JOURNAL OF MATERIALS SCIENCE 26 (1991) 2199–2207

Rapid mass spectrometric analysis of fragments of trinitrotoluene, picric acid and tetryl generated by laser irradiation

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Experiments have been made in which single crystals of nitroaromatic explosives such as trinitrotoluene, picric acid and tetryl were irradiated with a focused laser beam of wavelength 266 nm and of duration of ~5 n sec in an ultra-high vacuum system housing a sensitive and fast (microsecond time resolution) time-of-flight mass spectrometer. Both positive and negative ions of the products of decomposition were mass-analysed and it has been possible to propose the decomposition schemes of the different explosives. An important finding is that the substituents on the phenyl ring do not affect the breakdown schemes of the different explosives. This has important implications for understanding the different impact sensitivities of these explosives.

1. Introduction

The use of mass spectrometry in studies of the products of decomposition and detonation of explosives has been of considerable importance in understanding and elucidating the various chemical steps which lead to the breakdown of the parent molecules [1, 2]. In such studies it is particularly important that the mass analysis of the products is carried out as soon as they are formed, and at present instruments are available with which the effective time delay between the formation of the products and their detection is about a microsecond or less. (This is slow on the chemical time scale, but it is the best we can achieve at present.) Such short time delays make the investigations of the decomposition/detonation paths particularly attractive, and some recent results from laser decomposition of AgN_3, PbN_6, PETN and RDX can be found in Tang *et al.* [3].

One particular advantage of such investigations is that they may help us in understanding the reasons as to why some minor chemical differences in a series of explosives cause a considerable variation in their sensitivity to impact or other mechanical stimuli. For example, aromatic explosive molecules such as trinitrotoluene (TNT), picric acid (PIC) and tetryl (TET) are quite similar, except for the substituents $-CH_3$, $-OH$ and $N(CH_3)NO_2$, respectively. However, their sensitivity to impact is markedly different (see [4] and Table I below). It has been proposed by Owen and Politzer [4] that the electron-donating ability of the non-nitro substituents on the phenyl ring correlates with the relative impact and shock sensitivity. The electron-donating ability of the substituents affects the amount of charge on the carbon of the $C-NO_2$ bond, but has a much weaker influence on the charge on the nitrogen. Consequently the variation of the charge on the carbon results in the variation of the C–N bond strength. Therefore, the weaker the bond strength the greater is the impact and shock sensitivity. It is interesting that a somewhat similar explanation has been proposed by Cook and Haskins [5] for the sensitization of nitromethane by amines.

In the investigation described below we have examined with a time-of-flight mass spectrometer, having a submicrosecond time resolution, the breakdown behaviour of TNT, PIC and TET when these materials are irradiated with high-power laser pulses. The results show that, irrespective of the different substituents, the phenyl ring breaks up only after first losing the substituents. In other words, they do not appear to change the stability of the phenyl ring.

2. Experimental procedure

The experimental investigations were carried out under ultra-high vacuum conditions in a LIMA model 2A (Cambridge Mass Spectroscopy Ltd). The instrument incorporates a Q-switched Nd:YAG laser; its beam is frequency-quadrupled to give a pulse of ~ 5 nsec in duration and of a wavelength of 266 nm. The maximum output energy of this laser at this wavelength is up to 20 mJ, but that reaching the target is only up to

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~ 500 μJ. The power density at the target can be varied in the range of 10^9 to 10^{11} W mm^{-2}, mainly by defocusing the size of the laser spot. In this machine, the latter can be as small as ~ 1 μm. The ions produced from the irradiated spot on the target surface are immediately accelerated by a potential fall of + 3 or − 3 kV over a distance of 14 mm, before going into a 2 m long field-free drift tube. The ion detection system is located at the exit end of this drift tube. 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. This means that if there is no fragmentation of the ions during their passage through the field-free drift tube, the detected ions will represent the products existing within a microsecond of their formation at the target surface. Further details of the mass spectrometer may be found elsewhere [6].

The chemical formulae of the materials investigated, along with some relevant properties, are shown in Table I. Experiments were performed on individual single crystals of these materials, which were prepared by slow recrystallization from solution of each material in acetone at room temperature. Typically, the crystal sizes were ~ 2.5 mm across and ~ 0.5 mm thick.

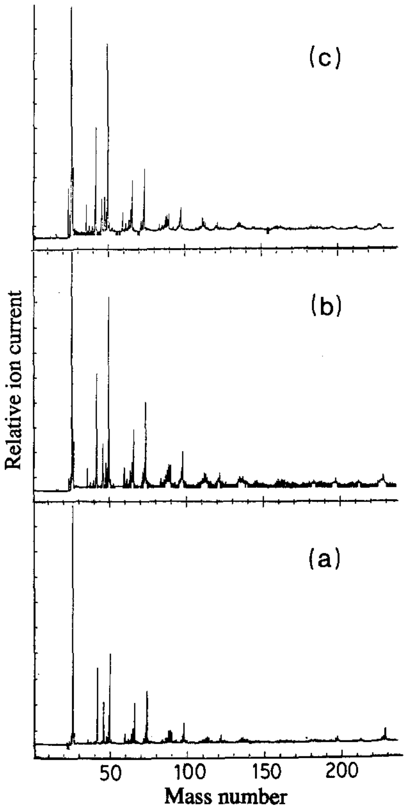


Figure 1 Negative-ion mass spectra of products of decomposition of TNT caused by laser irradiation of different relative powers: (a) 1, (b) 1.5, (c) 2.

