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TETRAHEDRAL $C_4R_4^{+\cdot}$ IN THE MASS SPECTRAL FRAGMENTATION OF THIONESSAL DIOXIDE

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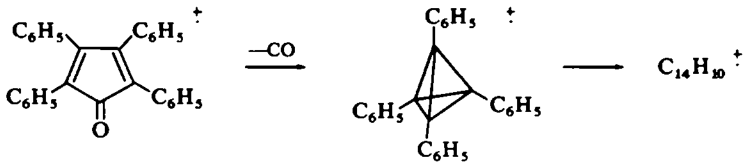
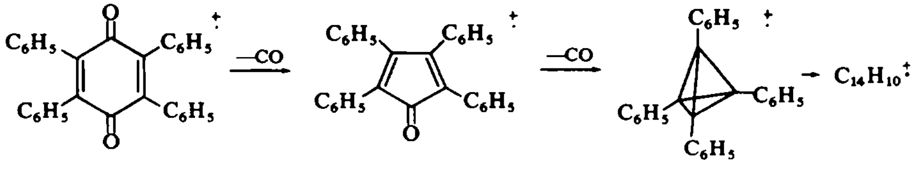
Abstract—On electron impact, tetraphenylthiophene-1,1-dioxide (thionessal dioxide) loses SO_2 to give $(C_6H_5)_4C_4^{+\cdot}$. The *p*-fluoro labeling technique has been used to determine whether this ion is acyclic, or whether it attains square or tetrahedral symmetry. The energetics for the loss of SO_2 are sufficiently similar to those for the loss of CO from tetracyclone that the $C_4R_4^{+\cdot}$ ion attains very nearly the same, i.e. distorted tetrahedral, symmetry.

Recently we have developed the *p*-fluoro labeling technique, a supplement to the more obvious isotopic labeling methods, for the study of symmetry in gaseous ions containing aryl groups.[1] This technique has its origin in the observations that in the mass spectra of typical aromatic compounds the *p*-fluoro substituent has very little effect on the rates of formation of ions[2] and very little effect on their rates of decomposition.[3,4] Our first application of this method to the study of gaseous ions was the demonstration that distorted tetrahedral symmetry is attained by the $(M - CO)^{+\cdot}$ ion in the mass spectrum of tetracyclone (Eq. 1).[1,5]



(1)

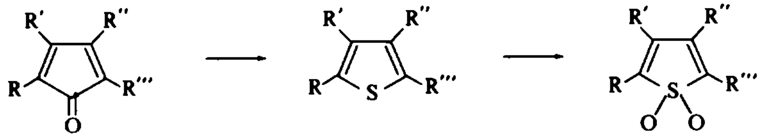
Tetraphenyl-*p*-benzoquinones also decompose by the loss of two molecules of CO to produce the same species of tetrahedral symmetry (Eq. 2).[6]



(2)

It was considered of interest to examine other possible sources of the $(C_6H_5)_4C_4^{+\cdot}$ ion in an attempt to determine how general the phenomenon of tetrahedral symmetry is, particularly in contrast to square or rectangular symmetry for such species. One closely similar example would be tetraphenylthiophene dioxide (IIIa), provided this molecule readily loses the small molecule SO_2 after electron impact. Such a loss, while reasonable by analogy to the case of the tetracyclone, seemed less than assured after examination of the literature on aromatic and heterocyclic sulfones. In fact, a number of laboratories have found these compounds of interest because of the rearrangements which must be invoked to explain their fragmentation patterns. For example, diaryl sulfones apparently undergo an S → O rearrangement of one aryl group before fragmentation.[7] Heterocyclic compounds also seem to suffer a similar fate, since ready losses of oxygen as CO, SO, and HCO are noted in the mass spectrum of benzothiophene dioxide,[8, 9] and at least CO and SO in dibenzothiophene dioxide.[10, 11] On the other hand, the loss of SO_2 is reasonably competitive with these strange losses in the spectra of thianthrene monosulfone and phenothoxin sulfone,[9] and is responsible for an important peak in a high temperature spectrum of a condensed system containing a dihydrothiophene ring, though pyrolysis products may be responsible for most of the ion current in this spectrum.[12]

A sample of tetraphenylthiophene was prepared from tetracyclone by heating with sulfur.[13] The heterocycle was then oxidized with hydrogen peroxide[14, 15] to the sulfone (Eq. 3), whose mass spectrum is illustrated in Fig. 1.



