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# Argentation Constants of Styrene Derivatives[*1]

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Equilibrium constants for the formation of silver ion complexes (argentation constants) of styrene derivatives in water were measured at 0 and 25°C by Andrews and Keefer's solubility method. The argentation constants for the 1 : 1 complex ($K_1$) decreased in this order: *cis-β*-alkylstyrene>α-alkylstyrene>*trans-β*-alkylstyrene, for a given alkyl group. This order was related to differences in the resonance stabilization of the double bond. The $K_1$ values of the α- and β-alkylstyrene series did not seem to correlate with Taft's steric substituent constant, $E_s$, within the respective series. However, when the hyperconjugation effect of alkyl substituents was considered, a good linearity between $\log K_1$ and Hancock's parameter, $E_s^c$, was obtained. Thus, the steric effect was separated from the hyperconjugation effect, and it was found that the steric effects for the three series are nearly identical. Thermodynamic data indicated that an isokinetic relationship holds between $\Delta H$ and $\Delta S$ and that the argentation equilibrium is controlled mainly by the entropy factor. The degree of methyl substitution at the double bond of styrene slightly influenced the $K_1$ values, although 1,2-dihydronaphthalene had an abnormally large $K_1$ value.

The argentation (silver ion complexation) equilibria of unsaturated compounds have been investigated by several groups of workers.[1–6] The stabilities of the complexes of the silver ion with unsaturated compounds may be interpreted as the sum of the independent contributions of polar, resonance, and steric effects of substituents. The polar effects were discussed in terms of the Hammett $\rho$–$\sigma$ relation for benzene derivatives by Andrews and Keefer[1] and for ring-substituted styrenes and other olefins by Fueno and his co-workers.[2–4] For the resonance effect, it has already been established that the argentation equilibria are affected by the conjugation of substituents with the reaction center.[5] Although the literature contains references to the steric effect of substituents on the argentation equilibria, the investigations have not been extended beyond qualitative discussions. Both Winstein and Lucas[5] and Fueno *et al.*[2] suggested that the reason for the reluctance of β-methylstyrene to argentate is the steric effect of the substituent. Muhs and Weiss[6] measured the argentation constants of many unsaturated compounds by the gas chromatographic method and discussed the steric effects of substituents qualitatively.

The present investigation was undertaken to obtain information concerning the steric effects in the argentation of styrene derivatives. In separate reports,[7,8] we have previously reported on our observations of the steric effects in the radical copolymerizations of α- and β-alkylstyrenes with acrylonitrile. From the difference in the steric effects of α- and β-alkylstyrenes in the radical copolymerizations, it was deduced that the transition state of the radical polymerization is not of the π-complex type but of the σ-complex type. Since it is known that the silver ion forms a π-complex with an unsaturated compound, the steric effect in the argentation of styrene derivatives may also give information concerning the transition state of the radical polymerizaion.

In the present investigation, the argentation constants of α- and β-alkylstyrenes in water were measured by Andrews and Keefer's solubility method.[1] Also, the argentation constants of *cis*- and *trans*-α,β-dimethylstyrenes, β,β-dimethylstyrene, 1,2-dihydronaphthalene, and indene were determined and compared with the values of the above styrenes.

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[1] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **72**, 3113 (1950).

[2] T. Fueno, T. Okuyama, T. Deguchi and J. Furukawa, *ibid.*, **87**, 170 (1965).

[3] T. Fueno, O. Kajimoto and J. Furukawa, This Bulletin, **41**, 782 (1968).

[4] T. Fueno, O. Kajimoto, T. Okuyama and J. Furukawa, *ibid.*, **41**, 785 (1968).

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

[6] M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4697 (1962).

[7] S. Hirose, S. Nozakura and S. Murahashi, to be published.

[8] K. Yasufuku, S. Nozakura and S. Murahashi, This Bulletin, **40**, 2146 (1967).

