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Collision-Induced Dissociation of Nitrobenzene Molecular Cations at Low Energies by Crossed-Beam Tandem Mass Spectrometry

Rahul Chawla,[†] Anil Shukla,*[,‡] and Jean Futrell[‡]

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

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The dynamics of the collision-induced dissociation (CID) of the nitrobenzene molecular ion have been investigated in the energy range of 3 eV−50 eV in the center-of-mass (CM) reference frame using a crossed-beam tandem hybrid mass spectrometer−supersonic molecular beam instrument. At these collision energies the dominant CID channel is loss of NO_2 from the molecular ion and contribution from competing channels is very small. At 3.1 eV collision energy, fragment ions, $C_6H_5^+$, are fully backward scattered and as collision energy is increased the most probable scattering angle moves in the forward scattering region but remains above zero up to 50 eV energy. These results suggest that small impact parameter impulsive collisions dominate this CID process in the low collision energy range. The energy transfer in the collisional activation step does not change significantly with increase in collision energy and corresponds to about 0.6 eV above the thermochemical threshold even though the molecular ions were formed by 70 eV energy electrons. There are no apparent changes in the dynamics features of the activation/dissociation process in going from 3 to 50 eV collision energy except the decrease in the maximum of the CM scattering angle. These results suggest that there is no change in the activation/dissociation mechanism for this CID process. We further suggest, based upon the energy loss measurements, that this dissociation process is not direct, instead it proceeds via ion−neutral complex $C_6H_5^+\cdots NO_2$, as proposed by Osterheld, Baer, and Brauman (Osterheld, T. H.; Baer, T.; Brauman, J. A. *J. Am. Chem. Soc.* **1993,** *115*, 6284) and competes with the loss of NO via nitro-nitrite rearrangement.

Introduction

Nitroaromatic compounds are among the most widely studied molecules because of their explosive properties and therefore need for accurate and highly sensitive detection requirements.[1,2] Mass spectrometry[3] provides a uniquely useful and suitable method to detect these compounds in trace quantities and also to understand their fast dissociation pathways/kinetics in the microsecond time window associated with their explosive characteristics.[4,5] Nitrobenzene, being the first in the series of nitro/substituted nitro aromatics, has undergone very extensive experimental mass spectral ionic dissociation studies.[6−15]

The simplest among all nitro compounds, nitromethane molecular ion, exhibited uniquely distinct activation and dissociation mechanisms[16] that were sensitive to collision energy when dynamics studies were performed on its dissociations to NO_2^+ and NO^+ fragment ions. The addition of an aromatic ring makes it into an extremely interesting system for mass spectrometric studies and that is clearly evident from the number of studies performed on the nitrobenzene cation,[5−15] anion[17,18] and substituted nitrobenzenes.[2,19−26]

Mass spectrometric dissociations of all nitro compounds mainly have two common pathways: direct C−N bond cleavage and C−O bond cleavage after nitro-nitrite rearrangement, although retention of charge on specific fragments varies from aliphatic to aromatic compounds.[6,15,16] Other dissociations involving chain/ring and different substituents vary.[19−26] These two processes involving NO_2 group have often been shown to follow different mechanisms for unimolecular dissociations as well as collisional activation/dissociation.

A photoelectron photoion coincidence (PEPICO) study of the dissociation of energy selected nitrobenzene cations by Panczel and Baer[12] suggested that loss of NO_2 is faster than the loss of NO from the same precursor ion and the former proceeds from an excited electronic state. It is surprising that these two dissociations are not in competition even though energetically the two are very similar, 1.02 eV for $C_6H_5O^+$ and 1.21 eV for $C_6H_5^+$ fragment ions. Also, the $C_6H_5O^+$ ions are formed with sufficient internal energy that they dissociate further via loss of CO and other channels. From a similar study using threshold PEPICO, Meisels and co-workers[11] concluded that dissociation of nitrobenzene cations could be explained adequately by statistical rate theories. Moini and Eyler[10] performed an infrared multiphoton dissociation (IRMPD) study of this ion and reached the same conclusion as Panczel and Baer since they could not observe the $C_6H_5^+$ fragments via loss of NO_2 from the molecular ion under their experimental conditions. These workers further suggested that $C_6H_5O^+$ is formed from two energetically different dissociation pathways leading to stable $C_6H_5O^+$ ions observed in the spectrum and excited $C_6H_5O^+$ that further dissociate to $C_5H_5^+$ via loss of CO neutral.

