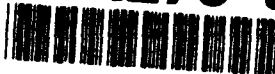**AD-A275 957**

OCUMENTATION PAGE

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 04 JAN 94	3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE

Thin Film Laser Pyrolysis of Nitramine Propellants

5. FUNDING NUMBERS

② ① DAAL03-90-G-0043

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FEB 2 4 1994
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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

ARO 27603.4-C

11. SUPPLEMENTARY NOTES

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13. ABSTRACT (Maximum 200 words)

A thin film laser pyrolysis technique has been developed to investigate initial steps in the thermal decomposition mechanism of RDX (1,3,5-trinitro-1,3,5-triazine) under rapid heating conditions. In this technique, thin films (10 microns or less) of RDX are irradiated with the pulsed output of a line-tuneable carbon dioxide laser to heat them from 77 K to approximately 1000 K in 35 microseconds. The films are then cooled back to 77 K in a few milliseconds by heat conduction into the film support. Initial pyrolysis reaction products are thereby trapped in the films for detection by transmission infrared spectrscopy. Results of numerous experiments on RDX films show that the initial step in the thermal decomposition mechanism under these conditions is unimolecular scission of a single N-N bond in the condensed phase. This reaction forms nitrogen dioxide, which is detected in its dimerized form, dinitrogen tetroxide.

14. SUBJECT TERMS

RDX; nitramine; laser; pyrolysis; thin film; infrared

15. NUMBER OF PAGES

13

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std 239-18
298-102

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Final Report

Charles A. Wight

January 4, 1994

U.S. Army Research Office

Grant No. DAAL03-90-G-0043

University of Utah

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94-05794

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I. Statement of the Problem

Cyclic nitramines such as 1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX) are energetic materials that are used as propellants and explosives. Although many of the physical characteristics of explosions and detonations of these materials are well described by modern hydrodynamic theories of detonation,[1,2] mechanistic details of how chemical energy is released in these materials is only beginning to emerge.[3,4]

A search for the chemical mechanism of thermal pyrolysis in RDX and HMX has been the subject of several experimental investigations[5,6,7,8,9,10,11,12,13,14] and computational studies.[15,16,17] Many of these studies suggest that N-N bond cleavage is the initial step in the reaction. Thermodynamic studies identify this as the weakest bond in the molecule[18] and experimental studies on other nitramines provide indirect support for this mechanism.[4] However, a gas phase molecular beam laser pyrolysis experiment[19] provides convincing evidence that a major decomposition route is the concerted depolymerization of gas phase RDX to form three molecules of methylenenitramine, CH_2NNO_2. Pathways involving initial cleavage of an N-N bond account for only about one third of the gas phase product yield. A classical dynamics study recently published by Sewell and Thompson supports the viability of this depolymerization pathway.[20]

Perhaps the most detailed studies of thermal decomposition mechanisms in RDX and HMX have been carried out by Behrens and Bulusu using simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) measurements.[21,22,23,24] These authors have identified four major decomposition pathways for RDX, two of which exhibit first-order reaction kinetics (accounting for about 40% of the observed products) while the other two involve higher order reactions in their rate-limiting steps. Many of the products exhibit significant deuterium kinetic isotope effects, in agreement with earlier studies,[12,25] indicating that hydrogen transfer reactions are rate-limiting in some of the pathways. In experiments of this type, samples are heated very slowly in comparison with the speed

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of product detection, so that the temporal information reflects the rate-limiting steps in the reaction mechanism rather than the *initial* steps. Nevertheless, some information about initial steps can be inferred from the data. Interestingly, little evidence was found for the concerted depolymerization route, and only one of the channels was clearly identified as being initiated by N-N bond scission.

