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Reactions Between Formaldehyde and Polyhydric Alcohols III.* An Unexpected Isotope Effect in the Mass Spectra of Deuterated 1,3-Dioxolanes

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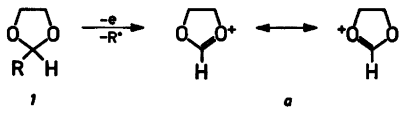
4-Methyl-1,3-dioxolane-2,2-d_2 (*2a*) displays in its mass spectrum an M − H peak which is more abundant than the M − D peak. From the study of the mass spectra of related compounds it was found that the hydrogen lost from *2a* originates from C-5. The kinetics are discussed and a mechanism for this unexpected reaction is proposed.

The mass spectra of 1,3-dioxolanes (*1*) have been extensively studied [2–5] and discussed [6] in previous work. The most outstanding feature of their spectra is the relatively low activation energy for loss of a group R (R = H or alkyl) from C-2, due to the relatively high stability of the delocalized oxonium ion *a* which is formed.



Scheme 1.

It was therefore extremely surprising to find that 4-methyl-1,3-dioxolane-2,2-d_2 (*2a*), displays in its mass spectrum an M − H peak which is more abundant than the M − D peak (Fig. 1). The present paper reports a study made to try to understand this surprising result.

* Part II, see Ref. 1.

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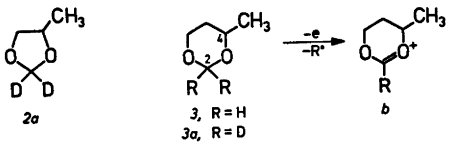
RESULTS AND DISCUSSION



Scheme 2.

Early evidence cited as supporting a low activation energy for the formation of a delocalized oxonium ion such as *a* was found in the mass spectrum of 4-methyl-1,3-dioxane (*3*), in which the M − H peak is over three times the abundance of the M − CH_3 peak.[6] It was argued [6] that since methyl radical loss is normally preferred over hydrogen radical loss in mass spectra (where this competition can occur for −H and $-CH_3$ substituents attached to the same carbon atom), then the dominant M − H ion must be due to the delocalized ion *b* (R = H). This conclusion has now been verified by an examination of the mass spectrum of 4-methyl-1,3-dioxane-2,2-d_2 (*3a*): the M − H ion from *3* is replaced by an M − D ion from *3a*.

The unusual phenomenon in the mass spectrum of *2a* was examined further through a comparison of the spectra of the parent compound *2* and the additional deuterated derivatives *2b* and *2c* (Fig. 1). Only deuterium is lost from the molecular ion of *2c*, establishing loss of D from positions C-2 and/or C-5 in forming the M − D ion in this case. The 5,5-d_2-derivative *2b*

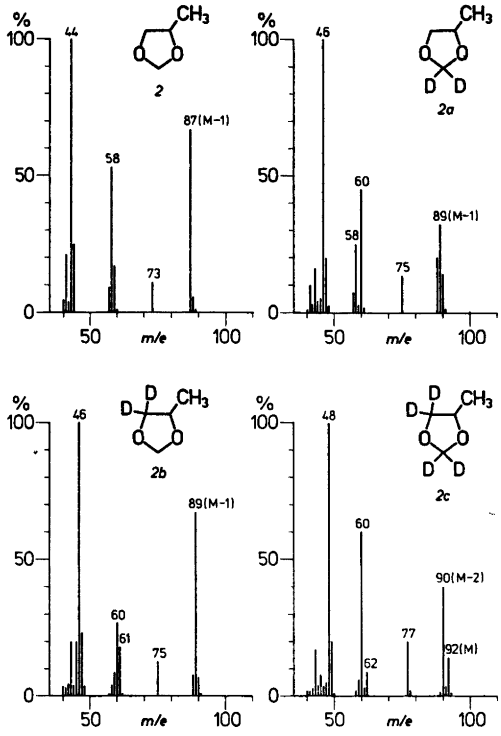
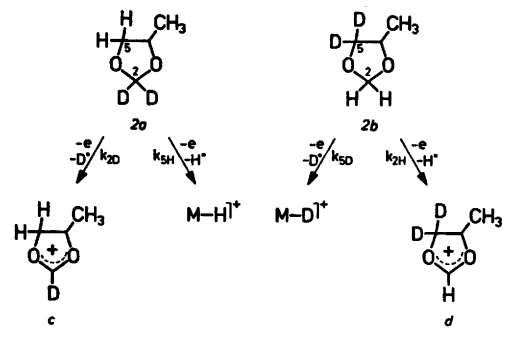


