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The Heat and Products of Detonation of Cyclotetramethylene
tetranitramine (HMX), 2, 4, 6-trinitrotoluene (TNT), Nitromethane (NM),
and Bis [2, 2-dinitro-2-fluoro-ethyl] -formal (FEFO)*

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1. INTRODUCTION

Calorimetric measurements combined with product analysis offer a precise method for obtaining fundamental information about the detonation process. This information can then be used to provide normalization and boundary conditions for thermodynamic-hydrodynamic codes that predict explosive performance.

Three pure CHNO explosives and one fluorine containing explosive were investigated. This work is an extension of the work reported¹ for PETN. Jointly, these studies span the range of oxygen balance in explosives that is of greatest interest.

Previous detonation calorimetric work with TNT²⁻⁵ and HMX⁶ is not amenable to theoretical interpretation because of the geometries used or the lack of reliable product information. No information concerning the experimental determination of the heat and products of detonation of NM and FEFO has been found in the literature.

2. EXPERIMENTAL

2.1 Apparatus and Operation

The apparatus and its operation have been described; however, some changes have been made.

The thermometric system is a quartz thermometer which has a sensitivity of 1×10^{-4} °C for differential measurements, is easily calibrated, and has direct digital readout.

The heat equivalent of the standard instrument, taken as the average of six calibration runs, was $15, 193 \pm 2$ cal/°C. The error is the standard deviation of the mean.

Charges are now completely confined by a 1.27-cm thickness of gold. Formerly the ends of the confining cylinder were left open. Since the bottom of the interior of the bomb was most damaged by flying fragments, it was protected by a 0.64-cm-thick, 6.4-cm-diameter stainless steel disc which we replaced after each experiment.

In order to contain NM under vacuum conditions, we sealed the gold cylinder 1.27 cm from each end with a translucent film which is a laminate of 0.025-mm polyethylene and 0.013-mm Mylar. A vacuum-tight seal was obtained by compressing the film between appropriately machined gold surfaces. The weight of film averaged 0.017 g per experiment.

NM was initiated through this film with a 0.75-g PETN booster at a density of 1.71 g/cc. HMX and FEFO were initiated with a 0.3-g booster. No booster was required for the TNT experiments since initiation was effected by means of the detonator alone.

2.2 Explosive Materials

Military specification, grade II HMX was used. Analyses by thin layer

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chromatography showed about 0.5% cyclotrimethylene-trinitramine (RDX) and less than 1% each of an incompletely characterized linear nitramine (compound C) and 1(N) acetal - 3, 5, 7 trinitrocyclotetranitramine (SEX). The melting point was 278-282°C. Charges were machined from billets which had been prepared with a special solvent-pressing technique.

Granular TNT, military specification, grade III was used. Analysis by thin-layer chromatography showed less than 2% impurities. These were identified as 2, 4, 5 TNT, 2, 4 dinitrotoluene and trinitrobenzoic acid. Elemental analyses for carbon, hydrogen, and nitrogen were in agreement with theory for pure TNT within the limits of the analyses. The melting point was 82.0°C. Charges were pressed in increments to a density at which TNT detonates reliably in small diameters.

Commercial grade NM was used. Chromatographic analysis showed a purity of 96.7%. Impurities were nitroethane 0.94%, 2-nitropropane 2.5%, 1-nitropropane 0.03%, and water 0.1% maximum. The empirical formula on which results are based was calculated from the above analyses and adjusted to carbon equals 1.00.

We de-aerated NM to avoid the formation of an air bubble between the booster and liquid when the bomb was evacuated. This was accomplished by subjecting frozen NM to vacuum, sealing the container, and then thawing the NM. This procedure was repeated several times.

FEFO, bis[2, 2-dinitro-2-fluoro-ethyl] -formal was available only in research quantities. It is a liquid with a vapor pressure of about 40 μ at 90°C. The sample was determined to be 94.4% pure by chromatographic analyses. The principle impurity is bis[2, 2-dinitro-2-fluoro-ethyl] -diformal and it contains 0.1% water as received.

Water was removed by vacuum distillation in order to avoid loss of FEFO from the confining cylinder when the calorimeter was evacuated. The empirical formula on which results are based was calculated from elemental analyses and adjusted to carbon equals 5.00.

3. RESULTS and DISCUSSION

3.1 Products from Heavily Confined Charges

Studies^{1,2,7} indicate that the products from heavily confined charges represent those found on the Chapman-Jouguet (C-J) isentrope at temperatures in the range of 1500 to 1800°K. Table 1 lists these products and the heats of detonation for HMX, TNT, NM and FEFO.

