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The study of the thermal decomposition of 3-nitro-1,2,4-triazol-5-one (NTO) by DSC, TGA–MS, and ARC

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Abstract

The thermal decomposition of NTO (3-nitro-1,2,4-triazol-5-one) was studied using DSC, TGA–MS, and ARC. The major gaseous products were identified, the approximate heat of decomposition was determined, and a chemical equation was suggested for the net reaction. It was found that the stability of NTO is sensitive to the thermal age of the sample. Kinetic analysis suggested an auto-catalytic mechanism. The thermal stability of NTO was compared with RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and its potential thermal hazard was assessed.

INTRODUCTION

When new energetic materials are identified, it is necessary to develop a thorough understanding of the potential thermal hazards relating to their safe manufacture, handling and storage. A number of thermal analysis techniques are available for obtaining the required data. These include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), TGA coupled with mass spectroscopy (TGA–MS), and accelerating rate calorimetry (ARC). We have employed all these methods to investigate fully the thermokinetic properties of the new, insensitive explosive, 3-nitro-1,2,4-triazol-5-one (NTO).

NTO is a compound which has recently been identified as a potential high explosive [1]. Although this material has been known in the literature for some years, interest in it has been active only since tests revealed it to be very impact-insensitive and thermally stable [2]. Since then it has been evaluated extensively in munitions [3,4].

Researchers at Los Alamos have reported some of the chemical, physical and explosive properties of NTO and found it to be much less sensitive than 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) or 2,4,6-trinitrotoluene (TNT)

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in all respects, and that its performance was similar to that of RDX [5]. Furthermore it possesses the high density of a small ring.

NTO is now being produced in multi-ton amounts for large-scale formulation and performance evaluation. In conjunction with this scaling-up of manufacture, it was felt that more should be known about its potential hazards; therefore, we set about conducting a thorough thermodynamic and kinetic evaluation of this material.

EXPERIMENTAL

Materials

NTO (3-nitro-1,2,4-triazol-5-one, $C_2H_2N_4O_3$, > 99% purity) was produced by Olin Corporation. Titanium powder (99% pure, 325 mesh, 0.0226 $m^2\ g^{-1}$) was obtained from Johnson Matthey Electronics.

Instrumentation, conditions and procedures

DSC (Du Pont 1090 Analyzer and DSC cell)

Runs were made using open aluminum sample pans, a heating rate of 10°C min^{-1} over the temperature range 25–350°C, and a nitrogen purge of 80 ml min^{-1}. A typical sample weighed 25 mg.

TGA–MS (Du Pont Instruments, TGA model 951, and Finnigan MAT Ion Trap Detector, model 700)

TGA runs were made using a heating rate of 10°C min^{-1}, a temperature range of 25–350°C, and a helium purge of 80 ml min^{-1}. A typical sample size was 25 mg. The gas evolved from the NTO decomposition was delivered to the ion trap detector (ITD) by a capillary transfer line heated to 250°C. Mass spectra were collected at a rate of 1 every 2 sec with a mass range of 10–100 atomic mass units.

Approximately 30 sec elapsed from the start of the TGA run to collection of the first mass spectrum.

ARC (Columbia Scientific Industries, model 851-0004)

Runs were made using a sensitivity of 0.02°C min^{-1}, a start temperature of 170°C, a stop temperature of 310°C, a heat step of 2°C, and a wait time of 10 min. In a typical ARC experiment, the rate of sample heating is not programmed. Instead, the calorimeter furnace heats up at a rate equal to the sample self-heat rate [6]. Reaction vessels were made of commercially pure titanium. A typical vessel weighs 27 g, and has a volume of 12 ml, an internal surface area of 24 cm^2 and a heat capacity of 3.52 cal K^{-1}. Sample vessels were cleaned by rinsing them first with deionized water, followed by acetone and then heating them in air to red heat over a Bunsen burner. They were allowed to cool in a desiccator. This process was repeated until a constant vessel weight was obtained. The reaction vessel was charged with the sample in ambient air. Initial charge weights were limited to between 0.1 and 0.5 g of NTO; an upper limit was necessary to prevent bursting of the vessel. It was calculated that the vessel atmosphere at the start of the test contained approximately 0.1 mmol of oxygen. During the test, the atmosphere in the vessel was self generated. On completion of the test, the vessel was cooled to room temperature, and after the internal pressure had been measured, it was vented and reweighed.

RESULTS

DSC

No endothermic transitions were observed on heating NTO through the temperature program. An exotherm having an extrapolated onset temperature of 270°C and a broad shoulder beginning at 232°C was observed.

TGA-MS

A typical TGA thermogram is shown in Fig. 1. The onset temperature for rapid decomposition occurred at 270°C, 22.13 min into the run. The rate of weight loss was a maximum at 276°C, 22.57 min into the run.

