PRODUCTS FROM THE DETONATION OF TRINITROTOLUENE AND SOME OTHER NAVY EXPLOSIVES IN AIR AND NITROGEN. I. LOW MOLECULAR WEIGHT GASES

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Summary

A method of sampling and analyzing the major and minor gaseous post-detonation products of 1.5–2.0 kg explosive charges in air and oxygen-deficient atmospheres has been developed. The oxygen-deficient atmospheres simulated underwater detonations. The system has been tested with a number of U.S. Navy explosives, including cast and pressed TNT, H-6, C4, cast PBXN-102, composition B, and pentolite. The data obtained experimentally from detonations in oxygen-deficient atmospheres was compared with compositions of post-detonation products predicted for underwater detonations. There was general agreement among the major products, but wide differences among the minor products.

Introduction

The purpose of this study was to identify the nature and the quantities of gaseous products produced by underwater and surface level detonations of typical U.S. Navy high explosives. We have separated these detonation products into two classes: (1) low molecular weight gases such as hydrogen, carbon monoxide, carbon dioxide and C_1–C_3 hydrocarbons and (2) high molecular weight organic compounds such as polycyclic aromatic hydrocarbons and phthalate esters. This report details the development of the experimental methods we used to collect and analyze the low molecular weight gas samples from the detonations. The data obtained from detonations in oxygen deficient atmospheres are compared to the gas compositions that have been calculated by theoretical methods.

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The sampling of the gaseous products resulting from the detonation of cast and pressed trinitrotoluene (TNT), cast PBXN-102, C4, H-6, composition B, and pentolite has been carried out in this study. The detonations have been studied in both air and in oxygen deficient (nitrogen) atmospheres. The detonations in the nitrogen atmospheres were carried out to simulate underwater detonations where the secondary oxidation of the detonation products cannot take place.

Renner and Short [1] have calculated the concentrations of the major detonation products which can be expected from the underwater detonation of a number of the explosives that we have studied. Ornellas and McGuire [2] have conducted small scale laboratory experiments where gram quantities of TNT were detonated under confined conditions and the products of the detonation were analyzed. We believe our study is the only one where detonation products were sampled from kilogram quantities of explosives.

Experimental

Detonation chamber

An experiment in which 1.5–2.0 kg of explosive is to be detonated in a controlled atmosphere with post-detonation sampling of gaseous products requires a special detonation chamber. To avoid the loss of the post-detonation products, the ideal chamber would be one that was totally enclosed. Preliminary experiments showed that a totally sealed chamber, approximately 30 m^3 in volume and constructed of heavy steel plate, could not withstand the blast of a 2.0 kg-charge of TNT. Other experiments showed that unless the chamber was totally enclosed the detonation products escaped before they could be sampled.

These problems were resolved with the detonation chamber (shown schematically in Fig. 1) that was used in this study. This chamber was a concrete-enclosed steel room with dimensions of 4.4 m × 3.3 m × 2.7 m and a volume of 38.0 m^3. The room had three shock baffle chimneys and an escape door that led to a short corridor with three sharp turns. The chimneys and door could be tightly sealed with plywood, polyethylene sheeting and tape prior to a detonation. These seals were broken by the detonation; however, samples of the gaseous detonation products could be obtained before they had escaped from the chamber.

The gas sampling probes used in this work were 1/2-inch stainless steel tubing. For tests 2-15 (see Table 1) gas sampling probes were inserted into the detonation chamber through one of the shock baffle chimneys. For tests 16-20 the probes were inserted through holes that had been drilled through one of the chimneys just above the roof line. For all experiments after test 20, the probes were inserted through a port in one of the walls to a position directly

across from the explosive. This final probe configuration is shown in Figs. 1 and 2.

Gas sampling system

The gas sampling system, shown in Fig. 3(a) was designed to sequentially take eight 1-liter gas samples in sets of two. By sampling at successive times after the detonation, it was possible to determine the rate at which the post-detonation products were escaping from the detonation chamber. The analysis of the first gas sample after the detonation is reported in the tabulation of results.

