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Thermochemical and detonation properties of 2,4,6-tris (3,5-diamino-2,4,6-trinitrophenylamino)-1,3,5-triazine as thermally stable explosive

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ABSTRACT

2,4,6-tris (3,5-diamino- 2,4,6-trinitrophenylamino)-1,3,5-triazine or PL-1 can be synthesized by amination of 2,4,6-tris (3,5-dichloro-2,4,6-trinitrophenyl amino)-1,3,5-triazine which, in turn, was prepared from condensation of cyanuric chloride and 3,5-dichloroaniline followed by nitration with mixed acid. PL-1 has considerably low hydrogen and high nitrogen content which can be introduced as good thermally stable explosive. The purpose of this work is to study theoretically some aspects of performance and thermochemical properties as well as sensitivity of PL-1. The results will be compared to reported measured values of TATB as a well-known thermally stable explosive.

KEYWORDS

PL-1;
Thermally stable explosive;
Detonation performance;
Thermochemical properties.

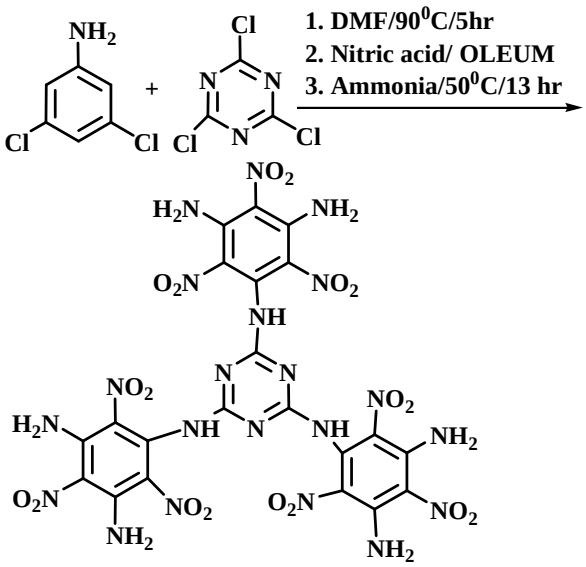
INTRODUCTION

There is continuous research purposes to develop new energetic materials with higher performance and enhanced insensitivity to thermal or shocks insults than the existing ones in order to meet the requirements of future military and space applications. 2,4,6-Tris (3,5-diamino- 2,4,6-trinitrophenylamino)-1,3,5-triazine or PL-1 is one of the interesting thermally stable explosives, which was recently synthesized[1].

This paper predicts some features of performance, shock sensitivity and thermochemical properties of PL-1. New methods will be used to study of mentioned properties. Detonation pressure and temperature as well as heat of detonation and gas phase heat of formation of PL-1 will be determined. Finally, shock sensitivity of PL-1 based on small-scale will be studied. The results will be also compared with that of TATB.

Synthesis of PL-1

Bapat and coworkers[1] synthesized PL-1by amination of 2,4,6-tris(3,5-dichloro-2,4,6-trinitrophenyl amino)-1,3,5-triazine which, in turn, was prepared from condensation of cyanuric chloride and 3,5-dichloro aniline followed by nitration with mixed acid. Its yield is 50% and has a density of 2.02g/cm^3. It has consider-



ably low hydrogen and high nitrogen content, and has good heat resistance with decomposition temperature 335°C (DTA 10°C/min).

Detonation pressure

Predicting of the performance of new energetic materials is very important to chemist because the calculated detonation properties of a notional energetic compound are recognized to be cost-effective, environmentally-desirable and time-saving in the decision to whether it is worth the effort to attempt a new or complex synthesis. The pressure associated with the state of complete reaction is an important parameter that has been regarded as principal measures of performance of detonating explosive for many years. Chapman and Jouguet (C-J) introduced a simple explanation of detonation so that as the shock compresses the material, the chemical reaction takes place instantaneously. It is reasonable to expect the calculated and experimental C-J pressures to differ by 10 to 20% because the nonsteady-state nature of the detonation wave[2]. The C-J pressure can be coupled with the adiabatic (gamma) exponent, i.e. the initial pressure-volume slope in the isentropic expansion of detonation products front the C-J state, to use an index of explosive's ability to accelerate metal[3].

To calculate detonation pressure, condensed phase heat of formation of PL-1 would be needed. The new empirical method can be used to predict condensed phase heat of formation of PL-1 via its molecular structure, which gives 27.2 kcal/mol[4]. Predicted heat of formation of PL-1 was used to determine its detonation pressure. Calculated detonation pressure for PL-1 is 307 kbar[5], which is close to measured value of TATB, i.e. 310 kbar[6].

