Organic Ions in the Gas Phase. XXVI. Decomposition of 1,3,5-Trinitrobenzene under Electron Impact

SEYMOUR MEYERSON* AND ROY W. VANDER HAAR

Research Department, Standard Oil Company (Indiana), Naperville, Illinois 60540

ELLIS K. FIELDS

Research and Development Department, Amoco Chemicals Corporation, Naperville, Illinois 60540

Received August 15, 1972

Metastable scanning of 23 fragment ions in the mass spectrum of 1,3,5-trinitrobenzene yielded 96 metastable peaks. Coupled with precise-mass measurement on selected peaks, this approach defines the underlying chemistry in considerable detail. Primary loss of NO_2 seems to play a central role in the network of competing and consecutive reactions, and may well be the rate-controlling step for a large part of it, releasing vibrational energy to drive further decomposition steps.

The mass spectrum of an organic compound is a representation of the products of ionization/dissociation of isolated gaseous molecules by electron impact, sampled a few microseconds after impact.[1,2] Deducing a molecular structure from mass spectral data thus consists in principle of defining the products and reactions involved and thence reconstructing the molecule on paper. With the growing realization that this chemistry often closely parallels that induced by heat, light, and ionizing radiation[1,3–5] and can therefore help both to rationalize and to guide exploratory work in these other contexts, the mechanistic interpretation of mass spectra has taken on added interest. Metastable peaks, which stem from ion decompositions in flight following acceleration[6] and have long been recognized as a valuable source of information in correlating mass spectra with molecular structures,[7–9] have become increasingly useful in this process as a result of recently developed instrumental techniques.[8,9] Several operating modes for double-focusing instruments have been described that defocus the ion beams giving normal peaks in a mass spectrum, and greatly increase the collection efficiency of those giving metastable peaks. The limit of detection for metastable peaks has thus been lowered to 2 to 5 $\times 10^{-8}$ of total ion yield,[9,10] estimated to be sufficient to detect metastable peaks for any breakdown path of the molecular ion.[10] For example, such "metastable scanning" produced 110, 60, 40, 30, and 25 metastable peaks, respectively, in the spectra of *n*-heptane, *n*-hexane, *n*-pentane, *n*-butane, and propane.[11] Similarly large numbers of metastable peaks have been found by metastable scanning of *n*-butane,[12] *n*-decane,[13] benzene,[14] vinyl fluoride[15] and other fluoroethylenes,[16] several C_2–C_7 nonaromatic hydrocarbons,[10] nitromethane,[17] and 4-nonanone.[18]

Following up our long-standing interest in nitroarenes,[3,5] we have studied the decomposition of 1,3,5-trinitrobenzene (TNB) under electron impact, placing particular emphasis on metastable scanning as an experimental approach.

Experimental Section

The 1,3,5-trinitrobenzene was Eastman reagent grade. Its melting point, 122°, was not changed by recrystallization from water.

The conventional 70-eV spectrum was measured on a CEC Model 21-103 mass spectrometer with the inlet system and ionization chamber both at 250°. Metastable scanning was done on a CEC Model 21-110 double-focusing instrument, following previously described procedures.[14,15,18,19] Briefly, after focusing on a selected fragment ion, the electric-sector voltage is decoupled from the ion-accelerating voltage and the latter is scanned to increasing values. This procedure defocuses the ions that produce normal peaks in the conventional spectrum, and it successively focuses the fragment ions arising *via* metastable transitions of various contributing precursors in the first field-free region. The mass of a precursor ion is calculated by multiplying the mass of the selected fragment ion by the ratio of the accelerating voltages associated with the metastable peak and the normal peak. Measurement of the accelerating voltages corresponding to the centers of the broad metastable peaks is facilitated in our system by use of a fast digital voltmeter, the output of which is recorded by one of the galvanometers in the oscillograph. Precise masses of selected peaks were also measured on the 21-110, by matching against appropriate perfluoroalkane reference peaks.

---

[1] H. M. Grubb and S. Meyerson, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10; S. Meyerson, *Record Chem. Progr.*, **26**, 257 (1965); F. W. McLafferty, in "Topics in Organic Mass Spectrometry," A. L. Burlingame, Ed., Wiley-Interscience, New York, N. Y., 1970, p 223.

[2] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967; J. H. Beynon, R. A. Saunders, and A. E. Williams, "The Mass Spectra of Organic Molecules," Elsevier, New York, N. Y., 1968.

[3] S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, **88**, 4974 (1966).

[4] N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D'Angelo, *ibid.*, **87**, 4097 (1965).

[5] E. K. Fields and S. Meyerson, *Accounts Chem. Res.*, **2**, 273 (1969).

[6] J. A. Hipple and E. U. Condon, *Phys. Rev.*, **68**, 54 (1945); J. A. Hipple, R. E. Fox, and E. U. Condon, *ibid.*, **69**, 347 (1946); J. A. Hipple, *ibid.*, **71**, 594 (1947).

