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THERMOLYSIS OF AMMONIUM NITRATE/POTENTIAL DONOR OF ACTIVE CHLORINE COMPOSITIONS

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The thermal stability of the ammonium nitrate (AN)/sodium salt of 1,3-dichlor-2,4,6-trioxo-1,3,5-triazacyclohexane (DC) composition has been studied. The factors of influence on the rates of reactions in the composition, namely, a water content, composition wetting methods, a dispersion of composition components, sample mass values, have been examined. The water presence in the composition reduces its thermal stability. The mechanism includes the partial dissociation of AN to HNO_3 and NH_3 and the hydrolysis of DC with the formation of some unstable Cl-containing compounds (chloramines, nitrogen chloride). The reaction of ammonium cation with active chlorine has been found to give rise to the explosion of the AN/DC composition. Such a situation is typical for other ammonium salt/DC compositions.

Keywords: *ammonium nitrate, composition, explosion, kinetics, mechanism, sodium salt of 1,3-dichlor-2,4,6-trioxo-1,3,5-triazacyclohexane, thermal decomposition*

Introduction

AN is a well-known solid oxidant. Commonly, AN is used as a fertilizer or as a component of industrial explosives. AN has a high thermal stability [1]. So, in contrast with most explosives AN does not need in special rules of manipulation. But there are some materials forming with AN dangerous compositions of low stability. Among these materials one can find mineral acids, sulphur, some inorganic chlorides, salts of transition metals. Documents regulating the rules of AN manipulation exclude AN contacts with these materials. The list of these materials together with the analysis of the main reasons of AN stability decrease one can find in [2–5]. Among these materials, the destabilizing effect of chloride has been studied in great detail [6–16]. Nevertheless, chloride is sometimes added to fertilizer formulations and to permissible AN explosives. Many researchers have noted the synergism between HNO_3 and Cl^- [8, 9, 11, 12], and several claimed acid is essential for chloride catalysis, but the acid may come from the decomposition of AN, itself [13]. It has been suggested [7, 10] that the key step to the destabilization is

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

It has been noted that there must be an initial excess of acid to allow formation of nitronium ion [11]. On the other side, the studies of thermal stability of compositions of AN with organic chlorides, that can be donors of active chlorine in definite conditions, are practically absent. Recently three works on physicochemical aspects of spontaneous explosion of AN in the contact with donor of active chlorine have been published [17–19] in connection with the accident in Toulouse, France in 2001. The investigation of kinetics and mechanism of AN reaction with these materials are of practical and scientific interest. This reaction can proceed in definite conditions in the mode of runaway, and data on kinetics and mechanism of this reaction are necessary to evaluate and predict these conditions.

Experimental

Materials

DC was selected as a model compound for experiments with AN. DC is a potential chlorine donor because it has two bonds N–Cl.

DC of trademark ONIACHLOR 60-G1500 (France) (with particle size distribution: 1.25 mm and more – 7%, 0.63–1.25 mm – 80%, 0.25–0.63 mm – 11%, and less than 0.25 mm – 2%) was used. DC particles have a well developed system of pores and capillaries. They can absorb large quantities of water (up to 15 mass%) without the loss of running properties.

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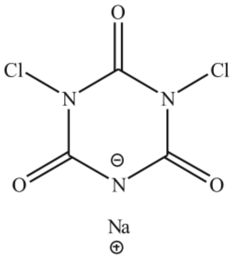

(DC)

French-made industrial grade, Grand Paroisse Co., AN was used. It consisted of compact porous granules (size of 0.1–0.3 cm, a granulometric density about 0.71 g sm^{-3}). These granules strongly absorb water, so most of water can be located on the granule surface. When the content of surface water reaches of 3–5 mass%, the granules stick together. Further increase of the surface water content results in covering the surface of a granule by the film of a saturated water solution of AN.

Chemically pure (Russian national standard) ammonium chloride (AC) and potassium nitrate (PN) were used.

Unless otherwise stated, both substances were used as-received. Before experiments the components were carefully dried up. In especial experiments ground substances were used. Grinding was performed with a mortar and pestle.

Moistening reagents was carried out by a direct water addition or by sample holding in air of 90% humidity.

Kinetic measurements were made by methods of calorimetry, thermogravimetry and manometry. Reaction products were identified by mass-spectrometry and IR spectrometry.

