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AND OTHER ENERGETIC MATERIALS(U) DELAWARE UNIV NEWARK
DEPT OF CHEMISTRY T B BRILL 01 OCT 87 AFOSR-TR-88-0169
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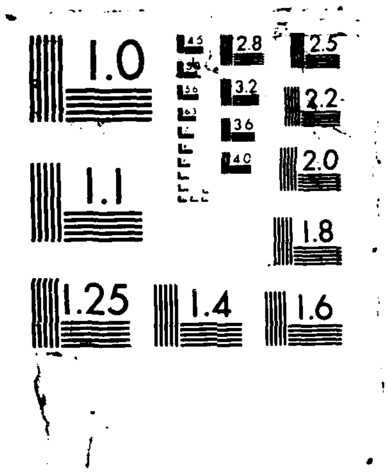
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19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

High heating rate thermolysis studies of energetic materials using rapid-scan Fourier transform infrared spectroscopy as the diagnostic technique have yielded considerable information on the origins of the pressure dependence of the process and structure/property/reactivity relationships. The pressure dependence of the observed gas products up to 1000 psi was shown for the first time to originate from heterogeneous gas/condensed phase reactions. The formation of NH_3 from alkylammonium nitrate salts occurs only if the O/H ratio is less than one. The thermochemistry of cyclic and acyclic nitramines is shown to be different in the condensed phase as a result of the different global molecular shapes. Hydrogen bonding as a stabilizing feature in the impact sensitivity of an energetic material was shown to be overridden by the presence of energetic functional groups. (Key words)

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I. Research Objectives

Our research program has several objectives. The fundamentals of fast thermal decomposition of energetic materials under conditions that approximate reality have been extremely difficult to acquire. This subject is a basic element of combustion modeling, hazard assessment, the development of new propellants and burn-rate improvements of current materials. We are attempting to reach a new level of understanding of these important subjects through development of new diagnostic techniques and the study of a large number of energetic materials. We have had considerable success in the last several years and this year was no exception.

We have continued to advance the understanding of structure/property/reactivity relationships of energetic materials by quantifying the first observed gas products immediately above the surface during fast thermolysis. This is a real-time experiment with a temporal resolution of about 100 msec. The heating rates are in the range of 50-400°C/sec and the static gas pressure on the sample is adjustable as desired in the 1-1000 psi range. These conditions are a much more realistic simulation of the rocket combustion environment than has been the case for most previous thermal decomposition studies, which largely involve slower heating rates and time delays between thermolysis and diagnosis.

A new technique has been developed that permits simultaneous, real-time, determination of the temperature of the condensed phase and the products ejected to gas phase at high heating rates. Endothermic and exothermic processes in the condensed phase can now be connected to the products that appear in the gas phase. This technique shows great promise for giving a deeper understanding of thermal decomposition mechanisms of interest in propellant combustion, for hazard analysis, and, especially, for fundamental studies of multi-component materials which are the "real world" of energetic compounds. That I am aware of, there are six organizations on four continents that have decided to reproduce this device and our procedures for the study of various combustion processes. These researchers are involved in studies of the combustion of wood, grass, tobacco and building materials, in addition, to energetic materials studies.

II. Status of Research

We have begun to apply FTIR/thermal profiling to the study of many energetic materials and feel that the payoff will be great. However, we are at a very early stage of this effort and will not report any of these results in this annual report. The work that has been completed has involved developing structure/property/reactivity relationships, an area in which we have been continuously interested and have had considerable success.[1-4] We have also achieved a major advance in understanding of the effect of pressure on thermolysis processes at the molecular level. These results are summarized below.

A. Pressure Effects

A major piece of research spanning several years was completed and published on the various effects of pressure on the first observed decomposition products of 34 energetic materials.[5] This work was conducted so that the heating rates were all about the same throughout the 1-1000 psi range of Ar buffer gas pressure. The compounds studied included nitramines, azides, C-NO_2 and O-NO_2 containing compounds. The compounds were found to separate into two major categories: Those in which the pressure dependence in the first observed gas products is large and those whose initial products were much less pressure dependent. Some further subdivision of these categories was found to be helpful but will not be discussed here. Figure 1 shows the concentration *vs* pressure profiles of the quantified gas products in the initial 200 msec of thermolysis at 100-130 K/sec of a compound from the first class of materials. The compound is RDX. A three zone behavior in the first observed products is found. The dominant early product at the lower pressures is the reactive gas product NO_2. In the mid-pressure range HCN and NO dominate. These gases are of intermediate stability in the scheme of nitramine decomposition. At the higher pressures the stable products, CO and CO_2, (N_2, which is not detected in the IR spectrum, is undoubtedly present as well) are dominant. Many compounds, not just nitramines, exhibit this three zone behavior.

