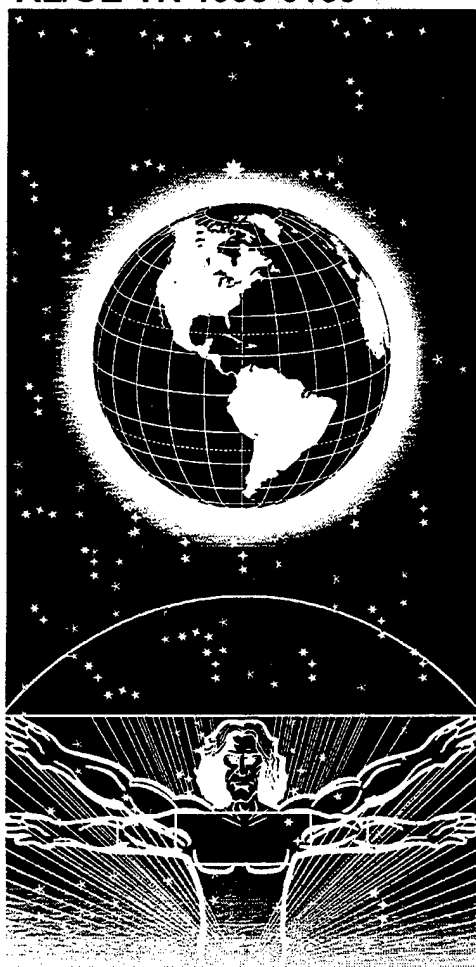




UNITED STATES AIR FORCE ARMSTRONG LABORATORY

AMMONIUM DINITRAMIDE: AN EPR/ENDOR STUDY

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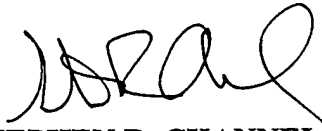
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The animal use described in this study was conducted in accordance with the principles stated in the "Guide for the Care and Use of Laboratory Animals", National Research Council, 1996, and the Animal Welfare Act of 1966, as amended.

This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

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

FOR THE DIRECTOR


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13. ABSTRACT (Maximum 200 words) Ammonium dinitramide (NH ₄ N[NO ₂] ₂ , ADN) is an oxidizer with potential applications in aerospace technology. Based on its chemical formula, ADN can decompose to form reactive nitrogen metabolites (RNMs). The decomposition characteristics of ADN powder following exposure to non-ionizing and ionizing radiation were studied. Electron paramagnetic resonance (EPR) spectroscopy was used to determine if radiation induces chemical change in ADN by formation of free radicals. Most free radicals are highly reactive and they will attempt to attempt to gain an electron from other compounds in order to pair with their odd electrons. Irradiated ADN powder generated two superimposed EPR spectra. These spectra have tentatively been identified as NO ₂ and NH ₃ radicals. To verify the EPR results, electron nuclear double resonance (ENDOR) was utilized. The initial results of these experiments suggest a proton interaction proximal to the NH ₃ radical center. In biological systems both reactive oxygen metabolites (ROMs) and RNMs play an important role in normal physiology and pathophysiology. The effects of decomposition products of ADN in biological systems should be studied by addressing ADNs effect on the balance between ROMs and RNMs.				
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PREFACE

This is one of a series of technical reports generated for the Air Force Office of Scientific Research for Environmental Initiative Program Work Unit # 2312A202. All work was performed at the Armed Forces Radiobiology Research Institute, Bethesda, MD or at the Naval Research Laboratory, Washington, DC while on temporary duty from the Occupational and Environmental Toxicology Division. The research described began in January, 1994. This technical report was presented as a poster at the Conference on Temporal Aspects in Risk Assessment for Noncancer endpoints, 18-20 April, 1994 at the Hope Hotel and Conference Center, Wright-Patterson AFB, May, 1994. All experiments performed in this study conform to NRC and OSHA requirements arranged by the safety officers of each facility. Lt Col Terry A. Childress served as Contract technical Monitor for the U. S. Air Force, Armstrong Laboratory, Toxicology Division.

