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# The Structure-Stability Relationship of the Metal Ion Complexes of Unsaturated Compounds. IV.[1,2]
# Argentation Equilibria of Alkenyl Alkyl Ethers

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The equilibrium constants, $K$, for the formation of 1 : 1 $Ag^+$ - alkenyl alkyl ether complexes were measured in the temperature range 10 to 30°C by the gas chromatographic method. It has been found (1) that *cis* isomers have the values of $K$ several times greater than those of the corresponding *trans* isomers, (2) that the $K$-value tends to diminish with the increasing degree of $\beta$-substitutions, (3) that, in a series of *cis* ethers, $K$ increases as the $\beta$-alkyl substituent becomes bulkier, and (4) that the variation of the alkoxy groups causes little change in the $K$-value. The difference in the $K$-values between the *cis* and *trans* complexes is found to be ascribable mainly to their difference in the enthalpy changes, $\Delta H$, accompanying the complexation. These trends have been discussed on a thermodynamic ground in comparison with those already noted for olefins.

The relations between the stability of the $Ag^+$-olefin complexes and the structure of the olefins have already been investigated and discussed to a considerable extent by several groups of workers.[3)]

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1) Part III: The preceding article.

2) Presented in part at the IUPAC International Symposium on Macromolecular Chemistry, Tokyo—Kyoto, September, 1966.

3) See, for example, Refs. 4, 5 and 6 and the papers cited therein.

Until recently, however, such investigations have never been extended to include "polar" olefins, *i. e.*, those olefinic compounds bearing polar groups. In the preceding paper of this series,1) we have dealt with some vinyl compounds and reached the conclusion that the inductive effect of the substituents is of primarily importance to the relative stabilities of the complexes.

In the present communication, we treat the silver ion complexation equilibria of various alkenyl alkyl ethers, $R_1R_2C=CR_3(OR_4)$, with particular attention to the effect of the geometrical structures on the stabilities of the complexes formed. In measuring the equilibrium constants, we have utilized the gas chromatographic technique which has recently been developed by Muhs and Weiss.4) This technique has greatly facilitated the comparison of the complexation abilities of *cis* and *trans* ethers as well as the examination of the temperature dependences of the equilibrium constants. Despite a possible influence of a large polarization of the carbon-carbon double bond in unsaturated ethers, the equilibrium data obtained for these compounds have manifested general features similar to those already recognized for olefins.4-6) Apparently, the difference in the mesomeric effects of various alkoxy groups on the complexation is overshadowed by the difference in other contributions such as the inductive and steric effects of various alkyl groups present as well as the effect of the substrate structure.

## Experimental

**Materials.** Silver nitrate, acetone and hexene-1 were of the best grade commercially available and were used without further purification. Ethylene glycol was obtained commercially and fractionally distilled immediately before use. Alkyl ethers were prepared by the methods described elsewhere7) and were checked for purity by gas chromatography. Geometrical isomers of the ethers, when these occurred, were not separated. In all cases, the ethers were rich in *cis* isomer.

**Equilibrium Measurements.** The equilibrium constants for the $Ag^+$-olefin complex formation in ethylene glycol were measured by the gas chromatographic method developed by Muhs and Weiss.4) It will be advantageous to briefly duplicate the principle here.

The distribution coefficient of the sample between liquid and vapor phases can be expressed as4)

$$H=\frac{3}{2}\cdot\frac{(P_i/P_o)^2-1}{(P_i/P_o)^3-1}\cdot\frac{Ft_r}{V_L} \tag{1}$$

where $P_i$ and $P_o$ are the inlet and outlet pressures, respectively; $F$ is the carrier gas flow rate; $V_L$ is the volume occupied by liquid phase at the column temperature; and $t_r$ is the retention time. The distribution coefficient varies with the $Ag^+$ concentration in the liquid phase as a result of complex formation. Thus, from the distribution coefficient, $H_0$, measured for a column without the $Ag^+$ ions and a similar coefficient, $H$, observed for an $Ag^+$-containing column, the equilibrium constant, $K$, for the complexation can readily be evaluated:5)

$$\begin{aligned} K &= [\text{Ether-Ag}^+]/[\text{Ether}][\text{Ag}^+] \\ &= (H-H_0)/H_0[\text{Ag}^+] \end{aligned} \tag{2}$$

