MASS SPECTROMETRY OF ARALKYL COMPOUNDS WITH A FUNCTIONAL GROUP—XIII*

THE STRUCTURE OF THE DECOMPOSING MOLECULAR ION OF m-HYDROXYBENZYLALCOHOL, ELUCIDATED BY ^{18}O- AND D-LABELING (SIX-MEMBERED- VERSUS SEVEN-MEMBERED RING)†

T. A. MOLENAAR-LANGEVELD and N. M. M. NIBBERING

Laboratory for Organic Chemistry. University of Amsterdam.
Nieuwe Achtergracht 129. Amsterdam. The Netherlands

Abstract—The mass spectra of m-hydroxybenzylalcohols. specifically labeled with ^{18}O in the benzylic hydroxyl group. with D in the methylene position and with D in both hydroxyl groups respectively. have been studied in order to determine whether or not the decomposing molecular ion is formed with ring expansion.

INTRODUCTION

IN THE formation of $XC_7H_6^+$-ions from substituted aromatic hydrocarbons upon electron impact, ring expansion of the molecular ions to cycloheptatriene intermediates has been proposed by some authors.[2-5] The results of appearance potential measurements on $XC_7H_6^+$-ions however, have shown that the possibility cannot be excluded, that certain $XC_7H_6^+$-ions have retained the six-membered ring.‡ Indeed, a ^{13}C- and ^{15}N-tracer study in our laboratory has shown that this is true for a substantial part of the decomposing molecular ions of (o-, m-, p) cyanobenzylcyanides $(C_7H_6(CN)_2)$.[1]

Even the molecular ion of 7-methylcycloheptatriene (C_8H_{10}) partly seems to collapse to a six-membered ring prior to loss of a methyl radical, as recently derived in our laboratory from the mass spectra of its 7-CD_3- and 7-$^{13}CH_3$ analogues.[6]

For a further evaluation of the problem of a six-membered versus a seven membered ring structure of aromatic molecular ions m-hydroxybenzylalcohol has been chosen. This compound and its O-d_2 analogue were studied mass spectrometrically several years ago by J. S. Shannon,[2] but the rationalization of the decompositions from the molecular ion, given at that time, appear to need drastical change as shown by

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* For Part XII, see ref. 1.

† This paper has been presented at the fifth meeting of the British Mass Spectroscopy Group, held at Bristol University on 13–15 July, 1971.

‡ Very recently a study of diffuse peaks in the mass spectra of some alkylnitrobenzenes has also strongly supported benzylic structures of $(NO_2C_7H_6)^+$-ions. R. Westward, D. H. Williams and A. N. H. Yeo, *Org. Mass Spectrom. 3*, 1485 (1970)

additional ^{18}O-labeling in the benzylic hydroxyl group and D-labeling in the benzylic position in the present investigation.

Results and Discussion

The most important decompositions of the molecular ion of *m*-hydroxylbenzylalcohol, supported by appropriate diffuse peaks observed in its mass spectrum, have been summarized in Scheme 1. In this Scheme three primary fragmentation reactions of the molecular ion can be discerned, *viz.* loss of a hydrogen atom, loss of
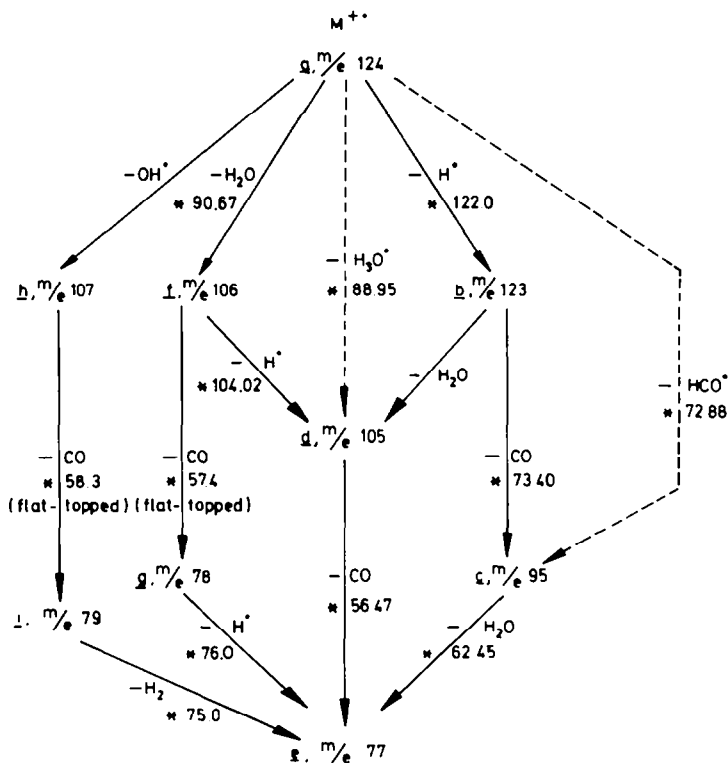
The dashed lines refer to the simultaneous expulsion of two neutral particles i e sequence a——→ d is in fact a——→ b——→ d and a——→ c is a——→ b——→ c (see text)
The numbers at the arrows correspond with the maxima of the diffuse peaks observed.

