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A MASS SPECTROMETRIC STUDY OF SOME MONOCYCLIC POLYCARBONYL COMPOUNDS

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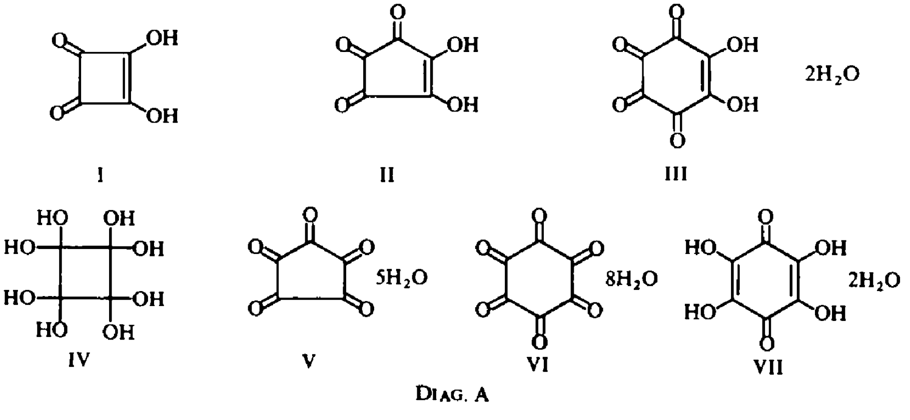
Abstract—The mass spectra of squaric acid, croconic acid, rhodizonic acid, and of their oxidation products octahydroxycyclobutane, leuconic acid, triquinoyl, and also of the related compound tetrahydroxy-*p*-benzoquinone have been studied. Characteristic features of the fragmentation of all these molecules are the elimination of carbon monoxide and ring contraction. The spectra of the acids show appropriate parent ion peaks, their oxidation products do not show parent ion peaks either of the fully hydrated or the fully dehydrated molecules.

INTRODUCTION

WEST *et al.*[1] observed that the di-anions of the di-enols squaric acid (diketo-cyclobutenediol) I, croconic acid (4,5-dihydroxy-4-cyclopentene-1,2,3-trione) II, and rhodizonic acid (5,6-dihydroxy-5-cyclohexene-1,2,3,4-tetrone) III, represent a new series of totally delocalized aromatic compounds, $C_nO_n^{2-}$. This and the structural ambiguities of their oxidation products octahydroxycyclobutane IV, leuconic acid pentahydrate (cyclopentane–pentone) V, and triquinoyl octahydrate (cyclohexane–hexone) VI, has prompted an investigation of the mass spectra of these interesting compounds. The synthetically important tetrahydroxy-*p*-benzoquinone dihydrate VII has also been studied. (Diag. A).



DIAG. A

The fragmentation, upon electron impact, of all of these compounds involves the scission of two C—C bonds with elimination of carbon monoxide followed by ring closure. The elimination of carbon monoxide is substantiated, in most cases, by the presence of the appropriate metastable peak.

This elimination of carbon monoxide in specific molecular re-arrangements in the mass spectra of oxygenated organic compounds has been discussed by Beynon *et al.*[2] The process is of wide occurrence and has been observed in the mass spectra of a large number of carbonyl compounds such as cyclic ketones,[3] quinones and polycyclic ketones,[4] tropone and tropolone derivatives,[5] substituted naphthoquinones,[6] and unsaturated cyclic ketones.[7]

RESULTS AND DISCUSSION

Mass spectral fragmentation of di-enols

The behaviour of squaric acid I, croconic acid II, and rhodizonic acid III, upon electron impact, is similar in that all three molecular ions break down with elimination of carbon monoxide followed by ring closure, yielding the next lower member of the series of di-enol carbonyl compounds, $C_{n-1}O_{n-1}H_2$.

Squaric acid I, the lowest known member of this series, was first synthesised by Park *et al.*[8] and its preparation and properties have been reviewed by Maahs and Hegenberg.[9]

The mass spectrum of squaric acid I (Fig. 1) shows a fairly intense parent molecular ion peak *m/e* 114. The occurrence of the base peak *m/e* 18 suggests that loss of water is of considerable importance in the fragmentation. The presence of ion peaks *m/e* 86, 68 and 58 can be envisaged as arising from the following fragmentation of squaric acid I. (Diag. B).

