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Synthesis of Keto-RDX and its Characterizations Calculation

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Abstract: Keto-RDX was obtained by one-step method with a certain amount of RDX as by-product. The effects of various parameters on high yield were studied. A simple analytical method was also introduced to determine simultaneously Keto-RDX/RDX mole ratio. Some important theoretical characterizations of Keto-RDX such as detonation performance at maximum nominal density and shock sensitivity were determined by new methods and compared with RDX.

Key words: physical chemistry; Keto-RDX; RDX; derivative spectrophotometry; performance; shock sensitivity; gas phase heat of formation

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1 Introduction

Keto-RDX (2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane or K-6) is one of the high energy density material (HEDM) bearing a cyclic dinitro-urea molecule. Mitchell and co-workers have reported synthesis of Keto-RDX via the condensation of formaldehyde, urea and amine and then nitration of condensed resultant. They scaled up and described some characteristics of Keto-RDX^[1]. Another method for preparing Keto-RDX was reported by Hunay which use either 2-nitroimino-5-nitrohexahydro-1,3,5-triazacyclohexanone or 2-nitroimino-5-nitrohexahydro-1,3,5-triazine as starting materials, with a mixture of reagents comprising $(CF_3CO)_2O$ and either HNO_3 or NH_4NO_3 ^[2]. Sikder and co-workers^[3] have shown that K-6 can be prepared through condensation of dinitrourea with nitrolysis products of hexamine in presence of P_2O_5 .

In this paper, the various research methods of the reactions and corresponding results in direct preparation method and one-pot synthesis of hexamine dinitrate (HDN) or hexamine and urea as reactants for preparing Keto-RDX are described. Since Keto-RDX is contaminated with RDX, a simple method is introduced to predict simultaneous determination of Keto-RDX and RDX. Finally, some important characteristics of Keto-RDX are calculated theoretically and compared with corresponding explosive RDX.

2 Experimental

2.1 Reagents, apparatus and measurements

Chemicals were purchased from fluka and merck chemicals companies. IR spectra were recorded on a Nicolet 800 FT-IR. 1H NMR spectra were recorded on a Bruker AC 100. UV-Vis spectra were recorded by Perkin-Elmer Lambda 2.

2.2 Preparation

Method A: Finely divided urea (10 g, 0.167 mol) was added in small portions with stirring and cooling to a solution of concentrated nitric and sulfuric acid (50 : 50, 65 mL). After the addition, temperature of the reaction mixture was maintained between 0 – 5 °C for 30 min. The milky mixture was cooled to – 5 °C and hexamine (10 g, 0.071 mol) was added slowly with stirring of the mixture. Temperature of the reaction vessel was kept below 0 °C during the addition of hexamine. It should be noted that addition of hexamine to reaction mixture is highly exothermic. After addition of hexamine, the mixture was allowed to warm to 10 °C and stirred for 35 min. The reaction progress was monitored by TLC method. The resulting suspension was transferred to a beaker containing crushed ice. The white precipitate was filtered, washed with plenty of water (to remove the excess acid) and dried. The crude product (14.3 g) of RDX and Keto-RDX were obtained with weight percent 60.4% and 39.6%, respectively. Pure Keto-RDX was prepared by recrystallization of crude product from acetonitrile or ethyl acetate solvent.

Method B: To 50 mL mixture of nitric and sulfuric acid

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(98%), as the same of method A, urea (4.5 g, 0.075 mol) was added. Hexamine dinitrate (HDN) (10 g, 0.038 mol) was added to milky mixture at temperature $< 5\text{ }^{\circ}\text{C}$. Addition of HDN is a mild reaction. After addition of HDN, the reaction mixture was allowed to warm $10\text{ }^{\circ}\text{C}$ and was stirred for 1 h. The reaction was monitored by TLC method. Finally, the reaction mixture was poured in crushed ice (400 g) to work-up the product. The white precipitate was filtered, washed and dried to give 8 g crude product that contain RDX (55%) and Keto-RDX (45%).

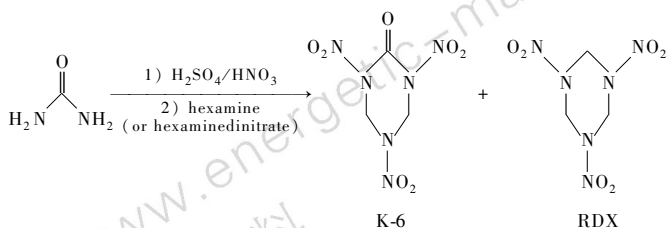
3 Results and discussion

3.1 Synthesis of Keto-RDX

In the process of preparing Keto-RDX by direct method via reaction of hexamine and dinitrourea in the presence of nitrating agents, hexamine can be nitrated continuously accompanied with bonding cleavage. There are a number of nitrolysis fragments formed in the whole hexamine degradation and nitration process that is called hexamine nitrolysis^[4].