The procedure by which the sampling was carried out is shown in Fig. 3(b). Before the detonation all the "pump solenoids" #1, #3, #5, and #7 were activated so that the sample flasks were being evacuated. A few seconds before the sampling was to begin (i.e., a few seconds before the detonation), these "pump solenoids" were closed. When sampling was initiated, "sampling solenoids" #2 were opened for 10 s, then closed, then "sampling solenoids" #4 were opened for 10 s, then closed etc., until all four sets of samples were collected. The gas samples remained isolated between the solenoids until it was safe to approach the area in which the sampling system was located. At this time the vacuum valves on the sample flasks were closed and the flasks were disconnected so that they could be returned to the laboratory for analysis.

Materials

The explosives used in this work were standard U.S. Navy explosives: cast and pressed trinitrotoluene (TNT), cast PBXN-102, C4, H-6, composition B, and pentolite. The mass of explosive used in each test was in the range of 1.5–2.0 kg. The detonations were initiated with a C4 booster and a standard detonator.

Analytical

The gas samples collected by the sequential gas sampling system were analyzed by gas chromatography (GC). The samples collected in the tests up to test 32 were analyzed with a Carle Model 8500 GC equipped with a thermal conductivity detector (TCD); those collected from tests 33-36 were analyzed with a Perkin-Elmer Sigma 2000 equipped with a TCD. The samples from test 37 were analyzed with the Sigma 2000 equipped with a flame ionization detector (FID). All samples analyzed were compared to standard samples and the concentrations listed are $\pm 2\%$.

When TCD detectors were used in the gas chromatographs, H_2, O_2, N_2, CH_4, and CO were separated with a 6 ft $\times$ 1/8 inch stainless steel 5A sieve column and CO_2, C_2H_4, and C_2H_6 were separated with a 6 ft $\times$ 1/8 inch stainless steel Porapak N column. Switching from one column to the other was accomplished by the Carle series/bypass valve which was supplied by the manufacturer of
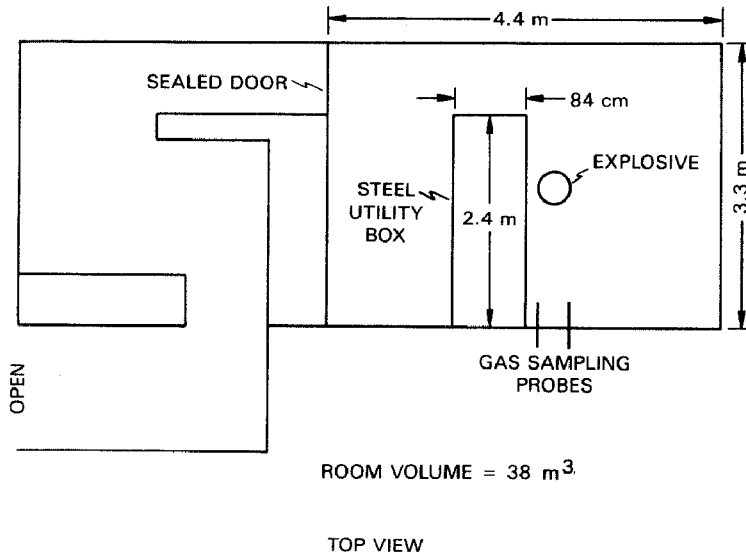
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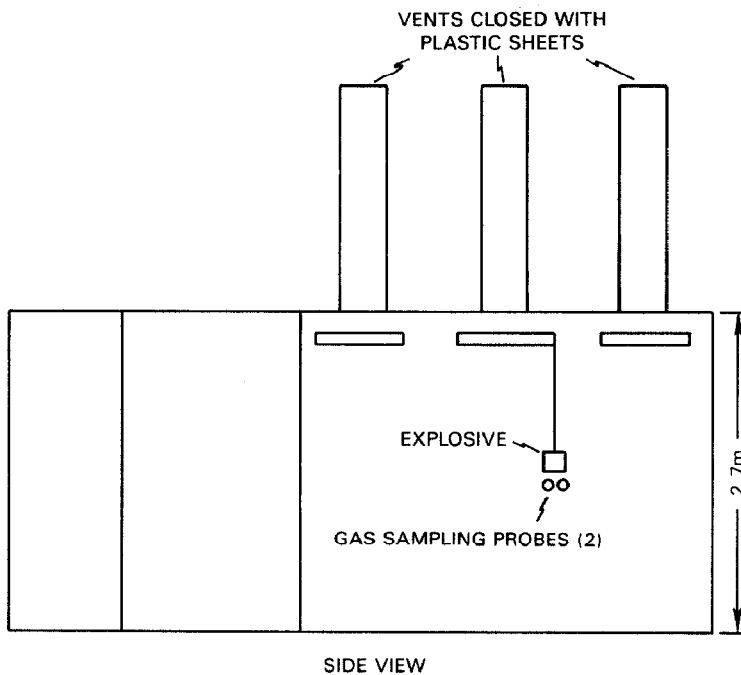Fig. 1. Top view of detonation chamber showing probes inserted through a port in the wall.