The most likely structure of the first breakdown product, *m/e* 86, is that of the unknown lowest member of the series of di-enol carbonyl compounds $C_nO_nH_2$ dihydroxycyclopropenone (n = 3), rather than mesoxalic dialdehyde.

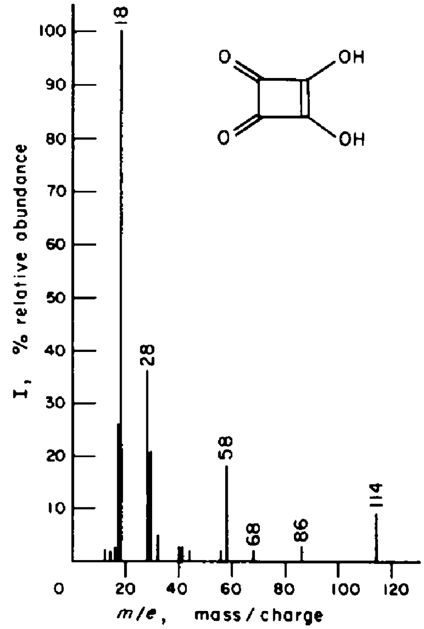
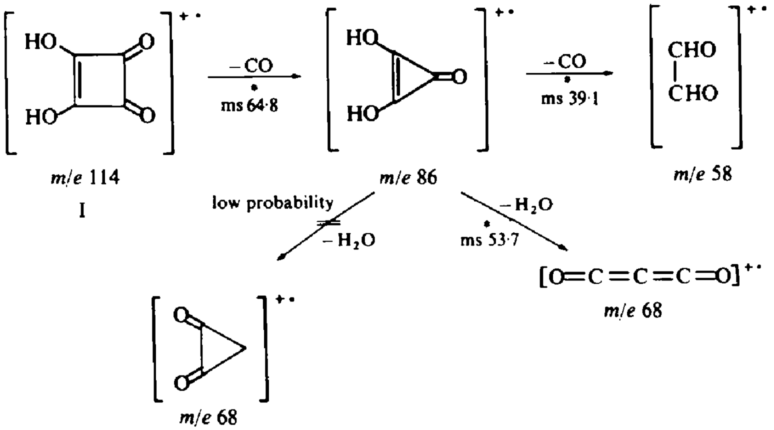


Fig. 1.



DIAG. B

Note: Fragmentation paths marked with an asterisk are substantiated by the appropriate metastable peak (ms).

Simple Hückel LCAO–MO calculations by West and Powell[10] predicted an unusually high resonance energy for the di-anion of dihydroxycyclopropenone, but, at the same time, they suggested that angle strain might reduce the stability of the di-anion. Recent studies on di-phenyl-cyclopropenone,[11a,b,c] mono-alkyl-cyclopropenones,[12] and cyclopropenone[13] itself, have fully established the unusual stability of this type of strained ring compound, and Farnum and Thurston[14] have been able to prepare the phenyl-hydroxy-cyclopropenone. It is difficult to construct a breakdown process in which mesoxalic dialdehyde, unknown in the free state, would lose carbon monoxide to give an ion *m/e* 58 rather than two formyl radical ions *m/e* 29. The loss of water from the postulated ion *m/e* 86 could give rise to either the carbon suboxide ion $C_3O_2^{+}$ *m/e* 68, or a cyclic 3-membered ring structure. The latter structure is energetically unfavourable[15] hence the former appears to be the most likely structure for this ion. Thus the proposed breakdown scheme appears to be the most likely one.

The 5-membered ring compound of the series, croconic acid II, has been known since 1825.[16] However, considerable ambiguity has existed regarding its structure. Hirata *et al.*[17] concluded, from a study of its UV and IR absorption spectra, that the structure II, is the most likely. This conclusion is supported by dipole moment measurements.[18]

The mass spectrum of croconic acid II (Fig. 2) shows a very intense parent ion peak *m/e* 142. The breakdown of this ion involves loss of carbon monoxide followed by ring closure to give the squaric acid I ion *m/e* 114. The breakdown then follows the pattern shown by squaric acid I, except that the base peak in the mass spectrum of croconic acid II is *m/e* 58 rather than *m/e* 18. Since *m/e* 58 is the base peak the corresponding molecular ion is very stable and it seems reasonable to suggest that this ion is the glyoxal rather than the dihydroxyacetylene ion. The formation of glyoxal would appear to involve a double hydrogen transfer. A similar transfer has been proposed by Bowie *et al.*[19] in the fragmentation of 2-hydroxy-5-methyl benzoquinone. It is noteworthy that the stability of the ion *m/e* 86, postulated as the

