Comparison of Thermodynamic Parameters Obtained by Gas Chromatographic and Spectrophotometric Methods for the Interaction of a Lewis Acid Transition Metal Complex with a Lewis Base

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Abstract: For the first time a GLC determination of thermodynamic parameters using *solutions* of one reactant on the column has been coupled with full corrections for adsorption effects to obtain an accurate enthalpy and entropy for an acid-base reaction in the liquid phase. The system studied involved the interaction of the Lewis base triethylamine with the Lewis acid bis(7,7,11,11-tetramethylheptadecane-8,10-dionato)nickel(II) in squalane. The equilibrium constants, enthalpy, and entropy all compare favorably with those obtained in solution using spectrophotometric methods. Previous studies have yielded different values for the equilibrium constants obtained by the GLC method than from other solution techniques (i.e., spectrophotometric and calorimetric procedures). A new modification of the method for elimination of adsorption contributions has been developed which significantly shortens the time required for analysis. The success of this experiment indicates that data from the GLC experiment may be used in a complementary fashion to standard procedures to determine the reactivity of transition-metal compounds in solution.

For some time gas-liquid chromatography (GLC) has been used to obtain thermodynamic data for acid-base reactions.[1] Two basic methods have evolved: the *neat liquid method,* which employs one reactant as a neat liquid phase on the GLC column,[2] and the *solution method,* which involves a solution phase on the column.[3] (This should not be confused with the use of "solution dominated" peaks advocated by Martire and Liao[11] for correction of adsorption effects.) Three basic techniques have been developed for adsorption effect corrections without which the thermodynamic data obtained by the GLC methods have little quantitative meaning.[4-8]

Recently we showed that enthalpies of hydrogen-bonding interactions obtained by the *neat liquid method* for long-chain aliphatic donors are in agreement with those obtained by calorimetric or infrared frequency shift techniques.[9] The GLC method used involved pure base on the column and corrections for interfacial effects were made using the solution-dominated approach.[8] This study demonstrated that the same enthalpies could be obtained by the GLC method as those for a comparable system in solution.

It has been shown that both of the basic GLC methods give the same equilibrium constant for certain systems.[10] It has also been established that the various methods for correction of adsorption effects give the same results.[11] However, to our knowledge, no one has coupled the use of the *solution method* with corrections for interfacial effects to obtain enthalpies that are comparable to those obtained from solution calorimetric or spectrophotometric methods.

We are primarily interested in utilizing the GLC technique to determine accurate solvation-minimized[12] enthalpies for acid-base interactions in which the acid is a transition-metal complex. For this reason we have prepared the squalane-soluble compound bis(7,7,11,11-tetramethylheptadecane-8,10-dionato)nickel(II), Ni(THDD)$_2$.[13] The enthalpy and entropy of interaction of this compound with triethylamine have been determined by both the *solution method* using data corrected for interfacial effects and by a spectroscopic technique. There is good agreement between the two methods. During the course of this work a new, rapid method has been developed for analysis of the data required to correct for the interfacial phenomenon and a method is presented for improving the precision of enthalpies obtained by the GLC technique. It is also important to note that, although lack of agreement between equilibrium constants obtained by GLC and alternate techniques has been previously reported,[14] the GLC equilibrium constants obtained by the method reported in this study agree with those obtained in the corresponding spectrophotometric study.

Thermodynamic Association Parameters from GLC

Net Retention Volume. When a volatile solute (or Lewis base), B, is injected onto a GLC column, a measure of the total interaction between B and the column packing is given by the net retention volume, V_N:[15]

$$V_N = \left[\frac{3}{2}\frac{(P_o/P_i)^2 - 1}{(P_o/P_i)^3 - 1}\right]\left[F_m\left(\frac{273.16}{T_m}\right)(P_o - P_w)\right](t_R - t_M) \tag{1}$$

The first term in brackets is a correction for the compressibility of the carrier gas and the second term in brackets is the flow rate, fully corrected to 0 °C and the vapor pressure of water (which contributes to the measured flow in a soap bubble flowmeter). P_o and P_i are the pressures (atm) of carrier gas at the outlet and inlet of the column. F_m is the volume flow rate (mL/min) measured in a soap bubble flowmeter, T_m is the temperature of the flowmeter (K), and P_w is the vapor pressure of water (atm) at that temperature. The quantity t_R is the time (min) between injection and the point of interest on the elution curve and t_M is the time between injection and elution of a noninteracting sample such as air. The t values are determined from the corresponding distances on the elution curve and the recorder chart speed.