The residual solid (at 350°C) amounted to roughly 12% of the original NTO mass. Elemental analysis proved it to have the empirical formula $C_2H_3N_3O$. An infra-red spectrophotometric examination of the residue showed that it was not 1,2,4-triazol-3-one.

The gases evolved during the TGA run were identified by mass spectroscopy as they were generated. The total ion count from the ITD mirrored

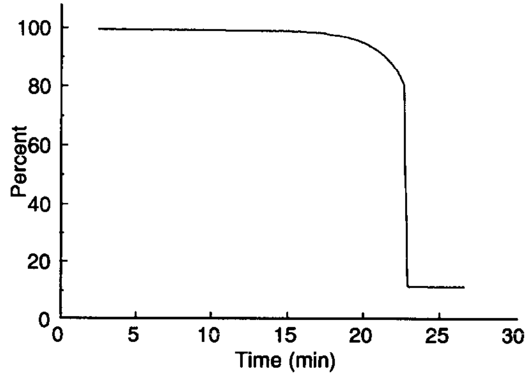

Fig. 1. TGA thermogram showing the percent $C_2H_2N_4O_3$ (NTO) weight loss as a function of run time. Rapid decomposition occurred at 22.13 min into the run and 270°C.

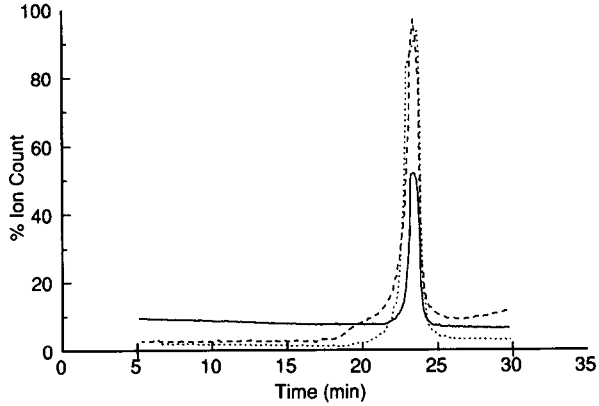

Fig. 2. Evolved gas profiles of the major $C_2H_2N_4O_3$ (NTO) decomposition products: ——, m/z 18; ······, m/z 30; ------, m/z 44.

the increasing NTO weight loss and reached a maximum at 22.26 minutes into the run, corresponding closely to the time of the maximum rate of NTO weight loss. The baseline of the ion count versus run time was flat up to a run time of 21.44 min. The evolved gas profiles of the major products (m/z 18, m/z 30 and m/z 44) are shown in Fig. 2. Also found were m/z 28 and m/z 46. To aid in the interpretation of the mass spectrum, an infra-red examination of the evolved gas was made. In this experiment a 13 mg sample of NTO was heated at 10°C min^{-1} in a 5 ml sample cell and under a static nitrogen atmosphere from 150 to 290°C. The gas evolved from the sample was admitted continuously into an IR cell through a capillary tube. The IR cell, which has a volume of 5 ml, was maintained at 150°C. The IR spectrum was scanned from 4000 to 600 cm^{-1} with a Nicolet, model 20 SXB, spectrophotometer using a resolution of 6 cm^{-1}. At equilibrium, the IR spectrum revealed the following: H_2O, NO, CO_2, CO, and N_2O. A spectrum taken 1 h later showed the presence of NO_2. These results suggest that NO_2 appears in the equilibrium gas mixture by oxidation of NO.

ARC

Decomposition of NTO in its as-received condition

Several features are apparent when the ARC data are presented as a plot of temperature rate (°C min^{-1}) against temperature (°C), Fig. 3. Two exotherms were observed. The first exotherm had an onset temperature (point J on Fig. 3) of 186°C and an adiabatic temperature rise (ΔT) of 1.6°C. The associated pressure increase was 0.69 atm and the maximum self-heat rate, which occurred at 186°C, was 0.072°C min^{-1}.

The onset temperature for the second exotherm (point O) occurred at 208°C. As a result of this exotherm, ΔT was 18°C and the pressure increase

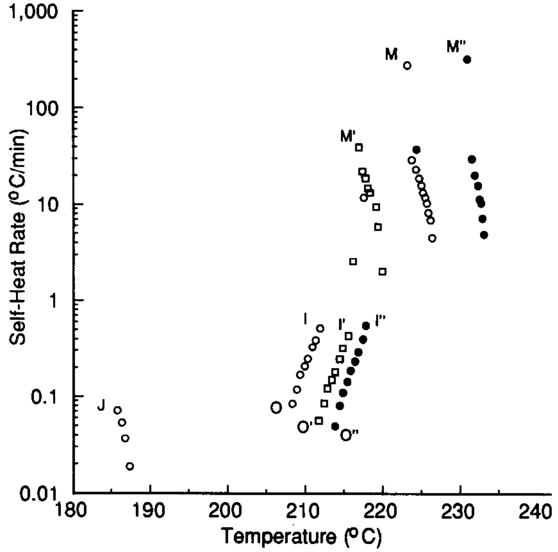

Fig. 3. ARC self-heat rate profiles for $C_2H_2N_4O_3$ (NTO): ○, 0.1066 g of NTO run in the as-received condition; ●, 0.1073 g of NTO run in the as-received condition; □, 0.1068 g of NTO run after being aged for 1 day at 185°C.

