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The Formation and Characterization of Three-Membered Ring Carbanions in the Gas Phase: An Experimental and Theoretical Investigation of the Conjugate Bases of Thiirane, Thiirane *S*-Oxide, and Thiirane *S*,*S*-Dioxide

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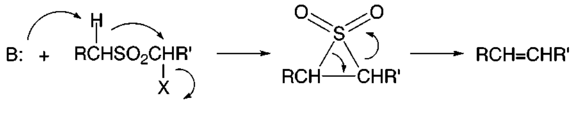
Deprotonation of thiirane, thiirane *S*-oxide, and thiirane *S*,*S*-dioxide was carried out in the gas phase, and the resulting anions were studied through a series of ion−molecule reactions. The cyclic conjugate bases of thiirane (**1b**) and thiirane *S*,*S*-dioxide (**3a**) are formed whereas a facile ring opening isomerization to vinyl sulfenate anion (**2d**, $CH_2{=}CHSO^-$) is observed in the thiirane *S*-oxide case. Vinyl thiolate, the rearrangement product of the conjugate base of thiirane, also is obtained. Proton affinities were determined for **1b**, **2d**, and **3a**. High-level ab initio calculations were also carried out, and the results compared with those obtained from experiment. Orbital arguments are advanced to explain the relative barriers to ring opening for the three anions of interest.

Introduction

Thiiranes,[1] thiirane *S*-oxides,[2] and thiirane *S*,*S*-dioxides[3] have attracted the attention of chemists for years.[4,5] Interest in these compounds derives largely from two sources. First, these species play key roles in a number of important organic transformations, the most notable being the Ramberg−Bäcklund reaction in which a thiirane *S*,*S*-dioxide is formed as an intermediate (eq 1).[6]

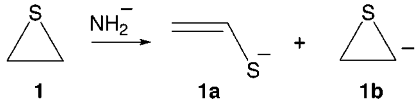


(1)

Second, like other strained ring systems, the study of these species allows the limits of covalent bonding to be explored. The presence of a heteroatom (S) in a variety of oxidation states permits carbon−sulfur as well as carbon−carbon bonding to be investigated.

α-Thio carbanions are synthetically useful reagents and as such have been studied extensively.[7] While some controversy persists, current thinking holds that the considerable stability enjoyed by these carbanions arises largely from the polarizability of a second-row heteroatom.[8,9] Accepting this hypothesis leads to the conclusion that geometrical constraints imposed upon a sulfur-containing substrate should have little impact upon the basicity of an α-thio carbanion. Unlike the first-row oxiranyl and aziridiryl analogues,[10] relatively little is known about the conjugate bases of thiiranes. The synthetic utility of the conjugate bases of thiirane *S*,*S*-dioxides, however, has been recently explored.[11]

In the gas phase, Nibbering et al.[12] have shown that deprotonation of thiirane (**1**) affords vinyl thiolate (**1a**) and small amounts of the cyclic α-thio carbanion (**1b**, eq 2). As this observation was part of a larger study of elimination reactions involving thioethers, no thermodynamic data on **1b** were reported, and its reactivity was not extensively explored. To the best of our knowledge, no gas-phase results have been reported on the conjugate bases of thiirane *S*-oxide or thiirane *S*,*S*-dioxide.



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Few computational studies concerning the anions of thiirane, thiirane *S*-oxide, and thiirane *S*,*S*-dioxide have

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appeared in the literature. Rajyaguru et al.[13] calculated barriers to inversion and ring opening for the thiiranyl anion at semiempirical and ab initio levels of theory. Similar ab initio computations were performed by Maccagnani and co-workers[14] on the cis and trans anions of thiirane *S*-oxide.

The results outlined in this paper come from a systematic gas-phase investigation of the structure and reactivity of the conjugate bases of thiirane, thiirane *S*-oxide, and thiirane *S*,*S*-dioxide. A parallel computational study was also performed to aid in the interpretation of the experimental observations. It is hoped that the present work will address a number of gaps in the literature regarding these unique compounds.[15]

Methods

Experimental. All of the gas-phase experiments were carried out with a variable-temperature flowing afterglow (VT-FA) apparatus or a Fourier transform mass spectrometer (FT-MS). The former device has been described previously in the literature.[16,17] Briefly, ions are generated by electron ionization and are carried down a 1 m long tube by a rapidly moving stream of helium buffer gas ($\bar{\nu}_{\mathrm{He}} = 8-10000$ cm/s, $P \sim 0.4$ Torr). Neutral reagents can then be added to the system at numerous points along the 1 m reaction region, and thus a series of ion−molecule reactions can be carried out. The charged products are subsequently mass filtered and detected via a triple quadrupole conversion dynode/electron multiplier setup. Fluoride (F^-) and amide (NH_2^-) ions, used in the deprotonation of thiirane *S*-oxide, were produced via electron ionization of nitrogen trifluoride (NF_3) and ammonia (NH_3), respectively.