Adsorption Effects. There are three contributions to V_N: partitioning of B with the liquid phase, adsorption of B at the gas-liquid interface, and adsorption of B at the surface of the solid support.[5]

$$V_N = K_R V_L + K_I A_I + K_S A_S \tag{2}$$

K_R is the apparent gas-liquid partition coefficient (hereafter referred to as the apparent partition coefficient), V_L is the volume of liquid phase on the column, K_I and K_S are the respective adsorption isotherms for adsorption at the gas-liquid interface and on the solid support surface, and A_I and A_S are their respective areas. K_R is obtained using the method of Conder[4] as modified by Cadogen and Purnell.[7] The treatment

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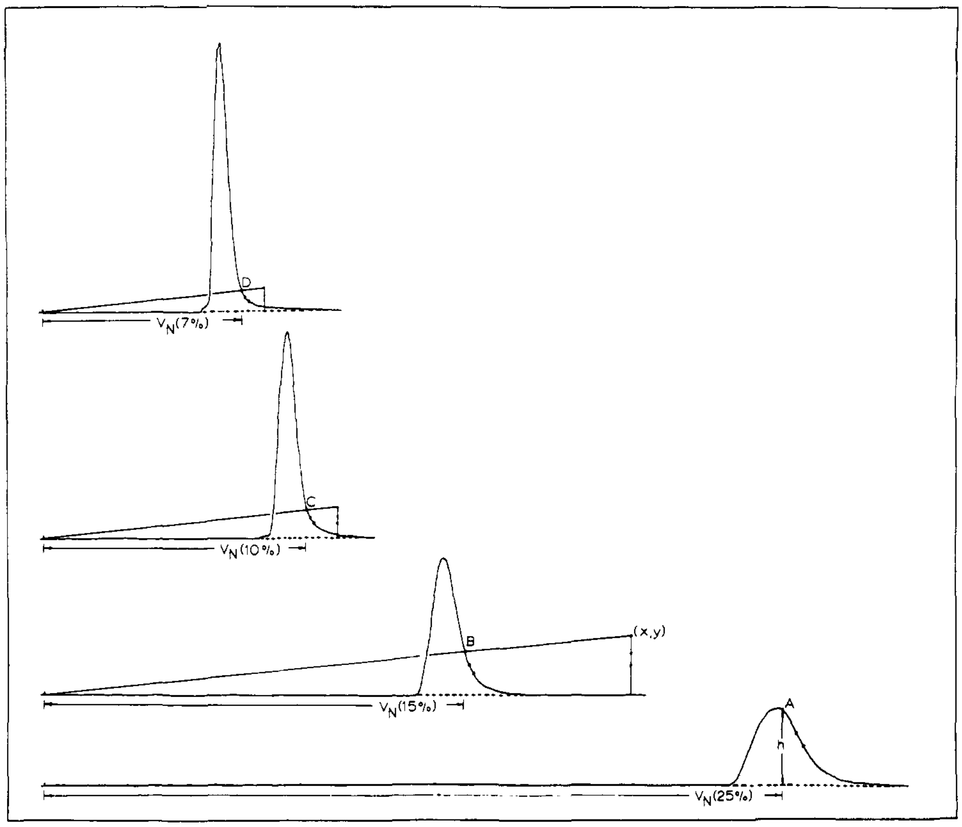

Figure 1. Chromatograms for Et_3N-$Ni(THDD)_2$ in squalane (40 °C). Each chromatogram is obtained from injection of the same amount of triethylamine at the same flow rate onto columns of different liquid-phase loadings (indicated by the number in parentheses). The points indicated were used to generate the data in Figure 2. The V_N scale on each chromatogram varies from the average slightly.

is based upon eq 3, which arises by dividing eq 2 by V_L:

