Combustion Mechanism and Kinetics of Thermal Decomposition of Ammonium Chlorate and Nitrite

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Abstract: Combustion data of ammonium chlorate and nitrite have been analyzed. The leading reactions of combustion of both NH₄ClO₃ and NH₄NO₂ at low pressures have been shown to proceed in the condensed phase, with the burning rate defined by the decomposition kinetics at the surface temperature. The kinetics of NH₄ClO₃ and NH₄NO₂ decomposition have been calculated by using a condensed-phase combustion model.

Keywords: ammonium chlorate, ammonium nitrite, combustion mechanism, decomposition, rate constant

Introduction

Ammonium salts of such oxidizing acids as HNO₃, HNO₂, HClO₄, and HClO₃ are energetic materials capable of exothermic decomposition. These compounds have the identical combustible part in their molecules, but differ in stability, heat of explosive transformation, and reactivity of the oxidizing part. The ability of some ammonium salts to burn was shown by Shidlovskii [1-3]. In works [4, 5], the combustion of these compounds was studied in the form of pressed strands (TMD is 0.85-0.95) in acrylic tubes of inner diameter 4 or 7 mm in a wide pressure interval (0.1-40 MPa). Their burning rates were shown to vary vastly. Authors of works [4, 5] suggested that the difference in the burning rates could be explained by different oxidation properties of acids, which are included in the composition of the salts rather than different thermal stability of the salts. They characterized oxidation properties of acids by the oxidation
potential and showed that the bigger the value of potential the higher the burning rate of corresponding ammonium salt.

This explanation implies that the leading reaction on combustion is a high-temperature oxidation-reduction process in the flame, since the decomposition is known to be the slowest process at moderate temperatures (and, moreover, in the condensed phase) [6]. However, it does not seem to be absolutely correct to assume that decomposition reactions are absent in the condensed phase for such unstable compounds as NH₄NO₂ and NH₄ClO₃. Moreover, it is well known now that burning rates of two other ammonium salts, ammonium perchlorate NH₄ClO₄ [7-11] and nitrate NH₄NO₃ [12-14] are determined by kinetics of their decomposition in the condensed phase.

Recently [15], it has been shown that the decomposition kinetics of an energetic material can be derived from its burning rate data provided its combustion is governed by condensed-phase reactions. In order for kinetic parameters of the rate-controlling reaction could be evaluated from an adequate combustion model, the experimental data on burning rates and surface temperatures must be obtained.

Decomposition kinetics of NH₄ClO₄ and NH₄NO₃ were studied widely [11], at the same time kinetic data on NH₄NO₂ and NH₄ClO₃ decomposition are practically absent in the literature.

In this connection, the purpose of the present work was an analysis of the existing combustion data for ammonium chlorate and nitrite aimed at determination of their combustion mechanism and decomposition kinetics.

**Results and Discussion**

**Ammonium chlorate**

Burning rates of ammonium chlorate are presented in Figure 1. Ammonium chlorate in the form of samples pressed into acrylic tubes of 4 mm diameter is capable of sustained combustion at atmospheric pressure [4, 5]. However, burning rates measured at atmospheric pressure are much lower than the general dependence of the burning rate vs. pressures (Figure 1) that may be connected with heat loses becoming significant at this pressure and sample diameter influencing the burning rate. In the pressure interval 0.4-40 MPa, the burning rate of NH₄ClO₃ can be described as: \( r_b = 12.96 P^{0.6} \). For comparison, burning rates of ammonium perchlorate (AP) [16] are also presented in Figure 1. As seen from the figure, ammonium chlorate, having chloric acid as oxidizer with standard oxidizing potential \( E_{\text{Cl}_2/\text{HClO}_3} = 1.47 \text{ V} \) burns much
faster than ammonium perchlorate, containing perchloric acid as oxidizer with $E_{Cl_2/HClO_4} = 1.39$ V [17]. At the same time, ignition point of NH$_4$ClO$_3$ (130 °C [18], 70-100 °C [19]) is much less than that of NH$_4$ClO$_4$ (350 °C) [20], which is an evidence of lower thermal stability of ammonium chlorate in comparison with ammonium perchlorate. In order to understand which factor has major effect on the burning rate, one needs to decide on the combustion mechanism, since reaction activity of the oxidizer is important for gas-phase combustion model, while kinetics of thermal decomposition is important for combustion governed by condensed-phase reactions.

