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Infrared Multiple-Photon Dissociation of the Nitrobenzene Radical Cation. A Paradigm for Competitive Reactions

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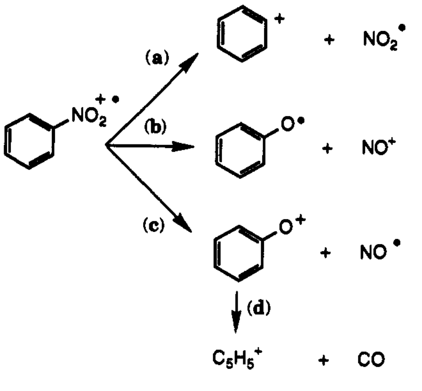
Abstract: The dissociation of nitrobenzene cation displays a variety of surprising and even apparently nonstatistical reaction behaviors. We have used infrared multiple-photon dissociation experiments to further study the reactions of this system. These experiments along with a previous photoelectron photoion coincidence study indicate that, for some products, the nitrobenzene cation dissociates to form an ion–neutral complex and then reassociates to give the phenyl nitrite cation. A reaction mechanism involving statistical dissociation is shown to account for the experimental data.

The nitrobenzene cation is among the most extensively studied ionic species.[1-15] Two photoelectron photoion coincidence (PEPICO) studies,[1,2] an infrared multiple-photon (IRMP) dissociation study,[3] and several UV/vis photodissociation studies,[4-9] as well as numerous conventional mass spectrometric studies,[10-15] have focused on this ion. The apparent complexity of its dissociation mechanism, however, has prevented the emergence of a clear understanding which is consistent with all of the evidence, some of it apparently contradictory. In this work, we present new IRMP dissociation[16-19] results in which a wide range of laser intensities is employed to dissociate the nitrobenzene ion. A mechanism involving competitive dissociation and isomerization/reassociation in an ion–neutral complex[20-33] is proposed to account for the present results as well as most previously reported data.



(1)

All studies agree that the nitrobenzene ion dissociates to four major fragments (eq 1) with activation energies ranging from 1.0 to 1.2 eV.[34] The simple interpretation of this system of equations is that the various decay channels are in competition[1,2,35,36] with each other so that the branching ratios to these channels are given by k_i/k_{tot}, where k_i is the rate constant for the ith reaction and k_{tot} is the sum of the rate constants for the three primary reactions. When all reactions are in competition with each other, the rate constants as measured by the appearance of the various product ions will be the same and will be equal to the total decay rate, k_{tot}. The rate constants for the individual reactions can be obtained from the branching ratios and k_{tot}.

It is expected that simple bond-cleavage reactions, such as the loss of NO_2, will proceed via loose transition states (high *A* factors) and thus dominate at high internal energies.[37-39] On the other hand, reactions involving *direct* rearrangement processes are expected to proceed via tight transition states (low *A* factors) and

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thus can be observed at low energies, if their activation energies are below those for the direct bond-cleavage reactions.[37-39] The rate measurements and breakdown diagrams (fractional ion yields as a function of the nitrobenzene ion internal energy) as determined by the PEPICO studies[1,2] as well as the UV photodissociation studies[4-6] are in qualitative agreement with these ideas. At an ionizing energy of 11 eV, most of the dissociation occurs via NO loss, while at 13 eV nearly 80% of the ions dissociate via NO_2 loss.

Even though this mechanistic description appears qualitatively correct, careful dissociation rate measurements are not consistent with direct competition. Panczel and Baer[1] found that nitrobenzene cations formed with 33.7 kcal/mol of energy predominantly lose NO (eq 1c). At this same energy, the nitrobenzene cation also loses NO_2 (eq 1a) in about one-tenth the abundance of NO loss. However, the rate of NO_2 loss at this same ion energy is at least 16 times faster than the rate for NO loss.[1] Thus NO loss and NO_2 loss are apparently not in direct competition and the competitive scheme in eq 1 cannot describe the reaction behavior. In addition, the NO_2 loss reaction, at its appearance energy, is faster than the rate which is predicted by a statistical (RRKM) calculation.[1]

In the mechanism proposed by Panczel and Baer, the loss of NO_2 occurs from an excited electronic state which exclusively dissociates to the $C_6H_5^+$ ion, while the NO loss channel proceeds, after internal conversion, to the ground electronic state followed by subsequent statistical dissociation. Thus, the immediate precursor ions for NO_2 and NO loss are different and the reactions are not in competition. This interpretation has not met with uniform acceptance. In a later PEPICO study, Nishimura *et al.*[2] interpreted their results in terms of the traditional mechanism in which all reactions are in competition. However, they apparently did not directly measure the NO_2 loss rate. Rather, they assumed that it was in competition and thus derived rates on the basis of this assumption. The derived rates were in agreement with the statistical theory (RRKM/QET). A subsequent IRMP activation study using a continuous-wave (CW) laser appeared to support the excited electronic state hypothesis.[3] Moini and Eyler found that IRMP activation resulted in NO loss but no NO_2 loss, presumably because the excited electronic state cannot be reached by a series of IR photon absorption steps.

