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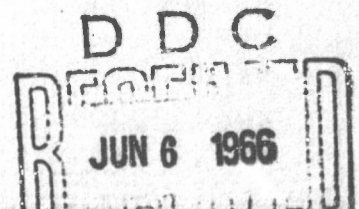THIRD ANNUAL SUMMARY REPORT

BASIC RESEARCH IN SOLID
OXYGEN OXIDIZERS (U)

Contract AF 04(611)9891
Supplemental Agreement #1

AFRPL-TR-66-108   May 1966

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JUN 6 1966

AEROJET
GENERAL TIRE
GENERAL

THIRD ANNUAL SUMMARY REPORT

BASIC RESEARCH IN SOLID OXYGEN OXIDIZERS (U)

Sponsored By

ADVANCED RESEARCH PROJECTS AGENCY
Propellant Chemistry Office
ARPA Order No. 398, Amendment #1

Monitored By

AIR FORCE SYSTEMS COMMAND
RESEARCH & TECHNOLOGY DIVISION
ROCKET PROPULSION LABORATORY
Edwards, California

Contract No. AF 04(611)-9891
Supplemental Agreement #1

Period Covered:
1 April 1965 to 1 April 1966

20 May 1966

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0856

AEROJET-GENERAL CORPORATION
A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY

FOREWORD

Work was initiated on this program on 1 April 1964 and this report covers
the period 1 April 1965 through 31 March 1966. It summarizes work carried out at
the Chemical Synthesis Department of Aerojet-General Corporation, Sacramento,
California, under Contract AF 04(611)-9891, Supplemental Agreement #1, entitled
"Basic Research In Solid Oxygen Oxidizers" (U), (ARPA Order No. 398, Amendment #1,
Program Code No. 4910). This program was administered by Mr. J. L. Trout, Air Force
Flight Test Center, Edwards Air Force Base, California. Previous work on N,N-
dinitroamines was performed under Contract AF 04(611)-8549 and is summarized in
Aerojet-General Report 0754-81S-1, 10 April 1964.

The primary emphasis of this program was to improve the thermal stability of
dinitroamines. With this objective in mind, the program was divided into two areas.
The first area had as its objective the quantitative determination of those factors
which affect the thermal stability of dinitroamines and the application of this
information to the stabilization of energetic, high oxygen content dinitroamines.
The second area had as its objective the synthesis and characterization of
dinitroamines which were expected to show enhanced thermal properties.

Also, this program consisted of the standard physical, stability, thermo-
dynamic and compatibility characterization of all interesting compounds synthesized.

The following personnel contributed to this program during this period:

E. E. Hamel (Project Supervisor)

R. E. Olsen (Principal Investigator)

R. H. Quacchia (Principal Investigator)

This technical report has been reviewed and is approved.

George F. Babits, Lt Colonel, USAF
Chief, Propellant Division

ABSTRACT

Several inorganic salts of N,N,N'-trinitroethylenediamine were prepared and characterized. These salts exhibit improved thermal properties over previously reported dinitroamines, showing decomposition at about 130°C. However, the salts were either deliquescent or contained difficult-to-remove impurities. Attempts to prepare organic salts of N,N,N'-trinitroethylenediamine were unsuccessful.

Attempts to prepare the aromatic dinitroamines, N,N,3,5-tetranitroaniline, N,N-dinitropentafluoroaniline and N,N-dinitro-2,3,5,6-tetrafluoroaniline, were unsuccessful.

A new type of oxygen oxidizer, 1,4-dihydro-1-nitro-4-nitriminopyridine, was prepared and characterized. The material forms a nonhygroscopic perchlorate salt, 1-nitro-4-nitraminopyridinium perchlorate. An analogous series of reactions was used to prepare 1,4-dihydro-1,3-dinitro-4-nitriminopyridine and 1,3-dinitro-4-nitraminopyridinium perchlorate. However, attempts to prepare 1,4-dihydro-1,3,5-trinitro-4-nitriminopyridine were unsuccessful.

It was shown that β-nitraza primary nitramines could be prepared by the acid hydrolysis of the corresponding β-nitraza N-nitro-t-butylcarbamate. However, treatment of the β-nitraza primary nitramine, 2-nitrazapropylnitramine, with nitronium tetrafluoroborate did not give the corresponding dinitroamine.

The decomposition kinetics of N,N-dinitro-n-butylamine were investigated and the data obtained were consistent with a unimolecular decomposition mechanism. It was shown that secondary carbinyl dinitroamines undergo a different thermal decomposition mechanism than the primary carbinyl derivatives.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont.)

TABLE OF CONTENTS (Cont.)

TABLES

FIGURES

I. INTRODUCTION

Compounds containing the N,N-dinitroamino functional group were first prepared at Aerojet-General in 1961 by the reaction of primary nitramines with nitronium tetrafluoroborate. These materials are high energy compounds and appear capable of providing theoretical specific impulse values of 295 seconds or greater; however, they were found to have poor thermal stability, showing explosive decomposition near 70°C on Differential Thermal Analysis.

In view of the excellent potential of dinitroamines as high energy oxidizers, a research program, funded by ARPA on 15 February 1963, was directed toward the synthesis of the following compounds: (1) N,N,N',N'-tetranitromethylenediamine, (2) pernitromethylenediamine, (3) hydrazinium bis(N,N-dinitroamino)methylnitronate and (4) N,N,2,2,2-pentanitroethylamine. The following year, the relationship of structure to thermal stability was studied; on the current program, funded on 1 April 1965, the primary emphasis was directed toward the improvement of thermal properties of dinitroamines.

II. SUMMARY

A. The potassium, lithium, silver and nickel salts of N,N,N'-trinitro-ethylenediamine were prepared and characterized. These salts exhibit significantly improved thermal properties over previously reported dinitroamines, showing decompositions at 130°C on a melting point block. However, the lithium, potassium and nickel salts were deliquescent, while the silver salt contained a difficult-to-remove impurity of metallic silver. Attempts to prepare organic salts of N,N,N'-trinitroethylenediamine led to decomposition of the dinitroamine.

B.   Attempts to prepare an aromatic dinitroamine, N,N,3,5-tetranitro-
aniline, by the reaction of N,3,5-trinitroaniline, or its ammonium, potassium,
lithium or silver salt, with nitronium tetrafluoroborate were unsuccessful; only
starting material or unidentified gums were isolated from the reaction mixtures.
Attempts to prepare fluorine-substituted aromatic dinitroamines were also unsuccessful;
treatment of the ammonium salts of N-nitropentafluoroaniline and 2,3,5,6-tetra-
fluoroaniline with nitronium tetrafluoroborate gave products which were unstable
at low temperatures.

C.   A new type of oxygen oxidizer, 1,4-dihydro-1-nitro-4-nitriminopyridine,
was produced by the reaction of 4-nitraminopyridine and nitronium tetrafluoroborate.
The structure of the nitration product was confirmed by elemental, infrared and
proton nuclear magnetic resonance analyses, and by comparison of its ultraviolet
absorption spectrum and apparent pK_A to two model compounds. The 1,4-dihydro-
pyridine product, m.p. 134°C (def.) was thermally stable for at least 240 hours
at 70°C and had an impact sensitivity of 2 cm (2 kg wt.); heat of combustion
measurements indicated a heat of formation of +26.3 kcal/mole for this material.
Treatment of the 1,4-dihydropyridine product with 70% perchloric acid gave a
quantitative yield of the corresponding salt, 1-nitro-4-nitraminopyridinium
perchlorate, a white, nonhygroscopic solid, m.p. 100-102°C, having an impact
sensitivity of 1.7 cm (2 kg wt.). Heat of combustion measurements indicated a
heat of formation of -2.2 kcal/mole for the salt.

The reaction of 3-nitro-4-nitraminopyridine with nitronium tetra-fluoroborate gave 1,4-dihydro-1,3-dinitro-4-nitriminopyridine, a yellow solid, m.p. 105°C, having an impact sensitivity of 6.7 cm (2 kg wt.). Treatment of this material with perchloric acid gave the corresponding salt, 1,3-dinitro-4-nitramino-pyridinium perchlorate, a white, nonhygroscopic solid, m.p. 163-164°C, having an impact sensitivity of 2.2 cm (2 kg wt.). The 1,3-dinitro-4-nitraminopyridinium perchlorate was the most promising pyridine compound prepared thus far, as it has the highest oxygen content and greatest thermal stability; it was stable at 90°C, but underwent extensive decomposition at 120°C.

D.   Attempts to prepare 1,4-dihydro-1,3,5-trinitro-4-nitriminopyridine by the reaction of 3,5-dinitro-4-nitraminopyridine with nitronium tetrafluoroborate were unsuccessful; only starting nitramine or a denitrated product, 3,5-dinitro-4-aminopyridine, could be recovered from the reaction mixtures.

E.   A new technique for the synthesis of primary nitramines under acidic conditions was developed as it was shown that N-nitro-t-butyl-n-butylcarbamate undergoes acid hydrolysis to give n-butylnitramine. A similar hydrolysis of t-butyl-2'-nitrazapropyl-N-nitrocarbamate gave fair yields of the previously unreported 2-nitrazapropylnitramine. Treatment of this nitramine with nitronium tetrafluoroborate did not give the corresponding N,N-dinitroamine, but rather gave 2,4,6-trinitrazaheptane.

F.   The kinetics of the thermal decomposition reaction of dinitroamines were studied in an effort to gain information which could be used to improve the stability of these materials. The decomposition rates of N,N-dinitro-n-butylamine were measured in the absence of solvent at 50, 60 and 70°C by gas chromatographic

techniques; the calculated activation energy, E_A, frequency factor, A, and entropy
of activation, ΔS^{*}, were consistent with a unimolecular decomposition mechanism.
The thermal decomposition of N,N-dinitro-n-butylamine was also studied in the
presence of acetic acid and styrene. The formation of n-butylacetate and styrene
polymers during the decomposition was consistent with the proposed reaction
mechanism.