Osterheld, Baer, and Brauman[15] conducted an IRMPD experiment using both pulsed and continuous wave (CW) lasers and observed that $C_6H_5^+$ fragment ion is formed when a pulsed laser is used but it is not formed when a CW laser is used. These authors suggested that since the laser intensity is several

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* Corresponding author. E-mail: anil.shukla@pnl.gov.

[†] Present address: Merck Research Laboratories, Rahway, N.J.

[‡] Present address: Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, MS: K8−96, P.O. Box 999, Richland, WA 99352.

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times higher in pulsed mode, enough energy is deposited for this dissociation to proceed which is not possible in the CW mode and that there are no higher excited electronic states contributing to this process. These results were further supported by rate constant calculations. To explain these experimental observations, Osterheld et al.[15] proposed that this dissociation proceeds via an ion−neutral complex $C_6H_5^+ \cdots NO_2$.

It is obvious from these studies that the dissociation of nitrobenzene molecular cation is far from fully understood. We have therefore extended our dynamics studies of the collision-induced dissociation (CID) of the nitrobenzene cation under similar experimental conditions as the previous studies of the nitromethane[16] and methyl nitrite cations.[27] Our angle- and energy-resolved studies of the CID of the nitromethane cation demonstrated earlier that the mechanism of activation and dissociation via direct cleavage of C−N bond leading to NO_2^+ fragment did not change significantly while that for the NO^+ fragment ion via nitro-nitrite rearrangement showed unique energetics and dynamical features. The results showed that as the collision energy was increased, a higher energy dissociation channel with distinct scattering characteristics begins to compete with and dominates the dissociation process above 50 eV. In this article, we present results from a similar dynamics study of the CID of nitrobenzene molecular cation.

Experimental Section

The tandem hybrid mass spectrometer used for the dynamics studies has been described in detail in an earlier publication[28] and only the salient features are given here. Nitrobenzene molecular ions were produced by 70 eV electron ionization, accelerated to 3 keV (nominal) for their passage through the electric and magnetic sectors. The energy and mass selected molecular ion beam was decelerated to desired laboratory energy at the collision center by a series of tube lenses and cylindrical rectangular lenses. The decelerated ion beam was collided at right angles with a vertically moving supersonic molecular beam of neat helium or argon at the collision center. The collision volume was maintained at the same potential as the last element of the deceleration lens to avoid any interference from stray potentials. Fragment ions were accelerated/decelerated for their energy analysis by a hemispherical energy analyzer operated under constant resolution and constant transmission mode and only the ions of desired mass were passed through a quadrupole mass filter set at a fixed mass. Ions were detected by a channel electron multiplier operating in the pulse counting mode. The detector assembly was rotated with respect to the collision center in the plane of the ion beam for measuring the energy and intensity distributions of fragment ions at a series of laboratory scattering angles.

The supersonic molecular beam was produced by expansion of neat argon (or helium) gas through a 100 μm diameter nozzle and passing the central core of the expanding gas by a skimmer of 1 mm diameter aperture located about 6 mm from the nozzle. The beam was passed through a collimating chamber with a 2 mm aperture before colliding the ion beam. The neutral beam was chopped inside the collimating chamber by a mechanical chopper at a frequency of 150 Hz for signal averaging and removing any contributions from the background CID.

