Study on reactivity of ammonium nitrate contaminated by sodium dichloroisocyanurate

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Abstract

A fatal 2001 explosion at a fertilizer plant in Toulouse, France, was possibly caused by an accidental mixture of sodium dichloroisocyanurate (DCCNa) and ammonium nitrate (AN). In this study, DCCNa was added into AN by the concentration of 0.01 %, 0.03 %, 0.1 %, 0.5 % and 1 %, respectively. A heat flux calorimetry C80 and an accelerating rate calorimetry (ARC) were used to analyze thermal decomposition of AN and its mixtures. The results showed that the initial decomposition temperature of the mixture decreased markedly compared to that of pure AN. It is considered that DCCNa catalyzes the decomposition of AN through key steps including the synergism between HNO_3 and Cl^-. Nonetheless, the results of the BAM 50 / 60 steel tube test did not show visible effect of added DCCNa on the detonation of AN.

Keywords: Ammonium nitrate (AN), Thermal hazard, Sodium dichloroisocynurate (DCCNa), Chlorine derivatives, Contamination

1. Introduction

Ammonium nitrate (AN) is an important industrial chemical as explosives and major agricultural fertilizers. However, the history of accidents involving AN, as an example of low probability-high consequence material by the occurrence of accidents from fire, explosion to decomposition, can be seen as a series of surprising and devastating events [1]. In the UN Recommendations on the Transport of Dangerous Goods (so-called Orange Book)[2], there are at least 1 entry classified as AN based fertilizer and assigned to Division 9, whereas 1 entry of AN based fertilizer classified as explosive and assigned to Division 1.1, and 5 entries of other ANs classified as oxidizers and assigned to Division 5.1. These classifications are dependent on their physical properties (particle size, porosity, density), chemical properties (purity, stabilizer, water content), environment factors and conditions (confinement, compatibility with other materials, temperature and pressure). The fatal explosion occurred at Atofina's Grande Paroisse site in Toulouse, France (September 2001), in which 29 people were killed and more than 2,500 injured, with a total loss of 2.5 billion Euros. It raised a severe concern of the inherent dangers associated with handling and storing AN and the importance of further understanding the hazardous properties of AN[1), 3)–5)]. Until now, the cause of the explosion is still uncertain, however, one of the possible causes was ascribed to contamination of AN by another chemical produced at the site[6]. The main products in the plant were AN and AN-based fertilizers. The explosion took place in a storage warehouse of 70 ha where rejected off-specs materials were stored. One of the other chemicals produced at the site was the sodium dichloroisocyanurate (DCCNa), a chlorine derivative that is often used to disinfect swimming pools. Just before the explosion, DCCNa might have been thrown in the AN storage. Therefore there has been recent interest in hazard characterization of mixtures of these two substances[7]. This research aimed to clarify the effects of possible contamination of DCCNa into AN in the accidental scenario on its decomposition and detonation properties by using calorimetries and the BAM 50 / 60 steel tube test.

2. Experimental
2.1 Chemicals

Crystalline AN (AN, Kanto ACS Grade, 99.0 % assay) and DCCNa (Nissan Chemical Co. INC) were ground. The latter was mixed with AN by weight percents of 0.01 %, 0.03 %, 0.1 %, 0.5 % and 1 %, respectively (where 1 wt% is defined as 1 g additive in 99 g AN).

2.2 Heat flux Calorimetry C80

A Setaram C80 heat flux calorimetry was used to characterize the decomposition of AN and its mixtures with DCCNa. In the experiments, 0.5 g sample was set in an 8 ml stainless steel cell and then heated at a rate of 0.1 K min⁻¹ from the room temperature to 300 ºC. The same amount of alumina was used in the reference cell.

