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Energy Output of Insensitive High Explosives by Measuring the Detonation Products [and Discussion]

F. Volk, C. Storm, W. Byers Brown and P. Gray

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Energy output of insensitive high explosives by measuring the detonation products

By F. Volk

Fraunhofer-Institut für Chemische Technologie (ICT), 7507 Pfinztal 1, F.R.G.

The detonation products of high explosives are dependent on pressure and also on the confinement under which the detonation reaction proceeds. To determine the detonation products of less sensitive high explosives such as trinitrotoluene/nitroguanidine and polymer bonded explosive charges with polybutadiene binder containing cyclotrimethylene trinitramine, together with or without aluminium, experiments have been performed in a stainless steel chamber of a volume of 1.5 m^3. These experiments were done under different ambient argon pressures up to 0.3 MPa. Gaseous reaction products were analysed by mass spectrometry and chemiluminescence analysis. Solid reaction products were analysed for measuring the carbon residue or unreacted aluminium. It was found that the detonation products were highly dependent on the ambient pressure of argon. The most important changes of the reaction products and therefore also of the energy output were found between vacuum and atmospheric pressure of argon. With increasing pressure, H_2 and CO decrease and CO_2, H_2, C_s, NH_3, HCN and CH_4 increase together with the reaction enthalpy. By analysing the physical structure of the carbon residue, diamonds have been observed between 4 and 7 nm in diameter.

1. Introduction

Some years ago, safety programs were started with the aim of developing so-called insensitive high explosives (IHE). These explosives should be safe, as far as possible, against heat, radiation, external fire, impact, friction and shock. The explosive charges are composed of insensitive explosive components such as 1,35-triamino-2,4,6-trinitrobenzene (TATB), nitroguanidine (NQ), NTO, etc. But also compositions with plastic bonded explosive (PBX) components exhibit properties of insensitive or less sensitive high explosives.

The energy output released during the detonation reaction of explosives depends on the following parameters: (i) energy of the charge; (ii) oxygen balance; (iii) grain size of the components; (iv) degree of confinement; and (v) completeness of the reaction of metals such as Al, with the reaction products of the explosive.

Confinement influences reaction in so far as it adds resistance to the expansion of the gaseous detonation products and maintains high pressures and temperatures for a longer period of time before lateral rarefactions quench reaction (Price & Zerilli 1981).

By using confinement, the Boudouard equilibrium

$$2\,\mathrm{CO} \rightleftharpoons \mathrm{CO}_2 + \mathrm{C}, \quad \Delta H = -172.7\ \mathrm{kJ\ mol^{-1}}$$

is influenced to form higher concentrations of CO_2 and C_s. Additionally, the amount of H_2O increases whereas H_2 and CO decrease (Ornellas 1982). Both reactions increase the heat of detonation of confined charges.

Earlier investigations have shown that less sensitive high explosives consisting of trinitrotoluene (TNT) and NQ produced very different detonation products when initiated in vacuum compared with those under one atmosphere of argon (Volk 1986), assuming that argon behaves as a confining medium, because the reshocking of the reaction products is reduced dramatically when going from vacuum to 0.1 MPa of argon.

To learn more about prepressurization, other high explosives such as PBX charges based on RDX and NQ with and without additional aluminium in a stainless steel containment were studied. By varying the argon pressure from vacuum up to 0.3 MPa, the detonation products were analysed with regard to the gas and the soot formation. Additionally the heat output was evaluated.

2. Experiments

For the experiments a stainless steel containment with a volume of 1.5 m^3 was used. The cylindrical high explosive charges had a mass of about 300 g without booster. For the initiation, a detonator cap No. 8 together with a 10 g RDX booster were used. Because of the corner effect a second booster of about 18 g having the same diameter as the main charge was glued onto the charge (Held 1989). After hanging the explosive horizontally inside the containment, the vacuum pump was started so as to provide a detonation at reduced pressure or under different pressures of argon. For the reduced pressure experiments we used a vacuum pump which produced after 15 minutes a pressure of about 2 mmHg.

After firing, gas samples were taken for the measurement of the NO content in an NO_x-analyser and the mass spectrometric analysis of the gas products. The reproducibility of the gas composition of several shots was about ±0.5 mol % relative to the mean value.

After the shot the containment was opened and the solid residue collected. This was analysed for carbon, hydrogen and nitrogen as well as for unreacted aluminium by measuring the H_2 formation after treating with HCl.

