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Influence of the substituent on the major decomposition channels of the NO_2 group in *para*-substituted nitrobenzenes: a tandem mass spectrometric study

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ABSTRACT: The relative extents of loss of NO_2 and NO were determined by 70 eV electron ionization and tandem mass spectrometry using B/E linked scans to investigate metastable (unimolecular) and collision-induced dissociation processes for molecular ions formed by electron ionization of *para*-substituted nitrobenzene compounds. The substituents used (NO_2, CHO, H, OCH_3) represent a wide range of electron donor–acceptor properties. Loss of NO_2 was favored by electron-withdrawing groups, while an electron-donor group favored loss of NO. Ion fragmentation mechanisms are consistent with the hypothesis that NO_2 to ONO (nitro to nitrite) isomerization precedes the loss of NO. Ring fragmentation (loss of CO) was observed only after all of the electron-withdrawing groups had dissociated. while the electron-donor group OCH_3 remained attached to the ring in the analogous CO elimination. These results are placed in the context of the thermolysis behavior of nitroaromatic explosives. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: tandem mass spectrometry; branching ratios; nitrobenzene compounds

INTRODUCTION

Nitroaromatic compounds comprise an important class of explosive materials. The identity of the parallel and consecutive pathways of thermal decomposition is central to defining the ignition, combustion and explosion characteristics of these highly reactive materials. Unfortunately, the mechanisms in the condensed phase are complex and difficult to define and characterize kinetically. Although it is generally risky to equate the findings of unimolecular chemistry in the gas phase directly to the dense condensed phase, it appears that the reaction schemes induced by heat, light and ionizing radiation in different phases of nitroaromatic compounds, and for the radical cations and anions in the gas phase, are similar.[1–4] Consequently, the unimolecular reaction of gaseous ions of nitroaromatic compounds will likely provide useful guides to the elementary processes in bulk compounds under more practical conditions.

The processes

$$C_6H_5NO_2{}^{+\cdot} \rightarrow C_6H_5{}^{+} + NO_2{}^{\cdot} \qquad (1)$$

$$C_6H_5NO_2{}^{+\cdot} \rightarrow C_6H_5ONO^{+\cdot} \qquad (2)$$

are widely indicated to be initial steps of decomposition and rearrangement of nitroaromatic ions[5–9] and neutral compounds,[10,11] especially in the absence of an *ortho*-related substituent. The presence of an *ortho* substituent frequently expands the number of reactions through interactions with the NO_2 group.[4] The process

$$C_6H_5ONO^{+\cdot} \rightarrow C_6H_5O^{+} + NO^{\cdot} \qquad (3)$$

usually follows process (2) for the formation of NO or C_6H_5O (neutrals or ions); hence, NO formation is described as a two-step process. Unlike nitroaliphatic compounds, where the nitrite isomer the analogous neutral molecule reactant of process (3) has been isolated[12] and its dissociation behavior studied by mass spectrometry,[13] no aryl nitrite compound appears to have been isolated to date. However, the most recent work on nitrobenzene ions, including reported multi-photon dissociation in a time-of-flight mass spectrometer (TOF-MS)[14–16] or a Fourier transform mass spectrometer (FT-MS),[17] the cavity-ring-down technique,[18] pyrolysis of nitrobenzenes in a mass spectrometer[19] and *ab initio* quantum mechanical calculations,[18,20] strongly supports the existence of process (2) as an intermediate step in NO elimination.

Our attention is mainly focused on the influence of substituents in the position *para* to the NO_2 group on the relative rates of decomposition reactions (1)–(3). The

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effect of the substituent on these processes is not apparent from the gaseous products liberated by pyrolysis of the condensed phase,[4b] although useful insights have been reported previously using spectrometry.[6] In this work, four *para*-substituted nitrobenzene compounds having substituents with widely different electron donor–acceptor properties[21] were investigated with tandem mass spectrometry (MS–MS) via metastable and collision-induced dissociation (CID) processes. These methods enable process (1) to be distinguished from processes (2) and (3) in the parent molecular ion without interference from secondary reactions. Substituent control[6] over processes (1)–(3) can thereby be obtained.

EXPERIMENTAL

Experiments were performed with a VG AutoSpec triple-sector hydrid mass spectrometer of EBEqQ geometry (E = electric sector, B = magnetic sector, q = r.f. quadrupole and Q = quadrupole mass filter). 1,4-Dinitrobenzene, 4-nitrobenzaldehyde, nitrobenzene and 4-nitroanisole were obtained from Aldrich Chemical.