[7] For early examples, see M. B. Wallenstein, A. L. Wahrhaftig, H. Rosenstock, and H. Eyring, in "Symposium on Radiobiology," J. J. Nickson, Ed., Wiley, New York, N. Y., 1952, p 71; S. Meyerson, *Appl. Spectrosc.*, **9**, 120 (1955); H. M. Rosenstock, A. L. Wahrhaftig, and H. Eyring, *J. Chem. Phys.*, **23**, 2200 (1955); P. N. Rylander and S. Meyerson, *J. Amer. Chem. Soc.*, **78**, 5799 (1956).

[8] For recent reviews, see J. H. Beynon, *Advan. Mass Spectrom.*, **4**, 123 (1967); F. W. McLafferty, T. Wachs, and W. T. Pike, *ibid.*, **4**, 153 (1967).

[9] J. H. Beynon and R. G. Cooks, *Res./Develop.*, **22** (11), 26 (1971).

[10] U. Löhle and C. Ottinger, *Int. J. Mass Spectrom. Ion Phys.*, **5**, 265 (1970).

[11] P. Goldberg, J. A. Hopkinson, A. Mathias, and A. E. Williams, *Org. Mass Spectrom.*, **3**, 1009 (1970).

[12] M. Barber, W. A. Wolstenholme, and K. R. Jennings, *Nature (London)*, **214**, 664 (1967).

[13] T. E. Mead, C. G. Warner, and F. W. McLafferty, *Anal. Chem.*, **39**, 1748 (1967).

[14] K. R. Jennings, *J. Chem. Phys.* **43**, 4176 (1965).

[15] K. R. Jennings, in "Some Newer Physical Methods in Structural Chemistry," R. Bonnett and J. G. Davis, Ed., United Trade Press, London, 1967, p 105.

[16] K. R. Jennings, *Org. Mass Spectrom.*, **3**, 85 (1970).

[17] E. K. Fields and S. Meyerson, *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.*, **16** (1), B96 (1971).

[18] G. Eadon, C. Djerassi, J. H. Beynon, and R. M. Caprioli, *Org. Mass Spectrom.*, **5**, 917 (1971).

[19] J. H. Futrell, K. R. Ryan, and L. W. Sieck, *J. Chem. Phys.*, **43**, 1832 (1965).

Results and Discussion

The 70-eV spectrum of TNB obtained on the 21-103 is shown in Table I, where intensity is expressed as per cent of total ion intensity from mass 26 to 215. It includes but two metastable peaks: 72.0 ($74^+ \rightarrow 73^+ + 1$), 73.0 ($75^+ \rightarrow 74^+ + 1$). Four additional metastable peaks were detected in a conventional 70-eV spectrum recorded on the 21-110: 45.6 ($120^+ \rightarrow 74^+ + 46$), 74.0 ($76^+ \rightarrow 75^+ + 1$), 75.0 ($77^+ \rightarrow 76^+ + 1$), 112.3 ($167^+ \rightarrow 137^+ + 30$).

TABLE I

SPECTRUM (70 eV) OF 1,3,5-TRINITROBENZENE

M/z	$\%\Sigma_{26}$	M/z	$\%\Sigma_{26}$
26	0.20	73	1.03
27	0.31	73.0 (m)	0.08
28	1.05	74	10.3
29	0.22	75	19.0
30	28.3	76	1.47
31	0.11	77	0.22
32	0.07	78	0.06
36	0.08	79	0.19
37	1.10	80	0.06
38	1.63	81	0.03
39	0.29	86	0.06
40	0.04	87	0.17
41	0.08	88	0.19
42	0.03	89	0.08
43	0.04	90	0.13
44	0.76	91	2.82
45	0.04	92	0.26
46	1.22	93	0.07
48	0.06	104	0.08
49	0.29	105	0.07
50	0.80	107	0.04
51	0.55	120	4.25
52	0.17	121	0.38
53	0.22	122	0.04
54	0.03	137	0.53
55	0.05	138	0.04
60	0.10	151	0.07
61	0.98	167	1.80
62	2.28	168	0.14
63	3.06	169	0.02
64	0.46	183	0.13
65	0.10	197	0.49
66	0.10	198	0.03
67	0.04	213	9.83
68	0.02	214	0.77
69	0.04	215	0.14
72	0.04		
72.0 (m)[a]	0.01		

[a] m denotes metastable peak.

Table II shows the parent–daughter pairs found by metastable scanning of the 23 fragment ions judged critical to understanding the decomposition chemistry. Of the 96 peaks detected, 5 are attributed to decompositions of naturally occurring heavy-isotopic ions, leaving 91 defined segments of decomposition paths. The peak heights shown are only crude measures of relative probabilities of the transitions, perhaps no better than an order of magnitude.[18] Nonetheless, the intensity ratio of the two metastable peaks that were also observed in the 21-103 spectrum is identical with that in the latter spectrum. If the proportionality holds approximately for all the peaks listed in Table II, the lower limit of detection by metastable scanning of the 21-110, scaled to the two metastable peaks observed in the 21-103 spectrum, was about 2×10^{-7} of total ion yield.

