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D. Chakraborty, R. Muller, S. Dasgupta, W. Goddard III

A Detailed Model for the Decomposition of Nitramines: RDX and HMX

Debashis Chakraborty, Richard P. Muller, Siddharth Dasgupta and
William. A. Goddard III *

Materials and Process Simulation Center
139-74 Beckman Institute

California Institute of Technology, Pasadena, CA-91125

Abstract:

A unified decomposition scheme for two very important cyclic nitramines used as primary explosives - RDX and HMX - has been constructed using ab initio Density Functional Theory (DFT) calculations. Molecular parameters such as vibrational frequencies and moments of inertia corresponding to the computed potential energy profile of unimolecular decomposition of these nitramines were then used to obtain the thermochemistry of all identified species and reaction rate constants of each individual channel. These primary decomposition reactions were then combined with:

- i) important secondary reactions of the key reactive radical intermediates, such as CH_2NNO_2 (Methylene Nitramine MN), CH_2N , NO , NO_2 , OH *etc.*
- ii) existing nitramine reaction networks (Yetter 1997).

We have developed an improved mechanism for the detailed chemistry of nitramines which can be applied to combustion and detonation phenomena of this class of energetic materials.

I. Introduction:

Cyclic nitramines, namely RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) are important energetic materials which release large amount of energy upon bulk decomposition. These are widely used from automobile air bags to rocket propellants and explosives. Thermal decomposition of these energetic materials has been observed to form very simple final product molecules such as HCN , NO , N_2O , NO_2 , CO , CO_2 , H_2O , H_2CO , *etc.* Understanding the underlying complex chemical processes is essential to obtain to an improved model for combustion or detonation of these energetic materials.

A number of experimental studies¹⁻⁵ have been done to elucidate the mechanistic

details of the thermal decomposition of RDX and HMX and various *plausible* reaction pathways have been proposed. Reported decomposition products vary greatly on the experimental conditions such as heating rate, sample dimensions and the composition of the surrounding matrix. Unambiguous identification of the primary decomposition products is difficult. In order to aid the determination of the initial steps of decomposition for these studies, mostly in condensed phase, we recently focused on the simpler gas phase primary and secondary decomposition of RDX and HMX using *ab initio* DFT methodology.^{6,7} The unified description helps us understand the formation mechanism of the key reactive radical intermediates such as MN, CH₂N, NO, NO₂, N₂O, OH etc. identified in the early stage of combustion or detonation of these nitramines.

Significant progress has been made in recent years in modeling the combustion chemistry of nitramines.⁸⁻¹³ However, most of these models are based on an assumed primary decomposition mechanism which provides estimated initial gas phase species concentrations. Moreover, the rate constants for the fragmentation of these large molecules and radicals are not known due to inherent experimental difficulty in monitoring these metastable species in the gas phase. Furthermore, no single kinetics experiment can cover the entire range of temperature and pressure that is relevant for combustion or detonation conditions. Thus in the present study, we have estimated the rate constants of the primary and secondary reactions of RDX and HMX in order to obtain an improved detailed chemistry model for this class of compounds. Theoretical studies on individual species and reactions, which provide the elemental input parameter necessary for development of the mechanism, is an important component of such model. The results of these calculations are reported here.

II. Computational Details:

B3LYP^{14,15} flavor of DFT in conjunction with 6-31G(d) basis set was used to evaluate the potential energy profile of the decomposition of RDX and HMX in our previous studies.^{6,7} Molecular parameters (vibrational frequencies, moments of inertia *etc.*) corresponding to the computed PES were then used to evaluate the rate constants for each individual reaction channel using Transition State Theory (TST) and Rice-Ramsperger-Kassel-Marcus (RRKM) theory.¹⁶ According to the RRKM theory, the

micro canonical rate constant for a unimolecular reaction at fixed energy E is given by,

$$k(E) = \frac{N^\#(E)}{h\rho(E)} \quad (1)$$

where $N^\#(E)$ is the sum of states at transition state and $\rho(E)$ is the density of states of the reactant. The unimolecular rate constant can be obtained by thermal averaging of the microscopic rate constant $k(E)$, at high pressure limit which becomes same as the conventional TST rate constant –

$$k(\text{uni}) = \frac{kT}{h} \frac{Q^\#}{Q} \exp\left(-\frac{E_0}{RT}\right) \quad (2)$$

where $Q^\#$ and Q are the partition function for the transition state and the reactant respectively and E_0 is the activation barrier for the reaction.

