

PRODUCTS FROM THE DETONATION OF TRINITROTOLUENE AND SOME OTHER NAVY EXPLOSIVES IN AIR AND NITROGEN.II. POLYCYCLIC AROMATIC HYDROCARBONS

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Summary

A method to sample and identify the higher molecular weight post-detonation products (in particular polycyclic aromatic hydrocarbons) from explosives has been developed. The procedure has been tested by sampling the post-detonation products of TNT, C4, H-6, pentolite, PBXN-102, and Composition B detonated both in air and in nitrogen atmospheres. The detonations in the nitrogen atmospheres are intended to simulate underwater explosions where atmospheric oxygen is not available to contribute to secondary combustion reactions. The concentrations and identities of the polycyclic aromatic hydrocarbons found in the post-detonation products have been evaluated. Those species present at the concentrations found do not constitute an environmental or health hazard. The sample analyses show no differences in the products produced in the air or in nitrogen atmospheres.

Introduction

The purpose of this study was to identify the nature and the quantities of products produced by the underwater and surface level detonation of a number of typical U.S. Navy explosives. In order to avoid the experimental difficulties of sampling the products of underwater explosions, detonations were carried out in a nitrogen or oxygen-deficient atmosphere to simulate an underwater detonation. In the nitrogen atmosphere, as in an underwater detonation, atmospheric oxygen would not be available for secondary oxidation processes.

In part I of this study [1], we have reported the results of the analysis of the low molecular weight gaseous post-detonation products, CO, CO₂, CH₄, etc.,

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sampled from cast and pressed trinitrotoluene (TNT), C4, H-6, cast PBXN-102, Composition B, and pentolite detonations. In this paper we will report on the sampling, analysis, and identification of higher molecular weight products and in particular polycyclic aromatic hydrocarbons (PAH).

A knowledge of the identities and concentrations of the post-detonation products from these explosives will make it possible to determine whether any toxins that are harmful to marine or human life are released by these detonations. In addition to the possible chemical hazards to marine life from underwater explosions, the products of surface level detonations not only diffuse into the atmosphere, but can also dissolve in seawater. For this reason, a knowledge of the post-detonation products of surface level detonations is also important when the protection of the marine environment is involved. Furthermore, primary detonation products of both surface level and underwater detonations may react with seawater to form secondary products which may be toxic.

Experimental

The detonation chamber, the sampling probe configurations, and the method to produce the oxygen-deficient atmosphere used in this study have been described previously [1].

Materials

The explosives used in these studies were blocks of standard U.S. Navy explosives withdrawn from magazines. The masses of the explosive charges were 1600 ± 100 g. Detonations of cast and pressed TNT, cast PBXN-102, C4, H-6, Composition B, and pentolite were initiated with a ~ 40 g booster and a standard U.S. Navy detonator.

Sampling systems

(1) Tenax traps

The design of the Tenax traps was patterned after that of Jones et al. [2] who used these traps to sample the exhaust of diesel engines for PAH. These traps contained approximately 50 cc of Tenax in a chamber 30 mm in diameter and 7.5 cm long. The traps were precleaned with methanol and pentane in a modified Soxhlet apparatus, dried in a vacuum oven, sealed, and stored in the dark until used for the collection of samples. The atmosphere of the detonation chamber was sampled at approximately 15 l/min through these traps. When the sampling was completed the traps were sealed and returned to the laboratory.

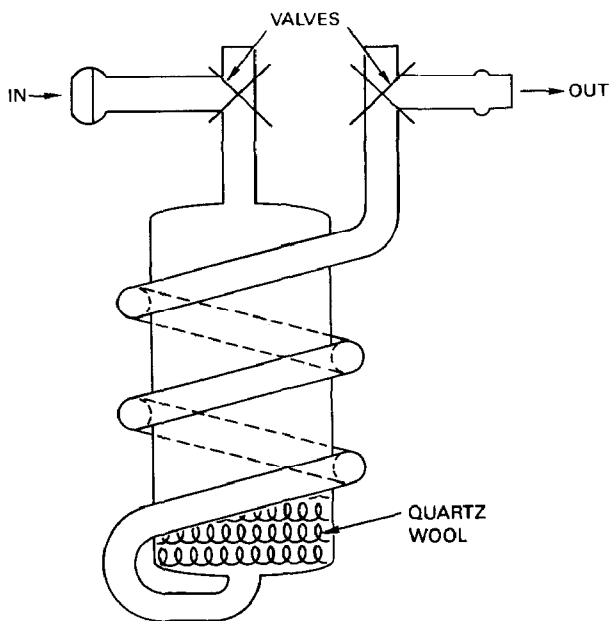


Fig. 1. Cryogenic trap.