## Experimental

**Materials.** The styrene and α-methylstyrene were obtained commercially. The other α-alkylstyrenes were synthesized by the Wittig reaction of alkyl phenyl ketones, much as in a previous paper.[8] By the Wittig reaction of the corresponding aldehydes, β-alkylstyrenes were prepared.[7] The *cis*- and *trans*-isomers of these styrenes were fractionated by distillation under reduced pressure, using a stainless-steel helipack column of about 30 theoretical plates. Also, the *cis*-and *trans*-α,β-dimethylstyrenes, and β,β-dimethylstyrene were obtained by the Wittig reaction. The 1,2-dihydronaphthalene was synthesized according to the literature.[9] The indene was obtained commercially. These olefines were purified by rectifications under reduced pressure and, immediately before use, were treated with lithium aluminum hydride overnight and redistilled under a high vacuum. The silver nitrate and potassium nitrate were of an analytical grade and used without further purification. The solvent for extraction, *n*-hexane, was purified in the usual way.

**Measurements of the Solubility.** All the experiments were carried out in the dark.

Samples of styrene derivatives (0.1—1.0 g) were added to 20 m*l* of aqueous silver nitrate solutions of varying silver ion concentrations, all the solutions containing enough potassium nitrate to maintain an ionic strength of unity. The mixtures were shaken vigorously in 50 m*l* glass-stoppered Erlenmeyer flasks for 3 hr in a constant-temperature bath at 0.00±0.05°C and 25.00±0.05°C in order to saturate the aqueous phase with styrenes. It was confirmed that one hour of shaking was sufficient for the argentation equilibrium to be reached.

After the two phases had been fully separated by being kept standing (5 hr), measured volumes of the saturated aqueous phase were pipetted out and extracted with 5—10 m*l* portions of hexane by shaking in glass-stoppered flasks for one hour. The optical density of the hexane phase was measured against a hexane blank on a Hitachi Spectrophotometer (EPS-3T) at a wavelength appropriate for each styrene, the molecular extinction coefficients having been previously determined. The spectra were scanned from 210 mμ through 360 mμ to check the impurity in the solutions. It was also checked whether one extraction for one hour is sufficient for the removal of all of the styrenes, both free and complexed, from the aqueous phase. The volume of the hexane phase was adjusted to obtain the optical density readings between 0.200 and 0.800.

The total styrene concentrations of the saturated aqueous solutions were calculated from the optical density of the hexane solutions. The wavelengths (λ) and the corresponding values of the molecular extinction coefficients (ε) are given in Table 1.

TABLE 1. EXTINCTION COEFFICIENTS OF STYRENE DERIVATIVES IN HEXANE SOLUTION*

| R | α-R–St | | *cis*-β-R–St | | *trans*-β-R–St | |
|---|---|---|---|---|---|---|
| | λ mμ | ε | λ mμ | ε | λ mμ | ε |
| H | 287 | $3.10\times10^2$ | | | | |
| Me | 285 | $1.40\times10^2$ | 290 | $1.15\times10^2$ | 293 | $6.30\times10^2$ |
| Et | 239 | $9.52\times10^3$ | 242 | $1.29\times10^4$ | 284 | $1.10\times10^3$ |
| *n*-Pr | 239 | $9.71\times10^3$ | 242 | $1.35\times10^4$ | 251 | $1.70\times10^4$ |
| *n*-Bu | 239 | $9.91\times10^3$ | 241 | $1.20\times10^4$ | 251 | $1.70\times10^4$ |
| *i*-Pr | 234 | $8.36\times10^3$ | 242 | $1.24\times10^4$ | 251 | $1.62\times10^4$ |
| *s*-Bu | 234 | $8.47\times10^3$ | 242 | $1.23\times10^4$ | 251 | $1.70\times10^4$ |
| *t*-Bu | 220 | $4.20\times10^3$ | 220 | $3.81\times10^3$ | 251 | $1.70\times10^4$ |

| | λ mμ | ε |
|---|---|---|
| *cis*-α,β-Dimethyl–St | 243 | $1.22\times10^4$ |
| *trans*-α,β-Dimethyl–St | 234 | $6.83\times10^3$ |
| β,β-Dimethyl–St | 244 | $1.46\times10^4$ |
| Indene | 281 | $3.02\times10^2$ |
| 1,2-Dihydronaphthalene | 295 | $4.59\times10^2$ |

