

Investigation of RDX flame structure at atmospheric pressure using probing mass-spectrometry and modeling.

P.D. Polyakov¹, O.P. Korobeinichev*^{1,2}, A.A. Paletsky², E.N. Volkov², A.G. Tereshchenko²

¹Novosibirsk State University,

²Institute of Chemical Kinetics and Combustion SB RAS,
Novosibirsk, Russia

Chemical structure of RDX flame at 0,1 MPa was investigated using method molecular-beam mass-spectrometric probing of energetic material flames. 12 species including RDX vapor were identified. Concentration profile of RDX vapor was measured in narrow zone, adjacent to the burning surface. Using obtained data modeling of RDX chemical structure was conducted. Experimental data results were compared with modeling results and literature data.

Introduction

Cyclo-trimethylene-trinitramine (RDX) is an energetic material that has been widely used as an oxidizer in composite propellants, producing high specific impulse, but little smoke, toxicity, and corrosion. The main purpose of scientific investigations of this object is creation a computational model which prediction of the combustion behavior may reduce the need for life testing. The main information source for creation a detailed mechanism of chemical reactions, which lays in the basis of such combustion model, is experimental investigation of RDX flame structure.

Combustion of RDX is a complicated two-stage process. The first stage is gasification of RDX – decomposition and vaporization RDX at the burning surface with formation of energy-rich species. These products react with release of stored energy in the second stage, in which formation of flame occurs. A wide variety of reactions involving many species occur in the gas flame until equilibrium is reached in the final flame zone.

The Yetter [2] gas phase mechanisms (45 species and 232 reaction steps) for an RDX flame was published in 1995 after a significant program comparing available kinetics parameters to various known reactions steps and simple flames. It allows to obtain the data on RDX flame structure using given flows of initial products at given temperature as a model boundary condition. This mechanism provided a basis for much of the followed works. The greatest uncertainties within the model are relative to the processes closest to the burning surface.

Zenin [3] experimentally proved, that two processes occur simultaneously in the condensed phase of RDX: evaporation and thermal decomposition. At low pressures (<5 atm) heat balance in the condensed phase (calculated from temperature profiles) is negative (<0) since the heat

absorption of the evaporation is greater than the heat release of the thermal decomposition. Heat feedback from the gaze phase compensates for the lack of heat. At elevated pressures increased heat release of the thermal decomposition produces a positive heat balance.

Most of the models assume that no reactions occur in the solid phase. Prasad et al [4] modeled the gases formed within the condensed phase as dissolved in the liquid, while Davidson et al. [5] and Liao et al. [6] modeled the gases within the condensed phase as bubbles. Liao et al. [6] used a suggestion that in condensed phase two processes occur: RDX evaporation and two condensed phase reactions by which RDX may decompose. The resulting species concentrations at the surface was used as the boundary condition for the gas phase modeling.

However, other ways to describe the processes in the condensed phase for modeling gas phase exist. Korobeinichev et al. [7] have measured the concentrations of main species in RDX flame at 0,05 MPa. at fixed distance (about 0,1 – 0,2 mm) from the burning surface. After that they used these experimentally determined values as a boundary condition feeding into the gas phase equations. Miller et al's [1] approach (based on intuition) consists in the assumption that the gas-phase reactant leaving the surface is all vapor phase RDX. They also assume an Arrhenius pyrolysis law exists relating the mass burning rate to a surface temperature (this assumption is based on Zenin [3] experimental observations).

Experiments on investigation of RDX chemical structure were conducted at self-sustained combustion [1, 8, 9] and at laser-supported combustion [8, 10]. In [1, 8] concentration profiles of OH, NO, CN and NH were obtained. Concentrations of H₂CO and HONO near burning surface were less than 1%. In [9, 11] chemical structure of RDX at 0,05 MPa is presented. In [10] profiles of H₂, H₂O, HCN, H₂CO, NO, HNCO,

* Corresponding author: korobein@ns.kinetics.nsc.ru
Professor, Head of Laboratory
Institute of Chemical Kinetics and Combustion
Novosibirsk, Russia

N_2O , NO_2 , N_2 и CO as well as H_2CNH , HONO , $\text{C}_2\text{H}_2\text{N}_2$, $\text{C}_2\text{H}_4\text{N}_2$, $\text{C}_2\text{H}_2\text{N}_2\text{O}$, $\text{C}_3\text{H}_3\text{N}_3$, $\text{C}_3\text{H}_3\text{N}_3\text{O}$ were measured.

