Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 443 (2006) 1–36

thermochimica acta

www.elsevier.com/locate/tca

Review

Thermal decomposition of ammonium perchlorate

V.V. Boldyrev[a,b,*]

[a] Research and Educational Center "Molecular Design and Ecologically Safe Technologies", Novosibirsk State University, 630090 Novosibirsk, 90, Pirogov str., 2, Russia
[b] Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Sciences, 630128 Novosibirsk, 128, Kutateladze str., 18, Russia

Received 16 May 2005; received in revised form 21 November 2005; accepted 21 November 2005

Abstract

This review represents an attempt to summarize literature data on thermal decomposition of ammonium perchlorate. The mechanism of thermal decomposition and various factors which influence on the thermal decomposition of ammonium perchlorate are discussed.

Keywords: Ammonium perchlorate; Thermal decomposition

Contents

---

* Tel.: +7 3833331424; fax: +7 3833321550.
E-mail address: Boldyrev@nsu.ru.

0040-6031/$ – see front matter
doi:10.1016/j.tca.2005.11.038

1. Introduction

Properties of ammonium perchlorate in general and particularly its thermal decomposition have been a subject of extensive literature including reviews [1–5].

It was revealed during investigation of thermal decomposition of ammonium perchlorate that the process is characterized by a number of features which were of purely scientific interest irrespective of applied problems at which these investigations had been aimed at first. It turned out that the character of thermal decomposition of ammonium perchlorate below phase transition at 240 °C and above this point is different.

Low-temperature thermal decomposition of ammonium perchlorate turned out to be extremely sensitive to the “biography” of a crystal, the presence of admixtures in it, preliminary mechanical treatment and irradiation. It was also revealed that addition of simple and complex oxides, which are typical catalysts of oxidation–reduction processes, has a very strong effect on the rate of thermal decomposition. It was established that low-temperature thermal decomposition of ammonium perchlorate proceeds not completely and runs through the formation and growth of reaction nuclei composed of unreacted NH_4ClO_4. Since no solid products are formed during thermal decomposition of ammonium perchlorate, a usual scheme of the process auto-localization due to catalysis by a solid product of the reaction could not be accepted; therefore, another scheme of feedback leading to auto-localization of the process, specific for ammonium perchlorate, had to be searched for. Below the phase transition at 240 °C reaction arrest after the decomposition of one-third of ammonium perchlorate is also unusual.

High-temperature thermal decomposition of ammonium perchlorate proceeds till completion; no dry residue is formed.

In the very beginning of study, the mechanism of thermal decomposition of ammonium perchlorate was not clear. There were at least three points of view on the elementary stages from which the process of thermal decomposition starts. According to one of these opinions, decomposition is considered to start with electron transfer from the anion to cation similarly to the case of heavy metal azide decomposition. According to another one, the decomposition process starts with the rupture of chlorine–oxygen bond, similarly to thermal decomposition of perchlorates of alkaline metals. According to the third point of view, thermal decomposition of ammonium perchlorate starts with proton transfer from the cation to anion, similarly to decomposition of all the ammonium salts.

2. Properties of ammonium perchlorate

2.1. Crystal structure

2.1.1. Phase transition

Ammonium perchlorate is a white crystalline substance. Two most important crystal modifications of ammonium perchlorate are: orthorhombic (region of existence: $T < 240\,^{\circ}C$) (Fig. 1) and cubic one, which is stable at temperatures $T > 240\,^{\circ}C$.

Heat of phase transition of ammonium perchlorate from orthorhombic to cubic modification is 11.3 kJ/mol [6].

The unit cell of the orthorhombic modification contains four molecules. The unit cell parameters are: $a = 0.9202$, $b = 0.5816$ and $c = 0.7449$ nm. Four oxygen atoms form a tetrahedron around the chlorine atom. The distance between chlorine and oxygen is 0.143 nm. Each ammonium ion is surrounded by 12 oxygen atoms. Eight of them are at a distance of 0.294–0.308 nm and four at a distance of 0.325–0.352 nm [7].

The high-temperature cubic modification has a structure of sodium chloride. The unit cell contains four molecules, $a = 0.763$ nm [8].

Investigation with the help of NMR, neutron diffraction [9] and ESR [10] shows that both the ammonium and perchlorate ions can rotate freely. In the cubic structure, both ions rotate; in the orthorhombic one, only ammonium does.

It was assumed that the phase transition of the first kind at 240 °C is preceded by the transition of the second kind, which is the reason of deviation from the normal behaviour observed in ammonium perchlorate under thermal decomposition [5]. It

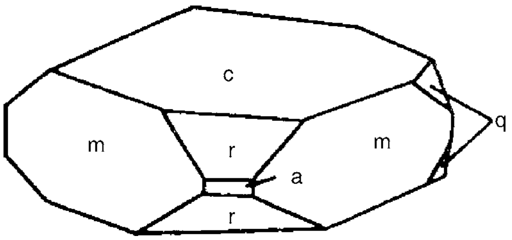


Fig. 1. The shape of ammonium perchlorate crystals. Designation of faces: a: (1 0 0); : (0 0 1); m: (1 1 0); r: (1 0 2); q: (0 1 1).

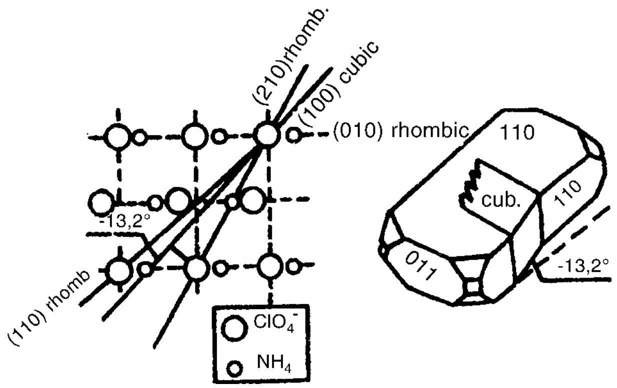


Fig. 2. A scheme of the observation of polymorphous transition in ammonium perchlorate crystals in the plane (0 0 1).

turned out later than the phase transition at 240 °C itself depends on the ability of perchlorate ion, hanging before the transition on N–H–O hydrogen bonds in the lattice, to rotate freely.

Polymorphous transition in ammonium perchlorate crystals was studied in [11]. It was discovered that there are two mechanisms of the transformation of the rhombic modification into cubic one. At low-temperature, the transition follows atom-by-atom mechanism. At temperature increased up to 243 °C, the transition is of martensite type. In both cases, the polymorphous transition proceeds through the formation and growth of the nuclei of the new phase; the growth of martensite nuclei occurs not continuously but jumpwise. The interface boundary can be coherent during the transition form rhombic modification into the cubic one [11]. During this process, the (0 1 1) plane of the rhombic modification corresponds to the (0 0 1) plane of the cubic one. The angle of surface relief is equal to 13.14° in the case when full coherence takes place, which happens, for example, during martensite transition (Fig. 2). During the atom-by-atom transition, which allows slow relaxation processes to occur, the angle of relief decreases. To measure the relief angle, the effect of preliminary irradiation on the rate of thermal decomposition of ammonium perchlorate was used [12], which allows one to develop a latent photographic image formed in a crystal during exposure to the ultraviolet radiation through a stencil with square orifices.

For martensite transition above the phase transition point distortion of the angle of the square stencil was 11.5°, which is close to the requirement provided by full coherence (13.2°). For atom-by-atom transformation, coherence angle could decrease to 2°. The course of phase transition from the orthorhombic modification into the cubic one was followed in [13] by heating the crystal and simultaneously recording X-ray diffraction patterns and IR spectra.

One more curious fact was revealed during investigation of thermal decomposition of ammonium perchlorate: the rate of thermal decomposition sharply decreases at the moment of phase transition [14,15] because rearrangement of the lattice from the rhombic into cubic at the moment of transition results in sharp worsening of the conditions for the accumulation of products catalyzing thermal decomposition in the system. In earlier works [16], this effect was explained by a decrease in the lattice parameters. According to the opinion of the authors of this hypothesis, compacting of the lattice should prevent the formation of interstitial ammonium ions, the process which was postulated to be one of the most important stages of the mechanism of thermal decomposition based on electron transfer from perchlorate ion to ammonium ion. However, this hypothesis was not confirmed experimentally because the density of ammonium perchlorate was observed not to increase but to decrease from 1.95 to 1.76 g/cm^3 as a result of the phase transition [5].

The reactivity of solids usually increases during the very moment of phase transition, and this phenomenon is well known in solid state chemistry as Hedvall effect. As we can see, thermal decomposition of ammonium perchlorate is an exception. Here we have, so to say, a reverse Hedvall effect.

Investigation of the behaviour of ammonium perchlorate under the pressure up to 25 GPa showed that at temperatures slightly above 240 °C (the point of transition from the rhombic modification to the cubic one), melting is observed [17].

2.2. *Conductivity of ammonium perchlorate*

Conductivity of ammonium perchlorate has long been the subject of discussions between researchers. There were three points of view on the mechanism of charge transfer in ammonium perchlorate crystals, and therefore on the mechanism of the conductivity process itself. One of the possible reasons of controversy about the mechanism of transfer processes in ammonium perchlorate crystals providing its conductivity was surely complicacy in arranging correct experiments on measuring the conductivity. A reflection of these difficulties is substantial scattering in conductivity values obtained by different authors (for example, see [4]). In part, poor reproducibility of the results can be explained by the use of pressed ammonium perchlorate tablets instead of single crystals as the objects of investigation. However, in the cases when single crystal samples of ammonium perchlorate were investigated, such factors as the presence of unintentional impurities or partial decomposition of ammonium perchlorate during measurements due to its thermal instability, polarization of the crystal during measurements involving direct current can also be the reason of deviations between the experimental data. In addition, in our opinion, it was not correct to study the conductivity of ammonium perchlorate separately from the conductivity of other ammonium salts.

2.2.1. *Mechanism of conductivity in ammonium perchlorate on the basis of the assumption about electron transfer*

The assumption about the existence of electron conductivity in ammonium perchlorate was made by Maycock and Verneker [18,19]. Having obtained four regions separated from each other by jogs in the curve of the temperature dependence of conductivity (Fig. 3), these authors concluded that if the low-temperature regions (up to 92 and 171 °C) corresponded to the surface and impurity conduction, above 171 °C they came across the bulk ion conductivity and above 233 °C, the electron one. No special confirmation of the existence of electron conductivity in ammonium perchlorate was reported, except coincidence of the

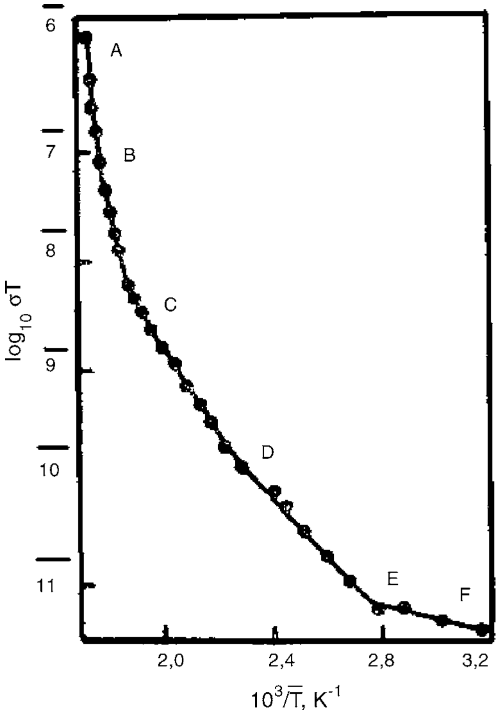


Fig. 3. Electroconductivity of ammonium perchlorate as a function of temperature [18]. AB: the region of electron conductivity; BC: conductivity due to ion defects of the cubic modification; CD: the same for the orthorhombic modification; DE: extrinsic conductivity of the orthorhombic modification; EF; the surface conductivity. (Interpretation of the curve by authors [18]).

activation energy determined experimentally (5.6 eV) with the activation energy values (6.06 eV), which can be obtained by investigating the absorption edge of ammonium perchlorate. The authors assume that this transition relates to the band-to-band type, which later became the grounds to criticize the electron mechanism of conductivity proposed by the authors because one can easily imagine that the probability of the process with such a large activation energy and small kT value should be extremely low.

Even if we admit that the electron transition proceeds not according to the band-to-band mechanism but according to a more probable hopping mechanism of electron transfer [20], the set of experimental data available at present make this assumption improbable.

2.2.2. *Mechanism of conductivity in ammonium perchlorate based on the assumption about charge transfer by the point ion defects*

Zirkind and Freeman were the first to propose the ion mechanism of charge transfer in ammonium perchlorate [21]. The assumption about charge transfer by ion defects was made in the work by Maycock and Verneker cited above [18], but it was assigned to the low-temperature region (90–150 °C). Small activation energy (0.5–0.6 eV) was interpreted by the authors of [18] as the confirmation of the fact that the charge is transferred by interstitial ions. Above 150 °C, when activation energy becomes equal to 2 eV, it is assumed that charge carriers are vacancies which are Schottki ion pairs.

Owen and Thomas adduce proofs in favour of the ion mechanism of conductivity [22–24]. They think that the ion mechanism of conductivity in ammonium perchlorate can be proved by coincidence between activation energy of conductivity in ammonium perchlorate and in rubidium perchlorate, the latter compound exhibiting undoubtedly the ion mechanism of conductivity. Crystal chemical similarity of lattices in rubidium perchlorate and the orthorhombic modification of ammonium perchlorate is sometimes mentioned as an additional argument [22–25].

Since simple equality of the data on conductivity activation energies for the two solid salts is evidently insufficient to prove the mechanism of transfer processes, and since the ion mechanism did not explain such features of transfer processes as a strong dependence of conductivity on the composition of gas phase atmosphere above ammonium perchlorate and especially on ammonia pressure, changes in conductivity during thermal decomposition, etc., the ion model of conductivity held its position not very long and then gave place to the mechanism based on proton transfer.

2.2.3. *Proton transfer*

2.2.3.1. Proton conductivity. The hypothesis of the proton mechanism of current arose as a result of the earliest investigations of conductivity of ammonium perchlorate. Wise [26] measured conductivity of ammonium perchlorate, discovered that is changes substantially in the atmosphere of ammonia and concluded that the conductivity is proton-type. The same conclusion was made by Khairetdinov and co-authors [27,28].

In order to establish the type of current carriers in ammonium perchlorate, a procedure described in [28] was used. A modified Schmidt coulometer was used as a measuring cell. Simultaneously with ammonium perchlorate, measurements were carried out also with the samples of monosubstituted ammonium phosphate which is known to be a typical proton conductor, and ammonium chloride. Since ammonium salts were subjected to electrolysis, electrodes were made of materials which were either proton conductors (for example, such a material is monosubstituted ammonium phosphate) or compounds forming complexes with ammonia thus binding ammonium evolved at the anode.

At first, Murthy's experiments with monosubstituted ammonium phosphate were repeated; it was confirmed that this compound is a proton conductor. Then the mechanism of conductivity was investigated for the sandwiches composed of the crystals of monosubstituted ammonium phosphate and perchlorate connected with each other. The results are shown in Fig. 4. One can see that the amount of gas evolved during electrolysis depends on electrode polarity. The slope of curves suggests that for the case when palladium electrode is the cathode, the ratio of the number of moles of the gas evolved to the quantity of electricity passed through is $\chi = 0.5/F$ mol/C, where F is Faraday number. According to Faraday's law, this is the necessary condition for proton conductivity. With opposite polarity, $\chi = 1.5/F$, which corresponds to the evolution of additional amount of gas (ammonia) from the anode region of the crystal. With silver electrode, χ is equal to $0.5/F$ for any polarity. Mass spectrometric analysis

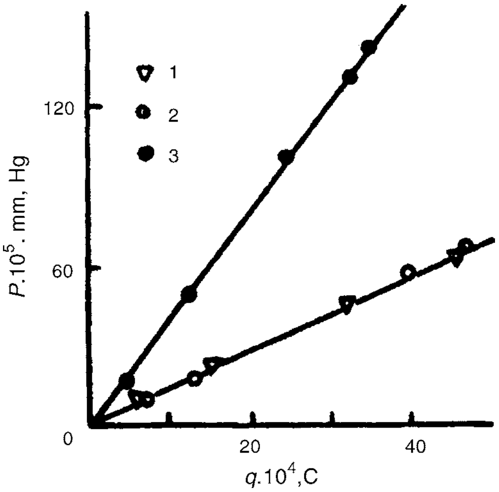


Fig. 4. Dependence of pressure of the gas evolved during electrolysis on the polarity of current and quantity of electricity passed through the ammonium perchlorate single crystal: (1) cathode region; (2) silver electrodes, anode region; (3) palladium electrodes, anode region.

showed that gas evolving at the cathode is hydrogen, while gas evolving at the anode is ammonia.

It was concluded on the basis of these data that the mechanism of conductivity is proton.

Later on, the hypothesis concerning proton conductivity was verified and confirmed experimentally by the investigations of Jacobs [29,30], who studied changes in the conductivity of ammonium perchlorate caused by doping with Ba^{2+} and SO_4^{2+}, the effect of water vapour, ammonia, and cycling for conductivity. The mechanism of proton conductivity in ammonium perchlorate proposed by Jacobs can be reduced to proton detachment from the ammonium ion, its transition to a trap and then transference of thus formed proton vacancy along the cation lattice.

Another mechanism of proton conductivity was proposed in subsequent works. It consists of three stages [31].

1. Proton transfer from cation to anion. Formation of current carriers.

   $NH_4{}^+ + ClO_4{}^- \rightarrow NH_3 + HClO_4$

2. Reorientation of the protonated anion.

   $HClO_4 \rightarrow ClO_4H$

3. Proton jump from one anion to another.

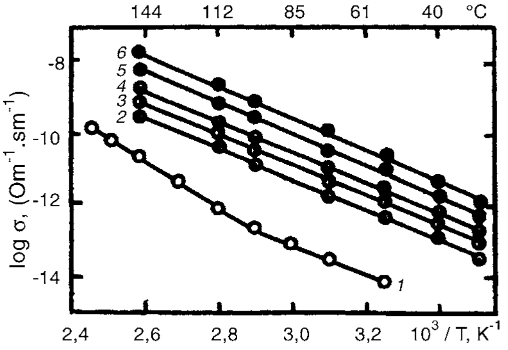


Fig. 5. Temperature dependence of the volume conductance of ammonium perchlorate crystals: (1) pure; (2) 8×10^{-4}; (3) 1.4×10^{-3}; (4) 3.5×10^{-3}; (5) 1.31×10^{2}; and (6) 3.9×10^{-2} mol% NH_4HSO_4.

Stages 2 and 3 correspond to transfer of the carrier along the lattice.

Doping of ammonium perchlorate crystals with $HSO_4{}^-$, which is donor of protons, causes an increase in conductivity (Fig. 5). At the same time, activation energy decreases.

Investigation of temperature dependence of the time of dielectric relaxation of ammonium perchlorate crystals with $HSO_4{}^-$ as a dopant gave activation energy Ed close to the value determined previously for mobility Em. This allowed concluding that the limiting stage of transfer is reorientation of the protonated ion, that is, stage 2. Table 1 shows the time of dielectric relaxation (τ_d) and time of correlation for proton diffusion process (τ_c) calculated on the basis of α and the modified Nernst–Einstein equation

$$\tau_c = \left(\frac{e\gamma\alpha^2}{\mu kT}\right),$$

where e is elementary charge, α is lattice parameter, γ is steric factor determined by the lattice geometry, k is Boltzmann constant.

One can see in Table that τ_d and τ_c values for ammonium perchlorate and for ammonium salts for which the proton conductivity had already been proven are close to each other.

Permittivity (dielectric constant) of ammonium perchlorate was measured within the frequency range from 100 to 10000 Hz and is equal to 5.1 ± 0.3 [32] (Fig. 6). It was shown in the work that the values of conductivity of ammonium perchlorate obtained directly from measurements coincide with those calculated using tangent of the loss angle.

A specific feature of the proposed mechanism is that proton migration proceeds over the anion sublattice with reorientation due to rotation of $ClO_4{}^-$ anion.

This idea was confirmed and adapted in later version of the mechanism of proton conductivity proposed by Jacobs [33,34].

Table 1
Parameters of dielectric relaxation and diffusion mobility of ions in NH_4ClO_4

Ammonium salt	Em (eV)	Ed (eV)	γ	α 10^{-8} (cm)	τ_d 10^5 (s)	τ_c 10^5 (s)
NH_4ClO_4	0.81 ± 0.05	0.76 ± 0.06	1/4	5.8	6.7×10^3	3×10^3
$NH_4H_2PO_4$	0.54 ± 0.03	0.50 ± 0.04	1/4	7.4	4.6	8.3
$(NH_4)_2SO_4$	0.49 ± 0.03	0.51 ± 0.03	1/6	6.0	5.5	3.3

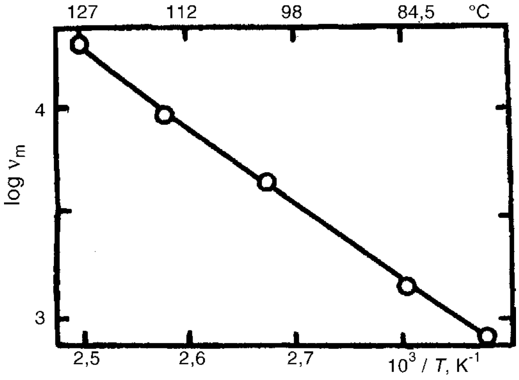


Fig. 6. Temperature dependence of the time of dielectric relaxation in ammonium perchlorate crystals containing 10^{-1} mol% NH_4HSO_4.

He showed in those works with the help of Raman spectroscopy that the additives used as dopants actually enter the lattice substituting NH4$^+$ and $ClO_4{}^-$. In addition, strong anisotropy of proton transfer was discovered in experiments with ammonium perchlorate, which the authors related to structural features of ammonium perchlorate and to the distances between ions in the lattice. It was assumed in [35] that proton conductivity is realized due to the formation of complex $N_2H_7{}^+$ between the ammonia molecule located in the interstitial space and one of the ammonium ions surrounding it. As a confirmation of the existence of such a complex, the authors refer to the results of their calculations carried out by means of molecular dynamics and the experimentally observed shift of the NH stretching peak into longer wavelengths. The formation of ammoniate in presence of gaseous ammonia can be the reason of large increase in conductivity of solid ammonium perchlorate [36]. Without denying principal possibility of the occurrence of such a channel of proton movement over the lattice along with the channel described above, it should be noted that this transfer process is likely to be valid for the subject of our present consideration, thermal decomposition, at the very beginning when proton gets liberated from $NH_4{}^-$ion.

Importance of proton transfer for thermolysis of alkyl- and aryl-substituted ammonium salts, including ammonium perchlorate, was considered in [37].

2.3. Dislocations in ammonium perchlorate crystals

The fact that the low-temperature decomposition of ammonium perchlorate starts from separate sites in a crystal stimulated search for defects as potential centres of the reaction where the reaction starts. These defects turned out to be dislocations; their presence in ammonium perchlorate crystals was studied by means of method of etching proposed by our laboratory. The etching agent was ethanol (95.5%). How we have selected this etchant, see [38]. It was shown that the maximal density of dislocations corresponds to the sites which had been mechanically deformed preliminarily. A more detailed investigation of dislocations in ammonium perchlorate was carried out in [39]. Etching was carried out at the rhombohedral and prismatic faces of ammonium perchlorate crystal. Results of these experiments indicated that the etch pits at the rhombohedral face, corresponding to the screw dislocations emergent from surface, are elongated along the longer axis of the rhombohedron. In addition, it was noted that dislocations are mainly grouped around the defects of crystal growth; dislocation picture itself, depicting the topography of dislocations on the faces of ammonium perchlorate crystal, is strongly dependent on mechanical treatment of the crystal.

Using the method developed by us to observe dislocations emergent from on the crystal surface, but using not only ethanol but also butanol, or mixtures of these etchants, the authors of [40] showed that etching proceeds in different manners at the prismatic and rhombohedral faces: etch pits are shaped as rhombs at the rhombohedral face, while they are rectangles at the prismatic face. The same authors showed that it is possible to obtain etch pits close in size, shape and areal density not only using solvent as etchants but also carrying out careful sublimation of ammonium perchlorate at 205 °C in vacuum. The basic dislocation glide planes in crystals were determined: (0 1 0) and (0 0 1).

The assumption that movement of dislocations occurs along densely packed planes of ammonium perchlorate crystal was confirmed in [41,42]. The ideas about the most active planes of dislocation movement were specified; these planes turned out to be (2 1 0) and (0 0 1); reliable data on the shape of etch pits were obtained: rhombs at the (0 0 1) face, parallelepipeds at (2 1 0) face chip, and triangles at (2 0 1).

The initial dislocation structure of ammonium perchlorate crystals depends, as shown in [43], not only on mechanical treatment but also on crystallization conditions. It recrystallization is carried out several times, the density of dislocations revealed by etching decreases substantially. By selecting supersaturation conditions during the growth of ammonium perchlorate crystals, one can grow the crystals containing no dislocations, the so-called dislocation-free whiskers [44].

