Electron Impact Induced Intramolecular Hydrogen Transfer Reactions in Polymethylene Glycol Di-*p*-toluenesulfonates

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The mechanisms of formation of the ionized acid and the protonated acid fragments in the electron impact induced fragmentation of the title compounds were investigated. The well known mechanisms of hydrogen transfer through mono- and bicyclic transition states that occur in the molecular ions of carboxylic esters are not the main pathways giving rise to these fragments. The major component of the *m/z* 172 peak corresponding formally to ionized *p*-toluenesulfonic acid in fact has a different structure; its formation involves a complex mechanism including a double hydrogen transfer reaction.

INTRODUCTION

In the course of our mass spectrometric studies of bifunctional aliphatic compounds[1,2] we have examined the mass spectra of a series of di-*p*-toluenesulfonic esters of polymethylene glycols with 4 to 8 carbon atoms in the aliphatic chain and more particularly those of the deuterated species **2–4** of the ditosylate derivative of 1,4-butanediol (**1**). We observed surprising results for the mass shifts of the ionized *p*-toluenesulfonic acid at *m/z* 172 and its corresponding protonated analogue at *m/z* 173. This has prompted us to study in more detail the mechanisms of formation of these two ions.

$CH_3C_6H_4—SO_2—O—\overset{\alpha}{C}H_2—\overset{\beta}{C}H_2—\overset{\beta'}{C}H_2—\overset{\alpha'}{C}H_2—O—SO_2—C_6H_4CH_3$ **1**

$CH_3C_6H_4—SO_2—O—CD_2—(CH_2)_2—CD_2—O—SO_2—C_6H_4CH_3$ **2**

$CH_3C_6H_4—SO_2—O—CH_2—(CD_2)_2—CH_2—O—SO_2—C_6H_4CH_3$ **3**

$CH_3C_6H_4—SO_2—O—(CD_2)_4—O—SO_2—C_6H_4CH_3$ **4**

RESULTS AND DISCUSSION

According to published work on the mass spectrometric fragmentation of esters,[3] and more specifically of alkylsulfonates,[4,5] one would expect Eqns (1) and (2) to account for the formation of the *m/z* 172 and 173 ions in the 70 eV spectrum of **1** (Fig. 1), the transferred hydrogen atoms coming from the alkyl chain.

$$[CH_3C_6H_4SO_2OR]^{+\cdot} \rightarrow [CH_3C_6H_4SO_2OH]^{+\cdot} + (R-H) \quad (1)$$

$$[CH_3C_6H_4SO_2OR]^{+\cdot} \rightarrow [CH_3C_6H_4SO(OH)_2]^{+} + (R-2H) \quad (2)$$

However, the observed mass shifts of *m/z* 172 and 173 (Table 1) in the spectra of the labelled derivatives cannot be explained on this basis. If one considers that *m/z* 172 cannot increase by more than 1 u in the spectra of **2** and **3** (i.e. there is no H/D exchange between the acid and the alcohol parts of the molecular ion prior to reaction (1)), then one can calculate the fractions of the total hydrogen transfer originating from the α,α' and β,β' positions using either of these two spectra. The spectrum of **2** leads to the conclusion that 65.3% $((44.7-15.5)/44.7\times 100)$ of the migrating hydrogen in reaction (1) originates from the positions α,α', while the spectrum of **3** shows that 66.7% $((44.7-14.9)/44.7\times 100)$ comes from the positions β,β'. This is illogical since with a normal isotope effect (i.e. favouring H transfer) the sum should be less than 100%.

On the other hand, if one also allows that *m/z* 172 cannot increase by more than 1 u in the spectrum of **4**, then *m/z* 173 can shift by 1 and 2 u but an abnormal isotope effect is again encountered. The relative ion current of *m/z* 172/*m/z* 173 decreases from 44.7/55.3 in the spectrum of **1** to 19.5/80.5 in the spectrum of **4**. It is obvious that the replacement of all possible migrating hydrogen atoms by deuterium atoms should lead to a change in the opposite direction. Moreover, the spectrum of **4** shows that the migrating H atom in reaction (1) does not originate exclusively from the alkyl chain; a fraction of the *m/z* 172 ion current does not shift.