The *N,N'*-dinitrourea was formed in the highest concentration in the nitrating media only through changing reaction time or temperature, and then it reacts with hexamine nitrolysis fragment, the highest yield of the Keto-RDX was obtained in the definite reaction rate^[5]. The scheme 1 shows the formation of Keto-RDX using hexamine and nitrourea in nitric-sulfuric acid mixture.

In order to obtain maximum yield of Keto-RDX production (scheme 1), several parameters, such as concentration of nitric-sulfuric acid mixture, the amount of hexamine and nitrourea and reaction time, were investigated and optimized.



In Figs. 1 and 2, the effect of sulfuric acid and nitric acid amounts on the yields of Keto-RDX and RDX were shown, respectively. As seen from Figs. 1 and 2, by increasing the amount of H_2SO_4 and HNO_3 up to mole

0.63 and 0.80, respectively, the content of Keto-RDX will increase up to 34% and decrease at upper concentrations of sulfuric acid and nitric acid. The yield of Keto-RDX production was decreased more than 0.63 mole H_2SO_4 and 0.80 mole HNO_3 .

In Fig. 3, it is seen that with increasing the mole ratio of HNO_3 /hexamine < 5 , the yield of Keto-RDX is increased and then decreased in the mole ratio of HNO_3 /hexamine > 5 . The presence of high concentration of HNO_3 also causes the degradation of Keto-RDX explosive.

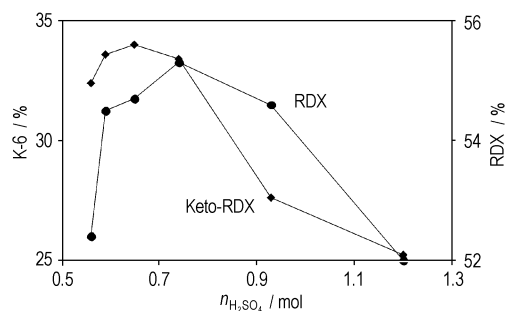


Fig. 1 The effect of mole of sulfuric acid on the yields of RDX and Keto-RDX in method A

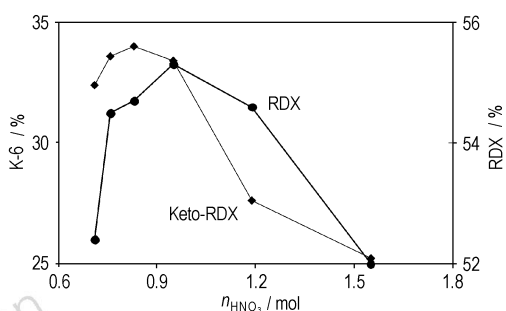


Fig. 2 The effect of mole of nitric acid on the yields of RDX and Keto-RDX in method A

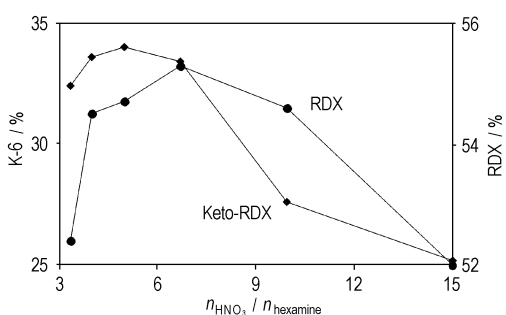


Fig. 3 The effect of mole ratio of HNO_3 /hexamine on the yields of RDX and Keto-RDX in method A

The highest percentage of Keto-RDX is in the mole ratio of hexamine/urea = 0.53. The reaction was uncontrollable by increasing the amount of hexamine in comparison with urea. The reaction was vigorously exothermic at

hexamine/urea mole ratio >0.53 .

The effect of reaction time was studied on the yield of Keto-RDX production. The maximum yield was obtained after 35 min and then was remained without any considerable change. As a result, the maximum yield of Keto-RDX ($\sim 34\%$) was obtained in optimized condition of 0.63 mole H_2SO_4 , 0.80 mole HNO_3 , mole ratio of $\text{HNO}_3/\text{hexamine} = 5$, mole ratio of hexamine/urea = 0.53 and reaction time = 35 min.