Since many of the radical association/dissociation reactions do not have a well-defined transition state (TS) because of the absence of reaction barrier, variational calculations have also been carried out. According to the variational theory, the rate constant k at a particular temperature T corresponds to the position of the dividing surface associated with the maximum free energy ($\Delta G^\#$).¹⁷ ΔG along the reaction coordinate was computed at temperatures in the range 500 - 2500 K to locate the position of the maximum at each temperature accurately. All molecular parameters corresponding to the structure at the maximum $\Delta G^\#$ for each temperature were then used in RRKM calculations for the association or dissociation rate. The pressure dependence of each unimolecular reaction was obtained by solving the master equation.¹⁶ The master equation in matrix form can be written as

$$-k_{\text{uni}} \mathbf{g} = \mathbf{J} \mathbf{g} \quad (3)$$

where \mathbf{g} is the eigenvector corresponding to the largest eigenvalue k_{uni} . The elements of the matrix \mathbf{J} are pressure dependent and hence the thermal rate constant obtained by solving eq. 3 is also pressure dependent.

III. Results :

III. A. Unified primary decomposition of RDX and HMX. The unified primary decomposition mechanism of RDX and HMX proposed by us recently^{6,7} is shown in Figure 1. The mechanistic details of the overall decomposition scheme including

structure, energy of key radical species and their comparison with available experiments have been compiled in detail in our earlier works. Molecular structure of all the reactive intermediates and products included in Figure 1 were described. Here a brief discussion of the overall mechanism is outlined since this will be the basis of our discussions in the following sections.

1. RDX can primarily decompose in four different pathways, a) concerted breaking to 3 MN molecules, b) N-NO₂ homolysis leading to the formation of MN, MNH, INT56¹, NO₂, CH₂N, HCN *etc.* c) successive HONO elimination to form HCN, OH and NO and d) oxygen migration from NO₂ to the neighboring C atom leading to the formation of MN, CH₂O and N₂O.
2. Two main primary decomposition pathways were identified for HMX, a) N-NO₂ homolysis leading to the formation of similar products MN, MNH, INT56, NO₂, CH₂N, HCN b) successive HONO elimination leading to HCN, OH and NO. No concerted decomposition pathway leading to 4 MN molecules has been identified for HMX.
3. Formation of RDR-o (the ring open structure of the radical RDR, obtained after elimination of first NO₂ group from RDX) from HMX N-NO₂ homolysis pathway and formation of INT222 (ring open RDX) from HMX via oxygen migration and N-NO₂ homolysis pathway connect the decomposition mechanisms of RDX and HMX.
4. Successive HONO eliminations leading to the formation of TAZ from RDX and INT108 from HMX were the only exothermic pathways in the overall primary decomposition scheme. Decomposition of RDX and HMX to HCN and HONO (and OH + NO on further decomposition) was also considered as one of the most important global reactions for nitramines, both from experimental⁴ and theoretical⁹ point of view.
5. The unified decomposition scheme presented in Figure 1 can successfully account for the key reactive species identified in the initiation stage of combustion experimentally¹⁻⁵ or by theoretical modeling,⁸⁻¹³ which corresponds mainly to gas phase chemistry at the burning surface. Gas phase chemistry is indeed important because it produces the bulk of the energy release.

¹ We have used the notation INTxxx for some of the intermediates where xxx stands for the molecular weight. This helps the correspondence with the observed fragments in mass spectrometric studies.

III. B. Rate constants for the primary decomposition reactions: The rate constants for the important primary and secondary reactions for RDX and HMX are shown in Table 1. Figure 2 shows rate constants of the major initiation reactions for RDX and HMX as functions of temperature.