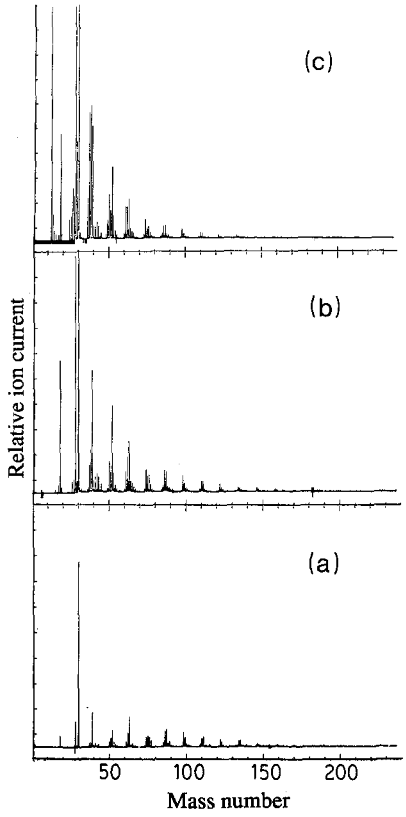
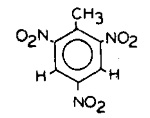
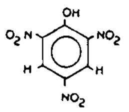
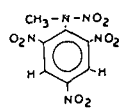


Figure 2 Positive-ion mass spectra of products of decomposition of TNT caused by laser irradiation of different relative powers: (a) 1, (b) 1.5, (c) 2.

For analysis in the LIMA, the crystal under study was mounted on a metallic stub with a piece of double-sided adhesive tape. A fine-wire stainless-steel mesh, in electrical contact with the stub, lightly pressed on to the crystal, covering it completely. Also it was made sure that the crystal surface to be irradiated with the laser beam was normal to it so that the energy density within the irradiated spot was uniform, thus enabling us to make a sensible comparison of the mass spectra of the products from different explosive materials at a given laser power. For crystals of each explosive, laser pulses of three different powers were employed. Their relative values were 1, 1.5, and 2; absolute power values were not measured.

TABLE I Chemical formulae and some relevant physical and chemical properties of TNT, picric acid and tetryl [7]

	TNT	Picric acid	Tetryl
Formula			
Melting point (°C)	80.6	122.5	129.5
Density (g cm^{-3})	1.65	1.77	1.73
Heat of explosion (J g^{-1})	5060	5025	5527
Impact sensitivity (Nm)	15	7.4	3
Deflagration point (°C)	300	300	185

The irradiated samples were taken out of the LIMA and examined with optical and scanning electron microscopy. In the case of the latter, the samples were coated with a thin film of silver, and the instrument employed was a Cambridge Stereoscan 250 Mk 2. The optical transmission spectra of thin crystals of the three explosives were obtained with a Perkin–Elmer λ-9 UV/visible spectrophotometer.

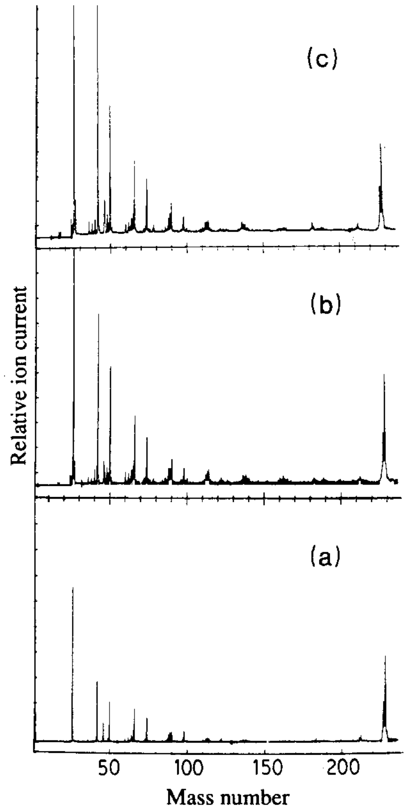


Figure 3 Negative-ion mass spectra of products of decomposition of picric acid caused by laser irradiation of different relative powers: (a) 1, (b) 1.5, (c) 2.

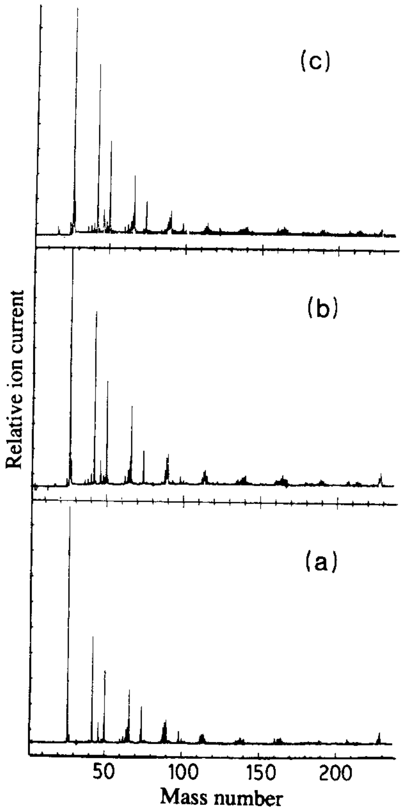


Figure 5 Negative-ion mass spectra of products of decomposition of tetryl caused by laser irradiation of different powers: (a) 1, (b) 1.5, (c) 2.