G. The secondary carbinyl dinitroamines, N,N-dinitro-i-propylamine and
ethyl N,N-dinitro-d-2-aminopropionate, and the bridgehead dinitroamine, N,N-dinitro-
1-apocamphylamine, were synthesized to study their decomposition rates and products.
The decomposition products and the rate data for the secondary carbinyl dinitroamines
indicate that the mechanism of thermal decomposition of the secondary dinitroamines
is different from that of the primary derivatives.

III. OBJECTIVE AND SCOPE

A. OBJECTIVE

The objective of this program was to improve the thermal stability
of N,N-dinitroamines. With this objective in mind, the program was divided into
two areas. The first area had as its objective the quantitative determination of
those factors which affect the thermal stability of dinitroamines. The second
area had as its objective the synthesis and characterization of dinitroamines
which were expected to show enhanced thermal properties.

B. SCOPE

The scope of this research program included: (a) determination of
the basic decomposition mechanism for several representative types of alkyl
dinitroamines, and (b) investigation of suitable methods for the synthesis of
previously unreported dinitroamines.

IV.   RECOMMENDATIONS

During the last month of the current program year, it was observed that secondary and primary carbinyl dinitroamines decompose by different mechanistic paths, evolving (as major gases) nitrogen in the first case and nitrous oxide in the latter. Furthermore, it was shown that for two secondary carbinyl dinitroamines, replacement of a methyl by the more electronegative carbethoxy group resulted in a four-fold decrease in the thermal decomposition rate. There was insufficient time available to determine if secondary carbinyl dinitroamines generally decompose at a rate proportional to the electronegativity of substituted groups. If this were the case, secondary carbinyl dinitroamines containing such electronegative moieties as trinitromethyl or difluoroamino could prove to be attractive and stable oxidizers.

It is therefore recommended that any future program concerning dinitroamines investigate the thermal decomposition of secondary carbinyl dinitroamines and determine if these materials can be stabilized by electronegative substituents.

V.   CURRENT STATUS

Funding for an ARPA-sponsored two man-year research program (monitored by Edwards Air Force Base) on N,N-dinitroamines was terminated on 1 April 1966.

VI.   TECHNICAL DISCUSSION

A.   SUMMARY OF WORK PERFORMED DURING FIRST THREE QUARTERS OF
CURRENT CONTRACT YEAR

1.   Synthesis and Characterization of Salts of
N,N,N'-Trinitroethylenediamine

The synthesis of N,N-dinitroamino-substituted salts was undertaken
since it was anticipated that such dinitroamines would show improved thermal
properties. Improved thermal properties were predicted because, in a crystalline
solid, an additional energy barrier (the lattice energy) must be overcome prior to
thermal decomposition. Attempts to prepare dinitroamino-substituted carboxylate
salts via the reaction of the corresponding esters with alcoholic potassium
hydroxide were unsuccessful as the base degraded the dinitroamino moiety.[1]
However, the preparation of N,N,N'-trinitroethylenediamine (TED) by the reaction
of N,N,N',N'-tetranitroethylenediamine with alcoholic potassium hydroxide and
subsequent acidification was successful.[1]

$$N(NO_2)_2CH_2CH_2N(NO_2)_2 + 2\ KOH \longrightarrow KN(NO_2)CH_2CH_2N(NO_2)_2 + KNO_3$$

$$\downarrow HCl$$

$$HN(NO_2)CH_2CH_2N(NO_2)_2 + KCl$$

$$TED$$
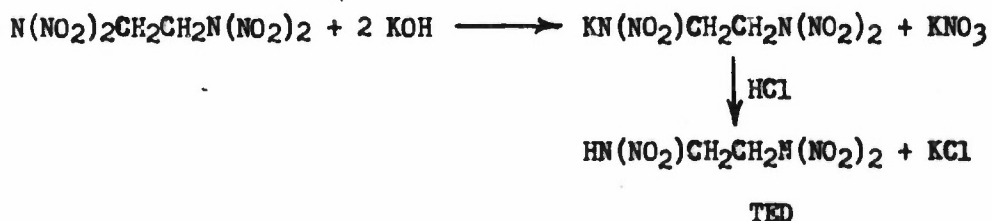
The N,N,N'-trinitroethylenediamine, which contains an acidic
proton, was obtained in high yields and was characterized by equivalent weight
and infrared and elemental analysis.

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1.   Aerojet-General Corporation, Report 0856-81Q-3, January 1965 (Confidential).

The lithium, potassium, silver and nickel salts of TED were prepared and partially characterized.[2] It was found that such salts have improved thermal properties over previously reported dinitroamines, showing decompositions at 130°C on a melting point block. However, the potassium, lithium and nickel salts of TED were hygroscopic, while the silver salt showed a slow decomposition at 75°C to give silver nitrate as one decomposition product. The thermal and impact properties of those salts are summarized in Table I.

TABLE I

PROPERTIES OF INORGANIC SALTS OF N,N,N'-TRINITROETHYLENEDIAMINE

Cation	M.P., °C	Exo. °C	Max. °C	Impact,[c] cm
Li	130[a]	-	-	-
K	130[a]	-	-	-
Ag	130[b]	105	120	7
Ni	130[b]	107	113	15

[a] Material charred at this temperature.
[b] Salt underwent deflagration when placed on block preheated to this temperature.
[c] 2 kg wt., RDX standard 32-35 cm.

Attempts were made to prepare the hydrazine and aminoguanidine salts of N,N,N'-trinitroethylenediamine since salts would be particularly attractive oxidizers.[2] However, these attempts were unsuccessful, as vigorous exotherms and evolution of gas were observed during neutralization of TED with the organic bases. The high reactivity of TED may preclude its use as a source of organic dinitroamine salts.

2. Aerojet-General Corporation, Report 0856-81Q-5, July 1965 (Confidential).

2. <u>Attempted Synthesis of Nonalkyl N,N-Dinitroamines</u>

    a.   Attempted Synthesis of N,N,3,5-Tetranitroaniline

        All of the alkyl N,N-dinitroamines synthesized to date on this program have shown limited thermal stability. It was of considerable interest to attempt the synthesis of aromatic dinitroamines, as it was expected they would exhibit improved stability. Previous attempts[3] to synthesize an aromatic derivative by the reaction of N,2,4,6-tetranitroaniline with nitronium tetrafluoroborate gave evidence for a nitro-oxygen substitution product.

$$ArN(NO_2)H + NO_2BF_4 \longrightarrow ArN=N(O)ONO_2 + HBF_4$$

        In the current studies,[4] N,3,5-trinitroaniline (prepared by the reaction of 3,5-dinitroaniline with nitronium tetrafluoroborate) was chosen as a model compound to investigate more fully the possible reactions leading to an aromatic dinitroamine as nitro groups in the 3,5-positions deactivate the phenyl ring to further substitution, but do not sterically inhibit reactions about the nitramino group. However, it was found that treatment of N,3,5-trinitroaniline, or its ammonium, potassium, lithium or silver salt with nitronium tetrafluoroborate in several solvents with temperatures ranging from -30°C to ambient did not give the desired dinitroamine, but resulted mainly in the recovery of starting primary nitramine.
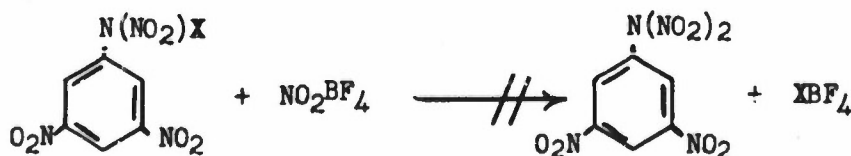
X= H, NH₄, Li, K, Ag

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3. Aerojet-General Corporation, First Annual Summary Report, AF 04(611)-8549, April 1964 (Confidential).
4. Aerojet-General Corporation, Report 0856-81Q-6, October 1965 (Confidential).

Attempts were also made to prepare fluorine-substituted N,N-dinitroamines,[5] as such materials would be useful in studying substituent effects in the thermal decomposition of dinitroamines. It was found that treatment of ammonium pentafluorophenylnitraminate (prepared by the nitration of pentafluoroaniline with nitronium tetrafluoroborate, followed by conversion of the unstable primary nitramine to its ammonium salt) with one equivalent of nitronium tetrafluoroborate gave an unstable product which evolved gas at 0°C. Removal of the reaction solvent under reduced pressure left a red oil which also evolved gas at about room temperature. Similar results were obtained when the ammonium salt of N-nitro-2,3,5,6-tetrafluoroaniline was treated with nitronium tetrafluoroborate.

$$\underset{X}{\overset{N(NH_4)NO_2}{\bigcirc}} + NO_2BF_4 \xrightarrow{\;\;/\!\!/\;\;} \underset{X}{\overset{N(NO_2)_2}{\bigcirc}} + NH_4BF_4$$
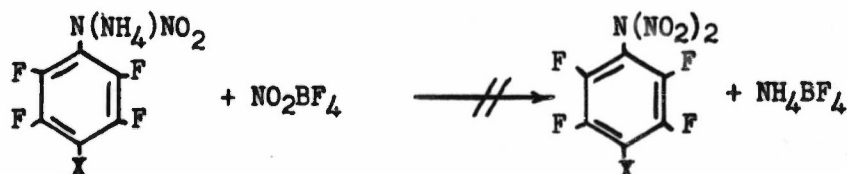
X= H, F

Due to the low thermal stability of these reaction products, no further work was done in the area of fluorine-substituted aromatic N,N-dinitroamines.

b. Synthesis and Characterization of 1,4-Dihydro-1-Nitro-4-Nitriminopyridine

In an attempt to prepare a heterocyclic N,N-dinitroamine, 4-nitraminopyridine was treated with nitronium tetrafluoroborate. Workup of the reaction solution gave excellent yields of a yellow solid which was identified as the previously unreported 1,4-dihydro-1-nitro-4-nitriminopyridine (I).[4]

