Mass spectra produced by field ionization relate more directly to larger molecules than the spectra produced by the usual electron impact technique. Field desorption is a new technique that extends even further the advantages of

Field ionization mass spectrometry

by H. D. Beckey

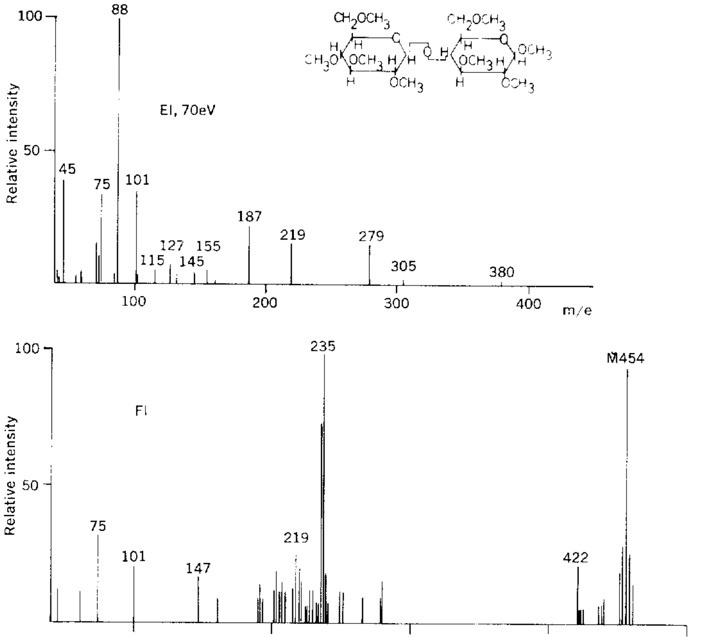

Fig. 1. Electron impact (EI) and field ionization (FI) mass spectra of 1-butanol. M is metastable peak (FI).

Mass spectrometry has become of growing importance to organic chemistry during the past decade. Mass spectrometers are powerful tools for elucidating the structure of organic molecules and for the analyzing complex organic mixtures. Moreover, mass spectrometry has greatly contributed to a more detailed understanding of the kinetics and mechanisms of unimolecular decomposition of organic molecules. In spite of the fact that the mass spectrometrically analyzed molecules are in the positively charged ionic state, many conclusions can be drawn regarding the decomposition kinetics of neutral molecules.

Ion Sources

The majority of experiments have been done with mass spectrometers equipped with electron impact ion sources. The reasons for this are twofold. Electron impact ion sources were developed to a high degree of technical perfection earlier than field or photo ionization sources, and commercial versions of ion sources other than electron impact sources have become available only recently. Further, the electron impact method is especially well suited for structure analysis of organic molecules because the large amount of internal energy transferred to the molecules by the impact of 70 eV electrons causes a variety of fragment ions that are specific for the molecular structure.

During the last few years, the field ionization method has become more popular because electron impact and field ionization mass spectra are to some extent complementary. Molecules that are extremely instable with respect to electron impact show no molecular ion peaks in the mass spectra—i.e., peaks due to the undecomposed parent ion. Reducing the energy of the impinging electrons to a value near the ionization potential increases only the relative molecular ion intensity; the absolute ion intensity is greatly reduced.

Field ionization (FI), on the other hand, became known as a "soft" method of ionization that causes only a minute amount of molecular excitation during the ionization process. Therefore, the most intense molecular ion peaks in the FI mass spectra of compounds are those that show no or only very weak molecular ion peaks in the electron impact (EI) mass spectra (Fig. 1). Exact molecular weight is one of the most important pieces of information one should obtain from a mass spectrum, and therefore, a combined electron impact and field ionization source offers the most versatile version of a mass spectrometer ion source. Field ionization of the molecules to be analyzed occurs when they come in contact with a field anode, which produces an electric field of the order of 5×10^7 V/cm. The field anode consists either of a thin wire of a few μm diameter or a sharp metal blade (a razor blade, for example) to which a positive potential of about 10 kV is applied. The distance between the wire and a plane cathode with a slit is about 2 mm; this distance is a few tenths of a millimeter in the case of a sharp blade. Electrons are drawn from the molecules to the field anode by the action of the extremely high electric field due to the quantum mechanical tunnel effect. A very small amount of internal energy is excited in the molecule by this process.

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A fine metal tip can also be used as the field anode. However, its use is more restricted to the study of surface phenomena like field evaporation of metal atoms or catalytic reactions. For structural or qualitative organic analyses, thin wires or sharp blades are preferable to tips because of the much larger emission area of the first mentioned anodes and because of the correspondingly larger field ion currents and the improved reproducibility of the mass spectra.

