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The Structure-Stability Relationship of the Metal Ion Complexes of Unsaturated Compounds. V. Stabilities of the Silver-Ion Complexes of Some *cis*-Stable Olefins

Tadashi Okuyama and Takayuki Fueno
Faculty of Engineering Science, Osaka University, Toyonaka, Osaka
and Junji Furukawa
Department of Synthetic Chemistry, Kyoto University, Sakyo-ku, Kyoto

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The silver-ion complexation equilibria of a few *cis*-stable olefins have been investigated in an aqueous phase at 25°C. The *trans* isomers of β-chlorovinyl ethyl ether and 1,2-dichloroethylene were found to have greater equilibrium constants than the corresponding *cis* isomers. It was concluded that the relative stabilities of parent olefin isomers play an exclusive role determining their relative complexation abilities.

The stability of the silver ion-olefin complexes in relation to the structure of the olefins has been investigated by several groups of workers[1-9] and discussed in terms of steric, strain, and electronic effects. The electronic effect was examined from the influence of substituents on the argentation equilibria of benzene,[2b] styrene,[7] and ethylene.[8] As for the steric and strain effects, various aliphatic[1,5,6] and alicyclic olefins[3,5] as well as some alkynes[4,5] have been investigated.

Some of the above investigations include several geometrical isomer pairs of alkenes, in which the greater complexation abilities of *cis* isomers have been interpreted in terms of the effects of steric hindrance and strain relief.[1d,5,6] We have previously studied similar complexations of a variety of *cis*- and *trans*-alkenyl alkyl ethers and found that the *cis* isomers form more stable complexes with the silver ion than do the corresponding *trans* isomers.[9] It was suggested that the greater complexation abilities of the *cis* isomers be due to their relative instability at the ground state. Although the origin of this is rather ambiguous as yet, it may be conceivable that, in cases where the instability is ascribable to the steric strain of the crowded *cis* substituents, the relief of strain on complexation would be a factor responsible for the greater stability of the complexes of *cis* isomers. However, such an interpretation of the effects of geometrical isomerism seems to be biased because all the olefins treated so far have been those that are known to be more stable in the *trans* form.

The present study will treat the silver-ion complexation of a few *cis*-stable olefins with particular interest in the relative stabilities of the complexes formed from *cis* and *trans* isomers. The *trans* isomers have proved to form more stable complexes in the present cases. This finding provides a favorable counterpart to the previous interpretation and supports the concept that the ground-state stability of the olefins is a major factor governing the effect of geometrical structure of olefins on stabilities of their silver-ion complexes.

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Experimental

Materials. *cis*- and *trans*-β-chlorovinyl ethyl ethers (CVE) were obtained as described previously.[10] *cis*- and *trans*-1, 2-dichloro- (DCE) and 1,2-dibromoethylenes (DBE) were purchased and distilled. Cyclohexane, toluene, silver nitrate and potassium nitrate were of the best commercial grade.

Procedure. The equilibrium constants, K, for the formation of the silver-ion complexes in the aqueous phase

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

were measured at 25°C by the solubility method in the same manner as described previously.[7] The volumes of the olefins and the aqueous phase were 1 and 10 m*l*, respectively.

The concentrations of olefins in the aqueous phase were determined by gas chromatography after extraction with cyclohexane. Five-hour shaking of an aqueous phase (5 m*l*) with cyclohexane (1 m*l*) was sufficient to complete the extraction of an olefin.[7] Cyclohexane used here contained 2 vol% toluene as an internal standard for the gas-chromatographic determination. A Shimadzu model GC-2C gas chromatograph was used with a column packed with polyethylene glycol (for DCE and DBE) or apiezon grease L (for CVE). It was found by calibration that the half-height width method fully sufficed for linearly correlating the obtained peak area to the olefin concentration.

Results

Solubility experiments were undertaken in the dark, and during that time no appreciable side reaction was observed. The solubilities of the isomeric pairs of β-chlorovinyl ethyl ether (CVE), 1,2-dichloroethylene (DCE) and 1,2-dibromoethylene (DBE) in aqueous $AgNO_3$-KNO_3 solutions are listed in Table 1. The experiments for DBE and CVE were conducted with the mixture of isomers, and the concentrations of respective isomers were determined separately. It was confirmed that such an expedience introduced no serious error into the K-values.[11] The composition of isomers in the organic phase was assumed to be invariant during the equilibrium experiments, as the amount of the substrate transferring from the organic to the aqueous phase was only of the order of 1% of the total olefin used.

The equilibrium constants, K, were calculated by the least squares treatment of the solubility data according to the equation[7]

$$K = ([M]-[M]_0)/[Ag^+][M]_0 \qquad (2)$$

where $[M]_0$ is the olefin concentration in the aqueous phase at $[Ag^+]=0$. The equilibrium leading to the formation of the 2 : 1 complex, Ag_2M^{2+}, was ignored since its contribution was immaterially small.

