

**SULFENIC ACIDS IN THE GAS PHASE.
PREPARATION, IONIZATION ENERGIES AND HEATS OF FORMATION
OF METHANE-, ETHENE-, ETHYNE- AND BENZENESULFENIC ACID**

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Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

Methane-, ethene-, and ethynesulfenic acids were generated in the gas phase by flash-vacuum pyrolysis of the corresponding tert-butyl sulfoxides at 400°C and 10⁻⁴ Pa. Benzenesulfenic acid was prepared from phenyl 3-buten-1-yl sulfoxide at 350°C and 10⁻⁴ Pa. The sulfenic acids were characterized by mass spectrometry. Threshold ionization energies (*IE*) were measured as *IE*(CH₃SOH) = 9.07 ± 0.03 eV, *IE*(CH₂=CHSOH) = 8.70 ± 0.03 eV, *IE*((HC≡CSOH) = 8.86 ± 0.04 eV, and *IE*(C₆H₅SOH) = 8.45 ± 0.03 eV. Radical cations [CH₃SOH][‡], [CH₂=CHSOH][‡], and [HC≡CSOH][‡] were generated by electron-impact-induced loss of propene from the corresponding propyl sulfoxides and their heats of formation were assessed by appearance energy measurements as 685, <824, and 927 kJ mol⁻¹, respectively. Heats of formation of the neutral sulfenic acids and the S—(O)(C), S—(O)(C_d), S—(O)(C_f), and S—(O)(C_B) group equivalents were determined. The experimental data, supported by MNDO calculations, point to sulfenate-like structures (R—S—OH) for the sulfenic acids under study.

Sulfenic acids, RSOH, belong to key intermediates in organosulfur chemistry that interconnect compounds containing bivalent sulfur with those containing sulfur in higher oxidation states.¹⁻⁴ Although a few stable sulfenic acids have been isolated^{5,6} most simple sulfenic acids are kinetically unstable in the condensed phase, undergoing rapid self-condensation to thiosulfonates.^{7,8} Kinetically unstable sulfenic acids have been assumed intermediates in the formation of the lachrymatory factor of the onion,⁹ and in oxidation of enzymes containing sulfhydryl groups.¹⁰ Methanesulfenic acid (*I*) has been postulated as an intermediate in the atmospheric

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oxidation of volatile sulfur compounds^{11,12} which belong to major industrial pollutants.¹³

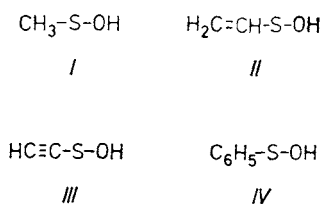
Sulfenic acids can be generated by thermolysis of sulfoxides (refs^{8,14-21}) in solution or in the gas phase. In solution they can be trapped by alkynes, giving rise to vinyl sulfoxides^{14,16,22} which are important ketone synthons. In the gas phase, *I* has been generated from tert-butyl methyl sulfoxide,^{8,23} while benzenesulfenic acid (*IV*) and 2-methylpropane-2-sulfenic acid have been trapped and studied in matrix.¹⁸

In spite of the considerable recent interest in the chemistry of sulfenic acids,⁸⁻²² some questions concerning the structure and energetics of these compounds have remained unanswered. A priori, sulfenic acids may exist in two isomeric forms corresponding to sulfenate-like (*A*) or sulfoxide-like (*B*) structures.

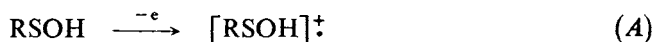


Methanesulfenic acid (*I*) has been shown convincingly by microwave spectroscopy to prefer the sulfenate structure *A* in the gas phase.²³ By contrast, *IV* and 2-methylpropane-2-sulfenic acid have been claimed to exist as mixtures of *A* and *B* (refs^{18,24}). The latter conclusion was based on the observation¹⁸ that the infrared spectra of pyrolysates measured in matrix contained bands attributable to S—H stretching vibrations.¹⁸ Energy parameters, e.g. the ionization energies and heats of formation in the gas phase, have been completely missing.²⁵

The goal of the present paper is to fill the gap by preparing four basic sulfenic acids *I-IV* in which the sulfur atoms are linked to carbons of different types.



The thermochemistry of *I-IV* can be approached by combining the energy parameters pertinent to ionization (Eq. (A)) and dissociative ionization (Eq. (B)), both yielding the same radical-cations.



The heat of formation of RSOH is then calculated from the heat of formation of the radical-cation $[\text{RSOH}]^+$ and the experimental threshold (ideally adiabatic) ionization energy, according to Eq. (1).

$$\Delta H_{f,298}^{\circ}(\text{RSOH}) = \Delta H_{f,298}^{\circ}[\text{RSOH}]^+ - IE(\text{RSOH}) \quad (1)$$

The knowledge of the heats of formation for $I-IV$ makes it possible to incorporate sulfenic acids into empirical thermochemical systems such as the Benson's additivity rules²⁶ and, in extenso, to predict heats of formation for homologous and analogous compounds. In the spirit of Benson's thermochemical kinetics²⁷ the ΔH_f° data may be useful in assessing activation energies for reactions in which sulfenic acids appear as transient intermediates.

EXPERIMENTAL

Mass spectra were measured on a Jeol D-100 double-focusing spectrometer (300 μA , 75 eV, 3 kV) furnished with a micro-oven.^{28,44} The ionization and appearance energies were measured with 50 μA emission current and the repeller voltage set to 0.00 ± 0.02 V. Ion intensities were recorded with a data system at slow scan rate (60 min/decade) in 50 meV steps starting from 0.5 eV below the threshold up to 2–3 eV above it. The intensities at each electron energy were averaged over 3–4 scans, normalized, and then treated with the inverse convolution procedure.³⁴ The deconvoluted ionization-efficiency curves were fitted with least-squares lines or polynomials. The reported threshold energy values are averages of 4–6 independent runs. The error limits are standard deviations including the uncertainties in calibration. Methyl iodide ($IE = 9.55$ eV) was used as internal standard to calibrate the energy scale. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-200 instrument (200.058 and 50.309 MHz for ^1H and ^{13}C , respectively, Fourier-transform mode) in deuteriochloroform at 23°C with tetramethylsilane as internal reference. The ^{13}C NMR spectra of the acetylenic sulfoxides were measured after adding to each sample a trace amount of chromium tris(acetylacetonate) to accelerate relaxation.