SCHEME 1. Partial fragmentation pattern of *m*-hydroxybenzylalcohol.

a molecule of water and elimination of a hydroxyl radical. These may be followed by further degradations as shown in Scheme 1, if the molecular ion has a relatively higher internal energy. The details of most of these reactions have been elucidated by ^{18}O- and D-labeling.

Loss of a hydrogen atom from the molecular ion and further degradations

Scheme 1 illustrates two pathways for decomposition, both starting with loss of a hydrogen atom from the molecular ion, *viz.* the reaction sequences **a → b → c → e** and **a → b → d → e**. Depending on the internal energy of the molecular ion these reaction sequences may proceed partially, thus enabling us to study the structure of decomposing molecular ions with increasing internal energy,

1. **a → b**	1. **a → b**
2. **a → b → c** and	2'. **a → b → d**
3. **a → b → c → e**	3'. **a → b → d → e**
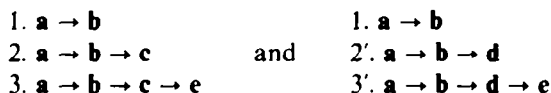
Formation of ion **b** *through sequence* **a → b.** In the mass spectrum of unlabeled *m*-hydroxybenzylalcohol peaks at *m/e* 123, *m/e* 122 and *m/e* 121 are present, as found earlier.[2] It is therefore complicated to determine quantitatively the origin of the hydrogen atom, eliminated during the formation of the $(M—H)^+$-ion through sequence **a → b**. Nevertheless, the mass spectrum of the O-d_2 compound suggests that the hydroxylic hydrogens do not participate in this expulsion, agreeing with previous work:[2] the mass spectra of the α-d_1- and α-d_2 analogues point to an extensive randomization of benzylic- and ring hydrogens prior to or during the formation of ion **b** (*cf.* Table 1).

TABLE 1. RELATIVE INTENSITIES[a,b,c] OF PEAKS DUE TO $C_7H_xO_2^+$-IONS FROM UNLABELED- AND LABELED *m*-HYDROXYBENZYLALCOHOLS, *m*-OH $– C_6H_4—\overset{\cdot}{C}H_2OH$, AT 70 eV (15 eV)

m/e	d_0	$—CH_2^{18}OH$	O-d_2	α-d_1	α-d_2
121	4 (−)	4 (−)	− (−)	5 (−)	4 (−)
122	2 (1)	3 (2)	4 (−)	1 (−)	− (−)
123	23 (8)	12 (2)	2 (1)	5 (2)	2 (−)
124	70 (89)	31 (41)	2 (1)	20 (7)	7 (2)
125	1 (1)	13 (4)	27 (10)	68 (90)	19 (6)
126	− (1)	36 (50)	62 (81)	1 (1)	67 (91)
127	− (−)	1 (1)	3 (7)	− (−)	1 (1)

[a] $\Sigma_{121\ to\ 127} = 100\cdot0$.
[b] Corrected for natural ^{13}C contribution.
[c] Average of at least three runs (estimated accuracy of $\pm\ 2\%$).

Formation of ion **c** *through sequence* **a → b → c.** Table 2 shows partial mass spectra of the various labeled analogues, relevant to the formation of ion **c**, *m/e* 95.
The data of this table illustrate:

(1) At both ionizing energies used, the peak at *m/e* 95 in the mass spectrum of the d_0 compound does not shift in the mass spectrum of the ^{18}O-labeled analogue, thus indicating that the molecule of carbon monoxide, eliminated from ion **b** in the ion source during the formation of ion **c**, contains (within experimental error) the benzylic oxygen atom exclusively.

