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The Structure-Stability Relationship of the Metal Ion Complexes of Unsaturated Compounds. III.[1] The Effects of Polar Substituents on the Silver Ion - Olefin Complexation

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The equilibrium constants for the formation of silver ion complexes of various vinyl compounds in water were determined at 25°C by the distribution method. It has been found that the equilibrium constants obtained are closely related to the Hammett sigma meta values of the relevant substituents, the reaction constant being $\rho=-5.07$ with the correlation coefficient $r=0.974$. The results have been interpreted in terms of the inductive effect of the substituents as the most dominant contribution to the stabilities of these complexes.

The polar effect of substituents in the argentation (silver ion complexation) equilibria of unsaturated compounds was first discussed by Andrews ant Keefer[2] for benzene derivatives in terms of the Hammett ρ-σ relation. We also reported the results of similar studies for the case of ring-substituted styrenes,[3] and presented a theoretical interpretation of the observed substituent effects.[1] For olefinic compounds, however, available experimental data, though may be numerous, only indicate the importance of inductive, steric and structural strain effects of alkyl

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[1] Part II: T. Fueno, T. Okuyama and J. Furukawa, This Bulletin, **39**, 2094 (1966).

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

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

groups on the relative stabilities of the complexes.[4-9] No work has ever been reported as to the role of polar substituents in the Ag^+-olefin complex stabilities.

In the present work we have measured argentation equilibrium constants of several "polar" vinyl compounds in water at 25°C, in order to compare the electronic contributions of various substituents to the stabilities of the ethylene complexes. It has been found that the equilibrium obeys the Hammett relation, provided the sigma meta values are used for the polar groups. Thus, the ease of complexation of an ethylenic bond appears to be governed primarily by the inductive effect of its neighboring groups.

Experimental

Materials. Silver nitrate and potassium nitrate were of the best grade commercially available. Carbon tetrachloride was washed successively with aqueous sodium hydroxide and water, dried over potassium carbonate and fractionally distilled. Most of the vinyl compounds studied were commercially obtained and purified by standard procedures. Phenyl vinyl ether was prepared by the methods of McElvain and Fajardo-Pinzón.[10] All these substrate compounds were checked for purity by gas chromatography before use.

Equilibrium Measurements. Equilibrium constants, K_1 and K_2, for the formation of the silver ion complexes in the aqueous phase

$$Ag^+ + M = AgM^+,$$

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

$$Ag^+ + AgM^+ = Ag_2M^{2+}$$

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

were measured at 25°C by the distribution method.[4] The polar olefins, M, were allowed to distribute between water and carbon tetrachloride by vigorously stirring the mixtures for 20 hr. The aqueous layer contained silver nitrate, whose concentration was in the range 0.1 to 0.6 M. The ionic strength of the layer was fixed at unity by the addition of a required amount of potassium nitrate. The initial concentration of the olefins dissolved in the organic layer was 1.0 M.

The constants, K_1 and K_2, may be related to an apparent equilibrium constant K in the following manner:

$$K = (k - k_0)/k_0[Ag^+] = K_1 + K_1K_2[Ag^+] \qquad (3)$$

Here, k_0 is the distribution coefficient of an olefin between the aqueous and organic layers measured in the absence of the Ag^+ ions, while k is a similar coefficient measured in the presence of the ions. Measurements of the values of K for varying silver-ion concentrations, $[Ag^+]$, permit the evaluation of both K_1 and K_2 for each olefin.

The magnitudes of k as well as k_0 were obtained from the initial concentration of olefin in the organic layer and its concentration in either organic or aqueous layer after distribution. In the case of unsaturated hydrocarbons, the total concentrations of these compounds, both free and complexed, in the aqueous phase were determined by the spectrophotometric method. The procedure adopted was the same as had been described previously.[3] In the case of polar olefins, on the other hand, the decreases in their concentrations in the organic layer were measured by gas chromatography. The conventional half-height width method was found to suffice for this purpose, insofar as the volume ratio between the organic and aqueous layers was so adjusted as to suit such measurements.

Results

The values of K were measured for various vinyl compounds at varying silver ion concentrations. In evaluating the K-values, the concentration, of the silver ion $[Ag^+]$, which remained intact in the aqueous phase was assumed to be equal to its initial concentration. In other words, the variations in the concentration of free silver ions, which were caused by the formation of the complexes, were assumed to be negligibly small compared with the initial concentration. It was ascertained that this approximation introduced practically no error into the values of K.

