the intensities were 1:3.0:3.0:1, in conformance with theory for free methyl radical. When the sample was warmed to 112°K., the four-line spectrum was considerably diminished while the superimposed three-line spectrum, marked on the 112°K. spectrum, did not change appreciably. The total spread for the three peaks is 46 gauss, or 23 gauss average, which could come from two equivalent protons after detachment of an hydrogen atom from a methyl group. As both the four-line and three-line spectra seem to be present at 77°K., it is probable that methyl radical is formed by carbon–carbon bond cleavage and that $R\dot{C}H_2$ radical is formed by carbon–hydrogen bond cleavage in the photochemical primary process.

Organic Ions in the Gas Phase. XVI.
## Isomeric $C_7H_5O^+$ Ions from Benzoic Acid

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Deuterium labeling reveals that 18% of the $C_7H_5O^+$ ions in the mass spectrum of benzoic acid arises by loss of a hydroxyl group containing hydrogen from the ortho position. The product is chemically distinct from the isomeric and more abundant benzoylium ion. It is formulated as the conjugate acid of the ortho isomer of a short-lived species recently reported among the products of flash photolysis of benzenediazonium-4-carboxylate.

The literature of mass spectrometry is replete with examples of ionic species the identities of which seem, at first glance, so obvious as to scarcely merit attention but upon close scrutiny are found to be quite different from what they seem.[1] A curious example of such a species occurs in the mass spectrum of benzoic acid.

The spectra of aromatic acids are characterized by intense peaks at the parent mass less 17 and less 45 units, corresponding to the $ArCO^+$ and Ar^+ ions.[2-4] Metastable peaks establish that the latter product arises, at least in part, by secondary loss of CO from $ArCO^+$ ion.[5] The data thus define the reaction path

$$\left[Ar-C\underset{OH}{\overset{O}{<}} \right]^+ \xrightarrow{-OH} Ar\!-\!C\!\equiv\!O^+ \xrightarrow{-CO} Ar^+$$
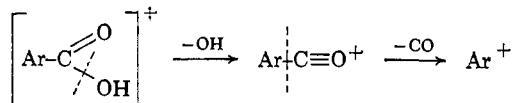
The neutral products lost in the reaction have been assumed[2,3] to consist solely of the original OH and CO groups. However, the spectrum of a sample of benzoic acid-2,3-d_2[6] suggested that about 9% of the parent-less-hydroxyl ions had lost a deuterium atom rather than protium. The possibility that part of the deuterium in the labeled acid was in the carboxyl group rather than in the ring was ruled out because the isotopic analysis of the acid was virtually identical with that of the toluene-2,3-d_2 from which it had been made.[7] The apparent incorporation of a ring hydrogen atom into the hydroxyl group lost prompted us to prepare and to study the mass spectra of benzoic acids labeled with a single deuterium in the ortho, meta, and para positions.

Experimental

The singly labeled acids were prepared from Eastman Kodak White Label bromotoluenes. These were converted to Grignard reagents and hydrolyzed with deuterium oxide; the resulting toluenes were oxidized to the acids with potassium permanganate. Chemical purity of the toluenes and benzoic acids was established by the mass spectra. Isotopic compositions, estimated from low-voltage spectra,[8] are shown in Table I.

Mass spectra of the acids were measured with 70-v. electrons on a modified[9] Consolidated Model 21-103c instrument with the inlet system at 250°.

Results and Discussion

Table II shows partial spectra of benzoic acids unlabeled, -2-d, -3-d, -4-d, and -2,3-d_2, corrected both for naturally occurring heavy isotopes and for isotopic impurities. An attempt to remove the d_1 impurity from the d_2 spectrum as the 2-d species left negative residues at masses 104 and 105, implying that the impurity must be, at least in large part, a species other than 2-d. In the spectrum shown, the d_1 impurity therefore was removed as the 3-d species. Table II lists metastable peaks and the transitions denoted by them.

Sequential Loss of OH and CO. The most abundant ions and the associated metastable peaks correspond to sequential loss of OH and CO. But both normal and metastable peaks show loss of OD as well as of OH in the 2-d and 2,3-d_2 spectra. Moreover, the isotopic

(1) For several such instances, see H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p. 453.

