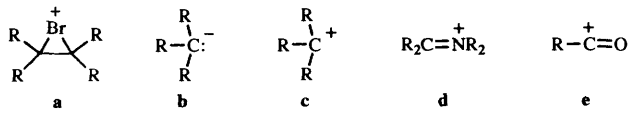
The generation, stability, dissociation and ion/molecule chemistry of sulfinyl cations in the gas phase

Fábio Cesar Gozzo, Ana Elisa P. M. Sorrilha and Marcos N. Eberlin *

State University of Campinas - UNICAMP, Institute of Chemistry, CP 6154 Campinas, SP 13083-970 Brazil

Sulfinyl cations [$R-S^+=O$ (R = CH_3, Ph, Cl, CH_3O and C_2H_5O)] have been demonstrated by MO calculations in conjunction with pentaquadrupole multidimensional (2D and 3D) MS^2 and MS^3 mass spectrometric experiments to be stable and easily accessible gas phase species, and their dissociation and ion/molecule chemistry have been studied. Potential energy surface diagrams indicate that the sulfoxides $(CH_3)_2S=O$, $Ph_2S=O$, $Cl_2S=O$, $(CH_3O)_2S=O$ and $(C_2H_5O)_2S=O$ do not undergo rearrangement upon dissociative ionization, yielding the corresponding sulfinyl cations as primary fragments. $Ph(CH_3)S=O^{+\cdot}$, on the other hand, is predicted to isomerize to $CH_3-S-O-Ph^{+\cdot}$ *via* a four-membered ring transition state, yielding upon further $CH_3^\cdot$ loss the isomeric ion $S=O^+-Ph$. The sulfinyl cations were found by *ab initio* calculations to be much more stable than their $S=O^+-R$ isomers, hence isomerization *via* [1,2-R] shifts is not expected. Direct cleavage of the $R-SO^+$ bonds and/or processes that are preceded by isomerization dominate the low-energy collision dissociation chemistry of the sulfinyl cations, thus providing limited structural information. On the other hand, a general and structurally diagnostic ion/molecule reaction with 2-methyl-1,3-dioxolane occurs for all the sulfinyl cations yielding abundant net oxirane (C_2H_4O) addition products. The reaction probably occurs *via* a transketalization-like mechanism that leads to cyclic 2-thia-1,3-dioxolanylium ions. This reactivity parallels that of several acylium ($R-C^+=O$) and thioacylium ions ($R-C^+=S$), and is not shared by the isomeric ions SO^+-Ph and $CH_2=S^+-OH$. While the corresponding acylium ions react extensively with isoprene by [4 + 2^+] cycloaddition, only the phenylsulfinyl cation $Ph-S^+=O$ yields an abundant cycloadduct.

Ionic species play a key role in various chemical processes. A characteristic example of such a role is provided by many synthetically useful reactions, which are driven or affected heavily by the properties of their ionic intermediates.[1] The driving force for these reactions is often provided by the great reactivity of the ionic intermediates, whereas some of their unique properties are responsible in many cases for the specific stereo- and regio-chemistry observed. Many changes in the structure (or connectivity) of the initial reactants also occur during the course of the reaction due to rearrangement of ionic intermediates. For instance, chloronium and bromonium ions **a** are the key intermediates in the very general and synthetically useful reaction of halogen addition to alkynes and alkenes,[2] and their structure and reactivity accounts for the high stereoselectivity of this reaction.[3] Carbanion intermediates **b** in the Aldol condensation reaction,[4] carbonium ions **c** in many nucleophilic substitution reactions,[1] immonium ions **d** in the Mannich reaction,[5] and acylium ions **e** in the Friedel–Crafts reaction[6] are other representative examples of key ionic intermediates in important chemical reactions. Ionic species also play a prominent role in other areas such as in ionosphere and flame chemistry.[7] A broad knowledge of the intrinsic properties of such ions is therefore indispensable for the understanding and control of the chemistry of reactions and other important chemical processes in which they participate as key intermediates.



a **b** **c** **d** **e**

The mass spectrometer provides a convenient 'solvent-free' environment in which to study the intrinsic properties of gas-phase ionic species and to seek parallels or to predict their chemistry in condensed phases. Many ions which are either difficult to isolate, elusive intermediates or even inaccessible species in solution, can be easily generated in the gas phase by mass spectrometric techniques.[8] In the gas phase, such ions usually display relatively long life-times which allow their isolation and the study of their intrinsic properties. For instance, acylium ions **e**, which are very reactive intermediates in solution,[6] are stable[9] and well characterized gas-phase species,[10] and they display a rich and unique reactivity in this environment.[11] Reactions without precedent in solution, such as those of polar [4 + 2^+] Diels–Alder cycloaddition with '*s-cis*' conjugated dienes[12] and a structurally diagnostic 'oxirane addition' reaction with 1,3-dioxolanes occur in the gas phase for many acylium ions.[13] Thioacylium ions ($R-C^+=S$), sulfur analogues of acylium ions, have also been found to display a rich gas-phase chemistry.[11f,g,h,12,13] In contrast to the well-documented solution chemistry of acylium ions,[6a] thioacylium ions are relatively unknown in solution.[14]

Studies of the chemistry of isolated ions in the gas phase can be appropriately performed by multiple-stage (MS^n) mass spectrometric experiments.[15] The complete set[16] of MS^2 and MS^3 experiments can be efficiently performed in pentaquadrupole mass spectrometers[17] (Fig. 1), which constitute very convenient 'laboratories' for gas phase ion chemistry studies. A large variety of ions can be easily generated in the ion source of this instrument by several different ionization techniques, purified (mass-selected in Q1) and then reacted in Q2 with selected neutral gases at controlled conditions ('temperature', *i.e.* collision energy, and 'concentration', *i.e.* reactant gas pressure). The structures of each individually Q3-selected ionic product can then be investigated *via* collision dissociation in Q4 followed by Q5 product analysis, or additionally by investigating their chemistry *via* structurally diagnostic ion/molecule reactions, a procedure to some extent similar to those commonly applied in condensed phase studies. Since in pentaquadrupole mass spectrometers two or even three mass-

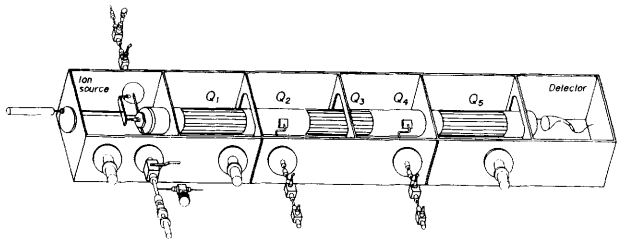


Fig. 1 The EXTREL pentaquadrupole mass spectrometer, a convenient laboratory for gas phase ion chemistry studies, with its three mass-analyser quadrupoles (Q1, Q3 and Q5) and two reaction chambers (Q2 and Q4). In a typical ion/molecule reaction experiment, ions are generated in the ion/source, purified (mass-selected) by Q1, and reacted with a neutral gas introduced in Q2 under controlled conditions (collision energy and pressure). Each of the product ions can then be subsequently mass-selected by Q3, and structurally analysed by either collisional dissociation or structurally diagnostic ion/molecule reactions in Q4, while the products formed in these processes are disclosed by scanning Q5.

analyser quadrupoles can be sequentially or simultaneously scanned, a complete view of the ion/molecule reaction process can also be obtained by applying several types of three-dimensional (3D)[12a,16] or even 4D (three m/z axis and a fourth intensity axis) MS^3 scans.[17b] The usefulness of this instrument and several MS^3 scans for detailed gas phase ion chemistry studies has been recently demonstrated.[12,13,18]

