



Combustion of potassium dinitramide and its binary mixtures with nitroester binder



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ABSTRACT

Steady-state combustion of potassium dinitramide (KDN) and binary mixtures of KDN with a nitroester-based energetic binder has been studied in a constant-pressure bomb in 0.1–15 MPa pressure interval. The thermal stability has been examined under nonisothermal conditions by means of TGA and DSC analyses. The temperature distribution in the combustion wave of the mixtures has been measured by using thin tungsten–rhenium thermocouples. The results obtained allowed conclusion that the observed increase in the burning rate on addition of KDN to the nitroester-based binder was caused by increasing temperature of the first flame zone and corresponding increase in the heat release rate.

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1. Introduction

At the present time a world-wide attention of researchers in the field of energetic materials is paid to the development of environmentally friendly components of solid propellants [1,2]. One of such components is ammonium dinitramide (ADN). ADN is an excellent solid rocket oxidizer which does not leave hydrogen chloride fumes and can provide a slightly higher specific impulse than commonly used ammonium perchlorate (AP) [3]. It was originally invented in the Soviet Union in 1970s [4,5], but had remained classified until it was discovered independently in the United States at Stanford Research Institute in 1989 [6,7].

As compared with AP, ADN demonstrates significantly higher burning rates [8–11]. Within the pressure interval of 2–10 MPa, the combustion of ADN is unstable: the propagation of the burning front is unsteady through the sample and the resultant burning rate might vary in more than two times at the same pressure [11].

Detailed thermocouple-aided study of the combustion wave of ADN using fine Π -shaped thermocouples along with numerous data on ADN thermal decomposition [12–18] allowed suggestion that the chemical transformation of ADN during combustion included two main pathways (mechanisms): ionic and dissociative [19]. Ammonium nitrate (AN), which is formed by the ionic mechanism, undergoes the endothermic reaction of dissociation into

ammonia and nitric acid at the burning surface and in the aerosol zone above the surface, thus controlling the burning surface temperature. Decomposition of dinitramidic acid, which is formed by the dissociative mechanism, proceeds immediately it appears in the condensed phase. Redox reactions between AN dissociation products are responsible for the temperature increase in the first flame, with the final combustion temperature determined by decomposition and redox reactions of nitrogen oxides NO and N₂O [19].

In contrast to ammonium perchlorate, an addition of any fuel to ADN did not appear to increase the burning rate [8,9,20–22]. It is an unbelievable result, but some 1000 °C increase in the flame temperature upon addition of the fuel did not cause the burning rate to increase, moreover the burning rate of the oxygen-balanced mixture with 7% of paraffin is less than that of neat ADN [20]. The combustion mechanism of ADN proposed in [19] allows an explanation of such combustion peculiarities. Redox reactions in both the condensed phase and the first flame of ADN are self-sufficient ones: they do not require an additional fuel since one molecule of ammonia formed from ADN molecule is quite enough for the reduction of the most active oxidizers, OH and NO₂. Any additional fuel to ADN, therefore, has little effect on the chemistry in both the condensed phase and the first flame zone, but exerts greatest influence on the temperature of the final flame. However, the low reactivity of oxidizers NO and N₂O in the final flame makes it stand far from the surface and exert little effect on the burning rate.

Studying of combustion of potassium salt of dinitramide (KDN) may reveal a good support for this concept. KDN contains an

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excess of oxygen and, therefore, may be also used as an oxidizer in various compositions. Since KDN molecule does not include any combustible species, one can expect that most active radicals will react with an external fuel, resulting in an increase in the temperature of the rate-controlling zone.

Obviously, the most promising options include formulations of KDN with nitroester-based energetic binders (NEBs). An important feature of nitroester-based energetic binders is the capability of self-sustained burning. Combustion of nitrocompounds is characterized by two-flame structure of the gas phase. Usually burning rate of nitrocompounds is controlled by reactions of NO_2 with fuel species in the first flame. Thermocouple-aided studies of the temperature distribution in the combustion wave of mixtures of energetic binders with AP [23] have shown that an addition of AP to the binder leads to a regular increase in the flame temperature and temperature gradient above the surface. The burning surface temperature, in turn, is controlled by boiling of the most volatile component i.e., nitroester.

Two reaction pathways were offered for KDN decomposition [24–26]: solid-state decomposition with formation of KNO_3 and N_2O and liquid-phase decomposition with formation of $\text{KNO}_3/\text{KNO}_2$ and $\text{N}_2\text{O}/\text{NO}$. The initial detachment of the nitro group in the last case is followed by conversion of NO_2 into $\text{N}_2\text{O}/\text{NO}$ in situ, i.e., without diffusing to participate in other reactions (so called “cage reaction”).

Since NO and N_2O are the oxidizing agents of low reactivity, they react in the second flame and exert little effect on the burning rate [27]. If the nitro group formed due to KDN decomposition really reacts without leaving the “cage”, an addition of KDN to a nitroester-based energetic binder, which burning rate is determined by reactions of NO_2 in the first flame, will not lead to an increase in the burning rate.

In this connection, the purpose of this work was to study the burning behavior and combustion mechanism of compositions of KDN with the nitroester-based binder.

