The Interaction of Iodine with Pyridine and 2,6-Dimethylpyridine in Carbon Tetrachloride and Cyclohexane

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Calorimetric and spectroscopic measurements of the formation constant and molar enthalpy of complexation for the interaction of pyridine and 2,6-dimethylpyridine with iodine, in carbon tetrachloride and in cyclohexane, have been carried out. Di-*ortho* substituents cause a decrease in the formation constant but do not greatly influence the value of the enthalpy of formation. Differences in results obtained by the two methods are interpreted as being due to the formation of ' contact ' complexes.

Recent combined spectrophotometric and calorimetric studies have indicated that the I_2–2,6-dimethylpyridine complex is not solvated by cyclohexane but is solvated by carbon tetrachloride.[1] However, the stability constant K_c for the 2,6-dimethylpyridine complex is less than the constant for the pyridine complex in spite of the fact that the pK_a for the methylated pyridine is significantly larger than the pK_a for pyridine itself. Similar conclusions have been reached by other workers [2] for the formation of di-*ortho*-substituted pyridine complexes with iodine and other acceptor molecules. This observed lack of correlation between pK_a values (and/or n-ionization potentials) and the K_c values for the complexes has been advanced as proof that pyridine bases act exclusively as n-donors.[3,4] The steric effect seems to manifest itself mainly by decreasing the value of the equilibrium constant. On the other hand, the $\Delta\bar{H}$ values, as shown in Table 1, exhibit the expected increase with increased electron-donating substituents, in spite of the accompanying steric hindrance.

It should be pointed out that the $\Delta\bar{H}$ values quoted in Table 1 were obtained both from the temperature variation of K_c values and from a combination of spectroscopic and calorimetric measurements. The extremely low value (−17.6 kJ mol^{-1}) for 2,6-dimethylpyridine and I_2 in an unspecified solvent was cited as evidence of a large steric effect.[7] In order to obtain comparable data it is advisable, however, to extract K_c and $\Delta\bar{H}$ values simultaneously from one type of measurement only. The method due to Bolles and Drago can be equally well applied to spectrophotometric and calorimetric results.[9] The analysis requires very precise data, however, since random error is magnified and propagated so that the extracted simultaneous values should still be interpreted with reasonable caution.

Numerical analysis of an arbitrary network of $\Delta\bar{H}$ and K_c values has been used to extract the best simultaneous values from titration calorimetry data for the system I_2–1,2-dithiane in ethylene dichloride.[10] Excellent agreement was found between the $\Delta\bar{H}$ value so obtained and the value derived spectroscopically. A similar analysis was applied to calorimetric titration data for a series of benzenoid–tetracyanoethylene complexes in methylene dichloride.[11] The K_c values obtained were uniformly smaller than those previously reported from spectroscopic measurements while the $\Delta\bar{H}$ values were, in the main, significantly higher than the corresponding published spectroscopic values. A systematic error in one or both of the methods was suspected. Since the treatment of the spectroscopic results was based on some form of the Benesi–Hildebrand equation, the observed differences were attributed, in part, to the fact that the Benesi–Hildebrand treatment does not exclude ' contact ' charge-transfer.[12]

An adaptation of the Scott equation [13] has also been used to analyse thermal measurements.[14]

Table 1. Molar enthalpy of complexation ($\Delta\bar{H}$/kJ mol^{-1}) of pyridine bases with I_2 at 25 °C

Solvent	Pyridine	2,6-Dimethylpyridine
CCl_4	−31.3 [5]	−32.5 [1]
n-Heptane	−34.2 [5]	
n-Hexane		−34.8 [1]
Cyclohexane	−31.4 [6]	−34.5,[1] −33.6 [6]
Unspecified		−17.6 [7]
Pyridine	−33.3 [8]	

