Thermodynamic Data for Olefin and Acetylene Complexes of Transition Metals

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Received September 6, 1972 (Revised Manuscript Received October 30, 1972)

Contents

I. Introduction

A knowledge of the thermodynamics of the interaction of a metal and a ligand can give considerable insight into the nature of the metal–ligand bond and the factors responsible for its stability. Accordingly, a large number of studies of the free energy, enthalpy, and entropy of formation of metal complexes have been reported.[1] Metal–olefin complexes have gradually assumed an increasing importance with the recognition of their involvement in a number of synthetically useful reactions such as the oxidation, hydrogenation, isomerization, and carbonylation of olefins, all of which are catalyzed both homogeneously and heterogeneously by transition metal salts. The vast literature on metal–olefin complexes has been sparingly sprinkled with reports of the thermodynamics of metal–olefin interactions. One reason for the scarcity of such data is that olefins, compared with many of the simpler widely studied ligands, present some rather special problems. First, the simpler olefins are gases necessitating the use of closed reaction vessels and a need to incorporate pressure measuring devices. Secondly, the ideal solvent for any thermodynamic measurement is water because of its lack of volatility and the ease with which a constant background ionic strength can be maintained, but only olefins with strongly hydrophilic functional groups such as OH, NH_3^+, or SO_3^- are reasonably soluble in water.

The object of the present review is, first, to consider the methods that have been used in studying the thermodynamics of metal–olefin interactions to enable the future worker in the field to readily choose the most suitable and most accurate method for his particular problem; secondly, to tabulate the thermodynamic data available up to mid-1972 as a convenient source of reference; thirdly, to analyze the available data to see what information it yields about the nature of metal–olefin interactions. While some of the necessary background to the thermodynamics of metal–ligand interactions is given here, the interested reader is referred particularly to the excellent text by Rossotti and Rossotti[2] as well as to other more recent works.[3-5] A number of detailed accounts of the chemistry of metal–olefin complexes have been given.[6-16]

II. Methods of Measurement

A. Free Energies of Formation in Solution

The determination of the free energy of interaction of a metal complex and an olefin in solution depends upon finding a reversible reaction in which an olefin displaces a ligand from the coordination sphere of the metal ion

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$$[ML_n] + ol \rightleftharpoons [ML_{n-1}(ol)] + L \qquad (1)$$

(eq 1). This reaction may be followed by the reversible displacement of further ligands L or, if the olefin contains more than one double bond, by coordination of the olefin to further metal ions. The necessary feature is that a finite time after the metal and olefin solutions have been mixed an equilibrium should be established. This may sound rather pedantic, but metal ions often catalyze the reactions of olefins so that the system does not come to equilibrium at all. For example, a solution of ethylene in water is quite stable, but in the presence of palladium(II) salts ethylene reacts with water to yield acetaldehyde, and the palladium(II) is reduced to metallic palladium.

For a system represented by eq 1 it is possible to write a *thermodynamic* equilibrium constant $K°$, where braces are used to represent activities.

$$K° = (\{ML_{n-1}(ol)\}\{L\})/(\{ML_n\}\{ol\})$$

This *thermodynamic* equilibrium constant is related to the free energy change by the expression

$$\Delta G° = -RT \ln K°$$

The associated enthalpy and entropy changes are given by the well-known equation

$$\Delta G° = \Delta H° - T\Delta S°$$

Thus, if it were possible to measure the activities of each of the species in eq 1 in solution, it would be possible to evaluate the free energy of formation of the metal-olefin complex. However, activities cannot be measured directly, although concentrations can. It is therefore convenient to rewrite the *thermodynamic* stability constant $K°$ as a *stoichiometric* stability constant K defined in terms of concentrations. The *stoichiometric* stability constant for eq 1 is given by

$$K = ([ML_{n-1}(ol)][L])/([ML_n][ol])$$

where brackets are used to represent concentrations. It can be seen that the *thermodynamic* and *stoichiometric* stability constants are related by the products of the activity coefficients (γ) of the reactants and products.

$$K° = K\left\{\frac{(\gamma_{ML_{n-1}(ol)})(\gamma_L)}{(\gamma_{ML_n})(\gamma_{ol})}\right\}$$

When measurements are made at very low concentrations, as in the determination of conductivities, the activity coefficients approach unity so that there is little error involved under these circumstances in considering *stoichiometric* stability constants to be *thermodynamic* stability constants. Occasionally it is possible to measure the *stoichiometric* stability constants over a range of ionic strengths and to extrapolate to zero ionic strength, so obtaining *thermodynamic* stability constants. More often, however, since almost as much information can be obtained for a series of olefins from the relative *stoichiometric* stability constants and their attendant free energies, enthalpies, and entropies, no such extrapolation is attempted. Instead, a high concentration of a background electrolyte is added to ensure that the activity coefficients of the species being studied remain effectively constant in spite of the change in concentration of these species. Since the activity coefficients are not evaluated but merely maintained at a constant (unknown) value, it is vital when recording the result to report not only the strength of the medium but also the nature of the inert background electrolyte used in the medium, since activity coefficients depend not only on the concentration but also on the nature of the electrolyte.[2]

In the case of reaction 1 the equilibrium constant is dimensionless. However, in the case of a chelating diolefin (diol) reacting according to eq 2, the equilibrium con-

$$[ML_n] + \text{diol} \xrightleftharpoons{K_2} [ML_{n-2}(\text{diol})] + 2L \qquad (2)$$

$$K_2 = [ML_{n-2}(\text{diol})][L]^2/[ML_n][\text{diol}]$$

stant K_2 will have the dimensions of concentration. For the resultant free energy, enthalpy, and entropy terms to have meaning, it is vital that the concentration be expressed in the correct units for the standard state, that is, in moles of solute per liter of solvent. So far the solvent has been omitted from all the equations in agreement with standard procedure. This is justifiable provided that the reactants are in such low concentrations that the activity of the solvent remains effectively constant throughout the series of measurements. For most methods of investigation, sufficiently low concentrations of metal ions are used for this to be true but in some methods, such as certain applications of gas chromatography, where very high concentrations of metal ions have been used, the results are likely to be in error on this account.

B. Methods Used to Measure Equilibrium Constants

Since the reliability of a given equilibrium constant depends to a considerable extent on the method used for its measurement, a brief discussion of the methods that have been used to measure the equilibrium constants in metal-olefin systems is given. Although these methods cover most of the important methods that have been used for other metal-ligand systems, there are a number of other techniques which it may be appropriate to use in the future. For these the reader should consult the literature.[2,4] In choosing a suitable method the following points should be carefully considered.

(a) Is the solvent being used one in which the activity coefficients of the reacting species can be controlled by the addition of a background electrolyte? It is this extremely important factor that has led to the widespread use of water as a solvent, although some organic solvents, such as acetic acid and ethylene glycol, are also capable of dissolving sufficient quantities of inert salts to enable activity coefficients to be controlled.

(b) Are all the so-called "constants" in the system truly constant? In a number of techniques parameters, such as partition coefficients in gas chromatography or extinction coefficients in electronic spectroscopy, are involved. It is obviously essential that these "constants" are truly constant and do not vary with the concentration of one or more of the reacting species. This is discussed in more detail below in connection with gas chromatography.

(c) Does the method give results in agreement with other independent methods, and what is its inherent accuracy?

(d) Is the apparatus available or obtainable? Thus potentiometry has been described[17] as "by far the most accurate and widely applicable technique currently available for the study of ionic equilibria." However, its application to a specific system does depend on the availability of a suitable electrode that is reversible in the solvent that is to be used.

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(17) Reference 2, p 127.

We now look at the techniques that have been applied so far to the study of metal-olefin equilibrium constants. The object of doing this is to give the reader some idea of the difficulties that have been met by previous workers in the field and hence an idea of the accuracy of the reported data. In addition it is hoped that the future worker in the field may get some feel for the techniques that are available. However, before applying a particular technique it will need to be studied in more detail than is given here.

1. *Potentiometry*

This is easily the most accurate and widely used method for the determination of equilibrium constants. However, its application is limited to those systems for which suitable reversible electrodes are available. Among the transition metals the principal electrodes that are reported to be reversible in aqueous solution are $Fe|Fe^{2+}$,[18] $Co|Co^{2+}$,[18] $Ni|Ni^{2+}$,[18] $Pd|Pd^{2+}$,[19] $Cu|Cu^{+}$,[20] $Ag|Ag^{+}$,[21] $Au|Au^{+}$,[2] $Hg|Hg^{2+}$,[22] and $Ag|AgCl$,[23] and only the latter appears to have been studied to any extent in nonaqueous solvents.[24] The potential of the electrode is given by the Nernst equation

$$E = E_0 - (RT/zF)\ln\{M\}$$

where $\{M\}$ is the activity of the free metal ion in solution. If the measurements are carried out in the presence of a sufficient concentration of a background electrolyte, the potential can be written in terms of concentrations.

$$E = E_0' - (RT/zF)\ln[M]$$

This equation is valid in a 3 *M* perchlorate medium for divalent metal ions up to 0.1 *M* concentrations and for trivalent metal ions up to 0.05 *M* concentrations.[25] The presence of a term in the Nernst equation dependent on the absolute temperature makes it doubly important in any potentiometric method to maintain the temperature within ±0.05° of a constant value, since changes in temperature affect not only the position of the equilibrium under study but also the emf generated by a given concentration of metal ions.

One of the major difficulties to be surmounted in any potentiometric measurement is the choice of a suitable reference electrode. In some cases it is possible to insert a reference electrode directly into the solution under test, but more often this is not possible and some kind of bridge has to be used. For this purpose the present author has found a Wilhelm salt-bridge with a "J-shaped" liquid junction to be very suitable.[26] Any salt bridge will develop a liquid junction potential although this can be minimized by using a salt such as potassium chloride where the mobilities of the cations and anions are very similar. In spite of a number of attempts no really accurate methods have been developed for calculating liquid junction potentials.[27] However, in the case of olefins the present author has shown that this is no real problem, because by titrating both the olefin and the corresponding saturated compound, which cannot, of course, complex with the metal ion, it is possible to measure accurately the liquid junction potential.[28]

If care is taken over all aspects of the measurement, it is possible to obtain stability constants using a potentiometric technique with an accuracy of better than 1%.

2. *Ultraviolet and Visible Spectrophotometry*

When an olefin displaces a ligand from coordination to a metal ion, there is a change in the electronic spectrum of the complex. This can be used to determine the equilibrium constant between the metal and the olefin and is very suitable because the extinction coefficients of complexes are generally large in some region of the electronic spectrum enabling small quantities of metal ions to be used, thus enabling activity coefficients to be readily held at a constant value with the aid of a background electrolyte. The method is unsuitable for studying very weak complexes, since these would require the use of very high concentrations of ligand. Such high concentrations of ligand would alter the nature of the medium, and the extinction coefficients of complexes are very sensitive to the nature of the medium, both the solvent and the nature and concentration of any added material such as the background electrolyte. Even in the absence of any specific interaction between particles, the presence of a high concentration of material (such as uncomplexed ligand) can lead to a change in the charge-transfer spectrum and hence extinction coefficient of the complex.[29] From this change apparent association constants of up to 0.2 l. mol^{-1} can be obtained, so that this represents the lower limit of stability constants that can be measured spectrophotometrically.

The absorbance (*A*) of a dilute solution is given by Beer's law

$$A = l\sum_i \epsilon_i c_i$$

where ϵ_i = extinction coefficient, and c_i = concentration of species *i*, and *l* = cell length. Before using a spectrophotometric technique it is essential to ensure that the solutions obey Beer's law. Failure to obey Beer's law can be due to either instrumental errors such as spectral impurity of the radiation, nonlinear response of the photocell, multiple internal reflection of the radiation or nonparallelism of the radiation, or to having too high a concentration of absorbing species present. Beer's law is not obeyed at high concentrations because neighboring molecules interact, causing changes in the extinction coefficients.

The accuracy of the method depends very much on the number of complexes formed, getting progressively less accurate as more complexes are formed. If one considers the simple system

$$[ML_n] + ol \rightleftharpoons [ML_{n-1}(ol)] + L$$

and if $[ML_n]$ and $[ML_{n-1}(ol)]$ are the only species that absorb at the wavelength being used, then it is apparent that as a result of the measurement there are five known parameters (total M, L, and ol concentrations, the extinction coefficient of ML_n, and the total absorbance). In general, there are six unknown parameters (final concentrations of $[ML_n]$, $[ML_{n-1}(ol)]$, free olefin, and L, the extinction coefficient of $[ML_{n-1}(ol)]$, and *K*, the equilibrium constant), but it is possible to add an extra known pa-

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rameter by varying the total concentration of olefin and then adding the condition that the equilibrium constant is independent of olefin concentration. In this way a least-squares analysis can be used to evaluate all the unknown parameters and hence the equilibrium constant. This procedure can in principle be extended to any number of complexes, but because of correlation of some of the constants with each other, the accuracy drops significantly. Using a single-beam spectrophotometer in the most accurate absorbance range (0.15–0.50), it is possible by taking all possible precautions to obtain stability constants for systems that only form a single metal–olefin complex that are accurate to better than 3%.[30]

3. *Infrared Spectroscopy*

Infrared spectroscopy is potentially very useful since the olefinic double-bond stretching vibration shifts in frequency on coordination, so that in principle the concentrations of both free and coordinated olefin could be determined from a single spectrum. The method, however, has not been used in this way for a number of reasons.

(a) The extinction coefficient of the double-bond stretching vibration is low so that high concentrations of olefin and olefin complex would have to be present. High concentrations are not only inconvenient but they are also detrimental to the accuracy of the determination as discussed in section II.A above.

(b) Most solvents, particularly water, absorb infrared radiation strongly in the same region as the olefinic double bond. The exclusion of water makes the control of activity coefficients difficult.

(c) An essential feature of the design of an infrared spectrometer is that polychromatic light is passed through the sample. This inevitably limits the accuracy of the resulting absorbance values.

Infrared spectroscopy has been used to measure the concentration of ethylene in the vapor phase above a saturated solution of the metal complex. The most intense band in the spectrum, which is at 952 cm^{-1}, was used, but even then the accuracy was only about 10%.[31]

4. *Raman Spectroscopy*

The resurgence of interest in Raman spectroscopy, which has followed the commercial manufacture of instruments using lasers as the source of exciting radiation,[32] has not yet led to its use in measuring equilibrium constants for the formation of metal–olefin complexes. This is undoubtedly partly due to the difficulty of thermostating the sample against the considerable heating effect of the laser beam and partly due to the low intensity of the Raman spectrum, necessitating the use of concentrated solutions. In principle, the method should be more useful than infrared spectroscopy because glass cells and aqueous solutions can be used. A neat answer has been found to the practical difficulty of setting up the instrument in an identical manner for every solution to be studied by comparing the relative intensities of two bands.[33] If one of these is due to the free olefin and the other to the metal–olefin complex, then the ratio of the integrated intensities can be used directly in evaluating the stability constant.

5. *Nuclear Magnetic Resonance*

Nuclear magnetic resonance is potentially a very attractive method for determining the position of equilibrium, since an integrated nmr spectrum immediately yields the relative number of magnetic nuclei in each environment. Ideally, therefore, in a system with two types of species present (*e.g.*, free and coordinated ligands) peaks due to each species would be observed and the concentration dependence of their relative areas measured. The keto–enol tautomerism of acetylacetone has been studied in this way.[34] One of the difficulties of applying nmr spectroscopy to the determination of stability constants is that the magnitude of the chemical shifts is often dependent on the nature and the concentrations of the inert ions present[35,36] and therefore, by implication, on the concentrations of the metal and ligand species. However, in the case of metal–olefin complexes a further, more serious, difficulty arises in that, because of the rapid exchange between free and coordinated olefins, it is not possible to observe two chemical shifts but only a single time-averaged shift. In order to use this time-averaged chemical shift, it is essential to know the chemical shift expected for the coordinated olefin. In the only olefin system studied so far this was determined by adding more and more metal salt until no further change in the chemical shift was observed when it was assumed that all the olefin had been complexed.[37] Such a technique is liable to underestimate the change in chemical shift on coordination and hence overestimate the equilibrium constant.

It is possible for systems in which only a single metal–olefin complex ([M(ol)]) is formed to determine the chemical shift indirectly by a similar technique to that used to evaluate unknown extinction coefficients in section II.B.2.[37a] For the system

$$[\mathrm{ML}] + \mathrm{ol} \rightleftharpoons [\mathrm{M(ol)}] + \mathrm{L}$$

in the limit of fast exchange, the observed chemical shift (τ_{obsd}) is given by

$$\tau_{\mathrm{obsd}} = \tau^{\mathrm{ol}}\chi^{\mathrm{ol}} + \tau^{\mathrm{M(ol)}}\chi^{\mathrm{M(ol)}}$$

where χ = mole fraction. Since

$$\chi^{\mathrm{ol}} = (n^{\mathrm{ol}} - X)/n^{\mathrm{ol}} \text{ and } \chi^{\mathrm{M(ol)}} = X/n^{\mathrm{ol}}$$

where n^{ol} = initial number of moles of olefin and X = number of moles of L and M(ol) at equilibrium

$$\tau_{\mathrm{obsd}} = \tau^{\mathrm{ol}}[(n^{\mathrm{ol}} - X)]/n^{\mathrm{ol}} + \tau^{\mathrm{M(ol)}}(X/n^{\mathrm{ol}})$$

Rearrangement gives

$$X = \frac{n^{\mathrm{ol}}\tau_{\mathrm{obsd}} - \tau^{\mathrm{ol}}n^{\mathrm{ol}}}{\tau^{\mathrm{M(ol)}} - \tau^{\mathrm{ol}}}$$

whence

$$K = \frac{X^2}{(n^{\mathrm{ML}} - X)(n^{\mathrm{ol}} - X)}$$

where n^{ML} = initial number of moles of ML. The equilibrium constants for a series of solutions of different metal

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and olefin concentrations are calculated using a "guessed" value for the chemical shift of the metal-olefin complex ($\tau^{M(ol)}$), and this value is adjusted until the calculated stability constant is independent of the initial metal and olefin concentrations. Such a procedure is clearly only possible where a single metal-olefin complex is formed.

