Ammonium Nitrate: Combustion Mechanism and the Role of Additives

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This paper is dedicated to the memory of Professor Boris N. Kondrikov, a great researcher in the field of energetic materials, who spent all his scientific life at Chemical Engineering Department, Mendeleev University of Chemical Technology.

Abstract

This paper presents an analysis of the observed combustion behavior of AN mixtures with different additives, fuels, and energetic materials. It has been determined on the basis of flame structure investigation by fine tungsten-rhenium thermocouples that the surface temperature of AN is controlled by the dissociation reaction of the salt occurring at the surface. Results obtained have indicated that the leading reaction of combustion of AN doped with additives proceeds in the condensed phase up to pressures of 20–30 MPa. A reason for the inability of pure AN to burn is suggested and the role of additives in the combustion mechanism is discussed.

Keywords: Ammonium Nitrate, Combustion Mechanism, Role of Additives, Surface Temperature

1 Introduction

Ammonium nitrate (AN) finds widespread application as both a fertilizer and a component of a variety of energetic compositions, mainly industrial explosives. AN is also used as an oxidizer in propellant formulations [1–3], but not so extensively as in explosive compositions. AN is hygroscopic, has rather low energy content, exhibits several crystalline phase transitions at temperatures within the range of normal usage, and endows AN-based propellants with a limited range of burning rates. For these reasons, AN has been used mainly in gas generators and other auxiliary power sources. However, AN is a very cheap, readily available, and safe energetic material that can be phase stabilized. It produces environmentally friendly and smokeless combustion products, which is an important feature. The current need for clean propellants to satisfy the high demand for automobile air bag systems gives rise to a new interest in AN combustion studies.

Notwithstanding the long history of AN combustion studies since the fifties and the present renewed interest in AN, the scientific understanding of the mechanism of AN combustion is far from satisfactory. This is especially true concerning the role of additives, without which pure AN will not burn at all. This paper presents an analysis of observed combustion behavior of AN mixtures with catalysts, fuels, and explosives. Burn rate data and data from flame structure investigations, using fine tungsten-rhenium thermocouples, have been considered in the formulation of a combustion mechanism of AN-based compositions and explanation of the role of additives.

2 Experimental

2.1 Sample Preparation

Pure crystalline AN was used in the burn rate experiments. 2-Methyl-5-nitrotetrazole (MNT) in the form of white plate-like crystals, with a density of 1.64 g/cm^3 and a melting point of 86 °C, was prepared according to [4]. Glycidyl azide polymer-diol (GAP) with a molecular weight around 1000 was synthesized from polyepichlorohydrin [5].

To obtain AN mixtures with additives, thoroughly comminuted and dried components were mechanically mixed, and cylindrical specimens, 7 mm in diameter and 10–15 mm long, with a relative density of 0.97–0.98, were obtained by compression in transparent acrylic tubes. This method enables steady-state combustion of the substance and prevents flame penetration between the particles into the strand and its propagation along the side surface.

An AN/GAP mixture with 86.7% solids loading was prepared by mixing AN with a particle size less than 50 μm with GAP.

2.2 Burn Rate Measurements

Burn rate measurements were carried out in a constant pressure window bomb with a volume of 1.5 liters. The pressure range studied was 0.1–36 MPa. A video camera was used to determine the character of the combustion process as well as the burning rates.

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DOI: 10.1002/prep.200500017

Table 1. The influence of some of the most typical additives on combustion characteristics of AN.

Additive	Low pressure limit (LPL) of burning MPa	Mass burning rate at LPL g cm^{-2} · s^{-1}	Pressure exponent (within pressure interval) (MPa)	Activation energy of leading combustion reaction kJ/mol (kcal/mol)
Catalysts				
7% NaCl	1.2	0.10	0.85 (3–20)	147.6 (35.3)
5% $BaCl_2$	3.0	0.25	0.87 (3–20)	145.4 (34.8)
5% NaF	5.0	0.18	0.94 (5–25)	162.5 (38.8)
Fuels				
5% Hydrocarbons				Will not burn
4% Charcoal	1.7	0.08	0.88 (3.6–10)	166.7 (39.9)
8.6% Charcoal	2.5	0.20	0.96 (2.5–20)	122.6 (29.3)
Explosives				
20% TNT	10	0.4	1.06 (10–80)	197.5 (47.3)
13.3% GAP	10	0.4	1.11 (15–36)	
15% MNT	6	0.3	1.12 (6–10)	

2.3 Temperature Measurements

Temperature profiles in the combustion wave were measured using Π-shaped thermocouples. The thermocouples were welded from 25 or 50 μm diameter tungsten + 5% rhenium and tungsten + 20% rhenium wires and rolled in bands to obtain 7 or 20 μm bead size. The thermocouples were embedded in AN pressed into acrylic tubes. A Tektronix TDS-210 digital oscilloscope was used to record the thermocouple signal.

3 Results and Discussion

3.1 Combustion Behavior

AN belongs to a class of onium salts, compounds formed by proton transfer from the acid to the base. A known characteristic of such compounds is their potential for the return proton transfer from cation to anion with the formation of the initial molecules of acid and base. This may occur in both the condensed (melt, solution) and gas phases. The process of the equilibrium proton transfer is referred to as dissociation. Dissociation of onium salts to give gaseous acid and base is similar to boiling of molecular substances and is characterized by the enthalpy of dissociation as boiling of molecular substances is characterized by the enthalpy of evaporation. The surface temperature during combustion of such salts is often determined by process of salt dissociation [6–8].

According to Glazkova [9, 10], neat ammonium nitrate does not burn in glass tubes of large diameter (30 mm) even at 100 MPa. In the present study, molten AN at atmospheric pressure was found to be incapable of burning in tubes of 7 mm diameter. The addition of small amounts of some mineral substances is known to increase its ability to burn strongly. Some kinds of fuels and explosives act in a similar way. The influence of some of the most typical additives on combustion characteristics of AN is presented in Table 1.

3.1.1 *Addition of Catalysts*

The influence of mineral additives on AN burning was studied in a number of works [10–15], in which it was found that the most effective catalysts of combustion were derivatives of hexavalent chromium and metal halides. It was shown that many mineral additives increased the rate and completeness of burning of both pure AN and related compositions. Thus, AN with 7% sodium chloride added undergoes sustained burning at pressures as low as 1.2 MPa [10] (Figure 1). Other chlorides of alkaline and alkaline-earth metals have a similar effect.

