UNCLASSIFIED

3

B.S

CRDV RAPPORT 4070/77
DOSSIER: 3621A-001
FÉVRIER 1977

DREV REPORT 4070/77
FILE: 3621A-001
FEBRUARY 1977

NITROSATION REACTIONS OF ETHYL CENTRALITE

K. Taymaz

B.T. Newbold

R. MacDonald

DDC
RECEIVED
APR 1 1977
A

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

Centre de Recherches pour la Défense
Defence Research Establishment
Valcartier, Québec

BUREAU - RECHERCHE ET DEVELOPPEMENT
MINISTERE DE LA DÉFENSE NATIONALE
CANADA

RESEARCH AND DEVELOPMENT BRANCH
DEPARTMENT OF NATIONAL DEFENCE
CANADA

NON CLASSIFIÉ

CRDV R-4070/77
DOSSIER: 3621A-001

UNCLASSIFIED

(14) DREV-R-4070/77
FILE: 3621A-001

(6)

NITROSATION REACTIONS OF ETHYL CENTRALITE

BY

(10) K. Taymaz*, B.T. Newbold [redacted] R. MacDonald

(11) Feb 77 (12) 29p.

*Université de Moncton, Moncton, N.-B.

CENTRE DE RECHERCHES POUR LA DEFENSE

DEFENCE RESEARCH ESTABLISHMENT

VALCARTIER

Tel: (418) 844-4271

Québec, Canada

February/février 1977

NON CLASSIFIE

404945

RESUME

Des expériences préliminaires décrivent l'action de l'acide nitreux de différentes concentrations sur la centralite d'éthyle, un stabilisateur d'usage courant dans les formulations de poudres à double base. Ces réactions chimiques provoquent la formation de plusieurs dérivés qui sont séparés, identifiés et analysés par chromatographie en couche mince et par spectroscopie d'absorption électronique. Les connaissances analytiques acquises seront utilisées avantageusement dans des études de stabilité sur le vieillissement accéléré des poudres. (NC)

ABSTRACT

Preliminary experiments are described in which ethyl centralite, a stabilizer frequently used in double-base propellants, was reacted with nitrous acid in various concentrations. The chemical reactions taking place led to the formation of numerous derivatives which were separated, identified and analysed by thin-layer chromatography and electronic absorption spectroscopy. The analytical knowledge gained will be used to advantage in stability investigations of artificially aged gun propellants. (U)

-A-

TABLE OF CONTENTS

ABBREVIATIONS

EC	Ethyl Centralite
4-NEC	4-Nitroethylcentralite
2-NEC	2-Nitroethylcentralite
2,2'-DNEC	2,2'-Dinitroethylcentralite
2,4'-DNEC	2,4'-Dinitroethylcentralite
2,4-DNEC	2,4-Dinitroethylcentralite
4,4'-DNEC	4,4'-Dinitroethylcentralite
2,4,4'-TNEC	2,4,4'-Trinitroethylcentralite
2,2',4,4'-TNEC	2,2',4,4'-Tetranitroethylcentralite
NEA	N-ethylaniline
2-NNEA	2-Nitro-N-ethylaniline
3-NNEA	3-Nitro-N-ethylaniline
4-NNEA	4-Nitro-N-ethylaniline
2,4-DNCC	2,4-Dinitrocarbanilyl Chloride
1,3-DNB	1,3-Dinitrobenzene
4-NNEAC	4-Nitro-N-ethylacetanilide
2,4-DNCB	2,4-Dinitrochlorobenzene
EA	Ethylamine
2,4,6-TNP	2,4,6-Trinitrophenol
1-P-3-EU	1-Phenyl-3-ethylurea
2,4-DNNEA	2,4-Dinitro-N-ethylaniline
2,4,6-TNNEA	2,4,6-Trinitro-N-ethylaniline
N,2,4,6-TNNEA	N,2,4,6-Tetranitro-N-ethylaniline
4-NNECB	4-Nitro-N'-ethylcarbanilide
2,4,6-TNNNNEA	2,4,6-Trinitro-N-nitroso-N-ethylaniline
NB	Nitrobenzene
NNNEA	N-Nitroso-N-ethylaniline
3-NNNNEA	3-Nitro-N-Nitroso-N-ethylaniline
4-NNNNEA	4-Nitro-N-Nitroso-N-ethylaniline
2-NA	2-Nitroaniline
3-NA	3-Nitroaniline
4-NA	4-Nitroaniline
2,4,-DNA	2,4,-Dinitroaniline
2,4,6-TNA	2,4,6-Trinitroaniline
3-NP	3-Nitrophenol
4-NP	4-Nitrophenol
4,4'-DNC	4,4'-Dinitrocarbanilide
1,3,5-TNB	1,3,5-Trinitrobenzene
Rg	$\frac{\text{Distance of sample spot from start point}}{\text{Distance of reference material spot (EC) from start point}}$
ϵ	Molar extinction coefficient
λ	Wavelength in nanometer (nm)
m-p	Melting point
b-p	Boiling point

1.0 INTRODUCTION

Ethyl centralite (EC) is a stabilizer often used in double-base propellants. It reacts irreversibly with nitrogen oxides produced during the slow decomposition of nitrocellulose and nitroglycerine, which are the two major components of propellants. The acidic products which could cause auto-catalytic decomposition are thus neutralized and the useful life of the propellant is greatly increased.

The reactions undergone by EC during the stabilization processes involve nitration, nitrosation and hydrolysis (1-2); the net result being a steady decrease in EC content and an accumulation of derivatives. The rate at which these reactions proceed is mainly dependent on the conditions to which the propellant is exposed during its service.

Since gun propellants have a finite life after which they are unfit for service applications or unsafe to store, it is important that accurate chemical methods be available to monitor the safe life of depot holdings. Regular inspections of this type reduce the hazards to personnel and property, as well as the expense of prematurely replacing propellant stocks.

A generally accepted method for verifying the chemical stability of a propellant is the determination of the residual amount of stabilizer at any particular time (3). This method becomes more and more empirical as the propellant ages because of the difficulty of separating the derivatives from the unreacted stabilizer before analysis. However, in general, the results obtained correlate well with the age and stability of the propellant.

A more elegant and informative method would be to separate EC and its derivatives from a propellant extract by thin-layer chromatography (4). Thus, the remaining stabilizer could be analysed in a pure form and the nitro and nitroso derivatives, many of which are highly coloured, could be examined visually. Such examination would give additional information on propellant stability since these derivatives are formed sequentially during ageing. The appearance of polynitro decomposition products would indicate instability. Periodic examination of propellants in storage using this technique would provide a stability history for each propellant. The chromatographic plates could be photographed so that a continuous visual record would be available.

In order to test the feasibility of applying these stability tests to propellants, a study, supported by Defence Research Board funding (Grant No. 9530-60), was started about six years ago at the Université de Moncton, Moncton, New Brunswick. This work was latterly done under contract with the Université de Moncton, under PCN 21A01 (formerly PCN 05101, Project No. 10-28-48), Explosives Technology.

The first part of the study dealt with the reactions of EC with nitric acid under various conditions, and showed that the transformations involved gave rise to numerous derivatives, which could be separated, identified and analysed by thin-layer chromatography (5). The second part of this investigation, described in this report, concerns a) the reactions of EC with nitrous acid in different concentrations and also with NO_2 gas; b) the separation, identification and analysis of the resulting products; c) the synthesis of some nitro- and nitroso-EC derivatives. Routes to account for the formation of the isolated products are postulated.

2.0 EXPERIMENTAL

2.1 Materials and Apparatus

2.1.1 Chemicals

The following compounds were purchased from Eastman Organic Chemicals, Rochester, New York: ethyl centralite (EC), 1,3-dinitrobenzene (1,3-DNB), N-ethylaniline (NEA), 2-nitroaniline (2-NA), 3-nitroaniline (3-NA), 4-nitroaniline (4-NA), 2,4-dinitroaniline (2,4-DNA), 4-nitrophenol (4-NP), 4-nitro-N-ethylacetanilide (4-NNEAC), 2,4-dinitrochlorobenzene (2,4-DNCB), and ethylamine (EA). The 2,4,6-trinitrophenol (2,4,6-TNP) was bought from Allied Chemicals, Morristown, New York.

