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DECOMPOSITION OF ENERGETIC MATERIALS COMBUSTION OF
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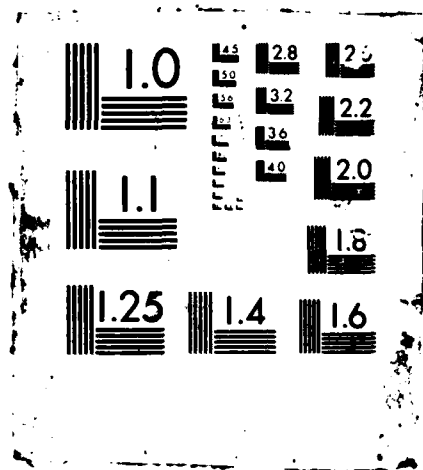
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from

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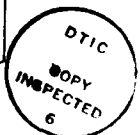
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16. Abstract → This report covers two areas of research. The first is an examination of the decomposition of dimethylnitramine using the method of laser powered homogeneous pyrolysis. The second is the spectral and product analysis of the combustion of a series of decoy materials.			
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Final Report on Contract N00014-85-C-2147

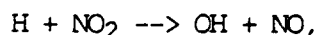
This is the final report on contract #N00014-85-C-2147. The work under this contract was carried out at the Naval Research Laboratory, Washington, DC. The report consists of two sections: Section I--Decomposition of Energetic Materials; and Section II--Combustion of Decoy Materials.

Section I--Decomposition of Energetic Materials

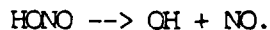
Dimethylnitramine (DMNA) has been studied as a model energetic material because of its structural similarity to the explosives RDX and HMX. The identification of the primary steps in the thermal decomposition of DMNA is the subject of some dispute. McMillen, et al., report two competing channels for the initial decomposition process: N-N bond scission to produce NO_2 and five-center molecular elimination of HONO [1]. Lloyd, Umstead, and Lin argue that the only primary decomposition step is the N-N bond scission [2]. This study was undertaken to determine whether HONO is a product in the initial decomposition of DMNA.

The experimental technique adopted was that of laser powered homogeneous pyrolysis. A CO_2 laser beam was directed into a reaction cell through which was flowing a gas mixture containing SF_6 , N_2 , and precursor. The SF_6 absorbed the CO_2 laser radiation in vibrational modes and, through rapid V-T transfer, heated the cylindrical volume of gas by 700-1,200 K in $\leq 15 \mu\text{s}$. Laser induced fluorescence (LIF) with an excimer-pumped dye laser was used to detect products at a variable time after the CO_2 pulse. In these experiments, the radical probed was OH. Temperatures of the heated gas were obtained by fitting the LIF intensities of the $J = 1$ through $J = 9$ transitions of the R_1 and R_1' branches to a Boltzmann distribution.

LIF spectra show the presence of OH in the reaction mixture even at short delay times. The amount of OH increases with delay time reaching a maximum at 700-800 μs before decreasing at longer times when the temperature is $850 \pm 50\text{K}$. The origin of the OH is not clear. The time dependence of the OH rise is not in agreement with that expected for production by a bimolecular reaction, i.e., the rise time does not vary appreciably with pressure of DMNA. Thus, it seems that processes, such as



are not the source of OH. If HONO were formed in the initial decomposition step, thermal decomposition of the HONO could lead to OH production



The estimated Arrhenius parameters [3] for the thermal decomposition of HONO show that process to be too slow to account for the OH production.

In an effort to further understand the initial decomposition process, a YAG laser was coupled into the experimental system. The purpose of the third laser was to photolyze any HONO formed thermally prior to detection of OH by LIF. The OH detected then would be the sum of that formed by thermal decomposition of DMNA and that formed by photolysis of the HONO produced by thermal decomposition of DMNA. Photolysis of HONO has been studied by Vasudev, Zare, and Dixon [4]. The feasibility of using the YAG enhancement approach to detect the presence of HONO was verified with experiments using 2-nitropropane which is known to produce HONO on thermal decomposition [5]. When the experiments were carried out using DMNA as the precursor, an enhancement of the OH signal due to the presence of the YAG beam was observed. The enhancement was present even at very short (≤ 10 ns) delay times between the YAG laser and the probe laser, thus precluding the possibility of formation of OH by chemical processes initiated by the YAG beam. Poor signal-to-noise prevented quantitative measurements of the YAG enhancement effect. Thus, while the results are suggestive of HONO formation, it cannot be demonstrated that HONO production does occur.

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Section II—Combustion of Decoy Materials

The Navy is interested in developing improved decoy materials to aid in ship defense against heat-seeking missiles. To aid in the design of effective decoys, a series of candidate materials has been tested under controlled conditions in the laboratory. The materials were formulated by a commercial vendor and were used as supplied. They were burned in a specially designed combustion chamber. The chamber was coupled through optical ports to three separate instruments: a radiometer, a UV-visible spectrometer, and an FTIR spectrometer. The radiometer was used to measure burn time of the samples by monitoring wavelengths in the visible region. The UV-visible spectrometer photographically recorded spectra over the 250-600 nm range with 160 nm sections recorded in a single exposure. The FTIR spectrometer scanned over the 2-14 μm region with a resolution of 4 cm^{-1} . In addition to the spectral analysis, particulate matter from the combustion plume was collected and analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) methods.

A total of 20 different sample compositions were tested with the type and amount of dopant added being varied in a systematic way. The UV-visible spectra revealed a number of lines which were assigned to particular atomic transitions. Also observed were diffuse features, some of which could be assigned to molecular emitters and some of which remain unassigned. Temporal and spatial characteristics of the emission could also be deduced from these spectra. The FTIR spectra allowed assignment of particular spectral features to emitting species. Ratios of total intensity in the wavelength windows of interest could also be calculated. These ratios are necessary for determining the suitability of candidate materials for use as decoys.

SEM and EDX techniques were used for examination of the particulate matter collected from the combustion plume above the burning samples. The morphology of the particulate matter ranges from very fine particles much less than 1 micron in size to large, spherical particles as large as 30 microns. The composition of the particulate matter varies with particle size and appearance. Although there are some similarities for different compositions, there is also a dependence of particulate composition on the formulation of the decoy materials. Correlation of the results of chemical analysis of the residue remaining after combustion with the original composition of the formulation gave further insight into the chemical changes occurring during combustion. More detailed discussion of the results of this research can be found in the references [1,2,3].

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