A Yanagimoto gas chromatograph model 3DH was operated at the column temperatures 10, 20 and 30°C with the hydrogen flow of 80 m*l*/min. A thermal conductivity detector and a soap bubble flowmeter were used. Special cautions were taken to minimize the scatters in the observed retention times which arose when the sample sizes were not strictly constant. The sample size finally adopted was 0.4 $\mu l$. The values of $K$ obtained as above were fairly well reproducible, irrespective of the $Ag^+$ concentration not greater than 1.0 M. Mixtures of a given pair of geometrical isomers were subjected to the equilibrium measurements as such, but their retention times recorded separately. This expedience proved to introduce no error into the final results.

**Preparation of Columns.** Yanagimoto Celite 545 (80—100 mesh) was immersed in a silver nitrate solution in ethylene glycol diluted with acetone. The mixture was stirred until it attained homogeneity. Acetone was then evaporated off at room temperature. The ratio of the liquid phase to the support was 3 : 10 by weight. A weighed amount of packing was placed in a 1-m stainless steel column of 5 mm in diameter. Columns required *ca.* 9 g of packing. Three columns with 0, 0.5 and 1.0 M silver nitrate were prepared.

## Results

**Operating Conditions.** Preliminary measurements of the equilibrium constants, $K$, indicated that the measured $K$-values were markedly dependent upon both the flow rate and the sample size adopted. Therefore, the effects of these factors had to be examined quantitatively in order to establish a routine operating condition.

For hexene-1, which showed relatively large variation in $K$ with operating conditions, the following trends were observed:

The value of $K$ tended to decrease considerably with the increasing sample size, whereas it slightly increased as the flow rate became greater. In magnitude, the effect of the sample size was the more appreciable, as may be seen in Fig. 1.

In such situations, it would be the most reasonable procedure in principle to extrapolate the $K$-values to both the zero flow rate and the zero sample size. Practically, however, a number of runs would then necessarily have to be performed for

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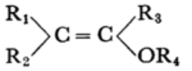
4) M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962).

5) R. J. Cvetanovic, F. J. Duncan, W. E. Falconer and R. S. Irwin, *ibid.*, **87**, 1827 (1965).

6) a) S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938). b) L. J. Andrews and R. M. Keefer, *ibid.*, **72**, 3113 (1950). c) J. G. Traynham and M. F. Sehnert, *ibid.*, **78**, 4024 (1956).

7) T. Okuyama, T. Fueno, H. Nakatsuji and J. Furukawa, *ibid.*, **89**, 5826 (1967).

TABLE 1. DATA FOR THE ARGENTATION EQUILIBRIA OF ALKENYL ALKYL ETHERS, ALKENYL



$R_1R_2C=C(R_3)OR_4$

| No.[a] | Compound |  |  |  | $K$, $l$ mol$^{-1}$ |  |  | $-\Delta H$[b] kcal mol$^{-1}$ | $-\Delta S$[c] e. u. |
|---|---|---|---|---|---|---|---|---|---|
|  | $R_1$ | $R_2$ | $R_3$ | $R_4$ | 10° | 20° | 30° |  |  |
| 1 | H | H | H | $C_2H_5$ | 9.08 | 6.72 | 5.55 | 4.4 | 11.0 |
| 2 | H | H | H | $n$-$C_4H_9$ | 8.72 | 7.76 | 5.66 | 3.7 | 8.8 |
| 3 | H | H | H | $i$-$C_4H_9$ | 8.77 | 6.83 | 5.56 | 4.0 | 9.8 |
| 4c | H | $CH_3$ | H | $C_2H_5$ | 4.00 | 3.13 | 2.55 | 3.9 | 11.0 |
| 4t | $CH_3$ | H | H | $C_2H_5$ | 0.67 | 0.54 | 0.47 | 3.2 | 12.1 |
| 5c | H | $C_2H_5$ | H | $C_2H_5$ | 5.62 | 4.24 | 3.13 | 4.5 | 12.6 |
| 5t | $C_2H_5$ | H | H | $C_2H_5$ | 0.95 | 0.73 | 0.63 | 3.3 | 12.0 |
| 6c | H | $i$-$C_3H_7$ | H | $C_2H_5$ | 5.98 | 4.46 | 3.48 | 4.7 | 12.9 |
| 6t | $i$-$C_3H_7$ | H | H | $C_2H_5$ | 0.77 | 0.59 | 0.50 | 3.5 | 12.9 |
| 7c | H | $CH_3$ | H | $i$-$C_4H_9$ | 3.58 | 2.86 | 2.34 | 3.7 | 10.4 |
| 7t | $CH_3$ | H | H | $i$-$C_4H_9$ | 0.77 | 0.60 | 0.55 | 2.8 | 10.6 |
| 8 | $CH_3$ | $CH_3$ | H | $C_2H_5$ | 0.27 | 0.21 | 0.17 | 3.5 | 15 |
| 9 | H | H | $CH_3$ | $CH_3$ | 9.51 | 7.35 | — | 4.7 | 12 |