Sulfinyl cations ($R-S^+=O$) represent an important class of closed-shell sulfur ions which are unknown in solution. However, they could in principle be easily generated and studied in the gas phase. Although these ions cannot really be considered as sulfur analogues of acylium ions ($R-C^+=O$) because of the significant changes in electron configuration caused by replacement of a carbon by a sulfur atom, structural similarities with acylium ions still permit one to predict by analogy a rich chemistry for sulfinyl cations. Their gas phase ion/molecule chemistry has, however, received no attention to date. It is also interesting to note that although the generation of sulfinyl cations has often been proposed to occur from dissociative ionization of sulfoxides, sulfones and related compounds,[19] little information[20] has been collected to substantiate their formation and gas phase stability towards isomerization. This fact becomes even more important when noting that the dissociation chemistry of ionized sulfoxides and sulfones often indicates the operation of several isomerization processes that precede dissociation,[19] and therefore the expected sulfinyl cations may not be formed as the primary fragments. In addition, sulfur ions in general display a greater proclivity to undergo rearrangements,[19j] hence the sulfinyl cations, if indeed generated as the primary fragments, may undergo further isomerization. The ion $CH_3-S^+=O$ **1** represents so far the only member of this class that has been conclusively demonstrated both experimentally[20a-d] and theoretically[20d] to be a stable and easily accessible gas-phase species. The complexity of such a system is demonstrated, however, by the fact that dissociative ionization of dimethyl sulfoxide generates **1**,[20a,b] while metastable dissociation generates the isomeric *O*-protonated sulfine $CH_2=S^+-OH$ **11**.[20c]

The present paper reports a theoretical and experimental study on the generation, stability, collision dissociation and ion/molecule chemistry of five representative members of the sulfinyl cation class **1–5**. Semiempirical or *ab initio* MO calculations have been applied to ionized sulfoxides and related compounds ($R_2-SO^{+\bullet}$), and their isomeric forms and connecting transition states in order to investigate the nature of primary ions of composition ROS^+, and the energetics of the [1,2-R] isomerizations of ions **1–5** to **6–10**. The gas-phase dissociation and ion/molecule chemistry of the sulfinyl cations **1–5** were investigated by fast 2D and 3D multiple stage mass spectrometric experiments performed in a high-transmission pentaquadrupole mass spectrometer.[17b]

1 R = CH_3
2 R = Ph
3 R = Cl
4 R = CH_3O
5 R = C_2H_5O

6 R = CH_3
7 R = Ph
8 R = Cl
9 R = CH_3O
10 R = C_2H_5O

Methods

The MS^2 and MS^3 experiments were performed using an Extrel (Pittsburgh, PA) pentaquadrupole mass spectrometer[17b] (Fig. 1) consisting of three mass analysing (Q1, Q3, Q5) and two reaction quadrupoles (Q2, Q4). Collision-induced dissociation (CID) and ion/molecule reactions were performed by MS^2 experiments in which Q1 was used to mass select the ion of interest. After dissociative collisions with argon or reactive collisions with a neutral reagent in Q2, the product spectrum was recorded by scanning Q5, while operating Q3 in the non-analysing rf-only mode.

For the 2D MS^3 experiments, ion/molecule reactions with the neutral reagent and CID with argon were performed in Q2 and Q4, respectively. The reactant ion generated in the ion source was mass-selected in Q1, the product ion of interest selected in Q3, while scanning Q5 to record the spectrum. The total pressures inside each differentially pumped region were, for a MS^3 experiment, typically 2×10^{-6} (ion-source), 8×10^{-5} (Q2) and 8×10^{-5} (Q4) torr, respectively, which correspond to multiple-collision conditions. The collision energy, calculated as the voltage difference between the ion source and the collision quadrupole, was typically ~0 eV for ion/molecule reactions and 15 eV for low-energy CID, in both MS^2 and MS^3 experiments.

The 3D MS^3 spectrum was obtained by mass-selecting in Q1 the m/z 79 reactant ion **4** and by performing reactions with 2-methyl-1,3-dioxolane in Q2 and 15 eV CID with argon in Q4, while scanning sequentially both Q3 and Q5. Instrumentally, this was accomplished by stepping Q3 one mass unit at a time while Q5 was scanned along the entire mass range of interest at each setting of Q3. Actually, a pre-scan procedure[17b] identified Q3 parent ions at m/z 59, 73, 79, 87, 89, 103 and 123; therefore, Q5 was scanned only while having Q3 set exactly at each of these pre-selected masses. This allowed very fast data acquisition, which took *ca.* 1 min.

AM1 molecular orbital calculations[21] were carried out using Spartan.[22] *Ab initio* calculations were carried out by using GAUSSIAN92.[23] The closed-shell ions were optimized at the restricted (RHF) Hartree–Fock level of theory by employing the polarization 6-31G(d,p) basis set.[24] Improved energies were obtained by using single point calculations at the 6-31G(d,p) level and incorporating valence electron correlation calculated by second-order Møller–Plesset (MP2) perturbation theory,[25] a procedure denoted as MP2/6-31G(d,p)//6-31G(d,p). Harmonic vibrational frequencies were calculated at the RHF/6-31G(d,p) level to characterize the stationary points and to obtain the zero-point vibrational energies (ZPE). The input and output structures from the Gaussian calculations were visualized by the aid of the XMOL program.[26]

Results and discussion

Molecular orbital calculations

(i) $(CH_3)_2S=O^{+\bullet}$. *Ab initio* calculations have been performed on ionized dimethyl sulfoxide (DMSO) and its three $C_2H_6OS^{+\bullet}$ isomers and on all of their fourteen conceivable CH_3OS^+ fragment ions.[20d] The theoretical results indicated that $(CH_3)_2-S=O^{+\bullet}$, excited a few eV above the threshold, dissociates upon

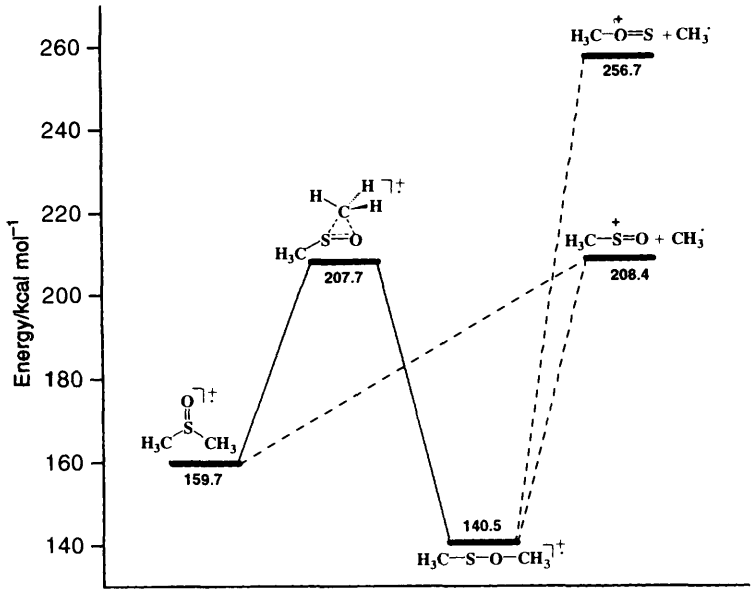


Fig. 2 Potential energy surface diagram for the [1,2-CH_3] isomerization process of ionized dimethyl sulfoxide and the thresholds for methyl radical loss