Generally the curve of burning rate (r_b) versus pressure (p) has a break at 20–25 MPa, with a strong pressure

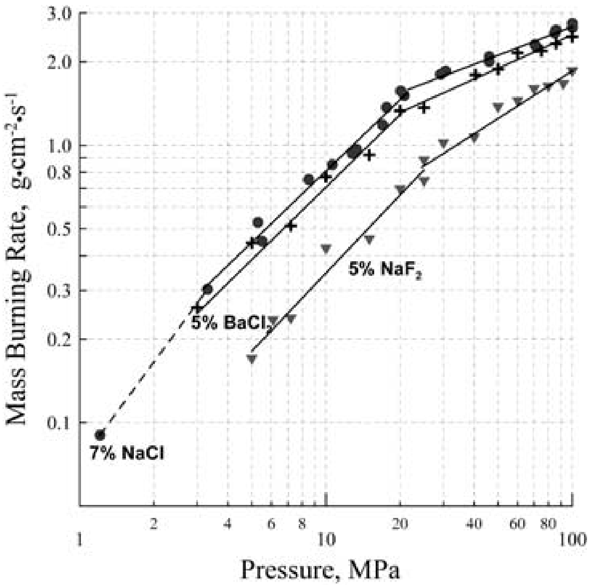


Figure 1. Pressure dependence of the burning rate for AN with addition of 7% NaCl (circles) [10], 5% $BaCl_2$ (crosses) [10], and 5% NaF (triangles) [10]. The particle size of the components is less than 100 μm.

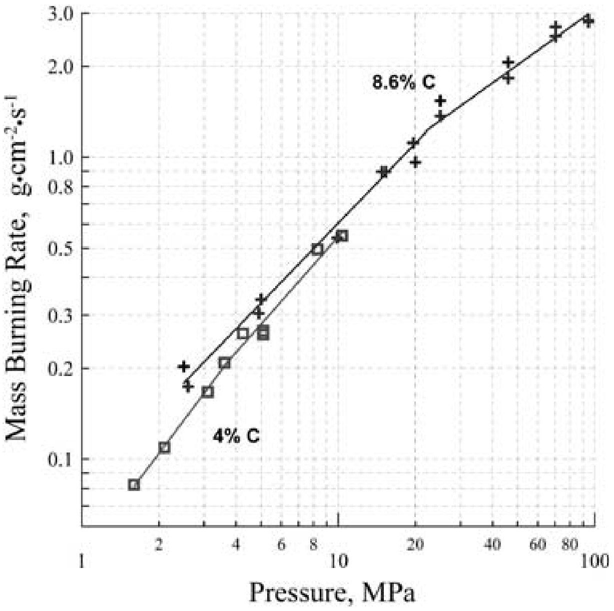


Figure 2. Pressure dependence of the burning rate for AN with addition of 4% (squares) and 8.6% (crosses) [10] of charcoal.

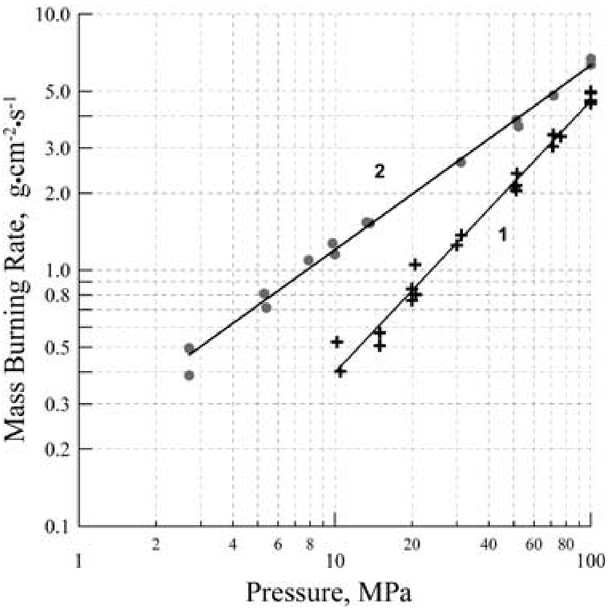


Figure 3. Pressure dependence of the burning rate for ammonite (20% TNT) (1) and ammonite with addition of 5% KCl (2) [10].

influence on the burning rate before the break (the pressure exponent, $n = 0.85-0.95$), and a weaker dependence after it ($n = 0.5-0.6$). According to Glazkova, the AN flame consists of separate flares and stands some distance off the surface at pressures below 20 MPa. This distance decreases with increasing pressure and the flame gets onto the surface at 20 – 25 MPa i.e., when $r_b(p)$ dependence changes.

3.1.2 Addition of Fuels

The ability of AN-fuel mixtures to burn and, especially, the low-pressure limit (LPL) of combustion depend strongly on the nature of the fuel. Many organic substances promote AN burning weakly, while mixtures with charcoal, wood flour and soot have the greatest ability to burn. Thus, a mixture of AN with hydrocarbons (ANFO explosive) does not burn below at least 40 MPa [16], whereas addition of 4% of charcoal results in a mixture capable of burning at 1.7 MPa (Figure 2). As the charcoal content increases, the burning rate of the mixture grows, passing through a maximum at 15.8% of charcoal (the stoichiometric mixture contains 7% of charcoal), and then falls [10]. It is necessary to note that structure and properties of such additives as charcoal can be slightly different, depending on the materials from which they were produced, the method of production, etc., so their influence on AN combustion behavior also can vary. The introduction of metal chlorides or chromium compounds in the AN mixture with charcoal or soot results in a further increase in the burning rate [10].

3.1.3 Addition of Energetic Materials

Addition of explosives to AN produces mixtures capable of sustained burning, beginning, however, at high pressures. Thus, the stoichiometric mixture of AN with trinitrotoluene (TNT) 80/20 (ammonite) begins to burn only at 15 MPa [10], although the adiabatic flame temperature increases from 1240 K for pure AN to 2030 K for the mixture (calculations at 10 MPa). An addition of 1% of polyethylene reduces the low-pressure limit of ammonite combustion to 10 MPa, showing an important role of dispersion of the molten surface layer in establishing the LPL. A polymeric additive suppresses dispersion, thus increasing a region of steady-state combustion of ammonite. Addition of metal halides to ammonite, as with neat AN, results in a substantial increase in the burning rate (Figure 3), with the pressure exponent, n, noticeably decreased.

With the growing demand for environmentally-friendly chlorine-free propellants and gas generators, many attempts have been made to investigate the combustion of AN with polynitrogen compounds like azides and tetrazoles [17 – 20]. These compounds are capable of sustained burning with high rates. Many of them start burning at atmospheric pressure. Combustion of AN mixtures with 15% of methylnitrotetrazole (MNT) and 13.3% of glycidyl azide polymer (GAP) is presented in Figure 4. As can be see from Figure 4, the low-pressure limits of combustion for these mixtures occur at high pressures. The burning rates are rather low, similar to those for burning of ordinary AN-based compositions.

