Quantum chemical modeling of the thermochemical characteristics and acidity of polynitroazole salts

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ABSTRACT

The thermochemical characteristics and acidity of polynitroazole ammonium salts were investigated. The Glasser–Jenkins method was modified with a view to estimate enthalpies of formation, which significantly improved the accuracy of calculations. A new modeling procedure for combustion enthalpies of polynitroazole salts with a computational error below 3% was developed. The acidity of a few polynitroazoles in water was computed and a lack of correlation between their acidity and the enthalpy of salt formation was revealed.

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1. Introduction

The thermochemical characteristics and primarily the enthalpy of formation (ΔH_f°) of high energy materials (HEMs) largely determine their performance. However it is often challenging to measure ΔH_f° experimentally because of quantities of HEMs needed for thermochemistry tests and in parallel with their instability and explosiveness. Methods of computer simulation of the HEM structure and properties, including quantum chemical approaches, let avoid these limitations and predict the thermochemical characteristics of such substances.

This paper discusses estimation of enthalpies of formation for five polynitroazoles (pyrazoles and imidazoles) and their salts by methods of quantum chemistry (DFT, CBS). Furthermore, since salt formation reactions directly depend on the proton elimination we considered it necessary to evaluate dissociation processes of azoles as NH acids, which are associated with the acidity.

Polynitroazoles and, in particular, pyrazoles and imidazoles have recently aroused much interest due to the high energy content and at the same time acceptable thermal stability and, as a rule, low impact sensitivity. The examined compounds can show promise as ingredients of explosive formulations and solid rocket propellants [1].

2. Computational method for evaluating enthalpy of salt formation

Whereas calculations of enthalpies of substance formation in the gas phase present no particular difficulty, the evaluation of the enthalpy of salt formation in the solid phase is rather challenging as it requires computing of the crystal lattice energy U_{POT}. One of the main approaches to the evaluation of U_{POT} is the method [2] that allows, knowing the structural formula of the compound and its charge distribution, estimation of the electrostatic term (Madelung term) in the expression of the crystal lattice potential energy and further on the calculation of the energy per se.

Also, alternative methods for estimating U_{POT} based on the evaluation of the mutual arrangement of ions in a crystal (Kapustinskii equations [3]) or of the molecular volume of ions (Glasser–Jenkins equations [4]) have been well recognized.

In this work we used the Glasser–Jenkins method, briefly described below, to calculate enthalpies of formation of salts (ΔH_f° (salt)).

Let the salt structure have the form M_qX_p, where M is the cation, X is the anion, and p and q are ionic charges of M and X, respectively. For example, for NaCl M = Na, X = Cl, $p = 1$, $q = 1$; and for

Na_2SO_4, M = Na, X = SO_4, $p = 2$, $q = 1$, etc. The Born–Haber cycle formed the basis of our approach [1] (Fig. 1).

In accordance with this cycle, the enthalpy of salt formation was established by the equation:

$$\Delta H_f^\circ(\text{salt, calc.}) = \Delta H_f^\circ(\text{cation}) + \Delta H_f^\circ(\text{anion}) - \Delta H_L, \qquad (1)$$

where ΔH_L is the enthalpy of the crystal lattice that is equal to the enthalpy of crystal sublimation taken with the opposite sign. Enthalpies of formation for the cation and anion were computed from the atomization energy values obtained by quantum chemical methods.

To estimate the enthalpy of sublimation of salts (ΔH_L) we used the following procedure: it is known [4] that the magnitude of 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). For MX salts (1:1), Bartlett's relationship is widely applicable to calculate enthalpies of formation [5–12]. The dependence of the lattice energy U_{POT} of the M_qX_p salt from the molecular volume (V_m) can be expressed by the equation:

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

where α and β are q-and-p-dependent coefficients (Table 1) and I is the ionic strength ($I = \frac{1}{2}\sum n_i z$ where n_i is the number of i type ions with charge z_i).

It should be noted that the coefficients α and β [4] were picked basing on the experimental selection from a large set of organic and inorganic compounds in such a way as to attain the best agreement between the calculated characteristics and their experimental values.

The relation between the energy (U_{POT}) and the lattice enthalpy (ΔH_L) for the solid phase can be expressed [13] by the equation:

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \qquad (3)$$

where 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 – absolute temperature (Kelvin).