The solid residue was dried in order to be able to analyse it completely for C, H, N and unreacted Al. For qualifying the analysis, in all cases the theoretical mass balance was calculated and compared with the experimental balance ratio of N/C, N/H and N/O. Because detonator caps consisting of copper sleeves were used, there was no contamination of the unreacted Al contained in the soot.

In some cases, the soot was examined in more detail at the Los Alamos National Laboratory by using X-ray diffraction and convergent-beam electron diffraction. Previous investigations have shown that X-ray diffraction powder patterns exhibit the same diamond spacings as an authentic diamond sample (Greiner *et al.* 1988). The following explosive charges have been investigated: (i) charges of TNT and spherical NQ with a grain size distribution of the NQ spherules of 28 % with 150–200 μm and 72 % with 500–1000 μm; (ii) charges with polybutadiene (PB), binder (PBX); and (iii) PBX charges containing aluminium. Table 1 gives the density and detonation velocity of the explosive charges.

The detonation velocity was measured using explosive charges with 40 mm in diameter and 350 mm in length. The charges were confined in hardpaper tubes with wall thickness of 1.5 mm. Ionization pins were used for the velocity measurements.

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Table 1

composition	density ($g\ cm^{-3}$)	detonation velocity ($m\ s^{-1}$)
TNT	1.64	6900
45% TNT/55% NQ	1.63	7724
45% TNT/55% NQ (glass confinement)	1.63	7724
HX 72		
80% RDX (10 µm)/20% PB	1.48	7750
HXA 123		
56% RDX class C/14% RDX (10 µm) 15% PB/15% Al Alcan 400	1.62	7350

Table 2. *Heats and products of detonation of TNT under varying conditions: comparison between ICT and Ornellas (1982)*

sample	ICT 28/30	detonation calorimeter Ornellas (1982)		
confinement	no	gold	Al_2O_3	no
charge				
density ($g\ cm^{-3}$)	?	1.533	1.533	1.000
diameter (mm)	50	12.7	12.7	12.7
mass TNT (g)	300	22	22	26
booster (g)	29	?	?	?
		products (mol%)		
H_2	3.4	4.3	4.1	20.4
CH_4	0.2	0.9	1.0	0.1
CO	17.2	18.5	18.9	53.9
CO_2	9.9	11.7	12.5	0.3
N_2	13.5	12.3	12.6	11.9
NO	0.07	—	0.01	0.01
HCN	0.8	1.9	0.5	0.3
NH_3	?	1.5	1.8	0.9
H_2O	19.6	14.9	13.3	3.4
C_s	35.4	34.0	35.2	8.8
		$\Delta H_{det}/(kJ\ kg^{-1})$		
experimental	—	4576	4480	2437
calculated from products	4320	4744	4091	2977

The critical diameter of NQ containing charges was about 20 to 25 mm. Because charge diameters of 50 mm, and charge lengths of more than 90 mm, were used, complete detonation must have been achieved.

3. Results

(*a*) *Reaction products of TNT*

The reaction products of a charge consisting of 300 g TNT and 29 g booster without confinement were compared with those published by Ornellas (1982) found using detonation calorimetry (see table 2). Two samples of Ornellas were tested under

Table 3. *Charges of 45% TNT/55% NQ in different* Ar *pressures*

sample no.	1450/1c	1450/2c	1450/3c
Ar pressure (MPa)	vacuum	0.05	0.1
O_2-balance (%)		−47.6	
charge mass/g	331	332	331
$\Delta H_f/(\text{kJ kg}^{-1})$	−661	−662	−657
products (mol%)			
H_2	20.7	8.3	5.0
CH_4	0.04	0.1	0.24
CO	32.1	17.9	14.3
CO_2	3.7	7.9	10.3
N_2	27.5	26.1	25.6
NO	0.1	0.1	0.13
HCN	0.3	3.2	3.6
NH_3	0.5	3.0	4.9
C_2H_2	0.02	0.03	0.1
H_2O	10.7	19.6	20.0
C_s	4.4	13.8	15.9
$\Delta H_{\text{det}}/(\text{kJ kg}^{-1})$	2999	3653	3763
C in residue (% of total C)	10.8	32.2	35.7
gas formation/(mol kg^{-1})	44.5	37.9	35.7

confinement: one in a cylinder of gold, the other in a cylinder of alumina (Al_2O_3). A third sample (26 g) was without confinement. It is interesting to see that the unconfined large TNT charge (300 g TNT + 29 g booster) exhibits nearly the same reaction products as the small charge (22 g) confined in gold, but is very different from the unconfined small TNT charge (26 g). This leads to the conclusion that for a large charge with a diameter of about 50 mm, argon behaves as a confining medium.