(2) F. W. McLafferty and R. S. Gohlke, Anal. Chem., 31, 2076 (1959).

(3) T. Aczel and H. E. Lumpkin, ibid., 33, 386 (1961).

(4) Products of competing decomposition paths important in the spectra of ortho-substituted acids are ignored here as irrelevant to the present system.

(5) Unpublished spectra, this laboratory.

(6) For the gift of this material, we are indebted to L. C. Leitch, of the National Research Council of Canada. See R. N. Renaud, D. Kovachic, and L. C. Leitch, Can. J. Chem., 39, 21 (1961).

(7) Our own isotopic analysis of the toluene-d_2 (see S. Meyerson, J. Am. Chem. Soc., 85, 3340 (1963)) agreed closely with that reported in ref. 6.

(8) D. P. Stevenson and C. D. Wagner, J. Am. Chem. Soc., 72, 5612 (1950).

(9) H. M. Grubb, C. H. Ehrhardt, R. W. Vander Haar, and W. H. Moeller, 7th Annual Meeting of ASTM Committee E-14 on Mass Spectrometry, Los Angeles, Calif., 1959.

Table I

	Toluenes				Benzoic acids			
	2-d	3-d	4-d	2,3-d₂[b]	2-d	3-d	4-d	2,3-d₂[b]
Unlabeled, %	12.7	14.3	12.0	0.6	12.5	14.1	12.0	1.5
d_1, %	87.1	85.5	87.3	16.5	87.3	85.5	87.4	16.3
d_2, %	0.2	0.2	0.7	82.7	0.2	0.4	0.6	81.4
d_3, %	...	...	...	0.2	...	...	...	0.8

Table II. Partial Spectra of Benzoic Acids

		Relative intensity[a]				
m/e	Ion[b]	Un-labeled	2-d	3-d	4-d	2,3-d₂
124		...	0.2	0.1	0.2	100.0
3		...	100.0	100.0	100.0	0.2
2	$C_7H_6O_2^+$	100.0	0.5	0.4	0.4	...
1		0.8	0.2	0.1	0.1	...
107		...	...	0.1	0.4	121
6		...	121	132	131	11.8
5	$C_7H_5O^+$	131	12.9	1.9	1.4	0.5
4		1.8	0.6	0.1	0.1	...
96		...	...	...	...	5.1
5		...	5.0	5.1	5.2	0.4
4	$C_6H_6O^+$	5.0	0.4	0.5	0.5	0.3
3		0.6	0.3	0.3	0.3	0.1
80		...	0.2	0.2	0.2	4.5
79		0.3	4.5	4.6	4.8	102.0
8	$C_6H_6^+$	4.7	105.0	104.0	105.0	8.1
7	$C_6H_5^+$	105.0	9.4	9.1	9.1	4.7
6		9.3	5.9	4.8	4.8	4.8
54		0.2	1.6	0.9	0.8	6.1
53.5		...	0.3	0.3	0.3	3.6
53		3.7	12.5	13.0	13.1	28.7
52.5	$C_7H_5O^{2+}$	3.3	...	...	...	...
52		11.0	47.3	46.1	45.1	49.2
51.5		0.1	...	...	...	...
51	$C_4H_3^+$	71.0	51.9	49.6	48.2	37.0
50.5		0.1	...	...	...	...
50		45.4	25.2	27.7	29.4	14.4
49		7.0	8.3	5.2	4.1	3.7
46		0.2	0.2	0.1	0.1	0.1
5	CHO_2^+	12.7	12.3	12.3	12.2	11.8
4		1.0	1.1	1.1	1.1	1.1

[a] Corrections have been made for naturally occurring isotopes except in the 49 to 54 mass range. [b] Formulas are shown opposite masses of the appropriate unlabeled ions only.