A Finnigan FT-MS model 2001 mass spectrometer was also employed. This instrument consists of two identical, cubic (5 cm/side) cells, separated by a common partition with a 2 mm orifice. The cells are housed within a 3.0 T superconducting magnet and are aligned collinearly with the field. A background pressure of approximately 10^{-9} Torr is maintained in both cells by two Edwards model 160M Diffstak diffusion pumps (pumping speed (air) = 805 L/s), each backed by an Alcatel model 2015 mechanical pump (pumping speed (air) = 4.15 L/s). In a typical experiment, a neutral precursor is pulsed at a pressure of about 10^{-7} Torr into one of the cells and is ionized via electron impact. The resulting ion of interest is isolated by ejecting all other ions with a frequency sweep ("chirp") or stored-waveform inverse Fourier transform (SWIFT)[18] excitation. This ion is then transferred to the other cell where it is allowed to react with neutral gases at static pressures of $10^{-8}-10^{-7}$ Torr. Again, ions of interest can be isolated via chirp or SWIFT excitations and subsequently permitted to undergo ion−molecule reactions. This process can be repeated many times. Thermalization of ions can be partially assured by pulsing an unreactive gas (e.g., Ar) into the cells at pressures up to 10^{-5} Torr. Ions are eventually excited using the "chirp" technique and detected. Dideuterioamide (ND_2^-) and F^-, used in the respective deprotonations of thiirane and thiirane *S*,*S*-dioxide, were generated via electron ionization of ammonia-d_3 (ND_3) and tetrafluoromethane (CF_4).

The following liquid samples were obtained from the Aldrich Chemical Co. and used as supplied unless otherwise noted: thiirane (preparative GC on a 6′ SE-30 column at ~100 °C), CS_2 (Fischer), CH_3OD, C_6H_5F, D_2O (Isotec), CH_3SH, CH_3CH_2SH, $(CH_3)_3CSH$, CH_3SSCH_3, aniline, *p*-fluoroaniline, and acetone oxime. $CF_3CF_2CH_2OD$, CF_3CD_2OD, and CH_3CH_2SD were prepared from the corresponding protic compounds via hydrogen−deuterium exchange with D_2O.[19] Noncondensable impurities were removed by carrying out several freeze−pump−thaw cycles. Gas sources and purities (minimum) were as follows: He (Genex, 99.9995%), Ar (Air Products, 99.9995%), NF_3 (Air Products, 99.0%), CF_4 (Matheson, 99.9%), NH_3 (Linde, 99.995%), ND_3 (Cambridge Isotope Laboratories, 99%), COS (Matheson, 97.5%), $(CH_3)_2NH$ (Matheson, 99.5%), N_2O (Air Products, 99.0%), and SO_2 (Linde, 99.98%). Thiirane *S*-oxide, thiirane *S*,*S*-dioxide, and trimethylsilylthiirane were prepared from standard procedures found in the literature.[20]

Computational. The theoretical approach employed was predicated upon the G2+ method of Gronert.[21] This level of theory has been shown to reproduce accurately anion thermochemistry. Like its G2 predecessor,[22] the G2+ procedure makes use of an additivity scheme whereby a series of simpler and less accurate calculations are combined in an attempt to approximate a more expensive and rigorous level of theory. The modified G2+ scheme used in this study is outlined in the next several paragraphs; where it deviates from the original prescription note has been made.[23]

Optimized structures were obtained at the MP2(fc)/6-31+G(d,p) level of theory.[23a] That these structures corresponded to stationary minima and transition states was verified via the calculation of their respective Hessian matrixes at the same level as used in the optimizations.[23b] These matrixes permitted vibrational analyses to be performed from which zero-point energies (ZPE) and finite-temperature corrections (ΔH) were computed.[24] Individual frequencies were scaled by an empirical factor of 0.9427, while ZPEs were multiplied by 0.9646.[23c,25]

Single-point calculations were carried out at three levels of theory: MP4(SDTQ)/6-311+G (2df,p); QCISD(T)/6-311+G(d,p); and MP2/6-311+G(3df,2p). From these energies, the so-called correlation, ΔE(QCI), and basis set, ΔE(3df,2p), corrections were computed (eqs 3 and 4).

$$\Delta E(\mathrm{QCI}) = E[\mathrm{QCISD(T)/6\text{-}311{+}G(d,p)}] - E[\mathrm{MP4(SDTQ)/6\text{-}311{+}G(d,p)}] \quad (3)$$

$$\Delta E(\mathrm{3df,2p}) = E[\mathrm{MP2/6\text{-}311{+}G(3df,2p)}] - E[\mathrm{MP2/6\text{-}311{+}G(2df,p)}] \quad (4)$$

A "higher-level correction", ΔE(HLC), was also determined from the number of α and β valence electrons (eq 5). The final

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(9) Negative hyperconjugation also has been invoked and is important in the case of $CH_3SCH_2^-$ (see ref 8d and references therein). In this instance, the effect amounts to about half of the stabilization of the sulfur atom relative to a methylene group (i.e., the rotation barrier about the CH_2−S bond is 12.5 kcal/mol, whereas $\Delta\Delta H°_{\mathrm{acid}}$ ($CH_3CH_2CH_3$ − CH_3SCH_3) = 25.4 kcal/mol). In the conjugate base of thiirane negative hyperconjugation cannot be very important since a periplanar arrangement between the CH lone pair and the CH_2−S bond cannot be achieved.

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(19) Residual water in the H/D exchange experiments has no significant effect given the large difference in acidity between D_2O and the deuterated acids.