Charges with 45% *TNT*/55% *NQ*

To determine the influence of different argon pressures on the detonation products of cast high explosives consisting of 45% TNT and 55% spherical (NQ), experiments were conducted in the containment described. In each case the detonation products of three experiments were analysed: one in the evacuated containment, the other under 0.05 MPa and the third under 0.1 MPa of argon pressure (see table 3).

Additionally, three charges of the same mass and the same composition, but in a glass confinement with a thickness of 9 mm were tested, also in vacuum and under 0.05 and 0.1 MPa of argon. The results are listed in table 4.

The results of the unconfined shots in table 3 show that the products formed under an evacuated condition are very different from those produced under 0.05 MPa and 0.1 MPa argon. With increased pressure we see a distinct decrease of H_2 and CO and a strong increase of CO_2, H_2O and solid carbon (C_s). The enthalpy of detonation (ΔH_{det}) increases markedly from vacuum to 0.05 MPa, but only slightly from 0.05 MPa to 0.1 MPa of argon. The highest value of the gas formation is obtained in vacuum.

It is also of interest to see how the concentrations of NH_3 and HCN increase with higher argon pressure; the same holds also for CH_4 and C_2H_2. It seems as if argon behaves as a confinement. It leads to a distinct increase in the heat of detonation

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Table 4. *Charges of 45% TNT/55% NQ in glass confinement and different* Ar *pressures*

sample no.	1451/1	1451/2	1451/3
Ar pressure/MPa	vacuum	0.05	0.1
O_2-balance (%)		−47.6	
charge/g	332	335	332
ΔH_f/(kJ kg^{-1})	−656	−658	−658
products (mol%)			
H_2	8.7	4.2	3.1
CH_4	0.2	0.4	0.44
CO	15.9	10.2	9.3
CO_2	7.9	11.9	12.7
N_2	27.3	26.0	25.6
NO	0.06	0.05	0.14
HCN	1.35	2.4	1.1
NH_3	1.15	4.7	5.3
C_2H_2	0.07	0.1	0.13
H_2O	20.5	20.7	21.0
C_s	16.8	19.2	21.3
ΔH_{det} (kJ kg^{-1})	3779	3960	4003
C in residue (% of total C)	39.8	43.3	47.2
gas formation/(mol kg^{-1})	37.1	34.4	33.0

Table 5. *Charges of 45% TNT/55% NQ in* Ar *pressures of* 0.1 *to* 0.3 MPa

sample no.	1450/3c	1450/2b	1450/3b
Ar pressure (MPa)	0.1	0.2	0.3
O_2-balance (%)		−47.6	
charge mass/g	331	328	327
ΔH_f/(kJ kg^{-1})	−657	−648	−646
products (mol%)			
H_2	5.0	4.2	4.4
CH_4	0.2	0.3	0.35
CO	14.3	11.4	11.4
CO_2	10.3	10.7	11.3
N_2	25.6	25.2	24.8
NO	0.13	0.22	0.3
N_2O	—	0.5	0.8
HCN	3.6	1.4	1.0
NH_3	4.9	3.4	3.6
C_2H_2	0.1	0.1	0.1
H_2O	20.0	21.7	20.8
C_s	15.9	20.8	21.2
ΔH_{det}/(kJ kg^{-1})	3763	3790	3706
C in residue (% of total C)	35.7	46.4	46.6
gas formation/(mol kg^{-1})	35.7	33.4	32.8

because of the increase of the species representative of a lower temperature isentrope such as CO_2, H_2O and solid carbon (C_s) and a corresponding decrease of the species representative of a higher temperature isentrope: CO and H_2 (Ornellas 1982).

From vacuum to 0.1 MPa of argon, the enthalpy of reaction increases from 2999 to 3763 kJ kg^{-1} by 20.6%. On the other hand, the glass confined charge exhibits at 0.1 MPa of argon a value of 4003 kJ kg^{-1}, which corresponds to an increase of only

Table 6. *Analysis of the residual soot of the charges 45% TNT/55% NQ*

sample no.	Ar pressure MPa	C (%)	H (%)	N (%)	O (%)	total carbon/g analysed	total carbon/g calculated
1450/1c	vacuum	72.5	3.5	8.5	15.5	5.9	8.1
1450/2c	0.05	83.5	2.4	7.7	6.4	20.9	24.2
1450/3c	0.1	78.5	2.2	11.5	7.8	31.6	26.6
1450/1b	0.1	73.8	2.4	13.8	10.0	31.7	36.6
1450/2b	0.2	65.7	3.0	20.4	10.9	36.1	34.6
1450/3b	0.3	61.9	3.0	23.4	11.7	35.6	34.6

6.4%, compared with the unconfined charge at the same pressure (see tables 3 and 4).