distribution of $C_7H_5O^+$ ions in the 2-d spectrum confirms the estimate of 9% derived from the 2,3-d_2 spectrum for the fraction of $C_7H_5O^+$ ions that have lost a tagged atom. The OH radical lost in this competing process evidently consists of hydrogen from the *ortho* position and oxygen most likely from the carbonyl position. Thus, the $C_7H_5O^+$ ion yield includes two isomeric species that are perhaps best represented as I[10] and II
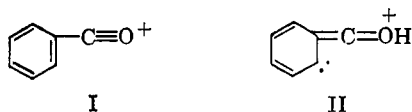
II may arise by a concerted reaction (1) or by a two-step reaction sequence *via* a rearranged parent ion (2). The labeling results imply that 18% of the $C_7H_5O^+$ ions in the spectrum of benzoic acid have lost a hydrogen atom from an *ortho* position. Thus, at least 18% have structure II rather than I. If hydrogen migra-

tion and loss of OH occur as two distinct steps, as shown in (2), with loss of identity of the hydroxyl

$$\qquad (1)$$

$$\qquad (2)$$
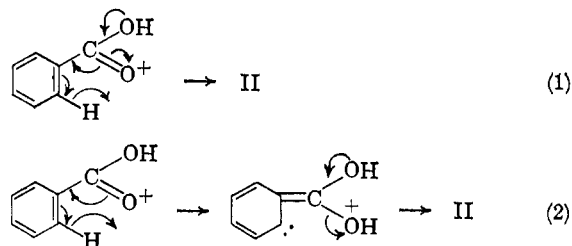
groups in the intermediate, then 36% of the $C_7H_5O^+$ ion yield must be assigned structure II.

The spectrum of benzoic acid-2-d shows no loss of deuterium in the process or processes leading to the $C_6H_5^+$ ion; therefore, none of these ions can be derived from a precursor that has lost the deuterium atom. In the 2,3-d_2 spectrum, the evidence is almost as conclusive. The difference between intensity of the d_2 species at mass 79 and that of the unlabeled species at 77 is slight; it may arise from an isotope effect. The finding that no measurable part of the $C_6H_5^+$ yield is derived from the intermediate II confirms the assumption that I and II are in fact isomeric species with different chemical properties and that loss of *o*-deuterium cannot be accounted for simply by hydrogen exchange in the parent ion.

Intensities of the corresponding doubly charged ions further support the view that $C_7H_5O^+$ ions that have lost an *o*-hydrogen are a second and chemically distinct species. The $C_7H_5O^{2+}$ peak at m/e 52.5 in the spectrum of the unlabeled acid is displaced to 53 in the spectrum of all three d_1 acids and apparently to 53.5 in that of the d_2 acid. The spectra give no evidence for a $C_7H_5O^{2+}$ ion that has lost any ring hydrogen; that is, II, unlike I, has no counterpart among doubly charged ions in the mass spectrum of benzoic acid.

Species II may well be the protonated *ortho* isomer of a recently reported short-lived molecule of mass 104, detected among the flash photolysis products of benzeendiazonium-4-carboxylate.[11] Conjugate acids of molecules with heteroatoms containing nonbonding electrons are often prominent in mass spectra—for example, CH_2OH^+ in the spectra of alcohols,[12] C_n-$H_{2n+1}C(OH)_2^+$ in those of aliphatic esters,[13] and $C_nH_{2n+1}SH_2^+$ in those of thioethers.[14] The relationship suggested here serves as a reminder that mass spectra are useful for detecting and identifying, among the products of electron impact on isolated molecules, chemical species that are not easily isolable, say, in a

(10) J. D. McCollum and S. Meyerson, *J. Am. Chem. Soc.*, **85**, 1739 (1963), and references cited there.

(11) R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Letters*, 1003 (1965).

(12) R. A. Friedel, J. L. Schultz, and A. G. Sharkey, *Anal. Chem.*, **28**, 926 (1956).

(13) A. G. Sharkey, J. L. Shultz, and R. A. Friedel, *ibid.*, **31**, 87 (1959).

(14) E. J. Levy and W. H. Stahl, *ibid.*, **33**, 707 (1961).

