



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

 ScienceDirect

Proceedings of the Combustion Institute 31 (2007) 2079–2087

Proceedings  
of the  
Combustion  
Institute

[www.elsevier.com/locate/proci](http://www.elsevier.com/locate/proci)

# Flame structure of composite pseudo-propellants based on nitramines and azide polymers at high pressure

Alexander A. Paletsky, Evgeny N. Volkov, Oleg P. Korobeinichev <sup>\*</sup>,  
Alexander G. Tereshchenko

*Institute of Chemical Kinetics and Combustion, Siberian Branch of Russian Academy of Sciences,  
Novosibirsk 630090, Russia*

## Abstract

The chemical and thermal structures of flame of composite pseudo-propellants based on cyclic nitramines (HMX, RDX) and azide polymers (GAP and BAMO–AMMO copolymer) were investigated at a pressure of 1.0 MPa by molecular beam mass spectrometry and a microthermocouple technique. Eleven species  $H_2$ ,  $H_2O$ , HCN, CO,  $CO_2$ ,  $N_2$ ,  $N_2O$ ,  $CH_2O$ , NO,  $NO_2$ , and nitramine vapor ( $RDX_v$  or  $HMX_v$ ), were identified, and their concentration profiles were measured in HMX/GAP and RDX/GAP pseudo-propellant flames at a pressure of 1 MPa. Two main zones of chemical reactions in the flame of nitramine/GAP pseudo-propellants were found. In the first, narrow, zone 0.1 mm wide (adjacent to the burning surface), complete consumption of nitramine vapor and  $NO_2$  with the formation of NO, HCN, CO,  $H_2$ , and  $N_2$  occurs. In the second, wider high-temperature zone, oxidation of HCN and  $CH_2O$  by NO and  $N_2O$  with the subsequent formation of CO,  $H_2$ , and  $N_2$  takes place. The leading reactions in the high-temperature zone of flame of nitramine/GAP pseudo-propellants are the same as in the case of pure nitramines. In the case of nitramine/BAMO–AMMO pseudo-propellants a presence of carbonaceous particles on the burning surface did not allow us to analyze the zone adjacent to the burning surface, therefore only one flame zone was found. Temperature profiles in the combustion wave of nitramine/azide polymer pseudo-propellants were measured at 1 MPa. The data obtained can be used to develop and validate a self-sustain combustion model for pseudo-propellants based on nitramines and azide polymers.

© 2006 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

*Keywords:* Nitramines; Azide polymers; Composite pseudo-propellant; Flame structure; High pressure

## 1. Introduction

Investigation of the combustion mechanism of energetic materials (EMs) is of significant interest from both fundamental and practical points of view. Knowledge of the real physicochemical pro-

cesses involved in combustion is necessary for solving the fundamental problem of developing combustion models for condensed phase systems based on the detailed kinetics in flame zones. The current status of computational methods and tools allows the simulation of combustion of energetic materials at the molecular level. However, in order to develop an adequate combustion model, it is necessary to know the combustion chemistry of EMs. To date most of the knowledge

<sup>\*</sup> Corresponding author. Fax: +7 383 3307350.

E-mail address: [korobein@ns.kinetics.nsc.ru](mailto:korobein@ns.kinetics.nsc.ru) (O.P. Korobeinichev).

on the mechanism and kinetics of chemical reactions occurring during combustion of EMs comes from studies of flame structure. An analysis of data on the structure of solid propellant flames provides information on the composition of the products formed in condensed-phase reactions (thermal decomposition and evaporation). This, in turn, helps to understand the mechanism of chemical reactions in the condensed phase. The product composition near the EM burning surface is an input parameter (boundary condition) for EM combustion modeling. On the other hand, the chemical structure of solid propellant flames provides information on the mechanism and kinetics of the further chemical transformations of gasification products responsible for heat release in gas phase. Development of combustion models for EMs requires detailed knowledge of reactions in both the condensed and gas phases. Without such information it is impossible to create a valid model for solid propellant combustion that would be able to predict propellant burning rate and other ballistic characteristics.

Propellants based on cyclic nitramines (RDX, HMX) and azide polymers [such as glycidyl azide polymer (GAP), 3,3'-bis(azidomethyl) oxetane polymer (BAMO), and 3-azidomethyl-3-methyloxetane polymer (AMMO)] have comparatively high values of specific impulse while generating minimum smoke. Therefore, investigation of these propellants is of considerable interest. There is fairly extensive literature on the combustion of nitramine/azide polymer pseudo-propellants. This paper deals with the combustion of HMX/GAP, RDX/GAP, HMX/BAMO-AMMO, and RDX/BAMO-AMMO pseudo-propellants. The thermal structure of the combustion wave of these pseudo-propellants was studied in Refs. [1,2]. The chemical structure of nitramine/azide polymer pseudo-propellant flames during laser-assisted combustion was investigated by microprobe mass spectrometry at atmospheric pressure in Ref. [3]. At present, combustion models for HMX/GAP and RDX/GAP pseudo-propellants exist and are presented in Refs. [4,5]. However, as noted in [4,5], sufficient experimental data (especially on the chemical structure of HMX/GAP and RDX/GAP flames) are not yet available to validate and improve these models. An alternative combustion model for RDX/GAP pseudo-propellants was proposed in Ref. [6]. Earlier we investigated the chemical structure of HMX/GAP flame during self-sustained combustion at a pressure of 0.5 MPa [7,8].