As one proceeds down the scale of oxygen balance - FEFO, HMX, TNT - the proportion of carbon which appears as solid carbon increases, and which appears as carbon dioxide decreases. Also, the proportion of hydrogen appearing as hydrogen gas increases, and which appears as water decreases. NM, a low-density explosive with a high hydrogen-to-carbon ratio, is the exception to these trends. It has the same oxygen balance as TNT, yet proportionally more carbon appears as carbon monoxide and less as solid carbon than one might expect from the TNT results. In addition, greater amounts of methane are present in the NM products than for any of the other explosives.

It is noteworthy that all of the fluorine in FEFO appears as hydrofluoric acid. Carbon tetrafluoride or other compounds containing the C-F structure were not observed.

The products from heavily confined charges attain equilibrium under non-ideal gas conditions since the pressure at 1500 to 1800°K is of the order of 5,000 to 50,000 atm. In order to calculate the product composition along the C-J isentrope, one must therefore use complex thermodynamic-hydrodynamic calculations. Calculations

were made by using the two best equations of state available, the Becker-Kistiakowsky-Wilson⁸ (BKW) equation in the RUBY⁹ code, and the LJD¹⁰ equation. The comparisons of observed products with calculated products for the four explosives studied (Tables 2, 3, 4, and 5) are fair. Data of this type will be used to improve equations of state for detonation products.

The ideal experiment to allow isentropic expansion of detonation products is an infinitely long, heavily confined, open-ended charge. For such a configuration end effects would be negligible. However, charge length is limited by the calorimeter dimensions, and end effects are such that some of the detonation products are sufficiently shock heated on colliding with the calorimeter wall to cause re-equilibration. Because of this the ends of the charges were also confined in gold. For oxygen-deficient explosives such as TNT, doing this increases the observed heat of detonation by almost 6%. The change is less for higher oxygen-balanced explosives.

3.2 Products from Unconfined Charges

It has been shown¹ that the temperature at which equilibrium becomes frozen can be found by comparing observed detonation products from unconfined charges with products calculated with ideal gas laws. Work with PETN¹ and the calculations of Jones and Miller⁷ indicated a freeze-out temperature of 1500 to 1800°C. Unconfined charges of HMX and TNT were fired and products were compared (Tables 6 and 7) to those calculated. The agreement is good, confirming the earlier work.

The TNT data indicate that solid carbon equilibrates rapidly during the reshocking of products that occurs with unconfined charges. The value for solid carbon, frozen out in the initial isentropic expansion, is 3.65 moles/mole TNT (from Table 1). If it were not equilibrating, the amount found in the products from unconfined charges (1.01 moles/mole TNT, Table 8) should be at least as large as that found in the products from heavily confined charges.

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Table 1

The Heat and Products of Detonation of Heavily Confined Charges of Explosives^{a,b}

Explosive	HMX	TNT	NM ^c	FEFO ^d
Density (g/cc)	1.89	1.53	1.13	1.60
Charge weight (g)	25	22	15	25
ΔH detonation, 298°K, H ₂ O _(l) , (cal/g)	1479 ± 5	1093 ± 5	1227 ± 5	1227 ± 5
Products (moles/mole explosive)				
CO ₂	1.92	1.25	0.261	3.16
CO	1.06	1.98	0.550	1.88
C(s) ^e	0.97	3.65	0.095	not detected
N ₂	3.68	1.32	0.394	1.99
H ₂ O	3.18	1.60	0.882	2.14
H ₂	0.30	0.46	0.294	0.046
HF	0	0	0	1.87 ^f
NH ₃	0.40	0.16	0.118	0.023
CH ₄	0.039	0.099	0.083	0.009
HCN	0.0081	0.020	0.0081	not detected
C ₂ H ₆	0.001	0.004	0.001	not detected

^aCylindrical charges, 1.27 cm diameter, confined in 1.27 cm gold.^bCorrected for PETN in the initiation system.^cNM = C_{1.00} H_{2.96} N_{0.96} O_{1.92} by analysis and adjusted to C = 1.00. Trace amounts of acetylene were observed.^dFEFO = C_{5.00} H_{5.74} N_{4.09} O_{10.06} F_{1.87} by analysis and adjusted to C = 5.00.

Results are corrected for reaction of HF with stainless steel. Charge not confined on the ends.

^eDetermined-by-difference.^fFrom total fluorine contained in FEFO.

