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REAL TIME ANALYSIS OF DETONATION PRODUCTS

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ABSTRACT

We have determined the mass spectrum and the time evolution of the freely expanding products of highly shocked and detonating substances. So far we have studied pentaerythritol tetranitrate (PETN), hexanitrostilbene (HNS), cyclotrimethylene trinitramine (RDX) and nitric oxide (NO). For the case of NO, we find that N_2 and O_2 are important products of the detonation. Other reaction products are N_2O and NO_2, some of which arise from secondary reactions between O_2 and unreacted NO. The other explosives give rise to a rich spectrum that includes many molecules not found in equilibrium spectra. Comparative spectra for two of these common explosives, RDX and HNS, are presented.

INTRODUCTION

The analysis of detonation products usually involves the mass spectrum of [illegible] obtained long after the detonation has occurred and after the temperature of these products has reached ambient conditions.[1] These spectra are simple and reflect nearly the lowest equilibrium conditions of the atomic mixture. Very little information is available about pathways through which the products pass to reach these final conditions. We have developed a method of analysis which allows us to determine the identity of the gaseous products several microseconds after the detonation has occurred.[2] We can also determine the relative time scales during which these products evolved.

By measuring the relative concentrations of the gaseous products we need to find the principal chemical reaction mechanisms that release energy to drive the detonation wave through the explosive. NO was of special interest to us because it has a simple molecular constituency while still having the characteristics of a high explosive. The product molecules have all been studied extensively,[3] at least under normal conditions, so that such characteristics as optical spectra, ionization efficiency, etc., are well known. NO seems to offer considerable promise for our mechanistic studies.

EXPERIMENTAL

All of our studies involve laboratory scale detonations utilizing explosive samples that consist of quantities of a gram or less, usually 25-50 mg. The experiments are conducted in high vacuum. After detonation, when the front of the expanding products has reached distances of several charge diameters, the flow becomes free molecular flow, i.e., collisionless. At this stage, we form the products into a molecular beam by collimating a small fraction of this "cloud" which passes unimpeded through a series of small apertures into a quadrupole mass filter detector. Fig. 1 is a schematic arrangement of the apparatus.

Fig. 1 is a sketch of the essential features of the detonation products analysis apparatus. The reaction chamber has a volume of [illegible] ℓ. The distance from the detonating charge to the skimmer is [illegible] cm. The total flight path is 1[illegible] cm. The [illegible] structure [illegible] placement of auxiliary experiments.

By measuring the time of flight of the molecules from the charge to the mass filter, the product velocity can be obtained, and the data transformed [illegible].

The figure also shows the special arrangement used for nitric oxide studies. Because of the physical characteristics of NO, we found it necessary to use it in its solid phase. Thus the rotatable carousel shown in the figure is capable of being cooled to 30-35 K. Six charges of up to [illegible] grams of NO were useable without the need to break the vacuum for recharging. For the more common explosives, PETN, etc., [illegible] to [illegible] charges at room temperature were accommodated.

Fig. 2 shows typical data as displayed by the multichannel scaler (MCS). The time axis is obtained simply by using the equation t = (n [illegible])Δt where n is the channel number displayed and Δt is the dwell time per channel.

Each set of data of the type shown in Fig. 2 is converted to a flux distribution, and the mass spectrum is obtained by summing these distributions. Usually, the sum is done over a short length of time; in the case of [illegible] this was [illegible] μs

Fig. 2 Plot of the number of ions detected in each channel of the MCS. These are for M = 28, 32 and 46 (N_2, O_2, NO_2) in the detonation of [illegible]. The channel number has been changed to time of arrival, the dwell time Δt = 10 μs.

Except for NO all of the charges were pure explosives, pressed into pellets having a density of [illegible] g/cm³. They were detonated by a copper bridge/Kapton slapper driven by 2.4 Joules delivered in 4-5 ns. In the case of NO, a 25 mg pellet of PETN acts as a booster. A foil of aluminum covers the pellet, which helps to keep the whole detonator assembly at 33 K. The NO is deposited from a gas jet positioned over the detonator, onto the foil.