Experimental

A thermistor calorimeter, similar to the one used earlier for heat of immersion determinations, but modified slightly for heat of solution measurements was used.[15] Additions of solids and liquids to the calorimeter were made following the procedure of Arnett *et al.*[16] Syringe addition was carefully calibrated by weighing and the amount of solvent or solution in the calorimeter was determined by weighing. Heats of solution of the pyridine bases in the solvents carbon tetrachloride and cyclohexane were measured in a batch-wise manner at 25 ± 0.1 °C over a range of concentrations. The procedure was then repeated but using a dilute solution of iodine (prepared by weighing) in the selected solvent. Depending on the amount of base to be added, the amount of iodine solution was adjusted so that the final analytical concentration of iodine was held constant. Concentrations were expressed as mol kg^{-1} of solution and the heat values were expressed as J kg^{-1} of solution. If it is assumed that the heat of dilution of the iodine solution is completely negligible,[17] then for any given pyridine base concentration, the difference between the heats of solution in the solvent and the iodine solution can be attributed to the formation of the complex.

The spectroscopic results were obtained on a Beckmann DK2A double-beam scanning spectrophotometer equipped with a thermostatted cell holder. Stock solutions of the bases and iodine were prepared by weighing and final concentrations were achieved by weighing various amounts of the stock solutions and the solvents into the spectrophotometer cell on a sensitive top-loading balance. Absorption spectra for solutions having a fixed concentration of iodine and varying concentrations of pyridine base were recorded between 350 and 650 nm. The procedure was repeated for each solution at fixed temperatures ranging between 4 ± 0.1 and 40 ± 0.1 °C.

The concentration of the uncomplexed iodine was calculated from the absorbance of the free iodine band at its maximum while the concentration of the complex was obtained in a similar manner using the absorbance of the shifted iodine band at its maximum absorbance. The uncomplexed pyridine base concentration was taken as the difference between the analytical base concentration and the concentration of the complex. Since there is a small overlap of the free and shifted iodine bands at their maxima, corrections to obtain the true absorbances had to be made. The maximum overlap of the free-iodine band can easily be obtained by the determination of the iodine spectrum in the pure solvent. Similarly, the maximum overlap of the shifted iodine band was obtained by swamping (200-fold molar excess) the system with pyridine base until the free-iodine band was completely suppressed and an increase in base concentration did not result in an increase in the shifted iodine-band absorbance. The maximum overlap for the free-iodine band at the shifted band maximum was about 3.5% of the maximum shifted band absorbance and the maximum overlap for the shifted band at the free band maximum was about 10% of the free band maximum absorbance. Since these are the extreme values, all intermediate concentrations will exhibit smaller overlap contributions to the observed absorbance. Corrections were made therefore by assuming that the shifted iodine absorbance was correct, within experimental error, and calculating a correction for the free band based on the maximum correction and the relative value of the shifted iodine absorbance to the previously determined maximum absorbance. K_c(spec) Values were computed only at the $\lambda_{max.}$ values for iodine and shifted iodine. $\Delta\bar{H}_c$(spec) Values were obtained by the standard use of the van't Hoff isochore and the values of K_c(spec) at 25 °C were calculated from the slopes and intercepts of the isochores.

The iodine, pyridine bases, and solvents used were the best available commercially (Aldrich Chemical Company Ltd.) and were used without further purification. The liquids were stored over activated 5A molecular sieve prior to use. No special precautions *i.e.*, dry-box preparation, were used. It has been shown that small amounts of water do not seem to affect the complexation reaction.[1]

