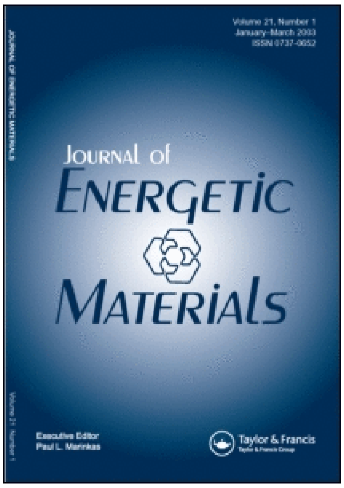

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Dong Shuan[a]; Wan Xingzhong[b]; Ou Yuxiang[c]; Feng Changgen[c]; Wang Yun[c]; Chen Boren[c]
[a] Department of Chemistry, Shandong Teacher's University, Jinan, China [b] Institute of Chemical Metallurgy, Chinese Academy of Sciences, Beijing, China [c] Beijing Institute of Technology, Beijing, China

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KINETIC STUDIES OF THERMAL DECOMPOSITION OF AANTO, BAED AND DAAP BY ARC AND DSC

Dong Shuan,

(Department of Chemistry, Shandong Teacher's University, Jinan 250014, China)

Wan Xingzhong*

(Institute of Chemical Metallurgy, Chinese Academy of Sciences, Beijing 100080, China)

Ou Yuxiang, Feng Changgen, Wang Yun and Chen Boren

(Beijing Institute of Technology, Beijing 100081, China)

ABSTRACT

In this paper, three new organic azids i.e. 2-azidoethylammonium-3-nitro-1,2,4-triazol-5-onate (AANTO), 1,1-dinitro-3-aza-5-azidopentane (DAAP) and bis(2-azidoethylamine)-ethyl-dinitramine (BAED) are synthesized and characterized, and their thermal decomposition reactions are studied using DSC and ARC. The approximate heat of decomposition is determined, and the the self-heating rates and pressure increasing rates are measured as the function of self-heating temperature. Their thermal stability is compared, and their potential thermal hazard is assessed.

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* Author to whom correspondence should be addressed.

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INTRODUCTION

As new energetic materials, the organic azides have various excellent performances due to the differences in molecular structures besides they have azido groups in common. These compounds may be applied to energetic plasticizers, energetic binders, energetic oxidizers and other additives [1]. Up to now, there are hundreds of organic azides have been synthesized, which are full of promises. It is expected that some azides may be used as ingredient of high performance and minimum signature propellants, and high energy density explosives in the future. Extensive works concerned to their properties and applications have been carried out.

In this paper, three typical compounds listed below have been synthesized via the following reactions.

2-azidoethylammonium-3-nitro-1,2,4-triazol-5-onate (AANTO),

1,1-dinitro-3-aza-5-azidopentane (DAAP),

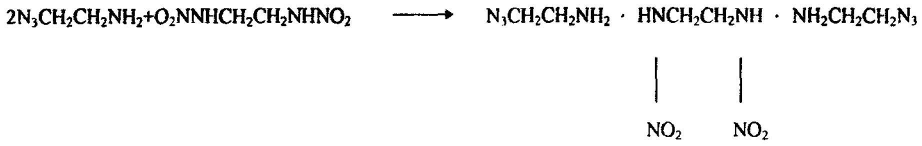
and bis(2-azidoethylamine)-ethyldinitramine(BAED). The routes of their syntheses are as follows:

$$N_3CH_2CH_2NH_2 + C_2H_2N_4O_3 \longrightarrow N_3CH_2CH_2N^+H_3 \cdot C_2HN_4O_3$$

(AANTO)

$$N_3CH_2CH_2NH_2 + HOCH_2C(NO_2)_2^-K^+ \longrightarrow N_3CH_2CH_2NHCH_2CH(NO_2)_2$$

(DAAP)



$$2N_3CH_2CH_2NH_2+O_2NNHCH_2CH_2NHNO_2 \longrightarrow N_3CH_2CH_2NH_2\cdot \underset{NO_2}{\underset{|}{HN}}CH_2CH_2\underset{NO_2}{\underset{|}{NH}}\cdot NH_2CH_2CH_2N_3$$

(BAED)

The ARC and DSC have been employed to study their thermal decomposition behaviors.