In the ion source shown in Fig. 2, a quick change from the EI to the FI mode of operation can be achieved by changing a few electric plugs, without breaking down the vacuum in the mass spectrometer. Solid samples are introduced into the source as a molecular beam. The electron beam crosses the molecular beam in the case of EI. For field ionization, the field anode, which is normally in a backward position, is shifted forward so that it comes to the position of the electron beam, which is switched off in this mode. Part of the molecular beam hits the field anode (thin wire or metal blade).

New Methods To Produce Active Field Anodes

Both thin wires and sharp metal blades have been introduced as field anodes into FI mass spectrometry by the author, but a certain preference is given to thin wires because the emitted ion intensity is larger at the same applied voltage and the reproducibility of the mass spectra is somewhat better than with metal blades. Until recently, thin platinum-Wollaston wires of about 2.5 μm were used as field anodes. The main disadvantage of these wires was their fragility. The high electric field exerts a large mechanical force on the wire. A number of means have been developed to increase the life of the wires, and an experienced operator can use a wire for several months. But on a routine basis of operations, the disadvantage of wire fragility still existed. The situation was much improved during the last few months in the following way.

A smooth wire of 2.5 μm diameter to which a voltage of 10 kV is applied produces a field strength of about 1×10^7 V/cm at its surface. This is insufficient for field ionization of the majority of organic substances. Normally $3–7 \times 10^7$ V/cm are necessary. This "ground field" can be enhanced by growing long, thin needles of length l and radius r_n. The local field enhancement on top of the needles is about l/r_n, provided that $r_n << r_w$ where r_w is the radius of the wire.

A method of growing a very large number (about 10^6 on a 2.5 μm wire of 1 cm length) of needles has been developed by the author using the field ionization process. Acetone at a pressure of about 3×10^{-3} torr is admitted to the FI wire, and a potential of about 10 kV is applied to the 2.5 μm wire. The field ion current increases with time by several orders of magnitude due to this procedure. Electron micrographs show that a very large number of long and thin micro-needles have grown during this activation process over a period of several hours (Fig. 3). The average length of these needles is about 2,000 A, and their diameters are a few hundred A. A number of points seemed to justify the assumption at the begin-

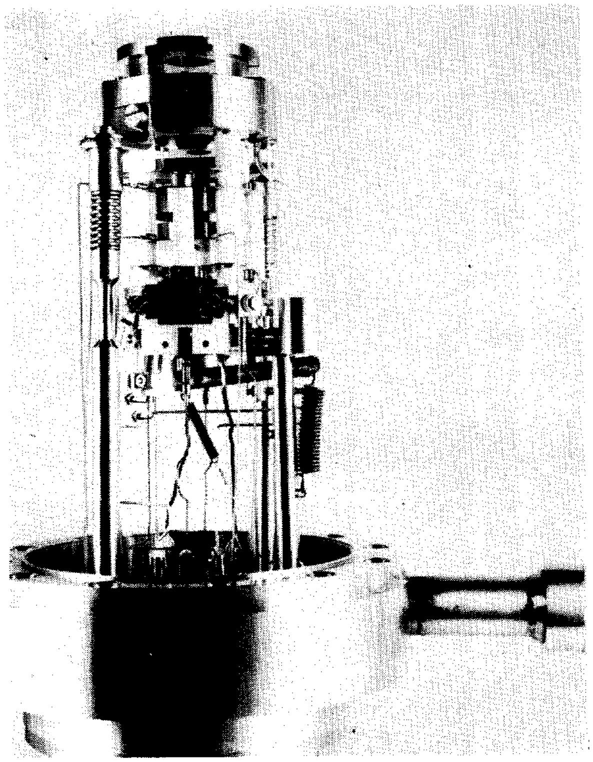

Fig. 2. EI-FI source used with mass spectrometer type CH5 or SM1 (Varian MAT). The lever (connected with two springs) driven by the rotatable feedthrough (lower right) moves the wire emitter either into the plane of the molecular beam or a few millimeters out of the beam. Ions produced in the central chamber are accelerated through the electrodes separated by ceramic spacers.

Fig. 3. Electon micrograph of a 3 μm platinum wire activated with acetone at a pressure of 3×10^{-3} torr and an anode-cathode voltage of 10 kV.