Fig. 1. Mass spectra of 4-methyl-1,3-dioxolane (*2*) and deuterated analogues (*2a* – *2c*).

forms almost exclusively M – H, establishing the preferential formation of ion *d* from this compound. Thus, the preferential loss of H from *2a* must occur from C-5, and the dominance of this process over D loss from C-2, to give *c*, must be due to an isotope effect.



Scheme 3.

Table 1. Abundances of M, M – H and M – D peaks in the mass spectra of *2*, *2a*, *2b* and *2c*.

Compound	% Σ_{40}[a] M	M – H	M – D	Metastable ion observed for
2 (d_0)	0.8	20.7	–	$M^+ \rightarrow [M-H]^+$
2a (2,2-d_2)	4.0	10.2	6.5	$M^+ \rightarrow [M-D]^+$
2b (5,5-d_2)	1.1	19.1	2.3	$M^+ \rightarrow [M-H]^+$
2c (2,2,5,5-d_4)	4.4	0.4	12.8	$M^+ \rightarrow [M-D]^+$

[a] Corrected for ^{13}C.

Relevant data for the abundances of M, M – H and M – D peaks in the spectra of *2*, *2a*, *2b*, and *2c* are given in Table 1.

The metastable ion data suggest that loss of H (or D) from C-2 is always the lowest activation energy process. Thus, $E_0(2D) < E_0(5H)$ and $E_0(2H) < E_0(5D)$. From the abundance of the M – H and M – D ions it can be concluded that on average, for reactions occurring in the ion source, $k_{5H} > k_{2D}$ and $k_{2H} > k_{5D}$. In total, the data indicated the following sequences of activation energies and frequency factors:

$$E_0(2H) < E_0(2D) < E_0(5H) < E_0(5D);$$

$$\nu_{2D} < \nu_{5H};$$

corresponding to crossing $\log_{10} k$ *vs.* E curves for the competing loss of H and D from ionized *2a*. It was not possible to observe any significant change in the (M – H)/(M – D) ratio for *2a* by lowering the electron energy from 70 eV to *ca.* 12 eV, indicating a rapid rise of k_{2D} and k_{5H} with E.

The dramatic effect of deuterium substitution on the activation energy for the most facile dissociation of these ionized dioxolanes may be illustrated by the molecular ion abundances which are evident in Fig. 1 and Table 1. The fraction of the total ion current (% Σ_{40}) carried by the molecular ion is increased by a factor of 5 in the presence of deuterium substitution at C-2, whereas substitution at C-5 only leads to an increase of *ca.* 40 %. This clearly indicates that the most facile decomposition mode of ionized *2* is the loss of H from C-2. Our observations show that increasing the strength of the C(2) – H bond towards homolysis by only *ca.* 4 kJ mol^{-1} (by deuterium substitution), the fraction of molecular ions

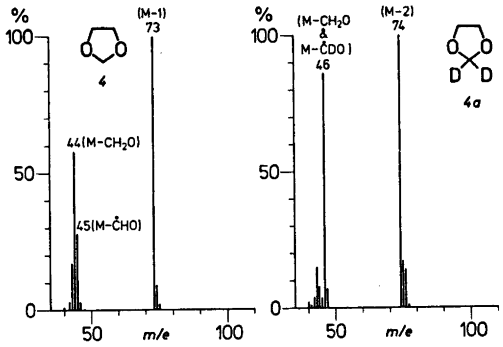
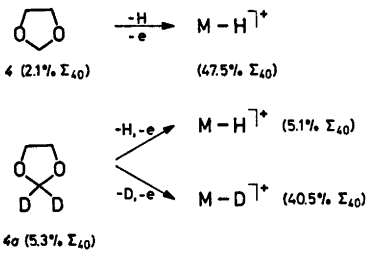


Fig. 2. Mass spectra of 1,3-dioxolane (*4*) and 1,3-dioxolane-2,2-d_2 (*4a*).

which do not decompose before reaching the collector is increased by a factor of 5.