Results and Discussion

The calorimetric results obtained are shown in Figure 1. The heat of solution of pyridine in carbon tetrachloride is endothermic over the range of concentration studied while the heat of solution of 2,6-dimethylpyridine in carbon tetrachloride is exothermic over most of the concentration range except for a small endothermic or zero heat at very low concentrations. The heat of solution of 2,6-dimethylpyridine in CCl_4 over a concentration range of 0.05—0.08 mol kg^{-1} has been reported as -1.26 kJ mol^{-1}.[1] The value obtained for the present data over a range of 0.005—0.08 mol kg^{-1} is -1.4 kJ mol^{-1}. The heat of solution of pyridine in CCl_4 at infinite dilution has been reported as $+1.0$ kJ mol^{-1}.[18] The present data yield a heat of solution value of $+0.77$ kJ mol^{-1} over the concentration range 0.003—0.075 mol kg^{-1}. Comparison cannot be made with the very precise work which has been reported,[19] since the concentration range used was much higher than the concentration used here. The heats of solution of pyridine and 2,6-dimethylpyridine in cyclohexane are endothermic with values of $+8.03$ kJ mol^{-1} for pyridine and 5.42 kJ mol^{-1} for 2,6-dimethylpyridine. These values may be compared with the heat of solution of pyridine in hexane of $+8.20$ kJ mol^{-1} [18] (infinite dilution) and with $+5.52$ kJ mol^{-1} for 2,6-dimethylpyridine in cyclohexane (0.013 mol kg^{-1}).[1] The endothermicity or exothermicity of the pyridine base-solution process has been interpreted as a consequence of the extent of self-association in the neat pyridine base coupled with the amount of solvation which occurs in solution.[19] Figure 1 indicates that for low base concentrations the enthalpies of solution depend on the base concentration in a linear fashion. Thus no important enthalpy of dilution contribution will be encountered when the data are used to calculate enthalpies associated with complex formation. The heats of solution of the pyridine bases in dilute iodine solutions, also shown in Figure 1, are all more endothermic than the heats in the pure solvent. On the assumption that the heat of dilution of iodine is negligible, the difference between the heat in the pure solvent and the heat in the dilute iodine solution yields a measure of the heat evolved when the pyridine base–iodine interaction occurs. The iodine concentration used (0.003 01 mol kg^{-1} for carbon tetrachloride and 0.006 21 mol kg^{-1} for cyclohexane) corresponds to an iodine molarity of 0.004M for both solutions. Figure 2 shows a plot of the differences in heat of solution, ΔQ, *versus* analytical base concentration for the iodine–pyridine system in carbon tetrachloride. The range of base analytical concentrations used was from about the analytical iodine concentration to a *ca.* 15-fold excess. The ΔQ values were calculated, for a given base concentration, by subtracting the value for the integral heat of solution of the base, obtained from a least-squares fit of the heat of solution data, from the observed heat at the same base concentration when the small amount of iodine was also present in the solution.

Although an attempt was made to treat the data *via* the Bolles–Drago method, it became obvious that only the data obtained at higher base concentrations had sufficient precision to give unequivocal simultaneous solutions. Discussion of the application and limitations of the Bolles–Drago method has been reported earlier.[9,14]

A modified form of the Scott equation [13] was used to treat the data in the following way. It is assumed that the complex is formed by a 1 : 1 reaction and activity effects are absent. The possibility that higher complexation reactions are involved cannot be entirely ruled out. However, it should be pointed out that the combination of the observed good isosbestic points and the constancy at $\lambda_{max.}$ for the I_2 shift indicates that higher complexes are present only in very low concentrations, if at all.

The reaction may be written as $a + b \rightleftarrows c$ where $[a]$ = iodine concentration (mol kg^{-1} solution), $[b]$ = base concentration (mol kg^{-1} solution), and $[c]$ = 1 : 1 complex concentration (mol kg^{-1} solution).