The ion signal was collected by pulse counting until a reasonable signal-to-noise ratio was obtained. The ion beam stability was monitored periodically since these experiments at most angles took several hours to obtain a good signal-to-noise ratio. The experiments at all angles were repeated several times over a period of several months. The energy analyzer was calibrated by performing energy measurement from the metastable decay of propane molecular ion to ethylene ion which has previously been thoroughly investigated by crossed-beam experiments.[29,30] Measured energy distributions were converted into velocity distributions using the relationship $v = (2\ eV/M)^{1/2}$, where M is the mass of the ion and eV is its kinetic energy. These velocity distributions were normalized to intensity distributions at each angle and necessary transformation Jacobians were applied as discussed in several previous publications.[31−34] Points of equal intensity were joined to draw contour plots and ion and neutral velocity vectors and scattering circles, etc., were superimposed on these diagrams before final presentation.

Results and Discussion

The crossed-beam method to study CID processes is often limited to study only those processes that have larger cross section and less interference from the unimolecular (metastable) decay of the parent ions in the collision region due to very low collision efficiency. We were therefore limited to detailed study of only the phenyl ion (m/z 77, loss of NO_2) via direct C−N bond cleavage. The phenoxy cation via loss of NO is well-known to proceed via nitro-nitrite rearrangement[6] and is associated with a metastable decay component that is several orders of magnitude stronger than the CID component in our experiments. Furthermore, cross sections for the NO^+ and $C_5H_5^+$ fragmentation channels were too small to obtain meaningful information on energy and intensity distributions for them. We have therefore concentrated our efforts on the phenyl ion which is actually the one that was earlier suggested by Panczel and Baer[12] to be formed from an excited state.

The threshold for the $C_6H_5^+$ fragment ion[11] is only 1.21 eV; however, we did not observe sufficient CID signal for this fragment ion below 3 eV collision energy to determine the CID dynamics near threshold. This is in agreement with the discussion by Osterheld et al.[15] who suggested from rate constant calculations using RRKM theory[35] and PEPICO measurements that NO_2 loss is observed at its competitive threshold rather than the thermodynamic threshold because of the intermediate ion−molecule complex $C_6H_5^+\cdots NO_2$ for both NO and NO_2 loss processes.

Figure 1 shows the velocity contour map for the CID of nitrobenzene ion to phenyl ion, $C_6H_5^+$, in collision with helium neutrals at 3.1 eV energy in the CM reference frame. It is interesting to note that majority of the contours are located in the backward scattering region and a significant intensity beyond the ESC. The maximum intensity contour is located inside the ESC at an energy loss of ∼1.9 eV and all contours are very broad. There are two factors that contribute to the width of these contours: kinetic energy release on dissociation that is amplified in the laboratory frame[36] and the data transformation process.[28,33] The ion intensity at each velocity point is divided by the corresponding velocity for necessary transformation from polar into Cartesian coordinates. Thus, the intensity of slower ions is amplified significantly for the data presentation in these contour maps. This anomaly is of course corrected when these contours are integrated over all angles.

The most probable energy transfer is ∼1.9 eV which is 0.7 eV higher than the threshold and the most probable scattering angle is ∼164 ± 8°. In other words, collisions between nitrobenzene ion and helium neutral are nearly head-on, very small (near zero) impact parameter collisions that result in sufficient energy transfer to cause the ion's dissociation. The broadening of contours in this case may also be due to the fact