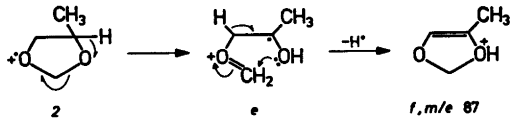
It remains to explain why 4-methyl-1,3-dioxolane (*2*) loses H from C-5 when substituted with deuterium at C-2. The phenomenon does not occur in the spectrum (Fig. 2) of 1,3-dioxolane-2,2-d_2 (*4a*) since this compound shows a great preference for D over H loss from M^+ in source reactions. The isotope labelling at C-2 in this case leads to an approximated doubling of the % Σ_{40} for the molecular ion.



Scheme 4.

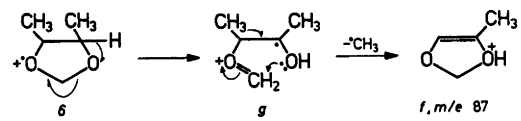
Thus, it is the presence of the C-4 methyl group in *2* and its deuterated analogues which gives rise to the phenomenon. This is further supported by the mass spectrum of 4-ethyl-1,3-dioxolane-2,2-d_2 (*5a*), which displays M−H and M−D peaks in the ratio 2.3:1. The presence of metastable peaks corresponding to the loss of H as well as D from ionized *5a* indicates, that the activation energy for loss of H from C-5 is only slightly greater than that for loss of D from C-2.

One possibility is that C−O bond cleavage in the molecular ion of *2* is favoured by participation of the C-4 hydrogen atom when the radical *e* so produced is secondary rather than primary; hydrogen radical loss from C-5 can then result in the formation of a cyclic oxonium ion *f*.



Scheme 5.

The striking anomaly in the spectrum of *2a* (Fig. 1) is emphasized by the greater abundance of the peak due to loss of H from C-5 compared to that due to loss of CH_3 from C-4, notwithstanding the greater stability of the latter radical by 79 kJ mol^{-1}. The sequence *2*→*e*→*f* not only accomodates this anomaly by using the methyl group to stabilize the radical centre while labilizing the hydrogen radical to be lost, but also leads to the prediction that, since a methyl radical is much more stable than a hydrogen radical, a 4,5-dimethyl-1,3-dioxolane (*6*) should undergo methyl radical loss (*6*→*g*→*f*) in preference to H expulsion.



Scheme 6.

This prediction is realized in the mass spectra of either diastereoisomer of *6* (Fig. 3; the spectra of *Z*-isomer being reproduced). Also as anticipated, the poor competition of H loss relative to CH_3 loss from *6* (1:6) is worsened in the 2,2-d_2-analogue *6a* [(M−H):(M−D): (M−CH_3) = 1:2:30], (see also Fig. 3).

EXPERIMENTAL

The mass spectra were recorded on an AEI MS902 mass spectrometer at 70 eV. The samples were introduced through the glass inlet system. The gas chromatographic separations were made on a Perkin-Elmer F21 pre-

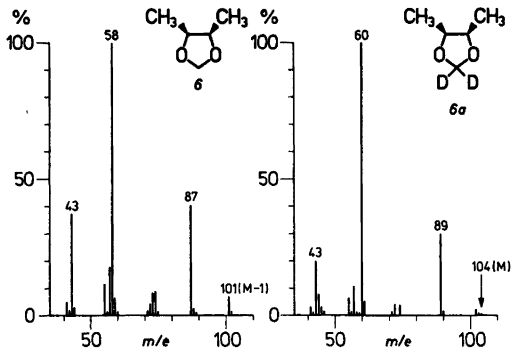


Fig. 3. Mass spectra of *Z*-4,5-dimethyl-1,3-dioxolane (*6*) and *Z*-4,5-dimethyl-1,3-dioxolane-2,2-d_2 (*6a*).

parative gas chromatograph using a 10 % Carbowax 1500 column at 70 °C. The 1,3-dioxolanes were prepared according to the general procedure given below. The diols were commercial samples unless otherwise stated. The perdeuterioparaformaldehyde and the lithium aluminium deuteride used were more than 98 % isotopically pure reagents. The purity of the products was checked by NMR spectrometry and GLC.

