Standard Enthalpies of Formation of Rubidium and Ammonium Acetates, and the Barrier opposing Ammonium Ion Rotation

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The correlation between the quantity $1/n\{\Delta_fH^\circ_m[(NH_4)_nX, s] - \Delta_fH^\circ_m[Rb_nX, s]\}$ and the rotational barrier in the ammonium salt has been strengthened by establishing the data point for the acetates. This point lies in a hitherto empty barrier-height region between 25 and 44 kJ mol^{-1}. It was obtained by determining $\Delta_fH^\circ_m(CH_3CO_2Rb, s)$ in a solution calorimeter. The value -722.6 ± 1 kJ mol^{-1} agrees very closely with a previously published prediction.

Two recent papers[1,2] have established a linear relationship between the barrier opposing rotation of the ammonium ion in a compound $(NH_4)_nX$, and the quantity $\Delta(X^{n-}) = 1/n\{\Delta_fH^\circ_m[(NH_4)_nX, s] - \Delta_fH^\circ_m[Rb_nX, s]\}$. Unfortunately, the correlation lacked corroboration for barrier heights in excess of 25 kJ mol^{-1}: only one point occurred in that region, and this was for the fluoride system where the barrier in NH_4F has the very high value of 44 kJ mol^{-1}. The acetate system therefore represents an important test of the correlation because the rotational barrier in the ammonium salt has the intermediate value[3] of 33 kJ mol^{-1}, $\Delta_fH^\circ_m(CH_3CO_2NH_4, s)$ is well established,[4] and $\Delta_fH^\circ_m(CH_3CO_2Rb, s)$ is unknown. This has already been acknowledged by using the correlation to predict a value of -723 ± 10 kJ mol^{-1} for $\Delta_fH^\circ_m(CH_3CO_2Rb, s)$.[2] In this note, we report a calorimetric determination of this quantity.

Results and Discussion

All auxiliary thermodynamic data were taken from ref. 4. The standard enthalpy of formation of rubidium acetate was determined by two different methods. Method 1 relied upon measurements of the enthalpy of solution of rubidium acetate [equation (1)]. Enthalpies of solution were determined to

$$CH_3CO_2Rb(s) \longrightarrow Rb^+(aq) + CH_3CO_2^-(aq) \quad (1)$$

dilutions in the range 800—2 200 H_2O at temperatures of 25 ± 2 °C. Small corrections to infinite dilution of about 0.5 kJ mol^{-1} were made by using data on potassium acetate whose enthalpies of solution lay within <1 kJ mol^{-1} of our determinations for the rubidium salt. Even smaller corrections to 298.15 K of <0.1 kJ mol^{-1} were estimated from the value of ΔC°_p for the dissolution of sodium acetate. The results are given in Table 1.

Method 2 depended upon the determination of ΔH°_m for reaction (2). The heat of solution of an equimolar mixture of

$$CH_3CO_2Na(s) + RbCl(s) \longrightarrow CH_3CO_2Rb(s) + NaCl(s) \quad (2)$$

CH_3CO_2Na and RbCl in 100 g of water was determined; the measurement was then repeated with the same mass of an equimolar mixture of CH_3CO_2Rb and NaCl, the reaction temperatures of the two measurements typically differing by less than 0.2 °C. The value of $\Delta H^\circ_m(2)$ at 298.15 K was then calculated from the difference, assuming that the correction to 25 °C for reaction (2) is negligible. The results are given in Table 2.

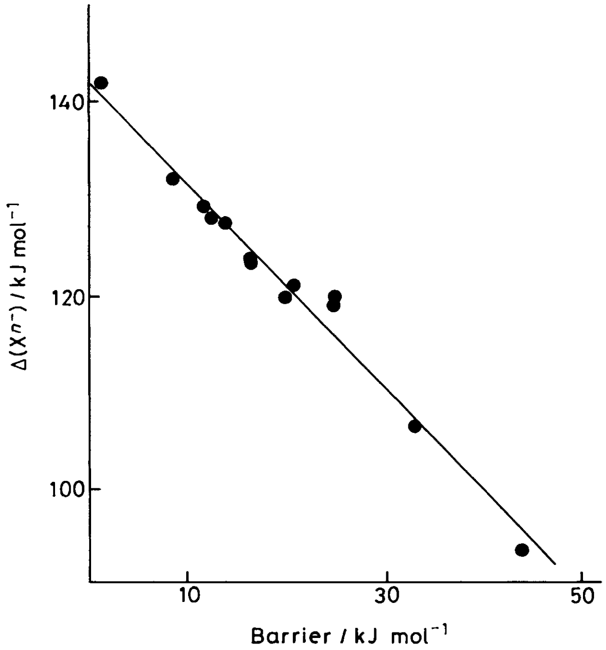

Figure. Correlation between $\Delta(X^{n-})$ and the energy barrier to ammonium ion rotation