If $[c] = \Delta Q/\Delta\bar{H}$, where ΔQ = excess of enthalpy (J kg^{-1} solution) and $\Delta\bar{H}_c$ = molar enthalpy of complexation (J mol^{-1}) then the Scott relationship may be written by rearrangement of the equilibrium expression (1), where $[a]_0$

$$\frac{[a]_0[b]_0}{\Delta Q} = \frac{1}{K\Delta\bar{H}_c} + \left(\frac{1}{\Delta\bar{H}_c}\ [a]_0 + [b]_0 - \frac{\Delta Q}{\Delta\bar{H}_c}\right) \qquad (1)$$

and $[b]_0$ are the stoicheiometric concentrations of iodine and base, respectively. Linear regression analysis of the $\frac{[a]_0[b]_0}{\Delta Q}$ *versus* $([a]_0 + [b]_0)$ data gives a preliminary value of $\Delta\bar{H}_c$ which can be used to approximate $[c] = \frac{\Delta Q}{\Delta\bar{H}_c}$. An iterative linear regression treatment of $\frac{[a]_0[b]_0}{\Delta Q}$ *versus* $([a]_0 + [b]_0 - \frac{\Delta Q}{\Delta\bar{H}_c})$ is now made to obtain a better value of $\Delta\bar{H}_c$. A three-fold repetition of this process gives constant values of $\Delta\bar{H}_c$ and K_c. This procedure uses all the data from low to high values of '*s*', the saturation coefficient (ratio of the concentration of the complex to the stoicheiometric concentration of the less concentrated component) and fulfils the requirement urged by