The influence of a *para* substituent on the fragmentation channels of the NO_2 group in the four nitrobenzene derivatives was investigated by the use of three techniques: 70 eV electron ionization (EI) relative ion intensity mass spectra and unimolecular (metastable) and CID processes in the first field-free region using *B/E* linked scans. The *B/E* unimolecular scan provides all of the fragment ions from a selected parent ion that are usually formed by low internal energy pathways, often requiring isomerization and/or rearrangement prior to dissociation. The *B/E* method has the advantage over the EI approach that the daughter ions specific to the parent ion are unambiguously determined. *B/E* CID experiments provide information on all possible dissociation pathways leading to fragment ions from a selected parent ion. The substituent effect is most clearly obtained in this manner, although it may be qualitatively indicated in the EI spectra. Some CID experiments were performed at low collision energies in the r.f.-only quadrupole to determine the lower energy dissociation pathway.

In addition to Hammett scale comparisons of substituent electron donor–acceptor properties, semiempirical MO calculations using the AM1 method[22] were carried out on these molecules. The mid-point potential, V_{mid}, of the C—NO_2 bond is defined[23] as $(V_C + V_N)/2R$, where V_C and V_N are the atom charges based on a Mulliken population analysis and R is the C—N bond distance. This model of the charge density variation has been used previously to correlate several properties of nitroaromatic compounds.[23–25]

RESULTS

The experimental findings for each compound are discussed below before comparisons and conclusions are made concerning this class of compounds.

1,4-Dinitrobenzene

The NO_2 substituent on the Hammett scale is highly electron withdrawing ($\sigma_p = +0.78$).[21] Consequently, the influence of electrophilic substitution on -NO_2 elimination is highest for this molecule. Figure 1 shows the fragmentation pathways for the molecular ion (*m/z* 168) determined by the metastable and CID reactions of the molecular ion and its fragment ions. The location of the positive charge on the even-electron cations is not specified in any of the fragmentation schemes of this paper, in recognition of the fact that some charge delocalization is expected. The dissociation scheme shows many more pathways than were observed by Yinon[26] from the CID of the same ion. However, it supports the fragmentation scheme proposed by Fields

Table 1. Substituent characteristics and ion current ratios (peak heights scaled to the peak height for NO for the parent ion) of *para*-substituted nitrobenzene compounds

Para substituent	σ_p	V_{mid}	*Technique*	(Loss of NO_2)/(loss of NO)
NO_2	+0.78	+0.63	CID	13
			Metastable	5
			EI	30
CHO	+0.42	+0.62	CID	3.3
			Metastable	1.5
			EI	20
H	0	+0.59	CID	1
			Metastable	0.5
			EI	10
OCH_3	−0.27	+0.54	CID	0.08
			Metastable	0.06
			EI	0.25