Four precursor ions—masses 181, 153, 135, and 106—were identified whose normal peaks were absent from the conventional 21-103 spectrum; they were detected, however, in the conventional spectrum measured on the 21-110 by virtue of the higher sensitivity employed. A few other cases have been reported of similar identification of a precursor ion for which the conventional spectrum contained no normal peak.[18,20]

A different problem occurs in the search for precursors of relatively low mass daughter ions, where the mass range that can be scanned is limited by the normal 21-110 instrumentation.[18] Thus, no precursors of NO^+ were detected in the accessible mass range of 30 to 64. Metastable peaks corresponding to formation of NO^+ directly from the molecular ions have been found in the conventional spectra of five other nitroarenes.[21] Likewise in TNB, NO^+ may well be formed directly from the molecular ion, in a process complementary to the well-known primary loss of neutral NO from nitroarenes.

Even a cursory examination of Table II reveals many transitions that doubtless involve more than one step. For many years, a metastable peak was widely assumed always to denote a single reaction step. Such an assumption is not justified by the early work,[6,22] which explicitly recognized that the decay process need only be completed while the moving ions are in the field-free region, and is not restricted to one step; even so, in the cases studied there[6] and in the vast majority of conventionally recorded metastable peaks reported since, the neutral products are most likely single particles. A metastable peak corresponding to a process $m_1^+ \rightarrow m_2^+ + n$ establishes only that an ion having mass m_1 at the point of entry into the field-free region of the flight path breaks down in that region to produce an ion of mass m_2. The mass difference n corresponds to the one or more neutral products formed before the ionic product emerges from the field-free region. Breakdown to yield more than one neutral product may occur in a concerted fashion, as assumed by some workers,[23] but concertedness is not demanded by the experimental data, and such data are today usually interpreted in terms of series of successive reaction steps.[10,15,22,24,25] For our system, TNB in the CEC Model 21-110 instrument, the estimated time spent in transit through the field-free region is 3 to 10 μsec; the time elapsed from

---

[20] J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier, New York, N. Y., 1960, pp 261, 312, 369–370.

[21] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, **29**, 311 (1964).

[22] *Cf.* D. P. Maier, G. P. Happ, and T. H. Regan, *Org. Mass Spectrom.*, **2**, 1289 (1969).

[23] W. D. Crow, J. H. Hodgkins, and J. S. Shannon, *Aust. J. Chem.*, **18**, 1433 (1965); D. Goldsmith and C. Djerassi, *J. Org. Chem.*, **31**, 3661 (1966).

[24] D. C. DeJongh, S. C. Perricone, and W. Korytnyk, *J. Amer. Chem. Soc.*, **88**, 1233 (1966); K. R. Jennings, *Chem. Commun.*, 283 (1966); J. Seibl, *Helv. Chim. Acta*, **50**, 263 (1967); E. Caspi, J. Wicha, and A. Mandelbaum, *Chem. Commun.*, 1161 (1967); T. H. Kinstle and R. L. Muntz, *Tetrahedron Lett.*, 2613 (1967); C. Fenselau and F. P. Abramson, *Org. Mass Spectrom.*, **2**, 915 (1969); R. W. Kiser, R. E. Sullivan, and M. S. Lupin, *Anal. Chem.*, **41**, 1958 (1969); J. H. Beynon, W. E. Baitinger, J. W. Amy, and R. M. Caprioli, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 309 (1969); E. Tajima and J. Seibl, *ibid.*, **3**, 245 (1969); U. Rapp, H. A. Staab, and C. Wünsche, *Tetrahedron*, **27**, 2679 (1971).

[25] R. D. Koob, M. L. Morris, A. L. Clobes, L. P. Hills, and J. H. Futrell, *Chem. Commun.*, 1177 (1969); L. P. Hills, J. H. Futrell, and A. L. Wahrhaftig, *J. Chem. Phys.*, **51**, 5255 (1969).