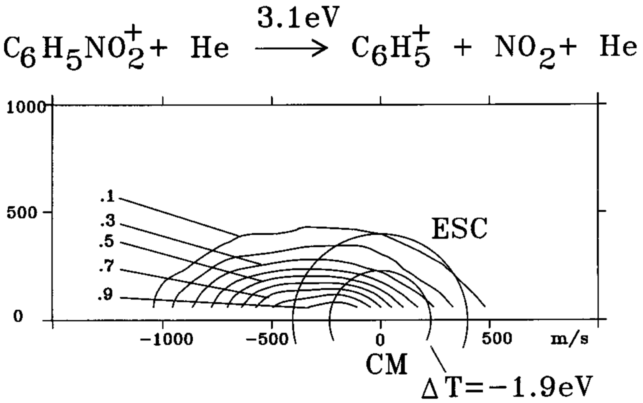

Figure 1. CM velocity contour plot for the CID of nitrobenzene molecular ion to phenyl ion on collision with helium neutral at a collision energy of 3.1 eV. CM refers to the CM of the nitrobenzene and helium collisions. The circle marked ESC represents the elastic scattering circle which defines the upper limit of the ion kinetic energy which the promary ions can have based upon conservation of momentum and energy restrictions. The circle marked $\Delta T = -1.9$ eV passes through the center of the peak intensity and corresponds to energy transfer of 1.9 eV energy from kinetic into interal modes of the dissociating ions.

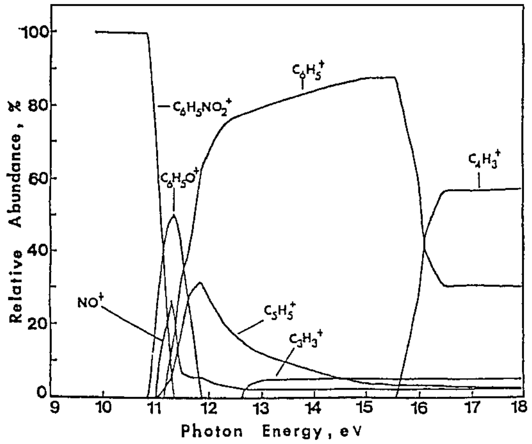

Figure 2. PEPICO breakdown graph of the nitrobenzene molecular cation. Taken from ref 11.

that $C_6H_5^+$ ions are formed from the primary ions in a very broad internal energy distribution range unlike other fragment ions as shown in the PEPICO breakdown graph (Figure 2) reproduced from ref 11. It is interesting (and not as commonly observed in many cases) to note from the Figure 2 that most fragment ion intensities peak quite sharply and then drop off while that for $C_6H_5^+$ has at least three distinct changes in the intensity curve. Whether these changes are associated with some unique features in its dissociation behavior is also a subject of our study.

Figure 3 shows the velocity contour plot for $C_6H_5^+$ fragment ions at 6.6 eV collision energy with argon collision gas. This plot is in sharp contrast with Figure 1 contour plot in that most of the scattered intensity is confined in the forward scattering region instead of the backward scattering region. The most probable scattering angle has decreased from ~164° to ~25° in the CM frame and the most probable energy transfer corresponds to ~2.1 eV. The shift in the scattering is quite large (decreased by a factor of 5) considering that energy is increased only by a factor of 2 in these experiments. Again, the contours are quite broad in this case also and hence the change in energy by 0.2 eV may not be experimentally significant.

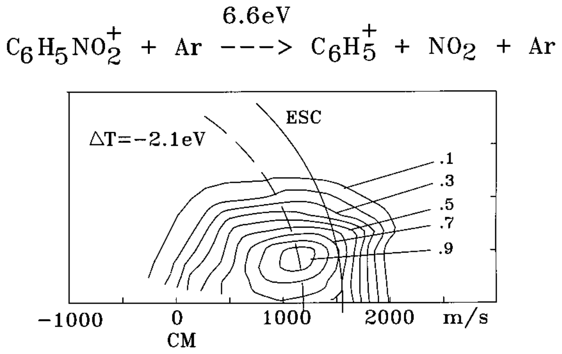

Figure 3. CM contour plot for the dissociation of 6.6 eV collision energy nitrobenzene ios to $C_6H_5^+$ ions.