Fig. 2. Side view of detonation chamber.

the gas chromatograph. Helium was used as the carrier gas at a flow rate of 15 cc/min and the columns were operated isothermally at 70°C. When the FID detector was used for the analysis of the gas samples from test 37, a 6 ft × 1/8

COPPER 1/2 IN. PROBE

STAINLESS 1/2 IN. PROBE

SOLENOIDS

3 – WAY SWITCH

1 ON   1 OFF 1 OFF
2 OFF 2 ON   2 OFF
BEFORE DURING AFTER

SOLENOID FLOW

OUT

IN

VALVE

IN   OUT

GLASS SAMPLE FLASK

PUMPS

TENAX TRAPS

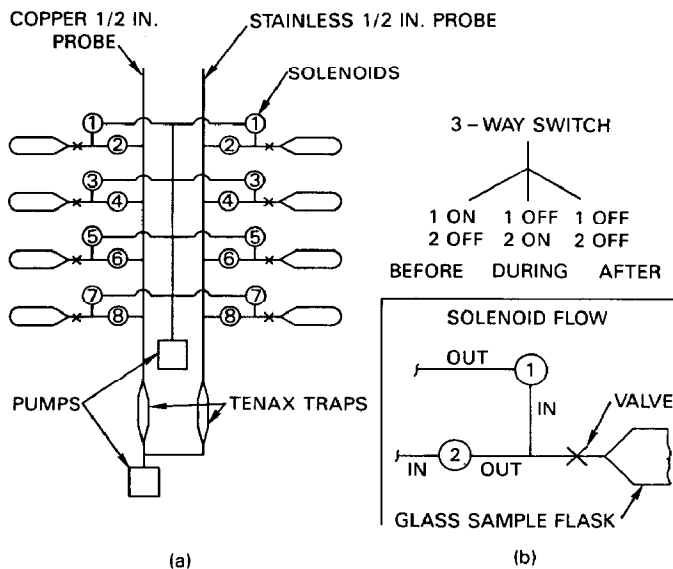(a)   (b)

Fig. 3. Gas sampling system showing gas sampling bottles for low molecular weight gases and Tenax Traps for high molecular weight gases (See Following Paper).

inch stainless steel Spherocarb column was used in the gas chromatograph. This column was followed by a catalytic converter that converted CO and CO_2 to CH_4 so that these gases could be detected by the FID. All gas chromatography columns were obtained from Analabs/Foxboro, New Haven, Connecticut.

All samples were analyzed either in duplicate or triplicate and these analyses varied by less than 1%. When the TCD's were used, the estimated detection limits (in mol%) are as follows: H_2, 0.07; CO, 0.02; CH_4, 0.02; C_2H_6, 0.03; C_3H_8, 0.02. When the FID was used, the detection limit for the hydrocarbons was 0.0001 mol% or 1 ppm.

The sampling times were so short that the collected gas samples were below atmospheric pressure. We developed a method to transfer these gas samples from the sample flasks to the gas chromatograph without air contamination. This procedure has been described elsewhere [3].

