbenes, would be related to x_{lv} by

$$E_{1/2} = -x_{lv}\beta - 1.05 \tag{9}$$

and actually obtained[5] this equation with $\beta = -2.23 \pm 0.02$ eV. It seems interesting to note that Equations (8) and (9) are in good agreement with each other.

According to Goulden and Warren,[9] 4, 4'-diacetyl-α,β-diethylstilbene is much more easily reduced (-1.78 V vs. S.C.E.) at the dropping-mercury electrode than any other derivative listed in Table 2. Substituting $E_{1/2} = -1.78$ into Equation (8), we obtain $x_{lv} = -0.3216$ for the stilbene derivative. Making use of the separation results for the reference compound V* in Table 1 we have

$$-0.4540 + 0.5302 k'_{CH_3} + 0.1304 k_O = -0.3216. \tag{10}$$

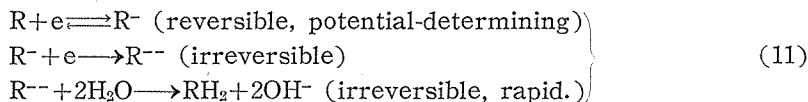Since $k'_{CH_3} = -0.2$, we obtain $k_O = 1.83$. This value of k is in good accordance with 2 that has been recommended by several authors[7,10,11] as the most suitable electronegativity characteristic for a carbonyl oxygen.

Thus, we may reach a possible conclusion that there exists a linear correlation between half-wave reduction potentials of some stilbene derivatives and their lowest vacant π-electronic energy levels.

The present method of obtaining the lowest vacant levels will also be applicable to other series of conjugated molecules containing heteroatoms. The favor of this method lies in easiness and rapidity with which the required levels can be approximated.

2. Relation between the Position of Polarographic Reduction and the π-Electronic Charge Distribution

On the experimental bases that the half-wave reduction potentials of unsaturated hydrocarbons are independent of the pH and that the logarithmic analyses of these reduction waves indicate potential-determining steps involving one electron, Wawzonek et al.[12,13] suggested the following mechanism for the electrochemical reduction of unsaturated hydrocarbons:

$$
\left.
\begin{array}{l}
R + e \rightleftharpoons R^- \text{ (reversible, potential-determining)} \\
R^- + e \longrightarrow R^{--} \text{ (irreversible)} \\
R^{--} + 2H_2O \longrightarrow RH_2 + 2OH^- \text{ (irreversible, rapid.)}
\end{array}
\right\} \tag{11}
$$

It may serve as another argument in favor of this mechanism that the half-wave reduction potentials of a great many unsaturated hydrocarbons could be linearly correlated to their lowest vacant π-electronic levels, i. e., the total

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* It should be noted that, for the $C = X_2$ bonds in the reference compound V, was assigned the resonance integral of $\sqrt{2}\ \beta$[7,10,11] which is believed to be the most recommendable for a carbonyl bond.

π-electronic energy differences between R and R⁻.[1-6]

According to the above reduction mechanism, it is to be expected that reduction involving the addition of protons will take place at the positions in R⁻⁻ where the last irreversible step in Equation (11) proceeds most preferentially. Hoijtink and Schooten[3,4] calculated the π-electronic charge distributions in various molecule ions using the simple molecular orbital method and made interesting predictions of structures of the reduction products, RH_2, by assuming that a proton would first add to the position in R⁻⁻ having the largest negative charge and that the successive proton addition toward RH⁻ would take place in a similar fashion to give RH_2. The structure of RH_2 seems unaltered if we assume more simply that two protons will add simultaneously to the two positions in R⁻⁻ at which the negative charges are largest.

There will be no reasons why the above consideration concerning the position of reduction will not be applicable to the substituted unsaturated hydrocarbons. For the purpose of checking up this point, we calculated the π-electron distributions of five double charged ions, I⁻⁻ to V⁻⁻. The results are collected in Table 3.

As to reference anions I⁻⁻, II⁻⁻, III⁻⁻ and IV⁻⁻, the negative net charges*

Table 3. The net charge distributions of the anions of stilbene derivatives[a].

Position	I⁻⁻	II⁻⁻		III⁻⁻	IV⁻⁻		V⁻⁻	
		$k_X=0$	$k_X=1$	$k_X=0$	$k_X=0$	$k_X=1$	$k_X=0$	$k_X=2$
1	0.3839	0.4701	0.4374	0.3970	0.4852	0.4452	0.3179	0.1547
2	0.0943	0.2076	0.1013	0.0387	0.1428	0.0646	0.0948	0.0601
3	0.1500	0.1367	0.1439	0.3624	0.1590	0.1630	0.1238	0.0626
4	0.0125	0.0700	0.0826	0.0034	0.1336	0.0899	0.0219	0.0072
5	0.1968	0.0798	0.0753	0.2903	0.1004	0.1077	0.1756	0.1370
6	0.0125	0.0700	0.0826	0.0189	0.1336	0.0899	0.0219	0.0072
7	0.1500	0.1367	0.1439	0.2413	0.1590	0.1630	0.1238	0.0626
8	0.3839	0.4611	0.3781	0.3839	0.4852	0.4452	0.3179	0.1547
9	0.0943	0.1367	0.1149	0.0984	0.1428	0.0646	0.0948	0.0601
10	0.1500	0.1867	0.1586	0.1520	0.1590	0.1630	0.1238	0.0626
11	0.0125	0.0200	0.0189	0.0131	0.1336	0.0899	0.0219	0.0072
12	0.1968	0.4089	0.2211	0.2010	0.1004	0.1077	0.1756	0.1370
13	0.0125	0.0200	0.0189	0.0131	0.1336	0.0899	0.0219	0.0072
14	0.1500	0.1867	0.1586	0.1520	0.1590	0.1630	0.1238	0.0626
15	—	+0.5911	+0.1363	+0.4155	+0.3137	+0.1233	0.0112	+0.2205
16	—	—	—	—	+0.3137	+0.1233	0.0112	+0.2205
17	—	—	—	—	—	—	0.1091	0.7291
18	—	—	—	—	—	—	0.1091	0.7291

a. All the charges should be multiplied by −1, unless a positive sign is prefixed.

