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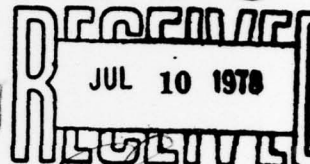
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EXPLOSION ON A SINGLE MOLECULE LEVEL: A CONCEPTUAL
MODEL BASED ON IONIZATION AND FRAGMENTATION
OF TNT UNDER ELECTRON IMPACT,

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11 JUN 1978

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INTRODUCTION: Several studies of the mass spectra of nitroaromatic compounds have appeared in recent literature (1) with emphasis on either analytical applications (2-4) or on the modes of electron impact fragmentation (5-7). The chemistry of the nitroaromatic compounds is of considerable interest to the field of explosives because of the central role played by TNT (2,4,6-trinitrotoluene) in a wide variety of armaments. Electron impact studies of explosives and related substances were initiated in this laboratory in order to provide a comparison with other modes of decomposition such as by heat (8,9), light (10) and ionizing radiation. The knowledge thus gained should provide an insight into the nature of the chemical species and processes preceding detonation. Under this program an investigation of nitramines under electron impact was previously published (11) and the present paper deals with 2:4:6-TNT which is the most important of the six isomeric trinitrotoluenes. In addition, to assess the effect of ortho orientation of the CH_3 and NO_2 groups on the fragmentation, comparative data will be presented on 3:4:5-trinitrotoluene which is the only isomer with no nitro groups ortho to the CH_3 group. The purpose of this paper is to indicate the major primary processes in TNT isomers under electron impact and draw attention to the similarities of these to the decompositions initiated by light and heat and to extend the analogies to the processes that precede detonation.

A comprehensive and highly noteworthy study of the electron impact decomposition of TNB (1:3:5-trinitrobenzene) was recently published by Meyerson, et al. (6), which utilized metastable scanning technique and identified a large number of ion transitions. This

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study delineates, in a remarkable detail, most of the competing and consecutive reactions which follow the ionization and dissociation of TNB and led to the important conclusion that the loss of NO₂ group was probably the rate determining step in the breakdown of the TNB molecule under electron impact. Our current studies, still in the early stages, are modeled along similar lines to provide a comparison of TNB and TNT in general and to elucidate the key bond breaking steps in the degradation of TNT when ionized by electron impact.

The mass spectra reported in this paper were obtained on a DuPont Model 21-492 double focusing mass spectrometer by introducing the samples via the solids probe. An ionization voltage of 70 ev and a source temperature of 200° were used. For metastable scanning the source temperature was maintained at 100° and the sample in the 50-70° range to prevent rapid loss of the sample by evaporation and allow time for the metastable scanning.

RESULTS AND DISCUSSION: The 70 ev mass spectra of 2:4:6-TNT and the isomeric 3:4:5-TNT are summarized in Tables -1 and -2, respectively. Table -1 for 2:4:6-TNT includes, in addition to the relative abundance, the percentage contribution of ions of each mass to the total ion formation.

Table -3 summarizes the metastable transitions observed by the scanning technique in the high mass end of the TNT spectrum. Current work is aimed to determine as many transitions as possible in the entire mass spectrum. The normal mass spectrum of TNT is rich in metastable peaks and those at the high mass end are shown in Table -4 along with the probable assignments.

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TABLE -1: Mass Spectrum of 2:4:6- Trinitrotoluene*

m/e	% Total Ion	RA	m/e	% Total Ion	RA
229	0.13	1.1	92	0.62	5.2
228	0.12	1.0	91	0.37	3.1
227	0.44	3.7	90	1.02	8.5
212	0.31	2.6	89	8.06	67.2
211	1.94	16.2	88	1.76	14.7
210	12.00	100.0	87	1.30	10.8
209	0.72	6.0	86	0.83	6.9
194	0.39	3.3	85	0.31	2.6
193	2.31	19.3	80	0.24	2.0
181	0.25	2.1	79	0.28	2.3
180	2.41	20.1	78	0.56	4.7
179	1.11	9.3	77	1.67	13.9
166	0.80	6.7	76	3.06	25.5
165	0.13	1.1	75	1.57	13.1
164	0.82	6.8	74	1.48	12.3
163	0.37	3.1	73	0.21	1.8
152	0.27	2.3	71	0.62	5.2
151	0.27	2.3	70	0.62	5.2
150	0.19	1.6	69	0.83	6.9
149	1.76	14.7	68	0.28	2.3
136	0.29	2.4	67	0.37	3.1
135	0.41	3.4	66	0.37	3.1
134	2.41	20.1	65	1.02	8.5
133	0.27	2.3	64	1.11	9.3
121	0.14	1.2	63	6.20	51.7
120	0.68	5.7	62	3.52	29.3
119	0.14	1.2	61	0.65	5.4
118	0.22	1.9	60	0.23	1.9
117	0.23	1.9	55	1.95	16.3
116	0.16	1.3	53	0.56	4.7
107	0.22	1.8	52	0.69	5.8
106	0.66	5.5	51	2.50	20.8
105	0.84	7.0	50	2.13	17.8
104	0.72	6.0	49	0.19	1.6
103	0.53	4.4	46	1.2	10.0
102	0.31	2.6	44	0.30	2.5
94	0.27	2.3	43	1.76	14.7
93	0.29	2.4	40	0.17	1.4