There are some interesting sidelights to the presence of three zones of products. First, the NO_2--→NO--→N_2 and CH_2O--→CO--→CO_2 reaction sequences found in this work are confirmed to be the natural pathways for nitrogen and carbon chemistry of many energetic materials. Second, these sequences are the ones that model nitramine flame chemistry which adds credence to the flame models that employ these mechanistic sequences.

Figure 2 illustrates an extreme example from the second class of compounds. That is, those that exhibit little pressure dependence. The data are for TNTO, *1*. It exhibits no pressure dependence in the quantified gas products.

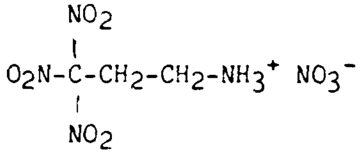
There are fluorohydrocarbons also present but no IR absolute absorption intensities are available for them and so they were not quantified. The reactive gas, NO_2, exhibits little pressure dependence because there are no gas species present with which it can react under these conditions.

The explanation for the pressure dependence of the gas phase species was shown in this study to be the increased amount of reaction between the gas molecules and condensed phase material as the pressure is raised.[5] The diffusion rate of gas molecules is suppressed by increasing the pressure so that they remain in contact with and can react to a greater extent with the condensed phase as the pressure is raised. Thus, the reactions move farther along in their multistep reaction pathway as the pressure is raised.

B. Structure/Property/Reactivity Relationships

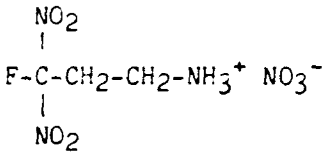
A study of the solid-solid phase transitions and solid-melt phase transition of seven cyclic and ten acyclic nitramines revealed a pattern when the ΔH values for each compound were summed and the value of ΔS of fusion for each compound was measured.[6] A statistically significant difference exists between the set of ΔH and ΔS values for the cyclic nitramines and acyclic nitramines. This difference is traceable to the global shape of the molecules and adds further insight into the condensed phase dynamics of these molecules. The cyclic molecules require more energy to mobilize from the condensed phase than do the chain-like acyclic molecules. This information is helpful for understanding the total energy balance involved in taking an energetic material from a cool solid through its decomposition temperature.

The high-rate thermolysis of amine nitrate salts containing additional energetic functional groups was initiated.[7] We investigated TNPAN, 2 and FDNPAN, 3.



$$O_2N\text{-}\overset{NO_2}{\underset{NO_2}{C}}\text{-}CH_2\text{-}CH_2\text{-}NH_3^+\ NO_3^-$$

2



$$F\text{-}\overset{NO_2}{\underset{NO_2}{C}}\text{-}CH_2\text{-}CH_2\text{-}NH_3^+\ NO_3^-$$

3

One question addressed was what are the relative stabilities of the functional groups: $-C(NO_2)_3$, $-C(NO_2)_2F$, and $-NH_3^+\ NO_3^-$? By careful thermolysis studies of these materials we were able to separate the effects of the two functional groups from one another and show that the order of stability is $F(NO_2)_2C- > -H^+\cdots NO_3^- > (NO_2)_3C-$. In fact, the nature of the functional group controls whether the backbone or the salt portion of the molecule decomposes first.

We have studied about a dozen aliphatic ammonium nitrate salts to date and have found that the O/H ratio can be used to predict whether the fuel, NH_3, will be a gas phase product or not. The O/H is a measure of the oxidizing power of the compound. Compounds with an O/H ratio greater than 1 liberate NH_3 upon fast thermolysis, while those with O/H < 1 do not produce NH_3. This information has potentially high payoff because NH_3 is a strong burn rate accelerator for nitramines. A comprehensive study of a wide range of ammonium nitrate salts is now underway on another program.

