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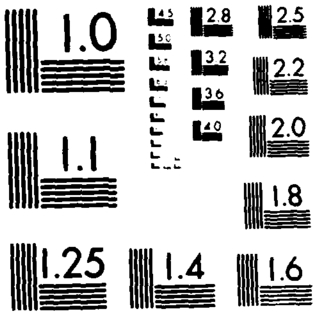
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DECEMBER 1983

FINAL REPORT ON RESEARCH INTO THE THERMAL DECOMPOSITION OF SELECTED ENERGETIC MATERIAL CANDIDATES (PROJECT ORDER ATL-2-094)

SALVATORE R. BOSCO
R. CAMERON DOREY

PROJECT 2303

AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE

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This document was prepared by the Energetic Materials Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado. The research was conducted under Project Work Unit Number 2303-F3-05, "Chemical Structure/Bonding Decomposition Relationship". Captain R. Cameron Dorey, III was the Project Scientist in charge of the work.

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This technical report has been reviewed and is approved for publication.

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The thermal decomposition of current and future energetic materials has been studied by electron paramagnetic resonance spectroscopy. The results of this study indicate that certain of these materials exhibit radical spectra when they decompose while others do not; in some cases, there is no evidence for decomposition at up to 250°C.

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By

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DECEMBER 1983

Approved for public release; distribution unlimited

Directorate of Chemical Sciences
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ABSTRACT

The thermal decomposition of current and future energetic materials has been studied by electron paramagnetic resonance spectroscopy. The results of this study indicate that certain of these materials exhibit radical spectra when they decompose while others do not; in some cases, there is no evidence for decomposition at up to 250° C.

PREFACE

The work described in this report was performed in Work Unit 2303-F3-05 in the Frank J. Seiler Research Laboratory, USAF Academy, Colorado. The work was performed under Project Order ATL-2-094 from the High Explosives Research and Development Laboratory, Air Force Armament Testing Laboratory, Eglin AFB, Florida, under the supervision of Thomas Floyd.

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2. Observed ESR spectrum of tetryl at 150°C.

INTRODUCTION

As the demands of the Armed Forces on ordnance increase, the materials which make up the explosives in the ordnance must improve. Many energetic materials due to their nature are inherently thermally unstable, and are not suitable for use in high-performance (extreme conditions) applications. Also, due to the development of "smart" (and expensive) ordnance, there is a premium on efficiency of the filling used. If plasticizers and binders can be developed which are energetic in their own right, they are more useful than those which are relatively inert.

When some energetic materials decompose thermally, they form free radicals-transient molecular fragments with unpaired electrons. The best characterized case so far is TNT (1)[a], although researchers have found free radical formation through irradiation of other explosives with spin trap agents (2) or of solid samples of explosives (3). Electron paramagnetic resonance (EPR) techniques are used to detect and characterize these free radicals in low concentrations in the presence of large amounts of similarly structured precursors and products.

At FJSRL, we have been investigating current and proposed future energetic materials for free radical formation at high temperatures. If free-radical intermediates are found, this will give a clue to the mechanism of thermal degradation. The materials in the present survey were supplied by AFATL to represent current military grade materials and items under development as energetic plasticizers and polymers.

The EPR system with heated sample have been described elsewhere (4). Since most materials in the study absorbed too much microwave energy to be

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[a] Chemical abbreviations used are found at the end of this report.

studied in conventional round tubes, they were placed in flattened tubes which had minimum cross section parallel to the magnetic field lines. Samples were heated to a maximum of 250°C if decomposition did not occur before this point. Materials which did not yield a measurable signal were combined with TNT in a separate experiment to demonstrate any synergistic effect. Recrystallized TNT itself gave a characteristic 21 line spectrum at about 230-240°C within 30 minutes.

EXPERIMENTAL

CURRENT INVENTORY MATERIALS

1. Military grade TNT (2,4,6-trinitrotoluene). An EPR spectrum, identical to that for recrystallized TNT was found (Fig 1). Onset of a weak spectrum began at about 100°C, however, all of the spectral lines were not distinguished until the temperature was raised to about 180°C. The spectrum was transformed to a single broad line after heating at 260°C for about two hours as does recrystallized TNT.

2. Comp-D2 is a wax used in TNT formulations as a binder. A broad weak triplet signal was observed superimposed on a broad singlet. The singlet appeared to be due to polymeric material. These spectra were taken at 150°C.

3. RDX recrystallized from DMSO. This is a proposed purification of RDX for economic reasons. The material decomposed at high temperature similar to standard military grade and recrystallized RDX. Any additional impurities left by this process do not seem to affect the thermal properties, as measured by EPR. The strongest signals were observed at 200°C after about 37 minutes of heating.

