

Decomposition of solid explosives by laser irradiation: a mass spectrometric study

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Experimental investigations have been made in which single crystals of solid explosives such as cyclotrimethylene trinitramine, RDX, pentaerythritol tetranitrate, PETN, AgN_3 and $\text{Pb}(\text{N}_3)_2$, were irradiated with a focused laser beam of wavelength 266 nm and duration ~ 5 nsec in an ultra high vacuum system housing a fast and sensitive time-of-flight mass spectrometer. From the mass spectra (both +ve and -ve ions) of the chemical species obtained, possible decomposition schemes of RDX and PETN have been proposed. For silver and lead azides, the laser irradiation did not cause explosions if the power density was sufficiently low, but micrometre size craters were formed. In the mass spectra of AgN_3 products N_3^- and silver cluster ions, Ag_n^+ , have been found for the first time. It has been suggested that such investigations may possibly throw some light on our understanding of the reactions taking place in a deflagration/detonation wave.

1. Introduction

The use of focused laser beams in conjunction with mass spectrometry has proven valuable in the micro-analysis of materials and the study of decomposition of solids over the past two decades [1]. Nearly ten years ago, a commercial instrument became available which combined a laser induced ionization source with a time-of-flight spectrometer under the generic name LAMMA, standing for laser microprobe mass analyser. These early machines all worked in the transmission or grazing incidence modes with the laser and mass spectrometer on opposite sides of the sample. More recently, a new commercial system has been developed which is capable of analysis in the reflection mode and therefore suitable for the analysis of bulk samples [2]. The system is called LIMA, an acronym for "laser ionization mass analyser". An important feature of this system is that ionized species are formed by the laser pulse alone.

The use of a Q-switched laser beam of the LIMA allows us to produce very localized heating in a region of diameter 1 to 3 μm to very high temperatures in a short time of ~ 5 nsec. Such high temperature conditions prevail in a detonation wave in which pressures of up to several hundred kbar may exist. The incident laser beam can also cause localized high pressures of magnitude of tens of kbar [3], and therefore the LIMA technique is especially attractive in possibly providing a simple laboratory method for studying the decomposition of reactive materials under conditions of transient high temperatures and pressures.

Our investigations have shown that the LIMA can be successfully employed for studying reactive materials and the findings from experiments on explosives such as RDX, PETN, AgN_3 and $\text{Pb}(\text{N}_3)_2$ are reported below.

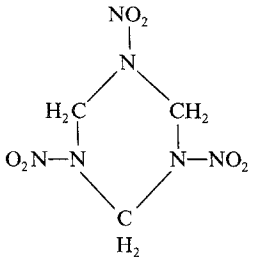
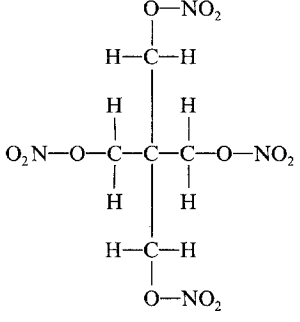
2. Experimental procedures

The experiments were carried out under ultra high vacuum conditions in a LIMA model 2A (Cambridge Mass Spectrometry Ltd) of the Department of Metallurgy and Materials Science of this university. The instrument incorporates a Q-switched Nd: YAG laser; its beam is frequency quadrupled to give a pulse of ~ 5 nsec in duration at a wavelength of 266 nm. The maximum output energy of the laser at this wavelength is up to 20 mJ but that reaching the target is only up to $\sim 500 \mu\text{J}$. The power density at the target can be varied in the range 10^9 to $10^{11} \text{ W mm}^{-2}$ by defocusing the laser spot. The ions produced from the irradiated spot (diffraction limited diameter: 1 μm) on the target surface are immediately accelerated by a potential fall of +3 kV or -3 kV over a distance of 14 mm, before going into the field-free drift tube, 2 m in length. This means that the time required to extract an ion of 1 atomic mass unit (a.m.u.) from the field region is ~ 40 nsec, whereas it is ~ 400 nsec for an ion of 100 a.m.u. Therefore, if there is no fragmentation of the ions during their passage through the field-free drift tube, the recorded mass spectra will represent the products which existed within a microsecond of their formation at the sample surface.

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TABLE I Chemical formulae of the various explosives

Explosive	Chemical formula
Cyclotrimethylene trinitramine (RDX)	
Pentaerythritol tetranitrate (PETN)	
Lead azide	$(\text{N}=\text{N}=\text{N})^- \text{Pb}^{++} (\text{N}=\text{N}=\text{N})^-$
Silver azide	$\text{Ag}^+ (\text{N}=\text{N}=\text{N})^-$

There is an electrostatic reflecting element at the end of the drift tube, which provides a correction for the spread in the initial energy of the ions. The mass resolving power of the instrument is better than 500 FWHM (full width half maximum) and the time spectrum of the ionic current, obtained over a period of up to 100 μsec , is digitized and stored on a computer. A detailed description of the instrument may be found elsewhere [2].