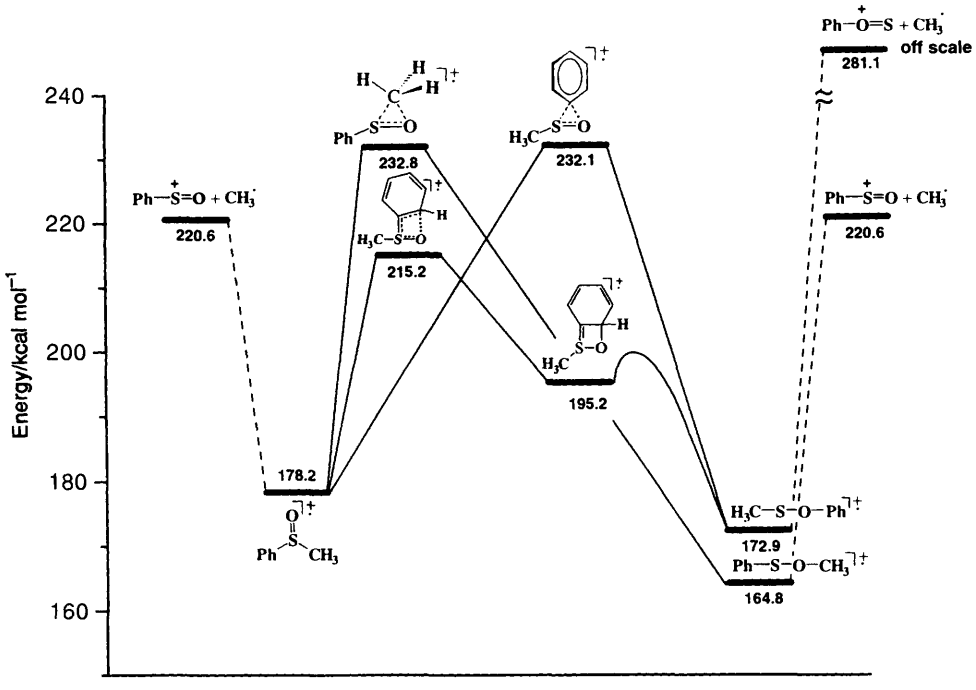


Fig. 3 Potential energy surface diagram for the [1,2-Ph] and [1,2-CH_3] isomerization processes of ionized methyl phenyl sulfoxide and the thresholds for methyl radical loss

methyl radical loss directly to **1**. Isomerization to the most stable $C_2H_6OS^{+\bullet}$ ion, *i.e.* CH_3–S–O–$CH_3^{+\bullet}$, was shown to be considerably exothermic (−25.1 kcal mol^{-1}) but connected by the most energetic transition state (40.3 kcal mol^{-1}), which is placed slightly below the threshold for direct methyl loss (42.6 kcal mol^{-1}). [1,2-CH_3] shift is therefore expected to be negligible, whereas the minor rearranged ion CH_3–S–O–$CH_3^{+\bullet}$ should dissociate by $CH_3^{\bullet}$ loss preferentially to **1**. Isomerization to the *aci*-form CH_2=S(OH)–$CH_3^{+\bullet}$, which dissociates by $CH_3^{\bullet}$ loss to **11** (CH_2=S^+–OH) but preferentially by $OH^{\bullet}$ loss to CH_2=S^+–CH_3, was shown to display the lowest activation barrier, but to be favourable only for low energy metastable ions. Ion **1** was also shown by *ab initio* calculations to lie in a deep potential well that hampers considerably its isomerization to a variety of other more stable CH_3OS^+ isomers.[20d]

The [1,2-CH_3] isomerization $(CH_3)_2S{=}O^{+\bullet} \longrightarrow CH_3$–S–O–$CH_3^{+\bullet}$, its transition state, and the thresholds for methyl radical loss dissociation of $(CH_3)_2S{=}O^{+\bullet}$ and CH_3–S–O–$CH_3^{+\bullet}$ were also evaluated by AM1 calculations (Fig. 2). Excellent agreement with the *ab initio* results was obtained; thus, AM1 calculations were also applied to the other precursors, their isomers and dissociation products, as summarized in Figs. 3 and 4, and discussed in the following text.

(ii) $Ph(CH_3)_3S{=}O^{+\bullet}$. Direct dissociation by phenyl or methyl radical loss from $Ph(CH_3)_3S{=}O^{+\bullet}$ should yield the sulfinyl cations **1** and **2** as primary fragments, whereas the occurrence of methyl or phenyl migration preceding dissociation could lead to formation of either **1** and **7** or **2** and **6** (Scheme 1).

The calculations show that the [1,2-CH_3] and [1,2-Ph] shifts for $Ph(CH_3)S{=}O^{+\bullet}$ are both exothermic, and that methyl migration to yield Ph–S–O–$CH_3^{+\bullet}$ is the most thermodynamically favourable process (Fig. 3). Transition state calculations show, on the other hand, that the most kinetically favourable process is that of phenyl migration, as expected by the greater

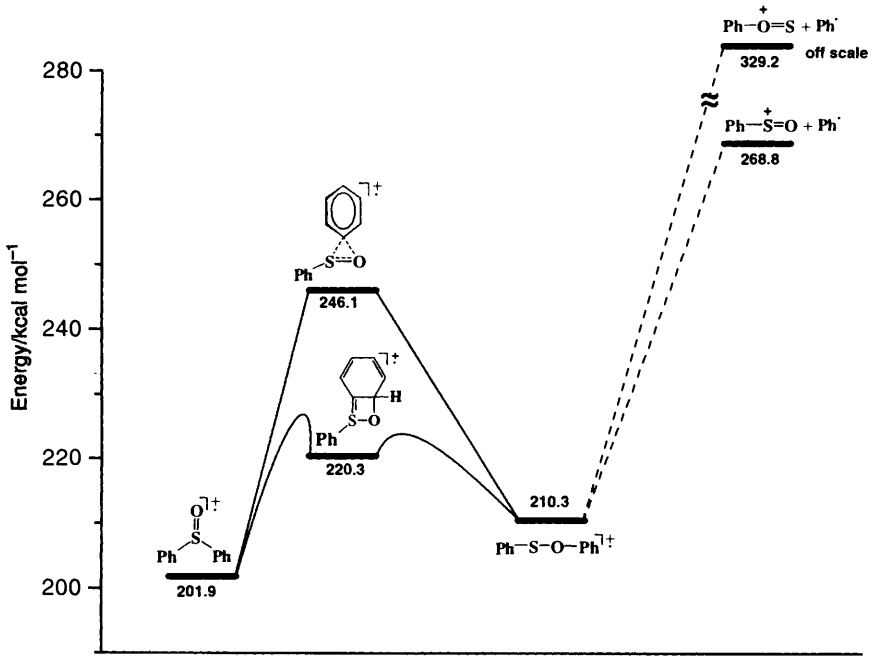
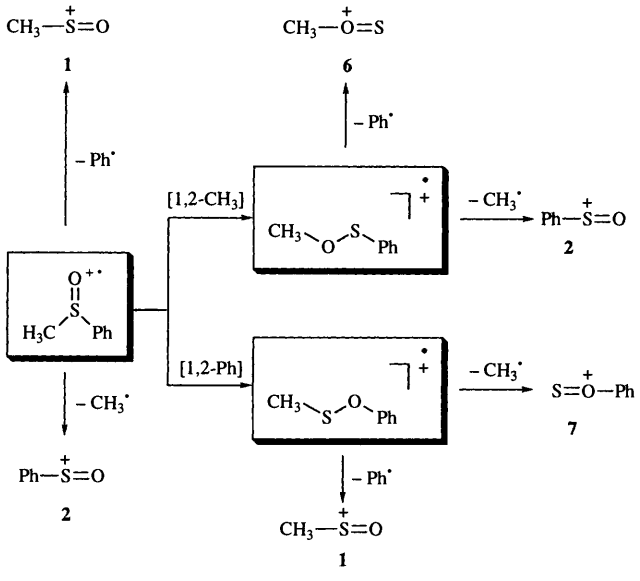