RESULTS

For each of the common explosives, we find that with only a few exceptions, all of the products have a common threshold time of arrival. That is, for one explosive, the ion counts exhibit a threshold at nearly the same channel number irrespective of mass. Mass 18, which is predominantly water, arrives at the same time as mass 44 which is CO_2 or N_2O. This indicates that the velocity of the molecules is determined by the hydrodynamic expansion of the products instead of by the initial temperature of the detonation products. That is, the mean velocity of the molecules at the temperature of the products is less than that imparted by the expansion, as occurs in a high Mach number jet expansion. For PETN, this velocity is about 10 km s^{-1}, while for HMX and RDX it is [illegible] km s^{-1}. A CO_2 molecule having this velocity has a kinetic energy of [illegible] eV.

The mass spectrum of these detonation products differs considerably from the stable product analysis taken 1 ms after detonation.[1] It is a richer spectrum, containing many radical species. Even for the stable products the intensities are much different than expected from equilibrium calculations. Fig. 3 is a composite showing the mass spectrum of HMX and RDX. RDX has a very similar spectrum to PETN, which has [illegible] reported. The intensities of both data have been adjusted for instrument sensitivities and corrected to unit ionization efficiency relative to N_2.[6] For both HMX and RDX, one mass is predominant, having an intensity of from 5 to 10 times larger than any other single feature. Mass 43, a combination of N_2 [illegible]

~~single feature~~. Mass 28, a combination of N_2 and CO, has that characteristic for HNS, while mass 18, H_2O, is that for RDX. We were able to obtain an atom balance for the HNS products that accounted for all of the C, N, H, but was short of O by 25%. In that case, N_2 and CO combined accounted for 50% of the product intensity. In contrast, in equilibrium measurements these only account for 38% of the product. The difference is even larger for the H_2O peak of RDX. The equilibrium measurements show it with an intensity of 29% of the total products, and also that N_2 has a higher intensity than H_2O.

Fig. 3 The mass spectrum of the indicated explosive. These are sums of all of the ion counts up to 400 μs for each mass. They have been adjusted for sensitivity and ionization efficiency when possible.

We call attention to the distribution in carbon clusters, C_n, that appear in the HNS spectrum. We were able to identify up to C_5, M = 60, but we did observe higher masses up to C[illegible].

Turning to HNS, we were able to account for all of the products using the overall mechanism shown in Table 1. Also shown in the Table are the observed products and their relative intensities.

Table 1. The observed products and their intensities. The reactions that lead to these products and the thermochemistry are shown below.

Product Molecule	Mass	Total Counts	Integrated flux Normalized
O Atom	16	97[illegible]	--
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	1,[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	0	
[illegible]	[illegible]	0	[illegible]
[illegible]	7[illegible]	0	[illegible]

REACTIONS AND THERMOCHEMISTRY

	ΔH, kcal/mole	Fraction Nitric Oxide
(1) $NO \longrightarrow 1/2\ N_2 + 1/2\ O_2$	-21.6	0.19
(2) $NO \longrightarrow 1/3\ N_2O + 1/3\ NO_2$	-12.4	0.36
(3) $NO + 1/2\ O_2 \longrightarrow NO_2$	-13.7	0.10
		0.65

(4) $[N_2O] + 2[N_2] = 2[O_2] + [NO_2]$.

The data support the mass balance of Eq. 4 to 5%.

Our data indicate that 65% of the NO was used up in reactions, 29% of that in the detonation reaction.

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4. [illegible], J. Chem. Phys. 46, 1686 ([illegible]); Kieffer LJ and Dunn GH, Rev. Mod. Phys. 38, 1 ([illegible]); Meyer RT and Lynch AW, High Temp. Science, 5, [illegible]; Cornu A and Massot R, "Compilation of Mass Spectral Data," VI (Heyden & Son, 1975).

