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CALORIMETRIC INVESTIGATIONS OF ASSOCIATION EQUILIBRIA: THE PYRIDINE–IODINE COMPLEX IN CYCLOHEXANE AND IN CARBON TETRACHLORIDE

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ABSTRACT

The results of two independent calorimetric investigations of the pyridine–iodine complex are reported. "Best" values are reported as $K_M = 128$ l/mol and $\Delta H^\circ = -8.4$ kcal mol^{-1} for the formation of the complex in cyclohexane at 25°C, and $K_M = 104$ and $\Delta H^\circ = -7.9$ kcal mol^{-1} in carbon tetrachloride. Evidence is presented to support the contention that association constants for weak complexes determined by calorimetric methods can be as reliable as those determined by spectrometric methods, and that values of ΔH° determined by the calorimetric method are much more reliable than those derived from the temperature dependence of equilibrium constants.

INTRODUCTION

Most recent investigations of equilibrium constants for formation of charge transfer and other weak complexes have been based on various spectrometric measurements[1–4]. Advantages of these methods have been adequately summarized and are not discussed further here. Equilibrium constants determined at several temperatures then permit calculation of ΔH° and ΔS° values. These latter calculations do merit some further discussion, as given in the next section of this paper. Throughout this paper, we have taken the infinitely dilute solution as the standard state for the enthalpy of the solute.

Calorimetry offers an appealing alternative to the difficulties and uncertainties associated with evaluation of ΔH° and ΔS° values from equilibrium constants determined at several temperatures. In addition to obtaining ΔH° values from the results of calorimetric measurements, it is also possible to obtain equilibrium constants. Along with the general references[1–4] already cited, we call special attention to pioneering calorimetric investigations[5–7] by Lamberts, Drago and Arnett. While these investigators have stressed the greater reliability of calorimetrically determined values of ΔH°, they have been somewhat apologetic for equilibrium constants based only on calorimetric data. Several reasons for this may be advanced. Obviously, the simultaneous solution of K_{eq} and ΔH° requires two experimental parameters. The use of an independently determined value of the equilibrium constant appears to permit greater accuracy in calculating the "best" value of ΔH°. This increased accuracy is largely illusory, however, since the equilibrium constant is normally but one of two parameters required in treating spectrometric data (the extinction coefficient or absorbancy index is an experimental parameter in many cases). By working at different wavelengths, a better estimate of the uncertainty of K_{eq} can be obtained with spectrometric data as opposed to calorimetric data. These uncertainties must be taken into consideration in estimating the uncertainty in the calculated value of ΔH°.

In many investigations of weak complexes, one or both of the components is capable of self-association. In many cases, the assumption of an ideal dilute solution is not valid at some of the concentrations studied. However, these effects compromise the reliability of spectrometric results as well as the results of calorimetric investigations. Without thorough theoretical and experimental investigation, it is impossible to state which results would be generally more reliable.

In order to show that the calorimetric method can be as reliable as the spectrometric method for the determination of equilibrium constants for weak complexes, we have chosen an example that is relatively free of interfering effects: the pyridine–iodine complex in cyclohexane and in carbon tetrachloride. The results of completely independent calorimetric investigations are compared with the results that have been reported for spectrometric investigations.

The inherently greater reliability of calorimetrically determined values of ΔH° for complex formation over those derived from the temperature dependence of equilibrium constants is easily recognized. However, we feel that it is worthwhile at this point to consider the source of some of the inaccuracies associated with this latter method.

CALCULATION OF ΔH° FROM EQUILIBRIUM CONSTANTS

Uncertainties in values of ΔH° and ΔS° derived from application of the van't Hoff equation to equilibrium constants determined at several temperatures are commonly underestimated. King[8] has described a thorough and rigorous analysis of the relationship between *random* errors in equilibrium constants and the thermodynamic quantities derived by differentiation. Because his statistical analysis specifically excludes systematic (possibly temperature dependent) errors, King's "statistical uncertainties" are lower limits for the "total uncertainties" that are of greater interest.

