Infrared multiphoton dissociation (IRMPD) of nitrobenzene cations has been shown to proceed via three pathways of ca. 1-2 eV activation energy to produce C\textsubscript{4}H\textsubscript{5}O\textsuperscript{+}, C\textsubscript{6}H\textsubscript{5}\textsuperscript{+}, and NO\textsuperscript{+} ions. Observation of these three fragment ions and not C\textsubscript{6}H\textsubscript{5}O\textsuperscript{+}, which has approximately the same appearance energy, suggests that they are produced from high vibrational levels of the ground electronic state of the cation, while the C\textsubscript{6}H\textsubscript{5}\textsuperscript{+} either has a higher appearance energy than previously reported or is produced by dissociation from an isolated electronic state. To explain all aspects of the observed formation of C\textsubscript{6}H\textsubscript{5}\textsuperscript{+} and C\textsubscript{6}H\textsubscript{5}O\textsuperscript{+} fragment ions from nitrobenzene cations by IRMPD two different dissociation pathways leading to C\textsubscript{6}H\textsubscript{5}O\textsuperscript{+} have been postulated. One produces stable C\textsubscript{6}H\textsubscript{5}O\textsuperscript{+} ions and one leads to unstable C\textsubscript{6}H\textsubscript{5}O\textsuperscript{+} which further dissociates to C\textsubscript{5}H\textsubscript{5}\textsuperscript{+}. 
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Infrared Multiphoton Dissociation

of the Nitrobenzene Cation

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INFRARED MULTIPHOTON DISSOCIATION OF THE NITROBENZENE CATION

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ABSTRACT

Infrared multiphoton dissociation (IRMPD) of nitrobenzene cations has been shown to proceed via three pathways of ca. 1-2 eV activation energy to produce C₆H₅O⁺, C₅H₅⁺, and NO⁺ ions. Observation of these three fragment ions and not C₆H₅⁺, which has approximately the same appearance energy, suggests that they are produced from high vibrational levels of the ground electronic state of the cation, while the C₆H₅⁺ either has a higher appearance energy than previously reported or is produced by dissociation from an isolated electronic state. To explain all aspects of the observed formation of C₅H₅⁺ and C₆H₅O⁺ fragment ions from nitrobenzene cations by IRMPD two different dissociation pathways leading to C₆H₅O⁺ have been postulated. One produces stable C₆H₅O⁺ ions and one leads to unstable C₆H₅O⁺ which further dissociates to C₅H₅⁺.
INTRODUCTION

The nitrobenzene molecular cation has been the subject of extensive studies in recent years. In fact, Porter et al. [1] have used nitrobenzene as an example to show various ways in which a contemporary mass spectrometer can be utilized to obtain a wealth of information about a molecular species. An understanding of the photochemistry of this cation has been facilitated by a number of investigations of the photoelectron spectrum of the parent neutral [2-6]. Stepwise and direct photoionization (PI) of nitrobenzene have been studied using pulsed lasers and photoionization mass spectrometry [7]. The ionization energy (IE) of the parent ion, the appearance energy (AE), and relative yields of various fragments have been measured. The IE of $\text{C}_6\text{H}_5\text{NO}_2^+$ was reported to be 9.87 eV and the AE of $\text{C}_6\text{H}_5\text{O}^+$ and $\text{C}_6\text{H}_5^+$ to be 10.95 and 11.15 eV, respectively. Based on the shape of the photoionization efficiency curve and the photoelectron spectrum it was concluded [7] that the main contribution to formation of the two ionic fragments of nitrobenzene is made by electronic excited states formed by detachment of an electron from non-bonding orbitals of the nitro group.

Laser photodissociation studies of the nitrobenzene cation [8-10] showed no $\text{C}_6\text{H}_5\text{O}^+$ peak (corresponding to loss of NO from $\text{C}_6\text{H}_5\text{NO}_2^+$), but the $\text{C}_6\text{H}_5^+$ peak (due to loss of NO$_2$) was very pronounced. However, fragmentation of collisionally activated nitrobenzene ions showed a different pattern [11] with peaks resulting from both the loss of NO and NO$_2$ observed (indicating that in this process the ions acquire a range of excitation energies).

