A Correlation of the Energy Barrier opposing Cation Reorientation in Ammonium Compounds with Thermochemical Data

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There is a good linear correlation between the energy barrier opposing cation reorientation in a compound $(NH_4)_nX$, and the quantity $\Delta(X^{n-}) = \{\Delta H_f^\circ[(NH_4)_nX,s] - \Delta H_f^\circ(Rb_nX,s)\}/n$, and at zero barrier height, $\Delta(X^{n-})$ is about 143 kJ mol^{-1}; depressions below this threshold provide some measure of cation–anion hydrogen bonding in $(NH_4)_nX$, and the estimated value of $\Delta H_f^\circ(NH_4^+,g)$, derived from the threshold, is 638 kJ mol^{-1}.

It was recently shown, for a number of ammonium compounds, that the quantity $\Delta(X^{n-})$ [equation (1)] was constant to within ± 10 kJ mol^{-1}, except for $X^{n-} = F^-$, when strong hydrogen-bonding occurs in NH_4F.[1] A nearly constant value of $\Delta(X^{n-})$ is consistent with a simple ionic model[2] because the nearly identical ionic radii of NH_4^+ and Rb^+ allow one to neglect variations in the difference between the lattice energies of $(NH_4)_nX/n$ and Rb_nX/n.

$$\Delta(X^{n-}) = \{\Delta H_f^\circ[(NH_4)_nX,s] - \Delta H_f^\circ(Rb_nX,s)\}/n \quad (1)$$

Examination of a wider range of thermochemical data[3] suggests that there is a pattern to the deviations from constancy; when $\Delta(X^{n-})$ is plotted against the energy barrier to cation reorientation in the ammonium compound, a good linear correlation is obtained. Table 1 contains data for those instances where both barrier data and reliable $\Delta(X^{n-})$ values exist. In the case of the energy barriers, no distinction has been made between activation energies derived by magnetic resonance, and estimated depths of potential wells obtained from spectroscopic and neutron scattering data. A correction for the distinction is not straightforward,[4] and if it is neglected, the agreement between the two kinds of quantity is generally good.[5]

The correlation is shown in Figure 1. Linear regression gives a slope of -1.063, and a correlation factor, r, of 0.987. The extrapolation to zero barrier height gives $\Delta(X^{n-}) = 143$ kJ mol^{-1} which should be an upper threshold. This threshold corresponds to free rotation of the ammonium ion, and therefore to the 'spherical cation' situation assumed by the simple ionic model. Now, $\Delta(X^{n-})$ is also given by equation (2), where $\Delta H_L^\circ(M_nX,s)$, the lattice enthalpy, is the value of ΔH_m° at 298.15 K for the process in equation (3). Assuming, on the basis of the simple ionic model, that the lattice enthalpies for ammonium and rubidium analogues are identical, then $\Delta H_f^\circ(NH_4^+,g) = 633$ kJ mol^{-1}.

$$\Delta(X^{n-}) = [\Delta H_f^\circ(NH_4^+,g) - \Delta H_f^\circ(Rb^+,g)] - \{\Delta H_L^\circ[(NH_4)_nX,s] - \Delta H_L^\circ(Rb_nX,s)\}/n \quad (2)$$

$$M_nX(s) = nM^+(g) + X^{n-}(g) \quad (3)$$
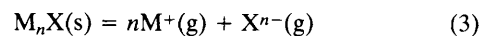
Alternatively, data on NH_4I and RbI[6,7] suggest that in six-co-ordination, the ionic radii of NH_4^+ and Rb^+ are 143 and 147 pm respectively. As the perchlorate point in Figure 1 is very close to the threshold, we may instead use the two-term Kapustinskii equation[2] to make a small correction for the

Table 1. Values of $\Delta(X^{n-})$ and the energy barriers to reorientation of the ammonium ion.

Anion	$\Delta(X^{n-})$[a]/ kJ mol^{-1}	Energy barrier[b]/ kJ mol^{-1}	$[\Delta(T) - \Delta(X^{n-})]$[j]/ kJ mol^{-1}
F$^-$	93.7	44	49
N$_3^-$	119.3	25	23
HF$_2^-$	119.7	25[h]	23
SeO$_4^{2-}$	119.8	20	23
Cl$^-$	120.9	21	22
CrO$_4^{2-}$	123.4	17	19
Br$^-$	123.8	17	19
SO$_4^{2-}$	127.4	14	15
I$^-$(1)[c]	128[f]	13	15
I$^-$(2)[d]	129[f]	12	14
NO$_3^-$	129.5	12	12
ReO$_4^-$	132[g]	9[i]	11
HSO$_4^-$	132.0	9	11
I$^-$(3)[e]	132.4	4	10
ClO$_4^-$	141.9	2	1

