

# **MASS SPECTROMETRY OF ORGANIC COMPOUNDS**

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## PREFACE

In November 1963 we made the following statement in the preface to our book Interpretation of Mass Spectra of Organic Compounds:

"The use of mass spectrometry in organic chemistry is becoming increasingly widespread and mass spectrometers are now being installed in many laboratories. Three years ago one had to search far and wide in the organic chemical literature to find examples of its use in structural problems. Three years hence it will be difficult to open a journal dealing with organic chemistry without encountering multiple applications of mass spectrometry. No physical tool in organic chemistry—not even infrared spectrometry—is so easily appreciated by the average organic chemist, and once used, none is so difficult to do without."

The present lines are written some three years later, and our prediction about the state of the organic-chemical mass spectrometry literature proved to be a gross underestimate. The veritable flood of papers in the field during these 40 months has been accompanied by nearly a dozen books, including two volumes entitled Structure Elucidation of Natural Products by Mass Spectrometry by ourselves. Under the circumstances, the reader may well inquire why we have the temerity to add to this volume of recent literature by still one more book.

One of the principal stimuli causing us to write our first book on mass spectrometry in 1963 was the belief that the most rapidly growing number of new users of this tool would be organic chemists and that a book addressed specifically to their needs was timely. We believed that the vast majority of organic chemists would not be measuring their own mass spectra—hence the omission of instrumental and other practical facets which are well covered in other books—but would indeed be interpreting their mass spectra themselves. For most organic chemists, mass spectrometry would be a tool, probably one of the two most important ones, used for the solution of their various research problems in the same manner that infrared or nuclear magnetic resonance spectroscopy have been employed. If this assumption were correct, then a "mechanistic" approach to organic mass spectrometry would be pedagogically the most sound one, and the organization of the material would then best be achieved by considering the fragmentation behavior typical of each functional group before delving into the more complicated problem of polyfunctional

molecules. The wide acceptance of our first book, and especially the frequency with which it was cited in journal publications, have convinced us that our original assumptions were correct.

In the intervening three years, the mass spectrometric fragmentation behavior triggered by virtually all common and even most esoteric functional groups in organic chemistry has been examined. Even more significant is the fact that the very rapidly increasing use of high resolution mass measurements and of isotopic labelling techniques has either strengthened or revised many earlier "mechanisms"; indeed the study of the behavior of organic molecules upon electron impact and its comparison with other organic chemical reactions of the same molecule has become a very respectable and active field of research. The quotation marks around the term "mechanism" are still well deserved and the term is hardly used throughout our present book; "rationalization" is a much better substitute. Since the fragment ions are not isolated, only indirect support can be presented to describe their nature, and the evidence is by no means as rigorous as in many other organic chemical reaction mechanisms. Nevertheless, the circumstantial evidence is now overwhelmingly in favor of the approach used in our first book—namely that much of organic mass spectrometry can be discussed in terms of the standard and really oversimplified language of the organic chemist. It is largely for that reason that mass spectrometry has found such rapid acceptance by organic chemists during the past few years, and it is precisely through the use of such oversimplified concepts and generalizations that the more detailed and refined knowledge of the future will be derived.

In view of the great deal of work performed during the past 40 months on the mass spectrometry of organic molecules, we felt that the time was ripe to revise Interpretation of Mass Spectra of Organic Compounds by including newer studies on functional groups already covered in that book and by discussing those functionalities which had previously not been exposed to mass spectrometric scrutiny. We soon discovered that with the exception of a few chapters (e.g., Chapter 18 on tropones and tropolones) revision meant nearly total rewriting. Furthermore, over two thirds of the book represents completely new material, and it is for these two reasons that we selected a different title, Mass Spectrometry of Organic Compounds, to emphasize that the reader is essentially dealing with a new book.

The present volume has been written with two groups of readers in mind. The first is typified by graduate students or advanced undergraduates, who know virtually nothing about mass spectrometry but are aware of the fact that they will probably employ this tool through much of their subsequent professional careers, and hence wish to become proficient in the utilization and interpretation of mass spectral data. It may be desirable, particularly for undergraduates, to consult one of the recent brief texts<sup>1,2</sup> for purposes of introduction. The second group of potential readers is exemplified by ourselves—organic chemists who are familiar with the technique, employ it every day in their chemical work, and even perform research on some specific topic in mass spectrometry. This group invariably has need at frequent intervals to refer to the voluminous literature on the mass spectrometric fragmentation behavior triggered by the many functional groups prevalent in organic chemistry. We know of no other up-to-date and fairly

comprehensive source wherein this information is conveniently available, especially since the relevant literature is spread over so many different journals.