To study the effects of argon in more detail, detonation products for argon confinement at 0.2 and 0.3 MPa were also analysed. The results are listed in table 5. As we see, an additional pressure of argon (0.2 MPa) increases the heat of reaction only by 27 kJ, and a further pre-pressurization to 0.3 MPa exhibits no additional improvement of the heat output.

Analysis of soot

After each shot, the residue in the containment was collected by using a dust cleaner, dried and then analysed for carbon, hydrogen and nitrogen. For comparison, the carbon residue was also calculated from the mass balance. Table 6 lists the elemental analysis of the soot as well as the analysed and calculated amounts of carbon. The carbon content clearly increases when going from vacuum to 0.05, 0.1 and 0.2 MPa of argon. The elemental analysis also shows that the nitrogen content increases when the argon pressure is raised. It is assumed that the formation of substances containing nitrogen increase in the same manner as HCN and NH_3 (Greiner *et al.* 1988). It is suspected that the formation of diamonds is also favoured by a stronger confinement (Greiner 1988).

(*b*) *Reaction products of* PBX

Detonation products of PBX-charges consisting of 80% RDX with a mean grain size of 10 μm and 20% of a PB binder are listed in table 7. The experiments were conducted in vacuum, under 0.05 MPa and 0.1 MPa of argon. The detonation products behave in the same way as discussed before. A decrease of H_2 and CO and an increase of CO_2, H_2O, C_S, NH_3, HCN, C_2H_2 and CH_4, going from vacuum to 0.05 and 0.1 MPa of argon. Additionally we see an increase of the enthalpy of reaction and a decrease of gas formation.

The reaction enthalpy is much higher than that of the charge containing 45% TNT and 55% of NQ. The reason for this is that the enthalpy of formation is much less negative for the RDX containing explosive (-94 kJ kg^{-1} than that of 45 TNT/55 NQ with a value of -646 kJ kg^{-1}).

(*c*) *Reaction products of* PBX *charges containing aluminium*

To find out how complete aluminium reacts in a detonation process under different pre-pressurization, a high explosive charge consisting of 56% RDX Class C, 14% RDX (10 μm), 15% Al Alcan 400 and 15% PB binder was detonated in vacuum and in argon atmosphere (0.1 MPa). The results are listed in table 8. We see that the

Table 7. PBX *charges with 80% RDX* (*10* μm)*/20% PB*

sample no.	HX 72/1	HX 72/2	HX 72/3
Ar pressure (MPa)	vacuum	0.05	0.01
O_2-balance (%)		−73.3	
charge mass/g	329	328	330
ΔH_f/(kJ kg^{-1})	−94	−90	−95
products (mol%)			
H_2	33.5	15.0	12.3
CH_4	0.1	0.7	2.9
CO	34.4	17.3	13.1
CO_2	1.2	3.5	6.6
N_2	18.8	18.0	18.8
NO	0.05	0.03	0.02
HCN	0.1	0.8	0.9
NH_3	0.5	2.9	2.8
C_2H_2	—	0.06	0.5
H_2O	4.8	19.6	19.9
C_s	6.6	22.2	22.2
ΔH_{det}/(kJ kg^{-1})	2949	4214	4440
C in residue (% of total C)	15.7	49.9	47.3
gas formation/(mol kg^{-1})	52.1	42.0	39.7

Table 8. PBX *charges with 15% PB/15% Al Alcan 400/56% RDX class C/14% RDX* (*10* μm)

sample no.	HXA 123/1	HXA 123/3
Ar pressure (MPa)	vacuum	0.1
O_2-balance (%)	−69.3	
charge mass/g	331	331
ΔH_f/(kJ kg^{-1})	−73	−71
products (mol%)		
H_2	29.5	25.8
CH_4	0.04	1.1
CO	26.1	20.1
CO_2	0.01	2.7
N_2	16.9	18.1
NO	0.07	0.05
HCN	0.1	2.35
NH_3	2.2	0.9
C_2H_2	0.04	0.3
C_2H_4	0.03	0.2
H_2O	4.2	7.2
Al_2O_3	4.6	3.9
Al	1.6	3.0
C_s	14.6	14.3
$K_p(T)$	?	2.018
freeze out temp/K		1365
ΔH_{det}/(kJ kg^{-1})	5143	5066
C in residue (% of total C)	35.6	34.5
unreacted Al (%)	15.0	28.0
gas formation/(mol kg^{-1})	38.6	37.0

reaction products analysed under vacuum conditions are much closer to those of 0.1 MP of argon than obtained in the previously described shots.

