

A Calorimetric Study of Phenol-Pyridine Complexes in Carbon Tetrachloride Solution¹

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The heats of reaction between a dilute solution of phenol in carbon tetrachloride and pyridine and the monomethylpyridines have been measured in an ice-calorimeter. The calculated enthalpy change per mol of hydrogen-bonded adduct formed appears to be insensitive to basicity and the position of the methyl group.

THERE is only a small variation in pK_a values for pyridine and the three monomethylpyridines and steric factors do not seem to exert any influence during neutralization in aqueous strong acids,² nor during the reaction between these bases and methanesulphonic acid in nitrobenzene solution,³ since in both cases plots of the calorimetrically measured enthalpy plotted against the pK_a values for the bases gave good straight lines. These results were obtained presumably because of the small size of the proton.

On the other hand, calorimetric studies have indicated that no such simple relationship exists for the reaction between these pyridine bases and the Lewis acid aluminium tribromide.⁴ Except for a lower value for the enthalpy of reaction in the case of the *ortho*-substituted compounds, 2-methyl- and 2,6-dimethyl-pyridine, the enthalpy values are reasonably constant for the series of pyridine bases investigated. Presumably steric hindrance by the bulky aluminium tribromide is the cause of the lower enthalpy observed for the reaction with the *ortho*-substituted pyridines. Steric effects caused by *ortho*-substitution on the pyridine base and a bulky Lewis acid have also been invoked to account for the fact that the 2-picoline adduct with trimethylboron is much more

unstable than the adducts formed by pyridine and 3- and 4-picoline.⁵ Also, although the introduction of a methyl group in the 3- or 4-position on pyridine causes only a small increase in the rate of reaction with alkyl halides, a methyl group in the 2-position brings about a marked decrease in reaction rate.⁶

Steric hindrance may or may not have an influence on the stability of hydrogen-bonded adducts with the methylpyridines. It appears from the work of Tamres *et al.*⁷ that the reaction between chloroform and the methylpyridines is not sterically hindered. Since, although enthalpy values for adduct formation were not calculated, the heats of mixing of chloroform and the bases were found to be roughly linear with the pK_a of the base. Bhaskar and Singh,⁸ on the other hand, have reported enthalpy values obtained from spectroscopic studies on hydrogen-bonded phenol-pyridine base systems in carbon tetrachloride that are insensitive to position and type of alkyl substituent on the pyridine ring and, in particular, no evidence of a steric effect arising from *ortho*-substitution in 2,6-dimethylpyridine was obtained. Similar results on the same systems have been reported also by Rubin and Panson,⁹ although they

¹ Based in part on B.Eng. Theses of T. R. Owen and L. J. Skinner, Royal Military College of Canada, 1966—1967.

² L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Amer. Chem. Soc.*, 1960, **82**, 3831.

³ H. C. Brown and R. R. Homes, *J. Amer. Chem. Soc.*, 1955, **77**, 1727.

⁴ J. W. Wilson and I. J. Worrall, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1357.

⁵ H. C. Brown and G. K. Barbaras, *J. Amer. Chem. Soc.*, 1947, **69**, 1137.

⁶ H. C. Brown and A. Cahn, *J. Amer. Chem. Soc.*, 1955, **77**, 1715.

⁷ M. Tamres, S. Searles, E. M. Leighly, and D. W. Mohrman, *J. Amer. Chem. Soc.*, 1954, **76**, 3983.

⁸ K. R. Bhaskar and S. Singh, *Spectrochim. Acta*, 1967, **23A**, 1155.

⁹ J. Rubin and G. S. Panson, *J. Phys. Chem.*, 1965, **69**, 3089.

found evidence that bulky *ortho*-substituents on the phenol molecule resulted in steric hindrance to hydrogen bonding.

