Ion–neutral–neutral complexes in unimolecular reactions: formation of proton-bound alkanol pairs from alkoxylated oxonium ions

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Received (in Cambridge, UK) 8th February 2001, Accepted 23rd May 2001
First published as an Advance Article on the web 26th June 2001

The proton-bound alkanol pairs, $[\mathrm{ROH}\cdots\mathrm{H}^+\cdots\mathrm{R'OH}]$, were generated in the unimolecular fragmentation reactions of alkoxylated oxonium ions $\mathrm{ROCH_2{-}O^+(R')(R'')}$ (where R, R′ = CH_3 or C_2H_5; R″ = *t*- or iC_4H_9). By means of collision-induced dissociative ionization mass spectrometry, the neutral counterpart of this reaction was identified to be a C_5H_8 hydrocarbon molecule. It is proposed that the reactions proceed through an intermediate ion–neutral complex in which *two* neutral alkanol molecules are associated with the 1,1-dimethylallyl cation, $\mathrm{CH_2{=}CH{-}C^+(CH_3)_2}$; the subsequent proton transfer leads to the formation of the proton-bound alkanol pair and neutral 2-methylbuta-1,3-diene (C_5H_8). This is the first three-component intermediate "ion–neutral–neutral" complex (where the ion is not a proton) identified in the unimolecular fragmentation of covalently-bonded organic ions in the gas phase.

Introduction

The unimolecular fragmentation of isolated organic ions in the gas phase has often been found to proceed *via* rearrangements involving various intermediate ion–neutral complexes.[1–4] The chemistry of ion–neutral complexes generated in unimolecular reactions is similar to those formed in bimolecular reactions.[5] An ion–neutral complex is stabilized by the interactions between the ionic and neutral partners, and it lies in an energy well relative to the separated species. Unimolecular reactions proceed while the two partners are electrostatically bound. Isomerization of the ionic moiety is a common reaction within ion–neutral complexes; other reactions are also observed, for example the transfer of a smaller ion, such as a proton, hydride or methyl cation, between the partners.

Ion–neutral complexes encountered in unimolecular reactions are most commonly in the form of an ion associated with one neutral species. Although a general definition has been given for these systems as "non-covalently bonded aggregates of an ion with one or *more* neutral molecules",[1a] ion–neutral complexes containing three bodies have only been proposed[6] for reactions of the proton-bound alcohol–alcohol or alcohol–ether pairs where there is at least one tertiary α-carbon atom. For example, *tert*-butyl alcohol so paired with another alcohol, ROH, loses water *via* an intermediate in which the *tert*-butyl cation is associated with H_2O and ROH on each side.[6] The ion–neutral complexes involved in the reactions of those proton-bound pairs are similar to that observed in ion–molecule reactions,[7] where the ion dissociates to generate a new ion–neutral pair while maintaining its coordination with the neutral reactant. In the unimolecular reactions of covalently-bonded organic ions however, intermediate ion–neutral complexes in which an ion (other than a proton) is associated with two neutral molecules have not been reported. The formation of a three-component "ion–neutral–neutral" complex in a unimolecular reaction requires that the first neutral fragment preserves its interaction with the ion when non-dissociative elimination of the second neutral molecule from the ion takes place. It could be anticipated that studies of the formation and fragmentation of a three-component ion–neutral complex could be a useful step towards understanding the chemistry of a microsolvated system.[8]

In studies of the chemistry of ion–neutral complexes, oxonium ions[9] have played a significant role.[3a,c] Most oxonium ions studied by mass spectrometry are equivalent to protonated alkanols,[10] protonated/alkylated ethers[11,12] or alkylated carbonyl compounds,[13] where the ion chemistry is focused at the central oxygen. We have recently described[14] the complex ion chemistry that results when an additional functionality is introduced into the simple trialkyloxonium ions. In this paper, we report observation of a novel unimolecular reaction of alkoxylated oxonium ions leading to the formation of the proton-bound dimer of alkanols and a neutral hydrocarbon. The reaction involves three-component ion–neutral complexes, in which two neutral alkanol molecules are associated with a tertiary carbocation.

