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Editorial

John Beynon 50 years ago

I heard great things about John Beynon's mass spectrometry at ICI, Manchester, before he was 30 years old. We then met in May 1955 when he stopped off at the Spectroscopy Laboratory of the Dow Chemical Co. in Midland, Michigan on his way to the San Francisco ASTM E-14 meeting on Mass Spectrometry. John had already obtained a high-resolution Nier–Johnson geometry mass spectrometer from Metropolitan Vickers, and he had very exciting results demonstrating that the elemental composition of an ion can be obtained by measurement of its exact mass value.

I am embarrassed to report that John also had offered to have us both buy such an instrument, generously giving me a chance also to pioneer what of course has turned out to be one of our most basic tools for mass spectral interpretation. But my enthusiasm for this promising idea was not even sufficient for me to request the purchase from Dow. It was not until 1961 that I actually ordered such an instrument at Dow, and I did not use a high resolution mass spectrometer in my research until I started at Purdue in 1964.

Beynon's 1955 San Francisco talk was, in my opinion, the real hit of the conference. As Fig. 1 shows, the short abstract with statements like "mentions new apparatus being designed especially for it" gave the audience almost no warning. As indicated in my "careful" notes, statements like "20,000 resolving power" caused an absolute sensation. I was particularly impressed by his total identification of the unknown 3-butenyl benzoate using only mass spectrometry. The mass spectrum not only told that the molecular weight was 176, but also that the elemental composition was $C_{11}H_{12}O_2$! In addition, interpretation of the fragmentation pattern showed the terminal allyl, the benzoate, and even the ester loss of 54, although this required an understanding of hydrogen rearrangements through a six-membered ring transition state. I do not remember details of our conversations in Midland and San Francisco, but I do remember that we had a great deal to talk about.

By the 1957 ASTM E-14 conference in New York City, John's talk abstract had become much more sophisticated. The veteran practitioner of this new art had to explain its fine benefits clearly to the rest of us who still were no where taking advantage of this breakthrough. But the new example of an unknown from the reaction of cyclopentanone with butylamine is still highly impressive; it would take a sophisticated interpreter today to come up with the correct structure. (But does dioxane really give a C_2H_6 peak?) Note also that John was far ahead of his time in using metastables to determine the molecular weight of compounds yielding no parent peak (I believe it was another dozen years before the CCl_4 example of this methodology was published). Last but not least, note the physicist instructing chemists in the importance of paying attention to the basics to do "Chemistry by Arithmetic."

In another unforgettable event at the New York City meeting, B.F. "Dude" Dudenbostel of Esso, New Jersey, took the three of us on the subway to a Brooklyn Dodgers baseball game. From the start, John was convinced that Baseball was what caveman played before they became sufficiently civilized to invent Cricket. He spent nine innings explaining this to us, but he had met his match in Dudenbostel. John: "That bowler didn't even hit the ground with his pitch"; Dude: "But our pitchers are actually strong enough to throw it all the way in the air"; John: "Why do those fielders have to wear a glove to catch that little ball?"; Dude: "Why do your batters have to wear so many pads when they are at bat?"; John: "Actually, that was a fair 6"; Dude: "With two men on base, that was actually a 3-run home run"; John: "Well, if that really was such a fine hit, why isn't he still batting?" And so on and on, with Fred collapsed with laughter. My only job was to get more beer (about which John also had pointed remarks about temperature and flavor).

Thus, John Beynon has been an anchor not only for our science in mass spectrometry but also for its social fabric. Conferences are always so much more stimulating, friendly, and fun if John is there. I would like to illustrate this with Fig. 2. There are no more wonderful scientific hosts for meetings than our Japanese colleagues in mass spectrometry. As you can see, a whole new research field was opened up here, with John the first to make a practical working system out of his version of electrospray ionization.

John, it has been wonderful to know you for these 50 years, and I look forward to many more.

