The Spark Source Mass Spectra of Organic Solids

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Spark source mass spectra of organic solids, obtained on an A.E.I. M.S.7 spectrometer, have been compared with the conventional mass spectra produced by electron impact ionization of the vapours of these same solids. Although fragmentation in the spark is very high, many more spectral lines being produced than by electron impact, the spark spectrum contains many features, including *meta-stable peaks,* that point to a similarity between the two ionization methods. It is suggested that electron impact of vaporised species is an important ionization process within the spark. This hypothesis is reinforced by the fact that those materials that could not be vaporised without thermal degradation for electron impact study also gave no spark spectra characteristic of their structure.

Improvements in the design of spark source spectrometers would permit identification, by means of accurate mass measurement, of the numerous ions, many of which do not occur in electron impact mass spectra. This might provide an insight into the processes of fragmentation, re-arrangement and ion-molecule reactions occuring in the spark.

Although spark-source mass spectrometry has gained acceptance as a tool for elemental analysis at low impurity levels, little attention has been paid to its potential use in organic chemistry, where the more conventional electron-impact mass spectrometry has found so many applications. Recently, however, Baun and his co-workers [1–3], and Hickam and his co-workers [4, 5] have described the spark-source mass spectra of a number of organic solids. They concluded that most of the spectra showed features characteristic of the molecular structure. On the other hand they did not in general consider what advantages, if any, spark spectra have over the conventional electron-impact spectra.

In this laboratory we have compared the spark-source mass spectra of a variety of organic solids with the electron-impact mass spectra of the vapour of these materials.

Experimental

Spark-source spectra were obtained on a standard A.E.I. M.S. 7 mass spectrometer [6] and interpretation of the photographically recorded spectra was facilitated by use of a Joyce Loebl recording microdensitometer. Electron-impact spectra not previously reported elsewhere were obtained on an A.E.I.M.S. 9 mass spectrometer [7]; a direct entry system was employed whenever involatility precluded the use of the reservoir inlet.

Much of the spark-source work has been on anthraquinone, a particularly suitable compound for examination because of its known chemical and thermal stability, and because its electron-impact mass spectrum has been thoroughly studied [8, 9]. Three methods were investigated for introducing anthraquinone to the spark: (a) an intimate mixture with powdered graphite was pressed in a die and the resultant "briquettes" used as electrodes; (b) the tips of short copper wires were immersed in molten anthraquinone to form, on withdrawal, electrodes having a central copper core surrounded by the sample; (c) small nickel tubes of internal diameter about 1 mm. were compressed at one end to leave a cup into which powdered sample was packed. All three types of electrode gave anthraquinone spectra negligibly different from each other. The third technique

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required the least amount of sample, was applicable to high melting solids, and did not contaminate the spectrometer with sublimed material as much as the others. It was therefore used for all the compounds whose spark spectra are described below.

A 30 kV, pulsed, radio frequency spark was used; the pulse length was generally 100 or 200 μs and the pulse repetition rate was between 30 and 300 per second. The sparking conditions selected were mainly governed by the rise in source pressure that resulted from vigorous sparking. The total ion charge to which the photoplate was exposed depended on the nature of the sample and also on the features of the spectrum to be demonstrated. Because the ion beam contained varying quantities of ions derived from the metal support tube, in addition to those derived from the substance under investigation, the optimum exposure was, of necessity, found by trial and error.

Mass measurements on the M.S. 9 spectrometer, accurate to about 2 parts in 10^6 were obtained by the standard peak-switching technique.

Mass measurements on the M.S. 7 spectrometer were obtained by interpolation between known standard peaks, derived from suitable inorganic materials added to the organic sample under examination. We have found that the position of the peaks on the photoplate does not strictly follow the relationship $x \propto \sqrt{m/e}$, where m/e is the mass to charge ratio of the ions responsible for a peak at position x. This arises from the fact that the plate in M.S. 7 spectrometers is not completely in the magnetic field; pure MATTAUCH-HERZOG geometry does not therefore apply. We have therefore adopted the following procedure.