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5. Aerojet-General Corporation, Report 0856-81Q-7, January 1966 (Confidential).
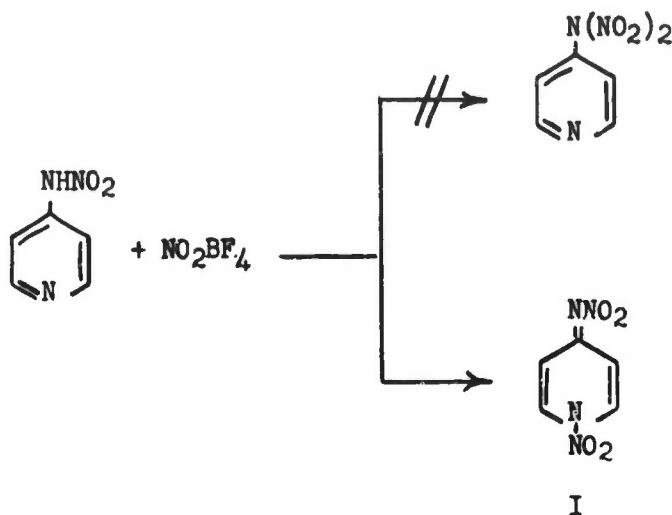
The product, which deflagrates at 134°C, gave elemental analysis values in excellent agreement with the proposed structure. It showed no decomposition after 240 hours at 70°C, and on impact testing, showed a sensitivity of 2 cm (2 kg wt.). A proton nuclear magnetic resonance spectrum was taken of the dihydropyridine derivative and two doublets of the A_2X_2 type ($\nu_{2,6}$ = 9.19, $\nu_{3,5}$ = 7.10 ppm, relative to TMS) recorded.

In view of the improved thermal stability of the nitrimino-pyridine, a considerable effort was made to establish conclusively the structure of the nitration product (I). The ultraviolet absorption spectra for the series 4-cyanopyridine, 4-nitraminopyridine, 1,4-dihydro-1-methyl-4-nitriminopyridine,[6] and 1,4-dihydro-1-nitro-4-nitriminopyridine were taken and compared under neutral and acidic conditions. These results are summarized in Table II and showed that the latter three compounds have similar structures.

X = CH_3, H, NO_2
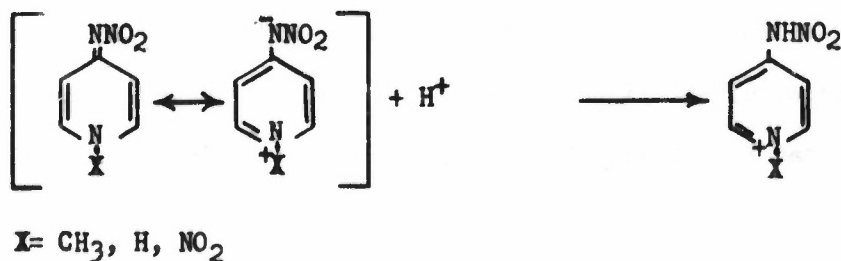
6. A. Albert, "Physical Methods in Heterocyclic Chemistry", Vol. 1, Ed. by A. R. Katutzsky, Academic Press, New York, 1963, p. 67.

TABLE II

ULTRAVIOLET ABSORPTION FOR 4-SUBSTITUTED PYRIDINES

Compound	Species[a]	λ_{max}[b]	$\epsilon \times 10^{-4}$
4-Cyanopyridine[c]	N	275	0.34
	C	276	0.57
4-Nitraminopyridine	N	334	1.05
	C	278	-
1,4-Dihydro-1-methyl-4-nitriminopyridine	N	342	2.37
	C	283	-
1,4-Dihydro-1-nitro-4-nitriminopyridine	N	334	1.97
	C	227	-

[a] N= neutral molecule, C= cation.
[b] Neutral spectra taken in 90% ethanol, acidic spectra
in 90% ethanol/0.1$\underline{N}$ hydrochloric acid.
[c] S. F. Mason, J. Chem. Soc., 1959, 1247.

As further evidence for the structure of the nitration
product (I), the apparent pK_A's were measured for the compounds 4-nitraminopyridine,
1,4-dihydro-1-methyl-4-nitriminopyridine and 1,4-dihydro-1-nitro-4-nitriminopyridine
and were compared to the reported pK_A's of electronegatively 4-substituted pyridines.
While the conjugate acids of electronegatively substituted pyridines usually shown
pK_A values of about 4,[6] it was found that 4-nitraminopyridine, 1,4-dihydro-1-
methyl-4-nitriminopyridine and 1,4-dihydro-1-nitro-4-nitriminopyridine had apparent
pK_A's of 1.69, 1.62 and 1.71, respectively.

The heat of formation of 1,4-dihydro-1-nitro-4-nitrimino-pyridine was determined by combustion calorimetry, using a Parr Adiabatic Calorimeter.[6] It was found that the dihydropyridine derivative had a standard heat of formation of +26.3 ± 2.5 kcal/mole.

$$\Delta H^e_f(298)\ C_5H_4N_4O_4 = +26.3 \pm 2.5\ \text{kcal/mole}$$

A quantitative yield of 1-nitro-4-nitraminopyridinium perchlorate (II) was obtained when 1,4-dihydro-1-nitro-4-nitriminopyridine was allowed to react with 70% perchloric acid in ether solution.[6]

II

The perchlorate salt, II, was a white, nonhygroscopic solid (m.p. 100-102°C) which showed a sensitivity of 1.7 cm (2 kg wt.) on impact testing. The heat of combustion of the salt as also determined by combustion calorimetry, giving a standard heat of formation of -2.2 ± 14.2 kcal/mole.[5]

$$\Delta H^\circ_f(298)\ C_5H_4N_4O_4 \cdot HClO_4 = -2.2 \pm 14.2\ \text{kcal/mole}$$

c. Preparation and Characterization of 1,4-Dihydro-1,3-Dinitro-4-Nitriminopyridine

Treatment of 3-nitro-4-nitraminopyridine with nitronium tetrafluoroborate gave good yields of 1,4-dihydro-1,3-dinitro-4-nitriminopyridine (III).

The dihydropyridine derivative, (III), was a pale yellow solid (m.p. 105°C) which showed a sensitivity of 6.7 cm (2 kg wt.) on impact testing. The dihydro structure was confirmed by elemental, infrared, ultraviolet and proton nuclear magnetic resonance analyses. Three proton signals of equal area intensities were observed from the NMR spectrum. The protons on the 5 and 6 positions of the pyridine ring were coupled ($J_{5,6}$= 9.05 cps) and the 2 and 6 protons were also coupled ($J_{2,6}$= 2.32 cps), giving rise to two doublets and a quartette (V_2= 9.85, V_6= 8.83, V_5= 6.99 ppm, relative to TMS).

1,3-Dinitro-4-nitraminopyridinium perchlorate (IV), the most interesting member of the series, was formed in quantitative yield by the action of 70% perchloric acid on 1,4-dihydro-1,3-dinitro-4-nitriminopyridine.
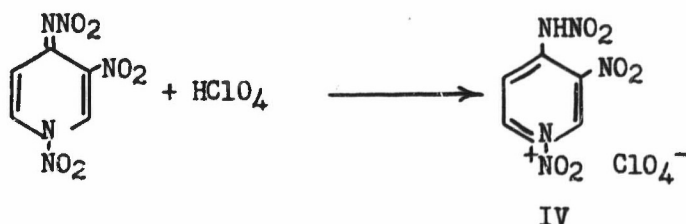
The salt, IV, was recrystallized from a nitromethane-methylene chloride mixture to give a white, nonhygroscopic solid (m.p. 163-164°C) which, on Differential Thermal Analysis, showed an exotherm at 163°C and a maximum at 168°C. On impact testing, the material had a sensitivity of 2.2 cm (2 kg wt.).

d.   Thermal Stability of Pyridine Derivatives

The thermal stability of the above pyridine derivatives was investigated utilizing thermogravimetric analysis and gas chromatography. The four compounds studied were: 1,4-dihydro-1-nitro-4-nitriminopyridine (I), 1,3-dinitro-4-nitraminopyridinium perchlorate (IV), 1,4-dihydro-1,3-dinitro-4-nitriminopyridine (III) and 1-nitro-4-nitraminopyridinium perchlorate (II); the first two compounds were studied by thermogravimetric analysis and the latter two by thermogravimetric analysis and gas chromatography.
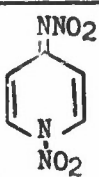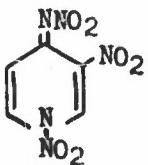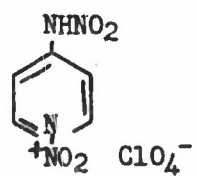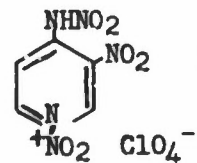
The thermogravimetric samples were decomposed in vessels open to the air, whereas the samples for gas chromatography were decomposed in sealed melting point tubes. The thermogravimetric data are presented in Table III and the gas chromatography data in Table IV.

TABLE III

THERMOGRAVIMETRIC ANALYSIS OF PYRIDINE DERIVATIVES

Compound[a]	Structure	M.P.,°C	Temp.,°C	Time	Initial Wt.,gms	% Wt. Loss
1)		130 (def)	70	22 hr	0.202	0.5
			90	18 hr	0.202	11.2
			110	25 min	0.208	Exploded
2)		105 (dec)	50	23 hr	0.202	1.8
			70	19 hr	0.202	9.3
			90	14 min	0.100	Exploded
3)		100-102	50	22 hr	0.202	0.1
			70	18 hr	0.103	21.7
			100	35 min	0.010	Exploded
4)		163-164	90	22 hr	0.210	0.2
			120	20 hr	0.109	13.8
			140	18 min	0.202	Exploded
			160	8 min	0.20	Exploded

----

[a]1) 1,4-Dihydro-1-nitro-4-nitriminopyridine.
 2) 1,4-Dihydro-1,3-dinitro-4-nitriminopyridine.
 3) 1-Nitro-4-nitraminopyridinium Perchlorate.
 4) 1,3-Dinitro-4-nitraminopyridinium Perchlorate.