The same is observed for decomposing ions **b**, having a lower internal energy: neither in the first—nor in the second field free region (at 70 eV as well as at 15 eV)

TABLE 2. RELATIVE INTENSITIES[a, b, c] OF PEAKS DUE TO $C_6H_xO^+$-IONS FROM UNLABELED- AND LABELED *m*-HYDROXYBENZYLALCOHOLS, m-OH—C_6H_4—CH_2OH, AT 70 eV (15 eV)

m/e	d_0	—$CH_2^{18}OH$	O-d_2	α-d_1	α-d_2
93	9 (1)	8 (—)	— (—)	8 (—)	7 (—)
94	8 (2)	7 (2)	7 (—)	3 (1)	2 (—)
95	81 (93)	83 (93)	4 (1)	27 (35)	4 (1)
96	2 (3)	1 (4)	11 (9)	60 (60)	51 (65)
97	— (1)	1 (1)	75 (79)	2 (4)	34 (31)
98	— (—)	— (—)	3 (10)	— (—)	2 (3)
99	— (—)	— (—)	— (1)	— (—)	— (—)

[a] $\Sigma_{93\ to\ 99} = 100.0$.
[b] Corrected for natural ^{13}C contribution.
[c] Average of at least three runs (estimated accuracy of $\pm 2\%$).

is any indication found for loss of carbon monoxide, containing the phenolic oxygen atom.

(2) Considering the incomplete labeling of the O-d_2 compound (Experimental) a practically complete shift of m/e 95 to m/e 97 is found at both ionizing energies used, showing that both original hydroxylic hydrogens are retained during the formation of ion c in the ion source. The extent of shift of m/e 95 to m/e 96 in the mass spectrum of the α-d_1 compound and to m/e 97 in that of the α-d_2 analogue appears to be 74% and 42% at 70 eV and 64% and 33% at 15 eV, respectively. These figures show that initially the molecular ion has preferentially lost a benzylic hydrogen atom, although less pronounced at 15 eV. This calculation cannot be applied to ions b decomposing in the first and second field free region due to the presence of diffuse peaks for both loss of CO from ion b (sequence b → c) and HCO˙ from ion a (sequence a → c), resulting in overlap of these peaks in the mass spectra of the deuterated compounds.

It is not known whether HCO˙ is ejected from ion a as a single entity: diffuse peaks however, observed for the reactions a → b and b → c, make a two steps elimination plausible. Similar observations have been reported earlier.[7]

Formation of ion e through sequence a → b → c → e. Ion e is generated from ion c by expulsion of a molecule of water. This process has been studied only in the second field free region as more reaction paths contribute to the formation of ion e (Scheme 1). The nature of the oxygen atom in the molecule of water, eliminated from ion c, appears to be exclusively phenolic as expected above.

The origin of the hydrogen atoms in the expelled molecule of water may be derived from Table 3.

This Table shows that at least one of the hydrogen atoms in the molecule of water is an original hydroxylic one, the other appears to originate from all the remaining positions. The ratio of the total loss of water from the $(M—H—CO)^+$-ion and from the $(M—D—CO)^+$-ion again demonstrates that the molecular ion a initially has preferentially lost a benzylic hydrogen atom, as also noted above.

Formation of ion d through sequence a → b → d. In the mass spectrum of the d_0 compound a diffuse peak is found for the reaction a → d, corresponding with the loss of 19 a.m.u. (i.e. one oxygen + three hydrogens) from ion a.

This must refer to a practically simultaneous expulsion of two neutral particles, a phenomenon described earlier.[7]

Also in the mass spectrum of the ^{18}O labeled analogue a diffuse peak is observed for the loss of 19 a.m.u. from the molecular ion, although to a large extent obscured by overlap with the diffuse peak for elimination of water from the molecular ion of

TABLE 3. RELATIVE PEAK AREAS[a, b, c] OF DIFFUSE PEAKS AT 70 eV, REFERRING TO THE LOSS OF WATER FROM THE $(M-H-CO)^{+}$- AND $(M-D-CO)^{+}$-IONS OF SITE-SPECIFICALLY LABELED m-HYDROXYBENZYLALCO-HOLS, m-OH $\cdot$ C_6H_4 – $\overset{\bullet}{C}H_2OH$

Labeled position	Loss of water from $(M-H-CO)^{+}$			Loss of water from $(M-D-CO)^{+}$		
	H_2O	HDO	D_2O	H_2O	HDO	D_2O
d_0	100	—	-	—	—	—
α-d_1	66	6	--	28	—	—
α-d_2	36	9	—	51	4	—
O-d_2[d]	—	90	10	—	—	—

[a] Sum being taken as 100-0.
[b] Corrected for natural ^{13}C contribution.
[c] Average of at least three runs (estimated accuracy of ± 2%).
[d] Corrected for isotopic impurities (Experimental).

the unlabeled compound, present in the sample (see sequence **a** → **f** in Scheme 1 and Experimental, respectively). A diffuse peak for the loss of 21 a.m.u. from the molecular ion however, calculated to be found in a region where other diffuse peaks appear to be absent, is definitely not observed. Thus, the phenolic oxygen atom participates exclusively in the loss of 19 a.m.u.