I II III (3)

a, $R = R' = R'' = R''' = C_6H_5$
b, $R = R''' = p\text{-}FC_6H_4$; $R' = R'' = C_6H_5$
c, $R = R'' = p\text{-}FC_6H_4$; $R' = R''' = C_6H_5$

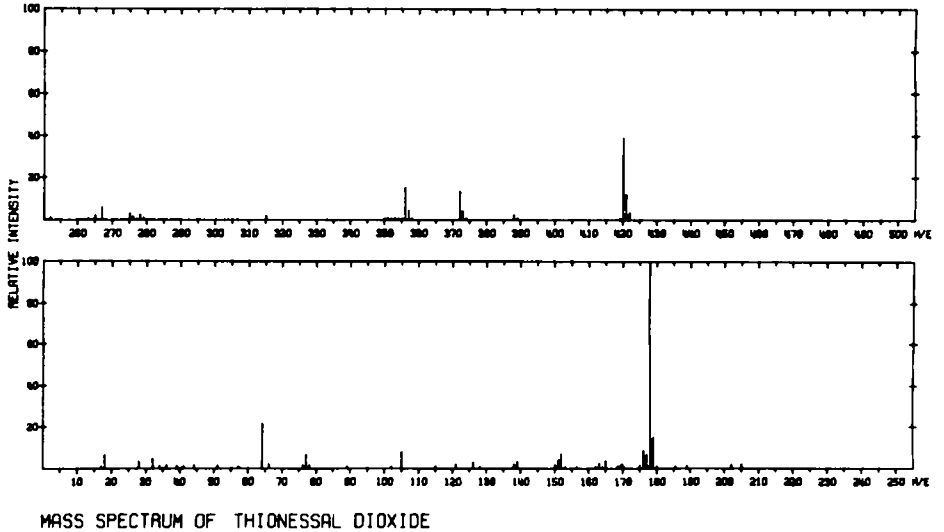
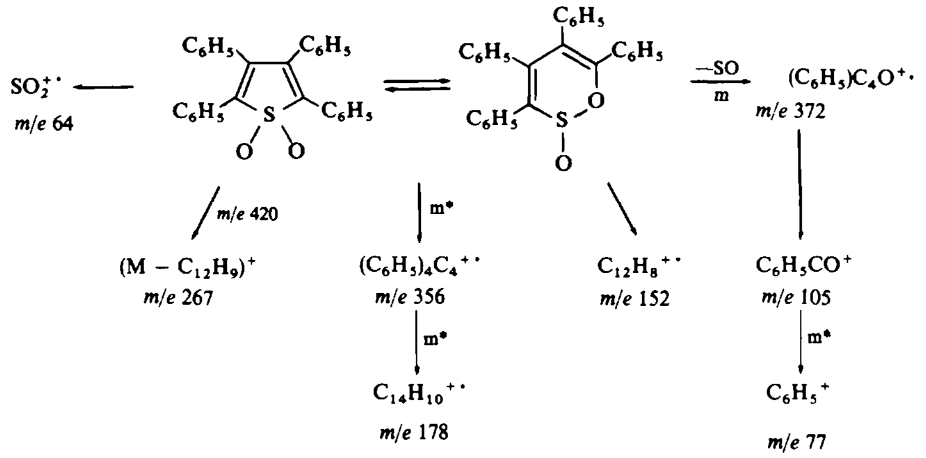


FIG. 1.

