# Electron Impact, Chemical Ionization and Negative Chemical Ionization Mass Spectra, and Mass-analysed Ion Kinetic Energy Spectrometry–Collision-induced Dissociation Fragmentation Pathways of Some Deuterated 2,4,6-Trinitrotoluene (TNT) Derivatives<sup>†</sup>

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Mass-analysed ion kinetic energy spectrometry (MIKES) with collision-induced dissociation (CID) has been used to study the fragmentation processes of a series of deuterated 2,4,6-trinitrotoluene (TNT) and deuterated 2,4,6trinitrobenzylchloride (TNTCl) derivatives. Typical fragment ions observed in both groups were due to loss of OR' (R' = H or D) and NO. In TNT, additional fragment ions are due to the loss of  $R_2'O$  and  $3NO_2$ , whilst in TNTCl fragment ions are formed by the loss of OCl and  $R_2'OCl$ . The TNTCl derivatives did not produce molecular ions.

In chemical ionization (CI) of both groups,  $MH^+$  ions were observed, with  $\{M - OR'\}^+$  fragments in TNT and  $[M - OCl]^+$  fragments in TNTCl. In negative chemical ionization (NCI) TNT derivatives produced  $M^-$ ,  $[M - R']^-$ ,  $[M - OR']^-$  and  $[M - NO]^-$  ions, while TNTCl derivatives produced  $[M - R]^-$ ,  $[M - Cl]^-$  and  $[M - NO_2]^-$  fragment ions without a molecular ion.

### **INTRODUCTION**

The mass spectrometry and fragmentation reactions and pathways of nitroaromatic compounds have been the subject of numerous studies<sup>1-12</sup> because of their use as explosives. Understanding the energy-releasing processes accompanying the decomposition of these compounds is therefore of great importance. Since there is a parallelism between the early stages of decomposition by explosive shock, and the fragmentation in the ion source of the mass spectrometer,  $^{13,14}$  it is of interest to study the mass spectra and the mass spectral fragmentation processes and pathways of explosives. As 2,4,6-trinitrotoluene (TNT) is the most widely used military explosive, its mass spectrometry has therefore been widely studied.<sup>3-12</sup> Electron impact (EI) mass spectra,<sup>3,7</sup> including fragmentation processes of labelled TNT,<sup>8,11</sup> chemical ionization (CI) mass spectra,<sup>5,6</sup> negative-ion mass spectra,<sup>4,9</sup> and tandem mass spectrometry (MS/MS) collision-induced dissociation (CID) spectra<sup>11,12</sup> of TNT have been reported.

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0030-493X/91/100867-08 \$05.00 © 1991 by John Wiley & Sons, Ltd. In order to contribute to the understanding of mass spectral fragmentation processes of TNT, compounds of type I and II (Table 1) were studied. Mass spectra in the electron impact (EI), chemical ionization (CI) and negative chemical ionization (NCI) mode were recorded, and mass-analysed ion kinetic energy spectrometry (MIKES) with collision-induced dissociation (CID) was used to determine fragmentation pathways.



## **EXPERIMENTAL**

The instrument used was a VG ZAB2-SEQ mass spectrometer of the BEQQ type with a PDP11-250J data system. The ion source was an EI/CI source with a variable slit. In the EI mode (70 eV), the source was operated at a temperature of 150-200 °C. The solids probe, through which the compounds were introduced, was

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Sample no.	Description	RMM	Struct	ure
1	TNT	227	1	R = R' = H
2	$d_2$ -TNT	229	1	R = D, R' ≃ H
3	d3-TNT	230	1	R = H, R' = D
4	d₅-TNT	232	E E	R = R' = D
5	TNTCI	261	- 11	R = R' = H
6	d <sub>2</sub> -Ar-TNTCI	263	11	R = D, R' = H
7	d <sub>2</sub> -Bz-TNTCI	263	н	R = H, R' = D

Table 1. Investigated compounds

not heated separately. In the CI mode, isobutane at a source housing pressure of  $2 \times 10^{-4}$  Torr, was used as reagent. For compounds 1 to 4, the source temperature was 100–150 °C, without separate probe heating. For compounds 5 to 7, the source and probe temperatures were 150 °C and 100 °C, respectively. In the NCI mode, methane, at a source housing pressure of  $5 \times 10^{-5}$  Torr, was used as electron energy moderator. The source temperature was 150–200 °C for all compounds and the probe temperature was 100–200 °C for compounds 5 to 7, and without separate heating for compounds 1 to 4. CID was carried out with the mass spectrometer in the MIKES mode, using the collision chamber between the magnetic sector and the electrostatic analyser. Argon was used as collision gas.