(2) Cryogenic traps

Cryogenic (cryocoil) traps, shown in Fig. 1, were incorporated into the sampling system in a parallel system with the Tenax traps. These traps were packed with quartz wool and immersed in liquid nitrogen. The atmosphere of the detonation chamber was sampled at approximately 15 l/min through these traps.

This duplicate sampling system served to check the efficiency with which small amounts of organic compounds were being trapped and eluted from the Tenax-GC traps and to determine whether any artifacts were being observed in the analyses due to the decomposition of the Tenax-GC. When it was concluded that the Tenax-GC was contributing artifact peaks, the use of the Tenax-GC traps was discontinued. The details of the problems of artifact peaks from Tenax-GC are discussed elsewhere [3].

(3) Particulate traps

Three types of particulate traps were used in this work.

(i) *Quartz fiber filters.* Pyrex tubes, 16 mm outer diameter \times 50 mm long and tubulated with 1/4 inch medium-wall glass tubing were packed with pre-fired quartz wool and installed as pre-filters in front of the Tenax-GC and the cryogenic traps to prevent particulates from entering these traps.

(ii) *Pallflex filters*. Teflon-coated, glass fiber filters of 0.2 micron porosity and 47 mm in diameter were used in a separate sampling system designed specifically for the collection of particulates.

(iii) *Sintered glass disk filters*. One-inch diameter sintered glass disks (40–60 microns) were sealed in Pyrex glass tubes, tubulated to 1/4 inch and used to collect particulate matter.

The detonation chamber atmosphere was pulled through all the filters by standard vacuum pumps. The flow rate through the filters was checked with rotameter flow meters before and after gas sampling.

Analytical

The Tenax traps were incorporated into the modified Soxhlet extraction apparatus described by Jones et al. [2] and extracted with 200 ml of pentane (Burdick and Jackson "distilled in glass" grade) for about 24 h as recommended by these authors. After the extraction was completed, 2.0 ml of an internal standard consisting of either anthracene- d_{10} or a mixture of naphthalene- d_8 , anthracene- d_{10} and pyrene- d_{10} in isooctane was added to the pentane extract. The sample volume was reduced to 0.5 ml by rotary evaporation [4]. The isooctane served to reduce the volatility of the final sample. Any further volume reduction was done by blowing pure, dry helium over the sample.

The cryocoil traps were rinsed with 200 ml of pentane in two 100 ml portions. The traps and solvent were placed in an ultrasonic cleaner for 5 min, 2.0 ml of the internal standard was added to the pentane washings, and the sample volume was reduced to 0.5 ml by rotary evaporation.

All particulate filters and particulate residues were extracted in a standard Soxhlet extraction apparatus with 200 ml of "distilled in glass" pentane for about 24 h. When the extraction was completed, 2.0 ml of internal standard was added to the solvent and the solvent was reduced to 0.5 ml by rotary evaporation.

The samples were analyzed with a Hewlett-Packard 5985 gas chromatograph-mass spectrometer (GC/MS) system. A 50 m SE-52 or OV-1 fused silica capillary column was used and splitless mode injections were made. (Fused silica capillary columns were purchased from Analabs/Foxboro, North Haven, CT 06473 and J and W Scientific, Rancho Cordova, CA 95670.) Temperature programming at 3–5 °C/min from 60 to 300 °C was used. Identification of peaks in the total ion chromatogram was aided by the Eight Peak Index of Mass Spectra [5], and by comparison of retention times of unknown peaks in the samples with those of standard samples. Quantitation was accomplished by comparing the peak areas in the samples to those of the internal standards.