Glazkova, reasoning from the strong $r_b(p)$ dependence in the pressure region 1 – 25 MPa for mixtures of AN with metal halides, assumed that gas phase reactions of the

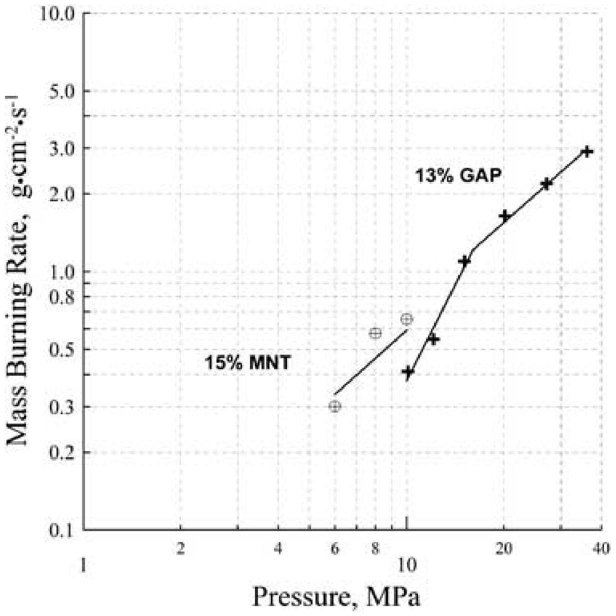


Figure 4. Pressure dependence of the burning rate for AN with addition of 15% of methylnitrotetrazole (circles) and 13.3% of glycidyl azide polymer (crosses).

second order controlled the combustion of these mixtures [10].

The authors of [1, 2], describing a model for combustion of AN composite propellants, also pointed to the leading role of gas phase reactions. They postulated that AN gasifies first at about 600 K by an endothermic reaction to form ammonia and nitric acid. These gaseous products then undergo exothermic redox reactions near the surface to establish an adiabatic flame of about 1250 K, which governs gasification of AN and pyrolysis of the binder. The authors of [1] suggested that burning catalysts could influence the burning characteristics of AN propellants mainly through heterogeneous catalysis of redox gas phase reactions.

In contrast to that, it was postulated in [16] and [21] that the leading reaction in combustion of AN-based compositions proceeded mostly in the condensed phase up to pressures of the order of hundreds of atmospheres. As confirmation, the thermocouple data from combustion of AN/TNT (80/20) mixture were considered in [16]: a plateau between the condensed and gas zones on the temperature profiles indicating the absence of heat flux from the gas phase, and significant superiority of the molten surface layer thickness over Michelson preheated layer pointing to reactions in the melt. A chemical mechanism of combustion of AN-based compositions was offered, in which it was postulated that the main reason for the inability of AN and its mixtures to burn at low pressures was the presence of a large amount of water in the reaction layer as a product of AN decomposition, which extinguished combustion by decreasing reaction rate and surface temperature. The role of catalysts in this combustion mechanism, according to the authors, is to enhance the rate of AN decomposition, which, in turn, results in water removal from the reaction mixture.

The hypothesis about the presence of large amounts of liquid water at the AN burning surface is obviously inconsistent with the data in [1] that show high surface temperatures during AN gasification in propellants. Furthermore, Egorshev's data on the combustion of water-impregnated AN-based explosives, also presented in [16], showed that the presence of 15–22% water in the compositions did not hinder sustained burning.

To gain a detailed understanding of the combustion mechanism of AN-based compositions, to find leading reactions and leading combustion zones, it was necessary to study the temperature distribution in the combustion wave of AN mixtures.

3.2 Temperature Measurements

Temperature distributions in the combustion wave of AN-based compositions were only studied in several works [22, 21, 1], and the data obtained are contradictory and not always reliable. It is necessary to note that the AN burning surface is not planar but rather consists of protrusions and depressions, that very strongly complicate the interpretation of temperature profiles.

In [22] it was shown that the surface temperature of catalyzed ammonium nitrate (2.5% CrO_3) remained constant and equal to 576 ± 12 K over a wide pressure range (from 7 to 30 MPa). This result is strange in light of the data on surface temperatures of other onium salts, and is apparently caused by some methodological mistake.

The existence of a dependence of the surface temperature on pressure within a pressure interval of 2.2–4.1 MPa was found for AN mixtures with magnesium and catalytic additives of ammonium dichromate (82/15/3) [21]. However, an extrapolation of this dependence to atmospheric pressure gives an unreal value of the surface temperature of 69 K, and the heat of evaporation estimated from this dependence is extremely low (~17 kJ/mol or 4 kcal/mol).

The surface temperatures of several composite AN-based propellants containing different fuels and 3% of ammonium dichromate were measured in [1] at atmospheric pressure only. All the measured temperatures for AN were found to fall into the area of about 580 K.

Temperature profiles for AN/TNT, AN/TNT/NaCl, and AN/TNT/wood flour mixtures given in [16] allowed only the maximum temperatures of burning to be determined.

In the present work, temperature profiles in the combustion wave of AN mixtures with 5% of KCl and 4% of charcoal were measured with the help of thin thermocouples. Typical temperature profiles of AN combustion at 5 MPa are shown in Figure 5. As seen from Figure 5, the surface temperature of AN doped with KCl, is visible rather clearly, despite fluctuations, as a point of inflection on the profile. The temperature gradient in the gas phase above the AN surface is very small, indicating a weak influence of gas phase reactions on AN combustion. The maximum temper-

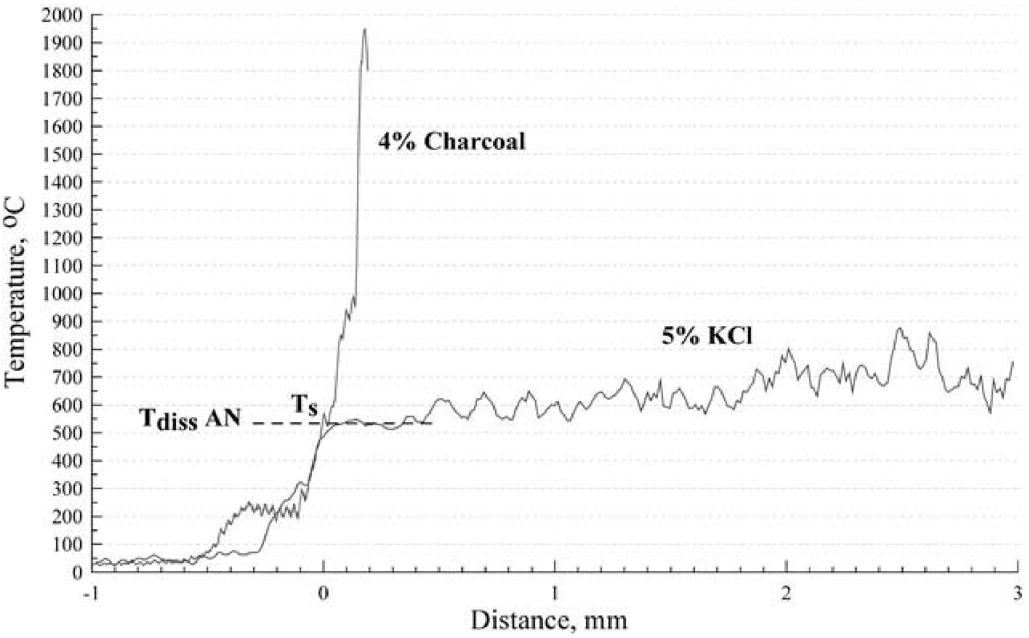


Figure 5. Typical temperature profiles for AN mixtures with 5% KCl and 4% charcoal at pressure of 5 MPa. The dashed line is AN dissociation temperature at this pressure.

ature (~1000 °C at pressure of 5 MPa) is achieved at a significant distance (3 – 4 mm) above the burning surface.