A reference ion is so chosen that it has the same integral mass M as the unknown ion. (If this reference ion is not completely resolved from the unknown ion, the attainable accuracy of mass measurement is usually inadequate.) By means of two other references ions of integral masses $(M-1)$ and $(M+1)$ the mass of the middle reference ion is calculated by interpolation according to the above square-root relationship. The difference between the calculated and true masses yields a correction that can be applied to the mass of the unknown ion as calculated by interpolation from the same two reference ions. The standard deviation of such measurements is estimated as ± 0.007 u.

Although all the spark spectra described were qualitatively reproducible, relative peak densities were found to vary when repeat spectra were run under nominally identical conditions. One reason for this variability is that the spark gap is not accurately reproducible in successive experiments. This is an important difference between the spark and electron impact ionization methods, the latter being accurately reproducible under controlled conditions.

Results

(a) Anthraquinone

At low exposure levels (Fig. 1 b and 2 a) only the most abundant ion species are recorded on the photoplate and the spark spectrum shows some resemblance to that obtained by the electron impact method[8, 9] (Fig. 1 a). Peaks at m/e 208, 180 and 152 are strong in both spectra, and have been attributed in electron impact to the anthraquinone molecular ion, fluorenone ion and biphenylene ion respectively. Such re-arrangements, following the loss of neutral carbon monoxide, are particularly characteristic of the quinone structure. The similarity between the electron impact mass spectra of anthraquinone (below m/e 180) and of fluorenone has been noted[8, 9]; the same similarity is shown when the spark-source spectra of these two materials are compared (Fig. 1b and 1c).

There are, however, several differences between the anthraquinone spectra obtained by the two ionization methods. The most immediately obvious is the occurrence, below m/e 120, of many more intense peaks in the spark spectrum than in the electron-impact spectrum. Clearly fragmentation is more prevalent in the former case.

The spark spectrum contains a prominent peak at m/e 163, whereas in the electron-impact spectrum this peak is only 0.3% of the peak at m/e 208. Mass measurement of this peak in the spark spectrum, with the dysprosium ions at m/e 162, 163 and 164 producing reference peaks, yielded (163.055 ± 0.005) u., (95% confidence limits derived from ten independent measurements). The accurate mass of the ion in the electron-impact spectrum, as measured on an M.S. 9 spectrometer, is 163.0542 u. with an expected error of less than 0.001u. It is therefore probable that the peaks in both spectra can be attributed to $C_{13}H_7^+$ (163.0548 u.). The mechanism of formation of this ion is not clear. We have obtained spectra of anthraquinone on the M.S. 9 spectrometer at various sample pressures; the height of the peak at m/e 163 relative to the parent peak

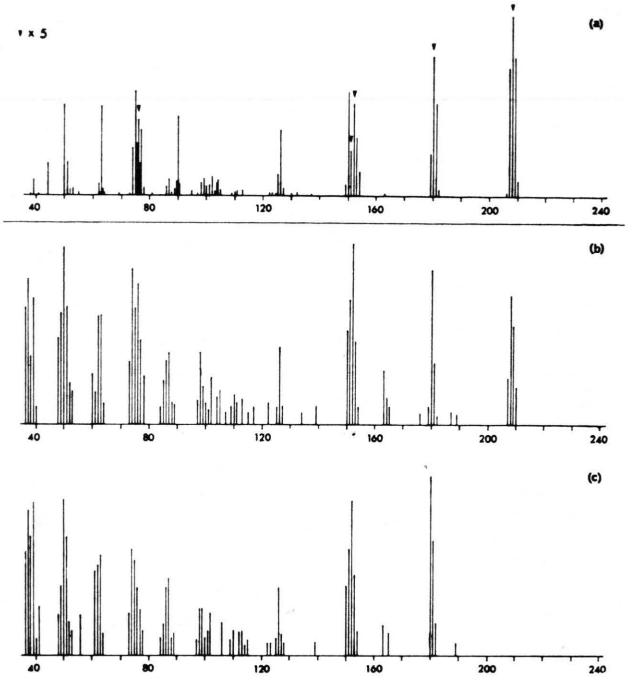

Fig. 1. (a) Electron-impact mass spectrum of anthraquinone, (b) Spark-source mass spectrum of anthraquinone, (c) Spark-source mass spectrum of fluorenone.