Experimental

All experiments were carried out on a modified[15] ZAB 3F tandem mass spectrometer with BEE geometry (VG Analytical, Manchester, UK). Metastable ion (MI) and collision-induced dissociation (CID) mass spectra were acquired with the ZABCAT program[16] by accumulating 6–8 consecutive scans, at an accelerating voltage of 8 kV. Helium was used as the collision gas for all CID experiments at a cell pressure of 5×10^{-8} mbar,‡ which caused 10–15% attenuation of the main beam. To obtain the CID mass spectra of the primary products, precursor oxonium ions were mass-selected by the magnetic sector; primary fragment ions generated metastably in the second field-free region (FFR) were then transmitted to the third FFR, where the above CID conditions were applied. Metastable peak widths ($w_{0.5}$) were determined using sufficient energy resolution to reduce the main beam width to 3–4 V at half height; the corresponding kinetic energy

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‡ 1 bar = 10^5 Pa.

Table 1 Structures and preparation of the alkoxylated oxonium ions $ROCH_2–O^+(R')(R'')$

	R	R′	R″	*m*/*z*	Preparation
1	CH_3	CH_3	*t*-C_4H_9	133	$CH_2(OCH_3)_2$ + *t*-C_4H_9-OCH_3
1-*d*$_3$	CH_3	CD_3	*t*-C_4H_9	136	$CH_2(OCH_3)_2$ + *t*-C_4H_9-OCD_3
1-*d*$_9$	CH_3	CH_3	*t*-C_4D_9	142	$CH_2(OCH_3)_2$ + *t*-C_4D_9-Br
2	CH_3	CH_3	$(CH_3)_2CHCH_2$	133	$CH_2(OCH_3)_2$ + $(CH_3)_2CHCH_2$-Br
3	CH_3	C_2H_5	*t*-C_4H_9	147	$CH_2(OCH_3)_2$ + *t*-C_4H_9-OC_2H_5
4	C_2H_5	CH_3	*t*-C_4H_9	147	$CH_2(OC_2H_5)_2$ + *t*-C_4H_9-OCH_3
5	C_2H_5	C_2H_5	*t*-C_4H_9	161	$CH_2(OC_2H_5)_2$ + *t*-C_4H_9-OC_2H_5

Table 2 Metastable ion and collision-induced dissociation mass spectra of the alkoxylated oxonium ions

Ion	Mode	− ROH	− R′OH	$[ROH + H + R'OH]^+$	Other
1	MI	101(100)[a]		65(6)	
	CID	101(100)		65(5)	77(12) 69(10) 57(11) 45(5)
2	MI	101(100)		65(6)	103(10) 77(2)
	CID	101(100)		65(5)	103(10) 77(25) 69(10) 57(15) 45(15)
3	MI	115(100)	101(30)	79(6)	103(3) 91(1)
	CID	115(100)	101(28)	79(6)	103(1) 91(30) 59(10) 57(10) 45(5)
4	MI	101(25)	115(100)	79(6)	103(1) 91(1)
	CID	101(25)	115(100)	79(6)	103(1) 91(30) 59(10) 57(10) 45(5)
5	MI	115(100)		93(6)	105(7) 103(25)
	CID	115(100)		93(5)	105(38) 103(55) 59(20) 57(15)

[a] *m*/*z* (relative intensity, %).

Table 3 Kinetic energy releases ($T_{0.5}$) for the major MI fragmentations and the CID mass spectra of their product ions

Precursor ion	Product ion *m*/*z*	$T_{0.5}$/meV	CID mass spectra of the product ion *m*/*z* (%)
1	65	11	47(10) 33(100) 31(5)
	101	16	85(5) 71(15) 69(100) 45(40) 41(5)
2	65	11	47(12) 33(100) 31(8)
	101	17	85(5) 71(20) 69(100) 45(40) 41(10)
3	79	12	61(2) 47(100) 33(15) 29(5)
	101	15	85(5) 71(18) 69(100) 45(42) 41(8)
	115	16	99(5) 71(100) 69(23) 59(32) 43(4) 41(6)
4	79	12	61(2) 47(100) 33(15) 29(5)
	101	15	85(5) 71(18) 69(100) 45(40) 41(8)
	115	16	99(5) 71(100) 69(25) 59(32) 43(6) 41(7)
5	93	13	75(4) 47(100) 45(5) 29(5) 19(1)
	115	16	99(5) 71(100) 69(25) 59(40) 43(4) 41(6)

release values ($T_{0.5}$) were calculated by established procedures.[17] Collision-induced dissociative ionization (CIDI) experiments[18] were performed in the second FFR, where oxygen was used as the ionizing reagent at a pressure of 5×10^{-8} mbar while +1 kV was applied to the deflector electrode in front of the ionizing cell.