Burning of AN mixed with charcoal is accompanied by a high-temperature, bright flame (1600 – 1900 °C), as little as ~0.2 mm from the surface. In most cases, adherence of the liquid layer to the thermocouple horizontal section is observed, followed by a sharp springing out of the thermojunction to the high-temperature gas zone. This leads to the apparent broadening of the molten surface layer and overstated values of the temperature gradient above the surface. Estimated values of the temperature gradient above the AN burning surface ($4 – 8 \cdot 10^6$ K/m) allow calculations of heat flux (795 – 1590 kJ $m^{-2} s^{-1}$ or 19 – 38 cal $cm^{-2} s^{-1}$) and corresponding heat feedback (305 – 607 J/g or 73 – 145 cal/g) from the gas to the condensed phase. This amount of heat is not enough to warm up AN to the surface temperature (1452 J/g or 347 cal/g) nor to evaporate it. Therefore, condensed-phase reactions continue to play an essential role in burning of the mixture.

All the surface temperatures measured are shown in Figure 6. Also presented are data for composite AN-based propellants from [1] and the surface temperature for AN mixture with magnesium taken from a temperature profile in [21].

It is known that another energetic oxidizer, ammonium dinitramide (ADN), decomposes in the melt to form N_2O and ammonium nitrate. The latter, being a salt of weaker acid, evaporates first, thus determining the temperature of the ADN burning surface [23]. The pressure dependence of the ADN surface temperature has been shown to be very close to the pressure dependence of the dissociation temperature of ammonium nitrate [24]. Data on the ADN surface temperature obtained in [23] are also presented in Figure 6.

The vapor pressure above the AN condensed phase is given in [24] and [25]. The experimental points and the fitting equations reported in these works agree very well.

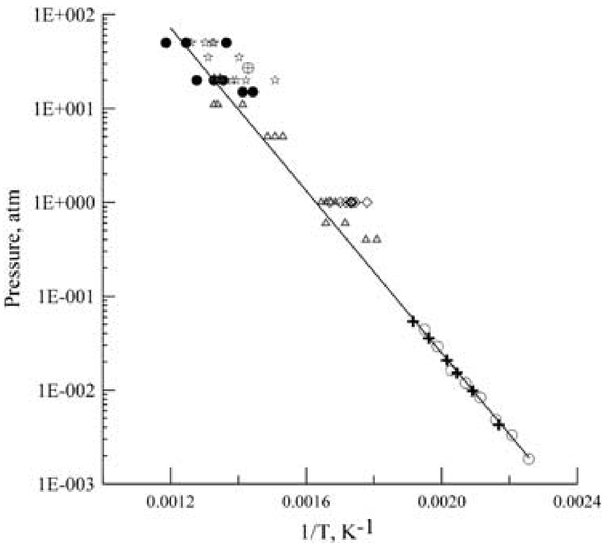


Figure 6. Relationship between vapor pressure and dissociation temperature of ammonium nitrate (solid line [25]). Points relate to: vapor pressure of AN (crosses [24] and empty circles [25] at the right bottom of the plot), ADN surface temperature (triangles) [23], surface temperatures of composite AN-based propellants (rhombs) [1], surface temperature of AN-magnesium mixture (crossed circle) [21], and surface temperatures of AN mixtures with charcoal (filled circles) and KCl (stars).

The enthalpies of dissociation given in [24] (166.9 kJ/mol or 39.9 kcal/mol) and in [25] (166.5 kJ/mol or 39.8 kcal/mol) are in good agreement with a value calculated from standard enthalpies of formation of the components (163.2 kJ/mol or 39.0 kcal/mol). In Figure 6, the pressure dependence of the AN dissociation temperature is presented as taken from [25].

As can be seen from Figure 6, the surface temperatures obtained for various AN-based systems are close to each other, grouping together around a straight line of vapor pressure above liquid AN [25]. As with other onium salts, experimental AN surface temperatures increase with pressure. The data obtained allow considering the surface temperature of burning of AN and many AN-based systems as determined by process of dissociation of the salt.

3.3 Mechanism of AN Thermal Decomposition

To gain an understanding of the AN combustion mechanism it is necessary to consider the processes proceeding in the condensed phase during combustion of AN. AN decomposition begins with proton transfer to form NH_3 and HNO_3 dissolved in the condensed phase, followed by thermal decomposition of nitric acid:

$$NH_4NO_3 \Leftrightarrow NH_3 + HNO_3 \qquad (1)$$

It has been shown by direct experiments [26, 6] that the rate of HNO_3 consumption is higher in the presence of NH_4^+ ions than in thermal decomposition of pure nitric acid. The change in the rate was directly proportional to the NH_4^+ concentration. It was assumed that the kinetics of this reaction was described by interaction of NH_4^+ ions not only with molecules of HNO_3, but mainly with molecules of N_2O_5.

There exists a somewhat different scheme of transformations in molten AN [27–29], based on formation of $NO_2^+NO_3^-$ rather than N_2O_5 as a nitric acid decomposition product.

$$2HNO_3 \Leftrightarrow H_2O + NO_2^+NO_3^- \qquad (2)$$

$$NO_2^+ + NH_3 \rightarrow NH_3NO_2^+ \rightarrow N_2O + H_3O^+ \qquad (3)$$

This scheme explains quite well the observable behavior of liquid-phase AN decomposition: acidic species increase the rate of AN decomposition dramatically, while bases, such as ammonia or water, retard decomposition. In a high-dipole environment, as is the case with molten AN, the ionic structure of $NO_2^+NO_3^-$ is quite acceptable, although its covalent counterpart N_2O_5 plays a certain role in the total process of AN decomposition.