This necessity to assume that only a single metal-olefin complex is formed is often a problem with the nmr method because while the nmr experiment can distinguish between free and coordinated olefin it cannot always distinguish between olefin complexes containing different numbers of olefins. The assumption that only one olefin complex is formed, even if valid at normal concentrations, may well break down in the presence of the high metal concentrations used in the direct method for determining the chemical shift of the coordinated olefin.

In conclusion, nmr does not appear to be a particularly satisfactory method for determining metal-olefin stability constants largely because of the rapid exchange of free and coordinated olefin and the problems that result from this.

6. *Solubility Methods*

Equilibrium constants for the formation of metal-olefin complexes have been determined both by measuring the solubility of the metal salt in the olefin solution[38] and by measuring the solubility of the olefin in the metal salt solution.[39] For accurate results three criteria must be met.

(a) A constant ionic medium must be used to ensure that the activity coefficients remain constant.

(b) Since the solubility product is fixed so that the concentration of olefin cannot be varied independently of the metal ion concentration, it is impossible to obtain sufficient data to ascertain whether or not polynuclear species are present. Accordingly, the method cannot be used in cases where polynuclear species are suspected.

(c) It is essential to ensure that the composition of the solid phase and hence its solubility product remains constant over the concentration ranges of metal and olefin being investigated.

Unless the olefin is a gas, the use of solubility methods[39a] depends upon the accurate analysis of the saturated solution. A wide range of analytical techniques is available;[40] high concentrations are often determined gravimetrically or volumetrically and low concentrations can be determined by polarography, spectrophotometry, or radiometry.

It has been suggested that instead of the *stoichiometric* stability constant K_1 ($K_1 = [\mathrm{Ag(ol)^+}]/[\mathrm{Ag^+}][\mathrm{ol}]$) the *thermodynamic* stability constant $K_1°$ ($K_1° = K_1\gamma_{\mathrm{Ag(ol)^+}}/\gamma_{\mathrm{Ag^+}}\gamma_{\mathrm{ol}}$, where γ = activity coefficient) is a more useful parameter to obtain from the solubility studies of hydrocarbons in aqueous silver salt solutions. Thus in the case of a series of acetylenes, increasing substitution on the acetylene had little influence on the value of K_1 although $K_1°$ decreased as expected.[41] *Thermodynamic* stability constants are normally very difficult to evaluate, but in the present case, for hydrocarbons that are virtually insoluble in water, it can be shown that, at very low silver ion concentrations, $K_1°$ is approximately equal to $K_1[\mathrm{ol}]$.

As the silver ion concentration tends to zero, $\gamma_{\mathrm{Ag(ol)^+}}/\gamma_{\mathrm{Ag^+}} = 1$.

If the activity of the pure hydrocarbon at 25° is taken as unity, then the activity of the hydrocarbon in aqueous solution will be approximately unity (it will not be exactly unity because the hydrocarbon phase will not be pure owing to the presence of some dissolved water). Thus $[\mathrm{ol}]\gamma_{\mathrm{ol}} \approx 1$, and since $K_1 = [\mathrm{Ag(ol)^+}]/[\mathrm{Ag^+}][\mathrm{ol}]$

$$K_1° = \{[\mathrm{Ag(ol)^+}]/[\mathrm{Ag^+}][\mathrm{ol}]\}\{\gamma_{\mathrm{Ag(ol)^+}}/\gamma_{\mathrm{Ag^+}}\gamma_{\mathrm{ol}}\} = K_1/\gamma_{\mathrm{ol}}$$

but $\gamma_{\mathrm{ol}} \approx 1/[\mathrm{ol}]$; therefore, $K_1° \approx K_1[\mathrm{ol}]$.

7. *Distribution Methods*

The distribution of a metal between two immiscible liquid phases, one of which contains the olefin, has been one of the most widely used methods for determining silver-olefin stability constants. The results, however, are not always consistent with those obtained from other methods for a number of reasons.

(a) It is essential to choose an organic solvent that is only very sparingly soluble in the aqueous phase. Further the miscibility of the two solvents must remain constant over the whole range of metal and olefin concentrations used.

(b) Although the activity coefficients in the aqueous phase can be controlled by the use of an ionic background electrolyte, this is impossible in the organic solvent since ionic salts are not generally soluble in solvents that are immiscible with water. In a system such as

$$[\mathrm{ML}_n] + \mathrm{ol} \rightleftharpoons [\mathrm{ML}_{n-1}(\mathrm{ol})] + \mathrm{L}$$

it is possible to determine the range of concentration over which the activity coefficients in the organic solvent remain constant by determining the concentration range over which the ratio of the total metal concentration in each phase is a function of the ligand (L) concentration in the aqueous phase (where L is an ionic ligand that is insoluble in the organic phase) and is independent of the total concentrations of metal and olefin. Such a result would be unlikely to be obtained unless the activity coefficients in both phases remained constant.[42]

(c) In the case of weak complexes large changes in the free olefin concentration must be made, and care must be taken to ensure that, if the olefin is appreciably soluble in the aqueous phase, these large changes in concentration do not lead to changes in the composition of the solvents and hence to gross changes in the activity coefficients. Furthermore, even when the olefin is insoluble in water, large changes in its concentration are liable to lead to variations in its activity coefficient in the organic phase.

(d) Great care must be taken to investigate the possibility of the formation of polynuclear species, since even if these are not formed in aqueous solution they may still be formed in the organic phase.

In general, distribution methods are not to be recommended for the determination of accurate stability constants. Their most important drawback is the difficulty of controlling the activity coefficients in the organic phase. An important aspect of stability constants obtained by distribution methods that must be borne in mind when studying the literature is that some authors record the

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values of K_1^* ($K_1^* = [Ag(ol)^+]_{H_2O}/[Ag^+]_{H_2O}[ol]_{\text{organic-solvent}}$, where the subscripts refer to the phase in which the concentration is determined). Such constants are not strictly stability constants at all, although they may give indications of trends within a group of hydrocarbons if the distribution coefficients of the hydrocarbons between the two immiscible solvents are virtually independent of the hydrocarbon.

8. *Polarography*

When polarography is used to determine stability constants, the effect of the ligand on the reduction potential of a metal ion at a dropping mercury electrode, or less commonly a rotating platinum electrode, is determined.[43] The method is very difficult to use successfully and also rather inaccurate, but it does have the important advantage that it can identify and determine the properties of a number of species simultaneously. If the electrode process is reversible, the potential of the dropping mercury electrode (E) is given by the Heyrovsky-Ilkovič equation[44] with an accuracy of about ±2%.

$$E = (E_{1/2})_{\mathrm{M}} - (RT/zF)\ln\{(i)/(i_{\mathrm{d}} - i)\}$$

$(E_{1/2})_{\mathrm{M}}$ = the half-wave potential of the free metal ion in the solvent, z = number of electrons involved in the electrode reaction, i_{d} = limiting diffusion current, and i = current corresponding to potential E.

On adding a ligand, such as an olefin, the half-wave potential of the system is shifted by an amount (ΔE) proportional to the stability constant of the complex.[45]

$$\Delta E = (E_{1/2})_{\mathrm{M}} - (E_{1/2})_{\mathrm{M-ol}} = (RT/zF)\{\ln \beta_i + i \ln\,[\text{ligand}]\}$$

$(E_{1/2})_{\mathrm{M\text{-}ol}}$ = the half-wave potential of the metal-olefin complex, and β_i = the overall formation constant of $[\mathrm{M(ol)}_i]$. The main limitations of the method, apart from the inherent limitations in the Heyrovsky-Ilkovič equation are (a) the problems associated with the electrical double layer; (b) the need to maintain the temperature very accurately since in addition to the equilibrium under study both the diffusion current and the half-wave potentials are temperature dependent; and (c) the fact that, when full precautions are observed, the half-wave potential can be measured with a reproducibility of ±0.2 mV. In many cases only small differences in the half-wave potential occur in the presence of the ligand, so that the overall accuracy of the resulting stability constant is limited. As a result in the copper(I)-allyl alcohol system

$$\mathrm{Cu^+ + CH_2{=}CHCH_2OH \rightleftharpoons [Cu(CH_2{=}CHCH_2OH)^+]}$$

the stability constant was evaluated as 50,000 ± 25,000.[46]

9. *Gas Chromatography*

Gas chromatography, which seems to have first been applied to the silver-olefin system,[47] is potentially a very fast, elegant method for determining stability constants. A sample of the olefin is introduced onto the column of a standard gas chromatograph and eluted with an inert carrier gas. The columns are generally packed with firebrick soaked in the stationary liquid phase which is a solution of the metal salt in either water[47a] or a solvent, such as ethylene glycol,[47] in which the activity coefficients can be controlled by the addition of an inert background electrolyte. The partition coefficient (H) for the distribution of the olefin between the liquid and the vapor is given by[47]

$$H = \frac{3Ft_{\mathrm{r}}\{(P_{\mathrm{i}}/P_{\mathrm{o}})^2 - 1\}}{2V_l\{(P_{\mathrm{i}}/P_{\mathrm{o}})^3 - 1\}}$$

P_{i} = inlet pressure, P_{o} = outlet pressure, F = carrier gas flow rate, t_{r} = retention time, and V_{l} = volume of the liquid phase at the temperature of the column.

Thus by measuring the retention time and knowing the values of the other factors, the partition coefficient can be evaluated. By measuring the distribution coefficient of the olefin in the presence (H) and absence (H_0) of the metal, the equilibrium constant can be evaluated since

$$K = \frac{[\mathrm{M(ol)}]}{[\mathrm{M}][\mathrm{ol}]} = \frac{H - H_0}{H_0[\mathrm{M}]}$$

whence $H = H_0 + H_0K[\mathrm{M}]$. Thus a plot of the distribution coefficient against the concentration of the metal should be a straight line of slope H_0K and intercept H_0. Unfortunately, this simple situation does not always arise,[48] and plots of H against the metal concentration are not linear owing to a salting-out effect at high metal concentrations. This salting-out effect can, however, be overcome by using very high concentrations (*e.g.*, 4 *M*) of an inert electrolyte in the liquid phase.

There are a number of major disadvantages connected with the use of gas chromatography.

(a) To get accurately measurable differences between the partition coefficients in the presence and absence of metal ions, it has been necessary in the case of silver ions to use high concentrations of the metal ion, up to 4 *M*. This in turn has undesirable consequences in that firstly the accurate control of activity coefficients over such a wide concentration range is impossible, and secondly the approximation normally made that the solvent can be neglected in evaluating the stability constant is less valid than with the much lower metal ion concentrations normally used. This problem of the high concentration of metal ion needed in the case of silver should be less for many other metals where higher stability constants are observed, leading to greater slopes on the plots of distribution coefficient against metal ion concentration.

(b) The value of the equilibrium constant is dependent on the flow rate of the inert carrier gas, increasing slightly with increasing flow rate.[49] This is a major problem, firstly, because it has generally been neglected in the literature and, secondly, because it is very difficult to take account of because, although in theory a series of flow rates could be used and extrapolated to a zero flow rate, in practice this is not possible (i) because the number of runs necessary would lead to deterioration of the column and hence the incorporation of further errors and (ii) because as the flow rate is lowered the peak broadens and so the accuracy of the measurement of the retention time drops.

(c) The value of the equilibrium constant is dependent on the sample size, decreasing with increasing sample

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size. Again, ideally an extrapolation to zero sample size would be made, but this involves an undesirable number of runs which would lead to deterioration of the column and does not give very accurate results because of the increasing difficulty of measuring the retention times as the peaks get smaller.

In conclusion, it would appear that because of the importance of both sample size and carrier gas flow rate a given set of metal-olefin equilibrium constants obtained by a single group of workers should be internally consistent, but any agreement with equilibrium constants obtained by other methods is likely to be fortuitous rather than an indication of the reliability of equilibrium constants obtained by gas chromatography.

10. Thermometric Titration Calorimetry

Although it has not been applied to the determination of thermodynamic data for metal-olefin systems, thermometric titration calorimetry is a method that is likely to be used in the near future as it can in suitable cases give rise to free energy, enthalpy, and entropy data simultaneously. Basically the method involves titrating a solution of the metal complex with the ligand in a calorimeter and measuring the temperature of the system as a function of the amount of ligand added. The method has three main advantages over conventional solution calorimetry: (a) it can be used to study a number of simultaneous equilibria; (b) more data can be determined in a given time than with solution calorimetry; (c) provided that (i) the equilibrium constants and the reaction conditions are such that the amount of reaction occurring is measurable, but the reaction is not quantitative and (ii) the enthalpy values for the reactions are measurably different from zero, it is possible to obtain free energy and entropy as well as enthalpy data. The interested reader is referred to a recent review on thermometric titration calorimetry.[49a]

11. Nonpolar Solvents

So far we have indicated that, because of the problem of controlling activity coefficients, water or an alternative highly polar solvent is the ideal medium for determining stability constants. This follows the classical work on stability constants led by the Swedish schools. However, it has been suggested recently[37a] that nonpolar solvents such as benzene and carbon tetrachloride have a number of advantages as media for studying metal-olefin systems. These include the following. (a) The solvation terms in a nonpolar solvent would be much smaller than in a polar solvent and hence would more closely cancel to zero when two olefins are compared. (b) The structure of the reactants and products can be characterized more readily in the absence of a high concentration of a relatively strong nucleophile such as, for example, water. (c) The majority of metal-olefin reactions are run in nonaqueous solvents. (d) Most olefins and metal-olefin complexes are soluble only in nonaqueous solvents.

The major drawback of nonpolar solvents is that of controlling the activity coefficients. However, with nonionic metal-olefin complexes in dilute solutions the activity coefficients should be close to unity. The deviations from unity will be greatest with complexes which have the largest dipole moments. The concentrations at which the approximation of considering activity coefficients to be unity ceases to be valid can be found by determining the concentration below which the vapor pressure-composition curve for the solution obeys Raoult's law.[49b,c]

C. Enthalpies and Entropies of Formation in Solution

There are essentially two types of methods that can be used for determining the enthalpies and entropies of formation of metal-olefin complexes in solution, namely, measurements of the temperature dependence of the free energy of formation and calorimetric methods. Although the former are less accurate they have been more widely used. Since

$$\Delta G = -RT \ln K = \Delta H - T\Delta S$$

it follows that

$$\ln K = (-\Delta H/RT) + (\Delta S/R)$$

so that a plot of ln K against $1/T$ should have slope $-\Delta H/R$ and intercept $\Delta S/R$. The accuracy of the resulting enthalpy and entropy values depends on a number of factors.

(a) The accuracy of the original free energy data as well as the accuracy of the thermostating system used. With sufficiently good data, enthalpies of about ±0.2 kcal/mol and entropies of about ±0.7 cal/(mol °C) can be achieved, but more often the errors are rather higher.

(b) The evaluation of enthalpies from the slope of a plot of ln K against $1/T$ presumes that ΔH is temperature independent. In practice enthalpies are dependent on the temperature so that two conflicting requirements must be resolved: firstly, the temperature range should be sufficiently small to ensure that the variation of the absolute value of the enthalpy is small; secondly, the temperature range should be sufficiently large to enable the slope of the plot to be evaluated with the minimum of error. A typical compromise that many workers have used is a temperature range of about 30°.

In view of the low accuracy of the enthalpy and entropy data obtained from the temperature dependence of free energies it is pertinent to enquire whether there are cases in which such methods must be used? In fact there are, since calorimetric studies can only be used to study relatively fast reactions, typically complete in about 20 min. Special calorimeters have been described that can measure heats of reactions that take up to 24 hr to go to completion, but such calorimeters in addition to being very elaborate to ensure that they have the required long term thermal stability require very sensitive temperature probes to determine the very small heats of reaction that are liberated over a given short interval of time. Accordingly the enthalpies and entropies of a reaction such as that of tetrachloroplatinate(II) ions with olefins, which at 30° takes about 14 days to come to equilibrium with a charged olefin such as $CH_2{=}CHCH_2NH_3^+$ and about 50 days with an uncharged olefin such as $CH_2{=}CHCH_2OH$,[50] can only be determined from the temperature dependence of the free energies.