TABLE II

PARENT-DAUGHTER PAIRS FOUND BY METASTABLE SCANNING

Mass of fragment ion scanned	Mass of precursor	Approximate peak height, arbitrary units
30[a]	None	
46[b]	151	tr[c]
	167	tr
62[b]	63	25
	89	6 }[d]
	90	4
	120	13
	137	tr
	167	tr
63[b]	64	16
	91	16
	121[e]	1
	137	tr
	167	tr
	183	tr
64[b]	92	11
	107	tr
	120	tr }[d]
	121	tr
	135[f]	tr }[d]
	137	tr
	151	tr
	167	1
	183	tr
65	66	3
	67	3
	92	2
	107	tr
	121	tr
	137	tr
	151	tr
	167	2
	213	tr

Mass of fragment ion scanned	Mass of precursor	Approximate peak height, arbitrary units
73	74	103
	120	0.4
	167	tr
	213	tr
74	75	800
	120	142
	167	1
	213	5
75	76	80
	121	33
	151	tr
	167	1
	197	tr
	213	14
76	77	11
	104	5
	121	1
	151	1
	167	3
	213	tr
77	78	8
	105	5
	120	2 }[d]
	121	2
	135[f]	1
	151	3
	167	2
	213	tr
90	91	7
91	106[f]	3
	137	104
	167	4
	183	tr
	213	1

Mass of fragment ion scanned	Mass of precursor	Approximate peak height, arbitrary units
92	120	2 }[d]
	121	4
	138[e]	20
	151	1
	167	2
	184[e]	tr
	214[e]	tr
104	121	3
	151	1
	167	2
107	137	3
	153[f]	0.2
	167	tr
	183	tr
	213	tr
120	151	tr
	167	20
	213	10
121	167	10
	214[e]	1
137	167	130
	183	4
	213	1
151	181[f]	1
	197	1
	213	tr
167	197	4
	213	10
183	213	2
197	213	tr

[a] The scan did not extend above mass 64 because of instrumental limitations. [b] The scan did not extend above mass 190 because of instrumental limitations. [c] tr denotes ≤ 1, where noise level precludes a more explicit value. [d] The peak profile and width suggest a pair of overlapping peaks. [e] The precursor and product are apparently heavy-isotopic ions. [f] The indicated precursor mass was not detected in the conventional spectrum, shown in Table I.

the moment of electron impact to entry into the field-free region would be about the same as in other instruments, of the order of 1 μsec.[6,26] The time scale is clearly sufficient to allow multistep processes.

The data in Table II, interpreted to allow a parent-daughter relationship to encompass multistep as well as one-step processes, were assembled into a decomposition scheme that should be a valid representation of the chemistry underlying the mass spectrum shown in Table I. In constructing such a scheme for TNB, the masses of neutral products pretty well define their elemental compositions (Table III). Most of these species occur commonly as neutral products in the mass spectra of nitroarenes.[3,21]

TABLE III

Mass	Assigned composition	Mass	Assigned composition
1	H	31	HNO
16	O	43	HNCO
17	OH	46	NO_2
27	HCN	47	HNO_2
28	CO	71	HC_2NO_2 (Nitroacetylene)
30	NO		

With the help of these neutrals, one can assign elemental compositions to successive ionic products. In a few cases, attempts to do so led to inconsistencies. (a) The formula assigned to the ion of mass 106 is $C_6H_2O_2^+$, leaving no way to lose 15 u to go to mass 91. (b) The ion of mass 89 appears as a precursor of mass 62, implying loss of HCN. We were unable to construct a plausible path to a nitrogen-containing ion of mass 89. (c) The formula assigned to the ion of mass 107 is $C_6H_3O_2^+$, leaving no plausible path for the loss of 43 u to go to mass 64, or of 42 u to go to mass 65.

In the hope of resolving these inconsistencies and also of establishing the identities and relative abundances of isobaric products where the preliminary decomposition scheme suggested two species of a given nominal mass, we measured the precise masses of selected peaks. The resulting assignments, from which naturally occurring heavy-isotopic species have been omitted, are listed in Table IV. Among the ions so found are several containing more hydrogen atoms than the original TNB

---

(26) S. Meyerson, *Appl. Spectrosc.*, **22**, 30 (1968).