EXPERIMENTAL

1 The materials and methods

The 2-azidoethylamine and its salts are synthesized according to the procedure used by Foster[2]. The potassium-2,2-dinitroethanol is synthesized based on the method used by Kaplan[3]. The ethyldinitramine is synthesized by the method developed by the present authors [4]

2. The instruments

In the present study, ARX-400 NMR, PE-1600 FTIR Spectrograph, Carlo Erba 1102

Elementary Analyzer and Finnigan-Mat TSQ-45B Mass Spectrograph have been used to identify the chemical structures of the synthesized compounds. On the basis of these analyses ARC, PE -DSC-7 are also used to study compound's thermal decomposition behaviors.

DSC

The DSC used in this study is the Perkin Elmer DSC-7. The test are carried out by using the open aluminum sample pans, and a heating rate of 10 ^{O}C min^{-1}over the temperature range of (150 ~ 350) ^{O}C. A typical sample is 5.82 mg in weight.

ARC

An accelerating rate calorimeter (ARC) instrument produced by the Columbia Scientific Industries, model 94063205) is used in these studies. The descriptions and schematics of the ARC have been described elsewhere[5, 6, 7]. The reaction vessels are the 2.54 cm diameter titanium spheres having a mass of approximately 10 g. A pressure transducer with a range of 0-17200 kP is connected to the reaction vessel through stainless steel capillary tubing. In a typical experiment, a cleaned and weighted reaction vessel is charged with AANTO, sealed and re-weighed. The reaction vessel is then connected to the pressure fittings, enclosed in the calorimeter and the operating sequence of the instrument starts. The heaters in the calorimeter increase the temperature of the reaction vessel until the lower detectable limit of the temperature rate (0.005 ^{O}C /min) is observed. Up to this point, heating is intermittent. Between the heating periods the calorimeter is isothermal for 5 minutes while searching for a detectable temperature rise. If no temperature rise is detected, the calorimeter repeats the heat-wait-search cycle. During an exothermic reaction, heaters are digitally controlled to maintain zero temperature difference between the reaction vessel and the calorimeter jacket. At the completion of the exothermic, the calorimeter and the vessel are cooled, the vessel reweighed.

3. The synthesis.

3.1. 1,1-Dinitro-3-aza-5-azidopentane (DAAP)

Dissolve 0.18g of potassium-2,2 dinitroethyl alcohol (1.03 mmol) and 0.13 g of 2-azido-ethylammonium chloride (1.06 mmol) in 15 ml of water. The pH of the reaction solution is adjusted to 8.0 using diluted aq. NaOH. The faint yellow crystals precipitates from the solution thorough the process. Washing with water, filtering and drying afforded 0.14 g (68% yield) of 1,1-dinitro-3-aza-5-azidopentane, mp 99°C, IR(KBr) 3160, 2100, 1583, 1340 cm^{-1}, MS (CI); m/e 205(M+1)$^{+}$; Anal. calcd. for $C_4H_8N_8O_4$: C, 23.5%; H, 3.92%; N, 41.11%;. Found: C, 23.80%; H, 4.04%; N, 40.95%.

3.2. Bis(2-azidoethylamine)-ethyldinitramine(BAED)

Add 23.0 ml 5% of aq. 2-azidoethylamine (13.4 mmol) dropwise to 1.0 g of ethyldinitramine (6.67 mmol). The mixture is heated with a water bath at 60°C until ethyldinitramine dissolved, and the solution was weak base. The water was removed by evaporation under a vacuum. The solution of water-ethyl alcohol (1:1) was used to recrystallise the residue, the product as colour-less blocky crystals (2.10 g) is obtained (97% yield), mp:133-134°C, IR(KBr):3000,2095,2085,1620,1283 cm^{-1}. ^{1}H-NMR (DMSD-D6): δ 4.86(6H,S), 3.24(4H,S), 3.18(4H,t), 2.65(4H,t)ppm; MS(CI):323(M+1)$^+$. Anal. calcd. for $C_6H_{18}N_{12}O_4$: C, 22.36%; H, 5.59%; N, 52.17%. Found: C, 21.73%; H, 5.45%; N,52.76%.