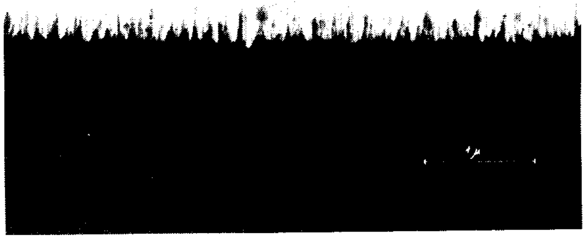

Fig. 4. Electron micrograph of a 15 μm platinum wire activated with benzonitrile at a pressure of 3×10^{-3} torr and an anode-cathode voltage of 10 kV.

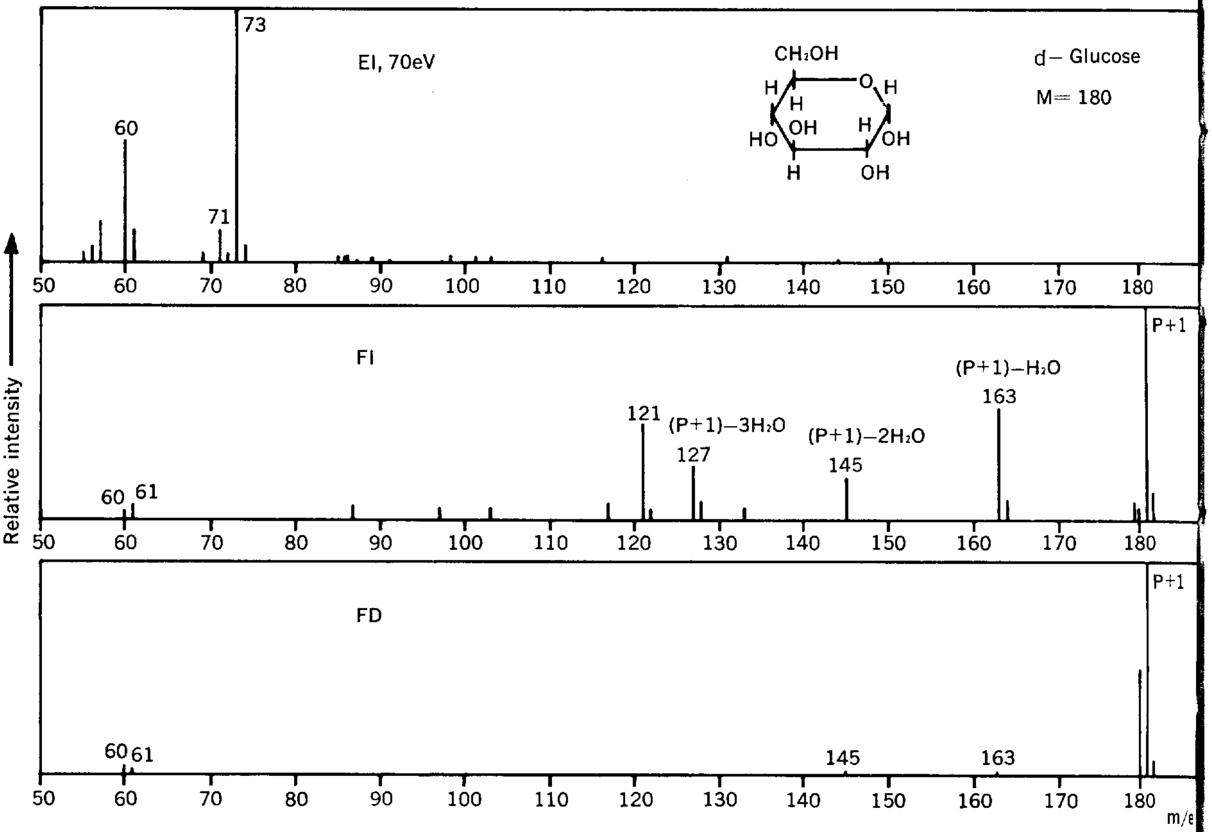

Fig. 5. Comparison of techniques is shown by these spectra for d-glucose. EI spectrum (top) was produced wit evaporation temperature of the substance about 100 C. FI spectrum (middle) was produced with evaporatio temperature of the substance about 115 C; the FI emitter was 2.5 μm activated platinum wire. FD spectrum (bottom was produced with emitter wire of 10μm activated tungsten heated by a 3.5 ma current.

ning of these studies that the micro-needles consisted of the wire metal. Therefore, they were termed "whiskers." However, more recent studies proved the needles do not consist of metal but of organic, semiconducting polymers. The crystallinity of the needles is still an open problem. Therefore, they are now termed "micro-needles." The average field enhancement factor on these acetone-grown needles is about seven.

