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Review

FAST ATOM BOMBARDMENT (FAB) MASS SPECTROMETRY: A NEW TECHNIQUE FOR THE ORGANOMETALLIC CHEMIST *

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Summary

Application of the new fast atom bombardment (FAB) mass spectrometry technique to various organometallic systems is reviewed and its potential explored briefly, especially with respect to polar or thermally labile systems, and heterogeneous catalysis.

Fast atom bombardment (FAB) mass spectrometry is a new (1981) technique [1] (ideal for polar and thermally labile molecules not suited for other MS techniques), which grew out of the surface chemistry technique, secondary ion mass spectrometry (SIMS). Whereas SIMS is accomplished by sputtering ions from a solid surface by means of an energetic (2–8 keV) beam of ions (and suffers from problems of surface charging when the sample materials are insulating, and difficulties in adapting to existing magnetic mass spectrometers), FAB uses a beam of fast neutral atoms, of similar energy, to sputter ions from solids or liquids. These fast atoms (typically argon, though xenon gives three times the sensitivity, and mercury has also been used for greater sensitivity) are generated in the same type of cold cathode discharge source as is used in SIMS, except that the energetic ions are charge exchanged in a collision chamber, yielding a beam of energetic neutral atoms. Non-volatile samples are supported on a metal probe tip (copper or stainless steel), either as a thin solid or liquid film, or as a film in a matrix liquid such as glycerol. The use of a matrix liquid provides for stable spectra over a period of many minutes, and also aids in the

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* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22 June, 1983. The author worked with Harry Emeléus in Cambridge as a National Research Council of Canada Overseas Postdoctoral Fellow, 1964–1966. At Professor Emeléus' suggestion, he joined Sidney Sussex College and completed a Cambridge doctorate as well as, in the collegiate atmosphere, pursuing interests in other sciences and the humanities. Unfortunately, current fee structures no longer permit such a beneficial situation for international and multidisciplinary cross fertilization which has proven to be of great professional and personal benefit.

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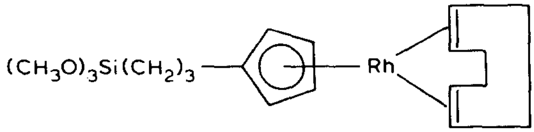
ionization process, for example by proton transfer giving quasi molecular ions MH^+ [1,2]. Cluster ions resulting from the matrix liquid do, however, complicate spectra, especially at low masses. The technique has been exploited, so far, primarily for molecules of biochemical interest, but as FAB sources are retrofitted to more existing mass spectrometers (kits are available from at least six manufacturers), the technique should find wide applicability for organometallic identification and characterization, using both positive and negative ions. The technique is ideal for polar molecules, ionic complexes, and high molecular weight species which may be thermally labile such as bio-organometallic systems and large cluster molecules. Unlike other soft ionization techniques, FAB gives both molecular ions and fragments. Several FAB reviews have appeared, stressing biological applications [3–8] though organometallics often appear at the end of these discussions [4–7].

The most ubiquitous organometallic compounds to be studied by FAB mass spectrometry were vitamin B_{12} and its co-enzyme. The mass spectrum was mentioned in the first published FAB paper [1], but by this time several commercial FAB sources had been delivered, and co-enzyme B_{12} was widely studied [9,10] and used as an example in the sales literature of various mass spectrometer manufacturers. The observation of vitamin B_{12} in mass spectrometry has been described as a "milestone" [11] and FAB has produced excellent results for cobalamines and related corrins [8–10,12–14], the most detailed work having come from Barber's group. In a recent paper, Schiebel and Schulter [15] compare FAB and FD (field desorption) techniques for cobalamine, though in their hands the latter is as good as the former, even though FD spectra are dominated by thermal decomposition products.