Detonation temperature

Detonation temperature with the other detonation parameters of a notional explosive compound is recognized to be cost-effective and time-saving in the decision to whether it is worth the effort to attempt a new or complex synthesis. It is one of the detonation parameters with least information in the C-J state which is measured experimentally from the brightness of the detonation front as it proceeds toward detector. Its measurement is difficult and is usually done by the brightness of the detonation front interacting with a detector with absolute accuracies estimated to be ±100 K for liquid explosives and ±200 K for solid explosives. Since it is not known how much it is absorbed from detonation products by the shocked and partially decomposed explosive between the detector and the end of the reaction zone, there is some uncertainty for determination of radiation in measurement of detonation temperature. Density discontinuities free system such as a liquid or a single crystal is to be useful for measurement of the detonation temperature. This may be attributed to any voids or density discontinuities which can lead to measurements of the brightness of the shocked air or shocked detonation products rather than the C-J detonation products.

Detonation temperature can be calculated through four decomposition pathways[7]. Calculated detonation temperature for PL-1 and TATB are 3467 and 4000 K, respectively[7]. As seen, detonation temperature of PL-1 is less than TATB, which can be attributed to high nitrogen and low oxygen contents of PL-1 with respect to TATB.

Heat of detonation

Detonation calorimetry allows the experimental evaluation and some recent methods can also be used to compute the heat of detonation[5,8-10]. Experimental or calculated heats of formation[4,11-12] can be used to evaluate the enthalpy change of detonation reaction. A positive heat of formation is favorable for an energetic

material because this leads to a greater release of energy upon detonation. If the heat of formation of an explosive is known, then using the standard heats of formation of assumed detonation products will lead to predict its heat of detonation.

New decomposition reaction for PL-1 was used to predict heat of detonation. Calculated heat of detonation for PL-1 is 2.5 kJ/g which is close to measured heat of detonation of TATB, i.e. 3.06 kJ/g[5].

Gas phase heat of formation

Gas phase heat of formation can used as to measure of energy content of an energetic material. Group additivity methods and quantum mechanics are two broadly methods for calculation gas phase heat of formation. Calculate gas phase heat of formation can be combined with heats of vaporization and sublimation to obtain condensed phase heat of formation. Group additivity methods commonly can be used to estimate thermochemical quantities of various organic molecules so that the properties of the molecules can be derived from atoms or functional groups from which they are made. Quantum mechanical methods can be used to develop new algorithms together with continuing improvement in computer processing to understand molecular problems with much more reliability. Two new methods were also introduced to predict gas phase heat of formation for aromatic and non-aromatic energetic compounds[13,14]. Since both PL-1 and TATB are aromatics, we can use the new method to determine their gas phase heat of formation. Calculated gas phase heat of formation of PL-1 (225 kcal/mol) is higher than TATB (40 kcal/mol)[14], which can be attributed to the existence of four aromatic rings in PL-1.

Shock sensitivity

Different gap tests can be used to qualitatively measure the shock wave amplitude required to initiate detonation in explosives, e.g. at Naval Surface Warfare Center (NSWC) and Los Alamos National Laboratory (LANL). A standard small scale gap test[15] is often used to measure shock sensitivity. It was recently found that small scale gap test can be predicted by simple method. This method can determine shock sensitivity based on small scale gap test as the pressure required to initiate material pressed to 90%, 95% and 98% of theoretical maximum density[16]. Calculated shock sensitivities for PL-1 are P_{90}=86.6 kbar, P_{95}=132.9 kbar and P_{99}=168.3 kbar, where P_{90}, P_{95} and P_{99} are the pressure in kbar required to initiate material pressed to 90%, 95% and 99% theoretical maximum density, respectively. Predicted results are close to reported values for TATB, i.e. P_{90}=70.38 kbar, P_{95}=121.92 kbar and P_{99}=164.86 kbar[17].

CONCLUSIONS

Detonation pressure can be regarded as an important detonation parameter to determine detonation performance. Explosives with higher density are preferred for warheads because its higher detonation pressure and compactness of warheads used in missiles and ammunitions. The main aim of this work was to study some aspects of performance, thermchemical and shock sensitivity of PL-1 as a new thermally stable explosive. Calculated detonation temperature of PL-1 is lower than TATB, which is one of the advantage of PL-1 with respect to TATB for some applications where lower detonation temperature is required. Moreover, calculated gas phase heat of formation of PL-1 is higher than TATB, which shows higher energy content of PL-1 in gaseous state as compared to TATB.

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