It is important to note that there is no direct experimental evidence presence of RDX vapor near burning surface. The purpose of this work is an experimental investigation of RDX flame structure at 0,1 MPa using method molecular-beam mass-spectrometric (MBMS) probing of energetic material flames. The most attention will be given to determination products compose near the burning surface, especially to identification RDX vapor and to measurement its concentration profile. After that based on obtained data fluxes of products from the burning surface were used as a boundary conditions for RDX flame structure modeling.

Methods of investigations

Method molecular-beam mass-spectrometric probing of energetic material (EM) flames [11] was used to investigate RDX flame structure at 0,1 MPa. This method allows to identify components, which present in a reacting gas mixture, and also to determine its quantitative composition. "Sound" probe was used for sampling products. It provides effective freezing of chemical reactions and possibility of conservation of vapor of substances with high boiling point. It is difficult to do using conventional mass-spectrometric analysis. The sample was delivered in analyzer as a molecular beam, which formed on setup with 3 stage differential vacuum system of pumping. It provides conservation of the sample. After that the sample is analyzed by time-of flight mass-spectrometer. In order to determine the quantitative composition of the sample calibration experiments to obtain mass-spectrum and calibration coefficients of individual species were conducted.

Experiments on vaporization of RDX hangings were conducted in a flow reactor combined with molecular beam sampling system. Flow reactor represented quartz tube of ~ 10 mm in diameter, with evaporator inside. The tungsten plate by thickness of 0.1 mm, width of 1 mm and length of 10 mm heated by electric current was used as a heater and evaporator. Temperature of the plate was measured by chromel-copel thermocouple welded to the plate. Drops of a solution of RDX in acetone were applied on the central part of the plate. After evaporation of acetone at room temperature the crystals of RDX ($< 40 \mu\text{m}$) were formed on the plate surface. The weight of a hanging was less than 1 mg. The probe represented a quartz cone. The tip of the probe was heated to $\sim 200 \text{ }^\circ\text{C}$ to prevent RDX vapor condensation on the inner walls of the probe orifice. The distance between the plate with hanging and probe orifice was ~ 2 mm. The experiments were conducted at atmospheric pressure in a flow (0.8-1.5 ml/sec) of nitrogen or argon. Melting of RDX is accompanied by partial decomposition, therefore specific conditions are necessary to increase vapor

fraction in products of decomposition and evaporation. The sizes of RDX crystals on evaporator at the initial moment of time should be as small as possible. The fast delivery of vapor to a probe and prevention of its condensation in a gas phase was achieved by increase of flow rate of carrier gas and decrease of a distance between evaporator and tip of a probe. For achievement of these conditions the following parameters were varied during the experiments: heating rate and maximal temperature of plate with hanging, temperature and flow rate of carrier gas, and also design of plate and mass of hanging.

The idea of the method of experimental investigation EM flame structure using MBMS is as follows: a burning EM sample moves with velocity exceeding the burning rate toward a probe, so that the probe is continuously sampling products from all the combustion zones, including a zone adjacent to the burning surface.

Aluminum (oxidized) probes was used to investigate RDX flame structure. Wall thickness of the probe was $\sim 70 \mu\text{m}$, and diameter of inlet orifice was also $\sim 70 \mu\text{m}$.

We have conducted experiments on combustion of RDX pellets in argon atmosphere at pressure of 0.1 MPa. RDX pellets with diameter of 8 mm and height of 7-8 mm were used. Density of the pellets was equal to 1.7 g/cm^3 (94% from density of RDX crystals). Ignition was performed using nichrome wire heated by electric current, which was situated at a distance of 0.5-1 mm from pellet surface.