The 3-Nitro-N-ethylaniline (3-NNEA), 2,4,6-trinitro-N-ethylaniline (2,4,6-TNNEA), 4,4'-dinitrocarbanilide (4,4'-DNC), 3-nitro-N-nitroso-N-ethylaniline (3-NNNNEA), and 1-phenyl-3-ethylurea (1-P-3-EU) were supplied by Defence Research Establishment Valcartier. The 2-Nitro-N-ethylaniline (2-NNEA), N-nitroso-N-ethylaniline (NNNEA), 2-nitro-N-nitroso-N-ethylaniline (2-NNNNEA), 4-nitro-N-nitroso-N-ethylaniline (4-NNNNEA), 4-nitroethylcentralite (4-NEC), 4,4'dinitroethylcentralite (4,4'-DNEC), and 2,2'4,4'-tetranitroethylcentralite (2,2'4'4,-TNEC) were synthesized earlier (5).

Derivatives synthesized at the Université de Moncton were 2,4-dinitroethylcentralite (2,4-DNEC), 4-nitro-N-ethylcarbanilide (4-NNECB), 4-nitro-N-ethylaniline (4-NNEA), 2,4-dinitro-N-ethylaniline (2,4-DNNEA), 2,4,6-trinitro-N-nitroso-ethylaniline (2,4,6-TNNNNEA), and N, 2,4,6-tetranitro-N-ethylaniline (N,2,4,6-TNNEA). The methods of preparation for these compounds are described in Section 2.2.1. Elemental analyses were done by Micro-Tech Laboratories Inc., Skokie, Illinois, U.S.A.

2.1.2 Absorbents

To obtain sufficiently pure samples for the determination of melting points when column chromatography was used, the absorbent was a mixture of silicic acid-celite 535.

In the thin-layer chromatographic separations Silicia Gel G (Brinkman Instruments) was employed.

2.1.3 Equipment

The thin-layer chromatographic equipment consisted of a Desaga Spreader Model S-II, glass plates (200 x 200 mm), rack, template and glass tanks, furnished by Brinkman Instruments. The ultraviolet sources were Black-Ray B-100A (366 nm) and R-51 mineralight (254 nm) lamps purchased from Ultra-violet Products Inc., San Gabriel, California.

Visible and ultraviolet absorption spectra were determined on a Beckmann DB spectrophotometer using 95% ethanol as a solvent. Infrared spectra were recorded on a 237B Perkin-Elmer Grating spectrophotometer using the KBr pellet technique.

2.1.4 Colour Test Reagents

The following reagents were prepared (1) and used to test products separated by means of chromatography: Ceric sulphate (1% solution of ceric ammonium sulphate in 85% H_2SO_4); diphenylamine (1% solution of recrystallized diphenylamine in concentrated H_2SO_4); 1-naphthylamine (1% solution of recrystallized 1-naphthylamine in concentrated HCl); and NaOH (6N aqueous solution). Aqueous NaOH produced red to purple colours with nitro compounds. λ-Naphthylamine reagent gave a pink colour upon reaction with nitroso compounds. Ceric sulphate reagent, which afforded various colours, was useful for detecting ethylcentralites.

2.2 Procedures

2.2.1 Synthesis and Characterization of Ethyl Centralite (EC) Derivatives and Possible Degradation Products

Initially, it was thought that 2,4-dinitroethylcentralite (2,4-DNEC) might be prepared by condensing N-ethylaniline (NEA) with N-ethyl-2,4-dinitrocarbanilyl chloride (2,4-DNCC). However, attempts to synthesize 2,4-DNEC from 2,4-dinitro-N-ethylaniline (2,4-DNNEA) and phosgene, using a procedure analogous to that of Wilcox and Schroeder (6), failed. Furthermore, several attempts to obtain 2,4-DNEC by refluxing N-ethylcarbanilyl chloride (prepared from NEA and phosgene with 2,4-DNNEA were not successful (6).

2,4-DNEC was finally obtained by nitrosation of EC with 20 molar equivalents of HNO_2, using the procedure described in Sec. 2.2.2. The reaction products were separated on a silicic acid-celite column using the technique of Schroeder et al (1) and benzene as solvent. The column was developed successively with benzene-petroleum ether (2:1) and ether-petroleum ether (1:2) to give a yellow band, followed by yellow and yellowish-brown bands.

Each band was run off and 25 to 50-μl samples of the eluents were analysed by two-dimensional thin-layer chromatography. The second yellow band contained 2,4-DNEC and small amounts of other reaction products. The eluent from this band was evaporated to give a brown residue, which was purified by thin-layer chromatography (600 plates). The 2,4-DNEC spots were collected, combined, extracted with ethyl alcohol, and the solvent was removed by distillation to give a minute quantity of very viscous yellowish-brown oil; b.p. 163°C/67 mm, which could not be crystallized; Rg 2.23; 0.10 (Lit. Rg 2.25; 0.10 (4). Hydrolysis of this oil with 65% H_2SO_4 gave the expected NEA and 2,4-DNNEA. The 2,4-DNEC produced a red colour with ceric sulphate reagent (indicating the presence of $C_6H_5\text{-}\overset{|}{N}\text{-}\underset{\underset{O}{\|}}{C}\text{-}$) and gave a λmax of 358 to 360 nm (ε,10,300).

4-Nitro-N'-ethylcarbanilide (4-NNECB) was obtained by refluxing 4-nitro-phenyl isocyanate (prepared by reacting 4-nitroaniline [4-NA] with phosgene [7]) with NEA. The resulting pale yellow crystals, m.p. 78.5-79°C (Lit., m.p. 79.5 - 80.5°C [6]), gave rise to 4-NA and NEA upon hydrolysis with 65% H_2SO_4 and subsequent thin-layer chromatography.

4-Nitro-N-ethylaniline (4-NNEA) was prepared by hydrolysis of 4-nitro-N-ethyl acetanilide (4-NNEAC). Two hundred millilitres of 70% H_2SO_4 were added to 20.8 g of 4-NNEAC, and the mixture was refluxed for 30 min to give a dark brown solution, which was then neutralized with 6N NaOH (while being cooled in an ice bath) to give a dark green precipitate. This product was filtered off, taken up in ethyl alcohol, and the extract was treated with animal charcoal and filtered to give a yellow solution. Evaporation to half volume and dilution with an equal volume of water precipitated 4-NNEA, 96%, as yellow needles, m.p. 94-95°C (Lit., m.p. 95°C [8]) and λmax, 385 nm (ε,19,200[9]).

The synthesis of 2,4-dinitro-N-ethylaniline (2,4-DNNEA) was achieved by dissolving 2,4-dinitrochlorobenzene (20.2 g) in ethyl alcohol (100 ml) and adding 10 ml of a 70% aqueous solution of ethylamine (EA). The mixture was allowed to stand overnight, then poured into an excess of water to precipitate yellow crystals. Recrystallization from ethyl alcohol gave pure 2,4-DNNEA, 95%, m.p. 113-114°C, alone or with an authentic sample, λmax, 347 nm (ε,16,700[9]).

2,4,6-Trinitro-N-Nitroso-N-ethylaniline (2,4,6-TNNNNEA) was obtained by reacting 0.5 g of 2,4,6-trinitro-N-ethylaniline (2,4,6-TNNEA) with 70% HNO_3 (10 ml) and $NaNO_2$ (0.3 g), the mixture being left to stand for 1 h and then poured into cold water (50 ml). The yellow crystals which formed were filtered off, dried over P_2O_5 in a vacuum desiccator, and recrystallized from ethyl alcohol to give 2,4,6-TNNNNEA as yellow plates, 72%, m.p. 78-79°C; λmax, 210 nm (ε,21,600). Anal. Calc. for $C_8H_7N_5O_7$: C, 33.70%; H, 2.46%; N, 24.57%; Found: C, 33.49%; H, 2.46%; N, 24.31%.