One of the important advances in this field has been the development of rapid heating and detection techniques for investigating early steps in the decomposition mechanisms. Brill and co-workers have developed rapid scan FTIR techniques for probing near-surface gas phase decomposition products after subjecting samples to temperature jumps (2000 K/s) to a final burning temperature.[26,27] This group has also pioneered FTIR methodologies to measure the burn rates of propellants while monitoring simultaneous mass and temperature changes (SMATCH/FTIR).[28] These techniques probe reaction products under conditions that closely resemble realistic combustion conditions at pressures of one atmosphere and higher.[29,30] These are crucial developments for determining combustion mechanisms under realistic conditions because the overall reaction kinetics and mechanistic pathways can be sensitive to the heating rates of molecules near the reaction zone.

This report describes a research program sponsored by the Army Research Office to develop a new experimental technique for detecting *initial* reaction products of thermal decomposition under conditions that simulate rapid combustion. We have already published three papers in the open literature describing the technique and initial results.[31,32,33] A fourth paper describing results of thin film laser pyrolysis of RDX isotopomers is currently in preparation.

II. Summary of the Most Important Results

A. Experimental Technique

Samples are prepared in a vacuum dewar cell illustrated schematically in Figure 1. This cell consists of a cold finger cooled with liquid nitrogen. An optical mount containing a 25 mm dia.
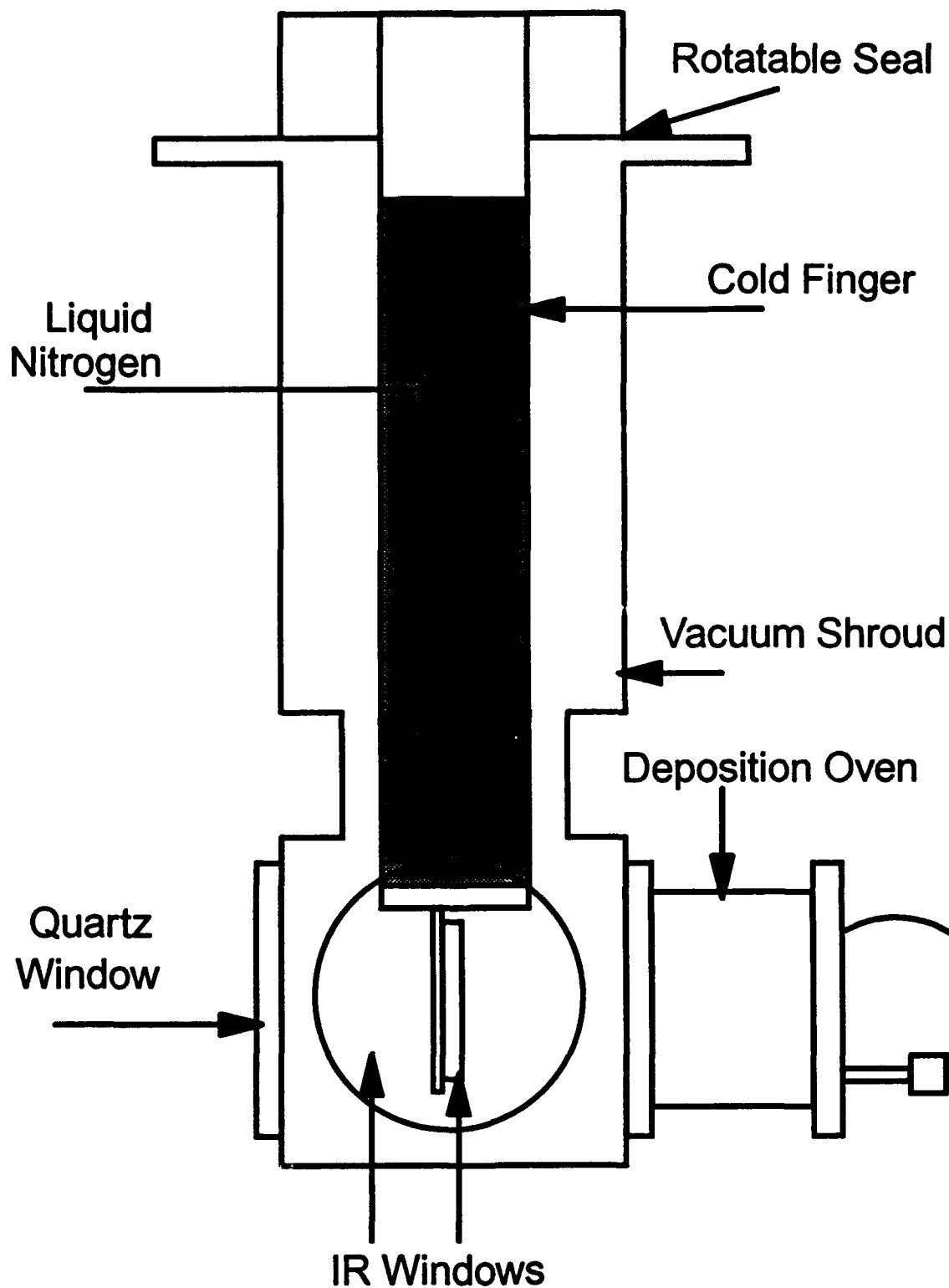
Figure 1 - Schematic diagram of the transient thin film laser pyrolysis apparatus.

