Transacetalization of 1,3-dioxane with acylium and sulfinyl cations in the gas phase

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Transacetalization occurs extensively in gas phase ion–molecule reactions of 1,3-dioxane with a variety of acylium ions [R–C$^+$=O; R = CH$_3$, C$_2$H$_5$, Ph, CH$_3$O, Cl, CH$_2$=CH, (CH$_3$)$_2$N] and a sulfur analogue, the thioacetyl ion CH$_3$–C$^+$=S. Six-membered 1,3-dioxanylium ions and analogues, *i.e.* cyclic 'ionic (thio)ketals', are formed, as evidenced by pentaquadrupole triple-stage collision-dissociation mass spectra and MP2/6–311G(d,p)//6–311G(d,p) + ZPE *ab initio* calculations, as well as by ^{18}O labelling experiments. Transacetalization with 1,3-dioxane is not a general reaction for sulfinyl cations (R–S$^+$=O). They react either moderately (CH$_3$–S$^+$=O) or extensively (CH$_2$=CH–S$^+$=O) by transacetalization, form abundant intact adducts (Ph–S$^+$=O) or undergo mainly proton transfer and/or hydride abstraction reactions (Cl–S$^+$=O, CH$_3$O–S$^+$=O and C$_2$H$_5$O–S$^+$=O). Competitive MS^2 experiments are employed to compare the transacetalization reactivity of different acylium ions, and that of two cyclic neutral acetals, that is 1,3-dioxane and 1,3-dioxolane. All the cyclic 'ionic ketals' dissociate exclusively under low-energy collision conditions to regenerate the original reactant ion species, a simple dissociation chemistry that is amply demonstrated to be a very general characteristic of the transacetalization products. The cyclic 'ionic thioketal' formed in transacetalization with CH$_3$–C$^+$=S is found, however, to dissociate exclusively to the oxygen analogue ion CH$_3$–C$^+$=O, a triple-stage mass spectrometric (MS^3) experiment that constitutes a novel gas-phase strategy for conversion of thioacylium ions into acylium ions.

Introduction

Acetalization and ketalization reactions of aldehydes and ketones with diols and analogues are classic, very general and synthetically useful reactions in the condensed phase.[1] Upon acid catalysis, cyclic acetals and ketals are formed promptly and in very high yields, and this very effective reaction is widely employed for protecting either carbonyl compounds or alternatively diols[2] against their most common reaction partners. Whereas the cyclic acetals and ketals are inert, for instance, towards powerful nucleophiles and reducing agents, they can however be hydrolysed easily to release the original carbonyl compounds. Transacetalization[2] with a second aldehyde or ketone can also be used to protect a second carbonyl compound or to regenerate the keto starting material [eqn. (1)].

$$(1)$$
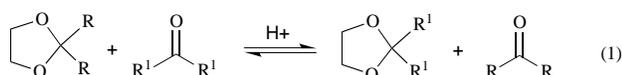
Acylium ions (R–C$^+$=O) are one of the most common and easily accessible classes of stable carbocations in the gas phase, whereby they display a rich and unique ion–molecule chemistry.[3] Recently, it was reported that a variety of acylium[4] and the related sulfinyl cations (R–S$^+$=O)[5] undergo a novel, structurally diagnostic[5] gas phase transacetalization reaction with two cyclic acetals (Scheme 1), a reaction that is in many aspects similar to transacetalization with neutral carbonyl compounds.[6] 1,3-Dioxanylium ions, *i.e.* cyclic 'ionic ketals', are formed *via* the replacement of the neutral aldehydes or ketones from the neutral cyclic acetals by the 'keto' ions [eqn. (2)]. Based on this


$$(2)$$
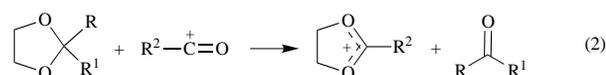
R = R^1 = H
R = H ; R^1 = CH$_3$

R^2 = CH$_3$, C$_2$H$_5$, Ph, OH, CH$_3$O, CH$_3$NH, (CH$_3$)$_2$N, Cl
CH$_2$=CH, PhCH=N, CH$_3$(OH)C=CH

specific reaction and a neutral gain–neutral loss MS^3 scan, a very selective test for the gas phase characterization of acylium ions has been devised.[7] Transacetalization was also shown recently to be very general, and to occur for a variety of five-, six- and seven-membered cyclic acetals and ketals, *i.e.* 1,3-dioxaheterocycles, and their sulfur and nitrogen analogues.[4c,d] Thus, transacetalization provides a very general method for the gas phase characterization of both the ions and the neutral cyclic acetals and ketals.