If the presumptions underlying Eq. (3) are basically correct, then, for a given substrate, plots of K against $[Ag^+]$ should give a straight line with the intercept K_1 and the slope K_1K_2. Such linear

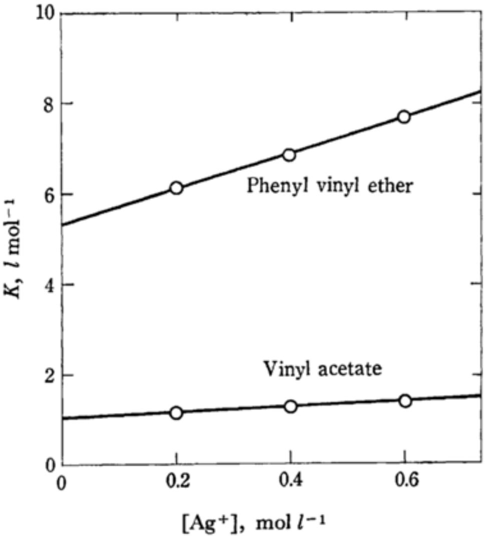

Fig. 1. Examples of the plots of K *vs.* $[Ag^+]$.

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[4] S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938).

[5] a) H. J. Lucas, R. S. Moore and D. Pressman, *ibid.*, **65**, 227 (1943). b) H. J. Lucas, F. W. Billmayer and D. Pressman, *ibid.*, **65**, 230 (1943). c) F. R. Hepner, K. N. Trueblood and H. J. Lucas, *ibid.*, **74**, 1333 (1952). d) K. N. Trueblood and H. J. Lucas, *ibid.*, **74**, 1338 (1952).

[6] L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); **72**, 5034 (1950).

[7] J. G. Traynham and J. R. Olechowski, *ibid.*, **81**, 571 (1959).

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

[9] R. J. Cvetanović, F. J. Duncan, W. E. Falconer and R. S. Irwin, *ibid.*, **87**, 1827 (1965).

[10] S. M. McElvain and B. Fajardo-Pinzón, *ibid.*, **76**, 650 (1945).

TABLE 1. THE EQUILIBRIUM CONSTANTS FOR ARGENTATION OF SOME VINYL COMPOUNDS IN WATER AT 25°C

Compound	Substituent	k_0	K_1, l mol^{-1}	K_2, l mol^{-1}	r	σ_m
Ethylene	H[a]	2.9×10^{-2}	85.3	0.15	—	0
Propylene	CH_3[a]	6.8×10^{-3}	87.2	0.11	—	−0.069
Styrene	C_6H_5	5.59×10^{-4}	19.1	1.5	10	0.06
Ethyl vinyl ether	OC_2H_5	8.7×10^{-2}	13.0	0.6	20	0.115[b]
Phenyl vinyl ether	OC_6H_5	1.10×10^{-3}	5.26	0.77	10	0.252
Vinyl acetate	$OCOCH_3$	4.5×10^{-2}	1.03	0.37	25	0.39
Methyl acrylate	$COOCH_3$	6.0×10^{-2}	0.37	0.28	25	0.37
Methyl vinyl ketone	$COCH_3$	0.47	0.42	—	2	0.376

a) Ref. 5d.
b) The value for the methoxy group was used.

relations were substantiated with sufficient precision with all the compounds studied here. Typical examples of such linearities are shown in Fig. 1.

The values of K_1 and K_2 obtained for the various vinyl compounds at 25°C are given in Table 1. Also listed in Table 1 are the distribution constant, k_0, of each compound between 1 N aqueous potassium nitrate solution and carbon tetrachloride and the volume ratio, r, between the aqueous and organic layers adopted for the distribution experiments of each compound.

Discussion

A number of workers[1-9] have already noted that the argentation equilibria of unsaturated compounds are sensibly influenced by the electronic, steric and strain factors of substituents. Among others, Muhs and Weiss[8] studied a large number of olefins by the gas chromatographic technique and extended detailed discussion of the steric and strain effects involved. As for the electronic contribution of substituents, the demonstrations that the relative stabilities of the silver ion complexes formed from substituted benzenes[2] and styrenes[3] obey the Hammett relation are noteworthy. In general cases, these factors join together in a complicated manner, and it is often extremely difficult to assess their relative importances in a simple yet general manner. All that has been possible to do is to isolate one major contributing factor or two, which may be different depending on the type of the substrate structures.