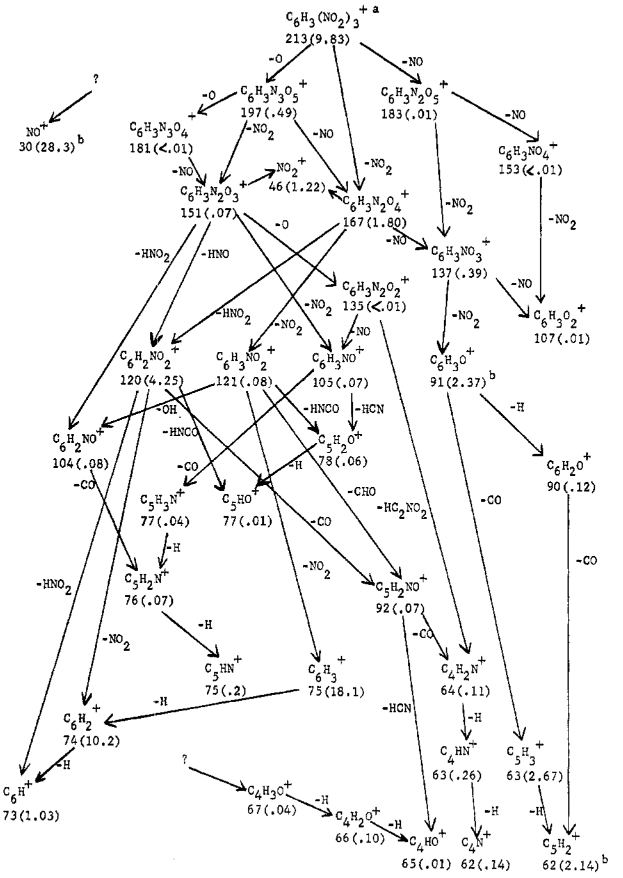

Figure 1.—Partial decomposition scheme for 1,3,5-trinitrobenzene: (a) the numbers below each ion formula give the nominal mass and, in parentheses, the relative intensity on the scale of the spectrum in Table I; (b) includes unknown contributions from dinitroaniline.

TABLE IV

IONIC SPECIES INFERRED FROM PRECISE-MASS MEASUREMENTS

Nominal mass	Species	% of intensity at nominal mass	Nominal mass	Species	% of intensity at nominal mass
62	C_4N^+	6	77	C_5HO^+	8
	$C_5H_2^+$	94		$C_5H_3N^+$	31
63	C_4HN^+	9		$C_6H_5^+$	61
	$C_5H_3^+$	91	89	$C_6H_3N^+$	100
64	$C_4H_2N^+$	35	90	$C_6H_2O^+$	94
	$C_5H_4^+$	65		$C_6H_4N^+$	6
65	C_4HO^+	7	91	$C_6H_3O^+$	84
	$C_4H_3N^+$	69		$C_6H_5N^+$	16
	$C_5H_5^+$	24			
			107	$C_6H_3O_2^+$	29
74	$C_6H_2^+$	100		$C_6H_5NO^+$	71
75	C_5HN^+	1	137	$C_6H_3NO_3^+$	74
	$C_6H_3^+$	99		$C_6H_5N_2O_2^+$	26
76	$C_5H_2N^+$	27	183	$C_6H_3N_2O_5^+$	6
	$C_6H_4^+$	73		$C_6H_5N_3O_4^+$	94

molecule and therefore not derivable from it. We were able to resolve the discrepancies by assuming that the anomalous data stem from a dinitroaniline impurity in the trinitrobenzene. The techniques that we employed are thus able to detect and characterize a low-level impurity whose contributions to the conventional spectrum are totally obscured by the main component. The finding for dinitroaniline is especially plausible in view of the evidence for inadvertent catalytic reduction of nitroarenes[27] and of nitromethane[17] to amines in the ionization chamber of the mass spectrometer.

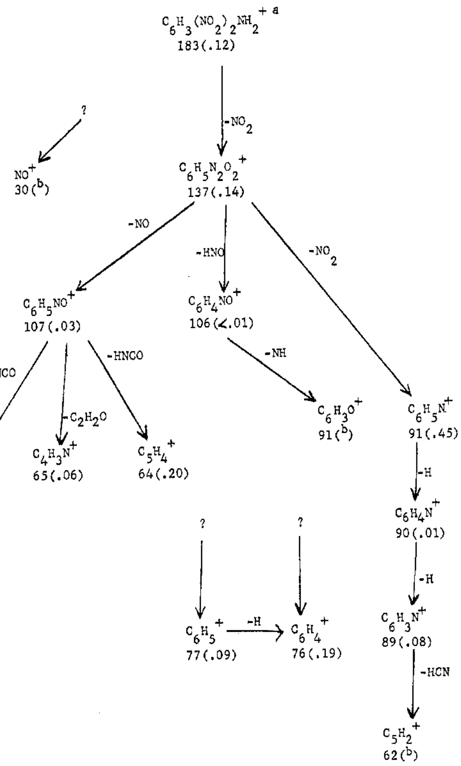

Figure 2.—Partial decomposition scheme for 3,5-dinitroaniline (in 1,3,5-trinitrobenzene): (a) the numbers below each ion formula give the nominal mass and, in parentheses, the relative intensity on the scale of the spectrum in Table I; (b) included in the intensities shown for trinitrobenzene (Figure 1).

All the available data are collected and summarized in Figures 1 and 2, partial decomposition schemes for TNB and the postulated 3,5-dinitroaniline, respectively. Below each ion formula are the nominal mass and, in parentheses, the relative intensity on the scale of the spectrum in Table I. Approximate corrections for heavy-isotopic contributions were made to the intensities listed in Table I, and the corrected values were pro-rated among isobaric components in accord with the distributions listed in Table IV. Of the total ion intensity in the spectrum in Table I, the species depicted in Figure 1 comprise 84.4% and those in Figure 2, 1.4%, although some ion origins, shown as question marks, remain unsettled. About 4.3% is attributed to heavy-isotopic contributions, and the remaining 9.9% is distributed among 34 peaks not studied in this work.

