Evidence of Isomerization During Ion Isolation in the Quadrupole Ion Trap

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Evidence of ion isomerization during isolation in an ion trap mass spectrometer is presented. An ion–molecule reaction that is specific for the tolyl cation was used to monitor the relative abundance of this species. In particular, it has been observed that ion isolation in the ion trap can impart sufficient energy to the tolyl cation to cause it to isomerize to a form (presumably either the benzyl or the tropylium ion) that is not reactive with the neutral reagent. These results are important to consider in ion trap applications involving ion species having activation barriers for isomerization lower than the activation barriers for dissociation. (*J Am Soc Mass Spectrom* 1992, 3, 680–682)

Knowledge of the ionic environment found within a mass spectrometer is important in understanding the chemical processes that occur in the instrument (e.g., ion reactivity and ion dissociation). This communication reports the use of the tolyl ion reaction with methane [1, 2] to monitor the relative abundance of tolyl cations after manipulating the ion trap electrode voltages to effect ion isolation. These results are important to consider when studying either dissociative or ion–molecule reactions of ions having activation barriers for isomerization lower than the activation barriers for dissociation in the quadrupole ion trap. Because ion isolation is typically performed prior to the dissociation step (whether by collisional activation or photodissociation), it is important to recognize that isomerization of some ion structures may occur.

A "pure" population of tolyl cations can be generated by methane chemical ionization (CI) of 3-fluorotoluene [3–5]. The ions observed in the methane CI mass spectrum of this compound in an ion trap mass spectrometer are listed in Table 1. Notice that the abundance of tolyl cations at m/z 91 is relatively small compared to that of the protonated molecule at m/z 111. In the course of other experiments using the ion trap rf and dc voltages to isolate the ions at m/z 91, it was discovered that the isolated m/z 91 ion population did not consist of pure tolyl cations because a substantial fraction of the m/z 91 ion population did not react with methane.

Tolyl cations react with methane to form ions at m/z 79, 105, and 107, which correspond to $C_6H_7^+$,

$C_8H_9^+$, and $C_8H_{11}^+$, respectively [2]. For example, the abundance of the ions at m/z 91 was reduced by 87% after 40 ms of additional reaction time subsequent to ejection of the CI reagent ions. A corresponding increase in the m/z 79, 105, 107 abundances was also observed. The other common $C_7H_7^+$ isomers, benzyl and tropylium, are not reactive with methane [1, 2].

Ion isolation is accomplished in the ion trap by manipulating the ion trap instrumental parameters to eject undesired ions from the trap. Ions can achieve large kinetic energies in the process of being ejected. It has been suggested by trajectory simulations that ions with mass-to-charge ratios close to those that are being ejected are also kinetically excited to some extent [6]. The heats of formation of the 3-tolyl, benzyl, and tropylium ions are 1054, 897, and 849 kJ/mol, respectively [3, 7, 8]. Thus, the tolyl cation is the least stable of these $C_7H_7^+$ isomers. If the tolyl cations are kinetically excited, and sufficient kinetic energy is converted into internal energy via collisions with the helium buffer gas, isomerization to one of the more stable, nonreactive forms may occur. This process can be monitored in the ion trap by measuring the relative abundance of $C_7H_7^+$ after a storage time sufficiently long to allow all the tolyl cations to react with methane. Using this approach, we have explored the effect of several ion isolation methods on the tolyl cation populations.

Experimental

All experiments were performed on an ion trap mass spectrometer (Finnigan MAT, San Jose, CA) with He as the buffer gas and the ion trap temperature set to 100 °C. Tolyl cations were generated by methane (Scott

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**Table 1.** Relative abundances for the methane chemical ionization mass spectrum of 3-fluorotoluene

m/z	Relative abundance
91	9.1
92	0.1
105	1.8
107	13.7
108	0.8
109	4.7
110	15.7
111	100.0
112	7.2
123	3.0