An investigation of the thermolysis of nitroguanidine (NGu) and trinitroethylnitroguanidine (TNENG) was undertaken in a further attempt to contribute to the understanding of the effects more than one energetic functional in the molecule.[8] In addition, the very large differences in the impact sensitivity between these two compounds was of interest. A crystal structure determination of TNENG was carried out (Figure 3). It has been proposed that hydrogen bonding is responsible for the low impact sensitivity of NGu.[9] The crystal structure revealed a similar amount of hydrogen bonding in TNENG, but TNENG is a highly impact sensitive material. Therefore, while hydrogen bonding may desensitize certain materials, the presence of a highly energetic group, such as $-C(NO_2)_3$, overrides this stabilizing influence and renders the hydrogen bonding ineffective. Work is continuing on structure/property/reactivity relationships and is currently being focused on high nitrogen compounds. These materials have been difficult for us to study in the past because N_2, which is IR inactive, is a major product. We are working on a new technique involving high heating rate thermogravimetric analysis combined with rapid-scan FTIR that may allow advances to be made in this area.

Work is beginning on applying our newly developed methods to multicomponent materials such as double based propellants with the hope of providing a much more detailed phenomenonological description of the decomposition processes taking place in an actual propellant.

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5. Y. Oyumi and T. B. Brill, Combust. Flame, 68, 209 (1987).
6. Y. Oyumi and T. B. Brill, Thermochemica Acta, 116, 125 (1987).
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9. J. P. Ritchie, D. T. Cromer, R. F. Stewart, H. J. Wasserman and R. R. Ryan, LA-UR-85-1088, Los Alamos Scientific Lab, NM, 1985.

Figure 1: The relative % concentrations of the gas products as a function of pressure from RDX heated at 100-130°C/sec. Note that three zones of products are found.

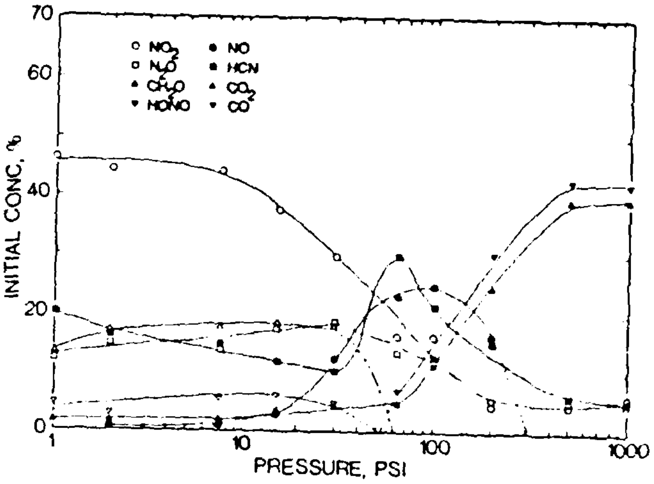


Figure 2: The relative % concentrations of the gas products as a function of pressure from TNTO heated at 100-130°C/sec. Note the distinct lack of a pressure dependence in the thermolysis gas concentrations which contrasts with the results in Figure 1.

