Thermochimica Acta, 53 (1982) 349–356
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

THERMOCHEMISTRY OF PICRATES. III. ENTHALPIES OF SOLUTION AND SOLUBILITIES OF PICRATE SALTS

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(Received 17 September 1981)

ABSTRACT

Using isoperibol solution-reaction calorimeters, the aqueous enthalpies of solution at 298.15 K of ammonium, caesium, potassium, silver, rubidium, tetramethylammonium and tetraethylammonium picrates have been determined as 45.81±0.35, 56.03±0.55, 51.14±0.55, 36.69±0.35, 55.01±0.36, 31.84±0.31 and 32.02±0.18 kJ mole^{-1}, respectively. Aqueous solubility data, as a function of temperature, have been measured for potassium, silver, ammonium, rubidium and caesium picrates by a precipitation method.

INTRODUCTION

Values of enthalpies of solution, $\Delta H_s^{\ominus}$, of picrate salts are important: the standard enthalpy of formation of the aqueous picrate ion, $\Delta H_s^{\ominus}\{C_6H_2(NO_2)_3O^-(aq)\}$, for example, is a key datum in the estimation of lattice energies, $U^{\ominus}$ and standard enthalpies of formation of ionic picrates. Reliable data both for $\Delta H_s^{\ominus}$ and for solubilities are sparse; determinations for several 1:1 picrates were hence made as part of a systematic investigation of thermochemical properties of nitroaromatic compounds.

EXPERIMENTAL

Materials and synthesis

$C_6H_2(NO_2)_3OK$
Stammler's [1] method was used, viz. neutralisation of a hot, 30% ethanol: water solution of picric acid by aqueous KOH.

$C_6H_2(NO_2)_3OAg$
This was prepared by the established method of addition of silver oxide to an ethanol/water solution of picric acid.

$C_6H_2(NO_2)_3ONH_4$

The more thermodynamically stable (yellow) modification was prepared as described recently from ammonium carbonate and picric acid.

$C_6H_2(NO_2)_3ON(CH_3)_4$

This was prepared by adding a small excess of tetramethylammonium bromide solution to silver picrate solution, filtering off the precipitated silver bromide. This was found to be preferable to the neutralisation method. Tetraethylammonium, caesium and rubidium picrates were similarly prepared from silver picrate and the appropriate bromides.

All picrates were recrystallised thrice from water, dried appropriately, and stored in desiccators until used.

CALORIMETRY

Either of two isoperibol calorimeters were used. For NH_4Pic, Me_4NPic and Et_4NPic a commercial system (LKB, Model 8700) was operated; for AgPic, KPic, CsPic and RbPic a calorimeter constructed in the department and described elsewhere was employed. The performance of each calorimeter was checked periodically, using the enthalpy of dissolution, $\Delta H_s^{\ominus}$, of 2-amino-2-hydroxy-propane-1,3 diol (THAM) in NaOH as a test reaction. Typical results were

LKB calorimeter, 16.67 ± 0.05 kJ mole^{-1} (0.10 M NaOH) (Lit. [2]: 16.698 kJ mole^{-1});

RHC calorimeter 17.18 ± 0.04 kJ mole^{-1} (0.05 M NaOH) (Lit. [2]: 17.189 ± 0.005 kJ mole^{-1})

SOLUBILITY MEASUREMENTS

A dynamic precipitation method was used. A picrate salt was weighed into a boiling tube and 10.00 cm^3 of distilled water added. The mixture was warmed to effect solution and then placed inside a transparent enclosure to exclude draughts. The solution was allowed to cool with constant stirring. A calibrated (N.P.L.) thermometer graduated to 0.05°C was used to note the temperature at which crystals first appeared. The solution was re-heated to restore homogeneity, and the process repeated to obtain concordant results (±0.1°C). From a burette, a measured aliquot of water was then added, and the procedure repeated to obtain a further result. This process of successive dilution, warming and cooling was continued as far as was practical.

A clear danger in this method is that of supercooling, which is irreproducible but common. Hence attention was directed to noting maximum temperature readings at crystallisation points, and to repetition to concordance. The smoothness of solubility, S, vs. temperature, T, plots and the linearity of ln S vs. $1/T$ plots were taken as further evidence of reliability.

RESULTS AND DISCUSSION

The calorimetric enthalpies of solution of these compounds in water are shown in Tables 1 and 2. Table 3 collates these results with those of other authors [3,8], and with values obtained using solubility data, fitted to general equations of the form $\ln S = A - 10^3 B/T$; "van't Hoff" enthalpies of solution are calculated using these plots. Table 4 lists values of the constants A and B for each picrate, as well as correlation coefficients.

There is good agreement between the independent calorimetric determinations for sodium, potassium, ammonium and tetramethylammonium picrates, but concordance between the calorimetric and van't Hoff enthalpies of solution is poor. This indicates the need for care in the interpretation of $\ln S$ vs. $1/T$ data uncorrected for activity and heat capacity effects.