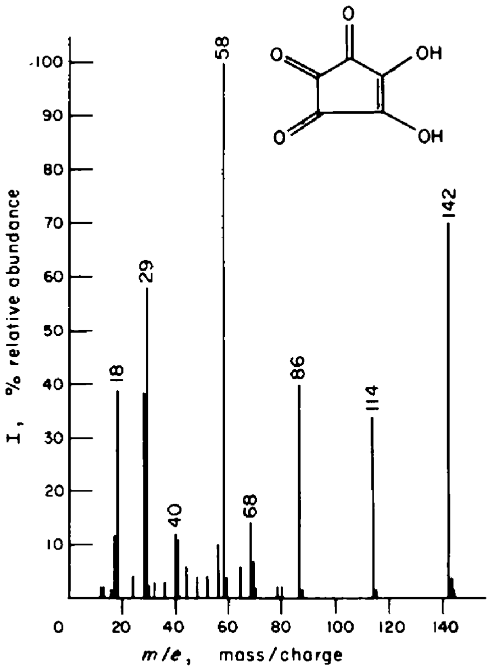
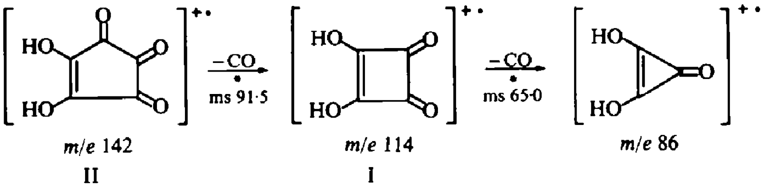


FIG. 2.



DIAG. C

dihydroxycyclopropenone ion, is reflected by the high intensity of this ion peak. (Diag. C).

The 6-membered ring of the series, rhodizonic acid dihydrate III, has been known since 1885[20] however, there has been some doubt about the role played by the two molecules of water.

The mass spectrum differs from those of the two lower members of the series in that the parent ion peak is observed at m/e 172 together with a peak of similar intensity at m/e 170 (Fig. 3). The peak m/e 172 appears to be due to the ion of tetrahydroxy-p-benzoquinone VII and can be visualised as arising from the loss of two OH-ions. (Diag. D).

The mass spectra at low source temperatures and pressures of rhodizonic acid dihydrate III, shows a parent peak at m/e 206. The presence of this peak, although of low intensity, indicates that the two water molecules must be relatively strongly bonded. Hence these are not present as water of hydration. The most likely structure is the *gem*-diol form as above. (Diag. D).

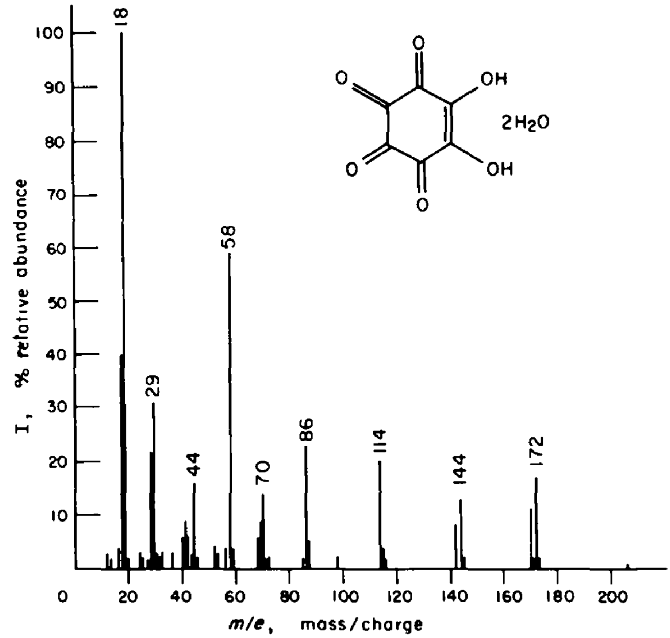
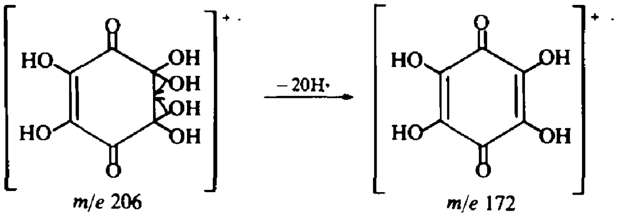


