FLAME STRUCTURE AND COMBUSTION CHEMISTRY OF AMMONIUM DINITRAMIDE/POLYCAPROLACTONE PROPELLANT

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Abstract

Flame structure and combustion mechanism of ammonium dinitramide(ADN)/polycaprolactone(PCL) composite solid propellant have been studied at 0.1 MPa by microthermocouple technique, probe mass spectrometry and videotape recording. Two types of PCL with molecular weight of 10000 (later on PCL(10000)) and 1250 (PCL(1250)) were used. Besides, an effect of CuO additive on propellant burning rate has been investigated. Combustion of ADN/PCL strands was dependent on type of polycaprolactone. In the case of PCL(10000) propellant strands burned without visible flame with low temperature of combustion products, whereas ADN/PCL(1250) showed a non-homogeneous non-stationary combustion with formation of luminous torches. Three zones of chemical reactions in flame have been detected. Vapor of ADN, products of decomposition of the oxidizer and binder, and also products of their interaction have been observed near the burning surface. It was shown that the composition of nitrogen-containing species in dark flame zone of ADN/PCL(1250) at 0.1 MPa is close to that of pure ADN at 0.6 MPa. Complete composition of combustion products in luminous flame zone was also determined. It was established that burning rate of ADN/PCL(1250) propellant (as in the case of pure ADN and ADN/HTPB propellant) is controlled by reactions in condensed phase. Computer modeling of chemical reactions in the dark flame zone using experimental data on composition and temperature of species near the burning surface has been conducted. The calculated temperature and concentrations of species in flame have been compared with experimental data. Obtained data on flame structure of ADN/PCL propellant can be used for development of combustion model of this propellant.

Introduction

Ammonium dinitramide (ADN) is a powerful chlorine-free oxidizer, which can replace ammonium perchlorate (AP) in solid rocket propellants. Since the combustion products of ADN-based propellants are not toxic, these propellants are environmentally friendly and investigation of them is of great interest. ADN-based propellant is convenient system for investigation of mechanism and chemistry of composite solid rocket propellant combustion, because of simplicity of oxidizer (ADN molecule contains only three elements: H, N and O). Important physicochemical properties and combustion characteristics of ADN and ADN-based propellants were published for the first time in the paper [1]. ADN has a higher heat of formation than AP, the common oxidizer of solid rocket propellant, therefore ADN-based propellants have higher specific impulse than AP-based propellants [1, 2]. The study of the combustion mechanism of pure ADN was the subject of several investigations [3 - 6]. It was found that the burning rate of ADN is controlled by reactions in the condensed phase. A multizone flame structure was also established. At present, however, there are only a few papers, which are devoted to the study of the combustion characteristics and combustion mechanism of the composite ADN-based propellants and sandwiches with different type of binder such as hydroxyl-terminated polybutadiene (HTPB) [7, 8], glycidyl azide polymer (GAP) [8, 9], paraffin [3, 10], poly(diethyleneglycol-4,8-dinitraza undeconate) (ORP-2A)/nitrate ester (NE) and polycaprolactone polymer (PCP)/NE [11], polybutadiene polymer [12].

One of the objectives of the study of propellant combustion mechanism is the development of a combustion model, which can predict combustion characteristics of solid propellants. The development of a combustion model describing composite solid propellant requires information on propellant flame structure. As a model of composite solid propellant, sandwiches based on oxidizer and binder are used. Flame structure of ADN-based sandwiches with various energetic and nonenergetic binders has been investigated in [13]. Results showed either no, or insignificant, effects of diffusion flames on the processes controlling the propellant burning rate in the pressure range from 0.1 to 1.4 MPa. However, the burning rates of sandwiches such as ADN/(ADN/HTPB)/ADN and ADN/PBAN/ADN increased nearly 1.5-fold with the pressure increase from 1.5 to 7 MPa (data of Ed. Price, George Tech. University, USA). This suggests a possible influence of the ADN-binder diffusion flames on the burning rate of sandwiches. It has been shown in [7] that the reactions in the condensed phase control ADN/HTPB propellant combustion.