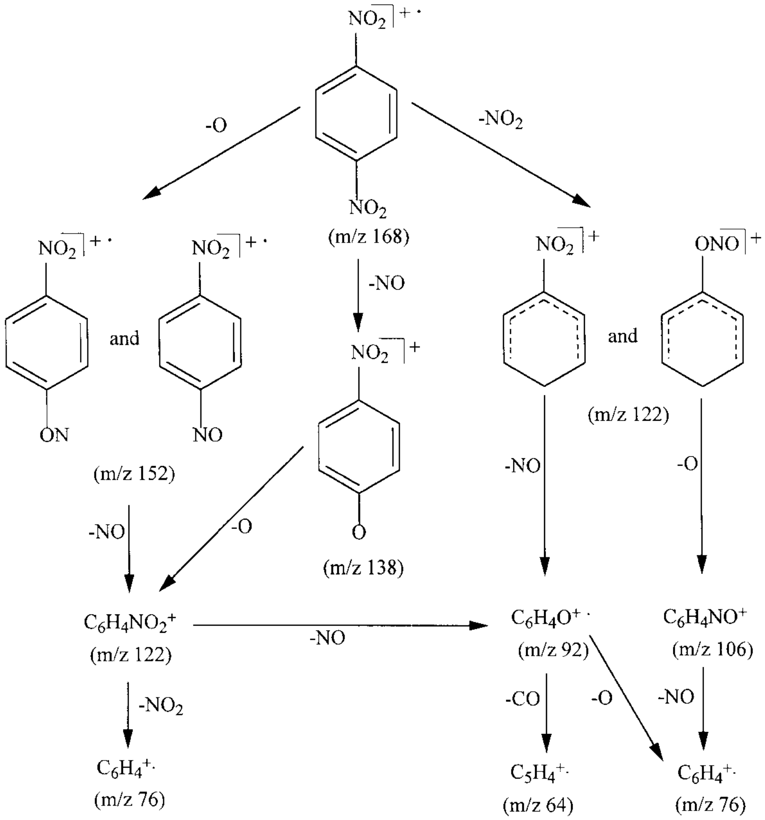

Figure 1. Fragmentation pattern of 1,4-dinitrobenzene determined from the *B/E* metastable and CID spectra

and Meyerson.[27] As summarized in Table 1, the EI, metastable and CID *B/E* scans all clearly show the preference for the loss of NO_2. It is widely known[7,9,14,16,17,28] that the $C_6H_4O^{+\cdot}$ cation (*m/z* 92) loses CO to form $C_5H_4^{+\cdot}$, again confirmed here by the *B/E* scan of the *m/z* 92 fragmentation. It is of interest that *m/z* 92 is the highest mass fragment in Fig. 1 to exhibit CO loss.

4-Nitrobenzaldehyde

The CHO group is moderately electron withdrawing ($\sigma_p = +0.42$) on the Hammett scale.[21] Figure 2 shows the fragmentation pathways of the *p*-nitrobenzaldehyde ion determined by *B/E* metastable and CID scans. The loss of NO_2 dominates over the loss of NO by the parent molecular ion in the EI and *B/E* CID spectra summarized in Table 1. The fragmentation pattern also shows the loss of HNO_2 and HNO, suggesting possibly the facile migration of H from the CHO group. HNO_2 is also lost from 4-nitrobenzoic acid,[29] possibly in the same manner or by abstraction of H by free NO_2. The abundances of HNO_2 and HNO may, therefore, not necessarily be simply related to a substituent effect because a multi-step internal rearrangement may have occurred. The loss of N from the *m/z* 134 cation to form the *m/z* 120 radical cation occurs with an abundance of 3% relative to the most abundant fragment ion, *m/z* 105, and is good evidence that the nitrite isomer has formed. We believe that the loss of N is not merely an artifact of linked scans because the sequential loss of N and O is seen in nitrobenzene (see below).

Nitrobenzene

The H atom is the baseline substituent in nitrobenzenes on the Hammett scale ($\sigma_p = 0$).[21] The fragmentation scheme shown in Fig. 3 was constructed from the *B/E* metastable and CID data. According to the (loss of NO_2)/(loss of NO) ratios in Table 1, these two processes are of approximately equal abundance when collisionally activated. Process 1 dominates processess (2) and (3) in the EI spectra, but does so to a lesser extent than the electron-withdrawing NO_2 and CHO substituents discussed above. In the metastable spectrum, dissociation of the parent ion via loss of NO by processes (2) and (3) is favored over process (1). The different results for the two *B/E* scans reflect the sampling of only low-energy decomposition mechanisms, while collisional activation increases the internal energy in the molecular ion and samples higher energy processes also found in the EI mass spectra. We may infer that processes (2) and (3)