N, 2,4,6-Tetranitro-N-ethylaniline (N,2,4,6-TNNEA) was obtained by nitration of 2,4-dinitro-N-ethylaniline (2,4-DNNEA). Thus 20 ml of 70% HNO_3 were added to 1.0 g of 2,4-DNNEA, and the mixture was allowed to stand at room temperature for 10 days, then poured into cold water (100 ml) to give a reddish-brown precipitate. This crude product was taken up in ethyl alcohol and the extract was treated with animal charcoal. Filtration gave a yellow filtrate which was evaporated to half volume and diluted with an equal volume of water. The yellow precipitate was filtered off and dried over P_2O_5 under reduced pressure to give N, 2,4,6-TNNEA, 69%, m.p. 91-92°C; λmax, 214 nm (ε,36,300). Anal. Calc. for $C_8H_7N_5O_8$: C, 31.90%; H, 2.33%; N, 23.26%; Found: C, 32.09%; H, 2.38%; N, 23.25%.

2.2.2 Detailed Nitrosation Studies of Ethyl Centralite

Nitrosation was carried out using two molar equivalents of HNO_2 and the following procedure: EC (1.0 g) was dissolved in glacial acetic acid (25 ml) and the solution cooled to 5°C in a flask equipped with a mechanical stirrer, thermometer, and dropping funnel. Concentrated hydrochloric acid (25 ml) was slowly added while stirring, followed by a solution of a $NaNO_2$ (6 ml, 10%) added dropwise to the stirred mixture; the temperature was kept below 8°C during the reaction. After the addition of $NaNO_2$ was complete (20 min), the reaction was allowed to continue for 1 h. Then the mixture was poured onto crushed ice, neutralized with 6N NaOH, and extracted with ethyl ether (150 ml). The extract was dried over $MgSO_4$, and the solvent was removed by distillation in vacuo to yield a brown residue (1.1 g), which was dissolved in acetone. The extract was examined by thin-layer chromatography and found to contain a mixture of EC, 90.1%; 4-nitroethylcentralite (4-NEC), 0.5%; and 2,4-DNEC, 0.7%.

Other nitrosations of EC were similarly carried out using 4,8,20,30 and 50 molar equivalents of HNO_2, respectively.

Ethylcentralite was also reacted with nitrogen dioxide in the following manner: EC (1.0 g) was placed in a flask and dry NO_2 gas was passed through the vessel, whereupon the EC immediately took on a brownish colour. This treatment was continued for 1 h and the resulting reddish-brown product (1.0 g) was dissolved in acetone (25 ml). The extract was analyzed by thin-layer chromatography and shown to contain 4-NEC, 31.2%; 2-nitroethylcentralite (2-NEC), 10.2%; 2,4'-dinitroethylcentralite (2,4'-DNEC), 14.1%; 4,4'-dinitroethylcentralite (4,4' DNEC), 26.8%; 2,4,4'-trinitroethylcentralite (2,4,4'-TNEC), 0.6%; 2,2',4,4'-tetranitroethylcentralite (2,2'4,4'-TNEC), 0.7%; 4-NNEA, 0.4%; 2,4-DNNEA, 3.1%; N-nitroso-N-ethylaniline (NNNEA), 0.1%; 4-nitro-N-nitroso-N-ethylaniline (4-NNNNEA), 1.3%; 2-nitro-N-nitroso-N-ethylaniline (2-NNNNEA), 0.1%; 4-NA, 2.2%; and 2,4-dinitroaniline (2,4-DNA), 0.4%.

2.2.3 Thin-Layer Chromatography Techniques and Quantitative Analysis

Silica Gel G absorbent was agitated in water until a homogeneous slurry was obtained, which was then applied to glass plates so that an absorbent layer 0.3 mm thick resulted. The plates were dried in air, activated at 120°C in an oven and stored in a dry container until used.

The residues from the nitrosations of EC were dissolved in acetone, a microliter sample was quantitatively applied to the chromatographic plates, and the solvent was allowed to evaporate. The plates were placed in the developing tanks and treated by ascending development using ethylene dichloride as a developer. In order to obtain sharper separations the plates were taken out of the tanks, dried in air, and rechromatographed in a 90° direction to the first development using a 75:25 petroleum ether-ethyl acetate solvent. After drying, the various reaction products were located by viewing the plates under short- and long-wavelength ultraviolet light. Based on the positions of the spots, tentative identifications were made by comparison of Rg values with those obtained from authentic samples (Tables I and II). The spots were removed using a zone collector and the absorbent was extracted with 95% ethyl alcohol. The extract was examined by ultraviolet spectroscopy to positively identify and analyse the components where authentic reference data were available (Tables III and IV). In some cases where complete reference data were lacking (2,2'-DNEC, 2,4'-DNEC) the results must be considered to be less reliable. Spot sizes were used in some cases (2,2'-DNEC, 2,4'-DNEC, 2-NEC, 2,4,4'-TNEC, 2-NNNNEA) to obtain semiquantitative data employing the Desaga template.

The mixture resulting from the reaction of EC with NO_2 gas was similarly analysed.

TABLE I

Recovery of Products from Nitrosations of Ethyl Centralite

Nitrosating Agent[a]	RECOVERY (%)[b]																			
HNO_2	EC	4-NEC	2-NEC	2,4-DNEC	2,4'-DNEC	4,4'-DNEC	2,2'-DNEC	2,4,4'-TNEC	2,2'4,4'-TNEC	NNNEA	4-NNEA	2-NNEA	2-NNNNEA	2,4-DNNEA	N,2,4,6-TNNEA	2,4-DNA	4-NNNNEA	2,4,6-TNNNNEA	1,3,5-TNB
2	90.1	0.5	-	0.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	84.0	4.4	-	3.9	-	-	0.1	-	-	-	-	-	-	-	-	-	-	-	-
8	68.1	10.3	1.1	8.3	-	0.1	3.9	0.1	-	-	-	-	-	-	-	-	0.3	-	-
20	24.7	18.2	2.9	9.8	-	0.1	6.6	2.6	2.2	3.8	4.2	-	-	-	-	-	2.0	T[c]	6.2
30	15.2	21.7	3.3	7.2	0.1	0.3	7.1	3.7	4.6	2.2	3.2	-	2.1	-	0.2	-	5.3	1.2	8.7
50	-	29.6	-	4.8	1.7	6.3	2.9	5.4	7.3	-	2.4	1.0	3.6	2.8	2.4	1.1[d]	6.2	0.8	9.1

a) Molar equivalents with respect to EC.

b) Tars were always present.

c) Traces.

d) Traces of 2-NA and 4-NA were also detected.

TABLE II

Rg Values for Ethyl Centralite and its Nitro Derivatives

Compound	Values (observed)		Values (literature)[a]	
	S_1	S_2	S_1	S_2
EC[b]	1.00	1.00	1.00	1.00
4-NEC	2.10	0.63	2.40	0.64
2-NEC	1.15	0.74	1.10	0.74
2,4-DNEC	2.23	0.10	2.25	0.10
4,4'-DNEC	2.96	0.22	2.55	0.25
2,4'-DNEC	2.80	0.45	2.54	0.44
2,2'-DNEC	2.10	0.30	2.20	0.30
2,4,4'-TNEC	3.60	0.24	3.50	0.24
2,2',4,4'-TNEC	5.50	0.41	4.50	0.50

(a) Values estimated from Ref. 4.

(b) EC used as a reference.

S_1) Ethylene dichloride.

S_2) Petroleum ether-ethyl acetate (75:25)

TABLE III

Rg Values for Degradation Products of Ethyl Centralite

Compound	Values (observed)		Values (Literature)[a]	
	S_1	S_2	S_1	S_2
NEA	6.15	1.43	5.80	1.40
4-NNEA	8.22	0.80	7.90	0.82
2-NNEA	11.00	1.45	10.50	1.45
2,4-DNNEA	10.40	0.68	9.50	0.68
2,4,6-TNNEA	11.15	1.40	10.25	1.35
N,2,4,6-TNNEA	12.40	0.95	11.00	1.05
NNNEA	8.70	1.51	7.60	1.40
4-NNNNEA	9.60	1.20	8.75	1.10
3-NNNNEA	8.12	0.95	--	--
2-NNNNEA	11.00	1.45	10.25	1.35
2,4,6-TNNNNEA	11.02	1.35	--	--
2-NA	9.40	0.83	8.50	0.85
3-NA	5.60	0.75	--	--
4-NA	6.00	0.46	5.90	0.30
2,4-DNA	5.90	0.40	5.70	0.25
NB	13.00	1.35	11.70	1.38
1,3-DNB	12.10	0.90	11.00	0.90
1,3,5-TNB	8.75	1.20	9.00	1.41
3-NP	6.20	0.65	--	--
4-NP	2.00	0.30	1.90	0.24

a) Estimated from Ref. 4.