FIG. 3.



m/e 206
III

m/e 172
VII

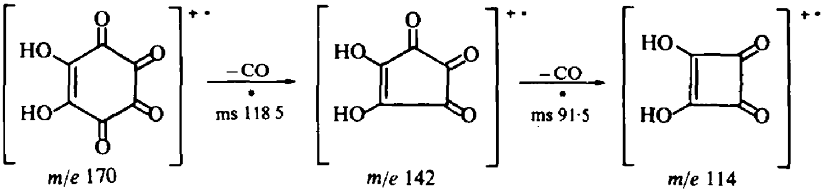
DIAG. D

The fragmentation of the anhydrous rhodizonic acid ion III m/e 170 follows the characteristic pattern observed in croconic acid II and squaric acid I. (Diag. E).

The base peak occurs at m/e 18, this is not surprising since dehydration of rhodizonic acid dihydrate III would be expected to occur under the high vacuum conditions in the mass spectrometer. Eistert and Bock[21] have found that upon heating in a high vacuum the anhydrous rhodizonicacid is obtained, while under normal pressure carbon dioxide is produced. The relatively intense peak at m/e 44, due to carbon dioxide, suggests that thermal breakdown as well as electron impact breakdown of rhodizonic acid has occurred in the mass spectrometer.

Mass spectral fragmentation of the oxidation products

Octahydroxycyclobutane IV has been prepared by the oxidation of squaric acid I, and from a study of its IR and Raman spectra West *et al.*[23] proposed a fully hydroxylated symmetrical planar structure.

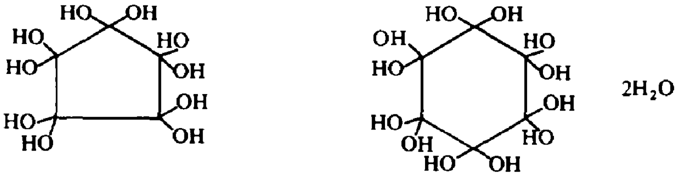


III II I

DIAG. E

Similarly, leuconic acid pentahydrate V[24] and triquinoyl octahydrate VI[25] can be prepared by the oxidation of croconic acid II and rhodizonic acid III (or tetrahydroxy-*p*-benzoquinone VII) respectively.

The structures of these compounds have been controversial for many years and the absence of a characteristic absorption band in the CO region of the IR spectra of these compounds led Person and Williams[26] to propose fully hydroxylated *gem*-diol structures for both leuconic acid pentahydrate V and triquinoyl octahydrate VI. (Diag. F).



V VI

DIAG. F

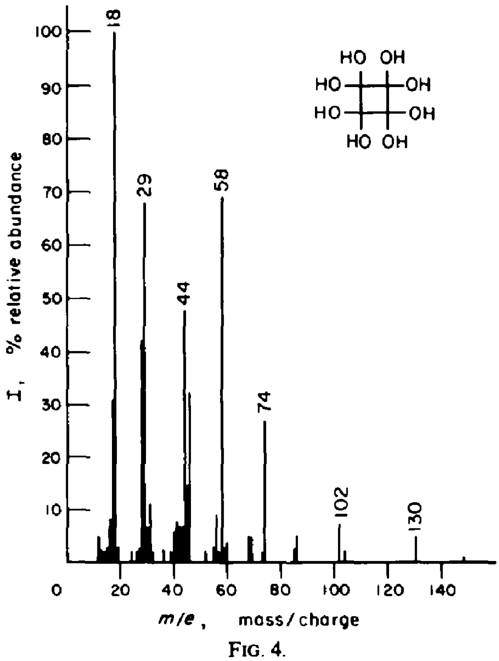
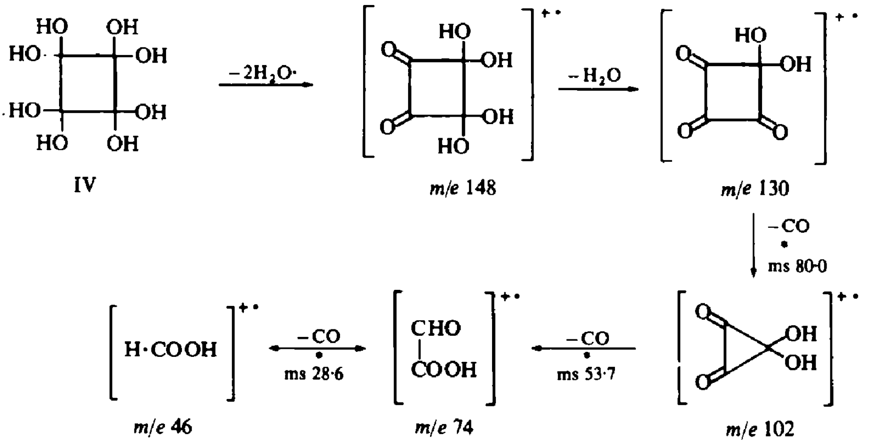