TABLE 1

Post-detonation from Navy explosives^a

	C ₆ H ₅ NC ^b	C ₁₀ H ₈ ^c	C ₁₁ H ₁₀ ^d	DNT	TNT	C ₁₆ H ₁₀ ^e
<i>H-6 in 5.93% O₂</i>						
Cryocoil (1)	0.32	0.98	0.16	0.18	19.0	0.49
Cryocoil (2)	0.30	0.78	ND ^f	ND	15.0	ND
Tenax (1)	ND	2.1	ND	ND	166.0	13.0
Tenax (2)	ND	ND	ND	ND	34.0	2.1
<i>H-6 in 21% O₂</i>						
Cryocoil (1)	ND	0.24	ND	ND	0.79	ND
Cryocoil (2)	ND	0.087	0.041	ND	1.4	0.12
Tenax (1)	ND	0.18	0.18	ND	2.8	ND
Tenax (2)	ND	0.13	0.8	ND	ND	ND
<i>Pentolite in 1.18% O₂</i>						
Tenax	ND	4.6	2.5	ND	ND	ND
Quartz fiber	ND	1.2	1.1	ND	ND	ND
Sample probe wash ^g	ND	1.0	1.3	ND	ND	ND
<i>Pentolite in 21% O₂</i>						
Tenax (1)	ND	6.8	9.8	ND	37.0	ND
Tenax (2)	ND	ND	ND	ND	ND	ND
Sample probe wash ^g	ND	1.0	2.0	ND	29.0	ND
<i>PBXN-102 in 0.44% O₂</i>						
Tenax (1)	D ^h	D	D	ND	ND	ND
Tenax (2)	ND	ND	ND	ND	4.4	ND
<i>PBXN-102 in 21% O₂</i>						
Tenax (1)	1.1	1.7	0.54	ND	ND	ND
Tenax (2)	ND	0.49	ND	ND	ND	ND
<i>C4 in 1.22% O₂</i>						
Cryocoil (1)	ND	0.70	0.27	ND	ND	0.20
Cryocoil (2)	ND	0.82	0.46	ND	ND	0.25
Sintered glass (1)	ND	ND	ND	ND	0.62	0.15
Sintered glass (2)	ND	ND	ND	0.34	0.99	0.42
<i>H-6 in 5.93% O₂</i>						
Cryocoil (1)	0.32	0.98	0.16	0.18	19.0	0.49
<i>Composition B in 1.16% O₂</i>						
Quartz fiber (1)	ND	ND	ND	ND	ND	ND
Cryocoil (1)	ND	ND	ND	ND	ND	ND
Quartz fiber (2)	ND	ND	ND	ND	ND	ND
Cryocoil (2)	ND	ND	ND	ND	ND	ND
Quartz fiber (3)	ND	ND	ND	ND	ND	ND
Cryocoil (3)	ND	0.033	ND	ND	ND	ND
Sintered glass (1)	ND	ND	ND	ND	ND	ND
<i>TNT in 1.27% O₂</i>						
Quartz fiber	0.008	0.13	0.028	ND	ND	ND
Cryocoil (1)	0.047	0.24	0.070	ND	0.027	0.39
Cryocoil (2)	ND	0.016	0.040	ND	ND	0.098
Sintered glass (1)	0.034	0.13	0.036	ND	0.062	ND
Sintered glass (2)	0.070	0.19	0.012	ND	ND	ND

TABLE 1 (Continued)