S_1)Ethylene dichloride.

S_2)Petroleum ether-ethyl acetate (75:25)

TABLE IV

Spectral Data for Ethyl Centralite and its Nitro Derivatives

Compound	Values (Observed)		Values (Literature)[a]	
	λmax, nm	ε[b]	λmax, nm	ε
EC	247	8,730	247	8,730
2-NEC	246	-	245-247	12,400
4-NEC	334	8,100	334-336	8,240
2,2'-DNEC	302	-	-	-
2,4-DNEC	358-360	10,300	-	-
2,4'-DNEC	324	-	323.5	-
4,4'-DNEC	324	15,200	323-324	15,200
2,4,4'-TNEC	308-310	-	309-310	14,400
2,2',4,4'-TNEC	293	11,800	293	11,800

a) Refs. 1 and 5.

b) ε, Molecular extinction coefficient.

Calibration experiments using authentic samples showed that the spectral analysis was reliable (experimental error 1.0 ± 0.5%) for yields as low as 0.4%. Quantitative determination via spot size was employed where the yields were < 0.5%. Analyses carried out by means of both spot size and spectral measurement were in relatively good agreement (± 0.5%). A correction was necessary for the spectral determination of EC since the Silica Gel G also absorbed at about 250 nm. Thus an ethanol extract of the absorbent from the same developed plate was taken as a blank. The same corrective technique was also used for some of the anilines.

Some of the results obtained on separating derivatives of EC after treatment with nitrosating solutions of increasing concentration are shown in Figs. 1 to 3; and the results achieved upon analysis of the EC-NO_2 reaction mixture are given in Fig. 4.

Quantitative estimations of the products resulting from treatment of EC with HNO_2 are listed in Table V.

Proposed routes by which some of the derivatives might form are shown in Fig. 5.

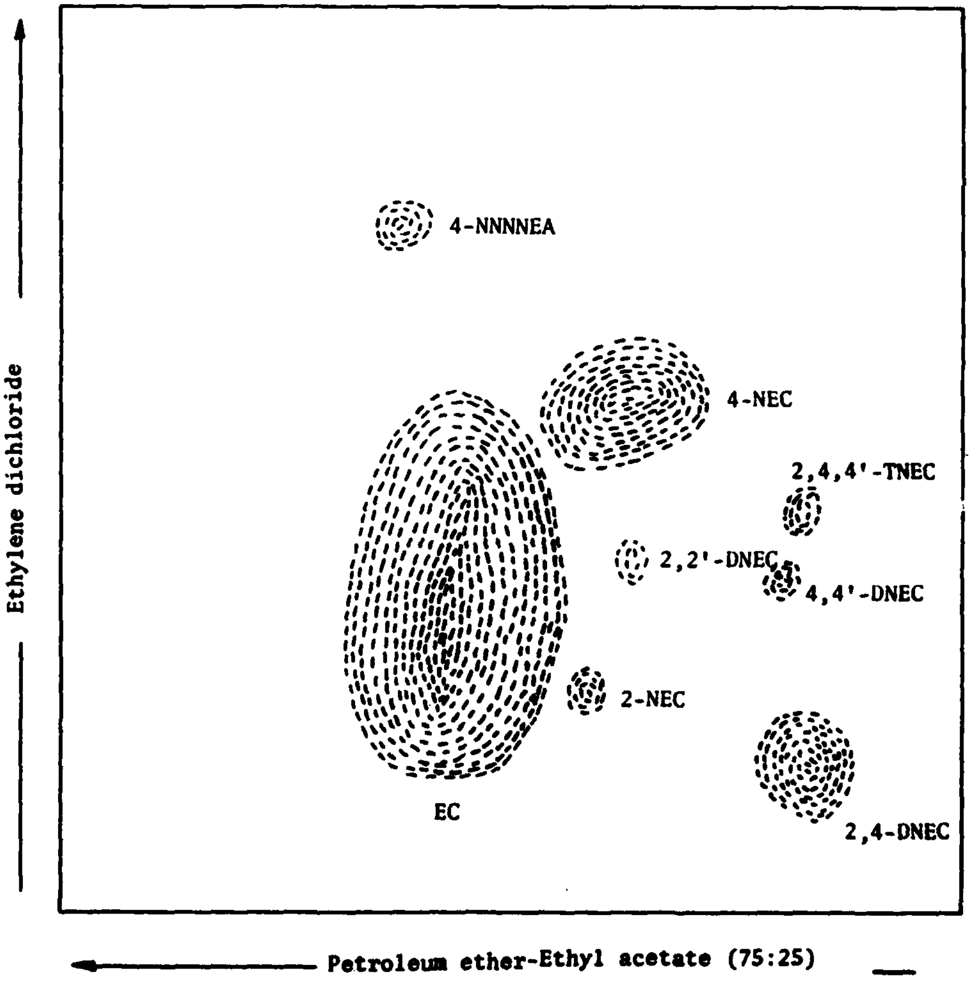

FIGURE 1 - Two-dimensional thin-layer chromatogram of mixture obtained from nitrosation of ethyl centralite using eight molar equivalents of HNO_2

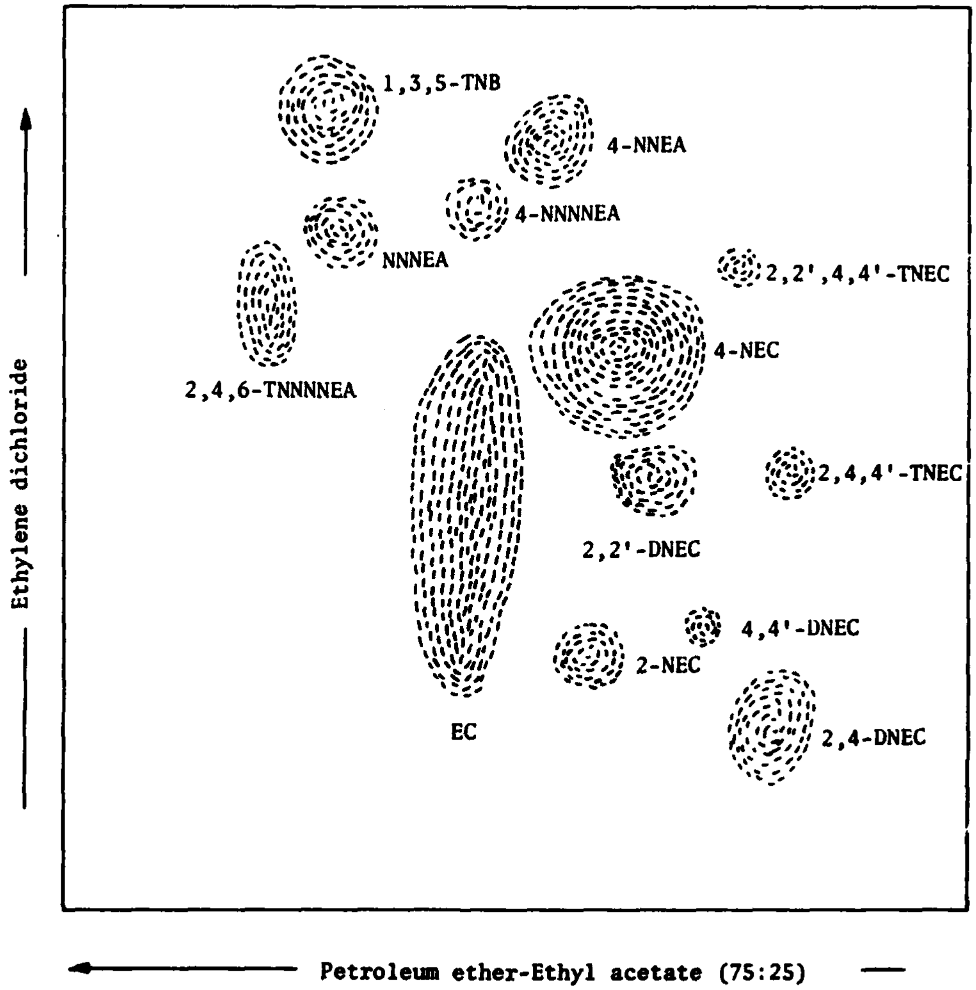

FIGURE 2 - Two-dimensional thin-layer chromatogram of mixture obtained from nitrosation of ethyl centralite using 20 molar equivalents of HNO_2