The sulfoxides used in this paper were prepared from the corresponding sulfides by sodium periodate oxidation^{51,52} in methanol. Vinylsulfides were prepared by a modified⁵³ Doumani protocol.⁵⁴ Ethynylsulfides were prepared according to literature.⁵⁵ All the intermediates had physical properties compatible with the literature data.^{53–56} The sulfoxides were purified by column chromatography (silica gel, elution with dichloromethane–ether 2 : 1), but final distillation was generally avoided because of thermal instability of these compounds. The products were characterized by spectral methods.

Methyl 3-buten-1-yl sulfoxides (VI): Mass spectrum (m/z , relative intensity): 119 (0.6), 118 (4.2), 117 (0.4), 103 (0.8), 102 (4.3), 91 (0.8), 90 (0.8), 88 (1.3), 87 (1.4), 85 (1.4), 77 (1.2), 75 (1.1), 74 (2.9), 71 (2), 65 (1.1), 64 (17.7), 63 (7.1), 62 (1), 61 (20.2), 60 (0.7), 59 (1.1), 58 (1), 57 (1.7), 56 (4.8), 55 (100), 54 (13.3), 53 (19.1), 52 (1.6), 51 (4.8), 50 (4), 49 (1.7), 48 (2.6), 47 (10.1), 46 (4.1), 45 (8.6), 44 (2), 43 (1.6), 42 (0.9), 41 (7.9), 40 (1.9), 39 (33.6), 38 (2), 37 (1), 35 (3), 34 (1.2), 33 (0.7), 31 (1.4), 30 (1.4), 29 (62.4), 27 (37.9), 26 (5), 15 (5.3), 14 (0.9). ^1H NMR: 5.85 (m, $W = 40$ Hz, 1 H); 5.17 (ddt, $J = 16.5, 3.0, 1.6$ Hz, 1 H); 5.11 (ddt, $J = 10, 3, 1.6$ Hz, 1 H); 2.78 (m, 2 H); 2.59 (s, 3 H); 2.52 (m, 2 H). ^{13}C NMR: 134.83 d, 117.12 t, 53.72 t, 38.62 q, 26.67 t.

tert-Butyl vinyl sulfoxide (VII): Mass spectrum (m/z , relative intensity): 132 (1), 117 (0.6), 116 (0.9), 115 (1.2), 108 (0.7), 106 (0.8), 105 (0.9), 92 (1), 91 (2.3), 85 (3.2), 84 (4.3), 83 (5.4), 80 (1),

79 (1), 78 (2·1), 77 (2·1), 76 (13·3), 75 (0·9), 65 (1), 64 (3·2), 60 (2), 59 (4·9), 58 (5·8), 57 (88·3), 56 (68·8), 55 (29), 54 (3·1), 53 (8·9), 52 (2·4), 51 (7·8), 50 (9·1), 49 (2·9), 48 (3·4), 47 (5), 46 (1·7), 45 (4·4), 44 (2·1), 43 (3·3), 42 (7·1), 41 (100), 40 (13·9), 39 (68·8), 38 (8·2), 37 (4·9), 34 (0·9), 31 (1·2), 29 (48·9), 28 (27·1), 27 (33), 26 (8), 15 (4·2), 14 (1·3). $^1\text{H NMR}$: 6·57 (dd, $J = 16·5$, 10 Hz, 1 H); 6·09 (d, $J = 16·5$ Hz, 1 H); 6·02 (d, $J = 10$ Hz, 1 H); 1·24 (s, 9 H). $^{13}\text{C NMR}$: 136·66 d, 123·78 t, 54·73 s, 22·89 q.

tert-Butyl ethynyl sulfoxide (VIII): Mass spectrum (m/z , relative intensity): 130 (0·3), 115 (0·3), 89 (0·4), 75 (0·9), 74 (4·1), 73 (1·1), 59 (9·8), 58 (4·5), 57 (100), 56 (12·3), 55 (9·5), 53 (2·6), 51 (1·8), 50 (1·8), 49 (1·2), 48 (2·1), 45 (3·7), 44 (2·3), 43 (5·1), 42 (3), 41 (71·2), 40 (3·4), 39 (21·4), 38 (2·1), 37 (1·1), 31 (4·1), 29 (41·3), 28 (6), 27 (11·3), 26 (2·2), 15 (2·3), 14 (0·5). $^1\text{H NMR}$: 1·40 (s, 9 H); 3·60 (s, 1 H). $^{13}\text{C NMR}$: 90·72 d, 79·28 s, 58·43 s, 22·76 q.

Phenyl 3-buten-1-yl sulfoxide (IX) has been described earlier.⁴⁴

Methyl propyl sulfoxide (X): Mass spectrum (m/z , relative intensity): 108 (1·2), 107 (1·4), 106 (21·1), 91 (1·9), 90 (8·7), 89 (3·5), 78 (1·2), 77 (2), 76 (1·2), 75 (2·4), 66 (4), 65 (3·1), 64 (84), 63 (15), 62 (1·2), 61 (19·8), 59 (1·3), 58 (1), 57 (3·9), 56 (1·4), 55 (3), 51 (1·8), 50 (1·1), 49 (4·2), 48 (8·1), 47 (18·8), 46 (7·1), 45 (11·8), 44 (2·4), 43 (64·5), 42 (9·2), 41 (100), 40 (3·6), 39 (27·8), 38 (3·8), 37 (1·7), 35 (3·3), 34 (1·6), 33 (1·1), 31 (2·9), 29 (10), 28 (20), 27 (73·4), 26 (3·9), 15 (12), 14 (1·4). $^1\text{H NMR}$: 2·70 (m, 2 H); 2·57 (s, 3 H); 1·78 (m, 2 H); 1·10 (t, 3 H). $^{13}\text{C NMR}$: 56·23 t, 38·41 q, 16·16 t, 13·26 q.