The nature of hydrogens involved in the expulsion of 19 a.m.u. (sequence **a** → **d**), is shown in Table 4.

TABLE 4. DISTRIBUTION AND RELATIVE PEAK AREAS[a, b, c] OF THE DIFFUSE PEAKS, CORRESPONDING WITH LOSS OF 18- AND 19 a.m.u. FROM THE MOLECULAR ION OF UNLABELED m-HYDROXYBENZYLALCOHOL, m-OH $\cdot$ C_6H_4 –$\overset{\bullet}{C}H_2OH$, IN THE SPECTRA OF SITE-SPECIFICALLY LABELED ANALOGOUS AT 70 eV.

Labeled position	Loss from M_0^{+} of			
	18 a.m.u.	19 a.m.u.	20 a.m.u.	21 a.m.u.
d_0	88	12	—	—
α-d_1	87	10	3	—
α-d_2	90	6	4	—
O-d_2[d]	—	--	88	12

[a] Sum being taken as 100-0.
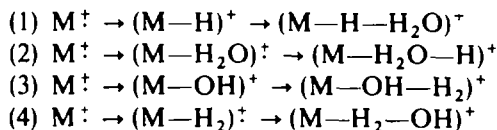[b] Corrected for natural ^{13}C contribution.
[c] Average of at least three runs (estimated accuracy of ± 2%).
[d] Corrected for isotopic impurities (Experimental).

Apart from the loss of 18 a.m.u. from the molecular ion, which will be discussed later, this Table illustrates that in the formation of ion **d** from ion **a** in the second field free region both original hydroxylic hydrogens are completely lost together with

a hydrogen atom, originating at random from the remaining positions. Although the character of the oxygen- and hydrogen atoms eliminated in the sequence $a \rightarrow d$, has now been elucidated. this reaction still must be separated in two processes.
Four possibilities can be considered:

(1) $M^{\ddagger} \rightarrow (M-H)^{+} \rightarrow (M-H-H_2O)^{+}$
(2) $M^{\ddagger} \rightarrow (M-H_2O)^{\ddagger} \rightarrow (M-H_2O-H)^{+}$
(3) $M^{\ddagger} \rightarrow (M-OH)^{+} \rightarrow (M-OH-H_2)^{+}$
(4) $M^{\ddagger} \rightarrow (M-H_2)^{\ddagger} \rightarrow (M-H_2-OH)^{+}$

The reaction paths, given in (2) and (3), can be ruled out, as will be shown later. Also the last reaction is very improbable, as it involves loss of a hydroxyl radical from the $(M-H_2)^{\ddagger}$-ion, which is supposed to be m-hydroxybenzaldehyde, as noted earlier.[8] Indeed, in the mass spectrum of m-hydroxybenzaldehyde itself, recorded in our laboratory, an (M-17)-peak is hardly observed and a diffuse peak for its formation is not found at all.
Thus, the elimination of 19 a.m.u. from the molecular ion of m-hydroxybenzyl-alcohol in the second field free region can be attributed to the successive loss of a hydrogen atom and a molecule of water.

Formation of ion e through sequence $a \rightarrow b \rightarrow d \rightarrow e$. When ion **d** has sufficient internal energy it may decompose further to ion **e** by loss of CO, a process only studied in the second field free region (Scheme 1). This molecule should be expected to contain exclusively the benzylic oxygen atom considering the observations, summarized earlier.
Ion **d**, however, also appears to be formed through the sequence $a \rightarrow f \rightarrow d$, where predominantly the ^{18}O label is lost as will be shown. This should imply that two kinds of ions **d** exist either possessing a ^{16}O-atom or a ^{18}O-atom.
Indeed. in the mass spectrum of the ^{18}O-labeled analogue two diffuse peaks are found for the transition m/e 105 $\rightarrow$ m/e 77 and m/e 107 $\rightarrow$ m/e 77 (sequence $d \rightarrow e$, Scheme 1), and their relative peak areas appear to be 45% and 55%, respectively, these figures corresponding (within experimental error) to the isotopic composition of the starting sample (Experimental).