TABLE IV

THERMAL DECOMPOSITION OF PYRIDINE DERIVATIVES AT 70°C, GAS ANALYSIS BY GAS CHROMATOGRAPHY

Compound[a]	Structure	Time, min.	O_2	N_2	CO	N_2O	% Wt. Loss in 24 Hrs.	
1)	NNO_2 / NO_2 / N / NO_2	0	170	600	–	–	N_2	10.9
		60	160	1150	–	–	CO	0.83
		120	152	4612	–	–	N_2O	1.06
		180	157	6000	–	–		
		1500	147	9040	604	1340		12.8%
		2930	10	11360	835	1330		
2)	$NHNO_2$ / N / NO_2 ClO_4^-	0	170	600	–	–	N_2	10.8
		60	135	560	–	–	CO	1.8
		120	200	843	–	–	N_2O	2.6
		180	149	745	–	–		15.2%
		1600	61	7448	1289	1052		
		2930	10	6616	1139	1015		

---

[a]1) 1,4-Dihydro-1,3-dinitro-4-nitriminopyridine.
2) 1-Nitro-4-nitraminopyridinium Perchlorate.

All of the pyridine derivatives tested by thermogravimetric analysis (Table III) exploded about forty degrees above the temperature where the thermal decomposition is negligible in twenty hours, with the observed order of thermal stability in the same order as melting points, i.e., the higher the melting point, the greater the thermal stability.

3.   Kinetics of N,N-Dinitroamine Decomposition

a.   Thermal Decomposition of N,N-Dinitro-n-butylamine

An investigation of the mechanism of the thermal decomposition of N,N-dinitroamines was initiated with a kinetic study of the decomposition of N,N-dinitro-n-butylamine. Ultraviolet absorption spectroscopy, nuclear magnetic resonance and gas chromatography were used for kinetic measurements. Gas chromatography proved to be the most suitable method for observing both the liquid and gaseous products from the thermal decomposition. First order decomposition rates based on nitrous oxide formation were measured for N,N-dinitro-n-butylamine in the absence of solvent at 50, 60 ($k_{obsd}= 1.15 \times 10^{-4}$ sec^{-1}) and 70°C using gas chromatographic techniques.[2] The calculated activation energy, $E_A= 23.6$ kcal/mole, frequency factor, $A= 4.38 \times 10^{11}$ sec^{-1} at 60°C, and entropy of activation, $\Delta S^*= 8.54$ e.u. at 60°C are consistent with a unimolecular reaction path.[2,7] Previous work indicated that the main reaction products from the thermal decomposition were n-butylnitrate and nitrous oxide with 1-butene and nitric acid as minor components.[3] Further workup of the liquid products by preparative gas chromatography and analysis of the fractions by infrared and nuclear magnetic resonance spectroscopy indicated that 1-nitrobutane and a higher molecular weight 1-nitroalkane were also formed in the decomposition.[2] The thermal decomposition of N,N-dinitro-n-butylamine in the presence of an equivalent of acetic acid formed n-butylnitrate and butyl acetate in approximately equal amounts as major liquid products. In the presence of an equivalent of styrene, the styrene was completely converted to polymer.

7.   "The Foundations of Chemical Kinetics", Chpt. XI, by Sidney W. Benson, McGraw-Hill Book Co., Inc., New York, 1960.

The first order kinetic data as obtained by UV (1.5×10^{-4} $\sec^{-1}$ at 60°C; disappearance of N,N-dinitro-n-butylamine), NMR (2.5×10^{-4} $\sec^{-1}$ at 60°C in $CDCl_3$; disappearance of N,N-dinitro-n-butylamine and appearance of 1-butylnitrate) and GLC indicate that the rate of formation of nitrous oxide and n-butylnitrate is approximately equal to the rate of disappearance of the dinitroamine. Thus, the rate determining step is either the direct formation of products or the formation of an intermediate prior to product formation. A possible reaction path is given in Equation (1).

$$CH_3CH_2CH_2CH_2N \begin{cases} NO_2 \\ NO_2 \end{cases} \quad \begin{array}{c} \nearrow CH_3CH_2CH_2CH_2N{=}\overset{O^-}{\overset{+}{N}}{-}ONO_2 \\ \rightleftharpoons \\ \searrow CH_3CH_2CH_2CH{=}N{=}\overset{O^-}{N} ; HNO_3 \end{array} \quad \begin{array}{c} \searrow \\ products \\ \nearrow \end{array} \qquad (1)$$
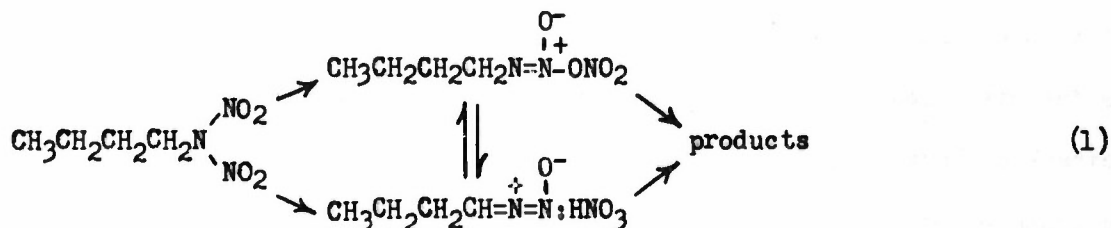
The formation of 1-butene and nitric acid by β proton abstraction, as well as the formation of n-butylnitrate by an intermolecular displacement, and n-butyl acetate by a bimolecular displacement, can be rationalized by the reaction path given in Equation (1). The loss of styrene can be accomodated by acid or cationic polymerization, but there is insufficient data to postulate the reaction path for the formation of the 1-nitroalkanes.

This decomposition path is similar to that advanced by White[8] for the decomposition of N-nitroso and N-nitro amides and urethanes, materials which are structurally similar to N,N-dinitroamines.

8. E. H. White and C. Aufdermarch, J. Am. Chem. Soc., 82, 1174 (1961);
    E. H. White and D. W. Grisley, ibid., 83, 1191 (1961).

b.   Synthesis of a Bridgehead N,N-Dinitroamine

The reaction mechanism given in Equation (1) suggests that an amino compound which has no α-hydrogens and cannot undergo carbonium ion formation should produce a relatively stable decomposition intermediate which could be isolated. A bridgehead amine such as 1-apocamphylamine would fit both criteria. For a further discussion, see this report, Section B, 3.

c.   Synthesis of N,N-Dinitro-i-Propylamine

Rate studies of the thermal decomposition reaction of branched alkyl N,N-dinitroamines were initiated[2] with the synthesis of N,N-dinitroisopropylamine by the nitration of the potassium salt of N-nitroisopropylamine with nitronium tetrafluoroborate in acetonitrile at -30°C. Differential Thermal Analysis showed an exotherm beginning at 30°C with a maximum at 80°C, followed by a minimum at 90° with another exotherm at 108°C. The latter exotherm may be due to the products from the first decomposition since most of the dinitroamine is decomposed prior to 90°C minimum. The decomposition kinetic data are presented and discussed in a subsequent section (this report, Section B, 3.).

B.   SUMMARY OF WORK PERFORMED DURING FOURTH QUARTER

1.   Attempted Preparation of 1,3,5-Trinitronitriminopyridine Derivative

Considerable effort was expended in attempts to prepare 1,4-dihydro-1,3,5-trinitro-4-nitriminopyridine (V), as this material and its perchlorate salt are attractive as potential oxidizers from both heat of formation and oxygen balance considerations. However, treatment of 3,5-dinitro-4-nitraminopyridine

(prepared from 3,5-dinitro-4-aminopyridine and nitrogen pentoxide in trifluoroacetic anhydride)[5] or its potassium or ammonium salt with nitronium tetrafluoroborate in acetonitrile, methylene chloride or nitromethane at temperatures from -30°C to ambient did not give the desired dihydropyridine structure; only starting material or a denitrated product, 3,5-dinitro-4-aminopyridine, could be isolated from the reaction mixtures.
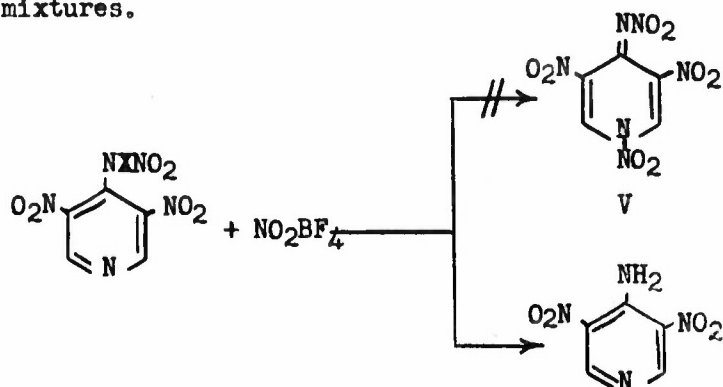
X= H, NH₄, K

Similarly, attempts to prepare 1,2-dihydro-1,3,5-trinitro-2-nitraminopyridine (VI) by the reaction of 2-nitramino-3,5-dinitropyridine (prepared by the reaction of 2-nitraminopyridine with two equivalents of nitronium tetra-fluoroborate)[4] or its potassium or ammonium salt with nitronium tetrafluoroborate were unsuccessful; only starting material or unidentified degradation products were recovered.
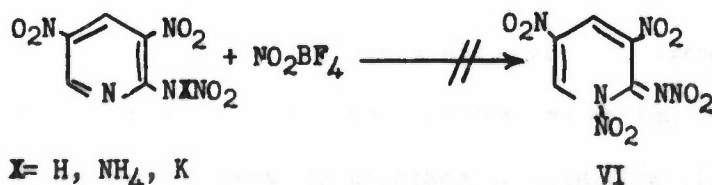
X= H, NH₄, K

