Central European Journal of Energetic Materials, **2005**, *2*(1), 3-20.
ISSN 1733-7178

Reason for Heat Instability of Combustion of Energetic Materials with Condensed Phase Leading Reaction

Valery P. SINDITSKII

Mendeleev University of Chemical Technology,
9 Miusskaya Square, 125047, Moscow, Russia
E-mail: svp@rctu.ru

Abstract: The paper presents an analysis of observable combustion instability of energetic materials with condensed phase leading reaction. The Zeldovich's and Novozhilov's criteria have been calculated by an example of two dinitramide salts, ADN and HMDADN, having a condensed-phase combustion mechanism. It is suggested an explanation of combustion instability observed.

Keywords: combustion instability, ammonium dinitramide, hexamethyle-nediamine bisdinitramide, temperature sensitivity of burning rate, surface temperature

Introduction

A comprehensive understanding of physicochemical processes occurring in the combustion wave of propellant ingredients is essential for modeling the combustion behavior of energetic materials (EM). EM are characterized by a large variety of chemical and physical properties, which in aggregate define a variety of combustion models. For example, burning wave propagation can be completely realized by reactions in the condensed phase. Such a process is described by the laws similar to the gas-phase burning with the only difference that the diffusion is supposed insignificant for the condensed-phase mechanism [1, 2]. However there is still very important distinction between two combustion models: in contrast to gas-phase model, the condensed-phase one has a limitation. In fact the burning rate in gas-phase model grows with pressure at the expense of increase of concentration in reacting substance in gas (if consider combustion temperature constant). In condensed-phase model the concentration of substance is constant and independent from pressure, the burning rate grows at the expense of surface temperature increase with pressure. Hence, at combustion of substances which surface temperature depends on pressure, there can come a moment when the heat effect of EM decomposition becomes insufficient for warming-up substance to the surface temperature. In most cases this moment masks by increasing gas-phase heat feedback with pressure and transition of leading reaction from the condensed phase to gas. However, there is a number of EM, which have high surface temperatures and rather low combustion temperatures. For these EM it is possible to consider the contribution of the gas phase to the burning rate insignificant within a rather wide pressure interval. The salts of strong acids, perchlorates and dinitramides have high surface temperatures. Many of them have instability regions on their burn rate *vs.* pressure curves. It would be interesting to establish a reason for heat instability of combustion for such energetic materials with condensed phase leading reaction.

Problem formulation

The main parameter determining the borders of stability of stationary process of EM combustion is the number of Ya. B. Zeldovich [1]:

$$k = \sigma(T_s - T_o) \ ,$$

where: σ is the temperature sensitivity of burning rate, T_s and T_o are the surface and initial temperatures. To take the melting of the condensed phase into account, L_m/c_p is added to the expression in brackets, where c_p is the average specific heat of the condensed phase, L_m is the heat of melting.

According to Zeldovich, the combustion process is steady if $k < 1$. Based on the main assumption of quasi-steady gas-phase behavior, Zeldovich's number was first suggested for designating the stability boundary of EM, burning with the gas-phase mechanism. In 1965 B. V. Novozhilov proposed [3, 4] an extended version of the phenomenological approach to combustion instability, which now is called in the literature the Zeldovich-Novozhilov (ZN) approach.

According to ZN approach, the exothermic chemical reaction may proceed both in the gas and condensed phases. The extent of the reaction zone in the condensed phase is assumed to be very thin in comparison with preheated layer of EM, due to high activation energy of chemical reactions. Therefore, it is assumed that the thermal relaxation time of the condensed-phase reaction zone is much shorter than the relaxation time of the preheated layer of EM.

So in the case if $k > 1$, the combustion process keeps stability under condition of:

$$\frac{(k-1)^2}{k+1} \le r$$

or analogical to Zeldovich's number one may write [5]:

$$k_N = \frac{(k-1)^2}{r(k+1)} \le 1, \text{ where } r = \left(\frac{\partial T_s}{\partial T_o}\right)_P .$$

If a reaction determining burning rate proceeds in the condensed phase, according to the combustion theory of Ya. B. Zeldovich [1], the expression for the mass burning rate (m) is as following:

$$m = \frac{\rho}{T_s - T_o}\sqrt{\frac{2\chi Q_c}{c_p}\left(\frac{RT_s^2}{E}\right)\cdot Z \cdot e^{-E/RT_s}}$$

where: χ is the thermal diffusivity of the condensed phase, Q_c is heat effect of leading reaction in the condensed phase, E and Z are activation energy and preexponential factor for this reaction. Taking the logarithm the above-stated equation and then differentiating by T_o, it is possible to receive expression for the temperature dependence of burning rate:

$$\frac{\partial \ln m}{\partial T_o} = \sigma = \frac{E}{2RT_s^2}\cdot\frac{\partial T_s}{\partial T_o} + \frac{1}{T_s}\cdot\frac{\partial T_s}{\partial T_o} - \frac{1}{T_s - T_o}\left(\frac{\partial T_s}{\partial T_o} - 1\right)$$

At burning of EM, which surface temperature is defined by evaporation process, it is possible to consider $\frac{\partial T_s}{\partial T_o}$ parameter as a very small value. In this case the temperature coefficient of burning rate is determined mainly by surface temperature (in the case of melting, L_m/c_p value may be added to the denominator):

$$\sigma \approx \frac{1}{T_s - T_o}$$

Hence, for combustion of energetic materials with condensed phase leading reaction, the Zeldovich's number for the steady combustion region should be close to 1 and the Novozhilov's number should be much less than 1.

