SHORT COMMUNICATION _____

Is the Volume-Based Thermodynamics (VBT) Approach Valid for the Estimation of the Lattice Enthalpy of Salts Containing the 5,5'-(Tetrazolate-1N-oxide) Dianion?

Leslie Glasser,*[a] H Donald B. Jenkins *[b] and Thomas M. Klapötke*[c,d]

In previous publications we have used volume-based thermodynamics (VBT) to estimate the lattice energies and enthalpies of new high-energy ionic materials. The use of the VBT approach for non-spherical ions such as the 5,5'-(tetrazolate-1N-oxide) dianion in TKX-50 [bishydroxylammonium 5,5'-(tetrazolate-1N-oxide)] has received some criticism. Here we show that the VBT approach is suitable for the estimation of lattice energies/enthalpies for such ions.

Introduction

TKX-50 [bis(hydroxylammonium) 5,5'-bis(tetrazolate-1N-oxide)] (Fig. 1) is one of the most promising ionic salts as a possible replacement for RDX.[1-3] Its superior calculated performance parameters, however, depend on the validity of the calculated enthalpy of formation of this compound, which itself depends on the estimated lattice energy and enthalpy values. We and others have used volume-based thermodynamics (VBT) [4-7] to obtain an estimate for the lattice energy and enthalpy using the experimentally (X-ray) determined volume (V_M) for a M_2X-type TKX-50 molecule, i.e., $[H_3NOH]^+_2[C_2N_8O_2]^{2-}$ (eq. 1, Table 1).

$$U_{POT}[kJ / mol] = | z_+ || z_- | v \left[\frac{\alpha}{V_m^{1/3}} + \beta \right] \qquad (1)$$

with V_m = molecular volume in nm³ (1 Å³ = 10^{-3} nm³)

Table 1: The values for the α and β constants for MX, MX₂ and M₂X salts.[4]

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* Prof. Dr. T. M. Klapötke
  Fax: +49-89-2180-77492
  E-Mail: tmk@cup.uni-muenchen.de
[a] Department of Chemistry,
  Nanochemistry Research Institute,
  Curtin University,
  GPO box U 1987,
  Perth, WA 6845,
  Australia
[b] Department of Chemistry,
  University of Warwick,
  Coventry CV4 7AL
  West Midlands, U.K.
[c] Department of Chemistry
  Energetic Materials Research
  Ludwig-Maximilian University of Munich
  Butenandtstrasse 5-13
  81377 Munich, Germany

[d] Department of Mechanical Engineering,
  Center for Energetic Concepts Development CED),
  University of Maryland (UMD),
  College Park, MD 20742
  USA

	α [kJ mol^{-1} nm]	β [kJ mol^{-1}]
M$^+$X$^-$	117.3	51.9
M^{2+}X$_2^-$	133.5	60.9
M$_2^+$X^{2-}	165.3	-29.8

Once the lattice energy has been estimated according to eq. 1, this value can easily be converted into the lattice enthalpy using eq. 2[8] for a material of formula M_pX_q

$$\Delta H_L = U_L + \left[p\left(\frac{c_{M^+}}{2} - 2\right) + q\left(\frac{c_{X^-}}{2} - 2\right) \right]RT \quad (2)$$

where $c_i = 3$ for monatomic ions, 5 for linear polyatomic, and 6 for polyatomic ions.

Using eq. 1 and 2 and the experimental molecular volume of 0.204 nm^3 and $Z=2$, we obtain a lattice energy of -1506 kJ mol^{-1}.
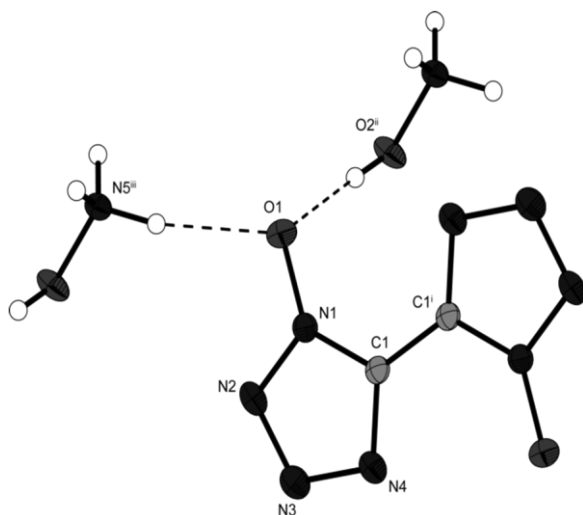

Figure 1: Molecular structure of **TKX-50** in the crystal (monoclinic, $P2_1/c$).[1]

Results and Discussion

Critics of the use of VBT for problems such as estimating the lattice energy of compounds like TKX-50 often have two principal reservations:

(i)   they doubt that the point charge model (as applied in VBT) is valid

and

(ii)   they argue that VBT is not valid for complex, non-spherical anions in which the charges may not be spread equally over the entire anion.