These observations show clearly that reaction (1) is not the only one giving rise to *m/z* 172. First, part of *m/z* 172 is produced by a mechanism involving the transfer of a H atom of the second *p*-toluenesulfonic

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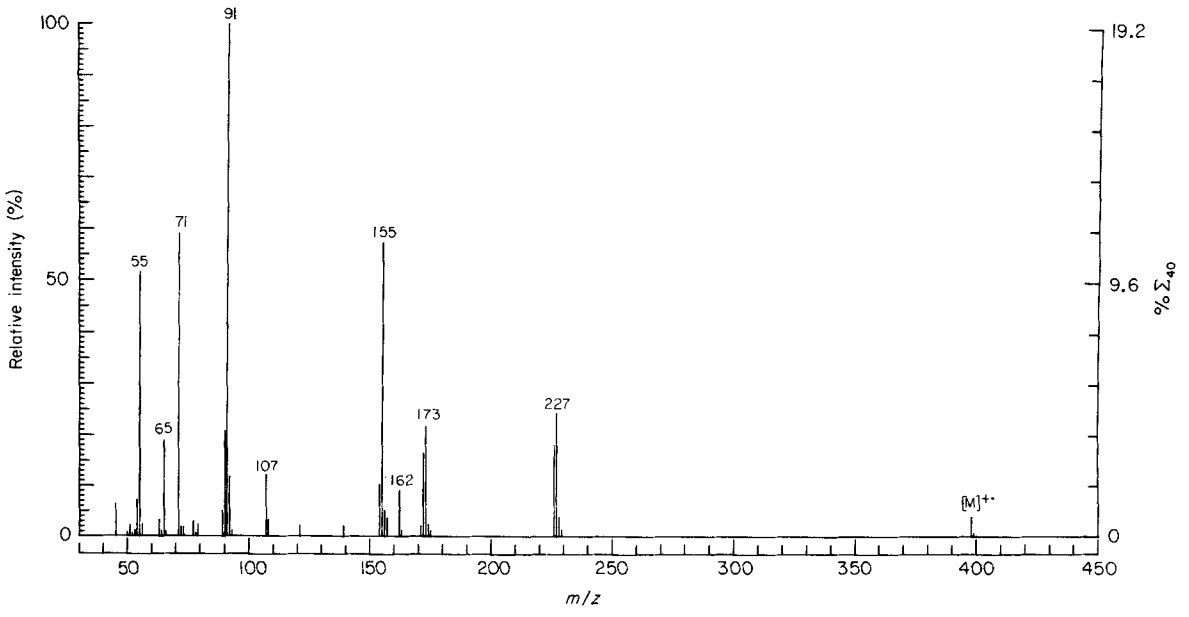


Figure 1. 70 eV mass spectrum of 1,4-butanediol di-*p*-toluenesulfonate.

moiety. For obvious steric and energetic reasons it seems difficult to conceive a direct transfer of tolyl hydrogen (aromatic or methyl) through a cyclic transition state in the molecular ion. Internal H/D randomization between the acid and alcohol moieties prior to reaction (1) is also improbable; such an exchange has not been noticed in the alkylbenzoate esters.[6,7] A precursor ion other than the molecular ion might explain the formation of that fraction and indeed, a close examination of the spectra shows that such a precursor could be the ion at *m/z* 326 (0.01% of the base peak in the spectrum of **1**) corresponding to ionized *p*-toluenesulfonic anhydride. Reaction (3) may then plausibly represent the formation of this fraction.

$$[M]^{+\cdot} \rightarrow \underset{m/z\ 326}{[CH_3C_6H_4SO_2—O—SO_2C_6H_4CH_3]^{+\cdot}} \rightarrow \underset{m/z\ 172}{[CH_3C_6H_4SO_2OH]^{+}} \quad (3)$$

To explain the apparently abnormal isotope effect a second fraction of *m/z* 172 could be produced by a process yielding a species that can shift by 2 u in the spectra of the labelled derivatives. This process would formally imply the transfer of two H atoms from the alkyl chain and the loss of one H atom from the ionized acid moiety. Again, a close examination of the spectra gives support to such a mechanism. The spectrum of **1** contains a pair of peaks at *m/z* 226 and 227 (24.7 and 18.0% of the base peak respectively). Both shift by 4 u in the spectra of **2** and **3** and by 8 u in the spectrum of **4**. Fragment *m/z* 227 is produced by the loss of a tosylate radical from the molecular ion by simple cleavage [Eqn (4)].

$$[CH_3C_6H_4SO_2O—(CH_2)_4—OSO_2C_6H_4CH_3]^{+\cdot} \rightarrow \underset{m/z\ 227}{[CH_3C_6H_4SO_2O—(CH_2)_4]^{+}} \quad (4)$$

The fragment at *m/z* 226 involves the expulsion of neutral *p*-toluenesulfonic acid and could be produced by a McLafferty rearrangement with the charge remaining with the olefin moiety. This is not the case, however, since the itinerant H atom does not originate from the β,β' positions but from the tosyloxy group of the ion. Again a cyclic transition intermediate of the molecular ion cannot explain such a transfer. Hence the loss of a H atom from *m/z* 227 [Eqn (5)] is probably the only mechanism leading to *m/z* 226 (*m** 227 → 226, calc. 225.0, obs 225.0).