Besides transacetalization, direct ketalization with acylium ions, in many aspects similar to direct ketalization of neutral carbonyl compounds,[1,2] has also been recently observed in the gas phase ion–molecule reactions of a variety of diols, their nitrogen and sulfur analogues, and their monoalkyl derivatives [eqn. (3)].[8] It is interesting to note that, whereas the cyclic 'ionic

$$(3)$$
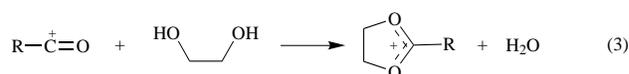
ketals' formed either by transacetalization or direct ketalization are inert towards a series of reactions that are characteristic of the original reactant acylium ions, they regenerate the reactant acylium ions in high yields upon low-energy collision-induced dissociation.[8] This process is therefore the most energetically favoured for the cyclic 'ionic ketals', being closely analogous to the hydrolysis of cyclic neutral acetals and ketals, which is the most facile reaction in solution by which the original carbonyl compound is readily regenerated.[1,2]

In the present work, multiple stage (MS^2 and MS^3) pentaquadrupole mass spectrometry[9,10] is used to investigate the reactions of a variety of acylium and sulfinyl cations with 1,3-dioxane. The latter molecule could be regarded as the cyclic-propane-1,3-diol acetal of formaldehyde and is therefore analogous to the cyclic neutral acetals alluded to in the above with reference to solution chemistry. Transacetalization is shown to be the dominant reaction of 1,3-dioxane with a variety of acylium ions as well as for the thioacylium ion

Table 1 Major ionic products from ion–molecule reactions of 1,3-dioxane with acylium and sulfinyl cations

| Ion | m/z | Products [m/z (relative abundance)] | | |
		Transacetalization	Proton transfer	Hydride abstraction
$C_2H_5–CO^+$	57	115 (100)	89 (3)	87 (19)
$(CH_3)_2N–CO^+$	72	130 (100)	89 (3)	87 (15)
$CH_3O–CO^+$	59	117 (100)	—	87 (76)
$CH_2=CH–CO^+$	55	113 (100)	89 (6)	87 (18)
$Cl–CO^+$	63	121 (100)	—	87 (36)
$Ph–CO^+$	105	163 (100)	—	87 (15)
$Cl–SO^+$	83	—	89 (18)	87 (100)
$CH_3–SO^+$	63	121 (62)	89 (73)	87 (100)
$CH_3O–SO^+$	79	—	—	87 (100)

$CH_3–C^+=S$. Experimental and *ab initio* theoretical evidence indicate the formation of *six-membered* cyclic 'ionic (thio)-ketals'. The structurally related sulfinyl cations, in contrast to their general reactivity observed with 2-methyl-1,3-dioxolane,[5] show instead a quite diverse reactivity with 1,3-dioxane. Some sulfinyl cations are found to react extensively or moderately, whereas others are completely unreactive towards transacetalization. Competitive studies were performed to compare the transacetalization reactivity of different acylium ions under identical experimental conditions, and that of the two homologous cyclic acetals, that is 1,3-dioxolane and 1,3-dioxane.

Methods

The MS[2] and MS[3] experiments were performed using an Extrel [Pittsburgh, PA] pentaquadrupole mass spectrometer described in detail elsewhere.[5,7] The instrument, which constitutes a very convenient laboratory for gas-phase ion–molecule reaction studies, is composed basically of three mass-analysing (Q1, Q3, Q5) and two 'rf-only' reaction quadrupoles (q2, q4). Ion–molecule reactions were performed by MS[2] experiments in which Q1 was used to mass select the ion of interest that was reacted further in q2 with a neutral reagent at near zero collision energy. The product spectrum was recorded by scanning Q5, while Q3 was operated in the non-analysing 'full-transmission' rf-only mode.

For the MS[3] experiments, an ion–molecule reaction product of interest was mass-selected by Q3 and further dissociated in q4 by 10–15 eV collisions with argon, while Q5 was scanned to record the spectrum. The total pressures inside each differentially pumped region were typically 2×10^{-6} (ion-source), 8×10^{-6} (q2) and 8×10^{-5} (q4) Torr, respectively, which correspond to multiple-collision conditions. The collision energies were calculated as the voltage difference between the ion source and the collision quadrupole.

Ab initio molecular orbital calculations were carried out by using GAUSSIAN94.[11] The closed-shell ions were optimized at the restricted (RHF) Hartree–Fock level of theory by employing the polarization 6–311G(d,p) basis set.[12] Improved energies were obtained by using single point calculations at the RHF/6–311G(d,p) level and incorporating valence electron correlation calculated by second-order Møller–Plesset (MP2) perturbation theory,[13] a procedure denoted as MP2/6–311G(d,p)//6–311G(d,p). Harmonic vibrational frequencies were calculated at the RHF/6–311G(d,p) level to characterize the stationary points and to obtain the zero-point vibrational energies (ZPE).

Results and discussion

Acylium ions

The products of ion–molecule reactions between the acylium ions and 1,3-dioxane are given in Table 1, whereas some representative cases are shown in Fig. 1. Note that transacetalization which leads to net addition of C_3H_6O (58 u) occurs extensively for all the acylium ions investigated (Scheme 1, X = C; Y = O).
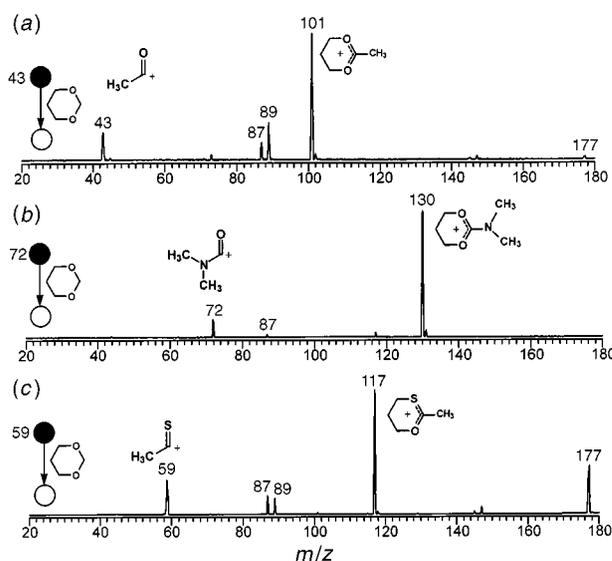

