The Mass Spectral Fragmentation of 1,4-Butanediol

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The behaviour of 1,4-butanediol under electron impact at 70 and 12.5 eV has been studied with the aid of high resolution mass spectra. Based on metastable ion decompositions and deuterium labelling, mechanisms are proposed for the formation of the abundant ions of this compound.

In a previous paper we reported on the mechanism of fragmentations occurring in α, δ-diols upon electron ionization.[1] Recently, the simplest of such diols, 1,4-butanediol, has been a source of $[C_2H_4O]^+$ ions used in a collisional activation study, and a mechanism was proposed for the formation of this ion.[2] The sentence '... the proposed fragmentation pathways are obviously speculative in the absence of labelling evidence'[2] revealed that some aspects of the mass spectral behaviour of 1,4-butanediol are still[3] open to question. Thus we report our investigations regarding the fragmentation of 1,4-butanediol (**1**). The fragmentation mechanisms proposed here are confirmed by the mass spectral data of the deuteriated analogues **2** and **3**.

XO—CR$_2$—CH$_2$—CH$_2$—CR$_2$—OX **1:** $X = R = H$
2: $X = {}^2H, R = H$
3: $X = H, R = {}^2H$

RESULTS AND DISCUSSION

The high resolution mass spectra of compounds **1–3** are shown in Figs. 1–3. The lines of the ions containing one oxygen atom are drawn exactly at the mass number marks, while those of ions with no and two oxygen atoms appear just above and below the marks, respectively. Results of measurements on metastable ion decompositions are given in Table 1. The mechanism proposed previously[1] for the elimination of water and for the accompanying processes in α,δ-diols also applies to the case of 1,4-butanediol. The relevant ions shown in Scheme 1 give rise to about 50% of the total ion abundance in the 70 eV spectrum of **1**. The formation of the ions *a*, *b*, *d*, *f* and *g* corresponds directly to that of the ions denoted by the same symbols in Ref. 1.

The stepwise nature of the fragmentation processes which follow the initial hydrogen rearrangement from one hydroxyl group to the other in α,δ-diols was recognized some years ago.[4] This means that the elimination of water does not take place in this case as a concerted reaction, but a rearranged molecular ion (as $[M']^{+\cdot}$ in Scheme 1) is formed in which the cation and radical sites are separated. In such an intermediate species hypothetically independent decomposition reactions may occur simultaneously at either site. Several observations attest that, in general, the homolytic fissions at the vincinity of an *isolated* radical site proceed at a higher rate than the heterolytic fissions at cation sites.[5] The detectability of the product of the faster homolytic reaction depends on the rate of the heterolytic fission, which in turn depends strongly upon the stabilities of the neutral molecule and the cation formed. This is the reason why a relatively abundant ion *e* occurs in the spectra of **1–3**, while the corresponding ion of 2,5-hexanediol does not exceed 1% relative intensity. As the neutral molecule eliminated is water in both cases this difference reflects the lower heat of formation of the secondary carbonium ion formed from ion *e* in the latter compound. The presence of ion *c* which decomposes to ion *d* (see Table 1) can be explained similarly.

The formation of ion *h* depicted in Scheme 1 supports the structure assigned to ion *b*. The analogous process, although not discussed,[1] also takes place in the case of 2,5-hexanediol.

Ion *f* is depicted in Scheme 1 as the cyclopropane radical cation because of the approximately random loss of $^{\cdot}$H and $^{\cdot}$D when giving ion *g* in the case of compound **3**. It should be noted in this context that the pictorial representations appearing in Scheme 1 may correspond rather to the ions decomposing further than to those which give rise to the peaks at the respective mass numbers in the spectra. These latter ions may be stabilized by electronic interactions and, occasionally, by rearrangements.

The deuterium contents of ions *a–h* in the spectra of **2** and **3**, as well as the 'metastable' data given in Table 1, are in accordance with the fragmentation pattern depicted in Scheme 1.