Although the enthalpies of formation of metal-olefin complexes that are formed rapidly can be measured directly by calorimetry, only one such study has been reported.[50a] There is an obvious need for work in this

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TABLE I. Thermodynamic Data for Rhodium(I)-Olefin and -Acetylene Complexes[a]

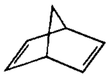
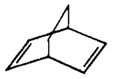
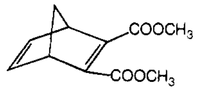
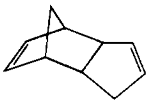
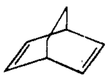
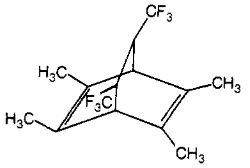
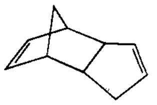
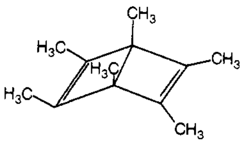
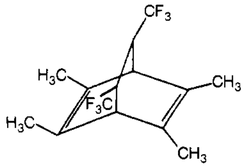
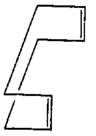
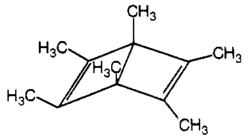
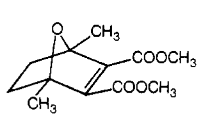
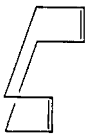
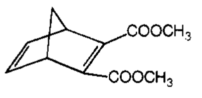
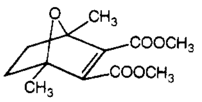
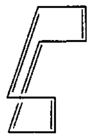
$K = ([(\text{acac})\text{Rh}(C_2H_4)(\text{olefin})][C_2H_4])/([(\text{acac})\text{Rh}(C_2H_4)_2][\text{olefin}])$[b]

Olefin	10^3K (25°)	10^3K(0°)	ΔH	ΔS
$CH_2{=}CHCH_3$	78 ± 7	63 ± 8	1.4 ± 0.9	−0.5 ± 0.5
$CH_2{=}CHC_2H_5$	92 ± 18	79 ± 12	1.0 ± 1.4	−1.7 ± 5.0
$CH_3CH{=}CHCH_3$ (cis)	4.1 ± 0.3	3.1 ± 0.3	1.8 ± 0.8	−4.9 ± 3.0
(trans)	2.0 ± 0.3	1.5 ± 0.1	1.9 ± 0.7	−6.1 ± 2.6
$(CH_3)_2C{=}CH_2$	0.35 ± 0.02	0.19 ± 0.02	3.9 ± 0.7	−2.6 ± 2.5
$CH_2{=}CHCl$	170 ± 19	150 ± 10	0.8 ± 0.8	−0.8 ± 2.9
$CHCl{=}CHCl$ (cis)	~0.07			
$CH_2{=}CCl_2$	No reaction			
$CCl_2{=}CCl_2$	No reaction			
$CH_2{=}CHF$	320 ± 22	410 ± 70	−1.6 ± 1.1	−7.5 ± 3.8
$FHC{=}CHF$ (trans)	1240 ± 360	1320 ± 410		
(cis)	1590 ± 330	2080 ± 460		
$CH_2{=}CF_2$	100 ± 10			
$CHF{=}CF_2$	88			
$CF_2{=}CF_2$	59			
$CH_2{=}CHOCH_3$	18 ± 2			
$CH_2{=}CHC_6H_5$	0.08			
$CH_2{=}CH{-}C{\equiv}N$	>50			
$CH_2{=}CHN(CF_3)_2$	0.1			

$K = [\text{RhL}I(\text{CO})(\text{PPh}_3)_2]/([\text{Rh}I(\text{CO})(\text{PPh}_3)_2][\text{L}])$[c]

L	K
C_2H_4	<1
C_2H_2	<1

$K = ([\text{Rh}_2(\text{diene-1})_2\text{Cl}_2][\text{diene-2}]^2)/([\text{Rh}_2(\text{diene-2})_2\text{Cl}_2][\text{diene-1}]^2)$[d]

Diene-1	Diene-2	K	Diene-1	Diene-2	K
		3			~1
		2			100
		~1			10
		80			6

[a] The concentration of C_2H_4 liberated was determined by measuring the concentration of C_2H_4 in the gas phase by ir absorbance and determining the solubility of C_2H_4 in toluene. [b] Measured in toluene (from ref 31). [c] In chlorobenzene at 20° (from ref 54). [d] K was determined by nmr at −60° in $CDCl_3$ (from ref 54a).

field, since an understanding of the nature of the interaction of olefins with metals requires enthalpy data as well as free energy data. The interested research worker is referred to texts on thermochemical measurements.[51,52]

D. Thermodynamic Data in the Solid Phase

So far only thermodynamic data in the solution phase have been considered. However, since the simpler olefins are gases, it is possible to derive thermodynamic data on solid olefin complexes by measuring the variation of the dissociation pressure with temperature. In making such measurements it is essential to ensure that true equilibrium conditions prevail by studying the effect of

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both increasing and decreasing the temperature. For the equilibrium

$$\mathrm{MX(cryst)} + n\ \mathrm{olefin(g)} \overset{K_p}{\rightleftharpoons} \mathrm{[M(olefin)}_n\mathrm{]X(cryst)}$$

the equilibrium constant K_p is equal to the inverse of the olefin pressure, and if the pressure (p) is expressed in the correct units for the standard state, namely atmospheres, then

$$\Delta G = -RT \ln (1/p)$$

and if the temperature range is sufficiently small for the temperature dependence of ΔH to be ignored, ΔH is given by[53]

$$\ln (p_1/p_2) = -\Delta H/R(1/T_2 - 1/T_1)$$

where pressure p_1 corresponds to temperature T_1.

It is, of course, impossible to determine the relative stabilities of metal-olefin bonds from solid-phase data because the lattice energies of the crystalline metal-olefin complexes are dependent upon the size of the olefin.

III. Thermodynamic Data

In tabulating the thermodynamic data it is immediately apparent that while many research groups have studied silver(I)-olefin complexes only a few have studied the olefin complexes of other metals. When comparing data for two different olefins it is essential to compare data obtained by the same technique under similar conditions and preferably by the same group of workers. This is because, as discussed in detail above, some methods such as gas chromatography give stability constants that are only relative values dependent on the precise experimental technique used. In such cases highly misleading conclusions may be drawn if care is not first taken to ensure that the data are comparable.

In Tables I-XII[54-97] the experimental technique is recorded alongside each result. The abbreviations for the techniques, which are all described in section II, are as follows: pot, potentiometry; sol, solubility; dis, distribution between two immiscible solvents; pol, polarography; glc, gas chromatography; nmr, nuclear magnetic resonance. In quoting the medium the inert background electrolyte has been reported. However, only the sum of the ionic strengths of the metal ion under study and the background electrolyte have been given so that in the case of the silver(I) results, for example, a medium referred to as 0.1 M $\mathrm{KNO_3}$ is x M with respect to $\mathrm{Ag^+}$ and $(0.1 - x)$ M with respect to $\mathrm{K^+}$. No units are quoted in the tables. In all cases the units of K can be determined from the relevant expression for K by expressing the concentrations of the species present in moles per liter. ΔH values are expressed throughout in kilocalories per mole and ΔS values in calories per mole per deg (°C) (entropy units).

TABLE II. Thermodynamic Data for Iridium(I)-Olefin and -Acetylene Complexes in Chlorobenzene

$K = [\mathrm{IrLX(CO)(PPh_3)_2}]/([\mathrm{IrX(CO)(PPh_3)_2}][\mathrm{L}])$

L	X	Temp, °C	K	ΔH	Ref
$\mathrm{C_2H_4}$	Cl	30	<1		55
$\mathrm{CH_2{=\!\!=}CHCN}$	Cl	30	1.2		55
$\mathrm{NCCH{=\!\!=}CHCN}$	Cl	30	1500		55
$\mathrm{(NC)_2C{=\!\!=}C(CN)_2}$	Cl	30	140,000 (in THF)		55
$\mathrm{C_2H_4}$	I	20	2.7	−12	54
$\mathrm{C_2H_4}$	I	30	1.1		55
$\mathrm{CH_2{=\!\!=}CHCN}$	I	30	0.4		55
$\mathrm{NCCH{=\!\!=}CHCN}$	I	30	87		55
$\mathrm{F_2C{=\!\!=}CF_2}$	I	30	>100		55
$\mathrm{CH{\equiv}CH}$	I	20	1.2	−9.3	54

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TABLE III. Thermodynamic Data for Nickel(0)–Olefin Complexes[a]

K_s = [Ni(dipyr)(ol)]/([Ni(dipyr)(solvent)][olefin])

Olefin	Temp, °C	K_s	ΔH	ΔS
Maleic anhydride	22.2	47,000	−12.8	−22.0
	36.1	21,000		
	40.1	17,000		
	46.7	14,000		
Acrolein	26.8	5,400	−19.0	−47.0
	32.5	3,100		
	35.6	2,300		
	42.5	1,400		
Acrylamide	22.4	3,700	−17.8	−44.2
	33.5	1,600		
	39.4	740		
	45.7	490		
Acrylonitrile	20.4	1,300	−16.0	−40.5
	30.6	600		
	36.5	490		
	41.8	350		
Methyl vinyl ketone	24.0	600	−13.7	−33.9
	30.0	470		
	35.6	360		
	41.1	280		
Methyl acrylate	18.3	790	−13.7	−34.3
	21.2	630		
	31.8	360		
	41.6	140		
Methacrylonitrile	21.9	510	−14.1	−36.2
	28.8	280		
	37.9	140		
	43.3	95		
Methyl methacrylate	17.3	24	−8.7	−24.1
	24.6	14		
	29.2	12		
	42.4	6.1		
Vinyl acetate	30.0	0.23		

[a] Studied in tetrahydrofuran using a spectrophotometric technique (from ref 56).

TABLE IV. Thermodynamic Data for Nickel(II)–Olefin Complexes[a]

K = [R_2Ni(dipyr)(olefin)]/([R_2Ni(dipyr)][olefin])

R	Olefin	K(200°K)	ΔH (200°K)	ΔS (200°K)
CH_3	Acrylonitrile	0.093	−2.15	−15.5
C_2H_5	Acrylonitrile	7.3	−4.55	−20.3
n-C_3H_7	Acrylonitrile	1.4 (5)	−4.90	−23.8
i-C_4H_9	Acrylonitrile	0.16	−1.67	−12.1
C_2H_5	Acrolein	1.9	−5.60	−26.8

[a] Studied in tetrahydrofuran using visual observation of the color of the mixture (from ref 56).

TABLE V. Thermodynamic Data for Palladium(II)–Olefin Complexes[a]

K = ([$PdCl_3L^-$][Cl^-])/([$PdCl_4^{2-}$][L])

Olefin	Temp, °C	Ionic strength, M	K		Ref
C_2H_4	15.0	2	18.7		57
	25.0	2	17.4		57
	35.0	2	9.7		57
C_2H_4	8.0	4	15.6	$\Delta H = 1.5$ $\Delta S = 0$	58, 59
	13.4	4	16.3		
	20.0	4	15.2		
	25.0	4	13.1		
	20.0	4	16.9		60
C_2H_4	14.8	2	18.7		61
	14.8	2.1–2.2	15.5		61
	14.8	3.1–3.2	15.9		61
	14.8	4.5	16.3		61
$CH_3CH{=}CH_2$	10.3	4	8.4	$\Delta H = 0$ $\Delta S = 4$	59
	14.9	4	8.6		
	20.1	4	7.9		
	20.0	4	7.6		60
$C_2H_5CH{=}CH_2$	5.0	4	13.9	$\Delta H = 0$ $\Delta S = 5$	59, 62
	10.0	4	12.6		
	14.8	4	13.6		
	20.0	4	12.4		
	20.0	4	14.3		60
$C_2H_5CH{=}CH_2$	14.8	2.1–2.2	13.8		61
	14.8	3.1–3.2	13.6		61
	14.8	4.1–4.2	13.6		61
	14.8	5.1–5.2	11.3		61

[a] Obtained by measuring the solubility of olefins in aqueous palladium(II) chloride solutions.

The order of the tables follows the position of the metal in the periodic table: rhodium(I), iridium(I), nickel(0), nickel(II), palladium(II), platinum(0), platinum(II), copper(I), silver(I), and mercury(II).

IV. Discussion of Thermodynamic Data

The thermodynamic data obtained for metal-olefin interactions can be used to answer two questions. The first is "which olefins form the most stable complexes?" and the second is "why does one olefin form a more stable complex than another?". The first question, which is of immediate importance to a chemist trying to apply existing knowledge either to the development of new synthetic organic reactions or to deciding which of a number of possible mechanisms for a particular reaction is the more likely, requires only free energy data. However, to answer the second question it is necessary to analyze the free energy change on complex formation into its enthalpy and entropy components. There are many examples in the literature where authors, having obtained stability constants at a single temperature, have attempted to interpret these in terms of both steric and electronic influences on the metal-olefin bond. While a number of such explanations have been shown by subsequent enthalpy studies to be valid, there are other cases where modification of the structure of the olefin has very little influence on the enthalpy of formation of the metal-olefin complex but a considerable effect on the entropy of formation of that complex and hence on the overall stability constant.

In this section we shall attempt to evaluate which properties of the olefin and the metal lead to the formation of a stable metal-olefin complex. We shall, however, only attempt to discuss why these properties lead to stable complexes when enthalpy and entropy data are available.

In order to rationalize the electronic influence of substituents on the overall stability of the metal-olefin bond, it is necessary to have a description of the bonding. The currently accepted explanation[16] of the bonding in metal-olefin complexes suggests that a σ bond is formed by donation of the pair of electrons in the π_{2p} orbital on the olefin to an empty hybrid orbital on the metal. This is complemented by π back-donation of electron density from a filled hybrid orbital on the metal to the initially empty π^*_{2p} (antibonding) orbital on the olefin (see Figure 1). The σ bond inevitably causes an unfavorable

TABLE VI. Thermodynamic Data for Platinum(0)-Acetylene Complexes[a]

$K = ([(PPh_3)_2Pt(PhC{\equiv}CH)][XC_6H_4C{\equiv}CH])/([(PPh_3)_2Pt(XC_6H_4C{\equiv}CH)][PhC{\equiv}CH])$

X	K	X	K
m-NO_2	125	*o*-Cl	3
p-NO_2	105	H	1
p-Br	10	*p*-CH_3O	1
p-Cl	10	*o*-CH_3O	0.5
m-CH_3O	6		

[a] Studied in cyclohexane at 28.8° using an ultraviolet spectrophotometric technique (from ref 63).

build-up of negative charge on the metal; however, the π bond relieves this, giving a synergic effect. This bonding scheme, which has been described in sufficiently general terms to be applicable to all metal-olefin complexes appears to give rise to two main types of olefin complexes, which have been described as class S and class T[97a] complexes.[16,98,99] The essential difference between the two classes of olefin complexes are listed in Table XIII. For the present purposes it is sufficient to mention that the π bond (metal to olefin) is relatively more important in class T than in class S complexes as is to be expected in view of the fact that in those cases where a given metal forms both classes of complex, the class T complexes are formed by the lower oxidation state, which has more d electrons potentially available for π back-donation, and the class S complexes are formed by the higher oxidation state (see Table XIII).

A. Properties of the Olefin

The properties of an olefin that influence the stabilities of metal-olefin complexes can usually be divided into two groups, namely steric and electronic. Of these the steric properties are generally far more important and accordingly are considered first.

1. *Steric Properties*

a. Substituents on the Multiple Bond

It is extremely difficult to separate the steric and electronic properties of a substituent. However, of the wide range of possible substituents that could be used to replace one or more of the hydrogen atoms on a double bond, methyl groups have the closest electronic properties to hydrogen atoms. Even a quick glance at the stability constant data, summarized in Table XIV, indicates that on replacing a hydrogen atom bound to one of the unsaturated carbon atoms by a methyl group there is a decrease in the stability constant. In all cases where enthalpy data are available (Ag(I), Rh(I), Pt(II), and Pd(II); for Pd(II), see Table V) it is apparent that replacement of a hydrogen atom by a methyl group is accompanied by an unfavorable enthalpy term, although in the case of silver(I) it requires the replacement of two of the hydrogen atoms on ethylene before the steric bulk of the methyl groups overcomes their electronic effect (which in the special case of silver(I) favors complex formation) and decreases the enthalpy of complex formation. In all cases, except palladium(II), there is a more favorable entropy change on complex formation with substituted olefins. The effect of replacing the hydrogen atoms on a double bond by groups such as cyanide or halides involves a much greater change in electronic properties than with methyl groups so that the resultant effect on the stability of the complex depends more on the susceptibility of the metal-olefin bond to electronic changes than on the steric effect of the substituent.

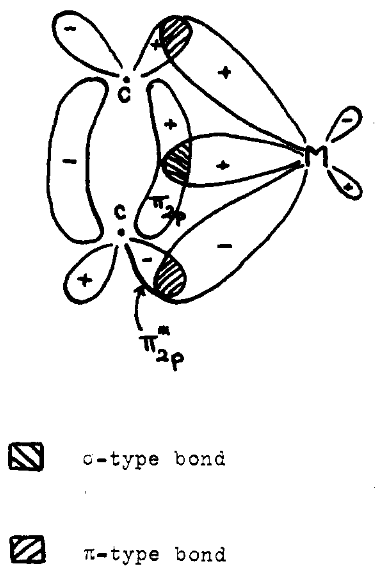

Figure 1. Bonding in metal-olefin complexes.

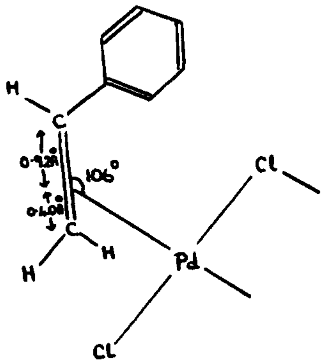

Figure 2. The structure of $[Pd(PhCH{=}CH_2)Cl_2]_2$ (from ref 100).

In general it would appear that any substituent on a double bond will have an unfavorable steric effect on the complexing ability of that olefin and that this is manifest in both the enthalpy and the entropy terms. There is some evidence from X-ray diffraction to support the contention that the steric bulk of the substituents prevents the optimum approach of the olefin to the metal. In styrenepalladium(II) chloride the bulky phenyl group prevents the double bond being either symmetrically disposed about the palladium-olefin bond or perpendicular to the $PdCl_2Pd$ plane[100] (Figure 2). The more unfavorable entropies of complex formation in the more substituted olefins suggest that there is a somewhat greater physical restraint in the complex when the olefin is more bulky. This is perhaps not surprising when it is remembered that for class S complexes (see Table XIII and section IV above) with ethylene there is only a very low energy barrier to free rotation of the olefin about the metal-olefin bond. As the bulk of the substituents on the olefin in-

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[97a] The letters S and T are taken from the square planar and trigonal structures of the model platinum complexes.