The data available on the effect of ammonium perchlorate doping with isomorphous ions are controversial. On the one hand, there are indications that ammonium perchlorate doping with $SO_4{}^{2-}$ and Ba^{2+} ions up to 0.01% causes an increase in dislocation density. An increase in micro-hardness corresponds to this observation. On the other hand, ammonium perchlorate doping with copper ions does not change the density of dislocations. However, the number of dislocation sliding systems changes substantially, which may be due to the formation of Cottrell's clouds surrounding the dislocations, which should prevent their motion [45].

3. General information about thermal stability and the composition of products formed under thermal decomposition of ammonium perchlorate

Ammonium perchlorate is considered to be rather stable chemical compound. Its decomposition starts at 130 °C. At this temperature, ammonium perchlorate is decomposed about 10 times slower than ammonium nitrate. However, thermal stability of ammonium perchlorate is strongly dependent on the method of obtaining crystals, preliminary treatment and storage time after obtaining the crystals [46].

The data reported by Dode [47,48] should be considered as being among the earliest data on the chemical composition of the products of thermal decomposition of ammonium perchlorate. Dode discovered that the composition of the products of thermal decomposition depends on temperature. Below 300 °C, ammonium perchlorate decomposes according to the scheme:

$$4NH_4ClO_4 = 2Cl_2 + 2N_2O + 3O_2 + 8H_2O$$

In addition to the decomposition products shown above, ClO_2, HCl and N_2 are formed.

At temperatures above 380 °C, the scheme of perchlorate decomposition can be presented as:

$$2NH_4ClO_4 = Cl_2 + 2NO + O_2 + 4H_2O$$

Additionally, traces of HCl, NOCl and NO_2 are formed.

Similar results on the composition of gas mixtures were obtained in [16]. The authors of [16] detected N_2, O_2, H_2O. NO_2, Cl_2 and ClO_2 by means of gas chromatography and mass spectrometric analysis. The presence of ClO_2 in the products was believed to have a special importance for explaining the behaviour of ammonium perchlorate under heating; ClO_2 was thought to initiate the combustion process in perchlorate. It should also be noted that ClO_2, which is a stable paramagnetic molecule, is detected with the help of electron paramagnetic resonance among the products of low-temperature thermal decomposition of ammonium perchlorate [49]. The rate of ClO_2 formation can be changed by adding heterophase catalytic additives, while the amount of ClO_2 formed during decomposition remains unchanged. The addition of homophase additives into NH_4ClO_4 crystals, for example, SO_4^{2-} ion, changes both the rate of ClO_2 formation and its yield.

Since the works cited above did not exclude the possibility of the effect of secondary processes taking place in the gas phase between the products formed during thermal decomposition, Heath and Majer [50] carried out mass spectrometric investigation of the products of thermal decomposition placing the furnace with the decomposing ammonium perchlorate near the ion source of mass spectrometer. As a result, at 111–120 °C, they discovered NH_3, HCl, Cl_2, O_2 and small amounts of nitrogen oxides among the products of decomposition; they did not detect a molecular complex NH_3HClO_4 the existence of which was assumed in previous investigations of thermal decomposition of ammonium perchlorate [51]. Analyzing the results obtained, the authors of [50] concluded that the primary products of thermal decomposition ammonium perchlorate are ammonia and perchloric acid. However, in the opinion of the authors of [50] who excluded the possibility of secondary reactions in the gas phase, the presence of $HClO_4$, NO, NO_2, O_2 and Cl_2 among the products under high vacuum indicates the occurrence of a parallel reaction proceeding in the condensed phase. Goshgarian and Walton [52] came to the same conclusion as Heath and Majer using a high-resolution mass spectrometer, Knudsen cell and ammonium perchlorate samples heated preliminarily to 200 °C and kept under high vacuum for 48 h. The shortcomings of both works were that they did not take into account: (a) the possibility of superposition of sublimation processes on thermal decomposition processes; (b) the possibility of secondary reactions in pores between the crystals of ammonium perchlorate. Rather substantial time, which is required to heat the sample to the required temperature, creates additional difficulties in separating the primary and secondary processes taking place during thermal decomposition of ammonium perchlorate.

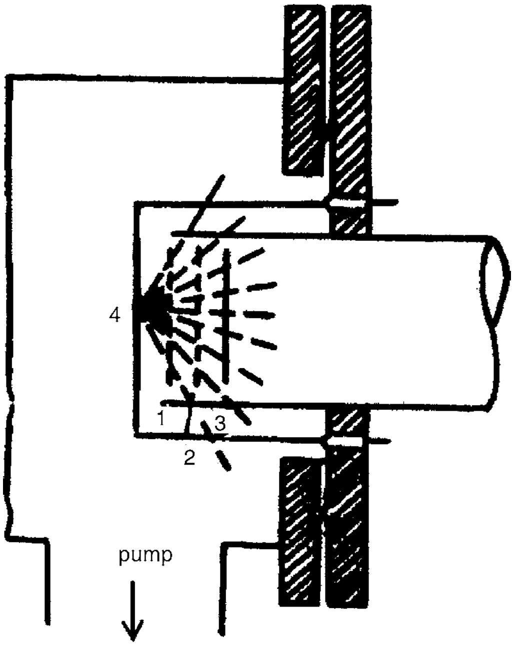


Fig. 7. The scheme of ion source according to Korobeinichev. (1–3) Nets of the ion source; (4) titanium tape.

Korobeinichev [53–55] studied thermal decomposition of ammonium perchlorate using pulse heating of small (10^{-6} g) amounts of ammonium perchlorate deposited as a thin layer on a titanium heating element, in combination with time-of-flight mass spectrometer (Fig. 7). A specific feature of the mass spectrometric procedure used in these investigation was that the distance from the ion source to the titanium tape, on which ammonium perchlorate was placed and which was directed to the wall of mass spectrometer, was only several millimeters. A special device allowed heating the tapes with crystals situated on them so that the time from the start of reaction to the start of recording was 1 ms. This allowed avoiding the loss of the main products, formed during the decomposition of ammonium perchlorate, in secondary reactions between them, as well as in their interaction with the metal parts of mass spectrometer, if the time of their consumption was shorter than the time that passed from the moment of their formation till the moment of their disappearance in mass spectrometer.

With the help of this procedure, mass spectrometric data on thermal decomposition of ammonium perchlorate at 400 °C were obtained (Table 2).

The reported mass intensity ratio 35:51:67:83:100 is close to the ratio of these masses in the mass spectrum of perchloric acid [56]. So, not only ammonium but also perchloric acid, which is the second product of ammonium perchlorate dissociation according to the proton mechanism, was detected in the mass spectra.

Table 2
Mass spectrometric data on thermal decomposition of ammonium perchlorate at 400 °C

m/*e*	Intensity
16 NH_2^+	53
17 NH_3^+ OH^+	93
35 Cl^+	13
51 ClO^+	13
67 ClO_2^+	73
83 ClO_3^+	100
100 $HClO_4^+$	53

The same conclusion was made by the authors of [57] investigating heat effect of thermal decomposition of ammonium perchlorate with the help of fast-operating pulsed adiabatic calorimeter designed by these authors [58], under the conditions excluding the possibility of secondary processes. A mixture of ammonium perchlorate with an inert diluent was placed as a thin layer (thinner than 10 mkm) on the inner part of a pack made of two sheets of titanium foil 40 μm thick. The pack was heated with a special device to a required temperature with electric current during time shorter than 10^{-2} s. Chemical reaction initiated by heating of the plates caused either cooling or heating of the foil, depending on the sign of heat effect. Measuring the accompanying changes in the resistance of titanium with the help of a fast-operating bridge, one could calculate the heat effect. For ammonium perchlorate, the heat effect coincided with the heat of dissociation of ammonium perchlorate into ammonia and perchloric acid (242–251 kJ/mol) [59].

Thermal decomposition of ammonium perchlorate under rapid heating with the help of CO_2 laser providing the possibility to obtain heat flow 39 to 222 cal/(cm^2 s) was studied in [60]. According to the data reported in that work, the primary products of pyrolysis are ammonia and $HClO_4$. The ratio of NH_3 to $HClO_4$ decreases permanently, which is an evidence that ammonia is removed more easily while the acid is accumulated in the crystal. Then, after 100–200 ms, H_2O, O_2, Cl_2, HCl, ClO_2, N_2O and N_2 appear; these compounds are the products of secondary reactions which are likely to proceed on crystal surface. After 200 ms, NH_3 and $HClO_4$ disappear gradually. These results can also be considered as a confirmation of the idea of proton mechanism of decomposition in ammonium perchlorate.

Since the earliest works on thermal decomposition of ammonium perchlorate, the nature of non-decomposed residue of the low-temperature decomposition was the subject of investigation of many scientists. At first, this residue was considered to be ammonium nitrate, which is often formed in the decomposition of ammonium salts containing oxidizing anion [47,48]. However, after the work of Bircomshaw and Newman, it turned out that the residue is ammonium perchlorate, indistinguishable by composition from the main substance. The newest investigations of the IR and UV spectra of the residue and of the initial ammonium perchlorate showed that they were completely identical.

Bircomshaw and Newman [16] investigating thermal decomposition of ammonium perchlorate discovered that below 240 °C decomposition proceeds only by 30%. Bircomshaw and Newman thought that the reason of the decomposition arrest was such a strong disordering of the lattice occurring during the reaction that this becomes an essential obstacle for electron transfer from anion to cation, which was postulated by these authors as the basis of the mechanism of thermal decomposition of ammonium perchlorate.

Schulz and Dekker [61] following the hypothesis of the proton mechanism of thermal decomposition in ammonium perchlorate explained the reaction arrest by the fact that at low-temperatures, the most active mozaic structure is burnt away. A similar point of view was reported in [51].

It was also established that the decomposition product after mechanical treatment and exposure in water vapour becomes again able to decompose thermally. Investigations carried out with the help of optical and electron microscopy showed that unreacted ammonium perchlorate contains micron-sized pores. It is assumed that the process arrest can happen due to several reasons. Among these reasons, accumulation of perchloric acid leading to the shift of the proton equilibrium to the left-hand side [62] or accumulation of ammonia due to its predominant adsorption on pre walls [63] was mentioned. A reason of the arrest of the process participated by gaseous decomposition products and ammonium perchlorate forming pore walls can also be selective removal of gaseous products from a pore [64] and accumulation of water which stabilizes thermal decomposition of ammonium perchlorate [65].

It was established that the addition of a residue formed under low-temperature decomposition of ammonium perchlorate can catalyze subsequent thermal decomposition of perchlorate subjected to thermal decomposition [66].

In spite of interest in revealing the reasons of the arrest of low-temperature decomposition of the orthorhombic modification of ammonium perchlorate and the continuing attempts to understand the mechanism of this effect, as evidenced by recent publications, the problem remains unsolved yet.

4. Topography of the process of thermal decomposition of ammonium perchlorate

4.1. The general characterization of the process topography

The early investigations into thermal decomposition of ammonium perchlorate showed that clearly exhibited localization and auto-localization of the process take place. In other words, thermal decomposition of ammonium perchlorate starts not over the whole crystal volume and not on the whole surface but in some sites near the outer and inner surfaces of a crystal. Having started at this active centres of a crystal, the reaction propagates near the place where it has already started, that is, the formation and growth of reaction nuclei occur. Reaction nuclei grow, merge each other forming the reaction region; its propagation is well seen with a microscope (Fig. 8) [16].

More detailed investigations [39,40,44] showed that localization of the nuclei formation process is connected with the screw and edge dislocations emerging from the crystal surface, and especially with their crossover points inside the crystal. It was established that there is a connection between the shape of nuclei, the geometry of their position, on the one hand,

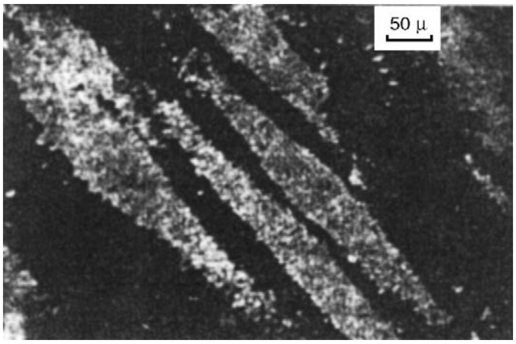


Fig. 8. Shape of decomposition centres in NH_4ClO_4 crystal.

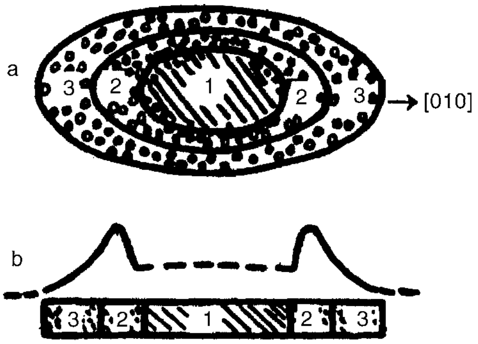


Fig. 9. Nucleus structure diagram for thermal decomposition of ammonium perchlorate (a) and mechanical strain distribution (b).

and crystal chemical features of the crystal structure, prevailing directions of dislocation glide planes.

Reaction nuclei are usually formed not at the very surface but at some distance from it, inside the crystal at a depth of 20–30 μm [42,44]. With large magnification (×1000), the nuclei are observed to be not continuous; they consist of separate seeds about one micron in size. The shapes of nuclei are different at different faces of the crystal and depend on temperature at which thermal decomposition is carried out. Below the phase transition point, the nuclei at the rhombic face of the crystal are cigar-shaped, while at the prismatic face they are round. Above the phase transition point, the nuclei are spherical. The growth of nuclei proceeds due to the formation of new seeds near the boundary of a nucleus. Photo-filming of the crystal during decomposition helped to establish that the nuclei are in the movement condition along the diagonal of the rhomb at a velocity of 7–10 μm per minute (for $T = 230\,^\circ\mathrm{C}$). With even larger magnification achieved by using the scanning electron microscope, it was shown that the nuclei are initially not round as it was suggested by studying them with electron microscope; they have a clearly exhibited shape corresponding to the crystal chemical features of a given face [67]. For example, on the rhombic face, the nuclei have a shape of rhomb, while on the prismatic face, they are rectangular. During decomposition, the nuclei reach the size of several microns and stop growing; their shape changes; they gradually become round.

The positions of nuclei with respect to each other are different for different faces. For the (1 1 0) face during thermal decomposition for 15 min at 205 °C, separate nuclei are located mainly along the directions corresponding to the directions of dislocation glide planes; for the (0 0 1) face, swarm-like formation of nuclei occurs. The "swarm" gets stretched along the [0 1 0] direction or, less frequently, along the [5 1 0].

The topography of processes taking place during thermal decomposition of ammonium perchlorate was investigated in more detail by Raevsky [44]. He concluded that a united topographic mechanism of thermal decomposition exists; this is a mechanism in which the active centres where the reaction starts are dislocations. According to Raevsky, the shape of reaction nuclei is a consequence of anisotropy in the mechanical properties of the lattice of ammonium perchlorate. These properties define the features of movement, multiplication and distribution of dislocations in the crystal.

Thermal decomposition of ammonium perchlorate starts at dislocations. This is evidenced by the correspondence between the geometry of etch pit positions and the sites from which the formation of nuclei starts during thermal decomposition of ammonium perchlorate. According to Raevsky, each nucleus formed during thermal decomposition of ammonium perchlorate is composed of three zones (Fig. 9): the region of a porous core formed by junction of seeds (1); the region of chemical reaction (2); and the periphery of he growing nucleus (3). Chemical reaction of thermal decomposition proceeds in the region (2) starting mainly on dislocations. Since the gaseous products evolved during the decomposition into the sub-surface pores can raise pressure up to 20 atm, the crystal of ammonium perchlorate gets subjected to mechanical strain and deformation in this zone. A consequence is multiplication of the existing dislocations and the formation of new ones along the periphery of the growing nucleus (region (3)).

The formation of new dislocations at the boundary between the nucleus and non-reacted ammonium perchlorate was demonstrated by Raevsky in direct experiments; he showed that the density of etch pits characterizing the dislocations wedging out on the surface is much higher near the boundary of a nucleus than in other parts of the crystal.

Raevsky showed that the crystals containing no dislocations, so-called whisker crystals are more stable than usual crystals. In addition, unlike for usual crystals, thermal decomposition starts in the whisker crystals at the maximal rate and is not accompanied by auto-localization of the process.

As far as the seeds comprising the nucleus are concerned, Raevsky succeeded in observing two kinds of them. The seeds of the first kind, which he called centres of partial decomposition, are formed mainly in the defect regions of a crystal, preferably in the sites where dislocations are accumulated. These centres are subsurface micro-cavities in the crystal. They grow until they reach a size of several microns in diameter, after which they stop to grow. It is these centres on which the evolution of a substantial amount of gaseous reaction products occurs; a crystal is deformed around them.

Unlike these centres of partial decomposition formed during thermal decomposition of the cubic high-temperature modification of ammonium perchlorate, Raevsky discovered also other centres and called them centres of complete decomposition. The centres of complete decomposition are filled with liquid and do not stop growing while the process runs. Completeness of total (overall) thermal decomposition depends on the kinds of centres on which it proceeds. If the centres are of the first kind, decomposition of ammonium perchlorate proceeds only by 30%; the product of reaction is porous perchlorate identical in its chemical composition to the initial compound. If decomposition occurs due to the centres of complete decomposition, thermal decomposition proceeds till completeness.

Since ammonium perchlorate is extremely sensitive to irradiation, Galwey and co-authors [68,69] carried out direct electron microscopic observation of the ammonium perchlorate surface using a special procedure which allowed them to exclude error connected with the use of electron beam for this purpose. In general, the results of these observations coincide with the earlier data obtained by Herley and Raevsky [40,44]; flat pits appear during the induction period; they do not overlap each other; while the process develops further on, some pits merge together; they also develop into the crystal depth along dislocation lines. The final result of such a development is a porous mass composed of ammonium perchlorate. The pore diameter according to the data obtained by Galwey is the same as that obtained by Raevsky: 1–2 μm; broadening of pores was observed at the sites of crossover points of the linear defects, as predicted by Raevsky [40].

Galwey observed the indices of the participation of the liquid phase in the development of centres which by description resemble the centres of complete decomposition; unlike Raevsky, Galwey thinks that the liquid phase is not an eutectic mixture of ammonium perchlorate with the products of its decomposition but nitrile perchlorate NO_2ClO_4, which he considers to be formed as an intermediate product resulting from oxidation of the ammonium ion with the oxygen-containing compounds of chlorine.

The results of similar investigations were described in [70]. The authors used nanosecond and picosecond laser irradiation of the surface of ammonium perchlorate and X-ray photoelectron spectroscopy to show that the primary decomposition product is ammonium chlorate. At temperature close to that on the surface of perchlorate incorporated into mix propellant, decomposition is localized on the defects of surface, cracks and so on, which then appear as a result of polymorphous transition at 240 °C during thermal decomposition and can be clearly detected with the help of optical, electron scanning and atomic force microscopy.

Relying on the data obtained, the authors proposed a model of decomposition based on initiation of the reaction at the sites of dislocations emerging out and on the development of reaction front due to the formation of new dislocations, similarly to the model proposed by A.V. Raevsky.

4.2. Anisotropy of the rate of nuclei formation and growth during low-temperature (up to 240 °C) thermal decomposition of ammonium perchlorate

In order to describe the kinetics of thermal decomposition of ammonium perchlorate before and after the polymorphous transition, different equations based on different models of its thermal decomposition were tested, starting from the first-order equation and ending with Prout–Tompkins and Avramy–Erofeev equations.

However, remembering that in the chemistry of heterogeneous processes with variable degree of heterogeneity, the very fact of coincidence of the experimental kinetic curve with the curve describing the process in the framework of the proposed theoretical model is yet not a proof of the process mechanism, we will not consider these works in detail.

The viewpoint described in [71] is likely to be close to this one, stating that the application of one of the topokinetic equations to complicated multistage processes at different regions of the kinetic curve has no sense.

This may be illustrated by the dependence of activation energy of ammonium perchlorate versus transformation degree plotted according to the data of different authors who applied different kinetic models to describe thermal decomposition of ammonium perchlorate using various methods [72].

One can see that activation energy values can be different at different stages of the process, and different values can be obtained for activation energies using different models for the kinetic analysis.

Since we came to this conclusion at the very beginning of our investigations, it was decided to use the method of direct measurement of the rate of formation and growth of reaction nuclei to study the dynamics of the process. This method allows determining not the overall reaction rate but specific rate of the process. If this rate is unknown, it is very difficult to carry out a correct kinetic analysis of the heterogeneous processes.

It was shown in [44] that the rates of nucleus growth along and across the direction [0 1 0] of ammonium perchlorate crystal differ about 10 times.

Considering the edge of a nucleus as a site where the heterogeneous chemical reaction proceeds at a given moment, a test was carried out to check correspondence between the total rate of the process, determined with an automated thermogravimetric set-up, and the rate of reaction zone propagation determined by means of microscopy [73–75].

Specific rate of reaction of low-temperature thermal decomposition of ammonium perchlorate was determined using two methods:

(a) on the basis of Rozovsky equation [76] proposed for anisotropic model;
(b) on the basis of the equation of contracted parallelepiped [77].

The values obtained were compared with the specific rate measured from reaction front propagation on the basis of microscopic observations. Unlike dehydration of magnesium sulphate heptahydrate, a process in which the character of reaction zone development is similar to the low-temperature thermal decomposition of ammonium perchlorate, and which was thus used as a reference, specific rate values determined on the basis of microscopic observations do not coincide with the specific rate values obtained on the basis of kinetic analysis. In the case of analysis according to Rozovsky, specific rate values are 1.2–1.7

Table 3
The influence of $Sr(ClO_4)_2$ additive on the rate of formation of the reaction nuclei ($dN/d\tau$), their maximal number per unit surface area (n_{max}), longitudinal (v_1) and latitudinal (v_2) rates of nuclei growth during thermolysis of NH_4ClO_4 at 230 °C

Sample	$dN/d\tau$ (1/mm^2 min)		n_{max} (1/mm^2)		v_1 (μm/min)		v_2 (μm/min)	
NH_4ClO_4 (pure)	5.9	±0.69 ±0.37	23	±4 ±2	20	±2 ±1	3.3	±0.2 ±0.1
NH_4ClO_4 + 0.032 mol% $Sr(ClO_4)_2$	10.9	±1.09 ±0.59	44	±9 ±5	20	±2 ±1	3.4	±0.2 ±0.1

Note: Confidence intervals are shown to the right of the rate values; the upper number is the confidence interval for reliability 95%, lower for 70%.

times lower than the rate determined from the direct microscopic observations; for the kinetic analysis on the basis of the equation of compressible parallelepiped, the difference could reach 1.6–3.4 times.

This discrepancy was considered as an indirect indication that the process of thermal decomposition is not localized on the flat boundary between non-reacted part of a crystal and a nucleus but proceeds within some diffuse layer.

The effect of homophase cation additives, incorporated into the lattice of ammonium perchlorate, on the rate of formation of reaction nuclei, their maximal number per unit surface, and the rate of nucleus growth along the principal axis of ellipse and perpendicular to it were studied in [74]. It was shown (Table 3) that the homophase heterovalent additives (divalent cations) cause a decrease in the induction period, an increase in nuclei formation and maximal number of nuclei per unit surface. At the same time, the additives do not affect the rate of nucleus growth both in lengthwise and crosswise directions.

The effect of water vapour was investigated in [73]. It turned out that the rate of nuclei formation is not affected by water vapour concentration. The nucleus growth rate is affected by the changes in water vapour concentration; however, the character of anisotropy of the nucleus development remains unaffected. Synchronous changes occur in the growth rate of nuclei both in the direction parallel to the principal axis of symmetry and perpendicular to it. Changes in nucleus growth rate occur in phase with the changes in the total rate of thermal decomposition process determined gravimetrically, and resemble Topley–Smith dependence known from experiments on dehydration of crystal hydrates.

Dependencies of the rate of nucleus formation, maximal number of nuclei and the induction period on partial pressure of ammonia and perchloric acid are shown in Fig. 10. One can see that an increase in the partial pressure of ammonia causes an increase in the induction period, a decrease in the rate of nuclei formation and in their number. An increase in perchloric acid pressure leads to an increase in the nuclei formation rate.