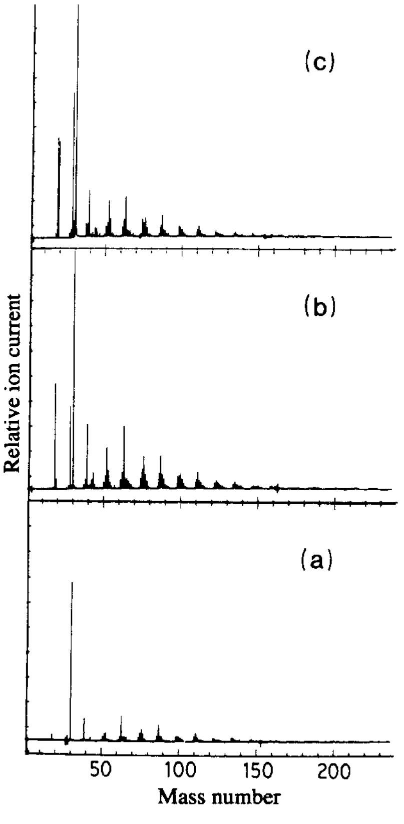


Figure 4 Positive-ion mass spectra of products of decomposition of picric acid caused by laser irradiation of different relative powers: (a) 1, (b) 1.5, (c) 2.

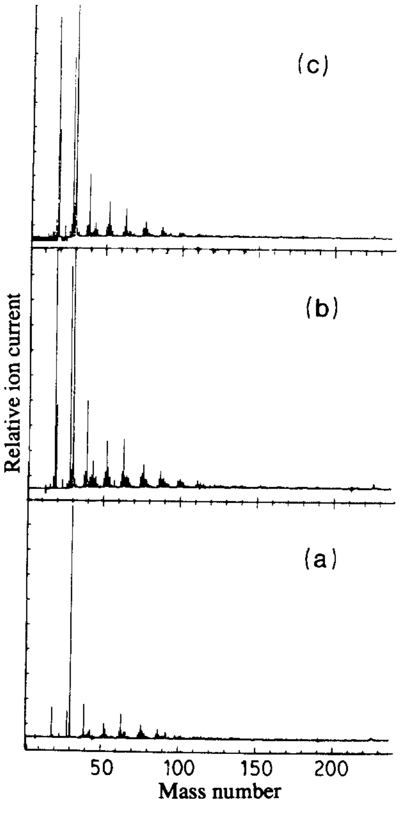


Figure 6 Positive-ion mass spectra of products of decomposition of tetryl caused by laser irradiation of different powers: (a) 1, (b) 1.5, (c) 2.

3. Results

It was found that none of the explosives showed any detectable amount of laser decomposition if the incident laser power was less than that corresponding to the minimum relative value of 1 (see below) used in this work. However, when the laser power was only just equal to this value, breakdown of the phenyl ring of the explosive molecules took place.

The positive and negative ion mass spectra of the three explosives corresponding to the three relative laser powers are shown in Figs 1 to 6. It will be seen from these figures that as the relative laser power is

TABLE II Positive and negative-ion fragments of TNT, picric acid and tetryl

TNT				Picric acid				Tetryl			
Positive		Negative		Positive		Negative		Positive		Negative	
m/e	Intensity[a]	*m/e*	Intensity	*m/e*	Intensity	*m/e*	Intensity	*m/e*	Intensity	*m/e*	Intensity
1	VW	1	VW	2	VW	1	VW	1	VW	1	VW
12	VS	12	VW	17	VW	12	VW	12	VW	16	VW
13	VW	16	VW	18	S	16	VW	13	VW	17	VW
14	VW	17	VW	19	S	17	VW	14	VW	24	VW
15	VW	24	W	26	VW	24	VW	15	VW	25	VW
		25	W	27	VW	25	VW	16	VW	26	VS
		26	VS	28	S						
		27	W								
17	VW	36	W	29	VW	26	VS	17	VW	27	VW
18	S	37	VW	30	VS	27	VW	18	VS	36	VW
19	VW	38	VW	31	VW	36	VW	19	S	38	VW
24	VW	39	VW	32	VW	38	VW	23	VW	40	VW
25	VW	40	VW	37	VW	40	VW	26	VW	42	S
26	W	41	VW	38	W	42	VS	27	VW	46	VW
27	W	42	S	39	VW	46	W	28	S	48	VW
28	VS	46	W	40	VW	48	VW	29	W	49	VW
29	W	48	W	41	VW	49	VW	30	VS	50	S
30	VS	49	VW	42	VW	50	S	31	VW	60	VW
31	VW	50	VS	43	VW	51	VW	32	VW	62	VW
35	W	51	VW	44	VW	60	VW	37	VW	64	VW
36	S			46	VW	62	VW	38	VW	65	VW
37	S	60	W	49	VW	64	VW	39	W	66	W
38	S	61	VW	50	VW	65	VW	40	VW	74	VW
39	VW	62	VW	51	VW	66	W	41	VW	88	VW
40	VW	63	VW	52	VW	72	W	42	VW	89	VW
41	VW	64	VW	53	VW	73	VW	43	VW	90	VW
		65	W	54	VW	74	VW	44	VW	98	VW
		66	VW	55	VW	75	VW	50	VW	112	VW
				57	VW	78	VW	51	VW	113	VW
42	VW	72	VW	60	VW	84	VW	52	W	114	VW
43	VW	73	VW	61	VW	86	VW	53	VW	115	VW
44	VW	74	W	62	VW	88	VW	54	VW	116	VW
45	VW	75	VW	63	W	89	VW	61	VW		
46	VW	84	VW	64	VW	90	VW	62	W		
47	VW	85	VW	65	VW	98	W	63	VW		
48	VW	86	VW	66	VW	99	VW	64	VW		
49	VW	88	VW	67	VW	110	VW	65	VW		
50	W	89	VW	68	VW	111	VW	66	VW		
51	VW	90	VW	72	VW	112	VW	74	VW		
52	W	93	VW	73	VW	113	VW	75	VW		
53	VW	97	VW	74	VW	114	VW	76	VW		
54	VW	98	VW	75	VW	115	VW	77	VW		
55	VW	99	VW	76	VW	116	VW	78	VW		
60	VW	108	VW	77	VW			79	VW		
61	W	109	VW	78	VW			80	VW		
62	W	110	VW	79	VW			86	VW		
63	W	111	VW	84	VW			87	VW		
64–68	VW	112	VW	85	VW			88	VW		
72–79	VW	113	VW	86	VW			89	VW		
84–91	VW	114	VW	87	VW			98	VW		
97–103	VW	115	VW	88	VW			99	VW		
109–113	VW	116	VW	89	VW			100	VW		
115	VW			90	VW			110	VW		
				91	VW			111	W		
				98–103	VW						
				110–116	VW						