Some of the peaks in the spectrum do suggest a rearrangement of the molecular ion, but for the purpose of this study the loss of SO_2 is the most important point. This loss produces a $(C_6H_5)_4C_4^{+\cdot}$ ion which decomposes by halving; both processes are supported by metastable peaks at m/e 302 (broad; calcd for 420 → 356, 301·8) and m/e 89·0 (calcd for 356 → 178, 89·0) respectively. The most intense ions in the spectrum can be interpreted on the basis of the Scheme. The loss of SO from the molecular ion is most easily envisaged by invoking the intermediacy of an isomeric molecular ion in which an S → O migration of a ring carbon has occurred. This reaction is possibly analogous to the loss of CO from 2-pyrones, an observation which has spawned energetic discussion.[16] None of the other ions are unusual; the simultaneous loss of most of two phenyl residues is parallel to many other systems.[17]



The structure of the $(C_6H_5)_4C_4^{+\cdot}$ ion produced in this system was studied further by p-fluoro labeling, since the necessary labeled tetracyclones (Ib, Ic) were available[5] for conversion to the thiophenes and thiophene dioxides. These compounds were prepared by analogous routes (Eq. 3). Their mass spectra are similar to those of the unsubstituted compound, the only item of interest being the distributions of the

TABLE 1. SIGNIFICANT IONS IN THE MASS SPECTRA OF p-FLUORO-LABELED TETRACYCLONES AND THIONESSAL DIOXIDES*

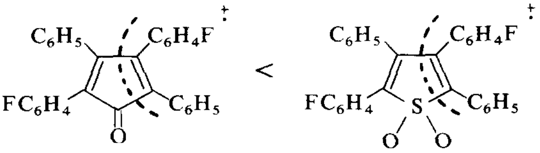
m/e	assignment	relative intensities			
		Ib	Ic	IIIb	IIIc
$M^{+\cdot}$		100	100	91	60
392	$(C_6H_5)_2(FC_6H_4)_2C_4^{+\cdot}$	33	35	23	20
214	$C_{14}H_8F_2^{+\cdot}$	17	7	7	4
196	$C_{14}H_9F^{+\cdot}$	97	80	100	100
178	$C_{14}H_{10}^{+\cdot}$	35	13	13	8

* All relative intensities were independent of temperature up to at least 180°. The data for Ib and Ic are taken from Ref. 5.

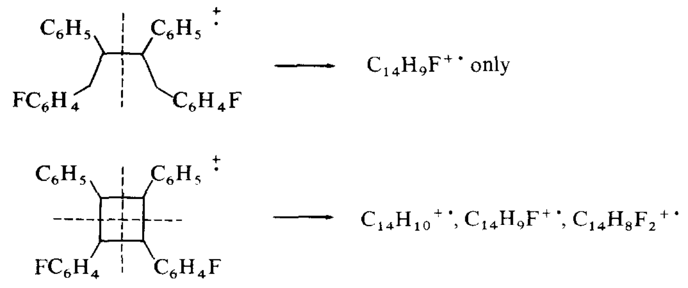
p-fluoro ladel in fragment peaks. In particular, the relative intensities of the fragment peaks corresponding to halving of the $(C_6H_5)_2(FC_6H_4)_2C_4^{+\bullet}$ ion reflect some of the symmetry features of that ion, particularly when they are compared with data for the corresponding ion in the spectra of the substituted tetracyclones (Table 1). Because of the existence of metastable ions, part (but not necessarily all) of the intensities at these masses may be ascribed to the processes in Eq. 4. The increased

$$\begin{tikzcd}
 & & m/e\ 214 \\
M^{+\bullet} \arrow[r] & m/e\ 392 \arrow[ur] \arrow[r] \arrow[dr] & m/e\ 196 \\
 & & m/e\ 178
\end{tikzcd} \tag{4}$$

intensity of the *m/e* 196 ion in the spectra of the sulfones, in comparison to those of the ketones, may reflect increased contributions from other sources, such as fragmentation of the molecular ion. However, there is at least qualitative similarity



between the sets of data, and qualitatively similar conclusions can be drawn. For example, it may be concluded that the $C_4R_4^{+\bullet}$ ion is not always acyclic; it could not produce $C_{14}H_8F_2^{+\bullet}$ unless the two carbons bearing fluorophenyl rings were joined (Eq. 5) after the molecular ion from IIIb lost SO_2. Further, this cyclic structure



(5)

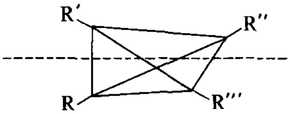
cannot be simply monocyclic, since $C_{14}H_{10}^{+\bullet}$ and $C_{14}H_8F_2^{+\bullet}$ are produced from IIIc. The simplest structure accounting for these results must have each ring carbon attached to each of the others at some point in its history; more complex descriptions could include sequential attachment of each carbon to the others in a series of rearrangements.