* Slit width 0.30 mm

## Results

**Argentation Constants.** According to Andrews and Keefer,[1] the equilibrium reactions of styrenes (St) with the silver ion in the aqueous phase can be explained in terms of these equilibria:

$$\mathrm{Ag^+ + St = Ag\text{–}St^+}$$

$$K_1 = [\mathrm{Ag\text{–}St^+}]/[\mathrm{Ag^+}][\mathrm{St}] \qquad (1)$$

$$\mathrm{Ag^+ + Ag\text{–}St^+ = Ag_2\text{–}St^{2+}}$$

$$K_2 = [\mathrm{Ag_2\text{–}St^{2+}}]/[\mathrm{Ag^+}][\mathrm{Ag\text{–}St^+}] \qquad (2)$$

here, $K_1$ and $K_2$ are the equilibrium constants for the formation of the Ag-St$^+$ and Ag$_2$-St$^{2+}$ complexes respectively.

An additional constant, $K$, introduced to facilitate the calculations of $K_1$ and $K_2$, is defined as:

$$K = \frac{[\mathrm{St}]_t - [\mathrm{St}]}{[\mathrm{Ag^+}][\mathrm{St}]} = K_1 + K_1K_2[\mathrm{Ag^+}] \qquad (3)$$

where $[\mathrm{St}]_t$ and [St] are the molar concentrations of all the styrene-containing species and of free styrene respectively, and where [Ag$^+$] is the molar concentration of the free silver ion.

The solubilities were measured for styrene derivatives at 25°C, and the values of $K$ were calculated from Eq. (3). If the equilibria (1) and (2) account for all the complexes formed, and if additional reactions do not contribute appreciably to the complex formation, the plots of $K$ against [Ag$^+$] should give a straight line. This was found to be the case, with reasonable accuracy, for all the styrene derivatives investigated. Figure 1 shows examples of these plots for *cis*-β-alkylstyrenes at 25°C. In such plots the ordinate intercept is $K_1$ and the slope is $K_1K_2$. The values of $K_1$ and $K_2$ thus obtained are given in Table 2. These values were determined by the method of least-squares with an error of about one percent.

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9) J. von Brawn and G. Kirchbaum, *Ber.*, **54**, 604 (1921).

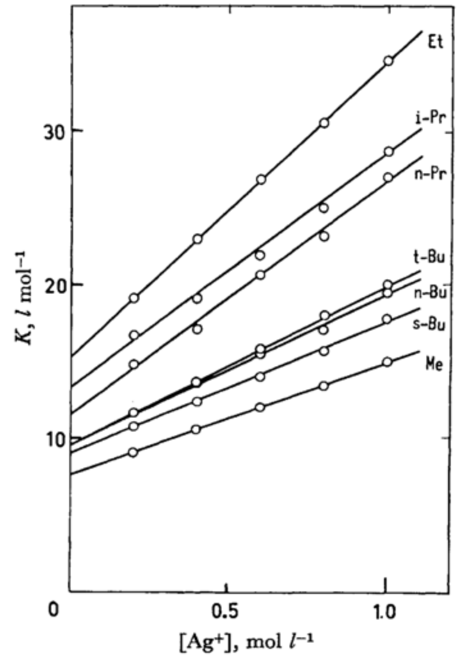

Fig. 1. Plots of $K$ vs. [Ag$^+$] for *cis*-$\beta$-R-styrene at 25°C.