Fig. 1 Double-stage (MS[2]) product spectra for ion–molecule reactions of 1,3-dioxane with the acylium ions (*a*) $CH_3–C^+=O$ and (*b*) $(CH_3)_2N–C^+=O$; and with (*c*) the thioacylium ion $CH_3–C^+=S$. Note the abundant transacetalization products of m/z 101, 130 and 117, respectively, whereas the proton transfer (m/z 89 and the 1,3-dioxane proton bound dimer of m/z 177) and hydride abstraction (m/z 87) products are minor. In the terminology used to describe the type of experiment and scan mode employed, a filled circle represents a fixed (or selected) mass; an open circle, a variable (or scanned) mass, while the neutral reagent or collision gas that causes the mass transitions are shown between the circles. For more details on this terminology see ref. 9*b*.
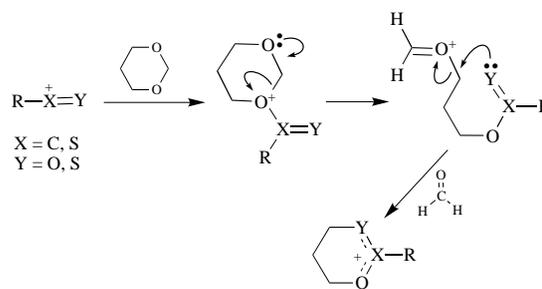
Scheme 1

The reaction proceeds *via* initial *O*-acylation that is followed by ring-opening–ring-reforming steps leading to the cyclic 'ionic ketals' *via* the elimination of a neutral formaldehyde molecule. Note that the ring-reforming step involves bond formation within a ring in an intramolecular analogue of an S_N2 reaction. The ions $CH_3–C^+=O$ [Fig. 1(*a*)] and $(CH_3)_2N–C^+=O$ [Fig. 1(*b*)], for instance, show abundant transacetalization products of m/z 101 and m/z 130, respectively, whereas proton transfer (m/z 89) and hydride abstraction (m/z 87) occurs to a moderate extent. The thioacetyl cation $CH_3–C^+=S$ also reacts extensively by transacetalization to form the corresponding cyclic 'ionic thioketal' of m/z 117 [Fig. 1(*c*)].
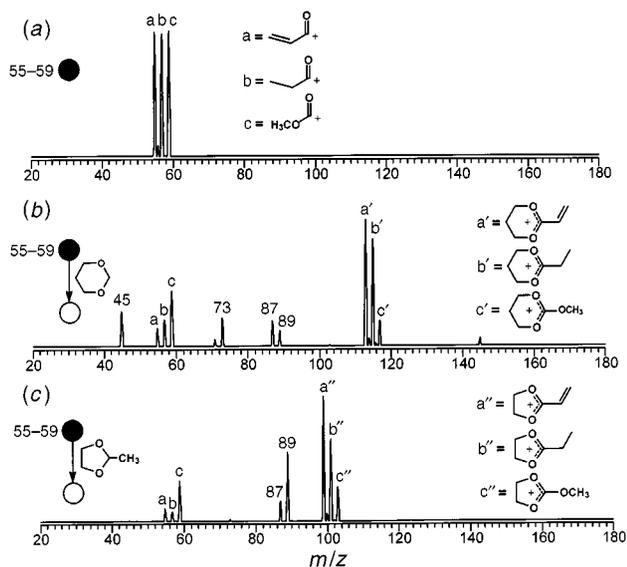
Fig. 2 (*a*) Double-stage spectra of an ionic bean constituted of an equal mixture of $CH_2=CH-C^+=O$ (*m/z* 55), $C_2H_5-C^+=O$ (*m/z* 57) and $CH_3O-C^+=O$ (*m/z* 59), which was mass-selected by Q1 operating in low resolution conditions, and the double-stage product spectra for ion–molecule reactions of the ions with (*b*) 1,3-dioxane and (*c*) 2-methyl-1,3-dioxolane. From the yields of the cyclic 'ionic ketals' the reactivity order: $CH_2=CH-C^+=O$ (*m/z* 55) > $C_2H_5-C^+=O$ (*m/z* 57) ≫ $CH_3O-C^+=O$ (m/z 59) is derived in both cases.