a) The suffixes c and t refer to *cis* and *trans*, respectively.
b) Probable error of each entry does not exceed 0.2 kcal mol$^{-1}$.
c) Accurate only to within ±0.6 e. u.

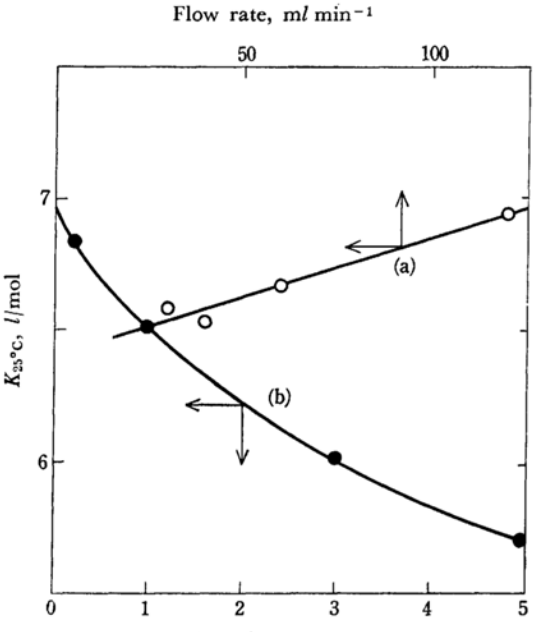


Fig. 1. Variations of $K$ for hexene-1 (a) with the flow rate at constant sample size 1.0 $\mu l$ and (b) with the sample size at constant flow rate 40 $ml$ min$^{-1}$.

each compound under study, which might lead to undesirable deterioration of the column packings, introducing even more crucial experimental errors into the final results. Furthermore, experiments with too slow a flow rate coupled with a small sample size would make it extremely difficult to get precise retention times because of the large broadening as well as the small height of the sample peaks.

Under these circumstances, we have decided to compromise the cumbers by adopting such operating conditions that the relative magnitudes of the equilibrium constants for the various compounds to be examined were not seriously affected. The choices of the flow rate ranging from 40 to 80 m$l$/min and the sample size in the range 0.4 to 1.0 $\mu l$ met this requirement. The flow rate and the sample size finally adopted as the routine conditions were 80 m$l$/min, and 0.4 $\mu l$, respectively, as has been specified in the experimental section.

**Equilibrium Constants.** The equilibrium constants were calculated from Eqs. (1) and (2). In obtaining the distribution constant, $H$, at a given $Ag^+$ concentration at a given temperature, three independent measurements were performed for each compound. The reproducibility of the equilibrium constants, $K$, was satisfactory. The values of $K$ listed in Table 1 are the averages of the three independent measurements at each of the temperatures 10, 20 and 30°C. It was observed that at both 20 and 30°C alkenyl alkyl ethers were liable to suffer solvolysis during the distribution measurements in the column containing silver nitrate. Yet, the peaks of the reactant ethers and the products were separated sufficiently far to enable the recordings of the retention times of the ethers with fair accuracy. Above 40°C, however, the alkenyl alkyl ethers were consumed to a considerable extent so that the measurements of $H$ were hardly feasible.