Vinyl propyl sulfoxide (XI): Mass spectrum (m/z , relative intensity): 118(4), 102(1·1), 101(6), 100 (11·4), 89 (1·1), 78 (4), 77 (3·9), 76 (84), 75 (3·4), 74 (1), 73 (5·2), 70 (1·4), 69 (16·4), 68 (3·6), 67 (1·1), 63 (6·7), 60 (15·3), 59 (13·6), 58 (9·6), 57 (3·2), 56 (1), 55 (1·9), 50 (4·7), 49 (3·8), 48 (8·1), 47 (24·9), 46 (9·3), 45 (19·5), 44 (3·6), 43 (76·1), 42 (9·2), 41 (93), 40 (4·4), 39 (33·3), 38 (4·3), 37 (2·2), 34 (1·8), 33 (1·1), 31 (7·2), 30 (0·8), 29 (11·1), 28 (7·2), 27 (100), 26 (11·1), 25 (1·1), 15 (8·7), 14 (1·9). $^1\text{H NMR}$: 6·61 (dd, $J = 16·5$, 9·8 Hz, 1 H); 6·10 (d, $J = 16·5$ Hz, 1 H); 5·95 (d, $J = 9·8$ Hz, 1 H); 2·71 (m, 2 H); 1·80 (m, 2 H); 1·09 (t, 3 H). $^{13}\text{C NMR}$: 140·59 d, 121·76 t, 55·32 t, 15·56 t, 13·23 q.

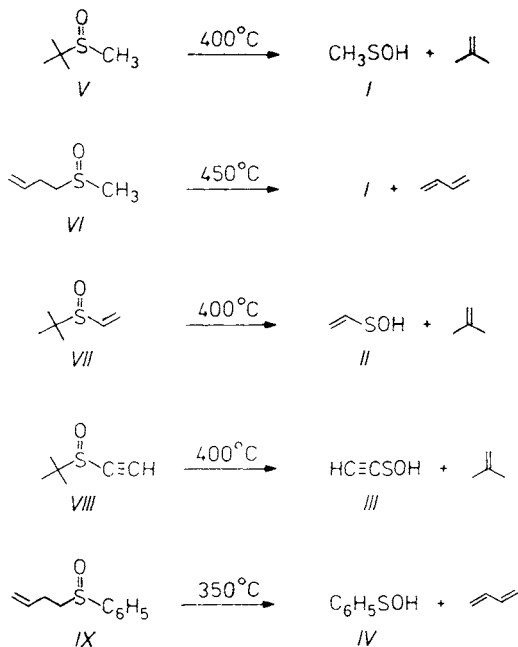
Ethynyl propyl sulfoxide (XII): Mass spectrum (m/z , relative intensity): 117 (0·7), 116 (1·5), 115 (0·5), 101 (1·1), 100 (4·1), 99 (2·3), 85 (2·3), 77 (0·8), 76 (3·3), 75 (3·3), 74 (34·3), 73 (7), 72 (0·8), 71 (3·1), 70 (1·7), 69 (1·2), 68 (2·2), 67 (6·5), 65 (1·5), 63 (1·8), 60 (1·9), 59 (2·8), 58 (10·8), 57 (11·1), 56 (1·6), 55 (2·4), 54 (0·9), 53 (1), 51 (1·1), 48 (4·9), 47 (6), 46 (6·3), 45 (17·1), 44 (5·2), 43 (100), 42 (12·5), 41 (96·8), 40 (5·7), 39 (39·4), 38 (5·7), 37 (3·1), 34 (1·6), 33 (1), 31 (2·2), 29 (6·2), 27 (72·2), 26 (7·5), 25 (2·2), 15 (5·7), 14 (1·7). $^1\text{H NMR}$: 1·12 (t, 3 H), 1·94 (m, 2 H), 3·10 (m, 2 H), 3·68 (s, 1 H). $^{13}\text{C NMR}$: 90·42 d, 80·83 s, 58·05 t, 15·98 t, 13·09 q.

RESULTS

Preparation and Characterization of Sulfenic Acids

Sulfenic acids I–IV were generated by flash-vacuum pyrolysis of the corresponding tert-butyl sulfoxides V, VII, VIII or 3-butenyl sulfoxides VI and IX (Scheme 1). The course of pyrolysis was conveniently monitored by electron impact mass spectrometry at 75 or 12 eV ionizing energy.²⁸ Under conditions of molecular flow, the molecules of the precursor underwent on average 40 to 50 collisions with the hot walls of the oven and decomposed within 1 ms to products which were cooled to

90–100°C by collisions with the walls of the ion source.²⁸ Decompositions of the tert-butyl sulfoxides *V*, *VII*, and *VIII* began at 280–300°C and were near completion at 380–400°C. This is documented by the $\log k$ vs T curves for the formation of *I–III* from *V*, *VII*, and *VIII*, respectively, shown in Fig. 1. The conversions were



SCHEME 1

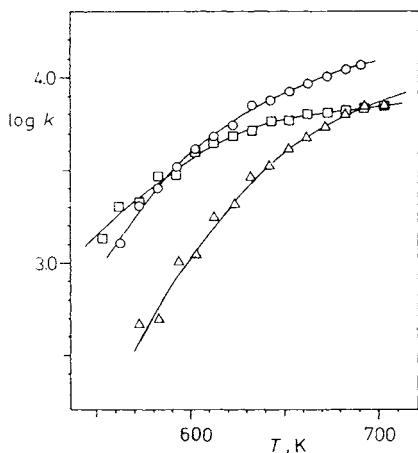


FIG. 1
Kinetic curves for the elimination of isobutylene from *V*, *VII*, and *VIII*. Δ $V \rightarrow I$, \circ $VII \rightarrow II$, \square $VIII \rightarrow III$

assessed from the $[\text{C}_4\text{H}_9]^+ / [\text{C}_4\text{H}_8]^+$ abundance ratios in the 75 eV mass spectra. These ratios dropped from the original values (e.g. 1.28 and 8.13 for *VII* and *VIII*, respectively) down to 0.04–0.05 at 400°C, indicating >95% conversions. Consistent with this, the 12 eV mass spectra of the pyrolysates at 400°C contained chiefly $[\text{C}_4\text{H}_8]^+$ and $[\text{RSOH}]^+$, both identified by accurate mass measurements. Sulfoxide *IX* decomposes readily starting at 300°C and achieves very high conversion to butadiene and *IV* at 350°C. This was inferred from the $[\text{C}_4\text{H}_7]^+ / [\text{C}_4\text{H}_6]^+$ abundance ratio that decreased from the original value of 14.3 in the 75 eV mass spectrum of *IX* down to 0.02 in the spectrum of the pyrolysate at 350°C. Pyrolysis of *VI* required higher temperatures and conversions of c. 85% could be achieved at 450–500°C.