The equilibrium constants, K, calculated from Eq. (2) for the isomeric olefins are given in Table 2, together with the related data available in the literature. Although the K values for the disubstituted polar olefins studied here are very small, the differences between the respective geometrical isomers are certainly significant. The *trans* isomers of CVE and DCE have greater K values than their *cis* isomers (**1** and **2**). This finding is the

TABLE 1. SOLUBILITIES[a] OF OLEFINS IN AQUEOUS $AgNO_3$-KNO_3 SOLUTIONS[b] AT 25°C

$[Ag^+]$, mol/*l*	$[M]\times 10^2$, mol/*l*	
	cis	*trans*
	$ClCH{=}CHOC_2H_5$[c]	
0.00	0.421	0.914
0.60	0.502	1.244
1.00	0.552	1.454
	$ClCH{=}CHCl$[d]	
0.00	5.78	3.45
0.60	6.55	4.20
1.00	7.56	4.96
	$BrCH{=}CHBr$[e]	
0.00	1.096	0.560
0.20	1.229	0.632
0.60	1.527	0.756
1.00	1.844	0.878

a) Averages of three or four independent measurements. Accurate to within ±6%

b) Ionic strength $\mu = 1.00$

c) Isomeric composition: *cis*/*trans* = 11.5/88.5

d) Isomeric purities: *cis*, 97.8%; *trans*, 97.6%

e) Isomeric composition: *cis*/*trans* = 56.9/43.1

TABLE 2. THE EQUILIBRIUM CONSTANTS FOR ARGENTATION OF SOME 1,2-DISUBSTITUTED ETHYLENES, $R_1CH{=}CHR_2$, AT 25°C

No.	Substituent		K, *l*/mol		Stable isomer
	R_1	R_2	*cis*	*trans*	
1	Cl	OC_2H_5	0.32	0.59	*cis*[c]
2	Cl	Cl	0.25	0.40	*cis*[d]
3	Br	Br	0.68	0.56	*cis*≃*trans*[e]
4	CH_3	CH_3	62.3[a]	24.6[a]	*trans*[d]
5	CH_3	OC_2H_5	3.13[b]	0.54[b]	*trans*[c]

a) Ref. 1d.

b) Ref. 9, in ethylene glycol at 20°C.

c) Ref. 12.

d) Ref. 13.

e) R. M. Noyes and R. G. Dickinson, *J. Am. Chem. Soc.*, **65**, 1427 (1943).

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[11] The solubilities of pure *cis*-CVE were 3.63, 4.34 and 5.06×10^{-2} mol/*l* for the silver ion concentrations of 0.00, 0.60 and 1.00 mol/*l*, respectively. These data lead to the equilibrium constant K=0.39 *l*/mol, which is in fair agreement with K=0.32 *l*/mol obtained from the experiments with the mixture of *cis*- and *trans*-CVE.

first demonstration that *trans* isomers of some α,β-disubstituted ethylenes can form more stable silver-ion complexes than the corresponding *cis* isomers. On the other hand, the K value of *trans*-DBE is comparable in magnitude with that of the corresponding *cis* isomer (**3**).

Discussion

The different abilities of geometrical isomers in forming complexes with the silver ion have already been reported for several alkenes[1d,5,6] and alkenyl alkyl ethers.[9] In all these cases, the *cis* isomers have greater equilibrium constants than the corresponding *trans* isomers, as shown in Table 2 (**4** and **5**). Such effects of the geometrical isomerism on the stabilities of the complexes have been interpreted in terms of strain effects.[1d,5,6] That is, the strain due to the group repulsions present in the *cis* isomers may be relieved on the formation of the complexes, which largely contributes to the stability of the complexes of *cis* isomers.

However, the concept of the strain relief effect is clearly inapplicable to the *cis*-stable olefins, because such a strain, if present, should be of minor importance. In fact, *cis* isomers of CVE and DCE, which were found to be more stable than the respective *trans* isomers,[12,13] have proved to form less stable complexes than do their *trans* isomers. On the other hand, all of the previous studies reporting the greater complexation abilities of *cis* isomers have been confined to the *trans*-stable olefins, where the strain may destabilize the *cis* isomers. In the case of DBE (**3**), in which both isomers are known to have nearly equal stabilities at the ground state, the K value of the *cis* isomer is only a little greater than that of the *trans* isomer. This result also accords with the expectation from the stability of the parent isomeric olefins. Thus, a more generalized idea might be that the isomers of lesser stability in the ground state lead to the more stable complexes. In other words, any structural difference between *cis* and *trans* isomers is relieved by the loosening of the olefinic double bonds on complexation, and hence the ground-state stability determines the stability of the complexes formed. In this sense, therefore, the term "stabilization effect" would be of more general use than the customary term "strain effect."

In conclusion, the relative stabilities of the silver-ion complexes of geometrical isomers are determined primarily by the relative stabilities of parent isomeric olefins. The less stable isomers, whether they are *cis* or *trans* and whatever the origin of their relative stabilities may be, have greater ability for the silver-ion complexation than their isomeric partners which are more stable.

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