Four important initiation channels have been identified for RDX decomposition as shown in Figure 2a. The computed barriers for the first NO₂ elimination to form RDR and first HONO elimination to form INT175 from RDX are comparable (39.0 and 39.2 kcal/mole respectively). However, the rate constant of the first reaction is higher because of the large pre exponential factor associated with the loose transition state. Rate constants for other two initiation processes, namely concerted breaking of RDX to 3 MN molecules and migration of NO₂ oxygen to the neighboring carbon atom to form CH₂O and N₂O via the formation of RDX-oring are relatively small at low temperature. At very high temperatures (~2500 K) the concerted breaking becomes the dominant reaction. This reaction has been considered as the most important unimolecular process in the infrared multi photon dissociation (IRMPD) study of RDX in a molecular beam.¹⁸ Figure 2a clearly shows that if the energy deposited by the laser beam in the IRMPD experiment was sufficient to access all these four initiation channels, the concerted breaking would be the dominant channel because of the large A factor. On the other hand, the direct CH₂O + N₂O formation reaction is the least favorable channel even at higher temperatures. Since these products have been identified as important in condensed phase, secondary decomposition of MN or some other inter molecular reactions might be responsible for their production in condensed phase.

The NO₂ elimination reaction does not have a well-defined transition state and hence the rate constants are computed using variational TST. Figure 3 shows the pressure dependence (fall-of curve) of this reaction rate constant at 1000 K. This is typical of barrier-less homolytic dissociation reactions, which are known to exhibit strong pressure dependences. Figure 3 clearly shows that at ~100 atm. and higher pressures, the rate constant approaches the high- pressure limit.

All important unimolecular reactions of RDX primary decomposition are tabulated in Table 1. Each individual unimolecular decomposition reaction rate constant [the general form of which is: $k_{uni} = A \times T^n \times \exp(-E_0/RT)$] is presented in three column

format (pre exponential factor(A), temperature coefficient(n) and activation energy(E_0)) used by the CHEMKIN²² program. Many of the unimolecular reaction rate constants have pre-exponential factors larger than predicted from collision theory due to the loose nature of the associated transition states. The N-N homolysis reaction has a pre-exponential factor of $\sim 3 \times 10^{15} \text{ sec}^{-1}$ while the HONO elimination reaction has $\sim 1.98 \times 10^{14} \text{ sec}^{-1}$.

Two major initiation reactions have been identified for HMX as shown in Figure 2b. The NO_2 elimination is the dominant reaction in the entire temperature range because of its low activation barrier and large pre-exponential factor compared to the HONO elimination. Because of the absence of concerted breaking of HMX to 4 MN molecules and the high barrier of the oxygen migration channel, the initiation of HMX decomposition is dominated by the N-N homolysis reaction for both thermodynamic and kinetic reasons. Formation of RDR-o in the HMX N-N homolysis pathway connects it to the decomposition reaction network of RDX. Our computed rate constant for the NO_2 elimination reaction compares well with the one recently reported by Zhang and Truong for α HMX.¹⁹ The rate constants for successive HONO eliminations from HMX to form INT108 and 4 HONO molecules and further dissociation of INT108 to 4 HCN are also tabulated in Table 1.

III. C. Decomposition of secondary products and secondary reactions:

Important products identified in the primary decomposition of RDX and HMX are MN, MNH, INT56, CH_2N etc. These reactive species can undergo further decomposition or reactions with other radical species such as NO, OH, NO_2 etc. These secondary dissociation and association reactions constitute the gas phase flame chemistry of RDX and HMX combustion. In the existing nitramine combustion models⁸⁻¹³ many of these reactions have been identified as important in different zones of the flame. Consider the CH_2N radical for example. This methyleneamino (CH_2N) radical is a key reactive intermediate in the combustion of RDX and HMX in their early stages. Our primary decomposition mechanism (Fig. 1) clearly shows that this radical could form directly from the fragmentation of RDX and HMX or indirectly from the decomposition of MN. In recent kinetic simulation studies of RDX combustion many important bimolecular

reactions of this pivotal radical with NO, NO₂, N₂O etc have been identified as key processes that control the chemistry in the dark zone.⁸⁻¹³