The dinitroaniline scheme includes reactions yielding neutral products of two masses in addition to those found in TNB (mass, assigned composition): 15, NH; 42, NCO or C_2H_2O (hydroxyacetylene or its tautomer, ketene).

The extent of the detail with which the complex network of competing and consecutive reactions is defined by metastable scanning supports the view that metastable peaks can thus be detected for nearly every con-

---

[27] J. H. Beynon, J. A. Hopkinson, and G. R. Lester, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 291 (1969).

tributing reaction step. The frequency of peaks corresponding to multistep sequences and the length of many of the sequences are unusual. Several such sequences (eq 1–6) comprise four and even five steps.

$$\underset{213}{C_6H_3N_3O_6^+} \longrightarrow \underset{167}{C_6H_3N_2O_4^+} \longrightarrow \underset{121}{C_6H_3NO_2^+} \longrightarrow \underset{78}{C_5H_2O^+} \longrightarrow \underset{77}{C_5HO^+} \tag{1}$$

$$\underset{213}{C_6H_3N_3O_6^+} \longrightarrow \underset{167}{C_6H_3N_2O_4^+} \longrightarrow \underset{121}{C_6H_3NO_2^+} \longrightarrow \underset{104}{C_6H_2NO^+} \longrightarrow \underset{76}{C_5H_2N^+} \longrightarrow \underset{75}{C_5HN^+} \tag{2}$$

$$\underset{213}{C_6H_3N_3O_6^+} \longrightarrow \underset{197}{C_6H_3N_3O_5^+} \longrightarrow \underset{151}{C_6H_3N_2O_3^+} \longrightarrow \underset{104}{C_6H_2NO^+} \longrightarrow \underset{76}{C_5H_2N^+} \longrightarrow \underset{75}{C_5HN^+} \tag{3}$$

$$\underset{213}{C_6H_3N_3O_6^+} \longrightarrow \underset{167}{C_6H_3N_2O_4^+} \longrightarrow \underset{120}{C_6H_2NO_2^+} \longrightarrow \underset{74}{C_6H_2^+} \longrightarrow \underset{73}{C_6H^+} \tag{4}$$

$$\underset{213}{C_6H_3N_3O_6^+} \longrightarrow \underset{167}{C_6H_3N_2O_4^+} \longrightarrow \underset{121}{C_6H_3NO_2^+} \longrightarrow \underset{92}{C_5H_2NO^+} \longrightarrow \underset{65}{C_4HO^+} \tag{5}$$

$$\begin{tikzcd}
 & & & \underset{90}{C_6H_2O^+} \arrow[dr] & \\
\underset{167}{C_6H_3N_2O_4^+} \arrow[r] & \underset{137}{C_6H_3NO_3^+} \arrow[r] & \underset{91}{C_6H_3O^+} \arrow[ur] \arrow[dr] & & \underset{62}{C_5H_2^+} \quad (6) \\
 & & & \underset{63}{C_5H_3^+} \arrow[ur] &
\end{tikzcd}$$

Strikingly, the molecular ion of mass 213 was detected as a precursor of every fragment ion scanned for it except those of masses 90, 92, 104, and 121. Likewise, the $[M^+ - NO_2]$ ion at mass 167 was detected as a precursor of every lower mass fragment ion scanned for it except those of masses 90 and 151. Thus, a substantial number of M^+ and $[M^+ - NO_2]$ ions, still intact upon entering the field-free region, about 1 μsec after electron impact, break down to give essentially all the observed products during the subsequent 3 to 10 μsec spent in this region. The low reaction rates associated with metastable transitions imply that the decomposing ions contain very little vibrational energy beyond that needed to drive the transition. Primary decomposition products that arise under these conditions and then proceed through one to four additional reaction steps must somehow have acquired the energy needed to drive the secondary and subsequent steps.[10,25,28] Such energy is most likely released early in a reaction sequence, not as translational energy, but rather as vibrational energy and perhaps as electronic excitation capable of undergoing internal conversion to vibrational energy. Previous electron-impact studies in our laboratories have led us to propose that decomposition/rearrangement processes release internal energy in a form available to drive further decomposition.[29] The seemingly crucial role performed by $C_6H_3N_2O_4^+$ in the overall decomposition of TNB makes the loss of NO_2 a prime candidate for consideration as a major source of excitational energy in the sense discussed here.