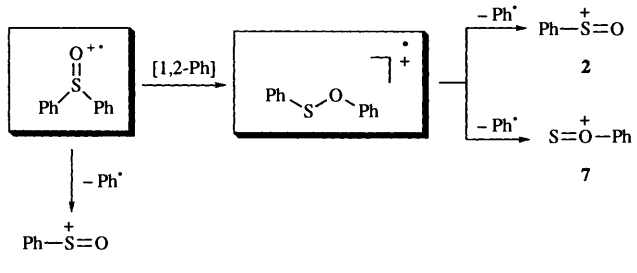
Fig. 4 Potential energy surface diagram for the [1,2-Ph] isomerization process of ionized diphenyl sulfoxide and the thresholds for phenyl radical loss



Scheme 1

migratory aptitude normally displayed by the phenyl group.[27] Note that this migration could be visualized to occur either directly *via* a three-membered ring transition state or *via* a bicyclic intermediate connected by a four-membered ring transition state, followed by ring opening and [1,2-H] shift (Fig. 3). The calculations predict the latter process to be considerably more favourable and, most importantly, that the activation barrier for phenyl migration (*via* the four-membered ring transition state) is 5.1 kcal mol^{-1} lower than the threshold for dissociation by direct methyl radical loss. The activation barrier for the competitive methyl migration is, on the other hand, placed 12.2 kcal mol^{-1} higher than the dissociation threshold for methyl radical loss (Fig. 3). Therefore, dissociative ionization of methyl phenyl sulfoxide is likely to be preceded by [1,2-Ph] isomerization and to yield mainly the isomeric **7** (not the sulfinyl cation **2**) and the sulfinyl cation **1** as the primary fragments (Scheme 1). An indication of phenyl migration is also provided by the *m/z* 94 fragment (CH_2S loss) observed in the mass spectrum of methyl phenyl sulfoxide.[19e] On the other hand, the entropically favourable direct dissociation that yields **2** could still occur or even predominate for excited $Ph(CH_3)S{=}O^{+\cdot}$ ions, as observed for $(CH_3)_2S{=}O^{+\cdot}$.[20d] The experimental results discussed in subsequent text shows, however, no or minor contribution of the direct dissociation process.

(iii) $Ph_2S{=}O^{+\cdot}$. In contrast with the previous case, analogous [1,2-Ph] migration is found to be a thermodynamically unfavourable process for $Ph_2S{=}O^{+\cdot}$ (Fig. 4). Phenyl radical loss would then be expected to occur mainly from the intact ion to yield **2** (Scheme 2). However, the transition state for [1,2-Ph]



Scheme 2

shift† is placed considerably lower in energy than the threshold for direct phenyl radical loss, hence energetic collisions could drive to some extent the [1,2-Ph] isomerization. In any case, however, phenyl radical loss from the rearranged Ph–S–O–Ph$^{+\cdot}$ is still predicted to yield the sulfinyl cation **2** as the primary fragment (Scheme 2), since both the semiempirical (Fig. 4) and the *ab initio* calculations (Table 1) show a considerably more energetically favoured threshold for dissociation to **2**. The greater stability of **2**, which according to the *ab initio* calculations lies −16.8 kcal mol^{-1} below **7** (Table 1), also discounts further [1,2-Ph] shift isomerization of **2**. Other isomeric structures could only be formed at the expense of the

† Many attempts to locate the four-membered ring transition state for ionized diphenyl sulfoxide have failed. This transition state is expected by analogy with the results obtained for methyl phenyl sulfoxide (Fig. 3) to lie lower in energy than the three-membered ring transition state shown in Fig. 4. The barriers for phenyl migration *via* both transition states should therefore be lower than the threshold for direct phenyl radical loss.

Table 1 Total, ZPE and relative energies from *ab initio* structure optimization calculations

Ion	MP2/6-31G(d,p)//6-31G(d,p) (hartree)	ZPE[a]/ kcal mol^{-1}	Relative[b]/ kcal mol^{-1}
1	−512.066 94	24.0	0
6	−512.031 61	25.2	23.4
2	−703.245 38	56.3	13.0
7	−703.219 33	56.7	29.8
12	−703.266 63	55.6	0
3	−931.884 55	3.3	0
8	−931.785 94	2.8	61.4
4	−587.113 46	27.7	0
9	−586.971 14	27.1	88.7
5	−626.308 91	44.5	0
10	−626.161 02	44.1	92.4

[a] Scaled by 0.89. [b] Including ZPE.

aromatic phenyl ring, which should hamper significantly the occurrence of such isomerization processes.

(iv) $Cl_2S{=}O^{+\cdot}$, $(CH_3O)_2S{=}O^{+\cdot}$ and $(C_2H_5O)_2S{=}O^{+\cdot}$. As with ionized diphenyl sulfoxide, the calculations show that the primary ionized forms of thionyl chloride, methyl sulfite and ethyl sulfite are far more stable than their corresponding isomeric species of general structure R–S–O–R$^{+\cdot}$ [179.9 kcal mol^{-1} (196.3), 78.5 (137.1), 60.9 (121.6), respectively]. The sulfinyl cations **3**, **4** and **5** should therefore be generated as the primary fragments upon direct dissociation by S–R bond cleavage. In the same way, any isomerization to the corresponding R–S–O–R$^{+\cdot}$ ions in the course of dissociation should still lead mainly to generation of the sulfinyl cations **3**, **4** and **5**, which are shown by *ab initio* calculations to be considerably more stable than the isomeric structures **8**, **9** and **10** (Table 1). These results also show that further isomerization of the primary ions **3**, **4** and **5** to the corresponding **8**, **9** and **10** is unlikely.

In conclusion, the MO calculations predict the sulfinyl cations **1**–**5** to be formed as the primary and stable fragments from dissociative ionization of dimethyl sulfoxide, diphenyl sulfoxide, thionyl chloride, methyl sulfite and ethyl sulfite, respectively. On the other hand, ionized methyl phenyl sulfoxide is predicted to isomerize by [1,2-Ph] shift, and to fragment further to the sulfinyl cation **1** and to the isomeric **7** (Scheme 2).

Collision dissociation chemistry

The methylsulfinyl cation **1** ($CH_3{-}S^{+}{=}O$) has been shown to display a somewhat complex dissociation chemistry (Table 2) that leads to formation of several indirect fragments, whose formation has been recently theoretically and experimentally investigated.[20d] Its structure is still characterized by two direct fragments (CH_3^+ and $SO^{+\cdot}$), which are not observed in the dissociation spectrum of isomer **11**.[20] However, the CH_3^+ and $SO^{+\cdot}$ fragments alone do not provide in principle an unequivocal characterization of **1** since similar dissociation could also occur for isomer **6**. The 15 eV MS^2 CID spectra of the sulfinyl cations **2**–**5** (Table 2) were then acquired in order to investigate their general ability to characterize this class of cations and for isomer distinction, particularly between the putative ions **2** (from $Ph_2S{=}O^{+\cdot}$) and **7** [from $Ph(CH_3)S{=}O^{+\cdot}$].