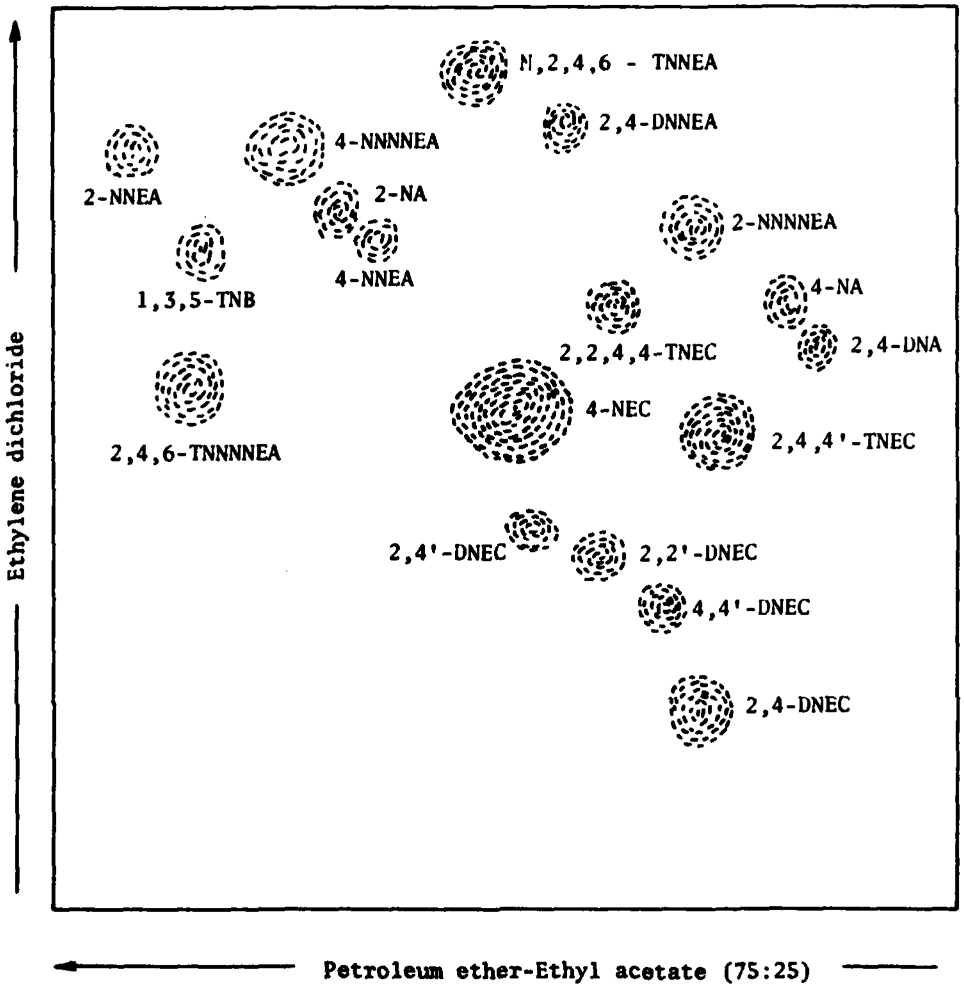

FIGURE 3 - Two-dimensional thin-layer chromatogram of mixture obtained from nitrosation of ethyl centralite using 50 molar equivalents of HNO_2

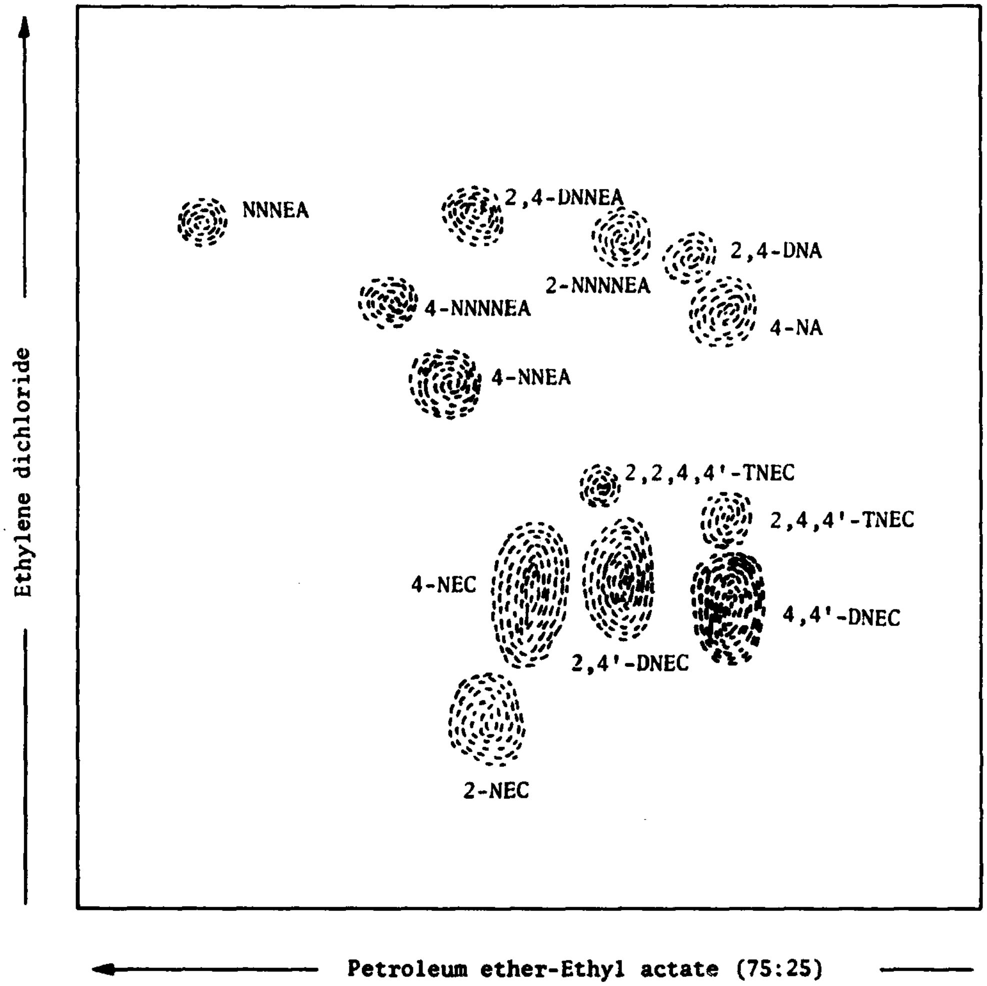

FIGURE 4 - Two-dimensional thin-layer chromatogram of mixture obtained from reaction of NO_2 with ethyl centralite

TABLE V

Spectral Data of Degradation Products of Ethyl Centralite

Compound	Values (Observed) λmax, nm	ε[b]	Values (Literature)[a] λmax, nm	ε
NEA	247	11,100	247	11,100
2-NNEA	423-425	6,000	425	5,200
3-NNEA	246	18,200	244	19,100
4-NNEA	385	19,200	385-386	19,300
2,4-DNNEA	347	16,700	347-348	16,600
2,4,6-TNNEA	336	15,000	336	14,900
N,2,4,6-TNNEA	214	36,300	-	-
NNNEA	272	6,600	271	6,800
2-NNNNEA	242	11,700	240-242	11,500
3-NNNNEA	264	14,100	264	14,100
4-NNNNEA	312-314	16,100	312-314	15,000
2,4,6-TNNNNEA	210	21,600	-	-
2-NA	404	5,400	403-405	5,300
3-NA	374	1,500	375	1,500
4-NA	372	16,300	373-375	16,400
2,4-DNA	336	14,800	336	14,800
NB	251	9,900	251	9,000
1,3-DNB	237	24,800	-	-
1,3,5-TNB	227	36,400	-	-
3-NP	272	5,960	272	6,000
4-NP	311-312	11,800	312	11,900

a) Refs. 10 and 15.

b) ε, Molecular extinction coefficient.