Methods

Thermogravimetry

Thermogravimetric experiments were carried out using electronic automatic thermobalance ATV-17M [20] designed and made in the Institute of Problems of Chemical Physics, Russian Academy of Sciences. A reaction vessel – a quartz glass of a cylindrical form (an internal diameter of 6 mm, a wall thickness of 0.1 mm) – was hung on the thin (of 0.1 mm) platinum filament. Experiments were carried out in air at linear heating with the rate of 4°C min^{-1} and at constant temperatures.

Manometry

For manometric measurements we used Bourdon glass manometers (reaction volume of 5–6 cm^3) with sensitive membranes [21]. Sample mass was of 100–150 mg. When we need to carry out our experiments in the presence of water the last was contained in the separate glass. So, water could be transported only as steam. In our experiments 100% humidity was provided by water surplus.

Isothermal microcalorimetry

The differential automatic calorimeter DAC-1 [22] designed and made in the Institute of Problems of Chemical Physics, Russian Academy of Sciences was used. It enables the heat release rate over the range of 10^{-5} to 1 Wt to be measured in a broad range of temperatures up to 400°C. Reagents were thrown down in a glass ampoule in two different manners: so AN was under or above DC. The area of an ampoule internal section was of 0.3 cm^2. Actually AN and DC contacted one to another at the points of a contact of spherical AN granules and small DC particles. It was impossible to determine the contact area so the heat release rates were calculated per the unit (1 cm^2) of the area of the geometric surface between AN and DC.

Mass-spectrometry

Mass-spectrometer MH1201-V (Stock Company 'Sumskoi Pribor', the Ukraine) was used to identify gaseous reaction products. Electrons energy was of 50 eV, accelerating voltage was of 5000 V.

IR spectrometry

IR spectra of condensed reaction products were recorded on a Specord 75-IR spectrophotometer in KBr pellets in a frequency range of 400 – 4000 cm^{-1}.

Results and discussion

Thermogravimetry

The initial experiments with AN and DC revealed their high thermal stability. When AN was heated linearly (Fig. 1, curve 1) no thermal decomposition was detected up to 170°C. A rapid AN decomposition was observed at the temperatures above 200°C. In the process of DC heating (curve 2) we observed a mass loss (2.2%) in the temperature range of 80–100°C. Water (≈0.5 mass%) and some compounds of a high molecular mass (≈1.7 mass%) were the products of this process. Up to 190°C DC is thermally stable. At the temperatures above 200°C DC decomposed with high rates. In contrast to individual AN and DC their composition (50:50 mass%) began to release the products at the temperatures above 90°C (Fig. 1, curve 3). At 145°C the process was sharply accelerated and at 150.5°C the composition was ignited with 20 mass%

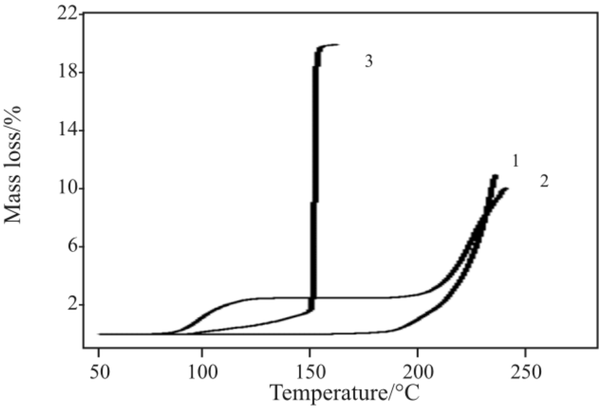

Fig. 1 TG curves of 1 – AN, 2 – DC and 3 – AN/DC composition in the air. Sample mass of 10.0–10.2 mg. Heating rate of 4°C min^{-1}

loss. Simultaneously we observed a considerable composition volume increase (the final volume was 5 times more than the initial one). It is a result of a reaction mass swelling up.

As it is shown in Fig. 2 at 140°C the components of the AN/DC composition (50:50 mass%) react with moderate rates (Fig. 2, curve 1). The total time of the process was about 40 min. AN and DC grinding gave rise to a sharp reaction rate increase. The AN/DC composition consisted of grinding components was ignited at 140°C after 25 s (Fig. 2, curve 2). It is interesting to note that a mass loss (≈20%) was the same as in the previous experiment (Fig. 1, curve 3). Moistening composition and grinding its components led to the process acceleration. Even without grinding the composition of dry DC and moistened AN (10.2 mass% H_2O) began to decompose at 47°C.

