

Thermodynamics of the Silver-Olefin Bond: the Influence of Chelation and the Symbiotic Effect

By D. S. BARNES, G. J. FORD, L. D. PETTIT,* and C. SHERRINGTON

(Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT)

Summary Enthalpy and entropy changes in the formation of chelated complexes in aqueous solution between Ag^+ and some thio- and seleno-alkenes demonstrate the thermodynamic origin of the symbiotic effect and the importance of using the lowest possible temperatures for reactions involving the co-ordination of olefins.

CO-ORDINATE bond formation between metal acceptors and olefinic bonds is one of the major aims of synthetic organometallic chemistry, yet surprisingly little is known of its thermodynamic properties or factors which influence its stability. In particular there is no quantitative information on the 'symbiotic' effect¹ of other ligands co-ordinated to the metal ion. We report the results of a study of the thermodynamics of complex formation in aqueous solution between Ag^+ and bidentate ligands containing both an olefinic bond and either S or Se donor atoms. The ligands studied were of general formula $\text{R}\cdot\text{X}\cdot\text{CH}_2\text{CO}_2^-$ where $\text{X} = \text{S}$ and Se and $\text{R} =$ but-1-enyl, pent-1-enyl, and butyl. It was assumed that the difference between complexes of unsaturated ligands and the butyl substituted ligands would give a direct measure of the effects of metal-olefin bonding.

character is significantly greater when a selenium atom is also bonded to the silver rather than a sulphur—a demonstration of the 'symbiotic' effect. A comparison of the results for the formation of the bis-complex with those for the formation of the mono-complex demonstrates this even more clearly. For both S and Se ligands the free energy change $\Delta(\Delta G)$ is unfavourable, presumably because the second step of the reaction ($\text{AgL} \rightarrow \text{AgL}_2$) corresponds to a change in co-ordination number for Ag^+ from 1 to 2 for the butyl substituted complexes and from 2 to 3 or 4 for the but-1-enyl analogues. This, however, disguises the fact that the step is strongly exothermic and the symbiotic effect is even more marked. This exothermic nature is presumably the result of the extensive orbital overlap in both the Ag-S (or Se) and the Ag-olefin bonds.

The large negative entropy changes are more interesting. Chelation would cause a reduction in the internal entropy of the ligands but this would not be sufficient to account for the entropy changes found. A more important contribution would be the influence of the ligands on the solvent. The free, long-chain ligands would be strongly structure-breaking. On chelation they would be constrained towards a tight spherical conformation allowing for more

Thermodynamic properties of silver complexes in kJ mol^{-1} at 25° and $I\ 0.20\ \text{M}$. Standard deviations in parentheses.

Ligand	$\text{Ag} + \text{L} \rightarrow \text{AgL}$			$\text{Ag} + 2\text{L} \rightarrow \text{AgL}_2$		
	$-\Delta G$	$-\Delta H$	$-T\Delta S$	$-\Delta G$	$-\Delta H$	$-T\Delta S$
$\text{C}_4\text{H}_9\text{SCH}_2\text{CO}_2^-$	22.39(2)	28.5(5)	6.1(5)	42.7(2)	58(2)	16(2)
$\text{CH}_2:\text{CH}(\text{CH}_2)_2\text{SCH}_2\text{CO}_2^-$	27.24(3)	46.1(6)	18.9(6)	40.1(4)	126(11)	85(11)
$\text{CH}_2:\text{CH}(\text{CH}_2)_3\text{SCH}_2\text{CO}_2^-$	23.91(2)	35.1(3)	11.2(3)	40.0(6)	55(10)	15(10)
$\Delta(\text{But-1-enyl} - \text{butyl})$	4.85	17.6	12.8	-2.6	68	70
$\text{C}_4\text{H}_9\text{SeCH}_2\text{CO}_2^-$	26.10(2)	32.6(8)	6.5(8)	45.8(1)	60(1)	14(1)
$\text{CH}_2:\text{CH}(\text{CH}_2)_2\text{SeCH}_2\text{CO}_2^-$	29.48(2)	54.5(8)	25.0(8)	45.4(2)	155(18)	110(18)
$\text{CH}_2:\text{CH}(\text{CH}_2)_3\text{SeCH}_2\text{CO}_2^-$	26.42(3)	38.2(18)	12(2)	43.8(2)	71(7)	27(7)
$\Delta(\text{But-1-enyl} - \text{butyl})$	3.38	21.9	18.5	-0.4	95	96

The species AgL , AgL_2^- , and Ag_2L^+ were shown to be present in significant concentrations under the conditions used. Silver complex formation constants were measured potentiometrically over the temperature range of $0-40^\circ$ at pH 5.8.² Some of the calculated constants are given in the Table. In all cases enthalpy changes favoured co-ordination while entropy changes opposed it as expected for typically 'soft' interactions.³ This effect is larger for Se than for S. Chelation through the but-1-enyl ligands is much more marked than through the pent-1-enyl analogues demonstrating clearly that the effect of ring size affects ΔH and ΔS to comparable amounts.

The results shown in the Table confirm that co-ordination through a double bond is strongly exothermic and opposed by a large unfavourable entropy change. This 'soft'

structure to the solvent. Hence, chelation should be accompanied by a negative entropy change: a reverse chelate effect.

Since co-ordination through a double bond is exothermic while being opposed by entropy changes, the temperature at which synthetic organometallic reactions involving such co-ordination is carried out is very important. It will be particularly important when chelation reactions involving other 'soft' donor centres (*e.g.*, σ -bonded carbon atoms) are also involved. Temperatures should be kept as low as the kinetics of the reaction permit. This should be an important consideration in the selection and design of catalysts for the reactions of alkenes and alkynes.

(Received, May 5th, 1971; Com. 707.)

¹ C. K. Jorgensen, *Inorg. Chem.*, 1964, **3**, 1201.

² D. S. Barnes, P. G. Laye, and L. D. Pettit, *J. Chem. Soc. (A)*, 1969, 2073.

³ S. Ahrland, *Helv. Chim. Acta*, 1967, **50**, 306.