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(modified) G2+ energy is defined in eq 6. The energy obtained from eq 6 effectively corresponds to that calculated at the QCISD(T)/6-311+G(3df,2p)//MP2(fc)/6-31+G(d,p) level of theory.

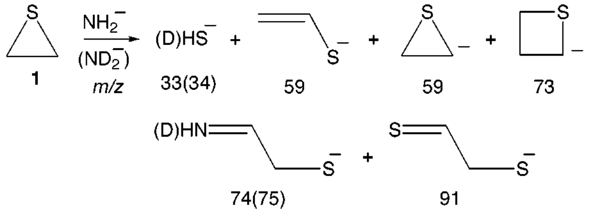
$$\Delta E(\mathrm{HLC}) = -0.00481(\beta) + -0.00019(\alpha) \qquad (5)$$

$$E(\mathrm{G2+}) = E[\mathrm{MP4(SDTQ)/6\text{-}311{+}G(2df,p)}] + \Delta E(\mathrm{QCI}) + \Delta E(\mathrm{3df,2p}) + \Delta E(\mathrm{HLC}) + \mathrm{ZPE} + \Delta H(298\ \mathrm{K}) \qquad (6)$$

All calculations reported in this paper were carried out with the G92/DFT, G94, and GAMESS program suites.[26-28] They were run on a series of UNIX-based IBM and SGI workstations at the University of Minnesota and Cray supercomputers at the Minnesota Supercomputer Institute.

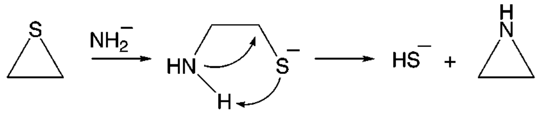
Results

Thiirane. The gas-phase investigations of thiirane (**1**) were carried out primarily with a Fourier transform mass spectrometer because of its MS^n capability. Deprotonation of **1** with NH_2^- or ND_2^- afforded an M − 1 ion (*m*/*z* 59) along with products at *m*/*z* 73, 74 (75 with ND_2^-), and 91 as previously described by Nibbering (eq 7).[11] We also



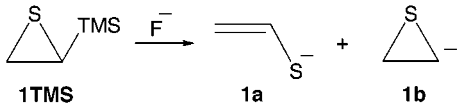
(7)

observed some HS^- (and DS^- when ND_2^- was used), which may arise as shown in eq 8. The M − 1 ion can be



(8)

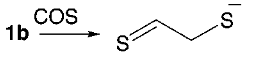
cleanly generated by reacting fluoride with trimethylsilylthiirane (eq 9). In this case, the different neutral precursor leads to different secondary products (eq 10).[29] In either instance, the M − 1 ion consists of a reactive species (**1b**) and an unreactive form (**1a**) as previously proposed by Nibbering et al.[11] For example, some of the



(9)

(10)

M − 1 ion reacts with carbonyl sulfide and carbon disulfide via sulfur-atom transfer (eqs 11 and 12). This is consistent with a reactive carbanionic structure (**1b**) and an unreactive thiolate (**1a**) as the latter species does not react with either of these reagents.



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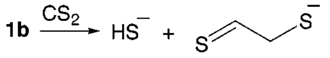


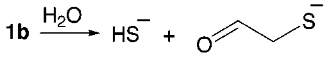
(12)

Table 1. Summary of Proton-Transfer Reactions with the M − 1 Anion of Thiirane (1b)[a]

ref acid (HX)	$\Delta H°_{acid}$ (kcal/mol)	proton transfer	H/D exchange
$(CH_3)_2NH$	396.5 ± 0.7	−	na
D_2O	392.0 ± 0.1	−	−
H_2O	390.7 ± 0.1	−	na
C_6H_5F	387.2 ± 2.5	+	na
CH_3OD	381.9 ± 2.1	+	−

[a] The + and − signs correspond to the occurrence and nonoccurrence, respectively, of the given reaction; na signifies that the reaction is not applicable.

The chemistry associated with the thiiranyl anion was probed further through a series of reactions with acids of varying strength, the results of which are summarized in Table 1.[30] Reaction of the M − 1 anion with methanol-OD led to the observation of methoxide anion. Proton transfer was also observed with fluorobenzene, but not with H_2O or D_2O. In the latter cases, addition−fragmentation products are observed along with the formation of HS^- (eq 13).[31] The least acidic reagent reacted with thiiranyl anion was dimethylamine. While HS^- is formed, dimethyl amide is not observed.



(13)

The observation of proton transfer vis-à-vis the appearance of the conjugate base of C_6H_5F serves to establish a lower limit of 387.2 kcal/mol for the proton affinity (PA) of thiiranyl anion (**1b**). The failure to detect OH^- and $(CH_3)_2N^-$ in the reactions with H_2O and $(CH_3)_2NH$ despite the fact that other reaction products are formed suggests an upper boundary of 396.5 kcal/mol for PA(**1b**); it is unlikely that the reaction with water could be exothermic by more than 5 kcal/mol and not lead to

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(23) All the following pertain to the original G2+ method (see ref 21 for details). (a) Structures are optimized at the MP2(fc)/6-31G(d,p) and MP2(fc)/6-31+G(d,p) levels for the neutral and anionic species, respectively. (b) The Hessian matrixes are calculated at the HF/6-31G-(d,p) and HF/6-31+G(d,p) levels for the neutral and anionic species, respectively. (c) ZPEs are scaled by an empirical factor of 0.9.