There is no direct calorimetric measurement of the enthalpy change for the reaction between phenol and the three monomethylpyridines which would support the findings of Bhaskar and Singh and Rubin and Panson. Arnett *et al.*¹⁰ reported an accurate value of ΔH_o , the enthalpy change per mol of adduct, for the pyridine-phenol reaction. By making measurements in carbon tetrachloride and in pure base these authors obtained evidence that the medium has only a small effect on ΔH_o and further that ΔH_o is not very sensitive to temperature change. However, ΔH_o data¹¹ for the reactions between the bases pyridine, 4-methylpyridine, 2,6-dimethylpyridine, and 2,4,6-trimethylpyridine and *p*-fluorophenol in carbon tetrachloride show clearly that no strong steric hindrance is offered by *ortho*-methyl groups to hydrogen bonding. The two *ortho*-substituted pyridines give significantly higher ΔH_o values than the unhindered 4-methylpyridine. It is possible that the influence of a small steric hindrance could be overshadowed by the increased basicity arising from the inductive effect of di-*ortho*-substitution in the 2,6-dimethyl- and the 2,4,6-trimethyl-pyridine.

In the present work, measurements of ΔH_o for the reaction between pyridine and the three monomethylpyridines with a solution of phenol in carbon tetrachloride were made at 0 °C in an ice-calorimeter.

EXPERIMENTAL

A simple ice-calorimeter similar to that described by Vallee¹² was used. The instrument was calibrated by dropping a weighed piece of pure aluminum on the end of a nylon thread from a jacket at known temperature above the calorimeter into an oil-filled reaction tube in the central well of the calorimeter. The calibration constant was found to be 1.23 cal cm⁻¹ reproducible to within $\pm 1\%$ when absolute amounts of heat of ca. 25 cal were used in the calibration. The uncertainty in the calibration constant is probably due largely to uncertainty in the correction for heat loss which was calculated from the fore and after drift of the mercury thread in the dilatometer tube.

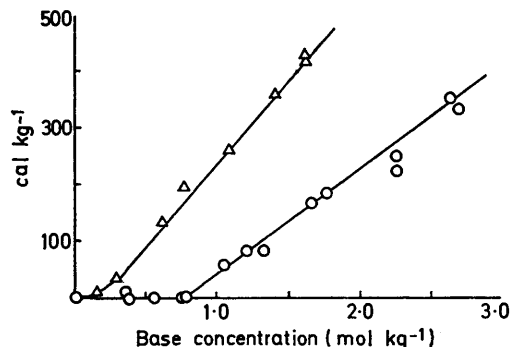
Spectrophotometric grade carbon tetrachloride and pyridine were used. The other bases were distilled and the following fractions were used: 4-methylpyridine, b.p. 142.8–143.7 °C at 760 mmHg; 3-methylpyridine, b.p. 141.5–142.5 °C at 750 mmHg; and 2-methylpyridine, b.p. 126–127 °C at 760 mmHg. Reagent phenol was doubly distilled in a simple distillation flask and the fraction boiling at 179.5–180.5 °C was used.

The pyridine bases were weighed and sealed into thin-walled glass ampoules which were broken under the surface of a volumetrically determined amount of carbon tetra-

chloride or a 0.050M-phenol solution in carbon tetrachloride in the calorimeter. The breaker was a piece of solid Pyrex rod which had been sharpened at one end. Stirring was accomplished by raising and lowering the breaker rod in the solution. A disc of Teflon slipped over the rod served as a stirrer. This breaking and stirring procedure has been tested and found to yield satisfactory results in similar heat determinations.¹³ Heats of breaking and stirring were determined in blank experiments and used to correct all heat measurements.

No attempt was made to eliminate the vapour space in the reaction tube in the calorimeter. Hence there will be a significant contribution to the measured heat from the heat of vaporization or condensation into the large and undefined vapour space when liquid mixing occurs.¹⁴ However since the interest here is in the difference in heat of solution when phenol is and is not present in the solvent it was assumed that the effect of vapour space remained constant for a given pyridine base-carbon tetrachloride concentration and was subtracted in the calculation of the heat due to hydrogen-bonding reactions.

The data for the pyridine-carbon tetrachloride system are shown in the Figure where the heat evolved, in cal per



Heat of mixing of pyridine bases and carbon tetrachloride in an open system at 0 °C; Δ 4-methylpyridine; ○, pyridine

kg of solution, is plotted against the concentration of pyridine expressed as mol per kg of solution. The line drawn through the linear part of the curve is derived from a least-squares determination of the apparently linear data. The zero heat effect observed up to pyridine concentration 0.8 mol kg⁻¹ probably reflects the decided change in sign of heat of mixing for the pyridine-carbon tetrachloride system which has been measured by Morcom and Travers.¹⁵

The results for 4-methylpyridine are also shown in the Figure. The apparently linear curve does not extrapolate through the origin and perhaps indicates that a reversal of the sign of the heat of mixing also occurs in this case. Similar results were found with 2- and 3-methylpyridine although indications of a reversal of sign are not apparent.

