Structure/Property/Reactivity Relationships among Nitramines and Newer Energetic Materials

Brill, Thomas B.

Final

FROM 10/1/85 TO 9/30/86

October 6, 1986

12. PERSONAL AUTHOR(S)

Thermal decomposition, Infrared spectroscopy, Pressure effects, X-ray crystallography, Nitramines, Phase transitions, Furoxan, Azides, Nitrate esters, Nitro compounds, Nitrate salts, Structure/property/reactivity relationships.

Rapid-scan infrared spectroscopy studies of the high rate thermolysis of energetic molecules containing CNO₂, NNO₂, ONO₂, N₃, NO₃, ClO₄⁻ and furoxan groups are reported. In addition, solid-solid phase transition studies by IR spectroscopy, DSC, solid-state NMR and X-ray crystallography have been conducted. Structure/property/reactivity relationships have been established for the formation of NO₂ and HONO. Understanding of some of the factors influencing the formation of CH₂O, N₃O and NO has also been acquired. The influence of the static applied pressure on the first observed decomposition products has been explored successfully.

DISTRIBUTION/AVAILABILITY OF ABSTRACT

UNCLASSIFIED/UNLIMITED

SAME AS REPORT

DTIC USERS

BACKGROUND

Aerospace and Defense

17. COSATI CODES

<table>
<thead>
<tr>
<th>FIELD</th>
<th>GROUP</th>
<th>SUB-GROUP</th>
</tr>
</thead>
</table>

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

Thermal decomposition, Infrared spectroscopy, Pressure effects, X-ray crystallography, Nitramines, Phase transitions, Furoxan, Azides, Nitrate esters, Nitro compounds, Nitrate salts, Structure/property/reactivity relationships.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Rapid-scan infrared spectroscopy studies of the high rate thermolysis of energetic molecules containing CNO₂, NNO₂, ONO₂, N₃, NO₃, ClO₄⁻ and furoxan groups are reported. In addition, solid-solid phase transition studies by IR spectroscopy, DSC, solid-state NMR and X-ray crystallography have been conducted. Structure/property/reactivity relationships have been established for the formation of NO₂ and HONO. Understanding of some of the factors influencing the formation of CH₂O, N₃O and NO has also been acquired. The influence of the static applied pressure on the first observed decomposition products has been explored successfully.
I. Research Objectives

The objectives of this research program are multifaceted. First, little is known about the chemical species contained in the dark zone that interfaces the surface of the condensed phase and the flame of a burning propellant. The problem is that in practice this transient zone is so thin that it has resisted diagnostic analysis. We are attempting to simulate this region by heating a solid material very rapidly under realistically high pressures without actually creating the flame. By the use of unusually fast scanning IR spectroscopy, the gas products that are ejected immediately above the surface can be identified and quantified. Since it is these gas products that feed the flame, this work also in effect simulates ignition chemistry.

Second, we are attempting to construct structure-property-reactivity relationships for the thermolysis of a wide variety of energetic materials. Such relationships would allow qualitative predictions of the initial gas products that are released on rapid thermolysis simply by examining the structure or measuring a particular physical property. Establishing such relationships is also a goal in other sectors of science such as the pharmaceutical industry and the catalysis industry. It should be possible to construct these relationships for the products initially liberated by the thermal decomposition of an energetic material.

Third, we are attempting to uncover the solid-solid phase transition patterns of energetic materials since solid-solid phase transitions influence the efficacy of handling and use of energetic materials. This work includes molecular structure studies by x-ray crystallography, thermal analysis studies by DTA, and phase transition-structural analysis by variable temperature IR spectroscopy. Kinetic data can sometimes be acquired for these phase transitions.
II. Status of Research

A. Development of new techniques

Rapid-scan infrared spectroscopy studies combined with fast pyrolysis methods developed in house is progressing well. Already a vast amount of new information and new levels of understanding of the decomposition processes of energetic materials have emerged.

Several generations of a homebuilt high-rate pyrolysis cell have been developed which now permit the observation and quantitation of gas products produced at heating rates of \(10^{-2} \text{ to } 250 \text{ K sec}^{-1}\). These products can be monitored as a function of time as evidence of further reactions among the products. While this facility is currently unsurpassed in the world for doing these sorts of experiments, we are not planning to rest on it. For instance, we are currently designing a residual gas analyzer system to permit combined infrared analysis and mass spectrometric analysis of the products. This procedure will allow quantitation of both IR active and IR inactive products, as well as helping to identify products we occasionally see that cannot be identified by IR spectroscopy alone.