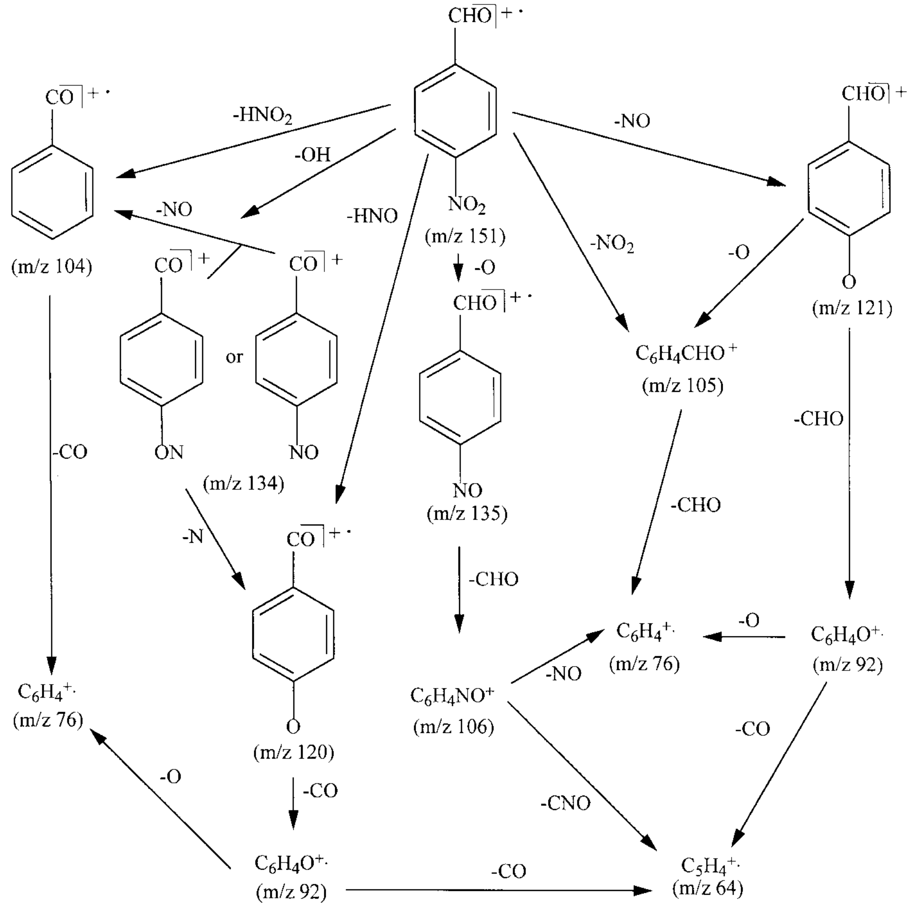

Figure 2. Fragmentation pattern of 4-nitrobenzaldehyde determined from the *B/E* metastable and CID spectra

have a lower overall activation energy than process (1). This explanation is in line with earlier experimental findings[30–33] regarding the activation energy of these processes from the molecular cation [process (1) ca 37–46 kcal mol^{-1}, processes (2) and (3) ca 9 kcal mol^{-1} (1 kcal = 4.184 kJ)] and from RRKM/QET calculations[9] [process (1) 27.4 kcal mol^{-1}, processes (2) and (3) 23.5 kcal mol^{-1}]. It is further supported in this work by performing low-energy CID experiments on the nitrobenzene parent ion using the r.f. quadrupole. The (loss of NO_2)/(loss of NO) ratio decreased to 1:8 at 10 eV energy consistent with a lower activation energy for the loss of NO.

A general result from this suite of experiments on $C_6H_5NO_2^{+\cdot}$ is clear evidence supporting the stepwise mechanism for NO loss. The CID spectrum of $C_6H_5NO^{+\cdot}$ (*m/z* 107) shows decomposition to both $C_6H_5O^+$ (*m/z* 93) and $C_6H_5^+$ (*m/z* 77). The O-bonded $C_6H_5O^+$ fragment ion can only be formed via isomerization/rearrangement of the N-bonded substituent since N atom elimination from $C_6H_5NO^{+\cdot}$ is impossible. Loss of N from *m/z* 107 is a minor channel with an abundance of about 4% compared with the most abundant channel which forms $C_6H_5^{+\cdot}$ via loss of NO. Finally, as was observed for 1,4-dinitrobenzene and 4-nitrobenzaldehyde, the ring remains intact until the $C_6H_5O^+$ fragment is formed which then fragments to $C_5H_5^+$ with the loss of neutral CO.

4-Nitroanisole

The methoxy substituent is electron donating on the Hammett scale ($\sigma_p = -0.27$).[21] Figure 4 shows the fragmentation pattern deduced as before from the metastable and CID processes. The dissociation tendencies in both the EI and *B/E* spectra clearly reveal that the parent ion loses NO [processes (2) and (3)] in preference to NO_2 [process (1)] under all experimental conditions. As was the case for nitrobenzene ion, process (2) must have occurred because $CH_3OC_6H_4O^+$ (*m/z* 123) comes from *m/z* 137 with about 7% efficiency. The latter ion implies the existence of the $CH_3OC_6H_4ON^{+\cdot}$ isomer in order to release N.

The low-energy CID spectrum of $CH_3OC_6H_4O^+$ (*m/z* 123) reveals that fragmentation of the ring takes place while the CH_3O substituent remains attached to the ring. This mechanism differs from that observed for electron-withdrawing substituents described above, all of which were eliminated prior to ring opening and loss of neutral CO.