	C ₆ H ₅ NC ^b	C ₁₀ H ₈ ^c	C ₁₁ H ₁₀ ^d	DNT	TNT	C ₁₆ H ₁₀ ^e
<i>TNT in 1.45% O₂</i>						
Quartz fiber (1)	ND	0.12	ND	ND	ND	0.23
Cryocoil (1)	ND	ND	ND	ND	ND	ND
Quartz fiber (2)	ND	0.34	ND	ND	ND	ND
Cryocoil (2)	ND	ND	ND	ND	ND	ND
Quartz fiber (3)	ND	0.043	ND	ND	ND	ND
Cryocoil (3)	ND	ND	ND	ND	ND	ND
Sintered glass (1) ^f	ND	1.0	ND	ND	ND	ND
Sintered glass (2) ^f	ND	1.0	0.50	ND	ND	1.3
<i>TNT in 2.63% O₂</i>						
Quartz fiber (1)	ND	1.44	0.61	ND	ND	ND
Cryocoil (1)	ND	ND	ND	ND	ND	ND
Quartz fiber (2)	ND	ND	ND	ND	ND	ND
Cryocoil (2)	ND	0.16	ND	ND	ND	ND
Quartz fiber (3)	ND	0.13	0.076	ND	ND	ND
Cryocoil (3)	ND	ND	ND	ND	ND	ND
Sintered glass (1)	ND	0.077	0.020	ND	ND	ND
Sintered glass (2)	ND	0.19	0.38	ND	ND	ND
Residue in detonation chamber ^g	0.61	1.0	0.56	ND	ND	ND
Pallflex filter ^h	ND	1.0	ND	ND	ND	0.72
<i>TNT in 5.05% O₂</i>						
Quartz fiber (1)	ND	ND	ND	ND	ND	ND
Cryocoil (1)	ND	ND	ND	ND	ND	ND
Quartz fiber (2)	ND	ND	ND	ND	ND	ND
Cryocoil (2)	ND	ND	ND	ND	ND	ND
Quartz fiber (3)	ND	ND	ND	ND	ND	ND
Cryocoil (3)	ND	ND	ND	ND	ND	ND
Residue in detonation chamber ⁱ	0.61	1.0	0.56	ND	ND	ND
<i>TNT in 21% O₂</i>						
Quartz fiber	ND	ND	ND	ND	ND	ND
Cryocoil	ND	0.28	ND	ND	ND	ND
<i>TNT in 21% O₂</i>						
Cryocoil (1)	ND	0.077	0.009	ND	ND	ND
Cryocoil (2)	ND	0.029	ND	ND	ND	ND
Sintered glass (1)	0.012	0.20	0.13	ND	ND	ND
Sintered glass (2)	0.004	0.046	0.014	ND	ND	ND

^aConcentrations are in $\mu\text{g/g}$ explosive as defined by eqn. (1) unless otherwise noted.

^bPhenyl isocyanide.

^cNaphthalene.

^dMethylnaphthalene.

^ePyrene.

^fNot detected.

^gconcentrations are compared to naphthalene = 1.0.

^hDetected, but not quantitated.

ⁱConcentrations are $\mu\text{g/g}$ residue.

Results

The results of the analyses of the post-detonation products that were collected on Tenax-GC, cryocoil, and filter traps are listed in Table 1. Only the major polycyclic aromatic hydrocarbons common to most samples, i.e., naphthalene, methyl naphthalene, and pyrene and its isomers, plus phenyl isocyanide, dinitrotoluene, and trinitrotoluene are reported in the table. Phenanthrene or anthracene ($C_{14}H_{10}$) were found in some samples but the peaks were masked by the internal standard anthracene- d_{10} . Quantitation was based on the $m/z = 178$ peak which made it easy to separate the deuterated from the undeuterated species. Hydrocarbons, oxygenated compounds, and compounds that could not be identified are not listed. These compounds appeared to be artifacts; they were not present in duplicate samples and were generally present in small concentrations. Products of the decomposition of Tenax-GC are also not included in Table 1. Phthalate and adipate esters were present in most samples, but the particular species and the concentrations varied widely; these are not included in Table 1. Table 2 gives a more complete list of the polycyclic aromatic hydrocarbons that are formed in the detonations; these were extracted from the residue after a detonation.

The concentrations of the post-detonation products reported in Table 1 are listed as micrograms of product per gram of explosive. These concentrations are calculated on the assumption that none of the products diffused from the chamber during the sampling period and that there was complete mixing of the post-detonation products in the chamber. In addition it is assumed that all the post-detonation products have equal response factors on the GC/MS. The concentrations are calculated by eqn. (1)

TABLE 2

Extract of residue collected after TNT detonation in 2.63% oxygen atmosphere

Compound	Collected mass ($\mu\text{g/g}$)
Phenylisocyanide	8.5
Trimethylbenzene	1.8
Indan	4.8
Dimethylethylbenzene	2.6
Methylphenylisocyanide	0.80
Naphthalene	13.9
1-Methylnaphthalene	3.9
2-Methylnaphthalene	3.9
Acenaphthene	4.4
Biphenylene	9.6
Methylacenaphthalene	5.7
Anthracene	4.1

$$a = A_{dp} M_{is} V_c / A_{std} V_s M_e \quad (1)$$

where a denotes mass of detonation product/unit mass of explosive ($\mu\text{g/g}$), A_{dp} area of the detonation product peak on the total ion chromatogram, M_{is} mass of the added internal standard (μg), V_c volume of the detonation chamber (l), A_{std} area of the internal standard peak on the total ion chromatogram, V_s volume of gas sampled from the detonation chamber (l), and M_e amount of explosive detonated (g).