If these two points were true, reservations (i) and (ii) would affect the calculation of the lattice energy of TKX-50 in particular, since the 5,5'-(tetrazolate-1N-oxide) dianion, $[C_2N_8O_2]^{2-}$, is planar, rather than spherical, and presumably contains a significant amount of negative charge localized at the two oxygen atoms.

(i): An important theorem of electrostatics, the Gauss theorem, [9, 10] states that the electric field outside a sphere of uniform surface charge (q) is identical to that produced by an equivalent point charge (q) placed at its centre. On this basis, we claim that if we treat our complex ions as single point charges, then the result cannot be too greatly in error. Indeed, we have already shown [10] that this procedure is successful for a large number of ions, including the planar nitrate ion and complex ionic systems such as ammonium sulfate.

(ii): If the counterions are sufficiently separated, then the charges on the complex ions will each be effectively at the same distance, and the multipole interaction terms will be negligible. At such distances (involved in the calculation of lattice energies), the shapes of the ions are irrelevant. The question is, how far apart should the counterions be, in order for this to be a good approximation?

According to the Oxford Dictionary of Chemistry [11]: "Multipole interactions are an important feature of intermolecular forces. … The interaction potential energy between multipoles falls off with distance increasingly rapidly as the order of the multipoles increases. If a 2^m-pole interacts with a 2^n-pole, the interaction potential energy, V, varies with distance r as $V = c/(r^{m+n-1})$, where c is a constant. The rapid fall-off with distance, as the order increases, is due to the set of charges appearing to tend towards neutrality (as seen from outside)."

Thus, the approach has to be rather close to cause large effects! This is further mitigated by the common practice of using the Ewald accelerated summation procedure [12] in evaluating the electrostatic lattice energy (via the Madelung constant) whereby the short-range charge-charge interaction is evaluated in real space, but its long-range contributions are summed in reciprocal space. Typically, the real space charge-charge interaction contributes only about 10% to the total electrostatic energy, thereby reducing any contribution to the overall error.

We have undertaken electrostatic calculations for the current molecular system. Since the anion is centrosymmetric, we placed a charge of -2 at the centre of the C1-C1' bond (at 0 0 0). With charges of +1 placed at the atomic centres of the cations, on N5, the electrostatic energy, E_m', is -1594 kJ mol^{-1}. This is converted to a lattice energy by the relation: [10] $U_{POT} = 0.963\,E_m'$, yielding the value -1535 kJ mol^{-1}, which is less than 2% different from the VBT result.

Using the lattice energy of -1506 kJ mol^{-1} obtained by eq. (2) and calculating the gas phase enthalpies of formation of the corresponding cation and anion (CBS-4M method, as explicitly described in ref. [1,13]) we have calculated an enthalpy of formation for TKX-50 of $\Delta H°_f$/TKX-50) = +447 kJ mol^{-1}. Using bomb combustion calorimetry, the experimental value for $\Delta H°_f$/TKX-50) was determined to be +439 kJ mol^{-1}.

We believe that the point is made - that it is a reasonable approximation to place charges at the ion centres - and this also tends to confirm our VBT values (which are not subject to any assumptions regarding charge distributions since they are calibrated against independent published values).

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There will, of course, be instances in which the VBT approximation will not provide quite as satisfactory results as those presented here for our TKX-50 system. Indeed, as our colleague Ingo Krossing has found, when dipole-dipole, U_{dd} and dipole-quadrupole, U_{qd}, dispersion energies are considerable in magnitude then lattice energies may be evaluated between 20 and 140 kJ mol^{-1} too low. [14] In a good many of our studies, however, it is comparative, rather than absolute, energies which are needed, and in these cases such peripheral dispersion energy effects often largely cancel out. The degree of covalency can perturb the ionic model adopted too. However, as mentioned in a recent text on the subject,[13] and recognised by its reviewer,[15] on balance experience has shown us that "theoretical calculations" - which have often involved VBT - "correlate well with actual experiments" with regard to high energy materials.

Conclusions

While recognising that VBT can never be suitable in all cases, we have shown that VBT is a suitable method for the estimation of lattice energies - even for complex, non-spherical anions in which the charges may not be spread uniformly over the entire anion.

Acknowledgement

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