TNT (1) and TNTCl (5) were prepared by standard methods.<sup>15-17</sup> The preparation of  $d_3$ -TNT (3),  $d_5$ -TNT (4) and  $d_2$ -Bz-TNTCl (7) has been described elsewhere.<sup>18</sup> These same general experimental details and the same general method for preparation of sodium of the remaining deuterated derivatives. The isotopic purities are given in Table 2.

### 2,4,6-Trinitro(3,5-D<sub>2</sub>)toluene (d<sub>2</sub>-TNT, compound 2)

A solution of 2,4,6-trinitro(D<sub>5</sub>)toluene (86.6 g) in dimethylformamide (935 cm<sup>3</sup>) was treated with the H<sub>2</sub>O (104 cm<sup>3</sup>) and tributylamine (1.77 g) and stirred for 6 h. The pH was adjusted to 5 with dilute HCl and the mixture was poured into cold water (3.5 l). The precipitate was collected, washed with water and dried. This material was subjected to the exchange reaction conditions a further three times and the product was recrystallized from carbon tetrachloride as light brown needles (64.5 g, 75%). Further purification by chromatography on silica gel plates in toluene and re-

Table 2.	The isotopic purities of the deuterated derivatives as determined by $^{1}H$ and $^{2}H$ NMR spectroscopy
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	Compound	Arª	Bzª		
2	d <sub>2</sub> -TNT	<1% H	<0.5% D		
3	$d_3^{-}$ TNT	≪0.5% D	<2% H		
1	d <sub>5</sub> -TNT⁵				
8	d <sub>2</sub> -Ar-TNTCI	<1% H	<0.5% D		
7	$d_2$ -Bz-TNTCI	3% D	<1.5% H		

<sup>a</sup> Ar: Aromatic ring; Bz: Benzyl.

<sup>b</sup> Proton incorporation of less than 2%. Determined using an internal standard (4-methoxybenzonitrile)

crystallizations from carbon tetrachloride gave white needles, m.p. 80.2-80.9 °C.

# 2,4,6-Trinitro(3,5-D<sub>2</sub>)benzyl chloride $(d_2$ -Ar-TNTCl, compound 6)

A solution of 2,4,6-trinitro(3,5-D)toluene (6.0 g) dissolved in tetrahydrofuran (60 cm<sup>3</sup>) and methanol (25 g) was stirred under argon and cooled to -38 °C. A chilled aqueous sodium hypochlorite solution (8.5% w/w available chlorine, 34.0 g) was added over 10 min



Figure 1. El mass spectra of compounds of type I.

and the temperature of the reaction mixture was controlled so that it was near, but did not exceed -20 °C. The agitated mixture was held at -20 °C for a further 6 min, the mixture temperature was lowered and dilute HCl (18.5% w/w, 38 cm<sup>3</sup>) was added over 7 min. The mixture was held at -20 °C for 5 min, allowed to rise to -10 °C over 15 min and then stirred at room temperature for 15 min. The mixture was diluted with water (400 cm<sup>3</sup>) and extracted with chloroform (3 × 250 cm<sup>3</sup>). These extracts were washed repeatedly with brine (6 × 400 cm<sup>3</sup>) and then dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent removed. The pale yellow oil was purified by TLC



Figure 2. Cl-isobutane mass spectra of compounds of type I.

(silica gel, toluene). Exposure of this compound to air on dry plates was minimized to avoid decomposition. Recrystallization from carbon tetrachloride gave the product (4.09 g, 59%). Two further recrystallizations gave pale yellow needles, m.p. 85.5-85.7 °C.