Modeling of RDX combustion was conducted using gas-phase mechanisms for RDX combustion. The starting mechanisms for this data base is from Carl Melius's RDX decomposition mechanism. A large percentage of this mechanism was derived from Miller and Bowman mechanism [12]. It has been updated and expanded using Tsang and Herron data [13]. PREMIX/CHEMKIN software, establishing a standard format that facilitates the solution of the gas phase equation for multiple reactions, was used.

Results and Discussion

In calibration experiments on RDX evaporation intensity of the following mass peaks 14, 27, 28, 29, 30, 42, 44, 46, 56, 75, 120, 128, 148, 222, corresponding to mass spectrum of RDX vapor, were measured (Tabl. 1). The obtained results are in the rather good agreement with literature data [14, 15], where the mass spectrum RDX vapor was measured at thermal decomposition in high vacuum. The basic peaks in a mass spectrum vapor are 28, 30 and 42 masses. Intensities of 75, 46, 29 mass peaks were more than 50 % from intensity of 42 mass-peak. Calibration coefficient for RDX vapor was determined. Data obtained were used for identification RDX vapor, and also for measurement of its concentration in RDX flame.

In all experiments during ignition of RDX a formation of big bubbles on the pellet surface was

Table 1.
Peak intensities in RDX mass spectrum.

| m/e | 14 | 15 | 27 | 28 | 29 | 30 | 42 | 44 | 46 | 56 | 74 | 75 | 120 | 128 | 148 |
|----------|----|----|----|-----|-----|-----|-----|----|-----|----|----|-----|-----|-----|-----|
| 1) | | | | | | | | | 189 | 75 | | 100 | 97 | 189 | 27 |
| 2) | 15 | 23 | 64 | 341 | 185 | 257 | 216 | 27 | 216 | 83 | 30 | 100 | 98 | 106 | 22 |
| Our date | 17 | | 34 | 404 | 129 | 339 | 244 | 51 | 188 | 76 | | 100 | 68 | 54 | 17 |

- 1) Stepanov et. al., evaporation in vacuum, [14]
2) Volk et al., evaporation in vacuum, [15]

Table 2.
Species concentrations (in mole fractions) near the RDX burning surface at different conditions.

| | P, MPa | H ₂ | HCN | NO | N ₂ | CO | H ₂ O | CO ₂ | N ₂ O | HNCO | NO ₂ | CH ₂ O | RDX _v |
|---|--------|----------------|------|------|----------------|------|------------------|-----------------|------------------|-------|-----------------|-------------------|------------------|
| 1 | 0,1 | 0,04 | 0,23 | 0,21 | 0,06 | 0,08 | 0,22 | 0,01 | 0,09 | Ident | 0,04 | 0,03 | - |
| 2 | 0,05 | 0 | 0,22 | 0,22 | 0,08 | 0,05 | 0,25 | 0,07 | 0,05 | 0,025 | 0,025 | - | - |
| 3 | 0,1 | 0,05 | 0,17 | 0,23 | 0,05 | 0,12 | 0,17 | 0,03 | 0,04 | Ident | 0,05 | 0,01 | 0,07 |
| 4 | 0,1 | 0,03 | 0,18 | 0,19 | 0,04 | 0,05 | 0,18 | 0,02 | 0,04 | - | 0,015 | 0,015 | 0,22 |
| 5 | 0,1 | 0,03 | 0,18 | 0,19 | 0,03 | 0,05 | 0,18 | 0,025 | 0,05 | - | 0,015 | 0,025 | 0,5 |
| 6 | 0,1 | 0,02 | 0,12 | 0,17 | 0,07 | 0,05 | 0,19 | 0,02 | 0,06 | - | - | - | 0,7 |
| 7 | 0,1 | 0,02 | 0,15 | 0,15 | 0,06 | 0,06 | 0,19 | 0,02 | 0,04 | - | - | - | - |

- 1) Lee et al., laser-induced combustion of RDX, 100W/cm² [10]
2) Korobeinichev et al. [9];
3) Our data;
4) Miller et al., modeling [1];
5) Liau et al., modeling [6];
6) Melius, modeling [16];
7) Yetter et al., modeling [4].