To understand the mechanisms of chemical reactions in the AN/DC composition we carried out some experiments with two model systems: ammonium chloride (AC)/DC and sodium nitrate (SN)/DC. When heated linearly (4°C min^{-1}), the composition of AC (8 mg) and DC (8 mg) was not ignited. Thermal stability of the AC/DC composition was not lower than that of individual AN and DC. An addition of small quantities of water (3 mass%) into the AC/DC composition led to an intensive heat release and foaming of the AC/DC composition. So the AC/DC/H_2O system is very similar to the AN/DC/H_2O composition. The SN/DC and SN/DC/H_2O systems were wholly inert at heating up to 200°C. While the SN/DC/H_2O composition thermolysis some DC was hydrolyzed. SN did not react when the SN/DC/H_2O composition was heated.

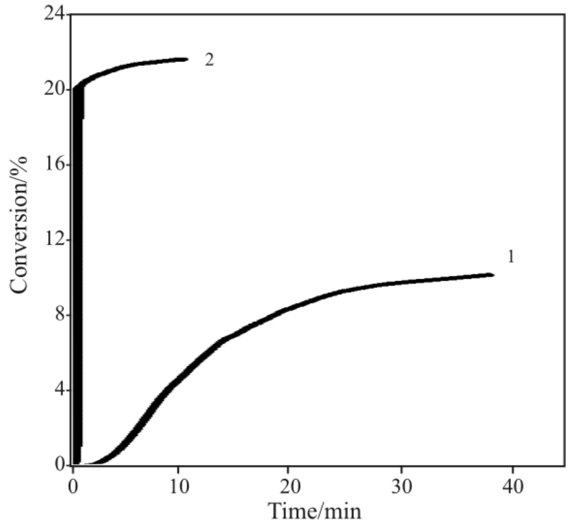

Fig. 2 Kinetics of chemical reaction in AN/DC composition (50:50 mass%) in air at 140°C . 1 – as-received components, 2 – ground components. Sample mass of 20 mg

Manometry

To elucidate mechanisms of the reactions it is important to clear up the question: either AN and DC react only between themselves or this reaction occurs with gaseous decomposition product participation. To clear up the question we carried out some special manometric experiments. AN and DC were disposed in Bourdon manometer separately under the condition of 100% humidity. The vessel was placed into the thermostat at 20, 40, 60 and 80°C. A very slow formation of gaseous products was noticeable at 80°C. A special experiment when individual DC was heated at 80°C in Bourdon manometer at 100% humidity condition proved that an observed gas evaluation in a ternary AN/DC/H_2O composition (all components were separated) was a result of a DC hydrolysis. Water and an environment humidity influenced compatibility AN with DC. It is well known that AN is a highly hydrophilic compound. When AN was in air with 100% humidity it absorbed water, which formed finally an AN solution in water. A reaction of H_2O with DC was a single reason of reducing AN/DC composition stability. So if AN and DC particles are disposed thus that, at first, water contacts with AN, the last absorbs water and protects DC. If, at first, water contacts with DC particles the chemical reaction is possible and as a result we observe a low compatibility of AN with DC. In a typical experiment the grinding DC (53 mg) was placed at the bottom of the glass cylindric vessel (an internal diameter of 5 mm), then a water drop (9 mg) was placed on the DC layer and finally the AN layer (52 mg) was disposed on the top of the composition (the water content was 8.6 mass%). The chemical reaction in this composition started immediately at 18°C. The initial rate of gas formation at 18°C was 0.42 mL g^{-1} min^{-1}. Initial rates of the process at 30 and 40°C were 1.1 and 2.5 mL g^{-1} min^{-1}. The value of 'effective' activation energy of the reaction in the AN/DC/H_2O composition was equal to 76.1 kJ mol^{-1}.

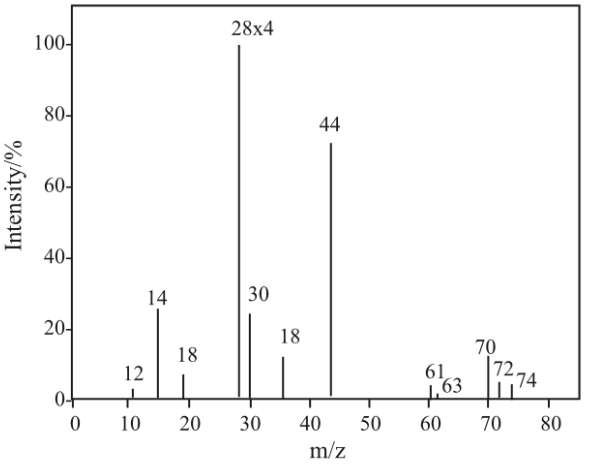

Fig. 3 Mass-spectrum of volatile at 25°C products of AN/DC (50:50 mass%) composition thermolysis (116°C, 30 min)

Mass-spectrometry

Mass spectrum of gaseous products of the AN/DC composition thermolysis is demonstrated in Fig. 3. The thermolysis at 116°C for 30 min was accompanied by formation of N_2, N_2O and H_2O (typical products of AN thermal decomposition) and also HCl, Cl_2 and very small quantities of Cl–C≡N.