The oxygen deficient atmosphere in the detonation chamber

The oxygen deficient atmosphere in the detonation chamber was achieved by displacing the air in the chamber with nitrogen. All ports in the chamber were sealed with plywood, polyethylene sheeting and tape, and the room air was displaced by pumping 240 kg of liquid nitrogen (the contents of two 150 l containers) into the detonation chamber over a period of about 15 minutes. Gas samples of the atmosphere in the detonation chamber showed that this procedure reduced the oxygen content to between 0.4–11.1%. Since this pro-

TABLE 1

Summary of detonation experiments

Test No.	Explosive	Mass (g)	Atmosphere (mol% O_2)
12	Cast TNT	1593	21.0
13	Cast TNT	1532	21.0
15	Pressed TNT	1565	21.0
16	Pressed TNT	1567	21.0
18	Pressed TNT	1578	11.1
19	Pressed TNT	1561	8.2
20	Pressed TNT	1566	0.7
21	Pressed TNT	1569	21.0
22	Cast PBXN-102	1629	0.44
23	Cast PBXN-102	1629	21.0
24	Pressed TNT	1588	21.0
25	Pentolite	1621	1.18
26	Pentolite	1702	21.0
27	H-6	1624	5.93
28	H-6	1630	21.0
30	Pressed TNT	1559	1.27
31	Pressed TNT	1559	21.0
32	Pressed TNT	1555	21.0
33	C4	1590	1.22
34	Pressed TNT	1557	1.45
35	Composition B	1609	1.16
36	Pressed TNT	1556	5.05
37	Pressed TNT	1556	2.63

cedure for displacing the oxygen from the detonation chamber cooled the explosive charge, the explosive charge was placed in a glass dewar flask when oxygen deficient tests were carried out.

Results

The detonation experiments reported in this work are listed in Table 1.

The results of the analyses of the post-detonation gas samples are listed in Tables 2–8.

Discussion

The data from all the post-detonation gas samplings show that when the detonations take place in air, secondary combustion reactions consume all or the major portion of the primary products that can undergo further oxidation. The concentration of carbon compounds formed at various oxygen concentra-

TABLE 2

Post-detonation gas samples from cast TNT tests in mol%[a]

Test No.	O_2	N_2	CO_2	CO
12	19.1	78.1	2.65	—
13	19.2	77.1	2.65	—

[a]Samples taken +5 to +15 s after detonation, unless otherwise noted.

tions in the detonation chamber is plotted in Fig. 4 for the pressed TNT experiments. This figure shows that: (1) the post-detonation concentration of CO decreases as the percentage of oxygen in the atmosphere of the detonation

TABLE 3

Post detonation gas samples from pressed TNT tests in mol%[a]

Test No.	O_2	N_2	CO_2	CO	CH_4	He
15[b]	19.6	77.5	2.15	0.004	—	—
16	19.6	78.7	2.47	0.003	—	—
21	19.9	76.7	1.73	0.02	—	—
24	18.5	76.8	2.15	0.03	—	—
31	19.1	76.2	1.94	∼0.02	—	—
32	19.9	76.4	1.54	∼0.02	—	—
18	7.87	89.8	0.68	0.57	0.02	—
19	5.15	93.1	0.59	0.74	0.02	—
36	4.77	84.2	0.35	1.06	trace	—
37[c]	4.12	85.1	0.37	1.07	0.04	10.08
20	3.08	94.7	0.47	0.68	0.02	—
30	2.87	83.9	0.43	0.90	0.04	9.75
34	1.42	88.0	0.43	1.16	—	8.95

[a]Samples taken +5 to +15 s after detonation, unless otherwise noted.
[b]Sample taken 0 to +10 s after detonation.
[c]C_2H_2, 32 ppm; C_2H_4, 16 ppm; C_2H_6, 1.2 ppm were detected with FID.

TABLE 4

Post-detonation gas samples from cast PBXN-102 in mol%[a]

Test No.	O_2	N_2	CO_2	CO	CH_4	H_2	C_2H_2 C_2H_4
23	20.3	78.7	1.07	0.03	0.00	0.00	0.00
22	1.18	97.8	0.38	0.28	0.12	0.25	trace

[a]Samples taken +5 to +15 s after detonation.

TABLE 5

Post detonation gas samples from Pentolite in mol%[a]

Test No.	O_2	N_2	CO_2	CO	CH_2	H_2	Freon 12
26	19.0	75.8	1.87	0.01	0.00	0.00	0.80
25	2.25	96.2	0.71	0.81	0.02	0.00	0.84

[a]Samples taken $+5$ to $+15$ s after detonation.

chamber increases and (2) the post-detonation concentration of CO_2 increases as the concentration of oxygen in the detonation chamber increases.

