
1984 Meeting and General Assembly

Hostellerie Rigi, 6356 Rigi-Kaltbad (LU), October 19-20, 1984.

Programme and Abstracts

FRIDAY, OCTOBER 19

Chairman : H. Milon (Orbe)

Instruments and Methodology

- 14.30 H. Milon (Orbe)
Welcome to the participants
- 60'
14.30 B. McFadden (San José, USA)
"Combined LC/MS with thermospray ionization and triple quadrupole MS/MS"
- 30'
15.30 D. Games (Cardiff, UK)
"Applications of moving belt and thermospray LC/MS"
- 15.50 C. Porter (Manchester, U.K.)
~~"MS-MS Studies using a Hybrid Mass Spectrometer"~~
- 20'
16.10 N. Neve (Lutry)
"ICP-MS analysis : new opportunities with old techniques"
- 20'
16.30 R. Lauber (Berne)
"A simple way to negative ions".
- 16.50 Coffee-break
- 30'
17.20 B. Willhalm (Geneva)
"What can we do if mass spectrometry fails to give the structural information we need ?"
- 18.30 GENERAL ASSEMBLY
- 19.30 Aperitif - dinner.

SATURDAY, OCTOBER 20

Fundamentals

Chairman : U. Schlunegger (Berne)

08.30 H. Schwarz (Berlin, GFR)

"Exploration of the mechanism of (C-C) cleavage in ionized carbonyl compounds"

09.30 T. Gäumann (Lausanne)

"To isomerize or not to isomerize, that is the question"

(10.30) D. Stahl (Lausanne)

"Experimental and theoretical studies of dications in the gas phase"

10.50 Coffee-break

Applications

✓11.20 F. West (Zürich)

"Dual MS in the study of urinary metabolites"

✓11.40 N. Oesch (Bern)

"Quantitative determinations of psilocin by MS/MS"

✓12.00 H. Eyer (Bern)

"Identification of mixture compounds by GC-MS-SISCOM"

12.20 W. Richter (Basel)

Concluding Remarks.

Acknowledgments

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Spectronex

Spectrospin

Sciex.

Combined LC/MS with Thermospray Ionization and
Triple Quadrupole MS/MS

Bill McFadden

Finnigan MAT Corp., San José, Calif. (U.S.A.)

Use of thermospray ionization has significantly extended the use of combined LC/MS for highly polar reverse phase systems and for samples of low volatility. However, one limitation of soft ionization methods in mass spectrometry is lack of ionic fragmentation leading to important structural information. By using a triple stage quadrupole (TSQ) in a collisional activation mode (CAD), the important molecular weight information is supplemented by fragmentation thus providing structural features of the unknown.

An example of thermospray LC/MS will be presented in which (1) the sample is run in LC/MS mode without CAD and the data reveal only the molecular weight of the components and (2) run in a TSQ using CAD so that structural features are observed. The data will further show the importance of TSQ/CAD with LC separation when several isomers and isobars exist in the sample. Without prior separation, the CAD fragmentation spectrum will have fragments from several compounds and will be confusing. In conjunction with LC separation both quantitative and qualitative data on each individual component is attained.

Applications of Moving Belt and Thermospray LC/MS

D.E. Games

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The combination of high-performance liquid chromatography and mass spectrometry (LC/MS) is becoming increasingly used to assist in the solutions of problems which were previously inaccessible or required the isolation of components from the liquid chromatograph prior to mass spectrometric study.

Moving belt interfaces for LC/MS have the advantage of providing both electron impact (EI) and chemical ionization (CI) mass spectra. If one is performing qualitative analysis where the nature of the compounds present is unknown the availability of EI data is invaluable, with CI providing confirmation of molecular weight. Using examples from studies of amino acids, peptides, environmental samples, extracts of natural materials and petroleum samples the advantages of this approach will be illustrated, together with the advantages of using microbore LC.

