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Thermochemical Properties of 2,4,6-Trinitro-1,3,5-triazine

MOHAMMAD HOSSEIN KESHAVARZ* and OMID RANAEE SYADAT†
Department of Chemistry, Malek-Ashtar University of Technology, Shahin-Shahr, P.O.Box 83145/115, Islamic Republic of Iran
Fax: (98)(312)5225068; Tel: (98)(312)5225071
E-mail: mhkeshavarz@mut.ac.ir; mhkir@yahoo.com

Theoretical studies of explosives continue to seek new compounds that can have higher performance and better thermochemical properties than RDX (cyclotrimethylenetrini-tramine) and HMX (cyclotetramethylenetetranitramine). 2,4,6-Trinitro-1,3,5-triazine is one of the interesting explosive with high performance as compared to HMX and RDX. The purpose of this work is to present computed or calculated thermochemical properties of 2,4,6-trinitro-1,3,5-triazine such as detonation temperature, adiabatic exponent, impact sensitivity, heat of detonation by using empirical and semi-empirical methods.

Key Words: Thermochemical properties, 2,4,6-Trinitro-1,3,5-triazine.

INTRODUCTION

High-density explosives are very interesting to chemist. In general, increasing the oxygen balance and heat of formation will increase the sensitivity of an explosive as well as the performance. Since detonation pressure is proportional to the cube of the density, increasing the density should do more to improve the performance without increasing the sensitivity. Theoretical studies show that 2,4,6-trinitro-1,3,5-triazine has high performance in compare to cyclotetramethylene tetranitramine (HMX) and cyclotrimethylene trinitramine (RDX)[1,2]. Quantum mechanical computations have been used to determine its structure and the energies of trimerization of nitryl cyanide[3].

The prediction of thermochemical properties and sensitivity of new explosive prior of its actual synthesis is appreciated to explosive user because they can help to reduce the costs associated with its synthesis, test and evaluation. In this paper, various properties of 2,4,6- trinitro-1,3,5-triazine were obtained by some empirical and semi-empirical methods. Detonation temperature, adiabatic exponent, impact sensitivity, heat of detonation is special importance that was investigated[4-8]. The results will be discussed in each case and compared to experimental data of some well-known explosives.

†Institute of Chemical and Science Technology, Tehran, Islamic Republic of Iran.

RESULTS AND DISCUSSION

Detonation temperature of 2,4,6-trinitro-1,3,5-triazine

Two important properties of an energetic molecule are condensed heat of formation and energy release in decomposition to stable species. The solid heat of formation of 2,4,6-trinitro-1,3,5-triazine can be obtained from the isodesmic reaction and experimental heat of formation of benzene, s-triazine and trinitrobenzene[1]. The estimated solid heat of formation by this method is 46 kcal/mol. Some new correlations were recently introduced for calculation of detonation temperature of $C_aH_bN_cO_d$ explosives[9]. These correlations are based on the relative amount of a, b, c and d in composition of pure and mixture of explosives. Since 2,4,6- trinitro-1,3,5-triazine with molecular formula $C_3N_6O_6$ follows the condition $d \geq a+b/2$ and $d \leq 2a+b/2$, the following correlation can be used for calculation of detonation temperature:

$$T_d = 298 + \frac{\Delta H_f(s) - 1158a - 252b + 848d}{-0.2964a - 0.0551b + 0.0187c + 0.1911d} \quad (1)$$

where T_d is detonation temperature and $\Delta H_f(s)$ is solid heat of formation of explosive. Calculated detonation temperature of 2,4,6- trinitro-1,3,5-triazine is 4869 K. Experimental detonation temperature of HMX is 4300 K. As seen, detonation temperature of 2,4,6- trinitro-1,3,5-triazine is 13.2% greater than HMX.

Adiabatic exponent

The Chapman-Jouguet (C-J) condition for a steady-state detonation chooses from all possible solutions the one that propagates with lowest velocity[8]. The adiabatic exponent γ_{CJ} is one of the important factors in evaluating detonation performance, which can be defined as the initial pressure-volume slope in the isentropic expansion of detonation products for the C-J state or:

$$\gamma_{CJ} = \left(\frac{\partial \ln P}{\partial V}\right)_S \quad (2)$$

The subscript S indicates constant entropy.

Conservation laws relate ρ_{CJ} and γ_{CJ} with loading density (ρ_0) in dense fluids where detonation products of mixture are obtained at high pressure:

$$\frac{\rho_{CJ}}{\rho_0} = \frac{\gamma_{CJ} + 1}{\gamma_{CJ}} \quad (3)$$

The adiabatic exponent can also be used as one of most sensitive tests of various equation of state (EOS) models. Since γ_{CJ} is a second-order derivative of free energy, it is extremely sensitive to slight deviation from true equation of state of detonation products. Kamlet and Short[10] introduced the following equation for estimating of γ_{CJ} as a criterion for choice

among conflicting experimental measurements of detonation properties of a number of $C_aH_bN_cO_d$ explosives:

$$\gamma_{CJ} = 0.702 + \frac{0.665}{\rho_0} + 1.107\rho_0 \quad (4)$$

The equation is valid only for $C_aH_bN_cO_d$ explosive with loading density above 1 g/cc. It can be changed to the following equation so that its range of validity[7] is above 0.8 g/cc.

$$\gamma_{CJ} = 0.442 + \frac{0.389}{\rho_0} + 1.335\rho_0 \quad (5)$$

The calculated γ_{CJ} for 2,4,6-trinitro-1,3,5-triazine is given in Table-1. The measured γ_{CJ} for HMX at its crystalline density[7], 1.89 g/cc, is 3.02. As indicated in Table-1, two methods can predict high performance for 2,4,6-trinitro-1,3,5-triazine as compared to HMX.