Photoelectron photoion coincidence (PEPICO) spectrometry studies of the dissociation dynamics of energy-selected nitrobenzene cations have been published by two groups [12, 13]. The appearance energies reported by Panczel and Baer [12] for $\text{C}_6\text{H}_5^+$ and $\text{C}_6\text{H}_5\text{O}^+$ agree with the previous PI study [7] within
experimental error. Additional values of AE's for $C_5H_5^+$, $C_4H_3^+$, and NO$^+$ were reported as 11.30, 11.40, and 11.04 eV, respectively. Based on their results, the authors concluded that part of the NO$^+$ and all of the $C_6H_5O^+$ products are formed by dissociation from the ground electronic state of $C_6H_5NO_2^+$. On the other hand, it was argued that dissociation to produce $C_6H_5^+$ takes place from an excited electronic state, following removal of a bonding electron from the C-N bond upon ionization of the nitrobenzene neutral.

The AE's reported by Nishimura, et al. [13] for $C_6H_5O^+$, $C_6H_5^+$, $C_5H_5^+$, $C_4H_3^+$, $C_3H_3^+$, and NO$^+$ were 10.98, 11.08, 11.08, 15.66, 12.63, and 10.89 respectively. Based on their results these authors concluded that formation of $C_6H_5O^+$ and NO$^+$ from the nitrobenzene ion proceeds via rate-determining tight transition states whereas near threshold the formation of NO$^+$ is probably preceded by nitro-nitrite isomerization. They also concluded that all aspects of nitrobenzene ion dissociation can be explained adequately by statistical theories in spite of the complexity of the reaction dynamics.

From the data given above, it can be seen that the AE's for most nitrobenzene fragments lie within 2 eV of the molecule's IE. Inspection of the infrared spectrum of neutral nitrobenzene [14] revealed several bands in the 10.6 μm region, so there was some possibility that the parent ion might absorb in this region as well. Successful attempts at using infrared multiphoton dissociation (IRMPD) to induce fragmentations requiring 1-2 eV of internal energy in nitrogen- and oxygen-containing hydrocarbon ions have recently been reported [15, 16] from this laboratory. The controlled nature of the IRMPD process usually guarantees that only a few fragment ions are formed, corresponding to the lowest activation energy pathway for dissociation [17]. For positive ions, only high vibrational levels of the ground electronic state, and not excited electronic states, have been accessed by
this technique. The IRMPD of the nitrobenzene cation was thus studied in order to investigate its fragmentation mechanism and to determine which fragment ions were produced from the ground electronic state.

EXPERIMENTAL

Nitrobenzene cations were produced by electron impact in a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer [18], with a nitrobenzene pressure of $3 \times 10^{-7}$ torr and an electron beam pulse of 15 ms duration. The ionizing electron energy was set to ca. 10 eV to guarantee that only the ground electronic state of the nitrobenzene parent ion was populated. This was monitored by observing the very low abundance of $C_6H_5O^+$ ions (the fragment ions of lowest appearance energy) formed by electron impact on the nitrobenzene neutral. (Due to the ca. 1 eV spread in electron energy, it was impossible to eliminate $C_6H_5O^+$ entirely without reducing the intensity of all ions to unacceptably low values. In order to investigate only the fragmentation of parent ions with low internal energy, this fragment ion was ejected from the cell before photodissociation). Nitrobenzene was purchased commercially and used without further purification except for repetitive freeze-pump-thaw cycles. No impurities were detected in wide mass range FTICR spectra. Laser irradiation was carried out using previously reported [16] instrument modifications.

