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REMPI-MS: Application to the study of the gas phase dynamics of radical cations

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ABSTRACT: Non-resonant and resonantly enhanced multiphoton ionization studies are presented for the isomeric propylamines, butylamines and *n*-pentylamine. Fragmentation patterns are described as a function of laser wavelength and fluence. These time-of-flight (TOF) mass spectra are compared with electron impact data and a discussion of the dynamics of the decomposition process is presented in terms of competitive ionic fragmentation pathways.

1. INTRODUCTION

Multiphoton ionization (MPI) and multiphoton ionization mass spectrometry (MPI-MS) have been employed in recent years to great advantage in the study of the mass fragmentation of fragile molecules as well as in the observation of photoinitiated chemical dynamics (Boesl, et al., 1978, Rockwood, et al, 1979). The technique has been especially valuable in those instances where electron impact mass spectrometry leads to extensive and somewhat indiscriminate fragmentation of the parent molecule.

We report here our efforts involving the use of MPI-MS in the study of the chemical dynamics of the isomerization of alkylamine radical cations (Siuzdak and BelBruno, 1990). In particular, the mass spectral fragmentation patterns of the propylamines, butylamines and *n*-pentylamine are presented and discussed in terms of the mechanism of parent radical cation fragmentation and rearrangement. A skeletal size threshold for isomerization and novel competitive kinetic pathways have been observed.

2. EXPERIMENTAL

The experiments described in this report were performed with a linear time-of-flight mass spectrometer of the standard Wiley-McLaren design. The sample was admitted to the source region via a molecular leak from a reservoir pressure of ~50-200 torr. The pressure in the source region was always less than ~8 x 10^{-5} torr and in the drift/detection region was maintained in the 10^{-6} torr range at all times. The resolution of the apparatus was 1 amu throughout the spectrum of the halocarbon calibration gases (m/z = 110).

The ionization potentials of all of the amines are clustered in a small range around 9 eV, so that depending upon the wavelength chosen for a particular experiment, 3 or 4 photon ionization of the parent molecule was expected. Resonant enhancement of the ionization process could occur through the n→3s Rydberg transition, which has previously been reported only for the lower alkylamines.

3. RESULTS

The electron impact (EI) mass fragmentation patterns for the target molecules are well-known. For *n*-propylamine, the most intense feature occurs at m/z 30 and corresponds to α-cleavage of the parent radical cation to a fragment with the empirical formula CH_4N^+. The *iso*-propylamine EI fragmentation pattern follows analogously with the major feature at m/z 44 and due to the $C_2H_6N^+$ fragment. Small quantities of lower m/z fragments and parent ion are also detected. The electron impact spectra for the butylamines exhibit pure α-cleavage of the amine cation, such that the largest neutral fragment is produced. Finally, the *n*-pentylamine EI mass spectrum is dominated by α-cleavage to produce the m/z 30 fragment as observed in *n*-propylamine. Very small yields of parent ion and *larger* fragments are also observed and are attributed to molecular rearrangements prior to fragmentation or higher order bond cleavage.

The 355nm non-resonant MPI mass fragmentation patterns for *n*-propylamine at low laser intensities (~10^7 W cm^{-2}) indicate only fragmentation to m/z 30 as in the EI mass spectrum. As the laser intensity is increased to 10^9 W cm^{-2}, more extensive fragmentation of the molecule is observed. Interestingly, a larger quantity of the M^+-H ion is produced at the higher energy. The MPI fragmentation patterns for *iso*-propylamine are analogous to those for *n*-propylamine. That is, the MPI spectrum at low energy resembles that obtained from electron impact, the total ion yield increases dramatically with laser energy and the fragmentation becomes more extensive at higher laser energies. Again, molecular rearrangements prior to fragmentation appear to be minimal and the presence of hydrogen atom loss channels, which do not appear to be readily available to the electron impact produced parent ion, are observed.

At 355nm excitation, the major mass fragment for *tert*-butylamine occurs at m/z 58, corresponding to an apparent α-cleavage and loss of a $CH_3\bullet$ group. The *sec*-butylamine also appears to follow an α-cleavage fragmentation pathway with the major mechanism involving loss of $C_2H_5\bullet$ (m/z 44) and a minor contribution from $CH_3\bullet$ elimination (m/z 58). However, the remaining two isomers exhibit mass fragments which cannot entirely be attributed to α-cleavage pathways. For *iso*-butylamine, the expected fragment due to formation of $CH_2NH_2^+$ is observed at m/z 30, but additional fragments with significant intensities were recorded at m/z 44 and m/z 58. Similarly, *n*-butylamine ionization results in the expected m/z 30 product, but fragments with m/z 58 and m/z 44 are also observed. At higher levels of laser intensity, higher yields of smaller fragments are observed.