In effect, we are postulating that primary loss of NO_2 is the rate-controlling step for a large part of the chemistry occurring in the wake of electron impact on an isolated TNB molecule. This view accords well with the evidently central role of primary NO_2 loss in the mass spectra of other nitroarenes,[3,5,21,30] and it probably applies equally to pyrolysis of nitroarenes.[5,31] Specifically in the case of TNB, the postulate that this primary reaction proceeds *via* a high-energy transition state is supported by the great difficulty of nitrating *m*-dinitrobenzene;[32] by the thermal stability of TNB at temperatures as high as 260°, where it is reported to undergo no detectable decomposition after 3 days;[33] and by its great explosive power once it is detonated, exceeding that of trinitrotoluene.[32] Homolytic cleavage of a series of tetranitrobiphenyls into NO_2 and the complementary radical has been proposed as a first step in thermal decomposition of these compounds.[34] Similar loss of NO_2 may be the unidentified first-order primary reaction suggested, on the basis of thermodynamic data, as common to trinitrotoluene and other explosives containing nitro groups.[35]

Attempts to define the thermal reactions that are important in the early stages of explosions are hampered by severe experimental difficulties.[33-37] A few other workers have already suggested that the decomposition reactions of explosives under electron impact in the mass spectrometer may closely parallel those in the early stages of explosions, and therefore that mass spectra can furnish helpful guidance in the study of such processes,[38] as in that of thermal reactions of organic compounds generally. Our findings on TNB prompt us to agree with this view. We suggest that, with a little latitude in the use of the term, the breakdown of TNB in the mass spectrometer may profitably be viewed as an "explosion" in a system whose dimensions are those of a single molecule.

Registry No.—1,3,5-Trinitrobenzene, 99-35-4.

---

(28) U. Löhle and C. Ottinger, 17th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, 1969.

(29) S. Meyerson and H. Hart, *J. Amer. Chem. Soc.*, **85**, 2358 (1963); S. Meyerson, *J. Chem. Phys.*, **42**, 2181 (1965); S. Meyerson and A. W. Weitkamp, *Org. Mass Spectrom.*, **2**, 603 (1969).

(30) A kinetic study of mass spectra of substituted toluenes suggests that $C_7H_7^+$ ions formed from *p*-nitrotoluene by bombardment with 20-eV electrons have a higher average energy content than those formed similarly from the several other compounds studied [S. Tajima Y. Niwa, M. Nakajima, and T. Tsuchiya, *Bull. Chem. Soc. Jap.*, **44**, 2340 (1971)].

(31) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 724, 3224 (1967); *Intra-Sci. Chem. Rep.*, **3**, 219 (1969).

(32) L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath, Boston, Mass., 1944, pp 580, 581.

(33) J. C. Hoffsommer, "Thermal Stability of Polynitropolyphenyl Compounds at Elevated Temperatures," Report NOLTR 67-118, U. S. Naval Ordnance Laboratory, Silver Spring, Md., July 28, 1967.

(34) J. C. Hoffsommer and J. F. McCullough, "Thermal Stabilities of Tetranitrobiphenyl Isomers at Elevated Temperatures," Report NOLTR 68-159, U. S. Naval Ordnance Laboratory, Silver Spring, Md., Oct 31, 1968.

(35) M. A. Cook and M. T. Abegg, *Ind. Eng. Chem.*, **48**, 1090 (1956).

(36) J. C. Hoffsommer and J. S. Feiffer, "Thermal Stabilities of Hexanitroazobenzene and Hexanitrobiphenyl," Report NOLTR 67-74, U. S. Naval Ordnance Laboratory, Silver Spring, Md., June 23, 1967.

(37) R. N. Rogers, *Anal. Chem.*, **39**, 730 (1967); J. Dacons, H. G. Adolph, and M. J. Kamlet, *J. Phys. Chem.*, **74**, 3035 (1970).

(38) K. Torssell and R. Ryhage, *Ark. Kemi*, **23**, 525 (1965); R. C. Musso, "3rd Combustion Conference," Chemical Propulsion Information Agency Publication No. 138, Vol. 1, Johns Hopkins University, 1967, p 69; J. T. Larkins, F. E. Saalfeld, and L. Kaplan, *Org. Mass Spectrom.*, **2**, 213 (1969).

Acknowledgments.—We are grateful to F. E. Saalfeld of the Naval Research Laboratory, Washington, D. C., and J. C. Hoffsommer of the Naval Ordnance Laboratory, Silver Spring, Md., for helpful suggestions and for guidance to relevant research reports. We are especially indebted to E. S. Kuhn for his care, skill, persistance, and good humor in coaxing our high-resolution instrument to answer our questions.

Reactions of Nitrosobenzene, *o*-Nitrosotoluene, and Pyridine *N*-Oxide with Phosphorus Pentachloride

ROBERT C. DUTY* AND GARY LYONS

Illinois State University, Normal, Illinois 61761

Received April 24, 1972

The products of the reaction of phosphrous pentachloride with nitrosobenzene (1), *o*-nitrosotoluene (2), and pyridine *N*-oxide (3) were identified by vpc with known samples. In all three compounds, phosphorus pentachloride deoxygenated the nitrogen and formed chlorinated aniline, toluidine, and pyridine products, respectively, in the anhydrous solvent methylene chloride.