2.3 ARC

An ARC (ADL. Co. Ltd., USA) was used to determine the self-heating and the pressure change during the thermal reaction at the HWS (heating-waiting-searching) mode in an adiabatic condition. 0.5 g sample was placed in a 10 ml spherical titanium vessel and the vessel was subsequently attached to the apparatus to form a closed, leak-tight assembly. The experiments were started at the room temperature. During the performance, the temperature of the vessel was raised from an initial temperature by increments (the heat period) of 5 K and the vessel was maintained in adiabatic condition during both a wait period (which allowed the dissipation of thermal transients) and a search period. The system searched and recorded an exotherm during the search period, and whenever the sample's self-heating rate exceeded a chosen threshold value of 0.02 K

min⁻¹, the surrounding temperature followed the sample temperature to minimize the temperature difference.

2.4 BAM 50 / 60 steel tube test

The BAM 50 / 60 steel tube test, test series A.1 in the UN Manual[2], was used to measure the ability of a substance to propagate a detonation by subjecting it to a detonating booster charge under confinement in a steel tube. A seamless steel tube of 500 mm length, 60 mm external diameter and 5 mm wall-thickness was closed by a malleable cast iron screwing cap. The tube was filled with 1000 g sample. The booster consisted of a cylindrical pellet of 50 g RDX / wax (95 / 5) compressed to a pressure of 1500 bar, and was placed centrally in the upper end of the tube. The wrapped booster was then attached to the malleable iron cap by means of thin wires passing through four additional drillings in the cap. The cap was carefully screwed onto the tube and the detonator was inserted into the booster through the central hole in the screw cap. The detonator was then initiated.

The dense powder AN as in 2.1 and granular AN of lower density were used in this experiment, with addition of 2 % DCCNa in these two types of AN. Two replicates were run and the test results were assessed on the basis of the type of fragmentation of the tube after the experiment.
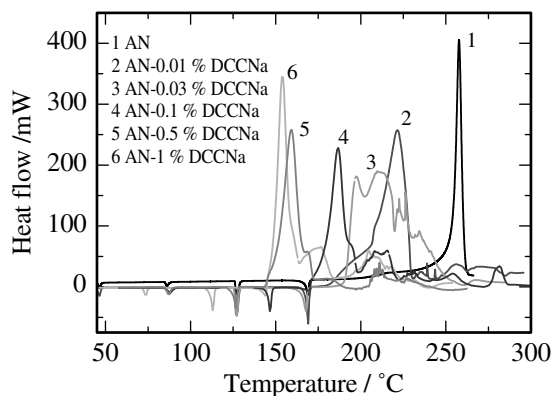

Fig. 1 Heat flow vs. temperature in the C80
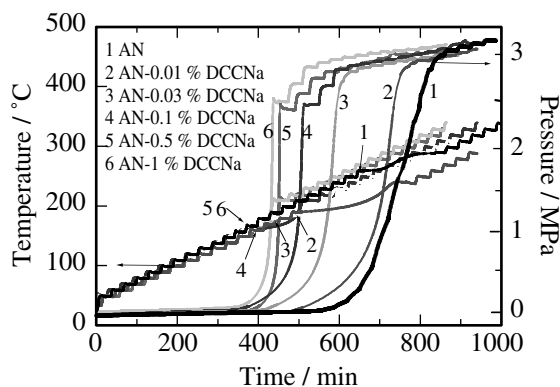(Sample: 0.5 g; heating rate: 0.1 K min⁻¹) .

