Field Ionisation Studies Using a Double Focussing Mass Spectrometer

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Intense field ionisation mass spectra have been obtained with an A.E.I. M.S.7 mass spectrometer, used with very simple modifications to the ion source.

Some features of the spectra of a variety of compounds are given and the spectrum of acetone is discussed in detail. A special feature of this spectrum is the variety of ions with a mass greater than that of a single molecule.

The relatively small energy spread of the field ion source enabled resolving powers, higher than those possible with a spark source, to be obtained. Multiplets occurring in the spectra were easily resolved.

Mass spectra arising from field ionisation of organic vapours have been obtained on a modified A. E. I. M. S. 7 mass spectrometer[1]. Beckey[2–4] and Robertson[5] have obtained field ionisation mass spectra on single focussing instruments. Beckey[4] has discussed peaks in such spectra that show a pronounced "tail" to low mass and has attributed this peak shape to the decomposition of short-lived molecular ions ($10^{-14}-10^{-9}$ seconds) moving down the electric field after ionisation has occurred near the edge. Peak broadening to low mass can also occur at the molecular ion peak if the ionising field is very high[6]. Mass resolution is therefore limited. Using an instrument capable of velocity as well as direction focussing, these distortions of peak shape are eliminated.

Experimental

In order to produce the spectra, simple modifications to the ion source of the M. S. 7 are required. The tantalum backplate and first slit are removed and a small piece of razor blade held in a small clamp is mounted on one of the manoeuvrable glass insulators of the M. S. 7 source so that it is adjustable to within about 1 mm of the second slit, which is at earth potential. The full 20 kV accelerating voltage of the M. S. 7 is applied to the blade. (The only previous preparation received by the blade was immersion in hot carbon tetrachloride to remove grease.) The use of sharp edges and thin wires to produce the high electric field required for field ionisation has also been described by Beckey[3, 4] and Robertson[5, 7]. Our experiments are limited to the use of razor blades.

Sample vapour is introduced to the ion source either from an unheated reservoir via a needle valve, or by a "direct inlet". The samples studied are therefore restricted to those that are reasonably volatile at room temperature. No modification to the spectrometer pumping system is made, and optimum field ionisation is obtained when the sample vapour is fed to a position close to the razor edge. The modified source is shown schematically in Fig. 1.

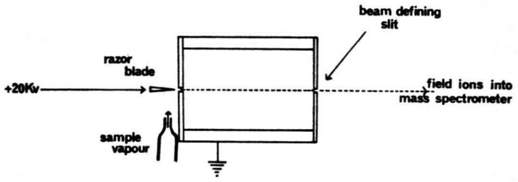

Fig. 1. The M. S. 7 source modified for field ionisation.

Using a nominally 0.005″ beam defining slit, the ion current indicated by the monitor was in the range 0.5 to 4×10^{-12} amps. The resolving power (50% peak height definition) was 1600 at m/e 20, 3000 at m/e 60 and 5000 at m/e 186, the last figure being determined from the parent ion peaks of ferrocene (Fig. 2). This compares with a figure of approximately 1500 at m/e 200 when the M. S. 7 is used with a spark source.

The spectra were recorded on a photoplate in the normal way for the M. S. 7.

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[1] R. M. Elliott, R. D. Craig, and G. A. Errock, Instruments and Measurements, Academic Press, London 1961.

[2] H. D. Beckey, Advances in Mass Spectrometry, Volume II, Pergamon Press, Oxford 1963.

[3] H. D. Beckey, Z. Instrumentenk. **71**, 51 [1963].

[4] H. D. Beckey, H. Knöppel, G. Metzinger, and P. Schulze, Advances in Mass Spectrometry, Volume III. Published by The Institute of Petroleum 1966.

[5] A. J. B. Robertson and B. W. Viney, Advances in Mass Spectrometry, Volume III. Published by The Institute of Petroleum 1966.

[6] R. Gomer, Field Emission and Field Ionisation, Oxford University Press, London 1961.

[7] A. J. B. Robertson, B. W. Viney, and M. Warrington, Brit. J. Appl. Phys. **14**, 278 [1963].

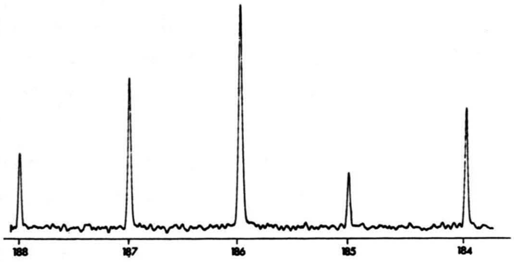

Fig. 2. Microdensitometer plot of the molecular ion peaks of Ferrocene (0.005″ slit).

Results

The first spectrum obtained was that of water. This spectrum was obtained to a greater or lesser extent as background in all subsequent spectra, and has been studied extensively by Beckey [2].