Table 2

Comparison of Calculated C-J Isentrope Products with Observed Products from Heavily Confined Charges of HMX

Products	Observed, Heavily Confined	Moles/mole HMX			
		Calculated			
		BKW C-J Isentrope		LJD C-J Isentrope	
		1520°K	1800°K	1490°K	1760°K
N ₂	3.68	3.97	3.97	3.98	3.97
H ₂ O	3.18	3.11	3.67	2.90	3.06
CO ₂	1.92	2.39	2.13	2.16	2.01
CO	1.06	0.10	0.071	0.77	0.93
C(s)	0.97	1.13	1.68	0.73	0.81
NH ₃	0.40	0.076	0.073	0.047	0.063
H ₂	0.30	0.005	0.001	0.36	0.34
CH ₄	0.039	0.38	0.11	0.34	0.26
HCN	0.0081	0	0	not allowed	

Table 3

Comparison of Calculated C-J Isentrope Products with Observed Products from Heavily Confined Charges of TNT

Products	Moles/mole TNT				
	Observed, Heavily Confined	Calculated			
		BKW		LJD	
		C-J Isentrope		C-J Isentrope	
	1505°K	1835°K	1500°K	1870°K	
C(s)	3.65	3.57	4.50	3.52	3.80
CO	1.98	0.56	0.32	1.60	1.58
H ₂ O	1.60	1.06	1.87	1.33	1.64
N ₂	1.32	1.49	1.48	1.50	1.50
CO ₂	1.25	2.19	1.91	1.53	1.39
H ₂	0.46	0.043	0.017	0.48	0.40
NH ₃	0.16	0.026	0.047	not allowed	
CH ₄	0.099	0.68	0.27	0.34	0.23
HCN	0.020	3.6×10^{-6}	1.3×10^{-6}	not allowed	
C ₂ H ₆	0.004	not allowed		not allowed	

Table 4

Comparison of Calculated C-J Isentrope Products with Observed Products from Heavily Confined Charges of NM

Products	Moles/mole NM				
	Observed, Heavily Confined	Calculated			
		BKW		LJD	
		C-J Isentrope		C-J Isentrope	
	1520°K	1835°K	1500°K	1800°K	
H ₂ O	0.88	0.75	0.77	0.81	0.85
CO	0.55	0.18	0.21	0.43	0.48
N ₂	0.39	0.47	0.47	0.5	0.5
H ₂	0.29	0.049	0.027	0.32	0.29
CO ₂	0.26	0.49	0.47	0.38	0.33
NH ₃	0.12	0.017	0.027	not included	
C(s)	0.095	0	0	0	0
CH ₄	0.083	0.33	0.32	0.19	0.18
HCN	0.0081	0	0	not included	

Table 5

Comparison of Calculated C-J Isentrope Products with Observed Products from Heavily Confined Charges of FEFO

Products	Moles/mole FEFO		
	Observed, Heavily Confined	Calculated BKW C-J Isentrope	
		1520°K	1820°K
CO ₂	3.16	3.92	3.82
H ₂ O	2.14	1.38	1.57
N ₂	1.99	2.04	2.03
CO	1.88	0.83	0.85
HF	1.87	1.87	1.85
H ₂	0.046	0.045	0.025
NH ₃	0.023	0.018	0.026
CH ₄	0.0009	0.24	0.16
CF ₄	0	0	0.005
C(s)	0	0	0.17

Table 6

Comparison of Calculated Equilibrium Products at Constant Volume with Observed Products from Unconfined Charges of HMX^a

Products	Moles/mole HMX		
	Observed Unconfined	Calculated for Ideal Gas	
		1500°K	1800°K
N ₂	4.01	4.00	4.00
CO	2.65	2.36	2.52
H ₂ O	2.50	2.36	2.52
H ₂	1.53	1.64	1.48
CO ₂	1.45	1.65	1.49
HCN	0.0006	0.00002	0.00002
NH ₃	not detected	0.0006	0.0002
CH ₄	not detected	0.0004	0

^a25-g charges at density 1.89 g/cc and 2.54 cm diameter.

Table 7

Comparison of Calculated Equilibrium Products at Constant Volume with Observed Products from Unconfined Charges of TNT^a

Products	Moles/mole TNT		
	Observed Unconfined ^a	Calculated for Ideal Gas	
		1500°K	1800°K
CO	5.89	5.97	6.00
H ₂	2.31	2.10	2.36
N ₂	1.36	1.49	1.47
C(s)	1.01	0.81	0.90
H ₂ O	0.17	0.007	0.003
CO ₂	0.063	0.009	0.003
HCN	0.024	0.018	0.056
NH ₃	0.022	0.0005	0.0003
CH ₄	0.0092	0.192	0.053

^a25-g charges at density 1.53 g/cc and 1.27 and 2.54 cm diameter.