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A Theoretical Interpretation of the Substituent Effects in Argentation Equilibria of Aromatic Hydrocarbons*

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The effects of ring substituents on the stability of silver ion complexes of benzene and styrene are discussed in terms of the delocalization energies as calculated by the simple LCAO MO method. It is demonstrated that the delocalization energy responsible for the formation of the σ-type molecular bond can predict the relative stabilities of the complexes; the calculated energies are linearly correlated with Hammett's sigma values. The π-type molecular bond energy arising from the delocalization of silver d-electrons decreases linearly with the increase in the σ-type bond energy. In cases where the two energies are comparable in magnitude, the substituent effects may well be controlled by the entropy term, as has previously been demonstrated experimentally. This apparent paradox encountered in the interpretation of substituent effects may best be reconciled by assuming that the behavior of the silver 4d-orbital in complexation is more closely associated with the entropy change than that of the 5s-orbital of the same atom.

Since Winstein and Lucas[1] first revealed evidence for the formation of silver ion complexes of olefins in the aqueous phase, the nature of such complexes has received considerable attention from physical and organic chemists. Thus, Andrews and Keefer[2] performed extensive measurements of the equilibrium constants for the silver ion complexation (argentation) of aromatic as well as olefinic compounds, hoping thereby to clarify the relation between the substrate structure and the complex stability. More light has recently been shed on these complexes through the structural studies of the isolated silver salt—substrate complexes, using the X-ray diffraction method[3,4] and the ultraviolet,[5,6] infrared[6,7] and NMR[5,8] spectroscopic techniques.

Admittedly, however, little is known about the nature of the complexation bonds formed between the silver ion and substrates. Dewar[9] proposed a complexation model in which the two components are bound by two types of molecular bonds; one is a *σ-type* bond formed by the delocalization of the carbon $2p\pi$ electrons of the substrates onto a vacant 5s-orbital of the silver ion, while the other is a *π-type* bond formed by the *backward* delocalization of the silver 4d-electrons onto a vacant $p\pi^*$ antibonding orbital of the substrates. Although there has been a growing tendency to accept the above customary picture, no direct confirmation of the role of the d-electrons has ever been provided.

Recently, Hosoya and Nagakura[6] made a theoretical analysis of the electronic structure of the cyclohexene - silver ion complex by evaluating the interactions among several possible electronic

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[*1] The Structure—Stability Relationship of the Metal Ion Complexes of Unsaturated Compounds. II. Reference 12 is the Paper I of this series.

1) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938).

2) a) L. J. Andrews and R. M. Keefer, ibid., **71**, 3644 (1949); b) ibid., **72**, 3113 (1950); c) ibid., **72**, 5034 (1950).

3) R. E. Rundle and J. H. Goring, ibid., **72**, 5337 (1950); H. G. Smith and R. E. Rundle, ibid., **80**, 5075 (1958).

4) F. S. Mathews and W. N. Lipscomb, *J. Phys. Chem.*, **63**, 845 (1959).

5) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, **1960**, 2519.

6) H. Hosoya and S. Nagakura, This Bulletin, **37**, 249 (1964).

7) H. J. Taufen, M. J. Murray and F. F. Cleveland, *J. Am. Chem. Soc.*, **63**, 3500 (1941).

8) D. F. R. Gilson and C. A. McDowell, *J. Chem. Phys.*, **39**, 1825 (1963).

9) M. J. S. Dewar, *Bull. soc. chim. France*, **18**, C79 (1951).

configurations of the components. From the results of this analysis, they drew the conclusion that the *d*-electrons of the silver ion contribute appreciably to the stabilization of the ground state of the complex. On the other hand, Fukui et al.[10] used the simple LCAO MO approximation to calculate the delocalization energies of 2pπ electrons alone and demonstrated that such energies could be used as a measure of the relative stability of the 1 : 1 argentation complexes of aromatic hydrocarbons.

It is to be expected that, in substituted aromatic hydrocarbons, the relative effects of substituents on the complex stability will be reversed, depending on which type of molecular bond is the more predominant, the σ-type or the π-type. According to Andrews and Keefer,[2b] the substituent effects in the case of benzene can roughly be interpreted in terms of the Hammett $\rho\sigma$ relationship;[11] the first equilibrium constants, K_1, of substituted benzenes are larger as the substituents are more electrondonating. A similar trend has been observed in our previous experimental work on substituted styrenes.[12] It would seem, then, that only the σ-type bond formation is important in the stabilization of complexes. However, it must be cautioned that, more precisely, such comparisons of substituent effects between theory and experiment should be directed toward the free-energy change in the complex formation rather than toward the enthalpy change, particularly when these changes are relatively small.

In the present paper, we will attempt to make theoretical examinations of the substituent effects observed for the stability of argentation complexes of benzene and styrene. The simple LCAO MO approximation will be used throughout in appreciation of its considerable simplicity. First, the above-mentioned simple delocalization model of Fukui et al.[10] will be tested for the substituted compounds. Second, a suggestion will be made as to the extent to which the d-electrons of silver would participate in the formation of argentation complexes. Finally, consequences of the above suggestion will be discussed, and the empiricism inherent in the present treatment will be assessed.