Results of measurements of the aqueous solubility of potassium picrate are listed in Table 5. Values obtained in this work are somewhat higher than the others; this may be due to a systematic error. However, the order of solubilities of these compounds and their variation with temperature, which is difficult to determine by other methods, is presumably sound (see Fig. 1).

Johnson [7] has formulated rules for predicting the solubilities of some series of salts. Briefly, he states that for compounds of the same anion and formula type, as the radius of the cation is increased, the standard free energy of solution rises (i.e. the solubility decreases), reaches a maximum and then falls steadily towards a limiting value. For some salts, however, the series of experimentally observed free

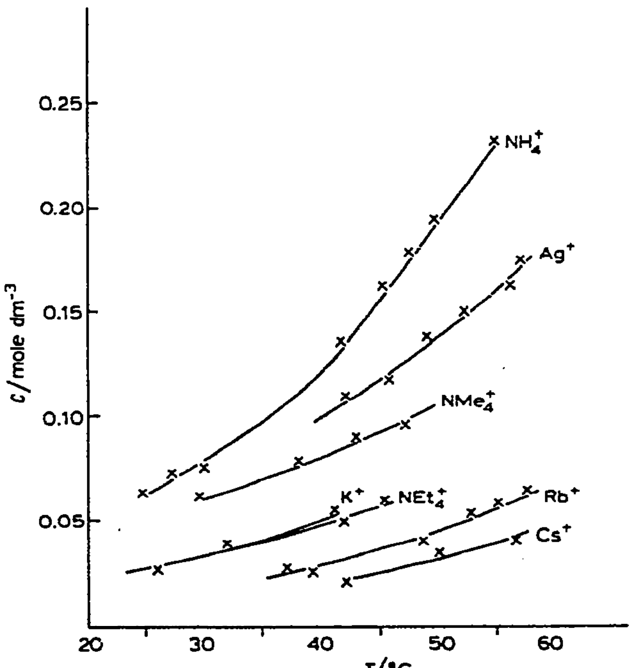

Fig. 1. Aqueous solubilities of picrates.

TABLE 1

Enthalpies of solution of ammonium, rubidium, tetramethylammonium and tetraethylammonium picrate in water at 298.15 K

Mass NH_4Pic (g)	n^*	ΔH_s° (kJ mole^{-1})	Mass RbPic (g)	n^*	ΔH_s° (kJ mole^{-1})	Mass Me_4NPic (g)	n^*	ΔH_s° (kJ mole^{-1})	Mass Et_4NPic (g)	n^*	ΔH_s° (kJ mole^{-1})
0.33957	4027	45.81	0.4751	7333	54.22	0.38062	4411	31.54	0.22145	8990	31.84
0.31901	4287	46.40	0.4691	7427	55.55	0.32448	5175	31.62	0.4342	9170	32.07
0.30780	4443	45.86	0.4658	7480	55.51	0.28571	5877	32.08	0.3415	11660	32.17
0.25396	5384	46.13	0.4389	7938	55.65	0.20253	8291	31.90	0.16561	12021	31.96
0.24986	5473	45.43	0.4239	8219	54.78	0.20030	8383	31.97	0.3054	13039	31.82
0.24152	5662	45.44	0.3857	9033	54.45	0.19626	8555	32.36	0.13842	14383	32.23
0.22225	6153	46.30	0.3591	9702	55.27	0.12948	12968	31.42			
0.21467	6370	46.24	0.3438	10134	54.87						
0.20487	6675	45.20	0.3056	11401	54.81						
0.17983	7604	44.88									
0.15146	9028	46.23									
Mean $\Delta H_s^{\circ} = 45.81 \pm 0.35$ kJ mole^{-1}			Mean $\Delta H_s^{\circ} = 55.01 \pm 0.36$ kJ mole^{-1}			Mean $\Delta H_s^{\circ} = 31.84 \pm 0.32$ kJ mole^{-1}			Mean $\Delta H_s^{\circ} = 32.02 \pm 0.19$ kJ mole^{-1}		

TABLE 2

Enthalpy of solution of silver, potassium and caesium picrate in water at 298.15 K

Mass AgPic (g)	n^*	ΔH_s° (kJ mole^{-1})	Mass KPic (g)	n^*	ΔH_s° (kJ mole^{-1})	Mass CsPic (g)	n^*	ΔH_s° (kJ mole^{-1})
0.8569	4355	36.40	0.5230	5678	50.84	0.6767	5927	54.73
0.7855	4752	36.35	0.5142	5775	52.18	0.5830	6880	56.02
0.7602	4910	36.21	0.5133	5784	50.43	0.5817	6895	56.00
0.6754	5527	36.97	0.5109	5811	52.08	0.5096	7871	55.73
0.6279	5945	37.03	0.5035	5898	50.50	0.4390	9137	56.27
0.6201	6019	36.50	0.4459	6657	50.64	0.4382	9154	56.72
0.5775	6464	37.60	0.4161	7136	51.26	0.4332	9259	57.29
0.4682	7973	36.70	0.4118	7210	52.26	0.3959	10132	55.73
0.4147	9001	36.47	0.3614	8212	50.46	0.3627	11050	55.76
			0.1177	25250	50.77			
Mean $\Delta H_s^\circ = 36.69 \pm 0.35$ kJ mole^{-1}			Mean $\Delta H_s^\circ = 51.14 \pm 0.55$ kJ mole^{-1}			Mean $\Delta H_s^\circ = 56.03 \pm 0.56$ kJ mole^{-1}		

