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Sulfenic Acids in the Gas Phase: A Photoelectron Study

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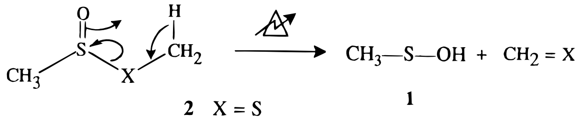
Abstract: Thermolysis of methyl methanethiosulfinate and methyl *tert*-butyl sulfoxide has been studied by photoelectron (PE) spectroscopy. The electronic structure of methanesulfenic acid (**1**) generated from both compounds has been determined, and the thermal stability of **1** was checked. **1** appears rather stable in the gas phase, giving rise to thioformaldehyde and water at high temperature. Thermolysis of vinyl *tert*-butyl sulfoxide gives rise to ethanethial *S*-oxide (**6**). At the thermolysis onset, sulfine **6** is observed in a mixture with a compound identified as ethenesulfenic acid (**4**). These results imply either an easy isomerization of **4** to **6**, in agreement with previous theoretical evaluations, or an alternative thermolysis pathway of the starting sulfoxide, directly leading to sulfine **6**. The obtained PE spectra complement previous microwave and/or mass spectrometry data and provide a further insight in the electronic structure and thermal stability of sulfenic acids **1** and **4**. The experimental ionization potentials are compared throughout this study with ab-initio calculated vertical ionization potentials either within Koopmans' approximation or by difference between the ionic and ground state energies.

Sulfur in sulfenic acids, R−S−OH, has an intermediate oxidation number (0) and thus stands between thiols (−II) and sulfinic acids, RSO_2H (II). For this reason, sulfenic acids and sulfenates are involved in the oxidation chain of reduced sulfur compounds such as thiols, sulfides, and disulfides (sulfur oxidation numbers −II and −I, respectively) and are of current interest in organic, bioorganic,[1] and atmospheric chemistry.[2] Furthermore, sulfenic acids participate in the reversible thermal rearrangment of sulfoxides bearing a β-hydrogen atom.[3] On the other hand, α,β-unsaturated sulfenic acids readily isomerize to sulfines, which are the active compounds in the chemistry of allium.[4]

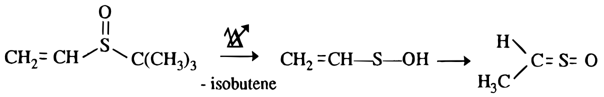
In spite of their importance, the great instability of simple alkyl or alkenyl sulfenic acids has hampered their direct characterization. The elusive methanesulfenic acid was studied in the gas phase for the first time by microwave spectroscopy[5] and later by mass spectrometry.[6,7] The characterization of ethenesulfenic acid is only based on mass spectrometry studies,[7,8] while heavier alkyl or aromatic sulfenic acids have been identified by matrix-IR spectroscopy in the condensed phase.[9,10] On the whole, sulfenic acids are easily trapped by alkynes to give α,β-unsaturated sulfoxides; this indirect method allows a reliable characterization of these compounds.[11]

In order to further investigate the structure of methanesulfenic acid (**1**), we undertook a photoelectron (PE) study of flash-vacuum thermolysis (FVT)[12] of two known precursors of $CH_3−S−OH$ (**1**), namely, methyl methanethiosulfinate (**2**) and methyl *tert*-butyl sulfoxide (**3**).



2 X = S
3 X = C(CH3)2
1

We also attempted to characterize by this way the even more reactive ethenesulfenic acid (**4**, $CH_2{=}CH−S−OH$) starting from vinyl *tert*-butyl sulfoxide (**5**), although **4** is known to isomerize into (*Z*)-ethanethial *S*-oxide (**6**):[13]



5 **4** **6**

Method

In the following, the results of these PE experiments are reported. The assignment of the spectra of sulfenic acids **1** and **4** or of their isomer(s), based on experimental arguments, is further supported by ab-initio calculations. Much of this theoretical work was aimed at estimations of ionization potentials (IPs) as extensive studies of the energies and geometries of these compounds have already been carried out.[8,14,15] Vertical

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IPs have been calculated either within Koopmans' approximation or more precisely as differences between the ionic and ground state energies, both obtained on the neutral ground state-optimized geometry.

The thermolysis of all precursors was performed in an FVT oven directly coupled to the photoelectron spectrometer; this assembly provides an efficient detection of reactive compounds from thermolysis.[16] In all our experiments, the compounds of interest are obtained in a mixture with FVP byproducts such as thioformaldehyde or isobutene. In the latter case, digital subtraction of a prerecorded spectrum of isobutene unmasks the ionization pattern of the sulfenic acids **1** and **4** or of their isomerization or decomposition products. Such a procedure has already proven valuable for the PE caracterization of short-lived species such as $ClPS_2$,[17] FPS_2 and FPS,[18] and *N*-cyanomethanimine,[19] among others.

Before describing the PE spectra, it is worth mentioning that on going from He I (21.21 eV) to He II (40.81 eV) excitation energies, the bands arising from the ejection of an electron from an orbital localized on sulfur decrease in intensity. Conversely bands arising from the ejection of an electron from oxygen orbitals smoothly increase. These relative intensity changes are attributed to variations in the one- and/or two-center contributions to the photoionization cross sections of the corresponding molecular orbitals.[20] These intensity changes are particularly useful for the assignment of the PE spectra of oxy sulfur compounds.

Thermolysis of Methyl Methanethiosulfinate (2) and Methyl *tert*-Butyl Sulfoxide (3)

The PE spectra of methyl methanethiosulfinate (**2**) and its thermolysis products at 793 and 1073 K are displayed in Figure 1. The spectrum of the starting compound is characterized by a set of three well-defined bands with decreasing intensity at 9.12, 9.51, and 10.38 eV. Three broader bands are then observed with higher IPs, namely, 12.26, 12.98, and 14.72 eV (Figure 1a). On going from He I to He II excitation energy, the relative intensities of the three first bands are strongly modified; the decrease of the intensities of the first two bands is evident, while the intensity of the third one at 10.38 eV remains unchanged. This observation clearly indicates that the first two bands arise from the ionization of orbitals heavily localized on sulfur, while the third band originates from an orbital weakly localized on sulfur.

