Identification of initial decomposition reactions in liquid-phase HMX using quantum mechanics calculations

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ABSTRACT

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, (HMX), also known as octogen, is a commonly used ingredient in solid propellants and explosives. As a result, many experimental and theoretical studies have investigated HMX to elucidate its liquid-phase and gas-phase decomposition behavior. In various experimental efforts, including both fast and slow thermolysis, the results indicate that ring opening occurs very early due to the presence of carbon-containing species, such as HCN, H_2CO, HNCO, CO and CO_2. After a lengthy search using quantum mechanics, ring-opening and subsequent reactions have been identified which may occur in both liquid and gas phases. Two existing pathways – 1) HONO elimination and 2) N–NO_2 homolysis – are re-examined for liquid-phase decomposition, and early ring-opening reactions have been identified. Three additional pathways – 1) reaction with NO and formation of ONTNTA, 2) prompt oxidation via HONO and $ONNO_2$ addition, and 3) hydrogen abstraction via NO_2– are also identified along with early ring-opening reactions in each pathway. The proposed pathways for decomposition of HMX are similar to that of RDX presented earlier [37]. The quantum mechanics calculations are performed using density functional theory (DFT) at the B3LYP/6-311++G(d,p) level. Conductor-like Polarizable Continuum Model (CPCM) is used to account for solvation effects with water as solvent within the Gaussian program package. Intrinsic reaction coordinate calculations have also been performed to verify that the reactants are indeed connected to the expected products. Similar to RDX, HONO elimination appears to be the initiation reaction followed by early ring-opening reactions. Results also indicate simultaneous formation of formaldehyde and N_2O from early ring-opening reactions. Competing bimolecular reactions with NO_2, HONO and $ONNO_2$ are also investigated in the liquid phase, which explain the experimentally observed autocatalytic behavior. These reactions can assist in the development of a detailed liquid-phase chemical kinetics mechanism of nitramine propellants containing RDX and HMX.

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1. Introduction

The cyclic nitramines RDX and HMX are used as energetic ingredients in various applications, such as rocket propellants and explosives, since a large amount of energy is released during their combustion. These ingredients are relatively stable and environmentally friendly. Thus, these nitramines have been the subject of many experimental and theoretical investigations with a focus on their use as a solid propellant [1–5] or an explosive ingredient [6–8]. Multiphase combustion modeling of RDX is presented in [1,2] whereas recent advances in ignition and combustion modeling of various solid propellant ingredients including RDX and HMX are reviewed in [3]. The ignition and combustion characteristics of cyclic nitramines are investigated in [4,5]. Tarver and Tran [6] used global multistep chemical kinetics models to investigate the ef-

fect of endothermic and exothermic binders on times to thermal explosion in HMX-based plastic bonded explosives. Phase-change and thermal decomposition kinetics were studied using Los Alamos radial cook-off test [7]. Thermal ignition and cook-off studies of HMX and HMX-based plastic explosives were also performed using Sandia instrumented thermal ignition (SITI) apparatus [8]. Critical analysis of the products from thermal decomposition of RDX and HMX is comprehensively reviewed in [9–11] and equation of state based thermodynamic models were recently developed for liquid HMX as well as four solid polymorphs (α-, β-, γ-, and δ-HMX) [12]. From these studies, it is evident that a knowledge of their chemical kinetics during thermal decomposition is of considerable importance, as it relates to the stability of the material and may be helpful in understanding ignition, combustion and detonation characteristics as well as developing novel propellants.

The four-step global decomposition model of HMX [6] has extensively been used to study ignition and cook-off in HMX, and results have been compared with the one-dimensional time to

explosion (ODTX) experiments [13,14] and scaled thermal explosion experiments (STEX) [15]. The first step in these global chemical kinetics models is solid–solid phase transition from β- to δ-HMX, which has been experimentally investigated by Henson et al. [16] and Brill and Karpowicz [17]. Second step describes the initial ring and bond-breaking endothermic processes via decomposition of δ-HMX to solid intermediates, which subsequently form gaseous intermediates modeled as step three. Most of HMX's chemical energy is released during the gas-phase formation of the final stable reaction products by second-order gas-phase reactions between the gaseous intermediates. The calculated times to explosion are in good agreement with the measured values [6]. However, the times to explosion measured at temperatures exceeding 558 K, the liquefaction temperature of HMX, are under-predicted by the four-step model. Above its melting point, RDX is known to exhibit faster decomposition, but little is known about HMX. The four-step global decomposition model does not include the melting and possible increased reaction rates for liquid HMX due to the lack of chemical kinetic data, but the authors have suggested to include it in more complex models.

Though the four-step global decomposition mechanism of HMX by Tarver and Tran [6] is able to accurately capture times-to-explosion during thermal ignition pertinent to explosives, it is not adequate for predictive modeling of burning characteristics of a complex reacting, multi-phase transport system relevant to solid-propellant ignition and combustion. A detailed chemical kinetic model is required for accurate prediction of the flame structure and the burn rate characteristics. This is reasonable because the conversion of RDX and HMX, with 20–30 atoms/molecule with several types of functional groups, into a few diatomic and triatomic reaction product molecules such as NO_2, N_2O, CO, CO_2, and HCN etc. requires considerable rearrangement which cannot be captured accurately by a four-step global mechanism. These global chemistry models have been developed for simulation of detonation. Such models are of limited use in simulation of deflagration.