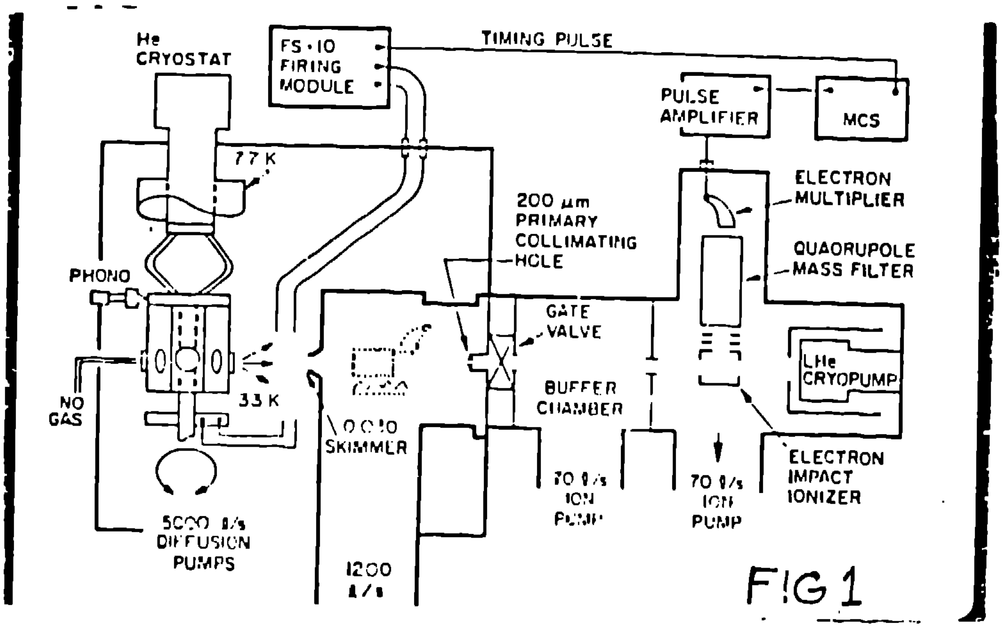
He CRYOSTAT
77 K
FS-10 FIRING MODULE
TIMING PULSE
PULSE AMPLIFIER
MCS
ELECTRON MULTIPLIER
QUADRUPOLE MASS FILTER
200 μm PRIMARY COLLIMATING HOLE
GATE VALVE
BUFFER CHAMBER
LHe CRYOPUMP
PHONO
NO GAS
33 K
0.010 SKIMMER
ELECTRON IMPACT IONIZER
70 l/s ION PUMP
70 l/s ION PUMP
5000 l/s DIFFUSION PUMPS
1200 l/s

FIG 1

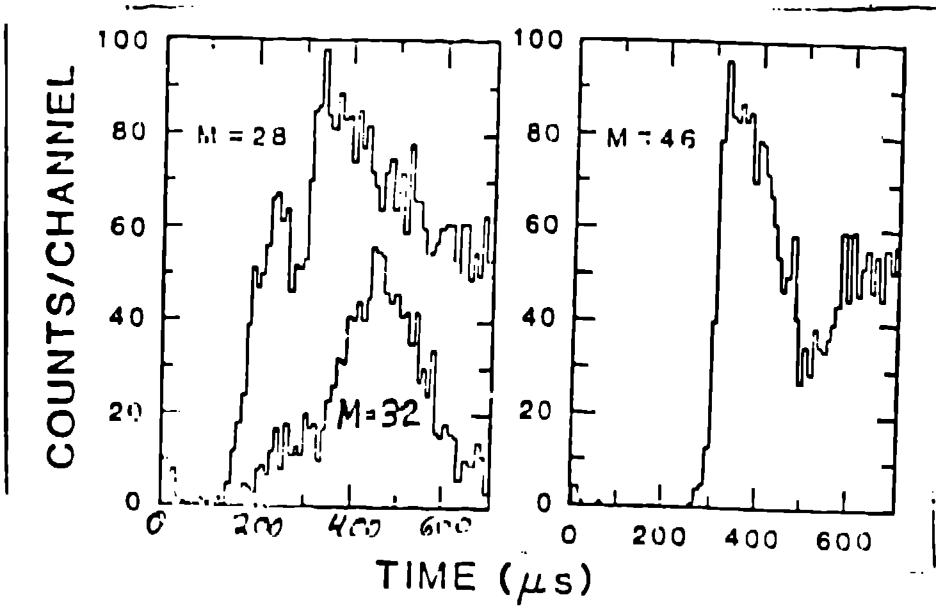
COUNTS/CHANNEL
100
80
60
40
20
0
M = 28
M = 32
0
200
400
600
100
80
60
40
20
0
M = 46
0
200
400
600
TIME (μs)