The effect of the concentration of oxygen on the secondary combustion products of pressed TNT is shown in a different way in Fig. 5. In this figure it is seen how the concentration of CO in the products of the TNT detonations relative to the sum of the concentrations of CO and CO_2 changes as a function of the concentration of oxygen in the detonation chamber. The results of the gas analyses for PBXN-102, pentolite and H-6 show the same pattern as TNT

TABLE 6

Post detonation gas samples from H-6 in mol%[a]

Test No.	O_2	N_2	CO_2	CO	CH_4	H_2	C_2H_4	C_2H_2	Freon 12
28	19.1	75.5	1.02	0.03	0.00	0.00	0.00	0.00	1.94
27	3.76	92.7	0.05	0.89	0.05	0.85	0.005	0.01	1.58

[a]Samples taken $+5$ to $+15$ s after detonation.

TABLE 7

Post detonation gas samples from C4 in mol%[a]

Test No.	O_2	N_2	CO_2	CO	He
33	1.77	89.95	0.25	0.87	7.27

[a]Samples taken $+5$ to $+15$ s after detonation.

TABLE 8

Post detonation gas samples from Composition B in mol%[a]

Test No.	O_2	N_2	CO_2	CO	He
35	1.87	87.2	0.39	0.90	9.58

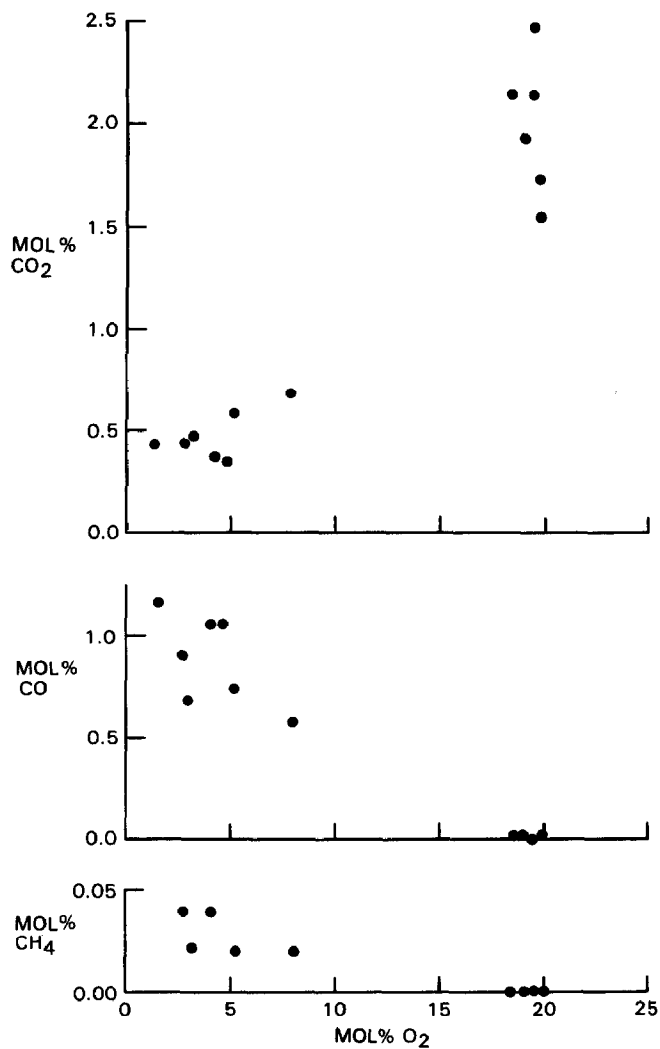[a]Sample taken $+1$ to $+11$ s after detonation.

Fig. 4. Concentration of carbon compounds formed at various detonation chamber oxygen concentrations in pressed TNT experiments.

when the detonations are carried out in atmospheres having a range of oxygen concentrations; that is, the concentration of carbon monoxide decreases as the concentration of oxygen in the atmosphere increases.