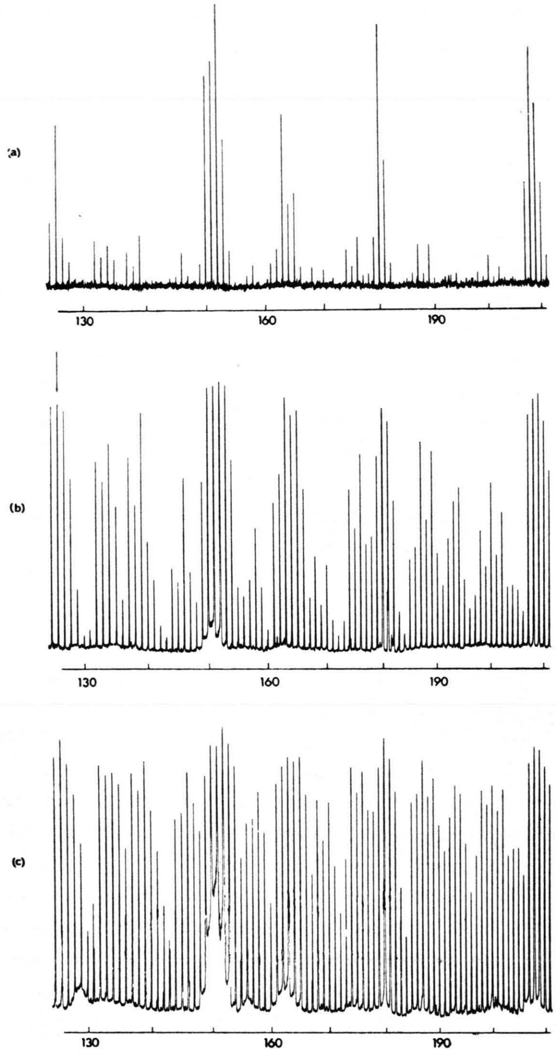

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Fig. 2. Microdensitometer traces of the spark-source mass spectrum of anthraquinone: (a) Low exposure, (b) Intermediate exposure, (c) High exposure.

was constant over a fifteen fold pressure range. In the electron-impact source, therefore, the low abundance ion at m/e 163 cannot be assigned as an ion-molecule reaction product. Whether or not the mode of formation of this ion is the same in the spark source as the electron-impact source cannot as yet be stated; it is, however, clear that conditions in the spark favour its formation.

A third difference involves the intensities of the peaks at m/e $(M+1)$ and $(M+2)$, where M is the mass to charge ratio of an abundant ion. Although the characteristics of the photoplate do not readily allow correlation of relative line densities with relative ion abundances, such peaks in the spark spectrum seem to be too strong to be accounted for entirely by ions containing heavy isotopes. It is probable that some of the ions contributing to these peaks arise from ion-molecule reactions occuring in the spark.

The appearance of the spark spectrum alters as the exposure of the photoplate is increased and new features, previously below the detection limit, are revealed (Fig. 2b and 2c). For instance, peaks occur at all mass numbers up to and even beyond the molecular weight. Unlike many of the weaker peaks observed in high sensitivity electron-impact spectra, they cannot be attributed to background effects, and provide further evidence of ion-molecule reactions in the spark. (The changes in apparent relative intensities are primarily due to the fact that the images of the strongest peaks in the spectrum attain the saturation density of the emulsion.)

A second new feature is the appearance of diffuse images, the most easily detected occurring near the peak at *m/e* 152. At intermediate exposures (Fig. 2b) this effect is seen as an inter-line darkening of the photoplate resulting in a rise of the base line of the densitometer trace between *m/e* 149 and 153. These observations are attributed to meta-stable transitions. When the exposure is further increased (Fig. 2c) this effect spreads from *m/e* 148 to 154.

Similar meta-stable transitions have been detected in the electron-impact spectra of anthraquinone obtained on an M.S. 9 spectrometer. In this case they were assigned to decompositions occuring during the passage of the primary ions through the electrostatic analyser. Variation of the ratio of accelerating voltage to the electrostatic analyser voltage produced the shift in the *meta-stable peaks* expected for ions of this type [10]. The same variation of this voltage ratio in the M.S. 7 spark spectra did not result in any observable shift. The difference in behaviour of the two instruments is attributable to the different geometry and mode of formation of the ions in each instrument. Ions formed from the spark source probably have a very wide distribution of energy. For inorganic ions the energy spread is usually much wider than the normal energy passband of the M.S. 7 (600 eV) [11]. Attempts to defocus the normal beam by altering the ratio of the accelerating voltage to electrostatic analyser voltage merely result in ions from a different part of the energy distribution being focussed. Slight differences that may be present in the energy distribution of different ions are masked by the normal variations associated with spark-spectra; this is true of daugther ions as well as their respective parent ions.

