Cumene hydroperoxide and *p*-carboxydimethyl-benzyl hydroperoxide show other differences in decomposition behavior in alkaline solution. Cumene hydroperoxide undergoes a rapid alkaline-catalyzed decomposition when heated above 60°, or at room temperature in the presence of an additive, such as succinonitrile.[3] No decomposition of the carboxylated hydroperoxide was detected after 72 hr. at 65°, pH 9.5, nor was any detected at room temperature in the presence of succinonitrile. In fact, at 100° a water solution of the free acid decomposes faster (partially by acid catalysis) than does the salt at pH 9.5.

Such differences in the reactivity of the two hydroperoxides in alkaline solution cannot be accounted for by the inductive effect of the *p*-carboxyl group. The *p*-carboxylate ion is a weak electron-withdrawing group with a Hammett σ-value +0.16.[19] When transmitted through the α-carbon out to the hydroperoxy group, this effect will be insignificant. A more attractive explanation lies in restriction of complex formation.

Perhaps by electrostatic repulsion the carboxylate group with a negative charge prevents the molecule from complexing with itself or with the anion of the hydroperoxide group. The ability of cumene hydroperoxide to form complexes is responsible for its more rapid decomposition in alkali.[3,20] If this complexing ability is repressed by the carboxylate group on the ring, stability is greatly enhanced, and the conditions for induced or catalyzed decomposition no longer exist.

The results reported for the action of other oxidizing agents on cumene hydroperoxide can be accommodated by the free-radical mechanism given here for a hypochlorite reaction. In an acid system, as in the lead tetraacetate reaction, the induced decomposition of cumene hydroperoxide is suppressed.

(19) E. Berliner and L. C. Monack, *J. Am. Chem. Soc.*, **74**, 1574 (1952).

(20) A. V. Tobolsky and L. R. Matlock, *J. Polymer Sci.*, **55**, 49 (1961); V. A. Belayaev and M. S. Nemtsov, *Zh. Obshch. Khim.*, **32**, 3113 (1962).

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The Electron Impact Fragmentation of 4-Pyrone

BY PETER BEAK, THOMAS H. KINSTLE, AND GLEN A. CARLS

A comparison of the mass spectral fragmentations of 4-pyrone and some isotopically substituted 4-pyrones is used to make structural assignments to the major fragments in the spectrum of the unlabeled compound. An estimate of the generality of the observed fragmentation pathways is made by a comparison of the predicted and observed fragmentation patterns of 3,5-dimethyl-4-pyrone and 2,6-dimethyl-4-pyrone.

The empirical correlation of the electron impact fragmentation patterns observed in mass spectrometry with the pathways of chemical processes has proved to be an intriguing and fundamental study, both for its own sake and for its utility in making structural assignments.[1] The present interpretation of the mass spectrum of 4-pyrone (1) provides additional confirmation of the utility of this approach and furnishes model pathways for the fragmentation of molecules which contain the 4-pyrone nucleus.[2,3]
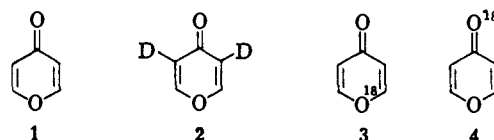
Results and Discussion

The partial mass spectra of 4-pyrone, 3,5-d_2-4-pyrone[4] (2) and an approximately 1:1 mixture[4] of 1-O^{18}-4-pyrone (3) and 7- O^{18}-4-pyrone (4) are presented in Table I, and the mass spectrum of the unlabeled 4-pyrone is shown in Fig. 1. The data for

1   2   3   4

the labeled compounds in Table I were obtained from the spectra of mixtures.

TABLE I

PEAK INTENSITIES IN THE MASS SPECTRA OF THE 4-PYRONES

1, 2, 3, and 4

m/e	1	2	3 and 4
98		32	32
96	32		
72			12
71		15	17
70	15	22	
69	17		
68	5		
43		14	
42	14		
41	3		
39	3		

The fragmentation pattern observed for 4-pyrone is rationalized below. The peak at m/e 97 is wholly accountable for on the basis of naturally occurring isotopes indicating that the ion-molecule collisions observed in the case of other basic compounds[5,6] is not

(1) For outlines and reviews of the concepts in this area see (a) F. W. McLafferty, "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachrod and W. D. Phillips, Ed., Academic Press, Inc., New York, N. Y., 1962, p. 93; (b) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 251; (c) J. H. Beynon, "Mass Spectrometry," Elsevier Publishing Co., Amsterdam, 1960, p. 325; (d) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden–Day, Inc., San Francisco, Calif., 1964; (e) F. W. McLafferty, Ed., "Mass Spectrometry of Organic Ions," Academic Press, Inc., New York, N. Y., 1963, Chapters 7 and 9–13.

