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Mechanisms of Formation of Trace Decomposition Products in Complex High Explosive Mixtures

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AMARILLO NATIONAL RESOURCE CENTER FOR PLUTONIUM/
A HIGHER EDUCATION CONSORTIUM

A Report on

Mechanisms of Formation of Trace Decomposition Products
in Complex High Explosive Mixtures

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Abstract

A significant concern in the nation's stockpile surveillance program is prediction of the lifetimes of the high explosives (HE) and their components as the weapons age. The Department of Energy's Core Surveillance and Enhanced Surveillance programs specifically target issues of degradation of HE, binders, and plastic-bonded explosives (PBX) for determination of component lifetimes and handling procedures. These material science topics are being

addressed at the DOE national laboratories and production plants, including Pantex. The principal goal of this project is to identify the mechanisms of decomposition of HE, plasticizers, plastic polymer binders, and radical stabilizers resulting from exposures to ionizing radiation, heat, and humidity. The following reports the work completed for the 1998, including a comprehensive literature review about some of the materials examined and the laboratory work completed to-date. The materials focused on in our laboratory are TATB, Estane 5301, and Irganox 1010.

TABLE OF CONTENTS

1. LITERATURE REVIEWS	1
<i>1.1 Summary of Literature Review of the Lifetime of DOE Materials</i>	<i>1</i>
<i>1.2 Literature Review of Synthesis of Nitroso Derivations of HMX and RDX.....</i>	<i>1</i>
2. LAB WORK COMPLETED.....	3
2.1 TATB	3
2.2 Estane 5301	3
2.3 Irganox 1010.....	3
3. FUTURE PLANS	5
3.1 TATB	5
3.2 Estane 5301	5
3.3 Irganox 1010	5
REFERENCES	7

LIST OF FIGURES

Figure 1: Chemical Structure of TATB.....	9
Figure 2: Chemical Structure of HMX and RDX.....	9
Figure 3: Chemical Structure of Estane 5301	9
Figure 4: Chemical Structure of Kel-F 800.....	9
Figure 5: Reaction to form the mononitroso-derivative of HMX	10
Figure 6: Reaction to form the trinitroso and 1,5-dinitroso-derivative of HMX	10
Figure 7: Reaction to form the tetranitroso-derivative of HMX	10
Figure 8: Diagram of the Aging Chambers Used to Expose TATB to Various Light, Heat and Humidity Conditions.....	11
Figure 9: Solid-State ^{13}C NMR CPMAS Spectrum of TATB Mixed with Silica Gel (10,000 Scans).....	11
Figure 10: EPR Spectrum of TATB	12
Figure 11: Mass Spectrum of TATB provided by Dr. Van Stipdonk and Dr. Sweikert of TAMU.....	12
Figure 12: Main Fragment Structure of Estane and the Solid-State ^{13}C NMR CPMAS of Estane	13
Figure 13: EPR of Estane Solid Aged in Air at 75°C for 8 Months	14
Figure 14: EPR of Estane Solid Aged in an Inert Atmosphere at 75°C for 8 Months.....	14
Figure 15: EPR of Estane Solution (CHCl_3) Aged in Air at 75°C for 8 Months	15
Figure 16: Possible Mechanism for the Hydrolytic Degradation of Estane.....	15
Figure 17: Chemical Structure of Irganox 1010.....	16
Figure 18: How a Hindered Phenol Reacts with a Peroxy Radical.....	16
Figure 19: Resonance Stabilization of Radical on Hindered Phenol	16
Figure 20: Solid-State ^{13}C NMR CPMAS of Irganox 1010 (Crystalline, Supplied by Ciba-Geigy)	17