TABLE 5. RELATIVE PEAK AREAS[a, b, c] FOR DIFFUSE PEAKS AT 70 eV, REFERRING TO THE LOSS OF CARBON MONOXIDE FROM THE $(M-H(D)-H_2O(D_2O))^{+}$-IONS OF SITE- SPECIFICALLY LABELED m-HYDROXYBENZYL-ALCOHOL. m-OH- $C_6H_4-CH_2OH$

| | Loss of carbon monoxide from | | |
Labeled position	$(M-H-H_2O)^{+}$	$(M-D-H_2O)^{+}$	$(M-H-D_2O)^{+}$
d_0	100	—	—
α-d_1	63	37	—
α-d_2	38	62	—
O-d_2[d]	--	—	100

[a] Sum being taken as 100·0.
[b] Corrected for natural ^{13}C contribution.
[c] Average of at least three runs (estimated accuracy of $\pm$ 2%).
[d] Corrected for isotopic impurities (Experimental).

So, CO, eliminated in the sequence **d** → **e**, contains exclusively the benzylic oxygen atom in spite of the expectations, suggested above. Apparently, ion **d** produced in the sequence **a** → **f** → **d** does not decompose further, whereas ion **d** produced in the sequence **a** → **b** → **d** (or **a** → **d**) does. With this knowledge it is possible to calculate the percentages for loss of H or D, initially eliminated from the molecular ions of the various deuterated compounds in the sequence **a** → **b** → **d** → **e** (or **a** → **d** → **e**). These correspond with the data of Table 5. These data again demonstrate that initially the molecular ion of m-hydroxybenzylalcohol preferentially has lost a benzylic hydrogen atom.

Conclusions and rationalizations of the reactions discussed. All observations, elaborated thus far, allow us to draw the following conclusions:

(1) The oxygen atoms in the molecular ion **a**, decomposing through ion **b** either to ions **c** and **e** or to ions **d** and **e**, retain their identity. Consequently, evidence both for a seven-membered ring structure of this ion **a** and for an earlier proposed dihydroxytropylium structure[2] of this ion **b** is not found.

(2) Equilibration of the benzylic—and the ring hydrogens in the decomposing molecular ion **a** occurs without expansion to a seven-membered ring, as found earlier in our laboratory from tracer studies of similar compounds.[1, 9]

Before attempting to rationalize the reactions with these conclusions, it is desirable to invoke the mass spectrometrical study on o-, m- and p-hydroxybenzylalcohol by J. S. Shannon.[2] This classical work has shown:

(1) The mass spectrum of o-hydroxylbenzylalcohol differs essentially from those of the m- and p-isomers because of an intramolecular hydrogen bonding within its molecular ion, *e.g.* peaks due to the reactions discussed are absent.

(2) The same peaks are found in the mass spectra of the m- and p-isomers, but they have considerably different intensities. Shannon has already suspected that this latter is governed by the position of the phenolic hydroxyl group with respect to the benzylic hydroxyl group, but at that time it has been impossible to differentiate between a six-membered- and a seven-membered ring structure for the molecular ions; both structures have seemed to account well for the differences in intensities of corresponding peaks in the spectra of the m- and p-isomers, when the relative positions of the hydroxyl groups are envisaged.

These considerations together with the present ^{18}O-labeling data suggest therefore strongly that the m-orientation in m-hydroxybenzylalcohol is retained during the electron impact. With this in mind, the reactions discussed may be rationalized by Scheme 2:

This scheme illustrates that after scrambling of α- and ring hydrogens in ion **a** a hydrogen atom from the benzylic position of ion **a'** is lost to produce ion **b**, having a m-hydroxybenzaldehyde structure, protonated at the carbonyl function. Further decomposition of ion **b** may be induced by transfer of the proton from the carbonyl function to the π-orbital of the phenyl ring, generating a π-complex represented by ion **b'**.* Then, through σ-bond formation the proton may get linked either to the phenolic oxygen atom or to one of the carbon atoms of the phenyl ring, producing