The processes connected with the other mechanism by which the molecular ion of 1,4-butanediol can lose water contribute about 30% of the total ion abundance in the case of the 70 eV spectrum of **1**. It should be noted that in the spectrum of 2,5-hexanediol this proportion is only $6.5\,\Sigma\%$. As shown in Scheme 2 these pathways start with a [1, 4] hydrogen rearrangement—a well known step in the elimination of water from aliphatic alcohols[6]—yielding the rearranged molecular ion $[M'']^{+\cdot}$. This intermediate state can be considered to possess separated radical and cation sites. The heterolytic fission at the cation site in

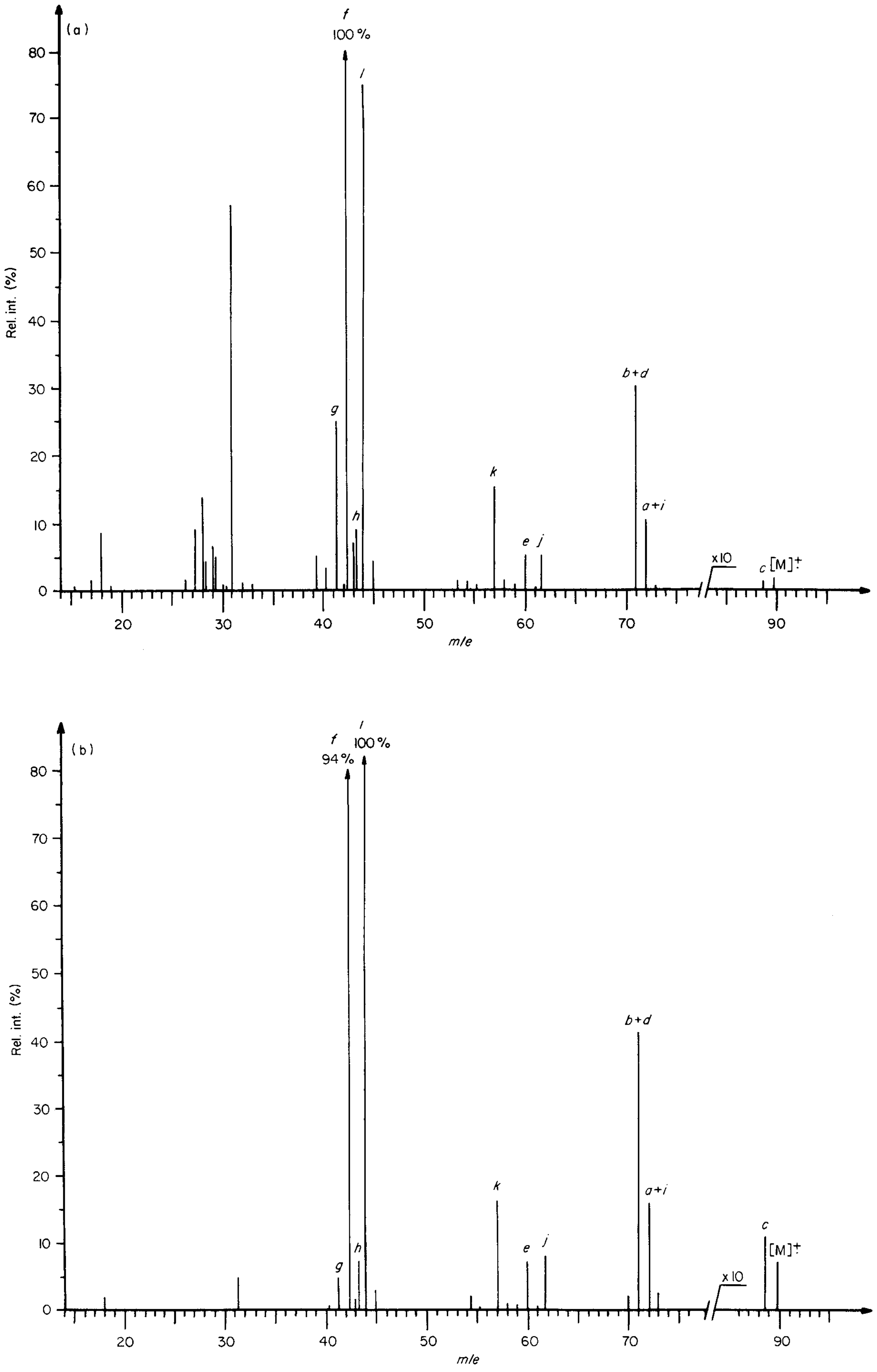


Figure 1. Mass spectra of 1,4-butanediol (1): (a) at 70 eV; (b) at 12.5 eV.