In an effort to disentangle the effects of polar substituents on the stabilities of the olefin complexes under study, we have plotted in Fig. 2 the values of $\log K_1$ against the Hammett σ_m values of the substituents. The result was that the $\log K_1$ was linearly related to the σ_m, though only roughly. The slope of the linear correlation was $\rho=-5.07$, and the correlation coefficient was $r=0.974$. As for the varia tions of the K_2 values with substituents, on the other hand, no simple generalization was possible to make.

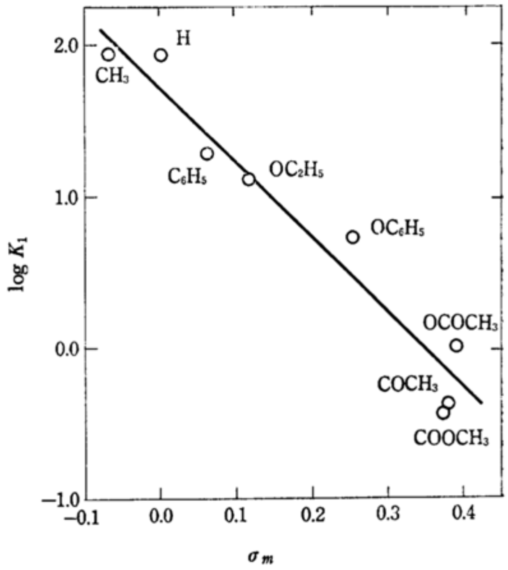

Fig. 2. Plots of $\log K_1$ *vs.* σ_m for the silver ion complexation equilibria of some vinyl compounds in water at 25°C.

The finding that a linear relation holds between $\log K_1$ and σ_m is not grossly fortuitous. The linearity may be rationalized as follows:

First of all, if the electronic effect of substituents is the most predominant contribution to the relative stabilities of polar olefin complexes, it will be nothing odd to expect that the values of $\log K_1$ will be correlated, to a first approximation, with the Hammett sigma values of the substituents. One may inquire at the second step why then the stabilities should be functions of the sigma meta rather than sigma para values. Perhaps, the most plausible answer to this question may be given in terms of the inductive effect of the polar substituents. The view that the σ_m values of polar groups are associated primarily with their inductive effects is of wide acceptance, even though the way how the effect would come into play and the extent to which it might contribute to the σ_m relative to the resonance contribution are still debatable.[11-14] No doubt, the argentation of vinyl compounds involves the interactions of the silver ion with the α-carbon just as well as the β-carbon of the vinyl linkage. Thus it is very likely that, in the case of vinyl compounds, the availability of the α-β bond for the complexation is greatly influenced by the inductive effect of its neighboring polar groups, and hence is correlated with their σ_m value.

The reaction constant, -5.07, obtained for a series of vinyl compounds as above is considerably larger in magnitude than the values of -1.6[2] and -0.766[3] which have previously been reported for ring-substituted benzenes and styrenes, respectively.[15] It may be said that the sensitivity of substrates toward the variation of substituents decreases in the order: ethylene > benzene > styrene. This order of sensitivity is readily understandable qualitatively in view that the polar effect of substituents should diminish with the increase in the distance between the substituents and the reaction center.

The above arguments, however, do not necessarily imply that the steric effect of substituents is wholly unimportant. For instance, one may clearly notice the importance of such an effect when he compares the K_1-values of heavily substituted ethylenes with those of the monosubstituted.[4,8,9] In the series of polar vinyl compounds studied here, possible steric effects of the various polar groups are apparently overshadowed by the more dominant contributions of their inductive effects. Hence, the steric effect is more conspicuous between ethylene derivatives of different degrees of substitution than between those that belong to the identical type of substitution but carry different substituent groups. Thus, it may be concluded that, so far as the silver ion complexation of vinyl compounds is concerned, the relative stabilities of the complexes formed is controlled most influentially by the inductive effect of the polar groups.

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11) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279, 285, 1554 (1952); **21**, 415 (1953).

12) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3539, 3548 (1962).

13) Y. Yukawa, Y. Tsuno and M. Sawada, This Bulletin, **39**, 2274 (1966).

14) T. Fueno, T. Okuyama and J. Furukawa, *ibid.*, **39**, 569 (1966).

15) The difference is significant, even though we admit that we have chosen sigma meta values somewhat deliberately in correlating the log K_1 of vinyl compounds with Hammett's substituent constants.