![Graph](image.png)

**Figure 1.** Comparison of combustion behaviors of ammonium chlorate and perchlorate.

The heat effect of decomposition reaction of solid NH$_4$ClO$_3$ to oxygen, gaseous water, and HCl (or chlorine) averages 42.5–49 kcal/mole or 419–482 cal/g depending on product composition. Calculated combustion temperature of NH$_4$ClO$_3$ is 1660 K at 10 MPa, which gives a heat effect of 452 cal/g taking
an average heat capacity \( (c_p) \) as 0.33 cal/g×K. Taking into account heat of condensation \( (\Delta H_{\text{cond}}) \) of water and HCl, the decomposition heat increases to 680-700 cal/g.

Knowing enthalpies of formation of solid \( \text{NH}_4\text{ClO}_3 \) (-65.1 kcal/mole [21]), gaseous \( \text{NH}_3 \) (-11.0 kcal/mole [22]), and \( \text{HClO}_3 \) (-13 kcal/mole, estimation) and taking into account heat of melting \( (\Delta H_m \sim 3 \text{ kcal/mole, estimation}) \), it is possible to calculate easily the thermodynamic enthalpy of \( \text{NH}_4\text{ClO}_3 \) dissociation in the melt to gaseous \( \text{NH}_3 \) and \( \text{HClO}_3 \) \( (\Delta H_{\text{diss}} \sim 38.2 \text{ kcal/mole or 376 kcal/kg}) \).

In work [23], the temperature distribution in the combustion wave of \( \text{NH}_4\text{ClO}_3 \) was measured by thin thermocouples. According to those data, the surface temperature at atmospheric pressure is 584 ±21 K. This temperature is significantly less than the surface temperature of AP (820 K) [24]. Knowing a dissociation temperature at one pressure and the enthalpy of dissociation, it is possible to calculate dissociation temperatures in a wide pressure interval: \( \ln P = -9612/T + 16.46 \). In turn, assuming that the salt is heated to the maximum possible temperature in the condensed state i.e., dissociation temperature, it is possible to estimate heat expenses for warming-up \( \text{NH}_4\text{ClO}_3 \) to the surface temperature and melting. In the pressure interval 0.1-40 MPa, heat needed for warming-up the condensed phase from initial temperature, \( T_0 \), to the surface temperature, \( T_s \), \( Q_{\text{need}} = C_p(T_s-T_0) + \Delta H_m \) is 136-256 cal/g. It is also needed \( 0.33(1660 - 584) = 355 \text{ cal/g} \) for warming-up the gas phase to the flame temperature at atmospheric pressure. A comparison of enthalpy change in the combustion wave of \( \text{NH}_4\text{ClO}_3 \), assuming warming-up the condensed phase to the surface temperature \( (T_s) \), melting, evaporation, and warming-up the dissociation products to the flame temperature \( (T_f) \) with heat released in combustion of \( \text{NH}_4\text{ClO}_3 \) is presented in Figure 2. The comparison of calorimetric value of \( \text{NH}_4\text{ClO}_3 \) (~690 cal/g) with heat expenses shows that the remaining heat \( (690 - 491 = 199 \text{ cal/g}) \) is not enough for complete transition of the substance into the gas phase (376 cal/g).

If combustion of a material obeys a gas-phase model, the lacking heat is provided by the ignition system. In the subsequent combustion events, heat of evaporation is transmitted from layer to layer. In the case when an energetic material decomposes in the condensed phase, amount of heat needed for evaporation is decreased. In the case of \( \text{NH}_4\text{ClO}_3 \) if we assume a condensed-phase combustion model, ~30% of the substance should be decomposed in the condensed phase at atmospheric pressure to provide for warming-up the condensed phase to the surface temperature and melting. The remaining part of the substance is thrown out into the gas phase by flowing-off gases (disperse) and decomposes in the condensed state in the aerosol flow above the surface.
Probably, the dispersion results in a significant scatter of the burning rate observed at low pressures (see Figure 1).