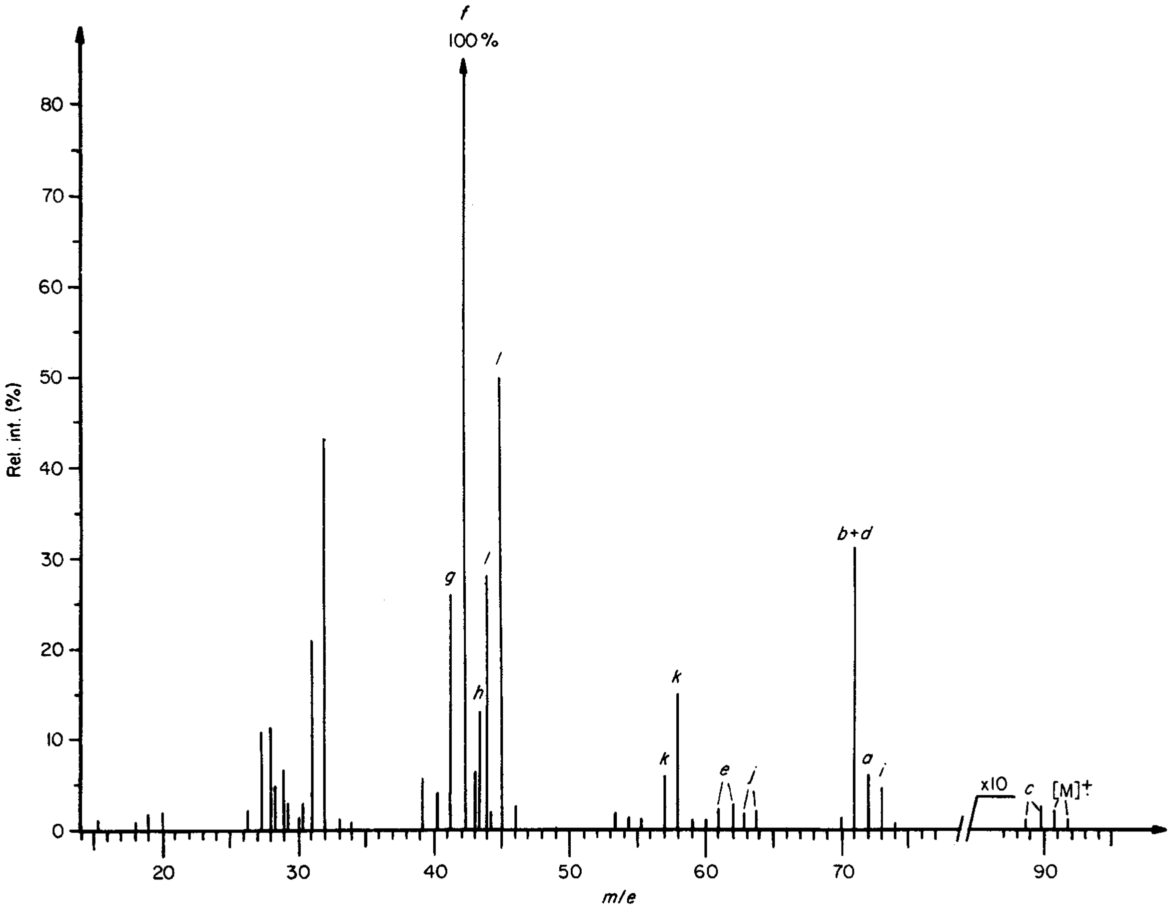


Figure 2. Mass spectrum of compound 2.