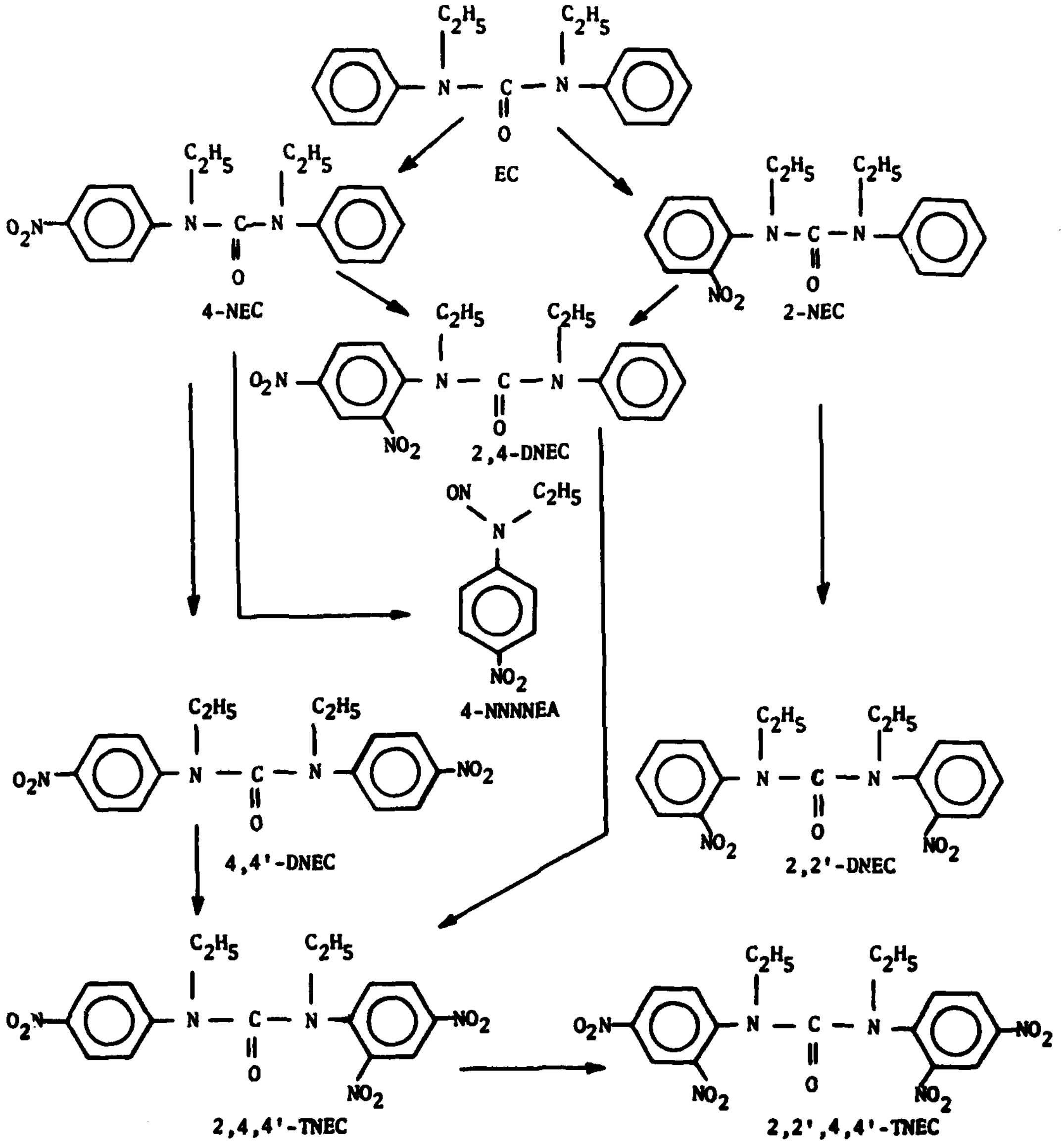

FIGURE 5 - Probable routes for the formation of major derivatives of ethyl centralite

3.0 RESULTS AND DISCUSSION

As far as the authors are aware, nitrosation reactions of EC with nitrous acid have not been previously described. The only literature reference concerning the treatment of a centralite with this agent reported that methyl centralite (1,3-dimethyl-1,3-diphenylurea) did not react when exposed to HNO_2 at room temperature for as long as six months (10).

In the present study, nitrosations of EC were carried out using concentrations of HNO_2 ranging from 2 to 50 molar equivalents, and the results obtained are summarized in Table I. EC was almost unaffected by two molar equivalents of HNO_2, and only very small quantities of 4-NEC and 2,4-DNEC resulted. Reaction with four molar equivalents of HNO_2 gave three products as well as EC, namely: 4-NEC, 2,4-DNEC and some 2,2'-DNEC.

Treatment of EC with eight molar equivalents of HNO_2 gave seven products. The yields of 4-NEC and 2,4-DNEC increased, and small amounts of 4,4'-DNEC, 2,4,4'-TNEC and 4-NNNNEA were detected. It is evident (Table I) that increasing the concentration of HNO_2 causes further reaction and cleavage. The chromatogram of the mixture obtained from this reaction is shown in Fig. 1. The precursor for the formation of 4,4'-DNEC could be 4-NEC, the processes being C-nitrosation followed by oxidation to the nitro group. Similarly 2,4,4'-TNEC could arise from 2,4-DNEC, 4,4'-DNEC and/or 2,4'-DNEC. It is interesting to note that 2,4-DNEC is formed in greater yield than 4,4'-DNEC, since reaction would be expected to occur at the more labile para positions, which are not sterically hindered by the bulky ethyl substituents. However, initial nitrosation on a nitrogen atom of EC and oxidation could give rise to N-nitro-EC; and in an acidic medium intramolecular rearrangement might well occur, producing 2-NEC. N-Nitroanilines undergo a similar rearrangement (11). 4-NNNNEA could have arisen via two routes, namely:

i) hydrolysis of 4-NEC followed by nitrosation; and
ii) hydrolysis of EC, nitrosation, followed by Fischer-Hepp rearrangement, then oxidation and further nitrosation.

Nitrosation of EC with 20 molar equivalents of HNO_2 produced twelve products, and unreacted EC was still present. The yields of 2-NEC, 4-NEC, and 2,2'-DNEC doubled. However, 4,4'-DNEC was still present in minute quantities. Increasing the concentration of HNO_2 gave rise to more degradation products. Figure 2 shows the chromatogram of the mixture obtained. A considerable amount of 2,2'4,4'-TNEC was also formed, which most probably arose from nitrosation of 2,4,4'-TNEC, followed by oxidation. Other possible ways in which 2,2'4,4'-TNEC could be produced are:

i) nitrosation of 2,4'-DNEC and oxidation to give 2,2'4-TNEC, followed by further reaction of the latter; and
ii) nitrosation of 2,2'-DNEC and oxidation to give 2,2',4-TNEC, followed by nitrosation and oxidation. However, no 2,2', 4-TNEC was observed in this study and this substance has not been detected previously (4,5). Therefore, the latter reaction sequences are considered improbable.