Table 3
Species concentrations (in mole fractions) near the RDX burning surface at modeling, using different suggestions about percentage of RDX vapor in overall flux.

| Π _{RDX} | H ₂ | HCN | NO | N ₂ | CO | H ₂ O | CO ₂ | N ₂ O | NO ₂ | CH ₂ O | RDX _v |
|------------------|----------------|-------|-------|----------------|--------|------------------|-----------------|------------------|-----------------|-------------------|------------------|
| 100% | 0.027 | 0.18 | 0.183 | 0.0357 | 0.046 | 0.186 | 0.0168 | 0.0372 | 0.0189 | 0.0146 | 0.218 |
| 60% | 0.0289 | 0.179 | 0.19 | 0.0368 | 0.0545 | 0.185 | 0.0185 | 0.038 | 0.0139 | 0.01534 | 0.2 |
| 25% | 0.0325 | 0.176 | 0.2 | 0.041 | 0.076 | 0.18 | 0.0227 | 0.041 | 0.021 | 0.0166 | 0.159 |
| 10% | 0.04 | 0.174 | 0.228 | 0.0476 | 0.11 | 0.176 | 0.028 | 0.041 | 0.039 | 0.013 | 0.096 |

observed. In some experiments these bubbles completely disappeared after ignition of pellet, in others they remain on the pellet surface during the combustion. When bubbles were presented on the burning surface, combustion of pellet was unstable or ceased in several seconds after ignition (incomplete burning of pellet). In other cases (~ 40% of experiments) regular combustion (without bubbles) with burning rate of ~ 0.27 mm/s was observed.

In RDX flame next species were identified: H₂, H₂O, HCN, CH₂O, NO, CO, CO₂, N₂, NO₂, HCNO + HNCO, RDX vapor. Concentration profiles of these species are presented on Fig. 1 and Fig. 3. Mass-peak 42 was identified as HCNO. Calibration coefficient for it was accepted equal to that of HCN. For the first time it was experimentally proved existence a narrow zone of RDX vapor near the RDX burning surface with zone width of ~ 0.16 mm. According modeling [1, 6] width of this zone is 0,07 mm.

Second reaction zone of NO₂, N₂O, CH₂O consumption is wider than zone of RDX vapor decomposition. Third reaction zone is connected with oxidation of HCN by NO and formation of final

combustion products. Zone of complete consumption of HCN comprises about 1 mm. It is in the agreement with data [1, 4, 6, 16] on RDX flame modeling. There is no complete consumption of NO, especially even at a distance of ~ 2 mm. Mole fraction of NO in final combustion products is equal to ~ 0.05 (0.025 according to [1, 4, 6, 16]).

Zone of complete consumption of N₂O comprises about 0,5 mm and 0,25 mm in [1, 4, 6] and in [16] accordingly. Experimental value - 0,3 mm. Zone of complete consumption of NO₂ in [1, 6] comprises 0,1 mm. It is less than experimental value - 0,4 mm. Product composition near RDX burning surface, obtained by different research groups, is given in Tabl. 2. Mole fractions of HCN, H₂O, N₂O, CH₂O as well as width of concentration profiles of main components, which were experimentally measured in this work (self-deflagrating combustion), are less than that in [10] (laser-supported combustion, 100W/cm²). Species concentration near the RDX burning surface in [1, 6] (Tabl. 2) are in good agreement with each other. However mole fractions of NO CO NO₂ are less and RDX vapor is more than those in this work.