We report here the use of IRMP activation of the nitrobenzene cation in its ground electronic state with both pulsed and CW lasers. The use of a pulsed laser allows for a considerably higher pumping rate so that the NO_2 loss channel, which proceeds via a higher activation energy, can be reached. We show that the surprising behavior and apparently conflicting experimental results can be reconciled by a mechanism involving an ion–neutral complex. The nitrobenzene cation dissociates to form an intermediate complex and then reassociates (after rotation of the ONO) to an isomeric structure—both steps involve relatively loose transition states. Previously, ion–neutral complexes have been proposed on the basis of hydrogen scrambling, reaction behavior, fragment isomerization, and similar appearance energies for more than one reaction.[20-33] Our experiment, combined with the previous PEPICO study, provides evidence based on the temporal reaction behavior that an ion–neutral complex is involved in the transformation of reactants to products.

Experimental Section

Materials. Nitrobenzene was purchased from J. T. Baker and used without further purification. Samples were degassed by several freeze–pump–thaw cycles, and then each liquid sample was pumped on for at least 15 min (to remove any impurities which are more volatile than nitrobenzene) prior to introduction into the high-vacuum system.

Experiment. Ions were trapped, photolyzed, and detected with a Fourier transform mass spectrometer (FT-MS)[40-42] using the OMEGA data system from IonSpec. The system is equipped with both chirp excitation and the IonSpec impulse excitation.[43-45] We detected with impulse excitation because it gives more accurate isotope ratios and more stable signals. Ions were formed by electron-impact ionization at low energies (about 14–17 eV), and then unwanted ions were ejected by standard notched ejection techniques. The ion of interest was then photolyzed by either a CW or a pulsed CO_2 laser followed by detection. None of the significant experimental observations appeared to depend on ionization energy, ion ejection parameters, or laser pulse energies. Additional information about the experimental procedure can be found elsewhere.[46] Photolysis scans were compared to scans with the laser blocked to make sure we had mass balance and to correct for any background chemical ionization.

The FT-MS cell is contained in a home-built vacuum system capable of background pressures less than 1×10^{-8} Torr. Neutral pressures were measured with a nude ionization gauge. When accurate pressures were desired, the ionization gauge was calibrated (on the same day as the experiment) for nitrobenzene using an MKS Baratron manometer. The Baratron itself was calibrated by MKS. Periodically, the calibration was checked by measuring the rate constant for protonation of methane by the methane cation. Neutral ion precursors or reactant species enter through Varian sapphire leak valves.

Pulsed laser photolysis was accomplished using the multimode output of a Lumonics TEA 103-2 CO_2 laser. The laser is line tunable using a grating element. We used a laser gas mixture containing nitrogen to achieve higher pulse energies. A desired pulse energy is obtained by attenuating the laser beam with CaF_2 flats of varying thickness. The laser beam is weakly focused using a 10 m radius of curvature mirror located about 2.3 m from the FT-MS cell. An iris, located about 45 cm in front of the cell, provides the desired spot size. Intensity profile measurements with an Eltec 420-2 pyroelectric detector indicate that this configuration gives a reasonable "top hat" profile at the location of the cell. The profile contains intensity variations because the laser is operated multimode to achieve higher pulse energies.

Pulse energies were measured using a Scientech 365 power and energy meter with a Scientech 38-0102 volume-absorbing disk calorimeter. The laser beam spot size was measured just in front of the KCl window to the vacuum chamber by burn spots on thermal paper. Reported fluences were calculated by taking the pulse energy divided by the spot size and then multiplying by 2. We multiply by 2 because the laser beam is reflected back on itself, so it passes through the cell twice and effectively doubles the number of photons as compared to a single pass.

Ions were also photolyzed using a home-built, grating-tuned, CW CO_2 laser. This laser provides 12–15 W of power on the R(20) line of the 10.6-μm transition. Fluence can be controlled by changing the irradiation time with a Uniblitz shutter. Laser power was measured using an Optical Engineering 25-B power meter.