Fig. 2 Temperature and pressure vs. time in the ARC
(Sample: 0.5 g; slope sensitivity: 0.02 K min⁻¹,
heating rate: 2 K min⁻¹, heat temperature step: 5 K;
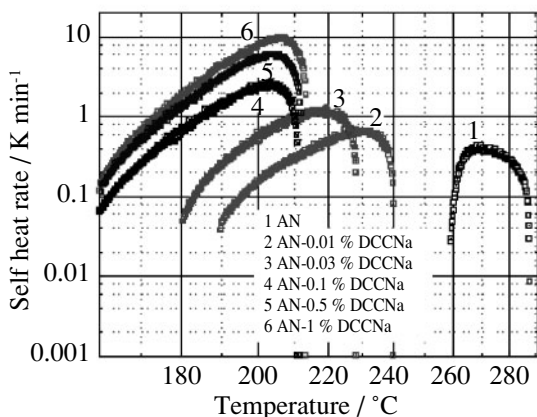Arrows point to the start of exotherm on each
temperature curve).
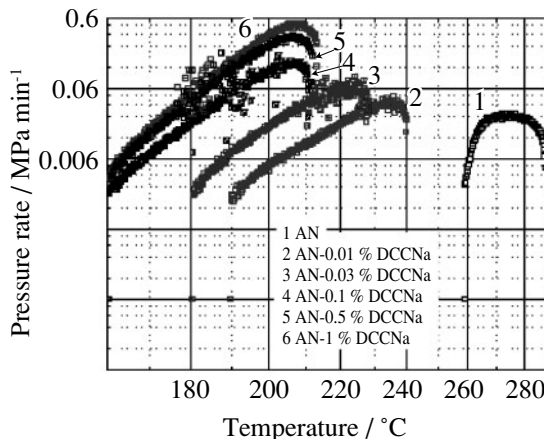

Fig. 3 Self heat rate in the ARC, derived from Fig. 2.

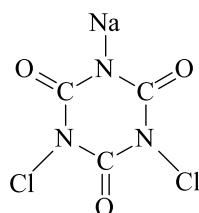Fig. 4 Pressure rate in the ARC, derived from Fig. 2.

3. Results and discussion

3.1 Effect of DCCNa on the thermal decomposition of AN

Figure 1 shows relations of heat flow of pure AN and DCCNa-added ANs versus temperature at a heating rate of 0.1 K min⁻¹ in the C80 experiments. It can be seen that AN started a slight reaction from 200 ˚C after its melting at 170 ˚C, and reached the major reaction above 250 ˚C. Its heat flow attained the maximum value, 400 mW, at about 258 ˚C. In the addition of DCCNa, the initial reaction temperature approached to lower values. The more the DCCNa was concentrated, the lower the onset temperature of the reaction was. For example, the onset temperature of the reaction was 180 ˚C for AN-0.01 % DCCNa, and 140 ˚C for AN-1 % DCCNa. Meanwhile, the heat flow split into two peaks in AN-0.01 % DCCNa and tended to reunite as one intense peak with increase of DCCNa content. Their maximum heat flow also moved towards lower temperatures. In the case of mixtures with more than 0.5 % DCCNa, it has moved into the melting range of AN. These results were identical to what happened in the mixtures of AN and various chlorides[8]. This implies that the effect of DCCNa on the thermal decomposition of AN follows the chlorine / chloride-catalyzing mechanism.

ARC experiments were also performed for AN and its mixtures with DCCNa. The temperature and pressure profiles are plotted in Fig. 2. The decomposition of AN occurred at 250 ˚C and became intense at 275 ˚C with the maximum self heat rate of 0.4 K min⁻¹ and pressure rate of 0.03 Mpa min⁻¹. The reactions of DCCNa-added mixtures took place at lower temperatures (190 ˚C for AN-0.01 % DCCNa, 180 ˚C for AN-0.0 3% DCCNa, 150 ˚C for AN-0.1 % DCCNa and 130 ˚C for AN-1 % DCCNa). Figures 3 and 4 derived from Fig. 2 show the self heat rate and pressure rate of these samples respectively. As can be seen, the maximum self heat rate and pressure rate increased gradually with the increased concentration of DCCNa. When 1 % DCCNa was added, the maximum self heat rate and pressure rate were 100 times as much as those of AN. These results were consistent with the C80 heat flows of the samples. The presence of DCCNa reduced the stability of AN dramatically. Moreover, it is noted in Fig. 5 that both the maximum self heat rate and the maximum pressure rate have a square-root dependence of the chloride concentration.