Detonations in oxygen deficient atmospheres resulted in the formation of a great deal of smoke. The smoke formation from a TNT detonation in an oxygen deficient atmosphere is shown in Fig. 6. A TNT detonation in air gave no black smoke. The observations for PBXN-102 and pentolite were the same as for TNT.
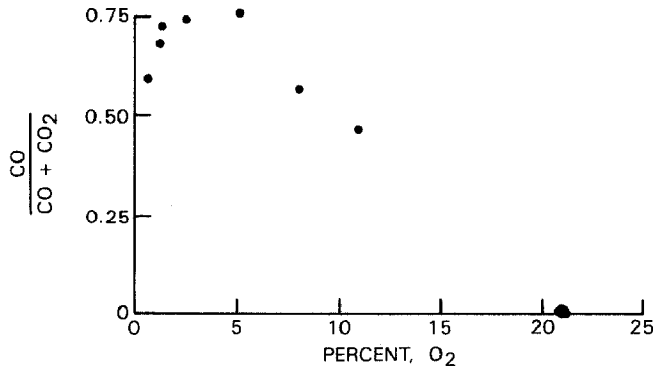
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Fig. 5. Dependence of the secondary combustion of carbon monoxide on the concentration of oxygen in the detonation chamber.
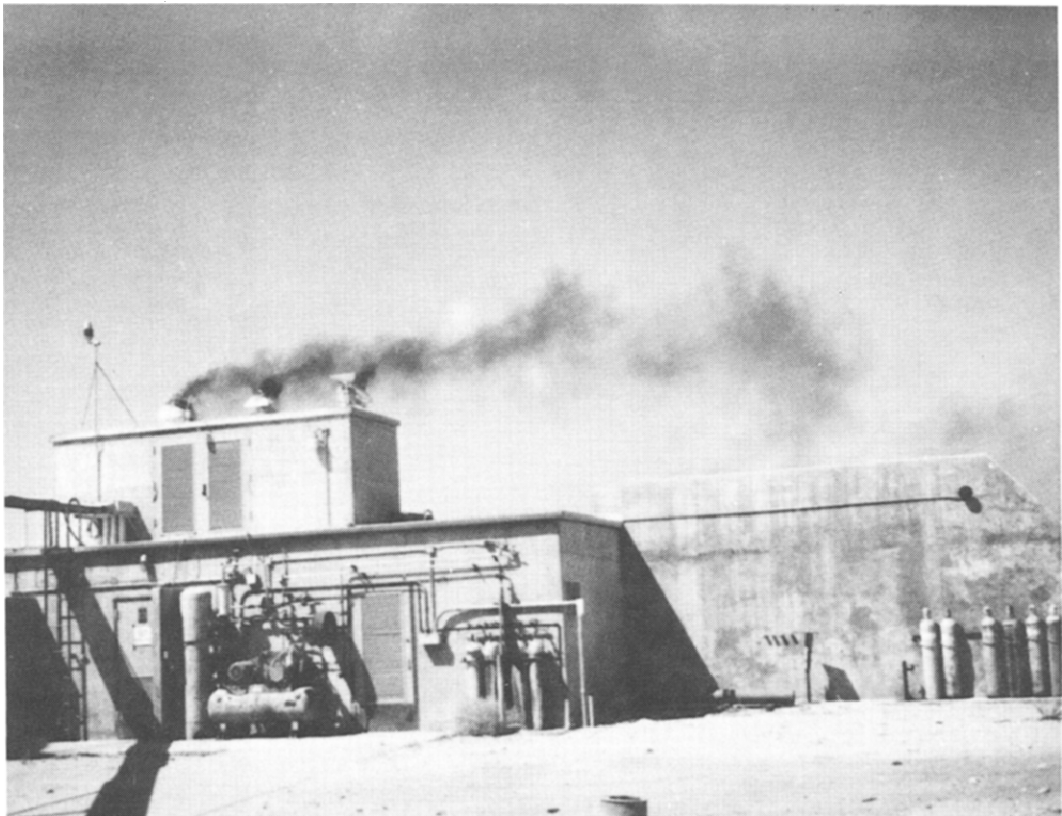

Fig. 6. Smoke formation from TNT detonation in oxygen deficient atmosphere.

As a result of the combustion of the carbon when the detonation takes place in an atmosphere where oxygen is present, the sum of the concentrations of the gaseous carbon compounds increases as the concentration of oxygen in the

atmosphere in the detonation chamber increases. This was observed for TNT, PBXN-102 and pentolite. In the case of H-6 however, the sum of the concentrations of CO, CO_2 and CH_4 was the same at ~ 4 and $\sim 20\%$ oxygen, and there was very little smoke at either oxygen concentration. The H-6 formulation contains sufficient oxygen to oxidize all the carbon so that the oxidation of carbon is not dependent on atmospheric oxygen.