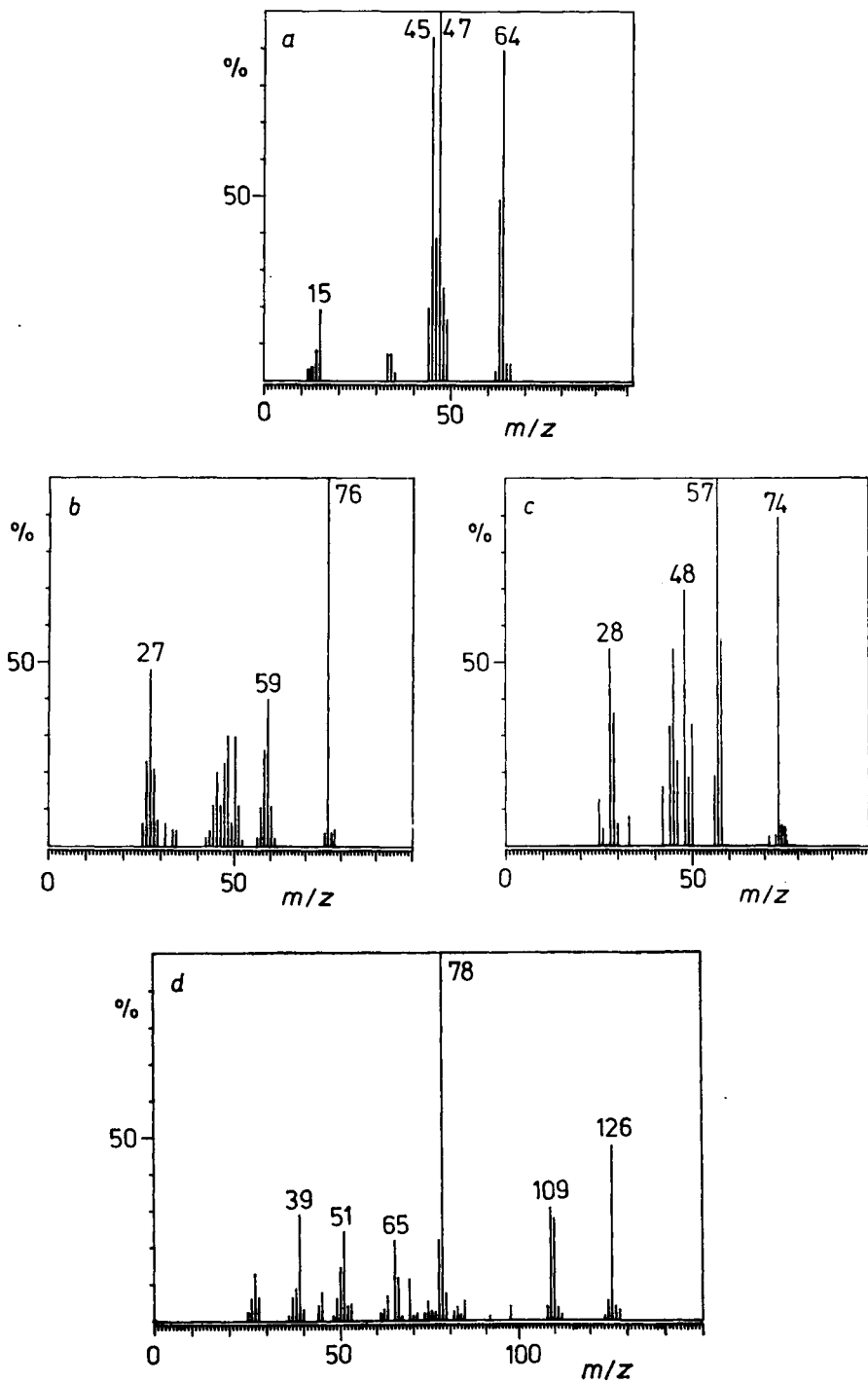
The 75 eV electron impact mass spectra are displayed in Fig. 2. The spectra were obtained after having subtracted from each spectrum of the pyrolysate the standard spectrum of the olefin formed, i.e. isobutylene for *I–III* and 1,3-butadiene for *IV*.²⁹ Wherever coincidences were possible, e.g. at m/z 56 and 57 in the spectra of *II* and *III*, the sulfur-containing ions were distinguished by high-resolution measurements, such that the reported relative intensities were free of any uncertainties due to corrections.

The electron-impact induced fragmentations of *I–IV* will be mentioned only briefly. All the sulfenic acids under study afford abundant molecular ions and $[\text{M–OH}]^+$ fragments, the latter representing the base peaks of the spectra of *I* and *III*. The facile loss of the hydroxyl radical from *I–IV* points to sulfenate (*A*) structures for the sulfenic acids being investigated. Sulfoxide-like compounds (*B*) could be expected to lose hydrogen atoms by analogy with the fragmentations of both thiols and sulfoxides (see Experimental and ref.²⁹). In contrast, $[\text{M–H}]^+$ ions are of negligible relative abundance in the spectra of *II–IV* (Figs 2*b–d*), suggesting that structures *B* are not populated to significant extent. Acid *I* whose structure is definitely of the *A*-type²³ deviates from this rule, giving abundant $[\text{M–H}]^+$ ions in the 75 eV mass spectrum (Fig. 2*a*). However, with *I* the hydrogen atom eliminated can originate from the methyl group (α -cleavage to heteroatom³⁰), while a similar hydrogen loss would be unfavourable in *II* and impossible in *III* and *IV*.

It should be noted that although the loss of hydroxyl radical from ionized *I–IV* is indicative of the suggested structures, it does not constitute a definite proof. Organosulfur compounds containing sulfur–oxygen bonds often undergo complex rearrangements following ionization, and these render mass spectrometry-based structure elucidation of such compounds somewhat uncertain (refs^{31–33}).

