Some Thermodynamic Parameters for Substituted Ammonium Salts of the Tetramethoxyborate Anion

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Thermodynamic parameters for the formation of piperidinium tetramethoxyborate from piperidine, trimethoxyborane, and methanol are presented. The results show that the formation of the salt is due to a favourable enthalpy change, the standard entropy change being negative. The fact that similar salts with larger tetra-alkoxyborate anions are thermodynamically unstable is discussed. The derived enthalpy of formation of piperidinium tetramethoxyborate ΔH_f° $C_5H_{12}NB(OMe)_4(s) = -1310{\cdot}91 \pm 1{\cdot}72$ kJ mol^{-1}. The derived enthalpy of formation of 2-aminoethylammonium tetramethoxyborate $\Delta H_f^\circ enH\,B(OMe)_4(s) = -1266{\cdot}5 \pm 1{\cdot}5$ kJ mol^{-1} and of ethylenediammonium ditetramethoxyborate $\Delta H_f^\circ enH_2[B(OMe)_4]_2(s) = -2486{\cdot}0 \pm 2{\cdot}0$ kJ mol^{-1}.

TRIALKOXYBORANES, $B(OR)_3$ where R = alkyl, have been shown to form ' onium ' salts with various amines.[1] These salts readily dissociate into starting materials (amine, trialkoxyborane, and the corresponding alcohol) with increase in temperature or in inert solvents, the tetramethoxyborates being the most thermally stable. From qualitative arguments it was deduced that the relative thermodynamic stability of a series of salts with the same anion appeared to be dependent upon the crystal lattice energy contribution to the overall enthalpy change for reaction (1) (see cycle below in which X represents the change in a thermodynamic parameter G, H, or S for each separate reaction). Quantitative thermodynamic studies on piperidinium and 2-aminoethylammonium tetramethoxyborate and ethylenediammonium ditetramethoxyborate are now reported.

RESULTS AND DISCUSSIONS

The enthalpy changes for reaction (1) were calculated by measuring the enthalpies of reaction of the salts with excess of distilled water in an Isoperibol calorimeter (Table 1) and combining these results with the enthalpy of reaction of liquid trimethoxyborane with an excess of water $\Delta H = -18{\cdot}03 \pm 0{\cdot}04$ kJ mol^{-1},[2] the enthalpy of solution of methanol $\Delta H = -7{\cdot}28$ kJ mol^{-1},[3] and the enthapy of solution of the amine.

TABLE 1

Enthalpies of reaction of ' onium ' salts with distilled water at 298·15 K

Compound	Number of measurements	Enthalpy of reaction (kJ mol^{-1})
$C_5H_{12}\overset{+}{N}\ \overset{-}{B}(OMe)_4(s)$	5	$-2{\cdot}72 \pm 0{\cdot}32$
$en\overset{+}{H}\ \overset{-}{B}(OMe)_4(s)$	4	$+11{\cdot}75 \pm 0{\cdot}07$
$en\overset{2+}{H_2}[B(OMe)_4]_2^-(s)$	4	$+32{\cdot}30 \pm 0{\cdot}52$

en = ethylenediamine

The Piperidinium Tetramethoxyborate System.—The enthalpy change for reaction (1) for this system $\Delta H_1 = -48{\cdot}78 \pm 0{\cdot}50$ kJ mol^{-1} using the value for the enthalpy of solution of piperidine $\Delta H = -26{\cdot}19$ kJ mol^{-1}.[4] The following values for ΔH_f° $B(OMe)_3(l) = -935{\cdot}12 \pm 1{\cdot}25$ kJ mol^{-1},[5] ΔH_f° $MeOH(l) = -238{\cdot}52 \pm 0{\cdot}21$ kJ mol^{-1},[6] ΔH_f° $C_5H_{11}N(l) = -88{\cdot}49 \pm 1{\cdot}05$ kJ mol^{-1},[6] give the standard enthalpy of formation of the crystalline salt ΔH_f° $C_5H_{12}N\,B(OMe)_4(s) = -1310{\cdot}91 \pm 1{\cdot}72$ kJ mol^{-1}. The value for $\Delta H_5 = -160{\cdot}22 \pm 2{\cdot}16$ kJ mol^{-1} is obtained from $\Delta H_5 = \Delta H_1 - (\Delta H_2 + \Delta H_3 + \Delta H_4)$ where $\Delta H_2 = 34{\cdot}72 \pm 2{\cdot}09$ kJ mol^{-1},[5] $\Delta H_4 = 37{\cdot}43 \pm 0{\cdot}02$ kJ mol^{-1},[7] and the enthalpy of vaporisation of piperidine $\Delta H_3 = 39{\cdot}29 \pm 0{\cdot}21$ kJ mol^{-1}.[6]

$$\begin{tikzcd}
B(OMe)_3(g) & + \text{Base}(g) & + MeOH(g) \arrow[dr, "\Delta X_5"] & \\
 & & & \text{Base}\ \overset{+}{H}\ \overset{-}{B}(OMe)_4(s) \\
B(OMe)_3(l) \arrow[uu, "\Delta X_2"] & + \text{Base}(l) \arrow[uu, "\Delta X_3"] & + MeOH(l) \arrow[uu, "\Delta X_4"] \arrow[ur, "\Delta X_1"'] &
\end{tikzcd}$$