General procedure for the preparation of 1,3-dioxolanes. Equimolar amounts (*ca.* 0.1 mol) of the diol and paraformaldehyde (or perdeuterioparaformaldehyde) and a catalytic amount of concentrated sulfuric acid were stirred and heated (oil bath, *ca.* 130 °C) in a flask equipped with a distillation condenser. The dioxolane and water formed during the reaction were distilled off as an azeotrope. With the exceptions of the cases of 1,3-dioxolane (*4*) and 1,3-dioxolane-2,2-d_2 (*4a*), the distillates separated into two phases. The dioxolane was isolated and dried over anhydrous potassium carbonate. The samples of *4* and *4a* contained an equimolar amount of water.

1,2-Propandiol-1,1-d_2 was prepared by the reduction of 5-methyl-1,3-dioxolan-4-one (prepared according to Salomaa and Laiho [7]) with lithium aluminium deuteride.

DL-E- *and Z-4,5-dimethyl-1,3-dioxolane (6) and* DL-E- *and Z-4,5-dimethyl-1,3-dioxolane-2,2-*d_2 *(6a).* From 2,3-butanediol (containing equimolar amounts of *meso-* and DL-2,3-butanediol) and paraformaldehyde a mixture of DL-E- and *Z*-4,5-dimethyl-1,3-dioxolane (*6*) was formed. The isomers were separated by preparative GLC. The d_2-analogues were obtained in a similar manner.

4-Methyl-1,3-dioxane (3). MS [*m/e* (% rel. int.)]: 102 (6, M), 101 (98, [M−H]), 87 (20, [M−CH_3]), 72 (59), 71 (5), 58 (20), 57 (25), 55 (73), 45 (43), 44 (18), 43 (100), 42 (39), 41 (25).

4-Methyl-1,3-dioxane-2,2-d_2 *(3a).* MS [*m/e* (% rel. int.)]: 104 (8, M), 103 (5, [M−H]), 102 (58, [M−D]), 89 (47, [M−CH_3]), 72 (77), 71 (6), 60 (22), 59 (5), 58 (7), 57 (14), 55 (47), 47 (16), 46 (20), 45 (25), 44 (21), 43 (100), 42 (42), 41 (23).

4-Ethyl-1,3-dioxolane (5). MS [*m/e* (% rel. int.)]: 102 (9, M), 101 (65, [M−H]), 73 (65), 72 (40), 57 (9), 55 (34), 46 (7), 45 (48), 44 (100), 43 (40), 42 (12), 41 (17); *m** 102→101, obs. 100.1, calc. 100.0.

4-Ethyl-1,3-dioxolane-2,2-d_2 *(5a).* MS [*m/e* (% rel. int.)]: 104 (15, M), 103 (35, [M−H]), 102 (15, [M−D]), 75 (67), 74 (27), 72 (21), 57 (7), 55 (20), 47 (38), 46 (100), 45 (15), 43 (19), 42 (13), 41 (15); *m** 104→103, obs. 102.1, calc. 102.1; 104→102, obs. 100.1, calc. 100.0.

REFERENCES

1. Nielsen, J. U. R., Jørgensen, S. E., Frederiksen, N., Jensen, R. B., Dahl, O., Buchardt, O. and Schroll, G. *Acta Chem. Scand. B 29* (1975) 400.
2. Collin, J. *Bull. Soc. Chim. Belg. 69* (1960) 585.
3. Beynon, J. H. *Mass Spectrometry and Its Applications to Organic Chemistry*, Elsevier, Amsterdam 1960, p. 368.
4. Marshall, J. T. B. and Williams, D. H. *Tetrahedron 23* (1967) 321.
5. Cooks, R. G., Yeo, A. N. H. and Williams, D. H. *Org. Mass Spectrom. 2* (1969) 985.
6. Budzikiewicz, H., Djerassi, C. and Williams, D. H. *Mass Spectrometry of Organic Compounds*, Holden-Day, San Francisco 1967, pp. 257 and 265, and references cited therein.
7. Salomaa, P. and Laiho, S. *Acta Chem. Scand. 17* (1963) 103.

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