3. 2-Azidoethylammonium-3-nitro-1,2,4-triazole-5-onate (AANTO)

Add 3.5 ml of 5% aq. 2-azidoethylamine (7.72 mmol) dropwise to 1.0 g 3-nitro-1,2,4-triazole-5-one (7.69 mmol) at room temperature. Stirr the mixture until the solid powder dissolved and the solution was weak base. The water was removed by evaporation under a vacuum to precipitate the light yellow powders. Recrystallising the residue with the solution of water-ethyl alcohol(1:1) gave 1.6 g of light yellow crystals (96% yield), mp:219°C; IR(KBr):3350, 3230, 3000, 2095, 1630 cm^{-1}, ^{1}H-NMR (DMSD-D6): δ 6.12(6H,S),3.26(2H,t),2.66(2H,t)ppm. MS(CI):217(M+1)$^+$; Anal. calcd. for $C_4H_8N_8O_3$: C, 22.22%; H, 3.70%; N, 51.85%. Found: C, 22.28%; H, 3.65%; N, 51.91%.

There is no suitable solvent for DAAP, therefore, it is unable to carried out the ^{1}H-NMR work for DAAP.

RESULTS AND DISCUSSIONS

In table 1 the characteristic data of the self heating are listed.

Table 1. ARC results of the thermal decomposition of AANTO, BAED and DAAP

Sample	m_s (g)	$(dT/dt)_0$ (℃/min)	T_0 (℃)	P_0 (kPa)	$(dT/dt)_t$ (℃/min)	T_t (℃)	T_c (℃)	P_c (kPa)	t (min)	ΔT_r (℃)
AANTO	0.4572	0.106	160.72	139.96	0.728	419.8	424.8	135.82	982.96	264.1
BAED	0.4250	0.009	103.74	147.55	0.218	177.9	186.8	146.17	1277.76	83.1
DAAP	0.4985	0.009	60.52	146.86	684.650	216.5	233.0	147.55	263.39	172.5

Table 1. continued

$(dT/d)_o$: initial self-heating rate;

T_o: initial self-heating onset temperature.

P_o: initial reaction pressure.

$(dT/dt)_t$: maximum self-heating rate.

T_t: temperature at maximum self-heating rate.

T_e: temperature at end of reaction.

P_e: pressure at end of reaction.

t: reaction time.

ΔT_r: temperature increase during the reaction under adabatic condition.

AANTO , BAED and DAAP show a transition from a controlled and reproducible self-heating to deflagration, characterized by the time t. The onset temperatures are far below the standard deflagration temperatures measured with the standard apparatus such as DSC at 10°C/min heating rate. Also the transition temperatures are still below these deflagration temperature. In figures 1 and 2 the temperature and pressure increase as function of time are shown for these compounds. The curves start at h = 0.005 °C/min. To this point the time zero is assigned. In Fig. 3 the self heating rate increase rate as function of temperature are illustrated. The coordinates are in lg (h[°C/min]) and 1/T[1/K], the scales are in °C/min, kPa/min and °C. Figure 4 shows the pseudo-rate constant as the function of temperature for AANTO, BAED and DAAP . The time- to- maximum rate for the thermal decomposition reaction of AANTO, BAED and DAAP are shown in figure 5. The kinetic data of AANTO, BAED and DAAP are shown in table 2.