A limitation of moving belt interfaces is the range of compounds which they can handle with EI or CI, the upper limit, with the best interface of this type being compounds which can be handled by desorption chemical ionization (DCI). Thermospray ionization LC/MS considerably extends the range of compounds amenable to LC/MS and has the advantage of working best with aqueous mobile phases at flow rates in the range 1-2 ml min⁻¹. For the first time we have been able to obtain molecular weight information from the LC/MS of penicillins using this technique. Using the Finnigan thermospray system mixtures of aromatic amino acids have been studied. The design of the interface enabled gradient elution to be used directly with the interface. One of the problems which we have encountered is that thermospray is a selective ionization method and hence when mixtures of compounds are studied some compounds exhibit no or very poor response. This will be illustrated with studies of a herbicide and its metabolites.

MS-MS Studies Using a Hybrid Mass Spectrometer

C.J. Porter

V.G. Analytical Limited, Floats Road, Wythenshawe, Manchester, UK

The V.G. 70-70EQ has EBQQ geometry and consists of a double focussing sector instrument followed by a quadrupole gas cell for studying collision - induced decomposition processes and a quadrupole analyser with a mass range of 1500 a.m.u. The combination of electrostatic, magnetic and quadrupole analysers as used on the V.G. 70-70EQ is characterized by high precursor ion selectivity, high transmission efficiency, unit mass daughter ion resolution and absence of artefact peaks.

Although GC-MS has been shown to be successful for the analysis of complex mixtures, the ability to also perform high resolution MS-MS under routine data system control can result in a more complete and often less ambiguous characterization of a complex sample. A number of examples demonstrating the necessity for greater than unit mass precursor ion resolution coupled with unit mass daughter ion resolution will be discussed.

Geological ion-marker compounds, such as pentacyclic triterpanes and steriodol alkanes are used extensively in oil/oil and oil/source - rock correlation studies. The total unseparated samples and the samples after G.C. separation show increased specificity and sensitivity when analysed using the V.G. 70-70EQ compared with the more traditional methods for such analyses. In particular, it has been possible to detect pentacyclic triterpanes upto carbon number C_{55} when analysing total oil samples.

Results for the analysis of protonated molecular ions produced by the fast atom bombardment ionization of typical peptides will also be discussed.

ICP-MS Analysis : New Opportunities with Old Techniques

N.F.B. Neve

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ICP and MS pose no problems for any of us either as acronyms or synonyms of analytical techniques, whereas not everyone feels as comfortable when the subject turns to ICP with MS. As yet the subject of only a handful of scientific papers and barely a dozen operating systems, this hybrid technique promises, even according to the most conservative opinion, to radically change the content of the analytical laboratory in the next decade.

Rapid multi-element analysis with high sensitivity, low detection limits and a large dynamic range as well as isotope dilution analysis and isotope ratio determinations all within one instrument, make ICP-MS an attractive and effective alternative to current instrumentation for inorganic and eventually organic analysis.

A presentation of the instrument and its applications will be given.

Exploration of the Mechanism of (C-C) Cleavage in
Ionized Carbonyl Compounds

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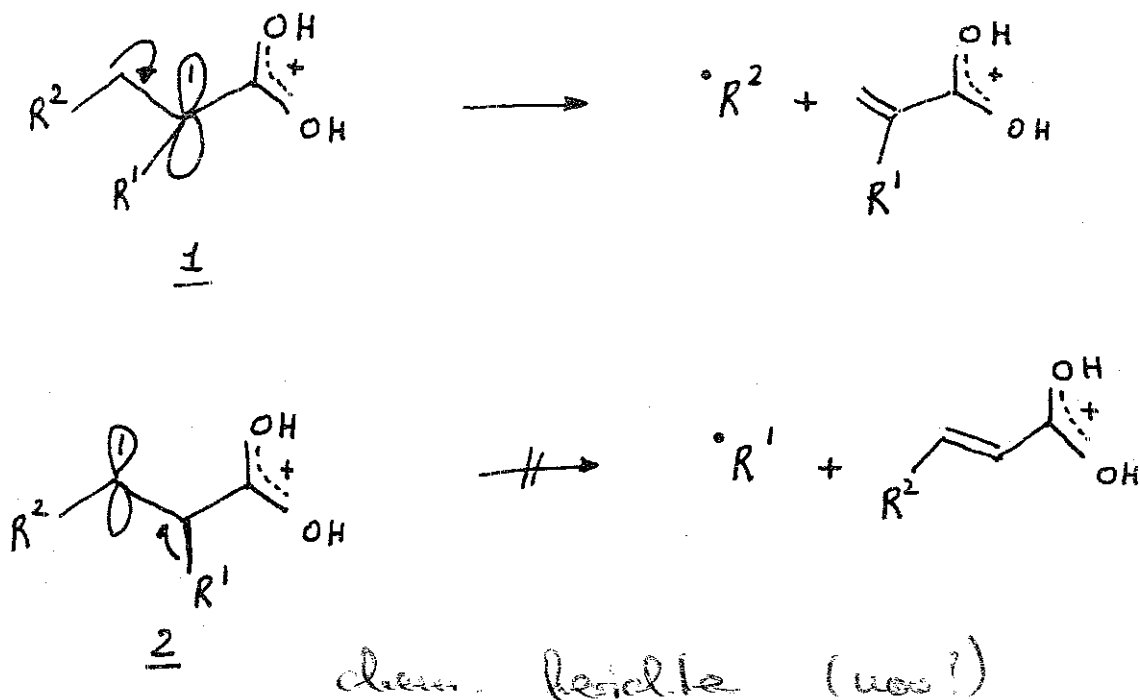
H. Schwarz

