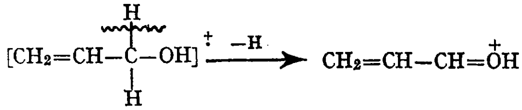
Mass Spectra of Deuterium-labelled Allyl Alcohols: Evidence for Rearrangement of the Molecular Ion

By J. J. KURLAND
(*Department of Chemistry, Harvard University, Cambridge, Massachusetts* 02138)

and R. P. LUTZ*
(*Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois* 60680)†

THE base peak in the mass spectrum of allyl alcohol[1] (I) occurs at *m/e* 57 and represents the $M-1$ ion, which is reasonably assumed[2] to have structure (II), formed with loss of hydrogen from the alpha position by a cleavage process analogous to those observed with saturated alcohols.[3] The stability associated with charge delocalization in (II) can account for its high relative abundance compared with $M-1$ ions derived from saturated alcohols.



$$[CH_2{=}CH{-}\overset{H}{\underset{H}{C}}{-}OH]^{+\cdot} \xrightarrow{-H} CH_2{=}CH{-}CH{=}\overset{+}{O}H$$

m/e 58 (I) *m/e* 57 (II)

We now report, however, that the assumed alpha-cleavage mechanism cannot account for the fragmentation pattern observed in the mass spectra of a series of specifically deuterium-labelled allyl alcohols. The labelling study shows that loss of hydrogen from every position in allyl alcohol, excluding hydroxy-group, contributes to the formation of the $M-1$ ion, which is probably best represented by a cyclic structure.

The compounds examined were, in addition to unlabelled allyl alcohol (I), the labelled alcohols shown below.

$CH_2{=}CH{-}CH_2{-}OD$ [O-^2H]-(I)
$CH_2{=}CD{-}CH_2{-}OH$ [2-^2H]-(I)
$CH_2{=}CH{-}CD_2{-}OH$ [1,1-$^2H_2$]-(I)
$CD_2{=}CH{-}CH_2{-}OH$ [3,3-$^2H_2$]-(I)

The carbon-labelled alcohols were prepared by pyrolysis at 375° of the corresponding anthracene adducts[4] and contained at least 98% of the indicated species. The hydroxy-labelled sample, prepared by the gas-chromatographic exchange method of Kallos and Westover,[5] was shown by its mass spectra (see below) to be at least 95% [O-^2H]-(I). The specificity of deuterium incorporation was verified in every case by n.m.r. spectroscopy.

Mass spectra of the carbon-labelled alcohols were obtained at 70, 14, and 12 ev (nominal) on an A.E.I. MS-9 mass spectrometer with the inlet at room temperature and ion source at 195°. The hydroxy-labelled sample was analysed on a Perkin–Elmer Model 270 mass spectrometer‡ equipped with a gas chromatographic inlet, using a Carbowax 20M column pre-conditioned with deuterium oxide. The ion source was at 195° and all components of the inlet system were at 100° or below. Relative abundances for peaks in the molecular ion region are given in Table 1, with values corresponding to the molecular ions themselves shown in brackets.

Two features of the fragmentation process are apparent from inspection of the data. First, simple alpha cleavage leads one to expect that the spectrum of $CH_2{:}CH{\cdot}CD_2{\cdot}OH$ should exhibit a negligible $M-1$ peak; this is not the case.

Second, the presence of significant $M-2$ peaks in the spectra of all three carbon-labelled derivatives shows that a deuterium atom is lost from each of the corresponding positions in allyl alcohol. [That these are actually $M-D$ peaks rather than $M-2H$ is shown by their high intensity compared to the $M-2H$ peak in (I).] If $M-2H$ ions are assumed to be negligible, the ratio of relative abundances, $(M-2)/[(M-2)+(M-1)]$, for a particular labelled alcohol reflects the fraction of the total atom loss from the molecular ion which occurs from the labelled position. The data at 70, 14, and 12 ev are presented in Table 2.

The sum of the numbers in each column is less than unity, indicating a small isotope effect[6] favouring loss of hydrogen over deuterium. This isotope effect is virtually insensitive to ionizing voltage in the range examined.

The values in Table 2 show that the extent of

---

† Present address: Department of Chemistry, Portland State College, Portland, Oregon 97207.