It must be emphasized that there are many other aspects of mass spectrometry, which are of interest to special groups of organic chemists and especially to physical chemists, and which are not covered here. These include virtually all of the instrumental features important to the experimental mass spectroscopist, the measurement of ionization and appearance potentials, applications to free radical chemistry, the use of negative ion mass spectrometry, theoretical studies (e.g., quasi-equilibrium theory) and many others. These are covered in great detail in numerous books that have appeared in English and in German during the past five years and no purpose would be served in duplicating such material in a book dedicated to structural applications of mass spectrometry in organic chemistry.

The literature is covered through early 1967; and because of the coopération of numerous authors, much unpublished work could also be included. We owe thanks to these investigators, as well as to many other individuals, who gave us permission to reproduce in somewhat modified form mass spectra first measured in their laboratories. The potentially complicated logistics, caused by having three authors several thousand miles apart, was simplified by the cooperation of the staff of Techdata, Inc., who prepared the final copy, and by Mr. Angus M. Babcock, who drew all of the figures. Finally, we acknowledge with admiration the assistance provided by three of our colleagues, Drs. Peter Brown, Alan M. Duffield, and Robert H. Shapiro, for reading the entire manuscript. This was no mean feat in view of our self-imposed deadline of having the book appear within 90 days from the completion date of our original manuscript.

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April 1, 1967

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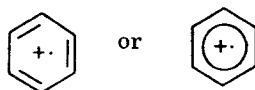
## NOTE TO THE READER

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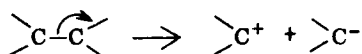
Perhaps the most useful of the ground rules established in our first book<sup>1</sup> is the attempt, whenever possible, to localize the positive charge in a molecular ion and to rationalize subsequent bond fissions in terms of such an ion. There is a great pedagogic value to such an approach, and the reasons for its use are outlined in the introductory chapter of the present volume. While the ionization conditions generally employed in the laboratory (ionizing energy of the order of 70 eV) may cause an electron to be abstracted from any part of the molecule, under conditions satisfying the Franck-Condon principle a "cascading" from higher energy levels to the lowest and most plausible one can follow (prior to any fragmentation or rearrangement processes). This is usually the one which corresponds to the a priori prediction for the position of localization of the positive charge—namely, on the heteroatom or the  $\pi$ -system of an unsaturated or aromatic moiety.

We have also emphasized the importance of proper "electron bookkeeping," which is implicit in the approach employed by us in the preceding volumes.<sup>1,2</sup> In order to avoid any misunderstanding, we utilize in the present book—as we have done in the research publications from our laboratories—a convention originated by Shannon.<sup>3</sup>

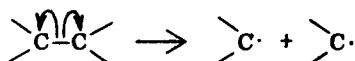
There are times when the site of the positive charge cannot be identified conveniently, because there are several or no plausible loci available for it. In such an event, it is best generally to enclose the molecular structure in brackets with a positive charge outside, as in  $[R]^+$ . In point of fact, such a species is a radical ion and according to Shannon's convention<sup>3</sup> may be more precisely written as  $[R]^{\cdot+}$ . The real utility of this more precise notation becomes clear when we consider the difference between odd- and even-electron species—a distinction which is very important in mass spectrometry.<sup>4</sup> Thus according to the original convention, the loss of a methyl radical from a molecular ion  $[RCH_3]^+$  would have been depicted as  $[RCH_3]^+ \rightarrow [R]^+ + CH_3^\cdot$ . In Shannon's formulation, the reaction would be written as  $[RCH_3]^{\cdot+} \rightarrow [R]^+ + CH_3^\cdot$ , thus showing immediately that the molecular ion  $[RCH_3]^{\cdot+}$  is an (odd-electron) ion radical and the cleavage product  $[R]^+$  an even-electron carbonium ion. Similarly, ionized double bonds may be written as  $R-\dot{C}H-\dot{C}H-R$  or  $[R-CH=CH-R]^{\cdot+}$  and aromatic rings as