The chemical mechanism of combustion of ADN-based propellants is not well understood. The main objective of this research was the experimental investigation of flame structure and combustion chemistry of ADN/PCL propellant at 0.1 MPa.

Experimental

The ADN used in this study was synthesized at the Zelinsky Institute of Organic Chemistry Russian Academy of Science. It contains 2% of ammonium nitrate as an impurity. The melting point (m.p.) of ADN is 365-367 K. Two types of PCL with different molecular weights of 10000 (PCL(10000)), and 1250 (PCL(1250)) were used. The former polymer at room temperature is flake (m.p. 333 K) and the latter one is a waxy solid (m.p. 309-321 K). Fine crystalline powder of ADN with an average particle size of ~ 40 μm was used for preparation of the composite propellants. Non-cured ADN/PCL propellant of stoichiometric composition (St_b) consisted of 89.08 wt% ADN and 10.92 wt% PCL. It was prepared by mixing of the ingredients in a dry cell at the temperature slightly exceeding melting point of the polymer. Strands with diameter of 6 mm and length of 10-12 mm were prepared by pressing propellant mixture under a pressure of ~ 390 MPa. Density of strands was 1.58 g/cm^3. The sides of the strands were protected with thin layer of high vacuum silicone grease. Addition of 2% CuO to St_b means that in this propellant mass fractions of St_b and CuO are equal to 98% and 2% respectively. CuO powder with particle size of ~ 2-5 μm and specific surface area of 33.6 m^2/g was used.

Probe mass spectrometry is the most effective and universal method for investigation of solid propellant flame structure [14]. It allows detecting all the stable species present in the flame and also to determine their concentrations and their spatial distributions. Flame structure has been studied at 0.1 MPa in argon using the set-up [15] with molecular beam sampling system combined with TOFMS. Calibrations [5] were conducted for N_2, O_2, CO, CO_2, N_2O, NH_3, NO, HNO_3 and H_2O. Calibration for water was conducted by vaporization of drop of water in argon flow. Accuracy of measurement of species mole fractions in the range of 0.1-0.4 (H_2O, N_2, N_2O, NO и CO_2) was ~ 10%. For species with mole fractions less than 0.1, the error was 20-30%.

The temperature profile in gas phase was measured by П-shaped WRe(5%)-WRe(20%) thermocouples with a shoulder length of ~ 3 mm, made of wire of 100 μm in a diameter. The thermocouples were located initially at a distance of ~ 2-5 mm from the strand surface. After ignition strand moved toward the thermocouple with rate exceeding the burning rate of propellant.

Results

Experiments showed that St_b(10000) propellant burned without visible flame at 0.1 MPa. Brown residue (apparently, undecomposed polycaprolactone) remained on strand holder after experiment. Temperature of combustion

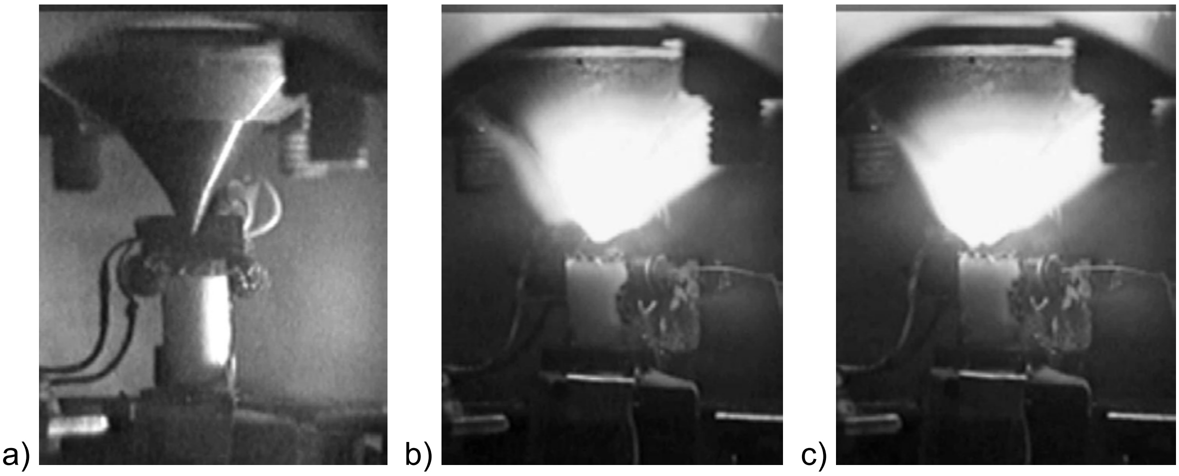

Fig. 1. Video images of combustion of propellant St_b(1250) at 0.1 MPa: (a) before the experiment, (b, c) in different times during combustion (Δt = 0.04 s).