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LIST OF ABBREVIATIONS

ADN	Ammonium dinitramide
C	Centigrade
DMPO	5,5-dimethyl-1-pyrroline N-oxide
g	gram
γ	gamma
Gy	Gray
L	liter
m	milli
min	minute
MNP	2-methyl-2-nitrosopropane
ROM	Reactive oxygen metabolite
RNM	Reactive nitrogen metabolite
T	Tesla
UV	ultraviolet
W	Watt

INTRODUCTION

Ammonium dinitramide (ADN) is an oxidizer which has potential applications in aerospace technology (Borman, 1994), therefore the biological risk assessment of this chemical has to be determined. Based on its chemical nature (SRI International 1992) the decomposition of ADN should yield nitrogen-centered radicals. Biological exposure to ADN may alter the natural balance between reactive nitrogen metabolites (RNMs) and reactive oxygen metabolites (ROMs) causing oxidative stress in cells. Oxidative stress in cells can be induced by metabolism of xenobiotics or by radiation through similar free radical pathways (Halliwell and Gutteridge, 1989). Oxidative stress can be caused by ROMs and RNMs forming peroxynitrite (ONOO^-) which is an oxidizing species (Beckman et al 1990, Radi et al 1991a,b, Carmichael et al 1993). Knowledge of the free radical decomposition of ADN is necessary to characterize its possible radical pathways in biological systems. Direct radiation effects on solids are known to generate free radicals which generally correspond to the free radical decomposition products of the substance (Swallow, 1973). Therefore radiation can be used to determine the free radicals in ADN which could possibly be formed during its decomposition in biological systems. The decomposition characteristics and chemical characteristics of ADN powder following exposure to non-ionizing and ionizing radiation are currently being studied. Electron paramagnetic resonance (EPR) spectroscopy is the most powerful method for directly detecting and characterizing free radicals (Wertz and Bolton 1972, Rice-Evans et al 1991). EPR was used to determine the radiation induced free radical products of ADN. The biological implications of these free radicals important for risk assessment are discussed.

MATERIALS and METHODS

Sample preparation: ADN powder 50 mg (SRI International, Menlo Park, CA) was irradiated in a ^{60}Co γ -ray field at a dose of 100 Gy per min, receiving a total dose of 2,500 Gy. UV radiation of ADN was carried out using a 1000 W Hg-Xe arc lamp.

EPR Apparatus: The EPR experiments were performed using a Bruker ESP 300E spectrometer. The EPR instrument was operated at a magnetic field set at 335 mT, microwave frequency about 9.41 GHz, microwave power 10 mW, receiver gain 2×10^5 , modulation frequency 100 kHz, modulation amplitude 1 mT, and temperature 25°C.

Electron-Nuclear Double Resonance Apparatus: The electron-nuclear double resonance (ENDOR) experiments were performed using a Bruker ER200 spectrometer.

RESULTS

The ADN powder used in the experiments was off-white in color and was hygroscopic. The physical and chemical data of the powder is shown in Table 1. This information was provided by the manufacturer (SRI International, 1992).

Formula	H₄N₄O₄
Names	Ammonium dinitramide, ADN SRI-12
Chemical Family	Oxidizer
Melting Point	90°C
Appearance	Solid, pale yellow to white
Vapor Pressure at 20°C	0
Solubility in water	500 g/L
Specific Gravity	~ 1.8

Table I Chemical and physical properties of ammonium dinitramide (SRI , 1992)

All the experiments were carried out at 25°C. This was within the safety margin estimated for these experiments. This chemical was not exposed to heat because preliminary studies showed it is only stable up to 55°C.