The pπ-Electron Delocalization Energies of the Complexes

In an attempt to interpret the relative stabilities of silver ion complexes of different aromatic hydrocarbons, Fukui et al.[10] have adopted Dewar's "bond-delocalization model" of the π-complex[13] in which only a pair of 2pπ carbon orbitals of a particular unsaturated bond overlap longitudinally with a vacant orbital of a complexing ion located equidistant from the two carbons. Assuming that the interaction is sufficiently small, they applied the perturbation technique to calculating, within the framework of the simple LCAO MO approximation, the stabilization energy of the complex due to the delocalization of pπ electrons. The result was expressed in the form:

$$\varDelta E_{rs}^{(\mathrm{p})} = 2\sum_{j}^{occ.} \frac{(c_{jr}+c_{js})^2}{m_j}\left(-\frac{\gamma^2}{\beta}\right) \qquad (1)$$

Here, r and s signify the carbon atoms constituting the bond at which the complexation takes place; γ is the resonance integral for the two weak bonds formed between the ion and the carbons, r and s; and the other symbols, which are associated with the isolated aromatic molecules, have their usual meanings. The energy, $\varDelta E_{rs}^{(\mathrm{p})}$, calculated from Eq. 1 has proven capable of providing a successful account of the relative stabilities of the silver ion complexes of aromatic hydrocarbons. The quantity, $\varDelta E_{rs}^{(\mathrm{p})}$, will henceforth be referred to as the pπ-delocalization energy.

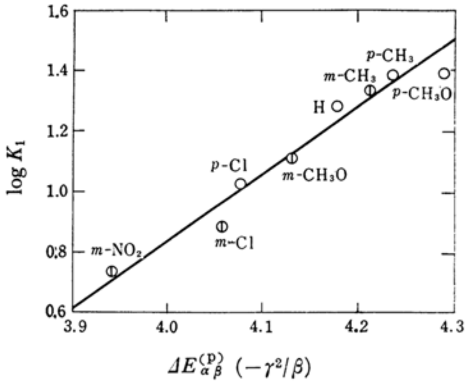

Fig. 1. Plots of the pπ-delocalization energies of argentation complexes of substituted styrenes against log K_1.

In the silver ion complexes of substituted styrenes, there are good reasons for believing that the primary center for the coordination of the silver ion is an extracyclic double bond, i. e., the α-β bond.[12] Using Eq. 1, the pπ-delocalization energies of the complexes of substituted styrenes are computed for the α-β bonds. The integral

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[10] K. Fukui, A. Imamura, T. Yonezawa and C. Nagata, This Bulletin, **34**, 1076 (1961).

[11] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y. (1940), Chapter 7.

[12] T. Fueno, T. Okuyama, T. Deguchi and J. Furukawa, *J. Am. Chem. Soc.*, **87**, 170 (1965).

[13] M. J. S. Dewar, *Discussions Faraday Soc.*, **2**, 50 (1947). He calculated a pπ-delocalization energy which is the same in principle as that of Fukui et al., but different numerically, because he solved the secular equations for the complexes in which the resonance integrals for the new bonds were assumed to have the value β.

TABLE I. THE pπ-DELOCALIZATION ENERGIES AND THE EQUILIBRIUM CONSTANTS FOR ARGENTATION COMPLEXES OF SUBSTITUTED STYRENES

Substituent	K_1[a) 1./mol.	$\Delta E^{(p)}_{\alpha\beta}$, $-\gamma^2/\beta$	$S^{(E)}_{\alpha}$	$S^{(E)}_{\beta}$	$S^{(E)}_{\alpha\beta}$
H	19.1(18.2[b))	4.1775	0.9113	1.2662	1.0000
p-CH_3	24.2	4.2357	0.9112	1.3055	1.0095
m-CH_3	21.7	4.2122	0.9113	1.2890	1.0059
p-CH_3O	24.2	4.2899	0.9084	1.3612	1.0101
m-CH_3O	12.9	4.1308	0.9115	1.2361	0.9916
p-Cl	10.6	4.0774	0.9088	1.2096	0.9795
m-Cl	7.58	4.0567	0.9111	1.1890	0.9783
m-NO_2	5.45	3.9413	0.9103	1.1174	0.9568

a) K_1 is the equilibrium constant at 25°C for the following reaction (Ref. 12):
$Ag^+ + St \rightleftarrows AgSt^+ \qquad K_1 = [AgSt^+]/[Ag^+][St]$.
b) Andrews and Keefer (Ref. 2c).