IR spectrometry

According to IR spectroscopy data isocyanuric acid and its derivatives were formed as condensed products of the AC/DC/H_2O composition thermolysis. In the case of the AN/DC/H_2O composition these products were not observed. It is important to note that Cl^- ions (6 mass%) were detected among condensed products of the AC/DC/H_2O composition ignition.

Isothermal microcalorimetry

For the moistened AN/DC compositions the chaotical oscillations of the reaction rate in the course of reaction were observed. Probably, the reason of this phenomenon was a change of the real area of surface of AN contacts with DC in the course of the reaction. The former contacts lost and the new ones formed. The rate changes observed in the case of moistened DC may be also the result of different rates of a water transport in the DC capillary system. To obtain more correct data on the heat release rates we found average values of experimental reaction rates. For this purpose a rate curve was integrated in a certain time interval. Then the calculated heat was divided by the time of integration.

For a layering composition of 0.1 g AN and 0.1 g DC without humidification of components at 25°C the very small heat absorption rate ($\sim 2–4\cdot 10^{-2}$ mW cm^{-2}) connected with vaporization of water, which was contained in the initial samples, was observed. The possible heat release rate due to interaction of AN and DC must be lower than this level. The very small heat absorption rate was also observed when 3.7 mass% of water was added to DC. When 7 mass% of water was added to DC the initial peak of a heat release rate of 22 mW sm^{-2} was observed. Then the heat release rate decreased so fast that in 10 min it was twenty times smaller of the initial value. In 3 h the heat release was about 5.3 J sm^{-2}. The measured initial rate of DC hydrolysis was about 1.5 mW sm^{-2}, after 6 min the rate was 10 times smaller, and after 25 min it approached to zero. The experiment results with direct water additions are listed in Table 1. The data on sample wetting by their exposure in air of a definite humidity are listed in Table 2.

When AN surface wetted, the oscillations of the rate in the course of the reaction were practically not observed as AN and DC granules were strongly adhered one to another due to the presence of significant amounts of water on the AN surface. In these conditions, the reaction proceeded on the practically constant contacts. The rate decrease determined by decrease of reactant contents on the contacts due to the replacement of some DC by its hydrolysis product, which did not contain chlorine.

The heat release rate did not depend on masses of components (experiments No. 3–8), and it was proportional to the area of a geometrical surface of a contact of components. In ampoules with a different inner diameter (experiments No. 56, 57) the heat release rate decreased in 1.2 times at decreasing a sectional area of the ampoule in 1.1 times. The heat release rate also increased essentially at preliminary intermixing AN and DC samples in the bottle (experiments No. 8 and 9, 52 and 53). The heat release rate for preliminary intermixed components (mass of 0.1 g) was 3 times higher than that in the layer system without intermixing. The greater a zone of intermixed components was, the higher the heat release rate was. The process spread all over the volume of intermixed AN and DC.

In Fig. 4 the dependence of the average heat release rate (W cm^{-2}) on water content in the AN/DC composition is demonstrated. DC was moistened in this experiment. Up to 4.1 mass% H_2O content in DC the process occurred with heat absorption because of an endothermal H_2O evaporation prevailed over an exothermal hydrolysis and oxidation. When water content in DC was of 4.1–6.4 mass% the exothermal processes predominated and we observed the heat release. The heat release rates did not depend on the water content in DC above 6.4 mass%. Probably, most part of water in DC disposed inside DC particles

Table 1 Results of microcalorimetric experiments at a direct water addition to the samples