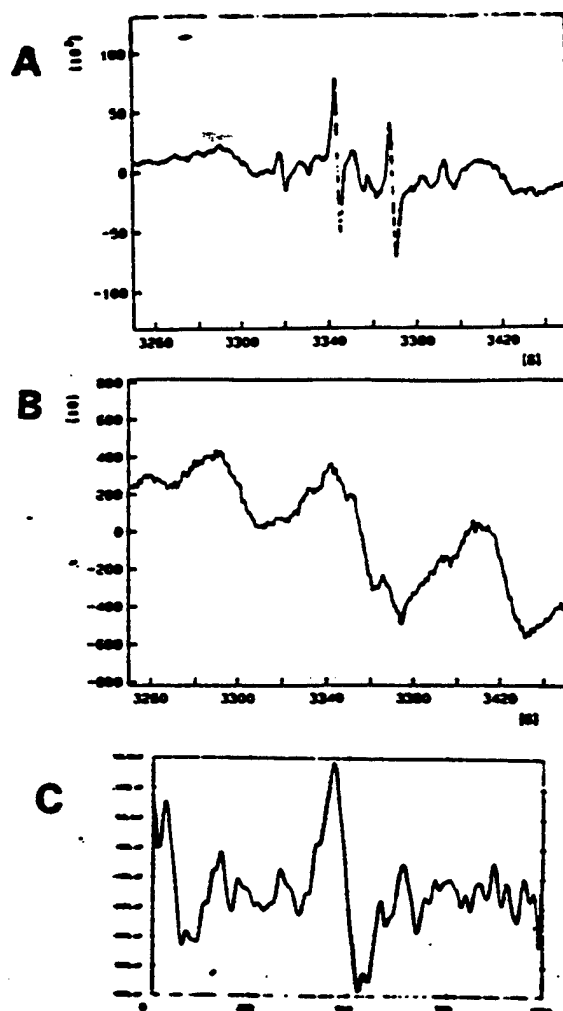


Figure 1 EPR spectra of ammonium dinitramide following 2.5 kGy irradiation in a ^{60}Co γ -ray field. (A) EPR spectra immediately following irradiation. (B) EPR spectra 20 h after irradiation. (C) ENDOR spectrum

Immediately after exposure to γ -rays the chemical produced the EPR spectrum shown in Figure 1A. This spectrum shows two radical species. One species yields an EPR spectrum similar to the $\text{NH}_3^\bullet$ radical generated after irradiation of ammonium perchlorate. In ADN the $\text{NH}_3^\bullet$ radical has an approximate lifetime of 20 h. The second species in Figure 2A yields an EPR spectrum consisting of a broad triplet and is attributed to the $\text{NO}_2^\bullet$ free radical. In ADN this radical persists well over 20 h. Figure 2B shows the EPR spectrum of the sample 20 h later. One of the radicals which was prominent immediately after irradiation ($\text{NH}_3^\bullet$) decayed over the 20 h period. To verify the radicals identified by EPR a preliminary ENDOR experiment was performed on γ -irradiated ADN soon after irradiation, Figure 1C. The ENDOR spectrum obtained at a proton resonance frequency 20.6 MHz (calculation below) suggests that one of the nitrogen radical species is interacting with a proton(s). This result supports the EPR assignment of the $\text{NH}_3^\bullet$ radical. Further ENDOR experiments are currently being performed to corroborate the results obtained in the EPR experiments.

$$25 \text{ G} \times 2.8 \text{ MHz/G} = 70 \text{ MHz}$$

$$\text{HFC}/2 \pm n_a ({}^1\text{H})$$

$$35 \text{ MHz} \pm 14.4 \text{ MHz}$$

$$35 - 14.4 = 20.6 \text{ MHz}$$

Data of the ultraviolet irradiation of ADN was presented by Dr M. D. Pace at a development and characterization of new energetic materials workshop 18-20 Apr 94 (Pace, 1994) and will not be shown in this report.

DISCUSSION

The products of ADN following γ -irradiation indicate that ADN can decompose to RNMs.

Recent reviews of free radical mechanisms in physiological and pathological conditions indicate that RNMs play an important physiological role (Grisham 1992, Moncada et al 1992). Reactions of active oxygen and nitrogen species have been studied by EPR and spin trapping (Carmichael et al 1993). Recent studies by Carmichael, 1994, suggest that there is a balance between ROMs and RNMs in biological systems. Table II shows proposed pathways in which the decomposition products of ADN can react in biological systems.

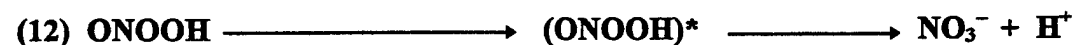
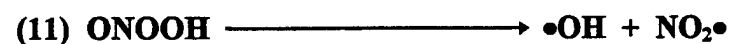
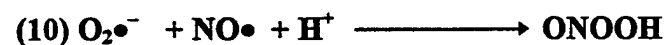
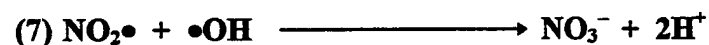
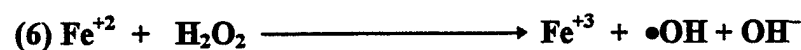
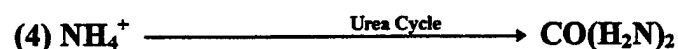
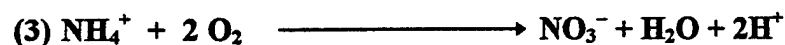


Table II The proposed interaction of decomposition products of ammonium dinitramide with ROMs and RNMs in biological systems.