$$\frac{V_N}{V_L} = K_R + (K_1A_1 + K_SA_S)V_L^{-1} \qquad (3)$$

Elution curves (Figure 1) for identical small amounts of injected B are obtained at the same detector temperature, injector temperature, attenuation, and recorder gain for four columns of different V_L or liquid phase loading (e.g., 25, 15, 10, 7% weight liquid/g packing). Points on the tailing side of each curve labeled A, B, C, and D are found which correspond to the same ratio of height above base line, h, to the net retention volume at that point. We have found a graphical method which eliminates much of the time required for this step since the elution curves are directly analyzed without replotting or iteration. This is done by first choosing a point, A, near the peak maximum on the 25% curve and determining the corresponding value h/V_N. A distance, x, on the 15% curve beyond the tail is arbitrarily chosen and the height, y, above this point necessary to satisfy the relationship $(y/x)_{15\%} = (h/V_N)_{25\%}$ is found. A line is drawn between the base of the air peak and the point (x, y); any point on the line corresponds to the value $(h/V_N)_{25\%}$. The intersection of the 15% elution curve with this line satisfies the relationship $(h/V_N)_{25\%} = (h/V_N)_{15\%}$. This is repeated for the 10 and 7% curves so that a set of four V_N values (corresponding to points A, B, C, and D) are obtained. When the ratios are identical the same concentrations of B exist in the liquid phase of each column.[4] Since the concentration of B in solution is constant, the concentration of B for the gas-liquid interface and the solid support surface must also be constant so the adsorption isotherms K_1 and K_S and the apparent partition coefficient K_R must be the same at these points on the four curves. Usually these absorption isotherms and sometimes the apparent partition coefficient are dependent upon the concentration of B. The usual method is then used to determine K_R by plotting V_N/V_L vs. V_L^{-1} according to eq 3; a smooth curve is generated whose intersection at the ordinate satisfies the relationship $K_R = V_N/V_L$ (Figure 2). Usually this is done for several values of h/V_N so that several curves are obtained, all intersecting the ordinate at approximately the same point. The value of K_R so obtained is

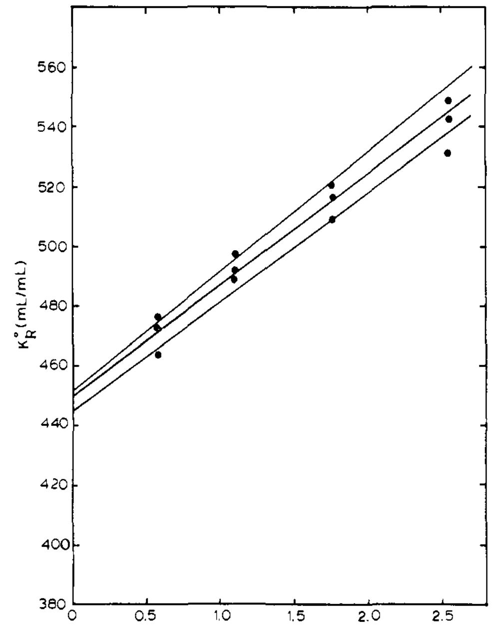

Figure 2. V_N/V_L ($=K^0_R$) vs. V_L^{-1} for Et_3N-squalane at 40 °C. The data for this graph were taken from the chromatograms given in Figure 1.

designated as the fully corrected apparent partition coefficient. This quantity is used in subsequent determination of thermodynamic parameters.

Thermodynamic Parameters for 1:1 Systems. Consider the interaction of the injected Lewis base, B, with a Lewis acid, A, which is in solution in the stationary liquid phase. After B is injected two interactions occur in addition to adsorption. Partitioning of B between the carrier gas (g) and liquid phase (l) occurs:

$$\mathrm{B(g)} \overset{K^0_\mathrm{R}}{\rightleftharpoons} \mathrm{B(l)} \tag{4}$$

Once B is in the liquid phase an acid-base interaction with A can occur. The most elementary case is given by

$$\mathrm{B(l)} + \mathrm{A(l)} \overset{K_1}{\rightleftharpoons} \mathrm{AB(l)} \tag{5}$$

The rigorous expressions for K_1 and K^0_R are given in terms of the activities of the species involved. The concentrations of B and AB are very low while that of A is usually larger. If it is assumed that the activity coefficients of B and AB are approximately unity, then K_1 is given by

$$K_1 = \frac{[\mathrm{AB}]}{[\mathrm{A}][\mathrm{B}]\gamma_\mathrm{A}} \tag{6}$$

γ_A is the activity coefficient of A. The subscript (l) has been eliminated since this and all subsequent expressions refer to interactions in the liquid phase.

The fully corrected apparent partition coefficient, K_R, is a measure of both the partitioning and the acid-base interaction:[3]

$$K_\mathrm{R} = K^0_\mathrm{R}(1 + K_1\gamma_\mathrm{A}[\mathrm{A}]) \tag{7}$$

In the literature γ_A has been assumed close to unity.