The oxonium ions studied were prepared by reactions of dimethoxy- or diethoxymethane with either appropriate butyl ethers or butyl bromide; their structures and preparation are summarized in Table 1. In the chemical ionization mode, dimethoxy- or diethoxymethane and the butylating reagent were introduced as a mixture (~1 : 1 ratio) through the septum inlet into the ion source; the source was maintained at a temperature of 150 °C and a total pressure of 8×10^{-5}–1×10^{-4} mbar. Dimethoxy- and diethoxymethane were commercially available (Aldrich Chemical Co., Milwaukee, WI) and used without further purification.

Results and discussion

The MI mass spectrum of *tert*-butylated dimethoxymethane, **1**, contains only two product ions at *m*/*z* 101 (100%) and 65 (6%, Table 2). The former is due to loss of methanol, but it is surprising that the latter was found to be the proton-bound dimer of methanol, from its CID mass spectrum (Table 3). Clearly, they both are the products of rearrangement processes. By using appropriate deuterium labelling (see Table 1 for labelling details), considerable information about the reaction mechanism was obtained from the results shown in Fig. 1. When one of the two methoxy groups is specifically labelled (by reacting dimethoxymethane with CD_3O–*t*-C_4H_9), the **1**-*d*$_3$ ion loses CH_3OH and CD_3OH with equal abundance (Fig. 1a); meanwhile, the proton-bound methanol pair shifts to *m*/*z* 68, and its CID mass spectrum (Fig. 1b) is wholly compatible with $[(CH_3OH)H^+(CD_3OH)]$. This shows that methanol loss is triggered by fission of the O–*t*-C_4H_9 bond, making the two methoxy groups equally accessible, and that the O–CH_3 linkage of both methoxy groups is retained. When the *tert*-butyl group is perdeuterated, the methanol lost from the **1**-*d*$_9$ ion involves only one label, while the methanol ion pair is found to be $(CH_3OD)_2D^+$, having three labels (Figs. 1c and d). For **1**-*d*$_9$, therefore, elimination of methanol involves one C–D bond cleavage in the *tert*-butyl methyls, whereas the formation of the proton-bound methanol pair requires rupture of up to three C–D bonds, one being the rate-determining step. The latter reaction should therefore show a significant kinetic isotope effect. Indeed, by comparing the MI mass spectra of **1** and **1**-*d*$_9$ in terms of the intensity of the paired ions (for **1**, *m*/*z* 65 = 6%, Table 2; for **1**-*d*$_9$, *m*/*z* 68 = 1.8%, Fig. 1c), $k_H/k_D > 3.3$ is found for this reaction, relative to the loss of methanol.