was 10.0 atm. The maximum self-heat rate (point M) was 282.5°C min^{-1} and occurred at 223°C. The maximum pressure-generation rate was 162 atm g^{-1} min^{-1} and occurred at 212°C. Ignition of the sample occurred at 212°C

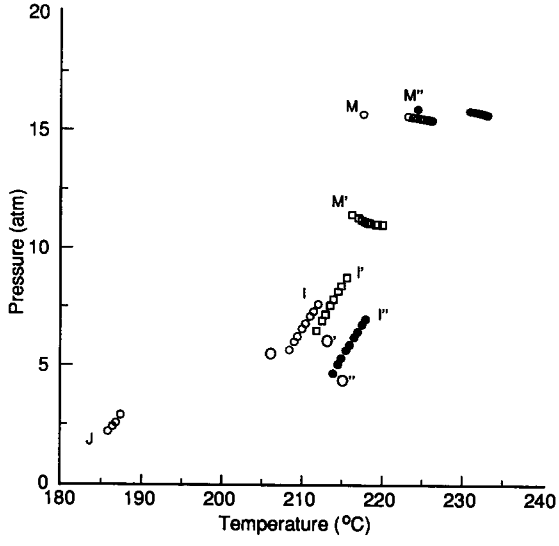

Fig. 4. ARC pressure profiles for $C_2H_2N_4O_3$ (NTO): symbols as in Fig. 3.

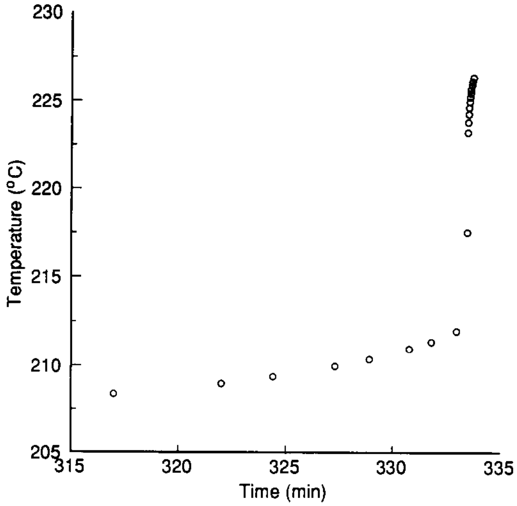

Fig. 5. Typical ARC result on $C_2H_2N_4O_3$ (NTO) showing the sample temperature during self-heating as a function of time. The rapid temperature increase occurred at 212°C. Only the major exotherm is shown. The clock started following detection of the first exotherm (not shown): o, 0.1066 g of NTO run in the as-received condition.

(point I). Figure 4 shows the corresponding pressure profile. Pressures of the order of 150 atm g^{-1} of NTO were developed in the adiabatic reactor.

Between the onset and ignition temperatures the temperature rise was 22% of its total and the pressure increase was 19% of its total for the run. Most of the heat and pressure generation for the run resulted from ignition of the sample. The rapidity of the ignition event is illustrated in the temperature versus time plot in Fig. 5. The adiabatic temperature rise amounts to a heat release of at least -77 kcal mol^{-1}. This represents 33% of the molar heat of combustion calculated from heats of formation assuming complete combustion to CO_2, H_2O, and N_2. A theoretical value for the heat of formation of NTO has recently been published [7].

At the end of the run the bomb was cooled to room temperature and the pressure in the bomb was measured. This pressure (corrected to 25°C) was used to calculate the number of moles of gas produced by the decomposition of 1 mole of NTO: the average of eight runs gave 3.3. Table 1 contains the pressure data used for this calculation.

After venting the bomb to ambient pressure, the difference in bomb weights before and after the run indicated the presence of a solid residue. This solid was, on average, present to approximately 10% of the initial charge weight. Results from eight experiments are given in Table 1.