TABLE 2. ARGENTATION CONSTANTS OF STYRENE DERIVATIVES AT 25°C IN WATER

| R | α-R–St | | *cis*-β-R–St | | *trans*-β-R–St | |
|---|---|---|---|---|---|---|
| | $K_1$ l/mol | $K_2$ l/mol | $K_1$ l/mol | $K_2$ l/mol | $K_1$ l/mol | $K_2$ l/mol |
| H | 17.4 | 0.9 | | | | |
| Me | 8.2 | 1.0 | 7.4 | 1.0 | 5.4 | 0.8 |
| Et | 11.1 | 1.6 | 15.3 | 1.3 | 8.1 | 1.3 |
| *n*-Pr | 8.2 | 1.7 | 11.6 | 1.3 | 5.5 | 1.7 |
| *n*-Bu | 6.5 | 1.5 | 8.5 | 1.1 | 2.7 | 1.0 |
| *i*-Pr | 13.6 | 1.4 | 13.8 | 1.1 | 10.5 | 0.9 |
| *s*-Bu | 7.0 | 1.3 | 8.7 | 1.0 | 5.1 | 0.9 |
| *t*-Bu | 8.6 | 1.2 | 9.3 | 1.1 | 6.6 | 1.4 |

| | $K_1$ l/mol | $K_2$ l/mol |
|---|---|---|
| *trans*-α,β-Dimethyl–St | 3.0 | 1.3 |
| *cis*-α,β-Dimethyl–St | 5.3 | 0.7 |
| β,β-Dimethyl–St | 5.0 | 0.8 |
| Indene | 8.5 | 0.9 |
| 1,2-Dihydronaphthalene | 28.4 | 1.4 |

It may be noticed that the values of $K_2$ are appreciably smaller than the $K_1$ values and are insensitive to the variation in the structure of styrenes. The values of $K_1$ which are a measure of the stabilities of the complexes, decrease in this order for a given alkyl:

*cis*-β-alkylstyrene>α-alkylstyrene>*trans*-β-alkylstyrene

The $K_1$ value obtained for styrene in our work is in reasonable agreement with the value obtained by Andrews and Keefer.[10] However, the $K_1$ values for β-methylstyrenes are larger than those given in the literature.[2,5] When rectificated samples of β-alkylstyrenes without further purification were used, abnormal peaks of benzaldehyde were found in the ultraviolet spectra of the extracted hexane solutions. Since the solubility of benzaldehyde in the aqueous phase is high, while the equilibrium constant is small, the $K_1$ values obtained were as small as the values in the literature. Samples which were treated with lithium aluminum hydride in order to remove the benzaldehyde gave smaller solubilities in the aqueous phase and larger $K_1$ values.

**Temperature-dependence.** The argentation constants were measured at 0 and 25°C for α- and β-alkylstyrenes. At temperatures higher than 30°C the solutions became turbid and silver metal precipitated during the equilibration, thus precluding measurements.

Listed in Table 3 are the values of $K_1$ and $K_2$ obtained at 0°C from the plots described above. The values of $K_1$ at 0°C are greater than those at

TABLE 3. ARGENTATION CONSTANTS OF STYRENE DERIVATIVES AT 0°C IN WATER

| R | α-R-St | | *cis*-β-R–St | | *trans*-β-R–St | |
|---|---|---|---|---|---|---|
| | $K_1$ l/mol | $K_2$ l/mol | $K_1$ l/mol | $K_2$ l/mol | $K_1$ l/mol | $K_2$ l/mol |
| H | 36.5 | 1.2 | | | | |
| Me | 22.2 | 1.1 | 13.9 | 1.4 | 10.3 | 2.2 |
| Et | 18.3 | 2.4 | 22.7 | 2.5 | 14.7 | 2.2 |
| *n*-Pr | 19.0 | 1.7 | 21.0 | 1.8 | 9.7 | 2.5 |
| *n*-Bu | 13.0 | 1.7 | 15.2 | 1.5 | 6.4 | 1.7 |
| *i*-Pr | 33.0 | 1.3 | 23.5 | 1.8 | 22.6 | 1.8 |
| *s*-Bu | 13.3 | 1.7 | 15.4 | 1.6 | 10.2 | 0.8 |
| *t*-Bu | 14.7 | 1.8 | 15.4 | 2.1 | 13.0 | 2.3 |