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* Intermolecular, interionic or intermolecular-interionic proton transfer may be ruled out as the spectrum of the d_0 compound does not change essentially, when the ion source pressure is increased from 0.1×10^{-6} Torr to 2.8×10^{-6} Torr by introduction of additional sample.
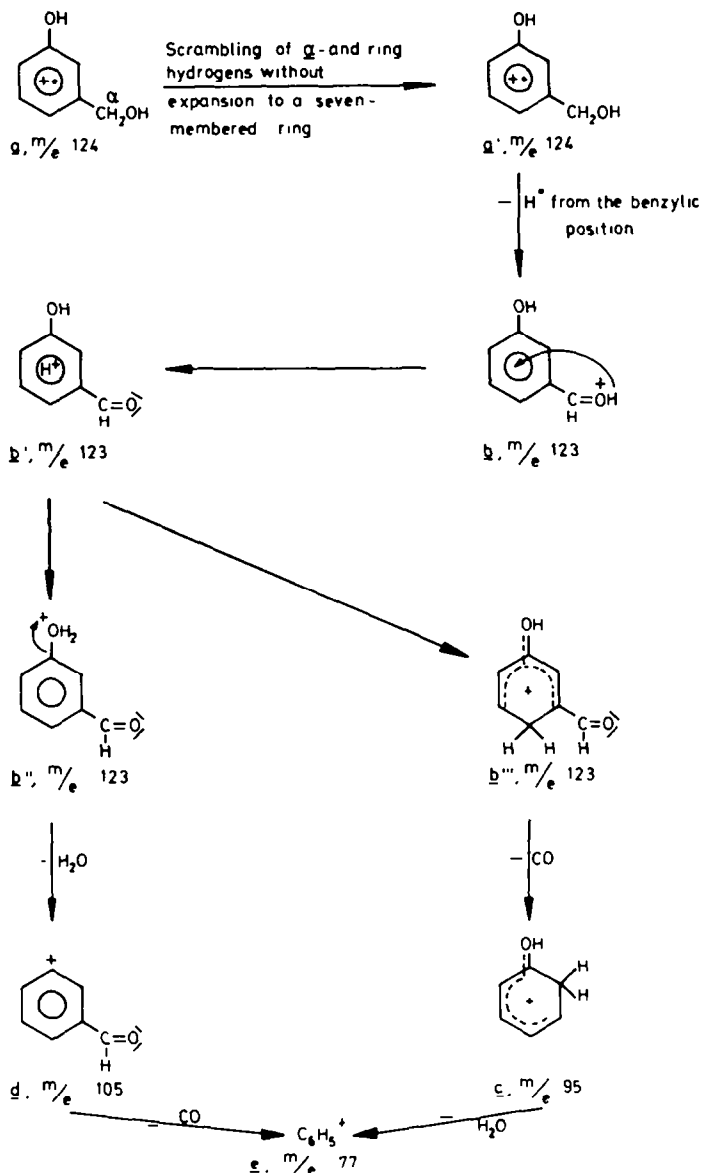
SCHEME 2. Rationalization of the loss of a hydrogen atom from the molecular ion of m-hydroxybenzylalcohol and further degradations.

ions **b″** and **b‴** respectively. Ion **b″** generates ion e by the subsequent elimination of water and CO possibly in a way, as shown in the sequence **b″ → d → e**.

Ion **b‴** loses CO to give ion **c**, possibly having a methylene group *ortho* with respect to the phenolic function (this orientation may be formed *via* a series of 1,2 shifts of hydrogen along the ring carbon atoms prior to or during or after the loss of carbon monoxide).

The latter structure may account for the loss of water in the sequence c → e.

Loss of a molecule of water from the molecular ion and further degradations

Formation of ion f through sequence a → f. The molecular ion a also appears to eliminate a molecule of water, producing ion f (Scheme 1). Table 6 shows partial mass spectra of the various labeled compounds, relevant to the formation of ion f in the ion source.

TABLE 6. RELATIVE INTENSITIES[a, b, c] OF PEAKS DUE TO $C_7H_xO_e^+$-IONS FROM UNLABELED- AND LABELED m-HYDROXYBENZYLALCOHOLS, m-OH—C_6H_4 CH_2OH, AT 70 eV (15 eV)

| m/e	d_0	—$CH_2^{18}OH^d$	O-d_2	α-d_1	α-d_2
105	37 (32)	22 (14)	34 (26)	15 (12)	1 (—)
106	24 (44)	23 (47)	25 (42)	23 (20)	26 (23)
107	37 (19)	47 (27)	6 (12)	25 (44)	12 (10)
108	2 (5)	2 (6)	34 (17)	35 (19)	24 (43)
109	– (—)	6 (6)	1 (2)	2 (5)	35 (19)
110	⋯ (—)	— (—)	— (1)	— (—)	2 (5)

[a] $\Sigma_{105\ to\ 110} = 100.0$.
[b] Corrected for natural ^{13}C contribution.
[c] Average of at least three runs (estimated accuracy of $\pm 2\%$).
[d] The partial shift of m/e 105 to m/e 107 is due to the sequence a → d, discussed earlier.

