Праці Одеського політехнічного університету, 2015. Вип. 2(46)

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

ХІМІЯ
ХІМТЕХНОЛОГІЯ
CHEMISTRY
CHEMICAL ENGINEERING

UDC 661.52+662.2-391

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INFLUENCE OF NITROGEN DIOXIDE ON THE THERMAL DECOMPOSITION OF AMMONIUM NITRATE

І.Л. Коваленко. **Вплив нітроген діоксиду на термічний розклад амоній нітрату.** В роботі наведені результати експериментальних досліджень термічного розкладу амоній нітрату у відкритій системі в звичайних умовах і в атмосфері NO_2. Показано, що ініціатором розвитку самоприскорюваного циклічного процесу екзотермічного розкладу амоній нітрату є нітроген діоксид. Введення NO_2 ззовні в умовах неізотермічного експерименту призводить до зниження характеристичної температури початку самоприскорюваної деструкції на 50…70 °С. Методом ізотермічних витримок доведено, що в атмосфері нітроген діоксиду термодеструкція амоній нітрату при 210 °С має автокаталітичний характер (реакція нульового порядку). Зроблено припущення про можливість підвищення чутливості і детонаційних характеристик енергоконденсованих систем на основі аміачної селітри за рахунок введення добавок, що забезпечать більш ранню появу NO_2 в системі.

Ключові слова: амоній нітрат, термоліз, нітроген діоксид.

I.L. Kovalenko. **Influence of nitrogen dioxide on the thermal decomposition of ammonium nitrate.** In this paper results of experimental studies of ammonium nitrate thermal decomposition in an open system under normal conditions and in NO_2 atmosphere are presented. It is shown that nitrogen dioxide is the initiator of ammonium nitrate self-accelerating exothermic cyclic decomposition process. The insertion of NO_2 from outside under the conditions of nonisothermal experiment reduces the characteristic temperature of the beginning of self-accelerating decomposition by 50...70 °C. Using method of isothermal exposures it is proved that thermal decomposition of ammonium nitrate in nitrogen dioxide atmosphere at 210 °C is autocatalytic (zero-order reaction). It was suggested that there is possibility of increasing the sensitivity and detonation characteristics of energy condensed systems based on ammonium nitrate by the insertion of additives which provide an earlier appearance of NO_2 in the system.

Keywords: ammonium nitrate, thermolysis, nitrogen dioxide.

Introduction. Ammonium saltpeter as a source of ammonium nitrate (AN) is widely used as a major component of modern energy condensed systems — explosives which do no contain TNT for the mining industry. One of the factors that determine the evolution of detonation processes in energy condensed systems based on ammonium saltpeter is the rate of exothermic decomposition in the system which, in its turn, is caused by the parameters of ammonium nitrate thermal decomposition.

Literature review. It is known [1...3] that AN thermolysis may extend in several directions through a series of stages and, in general, can be described by the equations

DOI 10.15276/opu.2.46.2015.28

$$NH_4NO_3 = N_2O + 2\ H_2O, \tag{1}$$

$$NH_4NO_3=0{,}8\ N_2+1{,}8\ H_2O +0{,}4\ HNO_3, \tag{2}$$

$$NH_4NO_3 = N_2 + 0{,}5\ O_2 + 2H_2O, \tag{3}$$

$$NH_4NO_3 = NH_3 + HNO_3, \tag{4}$$

$$NH_4NO_3 = NO + 0{,}5\ N_2 + 2\ H_2O. \tag{5}$$

Standard thermodynamic parameters of the reactions (1)…(5) are shown in Table.

As can be seen from the table AN decomposition by reactions (1) ... (3) and (5) is thermodynamically probable under standard conditions but due to the kinetic difficulties it proceeds very slowly [3…5].

Concerning the endothermic AN decay to ammonia and nitric acid, according to the thermodynamic calculations [6] this process becomes noticeable at temperatures above 250 °C. At the same time formed on the equation (4) nitric acid at these temperatures does not exist in the molecular form and is decomposed into nitrogen dioxide, oxygen and water (calculated degree of conversion at 250 °C exceeds 99 % [6])

$$2HNO_3=2\ NO_2+0{,}5\ O_2+H_2O. \tag{6}$$

The standard thermodynamic parameters of the ammonium nitrate decomposition

№ of reaction equation	ΔH_{298}^0, kJ/mol	ΔG_{298}^0, kJ/mol	K_{298}^0
1	–361,80	–169,156	$4{,}5\cdot10^{29}$
2	–218,37	–275,193	$1{,}6\cdot10^{48}$
3	–206,17	–341,879	$8{,}6\cdot10^{59}$
4	146,480	87,542	$4{,}2\cdot10^{-16}$
5	–269,30	–185,701	$3{,}6\cdot10^{32}$

As shown in [6], AN thermal degradation in the temperature range of 200...250 °C occurs according to the first order equation. At higher temperatures the self-accelerating cyclical process is implemented. It can provide explosive decomposition of AN under the conditions of complicated heat removal. Thus it was suggested that the nitrogen dioxide which reacts with the ammonium nitrate by the reaction

$$NH_4NO_3+2NO_2=N_2+2HNO_3+H_2O \tag{7}$$

is the initiator of decomposition.