(2) The 4-pyrone ring is found in a large number of naturally occurring compounds. A recent review of this area is given by F. M. Dean, "Naturally Occurring Oxygen Ring Compounds," Butterworths, London, 1963.

(3) R. I. Reed and J. M. Wilson, *J. Chem. Soc.*, 5949 (1963), have recently interpreted the mass spectral fragmentation patterns of some rotenoids and flavonoids by pathways which are analogous to those discussed herein.

(4) P. Beak and G. A. Carls, *J. Org. Chem.*, **29**, 2678 (1964).

(5) F. W. McLafferty, *Anal. Chem.*, **29**, 1782 (1957); (b) ref. 1b, pp. 55–56.

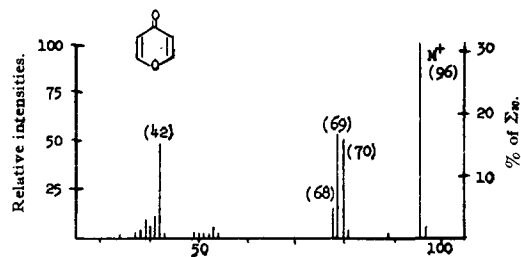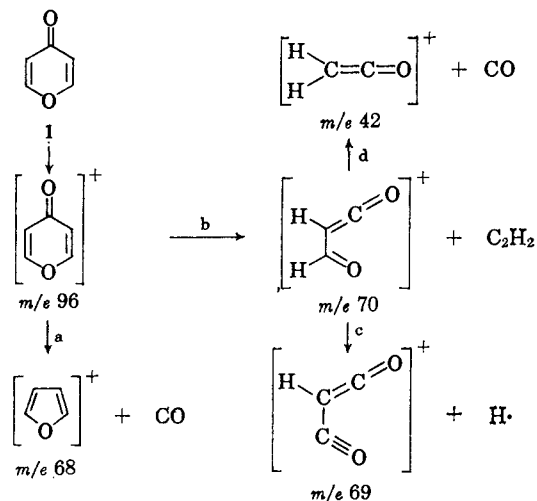(6) For evidence on the basicity of 4-pyrone see P. Beak, *Tetrahedron*, **20**, 831 (1964).

Fig. 1.—Mass spectrum of 4-pyrone.

particularly favored in the case of 4-pyrone under the conditions used.

Evidence for the fragmentation of the molecular ion (m/e 96) by pathway a to give furan ion (m/e 68) and carbon monoxide is provided by the presence of a metastable peak centered at m/e 48.5 (calcd. 48.2). The corresponding decomposition of the molecular ion of 3,5-d_2-4-pyrone gives a fragment at m/e 70 with the expected intensity[7] and with a metastable peak centered at 50.2 (calcd. 50.1). Support for this interpretation is found in the loss of carbon monoxide reported by Beynon, Lester, and Williams[8] for similar decompositions and more recently observed in the fragmentation of tropone,[9] xanthone,[10] and some rotenoids and flavonoids.[3] It is of more than casual interest that an analogous thermal loss of carbon monoxide has been reported for xanthone and 2,6-dimethyl-4-pyrone.[11]

The decomposition of the molecular ion by pathway b to acetylene and a positively charged substituted ketene fragment may be visualized as an example of the "retro-Diels-Alder" type[12] of fragmentation. A similar process has been postulated in the fragmentation of cyclohexenones,[13] xanthone,[10] and the rote-
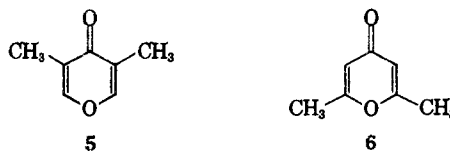
noids and flavonoids.[3] The analogous fragment in the spectrum of 3,5-d_2-4-pyrone, expected at m/e 71 with an intensity of 15%, is observed. The fragment at m/e 72 with an intensity of 12% in the spectrum of 3 and 4 also provides support for this pathway.