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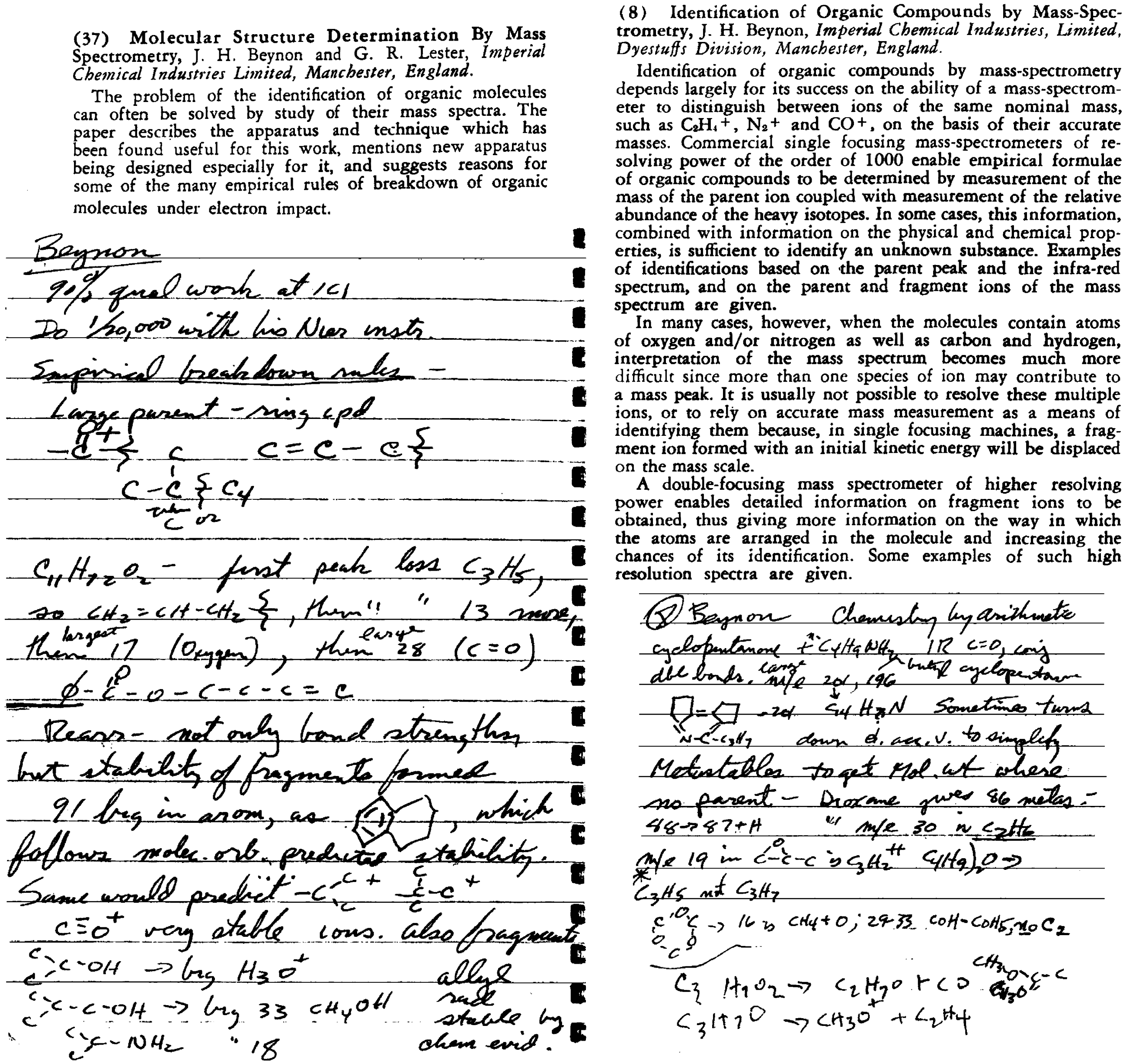

(37) Molecular Structure Determination By Mass Spectrometry, J. H. Beynon and G. R. Lester, *Imperial Chemical Industries Limited, Manchester, England.*

The problem of the identification of organic molecules can often be solved by study of their mass spectra. The paper describes the apparatus and technique which has been found useful for this work, mentions new apparatus being designed especially for it, and suggests reasons for some of the many empirical rules of breakdown of organic molecules under electron impact.

