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Mendeleev Commun., 2016, **26**, 134–135

Mendeleev Communications

Calculated enthalpies of formation of 5,5′-bitetrazole salts

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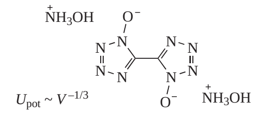
DOI: 10.1016/j.mencom.2016.03.017

The enthalpies of formation were calculated for a number of bitetrazole salts using classical quantum chemistry methods and an improved method of isodesmic reactions, and the latter was found most accurate in the assessment of this characteristic.



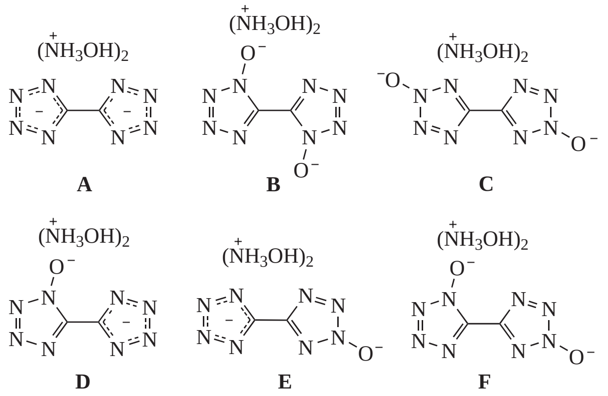
TKX-50

Energy materials (EMs) are widely used in both military and civilian applications. Nevertheless, many of these compounds were not implemented because they had a number of limitations in their use.

The key requirements imposed on EMs include[1] tailored performances, high energy and density, insensitivity, stability, vulnerability and environmental safety. Bitetrazole salts, in many respects, meet these requirements.

However, one of the basic characteristics, the enthalpy of formation, has a large scatter in the calculation values for bitetrazole salts, and the aim of this study was to clarify these values based on improved calculation methods.

The structures of the test compounds are shown in Scheme 1.

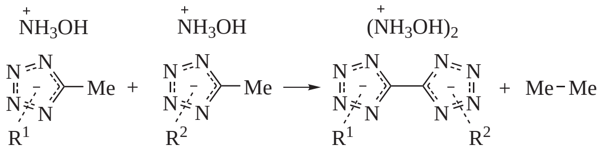


Scheme 1 Structures of the test bitetrazole salts (BTS).

We used two methods for calculating the enthalpy of formation (ΔH_f^0) of BTS in a gas phase based on (I) the direct calculations of ΔH_f^0 for a BT dianion and two hydroxylammonium cations and (II) the application of the formation enthalpies of small molecules in a hypothetical isodesmic reaction (Scheme 2). In both cases, the atomization energy[2] was applied and (CBS-4M)-calculations were used:

$$\Delta H_f^0(\text{gas, calc.}) = H^0(\text{molecule}) - \sum H^0(\text{atoms}) + \sum \Delta H_f{}^0(\text{atoms}),$$

where H^0(molecule) is the calculated enthalpy of molecule formation, H^0(atoms) is the enthalpy of calculated values of atoms, ΔH_f^0(atoms) is the experimental enthalpy of formation for atoms in a gas phase.



Scheme 2 Hypothetical isodesmic reaction for BTS.

For estimating the enthalpies of formation in a solid phase, we had to estimate the energy of a crystal lattice with the use of the Glasser–Jenkins method.[3]

It is well known that the lattice energy is a linear function of the inverse cube root of the molecular volume of a salt (*i.e.*, the sum of anionic and cationic volumes). The dependence of the lattice energy U_{POT} on the M_qX_p salt molecular volume (V_{mol}) can be expressed by the equation:

$$U_{POT}\ (\text{kJ mol}^{-1}) = 2I[\alpha(V_{mol})^{-1/3} + \beta],$$

where α and β are q- and p-dependent coefficients and I is the ionic strength ($I = {}^1/_2\sum n_i z_i^2$, where n_i is the number of ith ions with the charge z_i).