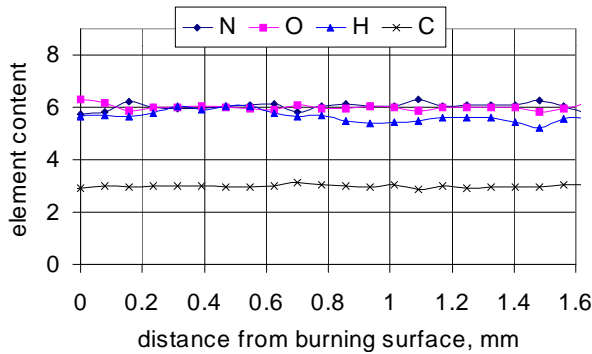
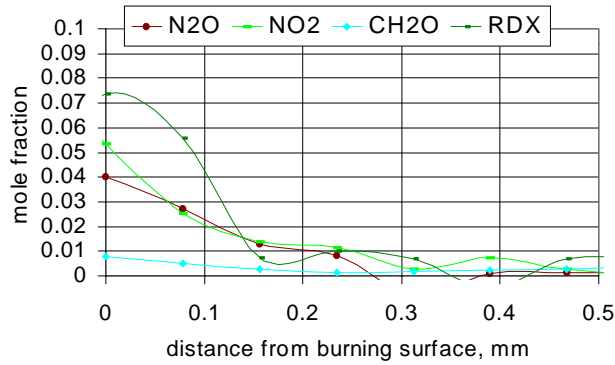
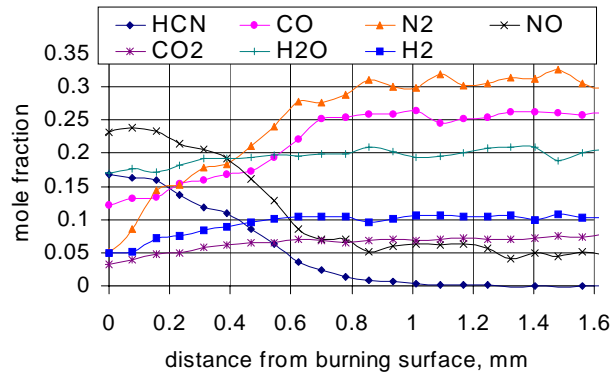


Fig. 1 Species profiles for self-deflagration RDX in argon at 0,1 MPa.

There are some disagreements in mole fractions of HCN and NO near burning surface between experimental data (this work) and data [4, 16].

In [6] modeling of physical-chemical processes in subsurface region of RDX burning surface was conducted. According to this work RDX vapor mole fraction (0,1) near the burning surface does not depend on pressure. This result contradicts Zenin data [30] who suggests, that mole fraction of RDX vapor on burning surface will decrease with pressure increase.

On the basis of the experimental data modeling of chemical structure of RDX flame was conducted. Following nomenclature is used: Π_{RDX} – RDX vapor flux, Π_i – fluxes of other species, $\rho_c v_c$ – overall flux from the burning surface.

A suggestion have been made, that percentage of RDX vapor in overall flux is equal 100, 60, 25 and 10%. Percentages of other species in overall flux proportional concentrations of these species near the

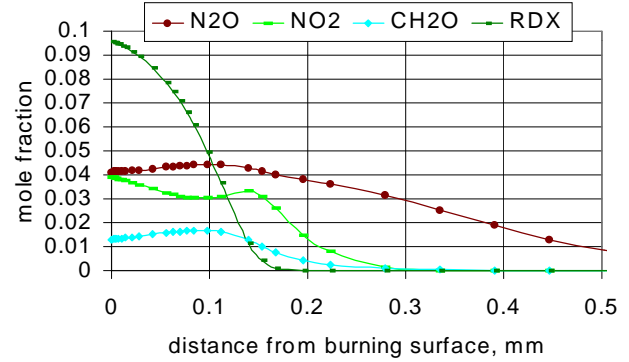
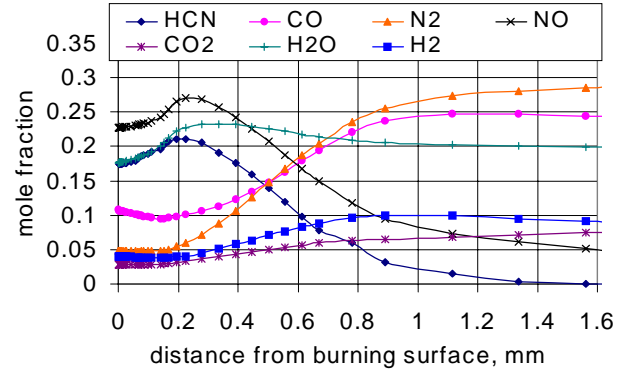


Fig. 2 Species profiles for RDX at 0,1 MPa. (modeling in suggestion that percentage of RDX vapor in overall flux is equal 10%).