RESULTS AND DISCUSSION

Nitrobenzene ions were trapped in the FTICR analyzer cell and subjected to gated irradiation from a continuous wave (cw) infrared laser [19] with a wavelength of 10.28 μ. Results for ions trapped for 300 ms without and with laser irradiation are shown in Figures 1a and 1b, respectively. The two peaks in Figure 1a with m/z 107 and m/z 93 are the result of ion/molecule reactions of the parent ion with nitrobenzene neutral and represent loss of O and NO,
respectively. (The peak at m/z 61.5 is the first overtone of the m/z 123 ion frequency, and not a doubly charged ion.) However, as can be seen in Figure 1b, IRMPD resulted in production of C$_6$H$_5$O$^+$ (m/z 93) as the most abundant fragment ion, but also some C$_5$H$_5^+$ (m/z 65) and NO$^+$ (m/z 30). The intensity of C$_6$H$_5$NO$^+$ (m/z 107) was essentially the same with and without laser irradiation, indicating that this ion is produced solely by an ion/molecule reaction. Ejection of this ion from the cell during the irradiation period had almost no effect on other fragments, indicating that it does not undergo IRMPD. No C$_6$H$_5^+$ (m/z 77) peak was observed, although this ion has an AE which is the same as [13] or even 0.15 eV lower than [12] C$_5$H$_5$O$^+$.

The IRMPD results suggest that the mechanism of formation of C$_6$H$_5$O$^+$ and NO$^+$ is different from that of C$_6$H$_5^+$, i.e. the former ions are formed from dissociation of C$_6$H$_5$NO$_2^+$ ions which are in high vibrational levels of the ground electronic state. This is in agreement with the conclusions of one PEPICO study [12], and also suggests that an excited electronic state (leading to C$_6$H$_5^+$) was accessed in the earlier [8-10] visible laser photodissociation studies.

Production of C$_5$H$_5^+$, as observed in Figure 1b, is a very interesting case. When C$_6$H$_5$O$^+$ was ejected during the course of laser irradiation no C$_5$H$_5^+$ was produced, indicating that C$_6$H$_5$O$^+$ is the precursor of C$_5$H$_5^+$ by some mechanism, dissociative or reactive. However, increased irradiation time of either the parent ion or of C$_6$H$_5$O$^+$ which was itself produced by IRMPD from the parent did not increase the relative intensity of the C$_5$H$_5^+$ fragment significantly. Thus the remaining C$_6$H$_5$O$^+$ ions do not absorb IR radiation. Also, no C$_5$H$_5^+$ was observed when C$_6$H$_5$O$^+$, which was formed by IRMPD, was allowed to react with background nitrobenzene molecules, eliminating the possibility of an ion/molecule formation mechanism.
The above observations suggest that IR laser irradiation of the nitrobenzene cation produces two different $C_6H_5O^+$ ions, a long-lived ($\tau \sim 100$ μs) unstable ion which further dissociates to $C_6H_5^+$ and a stable $C_6H_5O^+$ ion which does not dissociate. Support for this hypothesis may found in earlier metastable ion kinetic energy spectroscopy (MIKES) studies [20] of the metastable loss of NO from nitrobenzene to produce $C_6H_5O^+$. Two competitive unimolecular processes of approximately equal importance were postulated: one involving a three-centered cyclic transition state and the other involving oxygen rearrangement to the ortho position. The first process was postulated to involve a "tight" complex in which the ring and nitro group are in orthogonal planes, bonded in a spiro configuration. In this mechanism coupling of the degrees of freedom of the two parts of the molecule is very ineffective and the aryloxy cation is formed with a large kinetic energy release and relatively little internal energy. Stable $C_6H_5O^+$ ions formed in this manner could account for the m/z 93 peak seen in Fig. 1b.