As seen from Scheme 1, the RDX explosive is also as by product. The changes of RDX production were approximately as similar as Keto-RDX yield with variations of studied parameters. The maximum yield of RDX production was ($\sim 54\%$) under optimized conditions.

In method B, hexamine dinitrate (HDN) was used as an initial material. The reaction of HDN with urea in the presence of nitric-sulfuric acid mixture is an exothermic reaction, whereas, the reaction of hexamine-urea- H_2SO_4 - HNO_3 was done in vigorously exothermic conditions.

The influence of H_2SO_4 mole, HNO_3 mole, mole ratio of HNO_3/HDN , mole ratio of HDN/Urea and reaction time was studied on the yield of Keto-RDX. The maximum yield ($>37\%$) of Keto-RDX was obtained at 0.72 mole H_2SO_4 , 0.92 mole HNO_3 and mole ratio of HNO_3/HDN 18.

As a result, the yield of the Keto-RDX production in method B is grater than method A as well as moderate conditions of method B in comparison with method A. Thus, method B is more suitable than method A in the proposed system for production of Keto-RDX explosive.

3.2 Simultaneous determination of RDX and Keto-RDX using second-derivative spectrophotometric method

As seen from Scheme 1, RDX and Keto-RDX are formed simultaneously. Therefore, there is a need to obtain a suitable method for determination of each component in the mixture. Derivative spectrophotometry has been applied extensively to simultaneous analysis of binary, ternary and quaternary mixtures of substances with overlapping spectra [6-8].

In Figs. 4 and 5, the absorbance and second-derivative spectra of RDX and Keto-RDX in methanol solution are presented. As seen from Fig. 4, the normal absorption spectra of RDX and Keto-RDX have a clear overlapping. The result of second-derivative spectra is that zero-crossing wavelengths of RDX and Keto-RDX at 267 and

293 nm, respectively, can be used for simultaneous determination of RDX and Keto-RDX without any need for separation of these compounds. Therefore, the derivative amplitudes at wavelength of 267 nm are independent of Keto-RDX and can be used to plot the calibration graph for RDX. Conversely, the derivative amplitudes at 293 nm are independent of RDX. Thus, changes in derivative amplitude at this isodifferential point have been measured and plotted against Keto-RDX concentrations.

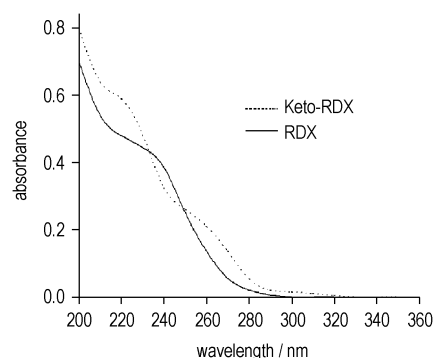


Fig. 4 The UV-Vis absorption spectra of RDX and Keto-RDX in methanol solvent

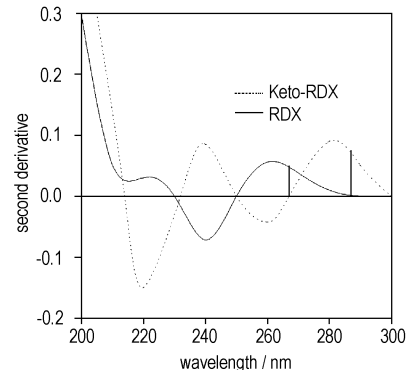


Fig. 5 The second derivative of UV-Vis absorption spectra of RDX and Keto-RDX in methanol solvent

For simultaneous determination of RDX and Keto-RDX in a solution, linear regression analysis of change in second-derivative amplitude at zero-cross over points (in mm) on the respective explosive concentration (mM) at 267 and 293 nm show the following relationship with a good linear fit as evidence by their residue values (r):

$$[\text{RDX}] = A_1 [d_1]_{267} + B_1 \quad (r = 0.9923)$$

$$[\text{Keto-RDX}] = A_2 [d_2]_{293} + B_2 \quad (r = 0.9937)$$

Where A and B are the slope and intercept of calibration curves, respectively, as well as $[d]$ is the second derivative amplitude at zero cross over points (in mm).