TABLE 3

Enthalpies of solution in water of picrates (M Pic)

M	$\Delta H_s^\ominus$ (kJ mole^{-1}) [a]	$\Delta H_s^\ominus$ (kJ mole^{-1}) [a]	$\Delta H_s^\ominus$ (kJ mole^{-1}) [b]
Li		6.40 ± 0.04 [3]	
Na		20.25 ± 0.17 [3]	
		21.16 ± 0.13 [8]	
K	51.14 ± 0.55	50.92 ± 0.21 [3]	62.65 ± 1.42
Rb	55.01 ± 0.36		73.74 ± 1.18
Cs	56.03 ± 0.55		72.40 ± 1.86
Ag	36.69 ± 0.35		54.32 ± 0.85
NH_4	45.81 ± 0.35	45.46 ± 0.30 [3]	71.88 ± 1.27
NMe_4	31.84 ± 0.31	31.97 [8]	42.75 ± 0.76
NEt_4	32.02 ± 0.18		52.66 ± 1.53

[a] Calorimetric method.
[b] Solubility method.

TABLE 4

Aqueous solubility data for picrates (M Pic)

	M						
	K	Rb	Cs	Ag	NH_4	NMe_4	NEt_4
A [a]	9.027	10.691	10.028	8.126	11.740	5.686	7.076
B [a]	3.768	4.435	4.354	3.267	4.323	2.571	3.167
r^2 [b]	0.996	0.998	0.995	0.995	0.997	0.998	0.995

[a] See text.
[b] Correlation coefficient.

TABLE 5

Solubility of potassium picrate

T(°C)	$10^3 S$ (mole dm^{-3})	Ref.
20	18.9	9
25	24.1	10, 11
25	23.1	12
25	24.2	13
25	23.3	14
25	26.7	This work
30	28.2	15
30	33.2	This work

energies may only cover the increasing or decreasing portion of the curve. One consequence is that, if the size of the cation in a salt of a particular anion and formula type is increased, a fall in the free energy of solution should never be succeeded by a rise.

Johnson's rules seem to hold for the solubilities of the alkali metal picrates. The maximum in the free energy of solution is probably observed at a cationic radius less than that of potassium, and the solubility of the picrates decreases from potassium to rubidium to caesium. This suggests that tetramethylammonium and tetraethylammonium picrates would be less soluble than caesium picrate. It is hence surprising to find that the solubilities of NMe_4Pic and NEt_4Pic are, respectively, greater than and comparable with that of potassium picrate. Tetrabutylammonium picrate is insoluble in water, so the aqueous solubility of these tetraalkylammonium picrates seems to decrease with increasing size of the alkyl group. Johnson's rules have been successfully applied to predicting the solubilities of some tetraalkylammonium salts e.g. iodides and perchlorates, but fail for some simple salts, e.g. alkali metal bromides and nitrates. They are not applicable to salts of cations such as silver, where there is considerable deviation from ionic character.

Calorimetric enthalpies of solution for lithium and sodium picrates were reported in 1934 [4] as 32.05 and 34.89 kJ mole^{-1}, respectively, but Vorob'ev et al. [3] account for the discrepancy with their work by explaining that these values are consistent with those obtained by using the hydrated salts. Lithium and sodium picrates, unlike the others mentioned here, which are anhydrous, crystallise from water as the monohydrate.

From our results, and some unpublished standard enthalpies of formation for these salts, an approximate value for the standard enthalpy of formation of the aqueous picrate ion, $\Delta H_f^{\ominus}Pic^-(aq)$, is calculated as -206 kJ mole^{-1}.

The constitutions of picric acid and potassium picrate solutions have been investigated by Moseley and Spiro [5], who suggested that, due to the anomalous concentration dependence of conductance in picric acid solutions [6], the possibility of the formation of hydrogen-bonded triple ions of type $HPic_2^-$ or picrate-ion dimers Pic_2^{2-} cannot be overlooked. Later experiments involving 0.02 M potassium picrate solution confirmed that dimerisation occurred. At a concentration of ca. 3×10^{-3} M, it has been calculated that a concentration of ca. 3.4×10^{-5} M of picrate-ion dimers, Pic_2^{2-}, should exist in aqueous potassium picrate at 25°C. In the solution calorimetry results reported here, the concentration of potassium picrate in the final solution varied between 4.4×10^{-3} M and 9.8×10^{-3} M.

ACKNOWLEDGMENTS

Financial support from the Procurement Executive, Ministry of Defence (A.E.S.), and helpful discussion from Mr. K. Holloway, Dr. P. Collins and Dr. R. McGuchan, are gratefully acknowledged.

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