Equation 1 is the decomposition products of ADN following γ -irradiation. The reactive products are $\text{NH}_3^\bullet$, $\text{H}^\bullet$, and $\text{NO}_2^\bullet$. $\text{NH}_3^\bullet$ radicals have been shown to be stable in other crystals (ammonium perchlorate, NH_4ClO_4), Carmichael et al. manuscript in preparation. However these $\text{NH}_3^\bullet$ radicals in ADN disappear over a 20 h period. This disappearance is not at the expense of the $\text{NO}_2^\bullet$ radical species which remains stable (Pace 1994 a ,b, Pace and Carmichael 1994). It is therefore possible that the $\text{NH}_3^\bullet$ radicals are reacting with a $\text{H}^\bullet$ to reform NH_4^+ (Equation 2). In a biological system NH_4^+ (Equation 2) can be converted to nitrate by microorganisms (Equation 3) or to urea by mammals through the ornithine cycle (Equation 4). The role NO_3^- plays in free radical pathway interactions are represented by Equations 5-12. The derivation of these equations has been described previously (Carmichael et al. 1993). The progenitor ROMs and RNMs often react by forming a $\text{ONOO}^\bullet$ (Equation 9-12). This intermediate when protonated either decomposes into $\text{OH}^\bullet$ and $\text{NO}_2^\bullet$, Equation 11 (Carmichael et al 1993) or prior to decomposition, forms an activated intermediate which reacts with similar fashion to the $\text{OH}^\bullet$ and $\text{NO}_2^\bullet$ radicals, Equation 12 (Moreno and Pryor 1992). Figure 2 A & B are results of recent experiments using EPR and spin trapping (Carmichael and Steel-Goodwin 1994). They show the decomposition of peroxyntrous acid (ONOOH) formed in the reaction between H_2O_2 and NO_2^- , Equation 9 (Carmichael and Steel-Goodwin 1994). Figure 2A is the EPR spectrum of the DMPO-OH adduct (1:2:2:1 quartet) superimposed on a triplet of triplets originating possibly from an NO_2 -like adduct (Carmichael et al. 1993).

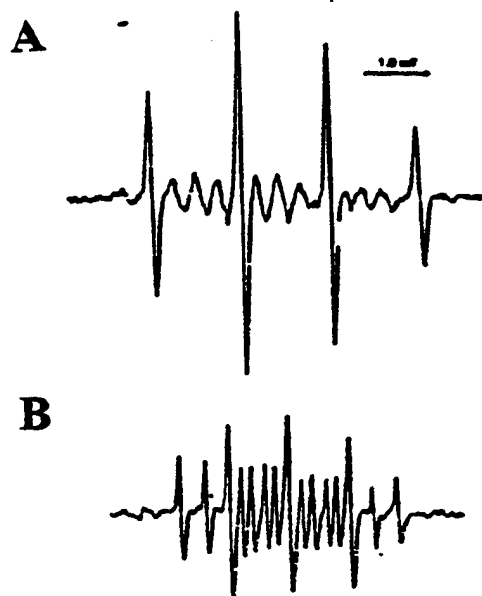


Figure 2 EPR/spin trapping of decomposition of ONOOH formed in the reaction of hydrogen peroxide and nitrite. (A). The EPR spectrum of the DMPO-OH adduct. (B) The EPR spectrum of the MNP-NHOH adduct

Figure 2B shows MNP-NHOH. The formation of an hydroxylamine is consistent with the known decomposition of organonitro compounds (March 1972, House 1972). As the study of the decomposition products of ADN following γ -irradiation show the presence of RNMs, toxicity experiments of this chemical in animal models should focus on nitrogen-centered free radical induced pathological changes. A symposium on biological effects of NO_2 sponsored by the Walter Reed Army Institute of Research (WRAIR, 1993) can provide background for studies on the biological effects of ADN. Chemical studies using EPR/spin trapping, planned to determine

these predicted equations for ADN decomposition, were presented at the International Symposium for Free Radical Research, Sydney, Australia in November, 1994 (Carmichael and Steel-Goodwin 1994).

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