products was ~ 670 K, which is close to that of pure ADN at 0.1 MPa [5]. So, one can suppose that at 0.1 MPa only ADN burns whereas PCL(10000) only melts and partially decomposes.

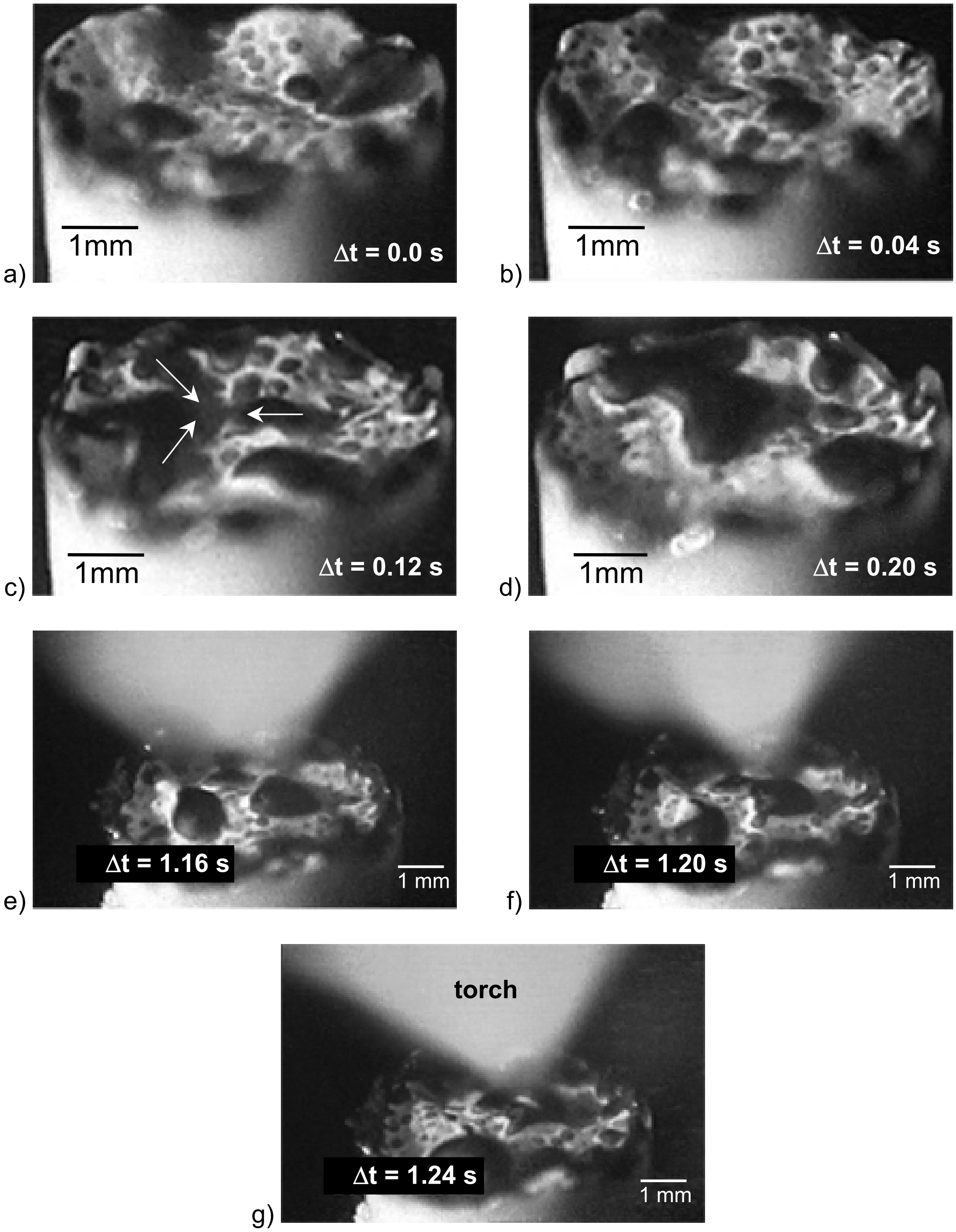

Fig. 2. Video images of the burning surface of propellant $St_b(1250)$ at 0.1 MPa.

