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Review

Evaluation of decomposition kinetics of energetic materials in the combustion wave

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ABSTRACT

Experimental data on burning rates and surface temperatures have been shown to allow deriving unique information on decomposition kinetics of energetic materials at high temperatures, provided combustion of these materials occurs in the condensed phase. In the paper, kinetic parameters of the leading reaction on combustion of four solid rocket propellant oxidizers: ammonium perchlorate (AP), ammonium nitrate (AN), ammonium dinitramide (ADN), and hydrazine nitroformate (HNF), as well as six energetic fillers: 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), bicyclo-1,3,5,7-tetranitro-l,3,5,7-tetraazacyclooctane (bicyclo-HMX), hexanitrohexaazaisowurtzitane (CL-20), 3,3′-diamino-4,4′-azofurazan (DAAzF), and 3-nitro-l,2,4-triazole-5-one (NTO) are evaluated from available combustion data.

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1. Introduction

Experimental evaluation of kinetic parameters of energetic materials decomposition at temperatures higher than 300–350 °C by using general methods based on monitoring sample mass change, heat or gas evolution, usually involves difficulties connected with very short conversion time. For example, time of half-decomposition of ordinary explosives such as RDX at 350 °C is not more than 0.0002 s, that is far below capabilities of existing recording devices.

The condensed phase of a burning energetic material is heated up to temperatures 250–1000 °C that can be recorded using microthermocouple technique with accuracy of 5–20 °C depending on the material nature and experimenter experience. Decreasing pressure leads in widening combustion wave zones, making measurements more accurate. At the same time, the burning rate measurements are usually feasible with an experimental error less than 5%. Using experimental data on burning rates and surface temperatures one can derive rate constants of the leading reaction from an adequate combustion model.

In the paper, experimental data on burning rates and surface temperatures for a series of energetic materials from different

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classes, such as onium salts (AP, AN, ADN, HNF), nitramines (HMX, RDX, bicyclo-HMX, CL-20), and heterocyclic compounds (NTO, DAAzF) were used to determine decomposition kinetics in the combustion wave.

2. Experimental

Syntheses of the substances, sample preparation technique, burning rate and thermocouple measurements are described in related papers, which are referred to in the text.

Most of burning rate measurements were carried out in a constant pressure window bomb with a volume of 1.5 l. Temperature profiles in the combustion wave were measured using fine Π-shaped thermocouples. The thermocouples were welded from 80% tungsten + 20% rhenium and 95% tungsten + 5% rhenium wires 20 μm in diameter and rolled into bands 7 μm thick. The thermocouple was embedded in the center of the strand so that the section with the junction was parallel to the combustion front.

3. Results and discussion

3.1. Theory

Decomposition of an energetic material begins with endothermic rupture of the weakest bond in the molecule. Subsequent secondary radical reactions have significantly less activation energy. A difference in the activation energies results in the leading reaction on combustion to be either initial endothermic decomposition of the original material to form active species or subsequent secondary heat-generating reactions, depending on the temperature interval. In the interval of 150–300 °C, within which thermal decomposition of energetic materials is most often studied, the limiting stage is usually characterized by high activation energy, with the secondary reactions being of low activation energy and proceeding fast. Associated autocatalytic processes can interfere in correct determination of kinetic parameters of bond cleavage, but are of insignificant importance in the combustion wave at high temperatures because of low activation energies of such reactions.

As temperature increases, secondary radical reactions get slower than the primary decomposition of the molecule, thus becoming rate-limiting ones in the heat generation process. Since the burning rate is determined by heat-release kinetics, the leading role can be switched to the secondary radical reactions starting from certain temperatures. Calculations [1], confirmed by experimental observations [2] show that this transition temperature is in the interval of 1000–1500 °C for nitrocompounds and above 2500 °C for endothermic substances such as organic azides. These temperatures lie above normal surface temperatures, suggesting that the rate-limiting process in the condensed phase of a burning substance is for the most part primary bond-cleavage reactions.

