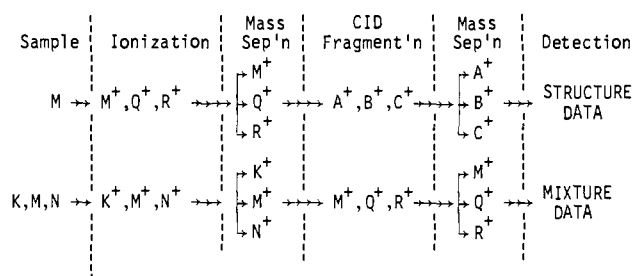


Selected Ion Fragmentation with a Tandem Quadrupole Mass Spectrometer

Sir:

An added dimension of mass spectral information is provided by a tandem mass spectrometer when it is used to create ion species from a sample, select one individual ion species, fragment it, and obtain the mass spectrum of the fragments. Metastable ion peaks and collision-induced dissociation (CID) have been used to relate daughter ions and their precursors.¹ Specialized "MIKES"² instruments have been developed to allow systematic acquisition of data on metastable and CID fragmentation spectra. The potential of such instruments for mixture analysis and structure elucidation is currently being explored. These processes are illustrated in Chart I. The second

Chart I



mass separation in MIKES instruments is actually an ion kinetic energy separation interpreted to provide the fragmentation mass spectrum. Impressive sensitivity has been achieved with a MIKES instrument³ despite the substantial ion losses and the ion energy spread produced by the CID process.⁴⁻⁶

Data presented here demonstrate that a selected ion fragmentation mass spectrometer based on tandem quadrupole mass filters is completely practical and that the CID process in the quadrupole instrument is effective and extremely efficient. The system consists of, in series, an electron impact (EI) ionization source, a quadrupole mass filter, an "RF-only" quadrupole CID region, a second quadrupole mass filter, and an electron multiplier. The use of quadrupoles for mass separation provides higher transmission efficiency than magnetic sectors operated as the same resolution and mass range,⁷ and unit mass resolution in the CID spectra is easily obtained.

Tandem quadrupole mass spectrometers have been developed for the study of ion-molecule reactions.⁸⁻¹⁰ A center RF-only quadrupole has been added for photodissociation studies^{11,12} and the investigation of long-lived metastable ions.¹³ Prior to this study, however, all of the reported selected ion fragmentation work has been performed on reversed-sector MIKES instruments.^{1,3-6,14}

Experiments demonstrating the practicability of selected ion fragmentation in a quadrupole system have been performed on a tandem quadrupole mass spectrometer¹² in the laboratory of J. D. Morrison at LaTrobe University, Bundoora, Victoria, Australia. The central quadrupole of three was used as the CID chamber by the admission of the collision gas and operation in the RF-only mode. The EI source sensitivity was 3×10^{-5} A/Torr of cyclohexane (1 ion/ 10^5 molecules). Transmission through the ion optics into the first quadrupole was 30%. In RF-only mode, quadrupole transmission was 30%. In mass filter mode, transmission dropped to 2.5%. Neglecting CID, this gives an overall sensitivity of 1.5×10^{-9} A/Torr of cyclohexane (5 ions detected/ 10^{10} sample molecules). The selected ions emerged from the first quadrupole and entered the CID quadrupole with a translational energy of 10 V. The RF oscillations of the ions in the CID quadrupole increase the ion energy by a few volts. However, the kinetic energy of ions in these experiments is very small compared with that of MIKES

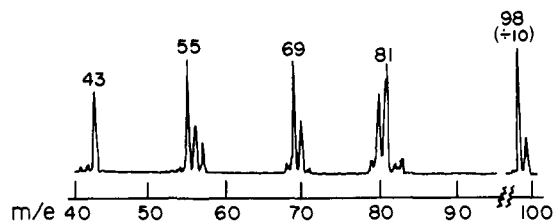


Figure 1. CID spectrum of the parent ion (m/e 98) of cyclohexanone present as 5% of a mixture.

instruments where ions enter the CID chamber with an energy of 3–10 kV. The CID spectra obtained in the quadrupole instrument resemble the 14–16-eV EI spectra of the pure compounds. Clearly the low translational energy combined with the relatively long ($\sim 5 \times 10^{-5}$ s) residence times of the ions in the CID region is sufficient to provide a characteristic and relatively rich fragmentation spectrum.