For both lasers, the laser wavelength was measured with an Optical Engineering 16-A CO_2 spectrum analyzer. Nitrobenzene was photolyzed using the R(20) line of the 10.6-μm transition.[3]

Results

Nitrobenzene cations activated at low energy give rise to four different reaction products (eq 1). Table I gives branching fractions (of products) for photolysis with a pulsed laser at a fluence of 5.3 J/cm^2 and branching fractions for photolysis with a CW laser after irradiation for 200 ms. Appearance energies from a previous PEPICO study[1] are also included in Table I. These are the only reactions observed with IRMP dissociation using our lasers. The branching fractions from CW laser activation are consistent with the previous CW IRMP study.[3] The total abundance of ions was the same in the "light on" and "light off" experiments. In other words, the sum of the product

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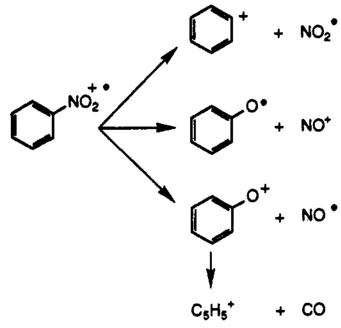
Table I. IRMP Dissociation Branching Fractions



	fraction (%) pulsed laser	fraction (%) cw laser	appearance energy[a] (kcal/mol)
+ $NO_2^\bullet$	24	0	29
+ NO^+	6	10	27
+ $NO^\bullet$	34	81	26
$C_5H_5^+$ + CO	36	9	33

[a] Reference 1.

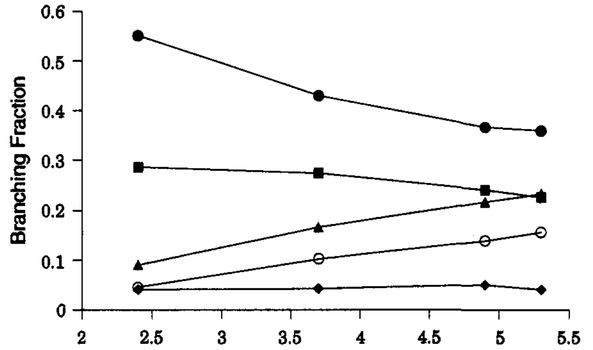


Figure 1. Dependence of branching fractions on fluence for the pulsed laser photolysis of the nitrobenzene cation: (●) nitrobenzene cation; (■) phenoxy cation; (○) phenyl cation; (▲) $C_5H_5^+$; (◆) NO^+.

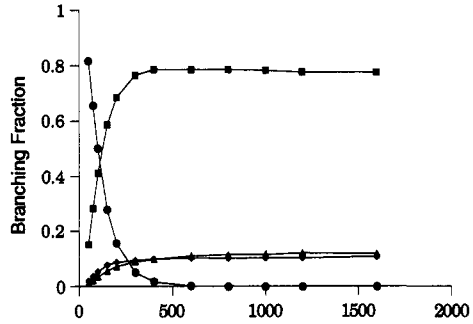


Figure 2. Dependence of branching fractions on irradiation time for the CW laser photolysis of the nitrobenzene cation: (●) nitrobenzene cation; (■) phenoxy cation; (▲) $C_5H_5^+$; (◆) NO^+.

ion abundances and the unreacted parent ion abundance measured in the photolysis experiments was the same as the unreacted parent ion abundance when the laser was blocked. This was true for both the CW and pulsed lasers.

Figure 1 gives branching fractions (of all ions) as a function of fluence (at constant pulse length) for the pulsed laser photolysis of the nitrobenzene cation. Increasing the fluence increases the photon intensity.[47] Note that significant amounts of the phenyl cation (open circles) are formed in the pulsed laser photolysis.

Figure 2 shows the dependence of branching fractions on irradiation time with the CW laser (laser intensity of 40–60 W/cm²).[48] Note that the phenyl cation is not a product in the CW laser photolysis.

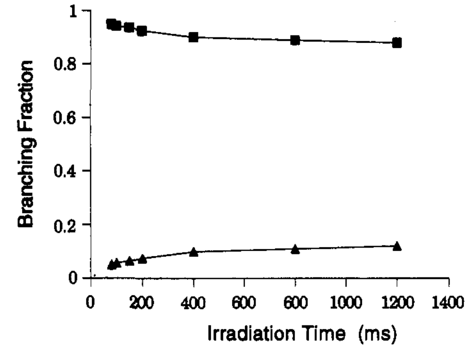


Figure 3. Dependence of branching fractions on irradiation time for the CW laser photolysis of the phenoxy cation: (■) phenoxy cation; (▲) $C_5H_5^+$. The phenoxy cation is formed by electron impact on nitrobenzene.

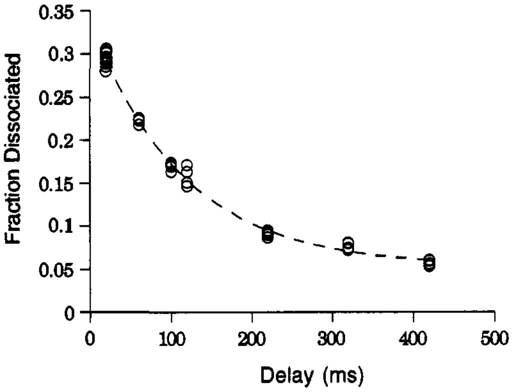


Figure 4. Dependence of product yield on the delay between formation of the phenoxy cation and firing of the pulsed laser. The phenoxy cation is formed by electron impact on nitrobenzene.