As the temperature increases, the ionic mechanism of AN decomposition is overtaken by radical reactions [30, 29], with homolysis of nitric acid being the rate-controlling step [29]:

$$HNO_3 \Leftrightarrow OH + NO_2 \qquad (4)$$

$$NH_3 + OH \rightarrow NH_2 + H_2O \qquad (5)$$

$$NH_2 + NO_2 \rightarrow NH_2NO_2 \rightarrow N_2O + H_2O \qquad (6)$$

The overall reactions of AN decomposition are the same for both modes of decomposition:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \qquad (7)$$

Besides the main reaction, there exist side reactions, which can be totally written as [6]:

$$NH_4NO_3 \rightarrow N_2 + 0.5O_2 + 2H_2O \qquad (8)$$

$$NH_4NO_3 \rightarrow 0.8N_2 + 1.8H_2O + 0.4HNO_3 \qquad (9)$$

Reaction (8) can be presented as a superposition of the dissociation reaction (1) and decomposition reaction of nitric acid:

$$HNO_3 \rightarrow NO_2 + 0.5H_2O + 0.25O_2 \qquad (10)$$

with subsequent oxidation of ammonium ion by nitrosonium ion:

$$NO_2 + NO_2 \Leftrightarrow N_2O_4 \rightarrow NO^+NO_3^- \qquad (11)$$

$$\begin{aligned} NH_3 + NO^+NO_3^- &\rightarrow HNO_3 + NH_2NO \\ &\rightarrow HNO_3 + N_2 + H_2O \end{aligned} \qquad (12)$$

The overall reaction (9) includes oxidation reaction of ammonia by nitrosonium ion as well.

The decomposition kinetics of liquid AN are described by a first-order equation of autocatalysis [6], with temperature dependence of the constants as follows:

$$k_1 = 10^{14.4} \exp(-23754/T)\ s^{-1} \qquad (13)$$

$$k_2 = 10^{7.3} \exp(-5736/T)\ s^{-1} \qquad (14)$$

In view of the conclusions made in [29] about ionic and radical mechanisms of AN decomposition, it is possible to assume that the constant k_1 describes the radical decomposition pathway with activation energy corresponding to $HO{-}NO_2$ bond rupture; and the constant k_2 describes the low-temperature ionic pathway of decomposition, which also includes side reactions.

3.4 Kinetics of the Leading Reaction in Combustion of AN-based Compositions

The heat effect of the main channel of high-temperature decomposition of AN to gaseous products is 49 kJ/mol (11.7 kcal/mol) or 611 J/g (146 cal/g). The heat effect of side reactions is much higher, but their contribution in decomposition of neat AN is insignificant and falls with increasing temperature. Thus, according to the data in [31], one mole of AN evolves less than 0.2 moles of nitrogen and about 0.8 moles of N_2O at 320 °C. The heat effect of side reactions is more than 125 kJ/mol (30 kcal/mol), hence the overall heat effect of decomposition of neat AN to gaseous products can be estimated as 67 – 71 kJ/mol (16 – 17 kcal/mol) or 837 – 877 J/g (200 – 210 cal/g). Assuming the average specific heat to be 2.34 J g^{-1} K^{-1} (0.56 cal g^{-1} K^{-1}) and considering phase transition effects, this amount will be enough to heat AN up to 570 – 590 K only, that is less than the dissociation temperature at atmospheric pressure (614 K). In our opinion, a reason for the inability of AN to sustain stationary combustion is the moderate heat effect of AN decomposition in the melt, which is not sufficient to warm the substance up to the temperature of dissociation.

It might seem strange that AN is incapable of burning without evaporation from the surface, as is the case of combustion of many gasless systems. Zeldovich showed [32] that failure of burning in gaseous systems due to heat losses appeared when there was a RT_f^2/E decrease in the temperature of the reaction zone, T_f. A similar situation obviously takes place in combustion of systems with the leading reaction zone in the condensed phase. Since the relaxation time of processes occurring in the reaction zone is much less than the relaxation time of the preheated layer, the temperature gradient in the layer under the reaction zone is responsible for steady-state burning. When ignited by an external heat source, the condensed phase is heated up to a maximum achievable temperature – the temperature of dissociation in the case of onium salts, including AN. If the self-heating in the condensed zone is insufficient to heat the substance to this temperature, the temperature in the reaction zone drops once the heat accumulated at ignition has been irreversibly consumed. The preheated layer has no time for readjustment, and combustion ceases.

3.4.1 Addition of Catalysts

AN can burn when small amounts of metal halides are added. As data of our thermocouple-aided measurements show, combustion of catalyzed AN proceeds because of heat release in the condensed phase; the role of the gas phase is insignificant. This fact allows us to calculate the rate constants of the leading reaction of AN combustion from a condensed-phase combustion model [33, 34], assuming first order reaction and using measured mass burning rate (m) and surface temperatures (T_S):

$$m = \sqrt{\frac{2\rho^2 \chi Q}{c_p (T_S - T_0 + \Delta_{pt} H / c_p)^2} \left(\frac{RT_S^2}{E} \right) \cdot A \cdot e^{-E/RT_S}} \tag{15}$$

In calculations, the average specific heat (c_p) varied from 2.34 (0.56) to 2.93 J g^{-1} K^{-1} (0.7 cal g^{-1} K^{-1}) [35] in the 0.1 – 20 MPa pressure interval, the thermal diffusivity (χ) was equal to $1.5 \cdot 10^{-7}$ m^2/s, and heat effect in the condensed phase (Q) was taken as 1883 – 1925 J/g (450 – 460 cal/g). The overall heat of phase transitions in the condensed phase ($\Delta_{pt}H$) was accepted as 143.9 J/g (34.4 cal/g) [36].

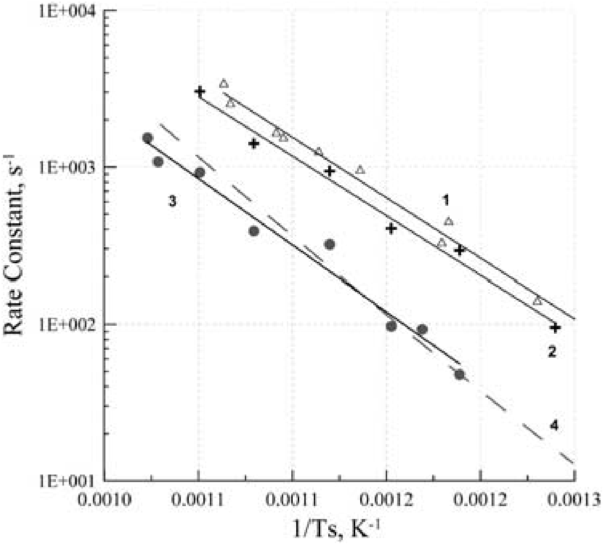


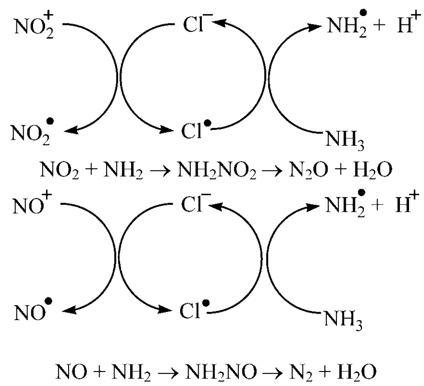
Figure 7. Comparison of rate constants of the leading reaction on combustion of AN containing 7% NaCl (1), 5% $BaCl_2$ (2), and 5% NaF (3) with decomposition kinetics of liquid AN (4).