Compound **2** begins to decompose around 573 K and disappears completely at 633 K, giving rise, up to 1073 K, to a clean new spectrum with the well-known ionization pattern of thioformaldehyde at 9.38 eV (narrow and high-intensity band), 11.76 eV (broad signal with a vibrational structure), and 13.85 eV[21] (Figure 1b). Besides these signals, five other bands are observed at 9.01, 11.08, 12.90, 14.95, and 16.80 eV. The He II thermolysis spectrum at 793 K indicates the obvious decrease of the intensity of the two first bands at 9.01 and 9.38 eV and the slighter decrease of the intensity of the fourth one at 11.76 eV (the two latter assigned to thioformaldehyde ionizations), while the intensity of the 11.08 eV band remains roughly constant.

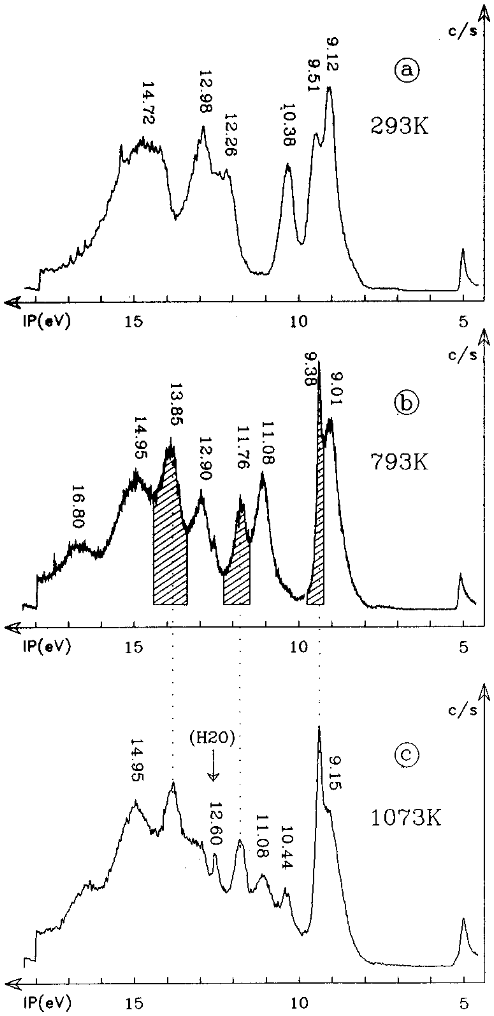

Figure 1. Photoelectron spectra of (a) methyl methanethiosulfinate (**2**), (b) its thermolysis products at 793 K, and (c) its thermolysis products at 1073 K.

On further heating, this new spectrum does not drastically change up to 1073 K. At this temperature the following changes are observed (Figure 1c): decrease of the intensity of the 9.01 eV band resulting in a slight shift toward higher IP of this band maximum (9.15 eV), decrease of the intensity of the 11.08 eV band relative to those of thioformaldehyde, and appearance of a new band at 10.44 eV and a narrow band at 12.60 eV assignable to water.

The spectra of methyl *tert*-butyl sulfoxide (**3**) and its thermolysis products are depicted in Figure 2. The sulfoxide **3** is characterized by two low-IP bands at 8.64 and 9.65 eV followed by broader signals centered at 12.12 and 15.31 eV (Figure 2a). On heating, this spectrum begins to change at 673 K and is completely different at 723 K (Figure 2b). A broad high intensity band is now observed at 9.18 eV followed by a set of broad signals centered at 11.10, 11.90, 12.92, and 14.94 eV. By digital subtraction of isobutene spectrum, the difference spectrum of Figure 2e is obtained; the position and intensity of the bands at 9.01, 11.10, 12.92, 14.94, and 16.80 eV closely match those of the new compound obtained by thermolysis of **2** between 633 and 1073 K (Figure 1b). However, the bands in the difference spectrum from **3** are less clear-cut than in the thermolysis spectrum of **2**, as broad shoulders on the low-IP

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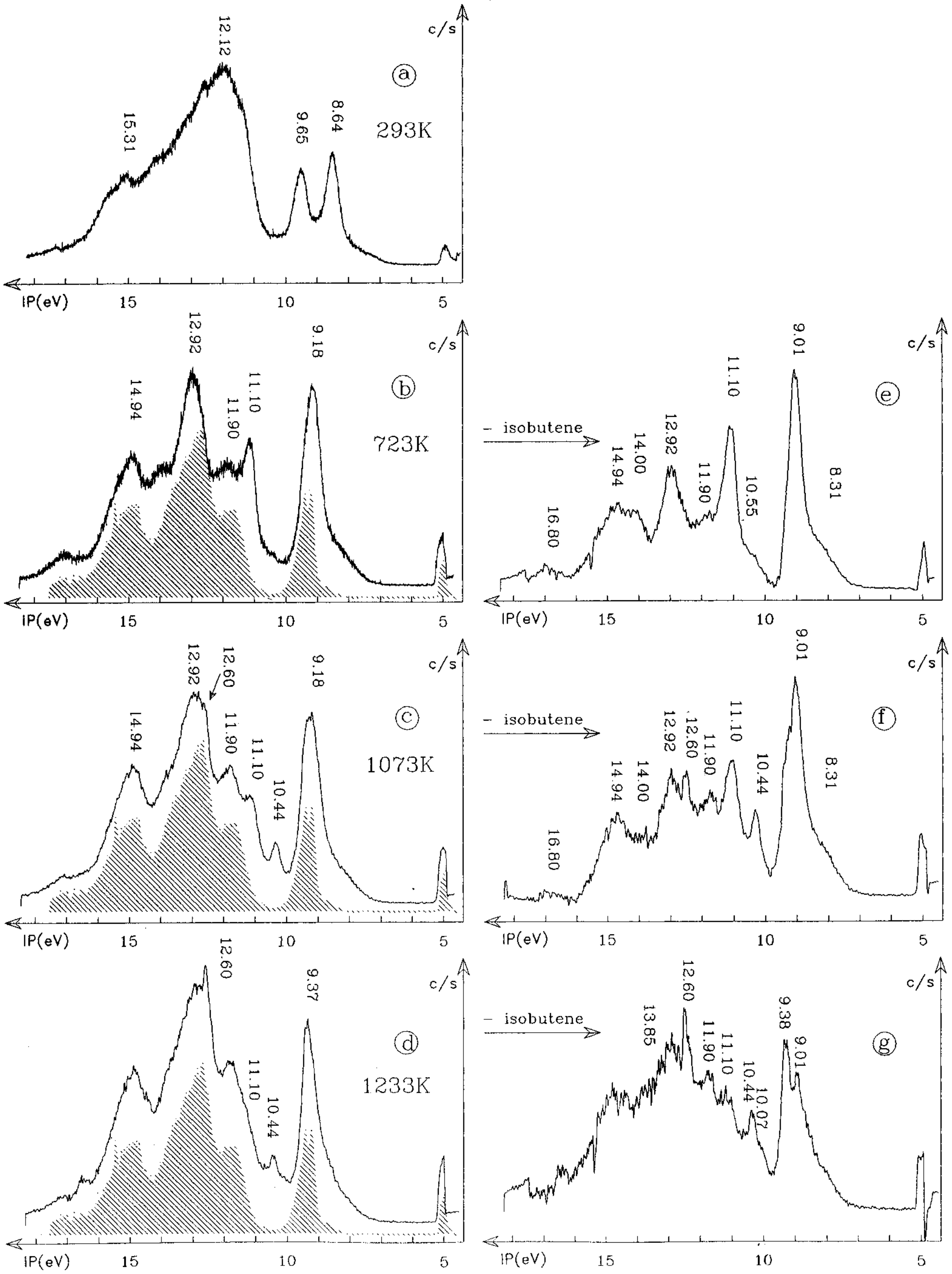