Institut für Organische Chemie, Technische Universität Berlin, (GFR)

By using field ionization kinetics, collisional activation, and extensive usage of labelling experiments a detailed insight into the mechanism by which carbon-carbon cleavage in ionized acids (and some analogues thereof) occurs will be presented.

The most important conclusion, which seems to be of general validity, is that enol cation radicals (1) act as the actual precursors for the elimination of R^2 (R =alkyl). Cation radicals in which the radical centre is not adjacent to the protonated carbonyl function, as for example in 2, do not serve as precursors for the C-C cleavage; instead, isomerization to 1 is required. The fact that enol cation radicals are of essential importance as intermediates in the cleavage of C-C bonds is a direct consequence of the fact that these dissociations can be viewed as the reversal of (1,4) additions of (nucleophilic) alkyl radicals to protonated α, β -unsaturated acids, which proceeds preferentially via enol cation radical intermediates.

The experimental findings are in line with semi-empirical molecular orbital calculations.



To isomerize or not to isomerize, that is the question

T. Gäumann

Institut de chimie physique, EPFL-Ecublens, 1015 Lausanne

Mass spectrometric fragmentation is a process that extends from a few picoseconds to milliseconds or longer. The "classical" mass spectrometer integrates the fragmentation over a given short time. The metastable decay opens an additional time window; the ion cyclotron resonance mass spectrometer yields a "total" fragmentation spectrum, i.e. a time span over more than ten decades. Any ion can do many things during this time. The simple fragmentation pattern of olefins is taken as an example to demonstrate what techniques are available to put some doubts on simple fragmentation schemes.

Experimental and Theoretical Studies
of Dications in the Gas Phase

D. Stahl

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Charge stripping mass spectrometry and other methods have led recently to the observation of a great number of stable dications in the gas phase, including even small molecules whose coulombic repulsion is expected to be quite substantial. High level ab initio molecular orbital calculations in conjunction with experimental studies provided a detailed description of many features of these emerging class of remarkable species. Although small dications have a tendency to fragment into two monocations because of Coulomb repulsion, many experiments have indicated that such doubly charged species may persist for several microseconds.

Several examples will be given to show the molecular parameters accessible by experiments and their link with results from ab initio molecular orbital calculations :

- ionization energy of monocations $IE (m^+ \rightarrow m^{2+})$
- structure of stable doubly charged species
- modes of decomposition of dications
- geometry and energy of transition states.

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Dual MS in the Study of Urinary Metabolites

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Low pressure negative CI has in the last few years been shown to be a useful complementary technique to positive EI (1-3). The quasi-simultaneous combination of both ionization techniques is made possible if we work at low reagent gas pressure, between 10^{-3} and 10^{-2} torr (4, 5). This dual method is now used daily in our toxicological studies (6). Its identification power will be demonstrated in the elucidation of drug metabolites detected in cases of overdose with hypno-analgesic mixtures. While the softer negative ionization mode usually provides a simple fragmentation pattern with an ion in the molecular range, other important information, i.e. concerning side chain structures, necessitates the hard ionization technique provided by conventional EI.

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