3. Results and discussion

Quantum chemical calculations were performed for the gas phase with the full optimization of the geometric parameters in the framework of the density functional theory (DFT) on B3LYP/6-31G(d) using Gaussian 98 [14]. The vibration spectrum was calculated for each localized stationary state on the potential energy surface (PES) and, if no imaginary frequencies in the Hessian matrix, the stationary point corresponded to the PES minimum.

Enthalpies of formation for ions and neutral molecules were calculated using the CBS-4M quantum chemical method [15]. Gas phase enthalpies for non-ionic substances were transformed to solid state enthalpies using Trouton's rule [16]. Molecular volumes of ions were determined by the Monte Carlo method (included in
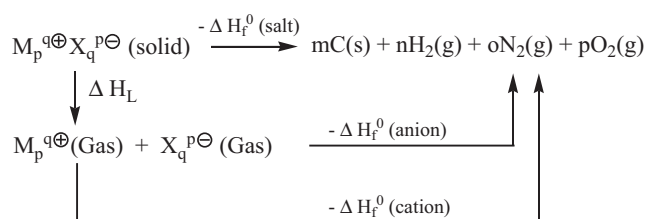

Fig. 1. The Born–Haber cycle for calculating enthalpies of salt formation.

Table 1
Values of coefficients α, β and I used to calculate ΔH_f° of salts.

Salt (charge ratio)	I, ionic strength	α, kJ mol^{-1} nm	β, kJ mol^{-1}
MX (1:1)	1	117.3	51.9
M_2X (1:2)	2	165.3	−29.8
MX_2 (2:1)	3	133.5	60.9
M_2X_2 (2:2)	4	101.6	91.5

the Gaussian software package) as the internal volume limited by the isosurface with the electron density 0.001 e/bohr^3.

First, we evaluated the applicability of the CBS-4M method to modeling of enthalpies of formation of organic compounds (azoles) based on the estimation of atomization energies.

Enthalpies of formation for compounds **1–5** in the solid phase (ΔH_f° (calc)) were calculated as:

$$\Delta H_f^\circ \text{ (calc)} = H^\circ \text{ (molecule)} - \Delta H^\circ \text{ (atoms)} + \sum \Delta H_f^\circ \text{ (atoms)}$$
$$- 188 * T_{melt} \qquad (4)$$

where H° (molecule) is the calculated enthalpy of the molecule (CBS-4M), H° (atoms) – the calculated values of the enthalpy of atoms (CBS-4M), ΔH_f° (atoms) – the experimental enthalpy of formation for atoms in the gas phase [17], and T_{melt} – melting point of the compound.

The calculation results for diazoles **1–5** are summarized in Table 2.

As seen from the calculation results, the obtained enthalpies of formation for azoles **1–5** are in good agreement with the experimental values. The imidazoles we dealt with have lower enthalpies of formation than the pyrazoles (with the same empirical formula), which is probably related to differences in the structure, namely to the location of nitrogen atoms in the five-membered ring.

Notably, for small molecules (water, carbon dioxide, ammonia, and elementary substances), the values obtained via the atomization energy of compounds are practically identical with the experiment (deviations do not exceed 1–2 kcal/mol), e.g. for the H_2O molecule, the difference between the calculated and experimental values is 0.27 kcal/mol.

Enthalpies of formation of ionic compounds **6–10** (ammonium salts of compounds **1–5**) were estimated by means of the Glasser–Jenkins equation [13] using enthalpies of formation for corresponding anions and cations in the gas phase according to the equation given above (without Trouton's correction) and the calculated molecular volume of ions (Eqs. 1–3). However, as shown by our calculations, the original method [4] appeared poorly applicable to complex anions of azoles because of low accuracy – that is

Table 2
Enthalpies of formation (ΔH_f°, kcal/mol) of compounds **1–5** in the condensed phase.

No.	Substance	Structural formula	ΔH_f° (exp) [18]	ΔH_f° (calc)
1	2,4-dinitroimidazole		1.9	2.15
2	4,5-dinitroimidazole		8.7	13.59
3	3,4-dinitropyrazole		28.7	29.79
4	3,5-dinitropyrazole		22.4	19.97
5	3,4,5-trinitropyrazole		22.2	32.64 31.91 [5]