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Performance Study of Energetic Compound 2,4,6-Trinitro-1,3,5-Triazine

MOHAMMAD HOSSEIN KESHAVARZ* and MOHASEN OFTADEH†
Department of Chemistry, Malek-ashtar University of Technology
Shahin-shahr, P.O. Box 83145/115, Islamic Republic of Iran
Tel: (0098) 0312 522 3071; Fax: (0098) 0132 522 5068; E-mail: mhkeshavarz@mut.ac.ir

2,4,6-Trinitro-1,3,5-triazine (TNTA) is an ultrahigh performance explosive with high density. Detonation pressure and velocity of TNTA at various loading densities are compared with RDX (cyclomethylene trinitramine) by some empirical and semiempirical methods. Relative specific impulse of TNTA with respect to HMX (cyclotetramethylene tetranitramine) is also calculated by simple method assuming the gaseous products are limited to CO, CO_2, H_2O, N_2 and H_2.

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

INTRODUCTION

Cyclic nitramine such as RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine) have found wide application as explosives and propellants. The most challenging immediate problem for explosive chemists is to develop explosives with higher performance than HMX. The compound 2,4,6-trinitro-13,5-triazine (TNTA), the cyclic trimer nitryl cyanide $(NO_2CN)_3$, is a high-energy material with high density which can be used as a high explosive and propellant. The σ acceptor affects NO_2 groups, by shortening the ring bonds and enlarging the bond angles at the carbons bonded to NO_2 groups, increases the effective electronegativity of carbon atoms and cyclic electron delocalization[1]. This effect enhances the stability of the ring structure of TNTA as compared to that of s-triazine. An *ab initio* study of TNTA has been performed in order to obtain its structure and the energies of trimerization of nitryl cyanide[2].

To obtain the highest C-J performance explosive one wishes to start with as an initial density of explosive as possible. The detonation performance of HMX and RDX are nearly identical at the same loading density, but 0.1 g/cc higher initial density of HMX explosives typically have C-J pressures 10% higher than RDX explosives[3]. Since the high estimated density (2.1 g/cm^3) and heat of formation of TNTA (46 kcal/mol)[1], TNTA can be introduced as an interesting high-energy density material which may be used as the most powerful energetic

†Department of Chemistry, Isfahan Payam-noor University, Isfahan, Iran.

material. In other words, TNTA can be initiated as an explosive or propellant to give powerful explosion or propulsion.

In this paper, detonation performance of TNTA is compared with measured values of RDX at various initial densities. Detonation performance of TNTA at various loading densities is studied by three methods, namely Becker-Kistakowsky-Wilson equation of state (BKW-EOS)[3], Kamlet's method[4–6] and the new correlation[7]. To obtain specific impulse as a measure of characterizing and evaluating performance, we have calculated the specific impulse of TNTA relative to that of HMX. The gas phase heat of formation of TNTA, which is obtained by semiempirical PM3 procedure[8], is used to calculate relative specific impulse.

Detonation Performance of TNTA

Detonation velocity and pressure have been regarded as the principal measuring of the detonation performance of explosives. The Chapman-Jouguet (C-J) pressure has been regarded as the principal parameter for determining detonating power of explositves. The calculations of C-J pressures are usually performed with equation of state (EOS) and a computer code such as TIGER[9], which combines the Rankine-Hugoniot conservation equation, the C-J condition, the laws of chemical equilibrium, the density and heat of formation of the explosive. Some of the complicated numerical codes, which use the EOS, *e.g.*, BKW-EOS, were developed for calculating detonation properties of condensed explosive[3]. Kamlet and coauthors[4–6], by assuming the reaction products consist of H_2O, N_2, CO_2 and solid carbon, derived the empirical formulas that interrelated the detonation properties to heat of detonation, density, etc. On the basis of relationship between combustion temperature and the number of moles of gaseous products per molecular weight of explosive, we have predicted P_{CJ} for any CHNO explosive by simple correlation relation[7]. In this simple method, there is no need to have accurate composition of detonation products. It is assumed that the gaseous products are limited to CO, CO_2, H_2O, N_2 and H_2. In particular, computed heat of formation of explosive by the PM3 procedure alone, without the correction for crystal effects, is used to calculate combustion temperature in determination of detonation pressure. To determine detonation velocity of any unknown CHNO explosive from detonation pressure, one can use the correlation between detonation pressure and velocity at any loading density[10]. Two later empirical methods, which determine the detonation velocity and pressure for a wide variety of CHNO explosives, have the same reliability as one might expect from the more complex computer codes.