IRMP activation of the phenoxy cation gives $C_5H_5^+$ (eq 1d). Our experiments confirmed previous conclusions that $C_5H_5^+$ is formed by a secondary mechanism (eq 1) in the photolysis of the nitrobenzene cation. Double-resonance ejection of the phenoxy cation during CW laser irradiation eliminated formation of $C_5H_5^+$. Figure 3 shows the dependence of $C_5H_5^+$ formation from the phenoxy cation as a function of CW laser irradiation. The phenoxy cation was formed by electron impact on nitrobenzene. About 10% of the phenoxy cation undergoes dissociation (eq 1d) within about 400 ms. Further conversion occurs at a significantly lower rate. The same behavior is observed for the phenoxy cation formed by CW laser photolysis of the nitrobenzene cation (Figure 2). This behavior was first reported by Moini and Eyler in their CW IRMP activation study.[3] Our experiments with a pulsed CO_2 laser demonstrate that the incomplete conversion occurs because only the nascent phenoxy cation can be photochemically decomposed. Radiative relaxation cools the phenoxy cation so that it cannot be activated (Figure 4).

Figure 4 shows photolysis of the phenoxy cation with a pulsed laser held at constant fluence. The delay in Figure 4 is the time between formation of the ions (measured from the end of the beam pulse) and firing of the pulsed laser. During the delay, ions can radiatively lose vibrational energy.[49] The behavior in Figure 4 does not result from relaxation of ions out of overlap with the laser—we changed the position of the laser at the longest delay and could not increase the yield. This behavior is not unique to the nitrobenzene system. IRMP dissociation of the phenoxy cation generated by electron impact on (trifluoromethoxy)benzene gives the same behavior[50] reported in Figure 4.

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[47] We actually want to measure branching fractions as a function of intensity, but because the laser pulse has two components, it is hard to define the intensity. For this reason, we simply report the branching fractions as a function of fluence and realize that any changes in branching fractions are a result of intensity changes. Two laser pulses with the same fluence should also have essentially the same intensity at a given time during the laser pulse.

[48] At longer times, the phenoxy cation (*m/z* 93) reacts with nitrobenzene to form ions at *m/z* 169 and 170. These abundances become noticeable for irradiation times longer than about 400 ms (when the experiment was done at a pressure of about 3×10^{-8} Torr). The $C_5H_5^+$ ion (*m/z* 65) reacts with nitrobenzene to form ions at *m/z* 142 and 143. Although these higher mass ions were present in sufficiently high abundance to be measurable, even after irradiation for 1.6 s they amount to less than 15% of the phenoxy cation or $C_5H_5^+$ intensity. A figure that has the higher mass ion abundances added to their precursors looks essentially the same as Figure 2.

Experimental Considerations

IRMP dissociation involves ions which dissociate after sequentially absorbing infrared photons. We use a CO_2 laser for which the energy increment (energy of one photon at the wavelength used in these experiments) is about 2.8 kcal/mol. The activation process involves energy pumping, which in most cases occurs at a steady-state rate dependent on the intensity.[16-19] Reaction starts to occur at the energy where the reaction rate competes with the pumping rate. Assuming an absorption cross section of 10^{-19} cm^2, photolysis with a CW laser involves a pumping rate of 10–100 s^{-1} so that the energy range for dissociation starts at the point where the lowest energy reaction has achieved a rate of 10–100 s^{-1}. The CW laser photolysis thus emphasizes the lowest energy reactions of the system. On the other hand, photolysis with the pulsed laser involves pumping rates of about 10^5–10^7 s^{-1}, and some reactions may not achieve this rate except at energies significantly above threshold. Pulsed laser photolysis, therefore, can shift the energy range of dissociation to higher energies, because an ion energized slightly above the reaction threshold will absorb another photon if its reaction rate does not compete with the pumping rate.

IRMP activation involves excitation of the ground-state ion, so that the excited vibrational states of only the ground electronic state of the nitrobenzene cation are directly produced. Reactions can only occur from the ground electronic state because conversion of vibrational energy into electronic energy (reverse internal conversion) will be extremely inefficient.[51] This differs from PEPICO experiments in which the ion is first produced in an excited electronic state and subsequent internal conversion transforms the energy into vibrational energy of the ground state.