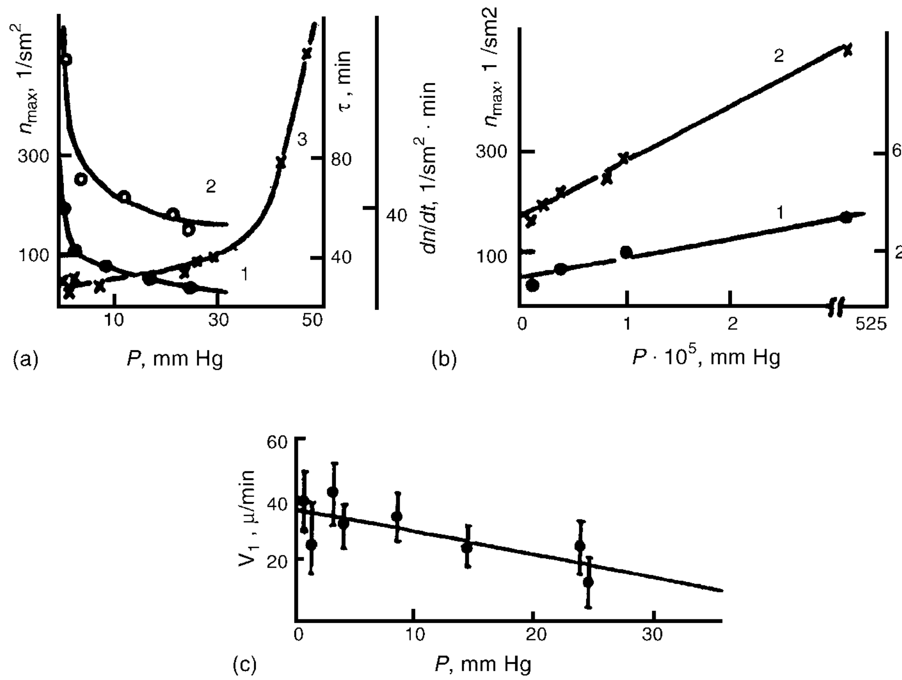


Fig. 10. Dependence of the rate of nuclei formation $dN/d\tau$ (1), n max (2) and induction period τ (3) for thermolysis of NH_4ClO_4 on partial pressure of ammonia (a) and equilibrium pressure of perchloric acid (b) at 230 °C. The influence of partial pressure of ammonia on the rate of reaction nuclei growth for thermolysis of NH_4ClO_4 (c).

Partial pressure of ammonia affects not only the formation rate but also the nuclei growth rate, which decreases as partial pressure of NH_3 increases (Fig. 10c).

5. Mechanism of thermal decomposition of ammonium perchlorate

It has already been mentioned above that different points of view on thermal decomposition of ammonium perchlorate existed.

According to one of them, the decomposition is a consequence of electron transfer from anion to cation, that is, the decomposition of ammonium perchlorate proceeds similarly to the case of thermal decomposition of azides, fulminates and other similar compounds.

One of the first versions of such a mechanism of that proposed by Bicromshaw and Newman [16]. According to Bircomshaw, at first electron transfer from perchlorate ion to ammonium ion occurs:

$$ClO_4^- + NH_4^+ \rightarrow ClO_4^0 + NH_4^0$$

Since electron transfer occurs locally, the probability of its realization is the higher, the smaller is the distance between the ions. Because of this, an efficient acceptor of electrons is considered to be not any ammonium ions but only those located in interstices. Another item is a postulate that the electron transfer occurs not in volume but on the surface, where the conditions for its realization are better due to the presence of local surface levels of Tamm or Shockley type.

After having captured an electron, the ammonium radical decomposes into ammonia and hydrogen atom:

$$NH_4^0 \rightarrow NH_3 + H$$

Hydrogen migrates over the lattice. Electron migrates exactly in the same manner over the anion sublattice:

$$ClO_4^0 + ClO_4^- = ClO_4^- + ClO_4^0$$

As a result of the interaction between ClO_4 radical and H, $HClO_4$ is formed. It may continue interacting with H:

$$HClO_4 + H \rightarrow H_2O + ClO_3$$

The ClO_3 radical is a trap for electrons. Having trapped an electron, it is transformed into ClO_3^- ion.

After that, chlorite ion and ClO_4 radical can decompose, interact with NH_4^+ ions, etc. As a result of interaction, secondary products are formed; among them, the major ones are chlorine, nitrogen hemioxide and water.

While Bircomshaw and Newman speak of a local electron transfer in their work, Raevsky and Manelis [42] consider electron transition within the energy-band theory, that is, as the transition of an electron from the valence band into conduction band.

Since ammonium perchlorate is a typical dielectric with the forbidden gap width about 5.6 eV, while kT value for decomposition temperature (450 °C) is about 0.2, it is evident that the probability of such a direct electron transfer is low.

Since thermal but not optical excitation is considered, in order to obtain a reasonable value for the activation energy close to the value determined experimentally, some advocates of the electron mechanism [51] applied the known Mott equation [78]. In this case, activation energy is determined to be 146 kJ/mol, which is close to the experimentally measured activation energy of thermal decomposition of ammonium perchlorate (134 kJ/mol); however, one cannot now speak of a direct band-to-band transition.

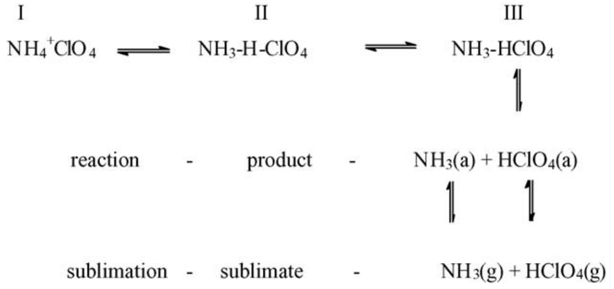
Understanding low probability of the band-to-band transition in a dielectric with such a broad width of the forbidden gap, instead of the band-to-band transition, Galwey and Jacobs [51] postulated the formation of molecular complex $[NH_4{\cdot}ClO_4]$ due to local electron transfer from anion to cation; the complex is then transformed into the final products. These authors considered the formation of perchlorate radical to be the limiting stage of nucleus formation process, while the decomposition of the molecular complex was considered to be the limiting stage nucleus growth. At first, water is formed during decomposition, and then chlorine dioxide and nitrogen. The mechanism of decomposition of ammonium perchlorate, based on electron transfer, had been discussed earnestly in literature for rather long time. Usual arguments in favour of the electron mechanism were sensitivity of thermal decomposition of ammonium perchlorate to irradiation and strong influence of the oxides, being typical catalysts of oxidation–reduction, on the reaction rate. Below we will show that these facts can be explained without enlisting the mechanism of electron transfer.

An argument against the electron mechanism was the fact that ammonium perchlorate is a typical dielectric; at low-temperature of thermal decomposition, the process cannot be sustained by electron transfer because of its low probability. Then, none of the attempts to discover the molecular complex assumed by Galwey and Jacobs was a success. On the contrary, primary products detected in the experiments of different researchers were ammonia and perchloric acid. This allowed assuming that the primary stage of the process of thermal decomposition of ammonium perchlorate is proton transfer.

5.1. Mechanism of thermal decomposition of ammonium perchlorate, based on the proton transfer from cation to anion

Arguments in favour of the proton mechanism were coincidence between the activation energies of thermal decomposition and sublimation [79], identical composition of the products of decomposition [80] and sublimation [81], inhibition of the reaction in ammonia vapour [80] and acceleration in the vapour of perchloric acid [74,75], the influence of dopants [82] and other factors that accompany thermal decomposition [83,84]. The inhibiting action of water vapour, which is known to stabilize perchloric acid, can also be considered as an indirect confirmation of competence of the proton mechanism.

A scheme of thermal decomposition of ammonium perchlorate proposed by Jackobs can be presented as a version of proton mechanism [79]:



State (I) corresponds to the pair of ions in perchlorate ammonium lattice. Decomposition or sublimation start with proton transfer from ammonium ion to perchlorate ion. At first, molecular complex (II) is formed; then it decomposes into ammonia and perchloric acid. The molecules of ammonia and perchloric acid either react in the adsorbed layer on the surface of perchlorate or desorb and sublime interacting in the gas phase.

At low-temperature (<350 °C), the reaction of the surface proceeds more rapidly than sublimation. Above 350 °C, inverse relation of these processes is observed.

For the reaction proceeding in the adsorbed layer, it is assumed that perchloric acid is desorbed more rapidly than ammonia; oxidation of ammonia becomes incomplete; the surface gets saturated with ammonia, which is the reason of cessation of the reaction and incomplete transformation of perchlorate.

However, the available experimental data showed that the scheme proposed by Jacobs is still simplified in comparison with the reality. For instance, this scheme cannot explain the fact that the addition of ammonia has an effect only at high pressure and stops acting at low pressure, in spite of the fact that its partial pressure is several times higher than the equilibrium one. In course of thermal decomposition, not ammonia but perchloric acid is accumulated in perchlorate [80,81]. From Jacob's viewpoint, the reason of localization and auto-localization of the process during thermal decomposition of ammonium perchlorate remains unclear.

These considerations made it necessary to develop the notions about the mechanism of proton transfer further on taking into account the physicochemical features of ammonium perchlorate, more detailed view of the chemical reactions that may occur, and topography of thermal decomposition of ammonium perchlorate.

In the previous sections, we have already stressed the proton character of conductivity in ammonium perchlorate, the presence of dislocation structure in the crystals of ammonium perchlorate, and a close connected of this structure with the centres from which thermal decomposition starts. These data should be supplemented with the data on accumulation and diffusion of perchloric acid in ammonium perchlorate crystals during thermal decomposition, obtained by Koroban [85,86], the data on the strong catalytic action of the ammonium perchlorate crystal on the decomposition of perchloric acid, and important role of chlorine oxides formed during decomposition, during oxidation of ammonia and ammonium ions. The important role which may be played by ClO_3^- ions present in ammonium perchlorate as admixture was demonstrated in [28,87]. Altogether, this allowed introducing essential corrections into the proposed model of the mechanism of thermal decomposition of ammonium perchlorate, and distinguishing the conditions under which thermal decomposition of ammonium perchlorate occurs and sublimation takes place.

The first thing to be taken into account when considering the mechanism with proton transfer is rather clearly exhibited localization and auto-localization of the process. In other words, thermal decomposition of ammonium perchlorate proceeds through the formation and growth of reaction nuclei. Therefore, the scheme of thermal decomposition mechanism should first of all take into account non-uniformity of different sites in ammonium perchlorate crystal with respect to chemical activity, and also it should establish the forms of the feedback due to which nuclei growth occurs.

At present, it may be considered to be established that the process of low-temperature thermal decomposition starts with the formation of nuclei. The nuclei, which are cavities filled with the gaseous products of decomposition of ammonium perchlorate (centres of partial decomposition, according to Raevsky [44]) or with liquid (centres of complete decomposition) are formed as a result of proton transfer and capture by a trap. The sites where these processes occur can be linear defects of the ammonium perchlorate lattice, for example dislocations. The most important factor for understanding the process of thermal decomposition of ammonium perchlorate is the presence of proton trap, which is ClO_3^- ion:

$$NH_4^+ + ClO_4^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_3 + HClO_4$$

$$HClO_4 + ClO_3^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} HClO_3 + ClO_4^-$$

The formed $HClO_3$ is unstable and decomposes. Its decomposition products include ClO_2, which was detected as an intermediate product during thermal decomposition of ammonium perchlorate as described in the works of different researchers, including ours.

Chlorine dioxide can interact with ammonium perchlorate [86,87]. It was demonstrated that the interaction proceeds mainly as a result of the reaction with NH_4^- ion. In addition, ClO_2 can enter chemical interaction with ammonia which is formed during the dissociation of ammonium perchlorate:

$$ClO_2 + NH_4^+ \rightarrow\ H_2O\ +\ N_2O\ +\ HCl\ +\ R_1$$

$$ClO_2 + NH_3 \rightarrow\ N_2 + H_2O\ +\ Cl_2 + R_2,$$

where R_1 and R_2 are the products of ammonia oxidation, which can be hydrazonium or hydroxylammonium ions, NO_2ClO_2 and so on.

As a result of these processes, the nucleus grows reaching the size of 2–3 μm. Then it stops growing. Since a pressure of the order to 20 atm arises inside the cavity [42], the crystal around the nucleus gets deformed. The fact that deformation of lattice actually occurs can be observed by examining the region of ammonium perchlorate crystal adjacent to the nucleus with the help of polarized light. A consequence of deformation can

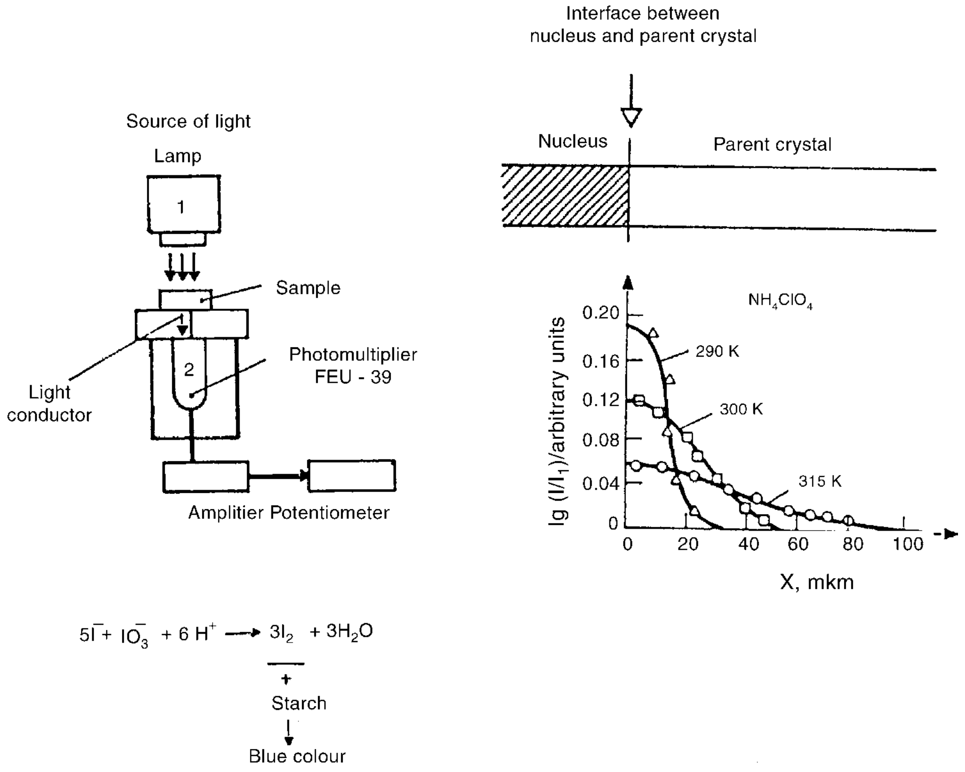


Fig. 11. Injection of the protons in parent crystal from nuclei.

be the formation of new dislocations. In addition, the accumulation of perchloric acid in the cavity of the nucleus may lead to proton migration into the region neighbouring with the nucleus, where a linear defect exists and ClO_3^- ion is available, which is an efficient renewable trap for protons [87]. The fact that perchloric acid can migrate from the region of a crystal where the reaction has already passed into the regions of unreacted ammonium perchlorate could be concluded from the works of Koroban cited above [85,86]; later on, direct experimental evidence was obtained that the acid actually drifts from the region of the nucleus into the adjacent regions of the crystal [88,89]. As already above mentioned migration of protons from the sites where perchloric acid is accumulated is one of reasons of auto-localization of low-temperature thermal decomposition of ammonium perchlorate. To demonstrate this special experiments were done. The scheme of experimental set up and main results are shown in Fig. 11. A partly decomposed crystal of perchlorate was placed in a sample holder of the microscope. The surface of the crystal was treated by an indicator (iodide-iodate solution mixed with starch) which changed colour in the presence of excess protons. The crystal was illuminated from the lamp. The light conductor placed under the crystal could be moved by micrometer screw. Moving the light conductor along the crystal from the nucleus to the parent crystal and measuring light absorption by photomultiplier connected via amplifier with potentiometer, it was possible to follow the change the protons concentration as a function of the distance from the nucleus (Fig. 11). It was assumed [90] that chlorine dioxide can also migrate in a neighbouring pore; however, this assumption was not confirmed by any theoretical or experimental data.

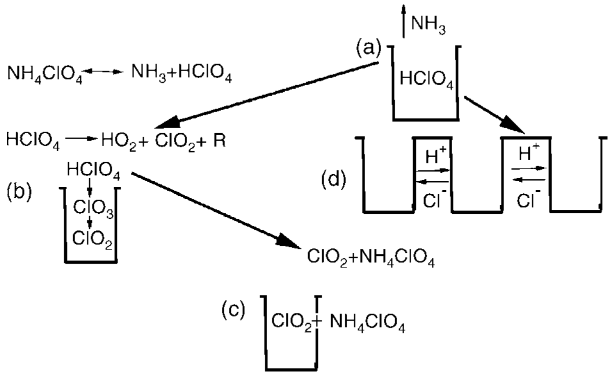


Fig. 12. Diagram of formation and growth of nuclei during thermal decomposition of ammonium perchlorate.

An essential feature of the process of thermal decomposition of ammonium perchlorate is that the process occurs not at the very surface but in pores beneath it at a distance of about several microns. This is a difference of thermal decomposition of ammonium perchlorate from its sublimation. This entails the necessity to understand the important role played by secondary processes in the arrangement of the feedback.

The general scheme of thermal decomposition of ammonium perchlorate at low-temperature is shown in Fig. 12 [64].

(a) At first, a proton passing from the ammonium ion to perchlorate ion becomes mobile. In agreement with the mechanism of proton conductivity, it starts migrating over the ammonium perchlorate lattice until it is captured with a proton trap. Proton trap can be ClO_4^- ion located in a special defectbearing site of the lattice. An efficient proton trap can be ClO_3^- ion [32,91,92]. The course in general chemistry suggests that the affinity of chlorate ion to proton is higher than that of perchlorate ion. This dependence existing for solutions is likely to be conserved for crystals. Chlorate ion is always present in ammonium perchlorate as a technological impurity [93].

(b) The formed perchloric and chloric acids can decompose. Chloric acid decomposes more rapidly since it is less stable. Chlorine oxides formed in the decomposition of chloric acid catalyze the decomposition of perchloric acid. ClO_2 which is formed during decomposition of $HClO_4$ can interact with ammonium ions located in the perchlorate lattice, and with ammonia formed during its dissociation. The essence of chemical processes occurring at this stage and the possibility of the influence of the cage effect on these processes allow concluding that the sites favourable for the chemical processes should be the regions of a crystal in which a free volume is present initially. As we assumed in [64] and Raevsky showed experimentally [44], these sites may be dislocation crossover points and the boundaries of blocks formed by them.

The accumulation of perchloric acid in a pore can proceed due to different reasons. This may happen as a result of separation of ammonia and perchloric acid because of difference in the rates of Knudsen diffusion of these gases. The rate of Knudsen diffusion is known to be proportional to the square root of molecular mass. Because of this, the rate of ammonia outflow from a pore should be about 2.5 times higher than that of perchloric acid.

As the acid is accumulated, some protons get drawn into the neighbouring defect sites in the lattice and “infect” them turning these centres from the potential into acting ones.

The accumulation of gaseous products in a pore leads to an increase in pressure, deformation of the crystal near the pore, subsequent formation of dislocations. This is how new potential centres appear which may afterwards (after proton migration into them) turn into nuclei; then the growth of the nucleus occurs.

(c) At the same time, during the interaction between chlorine anions with ammonia and the walls of unreacted ammonium perchlorate, an increase in pore diameter occurs; water is accumulated as the reaction product. Both these processes can be reasons for reaction arrest at a definite stage of the development of a nucleus. An increase in pore diameter can cause cessation of Knudsen diffusion, as soon as the size of a pore becomes larger than the free path of molecules. Accumulation of water, which is a stabilizer of thermal decomposition of both perchloric and chloric acids, should cause a decrease in the rate of secondary chemical processes in a pore. As a result, chemical reactions in the pore stop. Judging from the data reported by Raevsky, this happens when the pore size reaches 2–3 mkm.

The general scheme of feedback routes arising in this system, taking into account the stages mentioned above, is shown in Fig. 13 taken from [94,95]. One can clearly see in this scheme that thermal decomposition of ammonium perchlorate is a complicated process depending on diverse factors. Actually, the scheme of feedback connections of thermal decomposition of ammonium perchlorate is even more complicated because it should be taken into account that the nuclei can be of two types: the centres of partial decomposition and the centres of complete decomposition [44]. Since the growth of the former stops when a definite critical size is achieved, while the latter grow without stopping, they are likely to differ from each other in the nature of chemical processes involved in their development. Different intermediate products may be also expected (for example NO_2ClO_4) to be formed in secondary reactions occurring in these centres [96,97].

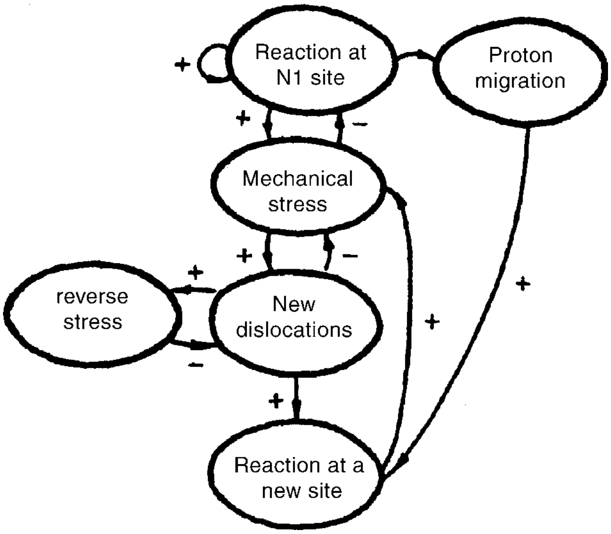


Fig. 13. Feedback contour proposed for thermal decomposition of ammonium perchlorate.

It follows from the above considerations that, in spite of essential advances in understanding the mechanism of low-temperature thermal decomposition of ammonium perchlorate, the problem remains not fully solved yet and requires additional investigations.

5.2. *The mechanism of high-temperature (>350 °C) thermal decomposition of ammonium perchlorate*

Bircomshaw and Newman [16] were among the first researchers who investigated thermal decomposition of ammonium perchlorate within this temperature range. Having determined activation energy of thermal decomposition of ammonium perchlorate, which was of the same order as that for thermal decomposition of potassium perchlorate (about 293 kJ/mol), they concluded that ammonium perchlorate decomposes under these conditions similarly to potassium perchlorate, and the process runs through the primary stage of rupture of the chemical bond between chlorine and oxygen.

Since high-temperature thermal decomposition of ammonium perchlorate is technologically important (within this temperature range ammonium perchlorate usually decomposes in the combustion zone of composite propellants), the hypothesis was tested in the works of numerous researchers in this area, and was not confirmed.

It was shown that the high-temperature thermal decomposition is dissociation of ammonium perchlorate into ammonia and perchloric acid, i.e. starts from the same elementary stage of proton transfer from ammonium ion to perchlorate ion. The difference is that the process starts not in a subsurface site but on the surface; secondary chemical reactions between the products of thermal decomposition of perchloric acid and ammonia occur either on the surface of ammonium perchlorate or in the gas phase above the surface. If the conditions allow avoiding secondary reactions, for example when the process is carried out in vacuum, sublimation of ammonium perchlorate occurs [60,98–100].

The mechanism of secondary reactions above the surface of ammonium perchlorate changes while temperature and pressure are changed. For example, with temperature rise, the NO to NO_2 ratio changes due to the decomposition of NO_2 at high temperature and due to the possibility of direct interaction between ammonia and perchloric acid [2].

The fact that the activation energy of thermal decomposition of ammonium perchlorate turned out to be smaller than the heat of sublimation (88 and 125 kJ/mol, respectively) had been the subject of discussion for some time. This contradiction can be overcome if we accept that quasi-equilibrium is established on the surface of ammonium perchlorate between the perchlorate and dissociation products, while the limiting stage is desorption of dissociation products: ammonia and perchloric acid. In this case, it may be shown that the activation energy is equal to 1/2 of the heat of sublimation. Another version of explanation of small activation energy of the high-temperature thermal decomposition of ammonium perchlorate can be consideration of Volmer model of stepwise evaporation [59]. According to this model, the transition of molecules from crystal into the gas phase in a single step is of low probability. More realistic is rupture of bonds made in turn; the number of bonds decreases gradually during this process. Physically, this looks like a transition from the most bound state at a step to a less bound state (for example, on a smooth surface).

In [101], an attempt was made to calculate, by means of molecular dynamics, the possible intermediate states through which the crystal of ammonium perchlorate passes during its thermal decomposition.

As a result of calculations, the structure of molecular complex was proposed, which is a precursor of the stage of removal of ammonia and perchloric acid molecules from the crystal.

In spite of recognition of the proton mechanism by the major part of researchers, works appear from time to time the authors of which try to revive the idea of participation of electron transfer in the initial stages of thermal decomposition of ammonium perchlorate [102,103]. The main arguments presented usually in favour of this idea are the features of catalysis with additives, the role of interparticle contacts between the catalyst and ammonium perchlorate, detection of NH_4^+ ions and NH_4 radicals with the help of high-resolution mass spectrometry, and other facts which from the point of view of above cited author can hardly be explained using the proton mechanism.

5.3. General remarks about the mechanism of thermal decomposition of ammonium perchlorate

Now one may say: it is quite well established that the process of thermal decomposition both at low and high temperatures has a common start, which is proton transfer from the cation NH_4^+ to the anion ClO_4^-. The difference between the decomposition of low-temperature orthorhombic modification and the high-temperature cubic one arises when the secondary processes occur. These secondary processes during the decomposition of orthorhombic and cubic modifications differ both in the character of chemical processes and in the topography of their course.

The decomposition of the low-temperature orthorhombic modification proceeds in the pores beneath the surface in the sites where the secondary products of dissociation can be accumulated, and in the sites where the conditions for regeneration of active centres exist, either due to pressure of the gases formed in a pore or due to decomposition of perchloric acid and interaction of the products of its decomposition with ammonia. It is the conditions for secondary processes, providing the feedback between the accumulation of reaction products and the formation of new active centres, that act as the main reasons of decomposition of the orthorhombic modification. Because of this, the action of additives, irradiation and other factors affecting the reactivity of the initial crystal is mainly restricted to the initial period of reaction, its initiation.