Reaction (7) is followed by significant release of heat (ΔH^0_T=–334,8 kJ/mol). This provides a heating of the entire system and the decomposition of resulting nitric acid according to reaction (6) with the release of new portions of NO_2 providing the cyclicity of process.

Aim of the Research is to confirm the effect of nitrogen dioxide on the nature and intensity of ammonium nitrate thermolysis in an open system.

Main Body. The nature of thermal decomposition of ammonium nitrate is investigated by differential thermal analysis (setting TERMOSKAN-2, Scientific and Production Enterprise “Analitpribor”, St. Petersburg) in open quartz cuvette 5 mm in diameter at a scan rate of 20 deg/min. Sample weight is 50 mg, standard is a sealed ampoule with Al_2O_3. Analysis of gaseous products of AN thermolysis is carried out using gas analyzer-signaling “Dozor-SM” (Scientific and Production Association “Orion”, Kharkiv). The selection of gas for analysis is implemented in differential thermal analysis process. The kinetics of ammonium nitrate mass loss is measured in a series of isothermal excerpts for samples weight of 5 g.

In the measurements with the feed of air or of nitrogen dioxide gas is fed directly into the open cuvette to the middle of height at a rate of 2 l/h. All connecting tubes of nitrogen dioxide feeding are made of fluoroplastic. Nitrogen dioxide is received by reacting the copper with concentrated nitric acid.

Thermogram of ammonium nitrate decomposition in an open system and the results of analysis of the gaseous products thermolysis are shown at Fig. 1.

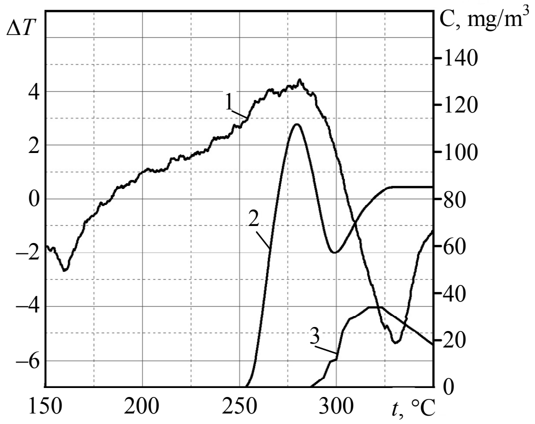
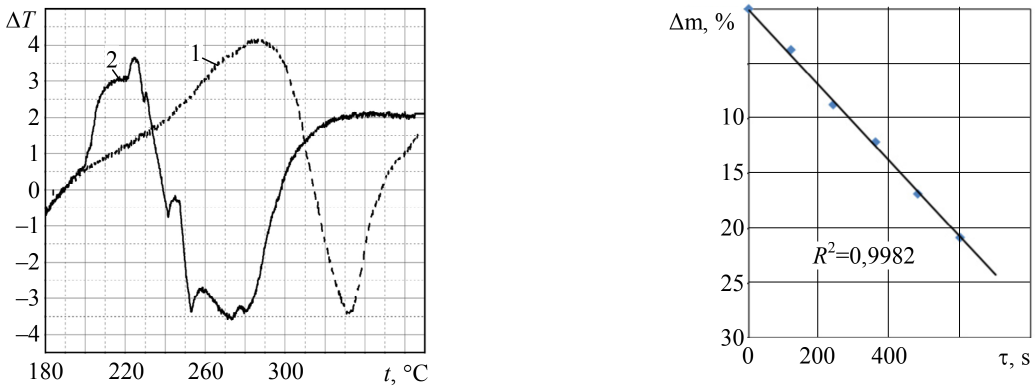


Fig. 1. Thermal decomposition of ammonium nitrate in an open system: differential thermal analysis — curve of ammonium nitrate thermolysis (1); NO_2 concentration (2); NH_3 concentration (3)

Thermal decomposition of the ammonium nitrate with feeding the nitrogen dioxide into the cuvette is studied to estimate the alleged initiating action of nitrogen dioxide. Thermolysis is carried out in two reproducible modes. At the first one into the cuvette at the constant rate at temperature up to 200 °C firstly the air is supplied and then from 200 to 350 °C with the same rate the nitrogen dioxide is supplied. The second mode is represented by the base of comparison — thermolysis of AN feeding into the cuvette at the entire range of air temperatures. The thermograms are shown at Fig. 2, *a*.