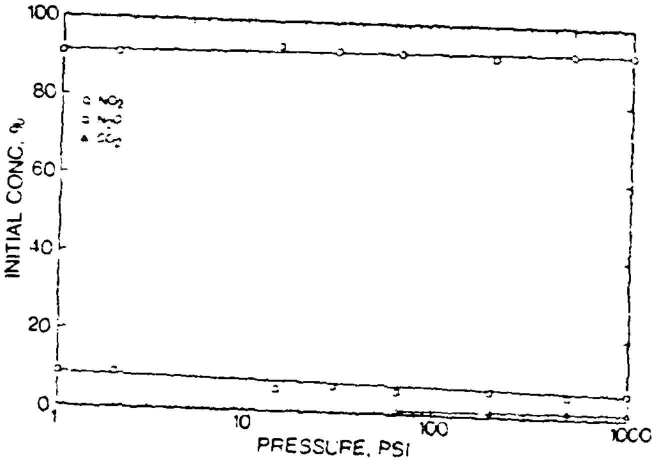
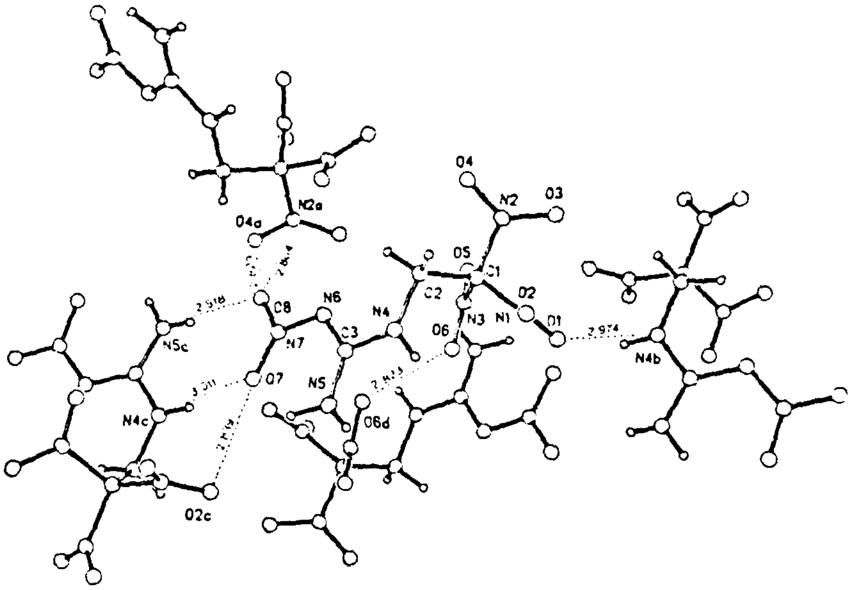


Figure 3: The crystal lattice packing of TNENG showing the hydrogen bonding network that is responsible for the organization of the structure. Unlike NGu, this packing does not stabilize the lattice toward impact.



III. Interactions

A. Meetings and seminars

My students or I attended and presented papers on various aspects of energetic materials at the following meetings or institutions. The starred papers dealt with and acknowledged our AFOSR supported work.

(1) FACSS Meeting - St. Louis, MO, Oct. 1986

*(2) ONR Workshop on Oxidizers, Great Oak Landing, MD, Nov. 1986

*(3) Naval Weapons Center, China Lake, CA, Jan. 1987

(4) Pittsburgh Conference, Atlantic City, NJ, March 1987

*(5) ARO Working Group Meeting on Sensitivity of Explosives (Member of Organizing Committees), Socorro, NM, March 1987

*(6) University of New Mexico, Albuquerque, NM, April 1987

(7) Aerojet Strategic Propulsion Co., Consortium Meeting, Sacramento, CA, May 1987

(8) Middle Atlantic Region of ACS Meeting, Atlantic City, NJ, May 1987

*(9) ONR Workshop on Condensed Phase Phenomena, Great Oak Landing, MD, May 1987

*(10) AFOSR/Rocket Propulsion Research Meeting, PSU, University Park, PA, June 1987

*(11) F. J. Seiler Research Laboratory, Colorado Springs, CO, July 1987

(12) Morton-Thiokol IR and D Review, Ogden, UT, July 1987

(13) ARO-Liquid Propellants Program Review, Aberdeen, MD, August 1987

*(14) International Conference on FTIR Spectroscopy, Vienna, Austria, August 1987

*(15) Fraunhofer Institut-ICT, Karlsruhe, FRG, August 1987

*(16) Symposium on Photophysics and Chemistry of Energetic Species, USC, Los Angeles, CA, September 1987

*(17) University of New Orleans, September 1987

B. Substantive Interactions with Other Laboratories

The nature of the work that we do requires that I discuss thermolysis processes and synthesis with many people throughout the country and world. Interactions have taken place with the following people this year (no significance to order).