Figure 21: Solid-State ^{13}C NMR CPMAS of Irganox 1010 (Amorphous, Supplied by Ciba-Geigy).....	17
Figure 22: Infrared Spectra of Irganox 1010 (Crystalline, Supplied by Ciba-Geigy).....	18
Figure 23: Infrared Spectra of Irganox 1010 (Amorphous, Supplied by Ciba-Geigy)	18
Figure 24: EPR of Powdered Irganox 1010	19
Figure 25: EPR of (a) Irganox 1010 in Solution with CHCl_3 and (b) Irganox 1010 in Solution with CCl_4	20
Figure 26: Mass Spectrum of Irganox 1010 (Average of 6 Scans) using SIMS	21
Figure 27: Theoretical Distribution of Mass at 1176 when Isotopes are taken into Account.....	22
Figure 28: Actual Distribution of the Mass at 1176.....	22
Figure 29: Solid-State ^{13}C NMR CPMAS of Irganox 1010 reacted with H_2	23
Figure 30: Infrared Spectra of Irganox 1010 reacted with H_2	23
Figure 31: EPR of Irganox 1010 reacted with H_2	24
Figure 32: Mass Spectrum of Irganox 1010 reacted with H_2	24

1. LITERATURE REVIEWS

1.1 Summary of Literature Review of the Lifetime of DOE Materials

A review on the lifetime of various materials associated with our nation's stockpile of nuclear weapons is included in ANRCP-1998-12, "Aging of Plastic Bonded Explosives and the Explosives and Polymers Contained Therein." The report can be downloaded from ANRC's website at www.pu.org. The materials that were focused on in the review are 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)/hexahydro-1,3,5-triazine (RDX), Estane 5301 and Kel-F 800. The structures of these compounds are shown in Figures 1-4.

TATB is an incredibly stable explosive that has been incredibly difficult to analyze due to its inability to be dissolved. Aging experiments have shown that even when exposed to γ -radiation for the equivalent of thousands of years, TATB still maintained its explosive integrity. However, with exposure to UV, X-ray, γ -radiation, TATB changes from yellow to green, the darker the green, the greater the exposure. Several attempts have been made to explain the green color, but publications to-date do not explicitly explain what happens as the molecule degrades. The PBX's formulated with TATB typically contain the polymer Kel-F to provide support to hold the explosive together. Kel-F does not degrade easily, but can become more crystalline (and possibly more brittle) with age.

HMX and RDX are less stable explosives than TATB. They are typically used in PBX's that contain Estane 5301, a polymer with both hard and soft segments. Estane 5301 can reduce the shock to the explosive due to its structure. The concern over PBXs that contain these components is degradation of the polymer. Estane 5301 can undergo hydrolytic degradation under relatively mild conditions. Radical stabilizers (e.g. Irganox

1010) are added to the PBX formulation in order to reduce Estane 5301 degradation, but the specific role of Irganox 1010 in the PBX formulation is not completely understood.

1.2 Literature Review of Synthesis of Nitroso Derivatives of HMX and RDX

Another facet of this research deals with the synthesis of 1-nitroso-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane (IV), 1,5-dinitroso-3,7-dinitro-1,3,5,7-tetraazacyclooctane (VIII), 1,3,5-trinitroso-7-nitro-1,3,5,7-tetraazacyclooctane (VII), 1,3,5,7-tetranitroso-1,3,5,7-tetraazacyclooctane and 1,3-dinitroso-5,7-dinitro-1,3,5,7-tetraazacyclooctane, which are suspected decomposition products of HMX. Bachmann et al. prepared the first of these compounds, IV, by reacting I with acetic acid, 98% nitric acid, and acetic anhydride to give II, reacting II with similar reagents to give III, and reacting III with nitrosyl chloride and acetic anhydride as shown in Figure 5 (Bachmann, et al, 1951). Synthetic routes for the next three of these compounds are outlined in Figures 6 and 7 and are based on reactions found in the literature.

We plan to prepare 1,5-dinitroso (VIII) and trinitroso (VII) derivatives of HMX as shown in Figure 6, where compound I is reacted with sodium nitrite and hydrochloric acid to form V. It is anticipated that reacting compound V with acetic acid, 98% nitric acid, and acetic anhydride will make VI. VII can be made by reacting VI with nitrosyl chloride and acetic anhydride and VIII can be made by reacting VI with 98% nitric acid, acetic anhydride, and ammonium nitrate. One possible route to the tetranitroso derivative of HMX is shown in Figure 7. This reaction involves reducing the nitro groups on HMX to the N-amino groups, and then oxidizing the N-amino groups to the tetranitroso compound. These reactions will first be tested using model compounds.