The Novozhilov's number contains parameter r, which is extremely difficult to determine experimentally. However, in the case of condensed-phase model of combustion, when the burning rate is determined only by surface temperature, parameter r can be expressed through other parameters. For such a case, according to [4]:

$$\left(\frac{\partial \ln m}{\partial \ln P}\right)_{T_o}\left(\frac{\partial T_s}{\partial T_o}\right)_P=\left(\frac{\partial \ln m}{\partial T_o}\right)_P\left(\frac{\partial T_s}{\partial \ln P}\right)_{T_o}.$$

Consequently

$$r=\left(\frac{\partial T_s}{\partial T_o}\right)_P=\left(\frac{\partial \ln m}{\partial T_o}\right)_P\left(\frac{\partial T_s}{\partial \ln P}\right)_{T_o}\left(\frac{\partial \ln P}{\partial \ln m}\right)_{T_o}=\left(\frac{\partial T_s}{\partial \ln P}\right)_{T_o}\cdot\frac{\sigma}{\nu},$$

where $\sigma=\left(\frac{\partial \ln m}{\partial T_o}\right)_P$, $\nu=\left(\frac{\partial \ln m}{\partial \ln P}\right)_{T_o}$.

At combustion of energetic materials with condensed phase leading reaction and surface temperature determined by evaporation processes, the exponent in the burning law is defined by the expression $\nu=\frac{E}{2L_v}$. So, Novozhilov's number can be expressed as:

$$k_N=\frac{(k-1)^2}{r(k+1)}=\frac{\nu(k-1)^2}{\sigma(k+1)}\cdot\left(\frac{\partial \ln P}{\partial T_s}\right)_{T_o}=\frac{E(k-1)^2}{2L_v\sigma(k+1)}\cdot\left(\frac{\partial \ln P}{\partial T_s}\right)_{T_o}.$$

To calculate Zeldovich's and Novozhilov's criteria it is necessary to know the dependence of the burning rate on pressure and temperature, the surface temperature (T_s) and its dependence on pressure. For a number of EM from the class of onium salts, for example, dinitramides, which combustion obeys the condensed-phase mechanism, such data were experimentally determined.

Results and discussion

Ammonium dinitramide (ADN)

One of the well-known representatives of dinitramide salts is ammonium dinitramide, which is considered as an environmentally friendly oxidizer capable of offering higher performance than conventional ammonium perchlorate (AP). As for now, there have been published results on ADN burn rate characteristics in a wide pressure range [6-8]. The dependence of burning rate on pressure *u(P)* for ADN is similar to that for AP. It is characterized also by three segments on the burning rate *vs.* pressure curve [8, 9] (Figure 1): the first one is the burning rate growth with pressure, the second one is the burning rate decrease, followed by increasing burning rate again at the third segment. For the first segment, at low pressures, the burning rate is obviously determined by reactions occurring in the condensed phase. Combustion of ADN within the pressure interval of 2-10 MPa is accompanied by a notable burn rate data scatter, which is indicative of ADN combustion instability. In the pressure interval of 10-36 MPa, the bright flame is visible just above the surface of the burning strand, therefore it is logical to assume that reactions occurring in the gas phase make a significant contribution to the burning rate on the third segment of the *u(P)*.

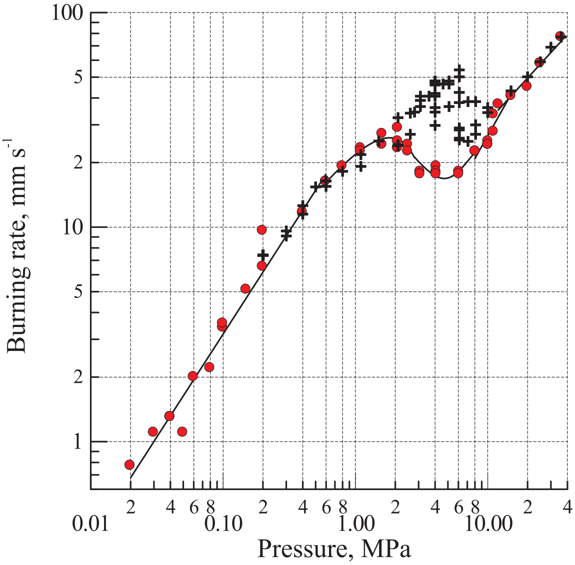

Figure 1. Comparison of the combustion behavior of pure ADN (black crosses) and ADN containing 0.2% of paraffin (light points and line), all pressed into acrylic tubes.