FIG.2

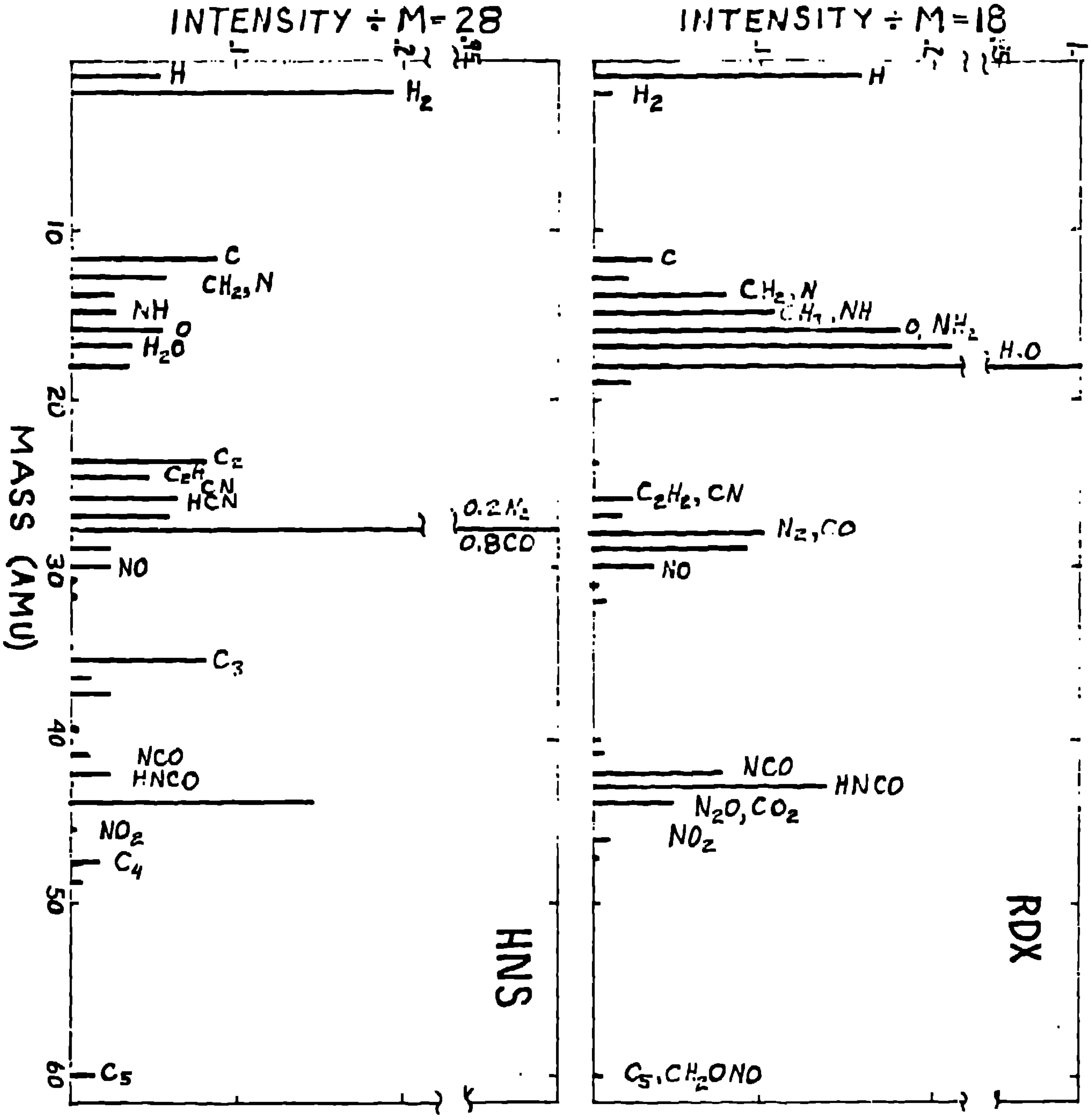
INTENSITY ÷ M=28
INTENSITY ÷ M=18
MASS (AMU)
10
20
30
40
50
60
H
H2
C
CH2, N
NH
O
H2O
C2
C2H
CN
HCN
0.2 N2
0.8 CO
NO
C3
NCO
HNCO
NO2
C4
C5
HNS
H
H2
C
CH2, N
CH3, NH
O, NH2
H2O
C2H2, CN
N2, CO
NO
NCO
HNCO
N2O, CO2
NO2
C5, CH2ONO
RDX

FIG. 3