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CONF-9009243--

LA-UR--90-2427

DE90 014906

Received by OSTI

AUG 0 6 1990

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TITLE **STUDY OF THE INDUCTION TIME IN ISOTHERMAL DECOMPOSITION OF EXPLOSIVES**

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SUBMITTED TO **Conference Proceedings of 19th Annual North American Thermal Analysis Society Conference**
**Boston, Massachusetts**
**September 23-26 1990**

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# STUDY OF THE INDUCTION TIME IN ISOTHERMAL DECOMPOSITION OF EXPLOSIVES

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The high explosives (HEs) HMX, RDX, and TATB, were studied in the isothermal-age mode in the accelerating rate calorimeter (ARC) in the solid state at temperatures well below their rapid decomposition temperatures. The ARC maintained the temperature chosen until it detected an exotherm greater than 0.01 °C/min, at which time heaters in the walls of the calorimeter were programmed to keep the calorimeter at the same temperature as the sample cell. If during its induction time at elevated temperature HMX was cooled and reheated, the total induction time remained the same as that of an uncooled sample. However, if the cooled sample was ground to release any trapped gases after the first heating, then the induction time was extended. Mass spectrometry was used to identify the trapped gases.

## INTRODUCTION

Safe handling and storage of explosives requires knowledge of their decomposition in thermal environments. Some explosives like nitrocellulose decompose slowly even at ambient temperature and produce products that catalyze their decomposition, which can accelerate to explosion. Other explosives do not decompose unless heated. The critical temperature is the lowest temperature at which a piece of explosive of a specific size, shape, and composition can self-heat catastrophically. Frank-Kamenetskii equations have been used to calculate the critical temperature for a specific piece of explosive from kinetics constants, heat of reaction, thermal conductivity, density, size, and geometry.[1] The induction times can be very long near the critical temperature and the explosive may appear stable; however, it may begin to self-heat after days if kept at this temperature. During the induction time, the explosive does not produce enough heat to overcome the heat lost to the surroundings. However, at the end of the induction time the heating rate increases, and a temperature rise can be detected on the surface of the HE. The heat-production rate continues to accelerate until explosion. The isothermal-age mode of the accelerating rate calorimeter (ARC) is a convenient way to measure the induction time because it will automatically record the beginning

of the exotherm and begin to store temperature/time data. Also, the sample size that can be safely heated in the ARC is large enough for analysis.

The reactions and products produced in the thermal decomposition in the solid state in RDX and HMX have been studied by other workers and reviewed by Schroeder.[2] Recent attempts to identify and measure rates of release of the products of thermal decomposition of solid HMX using simultaneous thermogravimetric, modulated-beam mass-spectrometry are reported by Behrens.[3] He noticed broken shells of a polymeric nonvolatile material in the residue after his treatment of HMX at 224°C. This observation gave him additional evidence that bubbles of gas formed inside the HMX crystals during decomposition. Behrens observed that formation of $N_2O$ and $CH_2O$ during the induction time was dependent on the surface area. During the acceleratory stage a wider range of products appeared, as bubbles grew and broke, including $N_2O$, $H_2O$, $CH_2O$, NO, and CO.

In the current study, lower temperatures and longer induction times on larger samples in sealed cells are used. The purpose of this work is to understand the chemical and physical processes that occur during the induction time. Better understanding may lead to new ways to stabilize explosives and will increase the safety of storage and handling of these explosives.

## EXPERIMENTAL

The ARC used in these experiments was developed at Dow Chemical Company, Midland, Michigan, and manufactured by Columbia Scientific Industries of Austin, Texas. Details on the instrument are found in the literature.[4,5] The instrument was calibrated every fifty degrees to give a flat base line, but slight changes in the jacket offset constants were made at the selected isothermal temperatures to produce a base line with a negative slope between -0.001 and -0.005 °C/min. Changes in room temperature affect the slope in an inverse manner. The radiant heater is programmed to heat the sample if the temperature on the surface of the cell drops 0.1°C below the set temperature. A type N (Nisil/Nichrosil) thermocouple is fastened to the equator of the cell. This type of thermocouple has good run-to-run repeatability.