Ionization and Appearance Energy Measurements

The ionization energies of *I–IV* were determined from the deconvoluted³⁴ ionization efficiency curves ignoring hot bands (Figs 3–6). The curve of *I* (Fig. 3*a*) displays



an onset at 9.07 ± 0.03 eV with a linear slope extending up to 1 eV above the threshold. A linear portion is also observed for the ionization-efficiency curve of *IV* which shows an onset at 8.45 ± 0.03 eV. By contrast, the curves for *II* and *III* are non-linear above the thresholds of ionization. Polynomial least-squares fits (Figs 4 and 5) show short pseudolinear intervals of low curvature some 0.4–0.7 eV above the thresholds, followed by upward bending portions. The non-linearity of the ionization-efficiency curves may be due to either low-lying excited states in radical-cations $[II]^{\ddagger}$ and $[III]^{\ddagger}$, or admixtures of isomers with higher ionization energies (*vide infra*).

In order to assess the heats of formation of *I–IV* it was necessary to generate the corresponding radical-cations and determine their ΔH_f° by appearance energy measurements. Ion $[I]^{\ddagger}$ has been prepared earlier by loss of ethene or propene from

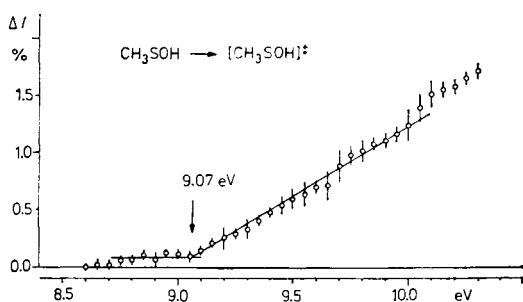


FIG. 3
Ionization-efficiency curve for $[I]^{\ddagger}$

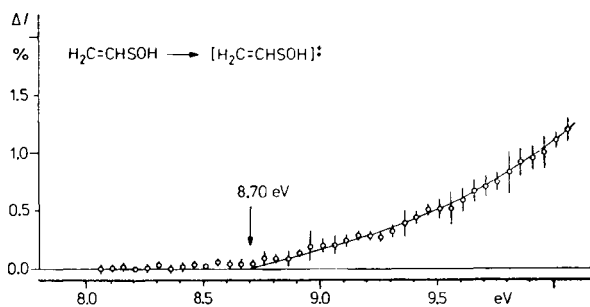


FIG. 4
Ionization-efficiency curve for $[II]^{\ddagger}$

←
FIG. 2
75 eV Mass spectrum of *a I*, *b II*, *c III*, *d IV*

ionized methyl ethyl sulfoxide or methyl isopropyl sulfoxide, respectively.³⁵ The appearance energies for the formation of $[I]^+$ from these precursors were determined by the retarding-potential-difference method, but showed rather large scatter, giving $\Delta H_f^\circ[I]^+ = 677-736 \text{ kJ mol}^{-1}$ (ref.³⁵). In this work we used propyl sulfoxides *X*, *XI*, and *XII* to prepare ions $[I]^+$, $[II]^+$, and $[III]^+$, respectively (Scheme 2). The sulfoxides *X-XII* afford abundant $[M - C_3H_6]^+$ fragments which become the base peaks of the spectra below 15–20 eV. Metastable $[X]^+ - [XII]^+$ show very weak to non-detectable signals for the loss of C_3H_6 . All this indicates that the elimination of propene from $[X]^+ - [XII]^+$ requires low critical energies³⁶ and proceeds very rapidly with $k \gg 10^6 \text{ s}^{-1}$. Both these characteristics are favourable for critical energy measurements since the competitive and kinetic shifts can be neglected.³⁷

The thermochemical data used to calculate the heats of formation are summarized in Scheme 2. Standard heats of formation for the sulfoxide precursors *X-XII* were estimated from the additivity rules.^{25,26} Unfortunately, the additivity scheme does

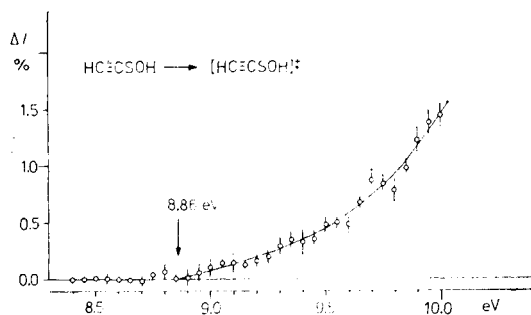


FIG. 5
Ionization-efficiency curve for $[III]^+$

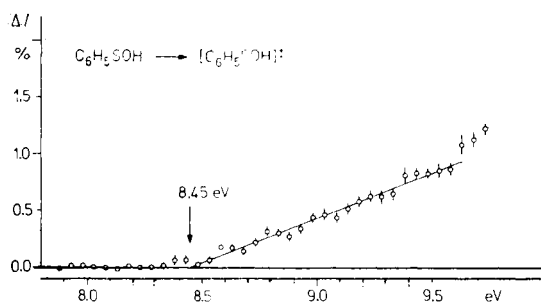
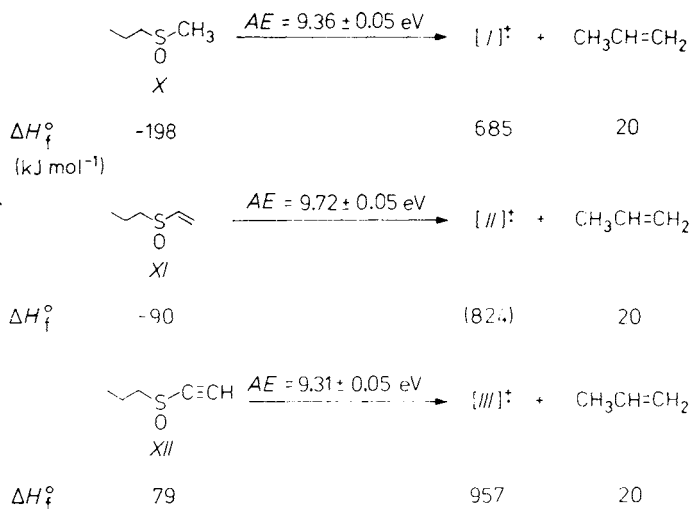


FIG. 6
Ionization efficiency curve for $[IV]^+$

not include terms for unsaturated sulfoxides. We used the standard $\text{SO}(\text{C})_2$ term²⁶ to calculate the heats of formation in a consistent manner while being aware of possible errors in the absolute values introduced by this approximation.