Replacement of PCL(10000) by PCL(1250) resulted in the appearance of the visible flame. However, flame did not cover the whole burning surface of strand. Separate jets of flame moving over the strand burning surface during the combustion were observed (Fig. 1). So, the combustion of $St_b(1250)$ at 0.1 MPa has a torch character with formation of separate seats of burning on the burning surface. Video recording of the burning surface with 16-fold magnification revealed processes, which take place on the propellant surface during combustion. Following processes should be noted (see Fig. 2): 1) appearance of sites of darkening on the burning surface (a) with consequent transition of them in small dark spots (b); 2) fusion of these small spots in large spots (c, d), arrows show the direction of fusion; 3) appearance of two torches over large spots, diameter of which is ~ 1 mm (e); 4) one of torches lift-off (f); 5) complete disappearance of one torch (g). These spots are probably drops of liquid undecomposed PCL on the surface of ADN. Fusion of small drops of PCL in bigger drops is caused by less melting point of PCL in comparison with ADN.

The measurement of temperature and the determination of combustion product composition were conducted in different experiments. The probe (or thermocouple) during the combustion was located either in luminous zone (torch) or in dark zone (between torches or far from them). Analysis of the videotape recording allowed the determination of the flame zone, where the probe or thermocouple was located at the moment of measurement.

Results of two experiments on measurement of the temperature profile in flame of $St_b(1250)$ at 0.1MPa are presented in Fig. 3. They confirm the conclusion regarding non-stationary torch combustion of this propellant. Curve 1 in Fig. 3 corresponds to the case when the thermocouple moved from the torch to the burning surface. Abrupt fallings of temperature on curve 1 are connected with changing of torch location with respect to thermocouple. Curve 2 corresponds to the case when the thermocouple moved to the burning surface from the dark zone. Abrupt increase of temperature at the distance of L ~ 2 mm relates to torch appearance near the burning surface. The videotape recording showed that a dark zone exists near the burning surface. The width of the dark zone varies from ~ 1 mm (near bottom of torch) to 3-4 mm (region between torches). Thermocouple measurements revealed existence of three zones in the flame (Fig. 3): 1) the narrow dark zone adjacent to the burning surface (width of the zone ~ 0.2-0.3 mm), where the temperature grew from ~ 600 K to ~ 1150 K, 2) the dark zone (width of the zone ~ 0.5 to ~ 3 mm), where the temperature slightly increased from ~ 1150 K to ~ 1450 K, 3) the luminous zone (torch), where the temperature increased to 2600 K at the distance of 4-8 mm.