2. <u>Attempted Synthesis of High Melting Alkyl N,N-Dinitroamines</u>

Since Thermal Gravimetric Analysis data have shown that solid dinitroamines exhibit greater thermal stability than their liquid analogs,[2] our synthesis efforts were directed toward the preparation of high melting materials, with particular attention directed toward dinitroamines containing nitraza groups. Based on earlier data, it was expected that dinitroamines where the dinitroamino moiety is separated from a nitraza group by a single carbon atom would be solids with relatively high melting points.[1] However, there appear to be no reported techniques available for the preparation of such primary nitramine precursors. Since such primary nitramines readily degrade under basic conditions, an investigation into the synthesis of primary nitramines under acidic conditions was undertaken. It was shown that treatment of the model compound $\underline{t}$-butyl-$\underline{n}$-butyl-N-nitrocarbamate (VII) with 70% nitric acid gave good yields of $\underline{n}$-butylnitramine.[4]

$$\underline{n}\text{-}C_4H_9N(NO_2)CO_2C(CH_3)_3 \xrightarrow{HNO_3} \underline{n}\text{-}C_4H_9N(NO_2)H + CO_2 + CH_2\text{=}C(CH_3)_2$$

VII
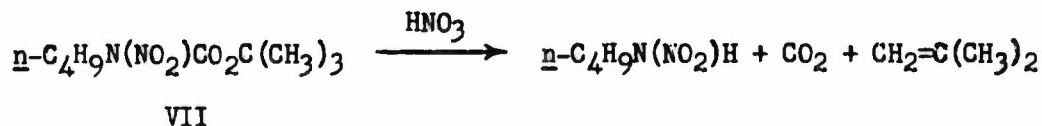
A similar hydrolysis of $\underline{t}$-butyl-2'-nitrazapropyl-N-nitrocarbamate (VIII) gave fair yields of the previously unreported 2-nitrazapropylnitramine (IX).

$$CH_3N(NO_2)CH_2N(NO_2)CO_2C(CH_3)_3 \xrightarrow{HNO_3} CH_3N(NO_2)CH_2N(NO_2)H$$

VIII   IX
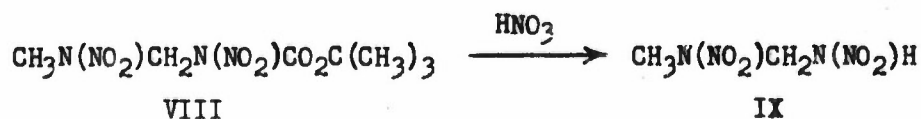
The nitramine, IX, was a white solid, m.p. 67-69°C, which was characterized by infrared, proton nuclear magnetic resonance and elemental analyses. The NMR spectrum (deuteroacetone solution) showed sharp, single absorption peaks at 3.59 and 5.52 ppm (relative to TMS), with area intensities of three to two for the methyl and methylene protons. The acidic nitramino proton was seen as a broad signal at 11.38 ppm.

Treatment of IX with nitronium tetrafluoroborate gave a fair
yield of a white solid (m.p. 159-160°C) which was examined by infrared and proton
nuclear magnetic resonance. Infrared analysis (KBr pellet) showed only the presence
of N-nitro (1565, 1555, 1540, 1295 and 1265 cm^{-1}), methyl (1450 and 1380 cm^{-1}) and
methylene (1470 cm^{-1}) absorption bands. The NMR spectrum (deuteroacetone solution)
again showed sharp, single absorption peaks at 3.53 and 5.85 ppm, with relative
intensities of three to two. The data are consistent with either the N,N-dinitro-
2-nitrazapropylamine (X) or the 2,4,6-trinitrazaheptane (XI) structure.

$$CH_3N(NO_2)CH_2N(NO_2)H \xrightarrow{NO_2BF_4}$$

$$\xrightarrow{//} CH_3N(NO_2)CH_2N(NO_2)_2$$

X

$$\longrightarrow [CH_3N(NO_2)CH_2]_2NNO_2$$

XI
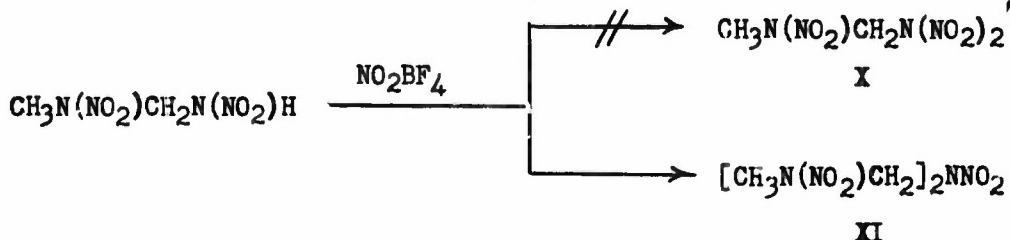
Elemental analysis, shown in Table V, established that the reaction product had
the 2,4,6-trinitrazaheptane structure.

TABLE V

ELEMENTAL ANALYSIS OF 2-NITRAZAPROPYLNITRAMINE NITRATION PRODUCT

	Calculated		
Element	Cmpd X	Cmpd XI	Found
C	12.3	20.1	20.3
H	2.56	4.20	4.45
N	35.9	35.3	35.1
O	49.3	40.3	40.2

3.   Kinetics of Dinitroamine Decomposition

  a.   Preparation of a Bridgehead N,N-Dinitroamine

The study of the mechanism of the thermal decomposition of N,N-dinitroamines was continued. N,N-Dinitro-1-apocamphylamine was synthesized with the expectation that the bridgehead dinitroamine would give a decomposition intermediate of sufficient stability to allow its isolation and characterization.

The reaction sequence shown below was used to convert dl-camphor-10-sulfochloride[9] (XII) to N,N-dinitro-1-apocamphylamine (XIV). The sulfochloride was oxidized with basic permanganate to give the corresponding keto acid, which was then reduced by the Huang-Minlom modification of the Wolf-Kishner reaction to yield 1-apocamphane carboxylic acid (XIII). The Schmidt reaction[10] was used to convert the acid to the amine, which was then treated with ethyl chloroformate, nitrated, and cleaved with morpholine to give the corresponding N-nitro morpholine salt. Treatment of the salt with two equivalents of nitronium tetrafluoroborate gave N,N-dinitro-1-apocamphylamine in fair yields. This reaction sequence was completed during the final two weeks of the program to give 0.02g of N,N-dinitro-1-apocamphylamine (XIV). The amount of product isolated was insufficient to allow decomposition studies and not enough time was left to repeat the synthesis and obtain larger quantities of material.

9. P. D. Bartlett and L. H. Knox, J. Am. Chem. Soc., 61, 3184 (1939).
10. D. N. Kursanov and S. V. Vitt, Zuhr Obshchii Khim, 25, 2509 (1955); C.A., 50, 9303 (1956).

R-CHSOCl $\xrightarrow{\text{MNO}_4^-}$ RCO$_2$H $\xrightarrow[\text{KOH}]{\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}}$ R'CO$_2$H $\xrightarrow[\text{H}_2\text{SO}_4]{\text{NaN}_3}$

$\qquad$ XII $\qquad\qquad\qquad\qquad\qquad\qquad$ XIII

R'NH$_2$ $\xrightarrow{\text{ClCO}_2\text{Et}}$ R'NHCO$_2$Et $\xrightarrow[\text{Ac}_2\text{O}]{\text{HNO}_3}$ R'N(NO$_2$)CO$_2$Et $\xrightarrow[\text{2) NO}_2\text{BF}_4]{\text{1) Base}}$ R'N(NO$_2$)$_2$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ XIV

R= $\qquad\qquad$ R'=
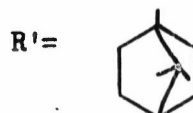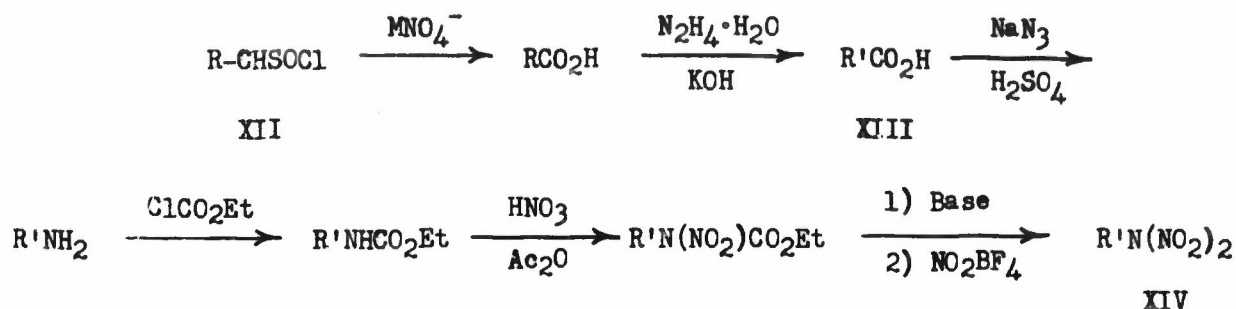
b. $\quad$ Preparation of Ethyl-N,N-Dinitro-d-2-Aminopropionate

$\qquad$ To further characterize the decomposition mechanism of N,N-dinitroamines, ethyl-N,N-dinitro-d-2-aminopropionate was synthesized in order to study the stereochemistry of the α-carbon in the decomposition reaction as well as the effect of substituents on the σ-carbon. The dinitroamine was prepared by the following route:

$\underset{\text{NH}_2}{\text{CH}_3\text{CHCO}_2\text{H}}$ $\xrightarrow[\text{HCl}]{\text{EtOH}}$ $\underset{\text{NH}_2}{\text{CH}_3\text{CHCO}_2\text{Et}}$ $\xrightarrow{\text{ClCO}_2\text{Et}}$ $\underset{\text{NHCO}_2\text{Et}}{\text{CH}_3\text{CHCO}_2\text{Et}}$

$\xrightarrow[\text{Ac}_2\text{O}]{\text{HNO}_3}$ $\underset{\text{N(NO}_2)\text{CO}_2\text{Et}}{\text{CH}_3\text{CHCO}_2\text{Et}}$ $\xrightarrow[\text{2) NO}_2\text{BF}_4]{\text{1) Base}}$ $\underset{\text{N(NO}_2)_2}{\text{CH}_3\text{CHCO}_2\text{Et}}$
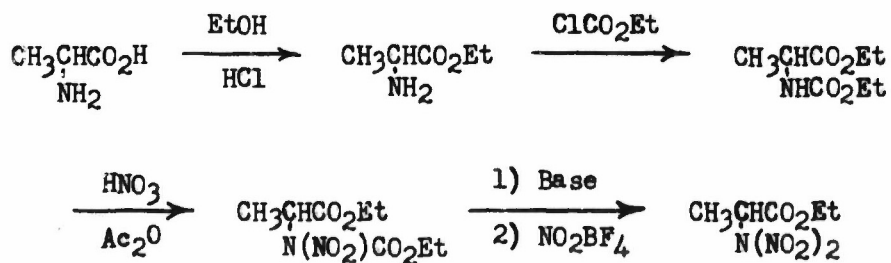
c. Thermal Decomposition Kinetics of Secondary Carbinyl
N,N-Dinitroamines

Thermal decompositions of the secondary carbinyl dinitro-
amines, N,N-dinitro-i-propylamine (Section A, 3, this report) and ethyl N,N-dinitro-
d-2-aminopropionate (Section B, 3, this report) were followed by gas chromatography
and the identity of the gaseous decomposition products was confirmed by mass spectral
analysis. It was apparent the secondary carbinyl derivatives follow a different
decomposition path than the previously investigated primary carbinyl derivative,
N,N-dinitro-n-butylamine. As shown in Table VI, the major gaseous decomposition
products from the secondary carbinyl derivatives were nitrogen, carbon dioxide and
nitric oxide, whereas the primary carbinyl derivative produced nitrous oxide as the
major product.

TABLE VI

GASEOUS DECOMPOSITION PRODUCTS FOR N,N-DINITROAMINES AT 60°C

Gas	$(CH_3)_2CHN(NO_2)_2$ Mole %	$CH_3CH[N(NO_2)_2]CO_2Et$ Mole %	$n-C_4H_9N(NO_2)_2$
CO	6.8	5.2	—
N_2	49.5	45.1	—
CO_2	13.3	22.6	—
NO	15.2	18.7	Minor[3]
N_2O	11.1	7.7	Major
NO_2	0.1	0.5	Minor
Propylene	3.8	—	—
1-Butene	—	—	Trace

The number of gases produced during the thermal decomposition of secondary carbinyl dinitroamines suggest that side reactions are occuring during the decomposition or products are further decomposing. Sufficient time was not available for an analysis of the nonvolatile decomposition products; however, infrared analysis of these products indicated the presence of C-nitro and C-nitrato groups. In addition, infrared analysis for the N,N-dinitro-i-propylamine nonvolatile decomposition product indicated the presence of carbonyl containing compounds. It was observed that during the decomposition of the isopropyl derivative, nitrous oxide was produced for a considerable period of time after nitrogen evolution had ceased. A similar study was not made on the propionate derivative. Again, the data indicate the presence of side reactions during the decomposition.

Thermal decomposition rates for N,N-dinitro-i-propylamine and ethyl N,N-dinitro-d-2-aminopropionate were measured in the absence of solvent at 60°C by following the production of nitrogen by gas chromatography. The rate data for both compounds gave good first order plots (see Figure 1). The data are summarized in Table VII; for comparison, the decomposition rate for N,N-dinitro-n-butylamine is also shown.

TABLE VII

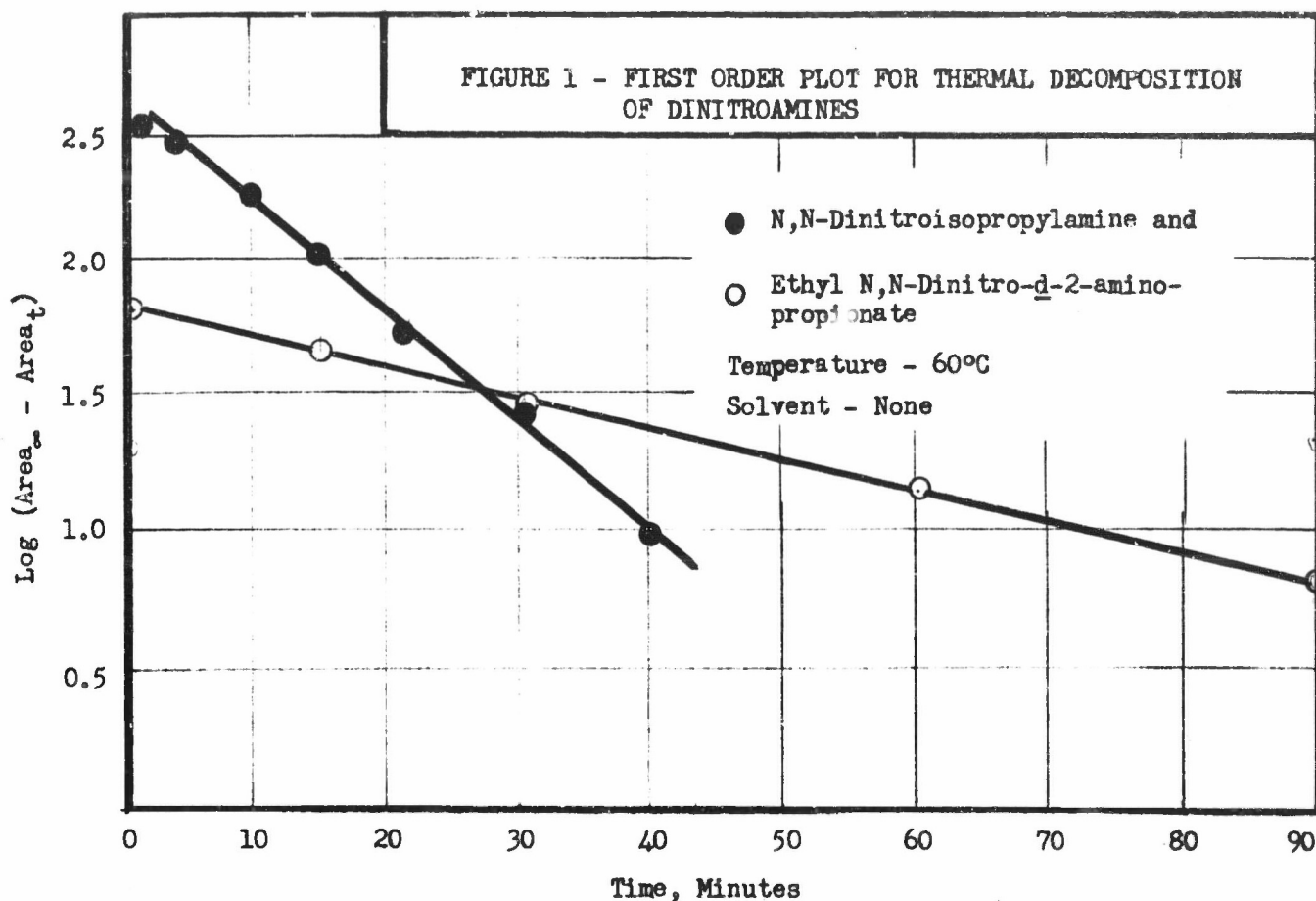THERMAL DECOMPOSITION RATES FOR N,N-DINITROAMINES AT 60°C (WITHOUT SOLVENT)

Compound	Observed Rate x 10^4, sec^{-1}	Half-Life, min.
$n-C_4H_9N(NO_2)_2$	1.15	100
$(CH_3)_2CHN(NO_2)_2$	16.0	7
$CH_3CH[N(NO_2)_2]CO_2Et$	4.2	28

FIGURE 1 - FIRST ORDER PLOT FOR THERMAL DECOMPOSITION
OF DINITROAMINES

● N,N-Dinitroisopropylamine and

○ Ethyl N,N-Dinitro-d-2-amino-
propionate

Temperature - 60°C
Solvent - None

[Y-axis: Log (Area$_\infty$ - Area$_t$)]

[X-axis: Time, Minutes]

As shown, there is a considerable difference in
decomposition rate between the two secondary carbinyl dinitroamines. This may
be attributed to electronic factors, but as the reaction was run in the absence
of solvent, this difference may also be attributed to the difference in polarity
of reactants and products.

With the limited experimental facts available, a
reasonable mechanistic path for the thermal decomposition of secondary carbinyl
dinitroamines cannot be formulated.

VII.   EXPERIMENTAL

Melting and boiling points are uncorrected. Reactions involving nitronium tetrafluoroborate were carried out in a dry box under a nitrogen atmosphere. The proton nuclear magnetic resonance spectra were obtained by Dr. R. M. Pearsen on a Model Varian DP-60 High Resolution NMR Spectrophotometer, while the infrared spectra were obtained on a Beckman IR-9 Infrared Spectrophotometer. The ultraviolet spectra were obtained using a Beckman DK2 Recording Spectrophotometer.