[a] W, weak; VW, very weak; S, strong; VS, very strong.

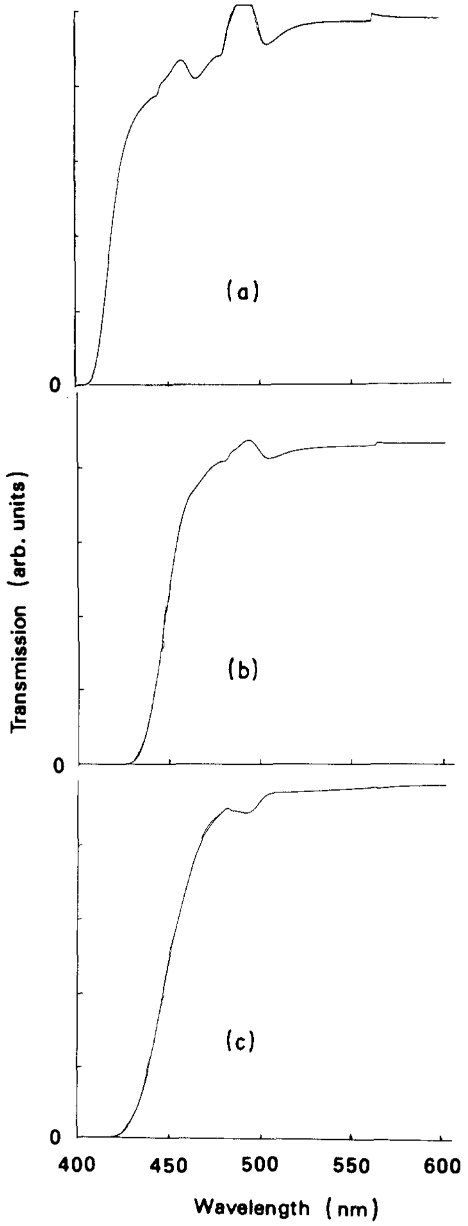


Figure 7 Transmission spectra of ~ 0.5 mm thick single crystals of (a) TNT, (b) picric acid and (c) tetryl.

increased, the number of peaks in the mass spectra also increases. The positive-ion spectrum of TNT at the highest relative laser power of 2 (see Fig. 2c) shows a strong peak corresponding to $m/e = 12$ which we interpret as being elemental carbon. The presence of the latter in the products could be attributed to the total breakdown of the molecule. It may be noted that the existence of elemental carbon in the decomposition products of other organic molecules has been seen before [3].

Assuming that the ions (both positive and negative) are singly charged, the decomposition products of TNT, PIC and TET are as shown in Table II. It is interesting to note that in both the positive and negative ion mass spectra, all the three explosives show strong peaks at $m/e = 18$, 28, 30 and 26, 42, 50, respectively. This indicates a similarity in the breakdown mechanism of the explosives.

The microscopic examination of the irradiated samples showed that in all explosive crystals ~ 4 μm diameter craters were formed at the irradiated sites