When TNT and other explosives are detonated in oxygen deficient atmospheres, traces of H_2, CH_4, C_2H_2, C_2H_4, and C_2H_6 are found in the post-detonation gas samples. These products are not observed when these explosives are detonated in air.

Comparison of the experimental and calculated values of the post-detonation gas samples

Renner and Short have calculated the detonation products for pressed TNT and a number of other explosives when these explosives are detonated under water [1]. We have compared these calculated values to our experimental results. The comparisons are shown in Tables 9–13.

The agreement of the identification and the concentrations of post-detona-

TABLE 9

Calculated and experimental post-detonation gas compositions for pressed TNT in mole-ratios[a]

Product	Renner and Short $\rho = 1.40$ g/cm^3	This work $\rho = 1.50$ g/cm^3
CO_2	100.0	100.0
CO	182.4	$203.6 + 87.1$[c]
H_2O	48.0	N.A.[d]
N_2	105.9	—
H_2	13.1	N.D.[b]
NH_3	3.24	N.D.
C_2H_6	28.12	0.03[e]
C_3H_8	5.91	N.D.
CH_4	2.56	$6.04 + 4$[f]
HCN	0.044	N.D.
CH_3OH	0.010	N.A.
CH_2O	0.015	N.A.
NO	0.00	N.A.

[a]All data are normalized to CO_2.
[b]Not detected; see text.
[c]Average and standard deviation of data from tests 18, 19, 36, 37, 20, 30 and 34. See Table 3.
[d]Not analyzed.
[e]Datum from test 37, see Table 3.
[f]Average of data from tests 18, 19, 37, 20 and 30, see Table 3.

TABLE 10

Calculated and experimental post-detonation gas compositions for pentolite in mole-ratios[a]

Product	Renner and Short $\rho = 1.67$ g/cm^3	This work $\rho = 1.56$ g/cm^3
CO_2	100.0	100.0
CO	43.0	114.1
H_2O	48.8	N.A.[b]
N_2	57.5	—
H_2	3.15	N.D.[c]
NH_3	2.56	N.D.
C_2H_6	12.6	N.D.
C_3H_8	3.15	N.D.
CH_4	0.66	2.8
HCN	0.0091	N.D.
CH_3OH	0.0060	N.A.
CH_2O	0.00090	N.A.
NO	0.00	N.A.

[a]All data are normalized to CO_2.
[b]Not analyzed.
[c]Not detected; see text.

tion products as calculated by Renner and Short and as determined experimentally in this work was not good.

The quantitative analysis of water vapor, methanol and formaldehyde by gas chromatography requires special chromatography columns and extensive preconditioning of the sampling equipment; therefore, these compounds were not analyzed in this work. On the other hand, the detection limit for hydrogen with our analytical equipment was far below that calculated to be present in the post-detonation products of all the explosives. It was detected only in the post-detonation products of H-6 detonated in a low concentration oxygen atmosphere and in this case the concentration was close to the calculated value. Methane and acetylene were also found in the post detonation products of H-6, methane and a trace of ethane were found in the post detonation products of pressed TNT, and methane was found in the post detonation products of pentolite. The relative concentrations of these products did not correspond to the concentrations calculated by Renner and Short. In the samples from all the other explosives, no hydrocarbons were detected. The detection limits for hydrocarbons were far below the predicted concentrations. In calibration tests HCN had been introduced into the detonation chamber, sampled with the gas sampler, and identified by both gas chromatography and mass spectrometry, but no HCN was found in any of the post-detonation gas samples.

TABLE 11

Calculated and experimental post-detonation gas compositions for H-6 in mole-ratios[a]

Product	Renner and Short $\rho = 1.74$ g/cm^3	This work $\rho = 1.71$ g/cm^3
CO_2	0.86	5.6
CO	100.0	100.0
H_2O	9.72	N.A.[b]
N_2	97.15	—
H_2	78.60	95.5
NH_3	8.65	N.D.[c]
C_2H_6	14.02	N.D.
C_3H_8	2.32	N.D.
CH_4	1.26	5.6
HCN	2.33	N.D.
CH_3OH	0.015	N.A.
CH_2O	0.018	N.A.
NO	0.00	N.A.
C_2H_2	0.46	1.12
PH_3	0.026	N.A.
C_2H_4	0.00[d]	0.56

[a]All data are normalized to CO.
[b]Not analyzed.
[c]Not detected; see text.
[d]Product entered in program but not found.