The reactions appear to involve the loss of single hydrogen atoms from the ions 155^+, 154^+, 153^+, 152^+, 151^+, 150^+ and 149^+. Since a transition such as $152^+ \rightarrow 151^+ + \mathrm{H}$ can produce a *meta-stable peak* anywhere between *m/e* 151 and 150, depending upon where in the flight through the spectrometer tube the decomposition occurs [10, 12] the overall superimposed effect of these transitions produces a broad peak extending from *m/e* 154 to 148.

In the spark spectra a similar set of meta-stable transitions, involving the successive loss of hydrogen atoms, is associated with the *anomalous* peak at *m/e* 163, but none is observed at the parent ion or the fluorenone ion. This suggests different stabilities of the ions concerned; those containing oxygen are apparently more resistant to loss of hydrogen than the hydrocarbon ions.

In the electron-impact type of double focussing mass spectrometers the majority of reported *meta-stable peaks* arise from decompositions occuring between the two analysers [12]: in anthraquinone the transitions $208^+ \rightarrow 180^+ + 28$ and $180^+ \rightarrow 152^+ + 28$ are readily detected by the presence of such *meta-stable peaks* at *m/e* 155.8 and 128.4 respectively. These *meta-stable peaks* are observed in M.S. 7 spark-source spectra only at high exposure levels, when faint diffuse images occur on the photoplate. The densitometer trace (Fig. 2c) illustrates this effect.

(b) Solids of Low Volatility

Whereas anthraquinone represents a fairly volatile solid, many of the compounds studied have been very much less volatile and required the direct entry system to produce their electron-impact spectra. The examples quoted are linear quinacridone (Fig. 3), indanthrone (Fig. 4), dibenzanthrone (Fig. 5) and 1,1′,5,1″ trianthrimide (Fig. 6), and their mass spectra are illustrated in Figs. 7 to 10.

These compounds all have high stability and are purified with great difficulty. The samples used were of unknown purity and interpretation of the spectra is complicated by this fact. However, certain features of the spectra are clearly representative of the molecules concerned.

(i) Electron Impact

Loss of carbon monoxide followed by re-arrangement is a characteristic fragmentation in cyclic ketones [9]. Furthermore all four compounds lose CHO fragments; with indanthrone and trianthrimide this occurs with greater probability than the loss of CO fragments and may be attributed to the proximity of the hydrogen atoms on the nitrogen to the carbonyl oxygen in these compounds.

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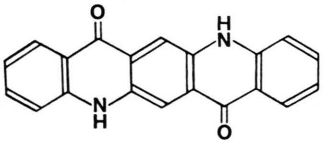

Fig. 3. The molecular structure of linear quinacridone.

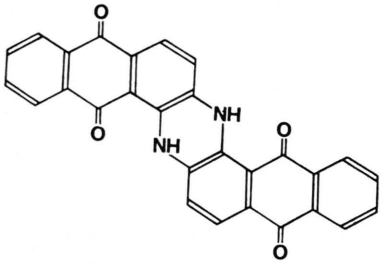

Fig. 4. The molecular structure of indanthrone.

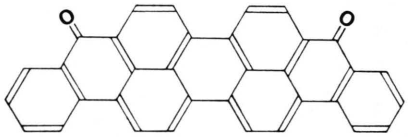

Fig. 5. The molecular structure of dibenzanthrone.

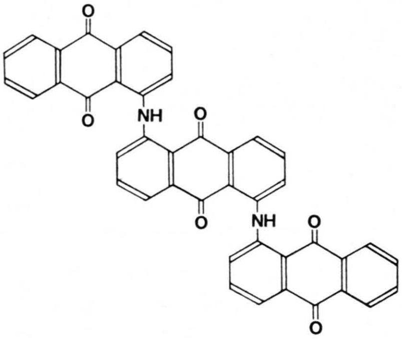

Fig. 6. The molecular structure of 1,1′,5,1″ trianthrimide.