Approximately 40% of the runs showed only the high-temperature exotherm. We compared self-heat rate (°C min^{-1}) versus T (°C) plots obtained from runs exhibiting one and two exotherms in Fig. 3. Both the onset

TABLE 1

Results of the ARC experiments

NTO weight [a] (g)	Onset of first exotherm (°C)	Onset of second exotherm (°C)	ΔT g^{-1} NTO (°C g^{-1})	ΔP g^{-1} NTO at 25°C (atm g^{-1})	% Residual solid (w/w)
Runs made on NTO in as-received condition					
0.4984	201	219	158	83.26	5.3
0.1534	185	214	180	29.00	8.5
0.1068	ND [b]	228	151	75.93	12.2
0.1106	202	220	183	68.52	13.0
0.1065	185	212	191	64.64	17.0
0.1066	186	208	169	58.43	20.2
0.1073	ND [b]	214	178	39.25	14.0
0.4979	186	218	165	74.50	5.7
Runs made on NTO previously aged at 185°C for 24 h					
0.1068	ND [b]	200	43	52.99	36.4
0.1066	ND [b]	212	77	32.70	30.4

[a] NTO stands for 3-nitro-1,2,4-triazol-5-one.

[b] ND stands for not detected; the rate was below our limit of detection.

temperature and the slope of the higher temperature exotherm are lower for the run that exhibits two exotherms. This observation was found to hold when all runs were compared and suggests that an auto-catalytic mechanism is involved in the NTO decomposition. The catalyst might be generated during the low-temperature exotherm and active in the high-temperature exothermic reaction.

Decomposition of NTO which was isothermally aged

Although no exotherm was detected during the isothermal wait period, the bomb pressure increased by 16.3 atm g^{-1}. On temperature ramping, an exotherm was detected at 212°C (point O′, Fig. 3). Ignition occurred at 217°C (point I′). Approximately 45% of the adiabatic temperature rise and 50% of the total pressure increase for the run was generated prior to ignition. A second sample yielded a single exotherm (onset at 200°C) and no ignition. Pressures of the order of 100 atm per gram of NTO were developed in the reactor.

The isothermally aged sample produced a smaller ΔT, fewer moles of gas and a larger percent residual solid, as shown in Table 1.

The fact that the onset temperature for the high-temperature exotherm was significantly lowered by isothermal aging is to be expected from an auto-catalytic mechanism, with the catalyst being formed in the isothermal aging period.

Effect of reactor surface, NTO particle size and confinement

Increasing the titanium surface area available to the reaction by 25% (by adding titanium powder to the sample) produced no detectable effect on the self-heat rate.

Runs made on samples of fine NTO powder and coarse NTO powder were not significantly different.

The approach to the ignition temperature (240°C) along the reaction exotherm was not as abrupt when NTO was heated in an open vessel. This could be the result of heat loss by the escape of product gases or a different reaction mechanism altogether. A low-temperature decomposition exotherm was not observed in either of the two runs made in this way.

Summary of product analysis

A chemical equation that accounts reasonably well for the products found is

$$\begin{aligned} C_2H_2N_4O_3(s) = {} & \tfrac{1}{6}C_2H_3N_3O(s) + \tfrac{1}{6}H_2O(l) + \tfrac{1}{3}CO_2(g) + \tfrac{1}{3}N_2O(g) \\ & + \tfrac{3}{2}CO(g) + \tfrac{4}{3}N_2(g) + \tfrac{1}{6}NO(g) + \tfrac{7}{12}H_2(g) \end{aligned}$$

DISCUSSION

Under adiabatic conditions, the thermal decomposition of NTO led to a thermal runaway which was characterized by an explosive rate of heat and pressure generation. The temperature of the onset of thermal runaway in a confined, adiabatic reaction occurred at 208°C. The decomposition mechanism changed abruptly at 212°C where an ignition event occurred. Ignition was observed in both confined and unconfined systems.

NTO is thermodynamically unstable with respect to decomposition products, yielding at least -77 kcal mol^{-1}, but is kinetically quite stable. This kinetic stability was evidenced by the high temperature required to initiate thermal decomposition and by the notably large rate increase produced by a 1° C change in the reaction temperature.

NTO was found to possess greater thermal stability than RDX [8]. Under nearly identical conditions, the onset temperature for an NTO thermal runaway was approximately 28°C higher than that found for RDX and its ignition temperature was approximately 12°C higher.

We have provided a reasonable chemical equation for NTO decomposition which accounts for the major products found.

Evidence of an auto-catalytic mechanism in NTO decomposition was provided by the ARC data. The catalyst could be one of the products of the exothermic, gas-producing reaction which was detected in our adiabatic reactor at temperatures as low as 185°C. The identity of the catalyst was not determined.

We have found that decomposition will consume a significant amount of NTO prior to ignition if the sample is held isothermally at 185°C in the closed ARC bomb for 1 day. In one case, such isothermal aging apparently prevented ignition from occurring on subsequent heating to 310°C.

Factors which effect the rate of thermal decomposition of NTO might have a significant effect on its performance and thermal stability. These factors do not appear to include the NTO particle size, at least over the narrow range studied, but do include the isothermal age of the sample.

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