The situation changes when higher temperature is employed, and when we come across decomposition of the cubic modification. In this case, the major role is played by the processes taking place on the surface of the crystal: adsorption and desorption of ammonia and chloric acid; so, the role of the primary processes connected with proton transfer increases. A result is larger effect of the introduction of dopants, which change the concentration of protons in the lattice during the decomposition of the cubic modification, and stronger effect of ammonia. The hypothesis formulated by Kaidymov [104,105] is likely to be worth mentioning; it says that the catalytic activity of the orthorhombic modification with respect to the decomposition of perchloric acid, an important stage through which thermal decomposition proceeds, is much higher than that of the cubic modification.

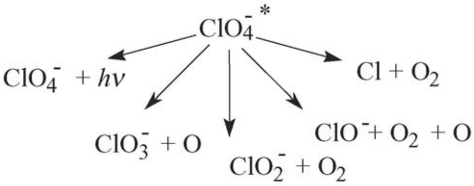
So, in spite of advances in investigating the mechanism of thermal decomposition of ammonium perchlorate, many aspects remain unclear and wait for researchers.

6. The effect of irradiation on thermal decomposition of ammonium perchlorate

The use of ammonium perchlorate as a component of solid propellants was one of the reasons of increased attention to radiation chemical processes taking place during its irradiation, and changes in the reactivity of ammonium perchlorate under irradiation.

The mechanism of processes occurring during the radiolysis of ammonium perchlorate was investigated in a number of works. According to their results, excitation of ions occurs under the action of irradiation both in the cation and in the anion sublattices.

Possible processes in perchlorate ion under excitation are the following [106,107]:



In addition to excitation, ionizing radiation can cause ionization of ClO_4^- ion:

$$ClO_4^- \rightarrow ClO_4^0 + e$$

and formation of ClO_4^0, which can either recombine with electron or further decompose:

$$ClO_4^0 \rightarrow ClO_3^0 + O$$

Ionization and excitation of the cation leads to the formation of NH_3^+ radicals:

$$(NH_4^+)^\bullet \rightarrow NH_3^+ + H$$

Some of the products of radiolysis, such as ClO_3^-, ClO^-, ClO_2 and NH_3^+, were detected in the irradiated ammonium perchlorate by means of chemical analysis [107], electron paramagnetic resonance [108–111], thermoluminescence [112]. Of special interest is the formation of NH_3^+ radical during radiolysis. This radical is rather stable and starts perishing at a temperature of 300–370 K.

The concentration of ClO_3 radicals is about two orders of magnitude lower than NH_3^+, because recombination of the former occurs more rapidly. Finally, in our opinion, one of the most important results of radiolysis is the accumulation of ClO_3^- ions in the crystals of ammonium perchlorate; these ions are one of the most efficient traps for protons regenerating during the process. It was shown that the accumulation of ClO_3^- ions takes place during irradiation of ammonium perchlorate, either pressed in tablets with KCl/KBr or pure. This increase in the concentration of chlorate ions reaches maximum at the dose of 0.5 MGy, then the concentration decreases [113].

Another result of radiolysis which is important for subsequent thermal decomposition was considered [114] to be the formation of additional number of dislocations in crystals, starting from the adsorbed dose of the order to 10^5 rad and higher.

Some of these chemical and physical results of radiolysis can lead and do lead to the acceleration of thermal decomposition process.

One of the first investigations of the effect of preliminary irradiation on the thermal stability of ammonium perchlorate was the works of Freeman and Anderson [115,116]. These authors showed that the curves of differential thermal analysis and thermogravimetric curves of perchlorate ammonium irradiated with X-rays and with gamma radiation substantially differ from the corresponding curves for non-irradiated ammonium perchlorate.

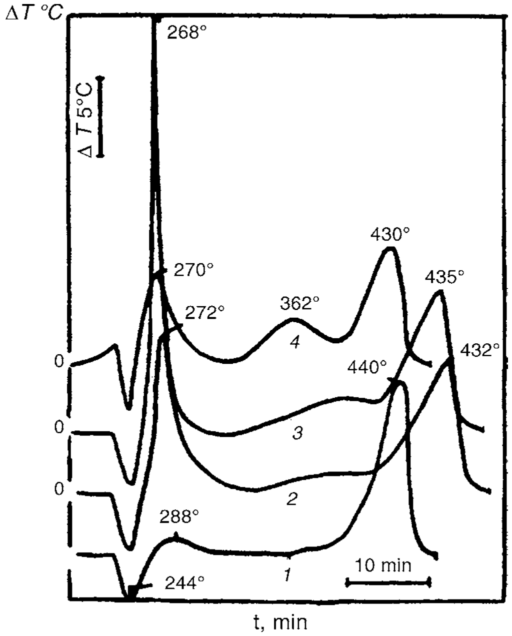


Fig. 14. The DTA curves for ammonium perchlorate after irradiation with X-rays. Heating in the air at a rate of 5°/min. Dose rate 1.4×10^{-3} eV molec.$^{-1}$ h^{-1}. Curve: (1) dose 0.27 eV/molec.; (2) dose 3.5×10^{-4} eV/molec.; (3) 5.4×10^{-5} eV/molec; (4) non-irradiated sample.

One can see in Fig. 14 that for an increase in the dose of X-ray radiation absorbed by perchlorate from 5.4×10^{-5} to 3.5×10^{-4} eV/molecule, thermal decomposition proceeds with a noticeable rate even below the phase transition point and especially immediately after it. In addition, irradiation causes the appearance of a new peak at 360 and a shift of the peak at 450 °C, corresponding to the high-temperature decomposition. During annealing the irradiated ammonium perchlorate at 100 °C for 200 h, the effect decreases but does not disappear completely. Similar results were obtained also in later investigations (for example see [117–123]).

For the decomposition of ammonium perchlorate carried out under isothermal conditions, a decrease in the induction period was noted first of all [117]. The dependence of induction period on the absorbed dose is described by equation:

$$I = C_1 - C_2 \log D$$

and is shown in Fig. 15.

It was shown in [123] that irradiation may affect even thermal decomposition at very low (145–140 °C) temperature, when induction period of thermal decomposition of ammonium perchlorate can reach several hundred or thousand hours. A feature of the effect of irradiation on the decomposition of ammonium perchlorate under these conditions is that the samples composed of coarse crystals turn out to be most sensitive to radiation. After grinding in a mortar, their sensitivity to radiation decreases sharply.

Comparison of preliminary irradiation of ammonium perchlorate, a pure sample and a sample with aluminium additive, with protons, fast neutrons, and gamma radiation carried out in [119] showed that the most effective radiation is that accompanied by the formation of thermal peaks, as happens during irradiation with fast neutrons and with protons. Irradiation with gamma rays, which does not cause the formation of thermal peaks in perchlorate, is less efficient.

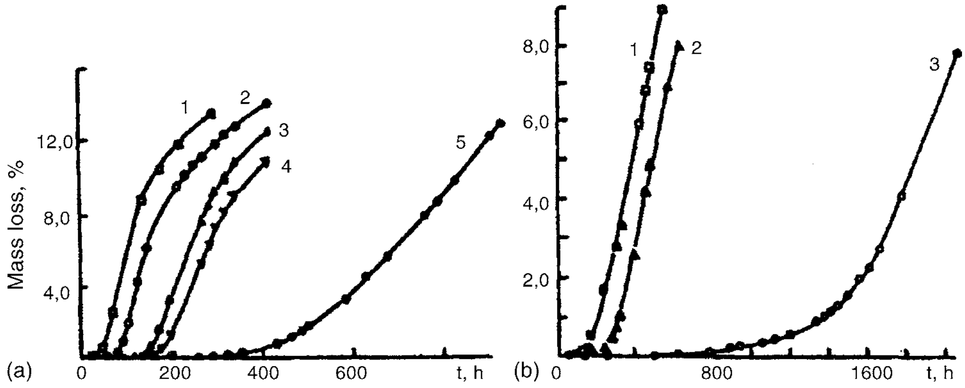


Fig. 15. Kinetic curves of decomposition of ammonium perchlorate at 135 °C after γ-irradiation. (a) The sample not treated mechanically: (1) 100, (2) 300, (3) 60 and (4) 30 s of irradiation with γ-rays, (5) non-irradiated sample. (b) The sample ground in a mortar: (1) 300 and (2) 60 s of irradiation with γ-rays, (3) non-irradiated sample.

The influence of gamma radiation of Co^{60} on the activation energy of thermal decomposition of ammonium perchlorate was studied in [120]. It was shown that irradiation with a dose up to 0.6 Mrad causes more than a two-fold decrease in activation energy.

Skorik and co-authors [124,125] carried out investigations of the rate of thermal decomposition of ammonium perchlorate under X-ray irradiation (dose rate 300 rad/min) during decomposition. It was discovered that irradiation during decomposition has no effect on the process rate.

As far as the reasons of the effect are conserved, they are connected both with chemical and with physical processes accompanying irradiation of ammonium perchlorate. Among chemical reasons, the main one is accumulation of chlorate ion during radiolysis [115]; the addition of this ion is known to produce a strong accelerating effect on thermal decomposition of ammonium perchlorate. An argument in favour of this assumption is considered to be the similarity of derivatographic curves of the irradiated ammonium perchlorate and that containing $ClO_3{}^-$ additive which was introduced into crystals during obtaining them (Fig. 16).

Komarov with co-authors [32] made an attempt to test this idea. Unlike Freeman [115] who introduced chlorate ions into the crystal of ammonium perchlorate by co-crystallization with potassium chlorate, in this work chlorate ions were introduced from ammonium chlorate solution, which made the experiment more correct. In this case, the effect of radiation treatment turned out to be higher that the effect observed after the introduction of chlorate ion into ammonium perchlorate crystal in the amount equal to that formed during radiolysis, as determined by the results of analysis.

So, it was assumed for radiolysis of ammonium perchlorate that, in addition to the formation of chlorate ion, the rate of thermal decomposition is affected by another factor causing an increase in the reactivity of ammonium perchlorate. Herley and Levy [114] discovered that irradiation of ammonium perchlorate causes, on the one hand, dislocation displacement in crystals, which can be observed as etch pits on mirror chips (Fig. 17, upper part); on the other hand, if the dose absorbed by the crystal exceeds 10^5 rad, an increase in the number of dislocations occurs (Fig. 17, lower part). Since dislocations are known to be the sites where the initial reaction centres are formed, an increase in the number of dislocations due to deformation of the walls of a pore in which radiolysis occurs became considered as the second reason of the influence of preliminary irradiation on the rate of thermolysis of ammonium perchlorate.

In [126,127], the dislocation model of the effect of preliminary irradiation was tested for the cases of influence of X-ray radiation (the source of radiation was Mars-2 set-up with copper cathode and the accelerating voltage of 18 kV) and UV light (the source was a mercury quartz lamp PRK-2).

The effect of development of a latent image by heating the irradiated crystal of ammonium perchlorate was used as a test fort he influence of preliminary irradiation.

It was shown in specially arranged experiments that even for small doses of irradiation with X-rays (10^2–10^3 rad), for which the corresponding density of dislocations is not changed, as demonstrated by etching of the mirror chips, the effect of preliminary irradiation is exhibited rather clearly. The same is true for the irradiation with the UV light.

The fact that the effect of preliminary irradiation is exhibited for the doses three orders of magnitude below the threshold, at which a noticeable increase in the number of dislocations is observed [114], serves as an indication that he main factor responsible for the influence of preliminary irradiation on the rate of thermal decomposition of ammonium perchlorate is the formation of $ClO_3{}^-$ ions (proton traps) in the lattice under the action of radiation. The presence of dislocations in the crystal is likely to affect the influence of irradiation on the rate of thermal decomposition process, but this influence should not be overestimated. It is likely to be of secondary character.

Unfortunately, a direct answer to the question concerning the importance of the dislocation mechanism of acceleration of thermal decomposition of ammonium perchlorate as a result of irradiation has not been given yet; the experiments mentioned above cannot serve as a direct confirmation of participation or non-participation of dislocations in the effect of preliminary activation. A more or less direct answer to this question is likely to be expected from experiments on the effect of irradiation on

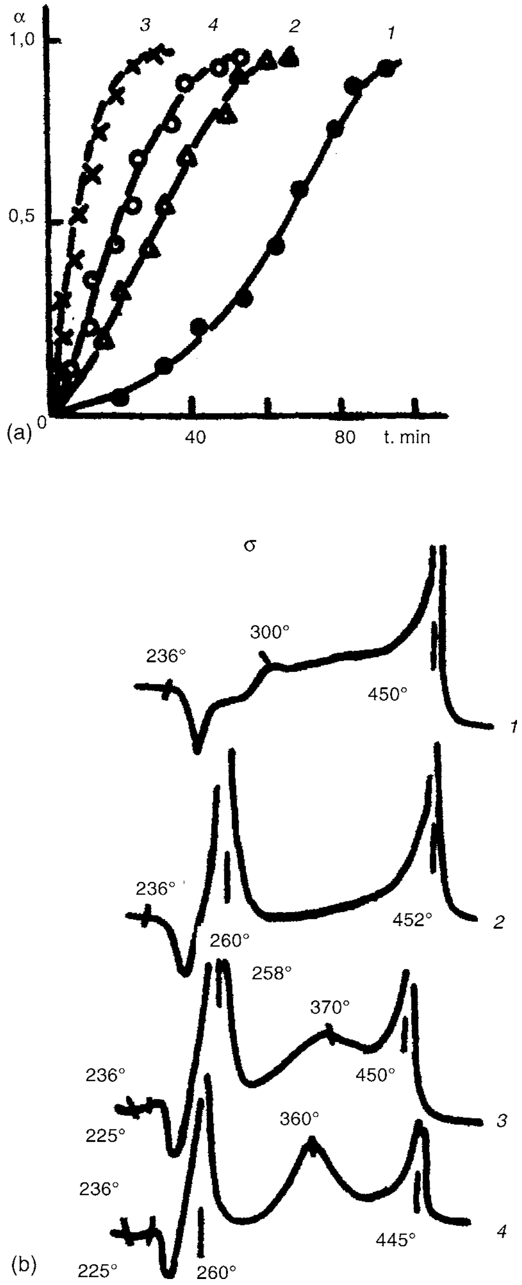


Fig. 16. The effect of irradiation and ammonium chlorate additive on thermal decomposition of ammonium perchlorate. (a) Kinetic curves of decomposition; (b) DTA curves. (1) Pure; (2) containing 0.153 mol% ClO_3^-; (3) containing 1.13 mol% ClO_3^-; (4) pure, irradiated with a dose of 4.5×10^6 rad.

dislocation-free ammonium perchlorate crystals; however, no such experiments have been carried out yet.

Preliminary irradiation with the UV light produces an effect similar to the effect of X-rays and gamma rays, which was observed by Bircomshaw [128]. The action of light, similarly to the action of ionizing radiation, is mainly restricted to the induction period. Similarly to the action of the ionizing radiation [117], the dependence of induction period on the absorbed dose is described by equation $\tau = \tau_0 - B \log \theta$, where θ is absorbed dose [127] (Fig. 18).

Chemical analysis indicates that the accumulation of chlorate ion occurs in the crystals of ammonium perchlorate during irradiation.

During subsequent decomposition, all the curves have a typical S-shaped appearance with the rate maximum corresponding to the inflection point at the transformation–time curve strongly shifted towards the axis of ordinates. The descending part of the rate–time curve is satisfactorily described by equation

$$\alpha = k(t - t_0)^n$$

As irradiation with light proceeds, the k and n parameters change.

Changes in the maximal decomposition rate $V_{\max}$ and the time of achievement of the maximal rate in course of irradiation of ammonium perchlorate with PRK lamp are shown in Table 3. One can see in these data that the number of potential reaction centres increases during irradiation; a decrease in the induction period corresponds to this observation. At the same time, the degree of localization of the process in course of irradiation changes, which is depicted in a decrease in factor n.

Specially arranged experiments showed that the efficiency of preliminary irradiation increases if the longer wavelength region is cut off with filters from the spectrum; the efficiency reaches maximum for $\lambda = 220–240$ nm.

As early as after three minutes of irradiation of ammonium perchlorate with light, the positive reaction with *o*-tolidine indicates that chlorine oxides ClO, ClO_2, ClO_3 and ions ClO^-, ClO_2^-, ClO_3^- are formed in ammonium perchlorate cerystals as a result of irradiation. This provides evidence that the scheme of photolysis of ammonium perchlorate corresponds in general to the scheme of radiolysis.

If ammonium perchlorate single crystal is irradiated with light through a stencil, it turned out that irradiation creates a latent photographic image in the crystals; it can be developed by heating the irradiated crystal at 230 °C. A sample of the negative image of the stencil thus obtained is shown in Fig. 19.

An interesting feature of this process is the fact that the image appears in the crystal not only on the side facing the light source and the mask but also at the opposite side. No substantial changes occur in the crystal volume. If we cleave the irradiated crystal and heat both parts, the latent image develops on both cleaved sides.

The longer is the distance from the cleaved surface to the irradiation source, the weaker is image.

A linear dependence of the optical density of image developed by thermal decomposition on ammonium perchlorate crystal chips taken at different distances from the irradiated surface corresponds to Bouguer–Lambert–Beer law which is usually used to describe absorption of light when passing through a light-absorbing medium:

$$I = I_0 \exp(-kx)$$

All these experiments provide evidence that under irradiation potential centres arise over the whole crystal volume. However, for these potential centres to be transformed into the active centres from which thermal decomposition of ammonium perchlorate starts and the nuclei of the products are formed, conditions

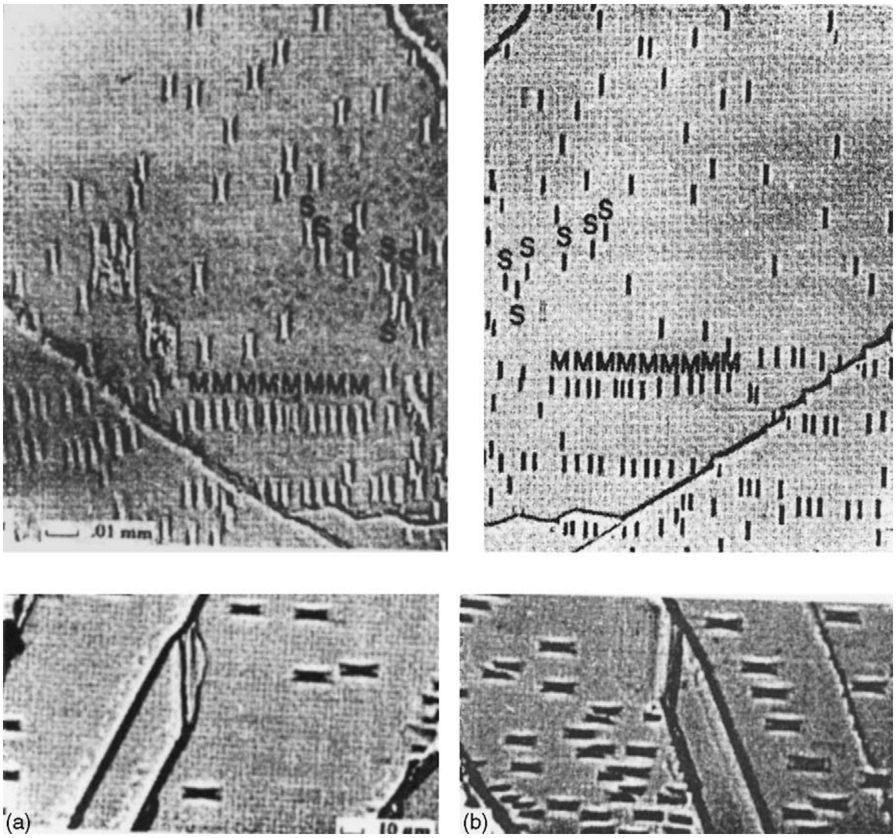


Fig. 17. (a) Radiation-caused movement of dislocations in ammonium perchlorate crystal, revealed with the help of etch pits. A mirror chip of the (2 1 0) plane. (a) Non-irradiated chip, (b) irradiated with γ-rays (10^4 rad). Dislocations shifted as a result of irradiation are marked with “M”, while those conserving their positions are marked with “S”. Shift of dislocations is substantially larger than that taking place during crystal cleavage without irradiation.

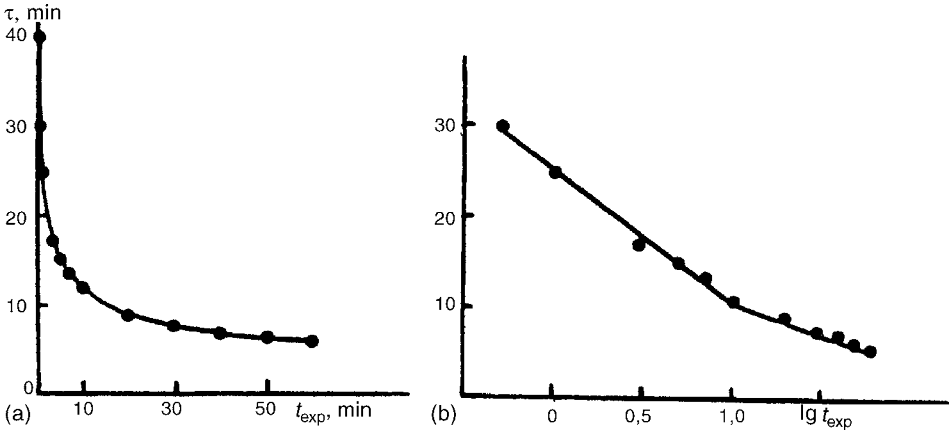


Fig. 18. Dependence of induction period τ for thermal decomposition of ammonium perchlorate on the time of preliminary UV irradiation. (a) In the ordinary coordinates, (b) in logarithmic coordinates.

are necessary under which a part of gaseous products could be removed from the reaction zone during heating the ammonium perchlorate. These conditions are likely to be realized in the subsurface layer of ammonium perchlorate crystal and cannot be realized in its volume due to the cage effect.

As one can see in Table 4, sensitivity of ammonium perchlorate to irradiation can be changed by introducing into ammonium perchlorate additives, which are the donor compounds (sen-

Table 4
Induction period (τ_d) of development of latent photographic image for pure ammonium perchlorate sample and for the sample containing additives

Sample	τ_d (min)
NH_4ClO_4	15
$NH_4ClO_4 + 5.1 \times 10^{-2}\%\ HSO_4^-$	9
$NH_4ClO_4 + 5.0 \times 10^{-2}\%\ CS(NH_2)_2$	20
$NH_4ClO_4 + 5.0 \times 10^{-3}\%\ HPO_4^-$	25

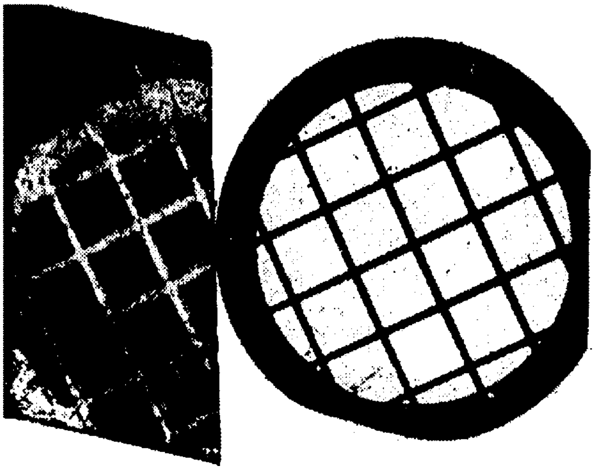


Fig. 19. A sample of photographic image obtained by combining the preliminary irradiation with UV light and thermal decomposition of NH_4ClO_4.

sitizers of the sensibility to irradiation) and proton acceptors (inhibitors).

7. The influence of additives on thermal decomposition of ammonium perchlorate

A specific feature of thermal decomposition of ammonium perchlorate is extremely high sensitivity to the action of various additives, either entering the lattice (homophase) or forming their own phase (heterophase). These additives can accelerate or decelerate the process of low-temperature thermal decomposition, which is important for the storage of ammonium perchlorate and mix compositions based on it. The additives may affect the deflagration delay time. It was assumed that there existed a correlation between the effect of the additives on the rate of thermal decomposition and their influence on the combustion rates of mix compositions incorporating ammonium perchlorate as the major component. This stimulated attention of many research groups, especially those dealing with the development of solid propellants, to the problem.

7.1. The influence of heterophase additives

As early as in the first works of Bircomshaw and Newman [16,128] the action of various additives on the rate of thermal decomposition of ammonium perchlorate was studied. These researchers discovered that the most efficient additive accelerating thermal decomposition of ammonium perchlorate is manganese dioxide. Less efficient catalyst of thermal decomposition is ferric oxide. Aluminium oxide did not affect the rate of thermal decomposition.

Hermony and Salmon [129] studied the effect of various additives on thermal decomposition of ammonium perchlorate within temperature range 170–200 °C. The results of their experiments are shown in Fig. 20. One can see that the maximal catalytic activity is exhibited under these conditions by cobalt and nickel oxides, which affect mainly the initial period of reaction. Manganese dioxide occupies intermediate position, while chromium and magnesium oxides affect later stages of the process.