The CID spectra of the putative **2** and **7** were, however, found to be nearly identical (Fig. 5). This could therefore indicate either an indistinguishable dissociation chemistry: that in fact the same ion **2** or **7** is formed from both precursors, or that **7** isomerizes to **2** prior to dissociation. The latter process appears to be particularly favourable since it is −16.8 kcal mol^{-1} exothermic (Table 1) and is likely to display a low activation barrier proportioned by a relatively stable phenonium ion intermediate [eqn. (1)].

The CID fragments provide no clue that could point to either

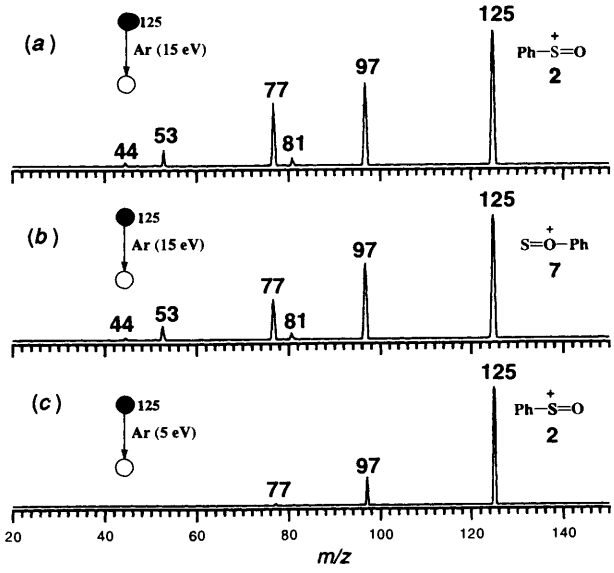
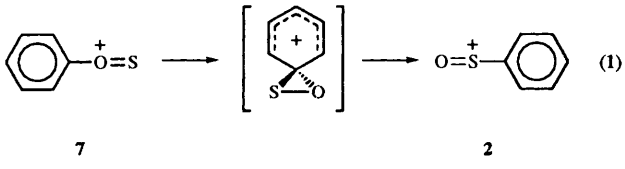
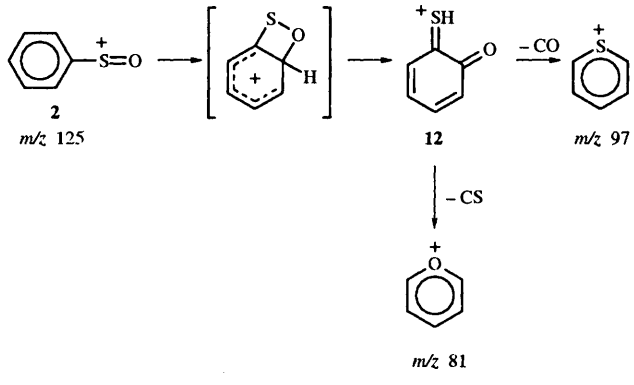


Fig. 5 MS^2 dissociation spectra of (*a*) ion **2** at 15 eV collisions, (*b*) ion **7** at 15 eV collisions and (*c*) ion **2** at 5 eV collisions. The dissociation spectrum of ion **7** at 5 eV collisions (not shown) is nearly identical to that of ion **2** (*c*). In the terminology used to describe 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, whereas the neutral reagent or collision gas that causes the mass transitions are shown between the circles. For more details on this nomenclature, see ref. 16.



of the two structures. The *m*/*z* 77 fragment (Ph^+, SO loss) is characteristic of the phenyl ring and could therefore be formed by direct dissociation of both **2** and **7**. Loss of, most likely, CO ($C_5H_5S^+$, *m*/*z* 97) must be, on the other hand, a dissociation process preceded by isomerization involving the phenyl ring. The CO loss appears to be the lowest energetic dissociation pathway since it greatly predominates for both ions at low collision energies [Fig. 5(*c*)], being still observed probably as a metastable fragment with no collision gas and at zero collision energy. A dissociation process involving **12** as the intermediate (Scheme 3), which is shown by *ab initio* calculations to be more



Scheme 3

stable than both **2** and **7** (Table 1), appears as the most likely alternative. This ion could then lose a CO molecule to form the stable, aromatic $C_5H_5S^+$ thiapyrilium ion. Note that CS loss also occurs (Fig. 5, *m*/*z* 81), likely preceded by intramolecular proton transfer, and would be similarly expected to yield the

Table 2 MS^2 Collision-induced dissociation (CID) spectra[a]

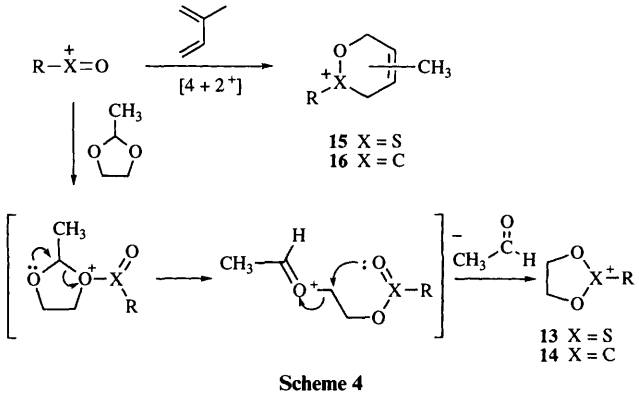
Ion[a]	Precursor	m/z	15 eV MS^2 CID spectra m/z (relative abundance)
1[b]	$(CH_3)_2S{=}O$	63	15 (5), 29 (4), 31 (19), 45 (72), 46 (43), 48 (100)
2[c]	$Ph_2S{=}O$[d]	125	97 (100), 81 (8), 77 (76), 53 (19), 44 (4)
3	$Cl_2S{=}O$	83	48 (100)
4	$(CH_3O)_2S{=}O$	79	15 (100)
5	$(C_2H_5O)_2S{=}O$	93	29 (100)
7[c]	$Ph(CH_3)S{=}O$	125	97 (100), 81 (7), 77 (54), 53 (17), 44 (3)
11	$(C_4H_9)_2S{=}O$[e]	63	29 (6), 31 (25), 45 (100), 46 (79)

[a] The ions were obtained from 70 eV dissociative ionization of the corresponding precursors. [b] Data taken from ref. 20*d*. [c] The complete spectrum is shown in Fig. 5. [d] Also obtained from diphenyl sulfone. [e] Ionized di-*n*-butylsulfoxide produces **11** by a [1,4-H] shift isomerization followed by losses of but-1-ene and C_3H_7; see ref. 20*b* and R. Smakman and Th. J. De Boer, *Org. Mass Spectrom.*, 1970, **3**, 1561.