The data of this table show, that at both ionizing energies the peak at m/e 106 ((M—H_2O) $^+$-ion) in the spectrum of the d_0 compound practically does not shift in the spectra of the ^{18}O- and O-d_2 analogues, if the incomplete labeling is considered (Experimental). Thus, the molecule of water, eliminated from the molecular ion a in the ion source, contains within experimental error exclusively the benzylic oxygen atom and both original hydroxylic hydrogens. Consequently, ion f must retain completely the deuterium atoms, incorporated in the α-d_1 and α-d_2 derivatives, as indeed observed (*cf.* Table 6). These observations exclude a seven-membered ring structure of this molecular ion a, as also discussed previously and invalidate the mechanism for expulsion of water, containing exclusively the phenolic oxygen atom, as proposed earlier.[2]

Assuming that the m-orientation is retained in the molecular ion a as noted above, a different mechanism for this reaction could involve initial transfer of the proton, generated by a heterolytic cleavage of the phenolic O—H bond, *via* a π-complex to the benzylic oxygen atom, followed by loss of molecule of water as depicted in Scheme 3.
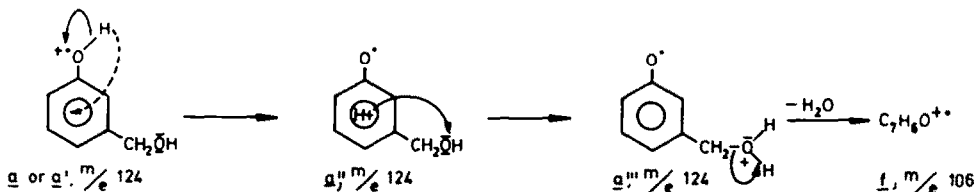
SCHEME 3. Rationalization of the expulsion of a molecule of water from the molecular ion of m-hydroxybenzylalcohol.

In the second field free region however, the molecular ion **a** appears also to lose a molecule of water, containing a phenolic oxygen atom as supported by a diffuse peak for the reaction $C_7H_8{}^{18}O{}^{16}O^{+\cdot}$ (m/e 126) $\rightarrow C_7H_6{}^{18}O^{+\cdot}$ (m/e 108) $+ H_2{}^{16}O$, observed in the spectrum of the ^{18}O-labeled analogue. Unfortunately, the diffuse peak for the reaction $C_7H_8{}^{18}O{}^{16}O^{+\cdot}$ (m/e 126) $\rightarrow C_7H_6{}^{16}O^{+\cdot}$ (m/e 106) $+ H_2{}^{18}O$ coincides practically with the diffuse peak for loss of 19 a.m.u. from the molecular ion of the unlabeled compound, present in the sample. Nevertheless, from the ratio of intensities and/or peak areas of the diffuse peaks under investigation at 70- and 15 eV it is estimated, that the phenolic oxygen atom participates to the extent of 15–20% in the sequence **a** $\rightarrow$ **f** (Scheme 1).

The data of Table 4 further show that both original hydroxylic hydrogens are lost during the formation of ion **f** in the second field free region.

These observations point to a possible rearrangement of a part of the molecular ions **a** to a seven-membered ring prior to their decomposition *via* the expulsion of a molecule of water in the second field free region.

Formation of ion **g** *through sequence* **a** $\rightarrow$ **f** $\rightarrow$ **g**. Considering the sequence **a** $\rightarrow$ **f** discussed above, both oxygen atoms and both original hydroxylic hydrogen atoms are expected to be lost in the formation of ion **g** through sequence **a** $\rightarrow$ **f** $\rightarrow$ **g** (Scheme 1). This should imply that the peak at m/e 78 in the spectrum of the d_0 compound does not shift in the spectra of the ^{18}O- and O–d_2 analogues, but does shift to m/e 79 and m/e 80 in the spectra of the α–d_1- and α–d_2 derivatives, respectively.

These suppositions are confirmed well by the 70 eV data and roughly by the 15 eV data, summarized in Table 7.