4. Tetryl. A weak spectrum characteristic of free NO_2 was seen at 150°C (Fig 2). No other signal or visible decomposition appeared after prolonged heating at that temperature and the temperature was not increased due to the explosive hazard.

5. Nitrocellulose. A weak NO_2 spectrum appearing below 150°C increased in intensity with time. However, no visible evidence (discoloration) of decomposition was seen from the sample.

6. Triaminoguanidine Nitrate (TAGN). No deterioration was visible at lower temperatures, but the material detonated after heating at 230°C for less than one hour. At this point the sample had not melted.

7. Nitroguanidine (NQ) mixed with TNT. Formation of the characteri c TNT spectrum was accelerated (appearance within 4 min at 180°C) althoug' second spectrum from nitroguanidine itself could be observed. This foll the pattern of many TNT "sensitizers".

OTHER MATERIALS OF INTEREST

1. Dimethylnitramine (DMNA) is a segment of both the RDX and HMX molecules. DMNA sublimed below 150°C without formation of any detectable spectrum. When heated with TNT, the TNT spectrum appeared faster than from pure TNT. No signals analogous to those from RDX-TNT mixtures (5) appeared.

2. Diethylene trinitramine (DETN). Nitropiperidine. Both of these materials melted below 120°C and discolored. No EPR signal was seen from the DETN sample. The nitropiperidine gave a weak polymeric signal at 190°C after about two hours.

3. Di(ethylene)trinitramine (DINA). Discolored about 120°C and showed no EPR signal.

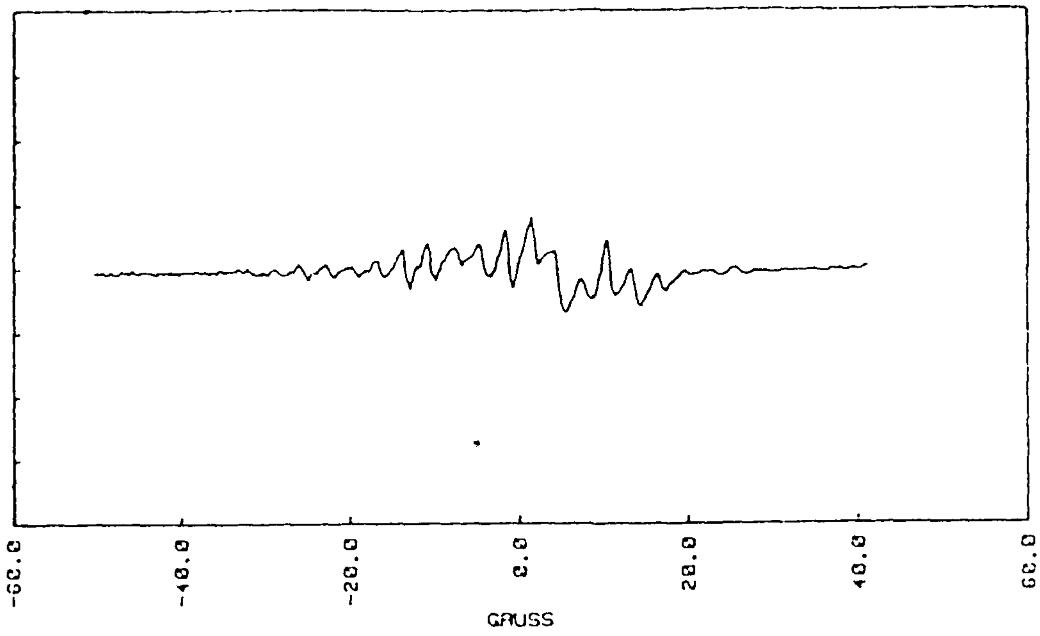

Figure 1. Observed spectrum of military grade TNT after heating at 260°C for 90 min.