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TABLE VII. Thermodynamic Data for Platinum(II)-Olefin Complexes

Part I[a]

$K = ([PtX_3L^-][X^-])/([PtX_4^{2-}][L])$

Ligand X	Olefin[b]	Temp, °C	K		Ref
Cl	$allNH_3^+$	30.2	2829	$\Delta H = -7.1$; $\Delta S = -7.6$	30
		44.0	1737		
		59.0	1022		
Cl	$allNH_2Et^+$	24.0	2348	$\Delta H = -5.9$; $\Delta S = -4.4$	30
		44.0	1233		
		59.0	806		
Cl	$allNHEt_2^+$	30.0	865	$\Delta H = -5.6$; $\Delta S = -5.0$	30
		45.3	551		
		59.0	386		
Cl	$allNEt_3^+$	25.0	260	$\Delta H = -4.9$; $\Delta S = -4.6$	30
		45.0	153		
		59.0	112		
Cl	$allPEt_3^+$	59.0	505		30
Cl	$allAsEt_3^+$	45.0	1320	$\Delta H = -5.9$; $\Delta S = -4.3$	30
		58.0	917		
Cl	$allNMe_3^+$	30.0	259	$\Delta H = -5.3\ (5)$; $\Delta S = -6.6$	30
		44.5	173		
		60.0	117		
Cl	$allN\text{-}n\text{-}Pr_3^+$	60.0	131		30
Cl	$allN\text{-}n\text{-}Bu_3^+$	60.0	308		30
Cl	$allNH(CH_2)_4^+$	60.0	649		30
Cl	$allNH(CH_2)_5^+$	60.0	437		30
Cl	$butNH_3^+$	30.0	4396	$\Delta H = -5.1$; $\Delta S = -0.2$	30
		44.5	3017		
		60.0	2038		
Cl	$butNEt_3^+$	30.0	7778	$\Delta H = -3.8$; $\Delta S = +5.4$	30
		44.8	5911		
		60.0	4449		
Cl	$butAsEt_3^+$	30.0	8962	$\Delta H = -3.3$; $\Delta S = +7.2$	30
		44.8	7014		
		60.0	5459		
Cl	$pentNH_3^+$	60.0	1124		64
Cl	*cis*-$CH_3CH{=}CHCH_2NH_3^+$	30.0	1075	$\Delta H = -6.0$; $\Delta S = -5.9$	65
		45.0	675		
		60.0	415		
Cl	*trans*-$CH_3CH{=}CHCH_2NH_3^+$	30.0	450	$\Delta H = -5.1$; $\Delta S = -4.6\ (5)$	66
		44.5	304		
		60.2	209		
Cl	$CH_2{=}CHCH(CH_3)NH_3^+$	30.0	2194	$\Delta H = -6.7$; $\Delta S = -6.9$	66
		45.3	1282		
		60.0	804		
Cl	$CH_2{=}C(CH_3)CH_2NH_3^+$	60.0	3.2		66
Cl	$(CH_3)_2C{=}CHCH_2NH_3^+$	60.0	2.6		66
Cl	allOH	30.0	13011	$\Delta H = -8.1$; $\Delta S = -7.6$	64
		44.5	7250		
		60.0	3890		
Cl	pentOH	60.0	2525		64
Cl	*trans*-$CH_3CH{=}CHCH_2OH$	60.0	3008		64
Cl	$allSO_3^-$	35.0	2884	$\Delta H = -6.1$; $\Delta S = -4.1$	67
		45.0	2123		
		55.6	1539		
Br	$allNH_3^+$	24.5	306		68
Br	$allNH_2Et^+$	0.0	506	$\Delta H = -4.8$; $\Delta S = -5.3$	68
		25.0	241		
		35.0	184		
Br	$allNHEt_2^+$	24.5	127		68
Br	$allNEt_3^+$	24.5	44.1		68
Br	$butNEt_3^+$	24.5	1190		68

Part II[c]

$K_D = ([trans\text{-}\{(XC_6H_4CH{=}CH_2)PtCl_2L\}][C_{12}H_{24}])/([trans\text{-}\{(C_{12}H_{24})PtCl_2L\}][XC_6H_4CH{=}CH_2])$

L	Z	Medium	*m*-CH_3O	*m*-CH_3	*m*-H	*m*-Cl	*m*-NO_2
Z-pyrO	CH_3O	$CHCl_3$	3.8	2.4	6.6	2.7	0.6
	CH_3		0.022	0.08	0.8	0.09	0.0011
	H		0.029	0.055	0.052	0.14	0.0041
	Cl		0.0040	0.023	0.10	0.10	0.033

TABLE VII *(Continued)*

			Part II[c]				
L	Z	Medium	*m*-CH_3O	*m*-CH_3	*m*-H	*m*-Cl	*m*-NO_2
	$COOCH_3$		0.026	0.20	0.13	0.043	
	NO_2		0.018	0.005	3.3	0.05	0.013
			p-CH_3O	*p*-CH_3	*p*-H	*p*-Cl	*p*-NO_2
Z-pyrO	CH_3O	$CHCl_3$	9.5	7.1	6.6	3.2	0.045
	CH_3		0.30	0.57	0.87	0.099	0.0017
	H		0.26	0.016	0.052	0.071	0.00035
	Cl		0.18	0.51	0.10	0.11	0.010
	$COOCH_3$		0.25	0.016	0.13	0.22	0.077
	NO_2		0.0032	0.078	3.3	0.052	0.0015
Cl		0.01 *M* HCl in EtOH	19.4	26	37		21

[a] In 0.1 *M* HCl + 1.9 *M* NaCl, studied using an ultraviolet spectrophotometric technique. [b] all = $CH_2{=}CHCH_2{-}$; but = $CH_2{=}CH(CH_2)_2{-}$; pent = $CH_2{=}CH(CH_2)_3{-}$. [c] Studied by an ultraviolet spectrophotometric technique at 25° (from ref 69 and 70).

creases, the resistance to free rotation would be expected to rise sharply.

For acetylenes, only in the case of silver(I) have sufficient studies been reported to confirm that replacing the hydrogen atoms bound directly to the unsaturated carbon atoms by methyl groups decreases the stability of the complex. Furthermore replacing the hydrogen atoms on the carbon atom adjacent to the unsaturated carbon atom also decreases the stability of the complex by a factor of about ⅓.[41] There are insufficient data to ascribe this strictly to an enthalpy or entropy effect although it is anticipated that both terms might be involved in a similar way to that found for olefins.

b. Branching in the Chain

The introduction of a branched group on the alkyl chain of an olefin causes a reduction in the stability of the silver(I)-olefin complex. The results for a series of heptenes[47] (see Table X under C_7H_{14}) indicate that this effect is greatest when the methyl side group is bound to the carbon atom next but one (*i.e.*, β) to the unsaturated carbon atom and least when it is next but two; methyl groups bound to the carbon atoms adjacent to the unsaturated carbon atom appear to have an intermediate effect. It will require enthalpy and entropy studies before an explanation for these observations, which are also found with acetylenes, can be advanced.

c. Chain Length

The effect of chain length is very difficult to generalize on. Before considering the data in detail it is important to reject any data in which an increase in chain length removes a group with a strong electronic influence to a greater distance from the multiple bond, since the interpretations of such results will depend on the electronic influence of the group being removed rather than the effect of chain length itself. With this limitation in mind, we are left with data for silver(I), palladium(II), and rhodium(I) (Table XV). In the case of silver(I) it is apparent firstly that the stability of complexes of $RCH{=}CH_2$ depends very much on the solvent. Thus in ethylene glycol the stability constant decreases steadily as R increases in chain length (R = H > CH_3 > C_2H_5 > *n*-C_3H_7 > *n*-C_4H_9 > *n*-C_5H_{11}), and over the series R = H to R = *n*-C_3H_7 there is very little change in the enthalpy of complex formation but a steadily more unfavorable entropy term. In aqueous solution, however, the stability constant increases steadily with increasing chain length of group R (R = H < CH_3 < C_2H_5 < *n*-C_4H_9), but no enthalpy or entropy data are available. For palladium(II) the stability constant order is R = H > CH_3 < C_2H_5, and now the entropy term becomes more favorable toward complex formation as the chain length of the olefin increases whereas the enthalpy of complex formation is comparable for propene and 1-butene and more favorable for ethylene. With rhodium(I) the stability constant trend is similar, though more dramatic, to that of palladium(II) (*i.e.*, R = H $\gg$ CH_3 < C_2H_5); however, in this case the entropy term gets steadily less favorable with increasing chain length while the enthalpy term is more unfavorable for propene than 1-butene relative to ethylene.

It is apparent that a great deal more work is needed before the influence of chain length on the stabilities of olefin complexes can be predicted. This work must be accompanied by enthalpy and entropy data if an understanding of how the chain length influences the stability of the metal-olefin complex is to be obtained.

d. Cis and Trans Isomers

In general cis olefins form more stable complexes than trans olefins (Table XVI). Further enthalpy and entropy studies have shown that there is very little difference between the entropies of complex formation of a pair of cis and trans isomers, although there is a considerable enthalpy difference in favor of the cis isomer. The greater enthalpy of formation of cis than trans olefin complexes has been ascribed to two effects.

(i) Cis olefins, as indicated by their higher heats of hydrogenation,[101] are generally more strained than trans olefins, and this strain is reduced on complex formation. Although it has been suggested[102] that on complex formation a slight rotation could occur about the double bond to relieve the bond oppositions present in a planar cis olefin, an X-ray diffraction study[65] of [Pt(*cis*-$CH_3CH{=}CHCH_2NH_3)Cl_3$] showed that the four carbon atoms of the *cis*-crotylammonium ligand were coplanar. Thus any relief of the bond oppositions in the cis olefins appears to result solely from the slight lengthening of the olefinic double bond on coordination to a metal. In support of this "relief of strain" hypothesis it has been found

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(101) R. B. Turner, D. E. Nettleton, and M. Perelman, *J. Amer. Chem. Soc.*, **80**, 1430 (1958).

(102) P. D. Gardner, R. L. Brandon, and N. J. Nix, *Chem. Ind. (London)*, 1363 (1958).

TABLE VIII. Thermodynamic Data for Copper(I)-Olefin Complexes in Solution[a]

$$K_1 = \frac{[\mathrm{Cu(olefin)^+}]}{[\mathrm{Cu^+}][\mathrm{olefin}]} \qquad K_a = \frac{[\mathrm{CuCl_3L^{2-}}]}{[\mathrm{CuCl_3{}^{2-}}][\mathrm{L}]} \qquad K_b = \frac{[\mathrm{CuCl_2L^-}][\mathrm{Cl^-}]}{[\mathrm{CuCl_3{}^{2-}}][\mathrm{L}]}$$

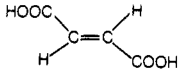
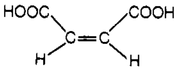
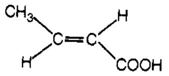
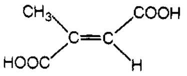
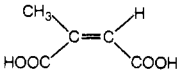
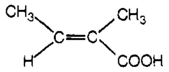
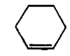
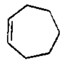
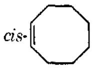
Molecular formula	Structural formula	Method	Temp, °C	Medium	*K*	Ref
C_3H_5Cl	$CH_2{=}CHCH_2Cl$	pot.	5	Various concentrations of HCl	$K_a = 7.7; K_b = 3.0$ $\Delta H_a = -17.1$	71
		pot.	15		$K_a = 2.7; K_b = 1.5$ $\Delta S_a = -57$	71
		pot.	25		$K_a = 1.0; K_b = 0.9$ $\Delta H_b = -7.1$ $\Delta S_b = -24$	71
C_3H_6O	$CH_2{=}CHCH_2OH$	sol	25	0.1 *M* $HClO_4$	$K_1 = 52{,}000$	38
		sol	25	0.1 *M* $NaClO_4$	$K_1 = 50{,}000$	46
		pot.	25	Various concentrations of NH_4Cl	$K_a = 21.0; K_b = 68.2$ $\Delta H_a = -6.0$	
		pot.	50		$K_a = 10.0; K_b = 53.0$ $\Delta S_a = -14$	71
		pot.	70		$K_a = 6.3; K_b = 45.1$ $\Delta H_b = -2.0$	71
		pot.	85		$K_a = 4.5; K_b = 40.1$ $\Delta S_b = 2$	71
C_3H_5OCl	$CH_2{=}CClCH_2OH$	sol	25	0.1 *M* $HClO_4$	$K_1 = 220$	38
$C_4H_4O_4$		sol	25	0.1 *M* $HClO_4$	$K_1 = 9200$	72
$C_4H_4O_4$		sol	25	0.1 *M* $HClO_4$	$K_1 = 1130$	73
$C_4H_6O_2$	$CH_2{=}CHCH_2COOH$	sol	25	0.1 *M* $HClO_4$	$K_1 = 34{,}000$	72
$C_4H_6O_2$		sol	25	0.1*M* $HClO_4$	$K_1 = 1600$	72
C_4H_8O	$CH_3CH{=}CH{-}CH_2OH$	sol	25	0.1 *M* $HClO_4$	$K_1 = 10{,}000$	38
C_4H_8O	$CH_2{=}CHC(CH_3)HOH$	sol	25	0.1 *M* $HClO_4$	$K_1 = 33{,}000$	38
C_4H_8O	$CH_2{=}C(CH_3){-}CH_2OH$	sol	25	0.1 *M* $HClO_4$	$K_1 = 9200$	38
C_5H_8		pot.	30	1 *M* $LiClO_4$ in 2-propanol	$K_1 = 725; \Delta H_1 = -12.7$	74
$C_5H_6O_4$	$CH_2{=}C(COOH){-}CH_2COOH$	sol	25	0.1 *M* $HClO_4$	$K_1 = 2200$	72
$C_5H_6O_4$		sol	25	0.1 *M* $HClO_4$	$K_1 = 410$	72
$C_5H_6O_4$		sol	25	0.1 *M* $HClO_4$	$K_1 = 22$	72
$C_5H_8O_2$		sol	25	0.1 *M* $HClO_4$	$K_1 = 210$	72
$C_5H_8O_2$	$(CH_3)_2C{=}CHCOOH$	sol	25	0.1 *M* $HClO_4$	$K_1 = 110$	72
$C_5H_{10}O$	$CH_2{=}CHC(C_2H_5)HOH$	sol	25	0.1 *M* $HClO_4$	$K_1 = 39{,}000$	38
$C_5H_{10}O$	$CH_2{=}C(CH_3){-}C(CH_3)HOH$	sol	25	0.1 *M* $HClO_4$	$K_1 = 4000$	38
$C_5H_{10}O$	$CH_3CH{=}C(CH_3)CH_2OH$	sol	25	0.1 *M* $HClO_4$	$K_1 = 3500$	38
$C_5H_{10}O$	$(CH_3)_2C{=}CHCH_2OH$	sol	25	0.1 *M* $HClO_4$	$K_1 = 11{,}000$	38
$C_5H_{10}O$	$CH_2{=}CH{-}C(CH_3)_2OH$	sol	25	0.1 *M* $HClO_4$	$K_1 = 25{,}000$	38
C_6H_8		pot.	30	1 *M* $LiClO_4$ in 2-propanol	$K_1 = 339; \Delta H_1 = -7.0$	74
C_6H_{10}		pot.	30	1 *M* $LiClO_4$ in 2-propanol	$K_1 = 123; \Delta H_1 = -8.3$	74
$C_6H_{12}O_2$	$CH_3C(OH)H{-}CH_2{-}C(CH_3){=}CH_2$	sol	25	0.1 *M* $HClO_4$	$K_1 = 16{,}000$	38
C_7H_8		pot.	30	1 *M* $LiClO_4$ in 2-propanol	$K_1 = 12{,}880; \Delta H_1 = -15$	74

TABLE VIII (*Continued*)

Molecular formula	Structural formula	Method	Temp, °C	Medium	*K*	Ref
C_7H_{10}		pot.	30	1 *M* $LiClO_4$ in 2-propanol	$K_1 = 18{,}200$; $\Delta H_1 = -10.8$	74
C_7H_{12}		pot.	30	1 *M* $LiClO_4$ in 2-propanol	$K_1 = 1{,}047$; $\Delta H_1 = -7.8$	74
C_8H_{12}		pot.	25	Acetone	$K_1 = 32{,}000$	75
C_8H_{14}		pot.	30	1 *M* $LiClO_4$ in 2-propanol	$K_1 = 2{,}884$; $\Delta H_1 = -15.3$	74

[a] All data refer to aqueous solution unless otherwise stated.

TABLE IX. Thermodynamic Data for Copper(I)-Olefin and -Acetylene Complexes in the Solid Phase[a]

Olefin or acetylene	*n*	Temp range studied, °C	ΔH
$HC{\equiv}CH$	0.5	0-42.5	−6.25
$H_2C{=}CH_2$	1	Not stated	−10.0
$CH_2{=}CHCH_3$	1	Not stated	−11.0
$CH_2{=}C(CH_3)_2$	1	Not stated	−11.0
$CH_2{=}CHCH{=}CH_2$	0.5	17-69	−8.5
$CH_2{=}C(CH_3)CH{=}CH_2$	0.336	10-40	−5.81

[a] Enthalpies of formation of copper(I)-olefin complexes according to the reaction CuCl(cryst) + *n* olefin(g) ⇌ [Cu(olefin)$_n$]Cl(cryst) obtained from measurements of the dissociation pressure of [Cu(olefin)$_n$]Cl (from ref 76).

that where the free trans olefin is more strained than the cis olefin, as in β-chlorovinyl ethyl ether[103] and 1,2-dichloroethylene,[104] the trans olefin forms the more stable complex with silver.[79] In the case of 1,2-dibromoethylene the cis and trans isomers of the free olefin are equally stable[105] and the silver complexes of the two isomers are of comparable stability.