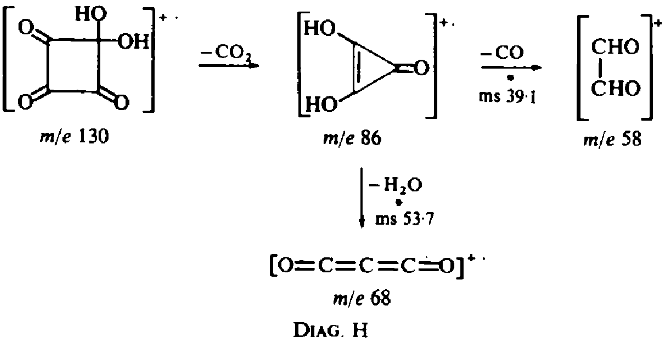
FIG. 4.

The mass spectrum of octahydroxycyclobutane IV (Fig. 4) shows no parent ion peak of the fully hydroxylated structure at *m/e* 184. Also it does not show an ion peak at *m/e* 112 due to the fully dehydrated compound cyclobutane–tetrone. The highest ion peak occurs at *m/e* 148 and is of very low intensity, indicating a rather unstable molecular ion. The first relatively intense peak occurs at *m/e* 130 whose fragmentation can be represented as follows. (Diag. G).



DIAG. G

The fragment ion peaks at *m/e* 86, 68, 58 can be envisaged as arising from the following fragmentation scheme: (Diag. H).



DIAG. H

The suggested elimination of carbon dioxide is supported by the presence of a relatively intense peak at *m/e* 44.

Leuconic acid pentahydrate V, upon electron impact, shows no parent ion peak at *m/e* 230 and also shows no peak for the fully dehydrated molecule at *m/e* 140 (Fig. 5). It breaks down to give a parent peak of the croconic acid ion, *m/e* 142. The fragmentation of this ion then follows a very similar pattern to that shown by croconic acid II. (Fig. 5 and Fig. 2). The base peak is *m/e* 18 so that dehydration must play an important part, however, it does not appear to go to completion. Eistert *et al.*[22] found that leuconic acid pentahydrate V upon heating at 150–160° decomposed with the production of carbon dioxide, water and a carbonaceous residue from which

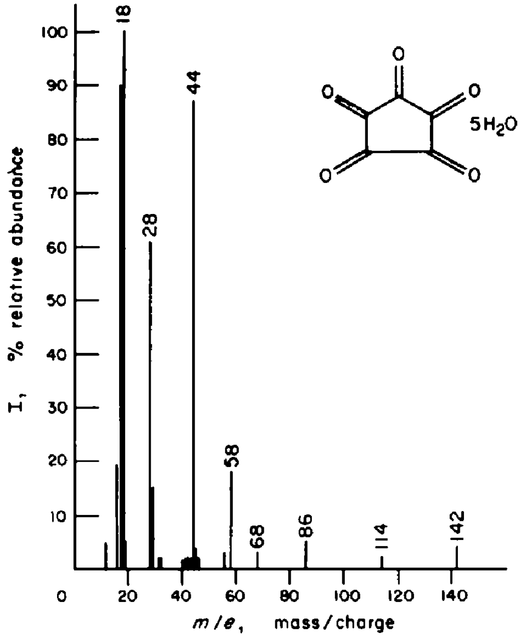


Fig. 5.

they were able to isolate a small amount of croconic acid. These results would indicate that both thermal and electron impact fragmentation is occurring in the mass spectrometer.

