

Laser Multiphoton Dissociation/Ionization of Butylamines: Competitive Processes in Radical Cations

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In Final Form: January 17, 1990)

Butylamine radical cations are produced by multiphoton ionization through the 3s Rydberg level. The nature of the intermediate state was confirmed by resonance-enhanced multiphoton ionization (REMPI) spectroscopy, and the optical data are reported for the first time. The high levels of excitation lead to competition among dynamical processes in the radical cation. Time-of-flight mass spectrometry is employed in the observation of these processes. It was observed that, for the less branched amines, isomerization effectively competes, on the nanosecond time scale of the experiment, with α -cleavage of the parent radical cation and further up-pumping of the parent cation to other reaction channels. The results of RRKM calculations are found to be in agreement with this observation.

Introduction

Multiphoton ionization mass spectrometry (MPI-MS) is customarily employed to generate structure-specific fragmentation patterns for molecules that are difficult to distinguish by other methods, especially electron impact.¹ Reactive species have been explored by using the MPI-MS technique with impressive results. In particular, a large body of data concerning the isomerization and fragmentation of alkyl cations has been reported.^{2,3} These experiments have shown that, until high levels of excitation are attained, isomerization is the dominant metastable pathway. However, on the nanosecond time scale, fragmentation is the major decomposition pathway and the spectra could be explained by means of a ladder-switching mechanism after molecular ionization.^{3,4}

Unlike alkyl iodides which are known to photodissociate with elimination of I^{*} in both the neutral and ion configurations, the alkylamines are expected to retain the -NH_x functionality ($x = 1$ or 2).⁵ In fact, the amine group is widely regarded as one of the most potent directing functionalities for ionic fragmentation.⁶ This class of molecules is an ideal subject for MPI mass spectrometry since the ionic fragmentation patterns are well-defined from electron impact studies and the required spectroscopic data may be readily obtained. Deviations from the expected fragmentation patterns result from either a new reaction channel or molecular rearrangement. The wealth of data which may be obtained in the MPI experiments permits assignment of the cause of any unexpected mass fragmentation pattern.

The UV spectroscopy of the lower alkylamines and of *tert*-butylamine has been reported.⁵ The lowest singlet excited state

has been assigned as $X \rightarrow \tilde{A}$, an $n \rightarrow 3s$ Rydberg transition with the origin at approximately 42 000 cm⁻¹. The excited-state geometry is planar about the N atom, and the change in geometry upon excitation results in a vibrational progression with a spacing of ~ 700 cm⁻¹. No direct evidence of photodissociation has been reported, but loss of an H atom from -NH₂ group, by analogy with the known photochemistry of NH₃,⁷ is a feasible pathway. Spectroscopic data have not been reported for the *n*-, iso-, and *sec*-butylamines. In order to clarify the kinetic processes observed in this study, REMPI spectra were also obtained for these molecules, and the data are reported here for the first time. In all cases, the $n \rightarrow 3s$ Rydberg transition was observed. However, the extent of vibrational excitation observed was isomer dependent.

Using this base of spectroscopic data, we have obtained the MPI mass fragmentation patterns for all four butylamine isomers. By comparison with the known unimolecular reactivity of the radical cations, the fragmentation patterns reflect the competition between "normal" fragmentation and rearrangement of the cation. In addition, a new high-energy fragmentation channel has been observed. On the nanosecond time scale of the experiment, the iso- and *n*-butylamine radical cations undergo substantial rearrangement prior to fragmentation, while the remaining two isomers are stable to rearrangements. As might be expected, the extent of the competition is excess energy dependent. The results of a series of RRKM calculations are consistent with the experimental observations.

Experimental Section

The experiments described in this report were performed with a linear time-of-flight mass spectrometer of the Wiley-McLaren design. The apparatus consisted of two independently pumped chambers, source and drift tube regions, separated by an aperture. The oil diffusion-mechanical roughing pump combination was capable of reducing the pressure to approximately 10⁻⁶ Torr in the absence of any sample flow. The source region contained a repelling plate and a pair of accelerating grids, with the repelling plate and grid assembly separated by 0.85 cm and the accelerating grids spaced 2.64 cm apart. Potentials of up to 3 kV could be applied to any two of the three plates, but for most of the reported work, only the repelling plate was employed with an applied

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