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Note

SOME THERMOCHEMICAL DATA FOR PYRIDINIUM BROMIDE

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Thermochemical data for pyridinium bromide is very sparse. Lilje and Macomber [1] have reported quantitative data relating to the solubility of pyridinium bromide in chloroform from which an approximate enthalpy of solution of —9 kJ mole^{-1} results. The structure of pyridinium bromide is also in doubt [1]. However, Macomber [2] has examined the proton NMR of this compound using $CDCl_3$ as solvent and has suggested that the multiplet at δ16.1 ppm suggests the presence of a highly acidic proton. The present paper reports the enthalpy of solution of pyridinium bromide obtained directly using a capsule-solution calorimeter and the enthalpy of fusion as derived using a differential scanning calorimeter. From these data the enthalpy of mixing of liquid pyridinium bromide and chloroform is derived.

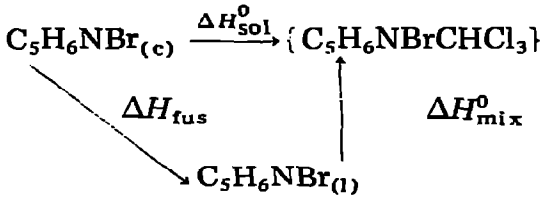
EXPERIMENTAL

Pyridinium bromide was synthesized by passing dry hydrogen bromide through a solution of anhydrous pyridine (90 cm^3) in pentane (45 cm^3) maintained at 273 K for 24 h. The white crystalline product was removed by filtration under nitrogen, washed with dry pentane and pumped dry. The product was purified by repeated sublimation: yield 7.7 g, m.p. 219.1 ± 0.3 K; literature 217.5—218.5 K [2]. Volhard analysis for bromide indicated a purity of 99.60 ± 0.21%. Chloroform solvent was purified by the well-established procedure [3]. The enthalpy of solution of pyridinium bromide in chloroform was derived using an L.K.B. solution/reaction calorimeter described elsewhere [4]. The enthalpy of fusion of pyridinium bromide was obtained using a Perkin-Elmer DSC IB differential scanning calorimeter and indium metal as the calibration standard (ΔH_{fus} = 3.35 kJ mole^{-1}) [5].

RESULTS AND DISCUSSION

The following simple thermochemical cycle (Scheme 1) inter-relates the enthalpy of solution, enthalpy of mixing and enthalpy of fusion of pyridinium bromide — the former two thermochemical quantities relate to chloroform as solvent.

Thus $\Delta H^0_{mix} = \Delta H^0_{sol} - \Delta H_{fus}$. ΔH^0_{sol} data are given in Table 1 and ΔH_{fus} data are recorded in Table 2. Thus $\Delta H^0_{mix} = -21.35 \pm 1.3$ kJ mole^{-1}.



Scheme 1

Lilje and Macomber [1] have given the solubility of pyridinium bromide in chloroform as 18% w/w at 0°C and 10% w/w at 60°C. If this data is interpreted as 18 g C_5H_6NBr is soluble in 82 g $CHCl_3$ at 0°C and 10 g C_5H_6NBr is soluble in 90 g $CHCl_3$ at 60°C, then based on these two data points, and assuming the presence of only one solute species, ΔH^0_{sol} is −9 kJ mole^{-1}. This is in excellent agreement with $\Delta H^0_{sol} = -9.97$ kJ mole^{-1} obtained by direct measurement. The relatively large enthalpy of mixing suggests significant interaction between pyridinium bromide and chloroform. Structural studies of solvent—solute interactions involving polar inorganic species in organic solvents are not numerous. Finch et al. [6] have studied the boron trihalide/benzene system and have confirmed the existence of a 1 : 1 complex based on IR data and ^{11}B NMR spectral data. However, the combined data is not consistent with the presence of a simple hydrogen-bonded complex. Since excellent agreement exists between the calorimetric ΔH^0_{sol} and that derived from the variation of solubility with temperature for the pyridinium bromide/chloroform system, it appears that the assumption of only one solute species is correct and dissociation of pyridinium bromide in chloroform is insignificant; however an NMR study of the pyridinium bromide/chloroform system is required to discern the structure of the complex species present.

TABLE 1

Enthalpy of solution of pyridinium bromide in chloroform at 298 K [a]

Run No.	C_5H_6NBr (mmole)	$-\Delta H^0_{sol}$ (kJ mole^{-1})
1	0.55	9.916
2	1.02	10.335
3	0.52	9.774
4	1.04	10.196
5	0.81	10.029
6	0.53	9.556

[a] For the reaction $C_5H_6NBr_{(c)} \rightarrow C_5H_6NBr_{(s)}$. (s) = infinitely dilute chloroform solution. Mean $\Delta H^0_{sol} = -9.97 \pm 0.30$ kJ mole^{-1}.

TABLE 2

Enthalpy of fusion of pyridinium bromide [a]

Run No.	C_5H_6NBr (mg)	Measured m.p. (K)	ΔH_{fus} (kJ mole^{-1})
1	5.91	219.50	12.740
2	8.55	219.25	11.569
3	5.43	218.50	11.837
4	3.45	219.25	10.255
5	4.38	218.75	10.502

[a] For the process $C_5H_6NBr_{(c)} \rightarrow C_5H_6NBr_{(\ell)}$. Mean $\Delta H_{fus} = 11.38 \pm 1.30$ kJ mole^{-1}.

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