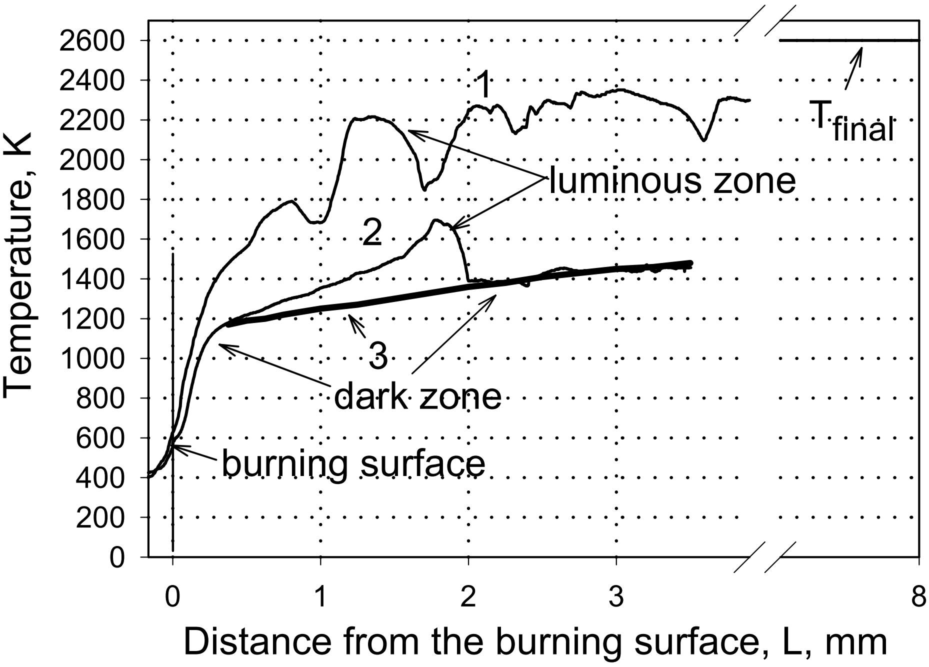

Fig. 3. Temperature profiles in flame of St_b(1250) propellant at 0.1 MPa. Curves 1, 2 – experimental data, curve 3 – modeling.

Compositions of the combustion products in the luminous and dark flame zones of St_b(1250) propellant are presented in Table 1. Temperature of the combustion products in luminous zone, which is equal to 2600 K, is slightly less than the calculated equilibrium temperature (2695 K [16]), i.e. 100% completeness of combustion is not achieved. Presence of NO in combustion products confirms this conclusion. The element balance in the luminous zone was in satisfactory agreement (±5%) with that in the propellant. The calculated deficiency of carbon in the combustion products determined in the dark zone near the burning surface is equal to ~ 50% of the initial amount. This fact indicates that identification of carbon-containing products in the dark zone was incomplete. Besides, we have obtained peaks of the following unidentified masses in mass spectrum of species near the burning surface of the St_b(1250) propellant: 55, 57, 60, 67, 69, 70, 71, 73, 79, 81, 95, 108, 115. We suggest that masses from 55 to 115 are responsible for decomposition products of PCL. The profile of intensity of mass peak 115 (Fig. 4) was also obtained. Figure shows that near the burning surface there is the zone with width of ~ 1.5-2 mm, where mass peak 115 is presented. Videotape recording showed that this zone is dark zone.

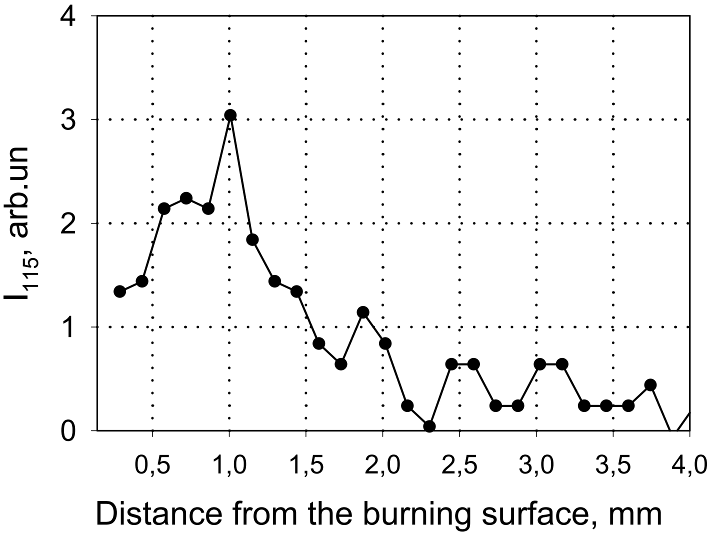

Fig. 4. The dependence of intensity of mass peak 115, I_{115}, on the distance from the burning surface of St_b(1250) propellant at 0.1 MPa.

