ane,[14] and dimethylbutane.[14] It seems unlikely that these values of K are significant. Other values in that table are probably large enough to be significant, although one should examine the original references to find the donor concentrations used in obtaining K for the weaker complexes. It is worth noting parenthetically that such detailed experimental information is not always easy to find in the literature.

Contact Charge-Transfer Pairs

From our discussion above, it is obvious that the concept of contact charge-transfer pairs[15] is connected with our analysis. Indeed, the experimental characteristic of contact charge-transfer pairs is an absorption band whose intensity is linearly dependent upon the initial concentration of the donor, to give a Scott plot with zero slope, as in the treatment above, or a Benesi–Hildebrand plot with zero intercept. From our analysis above, we see that such a plot can occur even for relatively strong complexes if the donor concentration is too low owing to poor choice of experimental conditions or limited solubility. It seems quite likely that the anthracene–iodine complex, for example, exists as a definite 1:1 complex, rather than as a weaker contact interaction, even though the experimental behavior of solutions at practical concentrations is identical with that for contact charge transfer.

The key question in attempts to distinguish between true complexes and contacts appears to be the question of whether the charge-transfer stabilization energy (which is greater than the ordinary van der Waals attraction energy) is greater than the translational kinetic energy of kT (or RT per mole). If it is, then we should consider the interaction to be best described as a "complex," stabilized by charge-transfer forces. If the energy of formation is less than kT, then the interaction is best described as a "contact," which may exhibit a charge-transfer absorption band. If the energy of formation is small, we should inquire as to whether it is due to an electrostatic energy greater between D and A than between D–D and A–A, or whether it is really due to the charge-transfer interaction. These questions are difficult, if not impossible, to answer.

Conclusion

The major conclusion which can be stated is that experimental error is important, and its effect on K and ϵ should be analyzed. This may seem obvious, but when one considers the amount of discussion in the literature of electron donor–acceptor complexes based upon erroneous data, or the discussion of discrepancies, such as "different" values of K in different solvents, which may agree well within the experimental error, then it does seem worthwhile emphasizing this conclusion. Perhaps further criteria for testing the reliability of the experimental data for these complexes may be stated which would permit critical use of the extensive data in the literature.

It should be noted that there are probably few data on donor–acceptor complexes in the literature which can survive the rigorous test on ΔK ($\Delta K > 3$ standard deviations). Failure does not necessarily mean that the complexes do not really exist or that their equilibrium constants are drastically different from the reported values. It just means that skepticism is warranted.

Finally, we note the danger in tabulating data from different complexes for comparison purposes when such tabulation separates K and ϵ. Because the use of eq. 1 gives $1/K\epsilon$ as the intercept, the experiment may well determine the product of $K\epsilon$ accurately, but the separation into K and ϵ individually may be seriously in error.

(14) S. H. Hastings, J. L. Franklin, J. C. Schiller, and F. A. Matsen, *J. Am. Chem. Soc.*, 75, 2900 (1953).
(15) L. E. Orgel and R. S. Mulliken, *ibid.*, 79, 4839 (1957).

Argentation Equilibria of Substituted Styrenes

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The equilibrium constants for the formation of silver ion complexes of various styrene derivatives in water have been determined at 25°. It is found that the equilibrium leading to the formation of 1:1 silver ion complexes of para- and meta-substituted styrenes obeys the Hammett relation with the reaction constant $\rho = -0.766$. The temperature dependence of the equilibrium has also been examined for styrene and its p-methyl and p-chloro derivatives. Analysis of the thermodynamic data obtained indicates that, in the ordinary temperature region, the substituent effects are entropy controlled. A possible aspect of the origin of the Hammett relation observed is presented.