This means that the influence of argon as a confining medium is reduced by using Al containing high explosives. This behaviour can also be derived from the values of the enthalpies of reaction, which only exhibit a difference of 1.5% between the detonation in vacuum and atmospheric pressure of argon.

Regarding the reaction of Al, the results show an amount of 15% unreacted Al for the vacuum shot compared with 28% Al for 0.1 MPa of argon. This means that the amount of unreacted Al is considerably higher when the detonation is performed under 0.1 MPa of argon. The reason for the incomplete Al reaction is the negative oxygen balance of -69.3% which is responsible for the very low formation of CO_2; CO_2 is needed for the reaction: $3\ CO_2 + 2Al \rightarrow Al_2O_3 + 3\ CO$; $\Delta H = -826.3$ kJ.

4. Conclusions

It has been shown that the analysis of reaction products formed during the detonation of high explosives in a containment of 1.5 m^3 is very useful for understanding the detonation behaviour under different conditions.

The influence of confinement on the detonation products and therefore also on the heat of detonation can be evaluated. In addition, the completeness of the reaction of aluminium or other ingredients can be analysed.

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Discussion

C. Storm (*Los Alamos, U.S.A.*). Have you done any chemical analyses of products from detonation of explosives with Cl/F binders? Additionally, could you comment on how your analytical results compare with calculated results?

F. Volk. We have no chemical analysis of detonation products of explosives with Cl/F binders.

The analytical results are not in a good agreement with calculated values because there is no possibility of calculating endothermic reaction products such as NO, N_2O, and HCN. In addition, it is very difficult to calculate the carbon formation because we have no Boudouard reaction as required from the BKW-code, going completely to CO_2 and C such as

$$2CO \longrightarrow CO_2 + C.$$

W. Byers Brown (*University of Manchester, U.K.*). What are the final pressures in the chambers due to the detonation product gases, and inert gases, if any in the various initial cases he describes?

Although I accept the assertion that kinetic processes are almost certainly involved in producing the differences in composition of the final detonation gas between detonations carried out *in vacuo* and those carried out in the presence of argon, to model the process adequately it will be necessary to use an equation of state (EOS) that is valid over a wide range of pressure. Neither the BKW EOS nor the Jacobs EOS (used in JCZ3) satisfies this criterion. For a recent review of EOS see W. Byers Brown and B. Arnold, *Review of equations of state valid to high density*. Health and Safety Executive, report no. RPG 2518 (1991).

F. Volk. The pressure that is measured immediately after the detonation in the 1.5 m^3 containment under argon atmosphere of 0.1 MPa using 300 g TNT/NQ (50:50) is about 0.132 MPa. This pressure decreases after 10 min to about 0.124 MPa because of condensation and cooling processes.

P. Gray (*Cambridge University, U.K.*). What is the reproducibility attained when working *in vacuo*. Maybe if the vacuum is around 10 mmHg there is still an appreciable mass of oxygen present: $1.5\ m^3 \times 1.4\ kg\ m^{-3} \times 1/76$ is about 30 g, whereas the total mass of explosive is about 330 g. If detonations are performed in air at atmospheric pressure, then the mass of oxygen is so much the greater (say 300 g). However, most interest attaches to the purpose behind the argon experiments: when choosing to do them what was the expectation, and how did they expect the argon to act?

F. Volk. The reproducibility of the vacuum shots was the same as the shots in argon: for the main components such as H_2, N_2, CO, CO_2, the reproducibility of several detonations with the same charge composition is better than 1% (vol.). If we evacuate for 15 min, we have a vacuum of about 1 mmHg. In this case we have only 2 dm^3 of air in our containment of 1500 dm^3. The interest of the experiments in argon was to be able to analyse the water gas reaction products H_2, CO, CO_2, H_2O and herewith the freeze-out temperature of the water gas reaction after the determination of the equilibrium constant

$$K_p = P_{CO}\, P_{H_2O} / P_{CO_2}\, P_{H_2}.$$

In addition, we know from combustion experiments of nitric ester containing propellants, that the combustion gases are very strongly dependent on the burning pressure, especially at the low-pressure range. Therefore we wanted to determine whether there is a pressure dependence in the detonation experiments.