Table 3 MS^2 Product spectra for ion/molecule reactions with 2-methyl-1,3-dioxolane[a]

Ion	Ionic products[b] m/z (relative abundance)
1	**107** (73), 89 (100). 87 (28), 59 (2), 73 (10), 45 (6)
3	**127** (21), 89 (19), 87 (22), 73 (100)
5	181 (19),[c] **137** (97), 117 (27),[d] 89 (100), 87 (31), 73 (77), 45 (5)
7	185 (15), 177 (3), **169** (16), 141 (65), 97 (99), 89 (15), 87 (100), 81 (3), 77 (13), 73 (4)
11	89 (100), 87 (25), 73 (9), 59 (3), 45 (10)

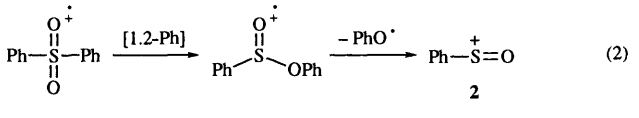
[a] The spectra for ions **2** [Fig. 6(*c*)] and **4** [Fig. 7(*c*)] are shown as Figs., see text. [b] The oxirane addition products are marked in bold. [c] The intact adduct. [d] The $C_2H_5^+$ transfer product, see text.



Scheme 4

pyrilium ion (Scheme 3). These rationalizations are supported by the MS^3 spectra of both the *m/z* 97 [*m/z* 70 (3%), 69 (5), 53 (100), 45 (41)] and *m/z* 81 [53 (100), 51 (4), 29 (2), 27 (28)] product ions, which are nearly identical to the MS^2 CID spectra of the authentic pyrilium and thiapyrilium ions.[18d]

The *m/z* 125 ion generated from dissociative ionization of phenyl sulfone was also subjected to CID, and a nearly identical spectrum to that obtained for the putative ions **2** and **7** (Fig. 5) was obtained. Ion **2** is the most likely primary *m/z* 125 fragment of ionized phenyl sulfone since the phenoxy radical loss must be preceded by a [1,2-Ph] shift [eqn. (2)].[28] This, therefore,



(2)

together with the theoretical predictions, points to the possibility that both isomeric ions **2** and **7** show an identical dissociation chemistry, most likely due to the occurrence of the relatively low energy demanding collision-induced isomerization **7** ⟶ **2** [eqn. (1)] although the possibility that **2** was formed from both precursors can not be entirely dismissed at this point. In contrast with ions **1** and **2**, the dissociation chemistry of the sulfinyl cations **3**, **4** and **5** (Table 2) is much simpler and completely dominated by cleavage of the S–R bonds. Ion **3** dissociates by Cl˙ loss to yield $SO^{+\cdot}$ (*m/z* 48, Table 2), whereas **4** and **5** fragment by neutral loss of SO_2 to form CH_3^+ (*m/z* 15) and $C_2H_5^+$ (*m/z* 29), respectively. As with ions **1** and **2**, even though these fragments are totally compatible with the sulfinyl cation structures, they cannot in principle be used for their unequivocal characterization, because the isomeric **8**–**10** could also dissociate directly to produce these same fragments.

Ion/molecule chemistry

In order to seek an efficient way of characterizing the sulfinyl cations, and to explore at the same time their gas phase chemistry, reactions with 2-methyl-1,3-dioxolane[29] and isoprene were carried out. Both reactions were chosen as candidates for structurally diagnostic reactions because they have already been shown to be able to clearly characterize many members of the acylium (and thioacylium) ion class and to distinguish them from several isomeric structures.[12,13] Considering that sulfinyl cations display some electronic and structural characteristics comparable to those of acylium ions, a similar reactivity could in principle be expected, as rationalized in Scheme 4.

The MS^2 product spectra displayed in Table 3, and exemplified for ion **2**‡ in Fig. 6(*c*) and in Fig. 7(*c*) for ion **4**, show that all the sulfinyl cations form abundant oxirane addition products (**13**, Scheme 4) in reactions with 2-methyl-1,3-dioxolane.§ Fig. 6 also exemplifies for ion **2** all the MS^n experiments employed in the pentaquadrupole mass spectrometer in producing, selecting, reacting and analysing by collision dissociation the ion/molecule reaction products of an ion of

‡ Similar product spectra were obtained for the *m/z* 125 ion formed from dissociative ionization of both diphenyl sulfoxide and diphenyl sulfone, thus indicating formation of ion **2** from both precursors.

§ The *m/z* 141 product seen in Fig. 6(*c*) and in the MS^2 spectrum of **7** (Table 3) corresponds to oxirane addition to *m/z* 97, the putative thiapyrilium ion. This assignment has been confirmed by separate experiments with the authentic ion. The product ions at *m/z* 103 [Fig. 7(*c*)] and at *m/z* 117 in Table 3 (ion **5**) correspond to transfer from **4** and **5** of CH_3^+ and $C_2H_5^+$ to 2-methyl-1,3-dioxolane, respectively. Ion **5** also transfers $C_2H_5^+$ very efficiently to several other compounds, such as nitriles and ketones (F. C. Gozzo and M. N. Eberlin, unpublished results).

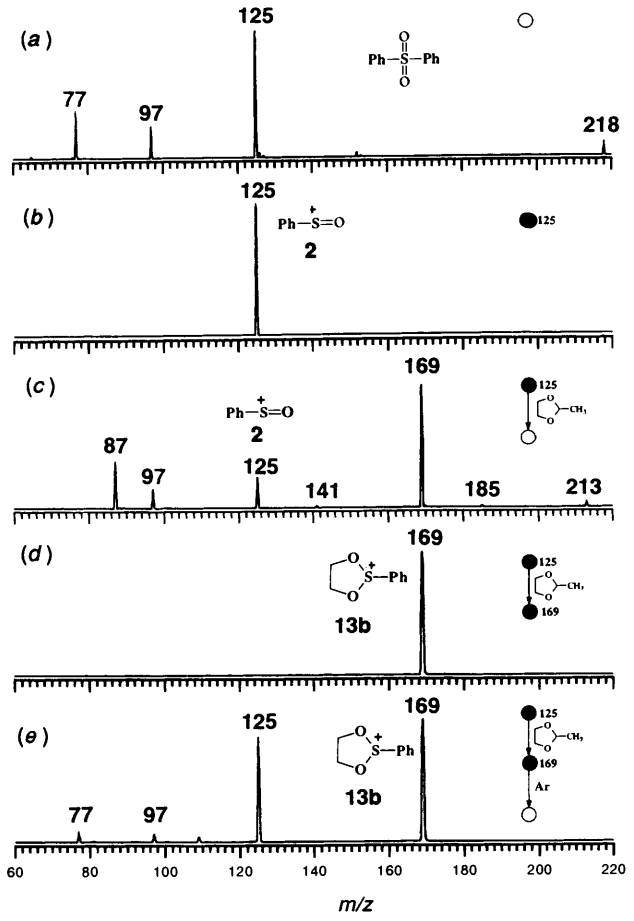


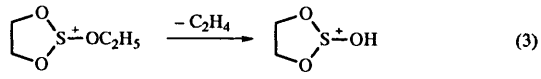
Fig. 6 The sequence of 2D MS^n (n = 1–3) experiments applied to study the ion/molecule chemistry of the sulfinyl cation **2** in the pentaquadrupole mass spectrometer. The ion of m/z 125 is (*a*) produced by 70 eV EI dissociative ionization of diphenyl sulfone, (*b*) mass-selected by Q1, (*c*) reacted with 2-methyl-1,3-dioxolane in Q2. A reaction product of interest (m/z 169) is (*d*) mass-selected by Q3, and (*e*) its dissociation induced by 15 eV collisions with argon in Q4, while Q5 is scanned to acquire the MS^3 sequential product spectrum. Note the distinguishing reactivity displayed by ion **2** (*c*) and its isomer **7** (Table 3).

interest. The mechanism proposed in Scheme 4 for the oxirane addition reaction is analogous to the one proposed for reaction of acylium and thioacylium ions.[13] The term 'oxirane addition' was chosen by analogy with the solution-phase reaction that occurs by oxirane addition to carbonyl compounds and leads to 1,3-dioxolanes derivatives.[30] The reaction most likely takes place *via* a 'transketalization-like' mechanism in which the 'keto' ions or the related sulfinyl cations ($R-S^+=O$) replace the aldehyde in the 1,3-dioxolane ketal.