2. LAB WORK COMPLETED

2.1 TATB

Aging experiments are underway at Texas Tech University. Figure 8 is a diagram of the aging chambers. The chamber conditions vary depending on combinations of exposure to 24°C and 50°C; 30, 50, and 80% humidity; and no fluorescent or UV light; 18 different conditions in all.

The first set of samples (3 months) were removed and delivered to WTAMU on November 23, 1998. EPR spectra are currently being run on each of these samples. Dr. Gene Carlisle of WTAMU has provided support on the EPR data collection.

Several baseline experiments were done on TATB using various analytical techniques to determine the best methods for analysis. Figure 9 shows a solid-state ^{13}C nuclear magnetic resonance (NMR) spectrum of TATB. The peaks shown have been the best obtained so far (and are quite noisy), so very little information can be provided in using this technique for analysis of TATB.

Electroparamagnetic resonance (EPR) was done on the unaged sample; the sample contained a small concentration of free radicals (Figure 10). Fine structure information from the EPR spectrum cannot be determined at this point. Mass spectrometry of TATB was provided by Dr. Mike Van Stipdonk and Dr. Emile Schweikert of Texas A&M University. Figure 11 is the mass spectrum of the solid TATB. The interesting feature of the mass spectrum is the large molecular ion peak at 257. It is the mass of TATB minus one amu. The next fragment is the loss of 16 amu from the molecular ion, which could be an ionization loss of oxygen or NH_2 . Future experiments include mass spectra of labeled TATB by ^{15}N , ^2H , or ^{18}O and mass spectra of severely degraded TATB as it turns green to provide accurate determination of the origin of the 16 amu mass fragment.

2.2 Estane 5301

Figure 12 shows the main fragment structure of Estane 5301 with carbons numbered and the solid-state ^{13}C NMR that correlates to the numbered carbons. Solid-state NMR cannot always provide the high resolution that solution NMR can obtain, so several carbons can be represented by one large peak.

Figures 13-14 show EPR of Estane 5301 solid (aged in air and inert atmospheres at 75°C for 8 months). No radicals were detected in the inert-aged sample, but the air-aged sample did contain a radical concentration. The sample was rerun in a solution of CHCl_3 , but radicals were not detected (Figure 15). Dr. Van Stipdonk is currently collecting mass spectral data on Estane 5301 at TAMU.

Based on data provided by Mike Lightfoot and Bobby Russell of Pantex, a hydrolytic degradation mechanism was proposed and is shown in Figure 16. More work will be done on other samples of Estane 5301 to determine other factors of degradation.

2.3 Irganox 1010

Irganox 1010 is a radical scavenger, a hindered phenol antioxidant. Irganox 1010 is included as part of a PBX to scavenge radicals that may degrade the polymer included in the PBX formulation. The radicals thought to be generated within the PBX are the nitro radicals ($\text{NO}_2\cdot$), and it is not known how the Irganox 1010 scavenges these radicals. Figure 17 shows the structure of Irganox 1010. Figure 18 shows how a hindered phenol reacts with a peroxy radical and a possible mechanism for Irganox 1010 to react with other radicals (Dexter, 1985; Pospisil, 1979). Once a radical is scavenged by Irganox 1010, the radical can move around the ring due to resonance stabilization (Figure 19).

Baseline experiments were done on Irganox 1010. Figure 20 shows the solid-state ^{13}C NMR and the structure with the carbons labeled. There were more peaks (and the

extra peaks shifted slightly) than the number of carbons, so the origin of the extra peaks was investigated. A literature search indicated the extra peaks were due to asymmetrical crystallinity of the Ciba-Geigy material (Barnedswaard, Moonen, and Neilen, 1993). If the Irganox 1010 is dried as an amorphous material, the extra peaks are not apparent (Figure 21). Figures 22-23 show the IR of Irganox 1010 in the crystalline and amorphous form. The crystalline spectrum shows some splitting of the OH peak at $\sim 3700\text{ cm}^{-1}$ and at the carbonyl peak at $\sim 1700\text{ cm}^{-1}$. When conducting EPR experiments, a free radical signal is detected, as a powder (Figure 24) and in solution (Figure 25). The signal shape can provide information on the structure of the free radical within the molecule, and work continues to determine this.