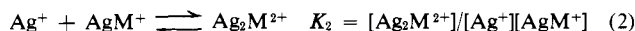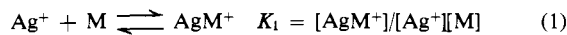## Introduction

It has been well demonstrated that transition meta cations such as Ag^+, Cu^+, and Hg^{2+} form coordination complexes with unsaturated compounds.[1,2] In par-

(1) R. N. Keller, *Chem. Rev.*, 28, 229 (1941).

ticular, complexation of silver ion with both aliphatic[3] and aromatic compounds[4] has been studied fairly widely. Yet, the structure of the complexes is still a controversial question.[2-7]

According to Andrews and Keefer,[4] the equilibrium reactions of unsaturated compounds with silver ion in the aqueous phase may be explained quantitatively in terms of the equilibria

$$Ag^+ + M \rightleftharpoons AgM^+ \quad K_1 = [AgM^+]/[Ag^+][M] \quad (1)$$

$$Ag^+ + AgM^+ \rightleftharpoons Ag_2M^{2+} \quad K_2 = [Ag_2M^{2+}]/[Ag^+][AgM^+] \quad (2)$$

The equilibrium constants K_1 and K_2 may be taken as the measure of relative stability of the water-soluble complexes AgM^+ and Ag_2M^{2+}, respectively.

It is expected that examination of the effect of substituents on the stability of silver ion complexes may shed some light on the physical basis underlying the complexation. The earlier work of Andrews and Keefer[4b] on substituted benzenes was certainly along this line but seemed to be somewhat limited in scope. In the present study, we have chosen several styrene derivatives as substrate and measured their argentation equilibrium constants at various temperatures. One major advantage of our choice of substrate lies in the possibility that, in the first equilibrium, silver ion is imbedded mostly in one particular site of substrates, i.e., the extracyclic carbon–carbon double bond of styrenes. The situation permits comparison of the effects of para and meta substituents, thus facilitating the analysis of the substituent effects on the complex stability.

Experimental

Materials. Silver nitrate and potassium nitrate were of the best grade commercially available. Cyclohexane was purified by passing through a 40-cm. column (2.5 cm. in diameter) packed with activated aluminum oxide. Styrene and β-bromostyrene were washed successively with aqueous sodium thiosulfate, dilute sodium hydroxide, and water and, after drying, were subjected to fractional distillation under reduced pressure. p-Methoxy-, m-methoxy-, and m-nitrostyrenes were prepared by decarboxylation[8,9] of p-methoxy-, m-methoxy-, and m-nitrocinnamic acids, respectively. Other substituted styrenes used in this work were obtained by dehydration[8,10] of the corresponding secondary alcohols. All samples were stocked at the Dry Ice–methanol temperature and distilled under reduced pressure immediately before use. Boiling point data of the various styrene derivatives are given in Table I.

Procedure. In conformity with the treatment of Andrews and Keefer,[4] the argentation equilibrium constants K_1 and K_2 are related to an additional constant K measured for the aqueous phase.

(2) J. Chatt, "Cationic Polymerization and Related Complexes," P. H. Plesch, Ed., W. Heffer and Sons, Ltd., Cambridge, England, 1953, pp. 40–56.
(3) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938).
(4) (a) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); (b) *ibid.*, **72**, 3113 (1950); (c) *ibid.*, **72**, 5034 (1950).
(5) M. J. S. Dewar, *Bull. soc. chim. France*, **18**, C79 (1951).
(6) K. S. Pitzer, *J. Am. Chem. Soc.*, **67**, 1126 (1945).
(7) K. Fukui, A. Imamura, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Japan*, **34**, 1076 (1961).
(8) W. S. Emerson, *Chem. Rev.*, **45**, 347 (1949).
(9) *Cf.* R. H. Wiley and N. R. Smith, *Org. Syn.*, **33**, 62 (1954).
(10) *Cf.* C. G. Overberger and J. H. Saunders, *ibid.*, **28**, 31 (1949).

$$K = ([St]_t - [St])/[St][Ag^+] = K_1 + K_1K_2[Ag^+] \quad (3)$$

Here, $[St]_t$ and $[St]$ are the molar concentrations of all styrene-containing species and free styrene, respectively, and $[Ag^+]$ is the molar concentration of uncomplexed silver ion. At varying silver ion concentration, the values of K were measured either by the solubility method[4] or by the distribution method.[3]

Table I. Boiling Points of Substituted Styrenes and Extinction Coefficients of Their Cyclohexane Solutions