The changes of enthalpy, $\Delta H$, and entropy, $\Delta S$, in complexation were evaluated from the $K$-values given in Table 1. Plots of the logarithms of $K$ against the reciprocal of temperature were satisfactorily linear for all the unsaturated ethers investigated. An example of such plots is shown in Fig. 2. The values of $\Delta H$ and $\Delta S$ obtained in the temperature range 10 to 30°C are given in the final two columns of Table 1.

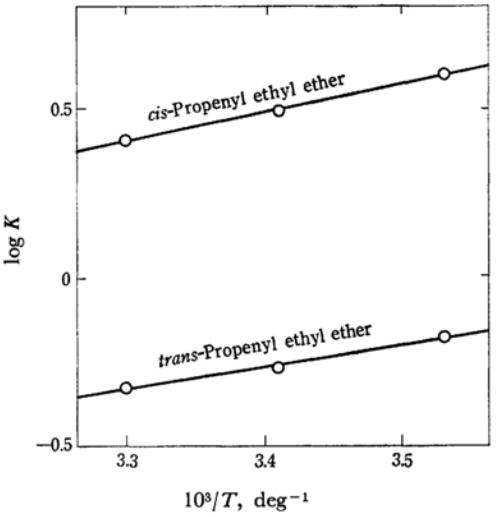


Fig. 2. Temperature dependence of log $K$ for the silver ion complexation of *cis*- and *trans*-propenyl ethyl ethers (4c and 4t).

## Discussion

**Effects of Alkyl Substitutions.** From the equilibrium constants listed in Table 1, the following generalizations can be made for the silver ion complexation of alkenyl alkyl ethers:

(1) The *cis* isomers have $K$ values several times greater than those of the corresponding *trans* isomers.

(2) The $K$ values largely decrease with the increasing degree of $\beta$-substitutions.

(3) As the substitutent on the $\beta$-position varies in the order $CH_3$, $C_2H_5$ and $i$-$C_3H_7$, the value of $K$ of *cis* ethers increases asymptotically in this order.

(4) The $K$-value varies little when the ethoxy group is replaced by the isobutoxy or $n$-butoxy group.

The features (1) and (2) are in agreement with those already noted in the olefin complexation and may most simply be interpreted in terms of the adverse steric effect of the alkyl substituents.[4,5,8] However, the effect appears, in some cases, to be coupled with the favorable inductive effect of the alkyl groups. Perhaps, the order of the effects of $\beta$-alkyl groups $CH_3 < C_2H_5 < i\text{-}C_3H_7$ mentioned in the item (3) is a result that the latter contribution outweighs the former. It is noteworthy in this connection that the $K$-values of the olefin homologs have been reported to *decrease* in this same order in one case[4] while they show a maximum in another,[5] as in the case of our *trans* ethers, depending on the environments where the measurements of $K$ have been made. This coupling of the two opposing contributions may also be a factor underlying the item (4).[*2]

In order to gain further insights into the nature of the complexation, it will no doubt be more advantageous to discuss the structure-stability relation in terms of the thermodynamic quantities, $\Delta H$ and $\Delta S$. Thus, in Fig. 3, the values of $\Delta H$ for the various alkenyl alkyl ethers were plotted against the $\Delta S$-values. It may be seen in Fig. 3 that the plotted points fall on a group of parallel straight lines which were drawn according to the types of $\beta$-substitution. We have found a similar relationship to hold (Fig. 4) between the $\Delta H$ and $\Delta S$ values for olefins which have recently been reported by Cvetanović *et al.*[5),*3] The slopes of these straight lines (*i. e.*, the isokinetic temperatures) corresponded to 310 and 350°K for the ethers and the alkenes, respectively.