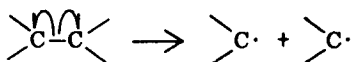
Finally, in following this emphasis on accurate "electron bookkeeping," we continue to employ the "fishhook" symbolism introduced in our earlier books.<sup>1,2</sup> The usual arrow denotes a two-electron shift as in



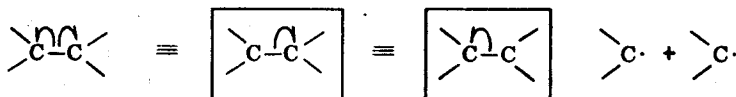
A homolytic bond fission is usually written by the organic chemist as



but many investigators dealing with mass spectral fragmentation processes either skip one of the small arrows or do not even differentiate between homolytic and heterolytic bond cleavages. To encourage precision, we select a "fishhook" to denote a one-electron movement:



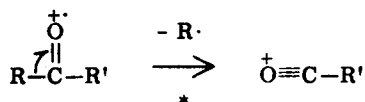
However, since so many mass spectral fragmentations may be visualized in terms of homolytic bond fissions (see introductory chapter), and since concerted processes are frequently encountered where at least six such bond uncouplings occur, we introduce for the sake of simplicity and brevity the final convention that only one "fishhook" needs to be written when homolysis of a bond is to be indicated. Thus the two expressions in the rectangles are synonymous and may be employed interchangeably.



The "fishhook" symbolism is, of course, not restricted to mass spectrometry but may be used profitably in many other areas of organic chemistry. Photochemistry, an area in which free radicals intervene frequently, is an obvious candidate, and various authors in that field<sup>5</sup> have accepted this convention.

Throughout this book we refer to " $\alpha$ -cleavage" as fission of a bond originating at an atom which is adjacent to the one assumed to bear the charge; the definition of  $\beta$ -,  $\gamma$ -, ..., cleavage then follows automatically. The following process

would thus be described as " $\alpha$ -fission of a ketone with expulsion of an alkyl radical"



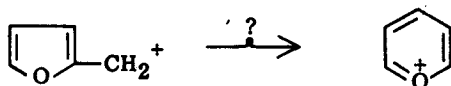
and the asterisk under the arrow denotes that an appropriate metastable peak (for definition, see section 5 in introductory chapter) has been observed in its mass spectrum.

Unless noted otherwise, all mass spectra refer to 70-75 ev spectra and are plotted in terms of relative abundance, with the most intense peak ("base peak") being taken as 100%. When the percent total ionization values of the peaks are also indicated, they are expressed as  $\Sigma$  on the right-hand ordinate (see, for instance, Fig. 7-3). The expression " $\Sigma_{40}$  15%" means that a given peak is responsible for 15% of the total ionization (or that the ion carries 15% of the total ion current) encompassed by the mass range  $m/e$  40  $\rightarrow$  molecular ion. The ion corresponding to the parent compound is referred to as the "molecular ion" and an abbreviation such as " $M - \text{CO}$ " or " $M - 28$ " refers to a fragment ion which has lost carbon monoxide or 28 mass units.

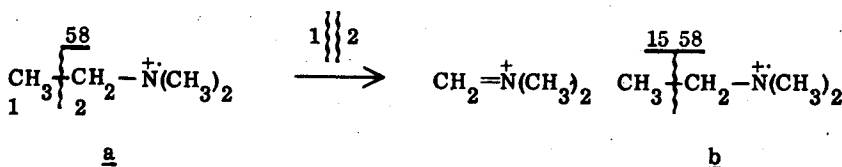
A few other conventions, which are nearly self-explanatory, are also described briefly below. The following type of arrow is employed to denote that a skeletal rearrangement has occurred, in this instance the conversion of a benzyl ion to the corresponding tropylium species



while a question mark over such an arrow indicates that such a rearrangement is suggested without any supporting evidence.



Finally, if a given bond fission is to be indicated schematically, such as the loss of a methyl radical from ethyl dimethyl amine to give an ion of mass 58, two devices can be employed which are exemplified below.





The convention "1||2" infers that the linkage between carbon atoms 1 and 2 is broken, while the wavy line with a perpendicular line bearing the mass number and pointing in the direction of the charge-retaining unit indicates which portion of the molecule encompasses the fragment of mass 58 (see a). Accordingly, formulation b indicates that both an ionized fragment of mass 58 and one of mass 15 are observed.

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