During the development of the technique, acetone was the sample material; its field ionisation mass spectrum has been studied in some detail and will be described.

The molecular ion peak (*m/e* 58) is the base peak of the spectrum. This enhancement of the molecular ion compared with the electron impact mass spectrum is well established and the spectrum observed is similar to that recorded by Robertson [5]. Thus, fragment ions are observed at *m/e* 43, 41, 31 and 29; the resolution of the M. S. 7 permits the identification of a doublet at *m/e* 29 corresponding to CHO^+ and $C_2H_5^+$. However, other peaks are observed that have not previously been recorded; these are all above the molecular ion on the mass scale, notably at *m/e* 71, 77, 97, 99, 115 and 117.

The reproducibility of the spectra obtained is not good. This is revealed when sets of spectra are run under nominally identical conditions. Significant differences are apparent in the abundances of many of the ions, those whose mass is greater than that of the parent ion seeming to be particularly susceptible to variation. This is especially noticeable when a new blade is inserted. In view of this it is very difficult to give more than an estimate of the relative abundances of the ions, as even a photoplate containing a series of lengthening exposures exhibited signs of erratic fluctuation of the ion beam. In general, however, fragment ion abundances were in the range 1% to 10% of that of the most abundant ion at *m/e* 58; *m/e* 59 and *m/e* 60 were of the order 50% and 5% respectively and the heavier ion abundances lay between 0.1% and 1%.

The figures quoted in Table 1 were obtained from a typical set of spectra, and the atomic constitutions were deduced by comparison of the spectra of acetone and hexadeutero-acetone. The electron impact spectrum is given for comparison [8].

m/e	Approximate Abundance %	Composition	Electron Impact
117	0.5	$C_6H_{13}O_2^+$	—
115	1	$C_6H_{11}O_2^+$	—
99	0.5	$C_6H_{11}O^+$	—
97	0.2	$C_6H_9O^+$	—
77	0.2	$C_3H_9O_2^+$	—
71	0.8	$C_4H_7O^+$	—
60	5	$C_3H_8O^+$	—
59	50	$C_3H_7O^+$	1
Molecular ion			
58	100	$C_3H_6O^+$	28
43	8	$C_2H_3O^+$	100
42	—		7
41	7	$C_3H_5^+$	2
39	—		4
38	—		2
37	—		2
31	2	CH_3O	1
29	2	$C_2H_5^+$ CHO^+	4
28	—		3
27			7
26			4
25			1
16			1
15			31

Table 1.

A histogram plot of the field ionisation spectrum of acetone together with air and water background is shown in Fig. 3. This figure was prepared from a microdensitometer scan of a photoplate showing saturation of the emulsion at the molecular ion.

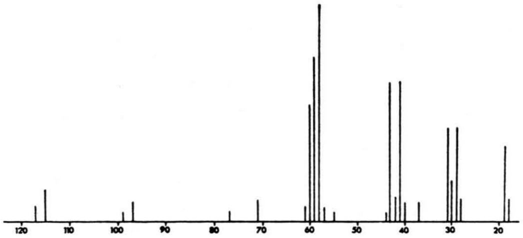

Fig. 3. Histogram of the field ionisation spectrum of acetone.

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[8] Mass Spectral Data, American Petroleum Institute Research Project 44, Serial No. 1647.

Attempts were made to plot the field ionisation spectrum of acetone as a function, firstly of voltage at the ionising edge, and secondly of sample pressure. During these operations occasional ion beam failure caused a whole exposure run to be abandoned since re-starting the beam usually necessitated re-adjustment of the razor edge position, which was found to be critical. Similarly, any exposure containing a large fluctuation of the ion beam was not considered. Despite precautions such as these, any trends which may have been detected in the plots were masked by the short term variations in ion beam constitution already mentioned.

When the exposure of the photoplate to the ion beam was 0.1 millimicro-coulombs or more, "metastable peaks" were observed in the spectra of acetone and hexadeutero-acetone at *m/e* 32.1 and *m/e* 33.2 respectively. These corresponded to the transitions:

$$(CH_3)_2CO^{+\cdot} \rightarrow C_2H_3O^+ + CH_3 . \quad m^* \text{ calculated} = 31.88 ,$$

$$(CD_3)_2CO^{+\cdot} \rightarrow C_2D_3O^+ + CD_3 . \quad m^* \text{ calculated} = 33.06 .$$

The former transition has been reported previously by ROBERTSON [5].

At these long exposures, the sensitivity of the method is illustrated by the detection, at an intensity level down to 0.1 p.p.m., of a weak hydrocarbon continuum and the ion peaks of the species, S_8^+, $S_7^+ \ldots\ldots S_1^+$ due to sulphur vapour evolved from rubber in the reservoir vacuum system.