The loss of a hydrogen atom from the substituted ketene fragment produced by pathway b to give the fragment observed at m/e 69 (pathway c) finds analogy in the fragmentations reported for a number of aldehydes.[9a,14] The fragment observed at m/e 70 in the mass spectrum of 2 with an intensity of 22% may be accounted for by a combination of the expected intensity of 17% for this process and that of 5% expected for the loss of carbon monoxide analogous to pathway a. Similar confirmation of pathway c is provided by the fragment at m/e 71 with a calculated and observed intensity of 17% in the spectrum of 3 and 4. The use of progressively lower ionizing voltages for the unlabeled 4-pyrone reveals that at lower voltages the process leading to the m/e 70 fragment is favored over the process leading to the m/e 69 fragment.[15] In the same experiment it is observed that the ratio of the m/e 68 to the m/e 70 peak increases as the ionizing voltage is reduced, indicating that decomposition of the molecular ion by pathway a is favored over decomposition by pathway b at lower ionizing voltages. These observations, however, do not completely rule out the possibility of a direct decomposition of the molecular ion to the m/e 69 fragment.

The decomposition of the positively charged ketene fragment via pathway d in the case of unlabeled 4-pyrone to give carbon monoxide and the ketene ion is analogous to pathway a and to the observations of carbon monoxide formation previously cited.[3,8-10] In the spectrum of 3,5-d_2-4-pyrone the expected fragment is observed at m/e 43 with a calculated and observed intensity of 14%.

In addition it seems likely that the fragment at m/e 41 in the mass spectrum of 4-pyrone arises from the ketene ion[16] and that the m/e 39 fragment is a direct decomposition product of the furan ion presumably to the cyclopropenyl cation in accord with previous assignments.[17] The latter process is supported by the presence of a metastable peak at m/e 22.5 (calcd. m/e 22.5). With these and the above assignments 89% of the peaks above m/e 30 in the mass spectrum of 4-pyrone can be accounted for.

An assessment of the applicability of these results to problems of structural assignment may be obtained in part by a comparison of the predicted and observed spectra of 3,5-dimethyl-4-pyrone[4] (5) and 2,6-dimethyl-4-pyrone (6). On the basis of the fragmentation

5   6

(7) For the purpose of these calculations no account was taken of a possible secondary isotope effect in the fragmentation. Such an effect would be expected to be small in terms of the present context.

(8) J. H. Beynon, G. R. Lester, and A. E. Williams, J. Phys. Chem., 63, 1861 (1959).

(9) (a) J. B. McCollum and S. Meyerson, J. Am. Chem. Soc., 85, 1739 (1963); (b) J. M. Wilson, M. Osashi, H. Budzikiewicz, and C. Djerassi, Tetrahedron, 19, 2247 (1963).

(10) Ref. 1a, p. 166.

(11) N. A. Orlov and V. V. Tishenko, Zh. Russk. Fiz. Khim. Obshch., 62, 2243 (1930); Chem. Abstr., 25, 3995 (1931).

(12) (a) F. W. McLafferty, Anal. Chem., 31, 82 (1959); (b) ref. 1a, p. 147; (c) ref. 1b. p. 102.

(13) (a) J. W. Chamberlin and J. B. Gurst, unpublished results cited in ref. 1d, p. 156. (b) H. Budzikiewicz, J. M. Wilson, and C. Djerassi, J. Am. Chem. Soc., 85, 3688 (1963); (c) A recent example of the absence of this

type of process in a system where it was suspected previously has been reported by D. H. Williams, T. M. Wilson, H. Budzikiewicz, and C. Djerassi, ibid., 85, 2091 (1963).

(14) (a) J. A. Gilpin and F. W. McLafferty, Anal. Chem., 29, 990 (1957).

(15) Careful examination of the m/e 67 to 70 region under these conditions reveals the presence of a small broad peak at ca. m/e 68. Presumably this is the metastable peak associated with pathway c (calcd. m/e 68.0).

(16) L. Friedman and F. A. Long, J. Am. Chem. Soc., 75, 2837 (1953).

(17) (a) Ref. 1a, p. 138; (b) J. Collin, Bull. soc. chim. Belges, 69, 449 (1960); (c) ref. 1d, p. 226.

pathway assigned above to 4-pyrone the mass spectrum of **5** would be expected to show major ions at m/e 124, 96, 84, 83, and 56 and **6** would have major ions at m/e 124, 96, 84, 69, and 56. The mass spectra observed for **5** and **6** are shown in Fig. 2.[18] It can be readily seen that the spectra are considerably more complex than predicted. In the spectrum of 3,5-dimethyl-4-pyrone the only predicted major fragment ion is the one at m/e 56 while in the spectrum of 2,6-dimethyl-4-pyrone the predicted fragment ions appear at m/e 96 and 69. These results, however, are not inconsistent with the predicted fragmentation processes. In the mass spectrum of 3,5-dimethyl-4-pyrone the operation of a pathway analogous to a is confirmed by the presence of a metastable peak at m/e 74.8 (calcd. m/e 74.4). The failure to observe a large fragment for the product of this decomposition at m/e 96 can be ascribed to the rapid loss of a hydrogen atom from this ion to give the fragment m/e 95 which may be tentatively assigned structure **7**. The operation of similar processes in the fragmentation of 2,6-dimethyl-4-pyrone is confirmed by the presence of a metastable peak centered at m/e 75 (calcd. m/e 74.4) and by the presence of a peak at m/e 95, presumably derived from the m/e 96 fragment by loss of a hydrogen atom, tentatively assigned structure **8**.[19] The ions observed at