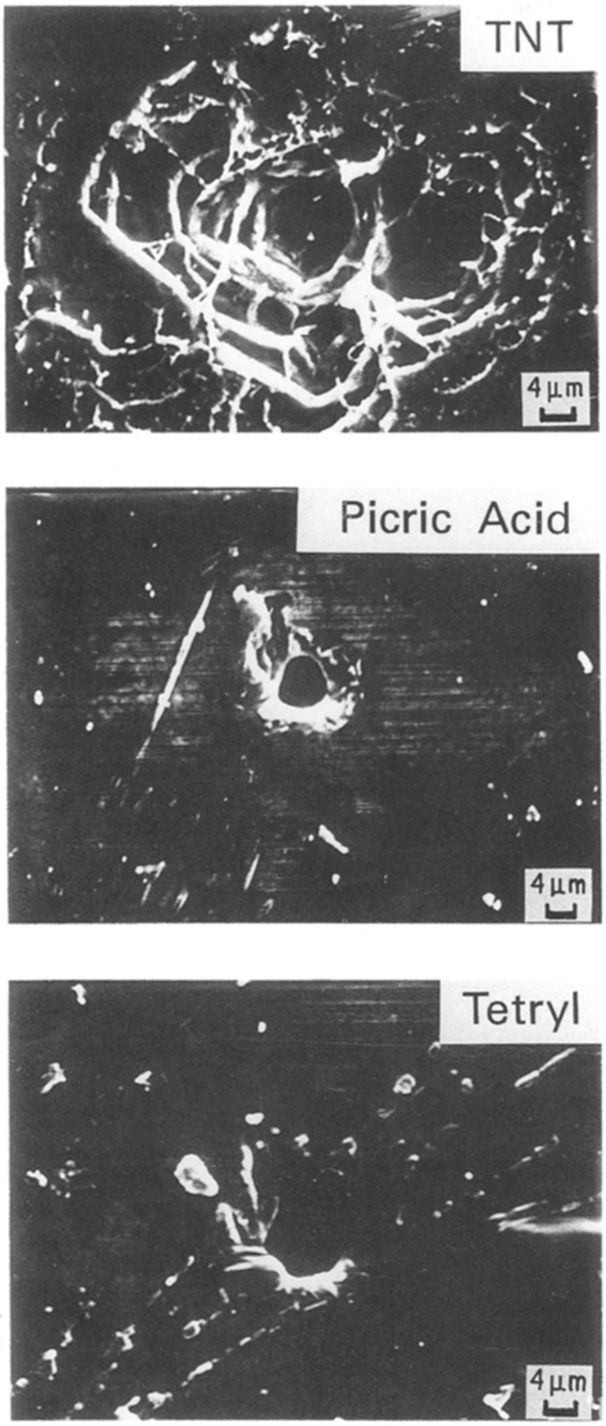


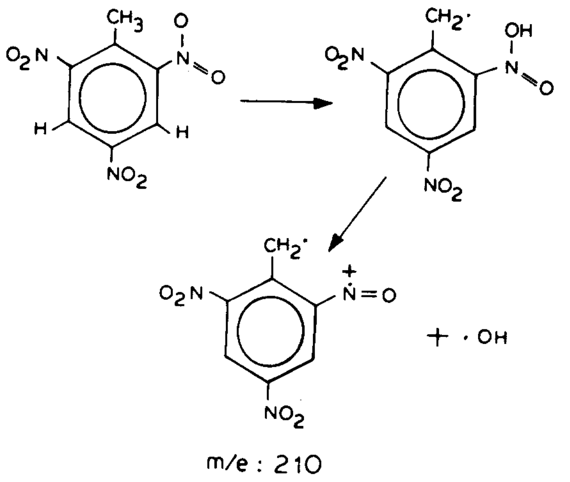
Figure 8 Typical scanning electron micrographs of craters in (a) TNT, (b) picric acid and (c) tetryl single crystals produced by laser irradiation.

(Fig. 7). Localized cracking around the craters was also observed. These observations are similar to those from laser irradiation of PETN, RDX, AgN_3 and PbN_6 single crystals [3].

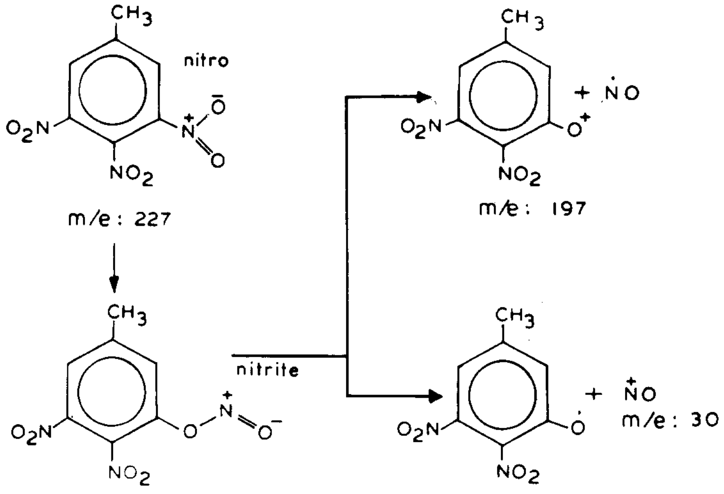
The optical transmission spectra of the three explosives are shown in Fig. 8; it will be seen that no transmission occurs for wavelengths below 407, 430 and 420 nm for TNT, PIC and TET, respectively.

4. Discussion

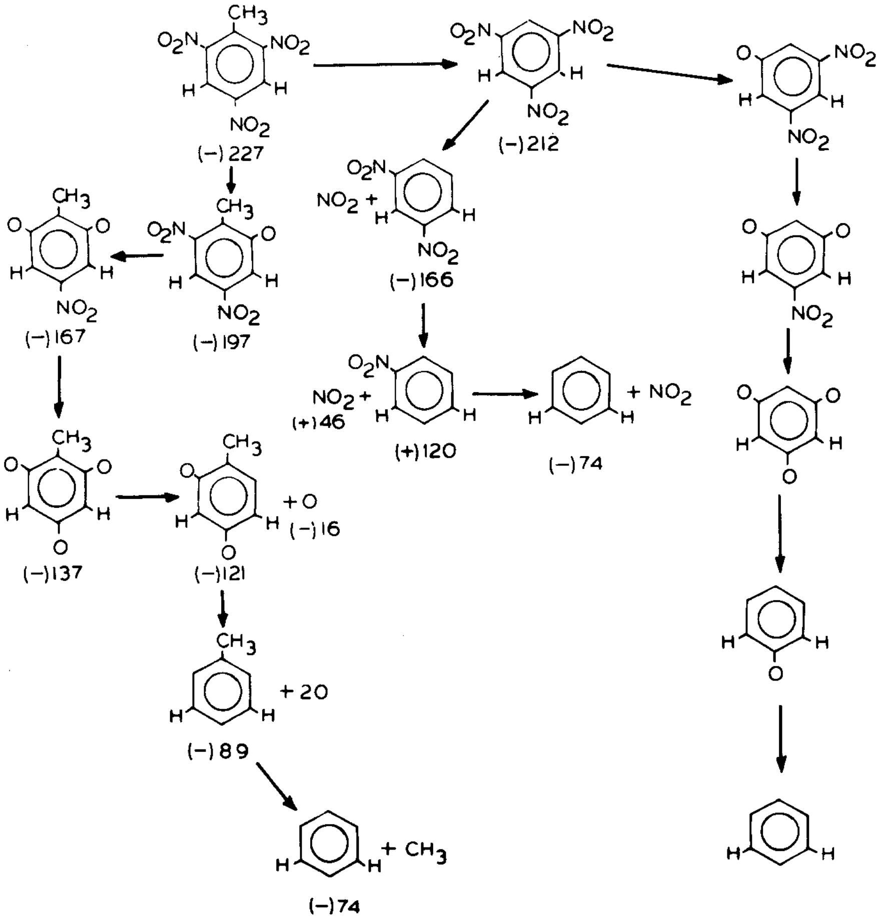
As shown in Fig. 7, in all three explosive crystals the laser beam of wavelength of 266 nm will be totally absorbed in a thin surface layer and the estimated temperature rise at the irradiated site can be of the order 10^5 K. (This is about a hundred times greater than the Chapman–Jouget plane.) Such high temperatures will lead to melting, material ejection in the form of jetting, high pressures and decomposition. These conditions are possibly similar to those existing during the propagation of deflagration and detonation waves. From the mass spectra of the products of decomposition caused by the laser pulse of the strongest power used, we have been able to propose the breakdown schemes for the different explosive molecules. For the sake of clarity, the results from the three explosives are discussed below separately.