To make further progress the three liquid reactants are assumed to behave ideally (*vide infra*). The equilibrium constant for reaction (5) is then given by $K_p = (27/P^3)$ atm^{-3} where P is the total vapour pressure of the system in atmospheres. Vapour pressure measurements on the salt over the temperature range 282—315 K gave the equation $\log P$ (mmHg) $= 12{\cdot}589 - (3386/T)$. The vapour pressure at 298·15 K is $2{\cdot}24 \times 10^{-2}$ atm giving a value for $K_p = 2{\cdot}41 \times 10^6$ atm^{-3}. The standard free energy change for reaction (5) is therefore $\Delta G_5^\circ = -36{\cdot}50$ kJ mol^{-1}. The standard entropy change for this reaction is $\Delta S_5^\circ = -415{\cdot}0$ J mol^{-1} K^{-1}. The free energy changes accompanying the vaporisation of the reactants at 298·15 K are $\Delta G_2^\circ = 4{\cdot}23$ kJ mol^{-1},[8] $\Delta G_3^\circ = 7{\cdot}99$ kJ mol^{-1},[4] and $\Delta G_4^\circ = 4{\cdot}35$ kJ mol^{-1},[3] giving a value for $\Delta G_1^\circ = -19{\cdot}93$ kJ mol^{-1} and $\Delta S_1^\circ = -96{\cdot}8$ J mol^{-1} K^{-1}.

Bearing in mind the original assumption of the ideality of the system these results show that for this system the spontaneous reaction at 298·15 K is due to the enthalpy change. The unfavourable entropy change is of little consequence at this temperature. However for other systems any dramatic decrease in

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[2] T. Charnley, H. A. Skinner, and N. B. Smith, *J. Chem. Soc.*, 1952, 2288.

[3] National Bureau of Standards, Technical Note 270—3, Washington, D.C., 1968.

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[5] A. Finch and P. J. Gardner, *Progr. Boron Chem.*, 1970, **3**, 177.

[6] J. D. Cox and G. Pilcher, ' Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London, 1970.

[7] J. Polak and G. C. Benson, *J. Chem. Thermodynamics*, 1971, **3**, 235.

[8] S. H. Webster and L. M. Dennis, *J. Amer. Chem. Soc.*, 1933, **55**, 3233.

ΔH_1 will result in the entropy term becoming the factor which controls the thermodynamic stabilities of the salts. It is believed that the failure of other systems, particularly those with large tetra-alkoxyborate anions, to produce crystalline products at room temperature is due primarily to a fall in the crystal lattice energy contribution to the overall enthalpy change for reaction (1).[1]

An indication that the piperidinium tetramethoxyborate system does not behave ideally is obtained when ΔH_5 is calculated from the vapour pressure data. The value of $-194{\cdot}9$ kJ mol^{-1} is somewhat higher than that obtained from measured enthalpy data. This indicates a positive deviation from Raoult's Law by the reactants. The fact that two of them (trimethoxyborane and methanol) form an equimolar low boiling point azeotrope is also consistent with a positive deviation.

The 2-Aminoethylammonium Tetramethoxyborate System.—The enthalpy change for reaction (1) for this system $\Delta H_1 = -68{\cdot}5 \pm 0{\cdot}5$ kJ mol^{-1} is obtained by using the value for the heat of solution of ethylenediamine in water $\Delta H = -31{\cdot}4$ kJ mol^{-1}.[3] Using the value ΔH_f° $C_2H_8N_2$(l) $= -24{\cdot}4$ kJ mol^{-1},[3] gives a value for ΔH_f° enH $B(OMe)_4$(s) $= -1266{\cdot}5 \pm 1{\cdot}5$ kJ mol^{-1}.

The Ethylenediammonium Ditetramethoxyborate System.—For this system $\Delta H_1 = -114{\cdot}3 \pm 0{\cdot}5$ kJ mol^{-1} refers to the reaction:

$$\text{en(l)} + 2\text{B(OMe)}_3\text{(l)} + 2\text{MeOH(l)} \longrightarrow \text{enH}_2[\text{B(OMe)}_4]_2\text{(s)}$$

The standard enthalpy of formation of ethylenediammonium ditetramethoxyborate ΔH_f° $enH_2[B(OMe)_4]_2$(s) $= -2486{\cdot}0 \pm 2{\cdot}0$ kJ mol^{-1}.

The enthalpy change for the disproportionation reaction:

$$\text{enH. B(OMe)}_4\text{(s)} \longrightarrow \tfrac{1}{2}\text{enH}_2[\text{B(OMe)}_4]_2\text{(s)} + \tfrac{1}{2}\text{en(l)}$$

is $\Delta H = 11{\cdot}3$ kJ mol^{-1}. Since this reaction proceeds readily at 348 but not at 298 K[1] the standard entropy change must be approximately $+38$ J mol^{-1} K^{-1}.

EXPERIMENTAL

The compounds were prepared, purified, and handled as previously described.[1] The calorimeter has been described elsewhere.[9,10]

Vapour Pressure Measurements.—The apparatus has been described.[10] Four different samples of piperidinium tetramethoxyborate were used giving 28 measurements. These were subjected to a least squares computer analysis.[10]

Errors.—Uncertainty intervals for the calorimetric measurements in this work are twice the standard deviation of the mean. The errors in subsidiary data are those given in the source reference. The uncertainties in data from refs. 3 and 4 are not yet available. The errors in derived enthalpies using these data therefore contain an arbitrary estimate of the unknown errors.

It should be noted that, even though the thermochemical measurements on the 2-aminoethylammonium tetramethoxyborate compound were reproducible, this compound could not be satisfactorily purified.[1]

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