The main goal of the present work was to study the self-sustained combustion of uncured composite pseudo-propellants based on cyclic nitramines (HMX, RDX) and azide polymers (GAP and BAMO-AMMO copolymer) at pressures of 0.5 and 1 MPa to obtain information on the flame structure of these pseudo-propellants.

Special emphasis was placed on studying a narrow flame zone adjacent to the burning surface in order to determine species compositions and elucidate the presence of nitramine vapor in this zone.

## 2. Experimental

The structure of nitramine/azide polymer flames at pressures of 0.5 and 1 MPa was studied using the molecular beam mass spectrometric (MBMS) system described in Ref. [8], a microthermocouple technique, and video recording. The experiments were performed in high-pressure combustion chambers in an argon atmosphere. Burning rates were determined by visualization of the motion of the burning surface using video recording with accuracy of  $\pm 5\%$  for pseudo-propellants with GAP and  $\pm 10\%$  for pseudo-propellants with BAMO-AMMO.

Temperature profiles in combustion wave of pseudo-propellants were measured using  $\Pi$ -shaped WRe(5%)-WRe(20%) ribbon thermocouples embedded in samples. The thermocouples had a thickness of  $\sim 6$  and  $\sim 14$   $\mu\text{m}$  and a length of shoulders of 1.2 and 3.0 mm, respectively. Temperature measured by thermocouple was corrected for heat loss by radiation. The temperature error in a single experiment was  $\pm 25$  K. Several temperature profiles were obtained for each pseudo-propellant but not all of them were taken into consideration. Reproducibility of selected temperature profiles comprised  $\pm 5\%$ . Video recording allowed us to choose temperature profiles that were measured correctly. A profile was taken into consideration only if (1) the thermocouple shoulders were parallel to the burning surface during its appearance in the gas phase and (2) the thermocouple surface was not covered by any residue, particles, etc.

Probing mass spectrometry is one of the most effective and universal experimental techniques for investigating the chemical structure of solid propellant flames. The possibility of using probing mass spectrometry at high pressures was substantiated earlier for the case of HMX/GAP burning at 0.5 MPa [7,8]. Quartz "sonic" probes with orifice diameter of  $\sim 15$   $\mu\text{m}$  and with an internal cone angle equal to  $\sim 40^\circ$  were used. However, with an increase in pressure from 0.5 to 1 MPa, the analysis of the flame structure of nitramine/azide polymer pseudo-propellants becomes more complicated. First of all, as the pressure increases, the width of the flame zone decreases. This implies that at a pressure of 1 MPa, it is necessary to use probes of smaller wall thickness (in order to minimize the distortion of the flame structure due to thermal influence of the probe). Therefore, at a pressure of 1 MPa, the flame structure was examined using probes of reduced wall thickness (0.15 mm). Second an increase in pressure from

Table 1

Main characteristics of pseudo-propellant ingredients: HMX, RDX, GAP, and BAMO–AMMO copolymer

Name	HMX	RDX	GAP	BAMO–AMMO copolymer
Formula	$C_4H_8N_8O_8$	$C_3H_6N_6O_6$	Brutto— $C_{60}H_{104}O_{21}N_{54}$	$C_{10}H_{17}N_9O_2$
MW (g/mole)	296	222	2000 <sup>a</sup>	2700 <sup>a</sup>
Density (g/cm <sup>3</sup> )	1.9	1.81	1.275	1.21
Enthalpy of formation (cal/g)	71.0 [9,10]	76.6 [9]	146	284.2 [11]

<sup>a</sup> Weight-average molecular weight (MW).

0.5 to 1 MPa leads to an increase in the burning rate (for example, from 0.96 to 1.62 mm/s for HMX/GAP) and, hence, to a decrease in the time available for flame probing. The residence time of the probe tip in the flame was less than 0.6 s.

The procedure used to calibrate the MBMS system for gaseous species was described in detail in Refs. [7,8]. Accuracy of determination of calibration coefficients for most of gas species was equal to  $\pm 5\%$ , for  $H_2O$ , HCN, and  $NO_2$ — $\pm 10\%$ , and for nitramine vapors— $\pm 15\%$ . It was a challenge to generate HMX and RDX vapor at atmospheric pressure and to measure their calibration coefficients. The calibration coefficients for HMX vapor and RDX vapor were determined as described in Refs. [7,8]. The values of the calibration coefficients are important for the correct determination of the species concentration near the burning surface of nitramine pseudo-propellants. Therefore, in the future we plan to perform calibration experiments by another method in order to check these values.