We are planning to add pressure to temperature as a variable in our condensed phase studies. This will be done with a heated diamond anvil cell.

B. Thermal Decomposition

A large amount of research has been conducted and written up during the initial year of this program. Product speciation for about 50 compounds (Figure 1) as a function of heating rate (up to 250 K sec\(^{-1}\)) and pressure (1-1000 psig) has been assembled so far. Common conditions have been used in almost all cases so that the data from one compound can be directly compared to that of another. Several patterns have begun to emerge and are summarized below.
Figure 1. Compounds studied to date in this program.
(1) Segmented decomposition patterns have been observed in nitrate esters wherein three classes of compounds emerge: those for which side chain products dominate, those for which side chain and backbone products compete, and those for which backbone products dominate.

(2) Convincing evidence that decomposition precedes deflagration in high heating rate thermolysis experiments has been obtained. This comes from capturing the transition from decomposition products to deflagration products in the same experiment on gem-trinitro and gem-fluorodinitro compounds. A representative result is shown in Figure 2.

(3) The asymmetric stretching frequency of the $-\text{NO}_2$ group in $\text{C}_2\text{NNO}_2$ containing nitramines is a good diagnostic of whether $\text{NO}_2$ will be the dominant decomposition product or will be mixed with comparable concentrations of other products. This correlation is shown in Figure 3.

(4) Compounds containing the $\text{O}_2\text{NN-CH}_2\text{NNO}_2$ fragment very frequently produce $\text{N}_2\text{O}$ and $\text{CH}_2\text{O}$ upon thermolysis. The exception so far is DNNC where the $\text{C(NO}_2)_2$ fragment seems to dominate the decomposition.

(5) Nitramines almost always liberate HONO as one of the thermolysis products whereas few other energetic materials do.

(6) Primary alkylamine nitrate salts appear to decompose initially by proton transfer leading to $\text{HNO}_3$. The $\text{HNO}_3$ thus produced then oxidizes the alkylamine. The equivalent proton transfer reaction does not occur with secondary or tertiary alkylamines.

(7) Solid-solid phase transitions among various polymorphs were discovered and studied for DNNC, TAGN, TNDBN, and DPT. TNDBN provides an example of a variation on conformational polymorphism which is an interesting and important phenomenon for HMX.
Figure 2

The concentration-time profile of the gas products from FEFO heated at 100K sec\(^{-1}\) under 65 psi of Ar.

![Graph showing gas product concentrations over time.]

Initial thermal reaction is decomposition by C-N bond fission.

Follow-up step is vigorous oxidation of the remainder of the molecule by NO\(_2\) to produce NO and deflagration products.

This figure demonstrates that decomposition occurs in advance of deflagration when a material is heated at a high rate. This may seem self-evident but it is devilishly difficult to prove and has not been proven before in real time as far as we are aware.
Figure 3. A structure-property-reactivity relationship for secondary nitramines (C₂NNO₂) showing the correlation of the asymmetric NO₂ stretching frequency with the N-N bond distance. Compounds to the upper left are strong NO₂ generators.

Figure 4. The relative % HONO produced in the initial 0.2 sec when nitramines are heated at dT/dt = 120-140 K sec⁻¹. There is a correlation with the H⁺ to NO₂⁺ ratio in the parent molecule.
(8) The decomposition of polymeric azide-containing compounds is relatively independent of pressure in the 1-1000 psig range suggesting that their decomposition pattern is dominated by a single process, probably decomposition of the azide group to the nitrene and N₂.

(9) The routine observation of HONO being liberated upon thermolysis of nitramines has permitted some understanding of its formation from the condensed phase. Rather than being formed by a concerted four or five-centered elimination step, HONO forms in the condensed phase largely by adventitious contact between H⁺ and NO₂⁻. The larger the H/NO₂ ratio in the parent molecule, the more HONO that is produced. Figure 4 shows this correlation.

(10) Primary nitramines were found to be strong N₂O generators while linear secondary nitramines produce much less N₂O and more NO₂ or HONO. The \( \text{NCH}_2\text{N}^- \) unit is less thermally stable than the \( \text{NCH}_2\text{CH}_2\text{N}^- \) unit.

(11) For mixed azidomethyl-nitramines, it has been possible to show that the azide group decomposes first and probably produces a radical that depolymerizes to N₂O and CH₂O. The N-N bond fission process in such molecules is strongly suppressed.