A.   PREPARATION OF PYRIDINE DERIVATIVE

1.   Attempted Preparation of 1,4-Dihydro-1,3,5-Trinitro-4-Nitriminopyridine

To a suspension of 1.00g (4.4 mmoles) of 3,5-dinitro-4-nitramino-pyridine[5] and 0.43g (4.4 mmoles) of potassium acetate, cooled to -20°C, was added with stirring, 0.64g (4.8 mmoles) of nitronium tetrafluoroborate. The mixture was allowed to warm to ambient temperature and was stirred for 24 hours, then quenched into 50 ml of ice water. An orange solid separated which was filtered and washed with acetone to remove the inorganic materials. Evaporation of the acetone left 0.73g of 3,5-dinitro-4-nitraminopyridine.

B.   ATTEMPTED SYNTHESIS OF HIGH MELTING ALKYL N,N-DINITROAMINES

1.   Preparation of t-Butyl-2-Nitrazapropylcarbamate

A solution of 2-nitrazabutyryl azide [prepared by treatment of 14.8g (0.10 mole) of N-methyl nitraminoacetohydrazide[11] with nitrous acid in chloroform solution] in chloroform was slowly heated to reflux, then refluxed for two hours. t-Butanol (30g, 0.40 mole) was added and the solution refluxed an additional hour, then allowed to stand overnight at ambient temperature. The

solvent was removed under reduced pressure to leave 14.0g (68% yield, based on N-methyl nitraminoacetohydrazide) of white powder (m.p. 80-81°C). The material was used without purification for subsequent reactions.

Analysis: Calcd. for $C_7H_{15}N_3O_4$: C, 41.0; H, 7.32; N, 20.5; O, 31.2.
Found: C, 40.8; H, 7.08; N, 20.8; O, 30.3.

2. Preparation of t-Butyl-2-Nitrazapropyl-N-Nitrocarbamate

A solution of 10g (0.05 mole) of t-butyl-2-nitrazapropylcarbamate in 35g of acetic anhydride was maintained between 15 and 20°C while 10g (0.15 mole) of 98% nitric acid was slowly added. The solution was stirred for 30 minutes at 20°C, then four hours at 5°C and finally quenched into 100 ml of ice water. The quench mixture was extracted with two 50-ml portions of methylene chloride and the combined extracts were washed with 5% sodium carbonate solution until the washings remained basic. The methylene chloride solution was dried over anhydrous magnesium sulfate and the solvent removed in vacuo to leave a white powder. Infrared and elemental analysis confirmed the identity of the powder (7.6g, 63% yield, m.p. 98-99°C) as t-butyl-2-nitrazapropyl-N-nitrocarbamate. The material was used without purification for subsequent reactions.

Analysis: Calcd. for $C_7H_{14}N_4O_6$: C, 33.6; H, 5.61; N, 22.4; O, 38.4.
Found: C, 33.7; H, 5.56; N, 22.0; O, 38.0.

3. Preparation of 2-Nitrazapropylnitramine

Nitric acid (70%, 10 ml) was cooled to 0°C and stirred while 2.0g (8 mmoles) of t-butyl-2-nitrazapropyl-N-nitrocarbamate was slowly added. The resulting yellow solution was maintained at 0°C and stirred for 15 minutes, then saturated with sodium chloride and extracted with three 10-ml portions of

ether. The ether extracts were combined and dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure left an off-white solid. The solid was recrystallized from hot (50°C) butyl chloride to give white needles identified as 2-nitrazapropylnitramine (0.9g, 74% yield, m.p. 67-69°C) by infrared, proton nuclear magnetic resonance and elemental analysis.

Analysis: Calcd. for $C_2H_6N_4O_4$: C, 16.0; H, 4.00; N, 37.3; O, 42.6. Found: C, 16.1; H, 4.12; N, 37.1; O, 42.4.

4. Attempted Preparation of N,N-Dinitro-2-Nitrazapropylamine

A solution of 3.0g (0.20 mole) of 2-nitrazapropylnitramine in 25 ml of acetonitrile was cooled to -30°C and 2.8g (0.21 mole) of nitronium tetrafluoroborate was added with stirring. The solution was allowed to warm to 0°C over a 45-minute period then quenched into 50 ml of ice water. A white solid separated which was removed by filtration and dried in vacuo over phosphorous pentoxide. The white solid was not the desired N,N-dinitro-2-nitrazapropylamine, but was identified as 2,4,6-trinitrazaheptane (1.3g, m.p. 159-160°C) by proton nuclear magnetic resonance and elemental analysis.

Analysis: Calcd. for $C_4H_{10}N_6O_6$: C, 20.1; H, 4.20; N, 35.3; O, 40.3. Found: C, 20.3; H, 4.45; N, 35.1; O, 40.2.

C. KINETICS OF DINITROAMINE DECOMPOSITION

1. Preparation of dl-Ketopinic Acid

dl-Ketopinic acid was prepared by adding, in three portions with stirring, 57g (0.31 mole) of dl-camphor-10-sulfochloride[9] to 500g of a 10% aqueous solution of sodium bicarbonate, heated on a steam bath between 85-90°C, with three corresponding portions of a hot solution of 500 gms of potassium permanganate in 300 cc of water. The reaction solution was heated for one hour,

acidified, and the excess permanganate and manganese dioxide destroyed by the addition of sodium bisulfite. The clear solution was cooled, extracted with ether and the ether extracts washed with aqueous 2N sodium hydroxide. The base washes were acidified and extracted with ether. After removal of the ether, the cream colored crystals were recrystallized from petroleum ether to yield 17.8g (38%) of white crystals of dl-ketopinic acid, m.p. 233-234°C. The infrared spectrum was identical to that listed in Sadtler Catalogue of Infrared Spectra (#2361) for dl-ketopinic acid.

2.   Preparation of 1-Apocamphane Carboxylic Acid[10]

dl-Ketopinic acid (13.1g, 7.0 mmoles) was refluxed with 100 ml of triethylene glycol, 15g of 85% aqueous hydrazine hydrate and 14g of potassium hydroxide in a three-necked flask equipped with a reflux condenser, magnetic stirrer, thermometer and heating mantle. After the solids in the flask were dissolved, the flask was arranged for distillation and the water and excess hydrazine were removed until the temperature of the reaction solution reached 202°C, whereupon the mixture was refluxed for 3.5 hours. The mixture was cooled and acidified with sulfuric acid. The gray precipitate of 1-apocamphane carboxylic acid was filtered and the aqueous filtrate extracted with carbon tetrachloride. The carbon tetrachloride solution was dried over anhydrous magnesium sulfate and the solvent removed by rotary evaporation. The remaining solid along with the filtered solid was recrystallized from petroleum ether to yield 8.4 gms (64%) of 1-apocamphane carboxylic acid, m.p. 217-218°C. The infrared spectrum was identical to that listed in Sadtler Catalogue of Infrared Spectra (#2360) for 1-apocamphane carboxylic acid.

3.   Preparation of 1-Apocamphylamine[10]

To 8.4g (0.05 mole) of 1-apocamphane carboxylic acid in 60 ml of benzene and 35 ml of concentrated sulfuric acid was added, in small portions, 4.6g (0.071 mole) of sodium azide while maintaining the temperature between 35-40°C. After addition was complete the reaction solution was heated at 50°C for one hour then poured onto ice; the benzene layer was removed and the aqueous phase washed with benzene. The aqueous phase was made basic and extracted with ether. The ether was dried with anhydrous sodium sulfate and removed by rotary evaporation to yield 6.9g of crude 1-apocamphylamine. The infrared spectrum was consistent for an alkylamine.

4.   Preparation of Ethyl-1-Apocamphylcarbamate

To a vigorously stirred solution of 6.9g of crude 1-apocamphylamine in 20 ml of water and 20 ml of ether, was added, from separate dropping funnels, 12g of a 20% aqueous solution of sodium hydroxide and 6.2g (0.057 mole) of ethyl chloroformate. The two reactants were added equally at such a rate as to maintain the temperature between 0-10°C. The ether phase was separated and the aqueous phase washed with ether. The combined ether solutions were dried over anhydrous magnesium sulfate and the solvent was removed by rotary evaporation to yield, after recrystallization from petroleum ether, 7.2 gms (69% from 1-apocamphane carboxylic acid) of ethyl-1-apocamphylcarbamate, m.p. 69-70°C.

5.   Preparation of Ethyl-N-Nitro-1-Apocamphylcarbamate

To a stirred solution of 7.2g (0.0475 mole) of ethyl-1-apocamphylcarbamate and 30 gms of acetic anhydride was added 3.3g (0.071 mole) of 98% nitric acid while the temperature was maintained between 15-25°C. The reaction mixture was allowed to stir at this temperature for one hour and was

then cooled to 0-10° and stirred for an additional one and one-half hours. The reaction mixture was poured onto ice and stirred overnight to hydrolyze the remaining acetic anhydride. The oil was separated from the reaction mixture and the aqueous phase was then neutralized with solid sodium carbonate and extracted with methylene chloride. The combined oil and methylene chloride extracts were washed with saturated aqueous sodium bicarbonate solution and then dried over anhydrous magnesium sulfate. The methylene chloride was removed by rotary evaporation to yield 6.7g (76%) of crude ethyl-N-nitro-1-apocamphylcarbamate. The infrared spectrum indicated the presence of the N-nitro group with an absorption at 1600 cm^{-1} and the shift of the urethane doublet from 1725 cm^{-1} to 1760 cm^{-1}.

6. Preparation of the Morpholine Salt of N-Nitro-1-Apocamphylamine

Ethyl-N-nitro-1-apocamphylcarbamate could not be cleaved with either ammonia or morpholine in ether at room temperature whereas alcoholic potassium hydroxide resulted in decomposition of the product. The morpholine salt was obtained by reacting morpholine (2.5 equivalents) and the carbamate (1 equivalents) without a solvent and with gentle heating on a steam bath. The white crystals were filtered and washed with cold ether. M.p. 144-146°C subl. Analysis: Calcd. for $C_{13}H_{25}O_3N_3$: C, 57.5; H, 9.29; O, 17.7; N, 15.5. Found: C, 56.9; H, 8.74; O, 17.3; N, 15.3.