The main characteristics of the pseudo-propellant ingredients are presented in Table 1. The mass fractions of nitramine and azide polymer in the pseudo-propellants were 80% and 20%, respectively. Uncured pseudo-propellant compositions were used. Pseudo-propellant samples were prepared by mixing a bimodal crystal nitramine powder (a coarse fraction with a particle size of 150–250  $\mu m$  and a fine fraction with a particle size less than 20  $\mu m$  in a 50/50 wt% ratio) and azide polymer. The BAMO–AMMO copolymer (B–A) in mole ratio 1:1 was used. The pseudo-propellant samples were 6 mm in diameter, and their height was 3–4 mm in mass spectrometric measurements and 8–10 mm in temperature measurements. The main characteristics of the pseudo-propellants studied are given in Table 2. Experimentally measured densities of the pseudo-propellant samples were close to the corresponding theoretical maximum densities (TMD).

### 3. Results and discussions

#### 3.1. Observations of pseudo-propellant burning

RDX and HMX are monopropellants with a small negative oxygen balance. The addition of

azide polymers to RDX or HMX results in formulations with even more fuel rich equivalence ratios. These pseudo-propellant compositions can sustain combustion at atmospheric pressure only in the case of additional heat flux to the burning surface. Self-sustained combustion of such pseudo-propellants is observed at elevated pressures. Oxygen deficiency in nitramine/azide polymer pseudo-propellants leads to incomplete combustion of the polymer. Therefore, during combustion carbonaceous particles and in some cases even a carbonaceous skeleton are observed on the burning surface. The amount of this residue (undecomposed polymer) on the burning surface depends strongly on pressure and the type of nitramine and azide polymer used. At 0.5 MPa, black particles of size 0.1–0.15 mm were observed on the HMX/GAP burning surface. Increasing the pressure to 1 MPa resulted in a considerable decrease in the amount and size of these particles. The RDX/GAP burning surface at 0.5 MPa was covered by a net-shaped thin carbonaceous structure. Increasing the pressure to 1 MPa decreased the amount of this residue on the burning surface. In addition, the RDX/GAP burning surface at 1 MPa was not covered by the residue all the time. This residue detached periodically from the burning surface, resulting in regions free of carbonaceous residue. During combustion of HMX/B–A at 0.5 MPa, a carbonaceous skeleton almost completely covered the burning surface. Parts of this skeleton detached from the surface and then burned in the gas phase. At a pressure of 1 MPa, the skeleton was absent but almost the entire burning surface was covered by fine carbonaceous particles. In the case of RDX/B–A, coarse carbonaceous flakes were found to form on the burning surface even at 1 MPa. The higher the pressure, the smaller the amount of carbonaceous residue on the burning surface. The pseudo-propellants containing B–A yielded larger amounts of carbonaceous residue on the burning surface than the corresponding pseudo-propellants with GAP. This is due to the more fuel rich equivalence ratio of the pseudo-propellants with B–A (see Table 2) and the higher molecular weight of B–A (see Table 1). The HMX-based pseudo-propellants produced smaller amounts of carbonaceous residue on the burning surface than the corresponding RDX-based pseudo-propellants.

Table 2

The characteristics of the nitramine/azide polymer (80/20 wt%) pseudo-propellants

Pseudo-propellant	HMX/GAP	RDX/GAP	HMX/B–A	RDX/B–A
Brutto-formula	$C_{17.1}H_{32.5}N_{27.2}O_{23.8}$		$C_{17.6}H_{33.1}N_{27.7}O_{23.0}$	
Equivalence ratio (F/O)	2.12		2.25	
Enthalpy of formation (cal/g)	86	90.5	113.6	118.1
Density (TMD) (g/cm <sup>3</sup> )	1.73	1.67	1.71	1.65
Density (exp.) (g/cm <sup>3</sup> )	1.69 ± 0.01	1.64 ± 0.01	1.71 ± 0.01	1.62 ± 0.01

This is most likely explained by the higher melting temperature of HMX; therefore, in the case of HMX-based pseudo-propellants, the degree of condensed-phase polymer decomposition is higher than that in the case of RDX-based pseudo-propellants.

### 3.2. Burning rate

Figure 1 compares the burning rate of RDX-based pseudo-propellant with 20% GAP and the burning rate of pure RDX. One can see that the burning rate of the pseudo-propellant is lower than that of pure RDX. The line describing the RDX burning rate in Fig. 1 is plotted using the RDX burning rate data from Refs. [12,13]. A comparison of our experimental data on the burning rate of RDX/GAP with experimental data of Zenin [1] shows that they are in good agreement with each other (Fig. 1, Table 3). The model of Beckstead et al. [6] adequately predicts the burning rate of 80% RDX/20% GAP, whereas the model of Yang et al. [5] gives overestimated values. The model of Yang et al. gives higher (than experimental) values of burning rate even for pure RDX.

Burning rates of HMX/GAP are discussed in details in Ref. [8]. According to our data, HMX/GAP burns faster than RDX/GAP (see Table 3).