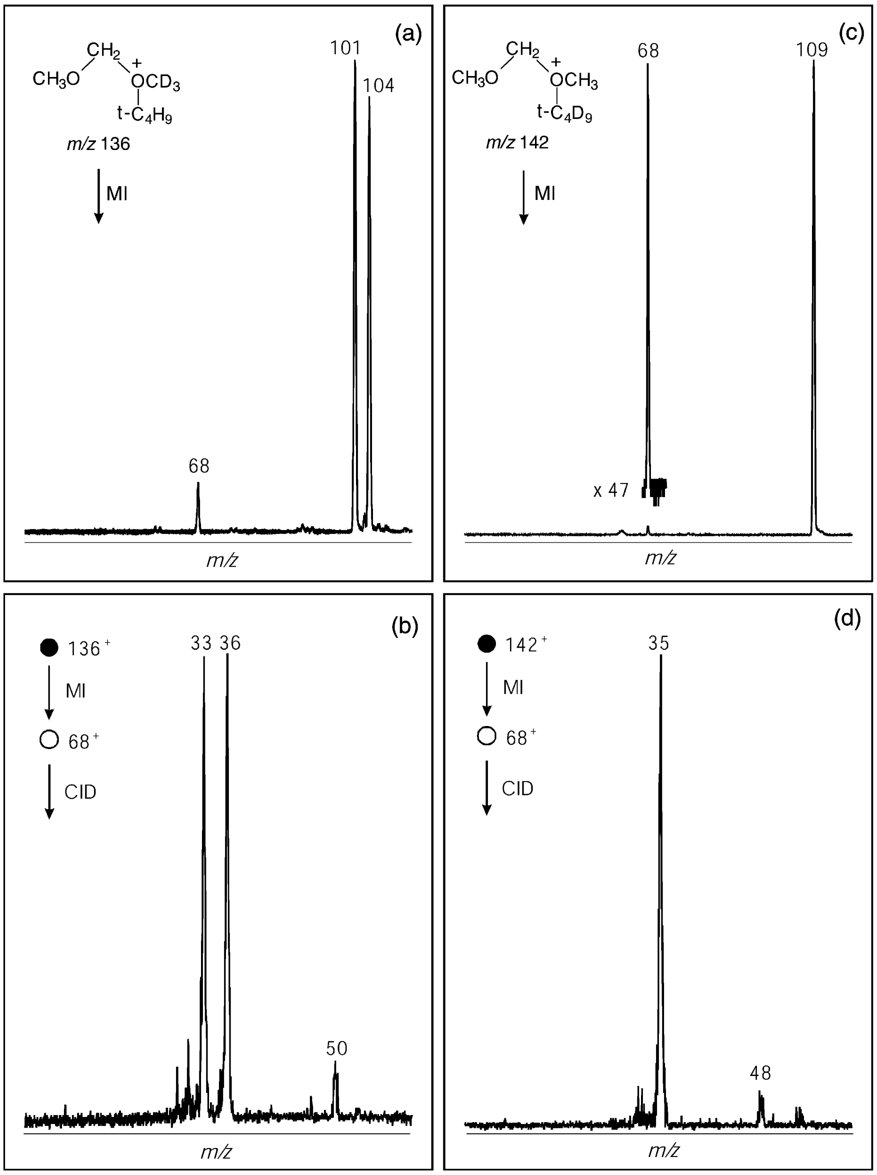


Fig. 1 (a) MI mass spectrum of oxonium ion **1**-d_3, (b) CID mass spectrum of the *m*/*z* 68 ion generated from **1**-d_3, (c) MI mass spectrum of **1**-d_9 and (d) CID mass spectrum of the *m*/*z* 68 ion from **1**-d_9. Note that **1**-d_3 was prepared from CD_3O–*t*-C_4H_9 and $CH_2(OCH_3)_2$ such that both CD_3 and the *t*-C_4H_9 groups are attached on the same oxygen atom.

With the origin and destination of all migrated hydrogen atoms determined, the simplified overall reaction mechanism presented in eqns. (1)–(3) can be interpreted in detail for the

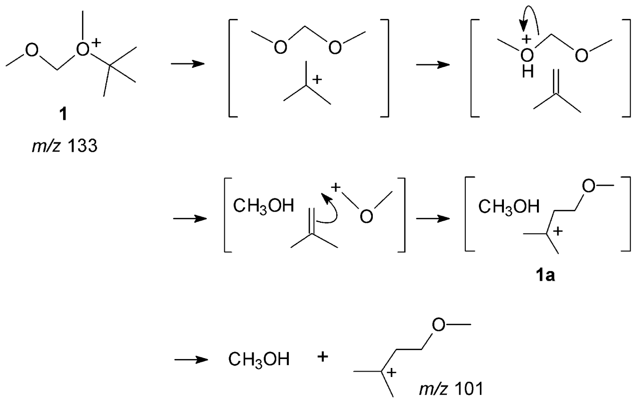
$$CH_3OCH_2\text{–}O^+(CH_3)(t\text{-}C_4H_9) \longrightarrow [C_6H_{13}O^+/CH_3OH] \quad (1)$$