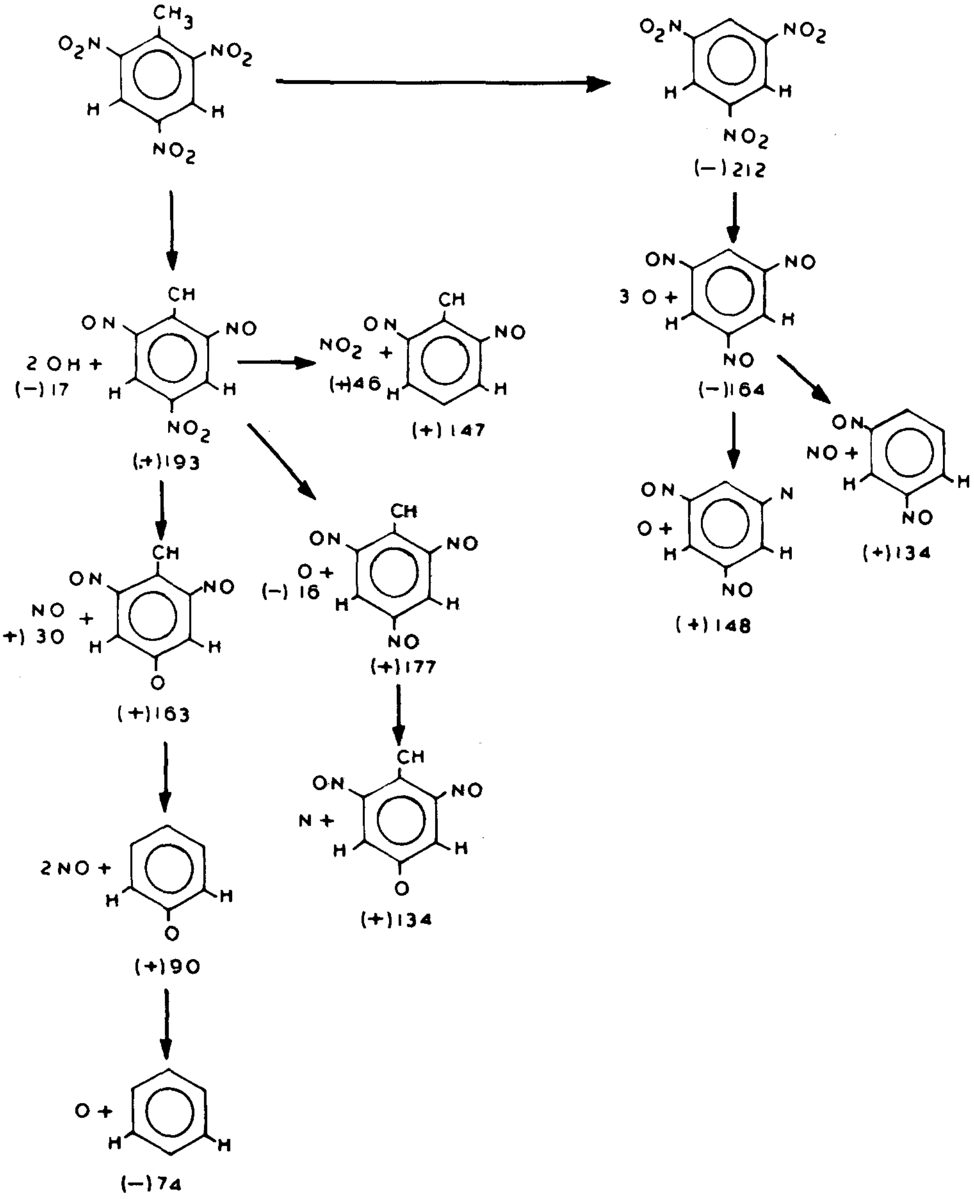
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

4.1. TNT

Since 2,4,6-TNT has been studied before by electron impact mass spectrometry [8, 9], it is worthwhile to compare the previous results with those from our LIMA experiments. The previous workers have ascribed the ion at $m/e = 210$ found in their 70 eV electron impact spectrum of 2,4,6-TNT to the well known *ortho* effect, also known as the hydrogen transfer mechanism found in the decomposition studies on *ortho*-substituted nitrobenzenes [8]. This mechanism is illustrated in Scheme 1.