Since the activation energy (E) of the self-catalyzed stage is much lower than the activation energy of the initial decomposition reaction (see Eqs. (13) and (14)), the contribution of self-acceleration is negligible in the field of high temperatures, i.e., at surface temperatures. Autocatalysis slightly reduces the activation energy of the overall decomposition kinetics only. Hence, calculated rate constants of the leading reaction in AN catalyzed combustion should be compared with the constant k_1 (see Figure 7).

As can be seen from the plot, the rate constants of the leading combustion reaction of AN with additives of 7% NaCl and 5% $BaCl_2$ exceed those of the decomposition reaction of neat AN and can be described by straight lines with smaller values of the activation energy of 142 – 159 kJ/mol (34 – 38 kcal/mol) as compared to E for neat AN (197.5 kJ/mol or 47.2 kcal/mol). Combustion of an AN mixture with 5% NaF is characterized by rate constants which are close to the decomposition rate constants of neat AN, but with the same activation energy as for the other additives.

The introduction of Cl^- ions in AN is known [6] to increase both the initial rate of decomposition (k_1), and the rate of self-acceleration (k_2), with the latter growing much faster than the former. Thus, introduction of 0.5% Cl^- leads to a 5-fold increase in k_1 and a 30-fold increase in k_2 at 200 °C. The greater increase in the degree of self-acceleration results in reduction of the activation energy of the leading combustion reaction of catalyzed AN.

By what means does an additive of halide ions enable AN burning? It is known that the addition of chlorides results in a decrease in AN stability, shifting the temperature of the AN exotherm from 326 °C to 246 °C for a mixture with 5%



Scheme 1.

KCl [31]. The mechanism by which halide-ions exert this effect is not completely established. Many researchers [37, 38] point to synergism in the action of HNO_3 and Cl^- as well as to the presence of an induction period [39]. Keenan with co-authors [39] suggested that the key reaction in the catalysis of AN decomposition by chloride ions is as follows:

$$NO_2^+ + Cl^- \rightarrow NO_2Cl \rightarrow NO_2 + Cl$$

Even in early works [37], it was found that alkali metal chlorides and ammonium chloride catalyze AN decomposition, reducing N_2O content and increasing the amount of N_2 in the products. Hence, the role of side channels in AN decomposition grows with addition of chloride ions. Therefore, catalysis of AN decomposition by chloride ions is apparently caused by interaction of Cl^- ions with both NO_2^+ and NO^+ species, formed from N_2O_4 during HNO_3 decomposition in the melt. It is known that the rate of bimolecular reactions between two ions of opposite charges is much more than the rate of reactions between uncharged particles. The catalytic process can be presented as shown by Scheme 1.

According to this scheme, the role of chloride ions is to accelerate ammonia oxidation by oxidizing particles formed in AN decomposition. In doing so, both the main and side processes are accelerated. The rate-controlling step of these processes is apparently splitting off a hydrogen atom from ammonia under the action of a chlorine atom. The subsequent reactions of NH_2 radical with NO_2 and NO proceed fast. This mechanism casts some doubt on a conclusion made in [29] that formation of NO_2^+ is the rate-limiting step in the ionic mechanism of AN decomposition. Indeed, in such an event, the acceleration of oxidation reactions of ammonia by oxidizing particles must not have an effect on the process rate. The closeness between the activation energies of autocatalysis and nitration reactions supports a rate-limiting role of the interaction of nitronium and nitrosonium with ammonia rather than reaction of their formation in the ionic mechanism of AN decomposition.

The heat effect of reactions resulting in formation of nitrogen is 1675–1880 J/g (400–450 cal/g). Therefore, the role of chloride ions in AN combustion is (1) to increase the condensed-phase heat effect, stabilizing the combustion process, and (2) to increase the decomposition rate, leading to increased burning rates.

Other halides, bromides and iodides, act in a similar way. Halide atoms react fast with ammonia to form strong halogen acids (pK_a HCl = −7, pK_a HBr = −9.5, pK_a HI = −10), which subsequently react with nitrate ion to form the initial halide ions and nitric acid:

$$HHal + NO_3^- \rightarrow HNO_3 + Hal^-$$

The nature of the metal cation in the chlorides can apparently exert a considerable effect on the kinetics of the rate-limiting reaction, determining the solubility of chlorides in melted AN and the degree of ionicity of the metal–chlorine bond. The replacement of chlorine by other halides, iodine or bromine, changes not only the physicochemical properties of the salt, but also the kinetics of the reaction of the halide atom with ammonia.

In contrast to chlorides, bromides, and iodides, the fluorides inhibit AN decomposition rather than catalyze it. Hydrofluoric acid is the weakest of the halogen acids (pK_a HF = 3.2), and fluoride ion, as well as other anions of acids weaker than nitric acid (pK_a HNO_3 = −1.64), retards HNO_3 decomposition, transforming it into the stable anion:

$$F^- + HNO_3 \rightarrow HF + NO_3^-$$

Most oxo-anions, as well as fluoride ion increase the temperature of AN exothermic decomposition. For example, an addition of 5% KF increases the temperature of the AN exotherm to 348 °C [31]. Analyses of gases produced show [31], that in this case too a contribution of side reactions increases and the N_2O/N_2 ratio decreases from 4.1 to 2–3.4. That is why addition of compounds that increase AN thermostability still results in the growing AN decomposition heat effect. AN with such additives becomes capable of sustained combustion, though it burns more slowly than AN with additives that catalyze decomposition.

3.4.2 Addition of Fuels

Fuel additives can exert different effects on AN stability: some of them (charcoal, mineral and diesel oils, sugar) lower the temperature of the exothermic maximum, whereas others (urea) raise it [31]. The first group of additives leads to the second high-temperature exotherm, with a considerable increase in the total heat release for all fuel additives. Some additives (for example, nitrobenzene) raise the temperature of the exotherm with little change in the general heat release, suggesting no reaction in the interval 200–400 °C [31].

In a detailed study of the influence of mineral oil additives on AN thermal stability [40], the first exotherm was assigned to oxidation of the organic fuel by nitric acid. In our opinion, the first exotherm is caused mainly by redox reactions of nitronium and nitrosonium ions, NO_2^+ and NO^+. The second high-temperature exotherm in the decomposition of AN mixtures with fuels is obviously connected with oxidation of the fuel by radical products of nitric acid decomposition.