Based on the stability of isodifferential points at 267 and 293 nm over a large concentration range, linear plots were obtained for RDX and Keto-RDX concentrations in the range 2.0×10^{-6} – 2.0×10^{-4} M of each compounds in the presence of $0 - 2.0 \times 10^{-4}$ M of the other compounds as an interfering component.

As a result, without need to use an expensive instrument such as HPLC, RDX and Keto-RDX, in an explosive mixture can be determined, simultaneously, using a simple and inexpensive method.

3.3 Theoretical determination of performance, shock sensitivity and gas phase heat of formation of Keto-RDX as compared to RDX

Calculated detonation velocity and pressure of Keto-RDX are 9.15 km/s and 368×10^5 Pa, respectively. Molecular structure of Keto-RDX was used to predict detonation velocity and pressure^[9-10]. Meanwhile, measured detonation velocity and pressure for RDX at its crystal density are 8.75 km/s and 347×10^5 Pa^[11]. This confirms previous investigation of Keto-RDX^[12] that inclusion of extra oxygen can increase significantly the performance of Keto-RDX with respect to RDX.

Detonation temperature is not well resolved measurements in contrast to detonation velocity^[13]. Fortunately, it can be predicted with good reliability with some well-developed new methods^[14-16]. Predicted detonation temperatures for Keto-RDX and RDX are 4587 and 4180 K^[16]. Higher detonation temperature of Keto-RDX is consistent with its detonation performance. Moreover, extra oxygen can produce more carbon dioxide with higher heat of detonation^[17].

Since factors in the impact experiment that might affect the formation and growth of hot spots could strongly affect the measurements as well as reported data of impact sensitivities are extremely sensitive to the conditions under which the tests are performed^[18], the results of impact sensitivity are often not reproducible but reliable shock sensitivity tests exist. For shock initiated studies, the collection of information has been gathered by NSWC using Navy small scale gap test^[19]. A new method has been recently introduced for reliable estimation shock sensitivity based on small scale gap test as the pressure required for initiating material pressed to 90%, 95% and 98% of theoretical maximum density^[20]. For nitra-

mines, two essential parameters have predominant effects which include distribution of oxygen between carbon and hydrogen to form carbon monoxide and water as well as the existence of nitramine groups^[20]. Predicted results for Keto-RDX pressed to 90%, 95% and 98% of theoretical maximum density are 5.95, 10.64 and 16.87 kbar, respectively, which are smaller than that of measured values for RDX (corresponding data are 10.97, 15.77 and 20.35 kbar^[19], respectively). As can be seen, increasing of oxygen balance in Keto-RDX can improve its sensitivity. However, high sensitivity of Keto-RDX is one of the shortcoming of this energetic compound that should be considered for its application in explosives industry.

Group additivity methods and quantum mechanics as well as some new methods^[21-22] are different procedures for calculation of gas phase heat of formation of energetic compounds. Predicted gas phase heat of formation by a new empirical method and PM3 semi-empirical molecular orbital methods are 4.7 and 8.0 kcal, respectively. As compared to experimental data of heat of formation for RDX (45.7 kcal/mol), we can observe that heat content of Keto-RDX in gas phase is less than RDX. This may be attributed to the existence of carbonyl group in Keto-RDX.

4 Conclusion

The use of cheapness materials and simplicity of the methods are the advantages of the synthesis method in this work. Although, the RDX explosive as well as Keto-RDX is a major product, but it should be noted that RDX also is a valuable explosive.

To determine Keto-RDX in presence of RDX, a simple method was also introduced. Detonation velocity and pressure at maximum nominal density as well as detonation temperature for Keto-RDX is relatively high than corresponding RDX values. Shock sensitivity of Keto-RDX is higher than RDX which is consistent with its oxygen balance. Calculated gas phase heats of gas formation for Keto-RDX with respect to RDX have shown that Keto-RDX in gas phase is thermodynamically more stable than RDX.

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Synthesis and Characterization of Energetic Konjac Glucomannan

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Abstract: Using Konjac glucomannan as the raw material, energetic glucomannan (EKGM) was synthesized in the mixture of fuming nitric acid, concentrated sulfuric acid and phosphoric anhydride, and was characterized by elementary analysis, FTIR, SEM, XRD and TG-DSC. The results indicate that the nitrogen content of EKGM is 13.59% due to the presence of —ONO₂, and crystallinity is higher than that of original KGM because of a loose network structure and the decomposition temperature is 161 °C with a high exothermic peak.

Key words: materials science; energetic materials; Konjac glucomannan; water resistant; modification