The transition from the lattice energy to the lattice enthalpy is determined by the equation:

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$$

$$\text{or}\quad \Delta H_L = U_{POT} + \Delta nRT,$$

where the coefficients n_M and n_X depend on the nature of ions and are equal to 3 for the monoatomic ion, to 5 for the linear polyatomic ion and 6 for the nonlinear polyatomic ion; R is the universal gas constant; T is the absolute temperature (K), Δn is the change of moles of gaseous components.

In our case, $q = 2$ and $p = 1$. The coefficients α and β are 165.3 kJ nm mol^{-1} and –29.8 kJ mol^{-1}, respectively.[4] Note that the coefficients can vary depending on the nature of the compounds.[5]

The ions were optimized by the Hartree–Fock method with the 3-21G basis for molecular volumes because this method/basis

Table 1 Molecular volumes of bitetrazole salts.

Salts	V_{mol}(SOI)/nm^3	V_{mol}(ISO)/nm^3	V_{mol}(X-ray)/nm^3
A	0.216	0.162	0.198
B (TKX-50)	0.199	0.196	0.204
C	0.230	0.218	0.215
D	0.223	0.179	0.205
E	0.205	0.190	0.209
F	0.238	0.207	0.224

gives good agreement with the X-ray data.[6] The molecular volumes of ions were determined by the Monte Carlo method (the Gaussian software package[7]) as the internal volume limited by the isosurface with an electron density of 0.001 e bohr^{-3}. Various models of molecular volumes were designated as the sum of ions (SOI) and isodesmic reaction (ISO). In the case of SOI, the molecular volume of BTS was calculated as additive (cations + anions). In the case of ISO, molecular volumes for two methyl-substituted tetrazoles were calculated as additive using the molecular volume of ethane. The calculated and experimental molecular volumes (from X-ray data) are given in Table 1.

Undoubtedly, the molecular volumes calculated by the Monte Carlo method depend on the selected methods and bases; therefore, experimental values should be used to assess the quality of calculations. As shown in Table 1, the calculated values of V_{mol} (SOI) are close to the experimental data, and they indicate the correctness and effectiveness of the selected methods and bases that we used for the calculations of the enthalpy of formation.

Table 2 shows the enthalpies of formation of BTS calculated using the two above methods.

As follows from the results for the gas phase, method II gives lower values of ΔH_f^0 in comparison with those in method I. These data reveal significant differences in the calculations in the case of classical quantum chemistry methods used for compounds with high molecular weights.

The main criterion for evaluating the effectiveness of the calculation methods is to compare the experimental and calculated enthalpies of formation. Unfortunately, information on ΔH_f^0 for BTS in the literature is limited, and these data are contradictory. Thus, the calculated enthalpy of formation for dihydroxylammonium-5,5′-bitetrazole-1,1′-diolate (TKX-50, salt **B**) was 446.6 kJ mol^{-1} in a solid phase.[8] The experimental values reported for this compound are 111±16,[9] 193±3[10] and 439 kJ mol^{-1}.[11] The latter experimental value is most consistent with the result of our calculations based on the improved isodesmic reactions method (II). In addition, the calculations should be based on the use of SOI molecular volumes.

Table 2 Enthalpy of formation of bitetrazole salts in gas and solid phases (I – using the sum of ions, II – using the isodesmic reactions).

Salts	ΔH_f^0(I)/kJ mol^{-1}		ΔH_f^0(II)/kJ mol^{-1}		
	Gas	Solid/SOI	Gas	Solid/SOI	Solid/ISO
A	1975.50	497.59	1710.66	232.76	64.26
B (TKX-50)	1945.57	420.19	1696.47	171.09	164.09
C	1878.99	435.03	1655.71	211.74	180.89
D	1971.27	510.52	1703.56	242.81	117.85
E	1924.99	418.11	1683.18	176.31	131.03
F	1923.56	496.75	1676.09	249.28	173.48

We are grateful to Professor T. M. Klapötke and M.Sc. P. C. Schmidt (LMU, Munich, Germany) for fruitful discussions and the provision of supplementary materials.

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Received: 7th July 2015; Com. 15/4673