Nitronium ion will react more easily with many of organic compounds than with ammonia. If the products of the interaction do not possess a high stability and there is no accumulation of free ammonia (for example, as is the case of sugar), the AN stability decreases. The interaction of nitronium ion with hydrocarbons or aromatic compounds results in formation of nitrocompounds whose stability is greater than the stability of AN, resulting in decreasing the heat release in first exotherm. These additives capture the nitronium ion, but they release heat at higher temperatures when the products of the nitronium ion-additive decompose. However, even more important is the fact that the formation of stable reaction products results in accumulation of free ammonia, which suppresses AN dissociation and reduces the nitronium and nitrosonium ions concentration. AN thermolysis in the presence of ammonia was found to shift the exotherm to a high-temperature area [40]. Obviously, the addition of urea to AN, which liberates ammonia upon decomposition, acts in the same manner.

The mixtures of AN with charcoal have the greatest ability to burn. The activation energy of the leading combustion reaction for a mixture of AN with 8.6% charcoal, calculated from the condensed-phase combustion model, is rather low (121 kJ/mol or 29 kcal/mol), suggesting that charcoal accelerates autocatalytic reactions of AN decomposition to a greater extent than halides do. As shown in [41], thermal decomposition of a mixture of AN with soot (3:1) at 110–140 °C follows the scheme:

$$2NH_4NO_3 + C \rightarrow 2N_2 + CO_2 + 4H_2O$$

Trace amounts of CO and N_2O are also formed. The heat effect of this reaction is rather high ~4100 J/g, (980 cal/g) suggesting that stable burning can take place when even a small part of AN is involved in this reaction. The activation energy of this process is very low, 46–54 kJ/mol (11–13 kcal/mol), so even a small contribution from the reaction will reduce considerably the overall activation energy.

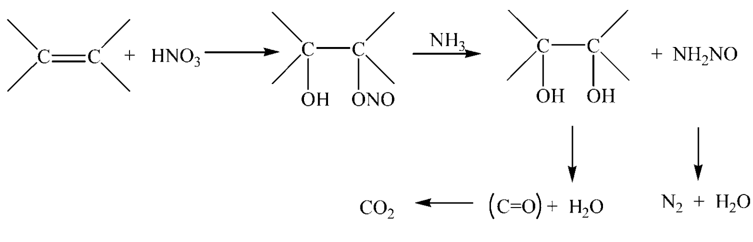
What is the mechanism of this process? In [41] the effect of soot is explained by its reaction with nitric acid, resulting in formation of NO_2 and water, which, in turn, give nitrous acid. Then the acid reacts with ammonia to form NH_2NO, which further decomposes to give nitrogen and water. However, it is difficult to agree with this mechanism, since NO_2 and water are typical products of nitric acid decomposition, and the interaction of NO_2 with ammonia is known to result in N_2O.

It is quite obvious that the role of soot is to shift the reaction of ammonia oxidation, changing the oxidation product from N_2O to N_2. The key moment for understanding the mechanism of catalytic action of soot came from the work described in [42], in which the composition of gases flowing off rapidly heated AN samples was studied with IR-spectroscopy. Charcoal added to AN was found to remove completely free ammonia from the gas phase. Analyzing the combustion products of mixtures of AN with charcoal (84.2:15.8) and halides, Glazkova [10] also noted that ammonia was oxidized first in such systems. Taking this fact into account, the mechanism of charcoal/soot action in AN decomposition can be assumed to include the addition reaction of nitric acid to unsaturated bonds of charcoal/soot with formation of nitrite first, which then reacts with ammonia to give alcohol and NH_2NO (Scheme 2)

Oxidized fragments of charcoal undergo pyrolysis to form water and carbon dioxide as final products. It is also possible to assume that hydroxyl groups formed on the charcoal surface serve as traps of nitrogen oxide, transforming it into nitrite, which then reacts with ammonia.

3.4.3 Addition of Energetic Materials

The above reasoning about the influence of fuel additives on the kinetic parameters of AN decomposition can be extended to additives of organic explosive compounds. However, explosives are capable of sustained burning and this property may be the determining factor. Trotyl is a more stable substance than AN. Its boiling point of 335 °C and heat of evaporation of 71 kJ/mol (17 kcal/mol), given in [43], suggest that, at pressures of more than 10 MPa, the boiling point of TNT will exceed the AN dissociation temperature and, hence, the temperature of the burning surface will be determined by the AN dissociation reaction. Mixtures of AN with TNT begin to burn only at 10–15 MPa. Temperature measurements during combustion of AN/TNT mixtures are given in [16]. They show that the leading reaction proceeds mostly in the condensed phase. Calculations of the leading reaction rate constants from the condensed-phase combustion model have been made, assuming that the surface temperature is determined by AN dissociation and using measured burning rates. The results are presented in



Scheme 2.

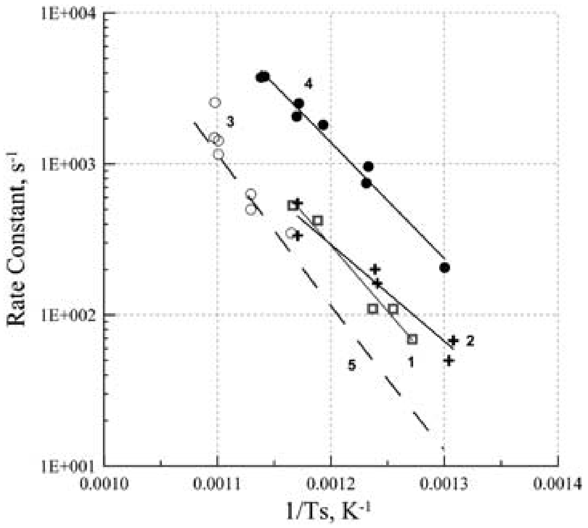


Figure 8. Comparison of rate constants of the leading reaction on combustion of AN with 4% (1) and 8.6% (2) of charcoal; ammonite AN-TNT 80/20 (3), and ammonite AN-TNT 80/20 + 5% KCl (4) with decomposition kinetics of liquid AN (5).

Figure 8. As can be seen from the figure, the kinetic data for ammonite coincide closely with kinetic parameters of AN decomposition. Although the presence of carbonaceous products was observed on the surface of extinguished samples [16], the degree of TNT decomposition in the surface layer is insignificant. As a trap for nitronium ion, TNT is a low-activity substrate also. Therefore, the occurrence of the stable burning region at pressures above 10–15 MPa for AN/TNT mixtures is most likely connected with a growing heat flux from the gas phase. The high pressures of onset of burning support this suggestion, because the part of the gas phase usually increases with pressure. The fact that TNT does not react with nitronium ion and does not suppress the autocatalytic channel of AN decomposition is in agreement with a substantial growth of the burning rate on addition of metal chlorides to this mixture (Figure 3). It is well known [38] that the catalytic action of chlorides manifests itself at high concentrations of HNO_3 in the system.