Table 2. Experimental kinetic data of AANTO, BAED and DAAP

Sample	Bomb weight (g)	ϕ	E (kJ/mol)	A (1/s)
AANTO	8.5	20.00	11.04	0.0014
BAED	8.5	17.06	15.68	0.014
DAAP	8.5	23.30	67.84	9.23×10^6

ϕ : thermal inertia

E : activation energy

A: preexponential factor

These tests show that AANTO has the highest self-heating onset temperature, among these three compounds. Therefore it is the most stable compound. However, the DAAP not only has the lowest self-heating onset temperature among those compounds, but its time from initial self-heating point to the transition point is the shortest one. Therefore it is the most unstable compounds. Figure 2 show that there is no obvious pressure change during the exothermal decomposition. There are not many gas products generated. The relationship between the self-heating rate and the system temperature is shown in figure 3. The self-heating rates of AANTO are linearly increase with the temperature. The self-heating rates of DAAP are also linearly increase with the temperature. However, the self-heating rates of

BAED appear to be quit complexed as the temperature increases. It indicated that the more complexed mechanism may be involved. The DSC results are shown in figure 6. The onset temperature of AANTO measured at the heating rate of 15 °C/min is about 180℃, which is higher than the ARC results. The transition temperature is about 195℃, which is also higher than the deflagration temperature determined with ARC.

CONCLUSION

The accelerating rate calorimetry has been used to study the adiabatic kinetics of the thermal decomposition reaction of AANTO, BAED and DAAP. The work shows that AANTO is the most stable compound among AANTO, BAED and DAAP. The DAAP is the most thermal unstable compounds. The amont of gas products released during the thermal decomposition of those organic azides is small. These compounds contain the groups of NTO (3-nitro-1,2,4-triazole-5-one), 1,1-dinitro, nitramine and etc respectively. This is the reason that there are large differences between those compounds regard to their thermal decomposition behaviors. The results show that the technique can be applied to high energy density explosives. The onset temperature of the self-heating is always much lower than the corresponding standard deflagration temperature, determined with the standard apparatus.

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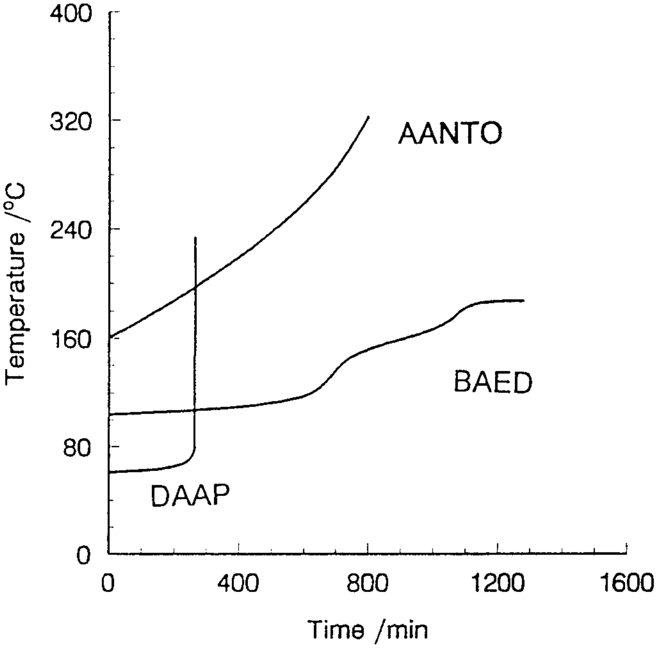

Fig. 1 Temperature increase as function of normalized time ($t-t_{0.05}$) from h= 0.05°C/min to transition.