TABLE -1: Mass Spectrum of 2:4:6- Trinitrotoluene*

m/e	% Total Ion	RA	m/e	% Total Ion	RA
39	3.61	30.1	29	0.58	4.8
38	0.65	5.4	28	0.65	5.4
37	0.36	3.0	27	0.43	3.6
31	0.12	1.0	26	0.22	1.8
30	8.61	71.8			

*Only peaks of 1% or higher relative abundance are included; however, the % total ion is based on true total ion current.

Several observations can be made from an inspection of the spectra (Tables -1 and -2) of the two trinitrotoluene isomers. In the following discussion only the main features of the spectra will be considered.

The Molecular Ions: In general, the chemical stability of the molecule parallels the stability of M^+ and is therefore reflected in the abundance of M^+ . The stability of M^+ depends on the energy needed to ionize the molecule. If less energy is required to ionize the molecule, more molecular ions will be formed with lower internal energy. Aromatic compounds are well known to yield abundant molecular ions. In the mass spectrum of 2:4:6-TNT the molecular ion at m/e 227 was quite small (3.7%) for an aromatic compound. 3:4:5-TNT, on the other hand, gave rise to a molecular ion of large abundance (70%). This contrast indicates that the instability of the molecular ion of 2:4:6-TNT stems from the position of the nitro group rather than an intrinsic instability associated with the NO_2 group in explosive molecules. This point will be further elaborated later in the following discussion.

The Base Peak in the Spectrum of 2:4:6-TNT: The base peak in the spectrum of 2:4:6-TNT was at m/e 210 (M-17). This represents the loss of an OH group since the elimination of the only other contender, NH_3 , is not a common process (15) and in any case, is unlikely to occur in TNT. A precise mass determination of the peak at m/e 210 assigned the formula, $C_7H_4N_3O_5^+$ to it and confirmed the above conclusion.

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Table 2

Mass Spectrum of 3:4:5-Trinitrotoluene*

<u>m/e</u>	<u>RA</u>	<u>m/e</u>	<u>RA</u>	<u>m/e</u>	<u>RA</u>
229	1.3	90	7.3	62	25.3
228	6.6	89	60.0	61	6.6
227	69.9	88	4.1	60	1.5
211	3.4	87	10.6	57	3.4
197	4.0	86	8.0	56	1.4
182	1.1	85	2.7	55	2.7
181	1.1	83	1.5	54	1.4
179	1.0	81	3.1	53	10.9
149	1.5	80	1.8	52	23.3
137	1.3	79	2.3	51	55.2
136	1.7	78	8.7	50	16.0
135	10.7	77	51.2	49	1.6
134	3.4	76	9.3	46	34.6
121	1.8	75	4.4	44	10.0
108	1.7	74	7.8	43	4.0
107	20.0	73	2.6	42	1.0
106	2.0	71	2.2	41	5.7
105	6.0	69	3.4	40	3.0
104	1.0	68	1.7	39	41.3
97	1.4	67	4.9	38	4.7
95	1.3	66	2.6	37	4.0
93	1.7	65	12.7	31	1.3
92	1.2	64	9.3	30	100
91	3.4	63	77.3	29	8.7
				27	8.0

*Only peaks of 1% or more of relative abundance are included in this table.

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Table 3
Transitions Observed by Metastable
Scanning Technique

<u>Fragment ion</u>	<u>Precursor ion</u>	<u>Approximate Peak Height*</u>
210	227	
193	210	
180	227	29
180	210	6
179	227	35.5
179	209	1.6

*Comparison is valid only when the same fragment was obtained from more than one precursor and gives the relative contribution of each transition to yield the same daughter ion.