Substituent	λ, mμ	$\epsilon \times 10^{-3}$	B.p., °C. (mm.)
H	282	0.781	54.0–54.2 (31)
p-CH$_3$O	293	3.02	54.5–55.0 (2)
m-CH$_3$O	296	2.22	84.5–85.0 (13)
o-CH$_3$O	312	2.28	79.5–80.5 (11)
p-CH$_3$	285	1.18	62.0–62.3 (16)
m-CH$_3$	296	0.588	39.5–40.0 (3)
p-Cl	288	1.19	56.0 (8)
m-Cl	299	0.488	53.0 (3)
m-NO$_2$	289	0.847	90.0–90.2 (4)
β-CH$_3$	273	1.28	176 (760)
β-Br	285	2.52	107.7–108.3 (19)

In the solubility experiments, *ca.* 1-g. samples of substituted styrene were added to aqueous silver nitrate-potassium nitrate solutions of varying silver ion concentration and a fixed total ionic strength of unity. The glass-stoppered flasks charged with the heterogeneous mixtures were immersed in a thermostat maintained at a specified temperature, and the mixtures were magnetically stirred vigorously for 20 hr. to saturate the aqueous phase with styrene.

In the distribution method, 5-ml. portions of cyclohexane containing a specified amount of styrene were added to 50 ml. of aqueous silver nitrate–potassium nitrate solutions. The styrenes were allowed to distribute between the aqueous and organic layers by stirring the mixtures in the same way as in the solubility method.

The total styrene concentrations $[St]_t$ of the aqueous phase treated as above were determined by the ultraviolet spectrophotometry. Ten milliliters of the aqueous phase of each sample was pipetted out and extracted with 10 ml. of cyclohexane by shaking for 10 hr. in a glass-stoppered flask. The optical density of the cyclohexane phase was measured against a cyclohexane blank on a Shimadzu spectrophotometer (Type QR-50) at a wave length λ selected for each substituted styrene. It was checked that one extraction was sufficient to remove all of the styrene, both free and complexed, from the aqueous phase. The total styrene concentrations were calculated from the optical densities measured and the values of molecular extinction coefficient ϵ which had been determined on cyclohexane solutions in advance. The spectrophotometric constants used for the various styrenes are listed in Table I.

The concentrations of free styrene $[St]$ in the aqueous phase were obtained in the following manner. In the solubility measurements, $[St]$ was considered to be equal to $[St]_t$ measured in the absence of silver ion. In the distribution experiments, $[St]$ was calculated for each run from the relation, $[St] = k_d(C_0 - 10 [St]_t)$, where C_0 is the initial concentration of styrene in cyclo-

Table II. Solubility of Methylstyrenes in Aqueous $AgNO_3$–KNO_3 Solutions[a] at 25°

[Ag⁺]ₜ, mole/l.	—p-Methylstyrene— [St]ₜ × 10³, moles/l.	K, l./mole	[Ag⁺]ₜ, mole/l.	—m-Methylstyrene— [St]ₜ × 10³, moles/l.	K, l./mole	[Ag⁺]ₜ, mole/l.	—β-Methylstyrene— [St]ₜ × 10³, moles/l.	K, l./mole
0.000	0.444	...	0.000	0.500	...	0.000	1.17	...
0.040	0.898	25.8	0.080	1.41	22.9	0.200	2.19	4.38
0.080	1.40	27.3	0.120	1.90	23.5	0.400	3.30	4.57
0.120	1.93	28.3	0.160	2.42	24.2	0.600	4.64	4.97
0.160	2.60	30.7	0.200	2.94	24.7	0.800	6.38	5.60
0.200	3.23	31.8				1.000	8.07	5.94

[a] Ionic strength $\mu = 1$.

hexane and k_d is the distribution constant of styrene between 1 N aqueous KNO_3 and cyclohexane.

Results

Substituent Effects. In evaluating the magnitudes of K, it may be assumed that $[Ag_2St^{2+}]$ is sufficiently small as compared with $[Ag^+]$ so that $[Ag^+]$ can be approximated as

$$[Ag^+] = [Ag^+]_t - [St]_t + [St] \qquad (4)$$

Here, $[Ag^+]_t$ denotes the molar concentration of all silver ions, both free and complexed. The values of K were calculated from eq. 3 and 4 for various substituted styrenes at 25°. Table II lists the results obtained for *p*-, *m*-, and *β*-methyl derivatives by the method of solubility measurements. Other derivatives were studied by the distribution method. The results are collected together with some supplementary data in Table III, where styrene is also included for the sake of comparison between the two methods (see below).