$$\longrightarrow [C_5H_9{}^+/2CH_3OH] \quad (2)$$

$$\longrightarrow C_5H_8 + (CH_3OH)_2H^+ \quad (3)$$

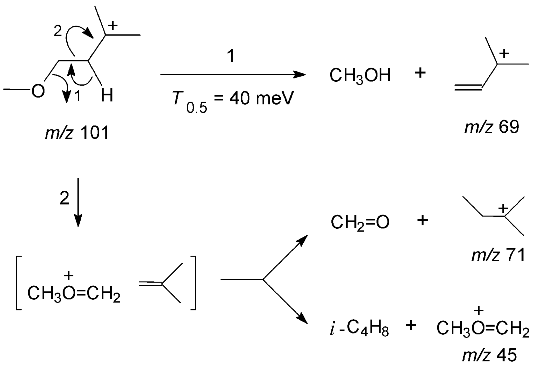
formation of the methanol pair in the metastable fragmentation of ion **1**.

Apparently, separation and the eventual loss of methanol from **1** [eqn. (1)] to give the *m*/*z* 101 ion is a multistep process. To make the two methoxy groups equivalent, the reaction should be initiated by heterolytic cleavage of the O–*t*-C_4H_9 bond, resulting in the $[CH_2(OCH_3)_2/t\text{-}C_4H_9{}^+]$ complex. The proton affinity (PA) of $CH_2(OCH_3)_2$ is estimated[14] to be 816 kJ mol^{-1}, higher than that of iC_4H_8 (PA = 803 kJ mol^{-1}).[19] Therefore, proton transfer from *t*-$C_4H_9{}^+$ to $CH_2(OCH_3)_2$ leads exothermically to isobutene (iC_4H_8) and protonated dimethoxymethane; the latter dissociates to give methanol and the $CH_3OCH_2{}^+$ ion. In the $[CH_3OH/CH_3OCH_2{}^+/iC_4H_8]$ aggregate, fast electrophilic addition of the $CH_3OCH_2{}^+$ ion to isobutene yields a much more stable tertiary carbocation associated with methanol, $[C_6H_{13}O^+/CH_3OH]$ (**1a**), as described in Scheme 1. This addition reaction[3a,c,20] has favorable thermochemistry and, as will be discussed later, is in keeping with the characterization of the neutral species formed in further fragmentation, which has a C_5 skeleton.



Scheme 1

The $C_6H_{13}O^+$ ion generated in methanol loss from **1** is an isomer of the $C_nH_{2n+1}O^+$ oxonium ions[3a,c,13] (that are equivalent to *O*-alkyl cationated carbonyl compounds); its fragmentation, however, is distinctly different from that of the oxonium ions.[3a,c,13] As outlined in Scheme 2, in the metastable ion time frame, the $C_6H_{13}O^+$ ion loses predominantly the second methanol molecule to give the *m*/*z* 69 ion, accompanied by losses of CH_2O (*m*/*z* 71, 15%) and iC_4H_8 (*m*/*z* 45, 1%). The latter two minor product ions arise from the reverse of the electrophilic addition (described in Scheme 1) and their difference in intensity can be rationalized by the difference in methyl cation affinity (MCA) of CH_2O and iC_4H_8. The proton affinities[19] of CH_2O and iC_4H_8 are 715 and 803 kJ mol^{-1}, respectively; therefore, the MCA of formaldehyde is considerably lower than that of isobutene.[21] In the CID mass spectrum of the $C_6H_{13}O^+$ ion, loss of the second methanol remains dominant while competition for the methyl cation between CH_2O and iC_4H_8 is reversed (*m*/*z* 71 = 15%; *m*/*z* 45 = 40%, Table 3). This is consistent with the *m*/*z* 45 ion arising from simple separation of the $[CH_3OCH_2^+/iC_4H_8]$ complex, whereas formation of the *m*/*z* 71 ion requires methyl cation transfer between the two partners in the complex.



Scheme 2

The interpretation of the fragmentation reactions of the $C_6H_{13}O^+$ ion (Scheme 2) is based on its structure, which is proposed to be a tertiary carbocation with a methoxy group at the position β- to the charge site. In the loss of methanol from this ion, an intraionic proton transfer is required. The presence of the positive charge will activate hydrogens both on the methylene and the methyl groups adjacent to the charge. The 1,5-H transfer from one of the methyl groups to the oxygen, followed by the O–C bond cleavage, would lead to a primary carbocation, CH_2=$C(CH_3)CH_2CH_2^+$. This would make this reaction very energy demanding even if further 1,2-hydrogen transfer could result in a secondary carbocation, CH_2=$C(CH_3)$-CH^+CH_3. In contrast, the 1,3-H shift from the methylene to the oxygen, as depicted in Scheme 2, gives rise directly to CH_2=CH–$C^+(CH_3)_2$, a stable, disubstituted allyl cation, and therefore should be energetically favoured.