The values obtained by the two methods were all weighted equally; the seven results in Tables 1 and 2 lie within 1 kJ mol^{-1}, and the average gives $\Delta_fH^\circ_m(CH_3CO_2Rb, s) = -722.6 \pm 1$ kJ mol^{-1}. This is in excellent agreement with the predicted value of -723 kJ mol^{-1}, and strongly corroborates the correlation. The resulting value of $\Delta(CH_3CO_2^-)$ is 106.5 kJ mol^{-1}, and the linear correlation, revised to include the new data point, is shown in the Figure. It now contains 15 points, the data for the other 14 being given in Table 1 of ref. 2. The slope is -1.072, the intercept at zero barrier height is 142.6 kJ mol^{-1}, and the correlation factor is 0.989.

Experimental

Enthalpies of reaction were determined in a Parr 1451 solution calorimeter. The initial mass of water in the Dewar was 100 g,

Table 1. Determination of $\Delta_f H^\circ_m(CH_3CO_2Rb, s)$ at 298.15 K from the enthalpy of solution [reaction (1)] in 100 g of water

Mass of acetate / g	Dilution / H_2O	T / °C	ΔH / J	$\Delta H_m(1)$ / kJ mol^{-1}	$\Delta H^\circ_m(1)$* / kJ mol^{-1}	$\Delta_f H^\circ_m$ / kJ mol^{-1}
0.9828	816	23.3	−95.12	−13.99	−14.55	−722.6
0.8453	949	23.6	−82.54	−14.11	−14.63	−722.6
0.8245	973	23.6	−80.02	−14.03	−14.53	−722.7
0.3779	2 123	26.8	−37.29	−14.26	−14.50	−722.7

* At 298.15 K; calculated from the figures in the preceding column using the corrections described in the text.

Table 2. Determination of $\Delta_f H^\circ_m(CH_3CO_2Rb, s)$ at 298.15 K from the enthalpies of solution of the mixtures CH_3CO_2Rb–NaCl and CH_3CO_2Na–RbCl in 100 g of water

Substances	Amount/mol	ΔH / J	$\Delta H^\circ_m(2)$ / kJ mol^{-1}	T* / °C	$\Delta_f H^\circ_m$ / kJ mol^{-1}
CH_3CO_2Rb–NaCl	0.005 23	−51.84			
CH_3CO_2Na–RbCl	0.005 23	3.93	10.66	26.7	−722.4
CH_3CO_2Rb–NaCl	0.004 91	−46.52			
CH_3CO_2Na–RbCl	0.004 91	4.53	10.40	24.3	−722.6
CH_3CO_2Rb–NaCl	0.005 46	−52.34			
CH_3CO_2Na–RbCl	0.005 46	4.93	10.49	24.3	−722.5

* Mean of the two reaction temperatures, typically differing by less than 0.2 °C.

and temperatures were measured with a thermistor, in appropriate cases to 0.0005 °C. The calorimeter was calibrated chemically, according to the manufacturer's instructions, using the heat of solution of aminotris(hydroxymethyl)methane in 0.1 mol dm^{-3} HCl. The calibration was checked by determining the enthalpy of solution of sodium acetate to a dilution of 500 H_2O (−16.78; lit.,[4] −16.73 kJ mol^{-1}).

Rubidium acetate (Johnson and Matthey, 99.5%) was oven-dried for 3 h at 110 °C, broken up with a spatula, and returned to the oven for another 5 h. Rubidium was determined gravimetrically as the tetraphenylborate compound (Found: 59.2. Calc.: 59.15%). Other chemicals, also from Johnson and Matthey, were of similar purity, and were similarly dried after being ground in an agate pestle and mortar.

References

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