Because of the interference by other possible pathways, as noted above, it is dangerous to assign significance to intensities of normal ions in this discussion; there is also the problem of evaluating the effect of the *p*-fluoro substituent on the further decomposition of the ion, so that the intensity of substituted ions will be raised or lowered by an unknown (though presumably small, as stated above) amount relative to unsubstituted ions. Both of these difficulties can be removed by the examination of the intensities of integrated metastable intensities for the transitions of interest; metastable peaks pinpoint only a single transition, avoiding both interference from other sources of the daughter ion and also consumption of the intensity of the daughter by the formation of further products (granddaughter ions). The appropriate metastable intensities, relative to the intensity of the metastable ion producing unsubstituted daughter ions (*m/e* 178) in each spectrum, are compared for the ketones and sulfones in Table 2. In this more accurate measure of the amounts of products formed in the halving of $C_4R_4^{+\cdot}$, the great similarity of the structures of the ions is obvious. To a very close approximation, the conclusions about the structure of $C_4R_4^{+\cdot}$ from tetracyclones[5] are equally applicable here. These are: at least some of the $C_4R_4^{+\cdot}$ ions have a tetrahedral structure; if there is only one kind of $C_4R_4^{+\cdot}$, then it is not a perfect tetrahedron, but is distorted; the similarity of intensities of *m/e* 117·0 in IIIb and IIIc (as in Ib and Ic) suggests that this distortion is elongation of one of the twofold axes of the tetrahedron, as in IV. There is evidence for singularity of structure: peak intensities do not vary to a great extent at low voltage. (The intensities of metastables being as reproducible as could be expected considering difficulty of measuring small peaks, overlap of the *m/e* 81·0 metastable with another at 84·5 which becomes of increasing relative size at low voltage, and superimposition of multiply charged ions on the metastable of highest *m/e*.) The low-voltage values obtained for IIIb have the ratio 1:3·4:0·65. The normal ion intensities at *m/e* 178, 196, and 214 in the same spectrum have the ratio 10:100:4·9, indicating somewhat increased importance of the alternate process suggested earlier for the *m/e* peak, but no change in the ratio of 178 to 214. These observations are certainly not conclusive with respect to demonstration of a single structure for the ion.

TABLE 2. METASTABLE PEAK INTENSITIES RELEVANT TO THE FRAGMENTATION OF $C_4R_4^{+\cdot}$ IN THE MASS SPECTRA OF TETRACYCLONES AND THIONESSAL DIOXIDES*

m/e	assignment	relative intensity			
		Ib	IIIb	Ic	IIIc
81·0	392 → 178	1	1	1	1
98·0	392 → 196	3·2	3·2	5·2	5·7
117·0	392 → 214	0·93	0·83	0·87	0·89

* The integrated intensities are reported as if they were recorded on a linear *m/e* scale. This was obtained by multiplying by the appropriate factor after measuring the actual scale contraction on each spectrum.