TABLE II. THE $p\pi$-DELOCALIZATION ENERGIES AND THE EQUILIBRIUM CONSTANTS FOR ARGENTATION COMPLEXES OF SUBSTITUTED BENZENES

Substituent	K_1[a) 1./mol.	$\Delta E^{(p)}_{om}$ $-\gamma^2/\beta$	$\Delta E^{(p)}_{mp}$ $-\gamma^2/\beta$	$S^{(E)}_{o}$	$S^{(E)}_{m}$	$S^{(E)}_{p}$
H	2.41	2.6667	2.6667	0.8333	0.8333	0.8333
CH_3	2.95	2.7356	2.7430	0.8734	0.8561	0.8730
CH_3O	2.50	2.7086	2.7537	0.9487	0.8021	0.9397
Cl	0.69	2.5042	2.5093	0.7938	0.7553	0.7857
F	0.46	2.5449	2.5769	0.8412	0.7605	0.8323
$COCH_3$	0.54	2.5014	2.4458	0.7427	0.7683	0.7296
$COOC_2H_5$	0.56	2.4843	2.4359	0.7408	0.7633	0.7301
NO_2	0.19	2.3221	2.2566	0.6761	0.6944	0.6552

a) K_1 is the equilibrium constant at 25°C for the following reaction (Ref. 2b):
$Ag^+ + Bz \rightleftarrows AgBz^+ \qquad K_1 = [AgBz^+]/[Ag^+][Bz]$.

parameters[14) used for the various heteroatoms and bonds are those given in a previous paper.[15) For *m*-nitrostyrene, the inductive model with $k = -1.1$ was used for the nitro group.

The calculated values of $\Delta E^{(p)}_{\alpha\beta}$ are listed in Table I, together with the first argentation constants, K_1, measured at 25°C.[12) Plots of $\log K_1$ against $\Delta E^{(p)}_{\alpha\beta}$ give a good linear correlation, as is shown in Fig. 1; the larger the $\Delta E^{(p)}_{\alpha\beta}$ value, the more stable are the complexes.

For the silver ion - substituted benzene complexes, Andrews and Keefer[2a,b) suggested a structure in which the silver ion is located above the plane of the ring at a position equidistant from the six ring carbon atoms, forming covalent bonds with any of these six carbons. However, it has been confirmed by the X-ray diffraction studies that, in the silver perchlorate - benzene complex salt, the silver ion is located above a carbon-carbon bond of the benzene plane and that it interacts primarily with the two nearest carbon atoms.[3)

Although the structure is not known for the complexes formed from substituted benzenes, we have assumed the bond-delocalization model as depicted above and have calculated the pπ-delocalization energies, $\Delta E^{(p)}_{om}$ and $\Delta E^{(p)}_{mp}$, for ortho-meta and meta-para bonds, respectively, of substituted benzenes. The results of the calculations are given in Table II.

Table II shows that, for a given benzene derivative, the pπ-delocalization energies for ortho-meta and meta-para bonds are nearly equal in magnitude. Since these bonds are little hindered sterically, it may reasonably be assumed that ortho-meta and meta-para bonds contribute equally to the coordination of the silver ion. On the other hand, since the steric effects on argentation are fairly large for the bonds adjacent to the carbon-substitutent bonds,[1) a neglect of the coordination of the silver ion on such bonds will not cause an appreciable error. Thus, the number, n, of the bonds effective for silver ion complexation may be assumed to be 4 for all the monosubstituted benzenes considered, while it is 6 for benzene itself.

If the above assumptions are basically correct, all the plots of $\log(K_1/n)$ against $\Delta E^{(p)}_{om}$ and $\Delta E^{(p)}_{mp}$ would fall in the vicinity of a single line. This has been roughly substantiated, as can be seen

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[14) The π-electron densities, q_r, calculated for the meta and para ring carbons by the use of our parameters are in a linear correlation with Taft's $\sigma°$-values[16) of the substituents:

$$\sigma_r° = 9.68(1 - q_r)^{15)}$$

[15) T. Fueno, T. Okuyama and J. Furukawa, This Bulletin, **39**, 569 (1966).

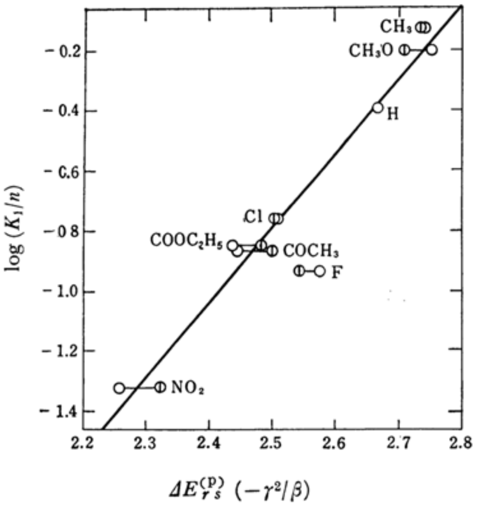

Fig. 2. Plots of the pπ-delocalization energies of argentation complexes of substituted benzenes against log (K_1/n).
n denotes the number of the bonds effective for the complexation. ⦶, $\Delta E_{om}^{(p)}$; ○, $\Delta E_{mp}^{(p)}$

in Fig. 2. These results may be taken as suggesting the validity of our proposal on the structure of the silver ion - benzene complexes. The value, $\Delta E_{om}^{(p)} + \Delta E_{mp}^{(p)}$, may therefore be regarded as a measure of the relative stabilities of the silver ion complexes of substituted benzenes.