The efficiency of the CID process is determined by two factors, the fragmentation efficiency and the collection efficiency. We can let P_0 and P symbolize the selected ion beam current at the entrance and exit of the CID region, respectively, and ΣF_i the total current of all fragment ions at the exit of the region. The fragmentation efficiency is $E_F = \Sigma F_i / (P + \Sigma F_i)$, the collection efficiency is $E_C = (P + \Sigma F_i) / P_0$, and the overall CID efficiency is $E_{CID} = \Sigma F_i / P_0 = E_F E_C$. The overall CID efficiency of the quadrupole system ranges from 15% for benzene to 65% for *n*-hexane. The CID efficiency of a MIKES instrument has recently been reported as $<10\%$.¹ The collection efficiency in the tandem quadrupole system is nearly 100%; there is virtually no scattering loss in the CID process, even at the 2×10^{-4} Torr CID pressure used in these studies. (Larger pressures could not be obtained with this instrument.) In this system, CID occurs in a strong-focusing quadrupole field; the field-free drift region used for CID in MIKES instruments produces scattering losses of 90% (collection efficiency of 10%) at similar CID pressures.¹⁴

The scattering losses in the MIKES CID chamber increase as the mass of the collision gas increases. This has led to a preference for hydrogen or helium as the collision gas.^{6,14} Because the collection efficiency is nearly 100% in the quadrupole CID region, heavier collision gases can be used to increase the fragmentation efficiency. Argon shows CID efficiencies three to four times higher than hydrogen in this system.

To demonstrate the mixture analysis capabilities of the quadrupole system, a mixture of cyclohexane and three minor components (benzene, *n*-hexane, and cyclohexanone, each present as 5% of the mixture) was analyzed. The mixture components were selected to minimize interference between fragment ions and molecular ions in the EI spectrum of the mixture. This, of course, would not be necessary if a low energy ion source such as chemical ionization (CI) were used. The CID spectrum of the parent ion of each of the four components was obtained; that for cyclohexanone is shown in Figure 1. The CID spectra of all of the mixture components are reproducible and show good agreement with the CID spectra of the pure compounds. On the basis of these results, the probability of being able to achieve a highly effective, yet fundamentally simple, quadrupole-based selected ion fragmentation mass spectrometer seems virtually certain.

A tandem quadrupole system for selected ion fragmentation is currently under construction in this laboratory. It will have a dual CI/EI source and more efficient quadrupoles with a larger mass range and be able to tolerate higher CID pressure than the instrument on which these experiments were performed. The ability to vary the translational energy of ions entering the CID region will also be incorporated. This instrument will be used to further characterize the low-energy

CID process and to explore selected ion fragmentation applications in mixture analysis and structural elucidation.

Acknowledgments. We gratefully acknowledge fruitful discussions with J. D. Morrison and the use of facilities in his laboratory in this work. Special thanks are extended to Don McGilvery and Dianne Smith for their assistance. This work was supported in part by the Office of Naval Research. One of us (R.A.Y.) gratefully acknowledges a National Science Foundation Graduate Fellowship, an American Chemical Society Division of Analytical Chemistry Fellowship sponsored by the Upjohn Co., and an L. L. Quill Memorial Fellowship from M.S.U.

References and Notes

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Book Reviews

Spectroscopic Properties of Inorganic and Organometallic Compounds. Volume 7. Edited by N. N. GREENWOOD (Department of Inorganic and Structural Chemistry, University of Leeds). The Chemical Society, Burlington House, London. 1975. 699 pp. £24.00.