Figure 2. Photoelectron spectra of (a) methyl *tert*-butyl sulfoxide (**3**) and (b−c) and (d) its thermolysis products at 723, 1073, and 1233 K and (e−g) the difference spectra of the thermolysis products at 723, 1073, and 1233 K after digital subtraction of isobutene spectrum (shaded: isobutene spectrum).

side of the first two bands may be noticed (8.31 and 10.55 eV) and broad signals remain around 11.90 and 14.00 eV.

On further heating, no changes are observed up to 853 K, where a weak intensity band begins to increase at 10.44 eV. At 1073 K, the intensity of this 10.44 eV band still increases (Figure 2c) and is clearly observed besides the previously described bands (9.01 and 11.10 eV) after digital subtraction of isobutene spectrum (Figure 2f). Bands due to water ionization begin to appear at 12.60 eV. At 1233 K the thermolysis spectrum is totally different (Figure 2d,g): The first band is slightly shifted toward higher IP (9.37 eV), and its shape is modified. The second band at 11.10 eV has strongly decreased; the previously described band at 10.44 eV is broadened with a shoulder at 10.07 eV, and the water band at 12.60 eV is clearly distinguished. After digital subtraction of the isobutene spectrum, the spectrum exhibits some features assignable to water (12.60 eV), some remaining compound observed at lower temperature (9.01 and 11.10 eV), unidentified bands at 10.07 and 10.44 eV, and a sharp band at 9.38 eV which is not inconsistent with thioformaldehyde. However, the other bands of this product (11.76 and 13.85 eV) are not clearly distinguished due to the presence of numerous thermolysis byproducts.

Assignment of the Spectra and Discussion. The starting compounds are the substituted sulfoxides **2** and **3**. For methyl *tert*-butyl sulfoxide (**3**), the interpretation is straightforward and follows from the known spectra of different sulfoxides.[7,22]

For methyl methanethiosulfinate (**2**) (Figure 1a), from the data on sulfoxides[7,22] and the He II experiment, the second (9.51 eV) and third (10.38 eV) bands are assigned to the ejection of an electron from the orbitals at the sulfoxide group (interacting

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Table 1. Calculated and Experimental Vertical IPs (eV) of CH_3SOH (**1**)

		Koopmans		$\Delta E = E(\mathbf{1}^{\bullet+}) - E(\mathbf{1})$		
IP	attribution	AM1[a]	Gaussian 92 MP2/6-311G** [b]	Gaussian 92 MP2/6-311G** [b]	CIPSI MP2/6-311G** [b]	expt
1	$n_s^{\perp} - \pi_{CH_3}$	8.74	9.63	8.86	8.92	9.01
2	$n_S - n_O$	11.31	12.08		10.65	11.08
3	σ_{SO}, σ_{CH}	13.03	14.38			12.92
4	σ_{CS}, σ_{CH}	14.42	15.68			14.95

[a] Geometry optimization at the AM1 level (*d* in Å, angles in deg): C−S, 1.745; S−O, 1.707; O−H_1, 0.961; C−H_4, 1.114; C−H_5, 1.115; C−H_6, 1.113; CSO, 100.70; SOH_1, 106.06; H_4CS, 111.51; H_5CS, 106.81; H_6CS, 112.25; H_1OSC, 101.83; H_4CSO, 42.91; H_5CSO, 161.87; H_6CSO, −78.93. [b] Geometry optimization at the MP2/6-31G* level (first and second values in parentheses refer respectively to MP2(FULL)/6-31+G(d)[14] and experimental data[5] : C−S, 1.797 (1.795, 1.806); S−O, 1.695 (1.699, 1.658); O−H_1, 0.976 (0.977, 0.957); C−H_4, 1.092 (1.095, −); C−H_5, 1.091 (1.091, −); C−H_6, 1.094 (1.095, −); CSO, 99.56 (99.3, 100.1); SOH_1, 106.24 (107.8, 107.7); H_4CS, 111.97 (110.4, −); H_5CS, 110.35 (112, −); H_6CS, 106.77 (106.5, −) ; H_1OSC, 92.38 (95.5, 93.9); H_4CSO, 66.40 (56, −).

with the sulfenyl orbital for the former) and the first one (9.12 eV) to the ejection of an electron from a nearly pure lone pair orbital at the sulfenyl sulfur.

Our PE experiments indicate that thioformaldehyde is obtained by FVT of **2** and isobutene by FVT of **3**. From the shape and relative intensities of the bands of the other FVT product in both cases, the formation of the same compound from these two precursors is obvious, thiosulfinate **2** being cleaved at lower temperature than sulfoxide **3**. The accompanying FVT product is thus most probably CH_3-S-OH. The question then arises on which isomer(s) we are dealing with.