* Net charge, q_{net}, is generally given by 1−q when the atom has one original p_π-electron and by 2−q when the atom has conjugating lone pair electrons, where q represents the total π-electron density at the position of the atom concerned.

are largest at the carbon atoms of ethylenic double bonds. For the molecule ions II⁻⁻ and IV⁻⁻, the net charge distributions were calculated with the Coulomb integral parameter $k=1$ for the heteroatom X; the results were found not to deviate largely from those in the corresponding reference anions except that the positive net charge for X decreases noticeably in either case. Possibly, the situation is also the case with the molecule ion of III. Since every value of k for dimethylamino-, hydroxy- or methoxy-group lies in the region of $0 < k < 1$, it might be reasonable to consider that, in the stilbene derivative with each of these groups as the nuclear substituent, the negative net charge will be largest at the ethylenic double bond. There will be no serious change in the charge distributions in the cases of their alkyl derivatives. Thus thee electrochemical reduction of any of the stilbene derivatives corresponding to the reference structures I to IV will be regarded as taking place at the extra-cyclic ethylenic bonds in agreement with the supposition made by Goulden and Warren.[9]

In the molecule ion V⁻⁻, on the other hand, the negative net charge is largest at the position of X_2 when the value of 2 was assigned to k_{X_2}. When the resulting neutral molecule traps two more electrons from the electrode, its charge distribution turns into what is represented in Fig. 2; the negative net charge of the anion is largest at the carbonyl carbons. These results might indicate that the reduction of 4, 4'-diacetyl-α,β-diethylstilbene would take place at the carbonyl groups contained, which is again in accord with Goudlen and Warren's supposition.
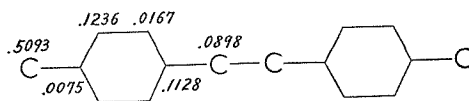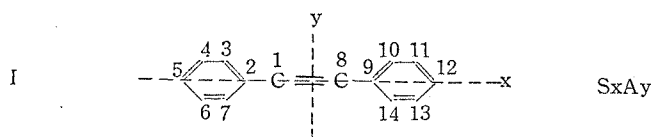

Fig 2. Diagramatic representation of the negative
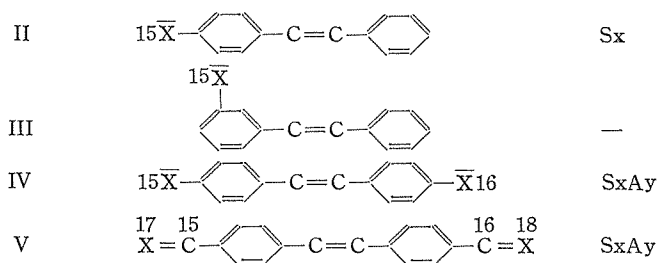net charge distribution in (VH₂).⁻⁻

In the addition reaction of protons toward molecule anions, the electrostatic interaction between the two species would play the more important role than any other factor does. It might be due to such a situation that the position of electrochemical reduction of substituted stilbenes seems to be related to the distribution of the net charge rather than to that of the total π-electron density. In the same way, the difference in the energy change accompanying the forma-tion of new σ-bonds in the coures of the proton addition will have less significant meaning compared with the contribution of the major factor mentioned above.

APPENDIX

The numberings of stilbene derivatives and the symmetries
of their lowest vacant levels.

Polarographic Reduction of Stilbene Derivatives

II   15$\overline{X}$—⟨ ⟩—C=C—⟨ ⟩   Sx

III   15$\overline{X}$
       ⟨ ⟩—C=C—⟨ ⟩   —

IV   15$\overline{X}$—⟨ ⟩—C=C—⟨ ⟩—$\overline{X}$16   SxAy

V   17 15   16 18
       X=C—⟨ ⟩—C=C—⟨ ⟩—C=X   SxAy

REFERENCES

(1) A. Maccoll, *Nature*, **163**, 178 (1949).
(2) A. Pullman, B. Pullman and G. Berthier, *Bull. soc. chim. France*, **17**, 591 (1950).
(3) G. J. Hoijtink and J. van Schooten, *Rec. trav. chim.*, **71**, 1089 (1952).
(4) G. J. Hoijtink and J. van Schooten, *ibid.*, **72**, 691 (1953).
(5) G. J. Hoijtink and J. van Schooten, *ibid.*, **72**, 903 (1952).
(6) G. J. Hoijtink, *ibid.*, **74**, 1525 (1955).
(7) R. W. Schmid and E. Heilbronner, *Helv. Chim. Acta*, **37**, 1453 (1954).
(8) S. Koide and I. Tachi, *J. Electrochem. Soc. Japan*, **23**, 522 (1955).
(9) F. Goulden and F. L. Warren, *Biochem. J.*, **42**, 420 (1948).
(10) T. Fueno, T. Tsuruta and J. Furukawa, *J. Chem. Soc. Japan, Pure Chemistry Section*, **78**, 1075, 1080 (1957).
(11) R. D. Brown, *Quart. Revs.*, **6**, 63 (1952).
(12) S. Wawzonek and J.W. Fan, *J. Am. Chem. Soc.*, **68**, 2541 (1946).
(13) H. A. Laitinen and S. Wawzonek, *J. Am. Chem. Soc.*, **64**, 1765 (1942).