Table 4

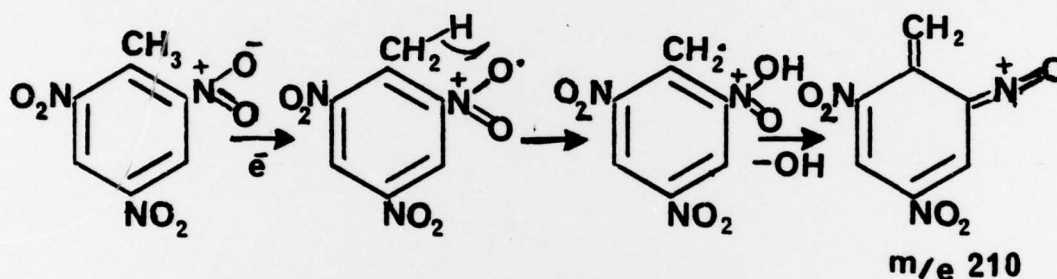
Well Defined Metastable Peaks Observed
in the Normal Mass Spectrum of 2:4:6-TNT
and their Probable Assignment to
Various Likely Transitions

Metastable Peak, m/e		Probable Assignment
Found	Calculated*	
194.2	194.3	227 $\xrightarrow{-OH}$ 210
192.5	192.4	227 $\xrightarrow{-H_2O}$ 209
177.5	177.4	210 $\xrightarrow{-OH}$ 193
-	164.1	227 $\xrightarrow{-2OH}$ 193
154.5	154.3	210 $\xrightarrow{-NO}$ 180
-	153.3	209 $\xrightarrow{-NO}$ 179
141.3	141.1	227 $\xrightarrow{-H_2O, NO}$ 179
		193 $\xrightarrow{-28}$ 165
128.2	128.1	210 $\xrightarrow{-NO_2}$ 164
124.1	124.0	179 $\xrightarrow{-NO}$ 149

Based on the well known relation, $m^ = m_2^2 / m_1$ for the transition $m_1 \rightarrow m_2 + \text{neutral}$, where m^* represents the apparent mass of m_2 (14).

The elimination of a hydroxyl group by T⁺ obviously requires a prior hydrogen rearrangement (Scheme -I). Such rearrangements by hydrogen atoms and even larger functional groups (e.g., NO₂ migration in HMX noted in Ref. 11) have often been observed (16) in electron impact fragmentations and are facilitated by the ortho orientation of the groups concerned. A very low energy

Scheme -I

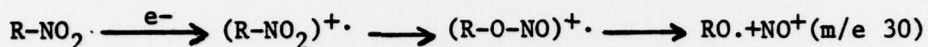


of the transition state involved in this reaction was probably responsible for the low relative abundance of the molecular ion (M^+) in the case of 2:4:6-TNT. When this pathway was preempted in the 3:4:5-TNT the relative abundance of the molecular ion (M^+) increased markedly (70%). Two close analogies are the mass spectra of *o*-nitroaniline and *o*-nitrotoluene both of which gave significant peaks due to the loss of a hydroxyl radical (1) arising from the "ortho" effect.

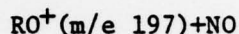
The Base Peak in the Spectrum of 3:4:5-TNT: The base peak in the spectrum of 3:4:5-TNT was at m/e 30, apparently due to the ion NO^+ . Elimination of a charged or neutral NO is one of the general features of the mass spectra of aromatic nitro compounds (14). If a neutral NO was eliminated, the complementary fragment would retain the charge as was the case here shown by m/e 197. However, the low abundance (4%) of ($M-NO^+$) (m/e 197) indicates its relative instability. Nevertheless, the presence of these ions, ($M-NO^+$) and NO^+ , suggests yet another interesting bond-forming rearrangement of the nitro group resulting in nitrite formation (Scheme -II).

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SCHEME -II



or



where $\text{R} = (\text{NO}_2)_2\cdot\text{CH}_3\cdot\text{C}_6\text{H}_2\cdot$

The Cleavage of the NO₂ Groups: The loss of NO₂ to give an (M-46)⁺ ion is a common process among nitroaliphatics (17), polynitro compounds (17c), nitrates (18), nitrites (19) and aromatic compounds (1). However, in the spectrum of 2:4:6-TNT the low abundances of the ions, (M-46)⁺ (m/e 181, 2.1%) and NO₂⁺ (m/e 46, 10%) indicated that the loss of NO₂ was either a relatively minor process or that the ions resulting from the NO₂ loss were highly unstable. On the other hand, in the spectrum of 3:4:5-isomer the ion NO₂⁺ was found to have a relative abundance of 35% while the ion (M-46)⁺ had only 1.1% relative abundance.