The replacement of GAP in HMX-based pseudo-propellant by B–A copolymer led to a decrease in the burning rate (Table 3). At the same time,

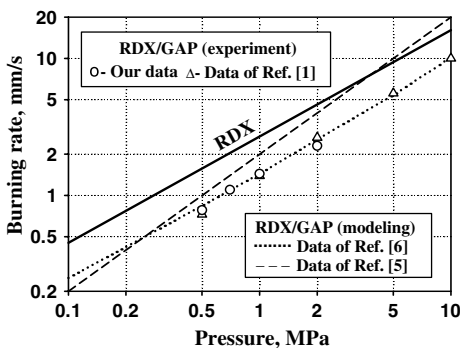


Fig. 1. Burning rate of RDX/GAP in comparison with burning rate of RDX.

our data on the burning rate of HMX/B–A at pressures of 0.5 and 1 MPa are slightly higher than those in Ref. [1], but they nevertheless agree with the overall dependence of the burning rate on pressure ( $r_b$  (mm/s) =  $1.25 \times P$  (MPa)<sup>0.87</sup>) obtained using the data of Ref. [1].

In the present study, the burning rate of RDX/B–A was measured only at 1 MPa, and the obtained value (1.4 mm/s) is close to that in Ref. [1] (Table 3).

### 3.3. Thermal flame structure

Averaged and smoothed temperature profiles for the HMX/GAP, RDX/GAP, HMX/B–A and RDX/B–A at a pressure of 1 MPa are presented in Fig. 2. All profiles were corrected for heat loss by radiation. For both pseudo-propellants with GAP, the experimental value of the final flame temperature is equal to 2580 K. However, the distance at which this final temperature is reached is different: 0.7 mm for HMX/GAP and 0.4 mm for RDX/GAP. In the case of HMX/B–A and RDX/B–A, the final temperature is reached at a distance of ~1.2 mm and is equal to 2475 and 2565 K, respectively. From Fig. 2 one can see that the pseudo-propellants with GAP have a narrower flame zone than the pseudo-propellants with B–A. The replacement of azide polymer in the pseudo-propellant composition leads to more significant changes in the temperature profile than the replacement of nitramine.

In the case of HMX/GAP, increasing the pressure from 0.5 to 1 MPa did not change the final temperature value (Table 4) but decreased (as might be expected) the distance at which this final temperature was reached from 1.2 to 0.7 mm [8].

Table 4 shows that in all cases (except for HMX/B–A at 0.5 MPa), the experimentally measured values of the final temperature are close to adiabatic temperature. The small differences between the experimental and calculated values of the final temperature are within the measurement error of the thermocouple technique. In the case of HMX/B–A at 0.5 MPa, the final flame temperature, which was reached at a distance of ~1.5–1.7 mm, is 100 K lower than adiabatic temperature. The incompleteness of combustion at a

Table 3  
Burning rates of nitramine/azide polymer pseudo-propellants

$P$ (MPa)	Burning rate (mm/s)							
	RDX/GAP		HMX/GAP		HMX/B–A		RDX/B–A	
	Our data	Ref. [1]	Our data	Ref. [1]	Our data	Ref. [1]	Our data	Ref. [1]
0.5	0.78	0.73	0.96	0.66	0.68	0.61	NM <sup>a</sup>	0.77
1.0	1.44	1.39	1.62	1.38	1.40	1.35	1.4	1.41
2.0	2.30	2.65	2.80	2.43	NM <sup>a</sup>	2.52	NM <sup>a</sup>	2.69

<sup>a</sup> NM, was not measured.

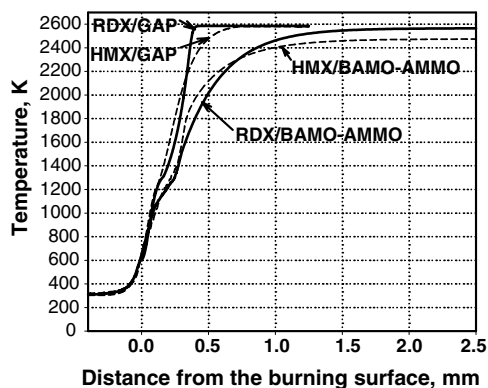


Fig. 2. Temperature profiles in flame of nitramine/azide polymer pseudo-propellants at 1 MPa.

pressure of 0.5 MPa can be attributed to existence of the carbonaceous particles during combustion.

The temperature profile obtained at 0.5 MPa has a peculiarity at a distance of  $\sim 0.13$ – $0.25$  mm, which is related to a decrease in the temperature gradient [8]. With an increase in pressure to 1 MPa, this peculiarity becomes less noticeable and is observed at a distance of  $\sim 0.1$ – $0.2$  mm. At 1 MPa, this peculiarity is less pronounced for HMX/GAP than for the other three pseudo-propellants. In contrast to the data of Ref. [1], the profiles obtained in our study do not have an extensive plateau (at a temperature of  $\sim 1300$  K). A plateau at a distance of 0.2–0.5 mm was observed in our experiments only in the case of HMX/B–A at 0.5 MPa. Joint consideration of data obtained using video recording and thermocouple measurements showed that the plateau on the temperature profile was observed only while thermocouple was inside the carbon skele-

ton. The plateau is possibly due to worsening of heat exchange between flame and the burning surface owing to presence of the carbon skeleton.