[a] All data from ref. 3 unless otherwise stated. [b] Ref. 5 unless otherwise stated. [c] Tetragonal low temperature structure. [d] CsCl low temperature structure. [e] NaCl structure. [f] Data for the NaCl structure of NH$_4$I was corrected by the enthalpies of transition recommended in ref. 5. [g] Calculated using the value of $S^{\ominus}$(NH$_4$ReO$_4$,s) obtained by R. D. Weir and L. A. K. Staveley, *J. Chem. Phys.*, 1980, **73**, 1386. [h] E. C. Reynhardt, A. Watton, and H. E. Petch, *J. Chem. Phys.*, 1979, **71**, 4421. [i] See also I. Svare, A. M. Raaen, and K. Otnes, *Phys. Scripta*, 1980, **22**, 519. [j] $\Delta(T) = 143$ kJ mol^{-1}; see text.

Figure 1. Correlation between $\Delta(X^{n-})$ and energy barrier for ammonium compounds.

lattice enthalpy difference at an anion thermochemical radius of 236 pm.[8] This gives $\Delta H_f^{\ominus}$(NH$_4^+$,g) $= 638$ kJ mol^{-1} which falls comfortably within the range 624—643 kJ mol^{-1} spanned by recent figures obtained by mass spectrometry,[9,10] and is identical with the photoionization value.[11]

Column 4 of Table 1 gives values of $[\Delta(T) - \Delta(X^{n-})]$ where $\Delta(T)$ is the threshold value of 143 kJ mol^{-1}. These represent estimates of the stabilization of the ammonium salt with respect to a hypothetical 'spherical-cation' state of the same compound. As the lowered cation symmetry in the real compound is associated with the distribution of hydrogen atoms, there is a sense in which $[\Delta(T) - \Delta(X^{n-})]$ is a measure of hydrogen bond energy in the ammonium salt. However, many ammonium and rubidium analogues are not isostructural, especially in cases where $[\Delta(T) - \Delta(X^{n-})]$ is substantial. This suggests that $[\Delta(T) - \Delta(X^{n-})]$ often incorporates differences in Madelung and other energies for the hydrogen-bonded and hypothetical non-hydrogen-bonded crystal structures of the ammonium salt. Such terms are not usually included in the concept of a bond energy although, following Kapustinskii,[2] we expect them to be small.

If $[\Delta(T) - \Delta(X^{n-})]$ is a legitimate index of hydrogen bond energy, then the correlation of Figure 1 should be high quality only when reorientation of the ammonium ion disrupts all the cation–anion hydrogen bonding. This is most likely when reorientation mainly takes place by rotation about a C_2 axis which seems generally to be the case in high barrier salts[4] and in the CsCl-related structures of the ammonium halides.[5] Thus, in Table 1, the low-temperature CsCl-type forms of NH$_4$I satisfy the correlation, but the room temperature rock salt structure NH$_4$I(3), which is not included in Figure 1, does not. In NH$_4$I(3), an important component of the cation motion seems to be a large-amplitude libration about a single
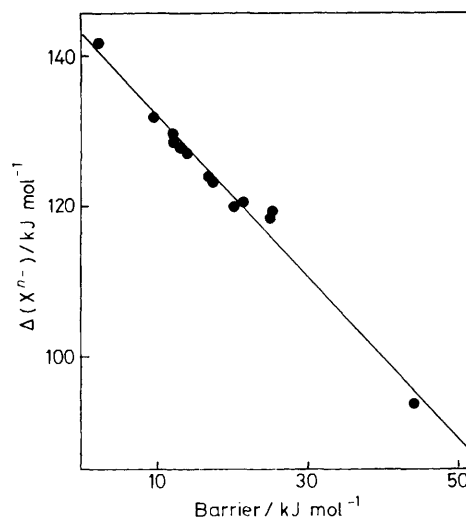
N–H$\cdots$I axis.[12,13] We can therefore argue that some hydrogen-bonding is preserved throughout the libration, and that the energy barrier in NH$_4$I(3) is lower than the correlation would suggest. Further and more accurate thermodynamic data on low-barrier salts, where rotation about C_2 axes is less dominant, may reveal more departures of this kind. It is noticeable that an attempt at a linear correlation of energy barriers with ν_1 (NH$_3$D$^+$) stretching frequencies breaks down when the barrier falls below about 10 kJ mol^{-1}.[14]

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