#### **RESULTS AND DISCUSSION**

Figures 1, 2 and 3 show the EI, CI and NCI mass spectra of the four deuterated compounds of type I,







Figure 4. CID fragmentation pathways map in El mode of compounds of type I.

respectively. In EI, low-abundance molecular ions are observed, whilst the  $[M - OR']^+$  ion forms the base peak. Other typical fragment ions are  $[M - 2OR']^+$ ,  $[M - R_2'O]^+$ ;  $[M - OR' - NO_2]^+$ ;  $[M - R_2'O - 2NO]^+$ ;  $[M - OR' - NO_2 - NO]^+$  and  $[M - 3NO_2]^+$ . All these fragment ions have been observed in the MIKES-CID spectra (in the EI mode) of the investigated compounds. The resulting fragmentation pathways map is shown in Fig. 4. Results show that a major fragment ion is due to the 'ortho effect', that is, loss of O from an o-nitro group and an R' from the methyl group, as has been previously reported.<sup>8</sup> There is no loss of OR, that is O from a nitro group and an R from the ring. This can be seen in Fig. 5, which shows the CID mass spectrum of the  $M^+$  ion at m/z 230 of compound 3 ( $d_3$ -TNT) in the range of m/z 209 to 213. Loss of OR would have produced a peak at m/z 213. The ions at m/z 212 and 210 are due to  $[M - OD]^+$ and  $[M - D_2O]^+$ , respectively. In the isotopic compound 2, this cannot be proved because loss of  $R'_2O$  $(H_2O)$  would be at a mass differing only by 0.0015 u



**Figure 5.** CID mass spectrum (in EI mode) of the M<sup>++</sup> ion at m/z 230 of compound **3** in the range of m/z 209 to 213.

from the loss of RO (OD), a difference indistinguishable by the equipment used.

In the CID spectrum of the  $[M - OD]^+$  ion at m/z212 of compound 3 ( $d_3$ -TNT) (Fig. 6) we find an additional loss of OD (m/z 194), but also a small loss of OH (m/z 195), which comes from a nitro group-O and an R from the ring. This has also been observed in the CID spectrum of the  $[M - OH]^+$  ion of compound 2 ( $d_2$ -TNT) (Figs 7 and 8). The possibility that the ion at m/z. 194 is due to loss of H<sub>2</sub>O has been dismissed, because in compounds 1 and 4 no ions due to loss of R'<sub>2</sub>O were observed.

Some fragment ions can be produced by direct loss from the molecular ion or by consecutive losses. For example,  $C_7R_2R_2'N_2O_3^+$  can be produced by loss of (OR' + NO<sub>2</sub>) from the molecular ion or by consecutive loss of OR' and NO<sub>2</sub>; similarly,  $C_7R_2R_2'NO_2$  can be produced by loss of (OR' + NO<sub>2</sub> + NO) from the molecular ion or by consecutive losses of OR' and (NO<sub>2</sub> + NO).

Only CID mass spectra of major fragment ions were



Figure 6. CID mass spectrum (in EI mode) of the  $[M - OD]^{\bullet}$  ion at m/z 212 of compound 3 in the range of m/z 192 to 196.



**Figure 7.** CID mass spectrum (in EI mode) of the  $[M - OH]^+$  ion at m/z 212 of compound 2.

recorded. Therefore the fragmentation map does not contain pathways in which the aromatic ring is cleaved.

The CI-isobutane mass spectra of the four deuterated compounds of type I (Fig. 2) contain a major  $MH^+$  ion and fragment ions  $[M - OR']^+$ ,  $[MH - NO]^+$  and  $[M - NO]^+$  and a major adduct ion  $[M + C_3H_6]^+$ . The NCI mass spectra contain an  $M^-$  ion and mostly an  $[M - R']^-$  ion. Other fragment ions observed include  $[M - OR']^-$  and  $[M - NO]^-$ . In compound 3 there seems to be some isotope exchange with the methane which serves as electron moderator, resulting in a molecule M', in which two deuterium atoms have been replaced by two hydrogen atoms.

Figures 9, 10 and 11 show the EI, CI and NCI mass spectra of the three deuterated compounds of type II, respectively. No molecular ions are observed. Typical fragment ions are  $[M - OR']^+$ ,  $[M - OCl]^+$ ,  $[M - R_2'OCl]^+$  and  $[M - R_2'OCl - NO]^{++}$ . A group of major fragment ions (one of them forms the base peak) observed in the mass spectra are probably due to  $[C_6 + NO_2 + R']^{++}$ ,  $[C_6 + NO_2 + R + R']^+$ ,  $[C_6 + NO_2 + R_2]^+$  and  $[C_6 + NO_2 + R_2 + R']^+$ . Another group of fragment ions are, with an additional NO<sub>2</sub> group, forming  $[C_6 + 2NO_2 + R']^+$ ,  $[C_6 + 2NO_2 + R + R']^+$ ;  $[C_6 + 2NO_2 + R_2]^{++}$  and  $[C_6 + 2NO_2 + R_2]^{++}$  and  $[C_6 + 2NO_2 + R_2]^{++}$  and  $[C_6 + 2NO_2 + R_2]^{++}$ . For example, in compound 5 these ions are observed in EI and in CI at m/z 119, 120, 121, 165, 166 and 167 (Figs 9 and 10). Similar ions were obtained in the EI mass spectrum of TNTBr (Fig. 12).