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(29) The conjugate base of **1TMS** could be isomerized. It also was noted that the **1b**/**1a** ratio decreases with time; i.e., **1b** apparently reacts with **1TMS** to afford **1a**.

(30) All acidities, unless otherwise noted, come from Lias et al. (Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phy. Chem. Ref. Data* **1988**, *17*, Suppl. 1) or the slightly updated form available on a personal computer, *NIST Negative Ion Energetics Database* (Version 3.00, 1993); NIST Standard Reference Database 19B.

(31) When D_2O is used some DS^- and $C_2H_2DOS^-$ are observed.

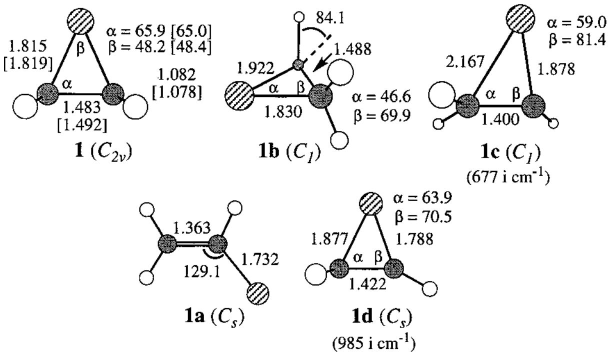

Figure 1. MP2(fc)/6-31+G(d,p) structures for the thiirane system. Bracketed values are from experiment. All structures are minima unless noted (e.g., 677i cm^{-1}). Bond distances and angles are in angstroms and degrees.

the formation of hydroxide ion. A thermoneutral or weakly exothermic process with H_2O might not lead to the formation of HO^-, particularly since it is known that hydroxide ion reacts readily with thiirane,[11] and would account for the failure to observe hydrogen−deuterium exchange. An experimental gas-phase PA of 392 ± 5 kcal/mol can, therefore, be assigned to thiiranyl anion. This contrasts with the much weaker basicity of the thiolate ion **1a** (PA = 348.0 ± 3.0 kcal/mol) previously reported by Zhang and Grabowski.[32]

Ab initio calculations were also carried out on the thiirane system. MP2(fc)/6-31+G(d,p)-optimized structures for the neutral, anions, and transition structures are reproduced in Figure 1. While no experimental data are available for the anionic and transition-state structures, a microwave spectrum exists for thiirane (**1**), the experimental geometric parameters of which are also listed in Figure 1.[33] Even a cursory inspection reveals that the experimentally determined and computed structures for **1** are in excellent agreement, the largest discrepancies being 0.009 Å for the C−C bond and 0.9° in the S−C−C angle. Upon deprotonation of thiirane, a 0.107 Å lengthening of the CH−S bond occurs; this shows the carbene character associated with the methine carbon atom and raises questions with regard to the possibility of α-eliminations. The CH_2−S and C−C bonds remain essentially unchanged. The methine group in the anion (**1b**), moreover, retains a pyramidal structure (84.1°). Mulliken population analysis (see Figure S1 in the Supporting Information) reveals that about two-thirds of the nascent negative charge in the anion resides at the methine carbon atom, while the remainder has been shifted to the sulfur atom.

The enthalpy associated with the deprotonation of thiirane (i.e., the PA of the thiiranyl anion) is calculated at the G2+ level to be 394.4 kcal/mol (Table 2), suggesting that the true value is somewhat on the high side of the experimental measurement (392 ± 5 kcal/mol). The PA for the vinyl thiolate anion (**1a**) at the sulfur atom is predicted at this same theoretical level to be 344.9 kcal/mol, which is in good accord with experiment (348 ± 3 kcal/mol).[32] This nearly 50 kcal/mol PA difference accounts for the vastly different reactivities of these ions.

Table 2. G2+ and Experimental Proton Affinities (PA) for the Anions of Thiirane, Thiirane *S*-Oxide, Thiirane *S,S*-Dioxide, and Related Species[a]

species	G2+	expt
thiirane anion (**1b**)	394.4	392 ± 5
vinyl thiolate (**1a**)	344.9	348 ± 3
cis-thiirane *S*-oxide anion (**2a**)	377.7	−
trans-thiirane *S*-oxide anion (**2b**)	379.3	−
cis-vinyl sulfenate (**2c**)	349.0 (342.8)[b]	−
trans-vinyl sulfenate (**2d**)	350.5 (356.7)[c]	354 ± 3
C1 anion of vinyl sulfenic acid (**4e**)	(365.7)[1]	−
thiirane *S,S*-dioxide anion (**3a**)	367.2	365 ± 2
vinyl sulfinate (**3c**)	332.1[d]	−

[a] All values in kcal/mol. See Figures 1, 5, and 6 for structures. [b] Parenthetical value corresponds to the transoid conjugate acid. [c] Parenthetical value corresponds to the cisoid conjugate acid. [d] **4′** is the conjugate acid.