optical window (CsI, CaF_2, or sapphire) is attached to the end. The cold finger is inserted into a rotatable vacuum shroud that is pumped to 10^{-5} torr. Attached to one side of the shroud is a modified Knudsen oven containing approximately 10 mg of propellant. When the oven is heated to approximately 120° C., the propellant is vaporized and condensed as a thin film on the cold optical window. A quartz window mounted on the shroud opposite the oven permits us to monitor the film thickness by laser interferometry during deposition. A pair of CsI optical windows are mounted on the two remaining sides of the shroud for obtaining transmission IR spectra of the sample using a Mattson model Polaris FTIR spectrometer. During deposition the shroud is turned so the cold optical window is normal to the path of the vaporized propellant coming from the oven. After deposition, the shroud is turned so the sample faces the two CsI windows. Spectra are obtained and pyrolyses are conducted in this configuration.

Pyrolysis of the samples is carried out with the use of a Pulse Systems Model LP140-G pulsed CO_2 laser tuned to the 10 μm P(20) line at 944 cm^{-1}. This laser has a nominal pulse length of 35 μsec and is used at a repetition rate of 1 pulse per second. Four types of pyrolysis experiments are conducted:

1) "Double window - threshold" experiments are performed by forming a film of RDX by vapor deposition from the Knudsen oven onto the substrate window (CaF_2 or CsI). The thin film is then warmed to room temperature to allow conversion from the amorphous to a crystalline state. A second window is then placed over the sample, and the "sandwich" arrangement is remounted in the vacuum Dewar vessel and recooled to 77 K. The entire sample is then subjected to a single low-fluence pulse from the CO_2 laser (typically 0.3 J cm^{-2}). FTIR spectra are obtained before and after the laser pyrolysis to record any physical or chemical changes in the sample. This cycle of laser pyrolysis and infrared spectroscopy is repeated on the same sample at successively higher laser fluence (to about 4.7 J cm^{-2}). The spectra are then

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analyzed to determine the fluence at which product formation is first detected. At 4.7 J cm^{-2}, the temperature of the film is raised to approximately 1000 K (based on measurements of the absorption coefficient at the laser wavelength and estimates of the heat capacity of the film) and is rapidly cooled ($\tau \approx 2$ ms) back to 77 K by conduction of the excess heat into the optical window.

2) "Double window - constant fluence" experiments are similar to the first type, except that samples are pyrolyzed several times at the same laser fluence.

3) "Single window" experiments are similar to the first type except that the sample is left uncovered during pyrolysis. Reaction products that are formed at temperatures high enough to vaporize the films are lost from the substrate window in these experiments.