Another distinction from the data of Ref. [1] is that in our case the temperature of the final products  $T_f$  is 200–280 K higher than that in Ref. [1]. It is difficult to determine the reasons (different characteristics or something else) for the difference between our and Ref. [1] temperature profiles because Ref. [1] and Ref. [2] give different data on HMX/GAP and HMX/B–A. For example, the characteristics of HMX/GAP pseudo-propellant (element composition, density, and adiabatic temperature) presented in Ref. [1] differ substantially from those in Ref. [2]. The element composition of HMX/GAP was revised. The density of the pseudo-propellant increased from 1.52 to 1.74 g/cm<sup>3</sup>, and the adiabatic temperature decreased from 2776 to 2693 K. At the same time, the HMX/GAP combustion parameters obtained by processing temperature profiles remained unchanged, and this is not explained in Ref. [2].

### 3.4. Chemical flame structure

Using mass spectrometric analysis of gas samples taken from flames of the nitramine/azide polymer pseudo-propellants, the following species were identified: H<sub>2</sub> (2), H<sub>2</sub>O (18, 17), HCN (27, 26, 14), CO (28, 12), N<sub>2</sub> (28, 14), CH<sub>2</sub>O (29, 30), NO (30, 14), CO<sub>2</sub> (44, 28, 22), N<sub>2</sub>O (44, 30, 28, 14), NO<sub>2</sub> (46, 30, 14), and nitramine vapor (75, 46, 42, 30, 29). The mass peaks used for the identification and determination of the species concentration are shown in parentheses. The concentrations of the identified species were determined using calibration coefficients. The location of the burning surface was found from abrupt changes

Table 4

Comparison of experimental values of final temperature ( $T_f$ ) in flame of nitramine/azide polymer pseudo-propellants with adiabatic temperatures ( $T_{ad}$ ) calculated using “Astra” code [14]

$P$ (MPa)	HMX/GAP		RDX/GAP		HMX/B–A		RDX/B–A	
	$T_f$ (K)	$T_{ad}$ (K)	$T_f$ (K)	$T_{ad}$ (K)	$T_f$ (K)	$T_{ad}$ (K)	$T_f$ (K)	$T_{ad}$ (K)
0.5	2580	2594	— <sup>a</sup>	2603	2400	2503	— <sup>a</sup>	2512
1.0	2580	2608	2580	2617	2475	2512	2565	2522

<sup>a</sup> Presence of carbonaceous skeleton on the burning surface did not allow to measure temperature correctly.

in most of the mass peak intensities at the moment of contact of the probe with the liquid layer on the surface. This was obviously related to density changes of the sampled products in a condensed to gas transition. In addition, the moment of contact of the probe with the burning surface was determined by video recording, which was synchronized with the mass spectrometric measurements.

The species concentrations (in mole fractions) near the burning surface of the nitramine/azide polymer pseudo-propellants at 1 MPa are presented in Table 5. The main features that distinguish the species compositions for the pseudo-propellants with B–A from those for the pseudo-propellants with GAP are (1) the higher concentration of  $N_2$  and (2) the absence of  $CH_2O$ ,  $NO_2$ , and nitramine vapor. The higher concentration of  $N_2$  near the burning surface of the pseudo-propellants with B–A is explained by the higher content of azide groups ( $-N_3$ ) in B–A than in GAP. It is most likely that  $CH_2O$ ,  $NO_2$ , and nitramine vapor were not detected near the burning surface of the pseudo-propellants with B–A because of the constant presence of carbonaceous particles (flakes) in a large amount on the burning surface.

The final combustion products of HMX/GAP and RDX/GAP are very close to those at thermodynamic equilibrium. For HMX/GAP, complete combustion is achieved even at 0.5 MPa. However, for HMX/B–A at 0.5 and 1.0 MPa, the final combustion product composition differs significantly (Table 6) from the equilibrium product composition as regards the concentration of hydrogen-containing species. In the final products, the main hydrogen-containing species is  $H_2O$ , and in the equilibrium composition,  $H_2$ . This is likely due to the incomplete combustion of the pseudo-propellant, as is evidenced by the presence of carbonaceous residue after burning.

As the pressure increased from 0.5 to 1.0 MPa, the  $H_2$  concentration in the final combustion products increased by a factor of  $\sim 1.8$  and the  $H_2O$  concentration decreased by a factor of 1.5. Thus, the measured concentrations of the hydrogen-containing combustion species at 1 MPa approached those for the equilibrium composition but still did not reach them. The composition of the final products for RDX/B–A is very close to that for HMX/B–A.

Thermocouple and mass spectrometric measurements were conducted in different experiments for all pseudo-propellants, but concentration profiles are similar to temperature profiles in the range of their scatter. In the case of RDX/GAP the influence of the probe on flame turned out to be more significant than in the case of HMX/GAP.