TABLE 1

Concentrations (in mole fractions) of species and temperature in flame of St_b(1250) propellant at 0.1 MPa and of ADN at 0.6 MPa

	T, K	H_2O	N_2	N_2O	NO	NH_3	HNO_3	H_2	CO	CO_2	O_2
Luminous zone (exp)	~2600	0.39	0.32	0	0.10	0	0	0.03	0.02	0.12	0.02
Thermodynamic calc. [16]	2695	0.40	0.34	0	0.01	0	0	0.03	0.05	0.09	0.03
Dark zone near surface (exp) at L ~ 0.5 mm	~1120	0.32	0.11	0.20	0.20	0.04	0.01	0.01	0.02	0.08	0.01
Pure ADN dark zone at L ~ 4mm (0.6 MPa) [5]	~920	0.31	0.10	0.28	0.23	0.07	0.02	-	-	-	-
Dark zone far from surface (exp)	~1400	0.38	0.15	0.20	0.15	0.01	0	0.01	0.01	0.09	0.01
Dark zone far from surface (calc) [17]	1410	0.38	0.15	0.19	0.16	0.01	0	0	0.01	0.08	0.01

The burning rate of St_b(1250) propellant at 0.1 MPa was equal to 2.3 mm/s. Addition of 2% CuO resulted in increase of the burning rate of St_b(1250) propellant by 2 times.

Discussion

Initially, fuel (PCL) and oxidizer (ADN) are distributed uniformly in propellant mixture. During the combustion of St_b(1250) at 0.1 MPa, redistribution of fuel on the burning surface, which is caused by formation of carbon-containing drops (Fig. 2), takes place. It results in variation of oxidizer/fuel ratio in gas phase near the burning surface. One can assume, that space near small drop is filled mainly by products of decomposition of oxidizer. Deficiency of carbon-containing products in dark zone confirms this statement. Thus, invisible lean diffusion flame (dark zone - Table 1) with low temperature of products occurs near the small drops of fuel. Fusion of several small drops of partially decomposed PCL in big one takes place on the burning surface (Fig. 2 c) during the combustion. Intense flow of products of gasification and/or decomposition of fuel exists over the big drop. An interaction of products of decomposition of oxidizer with it resulted in appearance of luminous diffusion flame directly over the drop. Lifetime of drop (after appearance of the torch) is equal ~ 0.1 s. The presence of luminous torch with high temperature of combustion products over the drop leads to increase of heat feedback from gas phase to the burning surface and increase of temperature of the drop. As a result, increase of decomposition rate of the drop occurs. Volume and thickness of the drop decrease during the combustion. The shape of the drop changes from near hemispherical to more flat form. Then, some drops fall into smaller drops under the influence of flow of oxidizer decomposition products from under the drop, and the torch disappears or exists over the rest part of the drop.

It was obtained earlier that ADN at 0.1 MPa burns without flame (temperature of combustion products ~ 620 K), and that the combustion products of pure ADN contain ADN vapor (ADN_v) [5]. During the investigation of flame structure of St_b(1250) at 0.1 MPa peaks with 17, 30 and 46 m/z were detected near the burning surface at temperature of ~ 600 K. Ratio between them corresponds to the ratio of this peaks in the mass spectrum of ADN vapor [5]. The profiles of intensities of these mass peaks near the burning surface are presented in Fig. 5. The comparison of combustion products composition of St_b(1250) in dark flame zone with that of pure ADN at 0.6 MPa at a distance from the burning surface ~ 4 mm (Table 1) shows that the compositions of nitrogen-containing species and the temperatures are close. A similar conclusion was made in the investigation of ADN/HTPB(97/3) propellant [7] and ADN/GAP(82.5/17.5) sandwiches [9]. One can suppose that in narrow (dark) flame zone of propellant (~ 0.3 mm at 0.1 MPa) mainly the same reactions as in the dark zone adjacent to the burning surface of pure ADN at 0.6 MPa occur. Temperature in dark zone of propellant is higher than that of pure ADN by 200 K. This fact can be explained by reactions of interaction between oxidizer and binder and (or) their decomposition products with formation of CO and CO_2, which occur in the CP and (or) in narrow zone near the burning surface.