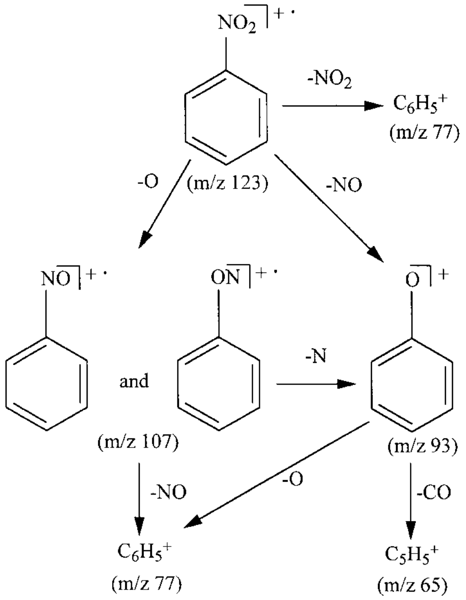

Figure 3. Fragmentation pattern of nitrobenzene determined from the *B/E* metastable and CID spectra

DISCUSSION

The elimination of NO was shown to proceed via the rearrangement process given by reactions (2) and (3) by determining the fragmentation patterns for the 4-nitroanisole and nitrobenzene ions. In these cases N is lost from an ion originating from the parent ion minus O. The loss of N can only occur if the C—O—N isomer of the NO substituent exists as m/z 107 from $C_6H_5NO_2^{+\cdot}$, m/z 134 from $CHOC_6H_4NO_2^{+\cdot}$ and m/z 137 from $CH_3OC_6H_4NO_2^{+\cdot}$. The transition state for process (2) has been proposed to be an ion–dipole interaction between $C_6H_5^{+\cdot}$ and $NO_2^{\cdot}$.[17]

Because the two decomposition channels of most interest in this work are process (1), the loss of NO_2, and processes (2) and (3), leading to the loss of NO, it is necessary to comment on the possibility that NO_2 might be lost by homolysis of the C—O bond after process (2) occurs. This would complicate the use of the loss of NO_2 and NO to measure the relative extents of process (1) and processes (2) and (3). A comparison of the rate constants for the loss of NO_2 (fast) and NO (slower)[7,17] suggests, however, that formation of NO_2 by process (2) is unlikely. The reasoning is that since the dissociation energies of the C—N and C—O bonds of $C_6H_5NO_2$ and C_6H_5ONO, respectively, are similar (ca 70 kcal mol^{-1}),[4,20] but the O—NO bond of C_6H_5NO is weak (17–24 kcal mol^{-1}),[20,34] the rates of loss of NO_2 and NO would be expected to be similar if NO_2 came from the $C_6H_5ONO^+$ isomer. As just noted, they have been found to be different.[17] The logical explanation is that NO_2 results from process (1), which is expected to be fast, whereas NO comes from processes (2) and (3) which

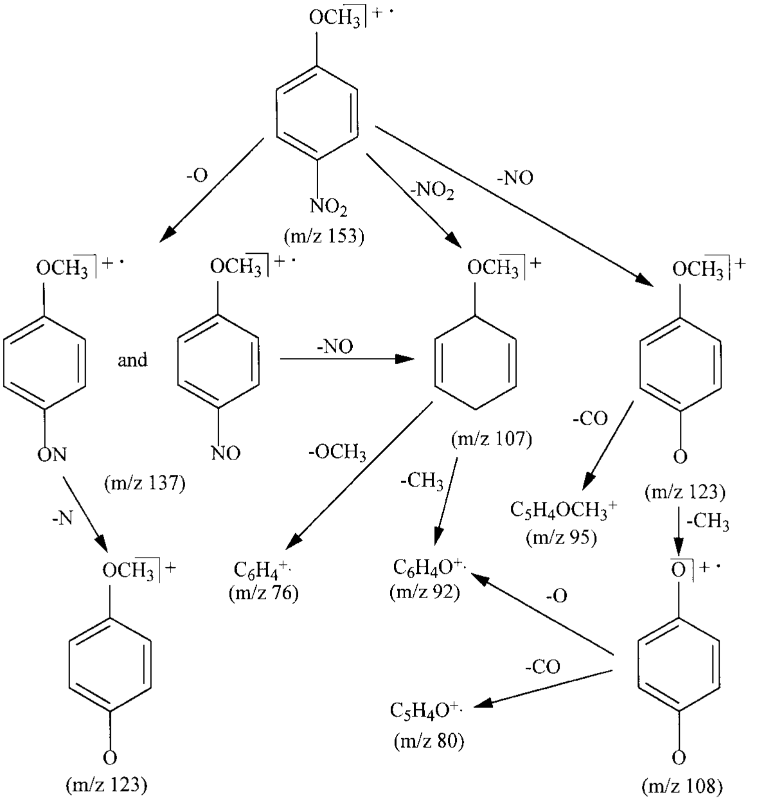

Figure 4. Fragmentation pattern of 4-nitroanisole determined from the *B/E* metastable and CID spectra