Thus an improved description of the kinetics and mechanism of these secondary dissociation/association reactions is important for the development of a detailed reaction network model. We added the computed rate constants for these early stage secondary reactions from the recent compilation of Chakraborty and Lin²⁰ to our detailed mechanism. These newly computed rate constants constitute an improvement over the assumed rate constants used in the existing models. For example, in the recent paper by Yetter *et al.*¹⁰ the direct abstraction reaction between CH₂N and N₂O leading to CH₂NO + N₂ had an assumed small activation barrier of 6.0 kcal/mole. Our computed barrier for this reaction is 42.4 kcal/mole.²¹ These secondary dissociation or association reaction rate constants were computed using a coupled channel RRKM approach.²³ The CH₂N + NO₂ → HCN + HONO and CH₂NO + NO reactions have negative activation barriers (see Table 1), typical for this type of radical association reactions. These secondary reactions also account for the formation of stable molecules such as N₂, H₂O etc in the early stage combustion of RDX and HMX.

IV. Discussions:

IV. A. Development of a Detailed Mechanism : Figure 4 shows a flow diagram of our approach. There has been many attempts to develop a balanced mechanism for nitramine combustion in recent years.⁸⁻¹³ Our approach starts from these existing network models. We have incorporated many reaction rate constants from *ab initio* calculations for the characteristic primary and secondary reactions of RDX and HMX.

A complete description of the nitramine mechanism should consist of:

- i) A good description of the primary and secondary reactions of RDX and HMX
- ii) HCN, NO₂, N₂O and CH₂O chemistry: CO oxidation, CH₂O oxidation, HCN oxidation *etc.*
- iii) H₂, NO, NO₂ and NH₃ chemistry: this relates nitramine with ADN chemistry. This also includes decomposition of NO₂ and N₂O.
- iv) Carbon chemistry related to binder.

Steps ii to iv are well established. The GRI mechanism²⁴ which adequately

describes the C, H, N, O chemistry is our starting point. We then combine the RDX gas phase mechanism of Yetter²⁵ by carefully removing the redundant reactions. Then the nitromethane mechanism of Melius²⁶ is added to include nitromethane initiation reactions. Finally addition of improved primary and secondary reactions of RDX and HMX results in an overall mechanism consisting of 89 species and 462 reactions as shown in Figure 4. Improved thermochemistry (C_p , H, S etc.) based on *ab initio* DFT calculations for all the species identified in the primary and secondary decomposition of RDX and HMX is also added.

The overall mechanism includes all important C, H, N, O reactions related to nitramine chemistry. Since we have taken a hierarchical approach to develop the overall mechanism, most of the reactions identified via sensitivity analysis²⁷ as important reactions for RDX/HMX burning are included in the present mechanism. Moreover, an improved description of many of the existing reactions (such as the one related to ADN chemistry) based on *ab initio* DFT calculations along with more detailed chemistry of RDX/HMX initiation makes the present mechanism a more complete one. We strongly believe that the present mechanism provides an improved model for RDX/HMX gas phase combustion chemistry.

IV. B. Modeling Detonation Chemistry: A number of hypotheses have been advanced to account for the initial reactions under detonation conditions. Possibilities such as electronic excitation,²⁸ multi-phonon-up-pumping,²⁹ intramolecular vibrational relaxation,³⁰ metallization³¹ etc. have been advanced to account for the sudden onset of chemical reactions within and behind the shock front. However the initiation process first requires a good description of the condensed phase reactions. Initiation due to a shock wave can occur through *inter molecular* reactions in condensed phase. Identification and inclusion of the important *inter molecular* initiation reactions in RDX and HMX will be important. It will also require *unimolecular* reaction rate constants for primary and secondary decomposition reaction of RDX and HMX in condensed phases.

In order to identify the important initiation reactions which trigger the chemistry in presence of a shock wave in the condensed phase, we have recently carried out simulation of shock induced initiation of RDX detonation using a reactive (Reaxff) force

field.³² Reaxff is a recently developed force field capable of simulating chemical reactions using modified forms of classical potentials. Our preliminary condensed phase simulation identified many of the unimolecular reactions presented in Figure 1. If this is confirmed, then the present mechanism can well describe the chemistry of detonation, provided the energetics and reaction rate constants for these individual reactions are obtained in the condensed environment. An effort is underway using hybrid quantum mechanics and molecular mechanics (QM-MM) approaches.