Discussion

Analysis of the data obtained in this work does not confirm the results of the theoretical studies by Renner and Short [6] that suggested that a number of minor toxic products are produced by the detonations. Renner and Short's studies predicted that hydrogen cyanide, ammonia, and nitrogen oxides would be present in the post-detonation products. None of these compounds were found in the 1-l gas samples taken from the detonation chambers [1] and none of these compounds have been found in this study where 50-100 l of gas were sampled through cryogenic and Tenax-GC traps. Hydrogen cyanide, ammonia, and nitrogen oxides were determined by gas chromatography and/or mass spectrometry in calibration sampling tests that were conducted in the detonation chambers. We feel that the absence of these compounds among the detonation products is not due to any shortcoming in our sampling or analytical techniques.

Renner and Short did not include polycyclic aromatic hydrocarbons among the post-detonation products of these explosives in their calculations. They did include methane and other light hydrocarbons among the products, and these were found in our gas samples when a flame ionization detector was used, but in much lower concentrations than predicted.

The analyses of Tenax-GC, cryogenic, quartz fiber, sintered glass, and residues all confirmed that a large number of polycyclic aromatic hydrocarbons are present in the detonation products. In spite of the fact that the Tenax-GC introduced a number of artifact peaks into the analytical data due to the liberation of Tenax-GC decomposition products when air flows over the Tenax-GC, it was possible to conclude from the Tenax-GC data, as well as the data from the other trapping systems, that polycyclic aromatic hydrocarbons are present in the post detonation products of all the explosives tested.

The aromatic compounds most consistently found in the post-detonation products were phenyl isocyanide, naphthalene, methylnaphthalenes, and pyrene and its isomers. (Anthracene and phenanthrene were also present but were not measured since they were masked by the anthracene d_{10} internal standard.) The number of polycyclic aromatic hydrocarbons found in the traps is

limited by the analytical sensitivity; the analysis of the residues shows that a much larger number is actually formed.

This study has also shown that the higher molecular weight post-detonation products are adsorbed on particulate matter and that these rapidly diffuse from or are expelled from the detonation chamber. When samples were taken at three time intervals after the detonation (0–1 min, 1–2.5 min, and 2.5–5 min), the analytical results showed that the high molecular weight compounds are adsorbed on particulate matter and that the concentration of the particulate matter in the detonation chamber dropped as rapidly as did the concentration of the helium [1]. The quartz fiber traps stopped all the high molecular weight post-detonation products before they reached the cryocool traps, and all the post-detonation products collected were found on the 0–1 min traps. In experiments where two quartz fiber traps were placed in series before the cryogenic traps, all the products were found on the first quartz fiber trap. The sintered glass traps contained concentrations of post-detonation products comparable to the quartz fiber traps, confirming that the products are adsorbed on particulate matter.

This work shows that neither the air nor nitrogen atmosphere detonations produce quantities of polycyclic aromatic compounds that could be considered a health hazard. Samples of post-detonation products from the detonations both in air and nitrogen atmospheres prove that only very small amounts of polycyclic aromatic compounds are produced in the detonations. This work also shows that there are no significant differences in the amounts of pollutants that are formed in the detonations in air and in the nitrogen atmospheres. We believe that the data obtained from the filters and traps are a reliable indication of both the number and concentration of products produced in the detonations and that these pose no hazard to the environment.

We are unable to explain the nonreproducible concentrations and the variety of species of phthalate esters found in all the samples. TNT and several of the other explosives that we have studied do not contain phthalate esters. All sampling equipment was carefully washed with chromatographic grade solvents and/or baked in a glass annealing oven at 550 °C with simultaneous air purge. The ~40 g of C4 used to initiate the detonation cannot be responsible since the samples taken from the 1590 g detonation of C4 did not contain as many phthalate esters as some of the other tests. A blank determination of the detonator and the firing cable was not made, but even if these items were the sources of the phthalates, it would not explain the nonreproducible quantities and types of phthalates found.

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