In the case of ADN single crystals as well as the supersaturated water solution the combustion instability area is emphasized very distinctly: the crystals are incapable of sustained burning within the pressure range of 2-10 MPa, whereas the supersaturated water solution has a local maximum of burning rate in this area (Figure 2) [9].

Even minor amounts of organic admixtures to ADN turned out to have a strong effect on the burning behavior [8, 9]. For example, an addition of only 0.2% of paraffin to crystalline ADN appeared to extend the low-pressure limit of ADN sustained combustion from 0.2 to 0.02 MPa (Figure 1). Within the pressure intervals of 0.2-2.1 MPa and 15-36 MPa the burning rate of the ADN + 0.2% paraffin mixture coincides well with that of pure ADN. Within the range of 2-10 MPa the burning rate of the paraffin-doped mixture is noticeably less and no marked scatter in the burn rate values is observed. The lower-pressure limit of ADN combustion turned out to be reduced by the addition of not only organic admixtures, capable to burn, but perhalocarbon oil and silica gel SiO_2 also, which hardly can be regarded as readily oxidizable fuels. This fact allows conjecture [9] that the surprising effect of some minor additives to ADN on the lower-pressure limit is connected to physical reasons rather than chemical ones.

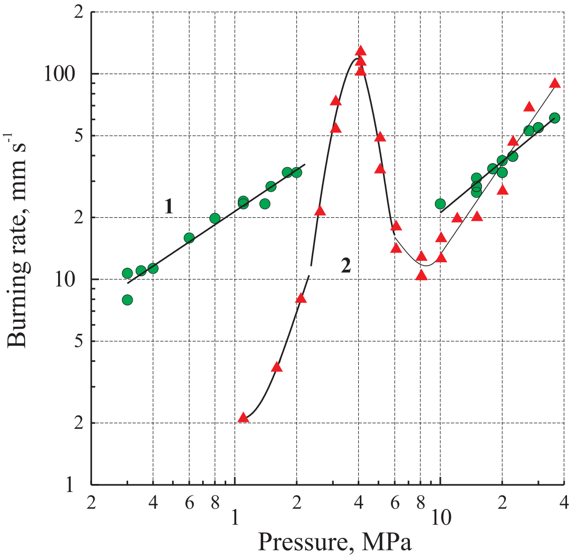

Figure 2. Comparison of burning characteristics of ADN single crystals (1) and supersaturated water solution of ADN (2).

ADN is a convenient substance for study since it has extended zones in flame that allows identification of the surface temperature in a wide pressure interval. It was revealed in work [8] that the temperature of the combustion surface corresponded to the temperature of dissociation of ammonium nitrate (AN) formed in the condensed phase (Figure 3). The dependence of the AN surface temperature on pressure expresses as $\log P = -\frac{4360}{T_s} + 7.101$ or $T_s = \frac{4360}{7.101 - \log P}$, where P in atm. The differentiation of this expression allows receiving the dependence of $\frac{\partial T_s}{\partial \ln P}$ on pressure: $\frac{\partial T_s}{\partial \ln P} = 36.92\ P^{0.146}$.

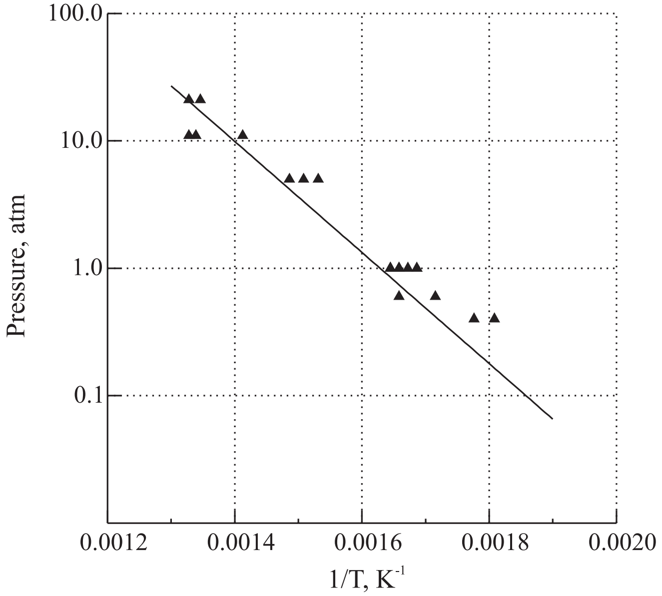

Figure 3. Dependence of the surface temperature of ADN on pressure. Line is vapor pressure above liquid ammonium nitrate.

The dependence of the burning rate of ADN, doped with 0.2% of paraffin, on initial temperature at atmospheric pressure is presented in Figure 4. As can be seen from the Figure, ADN is capable of burning even at temperature of liquid nitrogen (-196 °C) [10]. The differentiation of this dependence allows receiving the temperature sensitivity of burning rate σ at various initial temperatures. These data in comparison with calculated dependence are presented in Figure 5. Despite significant mistake of σ determination because of differentiation, quite good accordance between calculated and experimental data is observed.