Two sets of experiments are necessary to determine K_R and K^0_R, the corrections for adsorption being carried out as previously described. K_R is determined for B on a set of columns of concentration [A]. K_R is also determined for B on a set of columns containing neat solvent; in this case there is no acid-base interaction so that $K_\mathrm{R} = K^0_\mathrm{R}$. These two values are used to determine K_1:

$$K_1 = \left(\frac{K_\mathrm{R}}{K^0_\mathrm{R}} - 1\right)\frac{1}{\gamma_\mathrm{A}[\mathrm{A}]} \tag{8}$$

The enthalpy change (ΔH) and the entropy change (ΔS) for the acid-base reaction may be obtained by determination of K_1 at several temperatures, T_c, and use of the well-known relationship

$$-R \ln K_1 = \Delta H\left(\frac{1}{T_\mathrm{c}}\right) - \Delta S \tag{9}$$

where R is the universal gas constant.

Comparison of Two GLC Methods. A second method for GLC determination of thermodynamic parameters has been presented by Martire and Riedl[2] and is referred to as the *neat liquid method*. Two sets of columns are again used for determination of K_R for injected B. One set consists of a liquid phase which is neat A. This would correspond to the acid or base solution column of the *solution method*. The other set has as liquid phase a neat "reference liquid" chosen[2] such that its ability to partition B will be the same as that of neat A in the absence of the acid-base reaction. This set corresponds to the neat solvent columns of the *solution method*. In addition, for each set of columns K_R values are determined for an injected material (usually an alkane) which will not undergo the acid-base interaction. The values obtained are designated as $\overline{K}_\mathrm{R}$ and $\overline{K}^0_\mathrm{R}$ for the neat acid and neat reference liquid columns, respectively. Expression of K_1[2,9] in terms of fully corrected apparent partition coefficients yields

$$K_1 = \left(\frac{K_\mathrm{R}}{K^0_\mathrm{R}}\frac{\overline{K}^0_\mathrm{R}}{\overline{K}_\mathrm{R}} - 1\right)\frac{1}{\gamma_\mathrm{A}[\mathrm{A}]} \tag{10}$$

Although the original presentations of equations used to determine K_1 for the two different models appears different, comparison of eq 8 and 10 shows them to be of the same form.[10] The term $\overline{K}^0_\mathrm{R}/\overline{K}_\mathrm{R}$ is a correction for the inability of the reference liquid column to perfectly duplicate the partitioning ability of the neat A column. It probably could be used as a good approximation of the needed correction term for higher concentrations of A in the *solution method*.

Thermodynamic Parameters for 2:1 Systems

In the investigation of many transition metal Lewis acids, one must be concerned with the potential complication introduced by consecutive equilibria, e.g.

$$\mathrm{A(l)} + \mathrm{B(l)} \overset{K_1}{\rightleftharpoons} \mathrm{AB(l)} \tag{11}$$

$$\mathrm{AB(l)} + \mathrm{B(l)} \overset{K_2}{\rightleftharpoons} \mathrm{AB_2(l)} \tag{12}$$

When this situation exists, the GLC expression[16] for K_R is given by

$$K_\mathrm{R} = K^0_\mathrm{R}(1 + K_1[\mathrm{A}] + 2K_1K_2[\mathrm{A}][\mathrm{B}]) \tag{13}$$

If one desires to obtain K_1 by GLC, the third term in parentheses must be negligible with respect to $K_1[\mathrm{A}]$. Since $K_1[\mathrm{A}]$ appears in both the second and third terms in parentheses this condition is met if $2K_2[\mathrm{B}]$ is much less than one. This is true regardless of the value of K_1.[32] The term $2K_2[\mathrm{B}]$ is minimized by injecting small amounts of B. One should be able to test for the relative significance of $2K_2[\mathrm{B}]$ by investigating K_R as [B] is varied. Because of the common occurrence of the second equilibrium (eq 12) in transition-metal systems, care must be exercised to eliminate contributions from it to K_R.