Competitive studies. Although the extent of transacetalization varies considerably with the nature of the ion, it is always the dominant reaction for the acylium ions investigated (Fig. 1 and Table 1). The reactivity towards transacetalization of the ions is likely to be a combined result of the activation–deactivation effect of the substituent, and its proclivity to undergo the competitive proton transfer and hydride abstraction reactions. As exemplified in Fig. 2, differences in transacetalization reactivity are more appropriately compared when the ions compete for the neutral acetal. To perform the experiment, three acylium ions were generated in the ion source from 70 eV electron impact (EI) of a mixture of appropriate precursors, that is ethyl vinyl ketone (which generates both $C_2H_5-C^+=O$ and $CH_2=CH-C^+=O$), pentan-3-one ($C_2H_5-C^+=O$), and dimethyl oxalate ($CH_3O-C^+=O$). The simultaneous selection of the three desired reactant ions [Fig. 2(*a*)], which therefore guarantees that they all react in q2 under identical experimental conditions, was obtained by setting Q1 to work at very low resolution conditions. Approximately the same proportions of the three reactant ions were obtained by carefully adjusting the partial pressure of the precursors with the aid of a three-way needle valve inlet system. It is clear in Fig. 2(*b*) from the yields of the corresponding cyclic 'ionic ketals' **a′** (*m/z* 113), **b′** (*m/z* 115) and **c′** (*m/z* 117) that the transacetalization reactivity order is $CH_2=CH-C^+=O$ (*m/z* 55) > $C_2H_5-C^+=O$ (*m/z* 57) ≫ $CH_3-O-C^+=O$ (*m/z* 59). Thus, if one does not consider the effects of the substituent on the other competitive reactions, it can be concluded that alkoxy substituents on acylium ions decrease the extent of transacetalization, whereas substituents of the α,β-unsaturated type such as the vinyl group (as well as phenyl, see Table 1) favour the reaction. A similar trend in the reactivity of the acylium ions is observed when employing 2-methyl-1,3-dioxolane [Fig. 2(*c*)].

The transacetalization reactivity of two homologous neutral cyclic acetals was also compared. The very reactive $(CH_3)_2$-$N-C^+=O$ ion of *m/z* 72 (Fig. 3) was mass-selected in Q1 and allowed to react in q2 with an equimolar vapour mixture of 1,3-dioxolane and 1,3-dioxane. The greater reactivity of the higher homologue (1,3-dioxane), observed over a series of similar experiments and diverse setting conditions, is seen when comparing the relative abundances of their corresponding cyclic 'ionic ketals' of *m/z* 130 and 113 (Fig. 3).
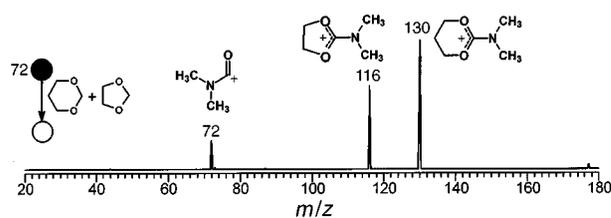

Fig. 3 Double-stage product spectrum for ion–molecule reactions of an equimolar vapour mixture of two cyclic acetals, that is 1,3-dioxane and 1,3-dioxolane with $(CH_3)_2N-C^+=O$. Note the greater transacetalization reactivity (product of *m/z* 130) of the higher homologue (1,3-dioxane) when compared to 1,3-dioxolane (*m/z* 116). The yields shown correspond to the average of several experiments.
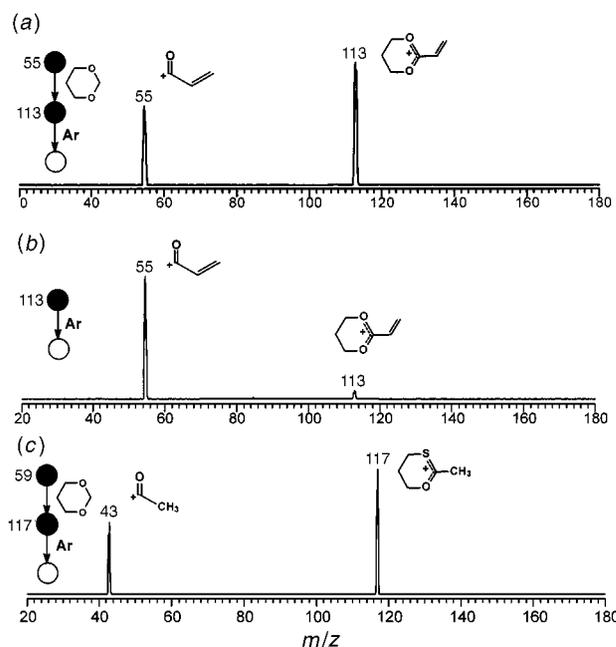

Fig. 4 Triple-stage sequential product spectra of the transacetalization products of 1,3-dioxane with (*a*) $CH_3-C^+=O$, (*b*) $CH_2=CH-C^+=O$ and (*c*) $CH_3-C^+=S$. Note that the cyclic 'ionic ketals' (*a* and *b*) dissociate extensively to regenerate the corresponding reactant acylium ions, whereas the 'ionic thioketal' forms exclusively the oxygen analogue ion $CH_3-C^+=O$ (*m/z* 43).
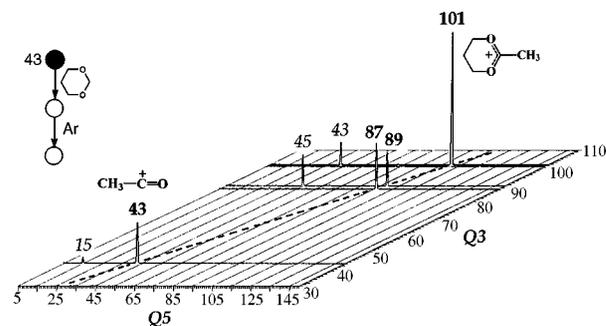

Fig. 5 Three-dimensional triple-stage intermediate-product domain spectrum for the ion–molecule reaction of the acetyl cation of *m/z* 43 with 1,3-dioxane. All the reaction products (bold numerals) are displayed along the diagonal dashed line, whereas their corresponding 15 eV CID fragments (italic numerals) are displayed along the horizontal Q5 axis.

