Supporting Information

for

Molecular Design and Property Prediction For A Series of Novel Dicyclic Cyclotrimethylene Trinitramine(RDX)-Derivatized as High Energy Density Materials

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Contents

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Kamlet-Jacobs equation[1]

The calculation of the detonation parameters such as detonation velocity (D), detonation pressure (P) and heat of detonation (Q) was performed with the Kamlet-Jacobs equation.[1] For a molecular formula form like $C_aH_bO_cN_d$, the equation is

$$D = 1.01\left(N\bar{M}^{1/2}Q^{1/2}\right)^{1/2}(1 + 1.3\rho) \quad (1)$$

$$p = 1.558\rho^2 N\bar{M}^{1/2}Q^{1/2} \quad (2)$$

Where D is detontion velocity, P is detonation pressure, Q is heat of detonation, N is the number of moles of the gas generated per gram, $\bar{M}$ is the average molecular weight of gaseous product, and ρ is crystal density.

In this paper these structure are all satisfied to $b/2 \le c \le 2a + b/2$, so there is enough oxygen to convert hydrogen to H20 while not enough to convert carbon to CO2,then the decomposition equation is shown as followed,

$$C_aH_bO_cN_d \rightarrow \frac{1}{2}d\ N_2 + \frac{1}{2}b\ H_2O + (\frac{1}{2}c - \frac{1}{4}b)\ CO_2 + \left(a - \frac{1}{2}c + \frac{1}{4}b\right)C \quad (3)$$

So, we have the following corollary to N, $\bar{M}$ and Q,

$$N = \left[\frac{1}{2}d + \frac{1}{2}b + (\frac{1}{2}c - \frac{1}{4}b)\right]/M = (b + 2c + 2d)/4M \quad (4)$$

$$\bar{M} = \frac{\frac{1}{2}d*28+\frac{1}{2}b*18+\left(\frac{1}{2}c-\frac{1}{4}b\right)*44}{\frac{1}{2}d+\frac{1}{2}b+\left(\frac{1}{2}c-\frac{1}{4}b\right)} = (56d + 88c - 8b)/(b + 2c + 2d) \quad (5)$$

$$Q \cong -\Delta H_0 = -\left[\Delta H_f^0(detonation\ products) - \Delta H_f^0(explosive)\right]/M \quad (6)$$

Then the standard heats of formation for H2O (g), N2 (g), and CO2 (g) and solid carbon are taken into this equation,

$$Q = \left[28.9b + 94.05(c/2 - b/4) + \Delta H_f^0(explosive)\right]/M \quad (7)$$

Here, the parameter unit of $\Delta H_f^0(explosive)$ is kcal/mol, the unit of Q is kcal/mol, so this equation can be obtained with the following formula,

$$Q * 10^{-3} = (28.9b + 94.05(c/2 - b/4) + 0.239\Delta H_f^0)/M \quad (8)$$

Where the parameter unit of ΔH_f^0 is kJ/mol, the unit of Q is cal/mol.

So when the structures are satisfied to b/2≤c≤2a+b/2, the parameters N, $\bar{M}$ and Q can be obtained as the following equation,

$$N = (b + 2c + 2d)/4M \quad (9)$$

$$\bar{M} = (56d + 88c - 8b)/(b + 2c + 2d) \quad (10)$$

$$Q * 10^{-3} = (28.9b + 94.05(c/2 - b/4) + 0.239\Delta H_f^0)/M \quad (11)$$

Thermodynamic Properties of R4

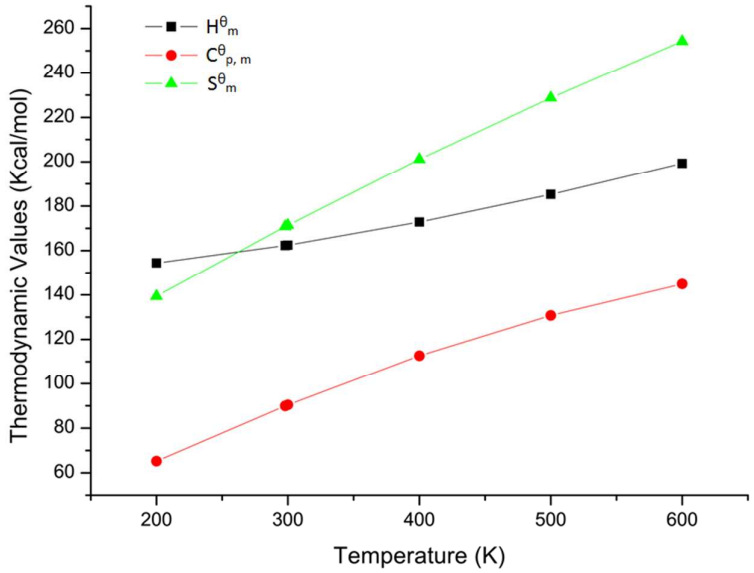
With the help of Gaussian03 program, the thermodynamic properties were obtained by analysis vibrational data. Then, standard molar thermal enthalpy H_m^θ, standard molar heat capacity $C_{p,m}^\theta$ and standard molar entropy S_m^θ from 200K to 600K were listed in **Table 5,**

Table 5. Standard Molar Thermal Enthalpy H_m^θ, Standard Molar Heat Capacity $C_{p,m}^\theta$ and Standard Molar Entropy S_m^θ of R4

Temperature(K)	**H_m^θ(Kcal/mol)**	**$C_{p,m}^\theta$(Kcal/mol)**	**S_m^θ(Kcal/mol)**
200	154.465	65.277	139.355
298	162.293	89.985	170.873
300	162.464	90.430	171.443
400	172.849	112.635	201.164
500	185.249	130.696	228.759
600	199.255	144.869	254.256

From this table we can see that the thermodynamic properties increase with temperature. This is mainly because the translations and rotations of the molecules are the key factors at lower temperature, while under high temperature the vibrational motion makes more contribution to the thermodynamic properties.

Figure 1. The Relationship between Temperature and Thermodynamic Properties



The relationship between temperature and thermodynamic properties have been calculated in following equations,

$$H^{\theta}_{m} = 143.975 + 3.1740 \times 10^{-2}T + 1.00911 \times 10^{-4}T^{2}$$

$$C^{\theta}_{p,m} = 2.95945 + 3.4783 \times 10^{-1}T - 1.85248 \times 10^{-4}T^{2}$$

$$S^{\theta}_{m} = 68.81084 + 3.7496 \times 10^{-1}T - 1.09915 \times 10^{-4}T^{2}$$

The correlation coefficients and standard deviations for standard molar thermal enthalpy H^{θ}_{m}, standard molar heat capacity $C^{\theta}_{p,m}$ and standard molar entropy S^{θ}_{m} from 200K to 600K are, in order, 0.99995 and 0.15842, 0.99996 and 0.23176, 1.00000 and 0.07624.

Reference

(1) Kamlet M. J.; Jacobs S. T. Chemistry of Detonation. I. A Simple Method for Calculating Detonation Properties of C, H, N, O Explosives. *J. Chem. Phys.* **1968**, *48*, 23-35.