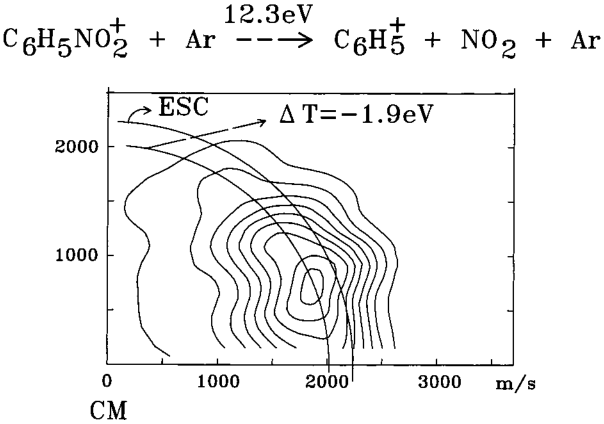

Figure 4. CM contour plot for the dissociation of nitrobenzene ions on collision with Ar at 12.3 eV collision energy.

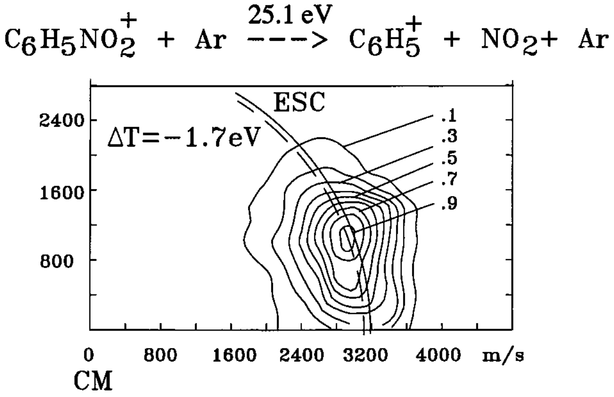

Figure 5. CM contour plot for the dissociation of nitrobenzene ions on collision with Ar at 25.1 eV collision energy.

CID experiments were extended to higher collision energies to explore the possibility of change(s) in the energy transfer, activation mechanism, and dissociation dynamics with energy. Figures 4−6 show velocity contour plots for the $C_6H_5^+$ fragment ions formed from collisions with argon neutrals at 12.3, 25.1, and 50.1 eV collision energy, respectively. All three contour plots show very similar features as observed at 6.6 eV energy plot shown in Figure 3. The most probable energy transfers at these energies correspond to 1.9 eV (for 12.3 eV collisions), 1.7 eV (for 25.1 eV collisions), and 1.5 eV (for 50.1 eV collisions). Considering the experimental measurement errors due to broad peaks, we can state that the difference is not significant and the average energy transfer in the CID of nitrobenzene molecular ion to phenyl ion via the loss of NO_2 is 1.8 ± 0.3 eV.

As expected, the most probable maximum intensity scattering angles decreased with increasing collision energies, suggesting

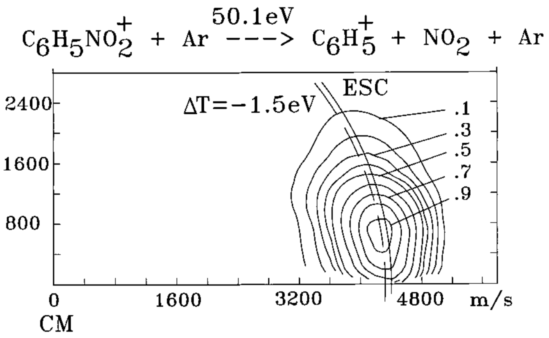

Figure 6. CM contour plot for the dissociation of nitrobenzene ions on collision with Ar at 50.1 eV collision energy.

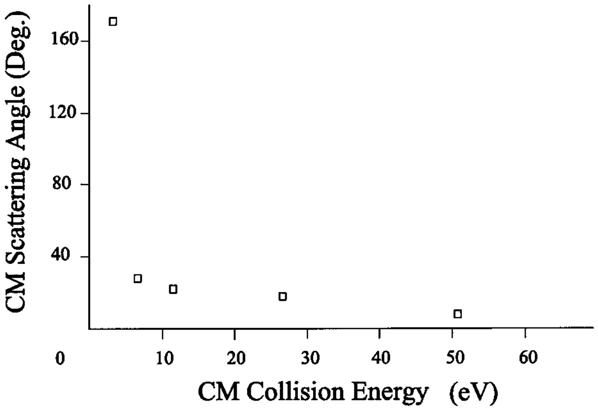

Figure 7. A plot of the most probable scattering angle versus the CM collision energy for the CID of nitrobenzene molecular ions.