Triple-stage mass spectra.[9] The characteristic dissociation chemistry of the transacetalization products observed *via* triple-stage (MS³) mass spectra provide evidence that six-membered cyclic 'ionic ketals' are indeed formed, as exemplified for two representative cases in Fig. 4(*a*) and 4(*c*), and in the three-dimensional spectrum shown in Fig. 5 (see discussion on the 3D spectrum that follows). Except for Fig. 4(*c*), the spectra

exclusively show dissociation to regenerate the reactant ions. This regeneration process can therefore be considered equivalent to the hydrolysis of neutral ketals that is used in the condensed phase to release the original reactant carbonyl compound.[1] A variety of five-membered cyclic 'ionic ketals' formed either *via* dissociative EI[4a] or transacetalization with acylium ions of cyclic acetals and ketals[4,8] also dissociate upon collision activation largely by the same process, a simple dissociation chemistry that is therefore amply demonstrated to be a general characteristic of cyclic 'ionic ketals'.
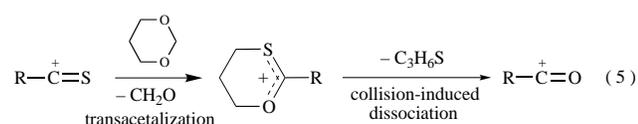
The 3D mass spectrum. Fig. 5 shows the 3D triple-stage spectrum acquired by mass-selecting the acetyl cation of m/z 43 in Q1, scanning sequentially both Q3 and Q5, and performing ion–molecule reactions with 1,3-dioxane in q2 and dissociative collisions with argon in q4. This interesting type of MS[3] scan[9b] is particularly useful for ion–molecule reaction studies[5] since it allows a detailed three dimensional view of the process by displaying in a single spectrum all the products of a specified mass-selected ion, each associated with their dissociation products. Across the diagonal line (Q3 axis), the surviving reactant ion of m/z 43 and all its reaction products (m/z 87, 89 and 101, bold numerals) are displayed, whereas the CID fragments (italic numerals) of each individually selected ionic product are seen across the Q5 horizontal axis. The reactant ion (CH$_3$–C$^+$=O) dissociates, as expected, to CH$_3^+$ of m/z 15 by CO loss. The protonated 1,3-dioxane product of m/z 89 fragments to m/z 45 by loss of a neutral molecule of 44 u; the transacetalization product of m/z 101 losses a neutral molecule of 44 u to regenerate the reactant acetyl cation of m/z 43, whereas the hydride abstraction product of m/z 87 does not dissociate under the collision conditions employed in q4.

Reference ion. A reference cyclic 'ionic ketal' was independently generated from dissociative EI of 2,2-tetramethylene-1,3-dioxane [eqn. (4)], and its double-stage dissociation spectrum

$$\text{(structure)} \xrightarrow{- C_2H_5^\bullet} \text{(structure)} \qquad (4)$$
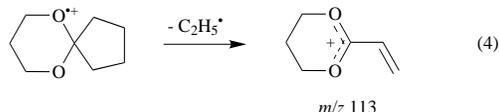
$$m/z\ 113$$

[Fig. 4(b)] compared to that of the transacetalization product of CH$_2$=CH–C$^+$=O with 1,3-dioxane [Fig. 4(a)]. The same dissociation chemistry for both m/z 113 ions, *i.e.* exclusive regeneration of the acylium ion of m/z 55, is seen in both spectra, and this provides additional evidence that six-membered cyclic 'ionic ketals' are produced upon transacetalization of 1,3-dioxane with acylium ions.

Conversion of thioacylium into acylium ions. The case of the cyclic 'ionic thioketal' shown in Fig. 4(c) is unique and indeed interesting. It does not regenerate the original reactant ion CH$_3$–C$^+$=S (m/z 59) upon collision-induced dissociation, but it dissociates exclusively to its oxygen analogue CH$_3$–C$^+$=O of m/z 43. Because of the relatively poor 2p–3p π overlap in multiple bonds between carbon and sulfur, thioacylium ions are anticipated to be less stable than the analogous oxygen acylium ions.[3g] Thus, dissociation of the 'ionic thioketal' yields predominantly the more stable acylium ion. This preference is also predicted by calculations, as discussed in the *ab initio* section that follows. The triple-stage mass spectrometric transacetalization–collision-induced dissociation sequence [eqn. (5)] therefore constitutes an efficient gas phase strategy for conversion of thioacylium ions into acylium ions.†

$$\text{R}-\overset{+}{\text{C}}=\text{S} \xrightarrow[- \text{CH}_2\text{O}]{\text{transacetalization}} \text{(structure)} \xrightarrow[\text{collision-induced dissociation}]{- \text{C}_3\text{H}_6\text{S}} \text{R}-\overset{+}{\text{C}}=\text{O} \quad (5)$$