(ii) The actual bonds formed between cis olefins and metals are stronger than between trans olefins and metals. This could arise from the different rotations needed to reduce the nonbonded interactions between the two isomeric olefins and the other ligands present around the metal. In the case of a cis-disubstituted olefin these nonbonded interactions could be reduced by rotation of the olefin about the olefinic axis in such a way as to take the substituents further away from the metal (Figure 3). This type of rotation, which will cause a small reduction in the orbital overlap resulting in a slight weakening of the metal-olefin bond relative to that formed by ethylene, has been observed in the nuclear magnetic resonance spectra of a number of complexes containing unsymmetrical olefins.[106-110] However its observation by X-ray diffraction is not so clear-cut for two reasons: firstly, all substituents are bent out of the plane of the olefinic double bond away from the metal on coordination,[16] and, secondly, in the complexes studied so far the olefinic hydrogen atoms have not been located. With these reservations in mind we may note that the angle α in Figure 3 by which the methyl and methylene groups are bent away from the ClPtCl plane in [Pt(*cis*-$CH_3CH{=}CHCH_2NH_3$)Cl_3] is 23°[65] as compared with a mean angle of about 18.4° for the methyl and methylene groups in [Pt(*trans*-$CH_3CH{=}CHCH_2NH_3$)Cl_3].[111] In the case of a trans-disubstituted olefin the steric interference between the olefin substituents and the cis ligands could be reduced by rotation about the metal-olefin bond axis (Figure 4). While not affecting the σ bond (olefin to metal), this will markedly reduce the overlap between the

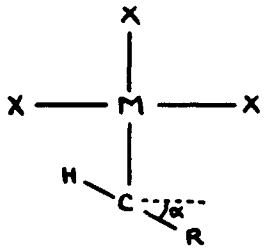


Figure 3. The rotation necessary to remove steric interference in a cis-disubstituted olefin complex (view down the olefinic double bond).

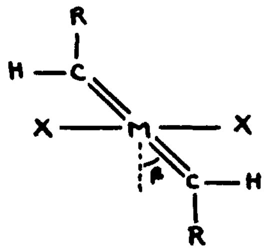


Figure 4. The rotation necessary to remove steric interference in a trans-disubstituted olefin complex (view down the metal-olefin bond).

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TABLE X. Thermodynamic Data for Silver(I) Complexes in Solution

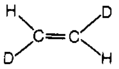
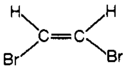
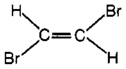
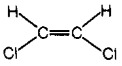
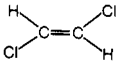
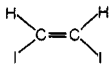
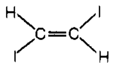
Molecular formula	Structural formula	Method	Temp, °C	Medium	K	Ref
				(i) Olefins^a		
	$K_1 = \frac{[\text{Ag(olefin)}^+]}{[\text{Ag}^+][\text{olefin}]}$; $K_2 = \frac{[\text{Ag(olefin)}_2{}^+]}{[\text{Ag(olefin)}^+][\text{olefin}]}$; $K_{1/2} = \frac{[\text{Ag}_2\text{(olefin)}^{2+}]}{[\text{Ag(olefin)}^+][\text{Ag}^+]}$; $K_1{}^* = \frac{[\text{Ag(olefin)}^+]_{\text{H}_2\text{O}}}{[\text{Ag}^+]_{\text{H}_2\text{O}}[\text{olefin}]_{\text{organic solvent}}}$ (see text)					
C_2H_4	$CH_2{=}CH_2$	sol	25	1 *M* CF_3COONa	$K_1 = 94.0$; $\Delta H_1 = -7.37$; $\Delta S_1 = -15.6$	39
		sol	25	1 *M* CF_3COONa	$K(\text{Ag(ol)OH} + \text{H}^+ \rightleftarrows \text{Ag(ol)}^+) = 2.2 \times 10^{-9}$	39
		sol	25	1 *M* CF_3COONa	$K(\text{AgA}^+ + \text{ol} \rightleftarrows \text{AgA(ol)}^+) = 57.0$	39
		sol	25	1 *M* CF_3COONa	$K(\text{AgA}_2{}^+ + \text{ol} \rightleftarrows \text{AgA(ol)}^+ + \text{A}) = 2.65$ (A = triethanolamine)	39
		dis	25	1 *M* KNO_3	$K_1 = 85.3$	77
		dis	25	1 *M* KNO_3	$K_{1/2} = 0.15$	77
		glc	40	Ethylene glycol	$K_1 = 22.3$	47
		glc	0	Ethylene glycol	$K_1 = 30.6$; $\Delta H_1 = -3.5$; $\Delta S_1 = -6.0$	78
		glc	25	Ethylene glycol	$K_1 = 17.5$	78
		glc	40	Ethylene glycol	$K_1 = 13.5$	78
		glc	0	Various concentrations of $AgNO_3$ in range 0–3.5 *M*	$K_1 = 203$; $\Delta H_1 = -5.5$; $\Delta S_1 = -9.1$	47a
			13.2		$K_1 = 127$	47a
			23.2		$K_1 = 95$	47a
			25		$K_1 = 85$	47a
$C_2H_2D_2$		glc	0	Ethylene glycol	$K_1 = 33.2$; $\Delta H_1 = -3.55$; $\Delta S_1 = -6.01$	78
		glc	25	Ethylene glycol	$K_1 = 18.7$	78
		glc	40	Ethylene glycol	$K_1 = 14.5$	78
C_2D_4	$CD_2{=}CD_2$	glc	0	Ethylene glycol	$K_1 = 35.6$; $\Delta H_1 = -3.63$; $\Delta S_1 = -6.2$	78
		glc	25	Ethylene glycol	$K_1 = 19.7$	78
		glc	40	Ethylene glycol	$K_1 = 15.2$	78
		glc	0	Various concentrations of $AgNO_3$ in range 0–3.5 *M*	$K_1 = 237$	47a
		glc	23.2		$K_1 = 105$	47a
$C_2H_2Br_2$		sol	25	1 *M* KNO_3	$K_1 = 0.68$	79
$C_2H_2Br_2$		sol	25	1 *M* KNO_3	$K_1 = 0.56$	79
$C_2H_2Cl_2$		sol	25	1 *M* KNO_3	$K_1 = 0.25$	79
		sol	25	1 *M* KNO_3	$K_1 = 0.16$	80
$C_2H_2Cl_2$		sol	25	1 *M* KNO_3	$K_1 = 0.40$	79
		sol	25	1 *M* KNO_3	$K_1 = 0.31$	80
$C_2H_2I_2$		sol	25	1 *M* KNO_3	$K_1 = 17.8$ $K_{1/2} = 1.06$ Note: these are not simple olefin complexes since the iodine atom is involved in bonding to Ag as shown by comparing CH_2I_2 with CH_2Cl_2 and CH_2Br_2	80
$C_2H_2I_2$		sol	25	1 *M* KNO_3	$K_1 = 5.5$ $K_{1/2} = 2.3$	80
C_3H_6	$CH_3CH{=}CH_2$	dis	25	1 *M* KNO_3	$K_1 = 87.2$; $K_{1/2} = 0.11$	77
		glc	40	Ethylene glycol	$K_1 = 9.1$	47
		glc	0	Ethylene glycol	$K_1 = 13.3$; $\Delta H_1 = -3.5$; $\Delta S_1 = -7.5$	78
		glc	25	Ethylene glycol	$K_1 = 7.5$	78
		glc	40	Ethylene glycol	$K_1 = 5.9$	78
		glc	23.2	Various concentrations of $AgNO_3$ in the range 0–3.5 *M*	$K_1 = 85$	47a
C_3H_5D	$CH_3CD{=}CH_2$	glc	0	Ethylene glycol	$K_1 = 13.9$	78

TABLE X *(Continued)*

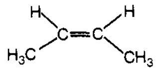
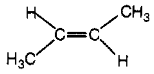
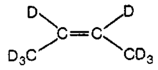
Molecular formula	Structural formula	Method	Temp, °C	Medium	K	Ref
		glc	25	Ethylene glycol	$K_1 = 7.8$	78
$C_3H_4D_2$	$CH_3CH{=}CD_2$	glc	0	Ethylene glycol	$K_1 = 14.3$; $\Delta H_1 = -3.61$; $\Delta S_1 = -7.8$	78
		glc	25	Ethylene glycol	$K_1 = 8.0$	78
		glc	40	Ethylene glycol	$K_1 = 6.2$	78
$C_3H_3D_3$	$CH_3CD{=}CD_2$	glc	0	Ethylene glycol	$K_1 = 14.8$; $\Delta H_1 = -3.65$; $\Delta S_1 = -7.8$	78
		glc	25	Ethylene glycol	$K_1 = 8.25$	78
		glc	40	Ethylene glycol	$K_1 = 6.35$	78
$C_3H_3D_3$	$CD_3CH{=}CH_2$	glc	0	Ethylene glycol	$K_1 = 13.7$; $\Delta H_1 = -3.57$; $\Delta S_1 = -7.7$	78
		glc	25	Ethylene glycol	$K_1 = 7.7$	78
		glc	40	Ethylene glycol	$K_1 = 5.95$	78
C_3D_6	$CD_3CD{=}CD_2$	glc	0	Ethylene glycol	$K_1 = 15.2$; $\Delta H_1 = -3.68$; $\Delta S_1 = -7.9$	78
		glc	25	Ethylene glycol	$K_1 = 8.45$	78
		glc	40	Ethylene glycol	$K_1 = 6.5$	78
C_3H_3N	$CH_2{=}CHC{\equiv}N$	glc	61	4 *M* $LiNO_3$	$K_1 = 0.703$	48
C_3H_6O	$CH_2{=}CHCH_2OH$	dis	25	1 *M* KNO_3	$K_1 = 12$; $K_2 = 3$	81
		sol	25	0.1 *M* KNO_3	$K_1 = 14$	38
		pot.	25	1.9 *M* $NaClO_4$ + 0.1 *M* $HClO_4$	$K_1 = 22.9 \pm 0.09$; $K_2 = 0.57 \pm 0.16$	28
		pot.	25	1 *M* KNO_3	$K_1 = 11.6$	82
$C_3H_8N^+$	$CH_2{=}CHCH_2NH_3^+$	pot.	25	1.9 *M* $NaClO_4$ + 0.1 *M* $HClO_4$	$K_1 = 1.30 \pm 0.01$	28
C_3H_2NCl	$ClCH{=}CHC{\equiv}N$	glc	61	4 *M* $LiNO_3$	$K_1 = 0.283$	48
C_4H_6	$CH_2{=}CHCH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 4.2$	47
		glc	0	Ethylene glycol	$K_1 = 7.6$; $\Delta H_1 = -3.2$; $\Delta H_1 = -7.7$	78
		glc	25	Ethylene glycol	$K_1 = 4.5$	78
		glc	40	Ethylene glycol	$K_1 = 3.6$	78
C_4D_6	$CD_2{=}CDCD{=}CD_2$	glc	0	Ethylene glycol	$K_1 = 8.9$; $\Delta H_1 = -3.44$; $\Delta S_1 = -8.2$	78
		glc	25	Ethylene glycol	$K_1 = 5.1$	78
		glc	40	Ethylene glycol	$K_1 = 4.0$	78
C_4H_8	$C_2H_5CH{=}CH_2$	dis	25	Corrected to 0 *M*	$K_1 = 119.4$	83
		glc	40	Ethylene glycol	$K_1 = 7.7$	47
		glc	0	Ethylene glycol	$K_1 = 16.1$; $\Delta H_1 = -3.7$; $\Delta S_1 = -8.0$	78
		glc	25	Ethylene glycol	$K_1 = 8.8$	78
		glc	40	Ethylene glycol	$K_1 = 6.8$	78
		glc	23.2	Various concentrations of $AgNO_3$ in the range 0–3.5 *M*	$K_1 = 120$	47a
C_4H_8		dis	25	Corrected to 0 *M*	$K_1 = 62.3$	83
		glc	40	Ethylene glycol	$K_1 = 5.4$	47
		glc	0	Ethylene glycol	$K_1 = 8.7$; $\Delta H_1 = -3.4$; $\Delta S_1 = -8.2$	78
		glc	25	Ethylene glycol	$K_1 = 4.9$	78
		glc	40	Ethylene glycol	$K_1 = 3.9$	78
		glc	23.2	Various concentrations of $AgNO_3$ in the range 0–3.5 *M*	$K_1 = 90$	47a
C_4H_8		dis	25	Corrected to 0 *M*	$K_1 = 24.6$	83
		glc	40	Ethylene glycol	$K_1 = 1.4$	47
		glc	0	Ethylene glycol	$K_1 = 2.6$; $\Delta H_1 = -2.6$; $\Delta S_1 = -7.7$	78
		glc	25	Ethylene glycol	$K_1 = 1.6$	78
		glc	40	Ethylene glycol	$K_1 = 1.4$	78
		glc	23.2	Various concentrations of $AgNO_3$ in the range 0–3.5 *M*	$K_1 = 29$	47a
C_4H_8	$(CH_3)_2C{=}CH_2$	dis	25	1 *M* KNO_3	$K_1 = 61.7$	81
		dis	25	Corrected to 0 *M*	$K_1 = 71.5$	83
		glc	23.2	Various concentrations of $AgNO_3$ in the range 0–3.5 *M*	$K_1 = 55$	47a
C_4D_8		glc	0	Ethylene glycol	$K_1 = 9.9$; $\Delta H_1 = -3.56$; $\Delta S_1 = -8.5$	78
		glc	25	Ethylene glycol	$K_1 = 5.9$	78
		glc	40	Ethylene glycol	$K_1 = 4.25$	78

TABLE X *(Continued)*

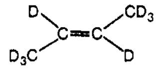
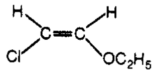
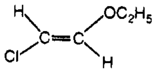
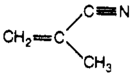
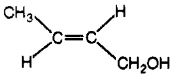
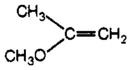
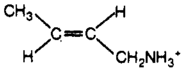
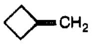
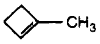
Molecular formula	Structural formula	Method	Temp, °C	Medium	K		Ref
C_4D_8		glc	0	Ethylene glycol	$K_1 = 3.0$	$\Delta H_1 = -2.75$ $\Delta S_1 = -8.0$	78
		glc	25	Ethylene glycol	$K_1 = 1.8$		78
		glc	40	Ethylene glycol	$K_1 = 1.55$		78
C_4H_7ClO		sol	25	1 *M* KNO_3	$K_1 = 0.32$		79
C_4H_7ClO		sol	25	1 *M* KNO_3	$K_1 = 0.59$		79
C_4H_5N		glc	61	4 *M* $LiNO_3$	$K_1 = 0.774$		48
C_4H_5N	$CH_3CH{=}CHC{\equiv}N$	glc	61	4 *M* $LiNO_3$	$K_1 = 0.940$		48
C_4H_6O	$CH_3CH{=}CHCHO$	dis	25	1 *M* KNO_3	$K_1 = 0.19$		81
		pot.	25	1 *M* KNO_3	$K_1 = 2.1$		82
C_4H_6O	$CH_3C({=}O)CH{=}CH_2$	dis	25	1 *M* KNO_3	$K_1 = 0.42$		84
$C_4H_6O_2$	$CH_3CH{=}CHCOOH$	dis	25	1 *M* KNO_3	$K_1 = 0.09$		81
$C_4H_6O_2$	$CH_2{=}CHCOOCH_3$	dis	25	1 *M* KNO_3	$K_1 = 0.37$; $K_{1/2} = 0.28$		84
$C_4H_6O_2$	$CH_3COOCH{=}CH_2$	dis	25	1 *M* KNO_3	$K_1 = 1.03$; $K_{1/2} = 0.37$		84
C_4H_8O	$CH_2{=}CHCH_2CH_2OH$	pot.	25	1 *M* KNO_3	$K_1 = 23$		82
C_4H_8O	$CH_3CH{=}CHCH_2OH$	dis	25	1 *M* KNO_3	$K_1 = 5.17$		81
	cis/trans mixture	sol	25	0.1 *M* KNO_3	$K_1 = 3.9$		38
C_4H_8O		pot.	25	1 *M* KNO_3	$K_1 = 5.6$		82
		pot.	25	1.9 *M* $NaClO_4$ + 0.1 *M* $HClO_4$	$K_1 = 7.87 \pm 0.02$; $K_2 = 0.57 \pm 0.07$		28
C_4H_8O		glc	10	Ethylene glycol	$K_1 = 9.51$	$\Delta H_1 = -4.7 \pm 0.2$ $\Delta S_1 = -12.0 \pm 0.6$	49
		glc	20	Ethylene glycol	$K_1 = 7.35$		49
C_4H_8O	$C_2H_5OCH{=}CH_2$	glc	10	Ethylene glycol	$K_1 = 9.08$	$\Delta H_1 = -4.4 \pm 0.2$ $\Delta S_1 = -11.0 \pm 0.6$	49
		glc	20	Ethylene glycol	$K_1 = 6.72$		49
		glc	30	Ethylene glycol	$K_1 = 5.55$		49
		dis	25	1 *M* KNO_3	$K_1 = 13.0$; $K_{1/2} = 0.6$		84
C_4H_8O	$CH_2{=}CHCH(CH_3)OH$	sol	25	0.1 *M* KNO_3	$K_1 = 14$		38
C_4H_8O	$CH_2{=}C(CH_3)CH_2OH$	sol	25	0.1 *M* KNO_3	$K_1 = 11$		38
$C_4H_{10}N^+$		pot.	25	1.9 *M* $NaClO_4$ + 0.1 *M* $HClO_4$	$K_1 = 1.28 \pm 0.05$		28
C_5H_6		glc	40	Ethylene glycol	$K_1 = 4.6$		47
C_5H_8	$CH_2{=}CHCH_2CH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 10.2$		47
C_5H_8	$CH_2{=}CH_aCH_b{=}CHCH_3$ (H_a,H_b *trans*)	glc	40	Ethylene glycol	$K_1 = 3.5$		47
C_5H_8	$CH_2{=}CH_aCH_b{=}CHCH_3$ (H_a,H_b *cis*)	glc	40	Ethylene glycol	$K_1 = 4.4$		47
C_5H_8	$CH_2{=}C(CH_3)CH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 3.1$		47
C_5H_8		dis	5	1 *M* KNO_3	$K_1^* = 0.266$	$\Delta H_1^* = -6.63$ $\Delta S_1^* = -26.5$	85
		dis	25	1 *M* KNO_3	$K_1^* = 0.119$		85
		dis	5	1 *M* KNO_3	$K_1^* = 0.267$	$\Delta H_1^* = -7.03$ $\Delta S_1^* = -27.9$	86
		dis	15	1 *M* KNO_3	$K_1^* = 0.164$		86
		dis	25	1 *M* KNO_3	$K_1^* = 0.114$		86
		glc	40	Ethylene glycol	$K_1 = 7.3$		47
		glc	25	Ethylene glycol	$K_1 = 10.2$	$\Delta H_1 = -4.3$ $\Delta S_1 = -9.9$	78
		glc	40	Ethylene glycol	$K_1 = 7.2$		78
C_5H_8		glc	40	Ethylene glycol	$K_1 = 5.8$		47
		glc	30	Ethylene glycol	$K_1 = 8.1$		87
		dis	5	1 *M* KNO_3	$K_1^* = 0.147$	$\Delta H_1^* = -4.04$ $\Delta S_1^* = -18.4$	85
		dis	25	1 *M* KNO_3	$K_1^* = 0.0900$		85
C_5H_8		glc	30	Ethylene glycol	$K_1 = 0.54$		87
C_5H_{10}	*n*-$C_3H_7CH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 4.9$		47
		glc	0	Ethylene glycol	$K_1 = 12.1$	$\Delta H_1 = -3.6$ $\Delta S_1 = -8.1$	78
		glc	25	Ethylene glycol	$K_1 = 6.7$		78
		glc	40	Ethylene glycol	$K_1 = 5.2$		78
C_5H_{10}	*i*-$C_3H_7CH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 5.1$		47