On the other hand, in the case of 3,4,5-TNT, the observed base ion (+) at $m/e = 30$ has been explained by the formation of nitro-nitrite isomerisation as shown in Scheme 2.

It has been shown by deuterium substitution that the hydrogen transfer mechanism is the rate-determining step in the thermal decomposition of TNT [8], though a nitro–nitrite mechanism is not ruled out.

In the positive-ion spectra of 2,4,6-TNT products produced by laser irradiation (see Fig. 2) no peak is observed at $m/e = 210$ for any of the three laser powers used*. The base (i.e. the strongest) peak is at $m/e = 30$, which corresponds to NO.

As the positive- and negative-ion spectra represent the positive and negative ions present at the impact site immediately after the irradiation, any suggested mechanism should account for both the positive and negative ions simultaneously. In the positive- ion mass spectrum, the base peak at $m/e = 30$ is likely to be NO, which could have been produced either by a nitro–nitrite-type mechanism or by a later-stage fragmentation of the products (see schemes 3 and 4). Similarly, the peak at $m/e = 26$ in the negative-ion spectrum is likely to be CN, which is also produced by a later-stage fragmentation. The other prominent low mass ions in the positive-ion ion spectrum are at m/e= 18, 28, 39, 42, 50, 52 and 63, which could be

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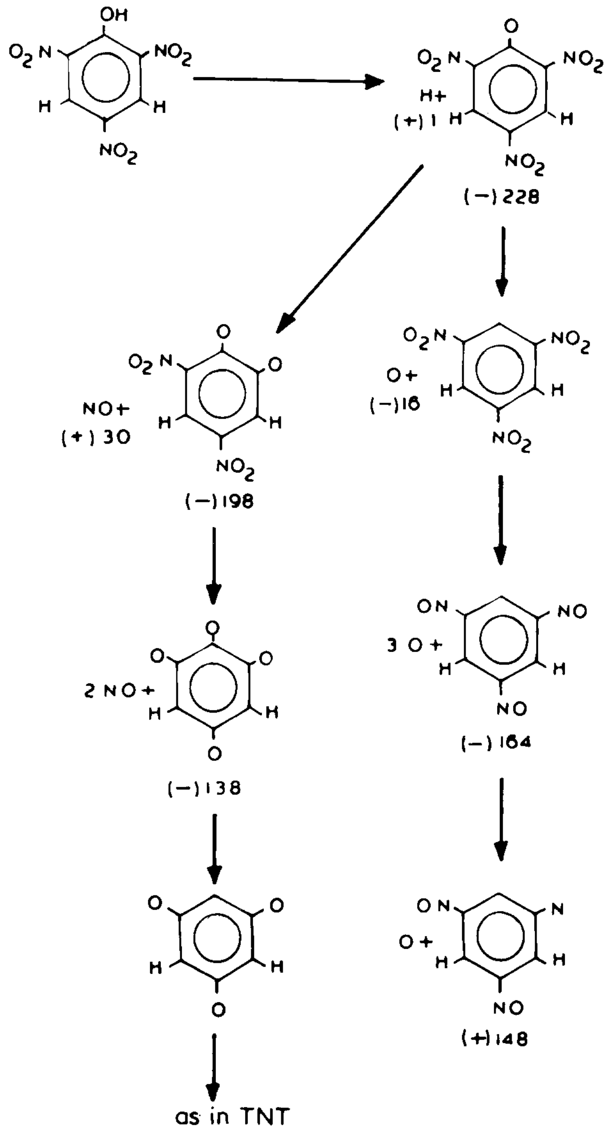
* Note that this finding is contrary to that of Bulusu and Axenrod [8], who found that the ion at $m/e = 210$ produced a very strong peak. This difference could possibly be due to the methods employed for fragmenting the TNT molecule.



Scheme 5.

ascribed to H_2O, CO, $HCCN/C(C)CH_3$, $N(CH_2)N$, C(CH)C(CH), C(C)CO and C_5H_3, respectively. In the negative-ion spectrum, the prominent low-mass ions are at $m/e = 26$, 27, 42, 46, 50 and 66; these masses could be ascribed to CN, HCN, $N(H_2C)N$, NO_2, CH(C)C(CH) and CCH(CO)CH, respectively. The pattern of the low-mass ions suggests that there is more than one fragmentation scheme. Based on the observed mass spectra, we propose two different schemes, 3 and 4, of the breakup of the 2,4,6-TNT molecule. The ions which have been observed in the positive- or negative-ion spectra have been marked with an appropriate sign in the schemes. It will be seen that the two schemes account for most of the ions observed. Moreover, it is interesting to note that the complete breakup of the phenyl ring occurs only for the highest powers used in this work. That this is so is indicated by the existence of the elemental carbon at $m/e = 12$ (see Fig. 2c).

4.2. Picric acid

As said in Section 1, picric acid differs from TNT only in that the methyl group in the latter is replaced by a hydroxyl group. The mass spectra (Figs 3 and 4) of the products produced by the laser irradiation show that the negative ion of the parent PIC molecule is much more prominent than the parent molecule in the case of TNT. It is also possible that the parent molecule of PIC is much more electronegative than that of TNT. Note that free electrons are present at the irradiation site due to the existence of high temperatures.

Our proposed breakup steps of PIC are represented by Scheme 5. As is to be expected, the scheme resembles those for TNT once the substituents have been removed from the phenyl ring. Moreover, the observed lower-mass ions in the positive- and negative-ion mass spectra of PIC are almost identical to those in the case of TNT. Again, as in the case of the latter, the complete breakup of the phenyl ring occurs at the highest laser powers used.