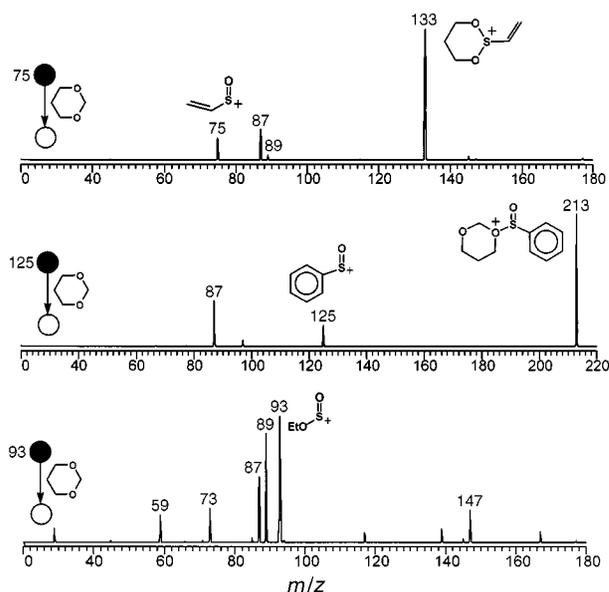**Fig. 6** Double-stage (MS²) product spectra for ion–molecule reactions of 1,3-dioxane with the sulfinyl cations (*a*) CH$_2$=CH–S$^+$=O, (*b*) Ph–S$^+$=O and (*c*) C$_2$H$_5$O–S$^+$=O. Note that CH$_2$=CH–S$^+$=O reacts extensively by transacetalization (m/z 133), whereas Ph–S$^+$=O forms an abundant adduct (m/z 213) and C$_2$H$_5$O–S$^+$=O reacts mainly by proton transfer (m/z 89) and hydride abstraction (m/z 87).

Sulfinyl cations (R–SO$^+$)
A series of sulfinyl cations were recently shown[5] to react with the cyclic acetal 2-methyl-1,3-dioxolane by transacetalization, a structurally diagnostic ion–molecule reaction that served as experimental proof for their generation and existence as stable species in the gas phase. However, sulfinyl cations show a quite diverse reactivity towards the higher homologue 1,3-dioxane. Both the CH$_3$–S$^+$=O (Table 1) and the vinyl, α,β-unsaturated sulfinyl cation CH$_2$=CH–S$^+$=O [Fig. 6(*a*)] react by transacetalization (Scheme 1, X = S, Y = O). CH$_3$–S$^+$=O reacts moderately to yield the cyclic 'ionic ketal' product of m/z 121, whereas the corresponding transacetalization product of m/z 133 is formed abundantly from CH$_2$=CH–S$^+$=O. The Ph–S$^+$=O ion, however, forms no transacetalization product of m/z 135 [Fig. 6(*b*)], reacting mainly by adduct formation (m/z 213). The chlorine-(Cl–S$^+$=O, Table 1) and the two alkoxy-substituted sulfinyl cations CH$_3$O–S$^+$=O (Table 1) and C$_2$H$_5$O–S$^+$=O [Fig. 6(*c*)] are also completely unreactive towards transacetalization, and their double-stage mass spectra (Table 1) are dominated by the products of proton transfer (m/z 89) ‡ and hydride abstraction (m/z 87).
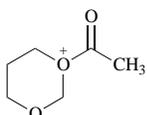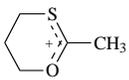
Triple-stage mass spectra. The cyclic 'ionic ketals' formed in reactions of CH$_3$–S$^+$=O and CH$_2$=CH–S$^+$=O with 1,3-dioxane [Fig. 7(*a*)] also dissociate exclusively to regenerate the reactant sulfinyl cation. This further demonstrates[4,8] that such unique dissociation chemistry is indeed a very general characteristic of a variety of cyclic 'ionic ketals', which includes five[5] and six-membered sulfur derivatives formed with the sulfinyl cations (Scheme 1, X = S, Y = O). It is interesting to note that the intact adduct of Ph–S$^+$=O does not lose formaldehyde even when activated upon collision [Fig. 7(*b*)], but it dissociates exclusively to regenerate the original reactant ion. This may be interpreted as evidence that it remains in cyclic form (see Scheme 1).

Ab initio calculations
Transacetalization. As already mentioned, experimental evidence supports the formation of cyclic 'ionic (thio)ketals' (**a**) in transacetalization with acylium, thioacylium and sulfinyl

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† A similar trend has been observed for the five-membered analogue, see ref. 4*a*.

‡ Proton transfer in the Cl–S$^+$=O case must be a secondary reaction involving any of the primary ionic products and the neutral reagent.