The mass spectrum of triquinoyl octahydrate VI (Fig. 6) is similar to both the

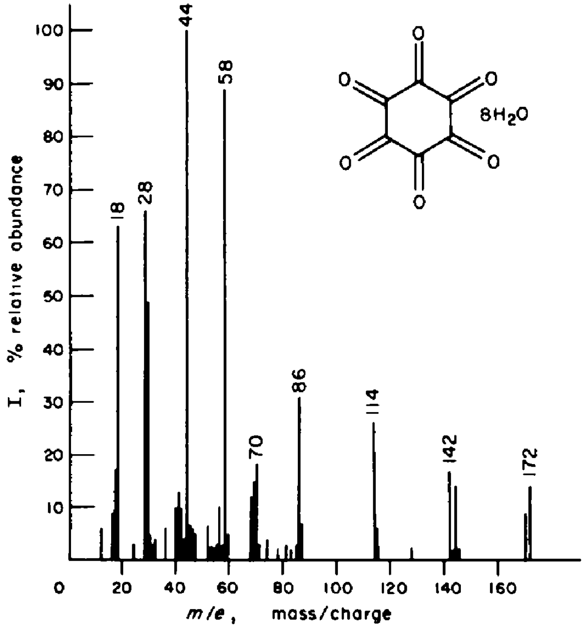
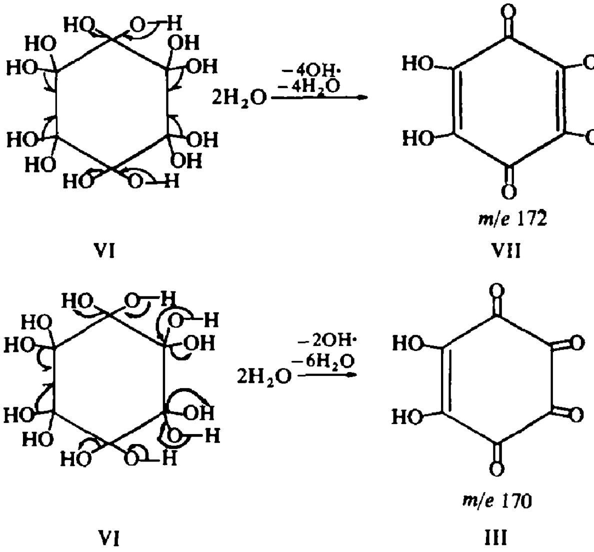


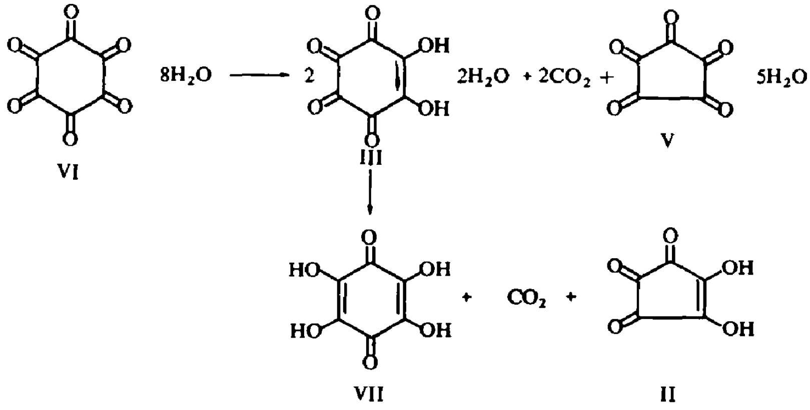
Fig. 6.

octahydroxycyclobutane IV and leuconic acid pentahydrate V spectra in that it does not show a parent ion peak of either the fully hydrated molecule at *m/e* 312 or the fully dehydrated molecule at *m/e* 168. Triquinoyl octahydrate VI breaks down to give a relatively intense parent ion peak at *m/e* 172, due to the tetrahydroxy-*p*-benzoquinone ion VII, and also gives a relatively intense peak at *m/e* 170, due to the anhydrous rhodizonic acid ion III. The production of these two ions can be visualised as arising from the loss of water and of hydroxyl ions from the fully hydroxylated triquinoyl. (Diag. I).



Diag. I

These two molecular ions then break down as in their individual mass spectra (Fig. 3 and Fig. 7). The base peak is at *m/e* 44, due to the carbon dioxide ion. This suggests that thermal degradation is also taking place in the mass spectrometer. Dehydration experiments carried out by Bergel,[27] and Eistert *et al.*[22] also yielded carbon dioxide.



Diag. J

Bergel found that triquinoyl octahydrate VI upon heating in a high vacuum at 135° lost water, carbon dioxide and yielded either rhodizonic acid III or croconic acid II.