Experimental Section

Materials. Matheson Coleman and Bell triethylamine was distilled from barium oxide and stored under nitrogen. Pure grade pentane was obtained from Phillips Petroleum Co. Squalane was obtained from Eastman Kodak Co. The solid support for GLC work was Johns-Manville Chromosorb W, 60-80 mesh, acid washed and DMCS treated. The preparation of bis(7,7,11,11-tetramethylheptadecane-8,10-dionato)nickel(II), $\mathrm{Ni(THDD)_2}$, is described elsewhere.[17]

Spectrophotometry. Solutions of about 0.017 M of $\mathrm{Ni(THDD)_2}$ in squalane were prepared with triethylamine concentrations in the range 0.001-0.4 M. This corresponds to about 5-95% complexation of $\mathrm{Ni(THDD)_2}$. Cells were 1.000-cm quartz cuvettes. The sample cell was placed in a cell holder which was a metal block through which was circulated water from a thermostated bath. The temperature was accurately maintained to at least 0.1 °C. The spectra over the range 4200-7000 Å were obtained using a Cary 14 spectrophotometer. The absorbance changes at 5350 Å were used to determine the equilibrium constants by a previously published procedure.[18-22] These were determined at 20.0, 39.7, 59.2, and 79.4 °C, the enthalpy and entropy being determined from the temperature dependence of the equilibrium constants (eq 9).

Gas-Liquid Chromatography. The thermal conductivity gas chromatograph has been described previously.[9] It was necessary to inject small amounts of triethylamine (~10 nL) with a reproducibility of about 1% to avoid complications from both overloading the column and problems related to forming both 1:1 and 2:1 complexes as described by eq 11-13. The best method found was injection of a dilute solution of the amine in pentane. The solution was placed in a vial sealed with a septum cap. The needle of a 10-μL Hamilton syringe was inserted through the cap into the solution, the plunger was removed, and the solution was then warmed slightly to build a positive pressure in the vial to force the solution out the top of the syringe. When the barrel was completely filled the plunger was reinserted. In this manner the volatile solution was loaded into the syringe without

Table I. Densities[a] (ρ_L) and Concentrations of Solutions as a Function of Temperature

	temp, °C						
	20	30	40	50	60	70	80
ρ_L(squalane)[b]	0.809	0.803	0.796	0.789	0.783	0.778	0.771
ρ_L(0.2 M Ni(THDD)$_2$)[c]	0.833	0.827	0.821	0.815	0.809	0.803	0.797
[Ni(THDD)$_2$], M	0.2009	0.1995	0.1980	0.1966	0.1951	0.1935	0.1922

[a] Densities are in units of g/mL. [b] The densities of squalane were obtained by linear interpolation between the three values given in ref 3 and the value listed in "Handbook of Chemistry and Physics", 53rd ed., CRC Press, Cleveland, Ohio, p C-492 (compound no. Ωs109). [c] These values are obtained by linear interpolation or extrapolation of values found at 61.5, 49.0, 40.0, 31.0, and 19.2 °C.

Table II. Thermodynamic Parameters Derived from Spectrophotometric Data

temp, °C	K_1, M^{-1}	σ_M/σ_C[a,c]	σ_C[b,c]
20.0	177.	2.2	1.2 (0.7%)
39.7	75.6	1.5	1.0 (1.3%)
59.2	35.2	1.8	0.2 (0.7%)
79.4	17.4	1.8	0.4 (2.%)

$-\Delta H$ = 8.0 (0.1)[d] kcal/mol

$-\Delta S$ = 16.9 (0.2)[d] eu

[a] Ratio of marginal standard deviation to conditional standard deviation. [b] Conditional standard deviation. [c] σ_M/σ_C and σ_C are measures of the reliability of a determination. Briefly, if σ_M/σ_C is less than 3.0 *and* σ_C is less than 5% of the equilibrium constant then the data is reliable. For a further explanation see ref 22. [d] Values in parentheses are experimental standard deviations.

Table III. Thermodynamic Parameters Derived from GLC Data

temp, °C	K_R[a]	K^0_R[a]	K_1, M^{-1}
20.0		1089	
40.0	6119	447	64.8
50.0	2700	303[b]	40.3
60.0	1351	212	27.9
70.0	776	163	19.5

$-\Delta H$ = 8.5 (0.3)[c] kcal/mol

$-\Delta S$ = 18.9 (0.8)[c] eu

[a] Milliliters of helium per mL of liquid phase. [b] Obtained by interpolation of a plot of ln V^0_g vs. T_c^{-1} (see Discussion). [c] Values in parentheses are experimental standard deviations.

bubble formation. The presence of the pentane, which was quickly eluted from the column, did not affect the retention time of the amine.

A 0.2 M solution of the nickel complex in squalane was prepared. The densities of the solution at the temperatures of interest were determined by finding the weight contained in a 5.00-mL volumetric flask. Column packing was prepared by placing the required amount of solution, solid support, and hexane into a flask, then removing the hexane on a rotary evaporator. The same procedure was used for preparation of the neat squalane column. Column packings of 7, 10, 15, and 25% weight liquid phase/g column packing were prepared for both the solution and neat squalane packings and used to fill 3.00-ft long, ¼-in. o.d. coiled copper columns.