The flame structure of HMX/GAP at 1 MPa is presented in Fig. 3. At a pressure of 1 MPa (as in the case of 0.5 MPa [8]) two zones of chemical reactions were found. The first zone 0.1 mm wide is the zone of consumption of HMX vapor and  $NO_2$  with the formation of  $NO$ ,  $HCN$ ,  $CO$ ,  $H_2$ , and  $N_2$ . In the second zone, at a distance of 0.1–0.4 mm, consumption of  $N_2O$ ,  $CH_2O$ ,  $NO$ , and  $HCN$  with the subsequent formation of  $CO$ ,  $H_2$ , and  $N_2$  occurs. The temperature in the first zone grows from 640 to  $\sim 1200$  K, and in the second zone, from  $\sim 1200$  to  $\sim 2350$  K. As in the case of 0.5 MPa, at a pressure of 1 MPa, the zone of  $HCN$  consumption is wider than that for the remaining species. Element content profiles were calculated ignoring the diffusion fluxes of species. The maximum deviations of N and O contents from the initial amounts are  $\sim 15\%$ . For elemental C and H, the maximum deviations are  $\sim 20\%$  and  $\sim 25\%$ , respectively.

The flame structure of RDX/GAP at 1 MPa is presented in Fig. 4. The species concentration

Table 5  
Compositions of species (mole fractions) near the burning surface of pseudo-propellants at 1 MPa

	$T_s$ (K)	$H_2$	$H_2O$	$HCN$	$N_2$	$CO$	$NO$	$CH_2O$	$CO_2$	$NO_2$	$N_2O$	HMX <sub>v</sub>	RDX <sub>v</sub>
HMX/GAP	638 <sup>a</sup>	0.12	0.16	0.12	0.09	0.12	0.08	0.04	0.02	0.05	0.04	0.17	—
RDX/GAP	635	0.12	0.11	0.10	0.01	0.11	0.04	0.02	0	0.09	0.06	—	0.33
HMX/B–A	665	0.17	0.17	0.11	0.36	0.10	0.04	—	0.01	—	0.03	—	—
RDX/B–A	643 <sup>a</sup>	0.05	0.22	0.15	0.22	0.12	0.17	—	0.02	—	0.05	—	—

<sup>a</sup> Data of Ref. [1].

Table 6  
Final product compositions (mole fractions) in nitramine/B–A flames in comparison with equilibrium composition calculated using “Astra” code [14]

	$P$ (MPa)	$H_2$	$H_2O$	$N_2$	$CO$	$CO_2$
HMX/B–A (exp.)	0.5	0.07	0.23	0.39	0.27	0.04
HMX/B–A (exp.)	1.0	0.12	0.15	0.42	0.28	0.03
RDX/B–A (exp.)	1.0	0.09	0.12	0.48	0.30	0.02
HMX/B–A, RDX/B–A (calc.)	0.5, 1.0	0.250	0.091	0.288	0.345	0.020

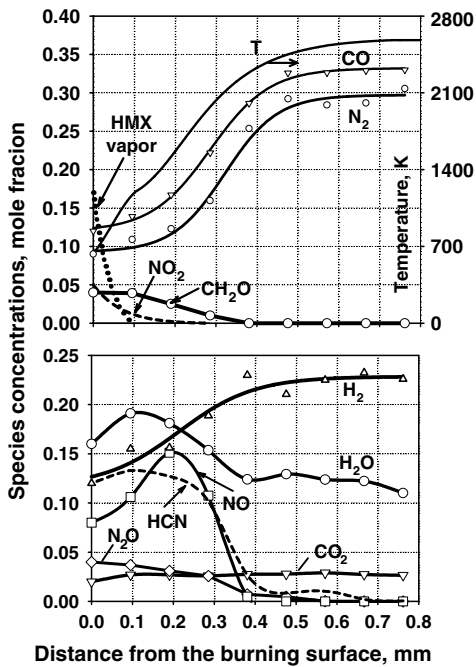


Fig. 3. Flame structure of HMX/GAP pseudo-propellant at a pressure of 1 MPa.

profiles in RDX/GAP flame at 1 MPa are similar to those in HMX/GAP flame; there are only some, mostly quantitative differences between them. In particular, the complete consumption of  $\text{CH}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{HCN}$  in RDX/GAP flame at 1 MPa occurred at a larger distance ( $\sim 0.6$  mm) from the burning surface than in the case of HMX/GAP ( $\sim 0.4$  mm).

In nitramine/GAP flames at a pressure of 1 MPa, two main zones of chemical reactions were observed. In the first low-temperature (dark) zone, consumption of nitramine vapor and oxidation of  $\text{CH}_2\text{O}$  by  $\text{NO}_2$  mainly occur. Most of  $\text{NO}_2$  and nitramine vapor is consumed at a distance less than  $\sim 0.1$  mm from the burning surface. This leads to the formation of  $\text{NO}$ ,  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{N}_2$ . In the second, high-temperature zone, the main reaction is the oxidation of  $\text{HCN}$  by  $\text{NO}$ , resulting in the final products  $\text{CO}$ ,  $\text{N}_2$ , and  $\text{H}_2$ . In Refs. [15,16], it was shown that this reaction is the main reaction in the high-temperature zones of RDX [15] and HMX [16]. Thus, in nitramine/GAP flames, the leading reactions are the same as in the case of pure nitramines. Influence of GAP on flame structure consists in changing of widths of consumption zones:  $\text{CH}_2\text{O}$  consumption zone becomes wider than those of  $\text{NO}_2$ , and  $\text{HCN}$  consumption zone becomes wider than those of  $\text{NO}$ .