Discussion

In this study we have used both CW and pulsed IRMP absorption to dissociate nitrobenzene ions. In agreement with the previous CW IRMP work,[3] we do not detect the NO_2 loss channel in the low-intensity CW experiment. However, when the laser intensity is increased by 5–6 orders of magnitude through the use of pulsed IRMP absorption, we do observe a significant signal from NO_2 loss. On the basis of this result, we conclude that the NO_2 loss reaction does not take place from an excited electronic state. Furthermore, we conclude that the activation energies for the two processes differ by at least 2.8 kcal/mol (consistent with the PEPICO studies).[1,2]

As pointed out in the introduction, the excited electronic state dissociation was invoked to account for the facts that (a) the NO_2 and NO loss channels are not in apparent competition and (b) the NO_2 loss rate at threshold was much larger than could be accommodated by the statistical theory. If the excited-state hypothesis is not correct, what can be the explanation for the PEPICO rate data?

The conclusions based on the PEPICO and the pulsed IRMP data are, in fact, not as incompatible as they might appear. The PEPICO results indicate that the NO_2 loss channel is not in competition with the other decay channels. This conclusion comes directly from the data. However, noncompetition does not necessarily imply the participation of excited electronic states. Rather, as Baer *et al.* have pointed out,[52,53] isomerization in competition with direct dissociation can also lead to noncompeting rates. Suppose that a molecule ABC rapidly and competitively dissociates to A + BC or isomerizes to a lower energy structure, ACB. If the isomerized structure produces a different product, *e.g.* AC + B, at a slow rate (because of the deep ACB well), the two products will be observed with different rates, but their branching ratios will be determined by the initial direct dissociation/isomerization rates and not by the final measured dissociation rates.

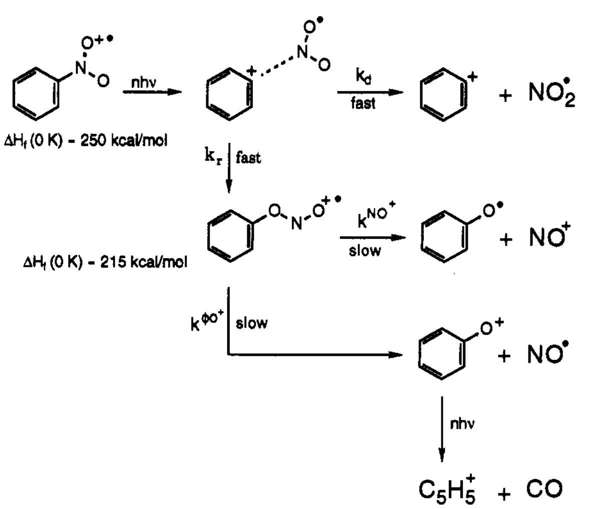
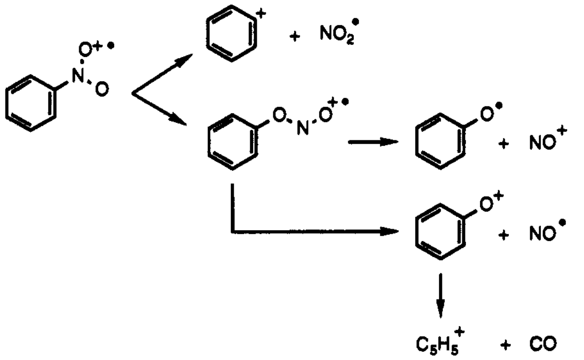


Figure 5. Overall mechanism for IRMP dissociation of the nitrobenzene cation. The heat of formation of the nitrobenzene cation comes from ref 1. The heat of formation of the phenyl nitrite cation comes from an AM1 calculation.

In order to explain the results in a quantitative manner, we carried out RRKM calculations for the mechanism given in eq 2, which we call the direct isomerization mechanism. It is similar to the one that was proposed by Nishimura *et al.*[2]



(2)

In order for such a mechanism to explain the simultaneous fast NO_2 and slow NO production, both the isomerization and the dissociation must be fast. However, we found that a tight transition state for the isomerization made this reaction too slow to compete with the NO_2 loss step. RRKM calculations for a direct isomerization using frequencies from the Nishimura study[2] gave a rate of only 10^5 s^{-1} at 7 kcal/mol above threshold. Yet, the PEPICO results,[1] which found the NO_2 loss rate to be very fast, coupled with the requirement for competition between dissociation and isomerization, indicate that the rate must be at least 10^7 s^{-1} at this energy (*vide infra*). No adjustments of frequencies and energy barriers within reasonable limits permitted the fitting of the results with this mechanism. We thus searched for an additional step which might allow the data to be reconciled.