Naval Surface Weapons Center-White Oak

H. Adolf M. Chaykovski J. Sharma
W. Koppes P. Miller

Ballistics Research Laboratory

A. Miziolek N. Klein E. Freedman
D. Beyer R. Frey R. Fifer
G. Adams B. Lengsfield

Sandia Livermore

C. Melius S. Vosen R. Karline
R. Armstrong R. Behrens

Naval Weapons Center

T. Boggs A. Nielson M. Chan
H. Richter J. Fischer T. Parr

F. J. Seiler Labs, USAFA

J. Wilkes S. Shackleford

Picatinny Arsenal

N. Slagg S. Bulnsu J. Alster
O. Sanders Y. Carignan F. Owens

Los Alamos NL

M. Coburn J. Ritchie R. Rogers
S. Agnew C. Storm B. Swanson
N. Blaise

Morton-Thiokol, Elkton

R. Willer R. Biddle W. Brundige
G. Conkle F. Goetz

Hercules

M. Trygstad T. Cassidy J. Graham
D. Pivonka

Lawrence Livermore NL

R. McGuire C. Coon
E. Lee

SRI International

R. Schmidt D. McMillen
D. Golden D. Ross

AFRPL

T. Edwards F. Roberto
D. Weaver

AFATL

R. McKenney T. Floyd
M. Caluda

ONR

R. Miller

ARO

R. Ghirardelli R. Seiders
D. Mann R. Shaw

Sandia, Albuquerque

A. Renlund R. Cummings
W. Trott

Naval Research Lab

R. Gilardi

Morton-Thiokol, Wasatch

D. Flanigan J. Hinshaw
J. Davidson

Morton-Thiokol, Huntsville

W. Graham J. Hightower

Aerojet

J. Campbell J. Manser F. Meyers
M. Todd

Georgia Tech

E. Price

New Mexico Inst. Mining & Tech

J. Oxley P-A. Pearson

Univ. of New Orleans

P. Politzer G. Griffin J. Boyer
E. Stevens

Fraunhofer Institut, Karlsruhe, FRG

H. Krause N. Eisenreich A. Pfeil
P. Duff

Yale University

M. McBride R. Chang

Fluorochem

T. Archibald K. Baum

Atlantic Research Corp.

R. Powers

Purdue University

J. Osborne

3rd Japan Defence Agency

N. Kubota Y. Oyumi

Univ. of So. California

H. Reisler K. Wittig

Nicolet Instruments

R. Rosenthal

IV. Publications

Y. Oyumi, T. B. Brill, and A. L. Rheingold, "Thermal Decomposition of Energetic Materials 20. A Comparison of the Structural Properties and Thermal Reactivity of an Acyclic and Cyclic Tetramethylenetetranitramine Pair," Thermochimica Acta, 114, 209 (1987).

Y. Oyumi and T. B. Brill, "Thermal Decomposition of Energetic Materials 21. The Effect of the Backbone Composition of the Products Evolved Upon Rapid Thermolysis of Linear Nitramines," Combust. Flame, 67, 121 (1987).

Y. Oyumi and T. B. Brill, "Thermal Decomposition of Energetic Materials 22. The Contrasting Effects of Pressure on the High-Rate Thermolysis of Thirty-four Energetic Compounds," Combust. Flame, 68, 209 (1987).

Y. Oyumi and T. B. Brill, "Thermal Decomposition of Energetic Materials 23. Thermochemical Differentiation of Cyclic and Acyclic Nitramines by Their Phase Transitions," Thermochimica Acta, 116, 125 (1987).

Y. Oyumi, A. L. Rheingold and T. B. Brill, "Thermal Decomposition of Energetic Materials 24. A Comparison of the Crystal Structures, IR Spectra, Thermolysis and Impact Sensitivities of Nitroguanidine and Trinitroethylnitroguanidine," Prop. Explos. Pyrotech., 12, 46 (1987).

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J. T. Cronin and T. B. Brill, "Thermal Decomposition of Energetic Materials 26. Simultaneous Temperature Measurements of the Condensed Phase and Rapid-Scan FTIR Spectroscopy of the Gas Phase at High Heating Rates," Appl. Spectrosc., 41, 1147 (1987).

V. Research Participants

A. Principal Investigator
  Thomas B. Brill

B. Faculty Collaborators (U. of Delaware)
  A. L. Rheingold (X-ray crystallography)
  M. K. Jain (Thermal analysis)
  J. Futrell/B. Munson (Mass Spectrometry)

C. Graduate Students
  Y. Oyumi (Ph.D. completed, Jan. 1987)
  J. Kiley
  C. Stoner

D. Postdoctoral
  Mark Timken

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