The leading role of the condensed phase in combustion of NH$_4$ClO$_3$ can be confirmed by an analysis of the temperature sensitivity of the burning rate. According to the condensed-phase model [25], the dependence of the burning rate on initial temperature is described by an expression $r_b = A/(T_S - T_0 + \Delta H_m/c_p)$, while for the gas-phase model this dependence is expressed as $r_b = A \times \exp(-B/(C+T_0))$, where $A$, $B$, and $C$ are constants. In coordinates $\ln r_b$ vs. $T_0$, the first dependence looks like a curve with convexity downwards, and the second one has convexity upwards. Hence, the shape of the $\ln r_b(T_0)$ curve can indicate to the leading role of one or the other combustion mechanism.

![Figure 2](image)

**Figure 2.** Comparison of the enthalpy change in the combustion wave of NH$_4$ClO$_3$ with heat released in combustion at atmospheric pressure.

In work [23], the temperature sensitivity of the burning rate of NH$_4$ClO$_3$ was determined at atmospheric pressure in the interval of initial temperatures of -68-80 °C. The authors described experimental points by a piecewise-linear method and obtained one value of the temperature sensitivity in the interval of -68-60 °C and significantly large value in the very narrow interval of 60-80 °C.
At the same time, experimental points are well described by a function of kind $r_b = A/(B-T_0)$, with scatter of data no more than 10% (Figure 3).

**Figure 3.** Effect of initial temperature on the burning rate of ammonium nitrite and chlorate at atmospheric pressure.

Differentiation of the received $r_b(T_0)$ dependence allows obtaining the temperature sensitivity of NH$_4$ClO$_3$ as a continuously growing function (Figure 4). Besides, in Figure 4 are presented two theoretical dependences of the burning rate temperature sensitivity. One is described by the formula $\sigma = 1/(T_s - T_0 + \Delta H_m / c_p)$ for the condensed-phase combustion model, using experimental surface temperature $T_s = 584$ K, and the other is defined by the formula $\sigma = E / 2RT_f^2$ for the gas-phase model, using experimental flame temperature $T_f = 1378$ K [23]. It is obvious that the gas-phase concept, which shows decreasing temperature sensitivity with initial temperature, contradicts experimental observations.
Knowing dependences of the burning rate and surface temperature on pressure it is possible to estimate kinetic parameters of NH₄ClO₃ decomposition by using a condensed phase combustion model [25]:

$$m = \sqrt{\frac{2\rho \lambda Q}{c_p^2(T_s - T_0 + \Delta H_m/c_p)^2 \left(\frac{RT_s^2}{E}\right) \cdot A \cdot e^{-E/RT_s}}}$$

Here $c_p$, $\rho$, and $\lambda$ are specific heat, density, and thermal conductivity of the condensed phase, $T_s$ and $Q$ are the surface temperature and heat of reaction, $E$ and $A$ are activation energy and preexponential factor of the leading reaction in the condensed phase. The expression $T_s - T_0 + \Delta H_m/c_p$ accounts for warming-up of the condensed phase from initial temperature, $T_0$, to surface temperature, $T_s$, and melting, where $\Delta H_m$ is heat of melting. A comparison of kinetics of the
leading reaction of combustion and decomposition for ammonium chlorate is presented in Figure 5. The following input data were used: \( c_p = 0.365 \text{ cal/g} \times \text{K} \), \( \lambda = 3.85 \times 10^{-4} \text{ cal/cm} \times \text{K} \), \( Q = 452 \text{ cal/g} \), and \( \Delta H_m = 3 \text{ kcal/mol} \). Since NH\(_4\)ClO\(_3\) decomposition data are not available, rate constants of decomposition have been estimated from the adiabatic thermal explosion model using known ignition temperatures. As seen from Figure 5, the kinetics of the leading reaction of combustion, calculated by the condensed-phase model, is in a good agreement with rate constants of decomposition, estimated by ignition points. The rate constants are described by the equation: \( k = 3.3 \times 10^{11} \times \exp^{-23700/RT} \). Kinetic data of the leading reaction of ammonium perchlorate combustion [26] and kinetic data of AP decomposition in the liquid state [27] are also presented in Figure 5. A comparison of the constants shows that the decomposition rate of NH\(_4\)ClO\(_3\) is almost three orders of magnitude more than that of the leading reaction of AP combustion. This is a reason for ammonium chlorate, having the same combustion mechanism and less surface temperatures than AP, to burn much faster than AP.