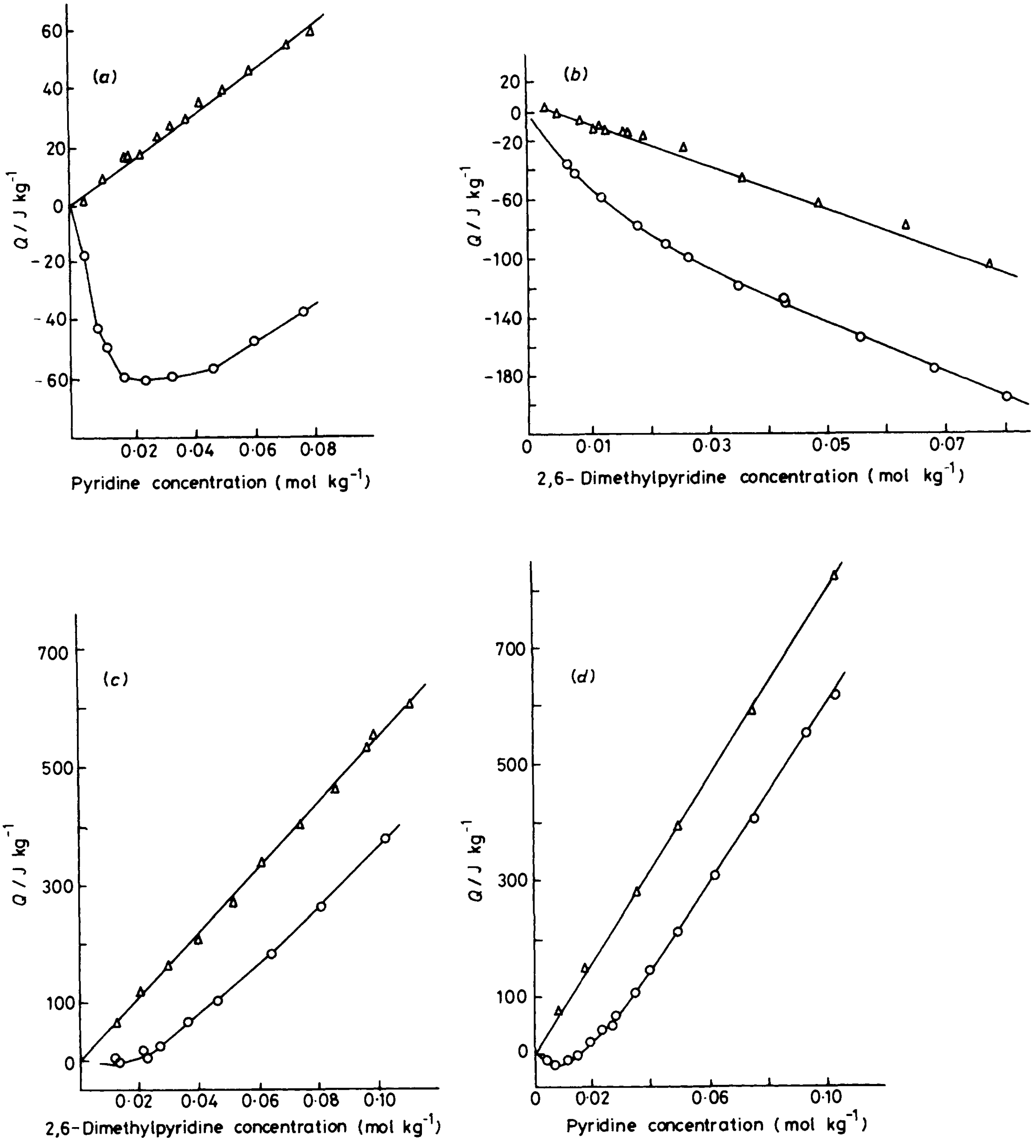

Figure 1. Heats of solution of pyridine bases in pure solvents and dilute iodine solutions. (*a*) Carbon tetrachloride (iodine concentration 0.003 01 mol kg^{-1}); (*b*) 2,6-dimethylpyridine + iodine in carbon tetrachloride (iodine concentration 0.003 01 mol kg^{-1}); (*c*) 2,6-dimethylpyridine + iodine in cyclohexane (iodine concentration 0.006 21 mol kg^{-1}); (*d*) pyridine + iodine in cyclohexane (iodine concentration 0.006 21 mol kg^{-1})

Deranleau that measurements should be taken over most of the saturation range in order that meaning may be assigned to the slope and intercept of the fitted data.[20] A typical iterated Scott plot is shown in Figure 3 and a typical ln K_c(spec) *versus* $1/T$ plot is given in Figure 4. Table 2 shows the molar enthalpies and equilibrium constant values obtained by the calorimetric and spectroscopic methods. The calorimetric results are identified as $\Delta\bar{H}_c$(cal) and K_c(cal) and the spectrophotometric results as $\Delta\bar{H}_c$(spec) and K_c(spec). The association constants are expressed both in kg mol^{-1} and the more usual dm^3 mol^{-1} units. The K_c(spec) values and the values of λ_{max} agree well with those of other workers [1,21-23] whereas the K_c(cal) values are uniformly smaller. A similar trend is shown in the data of ref. 11. The $\Delta\bar{H}$(spec) values are only in reasonable agreement with published $\Delta\bar{H}$(spec) values (see Table 1), and the $\Delta\bar{H}$ (spec) and $\Delta\bar{H}$(cal) values of this work are in general not in good agreement. The $\Delta\bar{H}_c$(cal) for pyridine–iodine is significantly higher than the value calculated from the heat of solution of iodine in pyridine (see Table 1) but this latter value presumably includes endothermic contributions from the dissociation of pyridine dimers. There is also a large discrepancy between $\Delta\bar{H}_c$, for pyridine–iodine in cyclohexane, found here and the value in ref. 6 (see Table 1). This lack of agreement possibly has its origins in the fact that the ref. 6 value was obtained by a combination of spectroscopic and calorimetric measurements. A complication also arises in that