Specialty Gases, Plumsteadville, PA) CI of 3-fluorotoluene (Aldrich Chemical Co., Milwaukee, WI) [3]. The existence of tolyl cations was confirmed by reaction of the $C_7H_7^+$ (m/z 91) ions with dimethylether (Aldrich Chemical Co.) to form a characteristic ion–molecule reaction product, $C_8H_{10}O^+$ (m/z 122) [3], in a separate experiment. The reagents and buffer gas were introduced into the vacuum system by variable leak valves (Granville-Phillips, Boulder, CO) and the pressure of each was measured by an ionization gauge (Granville-Phillips, Boulder, CO). The pressures were set to the following values for the experiments described in this communication: 3-fluorotoluene (2.2 × 10^{-7} torr), methane (7.5 × 10^{-6} torr), and helium (1 × 10^{-3} torr). These pressures were corrected using the method of Bartmess and Georgiadis with the assumption that the correction value for 3-fluorotoluene was approximately that listed for toluene [9].

Results and Discussion

There are a number of methods to isolate ions of a particular mass-to-charge ratio or range of mass-to-charge ratios in the ion trap [10, 11]. Two methods that use a combination of rf and dc voltages are shown in Figure 1. The most commonly used method involves raising the rf voltage on the ring electrode to a value corresponding to a q value of 0.781 for the ion being isolated and increasing the dc voltage to a value corresponding to an a value of 0.152 for the ion being isolated. Trajectories of ions with mass-to-charge ratios less than the selected mass-to-charge ratio and greater than the selected mass-to-charge ratio become unstable and these ions are ejected from the ion trap. This ion isolation method is sometimes referred to as "apex isolation" because these q and a values represent the upper apex of the stability diagram due to the intersection of the $\beta_z = 1$ and $\beta_r = 0$ stability boundaries (shown in Figure 1, point A). The scan function controlling this experiment utilized a 5-ms isolation step (i.e., the time interval where the dc voltage was applied to the ring and the ions of interest were at the apex of the stability diagram). The dc step was preceded and followed by an appropriate 2-ms rf ramp.
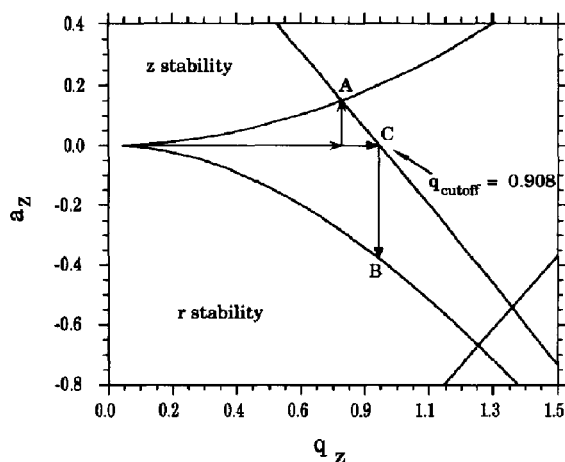
Figure 1. Stability diagram for the quadrupole ion trap showing apex isolation (point A), edge isolation (point B), and a combined RF ramp–resonance ejection (point C).

Another method of rf/dc ion isolation is accomplished by increasing the rf voltage on the ring electrode to a value close to q_{cutoff} for the ion being isolated (i.e., 0.908; point C in Figure 1). This rf ramp ejects all ions with a mass-to-charge ratio less than the ion of interest at the $\beta_z = 1$ boundary. The dc voltage on the ring is then increased to a value corresponding to an a value of -0.400, thus ejecting all ions with a mass-to-charge ratio greater than the ion of interest at the $\beta_z = 0$ boundary [12]. These a and q values represent a different edge of the stability diagram (shown in Figure 1, point B). The dc voltage was applied to the ring electrode for this isolation step for 5 ms and was preceded by a 3-ms rf ramp.

A third ion isolation method utilizes a combined rf ramp and resonance ejection. In this method, the rf voltage applied to the ring electrode is ramped up to a value close to q_{cutoff} (0.908). An ac voltage is simultaneously applied to the endcap electrodes to eject ions with mass-to-charge ratios larger than the ion of interest as they come into resonance with the ac voltage [11]. Resonant ejection at a β_z of 0.322 was used for these experiments. The rf was ramped at a rate of 180 μs per mass-to-charge ratio unit from a low mass cutoff of 45 with a resonant ejection ac voltage of 6 V.