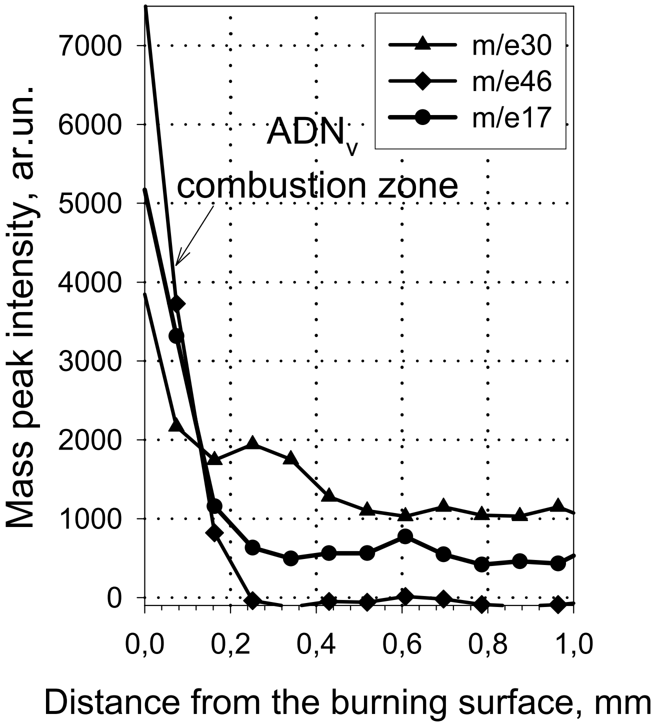

Fig. 5. Profiles of mass peak intensities responsible for ADN vapor in the flame of St_b(1250) propellant.

Using the composition of combustion products in the dark zone near the burning surface as a boundary condition, the modeling of the dark flame zone was conducted. Code PREMIX [17] was used. For calculations a mechanism containing developed earlier mechanism of chemical reactions in ADN flame [18] and consisting of 144 reactions for 34 species was used. Calculations with initial temperature of 1040 K gave temperature profile (curve 3, Fig. 3). It coincides with part of experimental profile (curve 2, Fig. 3) corresponding to the dark zone. Besides, the composition of combustion products obtained in calculations (corresponding to the temperature of 1410 K) coincides with experimentally measured composition of combustion products in the dark zone far from the burning surface (Table 1). So, the second (dark) flame zone of $St_b(1250)$ propellant was simulated. In this zone the consumption of HNO_3, NH_3 and partial consumption of NO with formation of H_2O and N_2 take place. Similar reactions occur in the dark zone of pure ADN flame at 0.6 MPa [5].

Conclusions

It was established that the molecular weight of PCL strongly influences on the combustion of ADN/PCL propellant of stoichiometric composition at 0.1 MPa. Polycaprolactone with molecular weight of 10000 weakly reacted with products of decomposition of ADN. It only melted and partially decomposed. The propellant with PCL(10000) burned similar to pure ADN. During the combustion of propellant with PCL(1250) the formation of torches above the propellant surface was observed. Observed appearance, disappearance and migration of torches are connected with fusion, fragmentation and moving of drops of partially decomposed PCL on the burning surface. Rather big drops can be the source of torch formation. The torch represents the diffusion flame between products of decomposition of ADN and PCL.

Combustion of ADN/PCL(1250) propellant at 0.1 MPa is neither steady nor one-dimensional process. Existence of three flame zones has been revealed. In the first narrow dark zone adjacent to the burning surface (width of the zone ~ 0.2-0.3 mm) the temperature grows from ~ 600 K to ~ 1150 K. In this zone the decomposition of ADN vapor takes place. In the second dark zone (width of the zone ~ 0.5 to ~ 3 mm) consumption of NH_3, HNO_3 and partial consumption of NO with formation of H_2O and N_2 occur. The temperature in this zone slightly increases from ~ 1150 K to ~ 1450 K. Calculated temperature profile and composition of combustion products are in very good agreement with experimental data for this zone. In the third luminous zone (torch) the temperature increases to 2600 K at the distance of 4-8 mm. The presence of

NO in the combustion products in the third flame zone shows that completeness of combustion at 0.1 MPa is not achieved.

Comparison of the flame structure of ADN/PCL(1250) propellant with that of pure ADN showed that in the first and second flame zones of propellant at 0.1 MPa the same reactions as in the case of pure ADN at 0.6 MPa occur.

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