On the basis of microwave spectrometric data,[5] it has been concluded that methanesulfenic acid exists in the hydroxyl form **1** in the gas phase rather than in its isomeric sulfoxide form $H-SO-CH_3$. From this experiment, and from high level of theory geometry optimizations (MP2(FULL)/6-31+G(d)),[14] methanesulfenic acid (**1**) is found with a gauche conformation of the hydroxyl relative to the CSO plane (experimental HOSC dihedral angle 93.9°). Ab-initio calculations at the MP2/6-31G* level indicate the sulfenic form **1** to be more stable than the sulfoxide isomer by 98.74 kJ mol^{-1}.[15] However matrix-IR spectroscopy studies on higher homologs of sulfenic acids have shown the existence of both isomers in the condensed phase.[9,10]

On qualitative grounds, it is evident that we are not dealing with the sulfoxide isomer between 573 and 853 K: Actually, the separation between the first two IPs of sulfoxide species $RSOCH_3$ or $RSOCH{=}CH_2$[7,22] is typically in the range 1−1.3 eV, whereas in the new spectrum (Figures 1b and 2b,e) the separation is 2.07 eV. Moreover, from substituent effects, it may be deduced that the first band of $H-SO-CH_3$ will appear at higher IP than the corresponding one of dimethyl sulfoxide (9.10 eV). The obtained value of 9.01 eV definitely rules out the occurrence of this isomer between 573 and 853 K.

The PE spectrum of methanesulfenic acid is probably close to the one of the structurally related cyclic sulfenate, 1,2-oxathiolane, for which the first two bands are observed at 8.51 eV (mainly n_S) and 10.89 eV (mainly n_O).[23] The important gap between the first two bands (2.38 eV) results from the CSOC dihedral angle which is estimated between 30° to 50°. According to the shape and position of the first (9.01 eV) and second (11.08 eV) bands ($IP_2 - IP_1 = 2.07$ eV) in the new compound spectrum (Figures 1b and 2b,e), and to the result of the He II experiment at 793 K (decrease of the intensity of the 9.01 eV band, constancy of the intensity of the 11.08 eV band), this new spectrum may thus be assigned to methanesulfenic acid (**1**).

The shape of both bands appears rather broad and poorly resolved. The shape of the former more closely matches the one of dimethyl disulfide rather than the thin and narrow one of methanethiol,[24] thus implying significant Franck−Condon effects upon ionization. Actually, the first ionic state has been calculated with a planar CSOH framework,[14] and according to this theoretical study, the difference between the adiabatic and vertical ionization energies amounts to 0.46 eV. From our measurements this difference appears similar, although the determination of the adiabatic IP is difficult because of the low-energy tail of the bands. As already stated by Turecek,[14] the previous mass spectrometry measurement of the first IP (9.07 eV)[7], inferred from the ionizing efficiency curve of $CH_3SOH^{\bullet+}$, "did not locate the true threshold corresponding to adiabatic ionization"; indeed, this value is much closer to our value of the vertical IP (9.01 eV).

The other point of concern is the thermal stability of CH_3SOH, as we observe neither isomerization nor decomposition under 853 K. At higher temperature, the appearance of a slowly growing new band at 10.44 eV from both precursors is noticed (Figures 1c and 2c,f). However owing to the presence of numerous products in our spectra, no conclusion may be drawn as to the structure of this new compound.

At still higher temperatures, our observations confirm the previous observation of thermal decomposition of CH_3SOH into $CH_2{=}S$ and H_2O.[5] These decomposition products appear at lower temperature from **2** (1073 K, Figure 1c) than from **3** (1233 K, Figure 2d,g).

In order to further confirm our assignment, vertical IP evaluations at different levels of calculations have been performed for CH_3SOH. Examination of our ab-initio results (Table 1) is a good illustration of the inadequacy of Koopmans' approximation for this molecule containing a third-row atom. The first two orbital energies are clearly too deep after the Gaussian 92 SCF calculation. This gives rise to overestimated IPs by 0.62 eV for the former and 1.00 eV for the latter. This inaccuracy may be accounted for by the neglect of polarization and correlation effets.

A good estimate of the first vertical and adiabatic IPs has been obtained[14] from the energetic difference between the first ionic and ground state energies at the G2 (MP2) level: IP(v) = 9.17 eV and IP(a) = 8.71 eV, while smaller values were calculated at the QCISD(T)/6-311+G(3df,2p) level: IP(v) = 9.04 eV and IP(a) = 8.58 eV. Our own estimation of the first vertical IP at a lower level (MP2/6-311G**) amounts to 8.86 eV. However owing to the lack of symmetry of the molecule, it is not possible to converge on the second ionic state with the Gaussian 92 set of programs. We thus attempted to estimate this energy within the CIPSI formalism which includes, through variational and perturbational configuration interactions treatment, both polarization and correlation effects. However in this

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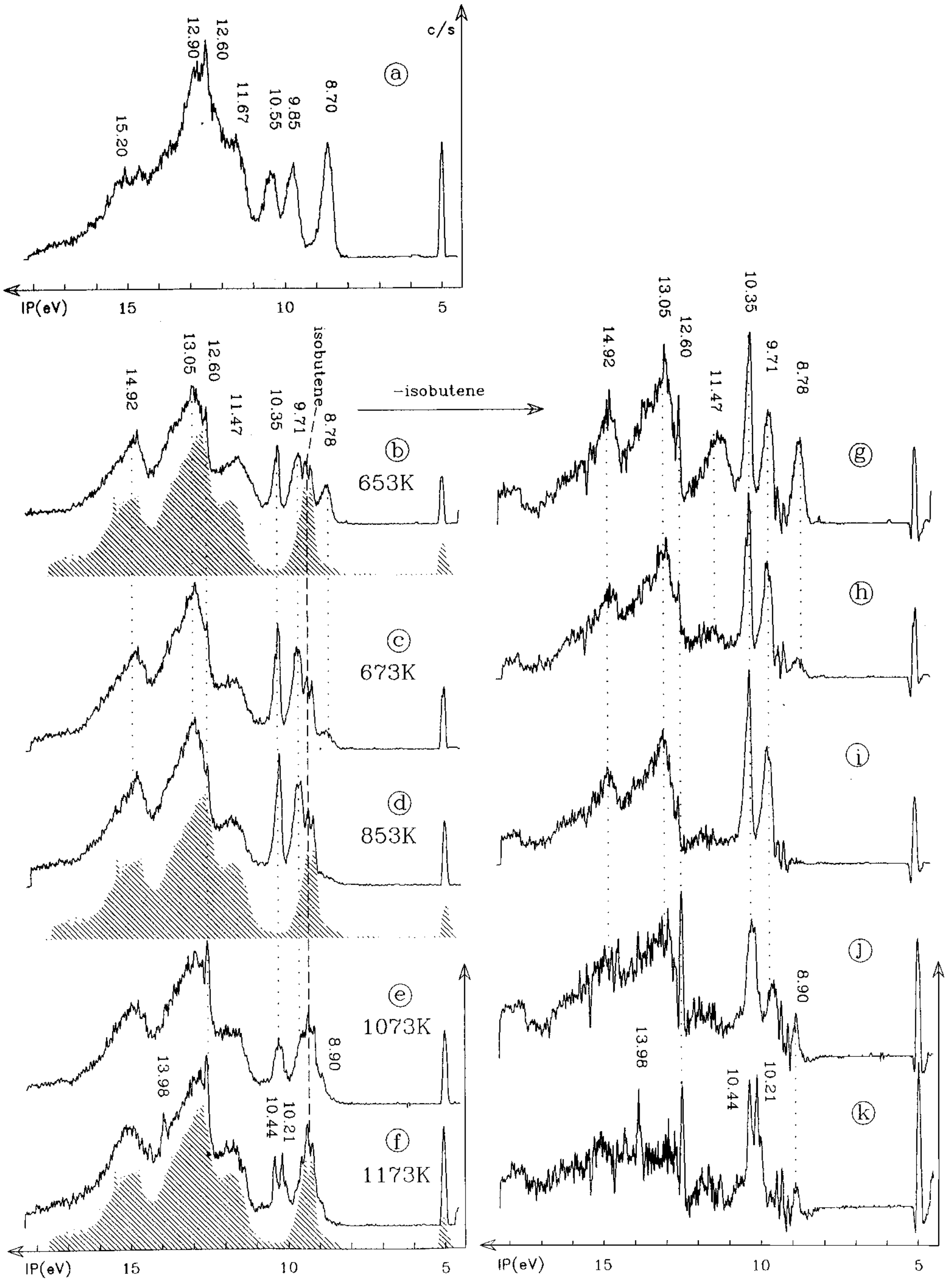