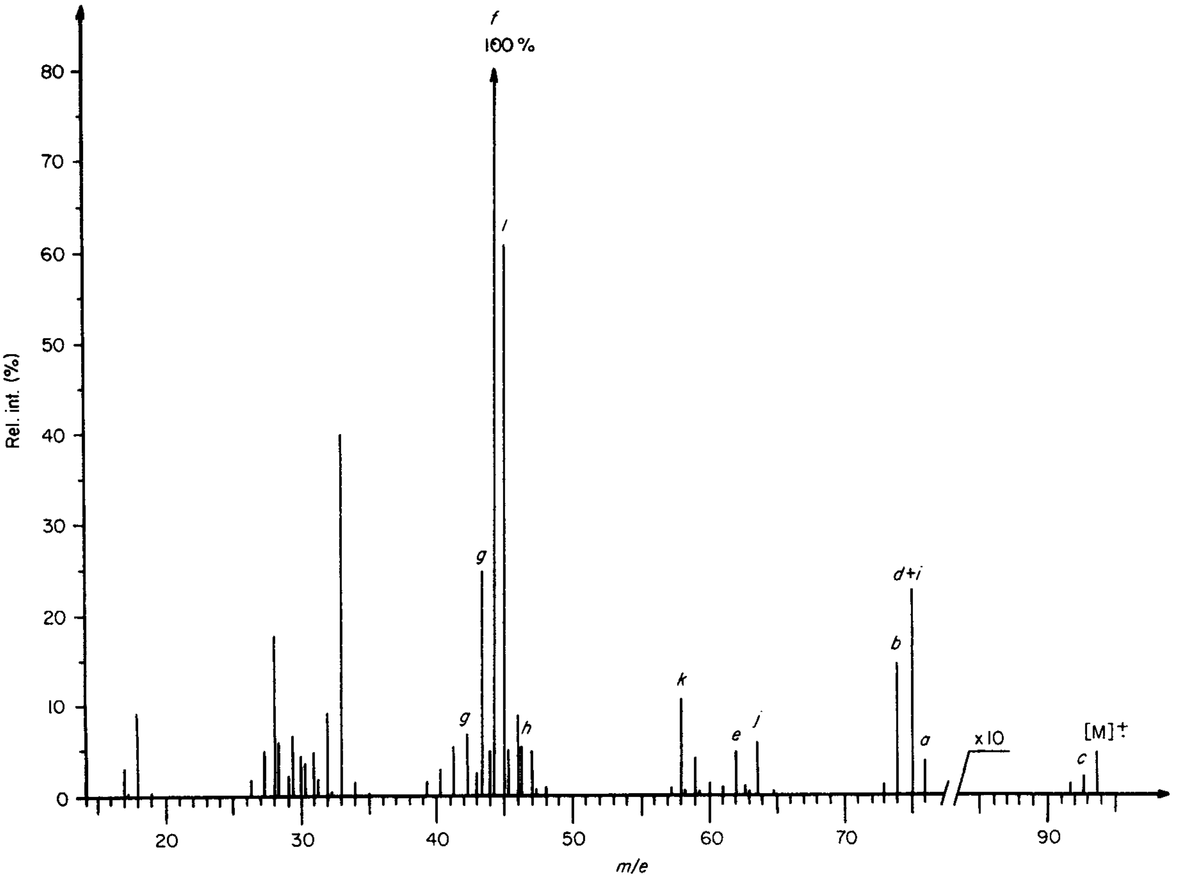


Figure 3. Mass spectrum of compound 3.

4A

Table 1. Metastable ion decompositions of compounds 1 and 3

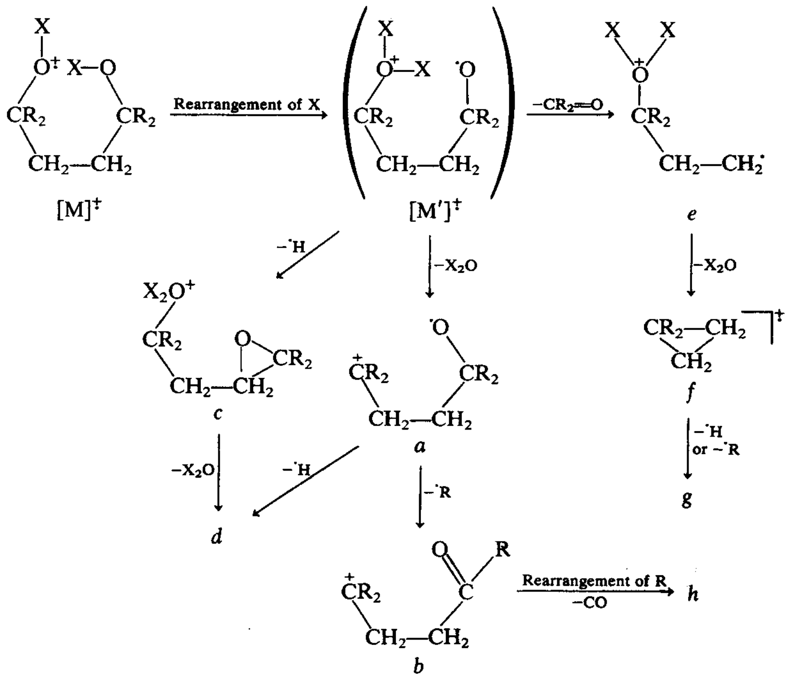
Scheme	Symbol	Compound	m_2	Voltage ratio	m_1	Intensity
1	*a*	3	76	1.240	94	weak (w)
	b	3	74	1.029	76	medium (m)
	d	1	71	1.253	89	very weak
	f	1	42	1.428	60	m
		3	44	1.472	62	m
	h	3	46	1.603	74	m
1, 2	*a, i*	1	72	1.253	90	m
2	*i*	3	75	1.254	94	w
	j	1	62	1.451	90	strong (s)
	k	1	57	1.265	72	s
	l	1	44	1.638	72	w
				1.410	62	w
		3	45	1.668	75	w
			46	1.391	64	w