SCHEME 2

Inspection of the data in Scheme 2 reveals a conspicuously high appearance energy for the loss of propene from XI. The ionization efficiency curve for $[II]^\ddagger$ from XI showed a clear onset which was reproducible within the given standard deviation over several independent measurements carried out on different days. In order to assess the critical energies (E_c) for the eliminations of propene from $[X]^\ddagger - [XII]^\ddagger$ we recorded the photoelectron spectra of sulfoxides X–XII (Table I). Approximating $E_c = AE - IE_1$ one obtains $E_c = 0.54, 0.9$, and 0.17 eV for the elimination of propene from $[X]^\ddagger$, $[XI]^\ddagger$, and $[XII]^\ddagger$, respectively. While the critical energies for $[X]^\ddagger$ and $[XII]^\ddagger$ appear reasonable, being similar to those for alkene losses from saturated⁴⁰ and unsaturated ketones^{41,42}, the value for the reaction $[XI]^\ddagger \rightarrow [II]^\ddagger$ is clearly too high. The photoelectron spectra of X–XII show that the first excited states in the corresponding radical-cations lie above the appearance energies for the loss of propene. This means that near the threshold the latter decompositions are induced by vibrational excitation of ground-state molecular ions, while being independent of the initial populations of higher electronically excited states which may be different in $[X]^\ddagger - [XII]^\ddagger$. In view of this we have no adequate explanation for the high E_c value of XI. A reverse activation energy or formation of isomeric ions or neutrals are just possibilities to be explored.

DISCUSSION

The energy data for neutral and ionized sulfenic acids *I–IV* are summarized in Table II and complemented with the results of MNDO calculations.⁴³ The ionization energies of *I–IV* are substantially lower than it would have been expected for sulfoxide-like forms *B*.⁴⁵ Comparison of the ionization energies in the series *I–III* with those of sulfoxides *X–XII* (Table I) points to quite distinct trends due to different orbital interactions in these two classes of compounds.

In vinyl sulfoxides the HOMO-energy increases, antibonding interaction of the filled n_s and $\pi_{C=C}$ orbitals is largely compensated by the σ -accepting effect of the vinyl group and, presumably, weakened by rotation about the C—S bond.³⁹ Consequently, replacing a methyl by the vinyl group in a sulfoxide has negligible effect on the first ionization energy³⁹ (see also Table I).

TABLE I
Photoelectron spectra of *X–XII*

Band ^a	Ionization energy, eV ^b		
	<i>X</i>	<i>XI</i>	<i>XII</i>
	8.35 ^c	8.4 ^c	8.7 ^c
$a', n'_O - n'_S$	8.82	8.82	9.14
a'', n_O	9.91	9.99	10.48
π_{C-C}	—	10.61	11.19
a', σ_{S-O}	11.87	11.92	12.1

^a Assigned according to ref.³⁸, for another assignment based on CNDO/2 calculations see ref.³⁹;
^b the first three bands ± 0.02 eV, the fourth band ± 0.05 eV; ^c adiabatic ionization energies as read from the onsets of the first bands in the photoelectron spectra.

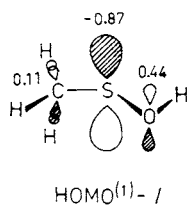
TABLE II
Energy data for *I–IV*

Compound	<i>IE</i> eV	$-\epsilon_{HOMO}$ eV	$\Delta H_f^\circ(\text{ion})$ kJ mol ⁻¹	$\Delta H_f^\circ(\text{neutr})$ kJ mol ⁻¹	$\Delta H_f^\circ(\text{MNDO})$ kJ mol ⁻¹	<i>S – (O) (C)</i> kJ mol ⁻¹
<i>I</i>	9.07 ± 0.03	9.85	685	–190	–155	11
<i>II</i>	8.70 ± 0.03	9.32	< 824	< –16(–77) ^a	–49	< 81(20) ^a
<i>III</i>	8.86 ± 0.04	9.54	957	102	122	27
<i>IV</i>	8.45 ± 0.03	9.56	780 ^b	–34	–22	48

^a Estimated from the comparison of the MNDO calculations and experimental data; ^b ref.⁴⁴.

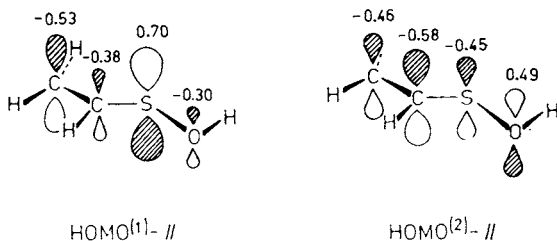
By contrast, with unsaturated sulfenic acids the $n_S-\pi_{C=C}$ interaction leads invariably to increased HOMO energies, a phenomenon which has also been observed for unsaturated sulfides.⁴⁶ The HOMO energies ($-\epsilon_{\text{HOMO}}$, Table II) calculated by MNDO for *I-III* correlate well with the experimental ionization energies, indicating that these compounds are structurally related. The differences in the absolute values of the *IE*'s and $-\epsilon_{\text{HOMO}}$ may be in part due to the threshold nature of the experimental data which are closer to adiabatic ionization energies. The corresponding vertical ionization energies are estimated to be shifted 0.3–0.4 eV higher, as judged by the $IE_{\text{vert}}-IE_{\text{adiab}}$ differences for simple thiols, sulfides and sulfoxides.^{38,39,46}

The shapes of the highest occupied orbitals in *I-IV* can be estimated from the MNDO wave function coefficients. The HOMO in *I* (denoted here HOMO⁽¹⁾-*I*)



consists largely of an antibonding combination $n_S - n_O$ which is mixed with a methylene pseudo- π -orbital. The latter is also antibonding with respect to n_S . The second HOMO is delocalized over the C—S—O—H σ -bond framework. Its energy, 2.7 eV below that of HOMO⁽¹⁾, indicates that there should be a large gap between the first and second ionization potentials in *I*, consistent with the long linear portion of the ionization-efficiency curve (Fig. 3).

