A Calorimetric Study of Complex Formation between Molecular Iodine and Pyridine or 2-Methylpyridine in Weakly Polar Solvents

Irmina Uruska * and Małgorzata Koschmidder
Department of Physical Chemistry, Technical University of Gdańsk, 80-952 Gdańsk, Poland

Heats of solution or dilution of pyridine and 2-methylpyridine in n-hexane, cyclohexane, carbon tetrachloride, benzene, and chlorobenzene and in solution containing iodine have been measured by calorimetry. Equilibrium constants for complex formation of the amines with molecular iodine have been determined by spectrophotometry. The results have been interpreted in terms of solvent effects on the thermodynamic characteristics of complex formation and on complex–solvent interactions (the enthalpies of transfer of complex from poorly solvating medium to a given solvent).

Few of the papers on complexes of pyridine derivatives with molecular iodine[1–14] report the entire thermodynamic characteristics of the process of complex formation, based on calorimetric measurements.[8,11,14] Such data have been reported for pyridine (py) and 2,6-dimethylpyridine (2,6-Me_2py) complexes in cyclohexane and carbon tetrachloride[8,14] and for 2,6-dimethylpyridine, 2,4-dimethylpyridine (2,4-Me_2py), and isoquinoline (iq) in five weakly polar solvents.[11]

We report here the results of calorimetric and spectrophotometeric measurements for pyridine and 2-methylpyridine (2-Mepy)–molecular iodine in several weakly polar solvents, n-hexane, cyclohexane, carbon tetrachloride, benzene, and chlorobenzene. No reliable results could be obtained for more polar media because of the instability of the solutions (ionic reactions).

The equilibrium constants K_c have been determined by spectrophotometry. The measured heats of solution of the amines $\Delta H_s(D)$ and the enthalpies of complex formation ΔH_r (calorimetry) have been used to calculate the heats of transfer of the complex from nonsolvating medium (n-hexane) to a given solvent, $\Delta H_{tr}(AD)$ [equation (1) where s and ref refer to the

$$\Delta H_{tr}(AD) = \Delta H_r(s) - \Delta H_r(ref) + \Delta H_{tr}(D) + \Delta H_{tr}(I_2) \quad (1)$$

given solvent and n-hexane, respectively].

Experimental

Reagents.—Solvent and iodine were purified by standard methods, as described previously.[10] Pyridine (POCH, Gliwice, pure) and 2-methylpyridine (Fluka AG, Busch SG, Switzerland, pure) were dried over KOH and distilled from molecular sieves (4A) *in vacuo*. Calorimetric and spectrophotometric measurements were performed in moisture-free conditions. A reaction calorimeter of the 'constant temperature environment' type[15] with reaction ampoules made of Teflon and thin-walled glass has been used. The temperature 298.16 ± 0.001 K was measured with a 33 kΩ thermister of sensitivity 7×10^{-5} K. The heat capacity of the calorimeter was tested by measuring the heat of solution of 1 mol of KCl in 275 moles of water, corrected for the known heat of dilution, 17.61 ± 0.04 kJ mol^{-1}. The molar enthalpies of the reactions, ΔH_r, were calculated as $\Delta H_r = (q_r - q_s)/n$, where q_r is the heat of solution of the pure amine in the iodine solution ([iodine] *ca.* 10^{-3} mol dm^{-3}) in the given solvent (*ca.* 90 cm^3), q_s is the heat of solution of the pure amine in the same solvent, determined in a separate experiment for the same conditions and with the same final amine concentrations, and n is the number of moles of the complex in the solution, calculated using the equilibrium constant values determined by a spectrophotometric method. The ratio of the complex to the initial iodine concentration was 0.7—0.9. The heats of solution, q_r and q_s, in n-hexane and cyclohexane were measured by adding a concentrated amine solution (1—3 mol dm^{-3}) instead of pure amine because the exothermic heats of complex formation (at [complex] *ca.* 10^{-3} mol dm^{-3}) are much lower than endothermic heats of solution of the amines. The ΔH_r values were not corrected for the heat of dilution of the iodine to the final concentration because they were found to be negligible.[8] The ΔH_s and ΔH_r values listed in Tables 1 and 2 are the average of 3—5 separate measurements. Electronic spectra (340—600 nm) were measured on Beckman 5 270 u.v. spectrophotometer in thermostatted (298.2 ± 0.1 K) stoppered cells. K_c Values were calculated by a modified Ketelaar equation. This accounted for the free iodine absorption[10] and was applied to the measured absorbances (perturbed iodine band) of every set of solutions containing constant iodine concentration (*ca.* 10^{-4} mol dm^{-3}) and varying amine concentration (10^{-2}—10^{-3} mol dm^{-3}). The K_c values listed in Table 1 are averages of at least two independent sets of solutions (not less than five solutions in the set). All manipulations were carried out in a dry-box containing P_2O_5.