$$\underset{m/z\ 227}{[CH_3C_6H_4SO_2O(CH_2)_4]^{+}} \rightarrow \underset{m/z\ 226}{[C_7H_6SO_2O(CH_2)_4]^{+\cdot}} \quad (5)$$

The fragment at *m/z* 226 then gives rise to a *m/z* 172 species (*m** 226 → 172, calc. 130.9, obs. 130.9) by a double hydrogen transfer reaction shown in Eqn (6).

$$\underset{m/z\ 226}{[C_7H_6\overleftarrow{SO_2O}—(CH_2)_4]^{+\cdot}} \rightarrow \underset{m/z\ 172}{[C_7H_6SO(OH)_2]^{+\cdot}} \quad (6)$$

Finally, a single hydrogen transfer reaction in the *m/z* 227 fragment [Eqn (7)] leads to a *m/z* 172 ion which shifts in the

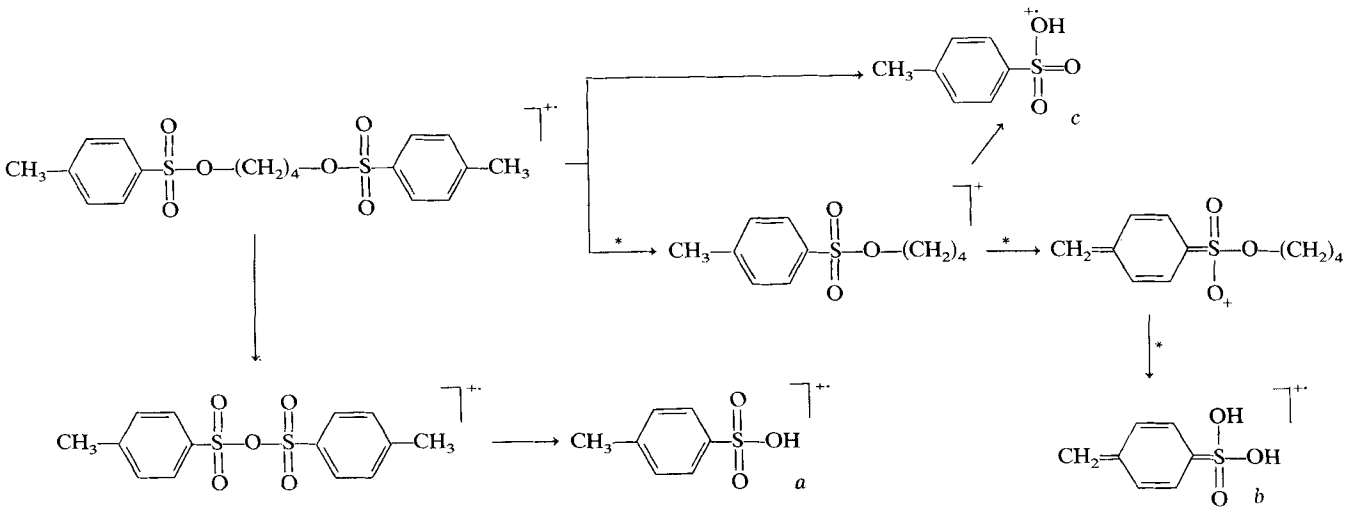
$$\underset{m/z\ 227}{[CH_3C_6H_4\overleftarrow{SO_2O}—(CH_2)_4]^{+}} \rightarrow \underset{m/z\ 172}{[CH_3C_6H_4SO_2OH]^{+\cdot}} \quad (7)$$

spectra of the deuterated derivatives in the same way as the one produced by the reaction given in Eqn (1). Thus, *m/z* 172 is produced at least by three different mechanisms, giving the ion species *a*, *b* and *c* as illustrated in Scheme 1.