‡ Extensive re-exchange of deuterium occurred in the A.E.I. MS-9 even after the inlet system had been conditioned with deuterium oxide.

TABLE 1. *Relative abundance*

	m/e	(I)	[O-^{2}H]-(I)[a]	[2-^{2}H]-(I)	[1,1-$^2H_2$]-(I)	[3,3-$^2H_2$]-(I)
70 ev	61			1	2	2
	60		1	2	[36]	[37]
	59	2	[30]	[28]	100	100
	58	[25]	100	100	44	48
	57	100	6[b]	17	3	7
	56	1	3	6	4	5
14 ev	61				3	3
	60		1	3	[65]	[69]
	59	2	[41]	[50]	100	100
	58	[38]	100	100	46	46
	57	100	7[b]	19	1	1
	56	1		1		
12 ev	61				6	6
	60	1	2	4	[100]	[100]
	59	3	[89]	[83]	90	77
	58	[58]	100	100	39	33
	57	100	7[b]	20	1	
	56	2	1			

[a] The reproducibility of relative intensities at 12 ev was poor.

[b] The relative abundances of the *m/e* 57 peaks in the spectra of [O-^{2}H]-(I) are accounted for by assuming a 5% or ess contamination with (I).

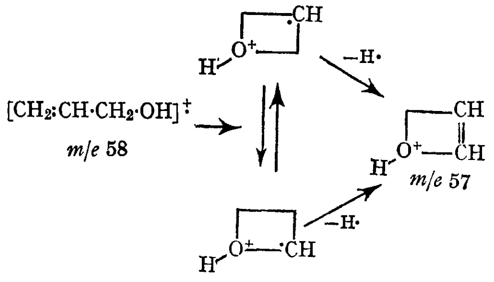
TABLE 2

Ratio of relative abundances, $(M-2)/[(M-2)+(M-1)]$

Compound	70 ev	14 ev	12 ev
[O-^{2}H]-(I)	0·00	0·00	0·00
[1,1-$^2H_2$]-(I)	0·31	0·32	0·30
[2-^{2}H]-(I)	0·15	0·16	0·17
[3,3-$^2H_2$]-(I)	0·32	0·32	0·30

deuterium loss from a given carbon position is roughly proportional to the number of deuterium atoms in that position. If the data are extrapolated to unlabelled allyl alcohol, the conclusion arises that in the formation of the $M-1$ (*m/e* 57) ion, about 40% of the hydrogen loss occurs from C-1, 20% from C-2, and 40% from C-3.

The relative values for the % hydrogen loss from each carbon position are those expected if the five carbon-bonded hydrogens of the original allyl alcohol become randomly distributed over all three carbons prior to hydrogen loss. The result can be rationalized by assuming that the original molecular ion cyclizes and undergoes extensive hydrogen rearrangement before losing a hydrogen atom.



Cyclization and rearrangement can also account for loss of the alkyl substituent from an allyl alcohol framework to give an *m/e* 57 ion as the base peak in the mass spectra of *trans*-but-2-en-1-ol,[1b,7] 2-methylprop-2-en-1-ol,[7] *cis*- and *trans*-hex-2-en-1-ol,[7b] and oct-2-en-1-ol.[7b]

This investigation was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society.

(*Received, July* 1*st*, 1968; *Com.* 872.)

---

[1] (a) "Catalog of Mass Spectral Data," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburg, Pa., No. 767; (b) S. Meyerson and J. D. McCollum, 'Advances in Analytical Chemistry and Instrumentation,' ed. C. N. Reilley, Interscience, New York, 1963, p. 206.

[2] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, 1967, p. 102.

[3] A review of the mass spectra of saturated and unsaturated alcohols is given in Chapter 2 of ref. 2.

[4] *Cf.* P. D. Bartlett and F. A. Tate, *J. Amer. Chem. Soc.*, 1953, **75**, 91.

[5] G. J. Kallos and L. B. Westover, *Tetrahedron Letters*, 1967, 1223.

[6] *Cf.* M. Corval and M. R. Viallard, *Bull. Soc. chim. France*, 1966, 3710.

[7] (a) R. S. Gohlke, Ed., 'Uncertified Mass Spectral Data.' Dow Chemical Company, Midland, Michigan, 1963; (b) A. Cornu and R. Massot, 'Compilation of Mass Spectral Data,' Heydon and Sons, Ltd., London, 1966.