![Figure 5](image-url).

Figure 5. Comparison of kinetic parameters of the combustion leading reaction (1 and 3) with decomposition kinetics in the liquid states (2 and 4) for ammonium chlorate and perchlorate.
Ammonium nitrite

By analogy with ammonium chlorate and perchlorate, ammonium nitrite burns faster than ammonium nitrate (AN) containing a combustion catalyst (Figure 6). Pressed samples of ammonium nitrite of 7 mm diameter are capable of burning even at pressure 0.55 atm [4, 5], while uncatalyzed ammonium nitrate will not burn at all. Combustion of NH₄NO₂ can be described by a line with two breaks: \( r_b = 5.97P^{1.05} \) at pressure 0.1-4 MPa, \( r_b = 13.62P^{0.44} \) at 4-20 MPa, and \( r_b = 2.57P^{1.01} \) at 20-40 MPa. As in the previous case, the standard oxidizing potential of nitrous acid \( E_{\text{NO}_2/\text{HNO}_2} = 1.45 \text{ V} \) is higher than the potential of nitric acid \( E_{\text{NO}/\text{HNO}_3} = 0.85 \text{ V} \) [17], and stability of nitrite is less than that of AN: its ignition point is 89-90 °C [3]. It was noted in paper [28] that a 0.25 g sample of NH₄NO₂ was decomposed completely for 2 minutes at 85-90 °C, and for 9 minutes at 55-60 °C. It was shown in [3] that NH₄NO₂ was decomposed to 10% at room temperature during 6 weeks.

Figure 6. Comparison of combustion behaviors of ammonium nitrite and nitrate.
Experimental points of the burning rate vs. initial temperature received in work [23] at atmospheric pressure can be well described by dependence $r_b = A/(B - T_0)$, that testifies to the leading role of the condensed phase reaction (see Figure 2). In work [3], it was revealed that catalysts of NH$_4$NO$_2$ decomposition also increased its burning rate, which argues for the condensed-phase mechanism of combustion.

The NH$_4$NO$_2$ surface temperature (dissociation temperature) at atmospheric pressure can be estimated from the $r_b(T_0)$ dependence; it is equal to 167 °C (440 K). This temperature is significantly less than the surface temperature of AN (580 K) [14].

![Figure 7](image_url)

**Figure 7.** Dependence of the temperature sensitivity of ammonium nitrite burning rate on initial temperature: 1 – condensed phase model (theory); 2 – experimental data; 3 – gas-phase model (theory).

Differentiation of the $r_b(T_0)$ dependence allows obtaining the temperature sensitivity of NH$_4$NO$_2$ burning rate at atmospheric pressure (Figure 7). Besides, Figure 7 shows theoretical dependences of the burning rate on initial temperature assuming either gas-phase ($T_f = 2180$ K) or condensed-phase
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(T_S = 440 K) mechanisms. As seen from the figure, the temperature sensitivity of NH_4NO_2 burning rate grows with initial temperature that is characteristic for the condensed-phase mechanism of combustion.

A comparison of enthalpy change in the combustion wave of NH_4NO_2, assuming warming-up the condensed phase to the surface temperature, melting, evaporation, and warming-up of the dissociation products to the flame temperature, with heat released in combustion provides us with additional information on combustion mechanism.