Figure 3. Photoelectron spectra of (a) vinyl *tert*-butyl sulfoxide (**5**) and (b−f) its thermolysis products at 653, 673, 853, 1073, and 1173 K and (g−k) the difference spectra of the thermolysis products after digital subtraction of isobutene spectrum (shaded: isobutene spectrum).

case, although the first calculated IP remains of the same order of magnitude as the previous one (8.92 eV), the second one is too low relative to Koopmans' approximation and amounts to 10.65 eV for an experimental value of 11.08 eV. Such an exaggerated correction has already been encountered within this formalism for the second A′ ionic state of phosphaethene localized on the phosphorus lone pair.[12b]

The results of AM1 calculations have been included in this table, as the calculated IPs, even within Koopmans' approximation, appears as reliable as the more expensive and time-consuming results of more elaborate ab-initio methods; actually the first IP is calculated at 8.74 eV (experimental 9.01 eV) and the second at 11.31 eV (experimental 11.08 eV) for a gauche AM1-optimized geometry (dihedral CSOH angle 101.8° close to the ab-initio result (95.5°)[14]).

On the whole, while a rather approximative evaluation of the IPs (and especially the second one) by different methods is evidenced for CH_3SOH, these calculations nevertheless confirm the consistency of our analysis as the experimentally observed large gap (2.07 eV) between the first two ionic states is calculated regardless of the algorithm used (AM1, $IP_2 - IP_1 = 2.57$ eV; Koopmans−MP2/6-311G**, $IP_2 - IP_1 = 2.45$ eV; CIPSI−MP2/6-311G**, $IP_2 - IP_1 = 1.73$ eV). From these studies, the experimental first band at 9.01 eV thus arises from the ejection of an electron from a pure sulfenyl lone pair orbital (perpendicular to the heavy atoms planes), and the second one at 11.08 eV arises from the ejection of an electron from the antibonding orbital between the sulfur and oxygen lone pairs (in the CSO plane).

Thermolysis of Vinyl *tert*-Butyl Sulfoxide (5)

The PE spectra of **5** and its thermolysis products are given in Figure 3. The spectrum of the unsaturated sulfoxide is characterized by three low-intensity bands on the low-IP side at 8.70, 9.85, and 10.55 eV followed by broad signals centered around 11.67, 12.90, and 15.20 eV (Figure 3a). (Some remaining water, identified by a sharp band at 12.60 eV, is observed in the spectrum of the starting product, even after extensive trap-to-trap distillation.) This compound begins to react at 573 K, and its spectrum is totally different at 653 K (Figure 3b). The first band, slightly shifted toward higher IP (8.78 eV), appears before a broader two-components signal: The former component of this band, centered around 9.32 eV, clearly displays a vibrational fine structure ($\upsilon = 1370\ \mathrm{cm}^{-1}$) and may be assigned to isobutene,[24] while the latter and broader part of the band is centered around 9.71 eV. Then, another thin band is observed at 10.35 eV followed by broad signals around 11.50, 13.00, and 14.90 eV. This spectrum is very sensitive to the pyrolysis temperature and is totally modified in the 653−853 K temperature range (Figure 3b−d). A careful examination of these spectra and their difference spectra with isobutene (Figure 3g−i) allows the following conclusions to be made. (1) A first set of two bands at 8.78 and 11.47 eV (this latter rather broad and probably containing two ionizations) very quickly disappears between 653 and 673 K and is no longer observed at 853 K. These bands are assigned to compound **A**. (2) Another set of four bands at 9.71, 10.35, 13.05, and 14.92 eV is already present at 653 K (Figure 3b,g). Their intensity smoothly increases with increasing temperature up to 853 K relative to the intensity of the band of isobutene (9.32 eV) and of the previously described bands of compound **A** (8.78 and 11.47 eV) (Figure 3b−d,g−i). This set of three bands is attributed to compound **B**.

An He II experiment, performed at 873 K (i.e., at a temperature where only compound **B** is present) indicates, after subtraction of isobutene, no intensity change for the first two bands of the spectrum (9.71 and 10.35 eV). This result implies that these two bands do not arise from the ejection of an electron from orbitals strongly localized on sulfur but rather from orbitals where sulfur and oxygen both participate.

At higher temperature (1073 K), another change is still noticed (Figure 3e,j): The 9.71 eV band decreases together with the sharp component at 10.35 eV, and a modification of the shape of the 9.32 and 10.35 eV bands is clearly observed. A new weak band is detected at 8.90 eV as a shoulder on the low-IP side of the 9.32 eV band, while the intensity of the 12.60 eV band, assignable to water, noticeably increases. The weak intensity narrow band at 8.90 eV may tentatively be assigned to minute amounts of thioketene,[25] although the other bands of this compound (11.32, 12.14, and 14.55 eV) are not observed in our complex pyrolysis mixture.