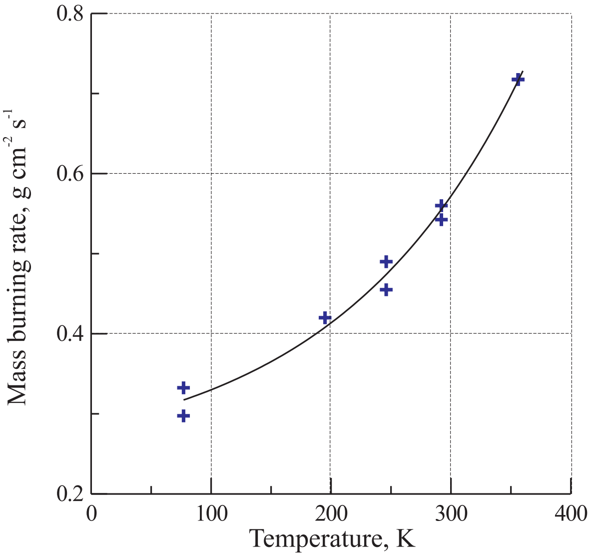

Figure 4. Effect of initial temperature on the burning rate of paraffin-doped ADN at 0.1 MPa.

At calculation of Zeldovich's and Novozhilov's criteria the heat of dissociation of ammonium nitrate L_v = 166.9 kJ mole^{-1} (39.9 kcal mole^{-1}) [5] was used, the activation energy E = 148.5 kJ mole^{-1} (35.5 kcal mole^{-1}) for the condensed-phase decomposition of ADN was given from work [11]. Calculated values are presented in Figure 6. As can be seen from the Figure, the average value of k for five various initial temperatures is slightly above than unit (1.15), and the average value of Novozhilov's number is close to zero (~0.1). At atmospheric pressure ADN, doped by paraffin, burns quite steadily, and as it can be seen from Figure 1, the low-pressure limit of burning lies much below. Thus, in fact, for energetic materials which combustion is propagated at the expense of exothermic reaction in the condensed phase, in the area of steady state burning, the Zeldovich's criterion is a little bit more than unit, and the Novozhilov's criterion remains less than unit.

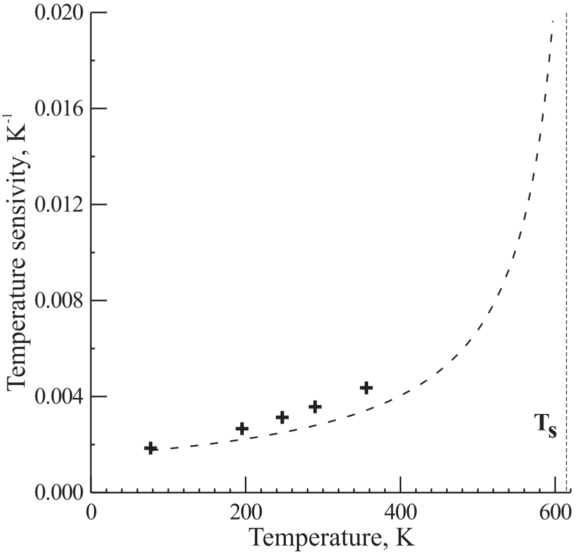

Figure 5. Comparison of the experimental temperature sensitivity of paraffin-doped ADN at 0.1 MPa with calculated one.

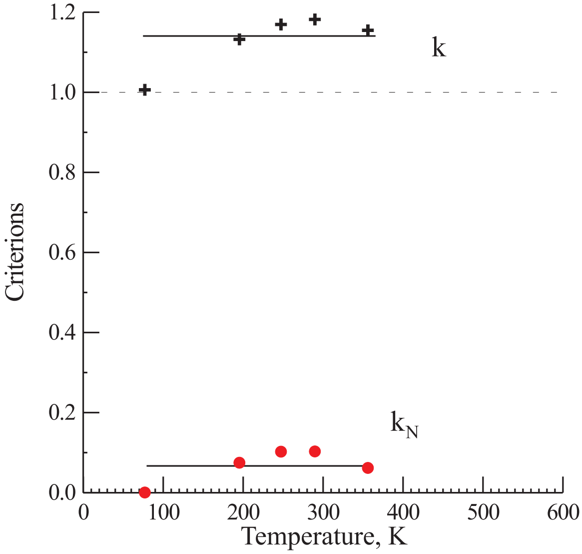

Figure 6. Experimental values of Zeldovich's and Novozhilov's numbers for paraffin-doped ADN at 0.1 MPa.