To demonstrate in simple fashion how small errors in K or pK values can lead to large errors in ΔH° (and thence in ΔS°), we write the van't Hoff equation in terms of the change in pK (ΔpK) associated with a change in temperature (ΔT) at some mean temperature T as

$$\Delta H \cong 2.3\, RT^2\, \Delta pK/\Delta T \qquad (1)$$

We now use $\delta(\Delta pK)$ and $\delta(\Delta H^{\circ})$ to indicate changes or errors in ΔpK and ΔH°, assuming that errors in ΔT are relatively small, and then have

$$\delta(\Delta H^\circ) \cong 2.3\ RT^2\ \delta(\Delta pK)/\Delta T \tag{2}$$

Uncertainties of 5–10% are commonly reported for equilibrium constants derived from careful spectrometric studies[9,10]. Therefore each pK value will have an uncertainty of about ±0.03, which represents a lower limit for $\delta(\Delta pK)$. Only rarely in these studies does the temperature range (ΔT) exceed 30 °C, and the results of studies over this and wider ranges of temperature might be compromised by temperature dependence of ΔH°. With these values of $\delta(\Delta pK)$ and ΔT, and $T \cong 300$ K, eqn (2) gives $\delta(\Delta H^\circ) = \pm 450$ cal/mol.

There is another matter of fundamental thermodynamics to be considered in connection with calculation of enthalpies of reactions by way of the van't Hoff equation

$$\mathrm{d}\ln K/\mathrm{d}T = \Delta H^\circ/RT^2 \tag{3}$$

Direct application of eqn (3) to K values based on different standard states or expressed in terms of different concentration units can lead to apparently different values of ΔH°, each of which supposedly refers to the enthalpy change of the same reaction at infinite dilution. The essential thermodynamic requirement for *direct* application of eqn (3) is that the standard states for the solutes must be independent of temperature[11], which is a formal way of saying that equilibrium constants to be used *directly* in eqn (3) must be expressed in terms of molalities or mole fractions rather than molarities or volume fractions.

One way to apply the van't Hoff equation correctly is to convert all equilibrium constants expressed in terms of molarities to new constants expressed in terms of molalities, using the density (ρ_s) of the solvent. For the formation of a 1:1 complex,

$$K_m = \rho_s K_M \tag{4}$$

It is often more convenient to apply the van't Hoff equation directly to equilibrium constants expressed in terms of molarities and to separately allow for thermal expansion of the solvent, $\alpha = (1/V)(\partial V/\partial T)_P$. Combination of eqns (3) and (4) leads to

$$\Delta H^\circ = RT^2(\mathrm{d}\ln K_m/\mathrm{d}T) = RT^2(\mathrm{d}\ln K_M/\mathrm{d}T) + RT^2(\mathrm{d}\ln \rho_s/\mathrm{d}T)$$

and

$$\Delta H^\circ = RT^2(\mathrm{d}\ln K_M/\mathrm{d}T) - RT^2\,\alpha_s \tag{5}$$

Because of the low thermal expansivity of water at normal room temperature ($\alpha \cong 2\times 10^{-4}$ deg^{-1}), the term $RT^2\,\alpha_s$ contributes very little to values of ΔH° determined in this solvent. For a "typical" organic solvent, however, $\alpha \cong 1.2\times 10^{-3}$ deg^{-1} at room temperature, and $RT^2\alpha = 220$ cal mol^{-1}.

EXPERIMENTAL

The ampoule calorimeter used in Rolla has been described[12]. Measurements in Lethbridge were made with an LKB Precision Calorimetry System used as a titration calorimeter with titrant delivered to the calorimeter by a Metrohm automatic titrator. All calorimetric measurements in Rolla and Lethbridge refer to 25.0 ±0.1 °C and are reported in terms of the defined calorie (1 cal = 4.184 J).