Comparison of the 355nm *n*-pentylamine spectra with those for EI indicates that MPI and electron impact ionization are nearly identical at low laser intensities, but that at higher laser intensities the *larger fragment ions are produced in much higher yields by MPI* than by EI. We note that H-atom loss channels again seem to be more prevalent with the MPI technique and that the spectrum has much the same appearance as a butylamine spectrum. Study of MPI fragmentation spectra, of all of the amines, for excitation at 532nm indicates a striking similarity to those recorded at 355nm. In this particular instance, the frequency dependent nature of the MPI fragmentation is lost.

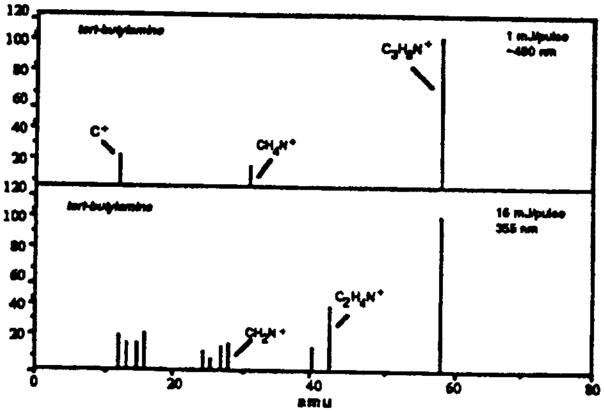

Figure 1. Comparison of MPI-MS for resonant (480nm) and non-resonant (355nm) excitation.

The mass spectra for resonant excitation at 480nm are different from the non-resonant results as shown in Figure 1. These spectra are obtained by excitation through low rovibrational states of the 3s Rydberg level. This result is a manifestation of the wavelength selectivity, i.e. the variable energy input, of MPI-MS, and one of its major advantages. The *tert*- and *sec*-butylamine mass spectra at this wavelength are intriguing, since they exhibit considerably more extensive fragmentation than for excitation with a greater laser energy at 355nm. Contrary to this observation is the indication that the remaining two isomers fragment along the expected reaction pathway, i.e., the additional peaks, attributed to some process other than α-cleavage, observed at 355nm are significantly reduced at this wavelength.

4. DISCUSSION

The MPI mass spectra, especially at the higher laser powers, exhibit considerably more extensive fragmentation than the EI spectra. This is typically observed in MPI-MS and is attributed to very efficient ladder-switching. Contrary to most MPI studies, the EI and MPI fragmentation patterns for the propylamines show many similarities. However, the butylamine and *n*-pentylamine results indicate that rapid (within the 6 ns laser pulse) isomerization mechanisms may effectively compete with direct fragmentation. *Isomerization is more favorable* than α-cleavage for the larger amines. One plausible explanation for the difference between the propyl- and larger amines is the fact that many fewer low frequency vibrational modes are available for the propylamines. The availability of such low frequency sinks for the excess excitation energy was found to be a critical factor in the opening of isomerization channels in the butylamine cations. It appears that the three carbon chain is simply below the threshold for the accessibility of isomerization pathways. The results involving the *n*-pentylamine mass spectrum are an interesting corroboration of this interpretation. The mass fragmentation pattern appears to indicate that aside from the expected α-cleavage, a significant number of the radical cations undergo γ-cleavage to produce the *n*-butylamine cation which is subject to both direct fragmentation as well as isomerization to the *sec*-butylamine cation (by a 1,2-methyl shift) with subsequent fragmentation. The greater probability of the M^+-H fragment ions for the amine cations at higher laser intensities is an intriguing and, initially, a counterintuitive result. However, this fragment lies ~1 ev above that resulting from C-C bond fission (in the parent ion). Therefore, absorption of an additional photon is required for creation of this product. Absorption of that photon is in competition with bond cleavage in the parent ion and the rates become comparable only at the higher laser intensities. This type of kinetic behavior in radical cations has not been previously reported.