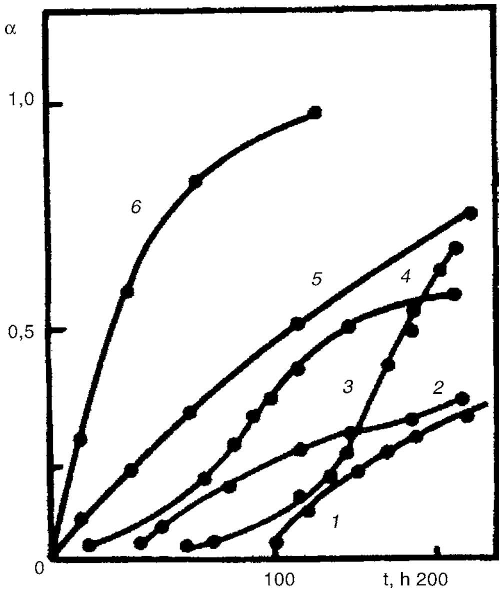


Fig. 20. The influence of oxide additives on thermal decomposition of ammonium perchlorate at 170 °C. Mixtures used: 100 mg of NH_4ClO_4 + 30 mg of an additive: (1) NH_4ClO_4; (2) NH_4ClO_4 + MgO; (3) $NH_4ClO_4 + Cr_2O_3$; (4) $NH_4ClO_4 + MnO_2$; (5) $NH_4ClO_4 + (Co_2O_3 + Co_3O_4)$.

Galwey and Jacobs [130] investigated the action of different manganese oxides on thermal decomposition of ammonium perchlorate in more detail. According to the results obtained by them, maximal catalytic activity is exhibited by manganese dioxide, but it affects the initial period of reaction while sufficient contact exists between the catalyst and ammonium perchlorate. Using MnO_2 labeled with ^{18}O oxygen isotope, it was shown that since the gaseous products of reaction do not get enriched with the label, chemical interaction between manganese oxide and ammonium perchlorate is excluded. In the presence of MnO_2 catalyst, transformation degree during thermal decomposition of ammonium perchlorate reaches 100%, while non-catalyzed decomposition is usually limited by the level of 30%. Deflagration delay time decreases, too. Manganese dioxide as the catalyst of thermal decomposition of ammonium perchlorate was also the subject of investigation in [131]; the authors of that paper thinks that MnO_2 catalyzes mainly high-temperature decomposition of perchlorate.

Oxides of monovalent and divalent copper were also studied as catalysts of low-temperature thermal decomposition of ammonium perchlorate. Jacobs and Kureishy [132] showed that addition of Cu_2O decreases deflagration delay time of perchlorate both due to the catalytic action itself and due to heat evolution during oxidation to copper oxide. The use of Cu_2O as efficient catalyst of thermal decomposition of perchlorate is also described in [131,133].

In the presence of copper(II) oxide, thermal decomposition of ammonium perchlorate starts at 180 °C, while usually it starts at a temperature about 200 °C; catalytic action of copper oxide manifests itself even in the case when its amount is only 0.5% mass. Similarly to the case of manganese dioxide, decomposi-

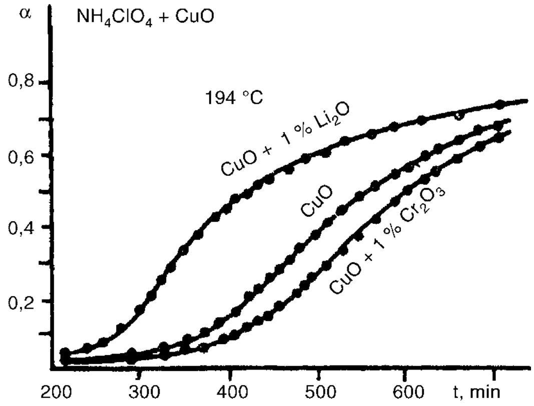


Fig. 21. The influence of doping of CuO on its catalytic activity in thermal decomposition of ammonium perchlorate at 194 °C. (Molar ratio NH_4ClO_4:CuO = 1:1).

tion of ammonium perchlorate in the presence of the catalyst proceeds almost till completion. It was established that doping of copper oxide with lithium increases its catalytic activity, while doping with chromium, vice versa, decreases it (Fig. 21) [134]. The author of [135] observed a decrease in the activity of copper oxide additive for perchlorate decomposition when doped with Cr^{3+} ions and an increase in the activity of chromium oxide when it was doped with Cu^{2+} ions.

The catalytic action of nickel oxide on thermal decomposition of ammonium perchlorate is similar to the action of copper oxides. Doping of nickel oxide with lithium and chromium leads to the same changes in the catalytic activity as those for the case of copper oxide. In addition to doping, catalytic activity of nickel oxide can be changed using thermal treatment. With temperature rise above 500 °C, the catalytic activity of the additive decreases substantially [4].

The effect of nanoparticles (∼10 nm) of nickel oxide on thermal decomposition of NH_4ClO_4 was studied in [136]. It was shown that addition to perchlorate about two weight percent of NiO brought about decrease of decomposition temperature and increase of heat of the reaction from 580 to 1490 J/g.

Iron(III) oxide is a catalyst of thermal decomposition of ammonium perchlorate mainly at high temperature (320–380 °C). The effect of the catalyst is observed at the later stages of the process [129,137]. It was shown that the efficiency of catalytic action of ferric oxide increases sharply when passing from micro-scale of the size of catalyst particles to the nano-size [138]. These authors also established a correlation between the specific surface of the catalyst and its catalytic activity toward decomposition of ammonium perchlorate.

Different opinions on the mechanism of catalytic action of ferric oxide exist. According to [139], the catalytic action of ferric oxide is due to the formation of iron perchlorate as an intermediate compound.

The authors of [140] think that the mechanism of the action of Fe_2O_3 is connected with the formation of nitryl perchlorate as an intermediate compound. These authors also established a correlation between specific surface of the catalyst and its activity. The authors of [141] showed that during decomposition of solid fuels ferric oxide catalyzes decomposition not only of ammonium perchlorate but also of the binder. Chromium(III) oxide, as well as other catalysts of oxidative-reductive processes, was used as an additive accelerating thermal decomposition of ammonium perchlorate. For this oxide as an example, as well as for the case of nickel and copper oxides, a strong effect of thermal treatment of an oxide and its doping with heterovalent foreign atoms on its catalytic activity was demonstrated. Similarly to ferric oxide, chromium oxide affects mainly not the initial stage but subsequent stages of thermal decomposition, and also affects deflagration delay time.

Burcat [142] and co-authors tried to reveal, using Cr_2O_3 labeled with ^{51}Cr isotope, whether the action of the additive on thermal decomposition of ammonium perchlorate involves oxidation of chromium(III) to chromate or the additive remains untransformed acting as a catalyst. Results of experiments showed that no traces of hexavalent chromium could be detected after thermal decomposition of ammonium perchlorate with the additive taken in the ratio 1:1. Moreover, it was established that if Cr_2O_3 additive is heated at a temperature of 300–310 °C in the air for 3 h, up to 4% of Cr_2O_3 is transformed into chromate. Therefore, under heating the additive with perchlorate, the factors inhibiting oxidation are actual.

Copper chromite, $CuCr_2O_4$ which is a component of traditional catalysts of combustion for solid fuels (for example Harshaw 0202P), was also the subject of investigation as an additive affecting the rate of thermal decomposition of ammonium perchlorate. According to the results described in [143,144], at low-temperatures up to 270 °C copper chromite has a slight effect on the rate increasing it by a factor of 2. However, at higher temperature (280–340 °C) its effect becomes more noticeable. Copper chromite affects the deflagration delay time decreasing it. Since industrial catalysts of combustion based on copper chromite contain not only copper chromite but also other compounds of copper and chromium, for example CuO and Cr_2O_3, the authors of [145] carried out comparative investigation of the catalytic activity of different components of the industrial combustion catalyst. The results are shown in Table 5.

It was shown in [146] describing investigation of the ignition of propellants based on ammonium perchlorate that copper oxide, copper chromite, iron(III) oxide and potassium permanganate change the lower ignition limit with respect to pressure. A typical dependence of the lower ignition limit with respect

Table 5
Comparison of catalytic activity estimated on the basis of flash temperature for the mixture catalyst + NH_4ClO_4 for different components of the copper-chromium catalyst of combustion

Catalyst	Specific surface (m^2/g)	Flash temperature (°C)
CuO	1.64	275.8
$Cu_2Cr_2O_4$	2.24	281.0
$CuCr_2O_4$	7.5	273.0
$CuCr_2O_4 + Cr_2O_3$		281.0
$CuCr_2O_4$ + CuO		284.0
$CuCrO_4$	21.2	275.5
Harshaw 0202P	23.25	276.0
Cr_2O_3	30.61	–
NH_4ClO_4 pure		435.0

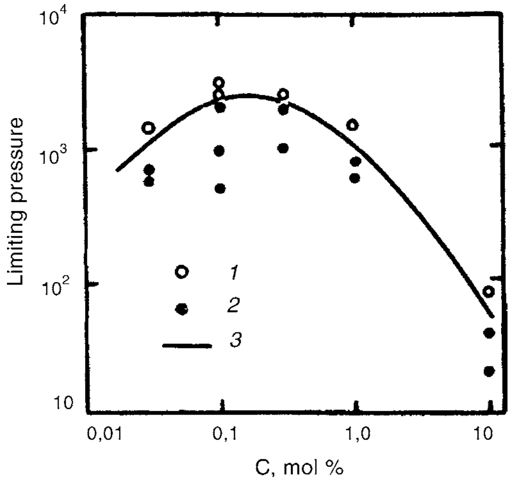


Fig. 22. Dependence of the lower ignition limit of ammonium perchlorate on the concentration of CuO mechanically mixed with ammonium perchlorate. With flash (1), without flash (2), lower pressure limit (3).

to pressure on the concentration of CuO additive is shown in Fig. 22 [144]. One can see that the limit with respect to pressure at first increases with an increase in the amount of the catalyst and then decreases. It is assumed that the occurrence of a maximum on the curve is a result of superposition of two effects: the catalytic action of the additives and heat losses connected with them [147]. A common feature for all the oxide catalysts of thermal decomposition is that they are known as the catalysts of oxidation–reduction. Because of this, their action of the rate and degree of transformation during thermal decomposition of ammonium perchlorate were often used as an argument to prove the scheme of decomposition mechanism based on the stage of electron transfer from anion to cation.

At the same time, as it was mentioned in the section describing the mechanism of thermal decomposition of ammonium perchlorate, the data on physicochemical properties of ammonium perchlorate and the decomposition process itself do not allow accepting the electron mechanism. The mechanism of catalysis at the contact between the solid ammonium perchlorate and the solid additive is not clear, too, if we take into account the fact that perchlorate is a typical dielectric with broad forbidden gap.

In order to try to eliminate this contradiction, it was assumed that the additives affect not only the solid ammonium perchlorate, but the reactions proceeding in the gas phase. The grounds for this assumption was the fact that the rate of thermal decomposition of ammonium perchlorate measured both gravimetrically and volumetrically relates not only to the reaction which proceeds within a definite subsurface layer, as suggested by the data on the process topography, but also inevitably includes dissociation of ammonia and chloric acid from the surface, and the secondary reactions with the participation of these products. Reasoning from the features of thermal decomposition of ammonium perchlorate, we may state that there are grounds to assume that the subsurface reaction, the reactions on the surface and those in the gas phase are closely connected with each other.

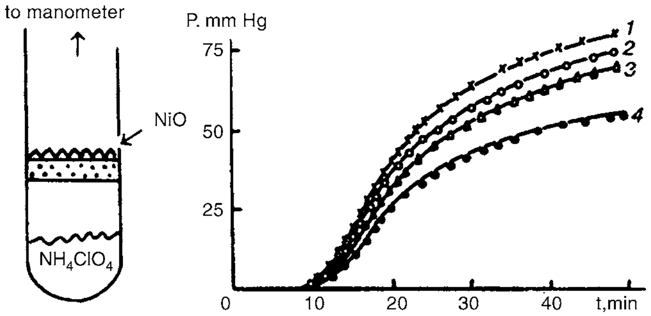


Fig. 23. The effect of NiO additive on thermal decomposition of NH_4ClO_4 at 250 °C, when the catalyst and ammonium perchlorate are separated by space (gap). Diagram of the experiment and the kinetic curves. (1) Without additive; (2–4) with NiO added, with the specific surface 2.0, 5.4 and 36.0 m^2/g, respectively.

In order to check the assumptions about possible role of catalysis in the gas phase, a series of experiments was carried out in [148]; in these experiments, perchlorate decomposing at 250 °C and NiO additive were separated with a glass filter. The scheme of this experiment and the results are shown in Fig. 23. One can see that the additive affects the rate and degree of transformation even under the conditions which are usually considered to be low-temperature ones. One can also clearly see in the data shown that the larger is specific surface of the additive, including both the outer geometrical surface and the inner surface, the higher is its catalytic action.

In subsequent experiments investigating the effect of the additive using the usual method, that is, by adding nickel oxide in the amount of 1% mass to ammonium perchlorate under simple mixing in a vibratory mixer for an hour and pressing tablets from the thus prepared mixture, it was shown (Fig. 24) that NiO additive, having larger specific surface, is more active, too. Similar results were obtained with copper oxide.

Special experiments were carried out which showed that if we take different weighed amounts of NiO and CuO preparations so that the surface of an additive was the same, the effect of an additive on the rate would be the same. For example, the action of 1% mass. NiO additive with specific surface 36 m^2/g

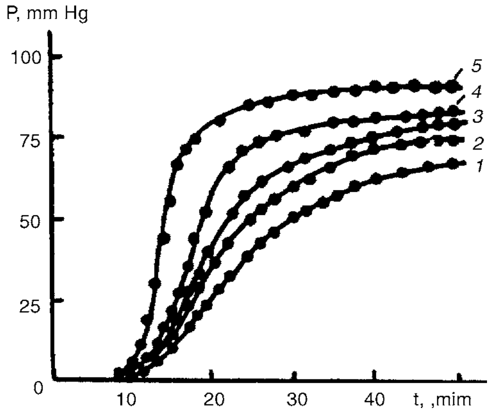


Fig. 24. The influence of specific surface of NiO additive on its catalytic activity toward thermal decomposition of ammonium perchlorate. (1) Without additive; (2–5) in the presence of NiO with the specific surface 0.7, 2.0, 5.4 and 36.0 m^2/g, respectively.

is equivalent to the action of 51% NiO additive with the surface of 0.7 m^2/g. Later similar results were obtained for catalysis of ammonium perchlorate decomposition by copper chromite additive [144].

As regards the processes catalyzed in the gas phase by oxide additives, these may be either decomposition of perchloric acid or oxidation of ammonia. This class of the data is likely to include also the data on the action of the palladium catalyst additive supported on γ-Al_2O_3 [149], as well as the experiments on the use of oxides of rare earths as catalysts [150] of thermal decomposition of ammonium perchlorate, though in the latter case one cannot exclude acceleration of the reaction due to possible chemical interaction of the oxides of rare earths with perchlorate, similarly to the situation with MgO. Addition of MgO, CdO, ZnO oxides accelerates thermal decomposition. However, the reasons of this acceleration are connected mostly not with the catalytic action of the additives but with the chemical interaction of these oxides with ammonium perchlorate or with perchloric acid, one of the products of perchlorate dissociation [151–155].

Several assumptions had been made with respect to the mechanism of the accelerating action of such additives as MgO and ZnO: (a) the reaction accelerates because zinc and magnesium perchlorate originating from the interaction between the oxides and ammonium perchlorate form easily melting eutectics. Due to the transition from the solid state into liquid, the rate of the process increases [153,154]; (b) the rate of the process increases due to the formation of intermediate amine compounds [156]; (c) the O^{2-} ions formed during decomposition of perchlorates and the surface of the oxides itself are proton traps and thus they simplify thermal decomposition, for example due to reaction [152]

$$2NH_4{}^+ + O^{2-} \rightarrow H_2O + 2NH_3$$

Addition of fluorides of transition metals were also tested as catalysts of thermal decomposition of ammonium perchlorate at 230 °C. The catalytic activity of fluorides changes in the sequence $Co^{2+} > Mn^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+}$; with other conditions being kept constant, it is always lower than the catalytic activity of the corresponding oxides [157].

The effect of the additives interacting with ammonium perchlorate is not always acceleration of the process. For example, the addition of lithium perchlorate in amounts more than 10% (or the compounds forming in the interaction with perchlorate an equivalent amount of lithium salt) causes strong inhibition of the process of thermal decomposition. Ammonium perchlorate with 1% mass of lithium perchlorate added can survive heating at 270 °C for up to 24 h without any noticeable indices of thermal decomposition [158]. The same happens also in the case when lithium fluoride is used as an additive. Interacting with ammonium perchlorate, it forms lithium perchlorate which inhibits subsequent decomposition [159].

Simchen [160] showed that during heating of ammonium perchlorate with additives – potassium and sodium chlorides, barium and strontium carbonates – the interaction of ammonium perchlorate with an additive occurs, resulting in the formation of the corresponding perchlorate which decomposes under subsequent heating.

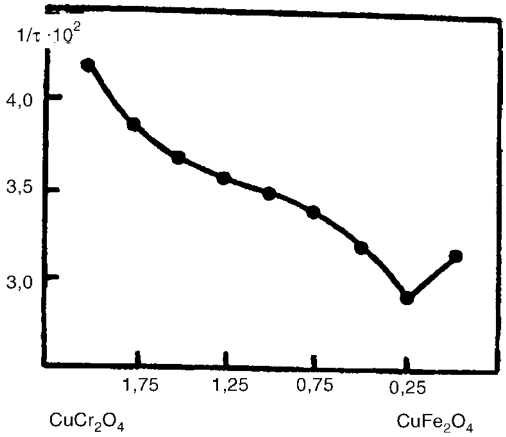


Fig. 25. Dependence of the catalytic activity of copper-chromium ferrites on their composition.

In [161], the effect of ferrite spinels as additives on the rate of thermal decomposition of ammonium perchlorate was studied. A series of spinels, belonging to the system of solid solutions copper chromite–copper ferrite with the composition chosen to provide the possibility of passing from copper chromite to ferrite by means of gradual substitution of Cr^{3+} ions with Fe^{3+}, was used as additives. The additives, with the specific surface approximately equal to 1 m^2/g, were mixed with ammonium perchlorate. The results of experiments on the kinetics of thermal decomposition of ammonium perchlorate are shown in Fig. 25, where the abscissa axis shows changes in the composition of spinel, while the ordinate axis shows the time within which the gaseous products reach a pressure of 14 mmHg; as a first approximation, this time can be considered as a characteristic of the reaction rate. One can see that all the studied additives catalyze thermal decomposition of ammonium perchlorate. As chromium is substituted with iron, the catalytic activity decreases until the composition $CuCr_{0.25}Fe_{1.75}O_4$, and then starts to grow.

In this respect, the behaviour of the catalysts of ammonium perchlorate decomposition does not differ from the behaviour of spinels in oxidation–reduction processes: passing from normal spinel to the inverted one, the catalytic activity drops down, provided that the cubic form of spinel is conserved. As soon as copper chromite containing iron and having cubic structure is transformed into the tetragonal form, its catalytic activity starts to increase. Thus, two opposite factors act in the system copper chromite–copper ferrite: inversion of spinel, which decreases the catalytic activity, and a decrease in the lattice symmetry, which increases catalytic activity. The observed effect is a result of superposition of these two factors. Attention should be paid to the fact that this dependence is conserved also for the combustion of mix model fuel.

To reduce the action of additives to simple catalysis of decomposition of one of the products of dissociation, namely, perchloric acid, means to simplify the question. The second component, ammonia, directly participates in catalysis. According to the data of works [162–164], the most active catalyst of perchloric acid decomposition is chromium(III) oxide. According to the data of different authors who investigated the effect of Cr_2O_3 additive on thermal decomposition of ammonium perchlorate, this effect was rather small. Moreover, though Al_2O_3, TiO_2 and SnO_2 catalyze decomposition of perchloric acid, these oxides have no effect on the decomposition of ammonium perchlorate. Vice versa, cobalt, nickel and copper oxides which are known as the most active additives have rather moderate activity when used as catalysts of decomposition of perchloric acid.

It was shown in the experiments carried out in our laboratory [165] to compare catalytic activity of different oxides when used as catalysts of thermal decomposition of ammonium perchlorate that the activity changes in the order:

$$MnO_2 > CuCr_2O_4 > Fe_2O_3 > SiO_2$$

Introduction of ammonium into the system in which the rate of catalytic decomposition of perchloric acid was studied caused a sharp (more than 10 times) increase in the rate of the process.

This is an evidence that the effect of catalytic additives on the decomposition of ammonium perchlorate is connected mainly not with the catalysis of decomposition of perchloric acid as it was initially assumed, but with other reactions which may occur in this system, for example oxidation of ammonia by the products of decomposition of perchloric acid. The most active catalyst should be considered to be the catalyst accelerating both the decomposition of he acid and oxidation of ammonia [163–167].

The opinion according to which the catalysis of thermal decomposition of ammonium perchlorate plays the major role in the action of additives during decomposition of combustion of fuel mixtures is reasonable not in every case. In [168], the effect of spinels $NiFe_2O_4$, $NiFeCrO_4$ and $NiCr_2O_4$, obtained by solid-phase interaction between the corresponding oxides, on thermal decomposition of ammonium perchlorate and its mixtures with polystyrene was studied. Relative efficiency of the catalysts for pure perchlorate decreases in the series $NiCr_2O_4 > NiFeCrO_4 > NiFe_2O_4$ and $NiFeCrO_4 > NiCr_2O_4 > NiFe_2O_4$ for the mixture. The catalytic action of these catalysts on polystyrene decomposition is characterized by the series $NiCrO_4 > NiCr_2O_4 > NiFe_2O_4$.

It was shown in [169] that boron additive can decrease the temperature of exothermal peak on DTA curve of AP and increase of enthalpy of all the process.

7.2. *The influence of additives introduced into ammonium perchlorate crystals by means of co-crystallization*

As early as in the first works on thermal decomposition of ammonium perchlorate, it was noted that the additives introduced into the lattice of ammonium perchlorate during its synthesis or during obtaining crystals have a substantial effect on physicochemical properties of ammonium perchlorate in general, and in particular on the rate of its thermal decomposition.

All the additives introduced into the lattice of ammonium perchlorate can be divided into three groups according to the character of their action: (a) the additives that cause changes in the conditions of proton, ion or electron transfer (if we assume the latter to take place) and therefore affect (accelerate or inhibit) thermal decomposition; (b) additives that decompose below the decomposition point of ammonium perchlorate (or together with it) and act as precursors for catalytically active products. These products, similarly to heterophase additives, affect the rates of secondary processes; (c) additives that cause the combined action of (a) and (b).

7.2.1. *The influence of additives on elementary stages of thermal decomposition of ammonium perchlorate*

Addition of foreign ions entering the lattice of ammonium perchlorate can change its physical and chemical properties. This is true also for thermal stability. Because of this, attempts were made to modify the properties of ammonium perchlorate by introducing the ions which could substitute wither NH_4^+ cation or ClO_4^- ion.

Maycock and Payne [170] introduced Ca^{2+}, SO_4^- and $C_2O_4^{2-}$ ions into ammonium perchlorate. According to the results obtained by them, Ca^{2+} ions create additional number of cation vacancies in the lattice in agreement with the electroneutrality principle. An increase in the number of vacancies decreases the number of interstitial NH_4^+ ions, which are considered to be electron acceptors according to the electron theory of thermal decomposition of ammonium perchlorate. According to Maycock, this is the reason of inhibition of thermal decomposition of ammonium perchlorate. According to the same principle of electroneutrality, the introduction of double-charged anions into the lattice of ammonium perchlorate should cause an increase in the number of anion vacancies. Interacting with the cation vacancies, the anion vacancies decrease their concentration in the lattice and therefore they prevent recombination of interstitial NH_4^+ ions with the cation vacancies. This causes acceleration of thermal decomposition of ammonium perchlorate. However, subsequent tests failed to confirm either experimental results of Maycock or his explanation of the effect of additives on the rate of thermal decomposition. First, it was established that doping with divalent cations of calcium [82], strontium [83], zinc [171] and barium [14] does not inhibit but, quite contrary, accelerates thermal decomposition of ammonium perchlorate. Moreover, it was shown that doping with a divalent cation affects the rate of thermal decomposition due to acceleration of the nuclei formation process and does not affect the rate of nuclei growth (Table 3).

The results obtained by Maycock on the accelerating action of doping with divalent SO_4^{2-} anions were not confirmed, too. It turned out that the addition of SO_4^{2-}, similarly to other di- and trivalent anions, does not accelerate thermal decomposition of ammonium perchlorate but inhibits this process [90] (Fig. 26).

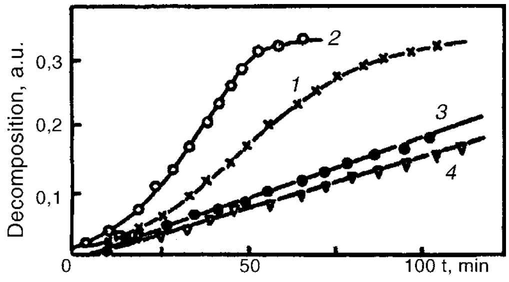


Fig. 26. Thermal decomposition of pure and doped ammonium perchlorate. (1) Without additive; (2) with addition of 2×10^{-2} mol% Ca^{2+}; (3) with addition of 1×10^{-2} mol% SO_4^{2-}; (4) with addition of 1.5×10^{-2} mol% PO_4^{3-}.