Chemicals

Lethbridge. Pyridine (BDH reagent grade) was distilled over BaO. Cyclohexane (BDH reagent grade) showed ultraviolet absorption corresponding to benzene (about 1%), so it was treated with fuming sulfuric acid, washed with aqueous $NaHCO_3$, dried over $MgSO_4$, and finally distilled and stored over sodium. This material showed no UV absorption corresponding to benzene. Iodine (BDH Analar) was used without further purification.

Rolla. Iodine was Fisher Certified ACS, cyclohexane and carbon tetrachloride were Fisher Certified ACS Spectranalyzed Reagent and pyridine was MCB spectranalyzed reagent. Solvents and pyridine were stored over molecular sieves.

Considerable care was taken in preparing and subsequent handling of all solutions to minimize contact with the atmosphere.

RESULTS

The calorimetric results were interpreted in terms of the reaction

$$\mathrm{Py} + \mathrm{I}_2 = \mathrm{Py}\text{–}\mathrm{I}_2 \tag{6}$$

through the relationships

$$\Delta h = M_{\mathrm{P-I}} V \Delta H^\circ \tag{7}$$

$$K_M = M_{\mathrm{P-I}}/(M_{\mathrm{P}}^\circ - M_{\mathrm{P-I}})(M_{\mathrm{I}}^\circ - M_{\mathrm{P-I}}) \tag{8}$$

The enthalpy change observed for a particular experiment (corrected for dilution effects) is represented by Δh, V is the volume of the solution in the calorimeter at the end of the experiment, M_{P}° and M_{I}° are the formal concentrations of pyridine and iodine in this solution, and $M_{\mathrm{P-I}}$ is the concentration of complex in this solution. Data were taken in the form of Δh as a function of M_{P}°, M_{I}°, and V. A computer has been used to find the values of K_M and ΔH° which give a minimum in the sum of the squares of the differences between observed and calculated values of Δh.

Pyridine–iodine in cyclohexane

Calorimetric measurements at Lethbridge involved the titration of concentrated pyridine solutions into dilute iodine solutions and the titration of iodine solutions into dilute pyridine solutions. Heats of dilution of the concentrated solutions into cyclohexane were measured separately. Both were small, with the heat of dilution of the iodine solution so small as to have no effect on the results. Fourteen measurements were made on solutions having a formal concentration of iodine of approximately 0.04 M and formal concentrations of pyridine ranging from 0.005 M to 0.5 M. "Best" values calculated for the parameters were $K_M = 130$ and $\Delta H° = -8.5$ kcal mol^{-1}.

By ampoule calorimetry (Rolla), heats of solution of pyridine were measured in cyclohexane and in solutions of iodine in cyclohexane. In each case, the formal concentration of iodine was about 0.007 M and the formal concentration of pyridine ranged from 0.03 to 0.14 M. In this case, Δh represents the difference between the heat of solution of pyridine in a solution of iodine in the solvent and the heat of solution of an equal amount of pyridine in an equal volume of pure solvent. "Best" values for the parameters were $K_M = 124$ and $\Delta H° = -8.3$ kcal mol^{-1}.

Equilibrium constants determined by spectrometric methods have been reported: $(\Delta)K_M = 135 \pm 8$ (ultraviolet measurements by Huong, Platzer and Josien)[9] and $K_M = 107 \pm 26$ (infrared measurements by Maki and Plyler, reported by Bist and Person[13]), both in excellent agreement with our calorimetric results. By consideration of all of the reported values, we have chosen $K_M = 128$ as the overall best value. Using this value with all of our calorimetric data, we calculate $\Delta H° = -8.4$ kcal mol^{-1} with a standard deviation of about 0.1 kcal mol^{-1}.

