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

J. U. R. NIELSEN, S. E. JØRGENSEN, N. FREDERIKSEN, R. B. JENSEN, GUSTAV SCHROLL
and D. H. WILLIAMS**

Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen,
DK-2100 Copenhagen, Denmark

4-Methyl-1,3-dioxolane-2,2-d₄ (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 mecha-
nism for this unexpected reaction is proposed.

The mass spectra of 1,3-dioxolanes (1) have been extensively studied ⁵⁻⁷ and discussed ⁸ 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 which is formed.

Scheme 1.

It was therefore extremely surprising to find that 4-methyl-1,3-dioxolane-2,2-d₄ (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.

Scheme 2.

Early evidence cited as supporting a low activation energy for the formation of a de-
localized 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−CH₃ peak.⁹ It was
argued ⁹ that since methyl radical loss is normally preferred over hydrogen radical loss in
mass spectra (where this competition can occur for −H and −CH₃ 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-d₄ (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 deriva-
tives 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-d₄-derivative 2b
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.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>%</th>
<th>M</th>
</tr>
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<tbody>
<tr>
<td>2 (d5)</td>
<td>0.8</td>
<td>M⁺&lt;M−H⁺</td>
</tr>
<tr>
<td>2a (2,2-d₅)</td>
<td>4.0</td>
<td>10.2</td>
</tr>
<tr>
<td>2b (5,5-d₅)</td>
<td>1.1</td>
<td>19.1</td>
</tr>
<tr>
<td>2c (2,2,5,5-d₅)</td>
<td>4.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

*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, $E_{o}(2D)<E_{o}(5H)$ and $E_{o}(2H)<E_{o}(5D)$. 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, $k_{H}>k_{D}$ and $k_{H}>k_{D}$. In total, the data indicated the following sequences of activation energies and frequency factors:

$$E_{o}(2H)<E_{o}(2D)<E_{o}(5H)<E_{o}(5D);$$

$v_{1D}<v_{1H};$

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 $k_{1D}$ and $k_{1H}$ 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 ( % $\Sigma_{40}$) 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...
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 CH₃ from C-4, notwithstanding the greater stability of the latter radical by 79 kJ mol⁻¹. The sequence 2→e→f not only accommodates 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 CH₃ loss from 6 (1:6) is worsened in the 2,2-d₄-analogue 6a [(M–H):(M–D): (M–CH₃) = 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$_4$ (6a).

Preparative gas chromatography using a 10% Carbowax 1600 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 perdeuterioparafomaldehyde 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 azo trope. With the exceptions of the cases of 1,3-dioxolane (4) and 1,3-dioxolane-2,2-d$_4$ (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$_4$** was prepared by the reduction of 5-methyl-1,3-dioxolane-4-one (prepared according to Salomaa and Laiho) 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$_4$ (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$_4$-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 (75), 45 (43), 44 (18), 43 (100), 42 (39), 41 (26).

**4-Methyl-1,3-dioxane-2,2-d$_4$ (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 (54), 46 (7), 45 (48), 44 (100), 43 (40), 42 (12), 41 (17); m*→102, obs. 100.1, calc. 100.0.

**4-Ethyl-1,3-dioxolane-2,2-d$_4$ (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, obs. 102.1, calc. 102.1; 104→102, obs. 100.1, calc. 100.0.

**REFERENCES**


Received October 5, 1976.