Similarly to the case of cation doping, the effect of doping of the anion sublattice on the rate of thermal decomposition is exhibited mainly as changes in the nuclei formation rate. The rate of their growth is not affected by doping of the anion sublattice (Table 7). According to [173], for doping the perchlorate crystals with barium ions, the rate of thermal decomposition decreases at first, then passes through a minimum and then increases with an increase in dopant concentration.

The reason of differences it the data obtained by different authors is not quite clear, because the description of an important and responsible operation of introduction of a dopant into a crystal is often very scarce, and there are no proofs that a dopant has entered the crystal and is not present as a heterogeneous admixture.

Experimental data obtained later by other researchers confirmed the results obtained by us on the effect of heterogeneous dopants (for example see review [4]). Theoretical notions about the mechanism of thermal decomposition of ammonium perchlorate have changed, too. The entire set of the data available at present provides evidence that the only mechanism according to which ammonium perchlorate decomposes is the proton mechanism. Because of this, the effect of dopants is to be explained basing on the fact that the reaction starts with proton transfer from cation to anion, followed by migration of proton over the anion sublattice.

From this point of view, the formation of additional number of cation vacancies during doping the ammonium perchlorate lattice with heterovalent cations should be considered as the formation of an additional number of proton traps in the lattice. Actually, since a cation vacancy is a site of local negative site due to the absence of positive ion in this site of the lattice, protons should be accumulated in this site; the formation of perchloric acid as the reaction product should occur in this site.

To the contrary, heterovalent anions, when introduced into the anion sublattice, form additional number of anion vacancies; they should inhibit the process due to elimination of a part of cation vacancies, because the anion–cation vacancy equilibrium should remain constant.

In addition to the effect on the rate of thermal decomposition of ammonium perchlorate through changes in the concentrations of ion defects, the dopant ions being donors or acceptors of protons can directly affect the processes participated by protons. For instance, the acceleration of thermal decomposition caused by the action of divalent copper ions introduced into ammonium perchlorate lattice by means of the joint crystallization of copper salts with ammonium perchlorate is explained by Keenan [174]: copper ions form amine complexes with ammonia, one of the products of dissociation of ammonium perchlorate; they bind ammonia and thus hinder the reverse reaction. In addition, it is assumed that ammonia bound in the amine complex would more easily enter the secondary reactions of its oxidation by the products of decomposition of perchloric acid.

Similarly, the inhibiting action of anion additives can be not only a consequence of the formation of anion vacancies but it can result from the fact that the additives themselves play roles of donors and acceptors of protons.

As an example of the action of proton donor additive, the effect of HSO_4^- ion additive on the rate of thermal decomposition of ammonium perchlorate should be considered. This ion has a size close to that of the perchlorate ion; judging from the results of conductivity measurements, it enters the ammonium perchlorate lattice rather well [172]. The data on the effect of proton donor additives on the rate of nuclei formation and growth are shown in Table 6.

With the introduction of proton accepting additives, according to the scheme of proton mechanism of ammonium perchlorate decomposition, a decrease in proton concentration should cause a decrease in the process rate. in [87,171], in order to check this assumption, the effect of $(NH_4)_2SO_4$, $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ on thermolysis rate was investigated.

The fact that these additives are indeed acceptors of protons can be demonstrated for the system $NH_4H_2PO_4$-NH_4ClO_4 as an example. The most probable reactions involving proton transfer in this system and the corresponding equilibrium constants can be written down as follows:

$$NH_4 + ClO_4^- \rightarrow NH_3 + HClO_4 \qquad K_1 = \frac{[NH_3]\,[HClO_4]}{[NH_4^+][ClO_4^-]}$$

$$NH_4 + H_2PO_4^- \rightarrow NH_3 + H_3PO_4 \qquad K_2 = \frac{[NH_3][H_3PO_4]}{[NH_4^+][H_2PO_4^-]}$$

$$H_2PO_4^- + ClO_4^- \rightarrow HPO_4^{2-} + HClO_4 \qquad K_3 = \frac{[HPO_4^{2-}][HClO_4]}{[H_2PO_4^-][ClO_4^-]}$$

$$2H_2PO_4^- \rightarrow H_3PO_4 + HPO_4^{2-} \qquad K_4 = \frac{[H_3PO_4][HPO_4^{2-}]}{[H_2PO_4^-]^2}$$

$$ClO_4^- + H_3PO_4 \rightarrow HClO_4 + H_2PO_4^- \qquad K_5 = \frac{[HClO_4][H_2PO_4^-]}{[ClO_4^-][H_3PO_4]}$$

Table 6
The effect of proton donor additive HSO_4^- on the rate of nuclei formation, maximal number of nuclei per unit surface area and rate of nuclei growth during thermal decomposition of ammonium perchlorate at 230 °C

	dN/dt (1/mm^2 min)		δ max (1/mm^2)		v_1 (||) (mkm/min)		v_2 ($\perp$) (mkm/min)	
NH_4ClO_4	45.7	±8.0 ±4.0	1003	±284 ±148	32.3	±5.4 ±2.7	4.3	±0.5 ±0.20
$NH_4ClO_4 + 5 \times 10^{-3}$ mol% HSO_4^-	149.0	±20 ±10	1680	±302 ±150	26.5	±3.9 ±1.9	4.3	±0.5 ±0.2
NH4ClO4 + 5×10^{-2} mol% HSO_4^-	210	±25.0 ±12.0	2229	±518 ±259	32.4	±5.6 ±2.8	5.5	±0.60 ±0.30

In this system of chemical equations, the three first ones are independent; because of this, only these equations will be considered below. The equations of material balance and charge equation are:

$$[H_3PO_4] + [H_2PO_4{}^-] + [H_2PO_4{}^{2-}] = [H_2PO_4{}^-]_o,$$

where $[H_2PO_4{}^-]_0$ is total concentration of the additive introduced into perchlorate, and

$$[HClO_4] + [H_3PO_4] = [NH_3] + [HPO_4{}^{2-}]$$

The equation of material balance can be rewritten taking into account the above equations as

$$\frac{[H^+](K_1 - [H^+]^2)K_2}{K_2[H^+]^2 - K_1K_3} + \frac{K_1(K_1 - [H^+]^2)}{K_2[H^+]^2 - K_1K_3} + \frac{(K_1 - [H^+]^2)K_1K_3}{[H^+](K_2[H^+]^2 - K_1K_3} = [H_2PO_4{}^-]_o$$

It may be shown that if the relation $K_2[H^+]^2 > K_1K_3$ is fulfilled, then $K_1 > [H^+]$, and the additive will be acceptor of protons.

If $K_1 < [H^+]^2$, the additive will be donor.

If $K_1 = [H^+]^2$, the additive will be neutral.

Let us rewrite $K_2[H^+]^2 > K_1K_3$ as $\dfrac{K_2}{K_3} > \dfrac{K_1}{[H^+]^2}$.

In order to make quantitative estimations, it is necessary to know constants K_2 and K_3. Let us admit that the constants in the solid are of the same order of magnitude as those in liquid, as a first approximation. Then we may use the relations known from general chemistry:

$$\frac{[H_2PO_4{}^-][H_3O^+]}{[H_3PO_4][H_2O]} = 10^{-2}; \qquad \frac{[NH_3][H_3O^+]}{[NH_4{}^+][H_2O]} = 10^{-10};$$

$$\frac{[HPO_4{}^{2-}][H_3O^+]}{[H_2PO_4{}^-][H_2O]} = 10^{-7}; \qquad \frac{[ClO_4{}^-][H_3O^+]}{[HClO_4][H_2O]} = 10^{10}$$

Dividing we will obtain:

$$K_2 = \frac{[NH_3][H_3O^+][H_3PO_4][H_2O]}{[NH_4{}^+][H_2O][H_2PO_4{}^-][H_3O^+]} = 10^{-8}$$

and

$$K_3 = \frac{[HPO_4{}^{2-}][H_3O^+][HClO_4][H_2O]}{[H_2PO_4{}^-][H_2O][ClO_4{}^-][H_3O^+]} = 10^{-17}$$

Here we obtain $K_2/K_3 = 10^9$. This means that $NH_4H_2PO_4$ will be proton acceptor with respect to ammonium perchlorate.

Evidently, if $NH_4H_2PO_4$ is proton acceptor, this will be even more for $(NH_4)_2HPO_4$ and $SO_4{}^{2-}$.

The data obtained by us when investigating the rate of thermal decomposition of ammonium perchlorate with proton acceptors as additives provide evidence that these additives indeed decrease the rate of thermal decomposition of ammonium perchlorate.

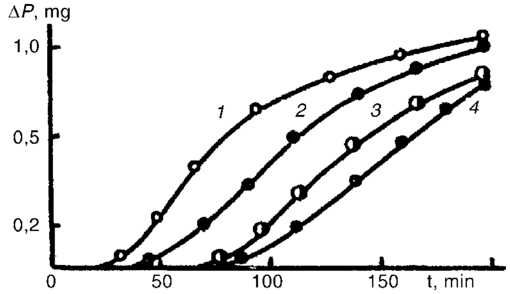


Fig. 27. The kinetic curves of NH_4ClO_4 decomposition at 235 °C in the presence of organic additives which are proton acceptors. (1) Without additive; (2) 1 mol% of diphenylamine; (3) 1 mol% of carbamide; (4) 1 mol% of thiocarbamide.

One can see in the data presented in Table 7 that the inhibiting effect of an additive is determined mainly by its proton acceptor activity. Generation of anion vacancies during doping is likely to be of secondary importance for this case. Because of this, $H_2PO_4{}^-$which does not produce additional anion vacancies when introduced into the lattice, turns out to be more active than $SO_4{}^-$.

Similarly, the rate of thermal decomposition of ammonium perchlorate decreases if the compounds known in organic chemistry as proton acceptors are added to ammonium perchlorate by means of the joint crystallization: diphenylamine, carbamide, thiocarbamide, that is, primary and secondary amines (Fig. 27).

7.2.2. *The effect of chlorate ion additive*

The effect of chlorate ion on thermal decomposition of ammonium perchlorate is of special importance. First, it is known that the addition of chlorate ion causes a substantial decrease in thermal stability of ammonium perchlorate [90–92]. Second, chlorate ion is one of the main products formed during storage and irradiation of ammonium perchlorate [4].

It was shown in [32,91,92] that the addition of chlorate ion into ammonium perchlorate causes a substantial decrease in the induction period of thermal decomposition. However, since only overall rate was studied in [32] and it was not clear if the additive affects the formation of nuclei or their growth, special investigation of this problem was carried out in [90]. The results of this investigation are listed in Table 8. Chlorate ion was introduced into the crystal by means of joint crystallization of ammonium chlorate and perchlorate. The content of the additive in crystals was determined using a known procedure with o-toluidine.

One can see in the data presented in Table 8 how strong is the effect of $ClO_3{}^-$ additive on the rate of decomposition. With an increase in $ClO_3{}^-$ concentration up to 0.1 mol%, the nuclei formation occurs at such a high rate that it can hardly be recorded; induction period decreases to 1 min and becomes comparable with the time of heating of the weighed portion to the required experimental temperature.

In order to answer whether chlorate ion is indeed proton acceptor and whether thermal decomposition occurs as a result of proton addition, experiments on thermal decomposition of chlorate ions in inert matrix in the presence of proton donors and without them were carried out [87]. Potassium perchlorate was used as inert matrix; $NH_4{}^+$ ion was used as proton donor.

Table 7
Dependence of the rate of nuclei formation (dN/dt), maximal number of nuclei formed per unit surface area (δ max), rate of nucleus growth parallel and perpendicular to the rhombic axis of ammonium perchlorate crystal during its thermal decomposition at 230 °C

	dN/dt (1/mm^2 min)	δ max (1/mm^2)	v_1 (||) (mkm/min)	v_2 ($\perp$) (mkm/min)
NH_4ClO_4	±8.0 45.7 ±4.0	±284 1003 ±148	±5.4 32.3 ±2.7	±0.5 4.3 ±0.20
NH_4ClO_4 3.2×10^{-3} mol% $SO_4{}^{2-}$	±9.0 28.2 ±4.5	±120 640 ±60	±5.0 35.5 ±2.5	±0.4 4.3 ±0.2
$NH_4ClO_4 + 4.5 \times 10^{-2}$ mol% $SO_4{}^{2-}$	±3.0 12.0 ±1.5	±61 448 ±30	±7.0 37.6 ±3.6	±0.4 4.8 ±0.2
$NH_4ClO_4 + 7.6 \times 10^{-2}$ mol% $SO_4{}^{2-}$	±2.5 7.5 ±1.2	±6.0 336 ±3.0	±6.0 35.8 ±3.0	±0.5 4.8 ±0.2
$NH_4ClO_4 + 6.1 \times 10^{-3}$ mol% $H_2PO_4{}^{-}$	±3.4 10.1 ±1.7	±64 374 ±32	±7.9 34.5 ±3.9	±1.1 4.7 ±0.5
$NH_4ClO_4 + 4.3 \times 10^{-2}$ mol% $H_2PO_4{}^{-}$	±3.2 5.8 ±1.6	±57 290 ±28	±5.0 35.5 ±2.5	±1.4 4.5 ±0.7
$NH_4ClO_4 + 3.0 \times 10^{-4}$ mol% $H_2PO_4{}^{-}$	±1.5 7.1 ±0.7	±92 371 ±46	±5.7 34.2 ±2.6	±0.7 4.7 ±0.4
$NH_4ClO_4 + 3.1 \times 10^{-2}$ mol% $H_2PO_4{}^{-}$	±1.6 3.3 ±0.8	±94 257 ±47	±5.9 31.9 ±2.7	±0.6 3.9 ±0.3

The introduction of chlorate ion and ammonium ion into the matrix was carried out by means of joint crystallization. Thermal decomposition was carried out at 320 °C. The composition of gaseous products was recorded with MSKh-4 mass spectrometer. The results of these experiments showed that the products of thermolysis are ammonia, water, oxygen, nitrogen oxide and hydrogen chloride. Kinetic data on thermolysis of $ClO_3{}^{-}$ ions in the matrix containing proton donor and containing no proton donor are shown in Fig. 28. One can see comparing the curves that the decomposition of chlorate ion occurs much more rapidly in the presence of proton donor additive than without it. It is natural to think that in the ammonium perchlorate crystal, in which $NH_4{}^{+}$ is every second ion, the route of $ClO_3{}^{-}$ decomposition through proton addition is the only one. Substan-

Table 8
The influence of chlorate ion additive on the rate of formation of the reaction nuclei (dN/dt), their maximal number per unit surface area (N_{max}), rate of nuclei growth parallel (v (||)) and perpendicular (v ($\perp$)) to the crystal axis, and the induction period (τ) at 230 °C

	dN/dt (1/mm^2 min)	δ max (1/mm^2)	v (||) (mkm/min)	v ($\perp$) (mkm/min)	τ (min)
NH_4ClO_4 recrystallized five times	±4.2 21.4 ±2.1	±59 612 ±31	±5.8 36.1 ±2.7	±0.6 4.7 ±0.2	±5.4 40.0 ±2.7
NH_4ClO_4 recrystallized two times	±8.0 45.7 ±4.0	±284 1003 ±142	±5.4 32.3 ±27	±0.5 4.3 ±0.2	±2.8 29.7 ±1.5
$NH_4ClO_4 + 8 \times 10^{-4}$ mol% $ClO_3{}^{-}$	±36 146 ±17	±155 1860 ±71	±5.8 30.7 ±3.0	±0.8 5.7 ±0.4	±4.7 23.0 ±2.1
$NH_4ClO_4 + 2 \times 10^{-3}$ mol% $ClO_3{}^{-}$	±99 481 ±52	±525 3632 ±275	±41 31.1 ±21	±1.1 5.9 ±0.6	±2.7 12.0 ±1.4
$NH_4ClO_4 + 6 \times 10^{-2}$ mol% $ClO_3{}^{-}$	±86 615 ±43	±575 4613 ±280	±2.9 30.6 ±1.6	±0.5 4.6 ±0.3	±0.8 10.0 ±0.4

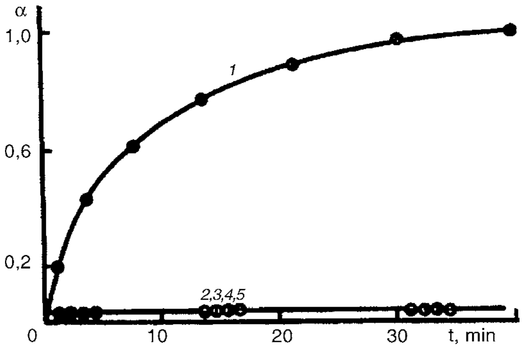


Fig. 28. The kinetic curves of thermal decomposition of the samples: (1) $KClO_4 + 1.7 \times 10^{-2}$ mol% $ClO_3^- + 1.0 \times 10^0$ mol% NH_4^+; (2) $KClO_4 + 3.1 \times 10^{-1}$ mol% ClO_3^-; (3) $KClO_4 + 2.5$ mol% NH_4^+; (4) $KClO_4$; (5) $KClO_3$. $T = 320\,°C$.

tial importance of ClO_3^- concentration for determining thermal stability of ammonium perchlorate is seen in the data on the dependence of induction period of thermal decomposition on the concentration of chlorate ion.

7.2.3. Additives introduced into the ammonium perchlorate lattice to serve as precursors of the catalysts of thermal decomposition of perchlorate

These additives include silver ions, which are transformed into metal silver during thermal decomposition, or MnO_4^- and $Cr_2O_7^{2-}$ ions, which form oxide catalysts as a result of decomposition. The addition of MnO_4^- ion introduced into ammonium perchlorate lattice attracted special attention of researchers. There were two reasons of this: first, it is well known that permanganate and perchlorate ions are isomorphous, so it was not difficult to obtain solutions of one of them in the other; second, thermal decomposition of permanganate, which is less stable than perchlorate, results in manganese dioxide, the catalytic action of which was established in the earliest works on thermal decomposition of ammonium perchlorate.

Schmidt and Stammler [175] introduced additives into ammonium perchlorate by means of its joint crystallization with potassium permanganate, potassium periodate, potassium iodate and calcium chromate. The results of investigation of thermal decomposition of ammonium perchlorate with 2% of permanganate added by co-crystallization are shown in Fig. 29. For comparison, the same Figure shows the curve of thermal decomposition of ammonium perchlorate into which $KMnO_4$ was added by means of mechanical mixing. One can see that isomorphically introduced $KMnO_4$ has a strong effect on the process rate.

The effect is strongly dependent on the size of particles of he solid solution. It is observed at higher extent for smaller particles. Thermograms of the solid solution indicate that its thermal decomposition occurs within temperature range below the phase transition. As far as the dependence of acceleration effect on concentration is concerned, the highest effect is caused when 50% of perchlorate is substituted by permanganate.

Since the experiments with mechanically added $KMnO_4$, K_2MnO_4 and MnO_2 did not reveal catalytic effect at low-temperatures, the authors assign a special mechanism of accelerating action to permanganate ion, which can (when introduced into the lattice) either directly oxidize ammonium ion or do this due to the atomic oxygen evolved during decomposition of permanganate:

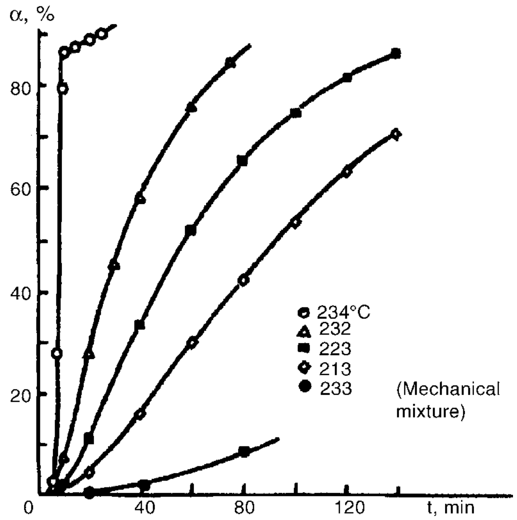


Fig. 29. Thermal decomposition of ammonium perchlorate crystallized together with $KMnO_4$.

$$MnO_4^- \rightarrow 1/2MnO_4^{2-} + 1/2MnO_2 + O$$

Unlike MnO_4^-, the IO_4^- ion causes much weaker action on the rate of thermal decomposition of ammonium perchlorate and only when the process has already started.

Addition of dichromate ion introduced into the lattice of ammonium perchlorate is likely to play a binary role. While the dichromate has not decomposed yet, which occurs at the initial stages of the process, it is an active proton acceptor and so inhibits the formation of reaction nuclei [64,176,177]. While the degree of ammonium perchlorate decomposition increases, especially at high temperatures, the dichromate ion decomposes, and the product of this reaction chromium(III) oxide can cause catalytic action on the rate of thermolysis of ammonium perchlorate.

Mixed crystals of ammonium perchlorate with cobalt, nickel and iron perchlorates, obtained by the joint crystallization of the salts, belong to the same class.

Thermal decomposition of these salts was studied in [178]. It turned out (Fig. 30) that the addition of cobalt ions is most efficient. Nickel ions occupy an intermediate position, while iron ions are the least active.

Three possible ways of the influence of additives were discussed: (a) Acceleration due to the formation of cation vacancies during the introduction of doubly charged ions into the lattice. As we have already mentioned this in the section dealing with the effect of homophase additives of alkaline metal additives, this way of process acceleration due to localization of protons in the lattice of ammonium perchlorate is principally possible if sufficient amount of the transition metal ions enters the lattice during co-crystallization. Versions of explanation are possible: transition metals are able to bind ammonia into ammoniates thus preventing ammonia from recombination with protons. (b) Per-

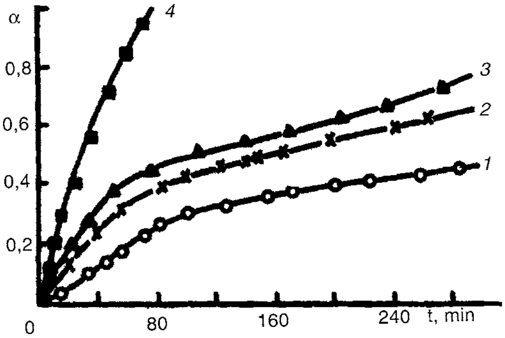


Fig. 30. Thermal decomposition of ammonium perchlorate dopes with Co^{2+}, Ni^{2+}, Fe^{2+} ion at 275 °C: (1) without additive; (2) Fe^{2+}; (3) Ni^{2+}; (4) Co^{2+}.

chlorates of transition metals decompose to form oxides. These oxides are catalysts of low-temperature thermal decomposition of ammonium perchlorate. This direction of influence is likely to be the major one. In any case, the curves of the effect of Co^{2+}, Ni^{2+} and Fe^{2+} on the rate of thermal decomposition of ammonium perchlorate and the curves of the effect of Co_2O_3, Ni_2O_3 and Fe_2O_3 additives on the rate of thermal decomposition of ammonium perchlorate are similar (Fig. 31 [178]).

Similar results were obtained by Pelly [179] who showed by means of DTA that the addition of Cu^{2+}, Mn^{2+}, Co^{2+} and Fe^{2+} affect the rate due to lattice modification and the formation of catalytically active oxides during decomposition.

7.2.4. The effect of heterophase additives which are precursors of the catalysts of thermal decomposition of ammonium perchlorate

A special place among the additives affecting the rate of thermal decomposition of ammonium perchlorate is occupied by the additives which themselves do not catalyze thermal decomposition but form the catalysts during thermal decomposition of the precursor or during its interaction with ammonium perchlorate.

As an example, we may cite the results of work [180] in which the comparison of the effect of different copper salts as additives on thermal decomposition ofammonium perchlorate was carried out. It was shown (Table 9, Fig. 32) that the efficiency of an additive depends on the features of its thermal decomposition. The rate of thermal decomposition of ammonium perchlorate is stronger affected by the additives which themselves can easily be decomposed or give rise to decomposition products accelerating thermal decomposition (for example, copper nitrate which forms nitrogen oxides during decomposition).

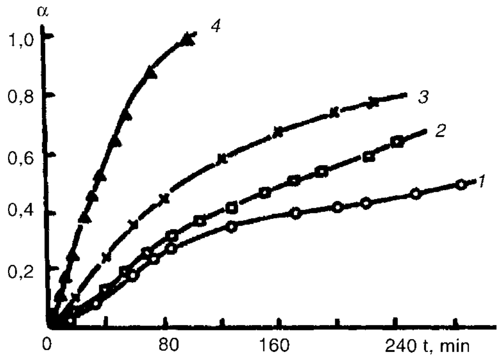


Fig. 31. The influence of oxide additives on the decomposition of ammonium perchlorate at 275 °C: (1) without additive; (2) 1% Fe_2O_3; (3) 1% Ni_2O_3; (4) 1% Co_2O_3.