$\text{NO}_2$ ,  $\text{CH}_2\text{O}$ , and nitramine vapors were not observed near the burning surface of HMX/B-A and RDX/B-A. The presence of carbonaceous

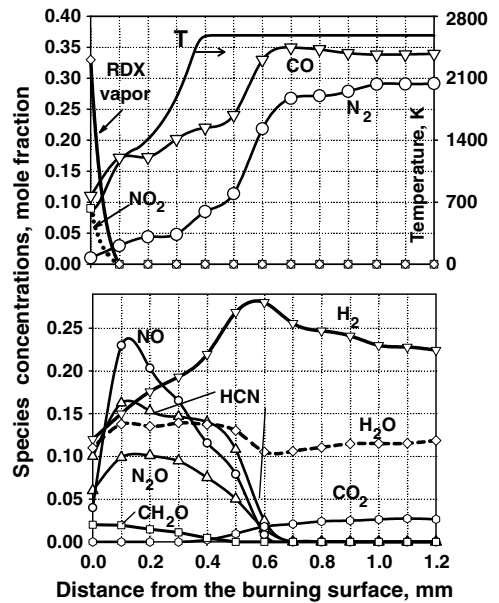


Fig. 4. Flame structure of RDX/GAP pseudo-propellant at a pressure of 1 MPa.

particles on the burning surface did not allow us to analyze the zone adjacent to the burning surface. Therefore, unlike in nitramine/GAP flames, in HMX/B-A and RDX/B-A flames, we found only one zone of chemical reactions at a pressure of 1 MPa in which consumption of  $\text{HCN}$ ,  $\text{NO}$ , and  $\text{N}_2\text{O}$  occurred.  $\text{N}_2\text{O}$  concentration decreased to zero at a distance of  $\sim 0.3$  mm. The zone of  $\text{NO}$  consumption was  $\sim 0.6$ – $0.7$  mm wide. Most of  $\text{HCN}$  also reacted before  $0.6$ – $0.7$  mm, but the zone of complete consumption of  $\text{HCN}$  was  $\sim 1.5$  mm wide.

#### 4. Conclusions

- Eleven species  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ , and nitramine vapor ( $\text{RDX}_v$  or  $\text{HMX}_v$ ) were identified, and their concentrations were measured in flame of nitramine/GAP pseudo-propellants (including a zone adjacent to the burning surface) at a pressure of 1 MPa. Profiles of species concentrations are similar; there are only some quantitative differences between them. Two zones of chemical reactions in flame of HMX/GAP and RDX/GAP pseudo-propellants were found. In the first, narrow, zone 0.1 mm wide, adjacent to the burning surface, complete consumption of nitramine vapor and  $\text{NO}_2$  with the formation of  $\text{NO}$ ,  $\text{HCN}$ ,  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{N}_2$  occurs. In the second, wider high-temperature zone, consumption of  $\text{N}_2\text{O}$ ,  $\text{CH}_2\text{O}$ ,  $\text{NO}$ , and  $\text{HCN}$  with the subsequent formation of  $\text{CO}$ ,  $\text{H}_2$ ,

and  $N_2$  takes place. The leading reactions in the high-temperature zone of flame of nitramine/GAP pseudo-propellants are the same as in the case of pure nitramines.

2. In the case of nitramine/BAMO–AMMO pseudo-propellants the presence of carbonaceous particles on the burning surface did not allow us to analyze the zone adjacent to the burning surface, therefore only one flame zone was found. The main features that distinguish the species compositions near the burning surface for the pseudo-propellants with BAMO–AMMO from those for the pseudo-propellants with GAP are (1) the higher concentration of  $N_2$  and (2) the absence of  $CH_2O$ ,  $NO_2$ , and nitramine vapor. The final combustion product composition of nitramine/BAMO–AMMO pseudo-propellants differs significantly from the equilibrium product composition.
3. The experimentally measured values of the final temperature of nitramine/azide polymer pseudo-propellants at 1.0 MPa are close to adiabatic temperature. But the pseudo-propellants with GAP have a narrower flame zone than the pseudo-propellants with BAMO–AMMO.

### Acknowledgment

This research was supported by US Army Research Office under the Grant DAAD19-02-1-0373.

### References

- [1] A.A. Zenin, S.V. Finjakov, *Energetic Materials: Synthesis, Production and Application*, Fraunhofer Institut Chemische Technologie, DWS Werbeagentur und Verlag GmbH, Karlsruhe, Germany, 2002, p. 6.1.