2. Experimental

KDN (KN_3O_4 , $\Delta H_f^\circ = -264.18 \text{ kJ/mol}$ [28]) was used for burning rate experiments as obtained by a technique given in Ref. 4 followed by recrystallization from ethanol. Precipitated KDN, as white non-hygroscopic crystals, were dried in vacuum at 60°C for 3 h and had a melting point $129\text{--}131^\circ\text{C}$. Two fractions of KDN with the mean particle size of $50 \mu\text{m}$ and $150 \mu\text{m}$ were used in the study. A composition of polyurethane rubber with nitroglycerine (NG), diethylene glycol dinitrate (DEGDN), and triethylene glycol dinitrate (TEGDN) with the general formula $\text{C}_{20.99}\text{H}_{35.39}\text{N}_{10.48}\text{O}_{35.34}$ and enthalpy of formation $\Delta H_f^\circ = -2574 \text{ kJ/kg}$ was used as the NEB. Previous thermocouple-aided study of this binder has shown that the combustion is governed by reactions in the gas phase [29]. Binary mixtures were prepared by mixing the crystals of KDN with the binder in a Teflon mortar.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with DSC 822e Mettler Toledo in the temperature range of $25\text{--}400^\circ\text{C}$ at different heating rates. The samples weighing between 1 mg and 3 mg were analyzed in aluminium pans under nitrogen atmosphere; in the case of mixtures the sample weight was increased to 10 mg.

Burning rates of KDN and its mixtures with the binder were measured in a window constant-pressure bomb of 1.5-l volume in the 0.1–15 MPa pressure interval. Samples to test were prepared by pressing fine particles of KDN into transparent acrylic tubes of 4 mm internal diameter or by compact filling the non-cured binary mixtures into the same tubes. To test the effect of sample diameter on the KDN burning rate several experiments have been done with samples pressed into 7-mm i.d. acrylic tubes. A video camera was

used to determine the character of the combustion process as well as to evaluate burning rates. Accuracy of the burning rate measurements was 5%.

Temperature profiles during combustion of the binder and its mixtures with KDN were measured using Π -shaped thin tungsten–rhenium thermocouples. The thermocouples were welded from 25- or $50\text{-}\mu\text{m}$ -diameter tungsten–5% rhenium and tungsten–20% rhenium wires and rolled in bands to obtain 5–7- μm bead size. The heat inertia for such a thin thermocouple is very small. The time constant of the thermocouple placed in the gas flame of a NG-based propellant was estimated as $10^{-3}\text{--}10^{-4} \text{ s}$ [30]. The method of preparation of samples with embedded micro thermocouples was described in [31]. The thermocouple signal was recorded with a Pico ADC 216 digital oscilloscope.

Adiabatic combustion temperatures were calculated with REAL thermodynamic code [32], intended for computer simulation of chemical equilibrium in the complex reactive systems at high temperature and pressure. The build-in database contains thermodynamic, thermochemical, and thermophysical properties of 2500 molecules and species which are composed of 79 chemical elements in total. The calculation algorithm is based on the fundamental principle of entropy maximum. All calculations of temperatures were performed for the adiabatic condition and constant pressure.

3. Results and discussion

3.1. Decomposition study

A DSC thermogram of KDN at the heating rate of 10 K/min is shown in Fig. 1. It demonstrates two endothermic peaks at 128°C and 338°C , the first one corresponding to melting of KDN (127°C) and the second one to melting of KDN decomposition products, as well as a broad exotherm composed of two overlapping peaks, attributed to the decomposition of KDN. In general, the observed DSC data are in accordance with previously published results [16,33,34]. Although the melting point of pure KNO_3 (334°C) falls within the second endotherm borders ($330\text{--}340^\circ\text{C}$), this temperature interval can be reasonably attributed to melting of a $\text{KNO}_2/\text{KNO}_3$ mixture with KNO_2 content ranging from 28% to 45%, as indicated by the $\text{KNO}_2/\text{KNO}_3$ temperature-composition phase diagram [35].

A TG curve for KDN decomposition in aluminium pans closed by pierced lids is shown in Fig. 1. The mass loss in the vicinity of 100°C is connected with evaporation of water absorbed by the sample. Literature data for KDN decomposition [33] has indicated ca 1.5% mass loss in this temperature range also. The mass loss of 31.3–34.3% (35.6% in [33]) observed in the temperature interval of $170\text{--}250^\circ\text{C}$ is attributed to the decomposition of the salt.

Assuming that the decomposition reaction in the liquid state proceeds as indicated in [25]:



the mass loss is 35.9%. If the decomposition products were N_2O and KNO_3 only, the mass loss would be 30.3%.

The heat effect of the KDN decomposition is measured as 528 J g^{-1} ($18.4 \text{ kcal mol}^{-1}$). At the same time, the heat effect calculated in accordance with Eq. (1) is considerably less ($8.8 \text{ kcal mol}^{-1}$ or 253 J g^{-1}). The decomposition of KDN to KNO_3 and N_2O will produce considerably more heat ($35.5 \text{ kcal mol}^{-1}$ or 1023 J g^{-1}).

Therefore, data of both DSC and TG analyses suggest that the decomposition of KDN can not be satisfactorily described by Eq. (1). Under given decomposition conditions, the proportion of KNO_3 formed must be higher than it follows from Eq. (1), with calculated fractions of NO and N_2O being close each other (0.65–0.7):

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