The dynamics of AN mass loss in the NO_2 atmosphere in a series of isothermal exposures at 210 °C is also determined (Fig. 2, *b*).



a *б*

Fig. 2. Influence of NO_2 on the nature of thermal decomposition of ammonium nitrate: differential thermal analysis — AN decomposition curves (a): with the air supply (1), with combined supplying of gas: air (up to 200 °C) and NO_2 (200...350 °C) (2); AN weight loss in the presence of NO_2 at 210 °C (b)

Results. Fig. 1 (curve 1) shows that the nature of dependence obtained by heating NH_4NO_3 in open system is similar to differential thermal analysis (DTA) curves observed in sealed ampoules [3]. From the t=200 °C the system starts an exothermic process, due to decomposition of NH_4NO_3 with forming N_2O and NO. At t=250 °C the curve has an inflection, indicating the change in the process. At the same temperature nitrogen dioxide excretion is fixed in the system.

Thus, it can be assumed that the exothermic maximum at temperatures 250…280 °C is a consequence of the interaction of ammonium nitrate with nitrogen dioxide (7), as well as interaction of NO_2 with formed by (4) ammonia:

$$NH_3+0,75\ NO_2 = 0,875\ N_2+1,5\ H_2O.$$

This maximum is not so explicit as in close systems [3] and while increasing of temperature it is replaced by deep endothermic minimum due to the prevalence of decay reaction of NH_4NO_3 (4) which goes with the absorption of heat.

At the same time, the compensation of endoeffect due to the interaction of ammonia and nitrogen dioxide in an open system does not happen in its entirety. This interaction occurs in the gas phase at a certain distance from the recording thermocouple junction, providing a certain error to the mapping of differential temperature at the range 280…350 °C.

Analysis of the set of experimental curves of ammonium nitrate thermolysis shows that the form of mapped DTA curve significantly depends on several factors, the main ones are: rate of temperature change, sample weight, AN humidity, diameter of the measuring cuvette. Changing of these parameters affect the height and location of the main exothermal peak, the shape and depth of subsequent endoeffect, as well as the ratio between the heights of the aforesaid extrema.

Thus, changing the heating rate from 1 to 20 deg/min (discretely 1,0; 2,5; 5,0; 7,5; 10,0; 20,0 deg/min) increases the mapped temperature difference between two extrema under consideration to a number of: 0,5; 1,2; 2,3; 3,6; 4,1; 8,5 deg. accordingly.

The ratio between the extrema of AN thermolysis also significantly depends on the diameter of the measuring cuvette at all other terms being equal.

So upon AN thermolysis in the cuvette of 5 mm in diameter at the temperature range 280…350 °C the signal of measuring thermocouple detects mainly endothermic processes corresponding to reactions (4) and (6), showing almost no exothermic processes implemented in the gas phase.

Increasing the diameter of the measuring cuvette from 5 to 7 mm and 9 mm leads to decrease of the temperature delta between the tops of exothermic and endothermic peaks of AN from 8,5 to 6,2 and 5,5 deg. accordingly.

But, as it is shown in [7], with increase of cuvette diameter and heating rate the growth of the temperature gradient occurs between the center and the surface of sample. Thus, when cuvette diameter is 2 mm and heating rate is 20 deg/min the temperature difference between the surface of sample and its center does not exceed 0,17...0,8 deg., and at 5 mm — 1...3,5 deg. [7]. These gradients even allow to consider the temperature field in the sample as uniform. Increasing the diameter of cuvette to 10 mm can provide the growth of temperature gradient in the sample to 20 deg. [7].

Since the main interest of this work is the area of the exothermic process (from melting of AN to the top of maximum exothermic effect), the predominant factor in the choice of the measuring cuvette diameter has become the optimum value of the temperature gradient, permitting the use of hypotheses about a uniform temperature field in the sample. Accordingly, the thermal decomposition of AN in dynamic mode is performed in cuvettes with diameter of 5 mm.

As can be seen from Fig. 2, *a*, while supplying nitrogen dioxide into the measuring cuvette the thermogram character is substantially changed. NH_4NO_3 intense exothermic decomposition starts at the temperature of 200 °C by reaction (7), which has a self-accelerating cyclic nature, and does not require prior endothermic decomposition of ammonium nitrate into ammonia and nitric acid. It is noteworthy that kinetics of the process is fundamentally changing in this case. If under normal conditions the decomposition of ammonium nitrate in the temperature range 210…250 °C can be described by the kinetic equation of the 1st order [6], then in the presence of nitrogen dioxide (Fig. 2, *b*) the dependence of mass loss on time is linear (zero order reaction). It is a confirmation of the initiating action of nitrogen dioxide on the nature and intensity of the exothermic decomposition of ammonium nitrate.

Thus, the exothermic decomposition of energy condensed systems based on ammonium saltpeter can be intensified by insertion of additives to such systems providing an earlier appearance of nitrogen dioxide. Reducing the temperature of the beginning and increasing the intensity of thermal degradation increase the sensitivity and detonation characteristics of energy condensed systems.

Conclusions. Intensive exothermic decomposition of ammonium nitrate occurs during the formation of nitrogen dioxide in the system. The insertion of NO_2 from outside reduces the temperature of thermolysis beginning on the 50…70 °C and runs the self-accelerating cyclic thermal decomposition process, which is capable to ensure the AN expansion on the mechanism of thermal explosion under the complicated heat sink.

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Received May 29, 2015