The loss of two CO fragments is possible with all four compounds and peaks are observed at (p-C_2O_2) and (p-C_2O_2H) in all spectra. The loss of more than two carbonyl groups is possible from indanthrone and trianthrimide. Indanthrone shows peaks at *m/e* 358, 357, 356, 355 and 330, 329, 328, 327 corresponding to (p-C_3O_3), (p-C_3O_3H), (p-$C_3O_3H_2$), (p-$C_3O_3H_3$) and (p-C_4O_4), (p-C_4O_4H), (p-$C_4O_4H_2$), (p-$C_4O_4H_3$) respectively. Trianthrimide, on the other hand, loses these further fragments with low probability, despite the fact that this molecule contains six carbonyl groups in its structure.

An interesting and unexpected fragmentation is observed in quinacridone and trianthrimide: both give peaks at (p-16) and (p-17). Accurate mass measurements have established that these correspond to loss of oxygen and hydroxyl fragments respectively. The loss of a fragment of mass 17 would seem to be analogous to that observed in anthraquinone to produce the ion of *m/e* 163 from the ion of *m/e* 180. As in this latter case the mode of formation of such ions is not clear. Despite their structural similarities to the other compounds discussed, indanthrone fragments in this manner to only a very slight extent whilst dibenzanthrone gives no detectable fragments of this kind.

(ii) Spark-Source

The spark-source spectra, in general, show more fragmentation than do electron-impact spectra; the ions observed in the latter process are, however, generally the most abundant ions in the spark. The molecular ion is formed quite readily and many of the fragment ions can be identified by comparison with the electron-impact spectra. Potentially it would seem that the spark spectra of involatile materials of the sort described here could provide added information as a result of the greater, though discrete, fragmentation. In quinacridone, for example, the identification of ions at *m/e* 267, 240, 214, 201, 164, 139 and 128 might yield very useful structural information. However, the relatively low resolving power of the instrument (about 3,000 on a 50% peak height definition) and the difficulties of selecting and introducing suitable reference compounds generally preclude mass measurement to the precision necessary to determine the elemental formulae of ions.

The spark-source spectra again show that ion-molecule reactions are highly probable; the height of the peak at $(p+1)$ (almost as high as the parent itself) is a striking illustration of this.

In general, the spark spectra show surprisingly few doubly charged ions (by comparison with the spark spectra of metals, which form many multiply charged species). They are only detected at exposures very much higher than those required to produce the spectra illustrated in Figs. 7 – 10; in the electron-impact spectra of these materials the doubly charged species are easily detected and in quinacridone, for example, the 312^{++} peak at *m/e* 156 is the third largest in the spectrum.

It is possible that the low abundance of doubly charged ions in the spark spectra is due to charge

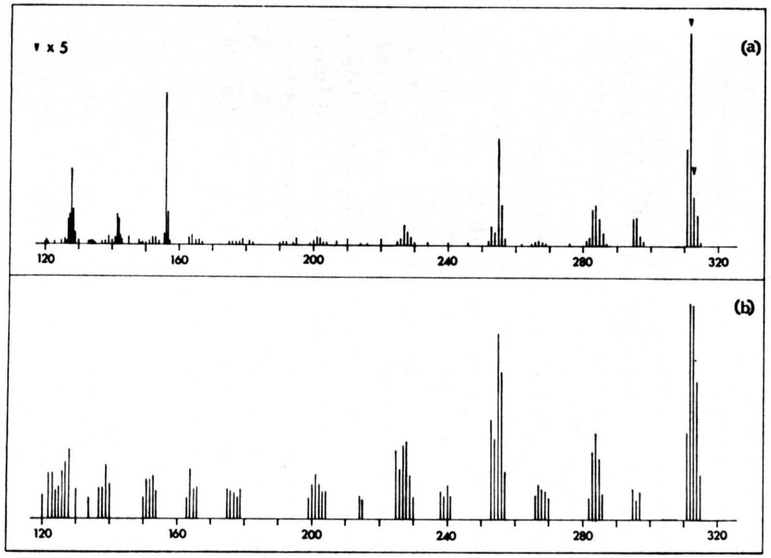

Fig. 7. (a) Electron-impact mass spectrum of quinacridone, (b) Spark-source mass spectrum of quinacridone.