TABLE 4. THERMODYNAMIC DATA FOR ARGENTATION OF STYRENE DERIVATIVES IN WATER

| R | α-R-St | | *cis*-β-R–St | | *trans*-β-R–St | |
|---|---|---|---|---|---|---|
| | $-\Delta H$ kcal/mol | $-\Delta S$ e.u. | $-\Delta H$ kcal/mol | $-\Delta S$ e.u. | $-\Delta H$ kcal/mol | $-\Delta S$ e.u. |
| H | 4.9 | 10.6 | | | | |
| Me | 4.9 | 11.6 | 4.0 | 9.2 | 4.3 | 11.1 |
| Et | 3.0 | 5.2 | 2.5 | 3.1 | 3.9 | 8.8 |
| *n*-Pr | 5.4 | 14.0 | 3.9 | 8.1 | 4.3 | 11.2 |
| *n*-Bu | 5.0 | 13.2 | 4.0 | 9.2 | 5.6 | 16.8 |
| *i*-Pr | 5.7 | 13.7 | 3.6 | 6.8 | 4.9 | 11.7 |
| *s*-Bu | 4.0 | 9.6 | 4.1 | 9.5 | 4.8 | 12.8 |
| *t*-Bu | 3.7 | 8.2 | 3.7 | 8.0 | 5.0 | 13.0 |

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[10] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **72**, 5034 (1950).

25°C. These results indicate that the silver ion complexes are stable at lower temperatures.

From the $K_1$ values at 0 and 25°C, the thermodynamic data for the argentation in water were obtained. Table 4 gives the entropy and enthalpy changes in the argentation for α- and β-alkylstyrenes in water.

## Discussion

**Alkyl Substituent Effect.** It has been established that, in the styrene molecule and in most styrene derivatives, the vinyl group is the center for the coordination of the silver ion.[2,10] On the basis of this consideration, it appears very likely that the $K_1$ values are related to the nature of the substituent about the double bond of styrenes. The effects of substituents on argentation constants may be divided into the independent contributions of the polar, resonance, and steric effects of the substituents. Thus, Taft's equation can be applied:

$$\log (K/K_0) = \rho^*\sigma^* + \delta E_s + \gamma E_\psi \qquad (4)$$

where $\sigma^*$, $E_s$, and $E_\psi$ are the polar, steric, and resonance substituent constants and where $\rho^*$, $\delta$, and $\gamma$ are the corresponding reaction parameters. $K_0$ is the equilibrium constant of a standard reaction (methyl substituent). In Fig. 2, the $K_1$ values for α- and β-alkylstyrenes at 25°C are plotted against the alkyl substituents, which are arranged in the increasing order of $E_s$. The plots shows zigzag curves, although they show similar patterns for the respective series. A similar tendency is shown by the results of Muhs and Weiss[6] for alkyl-substituted ethylenes.

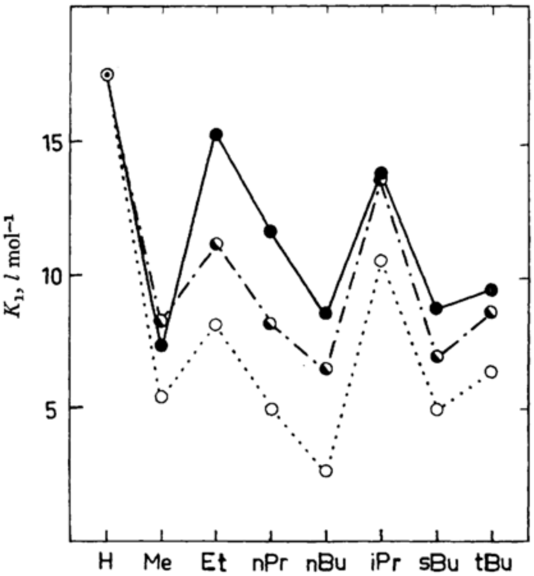

Fig. 2. Argentation constants of styrene derivatives at 25°C.
◐ α-R–St, ● *cis*-β-R–St, ○*trans*-β-R–St