Various groups have formulated theoretical models for studying deflagration of HMX with a focus on its application as a rocket propellant ingredient, such as burning rate prediction using eigenvalue method [18], HMX/GAP pseudo propellant combustion [19], three phase model for HMX combustion [20] and laser induced ignition modeling of nitramine propellants [21,22]. In these models, the entire combustion-wave structure is divided into three regions: solid phase, near-surface two phase, and gas phase. One-dimensional transient conservation equations for mass, momentum, energy and continuity of species are solved. Condensed phase, which consists of both solid-phase and near-surface two phase, is typically represented by two global reactions based on the work of Brill [23]. Detailed chemical kinetics mechanism is used in the gas-phase proposed by Yetter et al. [24]. Recently, the gas-phase chemical kinetics mechanism for nitramines was updated by Chakraborty et al. [25]. The RDX gas-phase mechanism of Yetter and coworkers [18,24] was added to the GRI mechanism [26] by carefully removing the redundant reactions. The nitromethane mechanism of Melius [27] was added to include nitromethane initiation reactions. Finally, they added reactions of RDX [28] and HMX [29], which resulted in an overall gas-phase mechanism consisting of 89 species and 462 reactions. However, most of the theoretical studies have investigated gas-phase unimolecular reactions only, and the liquid-phase decomposition is still represented by global reactions [1–3,21]. Hence, liquid-phase chemical kinetics including the bimolecular reactions needs further studies.

A wide variety of products are formed during thermal decomposition of HMX depending on the experimental conditions such as heating rate, sample size and environment [30–32]. The common decomposition products include small mass fragments such

as HCN, NO, N_2O, NO_2, CO, CO_2, H_2O, CH_2O etc. Experimental identification of initial reaction products and elucidation of reaction mechanism is a difficult task due to the great number of species observed and structural complexity of the reactant. However, based on final products, various decomposition pathways have been proposed by theoretical studies [29,33,34]. These pathways fall into four categories – 1) Concerted symmetric ring fission to four methylene nitramine molecules, i.e., CH_2NNO_2 2) N–NO_2 bond dissociation 3) C–N bond scission of the ring, and 4) HONO elimination.

The barrier for concerted symmetric ring fission is 71.8 kcal/mol in the gas-phase as calculated by Lewis et al. [33]. The C–N bond distance at the transition state is relatively large, and steric effects in the condensed phase would inhibit this reaction. This physical constraint coupled with a relatively large barrier indicates that this pathway is very unlikely in the condensed phase. The second pathway is N–N homolytic bond cleavage to form NO_2 and a radical intermediate HMR, which undergoes subsequent reactions [29]. The bond dissociation energy is estimated to be about 40 kcal/mol [29,33]. However, the backward reaction, i.e., radical recombination has no barrier. Hence, due to the barrierless reverse reaction, this step probably does not play a significant role in the condensed phase.

In the third pathway involving C–N bond scission of the ring, oxygen migration takes place from nitro group to the neighboring carbon atom leading to the formation of intermediate INT296. However, the barrier for this reaction is 55.3 kcal/mol in the gas phase [29]. Hence, we believe HMX is unlikely to undergo this reaction as well. In the fourth pathway, the barrier for HONO elimination is 44.6 kcal/mol in the gas phase [29]. This HONO elimination step leads to the formation of intermediate INT249 (HMX$_{-HONO}$) and HONO. Chakraborty et al. [29] considered successive HONO elimination in the gas phase from INT249 to form INT202 (HMX$_{-2HONO}$) which forms INT155 (HMX$_{-3HONO}$) and ultimately INT108 (HMX$_{-4HONO}$) after four successive HONO eliminations. Similar barriers for these HONO elimination reactions in liquid-phase are confirmed by the present study.

However, time evolution of final products from the experimental study [35] indicates early ring-opening reactions due to the presence of carbon containing species such as HCN, CH_2O, CO and CO_2. Also, HMX can decompose via various other pathways as evident from the wide variety of decomposition products observed experimentally, such as amides [36], which cannot be explained through simple unimolecular reactions. Behrens and Bulusu [35] used simultaneous thermogravimetric modulated beam mass spectrometry and isotope scrambling experiments to study thermal decomposition of RDX and HMX, and proposed four primary reaction pathways for condensed phase HMX as discussed below:

I. The first decomposition pathway is N–N bond cleavage, which results in the formation of NO_2, CH_2N and three methylenenitramine (CH_2NNO_2) molecules. CH_2N reacts with CH_2O to form amides such as CH_3NHCHO whereas NO_2 reacts with CH_2O to form H_2O, CO and NO. CH_2NNO_2 can decompose to HCN and HONO or CH_2O and N_2O.

II. The second pathway involves displacement reaction where NO_2 on HMX is replaced by NO leading to the formation mononitroso analogue of HMX, i.e., 1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocine (ONTNTA), which further decomposes to NO_2, N_2O, CH_2O and amides.

III. In the third pathway, HMX undergoes HONO elimination, and subsequently decomposes to HCN, HONO, NO, NO_2 and H_2O via methylenenitramine (CH_2NNO_2) molecule and HONO self-reaction.