The materials investigated were: (1) cyclotrimethylene trinitramine, RDX, (2) pentaerythritol tetranitrate, PETN, (3) silver azide, and (4) α - and β -lead azides. The chemical formulae of the materials are given in Table I. RDX and PETN are commonly-used secondary explosives, while the other two are primaries and are extensively used in the initiator devices as detonants. Single crystals of RDX, 3 to 4 mm across, were obtained by slow cooling of its solution in analar acetone at 70°C to room temperature, whereas single crystals of PETN of a similar size were prepared by slow evaporation of its saturated solution in analar acetone at room temperature. Single crystals of silver azide of size 100 μm \times 100 μm \times 10 mm were recrystallized from its solution in ammonia, whereas lead azide crystals of similar dimensions were grown by a diffusion method.

For analysis in the LIMA, the crystal under study was mounted on a metallic stud with a piece of double-sided adhesive tape. A fine wire stainless steel mesh, in electrical contact with the stud, lightly pressed on to the crystal, covering it completely. This mesh was necessary in order to avoid distorting the ion optics in the extraction region due to the electrical charging of the crystal surface during the laser irradiation.

The impact of the focused Q-switched laser beam caused craters in all specimens. Moreover, RDX and PETN showed some cracking around the craters. The damage was first photographed under an optical

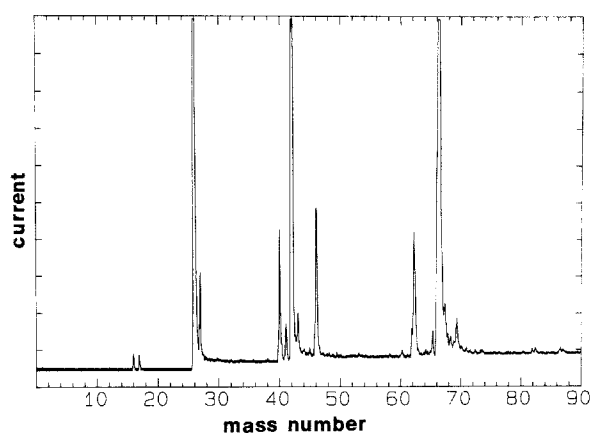


Figure 1 Negative ion mass spectrum of RDX. Small peaks exist for $m = 125$ and 134, but have not been shown.

microscope within 2 h of the irradiation. The specimens were then coated with a thin film of silver or gold and examined in a scanning electron microscope (Cambridge Stereoscan 250 mk 2).

3. Results

Representative results from the LIMA experiments are presented in Figs 1 to 6, which plot ionic current (either negative or positive) against mass number (all ions have been assumed to be singly charged and the identification of the peaks has been done according to the corresponding mass and the structure of the parent molecule). For this very short time in which the mass spectra are taken, it is not possible to give a thermodynamically stable charge distribution on the products. We first consider RDX (Fig. 1). The detected species can be identified as the negative ions of O, OH, CN, HCN, NCN, N(HC)N, N(H₂C)N and NO₂ for mass numbers 16, 17, 26, 27, 40, 41, 42 and 46, respectively.

For peaks at higher mass numbers, the assignment becomes ambiguous and uncertain. The one at $m = 62$ could be due to NO₃; that at 65 can possibly be due to CN(HC)NC; and that at 66 may be CN(H₂C)NC and/or C₂N₃. At still higher mass numbers peaks occur for $m = 86, 90, 93$ and 98, 134 and 176, which, excepting $m = 90$, may be due to the ions (CH)₂N-NO₂, (CH)(NCNC)(NN), (CH₂)₃N₂(NN), H₂C(N-NO₂)₂ and (CH₂)₃(N-NO₂)₂N, respectively.

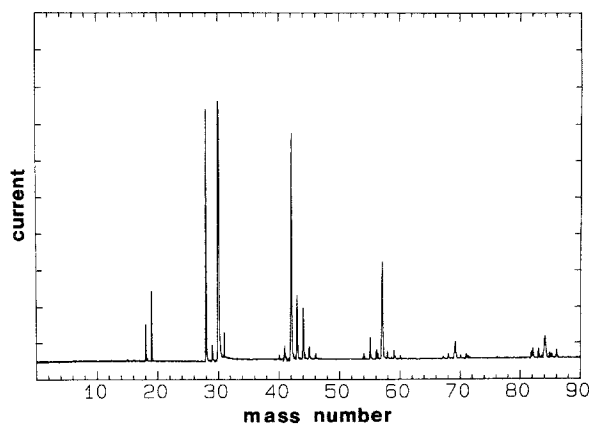


Figure 2 Positive ion mass spectrum of RDX. Small peaks at 125 and 130 have not been shown.