Transition structures for the two possible conrotatory ring-opening processes were also located. The lower energy structure (**1c**) differs from that of **1b** in that 0.044 and 0.088 Å contractions of the CH−S and C−C bonds have occurred, respectively, while the CH_2−S bond has expanded by 0.337 Å. Over two-thirds of the negative charge has also accumulated on the sulfur atom at this transition state (TS).

Calculations at the G2+ level of theory reveal an enthalpy for the ring-opening process that is exothermic by 49.1 kcal/mol and an activation energy (E_a) of 10.8 kcal/mol. A vibrational frequency along the reaction coordinate of 677i cm^{-1} is also predicted. The computed height of this barrier goes a long way in helping to explain the presence of two M − 1 isomers in the gas phase. While the preponderance of thiiranyl anions possess sufficient internal energy to overcome this barrier, a detectable fraction does not and is stable with respect to this isomerization.

The interconversion of identical thiiranyl anions is accomplished via inversion at the methine center, and a corresponding transition structure (**1d**) was located. The structure is characterized by C_s symmetry in which the methine proton resides within the plane of the ring. Noticeable contractions of the CH−S and C−C bonds are visible; a more modest expansion of the CH_2−S bond is also seen. Somewhat surprisingly, the charge distribution found for this structure is nearly identical to that of **1b**. A barrier to inversion of 26.0 kcal/mol is calculated at the G2+ level, and the TS is predicted to be tighter (985i cm^{-1}) than for that of the ring-opening process. Given the relative energies calculated for the TSs to inversion and ring opening, the thiiranyl anion should be conformationally stable, a fact that has been borne out by studies of substituted thiiranes in solution.[1b] The complete G2+ potential energy surface for the thiiranyl anion is reproduced in Figure 2.

Rajyaguru et al. have calculated E_a's and structures associated with the ring-opening and inversion pathways for the thiiranyl anion.[13] Their transition structures, determined at the HF/6-31+G level, differ significantly from those presented in Figure 1. The largest discrepancies are found for the C−S bonds (0.190 Å too long on average for the HF structures) and S−CH_2−CH angles (7.2° too wide on average for the HF structures). The corresponding E_a's for the inversion and ring-opening reactions, calculated at the MP4/6-31+G//HF/6-31+G level, are 3.8 and 7.1 kcal/mol too big and too small, respectively, relative to the G2+ values.

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(32) Zhang, L.; Grabowski, J. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1819−1821.

(33) Cunningham, G. L., Jr.; Boyd, A. W.; Myers, R. J.; Gwinn, W. D.; Le Van, W. I. *J. Chem. Phys.* **1951**, *19*, 676−685.

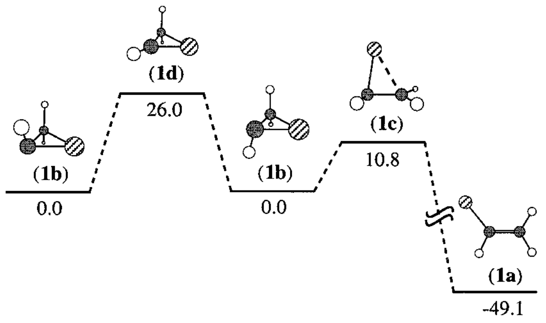


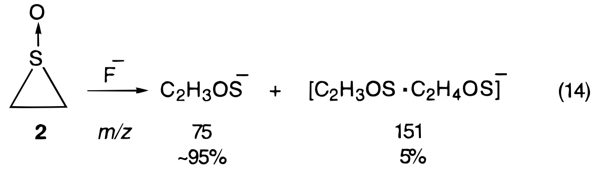
Figure 2. G2+ potential energy surface for the thiirane system. All energies are in kcal/mol.

Table 3. Summary of Proton-Transfer Reactions with the M − 1 Anion of Thiirane *S*-Oxide (2a)[a]

ref acid (HX)	$\Delta H°_{acid}$ (kcal/mol)	proton transfer	H/D exchange
pyrrole	358.7 ± 2.2	−	na
CH_3SH	356.9 ± 2.2	−	na
$CF_3CF_2CH_2OD$	356.7 ± 6.1	+	1 exch (slow)
CH_3CH_2SD	356.5 ± 2.2	+	1 exch (slow)
CH_3CH_2SH	355.2 ± 2.2	+	na
$(CH_3)_3CSH$	352.5 ± 2.2	+	na

[a] The + and − signs correspond to the occurrence and nonoccurrence, respectively, of the given reaction; na signifies that the reaction is not applicable.

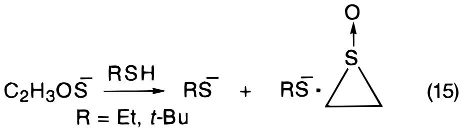
Thiirane *S*-Oxide. The gas-phase investigations of thiirane *S*-oxide (**2**) were conducted primarily within a FA apparatus because of its higher sample throughput. Deprotonation of the neutral precursor was effected with F^- to yield an M − 1 anion (m/z 75). Along with this product, an M·(M − 1) cluster (m/z 151) also is observed (eq 14). Deprotonation of thiirane *S*-oxide using the FT-MS only afforded the M − 1 ion; the m/z 151 cluster was not produced. This result is consistent with the low-pressure regimes typical of FT-MS experiments in which cluster formation is disfavored.