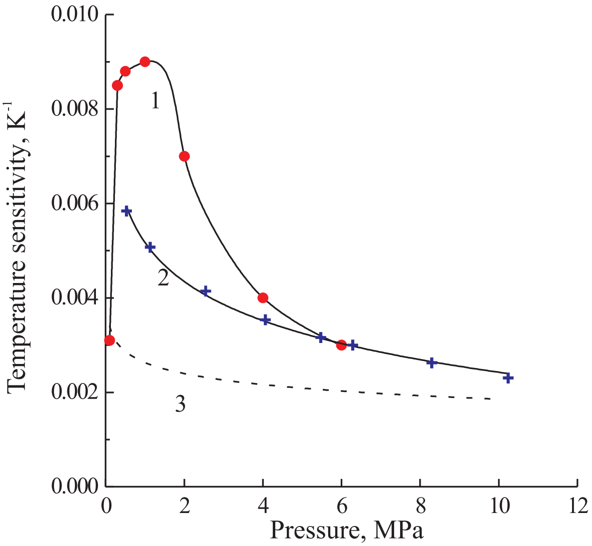

Figure 7. Comparison of the experimental temperature sensitivities of ADN measured at 123-298 K (1) and at 298-348 K (2) with calculated one (3).

The measurements of ADN burning rate at various pressures and initial temperatures were carried out in works [12, 13]. In work [13] measurements were carried out at -150, 20 and 80 °C in the interval 0.1-6 MPa, in work [12] at 20 and 75 °C in the interval 0.7-10.3 MPa. Our burn rate data obtained at atmospheric pressure are in the good agreement with data of work [13] up to T_o = 80 °C. At higher initial temperatures, samples of ADN, usually containing small amounts of ammonium nitrate as an impurity, melt that can result in substantial growth of burning rate for the account of turbulization of burning process. Therefore, only the data obtained in the interval -150 and 20 °C were taken from work [13]. Temperature sensitivities of ADN burning rate calculated on the basis of data [12, 13] are presented in Figure 7. The distinctions in the results are caused by not only significant scatter of ADN burning rates in the interval of 2-8 MPa, but first of all by the fact that the initial temperatures were various. The experiments carrying out at -150 °C result in sharp fall of burning rates which is reflected in value of σ. For calculation of the criteria the data of works [13] in the interval 0.3-6 MPa, complemented with our data at 0.1 MPa and data of work [12] at 8 and 10 MPa were used. Calculated criteria are presented in Figure 8. As can be seen from the Figure, both criteria k and k_N begin sharply grow with pressure and in the interval of 0.3-6 MPa they considerably exceed unit. At high pressures the Zeldovich's number approaches to the unit, remaining little higher, and Novozhilov's number tends to zero.

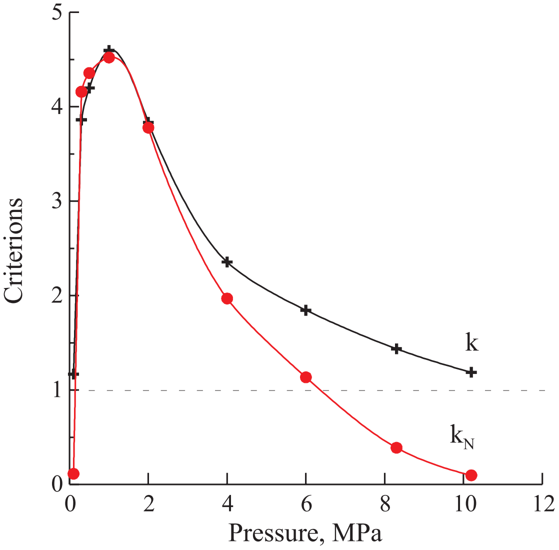

Figure 8. Experimental values of Zeldovich's and Novozhilov's numbers for ADN.

Hexamethylenediamine bisdinitramide (HMDADN)

Hexamethylenediamine bisdinitramide is a salt of dinitramide and a base hexamethylenediamine (HMDA) which possesses stronger basic properties than ammonia. Hence, for this salt it is possible to expect a higher surface temperature than in the case of ADN. Energetic characteristics of this salt concede to ADN. The luminous flame at HMDADN burning occurs only at pressure above 2 MPa, unequivocally suggesting that in the interval of 0.04-2 MPa the combustion is propagated at the expense of exothermic condensed-phase reactions. The flame structure of HMDADN has been investigated with tungsten-rhenium microthermocouples in [14, 10]. As in the case of ADN, HMDADN shows a local maximum on the burning rate *vs.* pressure dependence, situated at a pressure lower than one of ADN burning rate maximum (Figure 9).

