

Assigning Structures to Ions in Mass Spectrometry

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Assigning Structures to Ions in Mass Spectrometry summarizes the present knowledge of the structures and chemistry of small organic cations in the gas phase as obtained from very detailed research conducted over the last 40 years. The book consists of two parts, the first part consisting of an introduction and two chapters. The introduction gives the outline and purpose of the book, that is, to provide the background material that is essential for the proper interpretation and understanding of mass spectra. Chapter 1 briefly describes the various experimental and computational methods developed over the years to generate the ions and, in particular, to obtain qualitative and reliable quantitative thermochemical and structural data of gas-phase ions. It concludes with a cross-reference index to the mass spectrometric terms and methods in its text that is very convenient to the user of the book.

Chapter 2 discusses five landmark and historical case studies selected to illustrate how problems in gas-phase ion structure determinations can be solved by experiment, computational chemistry, and occasionally by required re-evaluation of available quantitative data. They concern: (1) the structure of the m/z 32 fragment ion from electron ionization-induced decomposition of ethylene glycol, shown by collision-induced dissociation (CID) experiments to be the distonic isomer of methanol, that is, the oxygen protonated hydroxymethyl radical (the relevant parts of the CID spectra of these isomeric species have been nicely reproduced on the front cover of the book); (2) the stepwise character of the McLafferty rearrangement shown by reversible H/D exchange in the distonic intermediate before metastable decomposition; (3) the structure of the b-type fragment ions of peptides shown by CID experiments to have a protonated oxazolone ring structure and not the open acylium ion structure, which is a transition state on the potential energy surface; (4) the elimination of a

mixture of methoxy and unexpectedly hydroxymethyl radicals from metastably decomposing methyl acetate radical cations where the neutral hydroxymethyl radicals were identified by collision-induced dissociative ionization and where the last step of the reaction involves the formation of a hydrogen atom-bridged acetyl/formaldehyde complex being fully confirmed computationally and by threshold photoelectron-photoion coincidence experiments; and (5) the revision of the heat of formation of neutral peroxy-ethanol to account for the experimentally determined heat of formation of the methylenehydroperoxy cation.

This chapter concludes with some advice for assigning structures to gas-phase ions by presenting four useful strategy diagrams for experimental work. Those strategies involve thermochemical data, metastable-ion phenomena as a comparative technique, metastable-ion phenomena on the basis of composite metastable peaks, and collision-induced dissociation mass spectra of isomeric mass-selected ions. In addition some relevant caveats about the use of metastable-ion spectra and published thermochemical data are given.

The second part covers (in Chapter 3) roughly 75% of the book and contains selected mass spectral and thermochemical data for ionized carbon clusters and ions containing one, two, and three carbon atoms and any of the elements H, N, O, S, P, and halogen. These four major subjects are covered in four sections, respectively. A brief introduction accounts for the chosen objectives and way of presentation of the huge amount of associated data in these four sections. That is, for any empirical chemical formula is given successively (1) a description of how a particular ion structure (an isomer) may be generated in a mass spectrometer's ion source or by mass-selected ion fragmentations or ion/molecule reactions; (2) experimental criteria on which basis the different isomeric species may be identified and confirmed; and (3) the best available thermochemical data obtained from experiment, by estimate, or by computation. Together with the index of chemical formulae and its associated sections and page numbers, given at the end of the second part and end of the book, the user can easily find the information provided for an ion and its isomers of interest. Moreover, many references to the original literature are presented at the end of each of the four sections of part two (and also at the end of part one) for further reading.

This pleasantly readable and well-organized book is prepared by experts in the field and contains interesting historical notes at various places in the text. It is an excellent handbook for all users of mass spectrometry, in particular, but not exclusively, for those practitioners who are dealing with organic compounds and who would be interested in and like to learn more about the many stories behind the ions that are represented by peaks in a mass spectrum.

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