IV

Several other ions in the spectra of the labeled compounds have some bearing on the structure of the $(C_6H_5)_2(C_6H_4F)_2C_4O^{+\cdot}$ ion at m/e 408. Metastable transitions confirm the decomposition of this ion to $(C_6H_5)_2FC_6H_4C_3^+$ (m/e 285, metastable at 199) and $(FC_6H_4)_2C_6H_5C_3^+$ (m/e 303, metastable at 225·0) by the loss of FC_6H_4CO and C_6H_5CO, respectively. The sum of these two peaks in the spectra of IIIb and IIIc is about 7%. The distribution of this faction m/e 285 and m/e 303 is 94:6 in IIIb and 47:53 in IIIc, essentially as would be expected if the original alpha and beta positions of the thiophene ring still retained identity up to the loss of the benzoyl or fluorobenzoyl ion. The process which appears to be conjugate to this, the formation of $C_6H_5CO^+$ or $FC_6H_4CO^+$, is not marked by significant metastable transitions, yet the ions of these structures comprise about 8% relative abundance. The distribution of this 8% between m/e 105 and m/e 123 is 43:57 in IIIb and 58:42 in IIIc. Obviously scrambling of the ring positions has progressed to a considerable extent before the benzoyl fragment ions are formed, and so the formation of these ions cannot be exactly conjugate to the formation of the m/e 285 and 303 ions. Whether they have a totally different source or whether they are formed from the distribution of ions of m/e 408 cannot be said. It is amusing to note that these scrambling results are almost the antithesis of the results for furan.[18] Deuterium labeling studies there indicate that positional identity of the ring carbons is retained in the formation of HCO^+, but the formation of the conjugate $C_3H_3^+$ shows some scrambling; the authors preferred another mechanism to the single-step loss of HCO from the molecular ion, however. Thus the structure of m/e 408 is not at all similar to the molecular ion of furan. Perhaps the ability of the phenyl substituents to interact with the charge or radical site has a great influence on the structure of the central part of the ion.

Further studies on the generation of $C_4R_4^{+\cdot}$, whether tetrahedral or planar, will be reported from our laboratory.

EXPERIMENTAL

Mass spectra were recorded on a Hitachi RMU 6E instrument with sample introduction by the direct insertion probe. The ionizing current was 80 μa; trap current, 50μa; ionizing voltage 75 eV, except for low voltage runs, where a nominal value of 15 eV was used. In such experiments the trap current was maintained at 2 μa.

Merck aluminium oxide "Suitable for Chromatographic Adsorption" was used for column purification of the thiophenes. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

The preparation of tetraphenylthiophene and tetraphenylthiophene dioxide followed literature procedures exactly.[13–15]

2,5-*Bis*(p-*fluorophenyl*)3,4-*diphenylthiophene* (IIb). A mixture of 2,5-bis(p-fluorophenyl)3,4-diphenylcyclopentadienone[5] (540 mg, 1·27 mmole) and S (65 mg, 2·01 mmole) was heated according to Fieser's procedure[13] and then chromatographed on alumina, eluting with 2% benzene to yield 400 mg (0·94 mmole, 74%) of white needles. Recrystallization from EtOH gave an analytical sample, m.p. 171–174°. (Found: C, 79·33; H, 4·31. $C_{28}H_{18}F_2S$ requires: C, 79·21; H, 4·27%).

2,4-*Bis*(p-*fluorophenyl*)-3,5-*diphenylthiophene* (IIc) was prepared in a similar fashion from S and 2,4-bis(p-fluorophenyl)3,5-diphenylcyclopentadienone[5] and recrystallized from EtOH, m.p. 167–172°. (Found: C, 79·25; H, 4·32. $C_{28}H_{18}F_2S$ requires: C, 79·21; H, 4·27%).

2,5-Bis(*p-fluorophenyl*)3,4-*diphenylthiophene* 1,1-*dioxide* (IIIb). The appropriate thiophene IIIb (275 mg, 0·65 mmole) was dissolved in 10 ml hot AcOH and 1·5 ml 30% H_2O_2 was added.[14, 15] The soln was refluxed for an hr. On cooling and partial evaporation of the solvent, yellow crystals (262 mg, 93%) were deposited. Two recrystallizations from benzene gave the analytical sample, m.p. 261–262·5°. (Found: C, 73·39; H, 3·94. $C_{28}H_{18}F_2O_2S$ requires: C, 73·66; H, 3·97%).

2,4-Bis (p-fluorophenyl)3,5-diphenylthiophene 1,1-dioxide (IIIc), m.p. 244·5–246·5°, was prepared in similar fashion. (Found: C, 73·56; H, 3·95. $C_{28}H_{18}F_2O_2S$ requires: C, 73·66; H, 3·97%).

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