A systematic study of the dependence of the activation efficiency on the chemical nature of the activating organic substance, carried out by M. D. Migahed of the author's group, led to the following results. The activation process is favored by a polar group in the activating substances, having a large dipole moment. It is favored further by a low ionization potential and a conjugated π-electron system. A number of substances besides acetone have turned out to be efficient for activation (crotone-aldehyde, nitrobenzene, for example), but the most efficient substance found so far is benzonitrile. This substance produces micro-needles that are about ten times longer than the acetone-grown needles. Figure 4 shows an electron micrograph of micro-needles grown by benzonitrile on a 15 μm platinum wire. Average length of the needles is about 20,000 A. The shape is dentritic.

The larger field enhancement factor of these needles enables one to reduce the ground field F_0 of the wire—i.e., to increase the diameter of the wire at the same applied voltage ($F_0 \simeq U/r_w$, where U is applied voltage). 10 μm wires can now be used instead of 2.5 μm wires. This makes possible the use of tungsten wires. Tungsten wires of 2.5 μm were not available commercially, and if so, they would have been difficult to handle and to connect to the wire supports. Tungsten wires of 10 μm, however, are commercially available, and it is no problem to spot-weld them on the supports. The strength of a 10 μm tungsten wire is about ten times greater than that of a 10 μm platinum wire, and since its cross section has been increased by a factor of 16 in comparison with the previously used 2.5 μm wires, the over-all gain in strength is about 160 fold. Thus, the danger of wire rupture is greatly reduced.

It is advisable not to activate the FI wire in the ion source of a mass spectrometer because solid deposits could be formed on the source insulators. Activation is carried out in a separate vacuum chamber. The benzonitrile pressure is about 3 × 10^{-3} torr, the applied voltage 14 kV at the beginning. The wire should be heated for two minutes by passing a current of 35 ma through it at the beginning. Then the wire is activated for one hour without heating. The voltage is gradually reduced during this period to 10 kV. Activation is then continued for five hours at 10 kV, succeeded by a 2 minute heating by 35 ma. Then another 3 hours activation at 10 kV follows, succeeded by a 2 minute heating by 35 ma. Finally, the wire is acti-

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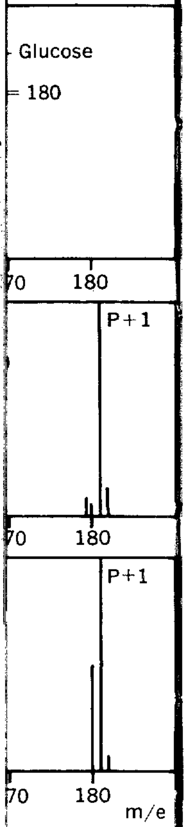

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vated by an additional period of two hours at 10 kV without heating, and is then inserted into the mass spectrometer. This activation program can be varied and shortened to some extent. The maximum ion current of a 10 μm wire of 5 mm length at 10 kV and 3×10^{-3} torr benzonitrile is about 1×10^{-5} a (including secondary electrons).

Thermally Instable Compounds Studied By Field Desorption

Recently, a new technique for the study of thermally instable compounds has been developed by the author. Although the FI method is a soft method of ionization, this feature is of little use if the molecules are already decomposed prior to the ionization process. This is the case if thermally instable solid organic compounds are evaporated from a micro oven. The lattice energy is sometimes greater than the energy required for removal of a smaller molecule from a larger one. (Elimination of water molecules from carbon hydrates during evaporation is a well known example.)

No molecular ions are found with EI in these cases, and strong $(M-H_2O)^+$ or other thermal fragment peaks are found besides the M^+-peak in the FI mass spectra of such substances.

The very large active area of the field anode achieved by the new method described in the preceding section establishes the possibility of direct adsorption of the substance on the field anode and of subsequent field desorption of the substance in its ionic state in the FI mass spectrometer. The activated field anode is immersed for this purpose in a concentrated solution of the substance to be analyzed. A minute droplet suffices for this procedure. After adsorption of the substance, the field anode is brought into the mass spectrometer, and the solvent is evaporated for a couple of minutes in high vacuum at room temperature. This temperature is too low for appreciable evaporation of the substance, which is normally of low volatility. A background spectrum is then taken at room temperature. The temperature of the field anode is subsequently raised gradually by passing a current of a few ma through the field anode (which is assumed to be a wire). Field desorption becomes noticeable after a certain temperature rise. If this threshold temperature has been carefully established and is not exceeded, steady field evaporation of the substance will occur for a quarter of an hour or more. This time is sufficient for taking useful mass spectra. The spectra should be scanned as fast as possible.