We have carried out RRKM calculations for all of the butylamine radical cations and these calculations are consistent with the following mechanism. For example (see Figure 2), production of the *iso*-butylamine ion requires absorption of three photons at 355nm. The ion is created with an excess energy as large as 1.7eV, enough to energetically lead to α-cleavage and isomerization. However, the rate of both processes is extremely slow and neither would not be observed on the timescale of the experiment. Absorption of an additional photon is necessary to produce any observable α-cleavage product. The additional energy also leads to isomerization at a rate which is competitive with fragmentation. The multiphoton mass spectra confirm that isomerization is occurring. The calculations also indicate that although production of a M^+-H fragment is energetically possible after absorption of a single photon by the parent ion, the rate of production is sufficiently slow as to render the product unobserveable. Only after absorption of a second photon, *in the parent cation manifold*, is this process kinetically feasible. Again, the experiments yield results consistent with the calculations. At the higher laser intensity, up-pumping of the parent ion successfully competes with decomposition to CH_4N^+ and isomerization. The cross section for further absorption may be estimated (for an allowed transition) as $\sim 10^{-17} cm^2$. At a laser intensity of $10^9 W \cdot cm^{-2}$, the transition probability is estimated to be $\sim 2 \times 10^{10} s^{-1}$. This is comparable to the α-cleavage rate constant, but a factor of ~3 less than the isomerization rate. However, the amount of product resulting from absorption and subsequent fragmentation would easily be sufficient for detection. At 480nm, the α-cleavage and isomerization rates after absorption of a single photon by the parent ion are nearly identical. Production of M^+-H is not expected to be significant even after absorption of two photons by the cation. Again, the calculations are in accord with the experiments. Finally, irradiation at 532nm requires absorption of two photons by the parent cation for either α-cleavage or isomerization. Fragmentation of the N-H bond requires yet an additional photon. These calculated results are in agreement with the observation that MPI mass spectra are only observed at high laser intensities for this wavelength.

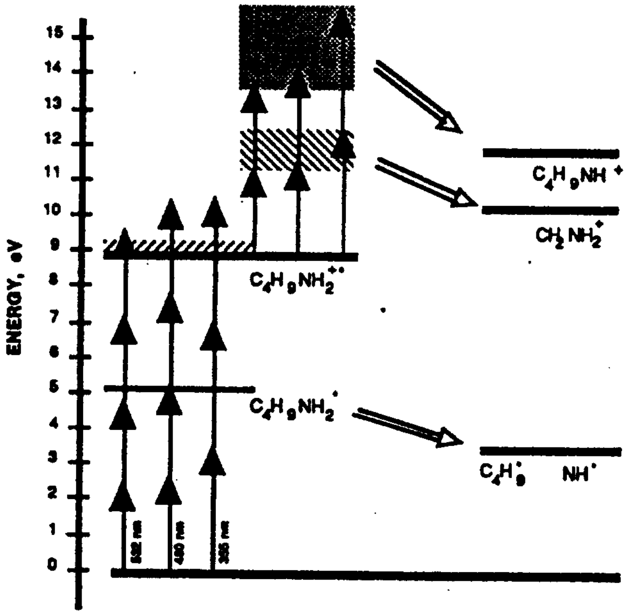

Figure 2. Relevant energy levels for the butylamines. Three possible fragmentation mechanisms are shown. The two uppermost shaded are correspond to one- and two-photon absorption by the radical cation.

One interesting aspect of this research is the lack of any wavelength specificity in the non-resonant excitation. Our butylamine research has indicated that the lowest electronic transition corresponds to an n→3s Rydberg excitation (X→A) with an origin at approximately 42,000cm^{-1}, depending upon the particular chain length of the alkylamine. The higher excited states have been relatively unexplored. Two photons at 355nm and three photons at 532nm would be required to attain an energy greater than the vibrationless ground state of the 3s level. Both of these excitation schemes would result in approximately 56,000cm^{-1} of energy input. Production of the molecular ion via either wavelength would result in an ion with excess energy and a high probability for fragmentation. One must also conclude from the similarity of the mass spectra, that the ions involved in ladder-switching mechanism readily absorb either wavelength.

The butylamine MPI spectra are wavelength dependent, implying more than one decomposition mechanism, and one which is not related to the electron impact pathway. The initial step in the MPI excitation mechanism at 480nm is absorption into the 3s Rydberg level. Other important differences for the three wavelengths used in the study are the order of the absorption process and the level of excitation in the lowest ionic state. The nearly equivalent and large levels of excess energy deposited in the amine at 355 and 532nm are expected to cause the pathways for these two wavelengths to be nearly identical. Previous studies have shown that the excitation from the Rydberg level to the ionic state occurs with little change in the vibrational quantum number, i.e., the geometry of the Rydberg state resembles that of the ion. Therefore, excitation with either 355nm or 532nm radiation will ultimately yield similar ions due to the approximate energy matching at the two and three photon level respectively. In contrast, excitation at ~480nm results in the formation of Rydberg molecules in the ground vibrational level and subsequent production of vibrationally cold ions. This difference could be cause of the variation in resonant and non-resonant mass spectra A second possible factor is that the *tert*-butylamine and *sec*-butylamine radical cations might possess larger absorption cross sections at 480nm than do the remaining isomers.

5. REFERENCES

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