ion $[M'']^{+\cdot}$ results in the formation of ion *i* which may be stabilized, e.g. as cyclobutanol. A similar pathway has been proposed for the loss of water from **1** by Van de Sande and McLafferty.[2] It seems likely that the stable $[M-RXO]^{+\cdot}$ ions correspond to structures *i* (and/or to other possible stabilized forms of the open chain product formed by this primary loss of water). According to the spectra of **2** and **3**, about two-thirds of the non-fragmenting $[M-\text{water}]^{+\cdot}$ ions are formed in this way.

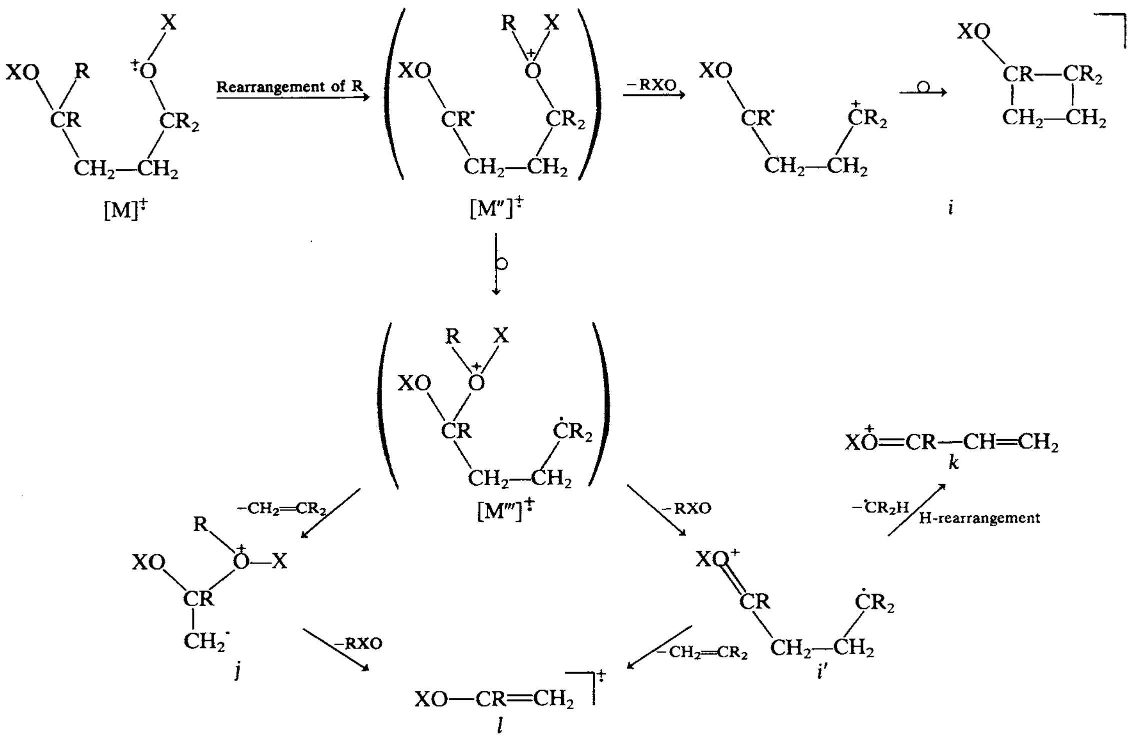
The mechanisms depicted in Scheme 2 for the formation of ion *l* which corresponds to the abundant ion at *m/e* 44 in the spectra of **1** are based on the following considerations. The presence of ion *j* in the spectra of **1–3** indicates that an unusual rearrangement can occur in the rearranged molecular ion $[M'']^{+\cdot}$, which leads to the formation of the intermediate species $[M''']^{+\cdot}$. This process can be rationalized as the interaction of the unpaired electron and the C—$\overset{+}{O}$(RX) bond in ion $[M'']^{+\cdot}$ being sterically close at the moment of the rearrangement of R. The rearrangement of 3-phenyl-1-nitropropane to 3-phenyl-3-hydroxy-1-nitrosopropane[7] shows some analogy to this process. The formation of ion *j* from the rearranged molecular ion is accompanied by an intense metastable peak (see Table 1). The deuterium content of ion *j* in the spectra of **2** and **3** supports the $[M'']^{+\cdot} \rightarrow [M''']^{+\cdot} \rightarrow j$ pathway.