The formation of the proton-bound methanol pair from ion **1** requires that *both* methanol molecules separate successively, while maintaining their interactions with the $C_5H_9^+$ ion as an ion–neutral complex (**1b**, see Scheme 3 below). This is the first three-membered intermediate ion–neutral complex involved in a *unimolecular* reaction of *covalently-bonded* ions, in which the ionic partner is associated with *two* neutral molecules (an "ion–neutral-neutral" complex). Proton transfer within the $[C_5H_9^+/2CH_3OH]$ complex yields 2-methylbuta-1,3-diene (C_5H_8) and the proton-bound methanol pair, $(CH_3OH)_2H^+$. The heat of formation of $(CH_3OH)_2H^+$ was reported[22] to be 230 kJ mol^{-1}, so that the PA of $(CH_3OH)_2$, nominally, would be as high as 900 kJ mol^{-1} (assuming no binding energy between the two neutral methanol molecules), which is considerably greater than that of 2-methylbuta-1,3-diene (PA = 827 kJ mol^{-1}).[19] Thus, this proton transfer is exothermic by 71 kJ mol^{-1} [eqn. (4)].

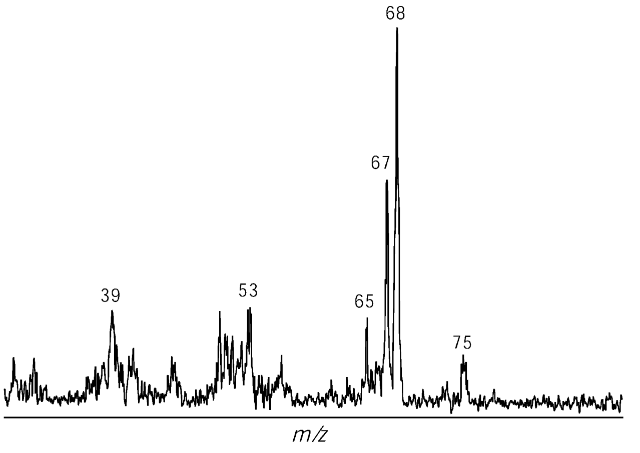
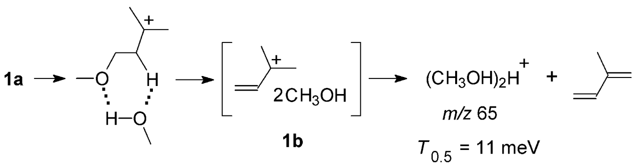


Fig. 2 CIDI mass spectrum of ion **1**. Deflecting voltage: +1 kV; ionizing reagent: O_2, 80% transmission. No signal was observed above *m*/*z* 90.

$$\begin{aligned} &CH_2\text{=}CH\text{–}C^+(CH_3)_2 + 2CH_3OH \longrightarrow \\ &\qquad CH_2\text{=}CH\text{–}C(CH_3)\text{=}CH_2 + (CH_3OH)_2H^+ \quad (4) \\ &\qquad \Delta H_{rxn} = -71 \text{ kJ mol}^{-1} \end{aligned}$$

In the formation of $(CH_3OH)_2H^+$, three hydrogen atoms are successively transferred from the *tert*-butyl group. The first hydrogen transferred (in the second step in Scheme 1) is one of the 9 identical H atoms of the *tert*-butyl group; the second (as in Scheme 2) would be from the methylene adjacent to the charge, and made acidic thereby, and the last [in eqn. (4)] should be from a methyl group of CH_2=CH–$C^+(CH_3)_2$. All the H atoms transferred in the reactions are originally from the *tert*-butyl group. This accounts well for the kinetic isotope effect observed for **1**-d_9 where the butyl group is fully deuterated.