3.2 Mechanism on the DCCNa-catalyzed thermal decomposition of AN

The chemical structure of DCCNa is shown as:

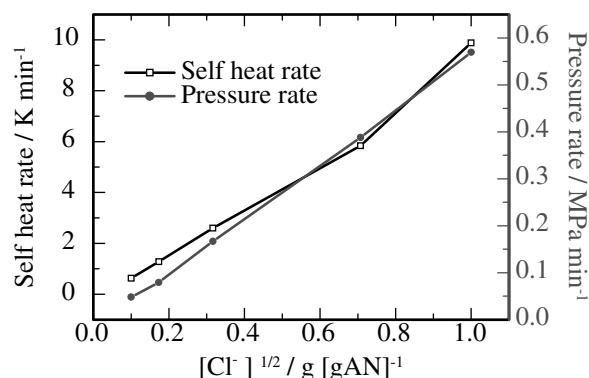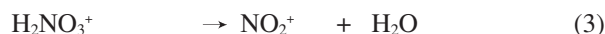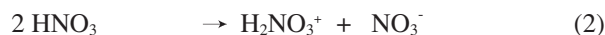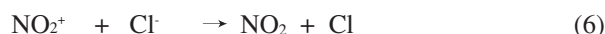It develops a radical catalysis to AN molecules after the release of chlorine.

Fig. 5 Maximum self heat rate and pressure rate vs. $[Cl^-]^{1/2}$ derived from Figs. 2-4.

As seen in Fig. 1, in the presence of DCCNa, the decomposition happened in the melting range of AN, indicating that the catalysis of DCCNa works actively at this stage. The melting of AN leads to an acidic environment due to preferential volatilization of NH_3. The decomposition products of a chlorine from DCCNa and simultaneous AN melt contain small amounts of Cl_2, HCl, HNO_3, and nitrogen oxides. The side reactions largely changed the shape of the plot of heat flow in Fig.1 in the mixtures and prolonged the reaction periods. The equiolibria set are given below as pertaining to the AN melt.

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 \quad (1)$$

$$2\ HNO_3 \rightarrow H_2NO_3^+ + NO_3^- \quad (2)$$

$$H_2NO_3^+ \rightarrow NO_2^+ + H_2O \quad (3)$$

$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^- \quad (4)$$

$$NH_4^+ + H_2O \rightarrow H_3O^+ + NH_3 \quad (5)$$

On the basis of the above equilibria, the obvious oxidizing agent in this system is NO_2^+ reacting as follows:

$$NO_2^+ + Cl^- \rightarrow NO_2 + Cl \quad (6)$$

$$Cl + Cl \rightarrow Cl_2 \quad (7)$$

$$Cl_2 + NH_3 \rightarrow [NH_2Cl]^{fast} \rightarrow N_2 + HCl \quad (8)$$

Equation (6) reveals that the reaction in the presence of Cl^- occurs through a radical reaction mechanism. Many researchers have noted the synergism between HNO_3 and Cl^-[9,10]. The excess HNO_3 is considered as an acidity environment to undergo the reaction of autoprotolysis and ionic self-dehydration. The fact that the chlorine concentration appears to the root-square relationship in the reaction rate, as shown in Fig. 5, indicates that the steady-state chlorine concentration is determined mainly by reactions (6) and (7), which are the key steps to the destabilization of AN. This is in agreement with the results studied by Keenan and Dimitriades[9]:

$$d[N_2] / dt = k_2[AN] + k_2[AN][Cl^-]^{1/2} \quad (9)$$

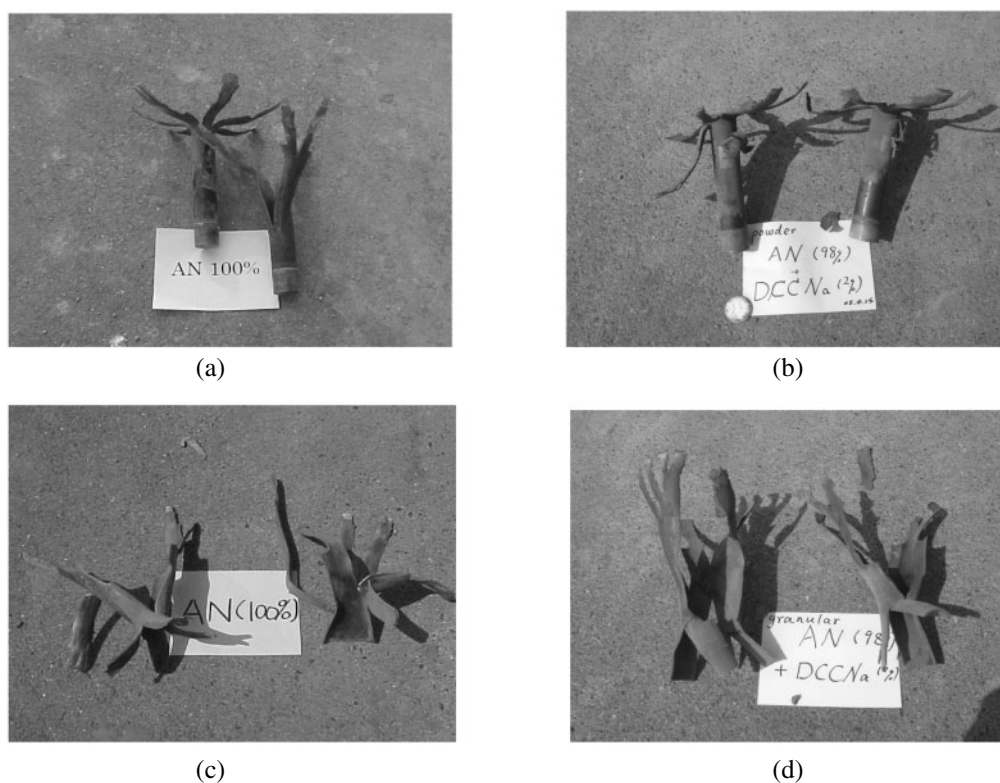in which the decomposition of AN is known as a first order reaction.

Fig. 6 Results of BAM 50 / 60 steel tube tests (1000 g sample; 50 g booster: RDX / wax=95:5).
(a) powder AN; (b) powder AN-2 %DCCNa; (c) granular AN; (d) granular AN-2 %DCCNa

3.3 Effect of DCCNa on the detonation of AN

Figure 6 shows the results of detonation for powder and granular ANs and their mixtures with 2 % DCCNa. The powder AN, either with DCCNa or not was assessed as "No detonation" on the basis of the types of fragmentation of the tube. Whereas the granular AN with or without DCCNa was assessed as "Detonation".

Generally, AN is supposed to detonate, and the detonation of the granular AN is feasible to be initiated. Whereas powder AN, as often used in fertilizer-based AN, is very difficult to initiate detonation due to its high density. The potential of the transition from a decomposition or deflagration developing in a detonation requires the right conditions[11]~[13]. The initiation is possible only when it delivers a shock wave strong enough to trigger the self-sustaining super-sonic decomposing reactions. In practice, whether or not a detonation occurs under given test conditions depends on the characteristics of the AN, the imposed conditions and the initiation strength. It is obvious that the small amount of DCCNa affects the rate of decomposition of AN at low temperatures, but it does not induce decomposition that converts to shock-wave detonation processes in "laboratory-size" samples.

4. Conclusions

(1) Both C80 and ARC results show a general and close correlation between contamination of DCCNa and its ability to destabilize AN thermal decomposition. The onset temperature of decomposition of AN approaches to much lower values in the presence of DCCNa.

(2) DCCNa concentration has a square-root dependence of the reaction rate of AN thermal decomposition. This suggests that a radical catalysis mechanism results from the synergism between the chlorine formation from DCCNa and the acidity by AN melting.

(3) A small amount of DCCNa can destabilize AN markedly. Nonetheless, the detonation was only observed in AN of low density in the BAM 50 / 60 steel tube test.

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