This the seventh volume in a continuing series devoted to the subject literature published during 1973. There are eight reviews in this volume, as follows: "Nuclear Magnetic Resonance Spectroscopy" by B. E. Mann; "Nuclear Quadrupole Resonance Spectroscopy" and "Microwave Spectroscopy" by J. H. Carpenter; "Vibrational Spectra of Small Symmetric Species and Single Crystals" by D. M. Adams; "Characteristic Vibrational Frequencies of Compounds Containing Main-group Elements" by S. R. Stobart; "Vibrational Spectra of Some Co-ordinated Ligands" by G. Davidson; and Mössbauer Spectroscopy by R. Greatrex.

As in past volumes of this series, a thorough compilation of the literature has been achieved. Because of the extensive number of books and papers involved, only very brief reference to each article can be made. However, by means of the many references listed, the reader can use the review to find details of relevant procedures and information in the papers cited.

In general the structure of the individual chapters has followed that of previous volumes. Changes are to be found in the chapter on NMR spectroscopy regarding discussion of techniques, coupling constants, chemical shifts, and relaxation measurements in that they have been omitted from the introductory section and absorbed into the rest of text. A new section in this chapter on metals in biological systems has been added.

James L. McAtee, Jr., *Baylor University*

Organic Syntheses via Metal Carbonyls. Volume 2. Edited by IRVING WENDER (Pittsburgh Energy Research Center) and PIERO PINO (Swiss Federal Institute of Technology). John Wiley & Sons, Inc., New York, N.Y. 1977. xiii + 743 pp. \$45.00.

This well-produced book is the second volume of the series, the first of which was published in 1968. Topics include carbonylation of various organic substrates, organic synthesis with iron pentacarbonyl, and decarbonylation reactions. The chapter on hydroformylation appears particularly thorough. The later chapters on hydrosilylation and symmetry restricted reactions although interesting contain few references to metal carbonyl complexes.

Since there are many contributors there is a range of style of treatment and some overlapping of material. The main criticism is that many of the articles were written several years ago and the more recent literature (up to mid-1975) is covered in brief supplements. This

results in the main review not being interpreted in the light of current available evidence, particularly mechanisms. The use of the newer metal carbonyl derivatives such as Collman's reagent, carbene complexes, or cluster compounds receive only the minimum of coverage. However, synthetic organic and organometallic chemists, who have often ignored the potential use of transition metal complexes in organic synthesis, should find this book valuable, especially since homogeneous catalysis is currently an area of intense research.

R. K. Pomeroy, *Simon Fraser University*

Excited States of Biological Molecules. Edited by J. B. BIRKS (University of Manchester). John Wiley & Sons, New York, N.Y. 1976. xviii + 652 pp. \$45.00.

This book is based on the Proceedings of the International Conference on Excited States of Biological Molecules, held in Lisbon, Portugal, April 18-24, 1974. The conference was divided into six sessions, each introduced by a plenary lecture, as is the book. The six sections are: (A) excited states of organic molecules (Sir George Porter) which is subdivided into (A1) primary processes and (A2) photochemistry and photobiology; (B) excited states of DNA and nucleotides (C. Helene); (C) excited states of photosynthetic pigments (H. T. Witt); (D) excited states of proteins and amino acids (G. Weber); (E) excited states of visual pigments (B. Rosenberg); (G) energy transfer in biological molecules (J. Eisinger). Texts of the plenary lectures are included plus most of the 73 contributed papers. The remainder are present in the form of an abstract only.

This is the fourth book in a series devoted to the photophysics of organic molecules. This volume suffers in comparison to the first three of the series. The previous volumes consist of high quality review chapters, which are effectively coordinated to give coherent coverage of the subject. Equally effective coordination of a large collection of presentations is made difficult by the diversity of topics plus their variation in quality. The meeting must have been very stimulating, and this collection communicates that to the reader. While it is not possible or desirable to report on all the papers, suffice it to say that many readers will find interesting reports here and should have access to it through a library.

David F. O'Brien, *Research Laboratories
Eastman Kodak Company*

Organolithic Macromolecular Materials. By ALAN D. WILSON and STEPHEN CRISP (Laboratory of the Government Chemist, London). Applied Science Publishers, Ltd., Barking, Essex, England. 1977. ix + 298 pp. \$32.00.