$$\mathbf{2} \xrightarrow{F^-} C_2H_3OS^- + [C_2H_3OS \cdot C_2H_4OS]^- \qquad (14)$$

m/z 75 (~95%), 151 (5%)

Reaction of the M − 1 anion with a number of reagents routinely used in structural determinations (N_2O, CS_2, COS, CH_3SSCH_3) failed to yield products characteristic of a carbanion. A series of acids of increasing strength was then allowed to react with the M − 1 anion. By noting the occurrence or nonoccurrence of proton transfer, the PA associated with the M − 1 anion was bracketed. The results from these reactions are summarized in Table 3. While proton transfer is not observed with pyrrole and methanethiol, the M − 1 anion is capable of deprotonating ethanethiol. A cluster between EtS^- and thiirane *S*-oxide (m/z 138) was also detected (eq 15). In an analogous fashion, reaction with 2-methyl-2-propanethiol leads to *tert*-butylthiolate and a cluster between $t\text{-BuS}^-$ and thiirane *S*-oxide. The facile nature of proton transfer from *t*-BuSH ($\Delta H°_{acid}$ = 352.5 ± 2.2 kcal/mol) and the failure to deprotonate MeSH ($\Delta H°_{acid}$ = 356.9 ± 2.2 kcal/mol) establishes a 4.4 kcal/mol range for the proton affinity of the M − 1 anion. The inefficient nature of proton transfer from EtSH ($\Delta H°_{acid}$ = 355.2 ± 2.2 kcal/mol) serves to narrow this range, suggesting a proton affinity for the M − 1 anion slightly less than that of ethanethiol (i.e., $PA(C_2H_3OS^-)$ = 354 ± 3 kcal/mol). In this regard, it should be noted that O'Hair et al. have recently examined the proton affinity for a related species (HSO^-), its estimated value being approximately 347 kcal/mol.[34]



$$C_2H_3OS^- \xrightarrow[R = Et,\ t\text{-}Bu]{RSH} RS^- + RS^- \cdot \qquad (15)$$

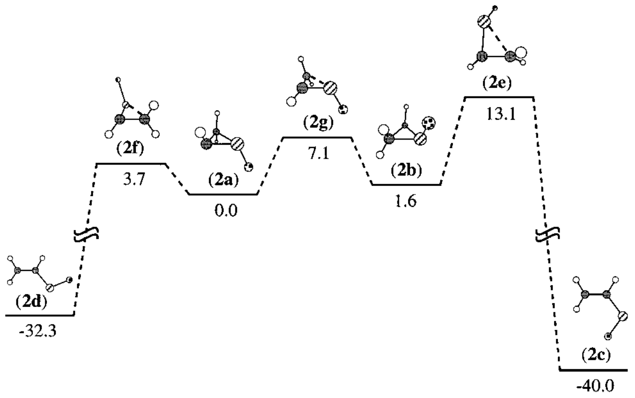


Figure 3. G2+ potential energy surface for the thiirane *S*-oxide system. All energies are in kcal/mol.

Computations were carried out in an attempt to corroborate the experimental PA for the M − 1 anion. Due to the C_s symmetry of thiirane *S*-oxide, two C_1 anions are possible upon deprotonation: one with the methine lone pair cis and the other trans to the sulfoxide group. At the G2+ level, the PAs are within 2 kcal/mol of one another. These computed values (PA(*cis*-thiirane *S*-oxide anion (**2a**)) = 377.7 and PA(*trans*-thiirane *S*-oxide anion (**2b**)) = 379.3 kcal/mol) are troubling in two respects. First, given the PA of F^- (371.5 ± 0.2 kcal/mol), deprotonation *without some subsequent isomerization* should be endothermic by over 5 kcal/mol. Processes that are endothermic by more than 4−5 kcal/mol do not take place in FA experiments where, given the relatively high pressures, ionic species are well-thermalized. Second, if the M − 1 anion was simply the conjugate base of thiirane *S*-oxide, it should be sufficiently basic to deprotonate pyrrole and methanethiol (a process that would be about 20 kcal/mol exothermic), and yet these conjugate bases were not observed.

The immediate inference to be drawn is that the anion does *not* possess a cyclic structure. A probable structure for the anion, suggested by studies of thiirane *S*-oxides in solution,[15] is that of vinyl sulfenate, $CH_2{=}CHSO^-$. Figure 3 reproduces the G2+ potential energy surface for the thiirane *S*-oxide anions. While there is a substantial barrier (11.5 kcal/mol) for ring opening from the trans anion, a much smaller barrier (3.7 kcal/mol) is found for the cis species. The barrier to cis/trans isomerization is, moreover, only 5.5 kcal/mol. The effective barrier to ring opening from the trans anion is thus reduced by 6.0 kcal/mol. When coupled with the extremely exothermic nature of the ring opening processes, an acyclic structure for the

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(34) O'Hair, R. A. J.; DePuy, C. H.; Bierbaum, V. M. *J. Phys. Chem.* **1993**, *97*, 7955−7961