TABLE X *(Continued)*

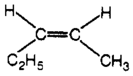
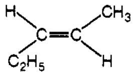
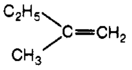
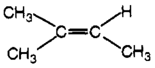
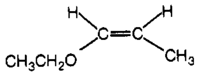
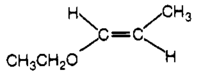
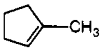
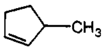
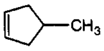
Molecular formula	Structural formula	Method	Temp, °C	Medium	K	Ref
		glc	0	Ethylene glycol	$K_1 = 15.2$ $\Delta H_1 = -3.9$	78
		glc	25	Ethylene glycol	$K_1 = 8.0$ $\Delta S_1 = -8.8$	78
		glc	40	Ethylene glycol	$K_1 = 6.1$	78
C_5H_{10}	$CH_3CH{=}CHC_2H_5$	dis	25	1 M KNO_3	$K_1 = 62.7$	81
C_5H_{10}		glc	40	Ethylene glycol	$K_1 = 4.3$	47
		glc	0	Ethylene glycol	$K_1 = 10.1$ $\Delta H_1 = -3.6$	78
		glc	25	Ethylene glycol	$K_1 = 5.6$ $\Delta S_1 = -8.5$	78
		glc	40	Ethylene glycol	$K_1 = 4.4$	78
		dis	25	1 M KNO_3	$K_1 = 112.5$; $K_1{}^* = 0.0312$	87a
C_5H_{10}		glc	40	Ethylene glycol	$K_1 = 1.1$	47
		glc	0	Ethylene glycol	$K_1 = 2.8$ $\Delta H_1 = -2.9$	78
		glc	25	Ethylene glycol	$K_1 = 1.8$ $\Delta S_1 = -8.7$	78
		glc	40	Ethylene glycol	$K_1 = 1.4$	78
		dis	25	1 M KNO_3	$K_1 = 62.2$; $K_1{}^* = 0.0111$	87a
C_5H_{10}		glc	40	Ethylene glycol	$K_1 = 3.0$	47
		glc	0	Ethylene glycol	$K_1 = 8.0$ $\Delta H_1 = -3.5$	78
		glc	25	Ethylene glycol	$K_1 = 4.4$ $\Delta S_1 = -8.6$	78
		glc	40	Ethylene glycol	$K_1 = 3.5$	78
C_5H_{10}		glc	40	Ethylene glycol	$K_1 = 0.8$	47
		glc	0	Ethylene glycol	$K_1 = 1.52$ $\Delta H_1 = -2.4$	78
		glc	25	Ethylene glycol	$K_1 = 1.01$ $\Delta S_1 = -7.8$	78
		glc	40	Ethylene glycol	$K_1 = 0.87$	78
$C_5H_{10}O$	$CH_2{=}CH(CH_2)_3OH$	pot.	25	1 M KNO_3	$K_1 = 29.2$	82
$C_5H_{10}O$		glc	10	Ethylene glycol	$K_1 = 4.00$ $\Delta H_1 = -3.9$	49
		glc	20	Ethylene glycol	$K_1 = 3.13$ $\Delta S_1 = -11.0$	49
		glc	30	Ethylene glycol	$K_1 = 2.55$	49
$C_5H_{10}O$		glc	10	Ethylene glycol	$K_1 = 0.67$ $\Delta H_1 = -3.2$	49
		glc	20	Ethylene glycol	$K_1 = 0.54$ $\Delta S_1 = -12.1$	49
		glc	30	Ethylene glycol	$K_1 = 0.47$	49
C_6H_8	*cis*-1,3,5-Hexatriene	glc	40	Ethylene glycol	$K_1 = 4.7$	47
C_6H_8	*trans*-1,3,5-Hexatriene	glc	40	Ethylene glycol	$K_1 = 5.1$	47
C_6H_8		glc	40	Ethylene glycol	$K_1 = 8.9$	47
C_6H_8		glc	40	Ethylene glycol	$K_1 = 4.9$	47
C_6H_{10}	$CH_2{=}C(CH_3)C(CH_3){=}CH_2$	glc	40	Ethylene glycol	$K_1 = 1.9$	47
C_6H_{10}	$CH_2{=}CH(CH_2)_2CH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 28.8$	47
C_6H_{10}		dis	5	1 M KNO_3	$K_1{}^* = 0.0371$ $\Delta H_1 = -5.58$	86
		dis	15	1 M KNO_3	$K_1{}^* = 0.0335$ $\Delta S_1{}^* = -26.6$	86
		dis	25	1 M KNO_3	$K_1{}^* = 0.0188$	86
		dis	5	1 M KNO_3	$K_1{}^* = 0.0369$ $\Delta H_1{}^* = -5.74$	85
		dis	25	1 M KNO_3	$K_1{}^* = 0.0184$ $\Delta S_1{}^* = -27.2$	85
		dis	0	1 M KNO_3	$K_1 = 191$	81
		dis	25	1 M KNO_3	$K_1 = 79.3$	81
		glc	40	Ethylene glycol	$K_1 = 3.6$	47
		nmr	33	CH_2Cl_2	$K_1 = 230$	37
		nmr	33	$C_6H_5NO_2$	$K_1 = 76$	37
		nmr	33	C_6H_5Cl	$K_1 = 32$	37
		nmr	33	CH_3NO_2	$K_1 = 15$	37
		nmr	33	C_2H_5OAc	$K_1 = 14$	37
		nmr	33	$(CD_3)_2CO$	$K_1 = 2.6$ (for $AgBF_4$)	37
		nmr	33	$(CD_3)_2CO$	$K_1 = 8.1$ (for $AgClO_4$)	37
		nmr	33	$CH_3OCH_2CH_2OCH_3$	$K_1 = 0.98$	37
		nmr	33	Dimethylformamide	$K_1 = 0.55$	37
C_6H_{10}		glc	30	Ethylene glycol	$K_1 = 2.9$	87
		glc	40	Ethylene glycol	$K_1 = 1.9$	47
C_6H_{10}		glc	30	Ethylene glycol	$K_1 = 12.0$	87
C_6H_{10}		glc	30	Ethylene glycol	$K_1 = 5.5$	87

TABLE X *(Continued)*

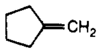
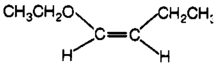
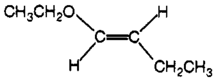
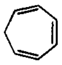
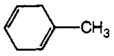
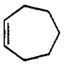
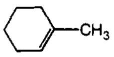
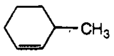
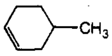
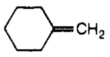
Molecular formula	Structural formula	Method	Temp, °C	Medium	K	Ref
C_6H_{10}		dis	5	1 *M* KNO_3	$K_1^* = 0.100$ $\Delta H_1^* = -3.31$	85
		dis	25	1 *M* KNO_3	$K_1^* = 0.0670$ $\Delta S_1^* = -16.5$	85
		glc	40	Ethylene glycol	$K_1 = 4.0$	47
		glc	30	Ethylene glycol	$K_1 = 6.0$	87
C_6H_{12}	$CH_3(CH_2)_3CH{=}CH_2$	dis	25	1 *M* KNO_3	$K_1 = 860$	81
		glc	40	Ethylene glycol	$K_1 = 4.3$	47
C_6H_{12}	$(CH_3)_2C{=}C(CH_3)_2$	glc	40	Ethylene glycol	$K_1 = 0.1$	47
		glc	0	Ethylene glycol	$K_1 = 0.45$ $\Delta H_1 = -1.9$	78
		glc	25	Ethylene glycol	$K_1 = 0.34$ $\Delta S_1 = -8.5$	78
		glc	40	Ethylene glycol	$K_1 = 0.29$	78
$C_6H_{12}O$		glc	10	Ethylene glycol	$K_1 = 5.62$ $\Delta H_1 = -4.5$	49
		glc	20	Ethylene glycol	$K_1 = 4.24$ $\Delta S_1 = -12.0$	49
		glc	30	Ethylene glycol	$K_1 = 3.13$	49
$C_6H_{12}O$		glc	10	Ethylene glycol	$K_1 = 0.95$ $\Delta H_1 = -3.3$	49
		glc	20	Ethylene glycol	$K_1 = 0.73$ $\Delta S_1 = -12.0$	49
		glc	30	Ethylene glycol	$K_1 = 0.63$	49
$C_6H_{12}O$	$CH_3CH_2OCH{=}C(CH_3)_2$	glc	10	Ethylene glycol	$K_1 = 0.27$ $\Delta H_1 = -3.5$	49
		glc	20	Ethylene glycol	$K_1 = 0.21$ $\Delta S_1 = -15$	49
		glc	30	Ethylene glycol	$K_1 = 0.17$	49
$C_6H_{12}O$	$CH_3(CH_2)_3OCH{=}CH_2$	glc	10	Ethylene glycol	$K_1 = 8.72$ $\Delta H_1 = -3.7$	49
		glc	20	Ethylene glycol	$K_1 = 7.76$ $\Delta S_1 = -8.8$	49
		glc	30	Ethylene glycol	$K_1 = 5.66$	49
$C_6H_{12}O$	$(CH_3)_2CHCH_2OCH{=}CH_2$	glc	10	Ethylene glycol	$K_1 = 8.77$ $\Delta H_1 = -4.0$	49
		glc	20	Ethylene glycol	$K_1 = 6.83$ $\Delta S_1 = -9.8$	49
		glc	30	Ethylene glycol	$K_1 = 5.56$	49
C_7H_8		glc	40	Ethylene glycol	$K_1 = 7.6$	47
C_7H_8		dis	20	1 *M* KNO_3	$K_1^* = 0.755$ $\Delta H_1^* = -11.18$	85
		dis	25	1 *M* KNO_3	$K_1^* = 0.572$ $\Delta S_1^* = -38.7$	85
		dis	32	1 *M* KNO_3	$K_1^* = 0.355$	85
		glc	40	Ethylene glycol	$K_1 = 33.7$	47
C_7H_{10}		glc	40	Ethylene glycol	$K_1 = 3.3$	47
C_7H_{10}		dis	5	1 *M* KNO_3	$K_1^* = 0.603$ $\Delta H_1^* = -6.68$	85
		dis	25	1 *M* KNO_3	$K_1^* = 0.268$ $\Delta S_1^* = -25.0$	85
		glc	40	Ethylene glycol	$K_1 = 62$	47
		pot.	25	1 *M* KNO_3	$K_1 = 900$	82
		dis	25	1 *M* KNO_3	$K_1^* = 0.270$	86
		nmr	33	$(CD_3)_2CO$	$K_1 = 420$	37
C_7H_{12}	$CH_2{=}CH(CH_2)_3CH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 14.7$	47
C_7H_{12}	$CH_2{=}C(CH_3)CH{=}C(CH_3)_2$	glc	40	Ethylene glycol	$K_1 = 1.6$	47
C_7H_{12}	$CH_2{=}C(CH_3)CH_2CH_2CH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 22.1$	47
C_7H_{12}		glc	40	Ethylene glycol	$K_1 = 12.8$	47
		dis	5	1 *M* KNO_3	$K_1^* = 0.0466$ $\Delta H_1^* = -6.49$	85
		dis	25	1 *M* KNO_3	$K_1^* = 0.0212$ $\Delta S_1^* = -29.4$	85
		dis	5	1 *M* KNO_3	$K_1^* = 0.0484$ $\Delta H_1^* = -6.61$	86
		dis	15	1 *M* KNO_3	$K_1^* = 0.0335$ $\Delta S_1^* = -29.8$	86
		dis	25	1 *M* KNO_3	$K_1^* = 0.0217$	86
C_7H_{12}		glc	30	Ethylene glycol	$K_1 = 1.25$	87
		dis	25	1 *M* KNO_3	$K_1^* = 0.00827$	85
		glc	40	Ethylene glycol	$K_1 = 0.5$	47
		nmr	33	$(CD_3)_2CO$	$K_1 = 0.52$ (for $AgBF_4$) $K_1 = 0.72$ (for $AgClO_4$)	37
C_7H_{12}		glc	30	Ethylene glycol	$K_1 = 5.5$	87
		glc	40	Ethylene glycol	$K_1 = 3.5$	47
C_7H_{12}		glc	30	Ethylene glycol	$K_1 = 5.1$	87
		glc	40	Ethylene glycol	$K_1 = 3.8$	47
C_7H_{12}		glc	30	Ethylene glycol	$K_1 = 9.6$	87
		glc	40	Ethylene glycol	$K_1 = 6.0$	47
		dis	5	1 *M* KNO_3	$K_1^* = 0.0872$ $\Delta H_1^* = -3.11$	85
		dis	25	1 *M* KNO_3	$K_1^* = 0.0598$ $\Delta S_1^* = -16.0$	85

TABLE X *(Continued)*

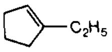
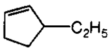
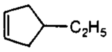
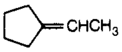
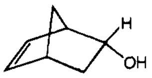
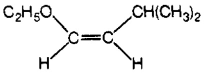
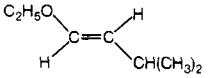
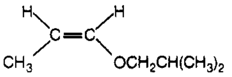
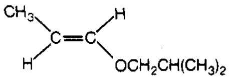
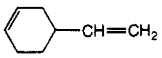
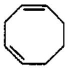
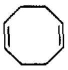
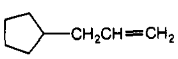
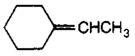
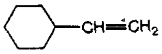
Molecular formula	Structural formula	Method	Temp, °C	Medium	K	Ref
C_7H_{12}		glc	40	Ethylene glycol	$K_1 = 2.3$	47
		glc	30	Ethylene glycol	$K_1 = 3.6$	87
C_7H_{12}		glc	30	Ethylene glycol	$K_1 = 11.8$	87
C_7H_{12}		glc	30	Ethylene glycol	$K_1 = 7.1$	87
C_7H_{12}		glc	40	Ethylene glycol	$K_1 = 0.7$	47
C_7H_{14}	$n\text{-}C_5H_{11}CH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 3.2$	47
C_7H_{14}	$C_3H_7C(CH_3)HCH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 2.7$	47
C_7H_{14}	$C_2H_5C(CH_3)HCH_2CH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 2.3$	47
C_7H_{14}	$(CH_3)_2CH(CH_2)_2CH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 3.1$	47
$C_7H_{10}O$		dis	25	1 *M* KNO_3	$K_1 = 333$	82
$C_7H_{14}O$		glc	10	Ethylene glycol	$K_1 = 5.98$ ⎫ $\Delta H_1 = -4.7$, $\Delta S_1 = -12.9$	49
		glc	20	Ethylene glycol	$K_1 = 4.46$	49
		glc	30	Ethylene glycol	$K_1 = 3.48$ ⎭	49
$C_7H_{14}O$		glc	10	Ethylene glycol	$K_1 = 0.77$ ⎫ $\Delta H_1 = -3.5$, $\Delta S_1 = -12.9$	49
		glc	20	Ethylene glycol	$K_1 = 0.59$	49
		glc	30	Ethylene glycol	$K_1 = 0.50$ ⎭	49
$C_7H_{14}O$		glc	10	Ethylene glycol	$K_1 = 3.58$ ⎫ $\Delta H_1 = -3.7$, $\Delta S_1 = -10.4$	49
		glc	20	Ethylene glycol	$K_1 = 2.86$	49
		glc	30	Ethylene glycol	$K_1 = 2.34$ ⎭	49
$C_7H_{14}O$		glc	10	Ethylene glycol	$K_1 = 0.77$ ⎫ $\Delta H_1 = -2.8$, $\Delta S_1 = -10.6$	49
		glc	20	Ethylene glycol	$K_1 = 0.60$	49
		glc	30	Ethylene glycol	$K_1 = 0.55$ ⎭	49
C_8H_8		glc	40	Ethylene glycol	$K_1 = 91$	47
C_8H_8	$PhCH{=}CH_2$	sol	25	1 *M* KNO_3	$K_1 = 18.2$; $K_{1/2} = 0.81$	88
		sol	0	1 *M* KNO_3	$K_1 = 23.9$ ⎫ $\Delta H_1 = -2.11$, $\Delta S_1 = -1.35$	89
					$K_{1/2} = 2.4$	89
		sol	40	1 *M* KNO_3	$K_1 = 14.1$	89
					$K_{1/2} = 1.8$ ⎭	89
C_8H_{12}		glc	40	Ethylene glycol	$K_1 = 11.2$	47
C_8H_{12}		glc	40	Ethylene glycol	$K_1 = 3.2$	47
C_8H_{12}		glc	40	Ethylene glycol	$K_1 = 14.4$	47
C_8H_{12}		glc	40	Ethylene glycol	$K_1 = 75$	47
C_8H_{12}		dis	25	1 *M* KNO_3	$K_1^* = 0.098$	86
		dis	5	1 *M* KNO_3	$K_1^* = 0.174$ ⎫ $\Delta H_1^* = -4.94$, $\Delta S_1^* = -21.2$	85
		dis	25	1 *M* KNO_3	$K_1^* = 0.0955$ ⎭	85
C_8H_{14}	$(CH_3)_2C{=}CHCH{=}C(CH_3)_2$	glc	40	Ethylene glycol	$K_1 = 0.8$	47
C_8H_{14}	$CH_2{=}C(CH_3)CH_2CH_2C(CH_3){=}CH_2$	glc	40	Ethylene glycol	$K_1 = 13.3$	47
C_8H_{14}	$CH_2{=}CH(CH_2)_4CH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 11.3$	47
C_8H_{14}		glc	40	Ethylene glycol	$K_1 = 3.9$	47
C_8H_{14}		glc	30	Ethylene glycol	$K_1 = 3.0$	87
		glc	40	Ethylene glycol	$K_1 = 1.6$	47
C_8H_{14}		glc	40	Ethylene glycol	$K_1 = 5.9$	47