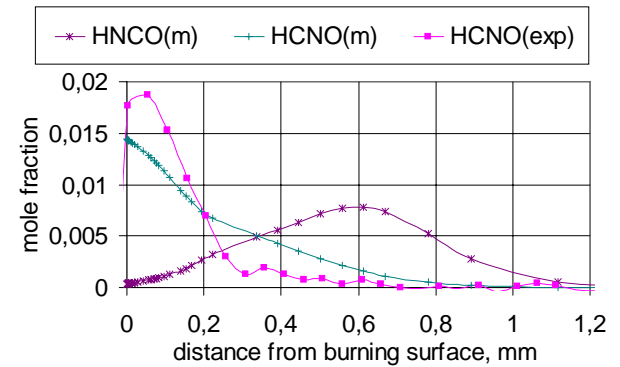


Fig. 3 Mole fraction of HNCO and HCNO in the gas phase of RDX at 0,1 MPa. (exp) – from experiment; (m) – from model).

RDX burning surface determined experimentally in this work. Then:

$$\Pi_i / \Pi_j = v_i / v_j,$$

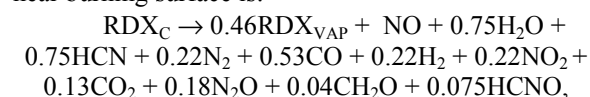
where v_i, v_j – species concentrations near the burning surface determined experimentally.

$$\Pi_{RDX} + \sum \Pi_i = \rho_c v_c.$$

Chemical structure of RDX flame, obtained in assumption that the gas-phase reactant leaving the surface is all RDX vapor, agrees with data [1]. A species concentrations at the burning surface concentrations calculated at modeling at different fluxes of RDX vapor are presented in Tabl. 3. RDX chemical structure obtained using a suggestion that RDX vapor flux is equal 10% of overall flux is presented on Fig.

2. It was determined that decreasing Π_{RDX} allows to achieve better agreement with experimental results. Species concentration of NO, CO, NO₂, RDX_{VAP} on burning surface are in satisfactory agreement with experimental data. Width of reaction zones is 0,07 mm for RDX vapor, 0,1mm for CH₂O, 0,15 mm for NO₂ (in case RDX vapor flux is equal 100% of overall flux) increase and become 0,16 mm for RDX vapor, 0,2 mm for CH₂O, 0,25 mm for NO₂ (in case RDX vapor flux is equal 10% of overall flux). These results are in satisfactory agreement with experimental data. However, widths of reaction zones (Fig. 3) of HCNO+HNCO are not in a good agreement with the experimental data. This disagreement can be eliminated by further improvement of existing combustion model.

Corresponding equation of chemical reaction (in case of RDX vapor flux is equal 10% of overall flux) near burning surface is:



where RDX_C – RDX condensed phase.

Heat release of this reaction is -50 cal/g. According [3] this value is -84 cal/g. The reason of disagreement can consist in errors both at conducting experiment (at thermocouple and mass spectrometric investigations) and at data processing. Elimination of these disagreements - task of the future research.

Conclusions

Chemical structure of RDX flame at 0,1 MPa was investigated using method molecular beam mass spectrometric probing of energetic material flames. 12 species including RDX vapor were identified.

Concentration profiles of RDX vapor and other species were measured in RDX flame. Three zones of chemical reactions were determined. The first and second zone are connected with consumption of CH₂O, NO₂, N₂O and RDX vapor with formation NO, H₂, H₂O, CO and N₂. The third zone is connected with oxidation of HCN by NO with formation final combustion products.

Modeling of chemical structure of RDX flame, using a suggestion that (0% 40% 75% 90%) percentage of RDX vapor may decompose in subsurface region, was conducted. It was determined that this approach allows to achieve better agreement with experimental results not only for composition near burning surface (NO, CO, NO₂, RDX vapor) but also for widths of consumption zones (RDX vapor, CH₂O, NO₂).

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