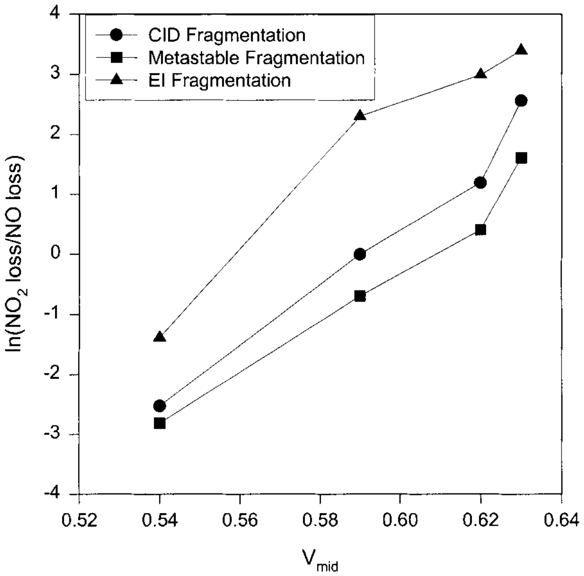

Figure 5. Correlation of V_{mid} (defined in the Experimental section) with the (loss of NO_2)/(loss NO) ratio from the parent ion

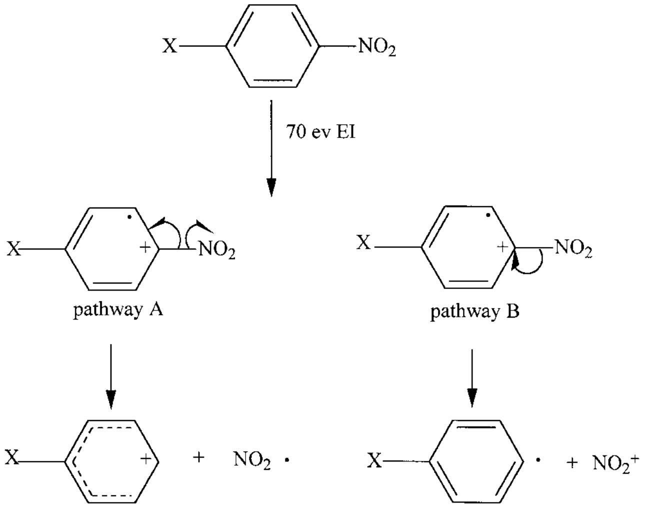

Figure 6. Mechanistic scheme for the effect of an electron-withdrawing *para* substituent on the decomposition pathway of the NO_2 group in nitroaromatic compounds. The charge shown is formal

are expected overall to be slower. Further support for this can be drawn from the dissociation behavior of the methyl nitrite ion, CH_3ONO^+, which does not have either CH_3^+ or NO_2^+ as dissociation channels of any significance.[13]

The relative order of the activation energies for NO_2 loss and NO loss is clearly indicated by the metastable and low-energy CID spectra. Lowering of the kinetic energy of collisional activation of the nitrobenzene cation using the r.f. quadrupole (~10 eV), rather than a keV collisional activation, favors processes (2) and (3) over process (1). This indicates that processes (2) and (3) have an activation energy that is overall lower than that of process (1). Similar conclusions have been reached on nitrobenzene from photodissociation,[14,17,32] shock tube data,[10] RRKM/QET[9] and *ab initio* quantum mechanical calculations.[20] At higher internal energy the simple bond-