Table 2 Total, ZPE and relative energies from *ab initio* full structure optimization calculations

Species[a]	MP2/6-311G//6-311G(d,p) hartree	ZPE[b] hartree	Total energy[c] hartree
CH_3–CO^+	$-152.558\ 706$	$0.042\ 505$	$-152.516\ 201$
CH_3–CS^+	$-475.140\ 116$	$0.039\ 963$	$-475.100\ 153$
CH_2=O	$-114.233\ 284$	$0.025\ 599$	$-114.207\ 685$
1,3-Dioxane	$-306.879\ 009$	$0.116\ 748$	$-306.762\ 261$
[structure]	$-459.486\ 263$	$0.163\ 065$	$-459.323\ 198$
[structure]	$-192.594\ 171$	$0.082\ 790$	$-192.511\ 381$
[structure]	$-515.209\ 581$	$0.079\ 754$	$-515.129\ 827$
[structure]	$-667.847\ 845$	$0.128\ 396$	$-667.719\ 449$
a	$-345.257\ 843$	$0.132\ 110$	$-345.125\ 733$
b	$-345.203\ 138$	$0.129\ 107$	$-345.074\ 031$
c	unstable		
d	$-345.224\ 217$	$0.126\ 773$	$-345.097\ 444$

[a] For the structures of **a**–**d** see Scheme 2. [b] Scaled by 0.89. [c] MP2/6-311G//6-311G(d,p) + ZPE.
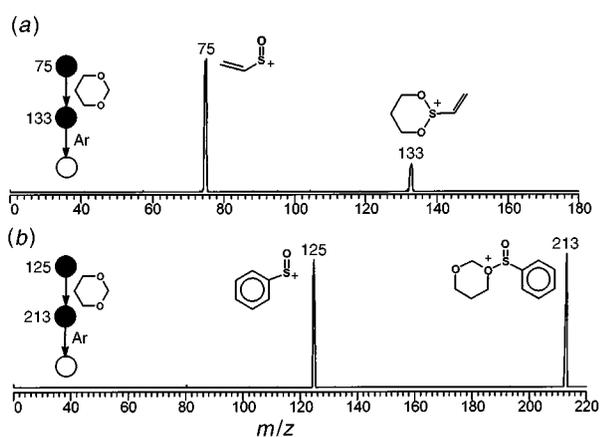

Fig. 7 Triple-stage (MS³) sequential product spectrum of (*a*) the transacetalization product of CH_2=CH–S^+=O and (*b*) of the intact adduct formed in reactions of 1,3-dioxane with Ph–S^+=O.

cations.[4,5] However, other alternative products (**b**–**d**) could also be proposed, as exemplified in Scheme 2.

Seeking theoretical support for the formation of the cyclic 'ionic ketals', the *ab initio* potential energy surface diagram was devised for a representative reaction, that is that of CH_3–C^+=O and 1,3-dioxane (Fig. 8, Table 2). Transacetalization that occurs *via* adduct (**a**) formation (-28.1 kcal mol^{-1}; 1 cal = 4.184 J) followed by formaldehyde loss and recyclization to **a** (-34.5 kcal mol^{-1}) is shown to be the most exothermic process (Fig. 8). Product **c** was found by the calculations to be unstable, and to undergo either isomerization to **d** or cyclization to **a** in the course of structure optimization. Note that formation of **d** *via* the unstable **c** must be hampered additionally by the activation barriers (not estimated) of the two consecutive 1,2-H shift processes (Fig. 8). Thus, transacetalization is shown by the *ab initio* calculations to be by far the most thermodynamically favourable reaction of 1,3-dioxane with CH_3–C^+=O. Note that formation of the cyclic 'ionic ketal' **a** would also be expected if one considers that the ring-opening process is assisted by an S_N2 intramolecular displacement, as proposed in Scheme 1. The exothermicity of the dissociation of the adduct to **a** and CH_2O
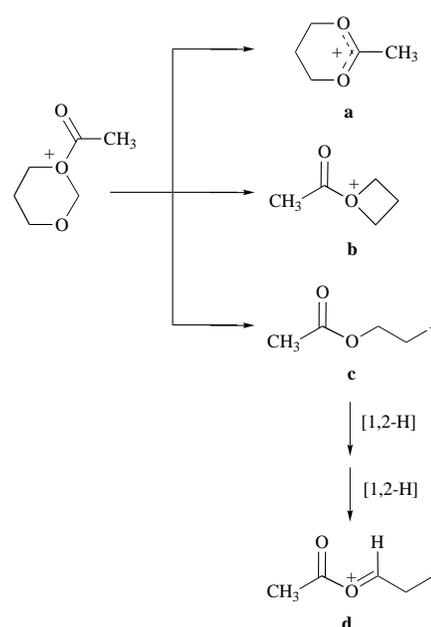
Scheme 2

indicates that the adducts should undergo rapid dissociation by formaldehyde loss, exactly as it is evidenced by the product spectra.

