Design of new high explosives by introducing N-oxides into 1H-tetrazole

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Computational Methods

The DFT-B3LYP method with the 6-311G(d, p) basis set was used to predict the HOFs of many organic systems via isodesmic reactions. Our designed isodesmic reactions used to obtain the HOFs of the BTZOA and TTZOA at 298 K are as follows:



(TTZOA)

For the isodesmic reaction, heat of reaction ΔH_{298} at 298 K can be calculated from the following equation:

$$\Delta H_{298} = \Delta H_{\rm f,p} - \Delta H_{\rm f,R} \tag{3}$$

where $\Delta H_{f,R}$ and $\Delta H_{f,P}$ are the HOFs of reactants and products at 298 K, respectively.

The calculations of HOFs of TZO, CH₃NHCH₃, (CH₃)₃N were carried out for the atomization reaction $C_aH_bO_cN_d \rightarrow aC(g) + bH(g) + cO(g) + dN(g)$ using the G2 theory to get an accurate value of ΔH_f . Now the most important task is to compute ΔH_{298} . The ΔH_{298} can be calculated using the following expression:

$$\Delta H_{298} = \Delta E_{298} + \Delta (PV) = \Delta E_0 + \Delta E_{ZPE} + \Delta E_T + \Delta nRT$$
⁽⁴⁾

where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔE_{ZPE} is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; ΔE_T is thermal correction from 0 to 298 K. The $\Delta(PV)$ value in eq. (4) is the *PV* work term and equals ΔnRT for the reactions of ideal gas. For the isodesmic reactions in this work, $\Delta n = 0$, so $\Delta(PV) = 0$.

Since most energetic compounds are in solid state, the calculation of detonation properties requires solid-phase HOF ($\Delta H_{f,solid}$). According to Hess's law of constant heat summation, the solid-phase HOF can be obtained from the gas-phase HOF ($\Delta H_{f,gas}$) and heat of sublimation (ΔH_{sub}):

$$\Delta H_{\rm f,solid} = \Delta H_{\rm f,gas} - \Delta H_{\rm sub} \tag{5}$$

Recently, Politzer et al. reported that the heat of sublimation correlates with the molecular surface area and the electrostatic interaction index $v\sigma_{tot}^2$ for energetic compounds. The empirical expression of the approach is as follows:

$$\Delta H_{sub} = aA^2 + b(\nu \sigma_{tot}^2)^{0.5} + c \tag{6}$$

where A is the surface area of the 0.001 electrons/bohr³ isosurface of the electronic density of the molecule, v describes the degree of balance between positive potential and negative potential on the isosurface, and $v\sigma_{tot}^2$ is a measure of the variability of the electrostatic potential on the molecular surface. The coefficients a, b, and c have been determined by Rice et al.: $a = 2.670 \times 10^{-4}$ kcal/(mol·A⁴), b = 1.650 kcal/mol, and c = 2.966 kcal/mol. The descriptors A, v, and $v\sigma_{tot}^2$ were calculated by using the computational procedures proposed by Bulat et al.. This approach has been demonstrated to predict reliably the heats of sublimation of many energetic compounds.

The detonation velocity and pressure were estimated by the Kamlet-Jacobs equations as

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1+1.30\rho)$$
(7)

$$P = 1.558\rho^2 N \overline{M} \,{}^{1/2} \,Q^{1/2} \tag{8}$$

where each term in the equations of (7) and (8) is defined as follows: D, the detonation velocity (km/s); P, the detonation pressure (GPa); N, the moles of detonation gases per gram explosive; \overline{M} , the average molecular weight of these gases; Q, the heat of detonation (cal/g); and ρ , the loaded density of explosives (g/cm³). For known explosives, their Q and ρ can be measured experimentally; thus their D and P can be calculated according to eqs. 7 and 8. However, for some compounds, their Q and ρ cannot be evaluated from experimental measures. Therefore, to estimate their D and P, we first need to calculate their Q and ρ .