4) "Amorphous" samples are prepared similar to type 3, except that no annealing cycle is performed. The sample is left in its amorphous state produced by the vapor deposition process in order to assess the effects of structural disorder on pyrolysis product yields.

B. Reaction Mechanism

The double window - threshold experiments (type 1) show that the first reaction product detected is N_2O_4, the dimer of NO_2. The threshold laser fluence for this product is 1.4 J cm^{-2}. Figure 2 shows FTIR spectra of a region where no strong RDX absorptions occur. The triplet of bands near 1735 cm^{-1} formed in the pyrolysis experiments is shown to be N_2O_4 by comparison with spectra of control experiments in which NO_2/N_2O_4 is deposited directly onto the cold window either in pure form or by co-deposition with RDX. The observation of NO_2 dimer as the initial reaction product is clear evidence that *N-N bond scission is the initial step in the thermal decomposition mechanism* under these experimental conditions.

At higher fluence, additional reaction products are formed due to subsequent steps in the thermal decomposition mechanism. These products include NO, N_2O, HCN, and CO_2.
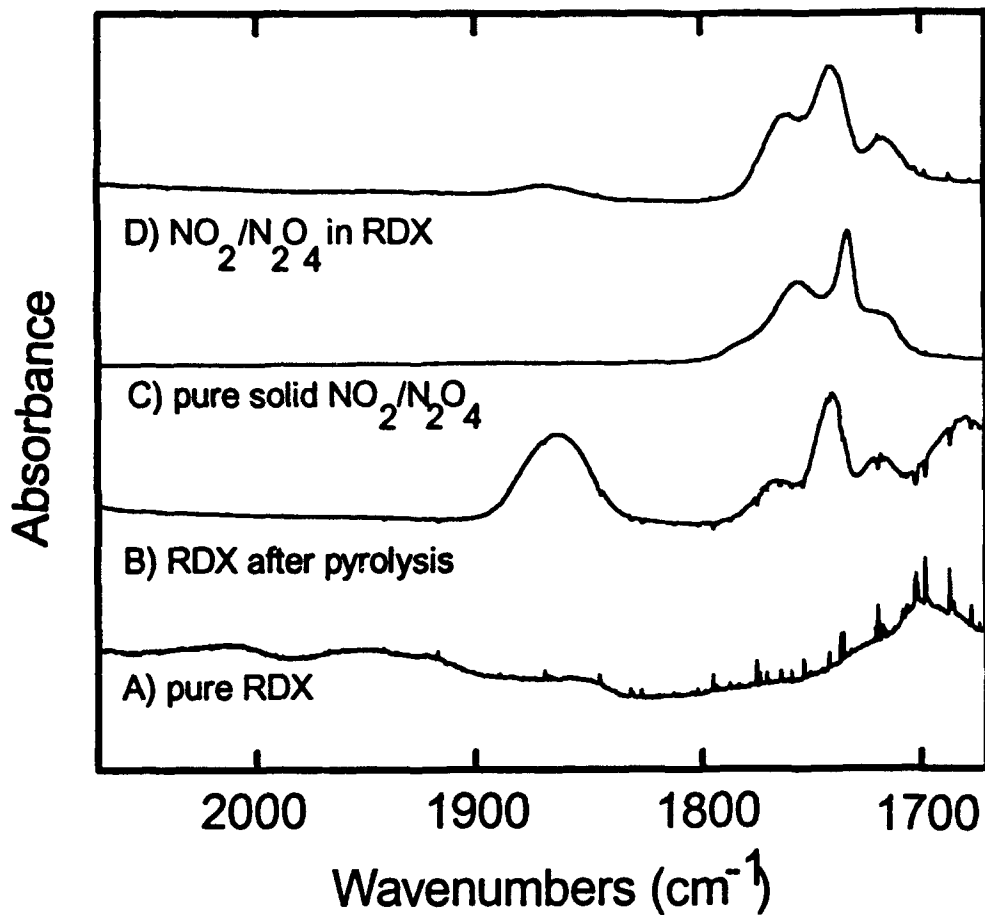
Figure 2 - Transmission FTIR spectra of the region showing N_2O_4 formation. A) Crystalline RDX film on a CsI substrate at 77 K. No RDX absorption bands occur in this region. The sharp bands are due to atmospheric water in the IR beam. B) Same RDX sample after pyrolysis with the P(20) line of a CO_2 laser at 4.7 J cm^{-2}. C) 1.9 torr NO_2 deposited onto a 77 K CsI window. D) 2.4 torr NO_2 codeposited with RDX onto a 77 K CsI window.