Co-enzyme B_{12} has a molecular weight of 1578 and displays an intense quasi-molecular ion $[M+H]^+$ at m/z 1579, and readily loses the axial deoxyadenosine ligand to give an intense ion at m/z 1329, characteristic of cobalamines [9,10,13]. Other related systems were the organometallic methylcobalamine and the cyano and hydroxy derivatives, the methyl, cyano or hydroxy groups being lost in the first stage of fragmentation. The relative intensities of the parent ions versus m/z 1329, i.e., loss of the various axial ligands, are $CN > CH_3 >$ adenosine $>$ OH. Below this region, the fragmentation is similar with metastable ions and linked scan data being available to assist in the assignment of breakdown products, as the corrin substituent fragments. Breakdown of the second axial ligand, dimethylbenzimidazole, followed by the sugar and phosphate linkages accounts for most of the fragments. Other losses in the positive ion spectra correspond to loss of water and either acetamide or cobalt. It is also possible to obtain exact mass information and element composition at higher resolution for these compounds [9,10] although, unless one can narrow down the number of elemental possibilities at these very high masses, the large number of possible combinations within the precision of the measurements will swamp one with computer output.

The negative ion spectra showed $[M-H]^-$ ions and less overall fragmentation than the positive ion spectra. Peaks are complementary [13] appearing two mass units lower than in the positive ion spectra.

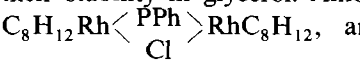
Although FAB usually produces best results for more polar or ionic species, an early example of FAB application to a neutral, relatively non-polar organometallic [8,12] was the silyl cyclopentadiene/cyclooctadienerhodium compound (I) which also contains silicon. This thermally labile compound, a liquid, gave good stable spectra without the need for glycerol (with which the compound, being water



(I)

sensitive, may have reacted), whereas no worthwhile mass spectra could be obtained using conventional techniques. A strong parent ion is observed at m/z 438, with loss of neutral C_8H_4, $(CH_3O)_3SiH$ and $(CH_3O)_3SiCH{=}CH$ being the most important high mass ions. The cyclopentadienerhodium core remains intact until ultimately a Rh^+ ion is observed. Prominent ions containing Si are $(CH_3O)_3Si^+$ and $(CH_3O)_2SiH^+$. These results are similar to what would be expected from normal EI fragmentation, if EI spectra could have been obtained.

In the case of ionic complexes, $(Ph_3P)_4Au^+ClO_4^-$, gave a simple positive ion spectrum which corresponds to that of the cation, and successive loss of ligands, though loss of biphenyl is also observed from $(Ph_3P)_nAu^+$ where $n = 1$–3. The negative ion spectrum corresponds to that of the anion.

Minard and Geoffroy [16] report on the use of 18-crown-6 (with 10% tetraglyme to depress the melting point) as an aprotic matrix for organometallics to avoid problems of their stability in glycerol. Among the compounds they studied were $(Ph_3P)_3Rh$,  $C_8H_{12}Rh\overset{PPh}{\underset{Cl}{\langle\;\rangle}}RhC_8H_{12}$, and the cluster compound $(Ph_2P)_3$-$Co_3(CO)_6$. Molecular ions or overlapping molecular and quasi-molecular $[M + H]^+$ ions were observed. Carbonyls show successive loss of CO as is observed in conventional mass spectrometry. Thus, the technique is useful in both identifying compounds by molecular weights and isotope abundance, and characterizing them from fragment ions. Other matrix liquids used successfully include 18-crown-6 in glycerol, glycerol with added acids or bases, thioglycerol, sulpholane [17], silicone oils, polyphenyl ethers etc. The newly developed liquid matrix techniques for FAB are now proving useful in SIMS which has also been applied to organometallics, with results basically similar to those of FAB. Solid ionic matrices (NH_4Cl or NaCl) were also used for SIMS [18] and applied to organometallics such as $(C_5H_5)_2TiCl_2$, $[C_5H_5Fe(CO)_2]_2$ and Ph_3SnCl, though in none of these examples were molecular ions observed.

FAB has been used to study the surfaces of zeolites [19], and in our lab we have begun a study of organometallic catalytic species on solid surfaces. This includes organometallics on silica or zeolite matrices and reactions of organic species with metallic surfaces. Species containing metal have been observed by reaction of matrix or sample liquids with the probe tip in the FAB beam [20,21], whereby copper/ligand ionic species are observed when copper probe tips are used.

In conclusion, work is just beginning on demonstrating the advantages of FAB mass spectra in characterizing organometallic compounds. As FAB instruments become common, the techniques will become a standard method in the organometallic chemist's repertoire.

Acknowledgement

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