Elution curves for injected amine were determined on each set of columns at each temperature, the flow rate being kept constant for all determinations. Fully corrected apparent partition coefficients and then equilibrium constants were determined as previously described. The enthalpy and entropy were determined as for spectrophotometry.

Results

The densities and associated concentrations of acid in the liquid phases are given as a function of temperature in Table I. It was found that the change of density with temperature was linear over the temperature range studied.

The results of the spectrophotometric study are give in Table II. Isosbestic points were observed at 6420 and 4450 Å.

The results of the GLC study are given in Table III. It should be noted that the V_N/V_L vs. V_L^{-1} plots were essentially linear, as in Figure 2. The same was found when B was tetrahydrofuran.

Discussion

The isosbestic points observed in the spectrophotometric experiment indicate[23] the formation of only one type of adduct. This must be the 1:1 adduct since the adsorption data fit a 1:1 expression so well. Collins and Henneike[24] have reported a study of the Lewis acid properties of bis(2,2,6,6-tetramethylheptane-3,5-dionato)nickel(II), Ni(THD)$_2$, which should be similar in Lewis acidity to Ni(THDD)$_2$. They found that most bases formed 1:1, then 2:1 adducts as described by eq 11 and 12. However, the triethylamine/Ni(THD)$_2$ system was found to form only the 1:1 adduct unless essentially neat base was used as the solvent. In the GLC study reported here, the Conder method[4-7,11] of correction for adsorption effects was used because small amounts of injected triethylamine are required. This keeps the concentration of triethylamine low, preventing formation of any 2:1 adduct on the column (eq 13), and also prevents overloading the column.[25]

To our knowledge, this is the first time the GLC *solution method* has been used in conjunction with corrections for interfacial effects to obtain enthalpies. The agreement between the enthalpies obtained by the two methods is fair:

$$-\Delta H(\text{GLC}) = 8.5\ (0.3)\ \text{kcal/mol}$$

$$-\Delta H(\text{spectro}) = 8.0\ (0.1)\ \text{kcal/mol}$$

We have attempted to improve the accuracy of the enthalpies obtained by use of the following considerations. Deviation of chromatogram base line linearity results in errors in values of K_R and K^0_R. It is known[26] that ln V^0_g is linearly related to $1/T_c$, where V^0_g is the specific retention volume for a GLC experiment in which no acid-base interaction occurs, and is calculated from

$$V^0_g = K^0_R \frac{273.16}{\rho_L T_c} \tag{14}$$

where ρ_L is the density of the liquid phase on the column.[26] An attempt to improve the accuracy of each K^0_R value can be made by linearization of the data by plotting ln V^0_g vs. $1/T_c$, finding the least-squares line, and converting the value of V^0_g on the line at the temperature of interest to the K^0_R value.

The K_R values may also be linearized if a similar relationship between some function of K_R and $1/T_c$ can be found. Assuming that γ_A is unity, eq 7 may be converted to the form

$$\ln K_R = \ln K^0_R + \ln K_1[\text{A}] + \{\ln (1 + K_1[\text{A}]) - \ln K_1[\text{A}]\} \tag{15}$$

Combining with eq 14, with the subscripts A and S referring to acid solution and neat solvent columns, gives

$$\ln (V^0_g)_A = \ln (V^0_g)_S + \ln K_1 + \ln ([\text{A}]\rho_S/\rho_A) + \{\ln (1 + K_1[\text{A}]) - \ln (K_1[\text{A}])\} \tag{16}$$

Table IV. Comparison of Equilibrium Constants Obtained by GLC and Spectrophotometric Methods

temp, °C	K_1(GLC), M^{-1}	K_1(spectro), M^{-1} [a]	% difference
40.0	64.8	73.8	12
50.0	40.3	49.6	19
60.0	27.9	34.2	18
70.0	19.5	24.1	19

[a] These values are obtained by interpolation on the van't Hoff plot of the spectrophotometric data, since the temperatures were not exactly the same in the two determinations.