Concentration of gaseous products in the detonation chamber immediately after detonation

When a detonation occurred in the detonation chamber, the plywood chamber door, polyethylene sheeting, and tape used to seal the chamber were blown away and the post-detonation products began to escape from the chamber. Gas sampling began within a few seconds of the detonation and lasted 10–15 seconds while the gas was escaping from the detonation chamber. In order to determine the validity of the gas sampling used in this work, the residence time of the post-detonation products in the detonation chamber must be known. The method selected to determine the residence time was to use an inert tracer gas. Freon 12 (CCl_2F_2) and sulfur hexafluoride were investigated as possible tracer gases and discarded. Freon 12 did not diffuse fast enough through the detonation chamber to give complete mixing and it reacted at detonation temperatures to give a series of fluorocarbons and chlorofluorocarbons. Sulfur hexafluoride was not used because of the possibility of the formation of toxic compounds. Helium was eventually selected as the tracer gas. Helium mixes rapidly and completely with the detonation products, it is unreactive and gas analysis showed that the helium and carbon dioxide are lost from the detona-

TABLE 12

Calculated and experimental post-detonation gas compositions for C4 in mole-ratios[a]

Product	Renner and Short $\rho = 1.60$ g/cm^3	This work $\rho = 1.59$ g/cm^3
CO_2	100.0	100.0
CO	79.79	348.0
H_2O	104.1	N.A.[b]
N_2	183.6	—
H_2	12.56	N.D.[c]
NH_3	9.19	N.D.
C_3H_6	36.29	N.D.
C_3H_8	7.81	N.D.
CH_4	2.28	N.D.
HCN	0.026	N.D.
CH_3OH	0.011	N.A.
CH_2O	0.0015	N.A.
NO	0.00	N.A.

[a]All data are normalized to CO_2.
[b]Not analyzed.
[c]Not detected; see text.

TABLE 13

Calculated and experimental post-detonation gas compositions for Composition B in mole-ratios[a]

Product	Renner and Short $\rho = 1.71$ g/cm^3	This work $\rho = 1.68$ g/cm^3
CO_2	100.0	100.0
CO	80.3	231.0
H_2O	60.0	N.A.[b]
N_2	134.1	—
H_2	7.18	N.D.[c]
NH_3	4.62	N.D.
C_2H_6	22.9	N.D.
C_3H_8	5.19	N.D.
CH_4	1.40	N.D.
HCN	0.23	N.D.
CH_3OH	0.0072	N.A.
CH_2O	0.0013	N.A.
NO	0.00	N.A.

[a]All data are normalized to CO_2.
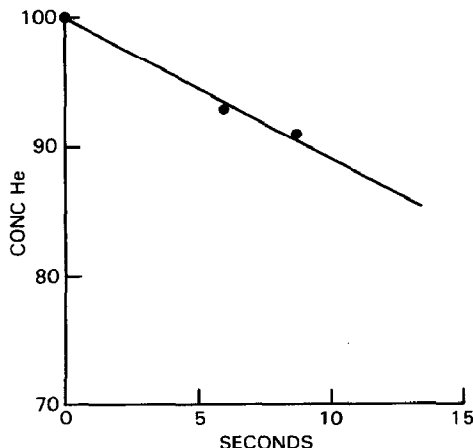[b]Not analyzed.
[c]Not detected; see text.

Fig. 7. Rate of escape of helium from chamber after detonation.

tion chamber at the same rate. For the analysis of helium it was necessary to use nitrogen as a carrier gas in the gas chromatograph.

The concentration of helium in the detonation chamber as a function of time after detonation is shown in Fig. 7. These data show that 18% of the helium and the detonation products have escaped from the detonation chamber by the time a sample taken between $+5$ and $+15$ s has been collected. A loss of this magnitude is not sufficient to explain the large differences between the concentrations of post-detonation products predicted by Renner and Short and the values determined experimentally in this work.

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