The two highest occupied orbitals in *II* (denoted as HOMO⁽¹⁾-*II* and HOMO⁽²⁾-*II*) are of π -type, both consisting of an antibonding combination $n_S - n_O$, but differing from each other in the interaction with the π_{C-C} part. However, the energy difference between HOMO⁽¹⁾-*II* and HOMO⁽²⁾-*II* (2.14 eV by MNDO) suggests that there is

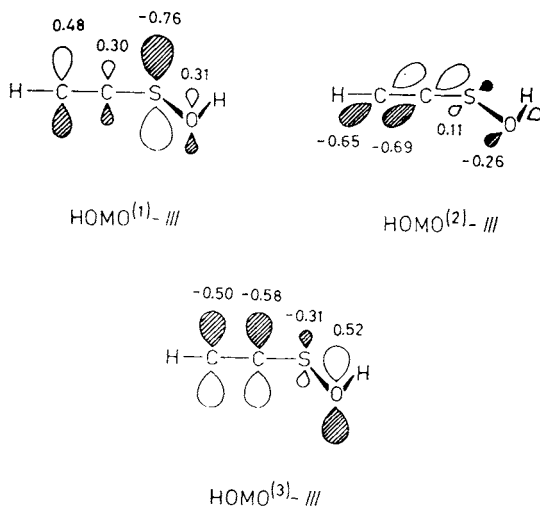


no low-lying excited state in the radical-cation [*II*]⁺ that would fall within 0.5–0.7 eV of the ground state. This shows that the early curvature on the ionization-efficiency

curve of *II*, starting at c. 9.4 eV (Fig. 4) is due to the presence of another C_2H_4SO isomer conformed with the sulfenic acid. We believe that the sulfoxide-like isomer *IIB* is an unlikely candidate, since its ionization energy can be expected to be substantially higher than 9.4 eV, according to the orbital energies calculated earlier by *ab initio* with the 3-21G basis set.⁴⁵ Based on the energy data, methylsulfine, $CH_3-CH=S=O$, *XIII*, appears to be a more plausible candidate. Isomer *XIII* can be expected to possess two closely spaced electronic states in the corresponding radical-cation, by analogy with the homologous sulfine $CH_2=S=O$.⁴⁷ The adiabatic ionization energy of the latter (c. 10.0 eV as read from the published photoelectron spectrum)⁴⁷ would give $IE_{\text{adiab}}(XIII) \doteq 9.3-9.4$ eV (ref.⁴⁸) which falls exactly within the region where we observe curvature on the ionization-efficiency curve of *II* (Fig. 4). The existence of two close electronic states in $[XIII]^+$ would explain the smooth upward rise of the curve instead of a single break. It should be noted that *XIII* has been postulated as an intermediate in the thermal loss of sulfur from *II*, though the latter sulfenic acid could not be detected directly.⁹

The three highest occupied orbitals in *III* (denoted $HOMO^{(1)}-III$, $HOMO^{(2)}-III$, and $HOMO^{(3)}-III$) are all of the π -type. According to MNDO, $HOMO^{(2)}-III$ and $HOMO^{(3)}-III$ are 1.75 and 2.52 eV lower in energy than $HOMO^{(1)}-III$. The large gap between $HOMO^{(2)}-III$ and $HOMO^{(1)}-III$ contrasts the upward rise of the ionization-efficiency curve of *III*, beginning 0.4–0.5 eV above the ionization threshold (Fig. 5). Hence we conclude that the rise is probably due to the presence of another C_2H_2SO isomer, conformed with *III*.

The two highest occupied orbitals in *IV* ($HOMO^{(1)}-IV$ and $HOMO^{(2)}-IV$) are calculated by MNDO to be nearly degenerate ($\Delta E = 0.095$ eV). $HOMO^{(1)}-IV$ consists of an antibonding combination of the sulfur *n* orbital with a benzenoid π -orbital.



$\text{HOMO}^{(2)}\text{-IV}$ is an almost purely benzenoid π -orbital with a nodal plane going through C-1, C-2 and the sulfur atom. $\text{HOMO}^{(3)}\text{-IV}$ is largely localized on the sulfur atom and its energy is 0.8 eV lower than that of $\text{HOMO}^{(1)}\text{-IV}$. The calculated orbital energies agree well with the course of the ionization-efficiency curve of IV (Fig. 6).

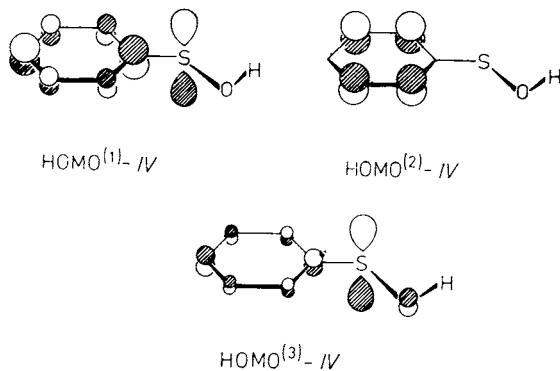
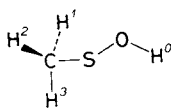


TABLE III

Bond lengths (nm) and angles (deg) in IA



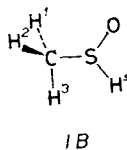
IA

Parameter	MNDO	STO-3G	Experiment ^{2,3}
Bonds			
O—H ⁰	0.0946	0.0945	0.0957
S—O	0.1614	0.1711	0.1658
C—S	0.174	0.1796	0.1806
C—H ¹ , C—H ²	0.1104	0.1086	—
C—H ³	0.1106	0.1086	—
Angles			
H ⁰ —O—S	107.1	102.5	107.7
O—S—C	103.3	95.8	100.1
S—C—H ¹	111.4	111.8	—
S—C—H ³	105.0	108.5	—
H ⁰ —O—S—C	180	180	93.9

The two highest electronic states are unresolved upon ionization, both contributing to the linearly rising portion. The third state becomes populated c. 0.9 eV above the ionization threshold as manifested by a break (Fig. 6).