The Correlation of $\Delta E_{rs}^{(p)}$ with π-Electron Distributions

The pπ-delocalization energy, $\Delta E_{rs}^{(p)}$, can be transformed into[10]

$$\Delta E_{rs}^{(p)} = \{S_r^{(E)} + S_s^{(E)} + 2S_{rs}^{(E)}\}(-\gamma^2/\beta) \qquad (2)$$

where $S_r^{(E)}$ and $S_s^{(E)}$ are the superdelocalizabilities for an electrophilic attack at the rth and sth carbon atoms respectively, and where $S_{rs}^{(E)}$ is a "bond-delocalizability" defined as[17]

$$S_{rs}^{(E)} = 2\sum_j^{occ.} c_{jr}c_{js}/m_j \qquad (3)$$

Thus, the pπ-delocalization energy does not depend upon only the $S_r^{(E)}$ and $S_s^{(E)}$; an important contribution comes into play from the $S_{rs}^{(E)}$ as well.

When the substituents are located sufficiently far from the r-s bonds,[20] the sum of the bond terms, $S_{rs}^{(E)}$, with respect to the s atoms adjacent to a fixed atom, r, becomes identical with the π-electron density, q_r, at the position r. That is,

$$\sum_s{}' S_{rs}^{(E)} = 2\sum_j^{occ.}\sum_s{}' c_{jr}c_{js}/m_j = q_r \qquad (4)$$

where the simple LCAO MO relation:

$$-c_{jr}m_j + \sum_s{}' c_{js} = 0 \qquad (5)$$

valid under the above conditions, has been utilized.

In the case of ring-substituted styrenes, $S_{\alpha\beta}^{E}$ is in itself equal to the π-electron density on the β-carbon:

$$S_{\alpha\beta}^{(E)} = 2\sum_j^{occ.} c_{j\beta}^2 = q_\beta \qquad (6)$$

Similarly, it can be shown that $S_\alpha^{(E)}$ is identical with Coulson's π-bond order, $p_{\alpha\beta}$, of the α-β bond:

$$S_\alpha^{(E)} = 2\sum_j^{occ.} c_{j\alpha}c_{j\beta} = p_{\alpha\beta} \qquad (7)$$

According to the results of numerical calculations, the values of $S_\alpha^{(E)}$ are nearly constant, irrespective of the sort of ring substituents. On the other hand, $S_\beta^{(E)}$ increases almost linearly with

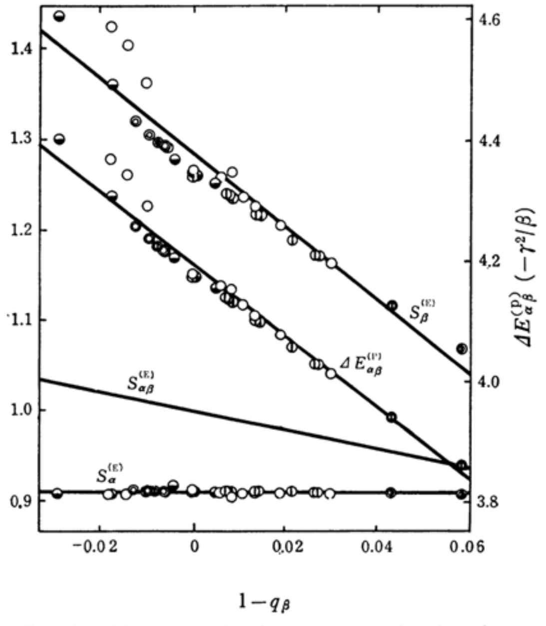

Fig. 3. Linear relationships between the β-carbon electron density and various π-delocalization quantities for substituted styrenes.

Calculations have been performed for various combinations of Coulomb and resonance integrals and the inductive parameters, δ. ○ and ⦶ correspond to para and meta substituents of the methylene-anion type with $\delta=0.3$; ◒ and ◓, to para and meta substituents of the same type with $\delta=0.1$; and ◎ and ⦶ indicate para and meta inductive-model substituents.

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[16] R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

[17] According to Ham and Ruedenberg,[18] the nondimensional bond quantities defined by Eq. 3 are intermediate in nature between "molecular-orbital" bond orders and bond populations. Further, it has been shown by Ham[19] that, in the case of even alternant hydrocarbons, the above bond quantities are mathematically identical with Pauling's "resonance-theory" bond orders.

[18] N. S. Ham and K. Ruedenberg, *J. Chem. Phys.*, **29**, 1215 (1958).