This study investigated the products of the reaction of phosphorus pentachloride with nitrosobenzene (**1**), *o*-nitrosotoluene (**2**), and pyridine *N*-oxide (**3**) in the solvent methylene chloride. The purpose of the investigation was to ascertain whether the tetrachlorophosphonium cation (PCl_4^+) would deoxygenate the nitrogen and chlorinate the ring. As expected, the oxygen from the nitroso group was removed to form phosphoryl chloride along with the hydrochloride salts of the chlorinated aromatic amines. Nitrosobenzene has been deoxygenated previously with triethyl phosphite. Bunyan and Cadogan[1] converted nitrosobenzene into azoxybenzene which subsequently can be converted into azobenzene with excess reagent.[2]

In the reaction with pyridine *N*-oxide, the phosphorus pentachloride would not react at the refluxing temperature of methylene chloride. Previously, Murakami and Matsumura[3] had treated pyridine *N*-oxide with solid phosphorus pentachloride at 140° to form 4-chloropyridine. Consequently, the reactants were placed in a sealed Pyrex tube and heated to 130° for 90 min. The solution turned a light brownish black, but no black-tarry residue remained as was the case with the nitroso compounds.

When phosphorus pentachloride dissolves in methylene chloride, the molecular ions, $(PCl_4^+)(PCl_6^-)$, are formed in equilibrium with molecular phosphorus pentachloride. This is substantiated from our experiments with 9-xanthone and 9-thioxanthone which immediately formed brilliant yellow and red complex ions, respectively, with the $(PCl_4^+)(PCl_6^-)$ molecular ions from phosphorus pentachloride.[4] Therefore, when nitroso compounds are added to a methylene chloride solution of phosphorus pentachloride, the initial reaction is undoubtedly the electrophilic attack of the tetrachlorophosphonium cation, (PCl_4^+), onto the negative end of the oxygen–nitrogen dipole of the nitroso group with the subsequent loss of a chloride ion.

The chlorination of the aromatic ring, as revealed from Table I, is probably an intermolecular chlorination. If intramolecular chlorination were occurring, one would expect the ratio of ortho/para isomers to be greater than 1; however, for both compounds **1** and **2** the ortho/para ratios were much less than 1 with values of 0.65 and 0.024, respectively.

TABLE I

REACTIONS OF PHOSPHORUS PENTACHLORIDE WITH NITROSOBENZENE, *o*-NITROSOTOLUENE, AND PYRIDINE *N*-OXIDE

Product	Yield, %
Nitrosobenzene: $POCl_3$, 61.2%	
Aniline	3.5
4-Chloroaniline	20.0
2,4-Dichloroaniline	18.5
2-Chloroaniline	13.0
2,4,6-Trichloroaniline	2.2
Total	57.2
o-Nitrosotoluene: $POCl_3$, 68.1%	
o-Toluidine	0.8
4-Chloro-*o*-toluidine	20.8
2,4-Dichloro-*o*-toluidine	18.7
2-Chloro-*o*-toluidine	0.5
Total	40.8
Pyridine *N*-Oxide: $POCl_3$, 55.0%	
Pyridine	65.4
2-Chloropyridine	10.2
3-Chloropyridine	10.2
4-Chloropyridine	1.9
Total	87.7

The actual species responsible for chlorination was not definitely established in this study. However, the additional experiments performed with chlorine, phosphorus trichloride, and phosphoryl chloride eliminated some of the possible precursors to chlorination. Phosphorus trichloride and phosphoryl chloride have previously been reported to chlorinate aromatic rings simultaneously with their ability to deoxygenate such compounds as pyridine *N*-oxide,[5] substituted pyridine *N*-oxides,[5,6] quinoline *N*-oxides,[5] lutidine *N*-oxides,[7] picoline *N*-oxides,[7] and pyrazine *N*-oxides.[8] Consequently, we treated compound **2** with excess quantities

---

[1] P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, 42 (1963).

[2] T. Mukaiyama, H. Nambu, and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962).

[3] M. Murakami and E. Matsumura, *J. Chem. Soc. Jap.*, **70**, 393 (1949); *Chem. Abstr.*, **45**, 4698 (1951).

[4] R. C. Duty and R. E. Hallstein, *J. Org. Chem.*, **35**, 4226 (1970).

[5] M. Hamana, *J. Pharm. Soc. Jap.*, **75**, 121 (1955); *Chem. Abstr.*, **50**, 1817 (1956).

[6] F. Gadient, E. Jucker, and A. Lindenmann, *Helv. Chim. Acta*, **45**, 1860 (1962).

[7] T. Kato, *J. Pharm. Soc. Jap.*, **75**, 1236 (1955); *Chem. Abstr.*, **50**, 8665 (1956).

[8] L. Bernandi, G. Palamidessi, A. Leone, and G. Larini, *Gazz. Chim. Ital.*, **91**, 1431 (1961); *Chem. Abstr.*, **57**, 2223 (1962).