In the earlier investigation (6) of the electron impact decomposition of 1:3:5-trinitrobenzene (TNB), metastable scanning revealed that the ion (M-46)⁺ was a precursor to almost all the lower mass ions found in its spectrum and not surprisingly, its own relative abundance was of the order of only 5%. This was interpreted to mean that the cleavage of NO₂ group released sufficient internal energy to sustain its decomposition to small fragments. In the two isomeric TNTs under study a similar situation could account for a low abundance of (M-NO₂)⁺ ions. A close comparison of the spectra of the two isomeric trinitrotoluenes shows that the 2:4:6-TNT gives rise to approximately 40% of the total ions in the high mass region (m/e 89) against about 20% for the 3:4:5-TNT in the same region. This difference is in accord with the ortho effect in the 2:4:6-TNT which should have a stabilizing influence on the molecule by providing a low activation energy pathway.

Metastable Scanning Experiments: Metastable peaks in mass spectra arise from ion decompositions in the field-free region of the analyzer following acceleration (12). With new instrumental techniques such decompositions can be identified and used as a source of information to reconstruct the breakdown paths of molecular ions. Table -3 summarizes the decomposition steps determined. Aside from confirming the one step elimination of OH group by the molecular ion

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to give m/e 210, the data indicate several primary steps involving the loss of 2 OH groups, HNO_2 , H_2O , and $\text{H}_2\text{O} + \text{NO}$. Table -4 illustrates the fact that the mass spectrum contains many more metastable transitions which can be potentially correlated with the structure and efforts are being made to accomplish this.

The Relationship of Electron Impact Fragmentation to Photochemistry and Thermal Decomposition of Organic Molecules: The mass spectrum of an organic compound represent the products of ionization and dissociation of isolated molecules in the gas phase which are detected within a few microseconds after electron impact. The lowest energy ionization of a nitro compound in the electron beam will in general remove a non-bonding electron from the nitro group. Much of the photochemistry of the nitro group can be attributed (20) to excitation in the non-bonding orbital. Reactions which emanate from a half-vacant non-bonding orbital should be similar whether the means of removing the non-bonding electron is electronic excitation with light or ionization by electron impact. This is borne out by the parallel between the two important processes observed in the mass spectra of TNTs and the photolysis of nitroaromatics including 2:4:6-TNT. Examples are the photochemical isomerization of *o*-nitrotoluene (21), 2:4-dinitrotoluene (22) and the nitro-nitrite rearrangement of nitroolefines (23) and 9-nitroanthracene (20). In this laboratory *o*-nitrotoluene was found (24) to convert to *o*-nitrosobenzyl alcohol representing an intramolecular hydroxyl migration after the initial hydrogen rearrangement. In fact, most recent ESCA studies (25) of 2:4:6-TNT photolysis showed that this reaction occurs both in the solid and gaseous phases. The loss of an oxygen atom under electron impact by the cleavage of the N-O bond in TNT also has a photochemical equivalent in the formation of nitrosodimethylamine by UV irradiation (10). Several other instances of similarities between mass spectrometric and photochemical reactions were described in the literature (26, 27).

Close parallels between mass spectral and pyrolytic decompositions have often been rationalized as reflecting parallelism of bond energies and vibrational modes in the vibrationally excited neutral molecules and their ionized counterparts. Recent mass spectral and thermal decomposition studies of nitroaromatics (8), polynitropolyphenyls (9) uncovered several reactions common to the two modes. A detailed review (Ref. 28) of these has appeared recently.

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The above comparisons between mass spectral reactions and reactions induced by light and heat will serve to support the suggestions often made (23, 26, 27) that the mechanistic mass spectral data helps to rationalize reactions in the other cases and guide the exploratory work.

CONCLUSION: This investigation of the mass spectral breakdown patterns of 2:4:6-TNT and its isomers, has uncovered several interesting reactions which are quite analogous to those inferred in photochemical and thermal decompositions and opened the potential of the metastable scanning approach to enable construction of a multistep decomposition scheme accounting for the disintegration of TNT molecule. Such a correlation was possible in the case of earlier TNB study (6) which showed that the cleavage of the C-NO₂ bond required a high energy transition state and probably constituted the rate-determining step in the disintegration of the TNB molecule. Because of the importance of such information to the understanding of the explosive behavior the authors (6) suggested that the breakdown of TNB in the mass spectrometer source may profitably be viewed as an "explosion" in a system whose dimensions are those of a single molecule. The present work supports this view as a helpful conceptual model.

ACKNOWLEDGEMENT: The author is highly thankful to Dr. Tung-Ho Chen of this laboratory for help with the metastable scanning experiments, and to Mr. J.R. Autera for assistance with instrumentation.

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