7. Preparation of N,N-Dinitro-1-Apocamphylamine

To 1.2g (0.0044 mole) of the morpholine salt of N-nitro-1-apocamphylamine in 25 ml of acetonitrile was added 1.3g (0.0097 mole) of nitronium tetrafluoroborate while the temperature was maintained at -30°C. The mixture was

stirred at this temperature for six hours and then allowed to warm slowly to 0°C whereupon it was quenched into 100 gms of ice water. The aqueous solution was extracted with methylene chloride and the methylene chloride extracts were washed with aqueous sodium bicarbonate, then dried over anhydrous magnesium sulfate. After removal of the solvent, the remaining oil (0.8 gms) was chromatographed over silica gel to yield 0.02g of N,N-dinitro-1-apocamphylamine as identified by infrared spectroscopy (shown in Figure 2).

8. Preparation of the Ammonium Salt of Ethyl-N-Nitro-d-
    2-Aminopropionate

Ethyl-N-nitro-d-2-aminopropionate (prepared from d-2-amino-propionic acid, Aldrich Chemical Company, by previously described methods)[1] dissolved in dry ether was treated with anhydrous ammonia. The white crystals were filtered and washed with dry ether. As the salt was hygroscopic it was not employed for subsequent reactions.

9. Preparation of the Morpholine Salt of Ethyl-N-Nitro-d-
    2-Aminopropionate

To 6.72g (0.0325 mole) of ethyl-N-nitro-d-2-aminopropionate in 10 ml of dry ether was added at room temperature 5.3g of morpholine (0.061 mole). The white crystalline plates were filtered and washed with dry ether to yield 6.95g (93%) of the morpholine salt.

10. Preparation of Ethyl N,N-Dinitro-d-2-Aminopropionate

To 6.95g (0.028 mole) of the morpholine salt of ethyl-N-nitro-d-2-aminopropionate in 50 cc of acetonitrile was added 8.25g (0.062 mole) of nitronium tetrafluoroborate while the temperature was maintained between -20 and -15°C. The mixture was allowed to stir for three hours at this temperature and then worked up in the usual manner.

The product was a yellow liquid (3.5g, 60%). The oil was
chromatographed over silica gel to obtain a pure sample which was characterized
by infrared and proton nuclear magnetic resonance spectroscopy and elemental analysis.
The Differential Thermal Analysis showed an exotherm beginning at 65°C with a maximum
at 118°C.

Analysis: Calcd. for $C_5H_9O_6N_3$: C, 29.0; H, 4.38; O, 46.3; N, 20.3. Found: C,
29.1; N, 4.90; O, 45.6; N, 20.4.

11. Rate of Thermal Decomposition of N,N-Dinitroisopropylamine and Ethyl N,N-Dinitro-d-2-Aminopropionate

A sample of the dinitroamine (0.2g) was sealed in a long neck,
5-ml volumetric flask (total volume of 10 ml) with a rubber serum cap and
pressurized to 2 lbs with argon. The tube was immersed in a constant temperature
bath and one milliliter gas samples were withdrawn and analyzed at various time
intervals on an F&M 500 gas chromatograph. The isothermal analysis was performed
on a 6' x ¼" stainless steel column packed with molecular sieve 13X (60-80 mesh)
at a temperature of 35°C, helium flow of 60 ml/min and a block temperature of 300°C.

12. Mass Spectral Analysis of the Gases From the Thermal Decomposition of N,N-Dinitroisopropylamine and Ethyl N,N-Dinitro-d-2-Aminopropionate

A small sample of the dinitroamine was sealed in an evacuated
(ca. 10 microns) ampule. The ampule was immersed in a 60°C constant temperature
bath for 48 hours, after which time the gases boiling below dry ice-acetone
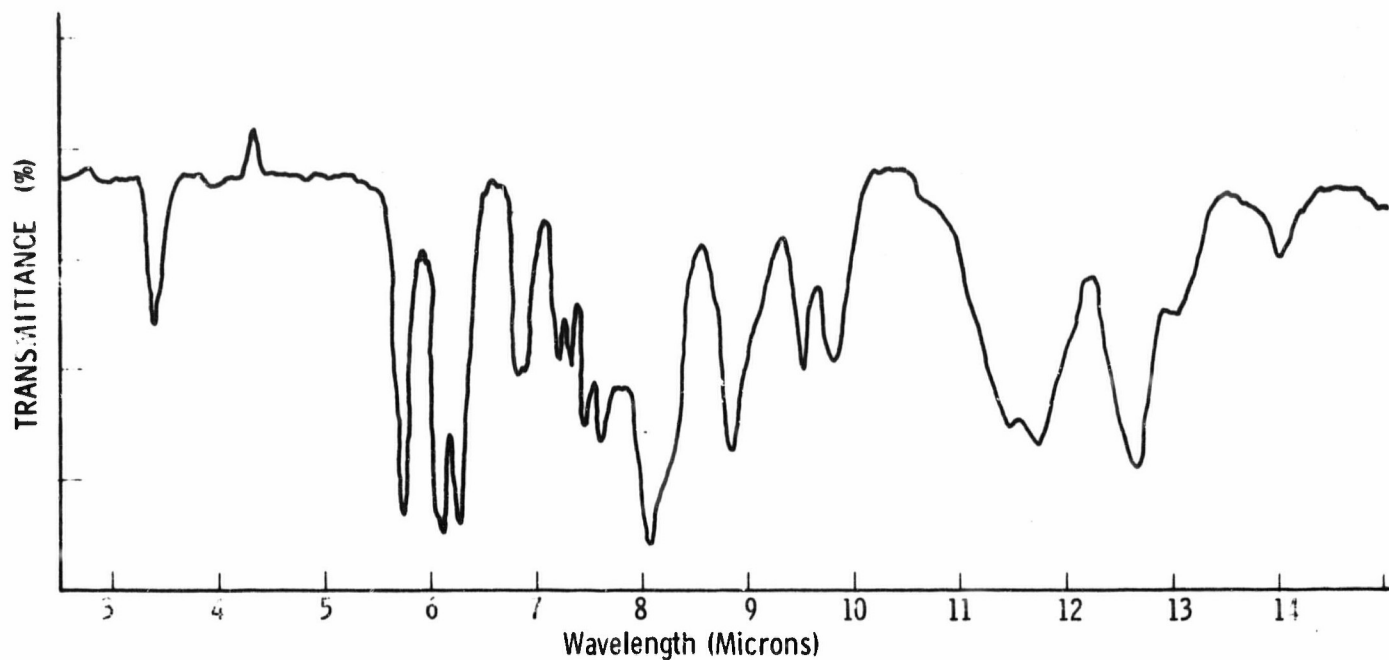temperature at 10 microns were analyzed on a Consolidated Mass Spectrophotometer.

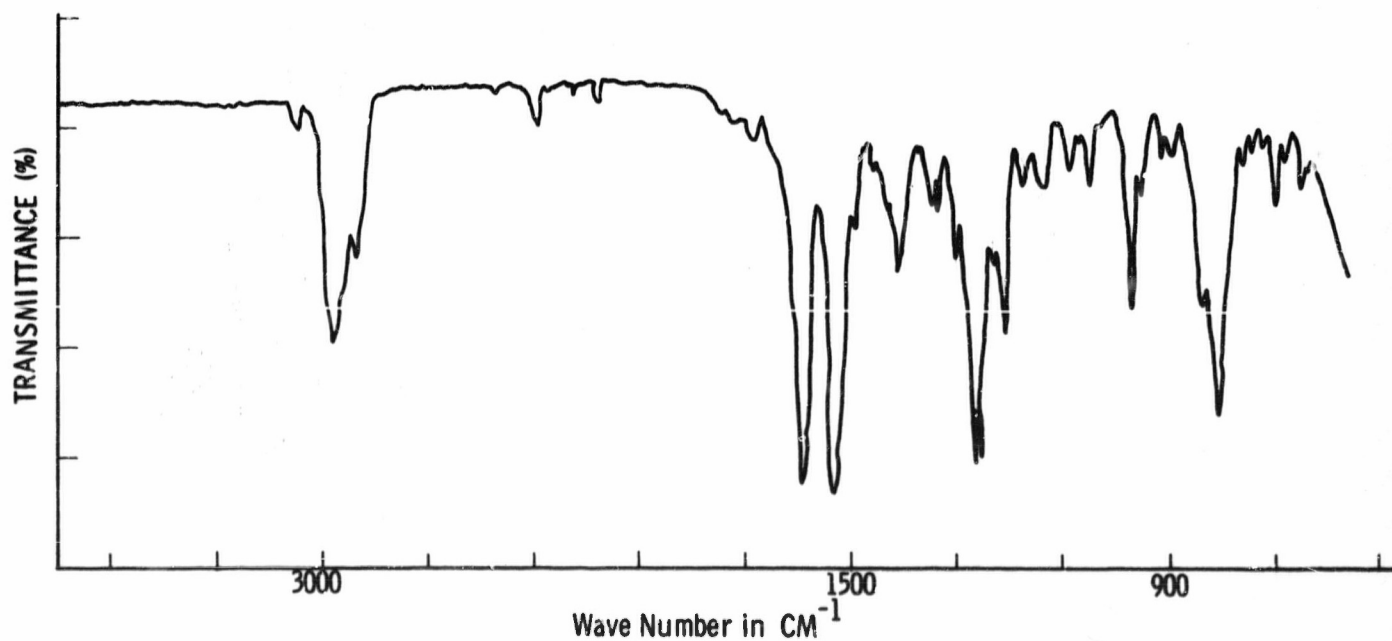FIGURE 2. INFRARED SPECTRUM OF N, N-DINITRO-d-2-AMINOPROPIONATE

FIGURE 3. INFRARED SPECTRUM OF N, N-DINITRO-I-APOCAMPHYLAMINE