Beynon

90% qual work at ICI

Do 1/20,000 with his Nier instr.

Empirical breakdown rules –

Large parent – ring cpd

$-\overset{O^+}{C}-$ ⌇ $\overset{C}{C}$ $C=C-C$ ⌇

$C-C$ ⌇ C_4 or C

$C_{11}H_{12}O_2$ – first peak loss C_3H_5,

so $CH_2=CH-CH_2$ ⌇, then " " 13 more,

then largest 17 (Oxygen), then large 28 (C=O)

$\phi-\overset{O}{C}-O-C-C-C=C$

Reasons – not only bond strengths but stability of fragments formed

91 big in arom, as , which follows molec. orb. predicted stability.

Same would predict $-C<^{C^+}_{C}$ $-\overset{C}{\underset{C}{C}}-C^+$

$C\equiv O^+$ very stable ions. also fragments

$C>C-OH$ → big H_3O^+

$C>C-C-OH$ → big 33 CH_4OH

$C>C-NH_2$ " 18

allyl rad stable by chem evid.

(8) Identification of Organic Compounds by Mass-Spectrometry, J. H. Beynon, *Imperial Chemical Industries, Limited, Dyestuffs Division, Manchester, England.*

Identification of organic compounds by mass-spectrometry depends largely for its success on the ability of a mass-spectrometer to distinguish between ions of the same nominal mass, such as $C_2H_4^+$, N_2^+ and CO^+, on the basis of their accurate masses. Commercial single focusing mass-spectrometers of resolving power of the order of 1000 enable empirical formulae of organic compounds to be determined by measurement of the mass of the parent ion coupled with measurement of the relative abundance of the heavy isotopes. In some cases, this information, combined with information on the physical and chemical properties, is sufficient to identify an unknown substance. Examples of identifications based on the parent peak and the infra-red spectrum, and on the parent and fragment ions of the mass spectrum are given.

In many cases, however, when the molecules contain atoms of oxygen and/or nitrogen as well as carbon and hydrogen, interpretation of the mass spectrum becomes much more difficult since more than one species of ion may contribute to a mass peak. It is usually not possible to resolve these multiple ions, or to rely on accurate mass measurement as a means of identifying them because, in single focusing machines, a fragment ion formed with an initial kinetic energy will be displaced on the mass scale.

A double-focusing mass spectrometer of higher resolving power enables detailed information on fragment ions to be obtained, thus giving more information on the way in which the atoms are arranged in the molecule and increasing the chances of its identification. Some examples of such high resolution spectra are given.

(8) Beynon Chemistry by arithmetic

cyclopentanone + $C_4H_9NH_2$ IR C=O, conj dbl bonds. large m/e 201, 196 butyl cyclopentane

-201 C_4H_9N Sometimes turns $N-C-C_3H_7$ down el. acc. V. to simplify

Metastables to get Mol. wt where no parent – Dioxane gives 86 metas: $48 \to 87+H$ " m/e 30 is C_2H_6

m/e 19 in $C-\overset{O}{C}-C$ is $C_3H_7^{++}$ $(C_4H_9)_2O \to$

* C_3H_5 not C_3H_7

$\to$ 16 is CH_4+O; 29-33 COH-COH5, no C_2

$C_3H_7O_2 \to C_2H_7O^+ + CO$

$C_3H_7O \to CH_3O^+ + C_2H_4$

Fig. 1. Abstracts and McLafferty's notes of the John Beynon talks at the ASTM E-14 mass spectrometry conferences in (left) San Francisco, May 1955 and (right) New York City, May 1957.

Fig. 2. Professor John Beynon (second from left) opening a new field of research at age 68. Although he has obviously obtained the first results, he has graciously allowed Professor Klaus Biemann (center) and others to assist him.

Notes added in proof

The reviewer provided two important additions:

(1) The Dodgers were playing the Yankees and Mickey Mantle hit the homer.
(2) The first over-enthusiastic blows with the mallet caused a spray of sake to emerge into the room.

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