(12) Linear and cyclic nitramines were found to have comparable patterns of decomposition.
C. Solid Phase Studies

Crystal structure determinations were undertaken on the compounds shown below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>DATH</td>
<td><img src="image" alt="DATH Structure" /></td>
</tr>
<tr>
<td>DNFP</td>
<td><img src="image" alt="DNFP Structure" /></td>
</tr>
<tr>
<td>BCEN</td>
<td><img src="image" alt="BCEN Structure" /></td>
</tr>
<tr>
<td>BCMN</td>
<td><img src="image" alt="BCMN Structure" /></td>
</tr>
<tr>
<td>OHMX</td>
<td><img src="image" alt="OHMX Structure" /></td>
</tr>
</tbody>
</table>

These studies augmented our work on trying to put some organization into the complex solid-solid phase transition patterns that are exhibited by various energetic materials. This is a very ambitious project which, not surprisingly, has been somewhat less successful than that described above at putting structure-property-reactivity relationships of energetic materials on a more sound footing. A preliminary and rather crude correlation of the enthalpy of the lower temperature solid phase with the molecular weight separates compounds according to whether they are cyclic or acyclic in their backbone.

III. Interactions

A. Meeting and Seminars

(1) Pittsburgh Conference on Analytical Chemistry, Atlantic City, NJ, for equipment examination, March 1986
The nature of this work requires that I regularly talk with synthesis chemists and persons involved in the characterization of thermally labile compounds. Through the past year of this program, interactions have been developed with the following persons (no particular order is meant).

Naval Surface Weapons Center-White Oak

Horst Adolf

Naval Surface Weapons Center-Indian Head

George Nauflett

Ballistics Research Laboratory

Andrzej Mizolek Robert Fifer
Mike Schroeder Nate Klein
Eli Freedman Dick Beyer

Lawrence Livermore National Laboratory

Raymond McGuire
Cliff Coon

Stanford Research International

Cliff Bedford
Dave Golden
Dave McMillan

Sandia Livermore National Laboratory

Carl Melius Rich Behrens
Sheridan Johnston Steve Vosen
Rob Armstrong

Picatinny Arsenal

Surya Bulusu Arthur Bracuti
Gilbert Sollott Yvon Carignan

Los Alamos National Laboratory

Mike Coburn Jim Ritchie
Ray Rogers Steve Agnew
Carl Storm Jerry Dick

Naval Research Laboratory

Robert Doyle
Richard Gilardi

Lawrence Berkeley National Laboratory

Yuan Lee

Aerochem

Don Olson
Rocketdyne
Dean Woolery
Milt Frankel
Joe Flanagan
Jim Weaver
Carl Christie

Georgia Tech
Ed Price

University of Colorado
Mel Branch

Rensselaer Polytech Institute
Arthur Fontijn

Aerojet
Gerry Manser
Mike Todd
Fred Meyers

Purdue University
John Osborne

United Technologies
D. Guimont

Systems Research Laboratory
Larry Goss

Morton-Thiokol, Elkton
Rod Willer
Ernie Sutton
Winston Brundige
Frank Goetz
Richard Biddle

Nippon Fats & Oils (Rocket Propellant Section)
Kenji Saumikawa
Koichiro Uchiyama

Office of Naval Research
Dick Miller

Morton-Thiokol, Wasatch
Dave Flanigan
Thomas Davidson

Institute of Space & Astronautical Science
(University of Tokyo)
Akira Iwama

Morton-Thiokol, Huntsville
William Graham
Jim Hightower

3rd Japan Defense Agency, Tokyo
N. Kubota

Hercules-Aerospace
Robert Earl
Kenneth McCarty
Mark Trygstad

Fraunhofer Institute, Karlsruhe
A. Pfeil
H. Schmidt

Fluorochem
Kurt Baum

Defense Research Center, Adelaide
T. T. Nguyen

MICOM
Walt Wharton
Bill Stevens

Other:

1. Reviewed proposals on Energetic Materials for:

   Army Research Office
   National Science Foundation
   Ballistics Research Laboratory
IV. Publications


V. Research Participants

A. Principal Investigator

Thomas B. Brill

B. Faculty Collaborators (University of Delaware)

Arnold L. Rheingold (X-Ray Crystallography)
Burnaby Munson (Mass Spectrometry)
Cecil Dybowski (Solid State NMR Spectroscopy)

C. Graduate Students

1. Full Effort

Yoshio Oyumi Ph.D. Expected December 1986
Jeff Kiley
Tom Russell
END

1–81

DTIC