This change is more evident at 1173 K (Figure 3f,k). At this temperature, the 10.35 and 9.71 eV bands disappear and the signal is completely modified to give rise to two thin bands at 10.21 eV (acetaldehyde)[24] and 10.44 eV (possibly H_2S).[24] Water (12.60 eV) and carbon monoxide (13.98 eV)[24] are also observed in these spectra besides isobutene (9.32 eV). At this temperature, the band at 8.90 eV is less intense than at 1073 K. Although the difference spectra at these temperatures (Figure 3j,k) are much less intense than at lower temperature (Figure 3g−i) and exhibit a rather poor signal-to-noise ratio, they nevertheless allow the identification of the previously described bands and have thus been included.

From this analysis, three temperature ranges are thus clearly defined for the thermolysis of **5:** (1) between 653 and 853 K where two products, **A** (8.78 and 11.47 eV) and **B** (9.71, 10.35, 13.05, and 14.92 eV), are observed besides isobutene, (2) between 853 and 1073 K where only compound **B** is obtained with isobutene, and (3) over 1073 K where decomposition products begin to appear which are the only thermolysis products at 1173 K (isobutene, acetaldehyde, carbon monoxide, water, and possibly H_2S and thioketene).

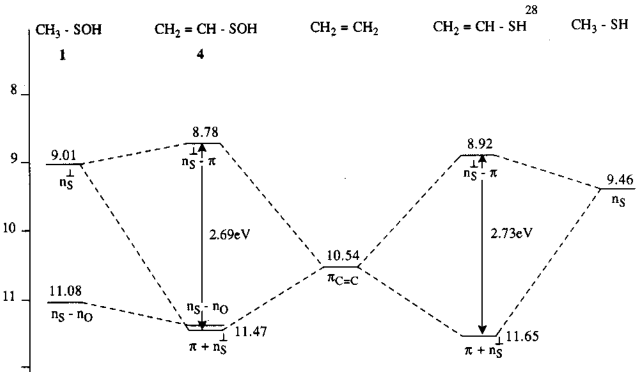

Figure 4. Correlation diagram between methanesulfenic acid (**1**) and ethylene and between methanethiol and ethylene (experimental IPs in eV) ($n_S^\perp$ refers to a lone pair sulfur orbital perpendicular to the heavy atoms plane).

Assignment of the Spectra. The spectrum of the starting vinyl sulfoxide **5** is easily analyzed according to the previous study on this class of compounds.[7,22] The presence of isobutene in each thermolysis spectrum makes it clear that the expected thermolysis reaction is going on (vide supra).

The spectrum of compound **B** alone at 853 K (Figure 3d,i) is more easily analyzed as it shows a close resemblance to the spectrum of methanethial *S*-oxide ($CH_2{=}S{=}O$, **7**)[26,27] in its overall feature (band shapes and relative intensities). The only noticeable difference concerns the shift of all bands to lower IPs relative to **7**: 9.71, 10.35, 13.05, and 14.92 eV vs 10.46, 10.70, 13.59, and 15.43 eV. Accordingly compound **B** is the methylated derivative of **7**, i.e., ethanethial *S*-oxide (**6**). This analysis is confirmed by the He II experiment. The constancy of the first two band intensities is in agreement with the description of the two highest orbitals from which the corresponding electrons are ejected: π_{nb} for the former (located on carbon, oxygen, and slighter on sulfur) and $n_S - n_O$ for the latter (located on sulfur and oxygen).[26]

A careful comparison of the starting product spectrum (Figure 3a) with the first two thermolysis spectra (Figure 3b,c) indicates that between 653 and 673 K another product (**A**) is present in minor amounts besides isobutene and ethanethial *S*-oxide (**6**). Owing to the known thermolysis pathway of **5**,[13] and to the fast disappearance of compound **A** in favor of sulfine **6** between 653 and 853 K, the tentative identification of compound **A** as ethenesulfenic acid (**4**) has been checked. A qualitative estimation of the first bands of ethenesulfenic (**4**) may be drawn from the correlation diagram of Figure 4 starting from the previously described PE spectrum of CH_3SOH. For **4** a planar CCSO framework with, as for parent CH_3SOH, the hydroxyl hydrogen orthogonal to the heavy atom plane (dihedral HOSC angle 88°) is inferred from the results of Turecek and al.[8] A parallel correlation diagram is drawn for ethenethiol, the PE spectrum of which is analyzed on the basis of a planar CCSH arrangment.[28]

The comparison between the spectrum of ethenethiol and the spectrum tentatively assigned to ethenesulfenic acid (**4**) further supports our analysis. (1) The important gap between the first

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Table 2. Total Energies in Hartree (1 Hartree = 2625.5 kJ mol^{-1}) of the Isomers of Ethenesulfenic Acid

isomer	HF/6-31G* [a]	MP2/6/-311G** [b]
$CH_2{=}CH{-}S{-}OH$ (**4**)	−550.371362	−551.056097
$CH_3{-}CH{=}S{=}O$ (**6**)	−550.356500	−551.057924

[a] Geometry optimization at the HF/6-31G* level. [b] Geometry optimization at the MP2/6-31G* level.

Table 3. Calculated Vertical IPs (eV) for **4**, **6**, and **7**[a]

	IP		
	1	2	3
	$CH_2{=}CH{-}S{-}OH$ (**4**)		
attribution	$n_S^{\perp} - \pi$	$n_S - n_O$	$\pi + n_S^{\perp}$
Koopmans	8.87	12.52	12.24
ΔE	8.40		
expt	8.78	11.47	
	$CH_3{-}CH{=}S{=}O$ (**6**)		
attribution	$\pi_{nb} - \pi_{CH_3}$ (A″)	$n_S - n_O$ (A′)	σ, π_b
Koopmans	9.69	11.32	14.34, 14.84
ΔE	9.59	10.23	
expt	9.71	10.35	13.05
	$CH_2{=}S{=}O$ (**7**)		
attribution	π_{nb} (A″)	$n_S - n_O$ (A′)	σ, π_b
Koopmans	10.18	11.65	14.72, 15.38
ΔE	10.08	10.58	
expt[26,27]	10.46	10.70	13.59