If the approximation 4 is feasible and if additional reactions do not contribute appreciably to the complex formation, then for a given substrate, plots of K against $[Ag^+]$ should give a straight line with the ordinate intercept K_1 and the slope K_1K_2. Such linear relations were substantiated with reasonable accuracy with all the styrene derivatives investigated.

Listed in Table IV are the values of K_1 and K_2 obtained for the various styrenes. It is noticed that the values of K_2 are sensibly smaller than the K_1 values except for the case of *β*-bromostyrene. Also, the solubility and distribution methods seem to yield essentially the same results; our K_1 value of 19.1 obtained for styrene by the latter method is in reasonable agreement with the value 18.2 obtained by Andrews and Keefer[4c] from the solubility study of the same compound.

In Figure 1 the logarithms of the K_1 values obtained for *meta*- and *para*-substituted styrenes are plotted against Hammett's σ-values. It does seem that these equilibrium constants fit the Hammett equation with the reaction constant $\rho = -0.766$, the correlation coefficient being -0.976. The negative ρ-value obtained indicates that the process leading to the formation of silver ion complexes is an electrophilic reaction.

Temperature Dependence. For styrene and *p*-methyl- and *p*-chlorostyrenes, the measurements of equilibrium constants were conducted also at 0 and 40°. The results are listed in Table V. The constants K_1 and K_2 both tended to be larger at lower temperatures, and so did the distribution constant k_d. The temperature de-

pendence of these constants was small; they varied less than a factor of two in the 0–40° range.

Table III. Distribution of Substituted Styrenes between Cyclohexane and Aqueous $AgNO_3$–KNO_3 Solutions[a] at 25°

[Ag⁺]ₜ, mole/l.	—Styrene— [St]ₜ × 10⁴, moles/l.	K, l./mole	[Ag⁺]ₜ, mole/l.	—p-Chlorostyrene— [St]ₜ × 10⁴, moles/l.	K, l./mole
$C_0{}^b$ = 1.832	$k_d{}^c$ = 3.06 × 10⁻⁴		C_0 = 0.983	k_d = 0.798 × 10⁻⁴	
0.000	5.59	...	0.000	0.785	...
0.040	10.04	20.2	0.040	1.14	11.3
0.080	14.9	21.3	0.120	1.91	11.9
0.160	25.8	23.1	0.160	2.40	12.8
0.200	32.5	24.8	0.200	2.88	13.4
—p-Methoxystyrene—			**—m-Chlorostyrene—**		
C_0 = 0.344	k_d = 5.28 × 10⁻⁴		C_0 = 0.550	k_d = 1.19 × 10⁻⁴	
0.000	1.76	...	0.000	0.656	...
0.080	5.35	26.1	0.100	1.18	7.96
0.120	7.27	26.9	0.300	2.40	8.85
0.160	9.38	28.1	0.400	3.13	9.24
0.200	11.49	28.8	0.500	3.79	9.56
—m-Methoxystyrene—			**—m-Nitrostyrene—**		
C_0 = 0.262	k_d = 6.60 × 10⁻⁴		C_0 = 1.568	k_d = 6.99 × 10⁻⁴	
0.000	1.73	...	0.000	10.9	...
0.100	4.18	14.2	0.200	22.8	5.60
0.200	7.04	15.5	0.400	35.7	5.88
0.300	10.03	16.1	0.600	48.1	5.93
0.400	12.9	16.3	0.800	61.9	6.14
0.500	16.6	19.4	1.000	76.0	6.34
—o-Methoxystyrene—			**—β-Bromostyrene—**		
C_0 = 0.268	k_d = 4.73 × 10⁻⁴		C_0 = 0.238	k_d = 1.23 × 10⁻⁴	
0.000	1.27	...	0.000	0.293	...
0.040	2.48	24.0	0.200	0.365	1.22
0.080	3.83	25.4	0.400	0.480	1.59
0.120	5.22	26.3	0.800	0.759	1.99
0.160	6.73	27.3	1.000	0.987	2.37
0.200	8.27	28.1			

[a] Ionic strength $\mu = 1$. [b] Initial concentration of styrene in cyclohexane solution in moles/l. [c] Distribution constant of styrene between 1 N aqueous KNO_3 and cyclohexane.