TABLE 7. RELATIVE INTENSITIES[a, b, c] OF PEAKS DUE TO $C_6H_x^{+}$-IONS FROM UNLABELED- AND LABELED m-HYDROXYBENZYLALCOHOLS. m-OH—C_6H_4—$\overset{x}{C}H_2OH$ AT 70 eV (15 eV)

m/e	d_0	$-CH_2{}^{18}OH$	O-d_2	α-d_1	α-d_2
74	2 (—)	2 (—)	2 (—)	2 (—)	2 (—)
75	2 (—)	2 (—)	1 (—)	1 (—)	2 (—)
76	2 (—)	2 (—)	1 (—)	2 (—)	1 (—)
77	53 (2)	54 (2)	17 (—)	21 (1)	6 (—)
78	29 (87)	30 (89)	64 (81)	36 (10)	30 (4)
79	10 (11)	10 (9)	7 (12)	26 (79)	21 (5)
80	1 (—)	– (—)	8 (6)	10 (10)	28 (82)
81	1 (—)	– (—)	– (—)	1 (—)	9 (9)
82	— (—)	– (—)	— (—)	1 (—)	1 (—)

[a] $\Sigma_{74 \text{ to } 82} = 100\cdot0$.
[b] Corrected for natural ^{13}C contribution.
[c] Average of at least three runs (estimated accuracy of $\pm$ 2%).

Ion **g** is also generated in the second field free region from ion **f** by loss of CO, but overlap of the flat-topped diffuse peak observed for this reaction with the flat-topped diffuse peak observed for the sequence **h** $\rightarrow$ **i** (Scheme 1) prevents us to determine the origin of the oxygen atom in the eliminated molecule of carbon monoxide.

Loss of hydroxyl from the molecular ion through sequence **a → h** (*cf.* Scheme 1)

The peak at m/e 107 in the mass spectrum of the d_0 compound indicates that the molecular ion **a** loses a hydroxyl radical in the ion source (*cf.* Table 6). The hydrogen atom in this radical originates from one of the hydroxyl groups as shown by a practically complete shift of this peak to m/e 108 in the mass spectra of the O-d_2- and α-d_1 analogues and to m/e 109 in the spectrum of the α-d_2 compound (*cf.* Table 6). In the mass spectrum of the ^{18}O-labeled analogue the peak under investigation partly shifts to m/e 109 (*cf.* Table 6), indicating that the eliminated hydroxyl radical may contain either the phenolic—or the benzylic oxygen atom. Considering the incomplete labeling (Experimental), the extent of shift to m/e 109 shows that 1/3 (3.5) of the eliminated hydroxyl radicals at 70 eV (15 eV) contains the phenolic oxygen atom.

These observations point to a ring expansion of the molecular ion **a** to a seven-membered ring in the ion source prior to or during the present reaction.

Further decomposition of ion **h** through sequence **h → i** (*cf.* Scheme 1) could not be studied, as noted above.

TABLE 8. MEASUREMENTS OF LABEL CONTENT (IN %) OF D- AND ^{18}O-LABELED m-HYDROXYBENZYLALCO-
HOLS, m-OH—C_6H_4—CH_2OH.

Ionization energy	Labeled position	unlabeled	d_1	d_2	d_3	^{18}O
9.0 eV	α-d_1	< 1	>99	—	—	—
	α-d_2	—	< 1	>99	—	—
	O-d_2	—	14	78	8	—
	—$CH_2^{18}OH$	46	—	—	—	54

* Average of at least five runs

EXPERIMENTAL

m-Hydroxybenzylalcohol and its labeled analogues were purified by recrystallization from benzene and hexane respectively. Label contents of all samples were measured, using such a low ionization energy, that in the parent mass region of the unlabeled m-hydroxylbenzalcohol only the molecular ion peak remained. The results of these measurements have been summarized in Table 8 (above).

Preparation of m-hydroxybenzylalcohol *and its* α-d₁, α-d₂ *and* ¹⁸O-*analogues.* m-Hydroxybenzylalcohol was obtained by reduction of m-hydroxybenzoic acid with LAH. The α-d_1- and α-d_2 analogues were synthesized from m-hydroxybenzaldehyde and m-hydroxybenzoic acid by reduction with LAD, respectively. For the synthesis of the ^{18}O-labeled analogue, m-hydroxybenzaldehyde was twice exchanged with ± 55% H₂¹⁸O as described earlier,[10] followed by reduction with LAH.

Preparation of the O-d₂ *analogue of* m-hydroxybenzylalcohol. The O-d_2 analogue was prepared dissolving m-hydroxybenzylalcohol in excess D_2O. This solution was then concentrated by evaporation in vacuo at room temperature and the wet residue introduced into the inlet system of the mass spectrometer. It appeared to be important to run the spectrum as quickly as possible, because exchange of a ring hydrogen, probably that between the substituents, occurs in the inlet system (*cf.* Table 8, showing the presence of d₃ molecules in the sample).

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