Considerable quantities of NNNEA, 4-NNNNEA, 2,4,6-TNNNNEA, and 4-NNEA were also present. Possible routes to NNNEA are: i) hydrolysis of EC followed by nitrosation; and ii) attack of NO$^+$ on the nitrogen atoms of EC followed by cleavage. However, EC has been found to resist hydrolysis in an acidic medium even under drastic conditions (12). Since the medium employed for the nitrosations was not very acidic, and the temperature was kept below 8°C, the first route is considered unlikely. On the other hand, attack by NO$^+$ on a nitrogen atom of EC would reduce the latter's stability, since there would be two adjacent positive charges (due to tetravalent nitrogen, and the polarized carbon atom of the carbonyl group), which could cause breakage of the $-\overset{|}{N}-\underset{\overset{\|}{O}}{C}-$ linkage. 2,4,6-TNNNNEA could arise via three routes: i) hydrolysis of the corresponding nitroethylcentralite followed by nitrosation; ii) attack of NO$^+$ on one of the nitrogen atoms of an appropriate nitroethylcentralite, and further reaction; and iii) rearrangement of NNNEA, oxidation and further reaction. However, nitroethylcentralites are resistant to hydrolysis under the nitrosation conditions used (13). Therefore, N-nitroso-N-ethylanilines are most likely formed by direct action of NO$^+$ on the corresponding nitro-EC.

1,3,5-TNB was also present in the mixture obtained from nitrosation of EC with 20 molar equivalents of HNO$_2$. Transformations leading to 1,3,5-TNB would involve dealkylation at some stage, the precursors being 2,4,6-trinitroaniline (2,4,6-TNA) and/or 2,4,6-trinitro-N-ethylaniline (2,4,6-TNNEA).

Nitrosation with 30 molar equivalents of HNO$_2$ caused further reaction. Some 2,4'-DNEC was detected, and recovered EC decreased to about 15%. The yields of 2-NEC, 4-NEC, 4,4'-DNEC, 2,2'-DNEC, 2,4,4'-TNEC and 2,2',4,4'-TNEC increased, whereas that of 2,4-DNEC dropped. This latter change could be due to further reaction to give 2,4,4'-TNEC and 2,2',4,4'-TNEC, and/or cleavage to produce 2,4-DNNEA and NEA. The increases in yield of the other nitroethylcentralites do not necessarily mean that these products do not undergo further reaction. While some of them are being formed by reaction of EC, loss might occur via further nitrosation and oxidation. Additional degradation products were 2-NNNNEA and N,2,4,6-TNNEA. The former is most likely derived from NNNEA via intramolecular rearrangement and oxidation. Cleavage of 2-NEC and/or 2,2'-DNEC via nitrosation would also produce 2-NNNNEA.

The precursor of N,2,4,6-TNNEA might be 2,4-DNNEA. We achieved this transformation by prolonged treatment with HNO$_3$ at room temperature. Clarkson et al (14) reported that N,2,4,6-tetranitro-N-methylaniline arises from 2,4-dinitro-N-methylaniline via the N,2,4-trinitro derivative. Therefore, N,2,4,6-TNNEA might be formed from N,2,4-trinitro-N-ethylaniline, rather than via 2,4,6-TNNEA. On the other hand, oxidation of 2,4,6-TNNNNEA would also yield N,2,4,6-TNNEA, which would be the end product from NEA under the reaction conditions employed. The decreases in the yields of NNNEA and 4-NNEA could be accounted for by the formation of 2-NNNNEA, 2,4,6-TNNNNEA and N,2,4,6-TNNEA.

EC underwent complete reaction with 50 molar equivalents of HNO_2. Figure 3 shows the chromatogram of the mixture resulting from this treatment. Neither 2-NEC nor NNNEA was detected. 4-NEC and 2,4-DNEC were the major EC derivatives and the degradation products were 2-NNEA, 2-NA and 4-NA. The disappearance of 2-NEC could be explained by further reaction to give polynitroethylcentralites and/or cleavage. The yields of 2,4-DNEC and 2,2'-DNEC decreased. 2-NA and 4-NA might arise from 2- and 4-nitrocarbanilide, respectively. There are two possibilities for the formation of 2,4-DNA, namely: cleavage of the corresponding carbanilide; and further reaction of 2-NA and/or 4-NA.

Increasing the concentration of HNO_2 caused more reaction of EC, such that with 50 molar equivalents no EC was recovered. The yield of 4-NEC increased steadily with the HNO_2 concentration, whereas that of 2,4-DNEC dropped when the concentration was increased from 20 to 50 molar equivalents. It can be seen from Table I that 4-NEC is much more readily formed than 2-NEC, a fact explainable on steric grounds. The decrease in the yield of 2,4-DNEC could be due to further transformations, such as nitrosation and oxidation to give 2,4,4'-TNEC; and/or cleavage to produce 2,4-DNNNNEA and NNNEA. The precursors of 2,4-DNEC are 2-NEC and 4-NEC.

The most abundant degradation products noticed in this study were NNNEA, 2-NNNNEA, 4-NNNNEA and 1,3,5-TNB. NNNEA was only present in the mixtures produced by nitrosation of EC with 20 and 30 molar equivalents of HNO_2 (Table I). Hydrolysis of EC in the presence of HNO_2 might have been expected to give NNNEA. However, since this was apparently not the case, it is more likely that cleavage of nitroethylcentralites occurred. NNNEA could result from cleavage of 2-NEC, 4-NEC, and also 2,4-DNEC, but from the product yields we can conclude that cleavage of 2,4-DNEC is the most probable source. The yields of 2-NEC and 4-NEC doubled when EC was treated with 20 molar equivalents of HNO_2, whereas there was only a slight increase in that of 2,4-DNEC.

2-NNNNEA was formed in nitrosations with 30 and 50 molar equivalents of HNO_2, and its precursors could be 2-NEC and/or NNNEA. The major nitroso derivative detected was 4-NNNNEA, whose recovery increased with the increasing HNO_2 concentration. Its formation would be preferred to that of 2-NNNNEA, due to the absence of steric hindrance in the former case. Possible precursors of 4-NNNNEA are 4-NEC and NNNEA, but the former is the much more likely source because 4-NNNNEA is formed earlier than NNNEA.

The presence of a considerable amount of 1,3,5-TNB is somewhat unexpected. A likely source of this compound would be a nitrocarbanilide. Cleavage of carbanilides would give anilines which can undergo nitrosation and oxidation to yield 2,4,6-TNNEA, which on deamination would produce 1,3,5-TNB. Therefore, 2-NA, 4-NA, 2,4-DNA, 2,4,6-TNA, and/or 1,3-DNB could be intermediates in the transformations leading to 1,3,5-TNB.

Probable routes for the formation of the major derivatives of EC are shown in Fig. 5.

4.0 CONCLUSIONS

The reaction of ethylcentralite with nitrous acid results in complex mixtures, the components of which can be separated, identified and quantitatively analysed using thin-layer chromotography and absorption spectroscopy. The reaction products become more complex as the concentration of nitrous acid is increased. At lower concentrations nitro and polynitro derivates of ethylcentralite are the main products while, at higher levels of reactant, degradation of the parent compound occurs leading to significant amounts of nitrated and nitrosated derivatives of ethylaniline and finally trinitrobenzene. The two main types of reaction appear to be C-nitrosation followed by oxidation, and N-nitrosation followed by cleavage of the ethylcentralite molecule with subsequent rearrangement and oxidative processes to yield the degradation products.

The most abundant and stable end product formed during treatment of ethylcentralite with nitrous acid is shown to be the 4-nitro derivative. Other nitro compounds are formed but are generally consumed under more drastic reaction conditions to form higher substituted compounds. Similiar processes occur in gun propellants where the stabilizer reacts with nitrogen oxides released by the slow decomposition of nitrocellulose and nitroglycerin to form nitroso and nitro compounds. As the propellant ages, more highly substituted derivatives of ethylcentralite appear. Analytical examination revealing highly nitrated compounds and degradation products would indicate a potential hazard. The detailed chemical interactions revealed during this study and, in particular, the separation analysis techniques will be applied in studies of chemical stability of propellants stabilized with ethylcentralite.

5.0 REFERENCES

1. Schroeder, W.A., Wilson, M.K., Green, C., Wilcox, P.E., Mills, R.S. and Trueblood, K.N., "Chromatographic Investigations of Smokeless Powders. Derivatives of Centralite Formed in Double-Base Powders during Accelerated Ageing", Ind. Eng. Chem. 42, 539-546, (1950).

2. Gagnon, P.E., MacDonald, R., Haggart, C. and Myers, J.L., "Stabiliser Degradation in Picrite Propellants", J. Appl. Chem. 10, 445-449, (1960).