Table 9
The effect of copper-containing additives on thermal decomposition of ammonium perchlorate

Additive	Temperature of salt decomposition (°C)	Flash temperature of the mixture ammonium perchlorate + additive (°C)
Ammonium perchlorate without additive	–	–
Copper oxide	–	259
Copper dichromate	400	298
Copper sulphate	600	333
Copper nitrate	220	245
Copper oxalate	240	251
Copper lactate	210	262

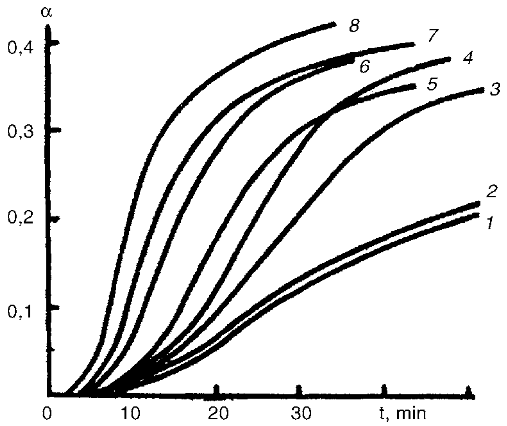


Fig. 32. The influence of copper salts as additives (1 mass%) on thermal decomposition of ammonium perchlorate at 250 °C: (1) copper bichromate and sulphate; (2) without additives; (3) copper benzoate; (4) copper benzoate heated preliminarily at 250 °C; (5) copper lactate; (6) copper oxalate; (7) copper oxide; (8) copper nitrate.

It is interesting to note that this dependence is also conserved for combustion of the model mix fuel based on ammonium perchlorate with copper salts as additives (Table 9).

Similar results were obtained by other authors, for example Singh [181] who used copper and chromium carbonates as precursors of the oxide catalysts of decomposition. A metal complex which contain iron or vanadium as a central ion had high activity during thermal decomposition of ammonium perchlorate. (see also [182–186]).

8. The effect of electric field on thermal decomposition of ammonium perchlorate

Since the edge components of dislocation in ion crystals are charged, an attempt was made in [187,188] to study the effect of the constant electric field on thermal decomposition of ammonium perchlorate. The results of experiments carried by the authors of [187,188] showed that a constant electric field with electrostatic intensity 0–10 kV/cm affects the character of thermal decomposition development in the crystal: anisotropy of reaction increases due to prevailing growth of nuclei along the main diagonal of the rhombic face of the crystal.

When the field is imposed along the direction [100], a decrease in the induction period and increase in the surface density of the initial reaction centres occur. Orientation of the field along [0 1 0] did not cause changes in these parameters.

The authors explain the first of the effects discovered by them in terms of Coulomb interaction of the field with the edge dislocations formed in the pore walls under the pressure of gaseous products, and in terms of reorientation of the dipole complexes of point defects in crystal located in the dislocation glide planes. The formation of new centres is assigned to an increase in the number of dislocations as a result of mechanical strain arising in the crystal under the action of the electric field.

The action of pulsed field on ammonium perchlorate crystals and on their thermal decomposition was studied in [189]. It was shown that under the negative pulse decomposition process is inhibited: temperature of the start of decomposition increases by 100 °C, while the rate of decomposition process itself decreases by 20%. Change in the polarity of the pulse leads to an inverse picture: decomposition accelerates substantially. In the opinion of the author of [189], under the action of the electric field, change in the limiting stage of thermal decomposition occurs: instead of the proton transfer from cation to anion activated thermally, the stage of activation of ion polarization under the action of the field appears.

9. The effect of crystal size and mechanical treatment on thermal decomposition of ammonium perchlorate

Anomalous dependence of the rate of thermal decomposition on crystal size was noticed even in the earliest works on thermal decomposition of ammonium perchlorate [16]. It turned out that with a decrease in the size of crystallites the rate of thermal decomposition passes through some optimal value; that is, as the specific surface area of ammonium perchlorate increases, no increase in rate is observed unlike the usual case of topochemical processes. A reason of such a specific dependence is likely to be the fact that the process of thermal decomposition of ammonium perchlorate, as we have already noted in the section describing topography of the process, starts not on the surface but in the subsurface layer on potential reaction centres formed as a result of interaction of dislocations with the point defects. These centres are renewed in course of the reaction; due to this, the chain character is sometimes assigned to the process. In order to put such a potential centre into operation, it is necessary that primary decomposition products accumulate in it. Because of this, crystal dispersing brings about two opposite factors. Since the removal of reaction products occurs through the surface, a decrease in crystal size improves the reaction conditions. On the other hand, starting from the moment when the crystallite size becomes of the same order of magnitude as the distance from the potential reaction centres to the surface, the conditions for accumulation of gaseous reaction products and formation of new dislocations as a result of their accumulation become worse, which causes a decrease in the reaction rate.

Along with these factors, we should also take into account changes in the density of dislocations in ammonium perchlorate crystals as a result of mechanical treatment. It was shown in [190] that mechanical treatment of ammonium perchlorate under the action of shock wave causes substantial acceleration of the process of low-temperature thermal decomposition. This may be seen from the comparison of thermograms of the mechanically treated ammonium perchlorate and the untreated ammonium perchlorate. While for the mechanically treated ammonium perchlorate the exo-peak corresponding to thermal decomposition lies on the DTA curve before the phase transition at 240 °C, for ammonium perchlorate not treated mechanically this peak is shifted to the temperature region above the phase transition.

Changes happening in ammonium perchlorate crystals under mechanical treatment in vibratory mill were investigated in [191]. It was shown that amorphization of the crystals under mechanical treatment leads to a decrease in the temperature of the start of thermal decomposition (see also [192,193]).

The rate of thermal decomposition of ammonium perchlorate is found to be significantly modified by precompression [194]. In author opinion precompression does not influence on reaction mechanism. This kind of treatment only modify the concentration of potential centres of reaction.

The nature of the shock sensitivity of ammonium perchlorate and mix compositions based on it was investigated with high-speed photography in the Cavendish Laboratory [195].

10. Conclusion

Studies of the thermal decomposition of ammonium perchlorate are interesting not only because of the application of the ammonium perchlorate as a component of solid propellants. The reaction provides a unique example of the auto-localization of thermal decomposition of a solid, when no solid products are formed, and the feed-back during the reaction is due to the secondary reactions, in which gaseous reaction products are involved.

As a consequence, a study of the mechanism of this reaction should consider both purely chemical stages at the elementary microscopic level, and the stages responsible for the spatial propagation of the reaction at the macroscopic level, the macrokinetics. A complex study should take into account all the details of the process in all their complicated interrelations. It would be erroneous, to over-estimate the role of any process and any effect. For example, an over-estimation of the role of the dislocations formed near a growing nucleus in the auto-localization of the reaction (“dislocation-chain theory of thermal decomposition”) [196] and an under-estimation of the role of point defects in the same process resulted in the discrepancy between the experimental data and the theoretical predictions [197].

A complex approach to the study of the thermal decomposition of ammonium perchlorate requires not only to consider all the facets of the process, but also to apply as many various techniques, as possible. For example, AFM, optical near field microscopy [198], synchrotron radiation diffraction experiments [199,200] might give a new knowledge on the structure of the reaction interface, on the characteristics and properties of the "solid product" of the incomplete thermal decomposition—the remaining unreacted ammonium perchlorate. The changes in the immediate surroundings of the ammonium cations and perchlorate anions during the reaction course and the dynamics of the ions in the structure could be studied by the solid-state multinuclei NMR [201] and some other techniques [202]. Thermal decomposition of ammonium perchlorate is one of the most extensively studied thermal decomposition reactions, and it still remains a mystery to a large extent. The studies of this old reaction might have a sort of renaissance, if the new techniques were applied and a new generation of researchers succeeded to combine seemingly contradictory observations and interpretations into a unifying picture of a complex process, which is so beautiful in its complexity.

References

[1] A.R. Hall, G.S. Pearson, Ammonium perchlorate. A review of its role in composite propellant combustion, Rocket Propulsion Establishment, Westcoff Techn. Report N 67/1, 1967.

[2] P.W. Jacobs, H.M. Whithead, Thermal decomposition and combustion of ammonium perchlorate, Chem. Rev. (4) (1969) 551–590.

[3] Mechanism of thermal decomposition of ammonium perchlorate: a collection of papers, in: G.B. Manelis (Ed.), Chernogolovka: Institute of Chemical Physics AN SSSR, 1981, p. 1–129 (in Russian).

[4] F. Solymosi, Structure and Stability of Salts of Halogen Oxyacids in the Solid Phase, Akademiai Kiado, Budapest, 1977, pp. 195–261.

[5] A.G. Keenan, R.F. Siegmund, Thermal decomposition of ammonium perchlorate, Quart. Rev. Chem. Soc. London 23 (3) (1969) 435–452.

[6] M.W. Evans, R.B. Beyer, L. McCulley, Initiation of deflagration waves at surfaces of ammonium perchlorate–copper chromite–carbon pellets, J. Chem. Phys. 40 (9) (1964) 2431–2438.

[7] H.G. Smith, H.A. Levy, Neutron diffraction study of ammonium perchlorate, Acta Crystallographica 15 (1962) 1201–1204.

[8] K. Herrmann, W. Ilge, Rontgenographische Structuren Forschung der Kubischen Modification der Perchloraten, Z. Krist., 1930, -Bd. 75, -pp. S41–44.

[9] J.A. Ibers, Nuclear magnetic resonance study of polycrystalline NH_4ClO_4, J. Chem. Phys. 32 (1960) 1448–1449.

[10] A.V. Dubovitsky, N.Ya. Buben, G.B. Manelis, Investigation of the movement of NH_4^+ ion in ammonium perchlorate by means of electron paramagnetic resonance, Russ. J. Struct. Chem. 5 (1964) 40–43.

[11] E.Yu. Ivanov, V.V. Boldyrev, On the mechanism of polymorphous transition in ammonium perchlorate crystals, Dokl. AN SSSR. 248 (4) (1979) 862–863.

[12] E.Yu. Ivanov, V.V. Boldyrev, T.V. Mulina, Ammonium perchlorate crystals as information recording system, Izv. SO AN SSSR, ser. khimich. nauk (5) (1976) 26–29, in Russian.

[13] L. Dauerman, H. Kimmel, Y. Wu, Application of internal reflectance spectroscopy to the study of solid propellants. II. Thermal decomposition of ammonium perchlorate, Combust. Sci. Technol. 5 (3) (1972) 129–133.

[14] P.W. Jacobs, Wee Lam. Ng, Thermal decomposition of ammonium perchlorate single crystals, J. Solid State Chem. 9 (4) (1974) 305–322.

[15] M.M. Pavlyuchenko, E.A. Prodan, L.I. Peshrovskaya, On the effect of temperature on the rate of topochemical transformations in ammonium perchlorate, Russ. J. Phys. Chem. 51 (3) (1977) 577–580.

[16] L. Bircomshaw, B. Newman, Thermal decomposition of ammonium perchlorate, Proc. Roy. Soc. A227 (1955) 228–237.

[17] M. Foltz, J. Meinschein, Ammonium perchlorate phase transitions to 26 GPa and 700 K in diamond anvil cell, Mater. Lett. 24 (6) (1995) 407–414.

[18] J.N. Maycock, V.R. Pai Verneker, G.A. Gorzinsky, Electrical conductivity of ammonium perchlorate, Solid State Commun. 5 (4) (1967) 225–227.

[19] J.N. Maycock, V.R. Pai Verneker, Role of point defects in thermal decomposition of ammonium perchlorate, Proc. Roy. Soc. A307 (1968) 303.

[20] K.V. Mikkelsen, M. Rather, Electron tunneling in solid state electron-transfer reactions, Chem. Rev. 87 (1987) 113–153.

[21] P. Zirkind, E.S. Freeman, Electrical conductivity of ammonium perchlorate, Nature 199 (1963) 1280–1281.

[22] G.P. Owen, J.M. Thomas, J.O. Williams, Comparison of the electrical conductivities of the perchlorates of ammonia and rubidium: a test for proton migration in the solid state, J. Chem. Soc. Dalton 7 (1972) 808–809.

[23] G.P. Owen, J.M. Thomas, J.O. Williams, Ionic conduction in ammonium perchlorate doped with divalent ions, J. Chem. Soc. Farad. Trans. 1 70 (1974) 1934–1943.

[24] G.P. Owen, J.M. Thomas, J.O. Williams, Electrical conduction in ammonium perchlorate, J. Chem. Soc. Farad. Trans. 1 68 (1972) 2356–2365.

[25] A.G. Keenan, M.G. Ohanian, The electrical conductivity of strontium doped ammonium perchlorate single crystals, J. Solid State Chem. 16 (1976) 215–217.

[26] H. Wise, Electrical conductivity of solid ammonium perchlorate, J. Phys. Chem. 71 (1967) 2843–2846.

[27] V.V. Boldyrev, E.F. Khairetdinov, Proton conductivity in ammonium perchlorate, J. Inorg. Nucl. Chem. 31 (1969) 3332–3338.

[28] E.F. Khairetdinov, A.A. Medvinsky, V.V. Boldyrev, On the initial stage of thermal decomposition of ammonium perchlorate, Kinetika i kataliz. 11 (5) (1970) 1343–1345.

[29] P.W. Jacobs, Wee Lam. Ng, Thermal decomposition of ammonium perchlorate single crystals, Solid State Chem. 9 (4) (1974) 315–322.

[30] P.W. Jacobs, Wee Lam. Ng, Proton transfer conduction in ammonium perchlorate, J. Phys. Chem. Solids 33 (1972) 2031–2039.

[31] E.F. Khairetdinov, V.V. Boldyrev, A.I. Burshtein, On the mechanism of conductivity of ammonium salts, J. Solid State Chem. 10 (1974) 288–293.

[32] V.F. Komarov, V.V. Boldyrev, V.K. Zhuravlev, G.V. Ivanov, On the reasons of the influence of preliminary irradiation on the rate of thermal decomposition of ammonium perchlorate, Kinetika i kataliz. 7 (B. 5) (1966) 788–791.

[33] A.M. Hor, P.W. Jacobs, Direct current conduction in ammonium perchlorate single crystals, J. Solid State Chem. 22 (1977) 77–86.

[34] A.M. Hor, S. Radhakrishna, P.W. Jacobs, Optical and electrical properties of ammonium perchlorate doped with chromate ions, Can. J. Phys. 54 (16) (1976) 1669–1675.

[35] L. Rosso, M.E. Tuckerman, Direct evidence of an anomalous charge transport mechanism in ammonium perchlorate crystal in an ammonia-rich atmosphere from first principles of molecular dynamics, Solid State Ionics 161 (2003) 219–229.

[36] J. Thomas, Reactivity of Solids, in: J.S. Anderson, M. Roberts, F. Stone (Eds.), Proceedings of the Seventh International Symposium, Chapmann and Hall, London, 1972, p. 428.

[37] G. Singh, I. Kapoor, J. Sing, F. Kaur, Role of proton transfer reactions in the thermolysis of alkyl and aryl ammonium salts, Indian J. Chem. B (2000) 1–9.

[38] V. Boldyrev, Topochemistry of thermal decomposition of solids, Thermochim. Acta 100 (1) (1986) 330.

[39] A.V. Raevsky, G.B. Manelis, V.V. Boldyrev, L.A. Votinova, On the role of dislocations in thermal decomposition of ammonium perchlorate crystals, Dokl. AN SSSR 160 (5) (1965) 1136–1137.

[40] P. Herley, P. Jacobs, P.W.A. Levy, Photomicrographic and electron microscopy study of nucleation in ammonium perchlorate, Proc. Roy. Soc. Lond. A318 (1970) 197–211.

[41] J.O. Williams, J.M. Thomas, Y.P. Savintsev, V.V. Boldyrev, Dislocation in orthorhombic ammonium perchlorate, J. Chem. Soc. Inorg. Phys. Theor. (11) (1971) 1757–1761.

[42] A.V. Raevsky, G.B. Manelis, On the mechanism of decomposition of ammonium perchlorate, Dokl. AN SSSR. 151 (4) (1963) 886–889.

[43] G.V. Sakovich, T.M. Moskovitina, E.D. Nesterova, Investigation of the influence of crystallization conditions of ammonium perchlorate on its

dislocation structure, Kinetics and mechanism of chemical reactions in solids: Expanded abstracts of reports at the VI All-Union Conference, Minsk, 1975, p. 66 (in Russian).

[44] Raevsky A.V. Topographic features of thermal decomposition of ammonium perchlorate, Mechanism of thermal decomposition of ammonium perchlorate. A collection of papers, G.B. Manelis (Ed.), Chernogolovka: Institute of Chemical Physics AS USSR, 1981, pp. 30–67 (in Russian).

[45] D. Thomas, D. Williams, V.V. Boldyrev, Yu.P. Savintsev, Investigation of the dislocation etch pits in NH_4ClO_4 doped with copper, Inorg. Mater. 11 (B. 6) (1975) 1035–1038.

[46] J.N. Maycock, V.R. Pai Verneker, L. Rooch, Influence of growth parameters on the reactivity of ammonium perchlorate, Inorg. Nucl. Chem. Lett. 4 (1968) 119–123.

[47] M. Dode, Sur la decomposition thermique du perchlorate d'ammonium. I. Influence de la temperature sur la nature des produits qui se forment lors de l'oxidation du perchlorate d'ammonium, Bull. Soc. Chim. France 5 (1938) 170–176.

[48] M. Dode, Sur la decomposition thermique du perchlorate d'ammonium. II. Partie experimentale, Bull. Soc. Chim. France 5 (1938) 176–183.

[49] V.I. Gritsan, V.N. Panfilov, V.V. Boldyrev, Investigation of the formation of chlorine dioxide during thermal decomposition of ammonium perchlorate, Dokl. AN SSSR. 187 (5) (1969) 1082–1084.

[50] G.A. Heath, I.R. Majer, Mass-spectrometric study of thermal decomposition of ammonium perchlorate, Trans. Farad. Soc. 60 (10) (1964) 1783–1791.

[51] A.K. Galwey, P. Jacobs, Thermal decomposition of ammonium perchlorate at low-temperatures, Proc. Roy. Soc. A.254 (1960) 455–469.

[52] B.B. Goshgarian, T.A. Walton, Mass-spectrometric study of ammonium perchlorate decomposition, US Air Force Rocket Propulsion Laboratory Techn. Report, 1965, pp. 65–87.

[53] O.P. Korobeinichev, V.V. Boldyrev, Yu.Ya. Karpenko, Application of pulse mass spectrometer to the investigation of the kinetics of fast processes during high-temperature decomposition of ammonium perchlorate, Fizika goreniya I vzryva. 1 (1968) 33–37, in Russian.

[54] V.V. Boldyrev, V.V. Korobeinichev, V.N. Pan'kov, On the mechanism of thermal decomposition of ammonium perchlorate, Kinetika i kataliz. 9 (B. 1) (1968) 218–219.

[55] V.V. Boldyrev, O.P. Korobeinichev, Yu.Ya. Karpenko, Investigation of the primary products of pulsed pyrolysis of ammonium perchlorate using time-of-flight mass spectrometer, Izv. AN SSSR, ser. khim (6) (1968) 1372–1373.

[56] I.P. Fisher, A mass-spectrometric study of thermal decomposition of perchloric acid and chlorinedioxide, Technical Report 66/13, Rocket Propulsion Establishment: Westcott, November 1966, pp. 31–37.

[57] V.V. Aleksandrov, V.M. Gladkykh, On the endothermic character of the initial stage of thermal decomposition of ammonium perchlorate, Kinetika i kataliz. 10 (3) (1969) 685–686, in Russian.

[58] V.V. Aleksandrov, V.G. Morozov, S.S. Khlevnoy, Procedure of measurement of quantity of heat and the kinetics of heat evolution in the condensed phase, Zhurn. prikladnoy mekhaniki i tekhnicheskoy fiziki. (4) (1969) 149–152, in Russian.

[59] V.V. Aleksandrov, E.F. Khairetdinov, On the sublimation of ammonium perchlorate, Kinetika i kataliz. 12 (5) (1971) 1327–1329, in Russian.

[60] G.L. Pellet, W.R. Cofer, Thermal decomposition of ammonium perchlorate by rapid heating, Seventh AIAA Aerospace Science Meeting, New York, 20 January 1969, p. 141.

[61] R.D. Schulz, A.O. Dekker, Transition-state theory of the linear rate of decomposition of ammonium perchlorate, in: Proceedings of the 6th Symposium on Combust., New York: Reihnold Publ. Comp., 1956, pp. 618–626.

[62] A. Russel-Jones, The mechanism of decomposition of inorganic perchlorates, Thesis, Imperial College of Science Techn. London Univ., 1964, pp. 20–41.

[63] J.V. Davies, P.W. Jacobs, A. Russel-Jones, Thermal decomposition of ammonium perchlorate, Trans. Farad. Soc. 63 (1967) 1737–1792.

[64] Boldyrev V.V., Savintzev Y.P., Mulina T.V., On the mechanism of formation and growth of the nuclei in thermal decomposition of ammonium salts, in: Proceedings of the 7th International Symposium on the Reactivity of Solids, 17–21 July 1972, Chapmann and Hall, Bristol, 1972, pp. 421–430.

[65] E.F. Khairetdinov, V.V. Boldyrev, The mechanism of the low-temperature decomposition of NH_4ClO_4, Thermochim. Acta 41 (1980) 63–86.

[66] A.L. Leu, T.F. Yeh, Thermal behavior of porous residual of the ammonium perchlorate, Thermochim. Acta 186 (1991) 53–61.

[67] K.J. Krautle, Thermal decomposition of orthhorombic ammonium perchlorate single crystals, J. Phys. Chem. 74 (1970) 1350–1355.

[68] A.K. Galwey, M.A. Mohamed, The low-temperature thermal decomposition of ammonium perchlorate, Proc. Roy. Soc. Lond. A396 (1984) 425–431.

[69] A. Galwey, P. Herley, M.A. Mohamed, Replication micrography of ammonium perchlorate surface during their initial stages of thermal decomposition, Reactivity Solids 6 (1988) 205–216.

[70] A. Ramaswamy, A. Shin, R. Armstrong, C. Lee, J. Sharma, Nanosecond and picosecond laser induced cracking and ignition of single crystals of ammonium perchlorate, J. Mater. Sci. 31 (1996) 6035–6042.

[71] S. Vyasovkin, Ch.A. Wight, Model-free and model fitting approach to kinetic analysis of isothermal and nonisothermal data, Thermochim. Acta 340–341 (1999) 53–68.

[72] S. Vyasovkin, Computation aspects of kinetic analysis. Part C. ICTAC – kinetic Project—the light at the end of tunnel? Thermochim. Acta 355 (2000) 155–163.

[73] V.V. Boldyrev, Yu.P. Savintsev, V.F. Komarov, The effect of water vapour pressure on the growth rate of nuclei during thermal decomposition of ammonium perchlorate, Kinetika i kataliz. 6 (4) (1965) 732–734.

[74] V.V. Boldyrev, Yu.P. Savintsev, T.V. Mulina, G.V. Shchetinina, On the physicochemical reasons of the formation and growth of reaction nuclei duirng thermal decomposition of ammonium perchlorate, Kinetika i kataliz. 11 (B. 5) (1970) 1131–1139.

[75] Yu.P. Savintsev, T.V. Mulina, V.V. Boldyrev, Thermal decomposition of NH_4ClO_4, Combustion and explosion,Moscow: Nauka, 1972, pp. 756–759 (in Russian).

[76] A.Y. Rozovsky, Kinetics of Topochemical Reactions, Khimiya, Moscow, 1974, 220 pp. (in Russian).

[77] B. Delmon, Introduction a la cinetique heterogene, Editions Technip., Paris, 1969.

[78] N. Mott, R. Gurney, Electron Processes in Ionic Crystals, Clarendon Press, Oxford, 1940, pp. 201–232.

[79] R.V. Jacobs, A.A. Russel-Jones, On the mechanism of decomposition of ammonium perchlorate, Raketnaya tekhnika i kosmotavtika 5 (4) (1967) 275–278, in Russian.

[80] B.S. Svetlov, V.A. Koroban, On the inhibition of thermal decomposition of ammonium perchlorate by the products of decomposition, Kinetika i kataliz. 8 (1967) 456–459.

[81] B.S. Svetlov, V.A. Koroban, On the mechanism of thermal decomposition of ammonium perchlorate, Fizika goreniya i vzryva. 6 (1) (1970) 12–18, in Russian.

[82] V.V. Boldyrev, On the mechanism of thermal decomposition of ammonium perchlorat, Dokl. AN SSSR. 181 (6) (1968) 1406–1409.

[83] V.V. Boldyrev, V.V. Alexandrov, A.V. Boldyreva, V.I. Gritzan, Yu.Ya. Karpenko, O.P. Korobeinichev, V.N. Panfilov, E.F. Khairetdinov, On the mechanism of thermal decomposition of ammonium perchlorate, Combustion Flame 15 (1970) 71–78.

[84] Yu.I. Rubtsov, G.B. Manelis, About the mechanism of thermal decomposition of ammonium perchlorate, in: Mechanism of Thermal Decomposition of Ammonium Perchlorate. A Collection of Papers, G.B. Manelis (Ed.), Chernogolovka: Institute of Chemical Physics AS USSR, 1981, pp. 123–129 (in Russian).