Results and Discussion

The calculated equilibrium constants for reaction (2) where D is

$$D + I_2 = DI_2 \quad (2)$$

the pyridine derivative, are listed in Table 1. The K_c values have been found to be independent of the wavelength of the measurement when measured at $\lambda_{max.}$, $\lambda_{max.} \pm 5$, and $\lambda_{max.} \pm 10$ nm, which indicates that only one equilibrium between D and I_2 is established in the solutions. In view of this fact the discrepancy between the K_c values obtained by spectrophotometric and calorimetric methods in earlier work[14] (Py–I_2–CCl_4; K_c 110 and 75 dm^3 mol^{-1}, respectively) cannot be explained by the simultaneous presence of the weak contact charge transfer D–I_2 complexes, as suggested by the authors.[14]

As can be seen from Table 1, the K_c values for both amines do not follow any regular dependence on dielectric permittivity of the solvent or the Hildebrand solubility parameter δ. The order of decreasing K_c values is: chlorobenzene > n-hexane ≃ cyclohexane > carbon tetrachloride > benzene > chloroform. A similar sequence was also found for other pyridine derivative–molecular iodine systems, irrespective of the basicity of the donor (pK_a 0.8—6.7) or the kind of substituent.[12] It is noteworthy, however, that for solvents with low dielectric constant ($\varepsilon < 2.5$), a fairly good linear correlation between ln K_c and the Hildebrand solubility parameter or one of the 'polarity functions', such as Taft's dipolarity/polarisability parameter,

Table 1. Thermodynamic characteristics of the reaction $D + I_2 = DI_2$ in weakly polar solvents; T 298.2 K

	ε[a]	$10^{-3}\delta$[b] / $\mathrm{Pa}^{-\frac{1}{2}}$	Final concentrations[c] $10^2[D]$ / mol dm^{-3}	$10^3[I_2]$ / mol dm^{-3}	$-\Delta H_r$[c] / kJ mol^{-1}	K_c[d] / dm^3 mol^{-1}	$-\Delta S_r$ / J K^{-1} mol^{-1}
			D = pyridine, pK_a 5.20				
n-Hexane	1.880	14.9	1.7	5.9	35.7 ± 0.9	133 ± 4	79 ± 3
Cyclohexane	2.015	16.8	1.9	5.7	34.6 ± 0.1	129 ± 4	76 ± 1
Carbon tetrachloride	2.228	17.6	1.8	6.4	30.4 ± 0.9	105 ± 3	63 ± 3
Benzene	2.274	18.8	20	5.6	29.9 ± 0.1	82 ± 3	64 ± 1
Chlofororm	4.726	19.0				66 ± 1	
Chlorobenzene	5.621	19.4	21	5.7	33.5 ± 0.6	182 ± 6	69 ± 3
			D = 2-methylpyridine, pK_a 5.96				
n-Hexane	1.880	14.9	1.9	5.3	37.6 ± 0.1	181 ± 9	83 ± 1
Cyclohexane	2.015	16.8	1.5	6.5	37.0 ± 0.9	186 ± 8	81 ± 3
Carbon tetrachloride	2.228	17.6	5.6	4.6	36.1 ± 0.6	143 ± 2	80 ± 2
Benzene	2.274	18.8	16	5.1	34.1 ± 0.5	100 ± 4	76 ± 2
Chloroform	4.726	19.0				76 ± 3	
Chlorobenzene	5.621	19.4	6	6.6	36.1 ± 0.6	249 ± 4	75 ± 2

[a] Dielectric permittivity. [b] Solubility parameter of the solvent; from ref. 17. [c] Calorimetric method. [d] Spectrophotometric method.