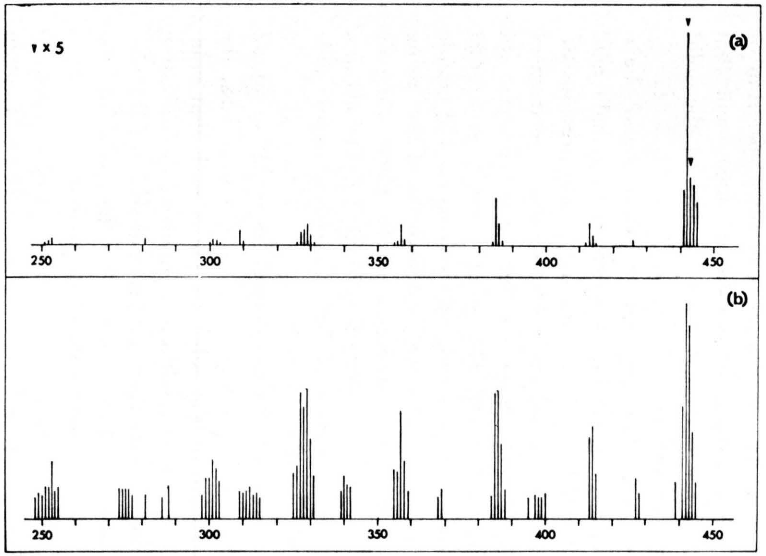

Fig. 8. (a) Electron-impact mass spectrum of indanthrone, (b) Spark-source mass spectrum of indanthrone.

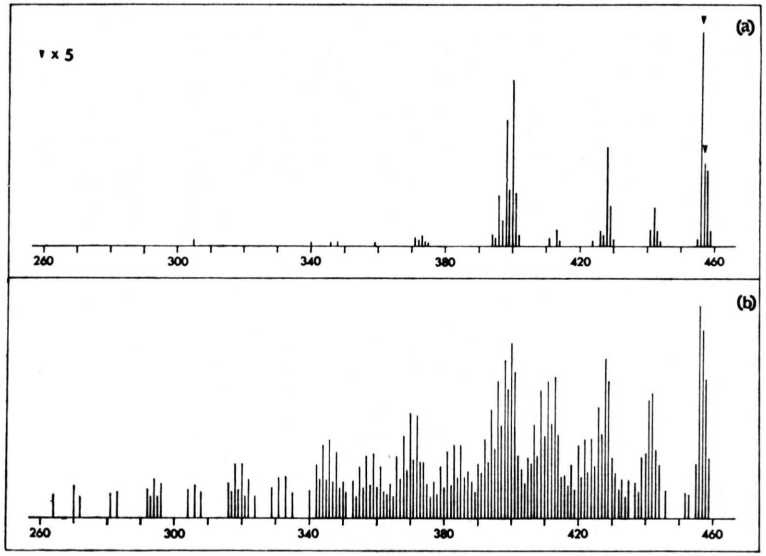

Fig. 9. (a) Electron-impact mass spectrum of dibenzanthrone, (b) Spark-source mass spectrum of dibenzanthrone.

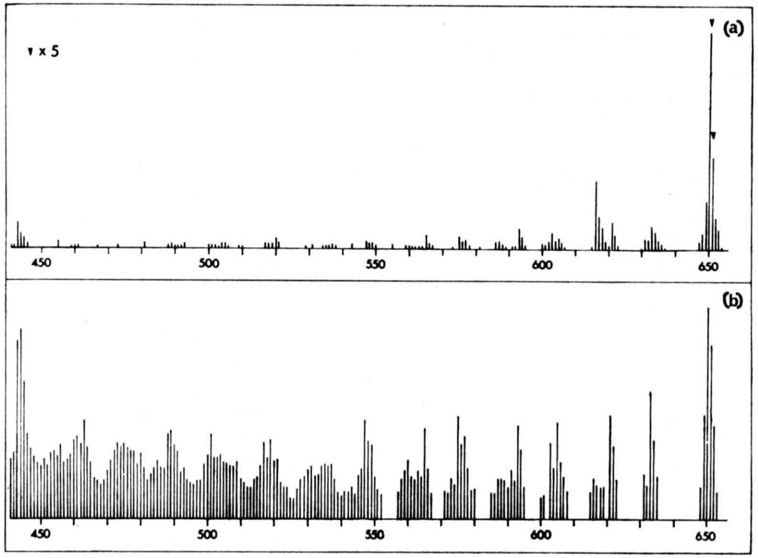

Fig. 10. (a) Electron-impact mass spectrum of trianthrimide, (b) Spark-source mass spectrum of trianthrimide.