[85] V.A. Koroban, B.S. Svetlov, V.M. Chugunkin, Combustion and explosion, in: Proceedings of the All-Union Symposium on Combustion and Explosion, Moscow: Nauka, 1972, p. 741, in Russian.

[86] V.A. Koroban, B.S. Svetlov, V.P. Guk, T.I. Smirnova, Mechanism of thermal decomposition of ammonium perchlorate, Mechanism of ther-

mal decomposition of ammonium perchlorate: collection of papers G.B. Manelis (Ed.), Chernogolovka: Institute of Chemical Physics AS USSR, 1981, pp. 5–29 (in Russian).

[87] E.F. Khairetdinov, T.V. Mulina, V.V. Boldyrev, Mechanims of nuclei formaiton during low-temperature decomposition of ammonium perchlorate, Mechanism of thermal decomposition of ammonium perchlorate: collection of papers G.B. Manelis (Ed.), Chernogolovka: Institute of Chemical Physics AS USSR, 1981, pp. 101–123 (in Russian).

[88] V.V. Boldyrev, O.I. Lomovsky, T.O. Zaykova, E.F. Gavrilov, The change of the reactivity of solids on interface reagent-product of topochemical reaction, J. Solid State Chem. 51 (1) (1984) 127–130.

[89] V.V. Boldyrev, O.I. Lomovsky, T.O. Zaykova, Changes in the reactivity of solid on the reagent-product surface, Dokl. AN SSSR. 271 (2) (1983) 368–370.

[90] T.V. Mulina, Investigation of nuclei formation process during low-temperature thermal decomposition of ammonium perchlorate: Thesis, Cand. Sci. Chem. Novosibirsk, 1976, p. 80–86 (in Russian).

[91] H. Osada, E. Sakamoto, Thermal decomposition of ammonium perchlorate, Kogyo Kayaku Kyokaishi. 24 (1963) 236–244.

[92] J.C. Petricciani, S.E. Wiberley, W.H. Bauer, T.W. Clapper, The effect of a chlorate impurity on thermal stability of ammonium perchlorate, J. Phys. Chem. 64 (1960) 1309–1311.

[93] I. Schumacher, Perchlorates. Their Properties, Production and Application, Khimiya, Moscow, 1963, 220 p. (in Russian).

[94] E.V. Boldyreva, Feed-back in solid state reactions, Reactivity Solids 8 (1990) 269–282.

[95] E.V. Boldyreva, Feed-back in chemical solid state reactions, Siberian J. Chem. (1) (1991) 41–50, in Russian.

[96] A.K. Galwey, M.A. Mohamed, The formation of NO_2ClO_4 as an intermediate during low-temperature decomposition of ammonium perchlorate, J. Chem. Soc. Chem. Commun. 18 (1984) 1197–1198.

[97] A. Galwey, N.J. Carr, M.A. Mohamed, Interface chemistry in solid state decomposition, in: Proceedings of the 10th International Symposium on Reactivity of Solids, 27–31 August 1984, Dijon, P. Barret, L.C. Dufour (Eds.), Amsterdam, Elsevier Sci. Publ., 1985, pp. 633–634.

[98] P.W. Jacobs, A. Russel-Jones, Sublimation of ammonium perchlorate, J. Phys. Chem. 72 (1968) 202–207.

[99] R.H. Waeshe, J. Wenograd, L.R. Femauer, Investigation of solid propellants decomposition characteristics and their relation to observed burning rates, in: Proceedings of the Second ICRPG/AIAA Solid Propulsion Meeting, Anaheim. Callif, June 1967, pp. 136–146.

[100] E.E. Hackman III, H.H. Hesser, H.C. Beachell, Detection of species resulting from condensed phase decomposition of ammonium perchlorate, J. Phys. Chem. 76 (1972) 3545–3554.

[101] Politzek, P. Lance, Energetics of ammonium perchlorate decomposition steps, Theochem. J. Mol. Struct. (454) (1998) 229–335.

[102] M.P. Kannan, Thermal decomposition of ammonium perchlorate, J. Thermal Anal. 32 (4) (1987) 1219–1227.

[103] V.G. Dedgaonkar, D.B. Sarawade, Effect of different additives on thermal decomposition of ammonium perchlorate, J. Thermal Anal. 36 (1) (1990) 223–229.

[104] B.I. Kaidymov, V.S. Gavazova, The influence of polymorphous transition in ammonium perchlorate on the catalytic effect of homogeneous and heterogeneous additives in its thermal decomposition, Fizika goreniya I vzryva. 10 (6) (1974) 801–810, in Russian.

[105] B.I. Kaidimov, V.S. Gavazova, A sharp change in the inhibiting effect of ammonia on thermal decomposition of ammonium perchlorate as a result of its phase transition, J. Inorg. Nucl. Chem. 36 (12) (1974) 3848–3849.

[106] G. Odian, T. Acker, T. Peltzke, γ-Radioolysis of ammonium perchlorate, J. Phys. Chem. 69 (7) (1965) 2477–2479.

[107] V.A. Nevostruev, Radiolysis of ammonium perchlorate and the effect of additives on this process: Thesis, Cand. Sci. Chem., Tomsk, 1969, 113 p. (in Russian).

[108] J.S. Hyde, E.S. Freemann, E.P.R. observation of NH_3^+ formed by X-ray irradiation of ammonium perchlorate crystals, J. Phys. Chem. 65 (1961) 1636–1638.

[109] M. Fujimoto, J.R. Morton, Electron spin resonance spectra of ^{15}N-centered radicals at low-temperatures. I. The radicals NH_3^+ trapped in NH_4ClO_4, Can. J. Chem. 43 (1965) 1012–1016.

[110] Yu.M. Boyarchuk, N.Ya. Buben, A.V. Dubovitsky, G.B. Manelis, Investigation of the irradiated ammonium perchlorate by means of EPR, Kinetika i kataliz. 5 (1964) 823–830, in Russian.

[111] R.V.G. Dedganka, A. Surawade, Radiation effects on thermal decomposition of ammonium perchlorate, J. Radioanal. Nucl. Chem. 165 (5) (1992) 269–275.

[112] S. Radhakrishna, M. Riggin, P.W. Whippey, P.W. Jacobs, Thermoluminiscence of irradiated ammonium perchlorate, Can. J. Phys. 54 (7) (1976) 766–770.

[113] J. Dedgaonkar, Radioanalytical Nucl. Chem. Lett., 199 (3) (1995) 191–196.

[114] P. Herley, P.W. Levy, Quantitative study on radiation induced dislocations and the decomposition kinetics of ammonium perchlorate, in: Proceedings of the 7th International Symposium on the Reactivity of Solids, Bristol, 1972, pp. 387–398.

[115] E. Freeman, D. Anderson, J.J. Camposi, The effect of X-ray and gamma-ray irradiation on thermal decomposition of ammonium perchlorate in solid state, J. Phys. Chem. 64 (1960) 1727–1732.

[116] E. Freeman, D. Anderson, Observations on the decomposition of X-ray irradiated ammonium perchlorate, J. Phys. Chem. 65 (1961) 1662–1664.

[117] P.W. Herley, P.J. Levy, Effects of X-and γ-ray radiation on thermal decomposition of solid orthorombic ammonium perchlorate, J. Chem. Phys. 49 (4) (1968) 1500–1509.

[118] P.W. Levy, P.J. Herley, Effects of radiation on thermal decomposition induction period in ammonium perchlorate and other pseudostable materials, J. Phys. Chem. 75 (2) (1971) 191–201.

[119] P. Herley, C.S. Wang, G. Varsi, P. Levy, Effect of fast neutron, gamma-ray and combined radiation on the thermal decomposition of ammonium perchlorate powders, J. Thermal Anal. 41 (23) (1994) 435–448.

[120] V.G. Dedgaonkar, D.U. Rajput, S. Devchandra, Intern. Symp. Rad. Chem. (Plutonium 50 years), Bombay, 4–7 February 1991.

[121] V.G. Dedgaonkar, D.U. Rajput, Radiation effects on thermal decomposition of ammonium perchlorate, Radiochem. Radioanal. Lett. 57 (1983) 281–286.

[122] V.G. Dedgaonkar, D.B. Sarawadze, TG, DTA studies on gamma-irradiated ammonium perchlorate and its mixtures with potassium chloride, potassium bromide, J. Thermal Anal. 35 (7) (1989) 2305–2310.

[123] S. Folger, D. Lawson, γ-irradiation effects on thermal stability and decomposition of ammonium perchlorate, J. Phys. Chem. 74 (1970) 1637–1639.

[124] A.I. Skorik, V.V. Boldyrev, V.F. Komarov, A.I. Baranov, Thermal decomposition of ammonium perchlorate at the moment of irradiation with X-rays, Izv. VUZov. Ser. khimiya i khimicheskaya tekhnologiya (7) (1968) 744–747.

[125] A.I. Skorik, V.V. Boldyrev, V.F. Komarov, Thermal decomposition of ion salts at the moment of irradiation, Kinetika i kataliz. 8 (B. 6) (1967) 1258–1263.

[126] E.Yu. Ivanov, E.F. Khairetdinov, T.V. Mulina, Photothermomechanical process in ammonium perchlorate crystals. I, J. Solid State Chem. 26 (1978) 209–215.

[127] E.Yu. Ivanov, V.V. Boldyrev, E.F. Khairetdinov, Photothermomechanical process in ammonium perchlorate crystals. II, J. Solid State Chem. 26 (1978) 215–219.

[128] L.L. Bircomshaw, T.R. Phillips, The kinetics of thermal decomposition of ammonium perchlorate, J. Chem. Soc. (12) (1957) 4741–4747.

[129] A. Hermony (Makovky), A. Salmon, The catalytic decomposition of ammonium perchlorate, Eighth Symp. Combust., The Williams and Wolkins Co, Baltimore, 1962, p. 656.

[130] A. Galwey, P. Jacobs, High-temperature thermal decomposition of ammonium perchlorate, J. Chem. Soc. (1959) 837–844.

[131] K. Kurotani, Some studies on solid propellants. Kinetics and thermal decomposition of ammonium perchlorate/Sci. Rep. Aeronautical Research Institute, University of Tokyo, Re 372, Tokyo, 1962, p. 23.

[132] P. Jacobs, A. Kureishy, The effect of additives on thermal decomposition of ammonium perchlorate, in: Eighth Symp. Combust., The Williams and Wolkins Co, Baltimore, 1962, pp. 672–677.

[133] A.A. Shidlovsky, L.F. Shmagin, V.V. Bulatova, The effect of some additives on thermal decomposition of ammonium perchlorate, Proc. High School USSR Ser. Chem. Technology (8) (1965) C.533–C.538.

[134] F. Solymosi, E. Kirx, Effect of doping of cupric oxide catalyst on thermal decomposition of ammonium perchlorate, J. Catal. 1 (1962) 468–480.

[135] A. Said, The role of copper-chromium oxide catalysts on the thermal decomposition of ammonium perchlorate, J. Thermal Anal. 37 (1991) 959–967.

[136] Y. Wang, J. Zhu, X. Yang, L. Lu, X. Wang, Thermochim. Acta 437 (2005) 106–109.

[137] F. Solymosi, L. Revesz, Catalysis of reactions in the solid phase. Thermal decomposition of ammonium perchlorate in the presence of ferric oxide, Kinetika i kataliz. 4 (1963) 88–96.

[138] Z.Y. Ma, F.S. Li, A.S. Chen, H.P. Bai, Acta Chimica Sinica 62 (13) (2004) 1252–1255.

[139] H. Nakamura, M. Akiyoshi, Combustion catalyst of non-pollutant solid rocket propellant, J. Jpn. Explos. Soc. 63 (4) (2002) 163–168.

[140] S.A. Halawy, M.A. Mohamed, The role of MoO_3 and Fe_2O_3 in the thermal decomposition of ammonium perchlorate, Czechoslovak Chem. Commun. 59 (10) (1994) 2253–2261.

[141] H. Bazaki, Mechanism of combustion of high energy solid rocket propellant, J. Jpn. Explos. Soc. 56 (3) (1995) 105–111.

[142] A. Burcat, A. Caimon, I. Pelly, M. Steinberg, A study on the mechanism of thermal decomposition of ammonium perchlorate, Israel J. Chem. 6 (1968) 859–864.

[143] F. Solymosi, Initiation of ammonium perchlorate—ignition by chromic oxide titanium dioxide catalysts, Combustion Flame 9 (2) (1965) 141–148.

[144] W.A. Rosser, S.H. Inami, H. Wise, Thermal decomposition of ammonium perchlorate, Combustion Flame 12 (5) (1968) 427–435.

[145] F. Solymosi, S. Borcsok, J. Rasko, J. Kiss, The effect of composite propellant catalysts on the stability of $HClO_4$ and $HClO_4$–NH_3 system, Abstr. of 14th Symp. (Intern.) Combustion, The Combustion Institute Pittsburgh, University Park, PA, 1972, pp. 239–240.

[146] F. Shadman-Yazdi, E. Petersen, The effect of catalysts on the deflargation limits of ammonium perchlorate, Combust. Sci. Technol. 5 (1972) 61–67.

[147] P.W. Jacobs, A. Russel-Jones, Thermal decomposition and ignition of mixtures of ammonium perchlorate + copper chromite, in: Eleventh Symp. (Intern.) Combustion, The Combustion Institute Pittsburgh, Penn., 1966, p. 457.

[148] A.V. Boldyreva, B.N. Bezrukov, V.V. Boldyrev, On the mechanism of the influence of additives on thermal decomposition of ammonium perchlorate, Kinetika i kataliz. 8 (2) (1967) 299–303.

[149] A.A. Said, The role of supported palladium oxide on alumina on thermal decomposition of ammonium perchlorate, J. Mater. Sci. Lett. 11 (16) (1992) 1093–1095.

[150] K. Raha, S. Ramamurty, D.G. Patil, The catalytic effect of rare earth oxide on thermal decomposition of ammonium perchlorate, J. Thermal Anal. 35 (4) (1989) 1205–12112.

[151] A.V. Boldyreva, V.N. Mozzhova, The influence of additives on thermal decomposition of ammonium perchlorate, Kinetika i kataliz 7 (1966) 734–736.

[152] R.J. Acheson, P. Jacobs, Thermal decomposition of magnesium perchlorate and of ammonium perchlorate mixtures, J. Phys. Chem. 74 (1970) 281–288.

[153] F. Solymosi, L. Revesz, Thermal decomposition of ammonium perchlorate in presence of zinc oxide, Nature 192 (1961) 64–65.

[154] F. Solymosi, K. Fonagy, The effect of cadmium oxide and cadmium perchlorate on decomposition and ignition of ammonium perchlorate, in: Proceedings of the 11th International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1966, p. 268.

[155] A. Hermony (Makovky), A. Salmon, Thermal decomposition of ammonium perchlorate in presence of magnesium oxide, Bull. Res. Council Israel 9A (1960) 206–207.

[156] K.C. Patil, V.R. Pai Verneker, S.R. Jain, The role of lithium and magnesium perchlorate amines in ammonium perchlorate decomposition, Combustion Flame 27 (3) (1976) 295–298.

[157] K.C. Patil, V.R. Pai Verneker, S.R. Jain, Role of transition metal fluorides in ammonium perchlorate decomposition, Indian J. Chem. Sect. A 16A (2) (1978) 109–111.

[158] F. Solymosi, M. Rauics, Thermal stability of the ammonium perchlorate lithium perchlorate system, Combustion Flame 10 (1966) 398–399.

[159] T. Mutani, T. Niioka, Double flame structure in ammonium perchlorate combustion, in: 20th Symposium on Combustion, Pittsburgh, 1983, pp. 2043–2049.

[160] A.E. Simchen, Livia. Inbar-Rozem, Thermal analysis of ammonium perchlorate and of its mixtures with inorganic substance, Israel J. Chem. 6 (1968) 937–948.

[161] A.V. Boldyreva, R.P. Mitrofanova, V.V. Boldyrev, V.F. Balakirev, G.I. Chufarov, Yu.T. Pavlyukhin, The influence of spinel additives on the rate of thermal decomposition of ammonium perchlorate and combustion of model mix compositions based on it, Fizika goreniya i vzryva (5) (1975) 715–721, in Russian.

[162] F. Solymosi, L. Gera, S. Borocok, Catalytic pyrolisis of $HClO_4$ and its relation to the decomposition and combustion of NH_4ClO_4, in: Thirteen International Symposium on Combustion, Salt Lake City, 1974, pp. 1009–1016.

[163] P.P. Rastogi, A.P. Rao, V. Syal, Catalyzed and inhibited decomposition of ammonium perchlorate, AIAA J. 21 (9) (1983) 1351–1352.

[164] F. Solymosi, S. Borocsok, Ammonium perchlorate pyrolisis in a stream of perchloric acids vapor, Mag. Kem. Foly. 81 (7) (1975) 332–333.

[165] O.P. Korobeinichev, Yu.I. Karpenko, V.V. Boldyrev, Investigation of the kinetics and mechanism of sublimation of ammonium perchlorate using mass spectrometric thermal analysis, Izv. AN SSSR. Ser. khimicheskaya (7) (1970) 1557–1560, in Russian.

[166] R.P. Rastogi, A.P. Rao, V. Syal, Unified model of catalyzed and uncatalyzed decomposition of ammonium perchlorate, Combustion Flame 51 (2) (1983) 177.

[167] A.P. Rao, Studies on mechanism of catalyzed combustion of ammonium perchlorate composite solid propellant: Thesis Ph.D. in Chemistry, Department of Chemistry, University of Gorakhpur, India, 1984, p. 78.

[168] B. Dubey, N. Singh, J. Srivastara, A. Ojha, The catalytic behavior of $NiFe2xCrxO_4$ ($O < x > 2$) during thermal decomposition of ammonium perchlorate, polystyrene and their composite propellants, Indian J. Chem. Sect. A 40 (2001) 841–847.

[169] Z.G. Moghaddam, Abdolsamad, P. Haseni, The role of boron in thermal decomposition of ammonium perchlorate, Iranian J. Chem. Chem. Eng. 19 (2000) 40–42.

[170] J.N. Maycock, C.E. Payne, Lattice modification to control the burn rate of ammonium perchlorate propellants, Presented Western States Section of Combustion Institute, 29.04.1969, N.W.G. Chine Lake, California.

[171] F. Solymosi, J. Rasko, Thermal decomposition and ignition of ammonium perchlorate in the presence of zinc perchlorate, Z. phys. Chem. N.F., 1969, Bd. 67, S. 75–85.

[172] E.F. Khairetdinov, T.V. Mulina, V.V. Boldyrev, Nucleation mechanism during low-temperature decomposition of ammonium perchlorate, J. Solid State Chem. 17 (1976) 213–219.

[173] T.G. Devi, M.P. Kannan, B. Hema, Thermal decomposition of ammonium perchlorate. The effect of Ba^{2+}doping, Thermochim. Acta 285 (1996) 269–276.

[174] A.G. Keenan, R. Siegmund, Kinetics of the low-temperature thermal decomposition of ammonium perchlorate and its catalysis by copper ion, J. Solid State Chem. 4 (1972) 362–369.

[175] W.G. Schmidt, M. Stammler, Thermal decomposition of catalyzed ammonium perchlorate, Bulletin of 21st Interagence Solid Propulsion Meeting, vol. 1, June 1965, pp. 77–88.

[176] B.I. Kaidimov, D.P. Draganova, V.D. Tsvetkov, Effect of permanganate and chromate impurity ion on the rate of thermal decomposition of ammonium perchlorate, Godishnic of Sophia University, Chemical Deptartment 66 (1975) 455–466.

[177] A.M. Hor, P.W.M. Jacobs, Thermal depolarization in ammonium perchlorate crystals doped with sulfate and chromate ion, J. Solid State Chem. 24 (1) (1978) 33–40.

[178] E.N. Gareeva, V.V. Boldyrev, The influence of homophase additives on thermal decomposition of ammonium perchlorate, Kinetika i kataliz 9 (2) (1968) 425–428.

[179] J. Pelly, Thermal decomposition of doped ammonium perchlorate, Thermochim. Acta 55 (1) (1982) 22–34.

[180] V.I. Plyusnin, A.V. Boldyreva, V.V. Boldyrev, The influence of copper salts on thermal decomposition of ammonium perchlorate and burning rate of model mixtures, Kinetika i kataliz 10 (4) (1969) 761–764.

[181] I. Singh, R. Singh, Kinetics of the catalyzed thermal decomposition of ammonium perchlorate, Indian J. Chem., Sect. A 16A (5) (1978) 405–409.

[182] H. Nakamura, M. Akiyoshi, K. Sakata, Y. Hara, J. Jpn. Explosives Soc. 61 (3) (2000) 101–107.

[183] A.A. Shidlovsky, L.F. Shmagin, V. Bulanova, The effect of additives on thermal decomposition of ammonium perchlorate, Izv. VUZov. Ser. Khimiya i khimicheskaya tekhnologiya 8 (1965) 533–538, in Russian.

[184] K.C. Patil, Pai Verneker, A.P. Juin, Role of metal perchlorate additives on ammonium perchlorate decomposition, Combustion Flame 25 (1983) 387–388.

[185] S.M. Shen, S.W. Wang, Y.S. Chin, S.I. Chen, F.M. Chang, C.C. Huang, Thermal decomposition of cured GAP-AP propellants containing catocene, Thermochim. Acta 216 (1993) 255–266.

[186] F.M. Chang, C.C. Huang, S.M. Shen, S.I. Chem, Effect of iron-containing catalyst on thermal decomposition of propellant, J. Thermal Anal. 44 (1995) 405–417.

[187] B.K. Laptenkov, A.V. Raevsky, G.B. Manelis, S.A. Abrikov, On the effect of electric field on thermal decomposition of ammonium perchlorate single crystals, Dokl. AN SSSR. 250 (5) (1980) 1185–1187.

[188] B.K. Laptenkov, S.A. Abrukov, On the effect of electrostatic field on the growth rate of reaction centres during thermal decomposition of ammonium perchlorate, Physics of combustion and methods of investigation. A collection of papers, vol. 8, Cheboksary, 1978, pp. 34–40 (in Russian).

[189] I.G. Khaneft, Thermal decomposition of ammonium perchlorate treated with pulsed electric field, Abstracts. 10th All-Union Conference on kinetics and mechanism of chemical reactions in solids, June 1989, Chernogolovka, 1989, pp. 105–106 (in Russian).

[190] A.N. Kiselev, V.N. Plyusnin, A.V. Boldyreva, A.A. Deribas, V.V. Boldyrev, The influence of preliminary treatment of ammonium perchlorate with shock wave on the rate of its thermal decomposition and combusiton of mix compositions based on it, Fizika goreniya i vzryva (4) (1972) 545–547, in Russian.

[191] S.M. Reshetnikov, S.G. Voronchikhin, T.D. Korotkova, The influence of disperse state on thermal stability of ammonium perchlorate, Heat and mass exchange in aircraft engines, Kazan (2) (1979) 53–56, in Russian.

[192] Y. Hagikawa, Effect of grinding on thermal decomposition of ammonium perchlorate, Rikogeku Kenhyn Hokous 18 (3) (1980) 343–348.

[193] N.P. Loginov, S.M. Murashov, V.B. Epifanov, Decomposition of ammonium perchlorate subjected to vibration, Fizika goreniya i vzryva 25 (1) (1989) 64–68, in Russian.

[194] G. Pramond, M.P. Kannan, A comparative study of the effect of precompression on the thermal stability of potassium bromate, ammonium perchlorate and potassium permanganate, J. Indian Chem. Soc. 77 (5) (2000) 261–263.

[195] J.E. Balzer, C.R. Siviour, S.M. Walley, W.G. Proud, J.E. Field, Behaviour of ammonium perchlorate based propellants and polymer-bonded explosive under impact loading, Proc. Roy. Soc. 460 (2043) (2004) 781–806.

[196] G.B. Manelis, G.M. Nasin, Yu.I. Rubzov, Thermal decomposition and combustion of explosive compounds and powders, Moscow, Science, 1994, 126 pp. (in Russian).

[197] L.P. Smirnov, Chemical Physics of decomposition of energetic materials. Problems and prospects, Russ. Chem. Rev. 79 (II) (2004) 1121–1141.

[198] G. Kaupp, Supermicroscopy: AFM, SNOM and SXM, in: J. Davies, J. Pirmeestev (Eds.), Comprehensive Supramolecular Chemistry, vol. 8, Pergamon Press, Oxford, pp. 381–423.

[199] V.V. Boldyrev, Yu. Gaponov, N. Lyakhov, B. Tolochko, T. Shakhtshneider, A. Politov, M. Sheromov, Experience in use of synchrotron radiation in solid state chemistry studies, Nuclear Inst. Methods Phys. 261A (1) (1987) 192–199.

[200] Y. Gaponov, N. Lyakhov, B. Tolochko, M. Sheromov, V. Boldyrev, Thermal decomposition of crystal hydrates by the Laue method, Nucl. Inst. Methods Phys. Res. 282A (2–3) (1989) 698–700.

[201] K.J.D. Mackenzie, Solid state multinuclear NMR a versatile tool for studying the reactivity of solid system, Solid State Ionics 172 (1–4) (2004) 383–388.

[202] A.K. Cheatham, P. Day, Solid State Chemistry Technique, Oxford Science Publ., Clarendon Press, Oxford, 1991, pp. 1–398.