In Figure 2 the values of K_1 obtained for the above three styrenes are plotted against the reciprocal of temperature. It seems that a linear relationship of the Arrhenius type holds for each styrene in the temperature range studied.

The linear relations observed in Figure 2 were utilized to estimate thermodynamic data for argentation equilibria in water at 25°. The results are given in Table VI.

Table IV. Equilibrium Constants for Argentation of Various Substituted Styrenes at 25°

Substituent	σ^a	$K_1{}^b$ l./mole	$K_2{}^b$ l./mole
H	0	19.1	1.5
		18.2[d]	0.81[d]
p-CH₃	−0.170	24.2[c]	1.6[c]
m-CH₃	−0.069	21.7[c]	0.68[c]
p-CH₃O	−0.268	24.2	0.54
m-CH₃O	+0.115	12.9	1.2
o-CH₃O	...	23.2	1.1
p-Cl	+0.227	10.6	1.3
m-Cl	+0.373	7.58	0.55
m-NO₂	+0.710	5.45	0.16
β-CH₃	...	3.86[c]	0.54[c]
β-Br	...	0.98	1.4

[a] Hammett's σ-constant: L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapter 7. [b] Distribution method, unless otherwise noted. [c] Solubility method. [d] Solubility method: Andrews and Keefer.[4a]

It can be seen in Table VI that the enthalpy change, $\Delta H°$, for the argentation reaction varies from compound to compound to a lesser extent than does the
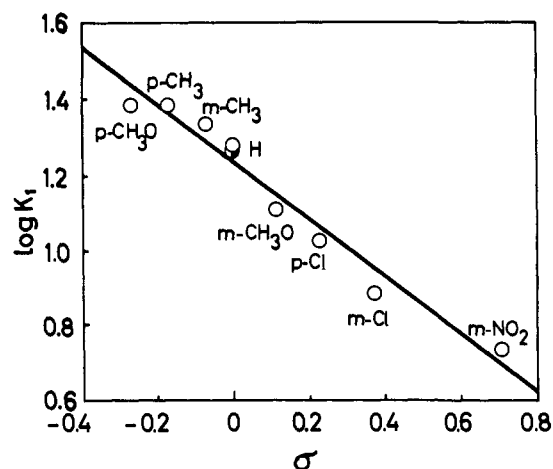
Figure 1. The Hammett plots of K_1 of substituted styrenes: ◑, ref. 4c.

to complexation than aromatic hydrocarbons. For instance, hexene-1 and pentene-2 have their respective K_1 values[3] of 860 and 62.7 l./mole, whereas benzene and

Table V. Argentation of Some Styrene Derivatives at 0 and 40°

[Ag⁺]ₜ; mole/l.	0° [St]ₜ × 10³, moles/l.	0° K, l./mole	40° [St]ₜ × 10³, moles/l.	40° K, l./mole
		Styrene (Solubility Method)		
0.000	2.26	...	1.40	...
0.040	4.55	26.2	2.22	15.1
0.080	6.94	27.5	3.17	16.3
0.120	10.2	31.3	4.11	16.6
0.160	13.1	32.0	5.37	18.3
0.200	16.7	34.4	6.55	19.0
	$K_1 = 23.9$	$K_2 = 2.4$	$K_1 = 14.1$	$K_2 = 1.8$
		p-Methylstyrene (Solubility Method)		
0.000	0.571	...	0.399	...
0.800	2.30	38.6	...	...
0.120	3.35	41.5	1.56	24.4
0.160	4.50	44.1	2.06	26.3
0.200	5.92	48.1	2.53	27.0
	$K_1 = 32.2$	$K_2 = 2.5$	$K_1 = 20.7$	$K_2 = 1.6$
		p-Chlorostyrene (Distribution Method)		
	$C_0{}^a = 0.877$	$k_d{}^b = 1.25 \times 10^{-4}$	$C_0{}^a = 1.267$	$k_d{}^b = 0.758 \times 10^{-4}$
0.000	0.109	...	0.0961	...
0.100	0.280	15.7	0.188	9.61
0.200	0.481	17.1	0.286	9.93
0.300	0.684	17.6	...	...
0.400	0.891	18.0	0.517	11.0
0.500	1.15	19.2	0.645	11.5
	$K_1 = 15.2$	$K_2 = 0.52$	$K_1 = 9.07$	$K_2 = 0.53$