TABLE-1
CALCULATED ADIABATIC EXPONENT FOR
2,4,6- TRINITRO-1,3,5-TRIAZINE

ρ_0	Kamlet-Short[10]	Keshavarz[7]
0.8	-	2.42
0.9	-	2.44
1.0	2.17	2.47
1.1	2.26	2.52
1.2	2.37	2.58
1.3	2.48	2.65
1.4	2.59	2.73
1.5	2.70	2.81
1.6	2.82	2.89
1.7	2.94	2.98
1.8	3.06	3.06
1.9	3.18	3.16
2.0	3.31	3.25
2.1	3.43	3.34

Impact sensitivity

Drop weight test is one of tests for evaluation impact sensitivity in which milligram quantities of an explosive material are placed between a flat tool steel anvil and the flat surface of a tool striker. Explosion or nonexplosion is recorded for some drops that are usually made by a 2.5 kg weight for different heights. H_{50} is frequently used to distinguish explosion, the height in centimeter at which the probability of explosion is 50%, for an arbitrarily set level of sound which produced by the explosive on impact. Maximizing performance as well as minimizing sensitivity is highly desirable in designing and formulating of energetic materials. Since all explosives are necessarily metastable and sensitive, organic explosives can

undergo very rapid and high exothermic reaction for which an understanding of sensitivity is in large part of chemical problem.

Kamlet and Adolph[11] introduced a very simple conventional scheme for estimating of impact sensitivity that can be applied for large number explosives. They relate the impact sensitivity to oxygen balance through:

$$\log H_{50} = A_1 + A_2 \times OB_{100} \quad (6)$$

where A_1 and A_1 are constants and OB_{100} is oxygen balance. OB_{100} can show a procedure of quantifying how well an explosive provides its own oxidant. It can be defined for $C_aH_bN_cO_d$ explosive as below:

$$OB_{100} = [2d\text{-}b\text{-}2c\text{-}2n(CO_2)]/MW \quad (7)$$

where MW is the molecular weight of explosive and $n(CO_2)$ is the numbers CO_2 moieties that are contained in the molecule. A new reliable model was recently introduced for estimation of sensitivity of selected class of explosives[12]. The following correlation can be used for polynitroarmatic explosives:

$$\log H_{50} = \frac{11.76a + 61.72b + 26.89c + 11.48d}{MW} \quad (8)$$

The calculated impact sensitivity for 2,4,6- trinitro-1,3,5-triazine is 5 and 17 cm according to eqns. 6 and 8, respectively. Application of the new correlation[12] for well-known polynitroaromatic explosives shows that the new correlation gives more reliable prediction than Kamlet and Adolph method[11]. The result indicates that this explosive is more sensitive than HMX and RDX because experimental data of impact sensitivity[12] for these explosives are 32 and 28 cm. Thus, high sensitivity of 2,4,6-trinitro-1,3,5-triazine is one of restriction of this explosive in laboratory synthesis and its scale up.

Heat of detonation

The effectiveness of an explosive depends on the amount of energy available in it and the rate of release of available energy when detonation occurs. In detonation process, the heat librated will raise the temperature of gases detonation because decomposition of an explosive is extremely fast, which will in turn cause them to expand and work on surroundings[5,6]. The heat of detonation can be determined from the heats of formation of the reactants and the products of detonation so that a positive heat of formation (per unit weight) is favourable for an explosive because this leads to a greater release of energy upon detonation and an improvement in performance of an explosive. It can be calculated through:

$$Q \cong \frac{\Delta H_f(\text{explosive}) - \Delta H_f(\text{detonation products})}{\text{formula weight of explosive}} \quad (8)$$

We can use eqn. 4 with the new method of Keshavarz-Pouretedal[4] for calculating heat of detonation. The calculated heat of detonation for 2,4,6-

trinitro-1,3,5-triazine is 1.519 kcal/g which is higher than reported values of 1.481 kcal/g for HMX[5]. This confirms higher detonation performance of 2,4,6-trinitro-1,3,5-triazine as compared to one of the most well-known powerful explosives namely HMX.

Conclusion

2,4,6-Trinitro-1,3,5-triazine is a hydrogen-free nitroheterocyclic compound which has high initial density, $\rho_0 = 2.1$g/cc. No information about synthesis or characterization of 2,4,6-trinitro-1,3,5-triazine is available in literature[1]. However, it contains excess oxygen to convert all of carbons to carbon dioxide in decomposition process. Its high density can improve the performance of this compound so that detonation pressure of 2,4,6- trinitro-1,3,5-triazine explosives within about 22 % is higher than RDX explosives[2]. The higher detonation temperature of 2,4,6-trinitro-1,3,5-triazine respect to HMX is one of the important factors for its high performance. High sensitivity of 2,4,6-trinitro-1,3,5-triazine may be taken as one of its limitation in explosive industry.

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