No.	T/°C	m_{AN}/g	m_{DC}/g	Component below	$(dQ/dt)_{t=0}$ /mW cm^{-2}	Q/J cm^{-2}
2	25.0	0.0	0.106+4.1% H_2O	DC	1.5	0.96 in 38.5 min
3	64.7	0.020	0.096+6.7% H_2O	DC	28	59 in 160 min
4	64.7	0.046	0.103+5.6% H_2O	AN	31	128 in 275 min
5	64.7	0.041	0.101+6.8% H_2O	DC	33	109 in 155 min
6	64.7	0.114	0.101+12.3% H_2O	DC	35	91 in 165 min
7	64.7	0.042	0.102+14% H_2O	AN	39	82.6 in 182.5 min
8	64.7	0.252	0.103+12.7% H_2O	DC	27	100 in 200 min
9*	64.7	0.103	0.102+13.7% H_2O	DC	83	60 in 43.5 min
10	53.3	0.105	0.104+14.5% H_2O	AN	13.6	22 in 50 min
11	53.3	0.099	0.102+13% H_2O	DC	14.2	75 in 262.5 min
12	53.3	0.102	0.100+13.8% H_2O	AN; DC grinded	6.7	64 in 205 min
15	53.3	0.101+7.1% H_2O	0.105	AN	18	27 in 200 min
16	47.5	0.103	0.102+12.7% H_2O	DC	8.6	70 in 367.5 min
18	47.5	0.100+10.0% H_2O	0.106	AN	52	105 in 120 min
19	41.0	0.041	0.097+12.4% H_2O	DC	6.1	140 in 480 min
20**	41.0	0.0	0.101+12.5% H_2O	–	1.9	4.7 in 420 min
21**	41.0	0.018	0.101+8.0% H_2O	DC	5	150 in 490 min
22	37.0	0.105	0.102+15.1% H_2O	AN	4.4	44 in 270 min
24**	37.0	0.100+12.6%H_2O	0.102	AN	19.4	280 in 970 min

*components were intermixed in the bottle; **ampoule sealed

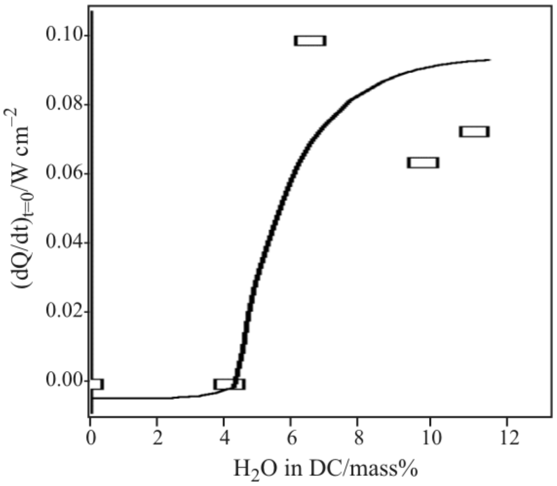

Fig. 4 The dependence of the initial heat release rate on the water content in AN/DC (moistened) composition

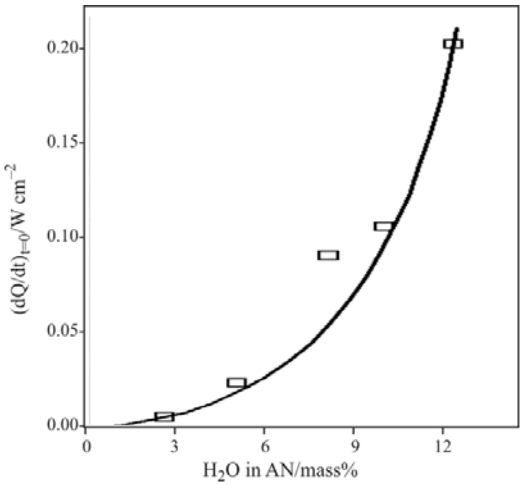

Fig. 5 The dependence of the initial heat release rate on the water content in AN(moistened)/DC composition

but the water content on the DC particle surface was close to a constant value.

Another situation was observed when the AN/DC composition contained a preliminary moistened AN (Fig. 5). The exothermal processes dominated at any water content in AN. The comparison of two compositions: AN (moistened)/DC and AN/DC (moistened) reveals that the heat release rates were strongly dependent on the water content in AN. When AN was moistened the heat release rates were significantly greater (5–10 times). In contrast to DC, most part of water disposed on the AN granule surface. The greater rates of the exothermal processes in the case of the moistened AN could be explained by the greater quantities of water which takes part in a DC hydrolysis and by the greater concentration of products of AN dissociation equilibrium (HNO_3 and NH_3) at the places of AN and DC contacts. From results of experiments

Table 2 Results of microcalorimetric experiments at introducing water by the exposure of the samples in wet air