TABLE X *(Continued)*

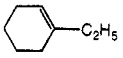
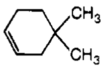
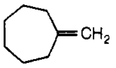
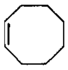
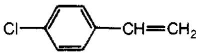
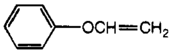
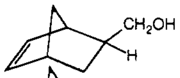
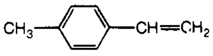
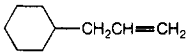
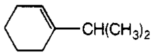
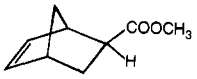
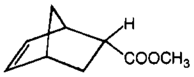
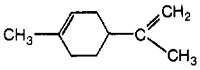
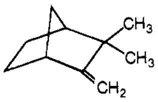
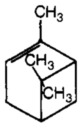
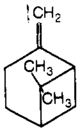
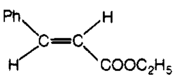
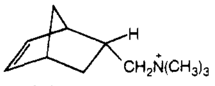
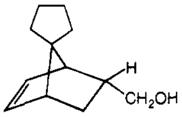
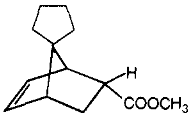
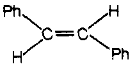
Molecular formula	Structural formula	Method	Temp, °C	Medium	K	Ref
C_8H_{14}		glc	30	Ethylene glycol	$K_1 = 1.3$	87
		glc	40	Ethylene glycol	$K_1 = 0.5$	47
C_8H_{14}		glc	40	Ethylene glycol	$K_1 = 1.4$	47
C_8H_{14}		dis	5	1 *M* KNO_3	$K_1^* = 0.107$ $\Delta H_1^* = -3.21$	85
		dis	25	1 *M* KNO_3	$K_1^* = 0.0725$ $\Delta S_1^* = -16.1$	85
C_8H_{14}	 (cis)	dis	5	1 *M* KNO_3	$K_1^* = 0.0083$ $\Delta H_1^* = -4.11$	85
		dis	25	1 *M* KNO_3	$K_1^* = 0.00504$ $\Delta S_1^* = -24.8$	85
		glc	40	Ethylene glycol	$K_1 = 14.4$	47
	(trans)	glc	40	Ethylene glycol	$K_1 > 1000$	47
C_8H_7Cl		sol	0	1 *M* KNO_3	$K_1 = 32.2$ $K_{1/2} = 2.5$ $\Delta H_1 = -1.88$	89 89
		sol	40	1 *M* KNO_3	$K_1 = 20.7$ $\Delta S_1 = 0.03$ $K_{1/2} = 1.7$	89 89
C_8H_8O		dis	25	1 *M* KNO_3	$K_1 = 5.26$; $K_{1/2} = 0.77$	84
$C_8H_{12}O$		dis	25	1 *M* KNO_3	$K_1 = 253$	82
$C_8H_{12}O$		dis	25	1 *M* KNO_3	$K_1 = 330$	82
C_9H_{10}		sol	0	1 *M* KNO_3	$K_1 = 15.2$ $K_{1/2} = 0.52$ $\Delta H_1 = -2.19$	89 89
		sol	40	1 *M* KNO_3	$K_1 = 9.07$ $\Delta S_1 = -2.62$ $K_{1/2} = 0.52$	89 89
C_9H_{16}	$CH_2{=}CH(CH_2)_5CH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 10.4$	47
C_9H_{16}		glc	40	Ethylene glycol	$K_1 = 3.2$	47
C_9H_{16}		glc	30	Ethylene glycol	$K_1 = 1.05$	87
$C_9H_{12}O_2$		dis	25	1 *M* KNO_3	$K_1 = 346$	82
$C_9H_{12}O_2$		dis	25	1 *M* KNO_3	$K_1 = 193$	82
$C_{10}H_{16}$		glc	40	Ethylene glycol	$K_1 = 5.9$	47
$C_{10}H_{16}$		glc	40	Ethylene glycol	$K_1 = 3.1$	47
$C_{10}H_{16}$		glc	40	Ethylene glycol	$K_1 = 1.1$	47
$C_{10}H_{16}$		glc	40	Ethylene glycol	$K_1 = 3.7$	47
$C_{10}H_{18}$	$CH_2{=}CH(CH_2)_6CH{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 7.8$	47
$C_{11}H_{12}O$		sol	25	1 *M* KNO_3	$K_1 = 1.0$; $K_{1/2} = 0.3$	88

TABLE X *(Continued)*

Molecular formula	Structural formula	Method	Temp, °C	Medium	K	Ref
$C_{11}H_{20}N+$	 (87% *endo*; 13% *exo*)	pot.	25	0.1 M KNO_3	$K_1 = 91$	82
$C_{12}H_{18}O$		dis	25	1 M KNO_3	$K_1 = 15$	82
$C_{13}H_{18}O_2$		dis	25	1 M KNO_3	$K_1 = 3.6$	82
$C_{14}H_{16}$		sol	25	1 M KNO_3	$K_1 = 6.3$; $K_{1/2} = 0.63$	88
$C_{14}H_{16}$	$(Ph)_2C{=}CH_2$	sol	25	1 M KNO_3	$K_1 = 2.3$; $K_{1/2} = 1.3$	88
(ii) Acetylenes^b						
$K_1 = \frac{[Ag(acetylene)^+]}{[Ag^+][acetylene]}$; $K_{1/2} = \frac{[Ag_2(acetylene)^{2+}]}{[Ag(acetylene)^+][Ag^+]}$						
C_2H_2	$HC{\equiv}CH$	sol	25	Corrected to 0 M ionic strength	$K_1 = 42.7$; $\Delta H_1 = -13.2$; $\Delta S_1 = -36.9$	90
C_6H_{10}	$CH_3CH_2CH_2C{\equiv}CCH_3$	glc	40	Ethylene glycol	$K_1 = 2.0$	47
C_6H_{10}	$C_2H_5C{\equiv}CC_2H_5$	glc	40	Ethylene glycol	$K_1 = 2.6$	47
		sol	25	1 M KNO_3	$K_1 = 17.3$; $K_{1/2} = 0.36$; $K_1{}^0 = 0.131$	41
		sol	35	1 M KNO_3	$K_1 = 17.3$; $K_{1/2} = 0.21$; $K_1{}^0 = 0.103$	41
C_7H_{12}	$CH_3(CH_2)_3C{\equiv}CCH_3$	glc	40	Ethylene glycol	$K_1 = 1.6$	47
		sol	25	1 M KNO_3	$K_1 = 11.9$; $K_{1/2} = 0.26$; $K_1{}^0 = 0.0204$	41
C_7H_{12}	$CH_3(CH_2)_2C{\equiv}CC_2H_5$	glc	40	Ethylene glycol	$K_1 = 2.1$	47
C_7H_{12}	$(CH_3)_2CH_2C{\equiv}CC_2H_5$	sol	25	1 M KNO_3	$K_1 = 20.5$; $K_{1/2} = 0.28$; $K_1{}^0 = 0.0386$	41
C_8H_{14}	$CH_3(CH_2)_4C{\equiv}CCH_3$	glc	40	Ethylene glycol	$K_1 = 1.2$	47
C_8H_{14}	$CH_3(CH_2)_2C{\equiv}C(CH_2)_2CH_3$	glc	40	Ethylene glycol	$K_1 = 1.5$	47
C_8H_{14}	$(CH_3)_3CC{\equiv}CC_2H_5$	sol	25	1 M KNO_3	$K_1 = 19.1$; $K_{1/2} = 0.30$; $K_1{}^0 = 0.0130$	41
C_9H_{16}	$(CH_3)_3CC{\equiv}CCH(CH_3)_2$	sol	25	1 M KNO_3	$K_1 = 23.4$; $K_{1/2} = 0.34$; $K_1{}^0 = 0.00529$	41
$C_{10}H_{18}$	$(CH_3)_3CC{\equiv}CC(CH_3)_3$	sol	25	1 M KNO_3	$K_1 = 12.8$; $K_{1/2} = 0.53$; $K_1{}^0 = 0.00191$	41
		sol	35	1 M KNO_3	$K_1 = 18.6$; $K_{1/2} = 0.33$; $K_1{}^0 = 0.00145$	41
(iii) Allenes						
$K_1 = [Ag(allene)^+]/([Ag^+][allene])$						
C_3H_4	$CH_2{=}C{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 0.8$	47
C_4H_6	$CH_3CH{=}C{=}CH_2$	glc	40	Ethylene glycol	$K_1 = 0.8$	47

[a] All stability constants except $K_1{}^*$ are in aqueous solution unless otherwise specified. [b] $K_1{}^0 = K_1/\gamma_{ac}$, where γ_{ac} = activity coefficient of acetylene (see text). All stability constants are in aqueous solution unless otherwise specified.

filled d orbitals of the metal and the empty π^* (antibonding) orbitals of the olefin, thus considerably reducing the overall bond strength. Nuclear magnetic resonance studies of class S olefin complexes have shown that this type of rotation does occur both in solution[110,112-114] and in the solid state.[115] Again, the observation of this type of rotation by X-ray diffraction is not clear-cut because no olefins lie exactly perpendicular to the square plane around the metal. However, in $[Pt(\textit{trans}\text{-}CH_3\text{-}CH{=}CH_2NH_3)Cl_3]$ the angle β in Figure 4 is 81.5°[111] compared with 85.5° in the corresponding *cis*-crotylammonium complex.[65] It might be thought that

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(112) A. R. Brause, F. Kaplan, and M. Orchin, *J. Amer. Chem. Soc.*, **89**, 2661 (1967).

(113) C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 53 (1969).

(114) R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964).

(115) S. Maričić, C. R. Redpath, and J. A. S. Smith, *J. Chem. Soc.*, 4905 (1963).

TABLE XI. Thermodynamic Data for Silver(I)-Olefin Complexes in the Solid Phase[a]

Olefin	*n*	X	Temp range studied, °C	ΔG	ΔH	ΔS	Ref
C_2H_4	1	BF_4	9.8–49.8	−2.42	−10.61	−27.5	91
	1.5	BF_4 (α form)	9.8–25.3	−3.28	−13.94	−35.7	91
	1.5	BF_4 (β form)	25.3–49.8	−3.28	−15.56	−41.2	91
	2	BF_4 (α form)	5.2–27.3	−3.67	−16.93	−44.5	91
	2	BF_4 (β form)	27.3–50.3	−3.67	−18.98	−51.3	91
	3	BF_4	−0.3–8.0	−3.08	−27.23	−81.0	91
	0.5	NO_3	−20–0		−5.3 (at −10°)		92
C_3H_6	2	BF_4	0.0–50.3	−4.59	−21.94	−58.2	91
	3	BF_4	−46.8–3.0	−3.88	−30.87	−93.9	91
$CH_2{=}CHCH_2CH_3$	1	NO_3	−5–25		−10.1		93
	2	BF_4	14.7–35.4	−5.20	−24.05	−63.2	91
	3	BF_4	−0.8–9.0	−5.10	−35.34	−101.3	91
cis-$CH_3CH{=}CHCH_3$	2	BF_4	24.6–54.6	−6.20	−25.79	−65.7	91
	3	BF_4	−4.1–10.5	−6.24	−37.67	−105.4	91
trans-$CH_3CH{=}CHCH_3$	2	BF_4	14.5–54.8	−4.26	−25.52	−71.3	91
$CH_2{=}C(CH_3)_2$	2	BF_4	14.9–51.6	−5.28	−22.28	−57.0	91
$CH_2{=}CHCH{=}CH_2$	0.5	NO_3	0–49		−6.5		94
	1	NO_3	−20–11		−10.8		94

[a] Thermodynamic data at 25° for the system $AgX(cryst) + n\ olefin(g) \rightleftarrows [Ag(olefin)_n]X(cryst)$ obtained from measurements of the dissociation pressure of $[Ag(olefin)_n]X$.

TABLE XII. Thermodynamic Data for Mercury(II)-Olefin and -Acetylene Complexes

Unsaturated ligand	Method	Temp, °C	Medium	*K*	Ref
$HC{\equiv}CH$	sol	25	Corrected to 0 *M* ionic strength	Solubility product $[Hg^{2+}][L]^2[OH^-]^2 = 10^{-37.10}\ mol^5\ l.^{-5}$	95
$H_2C{=}CH_2$	kin	25	1 *M* ClO_4^-	$K(Hg^{2+} + L \rightleftarrows HgL(OH)^+ + H^+) = 3.47 \times 10^6$	96
Cyclohexene	dis	25	1 *M* KNO_3	$K(Hg^{2+} + L \rightleftarrows HgL^{2+}) = 2.19 \times 10^4$	97
				$K(Hg^{2+} + L \rightleftarrows HgL(OH)^+ + H^+) = 5.0 \times 10^4$	97

since silver shows a preference for linear coordination, there would be no cis ligands present in silver complexes to give steric interactions causing the postulated rotations of the olefins. However, there is strong evidence[116,117] that in water the silver ion exists as $[Ag(H_2O)_4]^+$.

e. Monocyclic Olefins

The stability of the silver ion complexes of cyclic olefins decreases in the order $C_5 > C_7 > C_6 > C_8$ (Table XVII). This order apparently results almost entirely from enthalpy effects since there are only very small entropy changes across the series. With the exception of cyclohexene this stability and enthalpy order follows a similar pattern to the heats of hydrogenation of these cyclic olefins ($C_6 > C_7 \geq C_5 > C_8$[118]). Since heats of hydrogenation largely reflect the relief of strain, it is apparent that the strain in the cyclic olefin, modified somewhat by electronic and steric effects, is the most important factor in the bonding of the olefin to the metal. This probably arises from two effects: (i) the slight weakening and lengthening of the multiple bond that occurs on coordination relieves some of the strain present in the free olefin, thus giving a favorable enthalpy contribution; and (ii) the strain in the cyclic olefin facilitates deformation of the π orbital of the olefin thus promoting complex formation. In addition to strain the transannular hydrogen atoms can influence the stability of the complex. Thus cyclopentene

TABLE XIII. Classification of Olefin Complexes

	Class S	Class T
Model complex	$K^+[Pt(C_2H_4)Cl_3]^-$	$[(Ph_3P)_2Pt(C_2H_4)]$
Coordination number of the metal	4 or 6	3 or 5
Rotation of the olefin about metal-olefin bond?	Yes	No
Angle between axis of double bond and square plane of metal	77–90°	0–24°
Multiple bond lengthening on coordination, Å	~0.02	~0.15
Angle at which substituents on multiple bond are bent back away from metal	~15°	~35°
Examples of metal ions giving each class of complex	Pt^{II}, Pd^{II}, Fe^{II}, Rh^{I}, Re^{I}, Mn^{I}	Pt^0, Pd^0, Fe^0, Ir^{I}, W^{I}, Mo^{I}

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(116) H. B. Jonassen and P. C. Yates, "Symposium on Equilibrium and Rate Behaviour of Complex Ions," University of Chicago, Feb 21–23, 1951, Paper 25.

(117) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p 107.

(118) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, **79**, 4116 (1957).