**Figure 8.** CID mass spectrum (in El mode) of the  $[M - OH]^+$  ion at m/z 212 of compound 2 in the range of m/z 191 to 197.



Figure 9. El mass spectra of compounds of type II.



Figure 10. Cl-isobutane mass spectra of compounds of type II.

The CI mass spectra contain an  $MH^+$  ion as well as some major fragment ions such as  $[M - O]^+$  and  $[M - OCl]^+$ . The NCI mass spectra (Fig. 11) contain only a few major peaks,  $[M - R']^-$ ,  $[M - Cl]^-$  and  $[M - NO_2]^-$ .

As the EI mass spectra of the compounds of type II did not contain molecular ions, only MIKES-CID spectra of the major fragment ions were recorded. The resulting fragmentation map, as shown in Fig. 13, is therefore constructed of two parts: one is a hypothetical part (dashed lines), and the second part (full lines) is based on the experimental results. As in the case of compounds of type I, we have here loss of OR' but also loss of OCl and loss of OR'<sub>2</sub>Cl. Many of the end products are similar to fragmentation processes of the compounds of type I, such as  $C_7R_2R_2'N_02^+$ ,  $C_7R_2R_2'N_2O_3^+$ ,  $C_7R_2R_2'N_2O_4^+$ ,  $C_7RR_2'N_3O_4^+$  and  $C_7R_2R'N_3O_4^+$ . Loss of  $3NO_2$  was found to be a minor process, as the EI mass spectra contained only small abundance ions at  $[M - 3NO_2]^+$ .



Figure 11. NCI mass spectra of compounds of type II.

## CONCLUSIONS

In the TNT derivatives, the major fragment ion in EI,  $[M - OR']^+$ , is formed by loss of O from an *o*-nitro group and an R' from the methyl group, without any contribution from OR, that is O from a nitro group and an R from the ring. However, the  $[M - OR']^+$  ion loses an additional OR' group with a small OR contribution. Additional EI fragment ions are produced by losses of  $R_2'O$ , NO and NO<sub>2</sub>. Loss of three NO<sub>2</sub> groups produces a major fragment ion. In EI of TNTCl derivatives, no molecular ions were observed. Typical fragment ions are produced due to loss of OR', OCl,  $R_2'OCl$  and NO. Many of the EI fragmentation products in the TNT derivatives are similar to those in the TNTCl derivatives such as  $C_7R_2R_2'N_2O_4^+$ .



Figure 13. CID fragmentation pathways map in El mode of compounds of type II.

While in the TNTCl derivatives we find fragment ions of the type  $C_6R'N_2O_4^+$ ,  $CRR'N_2O_4^+$ ,  $C_6R_2N_2O_4^+$  and  $C_6R_2R'N_2O_4^+$ , in the TNT derivatives the fragment ions are rather  $C_6N_2O_4^+$ ,  $C_6RN_2O_4^+$  and  $C_6R_2N_2O_4^+$ . Loss of  $3NO_2$  was a minor fragmentation process in the EI of TNT Cl.

In CI both groups of compounds contained  $MH^+$ ions. In the TNT derivatives,  $[M - OR']^+$  fragment ions were produced, whilst in the TNTCl derivatives,  $[M - OCl]^+$  ions were produced. In NCI, TNT derivatives produced  $M^-$ ,  $[M - R']^-$ ,  $[M - OR']^-$  and  $[M - NO]^-$  ions, while TNTCl derivatives produced  $[M - R']^-$ ,  $[M - Cl]^-$  and  $[M - NO_2]^-$  fragment ions.

It seems that the Cl substitute produces some different fragmentation patterns, but in general does not contribute to the stability of the TNT derivatives in the mass spectrometer.

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