Rate constants for the leading reaction in combustion of catalyzed ammonite (containing 5% of NaCl, Figure 8) lie above the decomposition kinetics for neat AN and above rate constants of the leading reaction in combustion of AN catalyzed by addition of the same amount of chloride. Since TNT is a low-reactivity substrate for nitronium and nitrosonium ions, they basically enter into the oxidation of ammonia according to Eqs. (8) and (9). Now a contribution of this interaction to the overall decomposition determines the burning rate appreciably. The heat flux from the gas phase probably makes a small contribution to the burning rate also. The activation energy of the rate-limiting process is less than the activation energy of the leading reaction for combustion of ammonite with no chloride additive.

The situation looks more complex with combustion of AN mixtures with polynitrogen compounds: 2-methyl-5-nitrotetrazole and glycidyl azide polymer (Figure 4). The point is that the both substances are less thermally stable than AN, but evaporate at lower temperatures. Although there are no surface temperature data for these mixtures, the closeness of their $r_b(p)$ curves to the burning law of the AN/TNT mixture suggests similarity between their combustion mechanisms.

Combustion of endothermic methylnitrotetrazole, MNT, was shown in [44] and [45] to follow the mechanism of burning of volatile explosives, with the rate-limiting stage being MNT decomposition in the gas phase. MNT burns with high rates [44], which exceed by several times the burning rates of all AN mixtures with catalysts and fuels. The surface temperature of MNT is 535 ± 10 K at atmospheric pressure, which is almost 100 K lower than the AN dissociation temperature at the same pressure, and the tendency is retained at high pressures. This means that MNT evaporates from the melted AN layer, and then burns in the gas phase. The calculated temperature gradient in the MNT combustion wave at 5 MPa is $23 \cdot 10^8$ K/m [45], which allows 1380 J/g (330 cal/g) of heat to come back from the gas phase to the condensed phase. Additional heat feed back from the gas at the expense of MNT in an 85% AN/15% MNT mixture can be estimated as ~ 209 J/g (50 cal/g) (without the possible contribution of redox reactions between decomposition products of MNT and AN). Thus, a 209 J/g increase in the condensed-phase heat effect, which is equivalent to warming the condensed phase by more than 90 K, results in AN beginning to burn steadily from 6 MPa.

A similar mechanism can be put forward for combustion of AN mixtures with another endothermic polynitrogen compound, GAP. The burning behavior and flame structure of glycidyl azide oligomers of low molecular weights as well as compositions gelatinized with polymethylmethacrylate were investigated in [46]. At low pressures, the surface temperature of gelatinized GAP oligomer is much lower than the surface temperature of cured and cross linked GAP samples [47]. The surface temperatures are surprisingly weakly dependent on pressure, growing from 230 to 300 °C only when pressure increases from 0.1 to 4.5 MPa [46]. The burning rate of GAP oligomer is determined by the rate of the azide decomposition reaction in the gas phase. The appearance of stable burning of AN mixed with GAP from a pressure of 10 MPa is connected, therefore, with heat flux from the gas phase. Since both MNT and GAP are not likely to react with AN in the condensed phase, but can provide heat feedback, burning of the mixtures is determined by the decomposition of neat, non-catalyzed AN in the molten surface layer. Calculations show that kinetic parameters of the leading reaction in combustion of both AN/MNT and AN/GAP mixtures are in a good agreement with the decomposition kinetics of neat AN.

3.5 Pressure Sensitivity of Burning Rate of AN-based Compositions

The pressure exponent, *n*, for a system in which combustion is controlled by decomposition kinetics in the condensed phase [33] can be determined as $n = E/2L_{ev} = E/\Delta_{diss}H$. Using the activation energy of AN decomposition, 197.5 kJ/mol (47.2 kcal/mol), and taking the enthalpy of AN dissociation equal to 166.9 kJ/mol (39.9 kcal/mol) [25], the pressure exponent may be expected to be greater than unity: $n = 197.5/166.9 = 1.18$. Therefore, if an additive does not change AN decomposition kinetics in the condensed phase, as with explosives, the pressure exponent will be close to the calculated value 1.18. Indeed, the pressure exponent for ammonite is slightly more than unity (Figure 3).

In the case of combustion of AN with metal chloride additives, the pressure exponent must be less: $n = 142/166.9 - 159/166.9 = 0.85 - 0.95$. As can be seen from Figure 1 and Table 1, the pressure exponent of the low-pressure part of the $r_b(p)$ curve for AN with metal halide additives is 0.85 – 0.94. Addition of sodium chloride to ammonite results in decreasing the activation energy of the rate-limiting process, which is reflected in reduction of the pressure exponent at pressures below 20 MPa.

As mentioned above, many AN-based compositions exhibit a break in the $r_b(p)$ curves in the 20 – 30 MPa area. It may be suggested that the AN dissociation temperature reaches its critical value at these pressures and does not grow longer. Approaching the critical temperature is known to lead to a decrease in the heat of phase transition, which goes to 0 at the critical temperature. It may be suggested, therefore, that at pressures higher than 20 – 30 MPa the amount of heat required to warm the condensed substance is independent of pressure, whereas the burning rate increases with pressure due to increasing concentrations of the reacting gases. Thus, there is an opportunity for combustion to proceed through the gas phase mechanism. Since the combustion temperature of AN with the additives does not exceed 1300 K, it is possible to assume, based on the gas phase combustion model, that the leading reaction is monomolecular decomposition of AN with a pressure exponent close to 0.5, which is the case (see Figure 1).

4 Conclusions

Analysis of the observed combustion features of AN mixtures with inorganic additives, organic fuels and explosives shows that the leading reaction in combustion proceeds in the condensed phase at least up to pressures of 20 – 30 MPa. Flame structure investigations by fine tungsten-rhenium thermocouples have revealed that the surface temperature of AN is controlled by the dissociation reaction of the salt into ammonia and nitric acid, occurring at the surface. Data obtained allow kinetics of the leading reaction in combustion to be derived, based on a condensed-phase combustion model. The well-known combustion instability of pure AN has been suggested to arise from a moderate heat of decomposition in the liquid AN, which is insufficient to warm the condensed material to the dissociation temperature. It is proposed that additives increase heat generation in the condensed phase, which stabilizes combustion, first, and raise the decomposition rate, which increases the AN burning rate, second. The different behavior of $r_b(p)$ dependences for different AN-based compositions observed at pressures below 20 MPa is explained by the complex liquid-phase decomposition kinetics, comprising secondary reactions between AN decomposition products as well as the primary radical-type decomposition of nitric acid. It is the different contribution of secondary autocatalytic reactions, dependent on the amount, nature, and reactivity of an additive, that gives rise to the observed variety of burning rate – pressure dependences.

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Acknowledgements

The authors are grateful to Dr. S. A. Filatov and Mrs. S. N. Galtsova for the assistance in temperature profile and burn rate measurements.

(Received February 16, 2005, revised version April 14, 2005; Ms 2005/004)