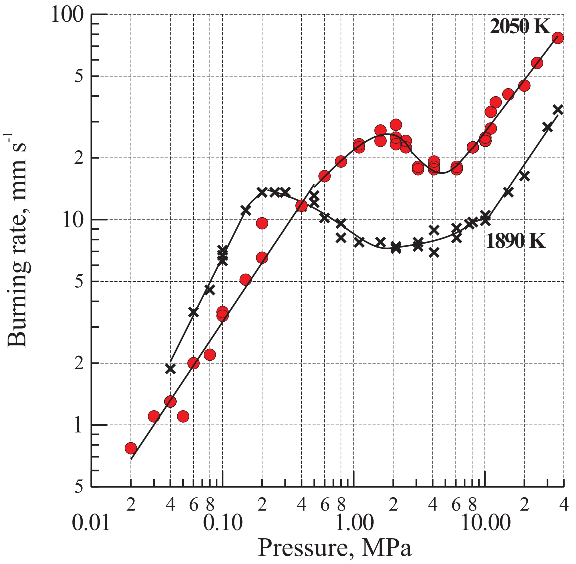

Figure 9. Effect of pressure on the burning rate of dinitramide salts of hexamethylenediamine (crosses) and ammonia (points). Figures are calculated adiabatic combustion temperatures.

It was proposed that the temperature of the combustion surface corresponded to the temperature of dissociation of nitrate salt formed in the condensed phase as in the case of ADN. The heats of dissociation of nitrate and dinitramide salts of HMDA have been calculated from the slopes of the curves constructed in the corresponding coordinates $logP\text{-}1/T_s$ and $logP\text{-}1/T_1$ to give values of 335 (80) and 464 kJ mole^{-1} (111 kcal mole^{-1}), respectively. These figures are in a good agreement with heats calculated as a difference between heats of formation of solid HMDA nitrate and dinitramide and gaseous products of their dissociation, 372 (89) and 435 kJ mole^{-1} (104 kcal mole^{-1}), respectively [14].

HMDADN is capable of self-sustained burning at atmospheric pressure even at temperature of liquid nitrogen (77 K), allowing burning rate-initial temperature dependence to be measured in a wide temperature interval (77-383 K) (Figure 10) [10]. The burning rate of the salt measured at low temperatures demonstrates rather significant data scatter, which is characteristic for combustion with the leading role of the condensed phase reactions.

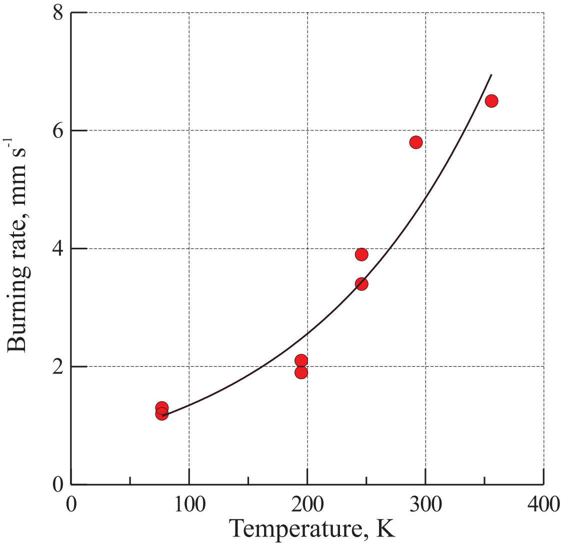

Figure 10. Effect of initial temperature on the burning rate of HMDADN at 0.1 MPa.

Burning rate temperature sensitivity of HMDADN at atmospheric pressure has been calculated from the experimental data. It increases from $4 \cdot 10^{-3}$ to $8 \cdot 10^{-3}$ K^{-1} as the initial temperature grows from 77 to 353 K. These values are several times more than the theoretical ones evaluated from the combustion model based on the dominant role of condensed phase chemistry (Figure 11). At calculation of Zeldovich's and Novozhilov's criteria the heat of dissociation of HMDA nitrate L_v = 372 kJ $mole^{-1}$ (89 kcal $mole^{-1}$) was used; the kinetics of decomposition were assumed to be close to kinetics of the ADN condensed-phase decomposition. The calculated criteria are presented in Figure 12.

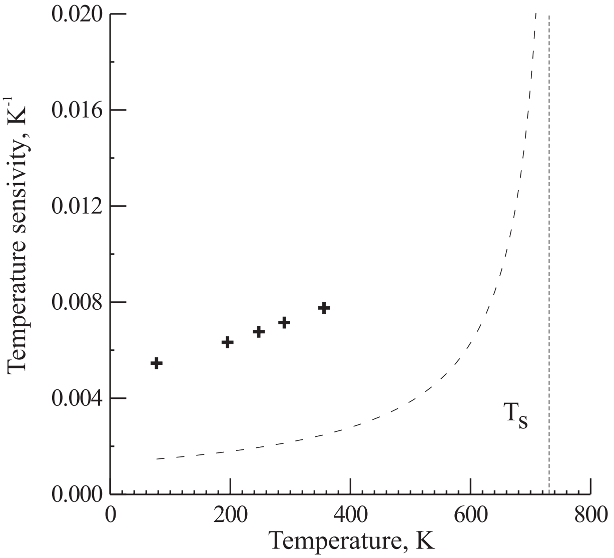

Figure 11. Comparison of the experimental temperature sensitivity of HMDADN (crosses) at 0.1 MPa with calculated one (dashed line).