[a] Gaussian 92 MP2/6-311G** results on MP2/6-31G*-optimized geometries. See ref[29] for optimized geometries.

and second band (around 2.7 eV) is of the same order of magnitude as for ethenethiol (2.73 eV) and results from a strong interaction between the sulfur lone pair perpendicular to the heavy atoms plane ($n_S^{\perp}$) and the π orbital in both cases. (2) The position of the first band (8.78 eV) slightly higher than the corresponding one of CH_3SOH (9.01 eV) is expected from the relative positions of the first bands of CH_3SH (9.46 eV) and $CH_2{=}CHSH$ (8.92 eV). Our value of the first vertical IP for **4** (8.78 eV) is furthermore in excellent agreement with the previous mass spectrometric determination (8.70 eV).[7] (3) The second broad band at 11.47 eV of **4** probably contains two ionizations, one arising from the ejection of an electron from the $\pi + n_S^{\perp}$ orbital and the other from the $n_S - n_O$ orbital in the molecular plane.

In order to further confirm this assignment, the previous calculations of Turecek and al.[8] on ethenesulfenic acid (**4**) and its isomer ethanethial *S*-oxide (**6**) have been completed by IP evaluations for both compounds (MP2/6-311G** level). In the case of sulfine **6**, a parallel calculation on parent methanethial *S*-oxide (**7**) (the spectrum of which has long been known[26,27]) has been carried out to assess the accuracy of our method. First, our energetic results and optimized geometries[29] are in agreement with Turecek's previous study:[8] Compounds **4** and **6** are found almost isoenergetic, the sulfine **6** being favored by 4.8 kJ mol^{-1} at the highest level of theory used (Table 2). It is worth noticing that the previously calculated activation energy between **4** and **6** amounts to 137 kJ mol^{-1} (MP4(SDTQ)/6-31G(d,p) level[8]) and is indicative of an easy isomerization pathway linking **4** to **6.**

As expected from both experimental and theoretical previous statements,[4,30] (*Z*)-**6** is calculated more stable than (*E*)-**6** by 9.86 kJ mol^{-1}, and once again our results are in good agreement with Turecek's study.[8] For both optimized structures **4** and **6**, the short hydroxyl hydrogen methylenic carbon (3.17 Å) or conversely oxygen−methyl hydrogen distance (2.57 Å) is worth noticing.[29]

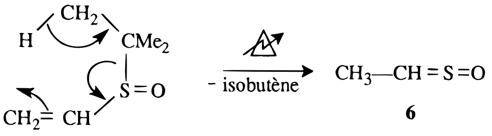
In Table 3, different vertical IP evaluations for the three studied compounds have been summarized. The more precise ΔE calculations between the ionic and ground states energies could only be performed on the first IP in the case of compound **4**; actually, due to the lack of symmetry of these molecule, no separation between ionic states can be achieved and no convergence on the second ionic state is obtained with the Gaussian 92 set of programs. On the contrary, sulfines **6** and **7** have a C_s symmetry, and the first two ionic states (A″ and A′ symmetry) are thus calculated.

The calculated vertical IPs for model compound **7** (10.08 and 10.58 eV) are in good agreement with experimental results (10.46 and 10.70 eV[26,27]), although slightly underestimated. Accordingly, the ΔE calculation for the first two ionic states of sulfine **6** (9.59 and 10.23 eV) agrees satisfactorily well with the experimental spectrum (9.71 and 10.35 eV) and further supports our qualitative assignment: 9.71 eV (π_{nb}), 10.35 eV ($n_S - n_O$).

One conclusion clearly arises from those results: The first vertical IP of sulfine **6** (9.59 eV) is calculated much larger than that of ethenesulfenic acid (**4**) (8.40 eV). For this latter compound , as for CH_3SOH, the gap between the first and second IPs is expected to be rather large (around 2 eV from Table 3) if the overestimation of the energy of the second ionic state by about 1 eV within Koopmans' approximation is taken into account as for CH_3SOH (Table 1). These theoretical results are thus fully consistent with the previous qualitative correlation diagram built for ethenesulfenic acid (**4**) (Figure 4) and further support our assignment. It is worth noticing that our calculated values of the first vertical IP are either identical with those of Turecek and al. at the MP4/6-31G* level[8] for sulfine **6** (9.59 eV) or very close for ethenesulfenic acid (**4**) (8.40 vs 8.35 eV[8]).

In summary, while the formation of ethanethial *S*-oxide (**6**) between 653 and 853 K is firmly estabished during the FVT of **5**, the identification of ethenesulfenic acid (**4**) in a mixture with **6** at 653 K only rests on the following arguments: (1) difference spectrum consistent with the qualitative correlation diagram built for **4**, (2) good agreement between mass spectrometry and PE data, (3) fast disappearance of **4** in favor of sulfine **6** observed between 653 and 673 K as already described,[13,8] and (4) consistency of the experimental and calculated IPs.

In any case, ethenesulfenic acid (**4**) is hardly at all observed by FVT of **5**, contrary to sulfine **6**. Two assumptions may account for this result: (1) either fast isomerization of sulfenic acid **4** into sulfine **6** (this assumption is supported by the relatively low calculated activation barrier between **4** and its more stable isomer **6** (137 kJ mol^{-1})[8] and by previous chemical trapping experiments of **4**[13]) or (2) a competitive thermolysis pathway leading directly, through a six-center transition state, to sulfine **6**.



5 **6**

Sulfine **6** is stable between 653 and 1073 K. Above this temperature, new decomposition products are observed indicat-

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(29) MP2/6-311G**-optimized geometries for (values in parentheses from ref 8): **4**, C_1C_2 1.339 (1.317), C_2S 1.753 (1.758), SO 1.687 (1.648), OH_4 0.977 (0.950), C_1H 1.084 (1.073), $H_1C_1C_2$ 120.2 (120.2), $H_2C_1C_2$ 121.7 (122.2), $H_3C_2C_1$ 121.9 (121.6), C_1C_2S 126.7 (127.4), C_2SO 101.3 (102.0), SOH_4 106.3 (108.8), OSC_2C_1 0.0 (3.6), $H_1C_1C_2S$ 180, $H_2C_1C_2S$ 0, H_4OSC_2 87.9 (88.1), distance C_1H_4 3.17; (*Z*)-**6**, C_1C_2 1.491 (1.498), C_2S 1.634 (1.593), SO 1.499 (1.466), C_2H_4 1.089 (1.077), C_1H 1.094 (1.086), $H_3C_1C_2$ 109.5 (110.5), $H_1C_1C_2$ 110.9 (110.2), $H_2C_1C_2$ 110.9, $C_1C_2H_4$ 122.15 (120.1), C_1C_2S 124.6 (126.5), C_2SO 114.3 (114.4), $H_3C_1C_2S$ 0 (0), $H_1C_1C_2S$ −120, $H_2C_1C_2S$ 120 (120.7), distance H_3O 2.57; **7**, CS 1.628, SO 1.495, CH 1.085, OSC 115.35, SCH_1 116.1, SCH_2 122.7, H_1CSO 180, H_2CSO 0.