It may be supposed therefore that the decomposition kinetics of a substance can be derived from its burning rate data if combustion is governed by condensed-phase reactions. In order for kinetic parameters of the rate-controlling reaction could be evaluated from available experimental data on burning rates and surface temperatures, an adequate combustion model must be chosen and considered.

Several combustion models with condensed-phase priority have created in the Soviet Union starting from the forties of past century. Zeldovich, one of the authors of the combustion model for gases and volatile explosives [3], proposed an expression for propagation of the exothermic reaction wave in the condensed phase of energetic materials. The equation was derived assuming the concentration of a reacting substance in the reaction zone equal to initial one, i.e., the degree of conversion was assumed to be small:

$$m = \sqrt{\frac{2\rho^2 \chi Q}{c_p (T_s - T_0 + L_m/c_p)^2} \left(\frac{RT_s^2}{E}\right) \cdot A \cdot e^{-E/RT_s}} \qquad (1)$$

where c_p, ρ, χ are specific heat, density, and thermal diffusivity of the condensed phase, T_s and Q are the surface temperature and heat effect, E and A are activation energy and preexponential factor of the leading reaction in the condensed phase. The expression $T_s - T_0 + L_m/c_p$ accounts for warming-up of the condensed phase from initial temperature, T_0, to surface temperature, T_s, and melting, where L_m is heat of melting.

In the subsequent years, a number of elementary condensed-phase combustion models were proposed and were summarized in Ref. [4]. According to Ref. [4], all the models can be divided into two groups. The first one includes models that consider full conversion of the substance in the combustion wave, i.e., when the reaction proceeds at the maximum combustion temperature $T_{\max} = T_0 + Q/c_p$. This type of models was developed in theoretical works by Novozhilov [5] and Khaikin and Merzhanov [6]. The burning rate here is independent of pressure, making these models suitable for describing combustion of materials which do not evaporate and do not produce gases at burning.

The modes of the second group consider formation of the burning surface of different physico-chemical nature. The value of T_s and degree of decomposition in the condensed phase, η, reflect the incompleteness of conversion ($T_s < T_{\max}$, $\eta < 1$) and determine the burning rate. Gas-phase reactions do not influence the rate of combustion and are not included into consideration. The burning surface of such materials is a result of dispersion or evaporation of the condensed phase [6–9]. As compared to Zeldovich's model [3], models developed in works [8–10] operate with different kinetic equations of heat generation process: zero-, first-, second-order reactions can be used. These models comply with the Zeldovich's equation for the zero-order reaction or, more specifically, for the first-order reaction with no change of the concentration in the reaction zone. If change in the concentration is taken into account, the first-order constant calculated with these models will grow 1.2–1.8 times depending on the degree of conversion in the condensed phase.

According to the models, the degree of conversion of energetic materials in the condensed phase is defined as the ratio between heat needed to warm up a material to the surface temperature, taking into account heat of modification and phase changes, and heat effect of the decomposition reaction. A part of the substance remains undecomposed at the surface and is ejected into the gas phase with flying-off gases. The following decomposition and evaporation of droplets does not exert essential influence on the burning rate.

The above model is most suitable for describing combustion of different energetic materials capable of evaporation, providing correct boundaries of application area. Flameless combustion, which obeys to the model best, is usually observed at low pressures. As pressure grows a high-temperature flame arises, and a judgment about location of the leading reaction can be done by analyzing temperature profiles of the combustion wave. It is generally believed that the leading role belongs to the condensed phase if the heat flux from the gas to the burning surface is negligibly small [11]. In addition, the model can be employed also in the case of substantial heat flux if the heat feedback, Q_g, is less than or comparable to the heat necessary for evaporation of unreacted in the condensed phase substance, $(1-\eta)Q_{\text{ev}}$. In this case, all the heat Q_g is consumed for evaporation of the dispersal phase above the surface, having no effect on the burning rate, which is determined by expression (1).

In the general case that the heat feedback from the gas becomes superior over the heat required for evaporation, the expression (1)