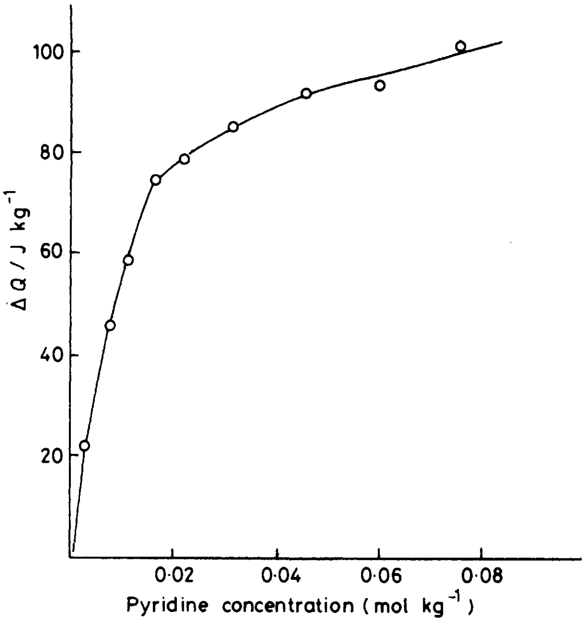

Figure 2. ΔQ *versus* pyridine concentration in carbon tetrachloride

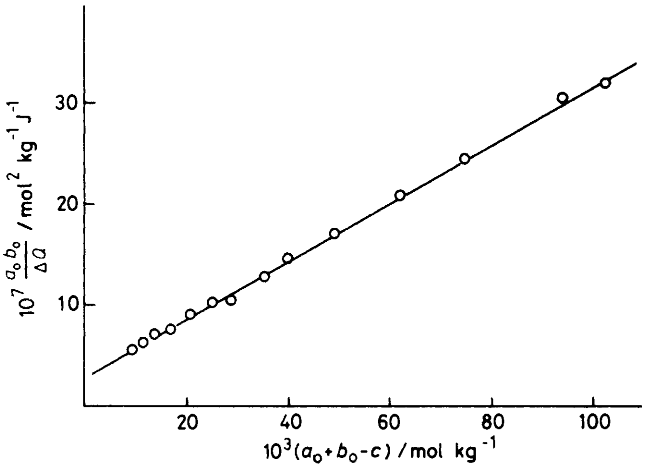

Figure 3. Scott plot after three iterations, pyridine + iodine in cyclohexane

it has been shown that ionic species begin to be formed when neat pyridine is the solvent.[24] A tacit assumption is made here that no ionic species are involved in the carbon tetrachloride or cyclohexane solvent systems.

The influence of the solvent on the complexation reaction is perhaps best expressed by the enthalpy of transfer of the equilibria from one solvent to another. The enthalpy of transfer ($\Delta\bar{H}_\mathrm{t}$) from cyclohexane to carbon tetrachloride may easily be obtained from the molar enthalpies of solution of iodine and the pyridine bases and the measured enthalpies of complexation. $\Delta\Delta\bar{H}_\mathrm{s}$ Values for the pyridine bases were calculated from the present data and the $\Delta\Delta\bar{H}_\mathrm{s}$ value for iodine, based on the published enthalpy of solution data,[25] was taken to be very close to zero. The $\Delta\bar{H}_\mathrm{t}$ results obtained are included in Table 2. The result for 2,6-dimethylpyridine–I_2 agrees closely with the result given in ref. 1 and supports the contention that the complex is more solvated by carbon tetrachloride than by cyclohexane. It would appear also that the pyridine–I_2 complex is even more strongly solvated by carbon tetrachloride. Furthermore, inspection of the $\Delta\Delta\bar{H}_\mathrm{s}$ values for the bases shows that the enthalpy of transfer ($\Delta\Delta\bar{H}_\mathrm{s}$) of pyridine from cyclohexane to carbon tetrachloride is less than the enthalpy of transfer of the complex while the $\Delta\Delta\bar{H}_\mathrm{s}$ for 2,6-dimethylpyridine is greater than the $\Delta\bar{H}_\mathrm{t}$ of the complex. Such results can be interpreted as indicating that competing equilibria involving the solvent and the pyridine base are significant.[1]