The degree of isomerization of tolyl ions, generated by methane CI of 3-fluorotoluene, was determined by measuring the m/z 91 ion current as a function of time using the above ion isolation conditions. Reaction of all of the m/z 91 ion current to the m/z 79, 105, and 107 ion–molecule reaction product ions was evidence that the m/z 91 ion population consisted of pure tolyl cations. The presence of a nonreactive component to the m/z 91 ion current, as measured by the cessation of further decreases in m/z 91 ion current with reaction time, was indicative of the presence of one or more of the nonreactive $C_7H_7^+$ isomers. The results

initially presented here were obtained assuming that isolation of the tolyl cations (m/z 91) required ejection of ions with mass-to-charge ratios of 90 and 92. The effect of ion isolation on the tolyl cation population is shown in Figure 2 using the ion isolation methods described above. It is clear from curve (a) of Figure 2 that methane CI of 3-fluorotoluene produces a "pure" tolyl cation population under the conditions used in the ion trap, because the ion current due to m/z 91 was reduced to zero at reaction times greater than 120 ms. When the ions appearing at m/z 91 are isolated as was the case for curves (b)–(d), a fraction of the m/z 91 ion current does not react with the methane. For example, isolation of m/z 91 using the upper apex of the stability diagram causes approximately 40% of the m/z 91 ion population to isomerize to $C_7H_7^+$ isomers not reactive with methane.

The degree of isomerization depends on the duration and resolution of the ion isolation step. The duration of the ion isolation is important because this determines the length of time that the ion population is kinetically excited. The resolution of isolation (i.e., how closely the ion is isolated from adjacent mass-to-charge ratios) is important because it determines the magnitude of the kinetic excitation. For example, ejecting an ion ten mass-to-charge units higher than the ion of interest causes significantly less excitation of the ion of interest than the ejection of an ion one mass-to-charge unit from the ion of interest. Accurately determining the relative degrees of isomerization among the isolation methods requires the use of an internal standard for calculating the degree of isolation of m/z 91. Therefore one should not infer the relative degrees
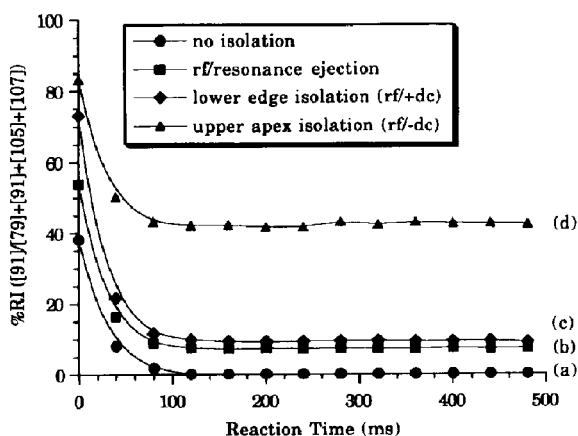
of isomerization for the three ion isolation methods from the data shown in Figure 2. The relative degrees of isomerization for ion isolation methods will be presented in a forthcoming publication [13].

Conclusions

This communication reports evidence of isomerization of tolyl cations during ion isolation using standard ion isolation methods with the quadrupole ion trap. A pure tolyl cation population (m/z 91) was observed from the methane CI of 3-fluorotoluene only when no isolation step was performed. Addition of an ion isolation step for m/z 91 to the scan function that controls the ion trap leads to various degrees of isomerization of the tolyl cations to one or more forms (probably benzyl and/or tropylium) that do not react with methane. The degree of isomerization depends on the duration and resolution of the ion isolation step. These results are clearly relevant in ion trap applications involving ion species with activation barriers for isomerization lower than the activation barriers for dissociation.

Acknowledgments

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Figure 2. Plot of relative intensity (%) (m/z 91) versus time for (a) no isolation, (b) rf/resonance ejection isolation, (c) lower edge rf/+dc isolation, and (d) upper apex rf/−dc isolation of m/z 91.