As attested by the metastable transition $j \rightarrow l$, the elimination of water from ion *j* is one of the processes by which ion *l* is formed. In the spectra of both **2** and **3** there is a deviation from the expected deuterium content of ion *l*, in the case of **3**, e.g. a d_2 content of about 10% occurs in this ion. This phenomenon can be explained by assuming that a hydrogen bond is formed in ion *j* between the oxygen atoms, resulting in a higher stability of that ion. In the case of **3**, H_2O can be ejected from such ions, giving the d_2-containing portion of ion *l* at *m/e* 46. The assumption that this latter ion is formed from ion *j* in a multistep process is supported by the fact that the metastable transition $j \rightarrow l$ leads mainly to the ion at *m/e* 46 in the case of **3** (see Table 1).

It is reasonable to suppose that—as a competitive process to the formation of ion *j*—the elimination of water may also take place from the intermediate species $[M''']^{+\cdot}$, giving ion *i'*. In our opinion ion *i'* and the open chain ion *i* are not 'canonical forms'[8] representing the same ionic species. The loss of ethylene from ion *i'* in a homolytic fission can give a part of ion *l*. It was not possible to differentiate experimentally between this process and the loss of ethylene from the open chain form ion *i* in a heterolytic fission. The cyclized form of ion *i* can be ruled out as a precursor of ion *l* (cf. Ref. 2), since it would give ion *l* and ion $[CD_2{=}CD{-}OH]^{+\cdot}$ with equal probability in the case



Scheme 1



Scheme 2

of **3**. However, the abundance of ion $[CD_2{=}CD{-}OH]^{+\cdot}$ is less than 2% in the spectrum of **3**.

The structure of ion *l* formed by either pathway depicted in Scheme 2 is in accordance with the result of the collisional activation study[2] on this ion.

The formation of ion *k* from ion *i′* is attested by metastable peaks in the case of both **1** and **3** (see Table 1). A study on the detailed mechanism of this process will be published subsequently.

EXPERIMENTAL

Mass spectra were taken on a Varian MAT SM-1 instrument under the following operating conditions: resolution, 1800; accelerating voltage, 8 kV; electron energy, 70 or 12.5 eV; electron current, 300 μA; source temperature, 150 °C; inlet temperature, 20 °C.

For low electron energy studies, the electron accelerating voltage was set to the ionization potential of oxygen (*c.* 12.5 eV).

Measurements on metastable ion decompositions were performed by scanning the accelerating voltage. Each voltage ratio given in Table 1 is that of the voltage necessary to observe the daughter ion m_2 formed from the appropriate metastable precursor ion m_1 versus the respective normal operating voltage.

The n.m.r. spectra were recorded on a JEOL C-60HL spectrometer, using TMS as internal standard.

1,4-Butanediol (**1**) was a commercial sample (Fluka), redistilled before use. N.m.r. (neat): δ1.62 ppm (4 H, m), δ3.58 ppm (4 H, m), δ5.06 ppm (2 H, s).

Compound **2** was prepared by refluxing **1** with tenfold D_2O for 1 h. The solution was evaporated and the procedure repeated three times. Deuterium content (m.s.): d_0 7.9%, d_1 40.5%, d_2 51.6%.

1,1,4,4-d_4*-1,4-Butanediol* (**3**).[9] 1.67 ml (10 mmol) of diethyl succinate in 3.5 ml dry dioxane was added to a suspension of 0.66 g (15 mmol) of $LiAlD_4$ in 10 ml dry dioxane. The reaction mixture was refluxed for 48 h, and then stored for 48 h at +5 °C. The solid material was filtered off, suspended in diethyl ether (10 ml) and a solution of K Na tartrate (1 g in 2 ml water) was added. The slurry formed was filtered and evaporated *in vacuo*. The residue was chromatographed on silica gel, using ethyl acetate as the solvent. The fractions containing the diol were evaporated and the residue was distilled at 1 Torr to give 0.4 g of pure compound **3** (yield: 45%). N.m.r. in dry pyridine: δ1.90 ppm (4 H, s) δ6.00 ppm (2 H, s). Isotopic purity (n.m.r.): $d_4 > 97\%$.

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