TABLE XIV. Influence of Substituents on the Multiple Bond on the Stability of Metal–Olefin Complexes

Metal	Olefin	Stability constant[a]	ΔH	ΔS	Ref
Ag^I	C_2H_4	$K_{Ag} = 17.5$	−3.5	−6.0	78
	$CH_3CH{=}CH_2$	$K_{Ag} = 7.5$	−3.5	−7.5	78
	cis-$CH_3CH{=}CHCH_3$	$K_{Ag} = 4.9$	−3.4	−8.2	78
	$(CH_3)_2C{=}CHCH_3$	$K_{Ag} = 1.01$	−2.4	−7.8	78
	$(CH_3)_2C{=}C(CH_3)_2$	$K_{Ag} = 0.34$	−1.9	−8.5	78
Cu^I	$CH_2{=}CHC(CH_3)HOH$	$K_{Cu} = 33{,}000$			38
	$CH_3CH{=}CHCH_2OH$	$K_{Cu} = 10{,}000$			38
	$CH_2{=}C(CH_3)CH_2OH$	$K_{Cu} = 9200$			38
Rh^I	C_2H_4	$K_{Rh} = 1$	0	0	31
	$CH_3CH{=}CH_2$	$K_{Rh} = 0.078$	1.4	−0.5	31
	cis-$CH_3CH{=}CHCH_3$	$K_{Rh} = 0.0041$	1.8	−4.9	31
	$(CH_3)_2C{=}CH_2$	$K_{Rh} = 0.00035$	3.9	−2.6	31
Pt^{II}	$CH_2{=}CHCH_2NH_3^+$	$K_{Pt} = 1022$	−7.1	−7.6	30
	trans-$CH_3CH{=}CHCH_2NH_3^+$	$K_{Pt} = 209$	−5.1	−4.65	66
	$CH_2{=}C(CH_3)CH_2NH_3^+$	$K_{Pt} = 6.2$			66
	$(CH_3)_2{=}CHCH_2NH_3^+$	$K_{Pt} = 2.6$			66

[a] K_{Ag} = [Ag(olefin)$^+$]/([Ag$^+$][olefin]) at 25° in ethylene glycol. K_{Cu} = [Cu(olefin)$^+$]/([Cu$^+$][olefin]) at 25° in 0.1 *M* aqueous perchloric acid. K_{Rh} = ([(acac)Rh(C_2H_4)(olefin)][C_2H_4])/([acac)Rh(C_2H_4)$_2$][olefin]) at 25° in toluene. K_{Pt} = ([Pt(olefin)Cl_3^-][Cl^-])/([$PtCl_4^{2-}$][olefin]) at 60° in aqueous 1.9 *M* NaCl + 0.1 *M* HCl.

TABLE XV. The Influence of Chain Length on the Stability of Metal–Olefin Complexes

Metal	Solvent	Olefin	Stability constant[a]	ΔH	ΔS	Ref
Ag^I	Ethylene glycol	C_2H_4	$K_{Ag} = 17.5$	−3.5	−6.0	78
		$CH_3CH{=}CH_2$	$K_{Ag} = 7.5$	−3.5	−7.5	78
		$C_2H_5CH{=}CH_2$	$K_{Ag} = 8.8$	−3.7	−8.0	78
		n-$C_3H_7CH{=}CH_2$	$K_{Ag} = 6.7$	−3.6	−8.1	78
		n-$C_4H_9CH{=}CH_2$	$K'_{Ag} = 4.3$			47
		n-$C_5H_{11}CH{=}CH_2$	$K'_{Ag} = 3.2$			47
	H_2O (1 *M* KNO_3)	C_2H_4	$K_{Ag} = 85.3$			77
	H_2O (1 *M* KNO_3)	$CH_3CH{=}CH_2$	$K_{Ag} = 87.2$			77
	H_2O (corrected to 0 *M*)	$C_2H_5CH{=}CH_2$	$K_{Ag} = 119.4$			83
	H_2O (1 *M* KNO_3)	*n*-$C_4H_9CH{=}CH_2$	$K_{Ag} = 860$			81
Pd^{II}	H_2O (4 *M*; 0.5 *M* HCl + 2.5 *M* $HClO_4$ + 1.0 *M* LiCl)	C_2H_4	$K_{Pd} = 15.2$	−1.5	0	58, 59
		$CH_3CH{=}CH_2$	$K_{Pd} = 7.9$	0	4	59
		$C_2H_5CH{=}CH_2$	$K_{Pd} = 12.4$	0	5	59, 62
Rh^I	Toluene	C_2H_4	$K_{Rh} = 1$	0	0	31
		$CH_3CH{=}CH_2$	$K_{Rh} = 0.078$	1.4	−0.5	31
		$C_2H_5CH{=}CH_2$	$K_{Rh} = 0.092$	1.0	−1.7	31

[a] K_{Ag} = [Ag(olefin)$^+$]/([Ag$^+$][olefin]) at 25°; K'_{Ag} = same at 40°. K_{Pd} = ([Pd(olefin)Cl_3^-][Cl^-])/([$PdCl_4^{2-}$][olefin]) at 20°. K_{Rh} = ([(acac)Rh(C_2H_4)(olefin)][C_2H_4])/([acac)Rh(C_2H_4)$_2$][olefin]) at 25°.

and cycloheptene are about equally strained, but in cycloheptene the transannular hydrogen atoms interfere sterically with the π bond and so lower the enthalpy of formation of the complex.[86]

f. Exocyclic Double Bonds

The stabilities, enthalpies, and entropies of formation of silver complexes with cyclic olefins in which the multiple bond is exocyclic are very similar for five-, six-, and seven-membered rings (Table XVIII). However, the stability and enthalpy of formation of the silver complex of methylenecyclobutane is rather higher, reflecting the much greater strain in the four-membered ring compound, which is slightly reduced on complex formation due to the introduction of some sp^3 character to the carbon atoms of the double bond.

g. Polycyclic Olefins

Polycyclic olefins, such as norbornene, interact with silver ions to give predominantly the sterically less hindered exo product in which the silver ion is on the opposite side of the C_6 ring to the bridge-head carbon atom. A comparison of the thermodynamic data for the formation of the silver complexes of norbornene, cyclopentene, and cyclohexene (Table XIX) shows that while the entropy terms are similar for all three, the enthalpies of formation put norbornene midway between the C_5 and C_6 monocyclic olefins.

h. Diolefins

The stability of the silver ion complexes of the diolefins $CH_2{=}CH(CH_2)_nCH{=}CH_2$ shows a maximum at $n = 2$ (stability constant (value of n): 4.2 (0), 3.1 (1), 28.8 (2), 14.7 (3), 11.3 (4), 10.4 (5), 7.8 (6)[47]). This may indicate that a six carbon atom chain is the optimum for chelate formation with silver.

2. *Electronic Properties*

a. Conjugation

Unfortunately thermodynamic data for conjugated olefins have only been obtained for silver where it is found

TABLE XVI. Thermodynamic Data for Cis and Trans Olefins

Metal	Olefin	Stability constants[a] Cis	Stability constants[a] Trans	ΔH Cis	ΔH Trans	ΔS Cis	ΔS Trans	Ref
Ag^{I}	$CH_3CH{=}CHCH_3$	$K_{Ag} = 4.9$	$K_{Ag} = 1.6$	−3.4	−2.6	−8.2	−7.7	78
	$CD_3CD{=}CDCD_3$	$K_{Ag} = 5.9$	$K_{Ag} = 1.8$	−3.56	−2.75	−8.5	−8.0	78
	$C_2H_5CH{=}CHCH_3$	$K_{Ag} = 5.6$	$K_{Ag} = 1.8$	−3.6	−2.9	−8.5	−8.7	78
	$C_2H_5OCH{=}CHCH_3$	$K'_{Ag} = 3.13$	$K'_{Ag} = 0.54$	−3.9	−3.2	−11.0	−12.1	49
	$C_2H_5OCH{=}CHC_2H_5$	$K'_{Ag} = 4.24$	$K'_{Ag} = 0.73$	−4.5	−3.3	−12.0	−12.0	49
Pt^{II}	$CH_3CH{=}CHCH_2NH_3^+$	$K_{Pt} = 1075$	$K_{Pt} = 450$	−6.0	−5.1	−5.9	−4.6	65, 66

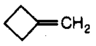
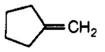
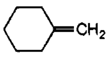
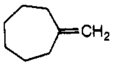
[a] $K_{Ag} = ([Ag^+][\text{olefin}])/[Ag(\text{olefin})^+]$ at 25°; K'_{Ag} = same at 20°. $K_{Pt} = ([Pt(\text{olefin})Cl_3^-][Cl^-])/([PtCl_4^{2-}][\text{olefin}])$ at 30°.

TABLE XVII. Thermodynamic Data for Silver(I) Complexes with Cyclic Olefins

Olefin	Stability constant[a]	ΔH	ΔS	Ref
Cyclopentene	0.114	−7.03	−27.9	86
Cyclohexene	0.0118	−5.58	−26.6	86
Cycloheptene	0.0217	−6.61	−29.8	86
Cyclooctene (*cis*)	0.00504	−4.11	−24.8	85

[a] Stability constant = $[Ag(\text{olefin})^+]_{H_2O}/([Ag^+]_{H_2O}[\text{olefin}]_{\text{organic solvent}})$ at 25° obtained by a distribution method.

TABLE XVIII. Thermodynamic Data for Silver(I) Complexes with Exocyclic Olefins

Olefin	Stability constant[a]	ΔH	ΔS	Ref
	0.0900	−4.04	−18.4	78
	0.0670	−3.31	−16.5	78
	0.0598	−3.11	−16.0	78
	0.0725	−3.21	−16.1	78

[a] Stability constant = $[Ag(\text{olefin})^+]_{H_2O}/([Ag^+]_{H_2O}[\text{olefin}]_{\text{organic solvent}})$ at 25° obtained by a distribution method.

that the diene gives a lower stability constant than the corresponding monoene (*cf.*, 1-butene and butadiene). The entropies of formation of the two complexes are similar while the enthalpy terms favor the monoene probably because only one of the double bonds in the diene bonds to silver yet the conjugation present in the free diene is lost.

b. Electronic Effects of Substituents

As mentioned above (section IV.A.1.a), it is generally extremely difficult to separate the steric and electronic influences of substituents, although it is possible in favorable circumstances either by considering unsaturated ligands in which the substituent under examination is remote from the coordination site as in para-substituted phenylacetylene and para-substituted styrene or by comparing substituents with similar steric substituent constants.[119] With this in mind, examination of the thermodynamic data indicates that metals fall into two groups. The first group, comprising silver(I) and copper(I), shows a decrease in the stability and enthalpy of formation of the metal-olefin complex as the electron-withdrawing ability of the substituent increases. By contrast metals in the second group, nickel(0), platinum(0), platinum(II), rhodium(I), and iridium(I), all show increases in the stability and enthalpy of formation of their olefin (or acetylene) complexes as the electron-withdrawing ability of the substituent is increased.

These results can be understood in terms of the molecular orbital description of the metal-olefin bond given above (section IV). In the case of metal ions in the first group, the σ (olefin to metal) bond is more important than the π (metal to olefin) bond for the formation of a stable metal-olefin complex, and so any reduction in the availability of the olefinic π electrons decreases the stability of the metal-olefin complex. In the case of the second group of metals it is the π-acceptor ability of the olefin that is more important for the formation of a stable metal-olefin bond, and so electron-withdrawing substituents on the olefin naturally increase the stability of the complex.

3. *Effect of Deuteration*

The replacement of a hydrogen atom in an olefin by deuterium increases both the stability constant and the enthalpy of formation of the silver-olefin complex.[78] The effect is greater where the deuterium is bound to one of the unsaturated carbon atoms than to the neighboring saturated carbon atoms. Although it is difficult to rationalize this isotope effect without a detailed knowledge of the structural parameters and vibrational characteristics of the complexes, it could be due to a combination of (i) the greater inductive release of electrons from C–D than from C–H bonds[120,121] and (ii) the smaller steric effect of deuterium than hydrogen[122] leading to less nonbonded interactions in the deuterated free olefins. A third possibility that the nonbonded interactions with silver are smaller can be eliminated since deuteration of the unsaturated carbon atoms in ethylene, propene, and but-2-ene gives a similar effect whereas it should give a decreasing effect if nonbonded interactions with silver were important.

B. Properties of the Metal

As already mentioned (section IV.A.2.b), metal ions fall into two classes, those in which electron-withdrawing substituents on the olefin decrease the stability and those in which the reverse effect occurs. The former group comprises silver(I), as can be seen from the effects of

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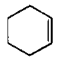
(119) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

(120) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

(121) E. A. Halevi, M. Nussim, and A. Ron, *J. Chem. Soc.*, 866 (1963).

(122) L. S. Bartell, *J. Amer. Chem. Soc.*, **83**, 3567 (1961).

TABLE XIX. Thermodynamic Data for Silver(I) Complexes with Polycyclic Olefins

Olefin	Stability constant[a]	ΔH	ΔS	Ref
	0.268	−6.68	−25.0	85
	0.0188	−5.58	−26.6	86
	0.114	−7.03	−27.9	86

[a] $K = [\mathrm{Ag(olefin)}^+]_{\mathrm{H_2O}}/([\mathrm{Ag}^+]_{\mathrm{H_2O}}[\mathrm{olefin}]_{\text{organic solvent}})$ at 25° obtained by a distribution method.

TABLE XX. Equilibrium Constants in Benzene at 25°, Obtained Using a Spectrophotometric Technique (from Ref 123), for the Reaction

$$ML_3 + C_2H_4 \overset{K}{\rightleftharpoons} [L_2M(C_2H_4)] + L$$

L	M	K
PPh_3	Ni	300
PPh_3	Pd	0.013
PPh_3	Pt	0.122
$P(p\text{-}C_6H_4CH_3)_3$	Pd	0.016
$P(p\text{-}C_6H_4CH_3)_3$	Pt	0.21
$P(m\text{-}C_6H_4CH_3)_3$	Pd	0.004
$P(m\text{-}C_6H_4CH_3)_3$	Pt	0.07

halide substitution, bearing in mind that methyl and bromide groups have comparable steric effects,[119] copper(I), as indicated by the lower stabilities of the α,β-unsaturated acids compared with the α,β-unsaturated alcohols. Although there are insufficient data at present, it is likely that when more data become available mercury(II) will be found to show the same characteristics. The relative stabilities of the olefin complexes of these three metal ions are mercury(II) > silver(I)[39] and copper(I) > silver(I).[38]

Although the stabilities of the olefin complexes of nickel(0),[56] platinum(II),[30] rhodium(I),[31] and iridium(I)[55] and the acetylene complexes of platinum(0)[63] increase with increasing electron-withdrawing power of substituents on the olefin or acetylene, it is significant that although the displacement of ethylene by tetrafluoroethylene at rhodium(I) is thermodynamically favored, it occurs slower by a factor of 10^6 than ethylene exchange. This behavior suggests a mechanism in which the rate-determining step is nucleophilic addition of the incoming olefin to the rhodium(I) complex, and further suggests that the formation of the σ (olefin to metal) and not the π (metal to olefin) bond is of critical importance in the formation of the activated complex.[31]

The results in Table XX might at first be thought to support other observations, such as the strength of chemisorption of ethylene on metal surfaces,[124] which suggest that platinum(0) forms stronger olefin complexes than palladium(0), although the high relative stability of the nickel(0) complex is obviously suspicious. However, as has recently been pointed out,[37a] it is impossible to use displacement reactions to compare the stabilities of metal–olefin bonds when the metal is being varied. Compare the two reactions

$$\mathrm{ML} + \mathrm{ol} \rightleftharpoons \mathrm{M(ol)} + \mathrm{L} \qquad (3)$$

$$\mathrm{M'L} + \mathrm{ol} \rightleftharpoons \mathrm{M'(ol)} + \mathrm{L} \qquad (4)$$

For reaction 3

$$\Delta G_{\text{reaction 3}} = \Delta G^{\mathrm{M(ol)}} - \Delta G^{\mathrm{ML}}$$

and similarly for reaction 4. Hence

$$(\Delta G_{\text{reaction 3}} - \Delta G_{\text{reaction 4}}) = (\Delta G^{\mathrm{M(ol)}} - \Delta G^{\mathrm{M'(ol)}}) - (\Delta G^{\mathrm{ML}} - \Delta G^{\mathrm{M'L}})$$

Thus the relative stability constants depend not only on the relative free energies of formation of the two metal–olefin complexes, but also on the relative free energies of formation of the two metal–ligand L complexes. It has been suggested[123] that *if* the relative stabilities of the metal(0)–triphenylphosphine bonds are such that the stability of the metal(0)–ethylene bonds do indeed increase in the order Pd(0) < Pt(0) ≪ Ni(0) (Table XX), then this may be due to the ability of the metal to donate electron density to the olefin through the π-metal–olefin bond increasing in the order Pd(0) < Pt(0) ≪ Ni(0). This electron donor ability was gauged from the ionization potentials of the metals, the electron promotion energies $(n-1)d^{10} \rightarrow (n-1)d^9np$ (Ni, 1.72 eV; Pt, 3.23 eV; Pd, 4.23 eV[125]) and the electronic spectra of the tris(triphenylphosphine) complexes of the metals.[123]

The nature of the other nonolefinic ligands coordinated to the metal is obviously of crucial importance to the stability of the metal–olefin bond. This aspect has, however, only received limited attention. The results, which are available for platinum(II)[68] and iridium(I),[55] show that replacement of a chloride ligand by a heavier halide decreases the stability constant, although analysis of the enthalpy data in the platinum(II) system indicated that the platinum(II)–olefin bond was actually stronger in the bromo than in the chloro complexes.[68] Investigation of the coordination of a series of bidentate chelate ligands, $CH_2{=}CH(CH_2)_2XCHCOO^-$, where X = S or Se, to silver(I) showed a similar effect in that replacing sulfur by selenium resulted in a more favorable enthalpy of formation that was to some extent opposed by an increasingly unfavorable entropy of formation.[126] The results for the three metals platinum(II), iridium(I), and silver(I) are thus all examples of a "symbiotic" effect whereby olefins form stronger complexes with metals when those metals are also coordinated to other soft ligands. A study[56] of the influence of the nonolefinic ligand in a series of dialkylnickel(II)–olefin complexes has shown that the stability increases as the alkyl group is varied in the series R = $CH_3 < C_2H_5 < C_3H_7$. This corresponds to an increase in the energy of the highest occupied orbital on nickel(II) in the order R = $CH_3 < C_2H_5 < C_3H_7$.[56] Since an increase in the energy of the highest occupied orbital on nickel(II) gives rise to an increase in the interaction between this orbital and the π^* (antibonding) orbital on the olefin, it may be concluded that the π (metal to olefin) component of the nickel(II)–olefin bond is more important than the σ (olefin to metal) component for the formation of a stable nickel(II)–olefin complex. When the alkyl group was increased to isobutyl a drop in stability occurred due to steric effects.

A similar conclusion, that the π component of the

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