Comparison of results from single and double-window experiments (types 1 and 3) show that *NO₂ is formed in the condensed phase.* This is an important observation because the burning rate of propellants depends not only on the rate of heat feedback from the flame to the solid (by conduction, convection and radiative mechanisms) but also by heat generated or used in condensed phase reactions. Experiments were also conducted at higher fluence to determine whether secondary reaction products were formed in the condensed phase or in the gas phase above the surface of the propellant. The results of these experiments were inconclusive because these secondary reaction products were only formed in significant amounts under conditions where the majority of the propellant film was vaporized by the laser.

In order to test whether the NO_2 reaction product is formed by unimolecular scission of an N-N bond or by a bimolecular reaction of two adjacent molecules in the solid, comparisons were made between experiments using amorphous and crystalline samples (types 3 and 4). The reasoning behind this is that bimolecular reactions are subject to steric constraints in which favorable orientations between neighboring molecules must be attained before reaction can occur. Unimolecular reactions are less sensitive to the relative orientations of neighboring molecules. The amorphous and crystalline samples afforded nearly identical yields of N_2O_4, leading us to conclude that *formation of NO_2 occurs by unimolecular N-N bond scission.*

Finally, it seems curious that NO_2 is detected in these studies only as the dimer (N_2O_4) rather than as the monomer. This could be due to facile diffusion and dimerization in the film, or it might be due to scission of two N-N bonds in each decomposing RDX molecule. To distinguish between these mechanisms, we conducted several "crossover" experiments on samples in which half of the RDX molecules are isotopically labelled with ^{15}N at all six positions. The isotopomers are mixed randomly with each other as a result of the vapor deposition process used to make the thin films, but each molecule remains either all ^{14}N or all ^{15}N. The pyrolysis experiments show that the N_2O_4 dimers

formed are isotopically mixed (i.e., a 1:2:1 mixture of $^{15,15}N_2O_4$:$^{15,14}N_2O_4$:$^{14,14}N_2O_4$). This observation proves that dimer formation is not due to combination of 2 molecules from a single parent RDX, and is instead due to diffusion of NO_2 monomers in the solid during the brief cooldown period after the laser pulse. This conclusion is supported by quantitative measurements of the N_2O_4 yield, which show that approximately 2 RDX molecules are destroyed for every N_2O_4 molecule formed by laser pyrolysis.

III. List of Publications and Technical Reports

1. C. A. Wight and T. R. Botcher, "Thermal Decomposition of Solid RDX Begins With N-N Bond Scission", J. Am. Chem. Soc. 114, 8303 (1992).

2. T. R. Botcher and C. A. Wight, "Infrared Laser Pyrolysis Studies of Thermal Decomposition Mechanisms in Nitramine Propellants", Proc. Mat. Res. Soc. Symp., 296, 47 (1993).

3. T. R. Botcher and C. A. Wight, "Transient Thin Film Laser Pyrolysis of RDX", J. Phys. Chem. 97, 9149 (1993).

IV. List of Scientific Personnel

1. Tod R. Botcher, Graduate Research Assistant, Ph.D. degree expected 3/94

2. Charles A. Wight, Principal Investigator

V. Report of Inventions

1. C. A. Wight and P. M. Kligmann, "Desensitized Energetic Materials", U. S. patent application filed February 1992

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