Dissociation of cyclic 'ionic thioketals'. *Ab initio* energy dissociation thresholds for the cyclic 'ionic thioketal' formed in reactions of 1,3-dioxane with CH_3–C^+=S were calculated (Table 2), and the results are summarized in Scheme 3. Thietane and
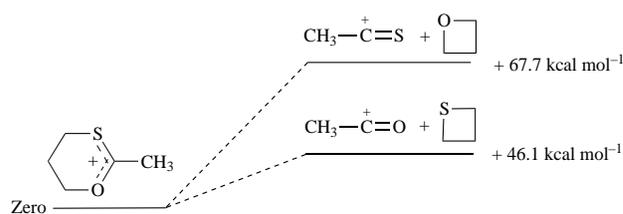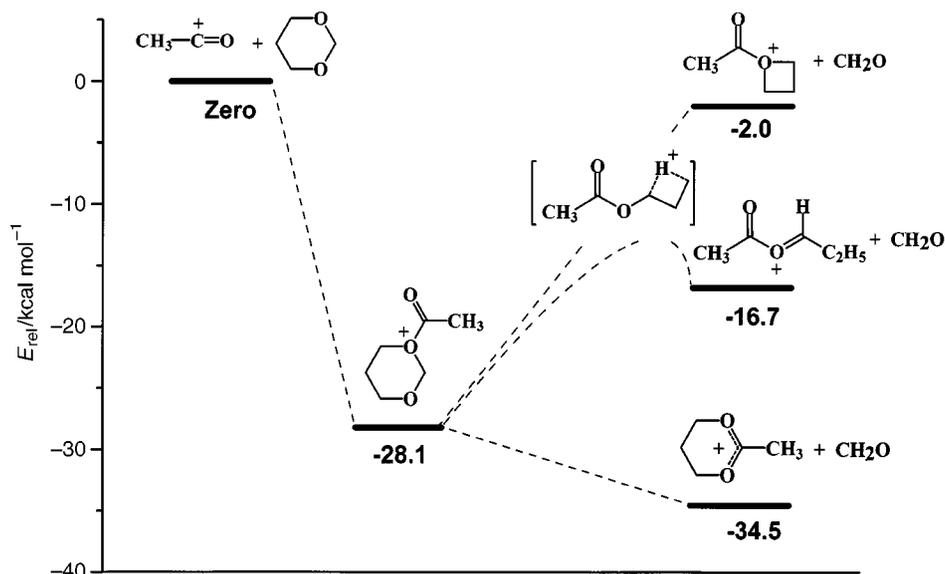

Scheme 3

Fig. 8 *Ab initio* MP2/6–311G(d,p)//6–311G(d,p) + ZPE potential energy surface diagram for the reaction of the acetyl cation with 1,3-dioxane. Note that transacetalization that leads to the cyclic 'ionic ketal' **b** is by far the most exothermic, therefore thermodynamically favorable, process.
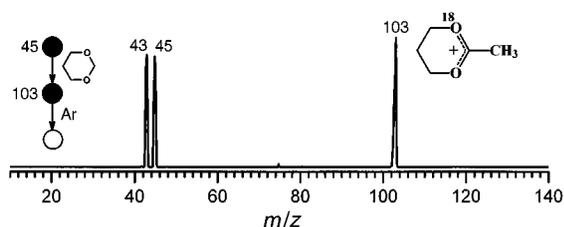

Fig. 9 Triple-stage (MS³) sequential product spectrum of the transacetalization product of 1,3-dioxane with $CH_3-C^+={}^{18}O$. Note the dissociation that regenates both the labelled ($CH_3-C^+={}^{18}O$, *m/z* 45) and unlabelled ($CH_3-C^+=O$, *m/z* 43) reactant ion.

oxetane were assumed to be the neutral fragments. A much less energy-demanding dissociation to $CH_3-C^+=O$ (*m/z* 43) is predicted, which nicely supports the dominance of this process during collision-induced dissociation [Fig. 4(c)].

¹⁸O Labelling

Conclusive evidence that cyclic dioxanylium ions ('ionic ketals') are formed *via* transacetalization of 1,3-dioxane with acylium ions is obtained when dissociating the product of the ¹⁸O-labelled ion $CH_3-C^+={}^{18}O$. The triple stage spectrum (Fig. 9) shows dissociation at the same extent to both the labelled ($CH_3-C^+={}^{18}O$, *m/z* 45) and unlabelled ($CH_3-C^+=O$, *m/z* 43) reactant ion, a result that can only be explained by assuming the ring-opening–ring-reforming 'oxygen-scrambling' mechanism depicted in Scheme 1.

Conclusions

Transacetalization is the dominant gas-phase reaction between the cyclic propane-1,3-diol acetal of formaldehyde, *i.e.* 1,3-dioxane, and a variety of acylium ions and the analogous sulfur ion, $CH_3-C^+=S$. The reaction is shown by *ab initio* calculations to be highly exothermic and hence thermodynamically favoured. Contrary to the case of 2-methyl-1,3-dioxolane, transacetalization of sulfinyl cations ($R-S^+=O$) with 1,3-dioxane is not general. Some sulfinyl cations react either moderately or extensively, whereas others are completely unreactive towards transacetalization.

Pentaquadrupole triple-stage (MS³) mass spectra and comparison with an authentic ion, as well as an ¹⁸O-labelling experiment, prove that six-membered cyclic 'ionic (thio)ketals' are formed. The cyclic 'ionic ketals' dissociate upon low-energy collision–activation exclusively to regenerate the reactant

acylium ion, a simple and characteristic dissociation chemistry that is amply demonstrated to be very general for the transacetalization products. The cyclic 'ionic thioketal' of $CH_3-C^+=S$, in contrast, does not dissociate to reform the reactant thioacylium ion to any measurable extent. As predicted by *ab initio* calculations, the oxygen analogue $CH_3-C^+=O$ ion is formed exclusively in this particular case. The efficient conversion of thioacylium ions into acylium ions can therefore be performed in the gas phase *via* this MS³ approach.

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