The first two terms on the right-hand side are known to be linear with $1/T_c$ (ref 26 and eq 9). The third and fourth terms can be examined for linearity with $1/T_c$ by substituting in the values for the variables, which are given in Tables I and III. It is not necessary that the K_1 values used be accurate, since only their sizes relative to unity and [A] determine the relationship of the fourth term to $1/T_c$. We have done this for the data presented here and find that both third and fourth terms are linear with $1/T_c$. Thus ln $(V^0{}_g)_A$ is linear with $1/T_c$. The corresponding K_R values may then be obtained from the linearized $(V^0{}_g)_A$ values.

The linearized values of K_R and $K^0{}_R$ were then used to determine values of K_1 at each temperature. These were then used to determine the enthalpy in the manner used previously:

$$-\Delta H = 8.1 \text{ kcal/mol (GLC linearized)}$$

If this method is to work, the third term in eq 15 must be linear with $1/T_c$. This may be determined experimentally. The linearity of the third term with $1/T_c$ will result when K_1[A] is significantly larger than unity (in this work it is 4 or higher). The method should be used with care since it will not work in all situations. It is promising since the calculated enthalpy differs from the spectroscopic enthalpy by only 0.1 kcal/mol. Further work is required to determine the limits of applicability of this linearization method.

The GLC equilibrium constants are about 20% lower than those for the spectroscopic determination (Table IV). It is quite possible that a minor modification of the GLC model used would give even closer agreement. The similarity between eq 8 and 10 coupled with the fact that an acid concentration of 0.2 M may cause some deviation between the true and determined partitioning ability of the acid column indicates that a modification of the model may be in order in this case. We have not chosen to do so at this time but we have found that $\overline{K}^0{}_R/\overline{K}_R$ for hexane on the 25% loaded columns is about 1.05 at 50 and 60 °C. This correction would bring the GLC and spectral equilibrium constants closer, while having a negligible effect on the enthalpy.

The thermodynamic data derived from GLC measurements may be inaccurate if there are substantial uncorrected contributions to the chromatograms from nonideality, i.e., band broadening resulting from diffusion and slow mass transfer.[4] Several checks for nonideality have been suggested, but these tend to be qualitative. For example, the steepness and linearity of the leading side of a peak may be examined,[29] but these factors suffer from dependence upon detector attenuation and recorder sensitivity. The locus of peak maxima from chromatograms of different injection volumes may be used to generate an "ideal" peak,[30] but this method has not been compared to independent thermodynamic determinations and peak maximum retention volumes are not necessarily thermodynamically significant. The ratio of slopes of trailing to leading boundaries of the chromatogram could be used in a rule-of-thumb approach to determining ideality, but would suffer quantitatively in that the cutoff would probably vary from system to system. It has been found for certain systems that the trailing edges of chromatograms resulting from different injection volumes lie on a common curve, but it is not known if this is a general phenomenon related to ideality.[7] In Figure 1 of ref 7 an illustration of peaks to be used for thermodynamic determinations was given; hence it is assumed that these peaks have little contribution from nonideality. Since these peaks of varying injection volume have a common trailing edge, analysis involving adsorption corrections as described above would give the same results, no matter which sample volume was chosen (as long as the sample volume was kept below a minimum value). The peak corresponding to the lowest injection volume also fits the above proposed criteria for the absence of nonideality (it lies on a common trailing edge with chromatograms of higher injection volume and also its trailing edge lies on an ideal chromatogram which could be generated from the peak maxima of the several peaks given in the figure), but does not rise sharply. In fact, it is about as symmetrical as the 25% chromatogram of Figure 1 of this paper. Thus, one must be cautious in assuming that a sharp rise is necessary for the absence of nonideality since this is clearly not always the case. Since rather high flow rates were used to generate the curves in the present paper, tending to limit contributions from nonideality, other factors must be contributing to the symmetrical nature of these curves. At the low injected solute concentrations on column, approximate symmetry may be a result of K_1 and K_S approaching constancy with decreasing solute concentration, and the increasing symmetry with increasing liquid phase loading on the columns (going from the 7% through the 25% loadings) reflects the increasing relative contribution to V_N/V_L from bulk partitioning. To conclude, much work has been done in an effort to determine the extent of nonideality in various systems. Since comparison of thermodynamic parameters obtained from data deemed free of nonideal effects via the above procedures and parameters from independent thermodynamic determinations has not been made, more study of the GLC system is required to gain a quantitative criterion as to when ideal behavior is achieved.