Noteworthy also is the fact that the isomeric ions **7** and **11** (Table 3) fail almost completely to undergo the oxirane addition reaction, and their MS^2 product spectra display mainly products of the proton transfer (m/z 89) and most likely hydride abstraction (m/z 87) reactions.¶ The small oxirane addition product (m/z 169) observed (Table 3) may correspond to oxirane addition to **7**, but could also indicate occurrence to a limited extent under the milder (near zero eV collisions) ion/molecule reaction conditions of the **7** ⟶ **2** isomerization. This isomerization, as already discussed, appears to occur extensively under 15 eV collisions with argon. The reactivity observed for the sulfinyl cations corroborates therefore their structures and indicates that this reaction can serve as a general method for their gas phase characterization, as is the case for acylium ions.[13]

The structure of the oxirane addition products. Considering that sulfinyl cations react with 2-methyl-1,3-dioxolane by a similar mechanism to that observed for the acylium and thioacylium ions, formation of the 2-thia-1,3-dioxolanylium ions **13** is expected (Scheme 4). The corresponding cyclic structures for the acylium ions **14** have been evidenced by ^{18}O labelling and comparison of their MS^3 spectra to those of authentic ions.[13] Such comparisons are not possible for the case of sulfinyl cations, since alternative ways to produce **13** are unknown. Evidence for structures **13** come, however, from their dissociation chemistry studied by MS^3 experiments known as the sequential product scan,[16] as discussed in the following text. Their relatively high resistance towards collision dissociation also discard any loosely bound structure, as for instance, the proton bound dimer between oxirane and the neutral sulfine $CH_2=S=O$.

The product ions **13a–d** (**a**, R = CH_3; **b**, R = Ph; **c**, R = Cl; **d**; R = OCH_3), when mass-selected by Q3 and collided with argon in Q4, dissociate extensively by C_2H_4O (44u) loss to regenerate most likely the original reactant ion, as exemplified for ion **13b** in Fig. 6(*e*) and **13d** in Fig. 7(*b*). This dissociation chemistry is therefore similar to that of the oxirane addition products of acylium ions **14**,[13] and that expected from the dissociation chemistry of several other analogous ions.[31] An interesting and drastic change in dissociation behaviour is observed, however, for the ethoxy-substituted ion **13e**. Dissociation by loss of most likely neutral ethylene (28u), not C_2H_4O (44u), yields the only observed fragment at m/z 109 (Fig. 8). This dissociation, highly favoured at the ethyl moiety, confirms the covalent nature of the oxirane addition products and reflects their great tendency to preserve the thiadioxolanylium ring structure. Such a structure is expected to be highly stabilized by charge delocalization promoted by both the 1,3-ring oxygens and, in this particular case, by both the *S*-ethoxy and *S*-hydroxy substituents [eqn. (3)].



13e *m/z* 137 *m/z* 109

The three-dimensional MS^3 intermediate-product domain spectrum

In Fig. 7(*a*) is presented the first example of a 3D MS^3 intermediate-product domain spectrum[16,17] applied to the study of ion/molecule reactions. This 3D spectrum was acquired‖ by mass-selecting the reactant ion **4** (m/z 79) in Q1 and by scanning sequentially both Q3 and Q5, while performing ion/molecule reactions with 2-methyl-1,3-dioxolane in Q2 and CID with argon in Q4. A detailed view of the whole ion/molecule reaction process is therefore presented in this spectrum. In the particular scanning setting in which equal masses in both Q3 and Q5 are selected [the dashed diagonal line in Fig. 7(*a*)], the surviving reactant ion (m/z 79) and all of its reaction products (m/z 59, 73, 87, m/z 89, 103 and m/z 123) are recorded. On the other hand, the CID fragments of each individually selected product can be seen across the Q5 axis. The oxirane addition product at m/z 123 (**13d**) is by far the main

¶ Proton transfer from acylium ions to 2-methyl-1,3-dioxolane has been previously assigned to yield the corresponding protonated molecule at m/z 89 and their loss of H_2, CH_4 and acetaldehyde fragments at m/z 87, 73 and 45, respectively, see ref. 13. However, the MS^3 spectrum of m/z 89 has shown that it fragments exclusively to m/z 45. Thus, the major m/z 87 ion appears to be the product of a hydride abstraction reaction. Charge-exchange followed by rapid hydrogen atom loss of the ionized dioxolane may also account for formation of m/z 87, although charge-exchange is somewhat unusual for closed-shell cations.

‖ See the Methods section for more details on the acquisition of the 3D spectrum.

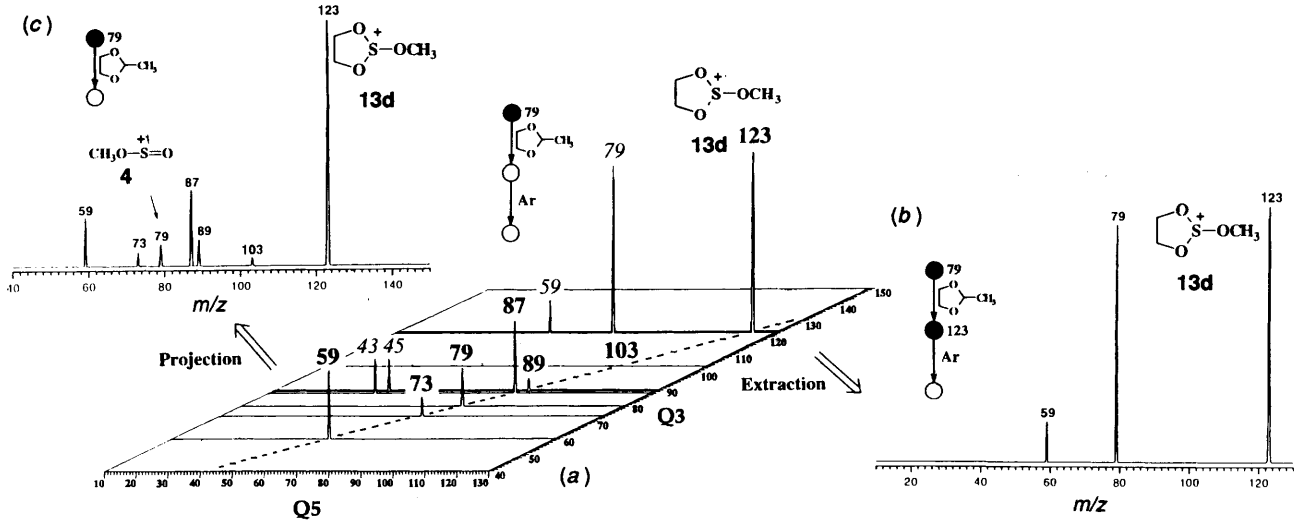


Fig. 7 (*a*) Three-dimensional (3D) MS^3 intermediate-product domain spectrum for the sulfinyl cation **4**. All the reaction products of **4** with 2-methyl-1,3-dioxolane (bold numerals) are displayed along the diagonal dashed line (equal Q3 and Q5 masses), whereas their corresponding 15 eV CID fragments (italic numerals) are displayed along the horizontal Q5 axis. (*b*) Extracted 2D MS^3 sequential product spectrum of the oxirane addition product at *m/z* 123 (**13d**), and (*c*) reconstructed (by projection towards the Q3 axis) 2D MS^2 product spectrum of ion **4**.