A mechanism only slightly more complex than the direct isomerization mechanism is one in which the dissociating nitrobenzene ion first forms a higher energy complex, or isomer (see Figures 5 and 6).[54] This intermediate species could be an ion–dipole complex between the $C_6H_5^+$ ion and the highly dipolar

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(49) An exponential fit to the curve in Figure 4 gives a decay rate of 8.75 s^{-1}. These experiments were done at (2.3–2.5) × 10^{-8} Torr of nitrobenzene. At this pressure, the rate for collisions between the phenoxy cation and nitrobenzene is 1.9 s^{-1} (calculated by the method in: Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183). The decay rate in Figure 4 is much faster than the collision rate.

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(54) An ion–neutral complex mechanism has been suggested for the reactions of the nitromethane cation on the basis of similar appearance energies for different dissociations. See ref 24.

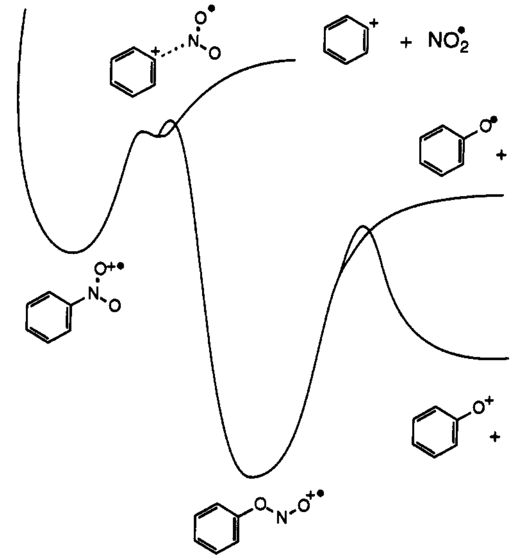

Figure 6. Potential energy surface for dissociation of the nitrobenzene cation.

NO_2 molecule. The purpose of invoking this complex is to allow the rates between the NO_2 loss and the isomerization to the phenyl nitrite ion to be both fast and competitive over a larger energy range. In addition, such an ion–neutral complex would readily both lose the NO_2 group and rearrange by rotation of the ONO group to the lower energy nitrite isomer. Theoretical work based on the unified transition state theory of Miller[55] and Chesnavich and Bowers[30–33] have shown that dissociation via such a complex is characterized by $k(E)$ curves that are high and vary rather more slowly with energy than they would in the absence of such a complex.

The overall rate of NO_2 loss through such a complex would be given by the RRKM rate constant expression[31] in eq 3, $G^\ddagger(\text{iso})$

$$k(E) = \frac{G^\ddagger(\text{iso})}{hN(E)}\,\frac{G^\ddagger(\text{diss})}{G^\ddagger(\text{iso}) + G^\ddagger(\text{diss})} \tag{3}$$

is the sum of states for the transition state for formation of the intermediate complex, $G^\ddagger(\text{diss})$ is the sum of states for the NO_2 loss transition state, $N(E)$ is the density of states of the nitrobenzene ion, and h is Planck's constant.[56] Since the complex formation step has a lower activation energy than the NO_2 loss step, it is energetically favored. Thus at low energies, $G^\ddagger(\text{iso}) \gg G^\ddagger(\text{diss})$ and the rate constant for loss of NO_2 is given by $G^\ddagger(\text{diss})/hN(E)$. However, at high energies, $G^\ddagger(\text{diss}) \gg G^\ddagger(\text{iso})$[30–33] so that $k(E) = G^\ddagger(\text{iso})/hN(E)$. Since the step for forming the complex involves a tighter transition state than the NO_2 loss step (fragments are separated by larger distances and involve relatively unhindered rotors in the NO_2 loss step), the resulting $k(E)$ curve at high energies varies more slowly with energy, E.[30–33]

Once the intermediate complex is reached, the mechanism branches between the fast overall cleavage of the C–N bond and the fast reassociation/isomerization (k_r) to give the phenyl nitrite cation. Formation of the nitrite is essentially irreversible because of its greater stability.[57] Subsequent reactions of the phenyl nitrite ion are slow because of the deep nitrite ion energy well. Competitive loss of NO and NO^+ results in slow rates for both of these reaction paths. In this scheme, the rate for overall NO or NO^+ formation can be much slower than k_d; only the k_r and k_d steps are fast and compete. Of course, the formation of the nitrite cation is not directly observed because it has the same mass as nitrobenzene.

Finally, it was noted that the NO_2 loss rate constant, measured at its appearance energy by PEPICO, is much faster than predicted by RRKM theory.[1] The intermediate complex mechanism explains this behavior. NO_2 loss is observed not at its *thermodynamic* threshold but at its *competitive* threshold. In other words, NO_2 loss is only observed when it has achieved a reaction rate which competes with conversion to the phenyl nitrite cation. Its appearance energy is higher than its thermodynamic threshold. Since NO_2 loss starts to appear only after its rate has achieved a value faster than 10^7 s^{-1}, the rate constant for the isomerization process must also be about 10^7 s^{-1} at this energy (7 kcal/mol above its threshold).