Discussion

The observed spectrum (Fig. 3) in which the molecular ion predominates over the fragment ions, is of the form expected from the field ionisation technique. However, the detection of a variety of ions above the molecular ion has not previously been reported in the acetone field ion spectrum. These ions presumably originate from ionisation in a condensed layer at the ionising edge as observed in the spectrum of water and methanol [2]. Some may be the result of ion-molecule reactions at the interface between the vapour and condensed phases at the emission edge, as reported when nitrogen is field ionised in the presence of water [2]. All the heavier ions observed, except that at *m/e* 77, can be attributed to acetone; that at *m/e* 77 moves to *m/e* 86 when hexadeutero-acetone is examined and therefore can be explained as being formed by the addition of H_3O^+ to an acetone molecule.

The mechanism of the field ionisation process has been discussed by GOMER [6] and by BECKEY [2, 9]. It consists of quantum mechanical tunnelling of an electron, through the field-distorted COULOMB potential of the molecule into the edge. Thus, as expected, the molecular ion, formed with no excess energy, is usually the most abundant in field ionisation mass spectra, though fragment ions derived from field dissociation of the molecular ion are observed together with fragment ions field desorbed from the tip. The phenomena of field dissociation and field desorption have been discussed by BECKEY [5, 9] and GOMER [6] respectively. GOMER [6] has also described a pulsed field method of differentiating between the two types of fragment ions.

Evidence of spectacular enhancement of the molecular ion, relative to other ions in the spectrum, by the field ionisation technique over electron impact ionisation has been observed for several other compounds studied. Some results are detailed in Table 2.

Compound	Field ionisation molecular ion abundance	Field ion base peak	Electron impact molecular ion abundance	Electron impact base peak
Dioxane	100	parent	30	*m/e* 28
2,2,4-trimethyl pentane	~ 10	*m/e* 57	0.02	*m/e* 57
2-methyl-1,3-dioxolane	~ 10	*m/e* 73	Nil	*m/e* 73

Table 2.

Microdensitometer plots of the molecular ion region of the field ionisation spectra of these compounds are shown in Fig. 4.

The field ionisation spectrum of toluene provides another good example of molecular ion enhancement. This consists only of the molecular ion peaks and a very small peak at *m/e* 91 (<1% of molecular ion peak). This latter ion forms the base peak in the electron impact mass spectrum of toluene in which

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[9] H. D. BECKEY, Bull. Soc. Chim. Belges **73**, 326 [1964].

the molecular ion peak at m/e 92 has an abundance 78% of that of m/e 91[10].

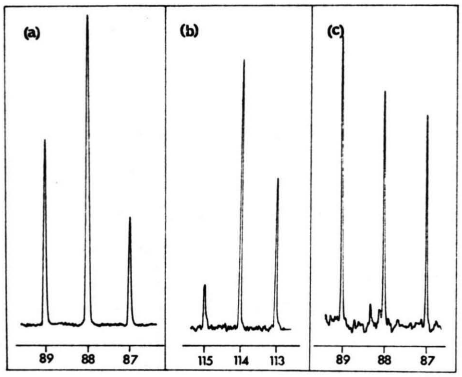

Fig. 4. The molecular ion region of: (a) 1,4-Dioxane, (b) 2,2,4-trimethylpentane, (c) 2-Methyl-1,3-dioxolane.

Other ions above the molecular ion on the mass scale have been observed in the field ion spectra of: acetic acid, m/e 61 (base peak) and m/e 121 $(2p+1)$; pyridine, m/e 158 $(2p)$; aceto-nitrile, m/e 42 $(p+1)$, m/e 83 $(2p-1)$ and m/e 85 $(2p+1)$ as well as the $(p+1)$ species of dioxane and 2-methyl-1,3-dioxolane illustrated in Fig. 4. (p represents the molecular ion).

While the reproducibility obtained was just good enough to give an estimate of ion abundances from graded exposures on a single photoplate, it did frustrate the attempts made to plot the abundances of the field ions formed as functions of voltage at the edge and the source pressure. It is likely that a major cause of the ion beam fluctuation is slight changing of the shape of the edge itself. For instance, the water etch effect, reported by BECKEY[2], could cause significant changes in the field strength, which in turn affects the thickness of the condensed layer, the distance from the edge at which ionisation can occur and the amount of field dissociation and desorption.

It is interesting to note that in the field ionisation spectrum of acetone, the most easily detected "metastable peak" arises from the loss of the neutral methyl radical from the molecular ion. In electron impact mass spectra this transition is not detected, whereas the transition

$$(CH_3)_2CO^{+\cdot} \rightarrow CH_2CO^{+\cdot} + CH_4 \quad m^* = 30.4$$

does occur[11].

A simple, easily removable modification of the M. S. 7 vacuum spark source enables relatively intense field ionisation spectra to be obtained. The photoplate detector confers great sensitivity on the system but for quantitative studies a detection system with a linear response is necessary.

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[10] Mass Spectral Data, American Petroleum Institute Research Project 44, Serial No. 418.

[11] A. E. WILLIAMS, unpublished work.