[19] N. S. Ham, ibid., **29**, 1229 (1958).

an increasing q_β value. These trends were not affected by the type (methylene-anion type or nonconjugative) or the position (meta or para) of the substituents investigated, nor did they depend on the integral parameters, which were arbitrarily chosen for the substituents (see Fig. 3). The net result is, then, that the calculated values of $\varDelta E_{\alpha\beta}^{(\mathrm{p})}$ and q_β are inherently in linear correlation with each other.

When we used the substituent parameters which had previously been adopted for the calculation of charge distributions in benzene derivatives,[15] the magnitudes of the imparted quantities, $S_\alpha^{(\mathrm{E})}$, $S_\beta^{(\mathrm{E})}$ and $S_{\alpha\beta}^{(\mathrm{E})}$, for substituted styrenes were found to be such as are listed in Table I. Comparisons of the $S_{\alpha\beta}^{(\mathrm{E})}$, i. e., q_β, with Hammett's σ-values revealed a satisfactory linear relationship between them, as is illustrated in Fig. 4.[21] Since the q_β in turn is in linear correlation with $\varDelta E_{\alpha\beta}^{(\mathrm{p})}$, as has been stated above, the $\varDelta E_{\alpha\beta}^{(\mathrm{p})}$ must also be linearly correlated with the σ-values (see Fig. 4). If the pπ-delocalization energy is a primary quantity governing the relative stabilities of the silver ion complexes, then the linearity found above between $\varDelta E_{\alpha\beta}^{(\mathrm{p})}$ and σ will suffice to explain our previous observations that the argentation equilibria of ring-substituted styrenes fit the Hammett $\rho\sigma$ relation.[12]

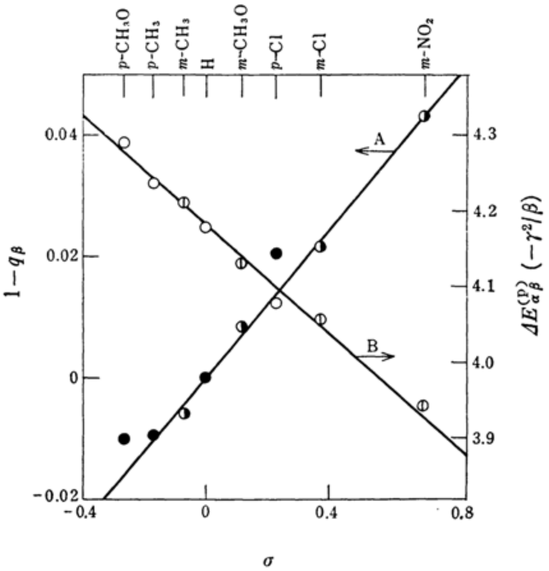

Fig. 4. Correlations of q_β and $\varDelta E_{\alpha\beta}^{(\mathrm{p})}$ of substituted styrenes with the Hammett σ.
A, plots of $1-q_\beta$ vs. σ: ●, para; ◑, meta
B, plots of $\varDelta E_{\alpha\beta}^{(\mathrm{p})}$ vs. σ: ○, para; ⦶, meta

In the case of substituted benzenes, we may write the following identities:

$$\begin{aligned}\varDelta E_{om}^{(\mathrm{p})} &= (S_o^{(\mathrm{E})} + S_m^{(\mathrm{E})} + 2S_{om}^{(\mathrm{E})})(-\gamma^2/\beta)\\ \varDelta E_{mp}^{(\mathrm{p})} &= (S_m^{(\mathrm{E})} + S_p^{(\mathrm{E})} + 2S_{mp}^{(\mathrm{E})})(-\gamma^2/\beta)\end{aligned} \tag{8}$$

where the subscripts o, m and p refer, respectively, to the ortho, meta and para ring positions with respect to the substituents. Again, from Eq. 4, we may write, to a good approximation, the equality:

$$S_{om}^{(\mathrm{E})} + S_{mp}^{(\mathrm{E})} = q_m \tag{9}$$

where q_m is the π-electron density on meta carbons.

The values of $S_o^{(\mathrm{E})}$, $S_m^{(\mathrm{E})}$ and $S_p^{(\mathrm{E})}$ were calculated for several monosubstituted benzenes. The results are included in Table II, where it may be seen that $S_o^{(\mathrm{E})}$ nearly equals $S_p^{(\mathrm{E})}$ with each compound. Aside from the p-CH$_3$O group, plots of $S_m^{(\mathrm{E})}$ and $S_p^{(\mathrm{E})}$ against the corresponding σ-values give a single straight line, as can be seen in Fig. 5.