impulsive small impact parameter collisions dominating the CID process in this energy range. It decreased sharply in going from 3.1 to 6.6 eV collisions and then only slowly with increasing collision energy. Qualitatively, these observations can be rationalized by the line-of-centers model[37] which has been used in several similar CID studies at low collision energies. It is rather difficult to state the mechanism(s) of energy transfer in this example since the scattering characteristics and most probable energy transfer values did not change significantly from 6.6 to 50.1 eV collision energy. Only at 3.1 eV collision energy, scattering changes from forward to backward region, most likely due to very small impact parameter collisions required for sufficient energy (same as in higher energy collisions) deposition for dissociation. If we plot the most probable scattering angle versus the collision energy, it becomes obvious that there is an exponential increase in the scattering angle from 6.6 to 3.1 eV CID as shown in Figure 7. It is therefore very likely that these very low energy collisions probe the repulsive part of the helium−nitrobenzene ion interaction potential to overcome the energy barrier for this dissociation. It is well understood that larger angle scattering is mainly due to the repulsive collisions (collisions at the repulsive portion of the interaction potential) at small impact parameters. A sharp increase in the most probable scattering angle, as shown in Figure 7, strongly suggests that the ion−neutral interaction potential well is deep and narrow. Since the energy transfer in the activation step did not change to any significant extent, we suggest that the nature of the CID process in this case did not change.

It is interesting to note that the energy transferred in the CID process is ~0.6 ± 0.3 eV higher than the threshold for the dissociation even though nitrobenzene ions are produced by 70 eV electrons and the NO_2 loss is a direct dissociation process. The presence of a strong metastable peak for the loss of NO clearly suggests that a fraction of these primary ions have internal energies ranging up to ~1 eV above the ionization energy. Why do nitrobenzene ions require more energy than the thermochemical threshold for the process? Is there a kinetic shift associated with this process or it proceeds from an isolated higher electronic state? Interestingly, both were convincingly discussed: the former by Nishimura et al.[11] on the basis of their RRKM calculations of the dissociation rate constant and the isolated state by Panczel and Baer.[12] In the last IRMPD study, Osterheld, Baer, and Brauman[15] suggested that the dissociation to $C_6H_5^+$ proceeds via an ion−neutral complex, $C_6H_5^+ \cdots NO_2$, rather than direct C−N bond cleavage. This intermediate complex then becomes precursor for both processes, loss of NO_2 as well as loss of NO via direct cleavage and nitro-nitrite rearrangement, respectively.

How do our experimental observations fit into the above picture described by Osterheld et al.?[15] We do not see any noticeable change in the dynamics of the CID process for $C_6H_5^+$ fragment ion as ion energy is increased. The energetics of the CID process does not change significantly when collision energy is changed. Further the transition from backward scattering to forward scattering and to smaller angles with increase in collision energy suggests only the role of varying impact parameter collisions in this CID process. Very similar experimental observations were made in the CID of propane[29] and methyl nitrite[27] molecular ions as well as in the CID of nitromethane ion[16] to NO_2^+ fragment ions where we concluded that there was no change in the activation and dissociation mechanism with increase in collision energy. The CID of nitromethane ion to NO^+ clearly showed a change in energy transfer as well as scattering characteristics leading us to conclude that there is a change in the activation and dissociation mechanisms. Nearly constant energy transfer and similar dynamical characteristics observed in our present study strongly suggest that there is no change in the activation mechanism either.