Table 2. Heats of solution (kJ mol^{-1}) of the donor, $\Delta H_s(D)$, heats of transfer of the donor, $\Delta H_{tr}(D)$, of molecular iodine, $\Delta H_{tr}(I_2)$, of the reactants, $\Delta H_{tr}(D + I_2)$, and of the molecular complex DI_2, $\Delta H_{tr}(DI_2)$, from n-hexane to the given solvent; T 298.2 K

Solvent	$\Delta H_s(D)$[a]	$\Delta H_{tr}(D)$	$\Delta H_{tr}(I_2)$[b]	$\Delta H_{tr}(D + I_2)$	$\Delta H_{tr}(AD)$
		D = pyridine			
n-Hexane	8.12 ± 0.02	0	0	0	0
Cyclohexane	8.31 ± 0.08	0.19 ± 0.1	0	0.2	1.3
CCl_4	0.80 ± 0.01	−7.32 ± 0.03	0	−7.3	−2.0
Benzene	0.07 ± 0.01	−8.05 ± 0.03	−6.5	−14.6	−8.8
Chlorobenzene	0.02 ± 0.02	−8.10 ± 0.04	−4.4	−12.5	−10.3
		D = 2-methylpyridine			
n-Hexane	5.81 ± 0.09	0	0	0	0
Cyclohexane	6.62 ± 0.07	0.81 ± 0.16	0	0.8	1.4
CCl_4	−0.46 ± 0.02	−6.27 ± 0.11	0	−6.3	−4.8
Benzene	0.11 ± 0.01	−5.70 ± 0.10	−6.5	−12.2	−8.7
Chlorobenzene	−0.93 ± 0.06	−6.74 ± 0.15	−4.4	−11.1	−9.6

[a] Approximate final concentrations are given in Table 1, column 4. [b] From ref. 19; the reported error in the heats of solution of iodine is: for n-hexane, cyclohexane, and CCl_4 0.8 kJ mol^{-1}; for benzene and chlorobenzene 0.2 kJ mol^{-1}.

π^*,[16] or the Kirkwood function, has been obtained. Both chloroform (ε 4.73) and chlorobenzene (ε 5.62) show strong deviations from the common dependence. This behaviour cannot, however, be entirely due to their dipolarity because the deviations are of opposite sign. Rather it reflects differences of solvation of the product and reactants by the two media: while in chlorobenzene the complex should be better solvated than would its less dipolar components, in chloroform the opposite should be true because the above effect is likely to be dominated by additional stabilisation of the donor through specific interactions with the solvent (hydrogen bonding).

Release of solvent molecules from the solvation shell of the reactants in the course of complex formation should also take place in media of low polarity ($\varepsilon < 2.5$). This effect may account for the regular decrease of K_c from n-hexane to benzene: though the increasing polarity of the medium should increasingly stabilise the complex with respect to the reactants, this contribution to the ΔG for complex formation should be rather small and dominated by desolvation of the reactants (the last effect also should increase in the sequence n-hexane–benzene).

The results can be compared with those reported in the literature for the extensively studied pyridine complex. The Figure reveals appreciable scatter of the K_c values reported by different workers for the same system. This can be due to different conditions of measurements or purity of the reagents rather than to the method used, because the calorimetric data obtained by Bertrand and his co-workers,[8] by both ampoule and titration calorimetry methods, agree very well with those calculated from absorptivities of solutions.

The K_c values for the α-substituted pyridine are higher than those for a much weaker base, pyridine (pK_a 5.97 and 5.2, respectively) and nearly as high as those for a base of intermediate strength (pK_a 5.4), quinoline.[11] This suggests that both a steric effect and the *n*-donor strength of the amine are operative in stabilising the iodine complex. The steric effect is clearly seen if we compare the K_c values for 2-methylpyridine with those obtained for the considerably stronger bases 2,6- and 2,4-dimethylpyridine (pK_a 6.7 and 6.6, respectively): the second CH_3 group in the *ortho*-position results in a pronounced decrease in K_c (72, 75, 58, 42, and 85 for n-benzene, cyclohexane,