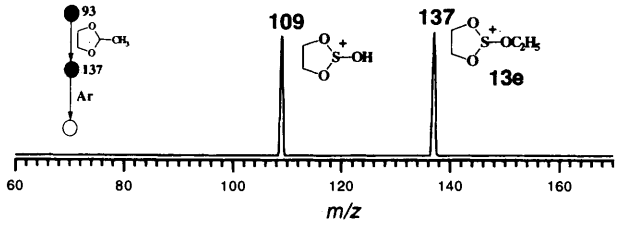


Fig. 8 MS^3 sequential product spectrum of the oxirane addition product *m/z* 137 (**13e**), showing exclusive and unique dissociation by neutral ethane loss (*m/z* 109)

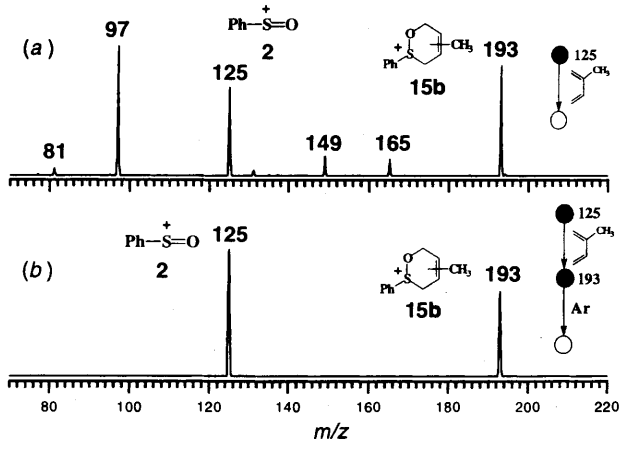


Fig. 9 (*a*) MS^2 product spectrum for ion/molecule reactions between **2** and isoprene, showing an abundant [4 + 2$^+$] cycloadduct at *m/z* 193 (**15**) and (*b*) MS^3 sequential product spectrum of **15a** showing exclusive dissociation by the retro cycloaddition process (*m/z* 125)

product and it fragments extensively by C_2H_4O loss to *m/z* 79 and moderately to *m/z* 59.** Protonated 2-methyl-1,3-dioxolane (*m/z* 89) fragments extensively to *m/z* 45; the 2-methyl-1,3-dioxolanylium ion at *m/z* 87, similarly to the analogous ion **13d**, fragments almost exclusively by C_2H_2O loss to *m/z* 43. The *m/z* 73 and the *m/z* 59 product ions show considerable stability towards dissociation under the collision conditions applied, although scarce fragments are observed at *m/z* 31 for *m/z* 59, and at *m/z* 45 for *m/z* 73.

Extractions from the 3D spectrum along the Q5 axis (fixed Q3 masses) produce MS^3 sequential product spectra,[17b] which display separately in 2D plots the dissociation products of each ion/molecule reaction product, as exemplified for *m/z* 123 (**13d**) in Fig. 7(*b*). It is also worth noting that the 2D MS^2 product spectrum for ion **4** can be properly reconstructed by performing a projection towards the Q5 axis [Fig. 7(*c*)]. The projection is actually done by adding to the abundance of the surviving ions those of their corresponding fragments. In the reconstructed spectrum, the effect of depletion of the abundance of the product ions caused by dissociation in Q4 is therefore cancelled out, and the correct yields of the ion/molecule products are displayed. The reconstructed spectrum should then be comparable to the MS^2 product spectrum of **4** obtained by a direct MS^2 scan, as it is indeed observed (spectrum not shown).

Reactions with the '*s-cis*' diene isoprene

Given the polar [4 + 2$^+$] cycloaddition reactivity displayed by many acylium ions,[12] and the similar reactivity observed for the sulfinyl cations with 2-methyl-1,3-dioxolane, the ability of **1–5** to undergo analogous [4 + 2$^+$] cycloadditions was investigated. The results show, however, that most sulfinyl cations are unreactive towards cycloaddition with isoprene. The competing proton-transfer reaction predominates and yields the primary ion at *m/z* 69 and a series of ions due to consecutive reactions, mainly at 81, 105, 137 and 149.[12] The phenylsulfinyl cation **2** is the only exception†† and yields an abundant product at *m/z* 193 [Fig. 9(*a*)], which is by analogy proposed to be the [4 + 2$^+$] cycloadduct **15a** (Scheme 4, R = Ph). Retro cycloaddition predominates the dissociation chemistry of the putative **15a**, as seen by the great abundance of the *m/z* 125 fragment in its MS^3 spectrum [Fig. 9(*b*)], whereas its considerable resistance towards dissociation eliminates any loosely-bound structure. Although the retro cycloaddition dissociation is, in principle, quite limited in revealing the structure (or the connectivity) of the putative cycloadduct **15a**, it is worth noting that extensive retro cycloaddition dissociation was also observed for the [4 + 2$^+$] cycloadducts of many acylium,[12] nitrilium and immonium,[32] and sulfonium ions,[33] which have been characterized both theoretically and experimentally as authentic cycloadducts. Retro cycloaddition is also very often observed as a main dissociation process for many authentic cycloadducts.[34]

** The *m/z* 59 fragment of **13d** has most likely the $C_2H_3O_2^+$ composition formed by $HSOCH_3$ neutral loss. The ion at *m/z* 59 also appears as an abundant ion in the product spectrum of **4** [Fig. 7(*a*) and (*c*)], likely due to dissociation of **13d** under the ion/molecule reaction conditions.

†† A scarce adduct at *m/z* 147 was also observed for ion **4**.

Conclusions

By combining semiempirical and high level *ab initio* calculations together with collision dissociation and ion/molecule reaction experiments performed by several 2D and 3D MS^2 and MS^3 scans, five representative members of the sulfinyl cation class **1–5** have been characterized as easily accessible and stable gas phase species. Therefore, the intrinsic properties and the chemistry of these unknown solution cations can be extensively investigated in the gas phase. Even though solvent effects are not easily estimated, the results could be useful in anticipating their behaviour in solution.

The dissociation chemistry of the sulfinyl cations **1–5**, which is dominated by simple cleavage of the S–R bond or *via* pathways that are preceded by isomerization, is compatible with their structures, but cannot be unambiguously used for their characterization. The gas-phase characterization of sulfinyl cations is, however, achieved in reactions with 2-methyl-1,3-dioxolane, in which they display a unique, general and structurally diagnostic ion/molecule chemistry. These reactions occur most likely *via* a transketalization-like mechanism, and yield the interesting cyclic 2-thia-1,3-dioxolanylium ions **13**, as indicated by MS^3 experiments. A convenient and so far exclusive method for gas-phase generation of this class of unusual ions is therefore available. In contrast with the quite general reactivity of acylium ions, efficient polar $[4 + 2^+]$ cycloaddition with isoprene was observed only for the phenylsulfinyl cation **2**. The unique behaviour of **2** can then be interpreted as a consequence of either or both a less favourable competitive proton-transfer reaction, a more favourable frontier MO interaction or product stabilization provided by the charge-stabilizing phenyl substituent.

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