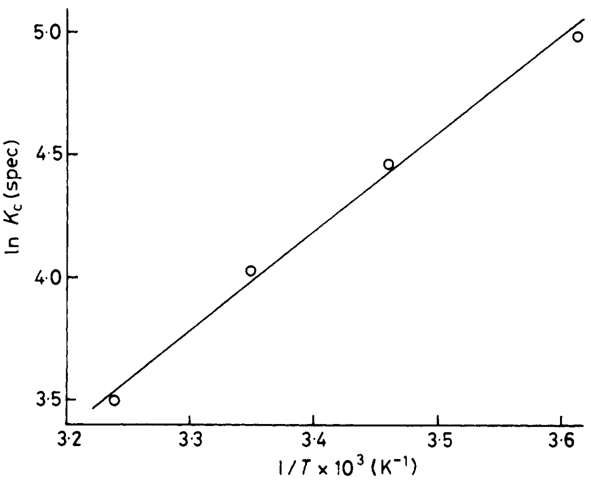

Figure 4. van't Hoff plot, 2,6-dimethylpyridine + iodine in cyclohexane

If $\Delta\bar{H}_\mathrm{c}$(spec) results are used in the $\Delta\bar{H}_\mathrm{t}$ calculation the increase of solvation on transfer from cyclohexane to carbon tetrachloride is still observed but the order for the two systems is reversed. It is believed that more reliance should be placed on the calorimetric enthalpies since it is possible that the calorimetric and spectroscopic methods do not detect exactly the same concentrations of complex. It has long been argued that contact charge-transfer can produce spectral changes.[26] Such contact complexes will not be detected by the calorimetric technique and so the observation that K_c(spec) are larger than K_c(cal) is expected. For the present data the largest difference is observed when carbon tetrachloride is the solvent. This observation coupled with the conclusions reached from the $\Delta\bar{H}_\mathrm{t}$ values implies that the more tightly bound solvation cage around the pyridine base may contain, on a statistical basis, I_2 molecules which although not complexed in the n–σ^* manner are,[27,28] in effect, fairly long lived ' contact ' complexes which contribute to the spectroscopic measurement. A similar conclusion was reached some time ago for the aromatic amine–nitro compound systems.[29] In the solvation shell in cyclohexane, which is not as strong, the ' contact ' complexes have smaller lifetimes so that the K_c(cal) and K_c(spec) values observed are much closer. Under these circumstances it is not to be expected that $\Delta\bar{H}_\mathrm{c}$(spec) values will be characteristic of only the n–σ^* reaction. On the basis of simple collision theory, $\Delta\bar{H}$ contact is *ca.* 0 [28] so that the van't Hoff plot of log K_c(spec) *versus* $1/T$ should yield $\Delta\bar{H}_\mathrm{c}$(spec) values which agree with the $\Delta\bar{H}_\mathrm{c}$(cal) values. On the other hand, ' contact ' interaction involving an iodine molecule as part of the solvent cage may well make an enthalpic contribution to the temperature variation of K_c(spec) which will not appear in the $\Delta\bar{H}_\mathrm{c}$(cal) measurement. In the calculation of ΔQ, the solvation enthalpy change is subtracted from the overall observed heat, as part of the enthalpy of solution of the base. If an additional requirement, that there be no enthalpy

Table 2. Thermodynamic and spectral data at 25 °C

The uncertainties cited are based on the standard deviation of the regression coefficients and shifts of the iterated Scott plots for the calorimetric results and of the van't Hoff isochore for the spectrophotometric results.

(a) Calorimetric

	Pyridine						2,6-Dimethylpyridine					
	$\Delta\Delta\bar{H}_s$ (cal)[a]/ kJ mol^{-1}	$\Delta\bar{H}_t$ (cal)[b]/ kJ mol^{-1}	ΔH_c(cal)/ kJ mol^{-1}	K_c(cal)/ kg mol^{-1}	K_c (cal)/ dm^3 mol^{-1}	K_2/ dm^3 mol^{-1}	$\Delta\Delta\bar{H}_s$ (cal)/ kJ mol^{-1}	$\Delta\bar{H}_t$ (cal)/ kJ mol^{-1}	ΔH_c(cal)/ kJ mol^{-1}	K_c(cal)/ kg mol^{-1}	K_c (cal)/ dm^3 mol^{-1}	K_2/ dm^3 mol^{-1}
CCl_4	−7.3	−9.4	−36 ± 1	119 ± 4	75	35	−6.8	−4.3	34 ± 1	77 ± 2	48	13
C_6H_{12}			−34 ± 1	106 ± 4	134	11			−37 ± 1	46 ± 2	59	13