7   **8**
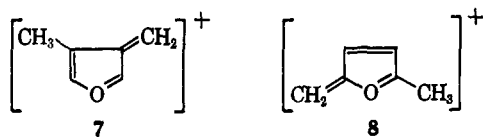
m/e 53 and 43 in the mass spectrum of **6** can be qualitatively assigned to the methylcyclopropenyl cation[19b] and the acylium ion[19b] arising from the decomposition of the 2,5-dimethylfuran ion. The use of lower ionizing voltages revealed that for the fragmentation of 2,6-dimethyl-4-pyrone the loss of carbon monoxide was by far the most favored pathway of fragmentation under these conditions. Although the analogous process was also the lowest energy fragmentation process for the molecular ion from 3,5-dimethyl-4-pyrone at lower ionizing voltages, it appeared to be less favored over competing processes than in the case of **6**. The above assignments account for 60% of the peaks above m/e 30 in the mass spectrum of 3,5-dimethyl-4-pyrone

(18) The mass spectrum of **4** has previously been obtained by Dr. F. W. McLafferty. We are grateful to Dr. McLafferty for making his results available to us.

(19) This assignment has previously been proposed in interpretations of the mass spectrum of 2,5-dimethylfuran by (a) Collin, ref. 17b, and (b) Budzikiewicz, Djerassi, and Williams, ref. 1d, p. 227.
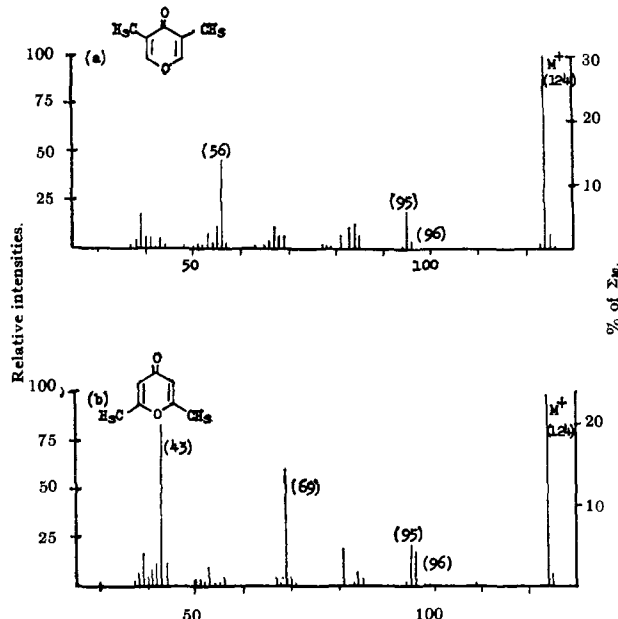
Fig. 2.—Mass spectra of 3,5-dimethyl-4-pyrone and 2,6-dimethyl-4-pyrone from m/e 30 to 130.

and 74% of the peaks above m/e 30 in the spectrum of 2,6-dimethyl-4-pyrone. Accordingly, it appears that the fragmentations of substituted 4-pyrones may be accounted for in part by using the fragmentations of 4-pyrone and its fragmentation products as models.

Experimental

The preparation of the pyrones used has previously been described.[4] The spectra were obtained on an Atlas CH 4 mass spectrometer using a variable temperature stainless steel inlet system and 70 e.v. as the ionizing potential.

The partial spectra in column 3 of Table I were calculated from the spectra of a mixture of 83% 3,5-d_2-4-pyrone, 12% 3-d-4-pyrone, and 5% unlabeled material. The intensities refer to the percent of total ionization above m/e 30[20] normalized to the values obtained with 4-pyrone and contain an error of ±2%. Column 4 of Table I was calculated from the spectra of a mixture of 88% 4-pyrone, ca. 6% 1-O^{18}-4-pyrone, and ca. 6% 7-O^{18}-4-pyrone. The intensities for the labeled material were calculated as above but with an error of ±5%.

(20) Ref. 1b, p. 42.