Table 5 collects the ultraviolet absorption spectra of α- and β-alkylstyrenes. It indicates that, for *cis*- and *trans*-β-alkylstyrenes, the extent of conjugation does not change appreciably within each series except for *cis*-β-*t*-butylstyrene. This means that the resonance factor varies little within each series. However, in the case of α-alkylstyrenes, the wavelengths of maximum absorption shift lower with an increase in the bulkiness of the alkyl substituents. It is generally known that an increase in the extent of conjugation causes a reduction in $K_1$ values. It appears, then, that the bulky alkyl groups of α-alkylstyrenes cause an increase in $K_1$ value as a result of the steric inhibition of conjugation. Table 5 also indicates that the resonance effect of styrene is different from those of alkylstyrenes.

TABLE 5. ULTRAVIOLET SPECTRA OF STYRENE DERIVATIVES IN HEXANE

| R | α-R–St | | *cis*-β-R–St | | *trans*-β-R–St | |
|---|---|---|---|---|---|---|
| | $\lambda_{max}$ m$\mu$ | log $\varepsilon_{max}$ | $\lambda_{max}$ m$\mu$ | log $\varepsilon_{max}$ | $\lambda_{max}$ m$\mu$ | log $\varepsilon_{max}$ |
| H | 244 | 4.08 | | | | |
| Me | 243 | 4.04 | 241 | 4.11 | 249 | 4.16 |
| Et | 239 | 4.03 | 242 | 4.11 | 251 | 4.19 |
| *n*-Pr | 239 | 3.97 | 242 | 4.13 | 251 | 4.23 |
| *n*-Bu | 239 | 3.97 | 241 | 4.08 | 251 | 4.23 |
| *i*-Pr | 234 | 3.86 | 242 | 4.09 | 251 | 4.21 |
| *s*-Bu | 234 | 3.93 | 242 | 4.09 | 251 | 4.23 |
| *t*-Bu | ~220 | 3.62 | ~220 | 3.58 | 251 | 4.23 |

Another important factor affecting the complex formation is the steric effect of the substituents neighboring the double bond. As has previously been mentioned, no correlation between $K_1$ and $E_s$ can be found in Fig. 2. From Fig. 2 it appears that the $K_1$ values in each series can be classified into three groups according to the number of α-hydrogen atoms in the alkyl substituent. This classification suggests the effect on argentation of the hyperconjugation of the alkyl group. Therefore, we tried to separate the effects of substituents into the independent contributions of the steric substituents and the hyperconjugation effects of alkyl substituents, as represented by the equation:

$$\log (K/K_0) = \delta E_s{}^c + h(n-3) \qquad (5)$$

where $n$ is the number of α-hydrogen atoms in alkyl groups and where $h$ is an adjustable parameter representing a measure of the hyperconjugation effect. We here used Hancock's $E_s{}^c$ values[11] rather than Taft's $E_s$ values, becuase the $E_s{}^c$ values are based upon the quantitative separation of the hyperconjugation effect from Taft's steric

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[11] C. K. Hancock, E. A. Meyers and B. J. Yager, *J. Am. Chem. Soc.*, **83**, 4211 (1961).

substituent constants. The correlation of $\log K_1$ by Eq. (5) gave a good linearity, as is shown in Fig. 3. The $h$ parameter was determined by trial and error. The negative value of $h$ in Fig. 3 indicates that the hyperconjugation effect serves to reduce the $K_1$ value. This is consistent with qualitative recognition that, as has already been mentioned, the conjugation between a substituent and the reaction center causes a reduction in the $K_1$ value.

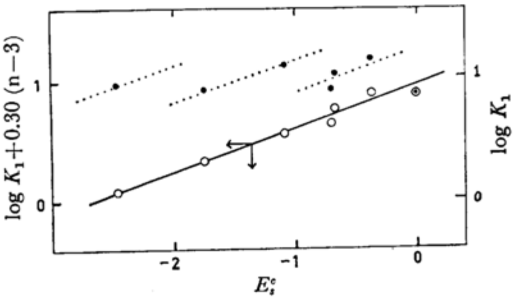

Fig. 3. Relationship between argentation constants of *cis*-$\beta$-R-styrene and $E_s^c$.