The second dissociation process, involving oxygen rearrangement to the ortho position, was postulated [20] to take place via a "loose" complex with an observed lower kinetic energy release and more internal energy remaining in the $C_6H_5O^+$ daughter ions. This excess internal energy is apparently just sufficient to permit further dissociation to $C_5H_5^+$, but with a lifetime of ca. 100 μs since that is the necessary time for ejection in the FTICR experiment. Such a long lifetime for dissociation is not unreasonable given the fact that IRMPD occurs when there is just sufficient energy to overcome the barrier to dissociation, leading to even longer lifetimes than those common for metastable ions in conventional mass spectrometry where a range of internal energies are imparted to the parents by electron impact ionization.

Observation of NO$^+$ and $C_5H_5^+$ ions of comparable intensities in Figure 1b
suggests that the activation energies for their formation are similar. This in turn implies that the more recent [13] PEPICO value of 11.08 eV for the AE of C$_5$H$_5^+$ should be preferred over the earlier [12] value of 11.30 eV. The former value is closer to the NO$^+$ AE of ca. 11.0 (10.89 [13] or 11.04 [12]) eV, and if the latter value were correct one would expect little or no C$_5$H$_5^+$ formation via IRMPD due to the 0.3-0.4 eV difference in activation energies for dissociation.

Dissociation channels leading to formation of NO$^+$ + C$_6$H$_5$O or NO + C$_6$H$_5$O$^+$ should be similar, basically depending on which fragment retains the positive charge. NO$^+$ ions corresponding to both low and high components of kinetic energy release (KER) have been observed in PEPICO studies [13] and similar results were discussed above for C$_6$H$_5$O$^+$ ions in MIKES experiments [20]. However, no C$_6$H$_5$O$^+$ corresponding to low KER was seen in PEPICO experiments. Failure to observe this component in PEPICO experiments could be due to a higher kinetic shift in these spectrometers and/or to greater sensitivity of the lower KER component of C$_6$H$_5$O$^+$ to fragmentation due to excess internal energy. Long ion residence times lead to extremely small expected kinetic shifts in the FTICR spectrometer.

Recently it has been shown [21-23] that disubstituted halo-benzene ions readily isomerize before fragmentation. The results of the present study suggest the importance of isomerization process in the nitrobenzene cation dissociation. Consideration of possible rearrangements in the more recent PEPICO study [13] facilitated interpretation of the photoelectron photoion coincidence results on nitrobenzene. On the other hand the earlier PEPICO work [12] did not rely on isomerization mechanisms in its explanations, while the present study indicates they may be important in C$_6$H$_5$O$^+$ formation. The isolated state assumption for C$_6$H$_5^+$ formation by Panczel and Baer [12] seems to
be more consistent with the IRMPD results and reported AE's for \( C_6H_5^+ \).

CONCLUSION

Production of \( C_6H_5O^+ \) and \( NO^+ \) by infrared multiphoton dissociation of the nitrobenzene cation indicates that these ions are produced from high vibrational levels of the ground electronic state of the ion. The mechanism of formation of these ions is different from that of \( C_6H_5^+ \), which is either produced directly from an excited electronic state or from the ground state via a pathway whose activation energy exceeds that of \( C_6H_5O^+ \), \( NO^+ \) and \( C_5H_5^+ \) by > ca. 0.2 eV, which is inconsistent with existing appearance energies. The results of this study also suggest that two different types of \( C_6H_5O^+ \) ions are produced by IRMPD, one stable with respect to dissociation and the other undergoing further fragmentation to give \( C_5H_5^+ \) on a >100 \( \mu \)s time scale.

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19. Apollo Laser Inc., 9201 Independence Avenue, Chatsworth, CA 91311.


FIGURE CAPTION

Figure 1. a. Mass spectrum resulting from reaction of nitrobenzene parent ions with nitrobenzene neutrals for 300 ms. Ionizing electron energy was ca. 10 eV and nitrobenzene pressure was $3 \times 10^{-7}$ torr. No laser irradiation.

b. Same conditions as in a. except laser irradiation of ca. 10 W/cm$^2$ during the 300 ms reaction period. Peaks normalized to $C_6H_5NO^+$ intensity from spectrum a. The small peak at m/z 116 is due to an indene impurity.
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