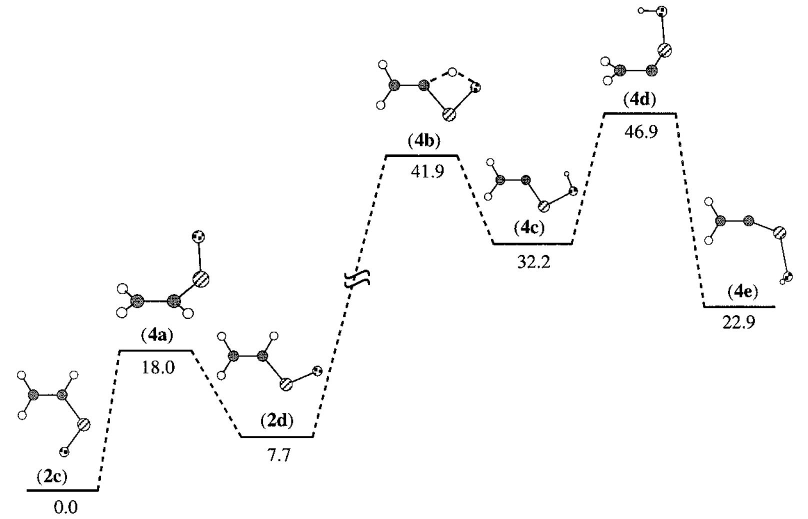


Figure 4. G2+ potential energy surface for the vinyl sulfinyl system. All energies are in kcal/mol.

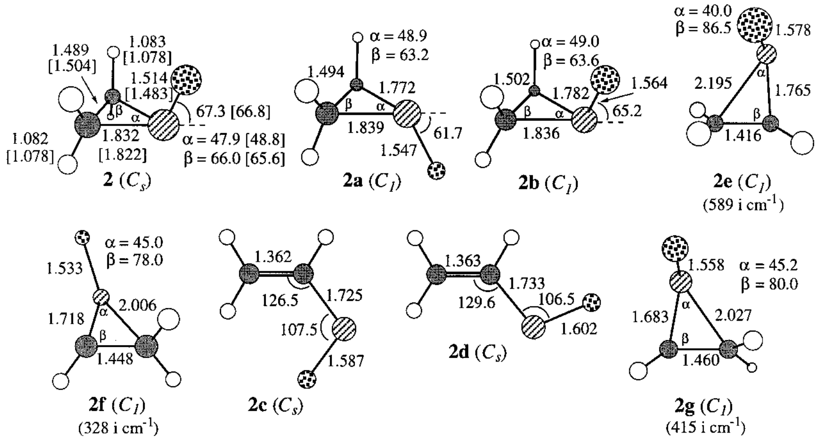


Figure 5. MP2(fc)/6-31+G(d,p) structures for the thiirane *S*-oxide system. Bracketed values are from experiment. All structures are minima unless noted (e.g., 328i cm^{-1}). Bond distances and angles are in angstroms and degrees, respectively.

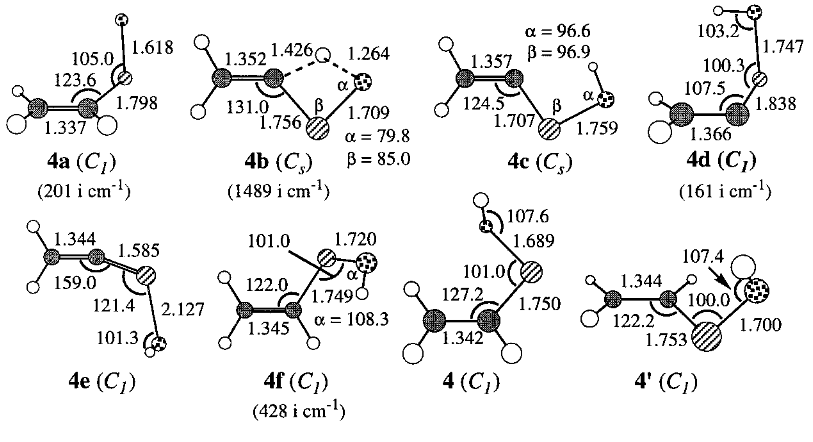
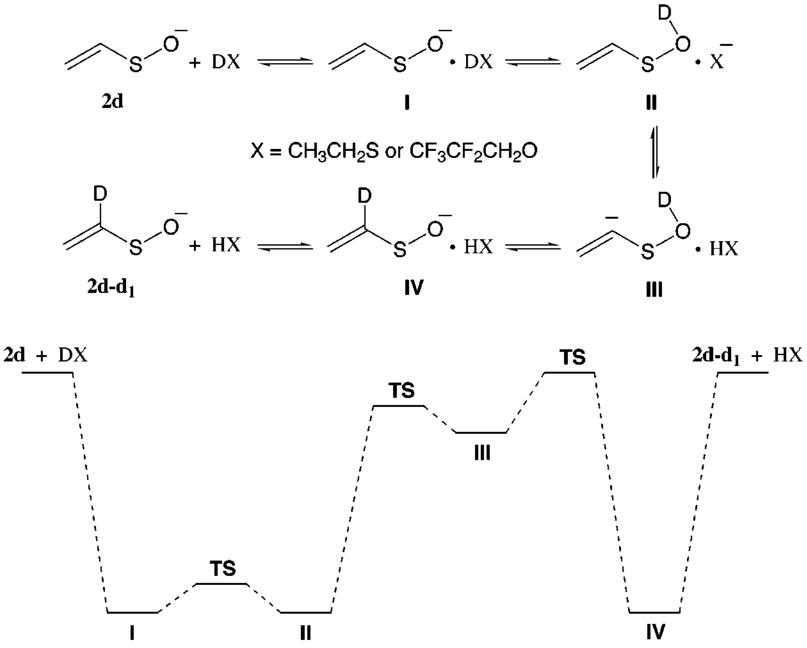


Figure 6. MP2(fc)/6-31+G(d,p) structures for the vinyl sulfinyl system. All structures are minima unless noted (e.g., 201i cm^{-1}). Bond distances and angles are in angstroms and degrees, respectively.