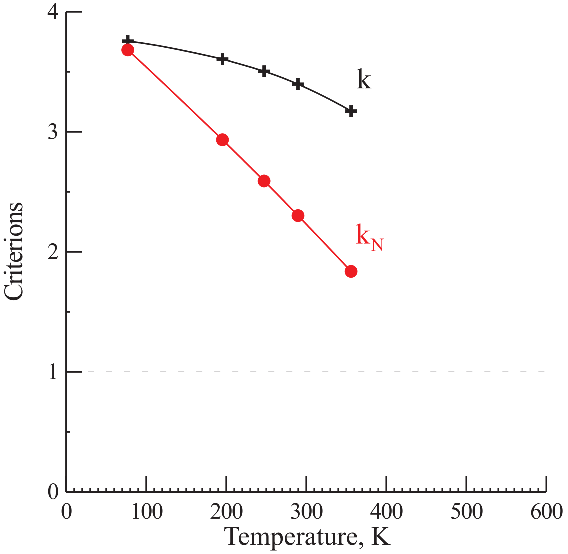

Figure 12. Experimental values of Zeldovich's and Novozhilov's numbers for HMDADN at 0.1 MPa.

As can be seen from the Figure, in the area of a local maximum of burning rate of HMDADN both criteria are more than unit that confirms the assumption of thermal instability of burning in this pressure region. This may be indicative of the thermal instability of combustion as a reason for the occurrence of the local maximum on the burning rate *vs.* pressure curve, as was the case of ADN.

What is the reason for combustion instability? Both dinitramide salts have similar combustion mechanism. At low pressures, the reaction of dinitramide salt decomposition to form N_2O and corresponding nitrate plays a dominant role in combustion. The temperature of the combustion surface of both salts corresponds to the temperature of dissociation of corresponding nitrates formed in the condensed phase. Temperature profiles obtained for ADN clearly indicate that at least up to 4 MPa there is a region between surface and first flame where temperature gradient is close to zero, that is the condensed phase can be warmed up only at the expense of a condensed-phase reaction. Similar observations have been done for combustion of HMDADN also. A comparison can be made between heat of ADN decomposition in the condensed phase (Q = 1674 kJ kg^{-1}, 400 cal g^{-1}) and heat required for warming-up the condensed phase to the surface temperature at different pressures. Calculations show that at pressures above 2 MPa, the heat released in the condensed phase is not enough to warm-up the condensed material to the surface temperature (Figure 13). Although there is a flame over the ADN surface at this pressure, the heat flux from the gas phase is consumed only for warming-up and evaporation of the condensed material in the aerosol flow above the surface and does not come to the condensed phase. Because of the lack of heat, the combustion process becomes unstable and assumes an oscillatory mode. Dispersion of the surface layer increases resulting in a notable burn rate data scatter; the critical diameter of combustion also increases.

It is interesting to note that the surface temperatures of HMDADN and ADN measured at the pressures corresponding to the burn rate local maximums are close together (~725 K). Since heat effects of the HMDADN and ADN decomposition in the condensed phase are close also, the similarity between surface temperatures supports the conclusion that the reasons for combustion instability of both substances are the same: a deficit in the reaction heat for heating-up the solid to the surface temperature and subsequent dissociation. Indeed, a comparison between available and required heats at different pressures shows that at pressures above 0.3 MPa the heat released in the condensed phase of HMDADN is not enough to warm-up the condensed material to the surface temperature (see Figure 13).

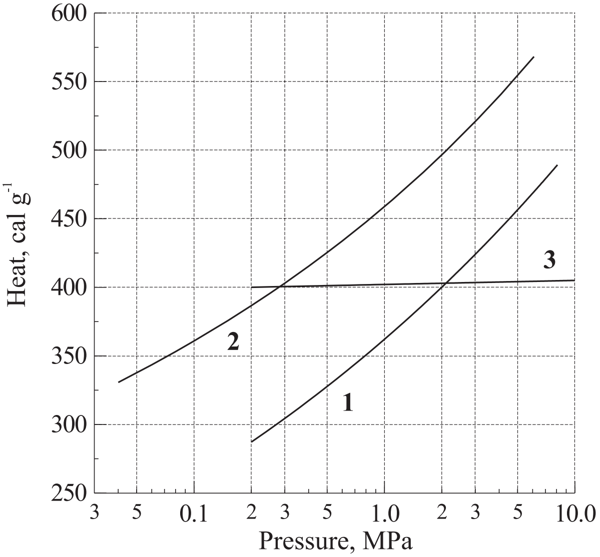

Figure 13. A comparison between heat of dinitramide decomposition in the condensed phase (3) and heats required for warming-up the condensed phase to the surface temperature for ADN (1) and HMDADN (2).

The occurrence of combustion instability area depends upon the fuel reactivity and, largely, the surface temperature, which is assumed to be dissociation one and dependent on the amine basicity. HMDA has a stronger basicity than ADN, which results in much higher surface temperature of the former (at the same pressures) and correspondingly, earlier occurrence of combustion instability area due to the disturbance of the balance between heat required and evolved in the condensed phase. At higher pressures a contribution of gas-phase redox reactions removes the combustion instability.