The experiments of Eistert *et al.*[22] led to the following scheme for the so-called "redox-disproportionation" of triquinoyl octahydrate VI. (Diag. J).

The mass spectral data support the postulated fully hydroxylated, *gem*-diol structures for these compounds and indicate that the fully dehydrated carbonyl compounds do not appear to be sufficiently stable to be detected in the mass spectrometer.

*Mass spectral fragmentation of tetrahydroxy-*p*-benzoquinone*

Tetrahydroxy-*p*-benzoquinone VII and its di-sodium salt are of importance in the preparation of all the 5- and 6-membered ring compounds discussed, and the quinone itself can be looked upon as the reduction product of rhodizonic acid dihydrate II and triquinoyl octahydrate VI. The structure of tetrahydroxy-*p*-benzoquinone dihydrate VII, is known from the work of Klug.[28]

The dihydrate of tetrahydroxy-*p*-benzoquinone VII, upon electron impact, gives a parent ion peak of the anhydrous quinone *m*/*e* 172, which is also the base peak, indicating the high stability of this structure. (Fig. 7).

The fragmentation pattern can be represented by the following scheme: (Diag. K).

The intensity of the ion peak *m*/*e* 144 suggests a high stability for the postulated tetrahydroxy-cyclopentadienone ion, which may break down via two paths by loss

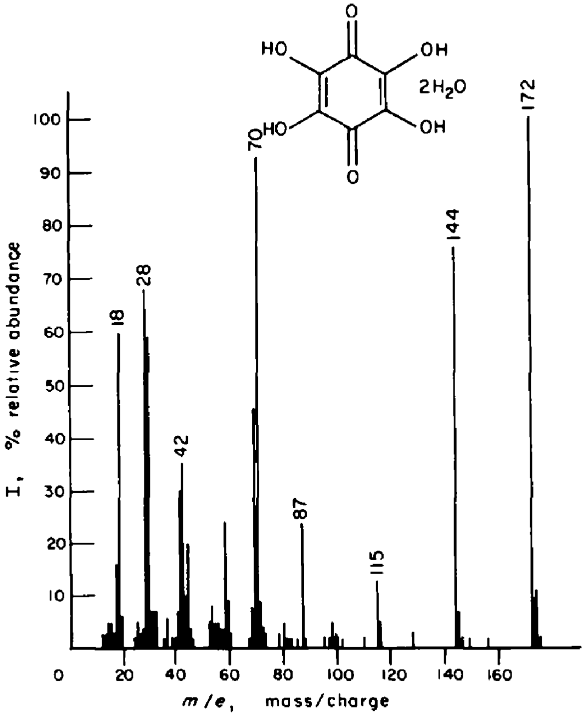
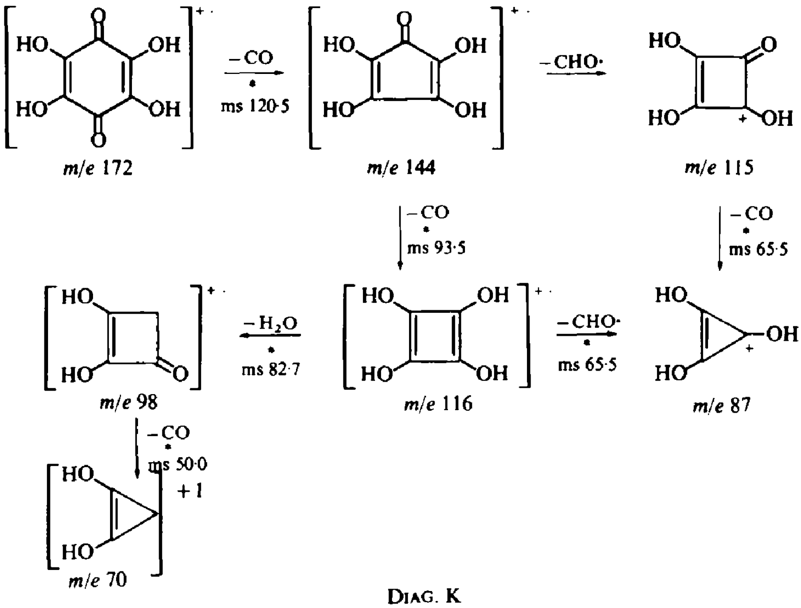


FIG. 7



DIAG. K

of a formyl radical and by the loss of carbon monoxide. The ion at m/e 116 can be postulated as the tetrahydroxy-cyclobutadiene ion which would be expected to be unstable. Simple Hückel LCAO–MO calculations[29] on the tetrahydroxy-cyclobutadiene molecule suggest that the molecule is a di-radical, with the two unpaired electrons in degenerate, anti-bonding orbitals.