No.	T/°C	m_{AN}/g	m_{DC}/g	Component below	$(dQ/dt)_{t=0}$ / mW cm^{-2}	Q/J cm^{-2}
27	64.2	0.1037	0.0892+4.1% H_2O	AN	–0.52	–7.6 in 450 min
28	64.7	0.09915	0.0851+11.1% H_2O	AN	28	45.7 in 114 min
29	64.7	0.0974+5.1% H_2O	0.971	AN	55.4	24.1 in 96 min
30	64.7	0.0943+8.2% H_2O	0.098	AN	178	102 in 150 min
31	74.0	0.10235	0.0901+6.4 % H_2O	AN	100	32.4 in 231 min
32	74.0	0.102	0.0965+9.7% H_2O	AN	64	22 in 48 min
33	64.0	0.0911+2.69% H_2O	0.10475	AN	6.8	2.7 in 15 min
34	74.0	0.0983	0.0883+11.1% H_2O	AN	72	18 in 10.2 min
35	74.0	0.1063	0.0992+4.1% H_2O	AN	–3.8	–5.0 in 228 min
36	54.5	0.0975+5.1% H_2O	0.10055	DC	7.69	13.6 in 87.6 min
37	60.6	0.0923+5.1% H_2O	0.103	DC	15.0	11.0 in 60 min
38	54.5	0.1004	0.0875+11.1% H_2O	DC	22	72.8 in 198 min
39	60.6	0.09425	0.09247+11.1% H_2O	DC	33	76 in 150 min
40	60.2	0.0898+5.1% H_2O	0.1045	AN	32	10.2 in 25.2 min
41	45.3	0.0911+5.1% H_2O	0.105	AN	22	14.6 in 100.2 min
42	50.3	0.0943+5.1% H_2O	0.10115	AN	168	12.0 in 100.2 min
43	45.3	0.0931+12.37% H_2O	0.103	AN	246	117 in 199.8 min
44	49.3	0.1022	0.0826+11.1% H_2O	AN	13	45.7 in 207.6 min
45	49.3	0.10065	0.064+11.1% H_2O	AN	5	53.2 in 252 min
46	45.3	0.0859+8.2% H_2O	0.099	AN	85	64.2 in 225 min
47	45.3	0.1022+2.69% H_2O	0.1006	AN	5.6	6.2 in 84 min
48	45.3	0.0945+10.0% H_2O	0.10265	AN	111	88 in 267 min
49	39.3	0.0974+5.1% H_2O	0.10635	AN	9.8	10.6 in 300 min
50	33.6	0.0879+5.1% H_2O	0.1089	AN	18	14.0 in 225 min
51	33.6	0.0957+5.1% H_2O	0.0910+13.0% H_2O	AN	5.6	53.7 in 420 min
52	25.4	0.0938+5.1% H_2O	0.0999	AN	9.6	14.3 in 174 min
53*	25.4	0.0873+5.1% H_2O	0.1046	AN	26.9	15.5 in 186 min
54**	25.4	0.10175	0.1042	AN	342	145 in 297.6 min
55	25.4	0.0957	0.0157+0.2580 g H_2O	5.75% solution of DC in H_2O	2.1	11.9 in 360 min
56	25.4	0.0882+5.1% H_2O	0.1053	AN	7.8	7.1 in 402 min
57	25.4	0.0948+5.1% H_2O	0.9965	AN	7.3	8.4 in 276 min
58	74	0.0932	0.10065	AN	–3	

*components were intermixed in the bottle; **0.1483 g of water was poured into the ampoule with the composition

No. 50 and 51 it has been seen that humidifying both components even decreases the heat release rate that in contrast with using AN humidified only. It is probable that the lower water content on the DC surface in contrast to AN can not change the total water content in the places of the AN and DC contacts. The vaporization of water from DC humidified reduces the total heat release rate. These results demonstrate that AN humidifying is most dangerous. Thus, calorimetric experiments supported the important role of water in the reaction of AN with DC.

In the experiment with an open ampoule the process stopped because of evaporation and some part of AN and DC did not react. When the ampoule was sealed (experiments No. 21 and 24) all the gaseous reaction products and water were retained in the reaction zone so we observed a process self-acceleration and its completion. The observed self-acceleration of the process was a result of a water content increase as the reaction of AN with DC accompanied by ammonium ion oxidation with water formation. The total heat of the process was 2.2 kJ g^{-1} AN. This value was higher than the total heat of AN decomposition. It means that stoichiometry of the process differs from stoichiometry of the AN decomposition and that DC was active in oxidation reactions. When one of the components was moistened and the reaction composition was placed in the sealed ampoule, water in quantities sufficient to hydrolyze DC was disposed all over the reaction composition. AN was accessible to gaseous products of a DC hydrolysis so an AN oxidation by these products took place all over the volume. As a result the reaction heat calculated per the unit of ampoule section area was proportional to AN mass.