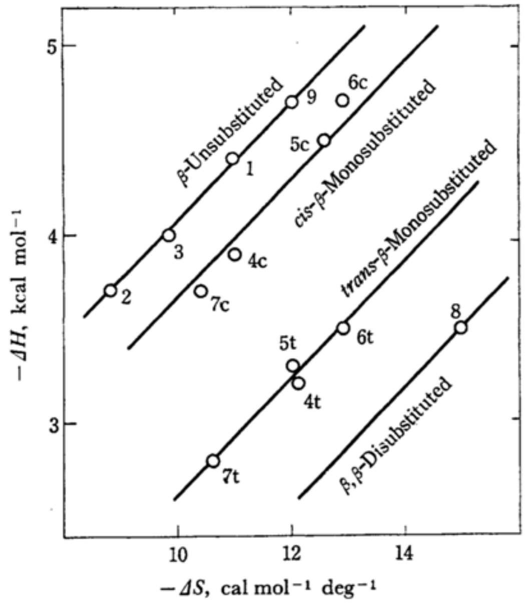


Fig. 3. Plots of $\Delta H$ *vs.* $\Delta S$ for the silver ion complexation equilibria of $\alpha,\beta$-unsaturated ethers in ethylene glycol.
The numbers 1—9 refer to the unsaturated ethers listed in Table 1.

The families of linear $\Delta H$-$\Delta S$ relationships in Figs. 3 and 4 may permit the following considerations:

First, since the isokinetic temperatures are only slightly above the temperatures at which the

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8) R. F. Hepner, K. N. Trueblood and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 1333 (1952).

[*2] The finding that an $\alpha$-methyl group produces no appreciable influence on the $K$-value (No. 9) may also have some bearing on this coupling effect.

[*3] The essential feature is discernible, even though the number of the experimental points is limited.

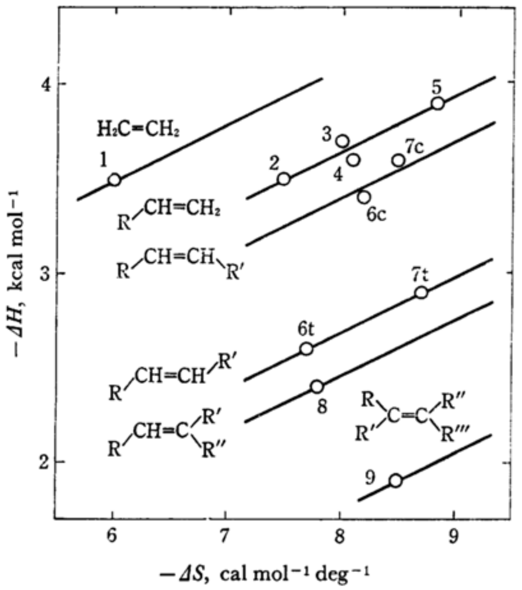

Fig. 4. Plots of $\Delta H$ *vs.* $\Delta S$ for the silver ion complexation equilibria of olefins in ethylene glycol. Data were taken from Ref. 5. The numbers 1—9 refer to the following olefins: 1, $CH_2=CH_2$; 2, $CH_3CH=CH_2$; 3, $C_2H_5CH=CH_2$; 4, $n\text{-}C_3H_7CH=CH_2$; 5, $i\text{-}C_3H_7CH=CH_2$; 6, $CH_3CH=CHCH_3$; 7, $C_2H_5CH=CHCH_3$; 8, $(CH_3)_2C=CHCH_3$; 9, $(CH_3)_2C=C(CH_3)_2$.

complexation studies have been carried out, it may not be quite proper to decide which of the two effects, enthalpy or entropy, is the more important factor to control the different complexation abilities of different alkenes or ethers of a given type of $\beta$-substitution. In fact, a closer examination of the thermodynamic data shows that the differentials in $\Delta H$ and $-T\Delta S$ between given pairs of substrate compounds are subject to complete cancellation between each other within the limit of experimental errors. As a consequence, no generalizations can possibly be made as to the relative importance of the two contributions in the temperature range studied.

Second, for compounds which belong to different classes of $\beta$-substitution, the relative importance of the enthalpy and entropy terms can be asscssed more easily. In particular, the greater stabilities of the complexes formed from *cis* ethers as compared with those from the corresponding *trans* isomers are evidently due to the greater enthalpy loss (*i. e.*, the greater heat evolution) of the former upon complexation.