[a] Initial concentration of p-chlorostyrene in cyclohexane solution in moles/l. [b] Distribution constant.

entropy term, $-T\Delta S°$. Further, although both the enthalpy and entropy effects observed are small, it seems that the variation of $\Delta H°$ is in the opposite direction both to that of the standard free energy change, $\Delta F°$, and to that of the entropy term. Hence, it may be concluded that, at least for H, p-CH₃, and p-Cl groups, the experimentally observed substituent effects are entropy controlled.[11]

Discussion

Insofar as the K_1 value for argentation is concerned, it is known that monoolefins are far more amenable

naphthalene have been reported to have the values[4a] 2.41 and 3.08 l./mole, respectively. This marked difference in complexation ability between different classes of unsaturated hydrocarbons may be related, to a first approximation, to the difference in double-bond character of the unsaturated carbon–carbon bonds involved. Undoubtedly, the π-bond orders (∿1) of the isolated olefinic bonds are greater than those (0.4 to 0.8[12]) of the unsaturated carbon–carbon bonds in aromatic rings. The mobile bond order (0.911[12]) of the external double bond of styrene is intermediate between the bond orders of the olefinic and aromatic bonds men-

(11) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 48.

(12) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 6.
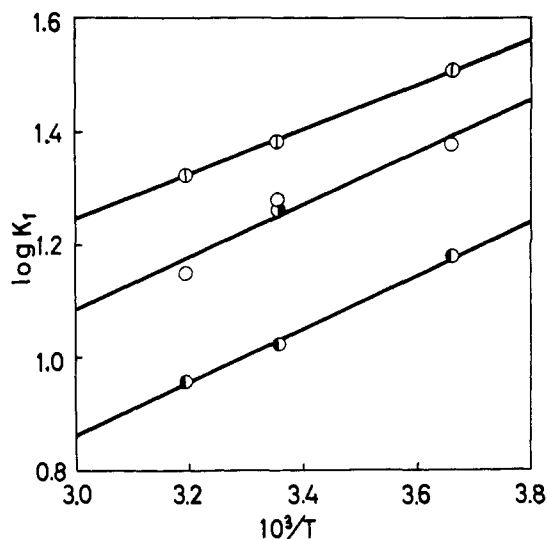
Figure 2. Temperature dependence of K_1 values: O, styrene; ◑' styrene (ref. 4c); ◔, p-methylstyrene; ◉, p-chlorostyrene.

tioned above, which is compatible with the fact that the K_1 value of styrene is of intermediate magnitude between the values of monoolefins and aromatic hydro-

Table VI. Thermodynamic Data for Argentation[a] of Some Styrene Derivatives in Water

	$\Delta F°,$[b] kcal./ mole	$\Delta H°,$ kcal./ mole	$\Delta S°,$[b] cal./mole deg.
p-Methylstyrene	-1.8_9	-1.8_8	0.0_3
Styrene	-1.7_1	-2.1_1	-1.3_5
p-Chlorostyrene	-1.4_1	-2.1_9	-2.6_2

[a] Formation of the 1:1 silver ion complexes at 25°. [b] The standard state has been taken to be the state of unit concentration, i.e., 1 mole/l.

carbons. On the basis of these considerations it appears very likely that in the styrene molecule, and probably in most of styrene derivatives also, the vinyl group is the primary center for coordination of silver ion.