This new method avoids the transfer from the solid to the gaseous state prior to ionization. The molecules to which this method is applicable are not decomposed during the dissolving process in the solvent. The molecules are bound to the adsorbents only by weak van der waals forces. Subsequent field desorption does, therefore, not lead to such a high degree of thermal decomposition as does evaporation.

Figure 5 shows the EI, FI and FD (field desorption) mass spectra of d-glucose. The EI and FI mass spectra were taken in the conventional way by evaporation of the solid substance from a micro-oven brought into a position near the ionization zone by a vacuum lock. The field desorption mass spectrum was obtained by immersion of a strongly activated FI wire in a small droplet of a concentrated aqueous solution of sugar. (The term "field desorption," FD, is used for the latter method because all of the molecules are ionized during the desorption process, whereas in the case of the molecular beam technique part of the molecules are "field ionized" during the approach to the field anode from the gas phase, and only a part of them are field desorbed.)

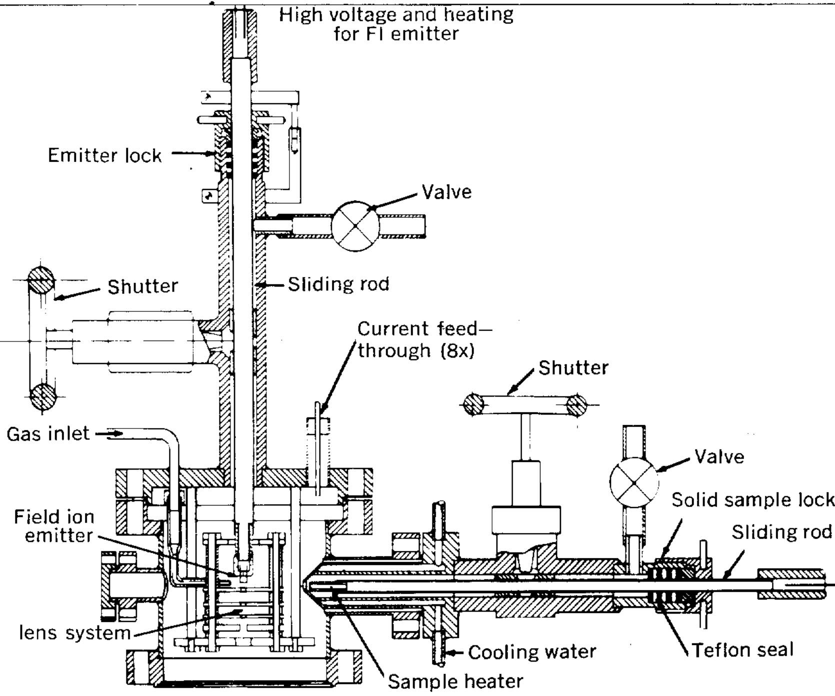

Fig. 6. Field ionization source with universal sample introduction system for gas, liquid or solid samples. This unit is also used for the field desorption technique.

It can be seen from Fig. 5 that the fragment peaks caused by thermal decomposition of the evaporated molecules are greatly reduced in the FD-mass spectra as compared with the FI-mass spectra.

The advantages of the new method are threefold.

1. Sensitivity of detection is greatly increased, because a very small droplet containing μg quantities of the substances suffices for adsorption of the substance on the FI anode. With the molecular beam technique, on the other hand, most of the substance does not strike the FI anode, and therefore, larger quantities of the sample are required.

2. Intensity of the molecular ion peak is increased in the FD spectrum as compared with the FI-spectrum.

3. One can determine which fragment peaks are due to thermal decomposition and which to dissociative ionization by comparing FD with FI mass spectra.

We have recently constructed an FI-FD ion source, which is universal in the sense that samples can be introduced in either the gaseous, liquid or solid state and analyzed either by the FI or FD-technique. Figure 6 shows a drawing of this source. Gaseous volatile liquid samples are expanded into a 5 liter vessel under a pressure of about 0.1 torr. They are then introduced into the ion chamber after expansion through a gold leak by a jet shown in Fig. 6. Solid samples are evaporated by a micro-oven inserted into the mass spectrometer by a vacuum lock in the conventional manner. A second vacuum lock mounted on top of the ion source serves for quick exchange of activated field anodes that have been immersed in a solution of the sample to be analyzed.

The universality of the ion source can be further increased by introduction of an electron beam unit. ☐