The mass spectrometric study of these polycarbonyl compounds adds support to the postulate that the cyclic di-enols are members of one series of compounds, $C_nO_nH_2$, and provides some evidence for the existence of the lowest member of this series, dihydroxy-cyclopropenone. The close similarity between the three oxidation products is indicated by their behaviour upon electron impact.

EXPERIMENTAL

The mass spectra were measured using an A.E.I. M.S. 12 mass spectrometer. This is a single focussing instrument with a 90° sector, 30 cm radius magnetic analyser. The standard Bleakney type source was used and the compounds were inserted via the direct insertion probes.

Some difficulty was experienced in maintaining the stable low pressures necessary to give a standard fragmentation pattern with some of the more volatile compounds. This was partly overcome by measuring the spectra of these compounds with the sample probe tip fully withdrawn into the probe tube and the source at a low temp, 70–100°.

The electron beam energy was at 70 eV run from a rhenium filament, with the ionizing current at 100 μA. Some 12 eV, 20 μA spectra were also run to give simplified spectra as an aid to interpretation.

Preparation of samples

(I) *Squaric acid* I. This compound was obtained from Fluka A.G. Switzerland, and purified according to the method of Park *et al.*[8] (Found: C, 42·24; H, 2·04. Calc. for $C_4H_2O_4$: C, 42·12; H, 1·78%).

(II) *Croconic acid* II. Croconic acid was obtained from tetrahydroxy-*p*-benzoquinone using the method of Yamada and Hirata.[30] (Found: C, 41·43; H, 1·60. Calc. for $C_5H_2O_5$: C, 42·27; H, 1·42%).

(III) *Rhodizonic acid dihydrate* III *and triquinoyl octahydrate* VI. Rhodizonic acid dihydrate was prepared by a modification of the method used by Eistert and Bock[21] to prepare triquinoyl octahydrate.

7·5 g of tetrahydroxy-*p*-benzoquinone dihydrate were suspended in 50 ml glacial AcOH and Br_2 added to the stirred suspension until a permanent brown colour was obtained. The stirring was continued for 15 min, at room temp. The brown solid was filtered off and washed thoroughly with glacial AcOH and a small amount of acetone, giving crude rhodizonic acid dihydrate. The filtrate was treated with a small amount of water and upon cooling in a refrigerator colourless crystals of triquinoyl octahydrate were obtained. These were filtered off, thoroughly washed with water, acetone and ether, and air dried, yield of triquinoyl octahydrate, 3·15 g. (Found: C, 23·36; H, 5·10. Calc. for $C_6O_6\cdot 8H_2O$: C, 23·08; H, 5·17%).

The crude rhodizonic acid was purified by dissolving in the minimum amount of warm THF, filtering, and re-precipitating rhodizonic acid by the addition of pet. ether. The solid was filtered off and washed with small amounts of acetone and ether. The purification was repeated, yield of rhodizonic acid dihydrate, 2·35 g, 31·6% of theory. (Found: C, 34·90; H, 3·02. Calc. for $C_6H_2O_6\cdot 2H_2O$: C, 34·96; H, 2·94%).

(IV) *Octahydroxycyclobutane* IV. Octahydroxycyclobutane was prepared according to the method of West *et al.*[23] from squaric acid. (Found: C, 26·13; H, 4·45. Calc. for $C_4H_8O_8$: C, 26·09; H, 4·38%).

(V) *Leuconic acid pentahydrate* V. Leuconic acid pentahydrate was obtained from croconic acid by the method of Sager *et al.*[31] (Found: C, 25·98; H, 4·79. Calc. for $C_5O_5\cdot 5H_2O$: C, 26·09; H, 4·38%).

(VI) *Tetrahydroxy*-p-*benzoquinone dihydrate* VII. The method of Preisler and Berger[32] was used in the preparation of tetrahydroxy-*p*-benzoquinone dihydrate. (Found: C, 34·66; H, 4·06. Calc. for $C_6H_4O_6\cdot 2H_2O$: C, 34·62; H, 3·87%).

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