3. Garman, N.S. and Murphy, J.M., "Long Range Study of Prediction of Safe Life of Propellants", Picatinny Arsenals Technical Memorandum 1609, 1965, Unclassified.

4. Yasuda, S.K., "Identification of Ethyl Centralite-Nitrogen Tetroxide Reaction Products", J. Chromatog. 16, 488-493, (1964).

5. Roy, E.J., Newbold, B.T. and MacDonald, R., "Nitration Reactions of Ethyl Centralite", DREV R-4013/75, Unclassified.

6. Wilcox, P.E. and Schroeder, W.A., "Synthesis of Certain Ethyl, Phenyl, and Nitrophenyl Derivatives of Urea", J. Org. Chem. 15, 944-949 (1950).

7. Blatt, A.H., Ed., "Organic Syntheses", John Wiley and Sons, Inc. New York, U.S.A. Collective Volume 2, 453, (1943).

8. Schweitzer, W., "Ueuber Aethilparaphenilendiamin", Ber. 19, 149, (1886).

9. Clark, G.G., N.O.I.L. Private Communication. 1956.

10. Moisak, I.E., "Products of Nitration of Centralite", Trans. Kirovi Inst. Chem. Tech. Kayan, 3, 153, (1935).

11. Brownstein, S., Bunton, C.A. and Hughes E.D., "The Intramolecular Rearrangement of Phenylnitramine, and the Benzidine and Semidine Changes", Chem. and Ind. 981, (1956).

12. Roy, E.J., "Chemical Reactions of Sym-Diethyldiphenylurea", M. Sc. Thesis, Université de Moncton, 1969.

13. Taymaz, K., "Nitrosation Reactions of Sym-Diethylphenylurea and Stabilizer Degradation in Double-Base Propellants", M. Sc. Thesis, Université de Moncton, 1970.

14. Clarkson, C.E., Holden, I.G. and Malkin T., "The Nitration of Dimethylaniline to Tetryl, 2,4,6,N'-Tetranitromethylaniline. The Course of The Reaction", J. Chem. Soc., 1556-1562, (1950).

15. Ultraviolet Spectral Data, American Petroleum Institute, Research Project 44, Volume 1, 1956.

DREV REPORT 4070/77 (UNCLASSIFIED)

Bureau - Recherche et Développement, Ministère de la Défense nationale, Canada.
CRDV, C.P. 880, Courcelette, Qué. GOA 1RO.

"Nitrosation Reactions of Ethyl Centralite"
by K. Taymaz, B.T. Newbold and R. MacDonald

Des expériences préliminaires décrivent l'action de l'acide nitreux de différentes concentrations sur la centralite d'éthyle, un stabilisateur d'usage courant dans les formulations de poudres à double base. Ces réactions chimiques provoquent la formation de plusieurs dérivés qui sont séparés, identifiés et analysés par chromatographie en couche mince et par spectroscopie d'absorption électronique. Les connaissances analytiques acquises seront utilisées avantageusement dans des études de stabilité sur le vieillissement accéléré des poudres.

DREV REPORT 4070/77 (UNCLASSIFIED)

Bureau - Recherche et Développement, Ministère de la Défense nationale, Canada.
CRDV, C.P. 880, Courcelette, Qué. GOA 1RO.

"Nitrosation Reactions of Ethyl Centralite"
by K. Taymaz, B.T. Newbold and R. MacDonald

Des expériences préliminaires décrivent l'action de l'acide nitreux de différentes concentrations sur la centralite d'éthyle, un stabilisateur d'usage courant dans les formulations de poudres à double base. Ces réactions chimiques provoquent la formation de plusieurs dérivés qui sont séparés, identifiés et analysés par chromatographie en couche mince et par spectroscopie d'absorption électronique. Les connaissances analytiques acquises seront utilisées avantageusement dans des études de stabilité sur le vieillissement accéléré des poudres.

DREV REPORT 4070/77 (UNCLASSIFIED)

Bureau - Recherche et Développement, Ministère de la Défense nationale, Canada.
CRDV, C.P. 880, Courcelette, Qué. GOA 1RO.

"Nitrosation Reactions of Ethyl Centralite"
by K. Taymaz, B.T. Newbold and R. MacDonald

Des expériences préliminaires décrivent l'action de l'acide nitreux de différentes concentrations sur la centralite d'éthyle, un stabilisateur d'usage courant dans les formulations de poudres à double base. Ces réactions chimiques provoquent la formation de plusieurs dérivés qui sont séparés, identifiés et analysés par chromatographie en couche mince et par spectroscopie d'absorption électronique. Les connaissances analytiques acquises seront utilisées avantageusement dans des études de stabilité sur le vieillissement accéléré des poudres.

DREV REPORT 4070/77 (UNCLASSIFIED)

Bureau - Recherche et Développement, Ministère de la Défense nationale, Canada.
CRDV, C.P. 880, Courcelette, Qué. GOA 1RO.

"Nitrosation Reactions of Ethyl Centralite"
by K. Taymaz, B.T. Newbold and R. MacDonald

Des expériences préliminaires décrivent l'action de l'acide nitreux de différentes concentrations sur la centralite d'éthyle, un stabilisateur d'usage courant dans les formulations de poudres à double base. Ces réactions chimiques provoquent la formation de plusieurs dérivés qui sont séparés, identifiés et analysés par chromatographie en couche mince et par spectroscopie d'absorption électronique. Les connaissances analytiques acquises seront utilisées avantageusement dans des études de stabilité sur le vieillissement accéléré des poudres.

DREV REPORT 4070/77 (UNCLASSIFIED)

Research and Development Branch, Department of National Defence, Canada.
DREV, P.O. Box 880, Courcelette, Que. G0A 1R0.

"Nitrosation Reactions of Ethyl Centralite"
by K. Taymaz, B.T. Newbold and R. MacDonald

Preliminary experiments are described in which ethyl centralite, a stabilizer frequently used in double-base propellants, was reacted with nitrous acid in various concentrations. The chemical reactions taking place led to the formation of numerous derivatives which were separated, identified and analysed by thin-layer chromatography and electronic absorption spectroscopy. The analytical knowledge gained will be used to advantage in stability investigations of artificially aged gun propellants.

DREV REPORT 4070/77 (UNCLASSIFIED)

Research and Development Branch, Department of National Defence, Canada.
DREV, P.O. Box 880, Courcelette, Que. G0A 1R0.

"Nitrosation Reactions of Ethyl Centralite"
by K. Taymaz, B.T. Newbold and R. MacDonald

Preliminary experiments are described in which ethyl centralite, a stabilizer frequently used in double-base propellants, was reacted with nitrous acid in various concentrations. The chemical reactions taking place led to the formation of numerous derivatives which were separated, identified and analysed by thin-layer chromatography and electronic absorption spectroscopy. The analytical knowledge gained will be used to advantage in stability investigations of artificially aged gun propellants.

DREV REPORT 4070/77 (UNCLASSIFIED)

Research and Development Branch, Department of National Defence, Canada.
DREV, P.O. Box 880, Courcelette, Que. G0A 1R0.

"Nitrosation Reactions of Ethyl Centralite"
by K. Taymaz, B.T. Newbold and R. MacDonald

Preliminary experiments are described in which ethyl centralite, a stabilizer frequently used in double-base propellants, was reacted with nitrous acid in various concentrations. The chemical reactions taking place led to the formation of numerous derivatives which were separated, identified and analysed by thin-layer chromatography and electronic absorption spectroscopy. The analytical knowledge gained will be used to advantage in stability investigations of artificially aged gun propellants.

DREV REPORT 4070/77 (UNCLASSIFIED)

Research and Development Branch, Department of National Defence, Canada.
DREV, P.O. Box 880, Courcelette, Que. G0A 1R0.

"Nitrosation Reactions of Ethyl Centralite"
by K. Taymaz, B.T. Newbold and R. MacDonald

Preliminary experiments are described in which ethyl centralite, a stabilizer frequently used in double-base propellants, was reacted with nitrous acid in various concentrations. The chemical reactions taking place led to the formation of numerous derivatives which were separated, identified and analysed by thin-layer chromatography and electronic absorption spectroscopy. The analytical knowledge gained will be used to advantage in stability investigations of artificially aged gun propellants.