transfer reactions; the high pressure in the spark would facilitate reactions of the type described by Melton and Wells [13] for the CO^{++} ion.

Dibenzanthrone is exceptional among the compounds studied by spark-source mass spectrometry in that the doubly-charged species are abundant; it is not clear why this is so. Fig. 11 illustrates the large number detected between *m/e* 170 and 230.

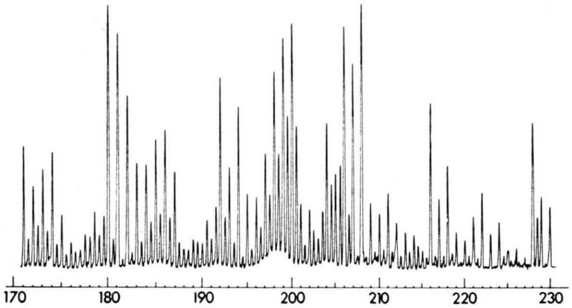

Fig. 11. Microdensitometer plot of part of the spark-source mass spectrum of dibenzanthrone.

Discussion

The vigorous nature of the spark and the complex ionization mechanisms that occur in it [14] make it a little surprising that spectra obtained by this method bear similarities to the electron-impact spectra and can be in part correlated with the molecular structure of the sample. The similarities between the two kinds of spectra lead one to suggest that the electron impact of vaporised molecules may be an important process in the spark. It is undoubtedly true that many of the electrons in the spark will be highly energetic, but the work of Kebarle and Godbole [15] using electrons with energies up to 12 keV suggests that the degree of fragmentation is not appreciably influenced by the energy of the bombarding electrons. Moreover, the high local pressure of vapour in the spark will provide the necessary conditions for the occurrence of the ion-molecule reactions indicated in the spark-source spectra. Support for this hypothesis of ionization of vaporised molecules is provided by the experiments of Hodgson and Katon [16], who have demonstrated, with the aid of specially designed electrodes, that the spark-source mass spectrum of anthracene vapour is indistinguishable from that obtained when the spark takes place at the solid anthracene surface.

However, Hodgson and his co-workers [3] have shown that a spark-source spectrum of phthalic acid is characteristic of its structure, while previous attempts to obtained the electron-impact spectrum of this material [17] have resulted in a spectrum of phthalic anhydride. This would seem to contradict our hypothesis concerning the vaporisation of sample into the spark. However, we have found that using the direct entry sampling system the electron-impact mass spectrum of phthalic acid can be obtained at a sample temperature of 100 °C, without appreciable degradation to the anhydride.

We conclude that, although degradation of all organic materials may occur within the spark, the temperature of the solid sample is such that volatilisation can occur without decomposition. Ionization probably occurs very quickly and some of the nascent ions are drawn away from the spark into the mass spectrometer by the fields present.

We have examined a wide range of compounds and have not found any from which we could obtain a spark spectrum when an electron-impact spectrum had not been obtained: all materials that degraded in the electron-impact sampling system also degraded in the spark. An example of this behaviour was dodecabromo tetrachloro copper phthalocyanine which degraded in the spark to produce halogenated phthalonitrile fragments in the manner reported by Hill and Reed [18].

There are undoubtedly more lines present in the spark spectrum than in the electron-impact spectrum. However, the accuracy with which the mass of the ions can be measured from the M.S. 7 spectrometer plates is insufficient to permit one to deduce unambiguously the elemental compositions of the ions. This imposes a severe limitation on the interpretation of spark spectra which might otherwise yield interesting information concerning the various processes involved in spark ionization of organic solids. A higher resolution spark-source instrument might overcome these difficulties.

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