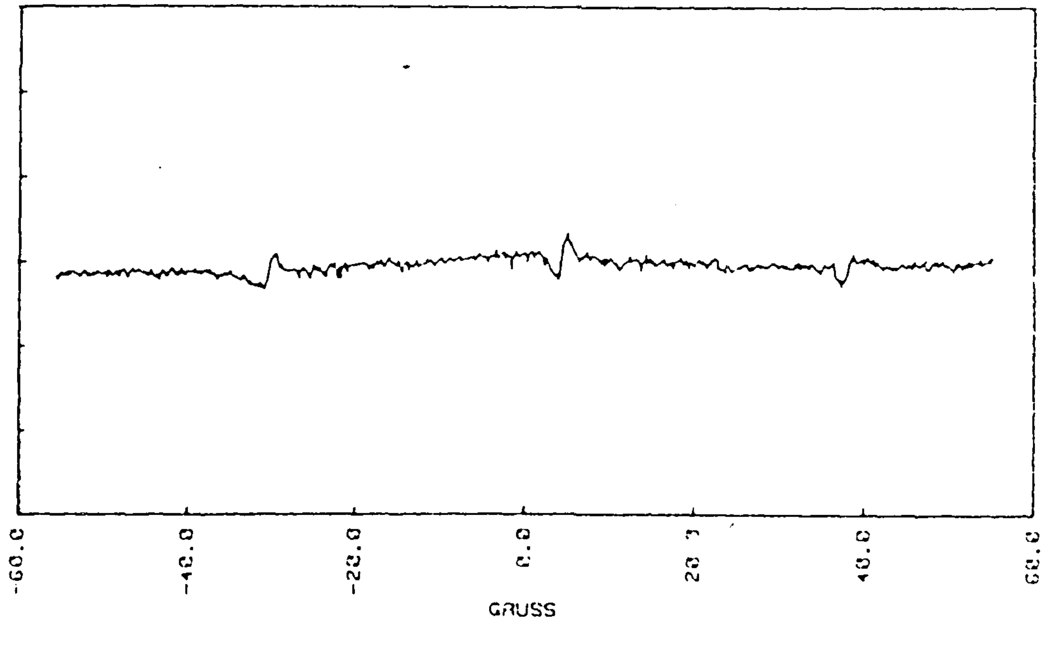

Figure 2. Observed spectrum of tetryl after heating at 150°C for 17 min.

4. Glycidyl azide polymer (GAP). A viscous yellow liquid at room temperature which discolored rapidly above 120°C, but gave no EPR signal even when heated up to 180°C.

5. Diazoethane nitramine. No change in the material was observed up to 180°C and no EPR signal could be detected.

6. Tripicrylmelamine (TPM). No physical changes in a neat sample were noted up to 250°C and no EPR signal was observed. When a 50/50 mixture of TPM and TNT was run, the characteristic TNT EPR spectrum was accelerated, appearing after about 3 minutes at 168°C.

7. Dinitropropylvinyl ether polymer (DNPVEP), Dichloromethyl diethylenetrinitramine (DCTNN), Alkyl (ethyl nitrate) nitramines (NENAs). All of these boiled at very low temperatures (below 150°C). At the boiling points no visible decomposition or EPR signal was observed except for n-pentyl NENA which displayed a weak triplet signal which could not be characterized.

DISCUSSION

Most materials failed to show any EPR spectrum, even when visible decomposition occurred rapidly. One possible explanation is a non-radical decomposition. This might occur in some species, particularly the nitrates. An alternative explanation is instrumental insensitivity, due to the high polarity (and thus dielectric constant) of the materials. If this is the case, it might be an insurmountable problem. What is needed is an inert high-temperature (250°C) solvent for those materials which decompose visibly. So far, we have not been able to find such a solvent, and the instability of most organic materials at high temperatures makes the search difficult. TNT itself is a very poor solvent, since any material we have conbined with it accelerates TNT decomposition, usually masking any other possible EPR signal. This may occur either by impeding hydrogen-bonding between TNT molecules, or by a charge-transfer mechanism from a decomposing solute molecule to TNT. Either case leads to a less stable composition than either of the pure substances.

In the case of the low-boiling energetic plasticizers, they should be tested in formulations with compatible materials, since this is how they will be used. Enough of the plasticizer might be entrapped to yield useful information at higher temperatures.

CONCLUSIONS

The results of this study indicate that, with the exception of tetryl none of the new materials displayed any evidence of thermal decomposition similar to TNT. Several of the materials tested acted as sensitizers and may have potential value as such. None of the new materials appeared to be suitable at higher temperatures. Until a high boiling solvent which will not generate an EPR signal masking any sample signal can be found, we recommend no further work be pursued on these compounds.

LIST OF ABBREVIATIONS

DCTNN	dichloromethyl diethylenetrinitramine
DETN	diethylene trinitramine
DINA	di(ethylenenitrate) nitramine
DMNA	dimethylnitramine
DMSO	dimethyl sulfoxide
DNPVEP	dinitropropylvinyl ether polymer
EPR	electron paramagnetic resonance
GAP	glycidyl azide polymer
HMX	cyclotetramethylene tetranitramine
NENA	ethyl nitrate nitramine
NQ	nitroguanidine
RDX	cyclo-1,3,5-trimethylene 2,4,6-trinitramine
TAGN	triaminoguanidine nitrate
TNT	trinitrotoluene
TPM	tripicrylmelamine

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