Supporting Information:

The complete mechanism is available for download from:

<http://wag.caltech.edu/home/rpm/projects/hedm>

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Table 1: Computed rate constants for some important primary and secondary decomposition reactions of RDX and HMX. (Table needs heading for columns)

Primary decomposition reactions of RDX and HMX

Reaction		A-factor	Temp. Coeff.	Act. Barrier Cal/mol
RDX	=> RDR + NO2	.310E+16	0.00	40230.0
RDX	=> 3MN	.374E+17	0.00	62670.0
RDR	=> RDR-o	.224E+14	0.00	27888.0
RDR-o	=> INT176	.112E+11	0.61	8390.0
INT176	=> INT149 + HCN	.312E+15	0.00	18470.0
INT149	=> MN + MNH	.290E+15	0.00	28307.0
RDR-o	=> INT102 + MN	.506E+14	0.00	26200.0
INT102	=> H2CN + MN	.675E+13	0.00	13300.0
RDR	=> INT130 + NO2	.269E+15	0.00	47235.0
INT130	=> MN + INT56	.116E+16	0.00	42504.0
RDX	=> INT175 + HONO	.198E+15	0.00	39924.0
INT175	=> INT128 + HONO	.107E+15	0.00	41514.0
INT128	=> TAZ + HONO	.571E+14	0.00	34650.0
TAZ	=> 3HCN	.725E+17	0.00	93661.0
INT128	=> 2HCN + MN	.102E+17	0.00	68792.0
HMX	=> HMR + NO2	.170E+16	0.00	40270.0
HMR	=> HMR-o	.100E+15	0.00	29000.0
HMR-o	=> RDR-o + MN	.843E+14	0.00	23780.0
HMX	=> INT249 + HONO	.327E+13	0.00	46065.0
INT249	=> INT202 + HONO	.306E+15	0.00	44066.0
INT202	=> INT155 + HONO	.919E+14	0.00	40368.0
INT155	=> INT108 + HONO	.890E+14	0.00	43672.0
INT108	=> 4HCN	.915E+18	0.00	113784.0

*Secondary dissociation/association reactions**

Reaction		A-factor	Temp. Coeff.	Act. Barrier Cal/mol
MN	=> H2CN + NO2	.246E+16	0.00	34200.0
MN	=> HONO + HCN	.621E+13	0.00	32500.0
MN	=> CH2O + N2O	.452E+12	0.00	38300.0
H2CNNO	=> HCN +HNO	.399E+03	2.66	6756.0
H2CNNO	=> CH2O + N2	.468E+04	1.80	4372.0
H2CNO	=> HCN + OH	.208E+14	0.00	58500.0
H2CNO	=> HCNO + H	.313E+16	0.00	55000.0
H2CN + NO2	=> HCN + HONO	.516E+06	1.54	-1252.0
H2CN + NO2	=> H2CNO + NO	.397E+02	2.65	-5167.0
H2CN + NO2	=> CH2O + N2O	.378E+05	1.57	2186.0
H2CN + N2O	=> H2CNO + N2	.171E+14	0.00	49481.0
H2CN + N2O	=> CH2O + N3	.276E+12	0.00	43321.0
H2CN + N2O	=> CH2N2 + NO	.598E+13	0.00	43718.0
H2CN + NO	=> CH2O + N2	.468E+04	1.80	4371.0
H2CN + OH	=> H2CNOH	.693E+31	-5.96	5365.0
H2CN + OH	=> HCN + H2O	.198E+12	0.0	1769.0

* Taken from ref. 18.

Figure Captions:

Figure 1. A unified decomposition scheme for RDX and HMX.

Figure 2. (a) Arrhenius plots of the rate constants for the four initiation decomposition reactions of RDX. (b) Arrhenius plots of the rate constants for the two initiation decomposition reactions of HMX.

Figure 3. Fall off curve for the N-N homolysis reaction of RDX at 1000 K.

Figure 4. A flow diagram for the hierarchical construction of the overall mechanism.