The sample cells are 1-in.-i.d. spheres with a 1.3-in. length of 1/8-in.-o.d. filler tubing made of lightweight Hastelloy C. Cajon fittings are used to seal to the gland and the pressure blowout seals. A diaphram pressure gauge was used in some experiments, but no significant pressure increase occurs during the induction time. Most experiments used a stainless-steel foil disk on the sample side plus a copper disk as blowout seals to keep the

gases in contact with the sample. The surface of the inside of the cell was passivated by heating at 600°C in a muffle furnace under a stream of oxygen for 1 hour. Samples weighed between 0.4 and 0.5 g and the thermal inertia,

$$\phi = 1 + \frac{Cp_{cell} \times mass_{cell}}{Cp_{sample} \times mass_{sample}}$$

ranged from 13 to 15. Samples of 99% pure RDX, HMX or TATB were heated isothermally in the ARC at temperatures 30 to 70°C below the exothermic temperature as observed by DTA scanned at 20°C/min.

The calorimeter changed to exothermic (adiabatic) mode if its heating rate exceeded 0.01°C/min during the search time and began to store data in the microprocessor. The time at the beginning of the exotherm is defined as the end of the induction time. If the exotherm slows to less than 0.01°C/min, the calorimeter returns to isothermal mode at that temperature and again searches for an exotherm.

Samples were cooled before the end of the induction time and shaken out of their cells for analyses. Trapped gas was analyzed by dissolving the sample in a degassed solvent in an evacuated tube and venting into a mass spectrometer. The solutions were analyzed by $^{13}C$-nuclear magnetic resonance on a JEOL 270-MHz spectrometer. Other samples were ground in a remotely operated mortar and pestle, sieved, and weighed into a clean cell to measure their induction times again.

## RESULTS AND DISCUSSION

The induction time for recrystallized HMX at 190°C was 32.2 ± 3.2 h on 13 runs. At 200°C it was 13.4 ± 1.3 h on six runs. Using the average time for these two temperatures together with induction-time values for other temperatures, the log of the induction time versus the reciprocal temperature (K) is a straight line, Figure 1, with the following equation:

$$\text{Log (induction time of HMX)} = -18.214 + 9.178\ (1000/T).$$

If the dependence of induction time on temperature follows Arrhenius kinetics, and the end of the induction time corresponds to the same percentage of decomposition in the sample at different

temperatures, the method of Kishore can be used to find the activation energy.[6] The slope of the plot times 2.3R gives an approximate activation energy of 41.9 kcal/mole, which agrees with other findings.[2]

Coarse HMX crystals (300 μm) received from the United Kingdom have an average induction time of 21.4 ± 3.2 h. To study the influence of the gas formed on the onset of the exotherm, samples (0.5 g) of HMX crystals were heated for 16 h at 190°C, then cooled, ground remotely, and sieved. Sieve fraction 125-177 μm of unheated HMX had an induction time of 23 h while that size fraction of heated HMX had an induction time of 8.7 h. The next smaller sieve fraction, 62-125 μm, of the heated HMX had an induction time of 10.8 h. For an unground heated sample, the exotherm began almost immediately after reheating to 190°C, 0.75 h; therefore, it appears that the product gases formed and trapped inside of the crystals have an effect on the onset of the exotherm. The induction times of the heated and ground samples were not as long as for the unheated HMX, indicating that nonvolatile decomposition products are also catalyzing the decomposition.