The heats of formation, calculated from the experimental energy data according to Eq. (1), made it possible to assign terms to sulfonate sulfur atoms bonded to sp^3 , sp^2 , sp^2 -ar, and sp carbon atoms (Table II). The energy data for *II*, and hence also the term for S-(C_d)(O), represent upper limits at best because of the uncertainty in the appearance energy of $[II]^+$. The heats of formation for *I*, *III*, and *IV* are somewhat overestimated by MNDO relative to the experimental values, while not being in gross error. Assuming that the difference between the MNDO-based $\Delta H_f^\circ(II)$ and the actual value can be interpolated from the same differences for *I* and *III*, one obtains a plausible estimate for $\Delta H_f^\circ(II) \doteq -77 \text{ kJ mol}^{-1}$ and S-(C_d)(O) (20 kJ mol⁻¹). The MNDO-optimized geometry parameters for structures *IA*, *IB*,

TABLE IV
Bond lengths (nm) and angles (deg) in *IB*

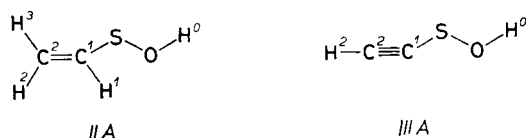


Parameter	MNDO ^a	3-21G* (ref. ⁴⁹)
Bonds		
S—O	0.1586	0.1490
S—H ^S	0.1354	—
C—S	0.1777	0.1794
C—H ¹ , C—H ²	0.1102	—
C—H ³	0.1105	—
Angles		
C—S—O	105.8	—
C—S—H ^S	97.9	—
S—C—H ¹	109.0	109.3
S—C—H ²	109.0	108.7
S—C—H ³	109.0	110.4
H ^S —S—C—H ³	37.7	—
O—S—C—H ³	143.0	—

^a With the minimum basis set STO-3G, SCF iterations failed to converge for the structure *IB*.

IIA, *IIIA*, and *IVA* are summarized in Tables III–VI and compared with experimental²³ or computational results.⁴⁹ Some of the bond lengths and angles calculated by MNDO and STO-3G for *IA* deviate significantly from the experimental ones (Table III). According to these methods the potential energy minimum for *IA* corresponds to a planar *trans*-form, while the *cis*-form is calculated as a saddle point c. 18 kJ mol⁻¹ higher in energy (MNDO). In contrast, the analysis of microwave spectra²³ yielded a *gauche*-form of *IA* as the equilibrium structure, while both the planar forms were postulated to be maxima (saddle points) of comparable heights.²³ The sulfoxide-like structure *IB* is highly destabilized against *IA* at the MNDO level ($\Delta E = 281$ kJ mol⁻¹). The MNDO-optimized geometry (Table IV) shows a very long S—O bond, much longer than obtained earlier by *ab initio* calculations with the 3-21G* basis set.⁴⁹ The destabilization of *IB* against *IA* is clearly exaggerated by the MNDO calculations, consistent with the unrealistically long S—O bond

TABLE V
MNDO bond lengths (nm) and angles (deg) in *IIA* and *IIIA*



Parameter	<i>IIA</i>	<i>IIIA</i>
Bonds		
O—H ⁰	0.0947	0.0947
S—O	0.1615	0.1621
C ¹ —S	0.1698	0.1621
C ¹ —C ²	0.1339	0.1197
C ¹ —H ¹	0.1089	—
C ² —H ²	0.1089	0.1051
C ² —H ³	0.1089	—
Angles		
H ⁰ —O—S	107.0	106.9
O—S—C ¹	103.0	102.1
S—C ¹ —C ²	121.3	180
S—C ¹ —H ¹	116.2	—
C ¹ —C ² —H ²	121.9	180
C ¹ —C ² —H ³	124.4	—

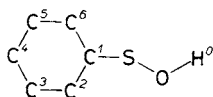
obtained for the former. By comparison, *ab initio* calculations of better quality⁵⁰ yielded $\Delta E = 84 \text{ kJ mol}^{-1}$ for the lowest homologues $\text{H}_2\text{S}=\text{O}$ and $\text{HS}-\text{OH}$, with the ΔE value being very sensitive to configuration interaction effects.⁵⁰

The unsaturated sulfenic acids *IIA* and *IIIA* (Table V) are also predicted by MNDO to assume planar *trans*-conformations. Clearly, calculations of better quality will be required to treat the rotational isomerism in *IA-III A* more reliably. The MNDO-based optimized geometries, as reported here, may serve as convenient starting points in higher-quality calculations.

In contrast to *I-III*, the MNDO-optimized equilibrium geometry for *IVA* is non-planar, showing large dihedral angles about the C—S and S—O bonds (Table VI). The out-of-plane twist about the latter bond closely resembles that found experimentally for *I* (cf. Table III).

We conclude that sulfenic acids *I* and *IV*, prepared from sulfoxides by flash-vacuum pyrolysis, exist predominantly as the sulfenate forms *A* in the gas phase. This is in agreement with the previous microwave study of *I* (ref.²³) but contradicts other observations concerning *IV* (refs^{18,24}). Unsaturated sulfenic acids *II* and *III*, prepared for the first time in this study, are formed in mixture with other isomers which have not been safely identified. An investigation of the relative stabilities of $\text{C}_2\text{H}_4\text{SO}$ and $\text{C}_2\text{H}_2\text{SO}$ isomers, both neutral and ionic, is in progress and the results will be reported in a future communication.

TABLE VI
MNDO bond lengths (nm) and angles (deg) in *IVA*



IVA

Parameter	<i>IVA</i>	Parameter	<i>IVA</i>
Bonds		Angles	
H ⁰ —O	0.0948	H ⁰ —O—S	109.8
S—O	0.1602	O—S—C ¹	105.3
C ¹ —S	0.1710	C ² —C ¹ —S	118.3
C ¹ —C ²	0.1411	C ³ —C ² —C ¹	120.0
C ² —C ³	0.1405	H ⁰ —O—S—C ¹	263.1
C ³ —C ⁴	0.1406	C ² —C ¹ —S—O	120.3

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