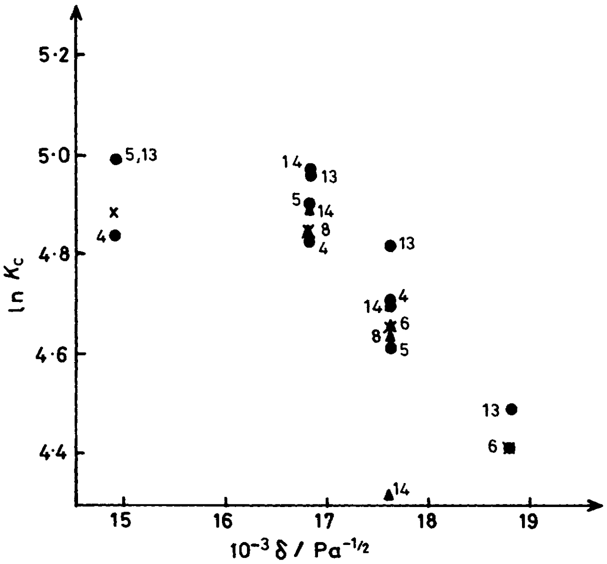

Figure. Dependence of ln K_c/dm^3 mol^{-1} on the Hildebrand solubility parameter of the solvent, δ, for pyridine–iodine complexes in weakly polar solvents. ●, spectrophotometric method; ▲, calorimetric method (the numbers denote references to the literature); × this work

carbon tetrachloride, benzene, and chlorobenzene)[11] while the second CH_3 group in the *para* position strongly increases the stability of the complex (K_c 390, 364, 284, 228, and 575, respectively).[11]

The measured molar enthalpies of complex formation ΔH_r show a similar dependence on the solvent as do the equilibrium constants: their absolute values decrease with increasing polarity of the medium in the sequence n-hexane ⩾ cyclohexane > carbon tetrachloride > benzene and then increase for the polar chlorobenzene. This sequence shows that the $|-\Delta H_r|$ values do not parallel the extent of charge transfer in the ground state of the complex (as expected on the basis of the Mulliken's theory of electron donor–acceptor complexes)[18] because the proportion of dative structure should regularly increase with the polarity of the medium. Such an increase in charge transfer has been reported for analogous complexes.[13]

The steric effect of the *ortho* substituent in the pyridine ring is not as pronounced in the case of ΔH_r values as it is for the equilibrium constants. It can be observed only for the *ortho* disubstituted compound, 2,6-dimethylpyridine (pK_a 6.7): the $-\Delta H_r$ values for 2,6-Me_2py (34.8, 34.5, 32.5, 28.6, and 35.6 kJ mol^{-1} for n-hexane, cyclohexane, carbon tetrachloride, benzene, and chlorobenzene, respectively)[11] are lower than those for the weaker base, 2-methylpyridine (Table 1) and comparable with ΔH_r values for the amine with the lowest pK_a value in the series, *i.e.* pyridine.

The fact that K_c values are more sensitive to steric effects than are the ΔH_r indicates that steric hindrance causes major unfavourable entropy effects in complex formation. This conclusion is supported by higher values of $|-\Delta S|$ for α-methylpyridine than for pyridine complexes (Table 1).

The $-\Delta H_r$ values for pyridine–iodine in cyclohexane and carbon tetrachloride reported here can be compared with literature values. They agree very well with those obtained by Bertrand and his co-workers[8] by calorimetric titration, calorimetric 'batch' method, and combined calorimetric–spectrophotometric measurements (35.5, 34.7, and 35.1 kJ mol^{-1} for cyclohexane and 32.6, 30.9, and 30.0 kJ mol^{-1} for carbon tetrachloride, respectively) and do not differ appreciably from those of Barton and Pottier[14] obtained by calorimetric titration in cyclohexane (34 ± 1 kJ mol^{-1}). The value, 36 ± 1 kJ mol^{-1}, reported by these authors for carbon tetrachloride solutions[14] may be in some error in view of the unusually low K_c value (75 dm^3 mol^{-1}) determined simultaneously in the experiment.

With the calculated molar enthalpies of complex formation, the molar enthalpies of solution of the donor amines (Table 2), and the ΔH_s value of iodine taken from the literature,[19] it is possible to obtain heats of transfer of the complexes from a poorly solvating medium (here n-hexane) to a given solvent [equation (1)]. Their values (Table 2) clearly show that the interactions of the molecular complex with the non-dipolar media such as benzene and carbon tetrachloride are non-negligible. It is interesting that solvation of the complex by dipolar chlorobenzene is not much stronger than by benzene. This suggests that non-specific interactions do not play the main role in complex solvation, though the overall trend in ΔH_{tr}(AD) values is a regular decrease with the solvent polarity. This decrease does not, however, quantitatively correlate with the dielectric permittivity of the medium or other polarity parameters. Such behaviour suggests that other schemes of complex solvation, *i.e.* specific interactions, should also be taken into account. The most probable are local solvent–amine π–π (aromatic hydrocarbons) or *n*–π (carbon tetrachloride) interactions and/or those between the complexed iodine (a donor site) and the solvent.

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