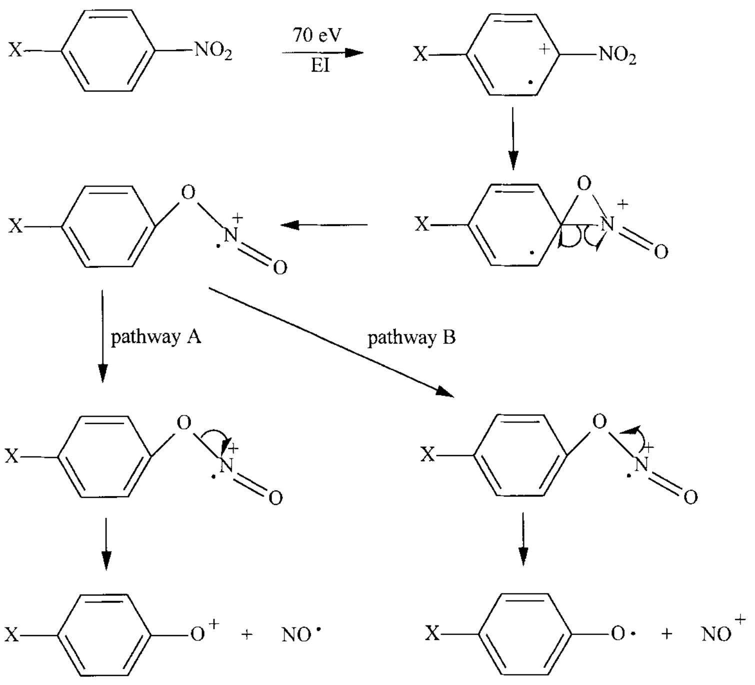

Figure 7. Mechanistic scheme for the effect of an electron-donating *para* substituent on the decomposition pathway of the NO_2 group in nitroaromatic compounds. The charge shown is formal

breaking reaction (1) becomes the dominant reaction path because of the lower frequency factor of rearrangement reactions.

The electron donor–acceptor characteristics of the substituent *para* to the NO_2 group influence the balance of process (1) and processes (2) and (3). The EI, CID and metastable *B/E* spectra indicate that process (1) is enhanced by electron-withdrawing substituents (Table 1), whereas electron-donating substituents favor processes (2) and (3). Figure 5 is a plot of V_{mid} of the C—NO_2 bond as a function of the *para* substituent vs the ratio of currents for the ions corresponding to the loss of NO_2 and loss of NO from the parent molecular ion. While monotonic relations do not exist, a trend is found among these variables, as well as the Hammett σ_{p} constants. Consequently, the electron density in the aromatic ring appears to have a major influence on the ratio of parallel reactions leading to the liberation of NO_2 and NO. Figures 6 and 7 give qualitative mechanistic schemes of how the electron-withdrawing and electron-donating properties of the substituent, respectively, may have affected the reaction pathways of the nitro group. Inductively electron-withdrawing substituents (e.g. CHO, NO_2) weaken the C— N bond, whereas a resonantly electron-donating substituent (OCH_3) will destabilize the nitrite intermediate and stabilize the single-bond cleavage product.

When an electron-withdrawing group is attached to the ring, the ring remains intact during fragmentation down to the phenoxy radical cation. The first evidence of ring dissociation is from the $C_6H_4O^{+\cdot}$ ion. This finding is in line with the findings of earlier mass spectral studies.[35,36] On the other hand, when an electron-donor substituent (CH_3O) is present, we observed that the ring dissociates before the electron donor substituent has reacted (Fig. 4). Hence the tendency of the aromatic ring to dissociate is also substituent dependent.

Finally, it is useful to comment on the possible relation between this work and the behavior of polynitroaromatic explosives in the condensed phase. Many such compounds, including 2,4,6-trinitrotoluene, are observed to produce a large amount of NO compared with NO_2 when they are heated slowly or flash heated.[37,38] When a much larger number (19) of substituents and flash heating are used, it is observed that electron-donating substituents produce much more NO than electron-withdrawing substituents.[39] It is not possible to quantitate this pattern because of the large number of possible intermolecular processes and competing secondary oxidation–reduction reactions in the condensed phase before NO appears in the gas phase. The pattern of substituent control over process (1) vs processes (2) and (3) found in the gas phase is, however, qualitatively reflected in the pyrolysis results of actual explosives in the condensed phase.

Process (1) has a faster rate (one step) and produces a stronger oxidizing agent (NO_2) than do processes (2) and (3) (two steps and NO as the oxidizing agent). Therefore, compounds with electron-donating substituents *para* to NO_2 would be less sensitive to impact initiation than those with electron-withdrawing groups in this position. Although the interactions among the substituents add an additional complication in polynitroamatic compounds, there is a rough tendency for electron-withdrawing substituents to produce more impact sensitivity than electron-donating groups.[39]

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