The polar effect of substituents on the argentation of benzene derivatives was discussed by Andrews and Keefer[1] in the Hammett $\rho$–$\sigma$ relation; they reported a reaction constant $\rho = -1.6$ for $\sigma_m$. Also, the two reaction constants $\rho = -0.766$[2] and $\rho = -5.07$[3] were reported by Fueno *et al.* for ring-substituted styrenes and vinyl compounds respectively. In our case, it is appropriate to discuss the polar effect using the reaction constant of vinyl compounds, $\rho = -5.07$, in the Hammett $\rho$–$\sigma_m$ relation. Table 6 shows only a small difference in the polar substituent effects $\rho\sigma_m$ of alkyl groups; therefore, the polar effect of substituents can be neglected.

TABLE 6. POLAR AND STERIC SUBSTITUENT CONSTANTS OF ALKYL GROUPS

| R | $\sigma_m$[a)] | $\rho\sigma_m$[b)] | $h(n-3)$[c)] | $E_s^c$[d)] |
|---|---|---|---|---|
| Me | −0.069 | 0.35 | 0.00 | 0.00 |
| Et | −0.07 | 0.35 | 0.30 | −0.38 |
| *n*-Pr | | | 0.30 | −0.67 |
| *n*-Bu | | | 0.30 | −0.70 |
| *i*-Pr | −0.068 | 0.34 | 0.60 | −1.08 |
| *s*-Bu | | | 0.60 | −1.74 |
| *t*-Bu | −0.10 | 0.51 | 0.90 | −2.46 |

a) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).
b) $\rho = -5.07$ from Ref. 3.
c) $h = -0.30$ from Fig. 3.
d) Ref. 11.

It was found that Eq. (5) holds in the case of the argentation of alkenes in ethylene glycol, which has been studied by Muhs and Weiss using gas chromatography (Fig. 4).[6] The substituent effect of alkenyl alkyl ethers on the argentation, which was investigated by Fueno *et al.*,[4] may be interpreted in a similar manner.

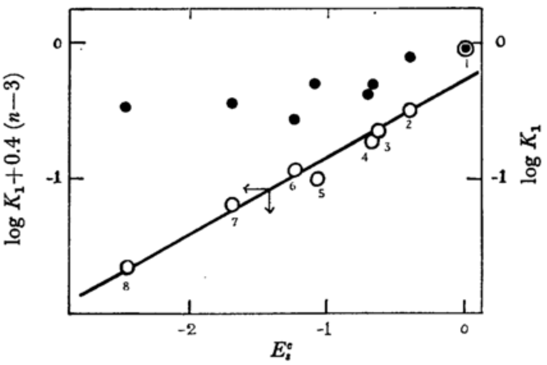

Fig. 4. Relationship between argentation constants of 1-alkene and $E_s^c$ at 40°C.
R-CH=CH$_2$: 1. Me 2. Et 3. *n*-Pr 4. *n*-Bu 5. *i*-Pr 6. *i*-Bu 7. *s*-Bu 8. *t*-Bu

The same treatment as in Fig. 3 was also applied to $\alpha$- and $\beta$-alkylstyrenes; all the results are given in Fig. 5. The slope of these straight lines corresponds to the $\delta$ parameter, the steric reaction constant. Figure 5 indicates that the $\delta$ parameters of *cis*-$\beta$- and *trans*-$\beta$-alkylstyrenes are practically the same. Figure 5 also indicates that the $\delta$ parameter of the $\alpha$-alkyl series is nearly equal to that of the $\beta$-alkyl series. However, since the $\alpha$-alkyl groups exhibit a steric inhibition of resonance, as has been shown above, the real steric effect of the $\alpha$-alkylstyrene series must be larger than the apparent value.