The enthalpy of NH_4NO_2 dissociation (27 kcal/mole or 422 cal/g) can be calculated from enthalpy of formation of the solid substance (-58.7 kcal/mole [21]), estimated enthalpy of melting (2.5 kcal/mole), and enthalpies of gaseous dissociation products NH_3 (-11.0 kcal/mole [22]) and HNO_2 (-18.34 kcal/mole [29]). Heat effect of the decomposition reaction NH_4NO_2 → N_2 + 2H_2O is equal to 864 cal/g for H_2O_{gas} or 1203 cal/g for H_2O_{l}. Heat effect of 1203 kcal/kg is consumed for warming-up the substance to the surface temperature (including melting) c_p(T_S-T_0) + ΔH_m = 111 kcal/kg, heating gaseous products to the flame temperature (2180 K) c_p(T_f-T_S) = 887 kcal/kg, and evaporating a part of the substance. In the case of condensed-phase combustion, the other part decomposes in the liquid state without evaporation. A comparison of heat needed for warming-up the substance to the surface temperature (including melting) with the heat effect of decomposition reaction to gaseous products (864 cal/g) shows that about 13% of NH_4NO_2 must be decomposed at atmospheric pressure to supply the required amount of heat. Hence, as with ammonium chlorate, combustion of NH_4NO_2 is probably characterized by partial decomposition in the condensed phase and formation of the aerosol flow above the surface, which serves as a buffer zone consuming heat flux from the gas phase. Thus, despite a considerable heat effect of decomposition, high flame temperature, and small decomposition depth in the condensed-phase, the low thermal stability of NH_4NO_2 leads to conclusion that its combustion at low pressures is determined by reactions in the condensed phase. The first break on the r_b(P) curve is observed at 4 MPa (see Figure 6). It is possible to assume that in this area the evaporation temperature (in case of salts the dissociation temperature) achieves its critical value and does not grow further. After achieving critical conditions, the enthalpy of dissociation turns to zero. The area of 4-20 MPa is transitive, and at pressure higher than 10 MPa, the leading role in ammonium nitrite combustion is probably passed to the gas phase.

Using experimental burning rates of NH_4NO_2 in the pressure interval of 0.1-4 MPa and calculated dependence of dissociation temperature on pressure lnP = -6794/T + 15.44, taking it as the surface temperature, it is possible to estimate kinetic parameters of the leading reaction of NH_4NO_2 combustion from
the condensed-phase model: \( k = 6.7 \times 10^{15} \times \exp^{31700/RT} \text{ s}^{-1} \) (Figure 8). The following parameters were used in the calculation: \( c_p = 0.49 \text{ cal/g}\times\text{K} \), \( \lambda = 1.42 \times 10^{-3} \text{ cal/cm}\times\text{K} \), \( Q = 864 \text{ cal/g} \), and \( \Delta H_m = 2.5 \text{ kcal/mol} \). Kinetics parameters derived from the \( \text{NH}_4\text{NO}_2 \) combustion data appeared to be in a good agreement with rate constants of its decomposition calculated from the ignition temperature and decomposition rate at 25 °C [3]. For comparison, the kinetics of the leading reaction of combustion of \( \text{AN} + 7\% \text{ NaCl} \) [14] are also presented in Figure 8. As seen from the figure, the decomposition rate of \( \text{NH}_4\text{NO}_2 \) is almost five orders of magnitude higher than the rate of the leading reaction of \( \text{NH}_4\text{NO}_3 \) combustion. This is a main reason explaining the fact that ammonium nitrite having the same combustion mechanism and less surface temperatures than AN, burns much faster than AN.

![Figure 8. Comparison of kinetic parameters of the leading reaction on combustion of ammonium nitrite (1) and ammonium nitrate (3) with kinetic parameters of ammonium nitrite decomposition (2).](image-url)
Conclusion

An analysis of combustion data of ammonium salts of oxygen-containing acids shows that the leading reaction of combustion of NH$_4$ClO$_3$ and NH$_4$NO$_2$ at low pressures proceeds in the condensed phase as it is the case of NH$_4$ClO$_4$ and NH$_4$NO$_3$. The burning rate is determined by decomposition kinetics at the surface temperature. Thus, the correlation between standard oxidizing potential of the acid-oxidizer and the burning rate previously offered for these salts seems to be a coincidence. The kinetic parameters of NH$_4$ClO$_3$ and NH$_4$NO$_2$ decomposition have been calculated from a condensed-phase combustion model.

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References