Observations were also made on changes of the properties of crystals. The loss of weight was small, 1.0 to 1.4%. The Type-12, 2.5-kg weight impact sensitivity remained the same -- 34.6 vs 34.2 cm drop height. The surfaces of the crystals, observed by microscope, changed from shiny translucent sharp faces to opaque, milky white particles with rounded corners such as would be expected of gas-containing particles. The HMX went through phase changes and the pseudomorphs were made up of microcrystals. Gases escaped easily when the crystals were ground because of discontinuities between the microcrystals. Mass-spectral analysis found the decomposition gas $N_2O$, but other gases were either masked by air from incompletely degassed solvent or dissolved in the solvent. $^{13}C$-NMR detected small peaks of decomposition products at 21.32, 46.68, 55.15, 65.38, 81.05, 174.19, and 180.07 ppm and $^{1}H$-NMR showed a water peak, which could have resulted in part from the hygroscopicity of the dimethylsulfoxide solvent.

The RDX crystals heated at 180°C, had an induction time of 39.8 ± 1.8 h. One sample heated for 28.5 h at 180°C, lost 5.6% of its weight after cooling. The sample was opened, evacuated, refilled with air, and reheated to 180°C. Exotherm began at 4.2 h to give a total induction time of 34.7 h. Removal of free gas did not lengthen the induction time.

TATB has been studied at different temperatures, but interrupted heating experiments have not been done. The log of induction time at several temperatures was plotted against reciprocal time and gave a straight line (Figure 1). The points for both RDX

and TATB were fitted with the following linear equations:

Log (induction time of RDX) = -30.58 + 14.61 (1000/T)
Log (induction time of TATB) = -15.23 + 8.62 (1000/T)

Activation energies were calculated for RDX and TATB to give 66.8 and 39.4 kcal/mol, respectively. The number is high for RDX[6] and low for TATB.[7] The assumptions for the simplified calculation of activation energy may not be valid.

## CONCLUSIONS

Mass spectroscopy and induction time experiments on heated samples of HMX confirm reports of bubbles inside the crystals containing decomposition products. These decomposition products catalyze the acceleratory decomposition because the induction time is lengthened when they are removed by crushing the crystals. Other nonvolatile decomposition products may also catalyze the decomposition because, after crushing the crystals, the induction time was not as long as for the original material. If the induction time is almost ended when the sample is cooled, it will go into an exotherm shortly after reheating to the isothermal temperature.

## ACKNOWLEDGMENTS

This work was performed under the auspices of the U.S. Department of Energy, Contract No. W-7405-ENG-36.

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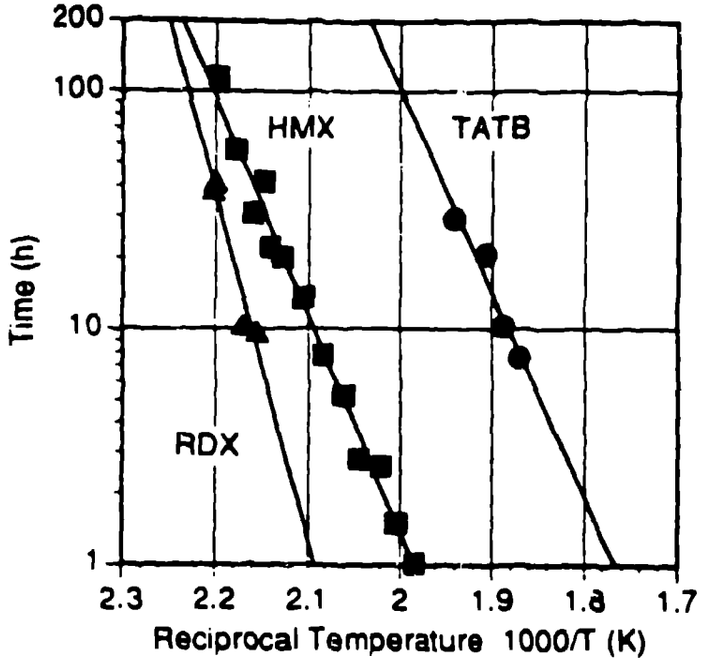


Fig. 1 Induction Time of HMX, RDX, and TATB.