The parameters of least-squares fits to the apparently linear portions of these curves were used to correct the heats measured when pyridine and the picolines were dissolved in 0.050M-phenol in carbon tetrachloride. The

¹⁰ E. M. Arnett, T. S. S. R. Murty, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 5955.

¹¹ E. M. Arnett and E. J. Mitchell, *J. Amer. Chem. Soc.*, 1971, **93**, 4052.

¹² R. E. Vallee, *Rev. Sci. Instr.*, 1962, **33**, 856.

¹³ S. S. Barton and G. Boulton, *J. Chem. Eng. Data*, 1970, **15**, 66.

¹⁴ M. L. McGlashan, 'Experimental Thermochemistry,' vol. II, ed. H. A. Skinner, Interscience Publishers, New York, 1962, p. 325.

¹⁵ K. W. Morcom and D. N. Travers, *Trans. Faraday Soc.*, 1966, **62**, 2063.

data are in the Table. Since the equilibrium constants for the hydrogen-bonding reaction have been reported to have

	[Base]	Q_0	Q	ΔQ	[phen]	ΔH_c
Pyridine	1.54	137	325	188	0.028	6.7
	0.853	18	231	213	0.029	7.3
	2.38	277	456	179	0.026	6.9
	1.20	76	294	218	0.029	7.5
	1.96	209	413	204	0.027	7.6
						7.2 ± 0.3
2-Picoline	0.940	240	443	203	0.030	7.0
	0.217	50	258	208	0.031	6.7
	2.43	523	694	171	0.024	7.1
	0.610	140	348	208	0.030	6.9
						6.9 ± 0.1
3-Picoline	0.973	223	436	213	0.029	7.4
	0.785	183	406	223	0.029	7.6
	0.539	105	329	224	0.030	7.5
	1.270	330	526	196	0.028	7.0
						7.4 ± 0.2
4-Picoline	1.019	241	440	199	0.029	6.9
	1.327	330	528	198	0.028	7.1
	0.951	221	445	224	0.029	7.7
	1.542	39	589	199	0.027	7.4
						7.3 ± 0.3

[Base] = Concentration of base (mol kg⁻¹). Q_0 = Cal per kg base-carbon tetrachloride solution. Q = Cal. per kg base-phenol-carbon tetrachloride solution. $\Delta Q = Q - Q_0$ = Cal per kg solution. [phen] = Concentration of phenol (mol kg⁻¹). ΔH_c = Enthalpy of adduct formation (kcal mol⁻¹).

values in the region 40–100 l mol⁻¹,^{8,9,16} and since on the average about a 40-fold excess of pyridine base over phenol was present, a simple calculation shows that effectively all the phenol present is engaged in hydrogen bonding. Hence

the concentration of phenol could be taken as a close estimate of the concentration of hydrogen-bonded adduct. The enthalpy change for the formation of one mole of hydrogen-bonded adduct is given by $\Delta Q/[\text{phenol}] = \Delta H_c$ cal mol⁻¹. In effect this method is a combination of Methods I and II of Arnett *et al.*¹⁰

RESULTS AND DISCUSSION

The Table shows that the values of ΔH_c for the adducts formed from phenol and the closely related series of bases are nearly constant. This is in agreement with the findings of Bhaskar and Singh⁸ and, within the precision of the measurements, no evidence for steric hindrance by *ortho*-methyl groups in hydrogen bonding of phenol to acceptors of similar basicity was obtained.

The ΔH_c value for the pyridine-phenol adduct agrees with that of Arnett *et al.*¹⁰ and with the values given by Bhaskar and Singh⁸ for pyridine-phenol and 4-methylpyridine-phenol adducts.

Not surprisingly the ΔH_c values show no trend with basicity, as measured by pK_a values. Such a trend may be hidden in the large uncertainties of the measurements which are of the same order as the increase in heat of reaction found by Sacconi *et al.*² and Brown *et al.*³ in comparing pyridine and 2-methylpyridine.

We thank the Defence Research Board of Canada for financial support.

[1/1677 Received, September 13th, 1971]

¹⁶ E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1970, **92**, 2365.