Within a series of substituted styrenes studied here, however, more influential factors seem to prevail over the contribution of the bond order. That is, there is a trend that styrenes bearing electron-releasing substituents on the ring are capable of forming more stable argentation complexes. Indeed, the K_1 values for para- and meta-substituted styrenes are found to fit the Hammett equation with the reaction constant $\rho = -0.766$, as is shown in Figure 1. Perhaps, this is an indication that, in the argentation reaction of substituted styrenes, the π-electron density on vinyl carbons is the most influential factor contributing to the determination of the relative magnitudes of the entropy change, which in turn controls the magnitude of log K_1. If so, the conjugative and inductive effects will both influence the complexation. A theoretical demonstration[13] that the Hammett σ-constants are closely related with the calculated π-electron densities on the reaction centers may lend support to the above interpretation of the experimentally observed substituent effects. However, the reasons why the distribution of

(13) T. Fueno, T. Okuyama, and J. Furukawa, unpublished work.

π-electrons influences the entropy change rather than the enthalpy change and why the larger π-electron density at the vinyl group lowers the entropy loss for complexation at that site are still open to question.

A similar plot of the Hammett type has been reported for a variety of substituted benzenes by Andrews and Keefer.[4b] It seems reasonable that our ρ-value (-0.766) found for styrene derivatives is less in magnitude than their value (-1.60) obtained for substituted benzenes.[14] However, quantitative comparison between the two values is of little significance at this stage, since, in a strict sense, the nature of the reaction centers may not necessarily be identical for the two series of substituted hydrocarbons.[16]

Another important factor affecting the complexation is steric hindrance of substituents neighboring the reaction center. Markedly small K_1 values for β-substituted styrenes (3.86 and 0.98 l./mole for β-methylstyrene and β-bromostyrene, respectively) seem to support this view.

At this point it is of some interest to compare the substituent effects on the argentation equilibrium with those on the polymerization reaction of styrene. It was shown that the Hammett relation roughly holds in the cationic copolymerizations of substituted styrenes with styrene, giving the ρ-constant of -1.7.[18] In the anionic copolymerizations of some para-substituted styrenes studied with living polystyrene, the substituent effect was characterized by a relatively large reaction constant $\rho = +5.0$.[19] The change in sign of the ρ-values for the two ionic reactions is quite understandable. However, copolymerizations between the same series of compounds, including a few meta derivatives, led to the negative value of $\rho = -0.95$,[20] when polymerization catalysts of the Ziegler–Natta type were used. For this last class of copolymerizations, which intrinsically follow an anionic mechanism, it has been suggested[20] that the coordination between monomer and the electron-deficient part (e.g., counter cation) of the reaction site controls the relative amenability of monomers toward chain propagation. The Hammett relation ($\rho = -0.766$) obtained in the present study on the complexation of silver cation with substituted styrenes may be considered to lend an additional support to the possibility of the coordination being influential in polymerizations of the Ziegler–Natta type.

(14) It seems reasonable to assume that, for a given reaction of different families of conjugated compounds, the effects of substituents diminish as the distance between the substituents and the reaction center increases.[15]

(15) H. H. Jaffe, J. Chem. Phys., 21, 415 (1953).

(16) In styrene derivatives the vinyl bond seems to be the predominant reaction center for complexation, whereas in the case of monosubstituted benzenes it remains unsettled whether the silver ion is coordinated on particular aromatic bonds[17] or on the entire ring.[4b] In correlating log K_1 of monosubstituted benzenes with Hammett's σ-value, Andrews and Keefer[4b] have deliberately chosen σ-meta values, by assuming that the argentation equilibrium constants for these compounds are controlled largely by inductive effects of ring substituents. However, the observed substituent effects appeared to be correlated with σ-para values nearly as well. As a result of these uncertainties about the reaction center and the choice of σ-values for benzene derivatives, it seems meaningless to compare the two ρ-values quantitatively.

(17) R. E. Rundle and J. H. Goring, J. Am. Chem. Soc., 72, 5337 (1950); H. G. Smith and R. E. Rundle, ibid., 80, 5075 (1958).

(18) C. G. Overberger, L. H. Arond, D. Tanner, J. J. Taylor, and T. Alfrey, ibid., 74, 4848 (1952).

(19) M. Shima, D. N. Bhattacharyya, and M. Szwarc, ibid., 85, 1306 (1963).

(20) G. Natta, F. Danusso, and D. Sianesi, Makromol. Chem., 30, 238 (1959).