The intermediate complex mechanism can explain a number of aspects of the reaction behavior in at least a qualitative manner. Whether it can do so quantitatively must await more information on ion structures, energies, and vibrational frequencies. All of these can, in principle, be calculated by *ab initio* MO methods. We did not feel that it was worth the effort at this time, since the experimental rates are not so well established due to the large thermal energy distribution of the previous two PEPICO studies. Thus, we summarize below a qualitative analysis of the dissociation dynamics.

The intermediate complex mechanism explains (a) why the products from nitrite formation compete with the cleavage reaction over a significant energy range,[1,2] (b) why the reaction has an effective threshold energy that is lower than that for the cleavage reaction, (c) how the isomerization process can achieve a rate of 10^7 s^{-1} only 7 kcal/mol above its threshold, and (d) why so many reactions appear within such a small energy range of each other.[21,24]

$C_5H_5^+$ Formation Mechanism. The incomplete conversion of the phenoxy cation to $C_5H_5^+$ during CW laser photolysis (Figures 2 and 3) has been observed previously.[3] This result, coupled with the observations in the PEPICO experiment,[1] appears to support an isolated electronic state mechanism.[3] However, the pulsed laser photolysis experiments (Figure 1 and especially Figure 4) show that the details of $C_5H_5^+$ formation are different in the two types of experiments. In the PEPICO experiment, $C_5H_5^+$ can only come from the phenoxy cation, which is formed with enough energy to dissociate because reactions occur subsequent to activation. On the basis of their thresholds,[1,2] nitrobenzene ions that gave $C_5H_5^+$ also had enough energy to form $C_6H_5^+$. In the IRMP activation experiments, however, $C_5H_5^+$ could be formed even though the nitrobenzene ion never obtained enough energy to give $C_6H_5^+$. This arises because the stepwise activation allows the phenoxy cation to absorb additional photons to obtain the energy to give $C_5H_5^+$ and because the phenoxy cation forms irreversibly under the conditions of the IRMP experiment. The experiment in Figure 4 shows that the phenoxy cation is formed with considerable vibrational energy (but not enough to dissociate), and this energy can be lost by a radiative process.[49] We propose that the CW laser pumping rate of the phenoxy cation does not compete well with radiative loss of vibrational energy. The phenoxy cation may also have a pumping bottleneck so that decay below the bottleneck eliminates the possibility of activation. Our proposed mechanism (Figures 5 and 6) allows the phenoxy cation to form with considerable vibrational energy, although not enough for it to dissociate, so that it must absorb additional IR photons to obtain enough energy to react.

The Competition and KER for NO^+ and NO Formation. Interestingly, both the phenoxy cation (eq 1c) and NO^+ (eq 1b) are observed even though the phenoxy cation plus the NO radical are about 16 kcal/mol more stable[1] than the phenoxy radical plus NO^+. In addition, the metastable ion peak of the phenoxy cation is bimodal,[12] which means there are two reaction channels forming an ion with the mass of the phenoxy cation. Previously, these results were explained by competing unimolecular reactions

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[55] Miller, W. H. *J. Chem. Phys.* **1976**, *65*, 2216.

[56] The actual expression for dissociation of the nitrobenzene ion should also include the sum of states for the transition state for isomerization to the nitrite structure (in the denominator of the ratio of the sum of states). This term has been omitted for clarity.

[57] AM1 calculations indicate that the phenyl nitrite cation is about 35–40 kcal/mol more stable than the nitrobenzene cation.

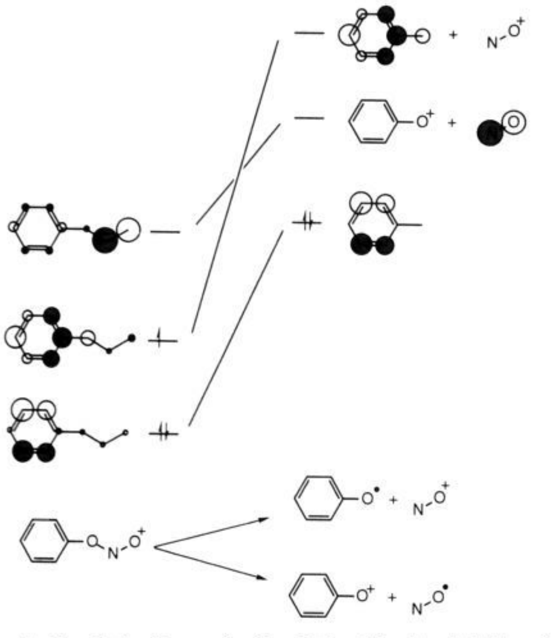
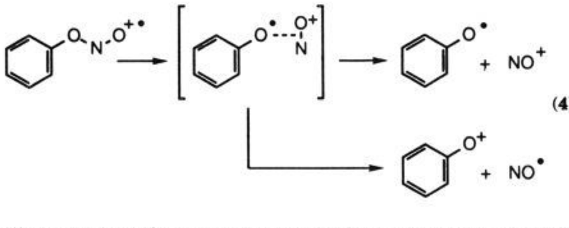