4.3. Tetryl

The positive- and negative-ion mass spectra of TET (Figs 5 and 6) show a resemblance to those of TNT and PIC, with the lower-mass ions being almost identical. These observations are consistent with the fact that the thermal decomposition of TET produces PIC and 2,4,6-trinitroanisol. Our proposed breakdown paths for TET are shown in Scheme 6. Again, once the non-nitro substituents have been removed, the fragmentation should be similar in all the three cases. This is indeed what is observed.

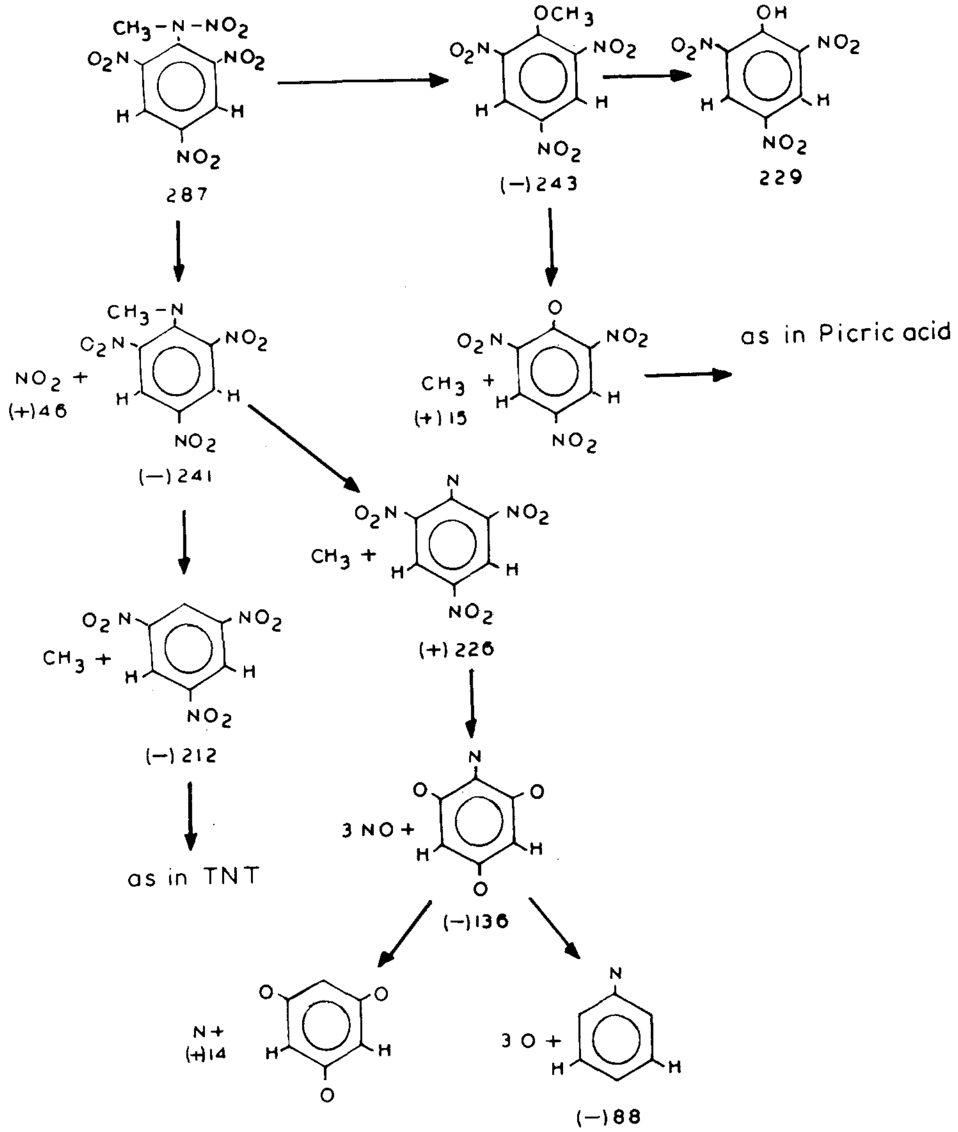
5. Conclusions

The positive- and negative-ion mass spectra of the three explosives TNT, PIC and TET by short-duration high-power laser irradiation have shown that the non-nitro substituents do not significantly affect the fragmentation patterns of the molecules. Moreover, in all cases the phenyl ring breaks up only after losing the substituents. We may conclude, therefore, that the differences in the impact and shock sensitivity between the three explosives are probably not due to the weakening of the phenyl ring by the substituents. It is possible, however, that the different explosives have different mechanical properties such as the coefficient of friction, uniaxial yield stress and hardness. These properties are also very important in controlling the initiation-of-explosion behaviour by mechanical stimuli and are being investigated.

We note a recent report by Dickenson *et al.* [10] on a mass spectrometric study of products of cyclotrimethylene trinitramine single crystals generated due to the impact of zons pulses of $\lambda = 248$ nm from an excimer laser. These workers detected charged particles, neutrals and electrons and suggested that the processes involved were nonthermal. On the contrary, we have proposed a purely thermal mechanism for the breakdown of the explosive molecules.

Acknowledgements

The work was supported by grants from the Ministry of Defence, UK (Procurement Executive) and the US



Scheme 6.

Government through its European Office. One of the authors (V.C.J.B.) would like to thank Dr J. E. Field for his interest and the management of IDL Chemicals Ltd, India, for allowing him to spend a year at the Cavendish Laboratory. We should also like to thank Drs P. Haskins and M. Cook of RARDE for their comments on the manuscripts.

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Received 19 February
and accepted 9 April 1990