Identification of the neutral products generated concurrently in a fragmentation reaction is complementary to the elucidation of the reaction mechanism. This information can be obtained from collision-induced dissociative ionization mass spectrometry.[18] The neutral products of the two MI channels of ion **1** are methanol and 2-methylbuta-1,3-diene (Schemes 1 and 3), whose ionization energies are 10.84 and 8.86 eV, respectively.[23] The latter is likely to be ionized and detected in the CIDI experiment. As shown in Fig. 2, indeed, the molecular ion (*m*/*z* 68) of a C_5H_8 hydrocarbon molecule is found together with its major fragments at *m*/*z* 67, 65, 53 and 39 in the CIDI mass spectrum. Note that the *m*/*z* 75 ion can be attributed to formation of dimethoxymethane (that is the neutral counterpart of the minor $C_4H_9^+$ ion upon collision, Table 2), which loses an H atom readily when ionized.[24] Although a neutral molecule may undergo isomerization in the CIDI process, Fig. 2 clearly shows that a C_5H_8 hydrocarbon molecule is generated as a neutral product in the fragmentation of ion **1**, and this is consistent with the reaction mechanism described above.



Scheme 3

As shown in Scheme 2, methanol loss from the isolated CH_3O–$CH_2CH_2C^+(CH_3)_2$ ion (*m*/*z* 101) involves a 1,3-proton transfer, which has a high energy barrier, and thus the kinetic energy release, 40 meV, is compatible with this. From the precursor oxonium ion **1**, however, formation of the proton-bound methanol pair, in which this high energy process is involved, has only a small kinetic energy release ($T_{0.5} = 11$ meV, Table 3) and is the only reaction that competes with loss of the first methanol in the metastable ion time frame. Therefore, methanol loss from $CH_3O–CH_2CH_2C^+(CH_3)_2$ and elimination of the second methanol molecule from oxonium ion **1** must involve different transition states. In the formation of the proton-bound methanol pair, the second methanol is expelled while the first methanol retains its interactions with the ion. The reaction here may be similar to that observed in systems where a neutral molecule acts as a proton-transport catalyst.[25,26] The first methanol molecule could assist the proton transfer as a transporter in a stepwise manner[25] to avoid a direct 1,3-H shift. Alternatively, the reaction could also have a transition state favouring a concerted process. As shown in Scheme 3, from the watershed complex **1a**, the first methanol reorientates to form a six-membered ring *via* hydrogen bonds. By way of this transition state, hydrogen transfer and methanol elimination take place simultaneously. Detailed energy information could be obtained from high level theoretical calculations.

As for oxonium ion **2**, upon the initial cleavage of the $O–C_4H_9$ bond the $iC_4H_9^+$ cation isomerizes spontaneously to the t-$C_4H_9^+$ ion, thereby making **1** and **2** identical; therefore, **1** and **2** indeed have similar relative intensities of their product ions (Table 2). Furthermore, ions **3** and **4** are indistinguishable in either their MI or CID fragmentations; in particular, methanol and ethanol losses are of similar abundance. This substantially supports the proposal that they involve the same ion–neutral complex, $[CH_3OCH_2OC_2H_5/t\text{-}C_4H_9^+]$, in the fragmentation. Therefore, the proton-bound hetero-alkanol pairs $[(CH_3OH)H^+(C_2H_5OH)]$ generated from **3** and **4** have similar intensity. When two ethoxy groups are present, as in ion **5**, the proton-bound ethanol pair was observed.

Conclusion

Alkoxylated oxonium ions $ROCH_2–O^+(R')(R'')$ (where R, $R' = CH_3$ or C_2H_5; $R'' = t$- or iC_4H_9) undergo unimolecular fragmentation to produce the proton-bound alkanol pairs, $[(ROH)H^+(R'OH)]$. The reaction involves a three-component ion–neutral complex in which two neutral alkanol molecules are associated with the $CH_2{=}CH–C^+(CH_3)_2$ ion. Proton transfer within the complexes leads to the formation of the proton-bound alkanol pairs and neutral 2-methylbuta-1,3-diene. The neutral species was identified by means of collision-induced dissociative ionization mass spectrometry.

Acknowledgement

The authors are indebted to the Natural Sciences and Engineering Research Council of Canada for continuing financial support.

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