The dependence of average values of the heat release rate for an initial reaction stage in the case of the AN/DC (preliminary moistened) layer composition with water content of 12–14 mass% on the temperature (interval 37.0–64.7°C) was described by the equation

$$(\mathrm{d}Q/\mathrm{d}t)_{\mathrm{t=0}}=8.5\cdot 10^{8}\exp(-67000/RT)\ \mathrm{W\ cm^{-2}}$$

This dependence is demonstrated in Fig. 6.

The heat release for the AN (moistened)/DC composition is the process of the first kinetic order (up to 70–80% conversion) in the temperature range of 25.5–66.0°C. Arrhenius dependence of the initial heat release rate is shown in Fig. 7. This dependence is described by Arrhenius equation

$$(\mathrm{d}Q/\mathrm{d}t)_{\mathrm{t=0}}=1.35\cdot 10^{7}\exp(-54000/RT)\ \mathrm{W\ cm^{-2}}$$

The lower value of activation energy for the composition with preliminary moistened AN in comparison with that of the AN/DC (preliminary moistened) composition is probably a result of whole water disposition on the AN granule surface.

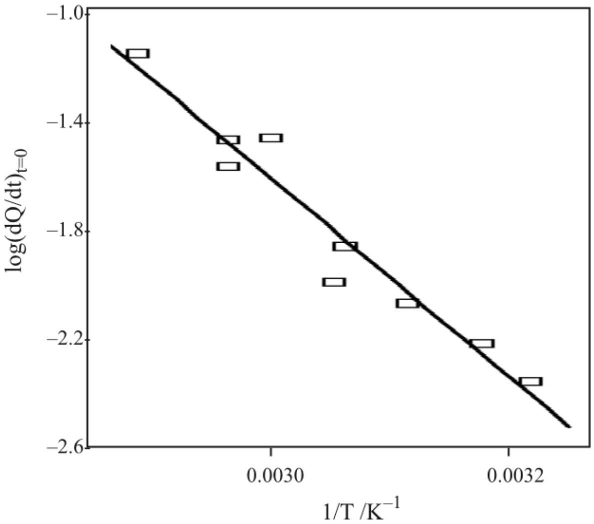

Fig. 6 Arrhenius dependence of the initial heat release rate (average value) for AN/DC (preliminary moistened) composition

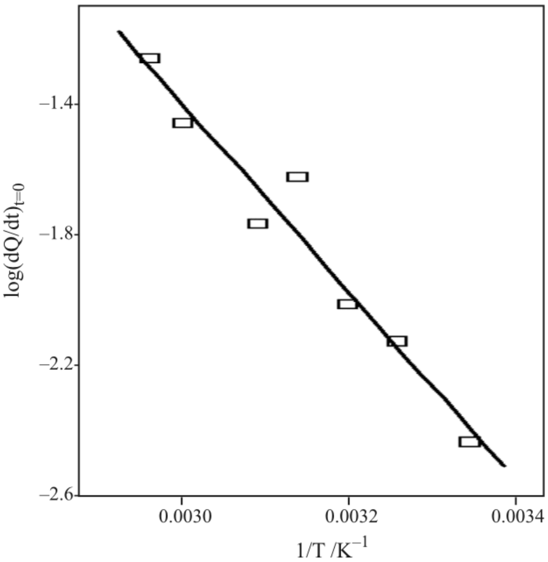

Fig. 7 Arrhenius dependence of the initial heat release rate (average value) for AN (preliminary moistened)/DC composition

To understand correctly kinetic regularities of reaction it is necessary to define the stage of the complex process which determines its rate. Considering an easy hydrolysis of DC by water with the release of chlorine and the necessity of water for interaction AN and DC, one can propose that namely the hydrolysis of DC determines the rate of the total process. However, this reaction is rather slow. At the ambient temperature the chlorine release from the aqueous solution of DC proceeds for several days. At the same time pouring approximately 42% of water (counting per the total mass) in the calorimetric ampoule with the dry layering AN/DC composition resulted in the sharp increase of the heat release rate from zero value up to 340 W sm^{-2} (experiment No. 54). The very intensive release of chlorine and other gases is also observed directly at filling the ampoule by water after carrying out an experiment to dissolve AN and DC stayed. It was possible to assume that AN increases the DC hydrolysis rate very sharply, and chlorine releasing interacting with AN. AN always contains some equilibrium quantities of ammonia and nitric acid, which can cause an acid-base catalysis of a hydrolysis of N–Cl bond in DC. To check this supposition, the experiment at 25°C (No. 55) with 5.75% aqueous solution of DC placed in the microcalorimeter ampoule was conducted using the microcalorimeter. After some time of the record of the heat release rate at DC hydrolysis AN sample was dropped in this solution. The rate of a hydrolysis was increased from value of 7 mW g^{-1} DC in aqueous solution up to 35 mW g^{-1} DC in the presence of AN due to its catalytic influence. These factors in connection with high rates of water absorbing by AN granules are responsible for a fast process in the AN/DC composition when AN was moistened.