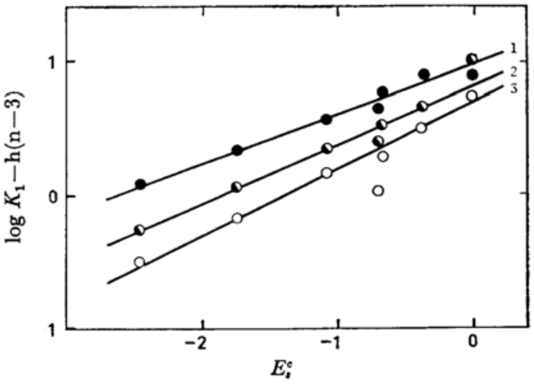

Fig. 5. Relationship between argentation constants of styrene derivatives and $E_s^c$.
1. *cis*-$\beta$-R–St 2. $\alpha$-R–St 3. *trans*-$\beta$-R–St

As has already been mentioned, Table 2 (or Fig. 5) shows a reasonable difference in the $K_1$ values of $\alpha$-, *cis*-$\beta$-, and *trans*-$\beta$-alkylstyrenes for a given alkyl. In the previous discussion using Eq. (4), the resonance factor was assumed to be constant within each series except the α-alkylstyrene series. When we compare the α-series, the *cis-β*-series, and the *trans-β*-series using the same equation, however, the difference in the resonance factor should be considered. The difference in the resonance factor between the three series corresponds to the large distance between the experimental lines of the α-, the *cis-β*-, and the *trans-β*-series in Fig. 5.

In order to obtain further information regarding the nature of the complexation of styrene derivatives, the thermodynamic data, $\Delta H$ and $\Delta S$, for complexation were evaluated from the $K_1$ values at 0 and 25°C. No simple relation between the $\Delta H$ (or $\Delta S$) and $E_s{}^c$ values of the substituent groups was found. However, as is shown in Fig. 6, a linear correlation was found to exist between $\Delta H$ and $\Delta S$ (isokinetic relationship); the plots for α-, *cis-β*- and *trans-β*-series fell on the same line, in contrast with the case of alkenyl alkyl ethers.[4] The isokinetic temperature, 250°K, was obtained from the slope of the straight line. Since the measurements of the argentation constants were carried out above the isokinetic temperature, the entropy factor is considered to be more important than the enthalpy in this equilibrium.

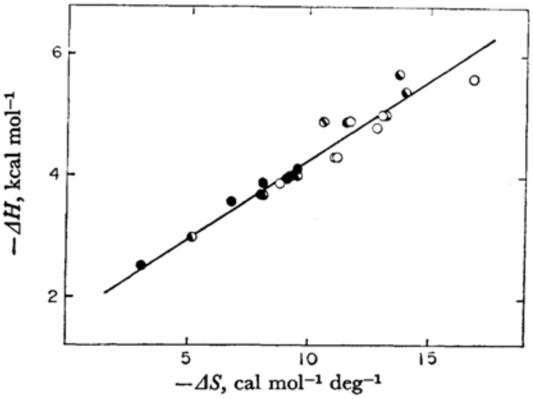

Fig. 6. Plots of $\Delta H$ *vs.* $\Delta S$.

⊘ Styrene ◑ α-R–Styrene ● *cis-β*-R–Styrene
○ *trans-β*-R–Styrnene

**Argentation Constants of the Other Styrene Derivatives.** Further substitution of methyl groups at the double bond slightly influenced the $K_1$ values. Table 2 indicates that the $K_1$ values for *cis-α,β*-dimethylstyrene, and *β,β*-dimethylstyrene are nearly equal to the $K_1$ value of *trans-β*-methylstyrene, although smaller than those of α- and *cis-β*-methylstyrenes. This is considered to be due to the fact that the inhibition of conjugation between the benzene ring and the double bond is more important than the steric effect in the complex formation of those styrenes.

Considering the structure and the strain of the olefin, the $K_1$ value of indene is reasonable. However, the very large $K_1$ value of 1,2-dihydronaphthalene was unexpected from the structure of this molecule.