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ing either dehydration through intermediate **4** (1073 K) or complete decomposition of **6** (1173 K) as already reported.[13]

Attempts have been made to better characterize **4** and **6**. However, tandem FVT experiments aimed at the study of the isomerization **4** → **6** could not be performed. Actually, with our device, such a tandem experiment can only be done in ovens external to the photoelectron spectrometer, thus noticeably increasing the length between the oven end and the ionization head. In such conditions, sulfenic acids do not survive over the increased residence time and their PE spectrum cannot be obtained. Furthermore, an alternative route toward sulfine **6** was checked starting from ethanesulfinyl chloride, CH_3CH_2SOCl.[26,31] However FVT of this latter compound gave rise to a complex mixture of products, while HCl elimination[32] over a solid base did not lead to the seeked sulfine **6**.

Conclusion

Thermolysis of thiosulfinate **2** or *tert*-butyl sulfoxide **3** produces the corresponding sulfenic acid **1** together with thioformaldehyde and isobutene, respectively. Methanesulfenic acid (**1**) appears rather stable in the gas phase, as only a very slight change of its spectrum is noticed above 853 K. Above 1073 K, methanesulfenic acid (**1**) decomposes into thioformaldehyde ($CH_2{=}S$) and H_2O, as already observed from a microwave experiment.[5]

On the other hand, thermolysis of vinyl *tert*-butyl sulfoxide (**5**) obviously leads, besides isobutene, to ethanethial *S*-oxide (**6**). However, another thermolysis product is present at the lowest FVT temperatures. A body of evidence indicative of the formation of transient ethenesulfenic acid (**4**) has been presented. These results imply either a poor stability of acid **4** quickly isomerizing to **6** or an alternative decomposition pathway of the starting sulfoxide **5** directly leading to sulfine **6**.

To our knowledge, this work constitutes the first experimental characterization of sulfenic acids **1** and **4** through their photoelectronic spectra. The assignment of these spectra, based on experimental grounds, has been completed by comparison with ab-initio calculated IPs (Koopmans and ΔE). Both acids are characterized by a large gap between the first two ionic states: 2.07 eV for **1** and around 2.7 eV for **4**. (In this latter case, the precise determination of the second IP is difficult due to poorly resolved overlapping bands at 11.47 eV.) The first band originates from the ejection of an electron from a lone pair orbital heavily localized on sulfur, in interaction with the ethylenic moiety in the case of **4**. The second band arises from the ejection of an electron from a $n_S - n_O$ orbital in the heavy atoms plane. This band is observed together with the one originating from the ionization of the $\pi + n_S^{\perp}$ orbital in the case of **4**. Our results fairly confirm the previous mass spectrometric determination of the first IPs of **1** and **4** by Turecek[7]. Moreover the spectrum of ethanethial *S*-oxide (**6**) is fully consistent with that of parent methanethial *S*-oxide **7**.[26,27]

Experimental Section and Calculation Methods

Photoelectron spectra were recorded on an Helectros 0078 photoelectron spectrometer equipped with a 127° cylindrical analyzer and monitored by a microcomputer supplemented with a digital analog converter. The spectra are calibrated on the known ionizations of xenon (12.13 and 13.43 eV) and argon (15.76 and 15.93 eV). The IPs are accurate within 0.02 eV. The short path thermolysis system has been described elsewhere.[33] Products are introduced at a partial pressure around 10^{-2} mbar. In these conditions, it is estimated that the detection of decomposition products with lifetimes in the $10^{-1}-10^{-3}$ s range may be performed.[19,34]

Methyl methanethiosulfinate (**2**) was prepared by careful oxidation of dimethyl disulfide with *m*-chloroperbenzoic acid in $CHCl_3$ at 273 K.[36] Methyl *tert*-butyl sulfoxide (**3**) was prepared by oxidation of methyl *tert*-butyl sulfide by hydrogen peroxide in glacial acetic acid.[37] Vinyl *tert*-butyl sulfoxide (**5**) was prepared in two steps from dimethyl sulfite. First, from a Grignard reaction between *tert*-butylmagnesium chloride and dimethyl sulfite, methyl *tert*-butyl sulfinate was prepared.[38] A second Grignard reaction was then performed between vinylmagnesium chloride and methyl *tert*-butyl sulfinate.[39] All the synthesized compounds were purified by extensive trap-to-trap distillation on a vacuum line and identified by comparison with reported data.

Preliminary calculations were performed in the AM1 formalism with the AMPAC set of programs[40] on fully optimized geometries. Ab-initio calculations were carried out with the Gaussian 92 program.[41] Full MP2 geometry optimizations were performed at the MP2/6-31G* level. Energies of ground and ionic states were then calculated at the MP2 level on the MP2/6-31G* ground state geometries, using the 6-311G** basis set.

In some cases where the second ionic state could not be calculated within this formalism due to the lack of symmetry of the molecule, both the ground and the first two ionic states were calculated with the CIPSI formalism[42] (6-311G** basis set) on the previously established MP2/6-31G* geometries of the ground state. In the CIPSI algorithm, the effects of electronic correlation are estimated by configuration interaction using a variation-perturbation method. A variational zeroth-order wave function is built up from an iterative selection of the most important determinants according to a threshold on the coefficients. The perturbative step is a multireference second-order Möller−Plesset treatment and includes all single and double excitations from the main determinants.

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(34) If it is assumed that the products vaporized at ca. 10^{-2} mbar generate a molecular flow, the maximum velocity of the molecules is calculated around 10^2 m/s. For a more realistic velocity between 1 and 10^2 m/s, the residence time of the species varies between 10^{-1} and 10^{-3} s for 10 cm length between the top of the oven and the ionization head.[19,35]

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