The dry AN/DC composition was highly thermally stable and safe. But it is important to note that this composition decomposes at the temperatures above 100°C in contrast to individual AN and DC, which are stable up to 190–200°C. Moistening composition (high atmosphere humidity or water addition) sharply decreased the compatibility of AN with DC in this composition. The action of water is rather complex. At first, dissolving AN and DC in water promotes the interaction between reagents because of homogenization of the reaction composition. At second, water takes part in some reactions. The experimental data prove that water hydrolyzes DC:

$$>N–Cl+H_2O \rightarrow >N–H+HOCl \quad (1)$$

The next reactions are possible:

$$2HOCl \rightarrow H_2O+Cl_2O \quad (2)$$

$$Cl_2O \rightarrow Cl_2+0.5O_2 \quad (3)$$

Probably small quantities of free Cl and O are formed as intermediate reaction products and a composition activity in different oxidations increases strongly. The next very important reaction is the reaction of chlorine and probably another chlorine-containing DC hydrolysis products with ammonium ion and ammonia (a product of AN dissociation):

$$2NH_3+3Cl_2 \rightarrow N_2+6HCl \quad (4)$$

This reaction occurs via intermediate monochloramine, dichloramine and nitrogen trichloride NCl_3. The important role of reaction (4) has been proved by the experimental fact that both AN and AC react with DC but SN does not. So ammonium ion (but not nitrate ion) is a reaction species interacting with DC. HCl is active in a reaction with HNO_3 forming from AN:

$$HNO_3+3HCl \rightarrow 2H_2O+NOCl+Cl_2 \quad (5)$$

$$2NOCl \rightarrow 2NO+Cl_2 \quad (6)$$

The products of reactions (5) and (6) are capable to oxidize ammonia also:

$$NOCl+NH_3 \rightarrow N_2+H_2O+HCl \quad (7)$$

In these reactions we observe N_2 and NO formation (but no N_2O, which is the main AN decomposition product). N_2 and NO formation instead of N_2O increases the reaction heat. Moreover, NO can oxidize DC forming CO_2 with an additional heat release. So, chlorine consumes in reaction (4) and forms in reactions (5) and (6), and evaporates partially. So when a DC hydrolysis ceases because of water evaporation, the chlorine content on the AN and DC contact surface decreases sharply and the whole process also ceases.

The results of calorimetric experiments show clearly that AN moistening accelerates the reaction of AN with DC more than DC moistening. But this statement does not contradict a main role of reaction (1). Being highly hydrophilic AN acts as water container, which moistens DC.

Undoubtedly, the number of chemical processes in the AN/DC/H_2O composition is not limited by reactions (1)–(7). It is known that chloride-ions can accelerate the AN decomposition at temperatures higher *m.p.* [8]. But at temperatures under study because of a high AN thermal stability [23] the role of this process may be not so important.

The most relevant factors to enhance possibility of thermal explosion in the system studied are to humidify AN on the surface up to the general water content of 5% and more and to intermix composition components even partially in the thin layer. The factors that counteract the thermal explosion are an easy vaporization of water at high temperatures and rather a low activation energy for the heat release rate. When the separate layers system does not possess of excess water the reaction practically does not proceed; also the thermal spontaneous combustion is impossible.

Conclusions

The interaction of AN and DC in the not intermixed composition at temperatures up to 65°C proceeds only in the thin layer on the contacts of components. The heat release rate depends on temperature and the interfacial area of components and does not depend on the masses of components. Introducing water in AN or DC increases sharply the heat release rate, AN humidifying influencing much more strongly. Intermixing composition components results in the essential increase of the rate as the reaction proceeds in the total volume of components intermixed. At humidifying DC the process proceeds with large oscillations of the heat release rate, at introducing water in AN these oscillations are small or not observed at all. There is not the heat release in the dry composition up to temperature 65°C, in the open ampoule even the very small heat absorption is observed. The kinetic regularities of the heat release, the dependences of its rate on the temperature and the water content have been obtained. These data can be used to calculate any thermal processes in the system studied.

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