One of the most important properties of an explosive is the solid state density. The performance characteristics of propellants and explosives, such as detonation velocity and pressure, are functions of density. In particular, density determines the quantity of material that can be packed into a limited volume. Our essential contribution here is to study how detonation pressure and velocity of TNTA can be varied at different loading density of three different BKW-EOS[3], Kamlet's method[4–6] and the new correlation[7]. The heat of formation of TNTA, as one of the required parameters for Kamlet's method and BKW-EOS, can be obtained

from the isodesmic reaction[1] that is 46 kcal/mol. The calculated detonation pressure and velocity *vs.* loading density from the above empirical and semi-empirical methods for TNTA and measured values of RDX are given in Table-1. As shown in Table-1, the detonation performance of TNTA from three methods is approximately near the values of RDX. Thus the higher density of TNTA, as compared to RDX and HMX, is an essential factor to justify its high detonating power.

TABLE-1
CALCULATED AND EXPERIMENTAL[13] DETONATION PROPERTIES AT DIFFERENT LOADING DENSITY FOR TNTA AND RDX

Loading density (g/cm^3)	TNTA (BKW-EOS)[3]		TNTA (Kamlet's method)[4-6]		TNTA (New correlation)[7]		RDX	
	Calcd. P_{CJ} (kbar)	Calcd. V_{CJ} (km/s)	Calcd. P_{CJ} (kbar)	Calcd. V_{CJ} (km/s)	Calcd. P_{CJ} (kbar)	Calcd. V_{CJ} (km/s)	Measrd. P_{CJ} (kbar)	Measrd. V_{CJ} (km/s)
1.07	105.5	5.83	115.8	6.15	112.1	6.03	117.5	6.26
1.10	111.2	5.92	122.4	6.25	117.8	6.14	121.6	6.38
1.29	151.9	6.50	168.4	6.89	163.8	6.80	166.2	7.00
1.46	194.8	7.02	215.4	7.46	211.1	7.39	210.8	7.60
1.77	292.3	8.00	317.0	8.50	312.5	8.44	338.0	8.70

TNTA as a propellant

When an energetic material undergoes combustion, expansion of gaseous products develops specific impulse (I_s). The specific impulse is widely viewed as a means of characterizing and measuring of propellant performance. Combustion of an explosive, as an energetic material, develops thrust due to discharge of gaseous products. High explosives such as HMX and RDX act as an oxidizer in formulations of propellants in order to increase the heat of combustion and performance. TNTA can be used as an energetic oxidizer in propellant formulation to achieve a higher performance characteristic. The relative specific impulse of TNTA is calculated relative to that of HMX, which is a high explosive extensively used in solid rocket propellants at present. To calculate the relative specific impulse, one can assume the stoichiometric decomposition reaction of one mole of TNTA to be perfectly oxygen balanced towards CO_2 and N_2 molecules. It is assumed that for decomposition of HMX and TNTA, the following reactions are satisfied:

$$C_4H_8N_8O_8 \longrightarrow 4CO + 4N_2 + 4H_2O$$

$$C_3N_6O_6 \longrightarrow 3CO_2 + 3N_2$$

In calculating the relative specific impulse, the method used for obtaining the heat of formation is not highly sensitive. In our work, we have used the gas phase

heat of formation of explosive, which is obtained by the semiempirical PM3 procedure, for calculation of enthalpy of combustion. It is assumed that steady state is satisfied and enthalpy of combustion is constant during the combustion process. There is no need to correct the enthalpy of formation for crystal effect in the case of relative specific impulse[11].

The assumption that the combustion products of HMX and TNTA are limited to CO, CO_2, N_2 and H_2O, does not change the calculated specific impulse values as those obtained using ISPBKW computer code[3] for determining the types and quantities of gaseous products. Relative estimated specific impulse of TNTA with respect to HMX is about 1.01, which is consistent with calculated detonation performance.

Conclusion

Increasing the oxygen balance and the heat of formation will generally increase the sensitivity of an explosive as well as performance. However, increasing the density should do more to improve the performance without increasing the sensitivity because the detonation pressure is proportional to the cube of the density. We can predict unusually high densities for two general classes of compounds: hydrogen-free nitroheterocyles and polycage compounds[12]. Table-1 gives a comparison between calculated and measured detonation properties of TNTA (as a hydrogen-free nitroheterocycle) and RDX. As shown in Table-1, the calculated detonation performances of TNTA by three methods are approximately the same as measured values for RDX. Density is the primary physical parameter in detonation performance and shock sensitivity. To obtain the highest CJ performance of explosive, one wishes first to maximize the CJ particle density or number of moles of gas per g of explosive and then to maximize the heat of detonation. The most important method of maximizing the CJ particle density is to increase the initial density of explosive as much as possible. The performances of TNTA and RDX at the same density are essentially identical; beside, TNTA has estimated initial density 2.1 g/cm^3 and RDX has an initial density of 1.82 g/cm^3. Thus TNTA exlosives typically will have CJ pressures 22% higher than RDX explosives.

In general, the low molecular weight of gaseous products per unit mass of propellant increases specific impulse. To have a high specific impulse for an energetic compound, it is also generally understood that the compound should have a large positive heat of formation. The gaseous products from decomposition of TNTA could reduce the effective performance of TNTA, but it has sufficient energy and density to act as a suitable propellant with respect to HMX.

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