Also plotted in Fig. 5 are the $\varDelta E_{rs}^{(\mathrm{p})}$ values; for the sake of convenience, the $\varDelta E_{om}^{(\mathrm{p})}$ values are plotted against σ_m, while the $\varDelta E_{mp}^{(\mathrm{p})}$ values are plotted against σ_p. The differences between $\varDelta E_{om}^{(\mathrm{p})}$ and $\varDelta E_{mp}^{(\mathrm{p})}$ for given substituents are, on the whole, smaller than the differences of either $\varDelta E_{om}^{(\mathrm{p})}$ or $\varDelta E_{mp}^{(\mathrm{p})}$ between different substituents. If we assume, as before, that ortho-meta and meta-para bonds contribute equally to the complexation, then an average of the two energies may

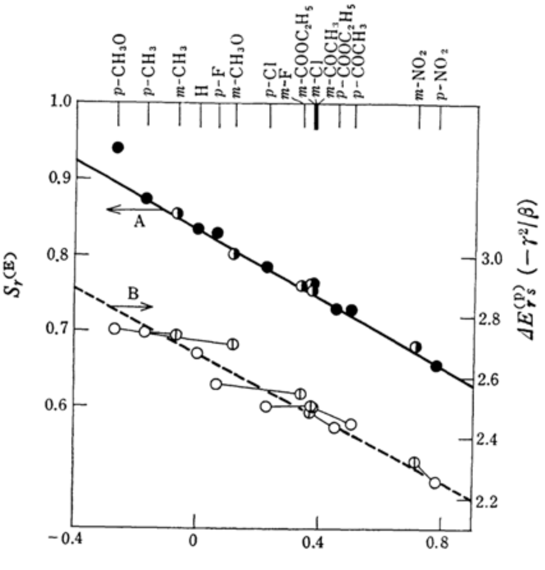

Fig. 5. Correlations of $S_r^{(\mathrm{E})}$ and $\varDelta E_{\mathrm{RS}}^{(\mathrm{p})}$ of substituted benzenes with the Hammett σ.
A, plots of $S_r^{(\mathrm{E})}$ vs. σ: ●, para; ◑, meta
B, plots of $\varDelta E_{rs}^{(\mathrm{p})}$ vs. σ: ○, $\varDelta E_{mp}^{(\mathrm{p})}$; ⦶, $\varDelta E_{om}^{(\mathrm{p})}$
For the sake of convenience, $\varDelta E_{om}^{(\mathrm{p})}$ are plotted against σ_m and $\varDelta E_{mp}^{(\mathrm{p})}$, against σ_p.

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[20] The condition is fulfilled if the substituents and reaction centers are spatially separated to the extent that the auxiliary inductive effect of substituents on the Coulomb integral of the carbon in question is negligibly small.

[21] Deviations in the p-chloro and p-methoxy points from Line A may suggest that the linearity between q_β and σ is only approximate and that it tends to be violated by the methylene-anion type para substituents.

perhaps be a convenient measure of the complexation ability. Thus, by combining Eqs. 8 and 9 with the approximation $S_o^{(E)} \simeq S_p^{(E)}$, we can write:

$$<E^{(p)}> \equiv (\Delta E^{(p)}_{om} + \Delta E^{(p)}_{mp}) \;/\; 2 \simeq (S_p^{(E)} + S_m^{(E)} + q_m)(-\gamma^2 \,/\, \beta) \qquad (10)$$

Equation 10 allows us to infer that, insofar as the pπ-delocalization energies in benzene complexes are concerned, the contribution of meta substituent effects might more or less outweigh that of para substituent effects. According to the results of numerical calculations, however, the variation in q_m with σ is less sensitive than that of $S_p^{(E)}$ and $S_m^{(E)}$, so that $\langle E^{(p)} \rangle$ is fairly well correlated with $(\sigma_m + \sigma_p)/2$. Such a relationship is marked with a broken line in Fig. 5. Thus, it may be more reasonable to correlate[22] log (K_1/n) with $(\sigma_m + \sigma_p)/2$ than to relate log K_1 directly to σ_m, as Andrews and Keefer did previously.[2b]

At this point it is worthwhile to compare the slopes of the $\Delta E^{(p)}$-σ lines for substituted styrenes and benzenes, i. e., Lines B of Figs. 4 and 5. The slope ratio is 1 : 1.46, which is qualitatively understandable because the effects of substituents should increase as the distance between the substituents and the reaction center decreases. Interestingly, this ratio is close to the corresponding ρ ratio, -0.766[12]: -1.36[22]$=1:1.78$, derived from the Hammett plots of the argentation equilibrium constants.

The Contribution of the Silver *d*-Electrons

So far, the relative stabilities of the silver ion complexes have been considered in terms of the delocalization energies of pπ-electrons alone. The complexation model underlying the treatments has been a simplification of the Dewar model[9] in that the participation of the silver d-electrons in the complex formation has been ignored. In the case of unsubstituted hydrocarbons, the contribution of these d-electrons to the complex stabilities will parallel that of the pπ-electrons hitherto considered, because, in the Hückel approximation, the bonding and antibonding π-orbitals of the isolated hydrocarbons are spaced in pairs and the distributions of the phantom electrons in the antibonding π-orbitals are the same as in the pairing bonding orbitals. In substituted compounds, however, this parity of orbitals breaks down, and the relative effects of substituents on the complex stability may be reversed, depending on which electrons, pπ or d, exert the more predominant contribution to the complex formation. According to the recent work of Hosoya and Nagakura,[6] the two contributions are almost equally important to the stabilization of the ground state of silver-monoolefin complexes.