### Comments

*M.Q. Brewster, University of Illinois, USA.* Your presentation showed one comparison slide with burning rate versus pressure calculations for two models, Yang and Beckstead, for RDX/GAP. Since models such as these presumably have the level of chemistry detail necessary for simulating effects of composition as well as flame structure I am interested in any additional model comparison results. First, were Yang's and Beckstead's model predictions done before or after the experiments? Second, were modeling predictions (or "post-dictions") done for HMX/GAP, RDX/BAMO-AMMO, or

- [2] A. Zenin, S. Finjakov, *Energetic Materials: Structure and Properties*, Fraunhofer Institut Chemische Technologie, DWS Werbeagentur und Verlag GmbH, Karlsruhe, Germany, 2004, p. 144.1.
- [3] T.A. Litzinger, Y. Lee, C.-J. Tang, in: V. Yang, T.B. Brill, W.-Z. Ren (Eds.), *Solid Propellant Chemistry, Combustion, and Motor Interior Ballistics*, American Institute of Astronautics and Aeronautics, Reston, VA, 2000, p. 355.
- [4] E.S. Kim, V. Yang, Y.-C. Liau, *Combust. Flame* 131 (3) (2002) 227–245.
- [5] Y.-C. Liau, V. Yang, S.T. Thynell, in: V. Yang, T.B. Brill, W.-Z. Ren (Eds.), *Solid Propellant Chemistry, Combustion, and Motor Interior Ballistics*, American Institute of Astronautics and Aeronautics, Reston, VA, 2000, p. 477.
- [6] K.V. Puduppakkam, M.W. Beckstead, in: 38th JANNAF Combustion Meeting, CPIA Publication 712, Vol. I, 2002, pp. 143–156.
- [7] O.P. Korobeinichev, A.A. Paletsky, E.N. Volkov, A.G. Tereshchenko, P.D. Polyakov, *Novel Energetic Materials and Application*, Grafiche GSS, Bergamo, Italy, 2004, p. 43.
- [8] A.A. Paletsky, O.P. Korobeinichev, A.G. Tereshchenko, E.N. Volkov, P.D. Polyakov, *Proc. Combust. Inst.* 30 (2005) 2105–2112.
- [9] G. Krien, H.H. Licht, J. Zierath, *Thermochim. Acta* 6 (5) (1973) 465–472.
- [10] J.L. Lyman, Y.-C. Liau, H.V. Brand, *Combust. Flame* 130 (3) (2002) 185–203.
- [11] R.D. Schmidt, *Energetic Materials Ignition, Combustion and Detonation*, Fraunhofer Institut Chemische Technologie, DWS Werbeagentur und Verlag GmbH, Karlsruhe, Germany, 2001, p. 140.
- [12] A.I. Atwood, T.L. Boggs, P.O. Curran, T.P. Parr, D.M. Hanson-Parr, C.F. Price, J. Wiknich, *J. Propul. Power* 15 (6) (1999) 740–753.
- [13] A.A. Zenin, *J. Propul. Power* 11 (4) (1995) 752–758.
- [14] G.V. Belov, "Astra" Code, ver. 2/24, MSTU, Moscow, 1990 (in Russian).
- [15] O.P. Korobeinichev, in: R.W. Shaw, T.B. Brill, D.L. Thompson (Eds.), *Overviews of Recent Research on Energetic Materials*, World Scientific Publishing Co. Pte. Ltd., Singapore, 2005, p. 75.
- [16] O.P. Korobeinichev, L.V. Kuibida, V.Zh. Madirbaev, *Comb. Explos. Shock Waves* 20 (3) (1984) 282–285.

HMX/BAMO-AMMO? Third, how do calculations for flame structure (temperature and species profiles) compare with your experimental results, both for calculations done before the measurements (if any) and for those done after?

*Reply.* According to both Yang and Beckstead ([5,6] in paper) model predictions were done without knowing our and Zenin's experimental data on burning rate of RDX/GAP. HMX/GAP combustion model was presented by Kim et al. ([4] in paper). However, calculations



of flame structure in this work were done only for the case of laser-assisted combustion. Calculations of RDX/GAP and HMX/GAP flame structures for the same conditions as in our experiments (self-sustained combustion, a pressure of 1.0 or 0.5 MPa) have not been yet published. As far as we know, there have not been any papers published, describing combustion models for RDX/BAMO-AMMO and HMX/BAMO-AMMO.

●

*Kenneth K. Kuo, Pennsylvania State University, USA.*  
I noticed that your micro-thermocouple traces for the HMX/GAP and RDX/GAP propellants are different from those of Zenin. I wonder whether the differences are caused by the difference in your GAP material and the GAP used by Dr. Zenin or due to the size differences of the micro-thermocouple beads.

*Reply.* We do not know the real reasons accounting for the differences between our and Zenin's temperature profiles, but size of thermocouples used by us and Zenin does not differ much and cannot cause so significant differences. All that is known about GAP used by Zenin is that it has molecular weight of 2000. Our GAP has the same molecular weight, but other properties (structure, amount of functional groups, etc.) can differ and therefore cause some differences in burning characteristics. Second, we used uncured pseudo-propellants. As to Zenin, we do not know for sure if his propellants were cured or uncured. Third, it should be noted that in contrast to Zenin we used video recording to ensure that our temperature profiles were measured correctly. We took a profile into consideration only if (1) the thermocouple shoulders were parallel to the burning surface during its appearance in the gas phase and (2) the thermocouple surface was not covered by any residue, particles, etc.