Pyridine-iodine in carbon tetrachloride

Heats of solution (Rolla) of pyridine in carbon tetrachloride and in solutions of iodine in carbon tetrachloride were measured and interpreted in terms of eqns (6)–(8). Formal concentrations were between 0.009 and 0.08 M for pyridine and between 0.005 and 0.012 M for iodine. Simultaneous solution for the equilibrium constant and standard enthalpy of reaction gave $K_M = 103$ and $\Delta H° = -7.9_5$ kcal mol^{-1}.

Beezer, Orban and Tyrrell[14] have used a titration calorimetric method similar to that used in Lethbridge to obtain $K_M = 108$ and $\Delta H° = -7.8_5$ kcal mol^{-1}.

TABLE 1

THERMODYNAMIC PARAMETERS FOR FORMATION OF THE PYRIDINE-IODINE COMPLEX AT 25.0°C

Solvent	*Cyclohexane*			*Carbon tetrachloride*		
Composition units	M^a	m^b	X^c	M^a	m^b	X^c
K (composition units)$^{-1}$	128	99	1180	104	165	1070
$-\Delta G°$ (kcal mol^{-1})	2.8_7	2.7_2	4.1_9	2.7_5	3.0_2	4.1_3
$-\Delta H°$ (kcal mol^{-1})	8.4	8.4	8.4	7.9	7.9	7.9
$-\Delta S°$ (cal deg^{-1} mol^{-1})	$18._4$	$19._1$	$14._1$	$17._3$	$16._4$	$12._6$

[a] M = moles/liter solution. [b] m = moles/kg solvent. [c] X = mole fraction.

Spectrometric equilibrium constants of $K_M = 102 \pm 6$ by Huong, Platzer and Josien[9] and $K_M = 101$ by Popov and Rigg as quoted by Bist and Person[13] are again in excellent agreement with calorimetric results. Taking $K_M = 104$ as an overall best value, we calculate $\Delta H^\circ = -7.9$ kcal mol^{-1} from our calorimetric data, with a standard deviation of less than 0.1 kcal mol^{-1}.

From our values of K_M and ΔH°, we have calculated ΔG° and ΔS° for formation of the pyridine–iodine complex. With the densities of the solvents, and the molecular weights, we have calculated the values of the equilibrium constants and thermodynamic properties in terms of other composition units, such as molality (m) and mole fraction (X). These parameters are listed in Table 1.

DISCUSSION

As noted above, equilibrium constants derived from our calorimetric measurements are in excellent agreement with those determined by spectrometric methods. The uncertainties in the values determined by the two methods appear to be comparable. Although there are no ($d \ln K/dT$) results for the pyridine–iodine complex to compare directly with our calorimetric values for ΔH°, it is clear that uncertainties in the calorimetric values (0.1–0.2 kcal mol^{-1}) are smaller than those that are likely to be derived by way of the van't Hoff equation.

The calorimetric method appears to be well suited for determinations of equilibrium constants of the order of 100–200 l mol^{-1}. Further investigation is needed to establish the general range of applicability of the method. In the case of very large equilibrium constants, it will be necessary to work at very low concentrations of donor and acceptor to obtain reliable results, thus requiring very great calorimetric precision. As Drago has pointed out[6c], one can determine ΔH° quite accurately under these conditions, even though K values may be relatively imprecise. In the case of very small equilibrium constants, relatively high concentrations of donor and acceptor may be required to produce a useable enthalpy effect. This problem is compounded by the fact that small values of ΔH° are usually associated with small values of K. However, Beezer[14] has obtained reasonable results with $K = 40$ and $\Delta H^\circ = -6.8$ kcal mol^{-1}, and Drago[15] has reported a study with $K = 5$ and $\Delta H^\circ = -4.0$ kcal mol^{-1}. As higher concentrations of donor and acceptor are used, however, there is increasing danger that the assumption of an ideal dilute solution will become invalid, and that other equilibria might interfere. Further investigation is required to assess the influence of these interfering effects on calorimetrically determined parameters, and to provide means for the detection of these effects.

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