It has been proposed that Irganox 1010 may be scavenging radicals from air and may limit its ability to perform. Other analytical techniques were employed to further understand the radical stabilizer.

Dr. Van Stipdonk and Dr. Schweikert of TAMU provided careful mass spectral analysis of Irganox 1010. Several mass spectral techniques were used to make sure the masses at the higher mass units were accurate. The techniques used were surface ionization mass spectrometry (SIMS), fast atom bombardment mass spectrometry (FAB), and plasma desorption mass spectrometry (PDMS). Figure 26 is the average of six separate mass spectra of Irganox 1010 using SIMS. The cluster of peaks at 1176 is the molecular ion. Other clusters of peaks at 231 and 278 indicate the fragmentation pattern of Irganox 1010 as pieces of the "arms" break off due to the

ionization energy within the mass spectrometer. The most interesting feature of the mass spectra is the "cluster of peaks" for each fragment, which differ in increments of one mass unit. In typical mass spectral analysis, the molecular ion will include the molecular mass of the material and the mass plus one amu (M+1) and M+2 due to isotopes of atoms (i.e. ^{13}C , ^{17}O ,). Figure 27 shows the theoretical distribution for Irganox 1010 for the molecular ion at 1176, which also includes ions at masses 1177 and 1178. However, when averaging six mass spectral scans of Irganox 1010 (Figure 28), the distribution includes peaks at 1173, 1174, and 1175. It is possible these fragments are generated from ionization of Irganox 1010 by loss of a hydrogen atom. However, due to EPR spectra indicating the existence of free radicals, the peaks at 1173-1175 could be the molecular ions of the radicals. The investigation continues in order to determine the origin of the masses at 1173-1175. To study this in more depth, we want to employ either a reaction to hydrogenate the radicals to pristine Irganox 1010 or a reaction of Irganox 1010 with free radicals. It is expected the products from these reactions will indicate a change when examining the various analytical techniques.

One attempt was made to hydrogenate the free radicals using H_2 (with Pt catalyst) by bubbling it through a solution of Irganox 1010 in ethanol. The ^{13}C NMR, IR, EPR, and mass spectra are shown in Figures 29-32. These spectra are identical to unreacted Irganox 1010 spectra, and therefore, either the reaction did not work or new radicals were generated as soon as the sample was exposed to air. Work will continue in this area.

3. FUTURE PLANS

3.1 TATB

EPR will be run on each aged TATB sample. Scans will be digitized and manipulated on the computer to determine changes in radical concentration. Mass spectral data collected on severely degraded TATB could provide information about TATB degradation. It is also possible we will either generate or find isotope labeled TATB in order to determine the degradation pattern of TATB in the mass spectrometer.

3.2 Estane 5301

Different solid-state ^{13}C NMR techniques will be employed to further understand aging of Estane 5301. Relaxation techniques can

provide information on changes in the mobility of the segments (i.e. if the Estane 5301 fragments into soft and hard segments, the relaxation technique might detect this). Radicals detected by EPR of Estane 5301 can establish a free radical degradation mechanism of the polymer.

3.3 Irganox 1010

Work will continue to determine the extent of degradation of Irganox 1010. Reactions with H_2 or radicals will be done to obtain either pristine or fully degraded Irganox 1010. Methods that appear to be the most useful in the analysis of Irganox 1010 are EPR and mass spectrometry. With these two methods, it may be possible to identify the radical that exists in Irganox 1010.

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Figure 4: Chemical Structure of Kel-F 800

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The carbons are numbered on the structure and then applied to the NMR spectra.

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Figure 32: Mass Spectrum of Irganox 1010 reacted with H₂