The goal of GLC studies of this type is to accurately determine the thermodynamic parameters. One may infer that the GLC methods and correction procedures, including assumptions regarding nonideality, are valid if the thermodynamic parameters obtained using other methods agree with those from the GLC experiment. One such favorable comparison for the triethylamine/$Ni(THDD)_2$ system has already been made in the present paper. We have also examined another system both calorimetrically and with the same GLC technique reported here. The results of this and related data are presented in full elsewhere,[31] but we review briefly some of the results that are relevant to the present discussion. The reaction

$$IrP_2(CO)Cl + SO_2 = IrP_2(CO)Cl(SO_2)$$

has been investigated where P is a triaryl phosphine. The GLC enthalpy was found to be −11.6 kcal/mol, which compares well with the calorimetric determination of −11.3 kcal/mol. The agreement between GLC and independently determined thermodynamic parameters for these two different systems implies that the GLC method, as described here, will yield reliable thermodynamic information. The limitations of the procedure can only be ascertained through further study in which very different systems and conditions are studied.

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Supplementary Material Available: The raw data used to calculate the spectrophotometric equilibrium constants (Table V) (1 page). Ordering information is given on any current masthead page.

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(32) This is to be contrasted to calorimetry and spectrophotometry in which the magnitude of K_1 often determines the feasibility of accurately determining K_1 and K_2.

Characterization and Reaction Studies of Dimeric Molybdenum(III) Complexes with Bridging Dithiolate Ligands. Catalytic Reduction of Acetylene to Ethylene[1]

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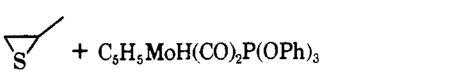
Abstract: The complexes $[C_5H_5MoSC_nH_{2n}S]_2$ (where $n = 2$ and 3) have been prepared by the reaction of ethylene sulfide and propylene sulfide, respectively, with $C_5H_5MoH(CO)_3$ or with $[C_5H_5Mo(CO)_3]_2$. Cyclic voltammetry shows that each complex undergoes two reversible oxidations at 0.13 and 0.79 V vs. SCE (in acetonitrile with 0.1 M Bu_4NBF_4). Both the one-electron and two-electron oxidation products have been synthesized and characterized by spectral and magnetic data. Electrochemical data for the oxidized complexes support the conclusion that the complexes have the same gross structural features in all three oxidation states. A single crystal of the monocation $[C_5H_5MoSC_3H_6S]_2BF_4$ has been characterized by an X-ray diffraction study. The compound crystallizes in the space group $C2/c$ with $a = 18.266$ (1) Å, $b = 9.206$ (4) Å, $c = 12.911$ (5) Å, $\beta = 100.83$ (3)°, and $V = 2128$ Å^3. The metal ions of the cation are bridged by two 1,2-propanedithiolate ligands. The four sulfur atoms of these ligands form a plane which bisects the metal-metal distance. The neutral dimeric complexes undergo a unique reaction with alkenes and alkynes in which the hydrocarbon portion of the bridging dithiolate ligands is exchanged. The reaction has been characterized with olefins with both electron-withdrawing and electron-donating substituents. When $[C_5H_5MoSC_2H_4S]_2$ (**1**) is reacted with acetylene at 25 °C, ethene is produced and the complex $[C_5H_5MoSC_2H_2S]_2$ is isolated. The latter complex is reduced by hydrogen (2 atm) at 60 °C to re-form **1**. The utility of these reactions in the catalytic reduction of acetylene to ethylene has been investigated. The role of the sulfur ligands in this catalytic cycle is discussed.

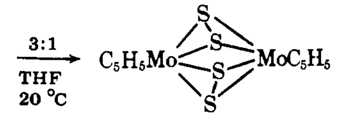
Introduction

There is evidence that molybdenum ions coordinated, at least in part, by sulfur donor ligands participate in a number of catalytic reactions. These include the homogeneous reactions of several molybdoenzymes,[2-8] as well as heterogeneous processes in Fischer-Tropsch[9-11] and hydrodesulfurization[12,13] catalyst systems. Despite extensive synthetic studies of molybdenum complexes with sulfur ligands, relatively few of these homogeneous systems have been found to display catalytic activity.[14-21] We are extending the study of reactions of new sulfur-containing molybdenum complexes in the expectation that this will increase our understanding of structural and mechanistic features which are important in catalyst development.

Dimeric cyclopentadienylmolybdenum complexes containing sulfido and disulfido ligands have been reported as products of reactions of hydridomolybdenum complexes with propylene sulfide (reactions 1 and 2).[22] However, the reaction



(1)



(2)