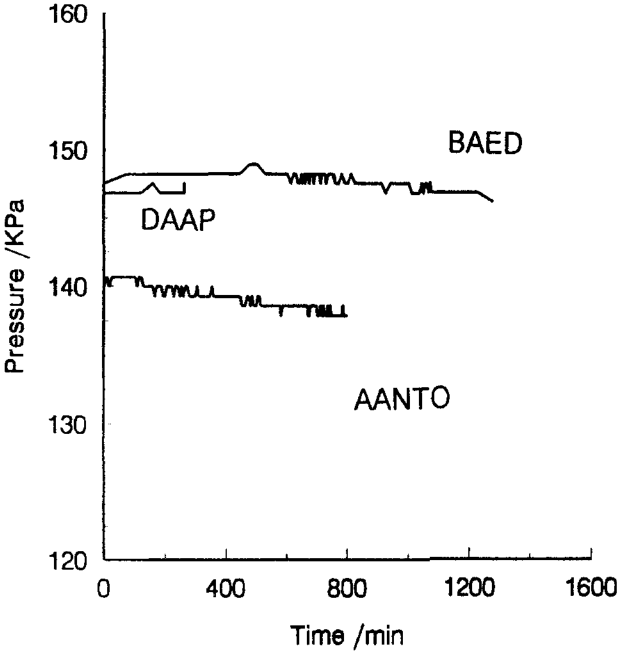

Fig. 2 Pressure increase as function of normalized time ($t-t_{0.05}$) from h= 0.05°C/min to transition.

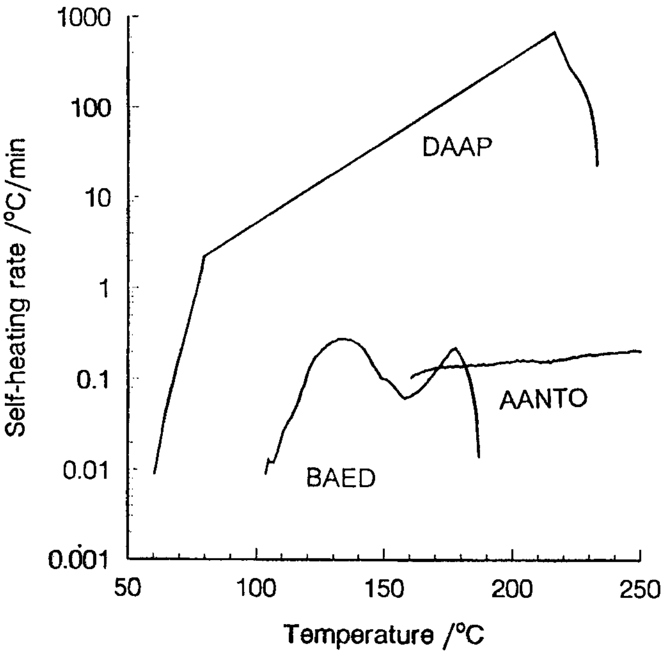

Fig. 3 Adiabatic self-heating rates vs. temperature for AANTO, BAED and DAAP.

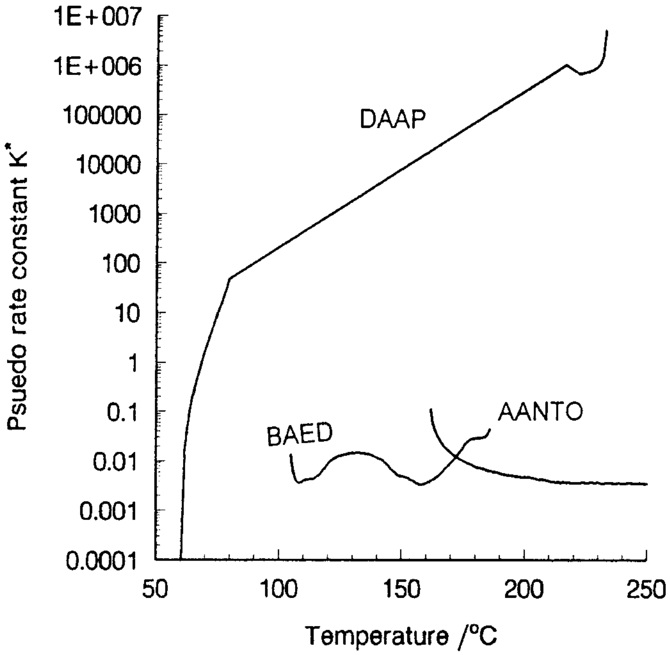

Fig. 4 The pseudo-order rate constant, k^*,vs. temperature for the thermal decomposition reaction of AANTO, BAED and DAAP.