If the energy level of the 5s-orbital of the silver ion is $h_s\beta$ relative to the 2pπ Coulomb integral of a benzene carbon, Eq. 1 should be modified to

$$\Delta E^{(p)}_{rs} = 2 \sum_j^{occ.} \frac{(c_{jr} + c_{js})^2}{h_s - m_j} \left(-\frac{\gamma^2}{\beta} \right) \qquad (11)$$

Likewise, we may express the delocalization energy, $\Delta E^{(d)}_{rs}$, of a pair of electrons originally belonging to the 4d$_{xz}$ atomic orbital of the silver ion as

$$\Delta E^{(d)}_{rs} = 2 \sum_j^{unocc.} \frac{(c_{jr} - c_{js})^2}{h_d - m_j} \left(-\frac{\gamma_d^2}{\beta} \right) \qquad (12)$$

where $h_d\beta$ is the energy level of the 4d$_{xz}$ orbital of the silver ion in the complex relative to the Coulomb integral of a benzene carbon; γ_d is the resonance integral for the bonds formed by the overlap of the silver 4d$_{xz}$ orbital and the 2p$_z$ orbitals of the *r*th and *s*th carbon atoms of the substrate molecules; and the summation extends over the unoccupied π-orbitals of the substrates. The energy, $\Delta E^{(d)}_{rs}$, may be referred to as the d-delocalization energy.

In order to evaluate these delocalization energies exactly, it is necessary to know the precise values of the energy level quantities, h_s and h_d, for the silver ion in the complexes. At the level of the present approximations, however, little can be predicted for these values. Yet, it is merely the relative effects of various substituents that we are primarily concerned with here. Thus we have decided to avoid the difficulty by proceeding, for the time being, by assuming somewhat arbitrary values for h_s and h_d.

To begin with, we calculated the d-delocalization energies for the various styrenes, assuming that $h_d=0$. The results are given in the third column of Table III. Comparisons of these $\Delta E^{(d)}_{\alpha\beta}$ values with the $\Delta E^{(p)}_{\alpha\beta}$ values previously obtained (Table I) show that there exists a linear correlation between them, as can be seen in Fig. 6. Since the slope of this linearity is negative, the relative effects of substituents in relation to the strengths of the σ- and π-type complexation bonds would tend to act in directions to cancel each other out. Thus a question remains whether the variation in the total complexation *energy* from one substituted styrene to another should parallel that of $\Delta E^{(p)}_{\alpha\beta}$, which has previously been used as a measure of the complex stability. This point will be discussed in the following section.

Next, we calculated the pπ- and d-delocalization energies for styrenes, varying the magnitudes of h_s and h_d. Table III lists the results obtained

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22) In fact, plots of log (K_1/n) against the average sigma result in as satisfactory a linear relation as the plots of log K_1 vs. σ_m, within the limits of the accuracy of experimental data. This new linearity gives a reaction constant of $\rho=-1.36$, while the Andrews and Keefer value is $\rho=-1.60$.

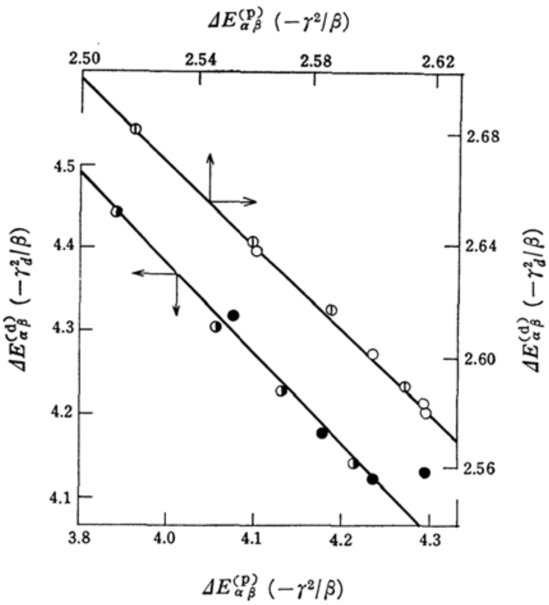

Fig. 6. Linear relationships between the pπ- and d-delocalization energies of silver ion - substituted styrene complexes.
●, para; ◑, meta, calculated with $h_s=0$ and $h_d=0$.
○, para; ⦶, meta, calculated with $h_s=-0.5$ and $h_d=0.5$.

from the choices of $h_s=-0.5$ and $h_d=0.5$ and 1. Comparisons of the $\Delta E^{(p)}_{\alpha\beta}$ values calculated for $h_s=-0.5$ with those previously obtained with $h_s=0$ (Table I) show that these two sets of data run linear. The same is found to be true among the three sets of $\Delta E^{(d)}_{\alpha\beta}$ values (Table III), except for some minor irregularities. This implies that we may expect a linearity of the type given in Fig. 6 without a loss of generality, as long as the d—s separation energy for the complexed silver ion is such that $-0.5<h_s<0<h_d<1$.