Third and finally, one should be cautioned against a risk of ascribing different complexation abilities of arbitrarily selected two alkenes or ethers to a difference in either enthalpy or entropy effect in a simple and general manner. By the same token, it should be realized that the complex stability is by no means directly associated with the strength of the complexation bonds. This phase of the problem has previously been emphasized by us[9,10] in regard to the substituent effects in the silver ion complexation of aromatic hydrocarbons.

In the coordination of the silver ions with the double bond of olefins, there seems to be a favorable space (line, surface or volume) around the double bond for the ions to be located. As this space gets narrowed by the increasing substitution of alkyl groups, the degree of freedom of the coordinated silver ions would decrease correspondingly and, as a consequence, the loss of entropy would become larger to that extent. In the case of the tri- and tetra-substitutions, the silver ion may rather experience hindrance against approaching the most favorable space, so that the complexation bond would become the weaker.

**Effects of the Geometrical Structure.** As has already been mentioned, the difference in stability between the complexes of *cis* and *trans* ethers may most simply be interpreted in terms of the difference in adverse steric effect of substituents. The steric hindrance to complex formation by the two bulky groups, one being a $\beta$-alkyl group and the other an alkoxy group, may be greater when they are *trans* to each other.[8] Thus, *cis* isomers may tend to give more stable complexes. Incidentally, this interpretation implicitly assumes that the difference in the free energies of geometrical isomers is a less important factor than that of the resulting complexes.

Alternatively, it may also be conceivable that the energy difference between the $Ag^+$-complexes of the geometrically isomeric substrates is small as compared to the difference in total energy between the substrate molecules themselves. If this is true, the isomers which are less stable in total energy will experience larger enthalpy loss upon complexation, thus forming more stable complexes. The greater heat of complexation of *cis* ethers may thus be ascribable, for instance, to the relief of strain[4,10] of the two bulky groups *cis* to each other, when the complex is formed.

It is not quite an easy task to decide which of the above two interpretations is more plausible. However, it may be pointed out with some emphasis that the latter view receives support from the results of independent studies of the relative stabilities of the geometrical isomers of olefins as well as alkenyl ethers. Specifically, studies of the geometrical isomerization equilibria of both olefins[12]

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

10) T. Fueno, T. Okuyama and J. Furukawa, This Bulletin, **39**, 2094 (1966).

11) R. B. Turner, D. B. Nettleton and M. Perelman, *J. Am. Chem. Soc.*, **80**, 1430 (1958).

12) a) D. M. Golden, K. W. Egger and S. W. Benson, *ibid.*, **86**, 5416 (1964). b) K. W. Egger and S. W. Benson, *ibid.*, **87**, 3311 (1965); *ibid.*, **88**, 236 (1966).

and alkenyl alkyl ethers⁽¹³⁾ have shown that the *cis* isomers are less stable than the corresponding *trans* isomers by approximately 1 kcal mol$^{-1}$. The energy difference roughly checks with the difference in the heats of complexation observed.

Thus, so far as the relative stabilities of the silver ion complexes of the *cis* and *trans* isomers of olefins or ethers are concerned, the concept of steric hindrance of bulky groups affecting the $\Delta H$ to different extents appears to be improbable. We feel that it is rather through the $\Delta S$ term that the steric effect of bulky groups influences the complexation to different extents depending on their placements, *cis* and *trans*. That is, the spatial limitation imposed on the location of the silver ion in the complexes of *trans* isomers perhaps has reflected in larger losses of entropy than would be expected if no such limitation existed. Thus, the entropy losses of *trans* isomers may well become comparable in magnitude with those of *cis* isomers, despite the smaller enthalpy losses of the former. This violation of the compensation rule between $\Delta H$ and $\Delta S$ must be an origin of such a separation of the $\Delta H$-$\Delta S$ linear relationships for the two isomers as has been shown in Figs. 3 and 4.

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13) T. Okuyama, T. Fueno, J. Furukawa and Y. Yonezawa, to be published.