(b) Spectroscopic

	Pyridine					2,6-Dimethylpyridine				
	$\Delta\bar{H}_c$(spec)/ kJ mol^{-1}	K_c(spec)/ kg mol^{-1}	K_c(spec)/ dm^3 mol^{-1}	$\lambda_{max.}$/nm I_2	$\lambda_{max.}$/nm I_2 shift	$\Delta\bar{H}_c$(spec)/ kJ mol^{-1}	K_c(spec)/ kg mol^{-1}	K_c(spec)/ dm^3 mol^{-1}	$\lambda_{max.}$/nm I_2	$\lambda_{max.}$/nm I_2 shift
CCl_4	−33.1 ± 0.1	174 ± 5	110 ± 3	515	416	−34.0 ± 0.8	96 ± 1	61 ± 1	515	427
C_6H_{12}	−34.6 ± 0.3	112 ± 5	145 ± 6	518	422	−33.8 ± 0.1	56 ± 1	72 ± 1	518	432

[a] $\Delta\Delta H_s$(cal) = molar enthalpy of transfer of base from C_6H_{12} to CCl_4. [b] $\Delta\bar{H}_t$(cal) = molar enthalpy of transfer of complex from C_6H_{12} to CCl_4.

change when an iodine molecule is exchanged for a solvent molecule in the solvation cage, is imposed then no part of the solvation enthalpy appears in the $\Delta\bar{H}_c$(cal) calculation. The enthalpy change for solvation will however make up part of the $\Delta\bar{H}_c$(spec) value. If the $\Delta\bar{H}_c$(spec), $\Delta\bar{H}_c$(cal) differences of Table 2 are real, it is apparent that the way in which ' contact ' interaction makes a contribution to $\Delta\bar{H}_c$(spec) is not clear.

If a simple multiple-equilibria model, where the mass action law governs the concentration of ' contact ' complexes,[30] is applicable to these systems then the K_c(spec) values observed are the sum of the formation constant for the n–σ^* complexes (K_1) and the corresponding constant for the ' contact ' complexes (K_2). K_1 May be identified as K_c(cal) so that subtraction of K_c(cal) from K_c(spec) gives values of K_2.

A theoretical value of K_2 has been calculated for a model involving random collisions in the absence of attractions between the donor and acceptor molecules.[31] This value, 0.2 dm^3 mol^{-1}, is far smaller than the values obtained here (see Table 2). This discrepancy may be accounted for either by an increased separation distance or by a much decreased value of the fraction of non-associated molecules (α in Prue's analysis [31]). For the pyridine–iodine system in carbon tetrachloride the K_2 value obtained here leads to a value of 20 nm for the contact charge-transfer distance. This value is obviously unrealistic. On the other hand, if the value for the separation distance proposed by Prue is retained then α becomes very small for pyridine–I_2 in carbon tetrachloride (*ca.* 0.04) and is larger for the other systems (*ca.* 0.13).

Speculation aside, the present data do show in an unambiguous manner that the effect of di-*ortho* substitution in creating a steric hindrance is confined mainly to a reduction in the size of the equilibrium constants, which are reduced by 30—40% depending on the solvent. The $\Delta\bar{H}_c$(cal) values depend in a more complicated way on the increased donor ability of the base and the solvent used but do not appear to be sensitive to steric hindrance.

Calorimetric data obtained at a single temperature appear to be capable of analysis by iteration of the Scott equation. The treatment yields values of the formation constant and the enthalpy of the interaction with the assumption that only 1 : 1 complexes are formed.

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