TABLE III. THE DELOCALIZATION ENERGIES FOR THE SILVER ION COMPLEXES OF SUBSTITUTED STYRENES:—EFFECTS OF ENERGY LEVELS OF THE ORBITALS OF SILVER ION

Substituent	$\Delta E^{(p)}_{\alpha\beta}$, $-\gamma^2/\beta$	$\Delta E^{(d)}_{\alpha\beta}$, $-\gamma_d^2/\beta$		
	$h_s=-0.5$	$h_d=0$	$h_d=0.5$	$h_d=1$
H	2.6004	4.1775	2.6004	1.9114
p-CH_3	2.6182	4.1224	2.5823	1.9017
m-CH_3	2.6112	4.1412	2.5884	1.9048
p-CH_3O	2.6186	4.1318	2.5794	1.8983
m-CH_3O	2.5861	4.2297	2.6163	1.9200
p-Cl	2.5604	4.3210	2.6347	1.9293
m-Cl	2.5595	4.3055	2.6409	1.9328
m-NO_2	2.5188	4.4440	2.6810	1.9534

Similar considerations hold for benzene derivatives. The results are found to be much the same as have been described for styrene derivatives.

Discussion and Conclusions

As has already been mentioned, the relative effects of substituents on the σ- and π-types of complexation energies act in opposite directions. If these effects are of comparable importance, as seems to be the case, it is conceivable that, in effect, the two contributions cancel each other out, so that the total complexation energies change but little within a given series of substituted compounds. This view is consistent with our previous observation that, for a few substituted styrenes, the differences in the enthalpy changes with respect to substituents, $\delta\Delta H$, are quite small despite the sensible differences in free energy change, $\delta\Delta F°$, the substituent effects thus being entropy-controlled in the ordinary temperature region.(12) A similar trend can be noticed in inspecting the argentation data for various α-olefins recently reported by Cvetanović et al.(25)

Nonetheless, it does appear that, at least in the cases of benzene and styrene, the effects of substituents on the stabilities of the silver ion complexes can be interpreted in terms of the pπ-delocalization energy, $\Delta E^{(p)}$, a contribution to the enthalpy change, ΔH. This apparent paradox may best be reconciled by invoking the conventionally accepted concept of the isokinetic relationship.(26) That is, the calculated $\Delta E^{(p)}$ somehow reflects the entropy contribution. In argentation equilibria of substituted compounds, the relationship is perhaps such that, the tighter a complexation bond, the greater is the accompanying entropy loss, $-\Delta S$, which in turn controls the substituent effects in prevalence over the contribution of ΔH.(12) Since $\Delta E^{(p)}$ is correlated with σ, whereas it antiparallels $\Delta E^{(d)}$, the entropy loss associated with $\Delta E^{(d)}$ should be a quantity which parallels σ. This would imply that the observed entropy loss is isokinetically associated more directly with $\Delta E^{(d)}$ than with $\Delta E^{(p)}$. It is, of course, hard to justify this implication theoretically. Offhand, however, this seems to be likely because of the directional properties of the silver d-orbitals in the complexes.

In conclusion, the pπ-delocalization energy, $\Delta E^{(p)}$, can successfully interpret the observed substituent effects on the argentation equilibria

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23) Considering the singlet d-s separation energy (5.7 eV.(24)) of the free silver ion, we may guess that the difference between h_s and h_d for a complexed silver ion will be of the order of unity.

24) C. E. Moore, "Atomic Energy Levels," Vol. III, National Bureau of Standards, Washington, D. C. (1958).

25) R. J. Cvetanović, F. J. Duncan, W. E. Falconer and R. S. Irwin, *J. Am. Chem. Soc.*, **87**, 1827 (1965).

26) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955); J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York (1963), Chapter 9.

of benzene and styrene despite some warnings raised against the Hückel calculations of π-complex stability.[27] However, the conclusion is only ostensibly correct, because the binding energy arising from the contribution of silver d-electrons, $\Delta E^{(d)}$, is of comparable importance, as is $\Delta E^{(p)}$, and because the two energies join together to suppress the enthalpy contribution to the relative substituent effects. The indications of such simple treatments may naturally be crude, but they seem to be significant so long as complexes merely of identical geometry are being compared. It seems, then, that only by assuming an isokinetic correlation between $\Delta E^{(d)}$ and ΔS can the observed substituent effects be cast into such a semiempirical theory of the free energy correlations as has been developed previously.[15]

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27) C. A. Coulson and M. J. S. Dewar, *Discussions Faraday Soc.,* **2**, 54 (1947).