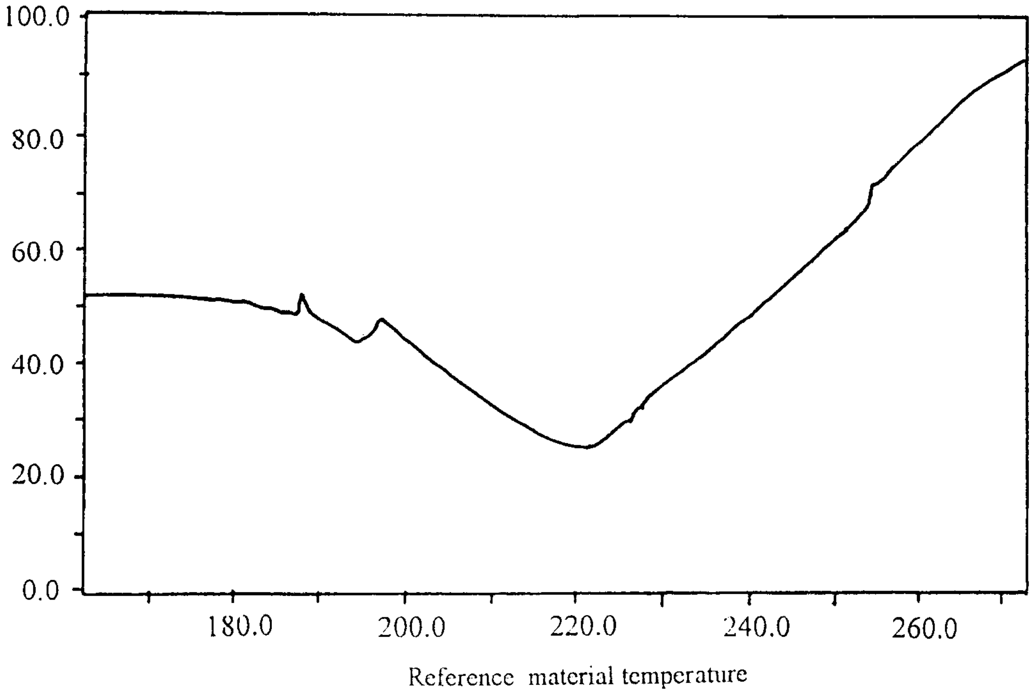

Fig. 5 Time to maximum rate vs. temperature for the thermal decomposition reaction of the AANTO, BAED and DAAP.

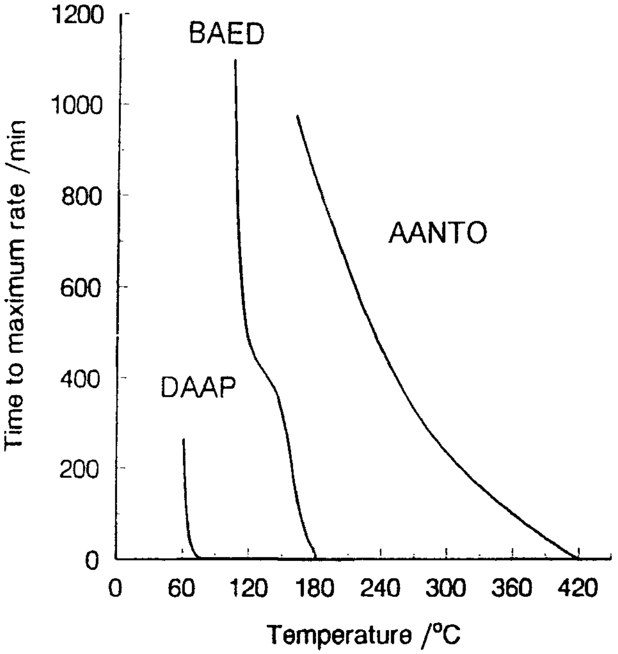

Fig. 6 DSC curve. Thermal decomposition of AANTO. Heating rate 15°C/min.