The remaining question is the activation mechanism: electronic excitation as once suggested or the kinetics effects on the dissociation process? It is easy to rule out any kinetic shift or similar related phenomenon responsible for more than necessary energy transfer in our CID experiments. In our experimental set up, the distance between the collision center and the entrance to the linear lens is of the order of 1.5 cm. The primary Ions after collisional activation must dissociate within this region for them to be properly accelerated for their true energy measurements by the energy analyzer. Any ions that decompose after the collision region (i.e., lifetimes between ~1 and ~2.5 μs for the energy range of the present experiments) would also be collected by the analyzer except that their measured energies would not reflect their true energies. This is due to their dissociation in different parts of the linear acceleration lens, which are at different potential fields. Further acceleration of the fragment ions between the collision region and the energy analyzer for their transmission through the energy analyzer at fixed transmission energy results in a shoulder/tail in the kinetic energy distributions alongside the main peak for the ions formed inside the collision region.[28] This behavior becomes very obvious in our experimental measurements and data analysis as we have demonstrated recently in the CID of enolic acetone ions.[38]

The photoelectron spectrum of nitrobenzene shows that its first two excited states, A and B, are only 1.11 and 1.30 eV, respectively, above the ground state. The dissociation threshold for the formation of $C_6H_5^+$ lies between these two states. It may therefore be a possibility that collisional activation results in excitation of these states. However, unlike nitromethane and acetone ions, the X, A, and B states in nitrobenzene have overlapping vibrational bands making the energy redistribution faster. On the other hand, propane and several other ions which have similar photoelectron bands as in nitrobenzene have shown that energy randomization in such ions is accomplished very fast. In these cases, even though energy transfer may be more than the thermochemical threshold, similar dynamical behavior was interpreted as CID proceeding from the ground electronic state following statistical unimolecular dissociation theories.

The larger than necessary energy transfer in the activation step but without any change in the dissociation dynamics suggest that there may be an energy barrier in the potential energy surface for this dissociation process. The competition between NO_2 and NO losses may result in a small competitive shift as observed in the present experiments. Kim and co-workers[39] performed a photodissociation study of the nitrobenzene ion in combination with RRKM calculations and concluded that fragmentation via NO_2 loss occurs statistically from the ground electronic state without significant reverse activation barrier. They concluded that both NO_2 and NO loss compete effectively in the dissociation of the nitrobenzene ions. This is in agreement with earlier PEPICO studies by Nishimura et al.[11] who also used RRKM theory to support their observations. Osterheld et al.'s[15] recent observations using IRMPD also support this conclusion. Thus, the experimental observations made in longer and shorter time frames both draw the same conclusion that the dissociation of nitrobenzene ion to phenyl ion is statistical.

Osterheld, Baer, and Brauman[15] proposed from their IRMPD studies that the dissociation of nitrobenzene molecular ion via loss of both NO_2 and NO proceeds via an ion−dipole complex, $C_6H_5^+\cdots NO_2$. The direct C−N bond cleavage for the loss of NO_2 competes with the C−O bond cleavage proceeding via nitro-nitrite rearrangement resulting in a competitive shift[40] that is responsible for an increase in the dissociation threshold for the phenyl ion. The NO_2 loss is experimentally observed only when its dissociation rate becomes comparable to the nitro-nitrite rearrangement. Thus, even though we do not have any direct evidence to support Osterheld's conclusion,[15] our experimental observations clearly point us only in that direction.

Conclusions

CID of nitrobenzene at lower collision energies is dominated by loss of NO_2 even though this is not the lowest energy dissociation pathway. There is no significant change in the activation and dissociation mechanism in the CM energy range from 3 to 50 eV since the energy transfer from kinetic to internal modes in the collisional activation step remains nearly the same, $\sim 1.8 \pm 0.3$ eV. The most probable scattering of the fragments correspond to backward scattering in the CM frame and decreases with increase in collision energy, suggesting that small impact parameter impulsive collisions dominate the CID process at all energies used in this study. Our experimental observations are consistent with the dissociation via intermediate ion−neutral complex suggested by Osterheld et al.[15]

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