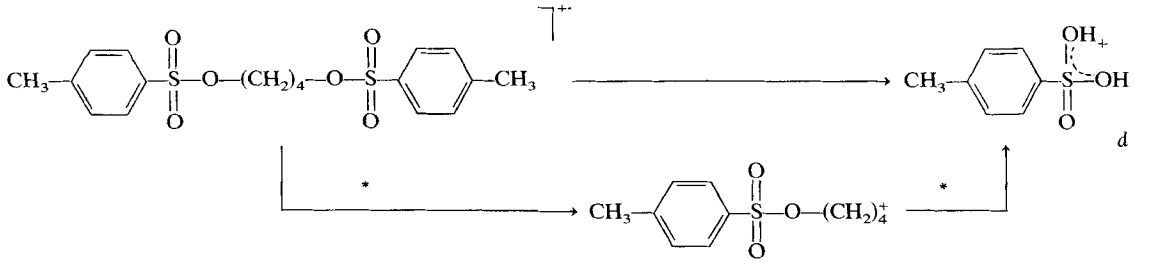
Table 1. Ion intensities[a] ($\%\Sigma I_{172\text{-}175}$) in the 70 eV mass spectra of 1–4

	Compound			
m/z	1	2	3	4
172	44.7	15.5	14.9	4.5
173	55.3	36.5	42.6	15.0
174		37.0	35.5	31.0
175		11.0	7.0	49.5

[a] Corrections have been made for naturally occurring isotopes.



Scheme 1



Scheme 2

On the other hand, at least part of the *m/z* 173 ion current originates from *m/z* 227 by a double hydrogen transfer reaction (*m** 227 → 173, calc. 131.85, obs. 131.9). The reaction given in Eqn (2), if present, is not the only one giving rise to protonated *p*-toluenesulfonic acid (Scheme 2). Regardless of the mechanism of its formation, *m/z* 173 involves two H atoms of the alkyl chain and it shifts totally to *m/z* 175 in the spectrum of **4**.

Knowing the occurrence of the different species *a*, *b* and *c* of the *m/z* 172 ions, one can deduce the relative abundances of ions *a*, *b*, *c* and *d* and also determine the origin of the H atoms that are transferred (Table 2).

Table 2. Relative abundances of the ion species *a*, *b*, *c*, *d* and origin of the migrating hydrogen atoms

Ion	*m/z*	Relative abundance[a] (%$\Sigma I_{172-173}$)	Migrating H atoms Number	Origin
a	172	4.5	1	Tolyl
b	172	31.0	2	52% α,α′; 48% β,β′
c	172	15.0	1	51% α,α′; 49% β,β′
d	173	49.5 (55.3)[b]	2	54% α,α′; 46% β,β′

[a] From the spectrum of **4**.
[b] From the spectrum of **1**.

CONCLUSIONS

With the present knowledge about these unexpected processes of formation for *m/z* 172, the mass shifts in the spectra of the labelled compounds (Table 1) can be explained easily. The decrease of the relative abundance of ion *d* from 55.3% in the spectrum of **1** to 49.5% in the spectrum of **4** results from a normal isotope effect. It is obvious that a similar isotope effect is also operative for the formation of ion *b*; its relative abundance of 31.0% in the spectrum of **4** is somewhat lower than the true value for the unlabelled compound **1**.

The non-specificity of the migrating H atoms (Table 2) may be due to various competing mechanisms involving transition states of different ring sizes, or to hydrogen randomization in the alkyl chain. It is now well established that no significant H randomization occurs in the alcohol moiety of the alkylmonoesters of carboxylic acids prior to formation of ionized acid and/or corresponding protonated fragments.[7,8] In the case of 1,4-butanediol dimethanesulfonate the formation of protonated methanesulfonic acid also involves non-selective H rearrangements and this was attributed to competing transfer mechanisms through bicyclic transition states of the molecular ion via 5-, 6-, and 7-membered rings.[5] However, the tendency to approach a purely statistical distribution for the origin of the transferred hydrogen atoms would rather indicate that there is a complete randomization in the alkyl chain as was observed previously for the electron impact induced fragmentation of α,ω-alkanediamines[1] and α,ω-alkanediols.[2]

EXPERIMENTAL

The mass spectra were obtained with a Varian MAT CH-4 spectrometer at 70 eV, using a direct insert

probe. The source temperature was 140 °C. *p*-Toluenesulfonate esters were prepared from the corresponding diols and *p*-toluenesulfonylchloride in the usual way. The preparation of the tetradeuterated diols has been described elsewhere.[2] Deuterium incorporation was better than 98% for the labelled compounds **2, 3** and **4**.

1,1,2,2,3,3,4,4-d_8-1,4-Butanediol

To a solution of 5 g of dimethylacetylenedicarboxylate in 50 cm^3 ethylacetate, 0.5 g of 10% Pd/C was added. Deuterium gas was introduced at a pressure of 3 atm. (Parr apparatus). Deuteration was achieved after 1 h and the catalyst was filtered off. Removal of the solvent at reduced pressure yielded 5 g of 2,2,3,3-d_4-dimethylsuccinate. The reduction of this ester with $LiAlD_4$ afforded 2.8 g of the desired octadeuterated 1,4-butanediol.

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