Figure 7. Correlation diagram for dissociation of the phenyl nitrite cation (see text).

of the nitrobenzene cation.[12] The PEPICO study, however, is not consistent with such a description[1] (*vide supra*). It would also be fortuitous if so many competitive transition states could occur within the available energy range. The scheme in Figures 5 and 6 can explain the reaction behavior. In this scheme, the dissociations involve cleavage reactions of the phenyl nitrite cation and not rearrangements of the nitrobenzene cation.

Figure 7 gives part of a correlation diagram for these reactions. We constructed the correlation diagram using AM1 calculations.[58,59] The calculated electronic structures and heats of formation were consistent with studies[60,61] of NO^+ and the NO radical as well as the previously analyzed photoelectron spectrum of the phenoxy radical.[62] Consideration of orbital occupancies shows that the phenyl nitrite cation tends to dissociate diabatically to give the phenoxy radical and NO^+. Direct formation of the lower energy phenoxy cation plus the NO radical occurs by an avoided crossing, as indicated in Figure 7, resulting in a significant barrier. Thus, NO^+ formation is competitive even though its products are 16 kcal/mol less stable than the phenoxy cation plus NO.

The phenyl nitrite cation could also form the phenoxy cation by an ion–neutral complex mechanism (eq 4). The phenoxy radical can transfer an electron to NO^+ in the complex to give the phenoxy cation and the NO radical. Such a pathway would be lower in energy than complete cleavage to NO^+, so it should be competitive. The electron transfer should be about 16 kcal/mol exothermic.[1] We believe that this pathway gives an energy release different from that of the avoided-crossing pathway, hence the bimodal energy release. Formation of the phenoxy cation via the complex of the phenoxy radical and NO^+ would give a small kinetic energy release because it is a simple electron transfer which would presumably produce vibrationally excited products and not impart significant translational energy. We expect that formation of the phenoxy cation by an avoided crossing gives a large energy release because of the barrier for the reaction. The pathway involving an electron transfer in the complex would disappear at higher energies because the ion–neutral complex would be too short-lived at the higher energies. This is consistent with the PEPICO experiment not giving a measurable amount of the low-energy kinetic energy release—the parent ions in the PEPICO experiment (when measuring kinetic energy releases) have considerably higher energies than metastable ions.[1]



(4)

Cooks and co-workers studied phenoxy cation formation from many para-substituted nitrobenzene cations.[12] They found that electron-donating substituents predominantly gave the large energy release component of the bimodal peak (avoided-crossing pathway in our mechanism). Electron-withdrawing substituents gave more of the small energy release component of the bimodal peak (electron-transfer pathway in our mechanism). Electron-donating substituents stabilize the phenoxy cation in comparison to the phenoxy radical, while electron-withdrawing substituents destabilize the phenoxy cation. The electron-donating substituents should therefore lower the threshold for the avoided-crossing pathway compared to the electron-transfer pathway, giving more of the large energy release component (as is observed). Less of the large energy release (avoided-crossing pathway) will be observed for electron-withdrawing substituents because NO^+ formation (and the electron-transfer pathway) becomes more competitive. In fact, inspection of the 70-eV mass spectra[63] shows that NO^+ formation is preferred for the strongly electron-withdrawing substituents while phenoxy cation formation is preferred for electron-donating substituents.

An alternative explanation for the bimodal peaks would involve forming two different electronic states of the phenoxy cation by the electron-transfer pathway. The photoelectron spectrum of the phenoxy radical[62] indicates that the lowest energy excited state is about 19 kcal/mol less stable than the ground state, and that is within the available energy. However, one would not expect to see much of this pathway because its transition state would have a much lower sum of states due to the higher energy. For this reason we do not think that such a mechanism adequately describes the experimentally observed behavior.

Conclusion

The rich chemistry of the nitrobenzene cation derives from branching in an ion–neutral complex of the phenyl cation and NO_2, which is the first step for many of the dissociation reactions. This mechanism can reconcile many surprising and even apparently inconsistent observations.

The pulsed laser IRMP dissociation experiment requires a thermal reaction mechanism. The PEPICO rate measurements require a mechanism with an early product-determining branching step that is not necessarily rate determining. The combination of these experimental results along with the magnitude of the reaction rates points to an ion–neutral complex in the transformation of reactants to products and provides evidence in real time that this intermediate exists as a short-lived transient species.

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