Conclusion

The Zeldovich's and Novozhilov's criteria have been calculated by an example of two dinitramide salts, ADN and HMDADN, having a condensed-phase combustion mechanism. It has been concluded that for the steady-state burning of these energetic materials the Zeldovich's criterion is a little bit more than unit, and the Novozhilov's criterion remains less than unit. At certain pressures an occurrence of combustion instability area is observed where both criteria are much greater than unit.

It is suggested an explanation of combustion instability observed. Since the burning surface of the salts grows with pressure, there comes a point when the heat of the condensed-phase reaction is no longer sufficient for heating-up the solid to the surface temperature and subsequent dissociation, while exothermic redox reactions in the gas do not contribute noticeably to the condensed phase heat balance.

Acknowledgements

The author is grateful to Prof. B. V. Novozhilov for valuable discussion and critical remarks. The author is grateful to his colleagues V. Yu. Egorshev, V. V. Serushkin and A. I. Levshenkov for the help in preparation of the paper.

References

[1] Zeldovich Y. B., Theory of Combustion of Propellants and Explosives, *Zh. Eksperimentalnoy i Teoreticheskoi Fiziki (J. Experimental and Theoretical Physics)*, **1942**, *12*(11-12), 498-524.

[2] Belyaev A. F., Connection between Flameless Combustion of Double Base Powder and its Kinetics Constants, *Doklady Akademii Nauk (Bull. Russian Academy of Science)*, **1959**, *129*(3), 635-637.

[3] Novozhilov B. V., Criterion of Stability of a Stationary Combustion Mode of Powder, *Zh. Prikladnoi Mekhaniki i Tekhn. Fiziki (J. Applied Mechanics and Technical Physics)*, **1965**, *4*, 157-160.

[4] Novozhilov B. V., *Non-stationary Combustion of Solid Rocket Propellants*, Moscow, Nauka, **1973**, p. 176 (in Russian).

[5] Manelis G. B., Nazin G. M., Rubtsov Yu. I., Strunin V. A., *Thermal Decomposition and Combustion of Explosives and Propellants*, Nauka, Moscow **1996**, p. 223 (in Russian).

[6] Denisuik A. P., Kuleshova T. M., Shepelev Yu. G., Combustion of Ammonium Dinitramide and their Mixtures with Organic Fuels, *Doklady Akademii Nauk (Bull. Russian Academy of Science)*, **1999**, *368*(3), 350-353.

[7] Strunin V. A., D'yakov A. P., Manelis G. B., Combustion of Ammonium Dinitramide, *Combustion and Flame*, **1999**, *11*(1-2), 429-434.

[8] Fogelzang A. E., Sinditskii V. P., Egorshev V., Levshenkov A. I., Serushkin V. V., Kolesov V. I., Combustion Behavior and Flame Structure of Ammonium Dinitramide, *Proceeding of 28th International Annual Conference of ICT*, Karlsruhe, FRG, 24-27 June, **1997**, paper 90, pp. 1-14.

[9] Sinditskii V. P., Fogelzang A. E., Egorshev V. Y., Levshenkov A. I., Serushkin V. V., Kolesov V. I., Combustion Peculiarities of ADN and ADN-based Mixtures, in *Combustion of Energetic Materials*, ed. Kuo K. K., DeLuca L. T., Begell House Inc., New York **2002**, pp. 502-512.

[10] Sinditskii V. P., Levshenkov A. I., Egorshev V. Yu., Serushkin V. V., Combustion of Dinitramide Salts, *Proceeding 7th Inter. Seminar New Trends in Research of Energetic Materials*, Pardubice, Czech Republic, April 20-22, **2004**, pp. 636-646.

[11] Manelis G. B., Thermal Decomposition of Dinitramide Ammonium Salt, *Proceeding 26th International Annual ICT Conference*, Karlsruhe, 4-7 July, **1995**, paper 15, pp. 1-17.

[12] Atwood A. I., Boggs T. L., Curran P. O., Parr T. P., Hanson-Parr D., Price C. F., Wiknich J., Burn Rate of Solid Propellant Ingradients, Part 1: Pressure and Initial Temperature Effects, *J. Propulsion and Power*, **1999**, *15*(6), 740-748.

[13] Zenin A. A., Puchkov V. M., Finjakov S. V., Physics of ADN Combustion, *AIAA Paper 99-0595*, *37th AIAA Aerospace Sciences Meeting and Exhibit*, Reno, NV, USA, Jan.11-14, **1999**, pp. 1-9.

[14] Sinditskii V. P., Levshenkov A. I., Egorshev V. Yu., Serushkin V. V., Combustion of Dinitramide Salts, *Proceeding 3rd Inter. Seminar "Intra-Chamber Processes, Combustion and Gas Dynamics of Dispersed Systems"*, Saint Petersburg, 26-30 June, **2000**, pp. 75-78.