Table III. Metastable Peaks in Benzoic Acid Spectra

Apparent mass	Transition denoted	Relative intensity[a]				
		Unlabeled	2-d	3-d	4-d	2,3-d₂
92.3	$(124^+) \rightarrow (107^+) + 17$	...	...	...	...	0.35
91.3	$(123^+) \rightarrow (106^+) + 17$	...	0.41	0.43	0.39	...
90.6	$(124^+) \rightarrow (106^+) + 18$	...	...	...	...	≤0.15
90.4	$(122^+) \rightarrow (105^+) + 17$	0.42	...	...	...	...
89.6	$(123^+) \rightarrow (105^+) + 18$	...	≤0.15	...	...	...
58.3	$(107^+) \rightarrow (79^+) + 28$	...	...	...	...	1.08
57.4	$(106^+) \rightarrow (78^+) + 28$	...	1.10	1.11	1.07	...
56.5	$(105^+) \rightarrow (77^+) + 28$	1.29	...	...	...	...
35.6	$(79^+) \rightarrow (53^+) + 26$	...	...	...	...	0.13
34.7	$(78^+) \rightarrow (52^+) + 26$	...	0.23	0.21	0.22	...
34.2	$(79^+) \rightarrow (52^+) + 27$	...	...	...	...	0.20
33.8	$(77^+) \rightarrow (51^+) + 26$	0.39	...	...	...	...
33.3	$(78^+) \rightarrow (51^+) + 27$	...	0.15	0.17	0.16	...
32.9	$(79^+) \rightarrow (51^+) + 28$	...	...	...	...	0.05

[a] Intensity at parent mass = 100.0.

Table IV. Relative Intensities of Metastable Peaks for Processes Leading to $C_4H_3^+$ Ions

Isotopic species of $C_4H_3^+$	2-d		3-d		4-d		2,3-d₂	
	Obsd.	Calcd.[a]	Obsd.	Calcd.[a]	Obsd.	Calcd.[a]	Obsd.	Calcd.[a]
Unlabeled, %	39	40	45	40	42	40	13	10
d_1, %	61	60	55	60	58	60	53	60
d_2, %	..	..	..	..	..	..	34	30

[a] Calculations based on assumption of complete loss of identity of H and D atoms in the $C_6H_5^+$ intermediate.

test tube. Thus, mass spectra permit fairly direct observations on isolated protonated molecules without the added complications introduced by working with solutions. Mass spectral evidence for the existence and comparative stability of II suggests that extension of the benzenediazonium carboxylate photolysis experiments to work in proton-donating solvents might prove fruitful.

Other Processes. The spectral data in Tables II and III also give information about other products of benzoic acid decomposition under electron impact.

The ion that has mass 94 in the unlabeled species appears in low but constant yield in the spectra of all the isotopic species studied, and it retains all the original labels. The reaction involved must therefore effect loss of CO. The product has the composition $C_6H_6O^+$ and may be represented as phenol.[15] The process has parallels in loss of CO from benzaldehyde[10] and nicotinamide[5] under electron impact and bears a formal resemblance to nickel-catalyzed decarbonylation of benzamide[16] and benzoyl chloride.[17]

(15) The structure is, of course, not certain. The most abundant ion in the spectrum of phenol is apparently formed via a cyclohexadienone intermediate. See J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959).

The similarly low but constant yield of the ion that has mass 78 in the unlabeled species, coupled with retention of all original labels, identifies this ion as $C_6H_6^+$, evidently formed by loss of CO_2 from the parent ion.

Relative intensity at mass 45 is essentially the same in all the spectra. This peak is unquestionably due to the $COOH^+$ ion, consisting solely of the elements of the original carboxyl group.

Metastable peaks in the mass range 32.9 to 35.6 correspond to further breakdown of the $C_6H_5^+$ ion to $C_4H_3^+$ and C_2H_2. Label retentions in the $C_4H_3^+$ ion in the spectra of the labeled species cannot be calculated with confidence because of interference from other C_4 hydrocarbon ions, doubly charged ions, and probably singly charged oxygen-containing ions. However, as shown in Table IV, intensity distributions of the metastable peaks agree surprisingly well—when one considers the low intensity of these peaks and the difficulty of measuring them accurately in the presence of superimposed normal peaks—with complete loss of identity of the protium and deuterium atoms in the $C_6H_5^+$ intermediate.

(16) A. Mailhe, *Bull. soc. chim. France*, [4] **37**, 1394 (1925).
(17) A. Mailhe, *Compt. rend.*, **180**, 1111 (1925).