Dear Sir

Thermochemical vs. Kinetic Control of Reactions in an Ion Trap Mass Spectrometer

Gas phase dehydration and deamination are competitive fragmentation processes of protonated \( \alpha,\omega \)-amino alcohols upon collisional activation (1,2). The dissociations proceed via acid-catalyzed intramolecular cyclization of the straight chain amino alcohol and subsequent loss of either H\(_2\)O or NH\(_3\) depending on the reaction conditions. In a previous study (17, it was found that the thermodynamically favored dehydration product was the major ion produced in the chemical ionization source of a conventional mass spectrometer whereas in the collision region of a tandem mass spectrometer either deamination or dehydration was predominant depending upon the carbon chain length.

Thermochemistry for two representative amino alcohols is shown in Figure 1. For the two and three carbon compounds, the thermodynamically more stable product is also the product with the lowest energy barrier for formation. However, for the four and five carbon amino alcohols, the most stable product is formed through the route of highest activation energy. This accounts for the observed differences in the extent of dehydration and deamination within the amino alcohol series under different reaction conditions. For example, in the chemical ionization source of a mass spectrometer where an ion may undergo many low energy collisions, the thermodynamically more stable product is formed because the ionic population presumably is approaching equilibrium. On the other hand, an isolated ion in the collision region of a tandem mass spectrometer undergoes energetic collisions and the dominant products are the ones that proceed through the pathways of lowest activation energies.

![Figure 1. Enthalpies associated with deamination and dehydration of protonated \( \alpha,\omega \)-amino alcohols (2).](image)

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It was of general interest to study the protonated amino alcohols and their corresponding reaction pathways in an ion trap mass spectrometer, a new type of tandem mass spectrometer. In this instrument, which is based on the Paul ion trap (3,4), ionization, parent ion selection and activation, and mass analysis all occur in one chamber (5). The pressure in the trap is similar to that used in the collision region of a triple quadrupole mass spectrometer (at 

torr range), but the activation time is about one thousand times longer, so that parent ions are expected to undergo many more collisions of lower energy than they would experience under multiple collisions in the triple quadrupole instrument. The many collisions which the parent ions experience with the helium buffer gas may be activating, in which part of the kinetic energy of the ion is converted into internal energy, or deactivating, in which internal energy is lost. In addition, product ions are expected to undergo many collisions including those in which proton transfer could occur to yield the thermodynamically most stable products.

The ion trap used was the prototype Finnigan-MAT ITMS (5). Sample ions were generated through chemical ionization (6) with isobutane at 2.0 x 10⁻⁶ torr. The amino alcohols were introduced through metering valves to 3.0 x 10⁻⁷ torr. Helium buffer gas was added to attain a nominal pressure of 1.5 x 10⁻⁴ torr. The supplementary ac voltage was tuned for each parent ion and was applied for 20 ms at about 1 V (pp). During the activation interval, the rf voltage was applied at 300-500 V (pp) depending on the mass-to-charge ratio of the selected parent ion.

The ratio of ions formed by dehydration to total ions formed by both dehydration and deamination is plotted in Figure 2 as a function of the amino alcohol carbon chain length. The results for the trap bear a close resemblance to the data obtained using a triple quadrupole instrument and a MIKES spectrometer. In every case, dehydration is the dominant fragmentation process for the two and three carbon compounds, but the trend reverses sharply for the four and five carbon compounds. These results suggest that the reaction occurs under kinetic control even for

![Figure 2. Competitive dehydration and deamination of protonated amino alcohols studied at 10 eV (single collision conditions) in the collision region of a triple quadrupole mass spectrometer (2), at 7000 eV in the collision region of a reverse geometry (MIKES) mass spectrometer (2) and using 1 V ac voltage for activation in an ion trap mass spectrometer. The dashed line represents the competitive dehydration and deamination studied in the ion source of a MIKES spectrometer in which the chemical ionization conditions induce thermochemical control of the reactions.](image-url)
conditions of multiple activating collisions in the ion trap (7). Upon 20 ms collisional activation in the ion trap, equilibrium is not achieved.

The ability to operate the ion trap under conditions which produce conventional collisional activation spectra, as well as under conditions which allow further reaction of collisional activation products, is an advantage of the ion trap over conventional MS/MS instruments. Information about the structures and relative proton affinities of the collisional activation products may be obtained by introducing a "wait" period or reaction period following collisional activation. If a wait period is introduced following collisional activation of the four or five carbon compounds, the ratio of the abundance of the dehydration product to the abundance of the deamination product increases. For example, if a wait period of 60 ms is added following collisional activation of protonated 5-amino-1-pentanol, the percent dehydration versus total dehydration plus deamination increases from 35% to 56%. Concurrently, the ratio of the abundance of the protonated amino alcohol to the sum of the abundances of the dehydration product plus the deamination product also increases. The amino alcohol has a higher proton affinity than the dehydration product (an amine) which has a higher proton affinity than the deamination product (an ether). The variation in the abundances of these species with time indicates that the system approaches equilibrium and reflects the relative proton affinities of the compounds involved. Application of the ion trap to the determination of relative proton affinities is currently being explored.

Yours

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References


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