The theoretical density was obtained by an improved equation proposed by Politzer et al, in which the interaction index $v\sigma_{tot}^2$ was introduced:

$$\rho = \alpha \left(\frac{M}{V(0.001)} \right) + \beta \nu \left(\sigma_{tot}^2 \right) + \gamma \tag{9}$$

where *M* is the molecular mass (g/mol) and *V*(0.001) is the volume of the 0.001 electrons bohr⁻³ contour of electronic density of the molecule (cm³/molecule). The coefficients α , β , and γ are 0.9183, 0.0028, and 0.0443, respectively.

The heat of detonation Q was evaluated by the HOF difference between products and explosives according to the principle of exothermic reactions. The products are supposed to be only CO₂, H₂O, and N₂, so released energy in the decomposition reaction reaches its maximum. Based on the ρ and Q values, the corresponding D and P values can be evaluated. The theoretical density of the compounds in this work is slight greater than practical loaded density. Therefore, according to the Kamlet-Jacobs equations, the D and P values can be regarded as their upper limits.

The strength of bonding, which could be evaluated by bond dissociation energy (BDE), is fundamental to understand chemical processes. The energy required for bond homolysis at 298 K and 1 atm corresponds to the enthalpy of reaction $A-B(g)\rightarrow A \cdot (g) + B \cdot (g)$, which is the bond dissociation enthalpy of the molecule A–B by definition. For many organic molecules, the terms "bond dissociation energy" and "bond dissociation enthalpy" usually appear interchangeably in the literature. Thus, at 0 K, the homolytic bond dissociation energy can be given in terms of Eq. (10):

$$BDE_0(A-B) = E_0(A \cdot) + E_0(B \cdot) - E_0(A-B)$$
(10)

The bond dissociation energy with zero-point energy (ZPE) correction can be calculated by Eq. (11):

$$BDE(A-B)_{ZPE} = BDE_0(A-B) + \Delta E_{ZPE}$$
(11)

where ΔE_{ZPE} is the difference between the ZPEs of the products and the reactants.

The free space per molecule in the unit cell, designated ΔV , can be used to estimate the impact sensitivity (h_{50}) of an energetic compound. ΔV can be represented as the difference between the effective volume per molecule that would be required to completely fill the unit cell, V_{eff} , and the intrinsic gas phase molecular volume, V_{int} :

$$\Delta V = V_{eff} - V_{int} \tag{12}$$

 V_{int} is defined as the volume enclosed by the 0.003 electrons/bohr³ contour of the molecule's electronic density. V_{eff} can be calculated exactly from the dimensions of the unit cell and the number of molecules that it encompasses, or alternatively by the formula:

$$V_{eff} = M / \rho \tag{13}$$

where *M* is the molecular mass and ρ is the crystal density.

The above calculations were performed with the Gaussian 03 package. In the geometry optimization, the maximum force was converged less than 0.00045 eV/Å, the RMS force less than 0.0003 eV/Å, the maximum displacement less than 0.0018 Å, and the RMS displacement less than 0.0012 Å. All of the optimized structures were characterized to be true local energy minima on the potential energy surfaces without imaginary frequencies.

Results

Table 1. Calculated heats of formation (HOF, kJ/mol) ρ (g/cm³), *D* (km/s), and oxygen balance (OB, %) values of BTZOA, TTZOA and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazoctane).

	BTZOA	TTZOA	HMX
HOF _(solid-phase)	577.8	954.6	120.0 (105.8 ^a)
ho(solid-phase)	1.95	1.90	1.92 (1.91 ^a)
$D_{(\text{solid-phase})}$	9.0	8.9	9.2 (9.1 ^a)
OB	0	0	-21.6

^a The experimental values.

Table 2. Calculated lowest BDE and h₅₀ values of BTZOA, TTZOA and HMX.^a

Compounds	BDE (kJ/mol)	$h_{50}(cm)$
BTZOA	202.7	100
TTZOA	215.9	65
HMX	166.5	30 (29 ^b)

^a The lowest BDE value is obtained by comparing the BDE values of four (for BTZOA and TTZOA) and two (for HMX) relatively weak bonds (according to the bond order). ^b The experimental value.