M − 1 anion (specifically, that of vinyl sulfenate) seems more likely than that of a cyclic one (i.e., **2a** or **2b**).

The calculated proton affinities for the vinyl sulfenate anions are also summarized in Table 2. The most stable conformations for the anion (**2c**) and corresponding neutral (**4**) are cisoid with C_s and C_1 symmetries, respectively (Figures 5 and 6). The G2+ proton affinity for the *cis*-sulfenate (**2c**) is 349.0 kcal/mol. While this value is somewhat lower than that determined experimentally (354 ± 3 kcal/mol), the lowest energy pathway for ring opening is predicted to proceed from the *cis*-thiirane *S*-oxide anion through a syn transition structure to the *trans*-vinyl sulfenate anion. A sizable barrier to the interconversion of the *trans*- and the *cis*-vinyl sulfenate anion is calculated at the G2+ level of theory (see **2c** → **2d** in Figure 4). Upon deprotonation of thiirane *S*-oxide, therefore, a relatively stable population of the higher energy *trans*-vinyl sulfenate isomer should result, and

Scheme 1



it is this species PA that is actually being probed in the gas phase. The G2+ PA for *trans*-vinyl sulfenate is computed to be 350.5 kcal/mol for the formation of the transoid conjugate acid (**4′**) and 356.7 kcal/mol for formation of the cisoid (**4**) species. The former value is somewhat lower than that determined experimentally, while the latter is in good accord with that observed (Table 2).

In an attempt to further elucidate the structure of the M − 1 anion, its H/D exchange behavior was examined via a series of reactions with deuterated acids. Reaction with CH_3CH_2SD or $CF_3CF_2CH_2OD$ leads to the slow incorporation of one deuterium into the M − 1 ion. This result is independent of whether F^- or NH_2^- is used to generate the M − 1 ion. Since the computed difference between the cis and trans positions in thiirane *S*-oxide is less than 2 kcal/mol and the less selective base (NH_2^-) also leads to 1 inefficient H/D exchange, it would be difficult to attribute this result to the *cis*- or *trans*-thiirane *S*-oxide anion. These data are consistent with the assigned proton affinity, 354 ± 3 kcal/mol, but at first glance appear to be inconsistent with a sulfenate ion; the most acidic site in vinyl sulfenic acid is at the hydroxyl group, so the conjugate base would not be expected to undergo any H/D exchange.

An explanation for this surprising H/D exchange behavior is outlined in Scheme 1. In the first step of the proposed mechanism, ion−molecule complex I is formed between the exchange reagent (CH_3CH_2SD or $CF_3CF_2CH_2OD$) and *trans*-vinyl sulfenate (**2d**). Formation of such a species is typically exothermic by 20−30 kcal/mol,[35] and it is this decrease in potential energy that drives the reaction process. Deuterium transfer between the exchange reagent and *trans*-vinyl sulfenate to afford II is computed to be essentially thermoneutral. The conjugate base of the exchange reagent can then abstract the C1 proton of vinyl sulfenic acid (**4′**) to yield III, an ion−molecule complex between the C1 anion of vinyl sulfenic acid (**4e**) and HX (X = CH_3CH_2S or $CF_3CF_2CH_2O$). This step is calculated to be endothermic by ∼9.2 kcal/mol; this value is based upon the experimental and G2+ proton affinities for $CH_3CH_2S^-$ and **4e**, respectively, which increases ∼9.3 kcal/mol if the transition is to structure **4c**. Intramolecular isomerization of the vinyl anion back to a *trans*-vinyl sulfenate containing a deuterium atom gives IV. Examination of the G2+ potential energy surface for the free ions (Figure 4) reveals that this isomerization is exothermic by 24.5 kcal/mol. Finally, dissociation of the protonated exchange reagent (HX) and the vinyl sulfenate anion can occur to complete a thermoneutral exchange reaction. The activation energy associated with this mechanism will depend on the barrier to the intramolecular isomerization (III to IV in Scheme 1). Our calculations indicate that the transition structure should be similar in energy to the starting materials, which is consistent with the experimental observation that this reaction is inefficient in the gas phase.[36]

It is worth noting with regard to the above explanation that Squires et al.[37] have observed that it is possible to exchange less acidic sites in an acid with D_2O. This phenomenon, referred to as “extraordinary exchange”, differs from the mechanism detailed in Scheme 1 in one important respect: unlike D_2O, which has two exchangeable deuteriums, the acids used to probe the H/D exchange behavior of the vinyl sulfenate anion have only one. Exchange of the less acidic C1 position of vinyl sulfenate would not be possible if not for an intramolecular isomerization that allows the more basic site to be exchanged.

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(35) Chabinyc, M. L.; Brauman, J. I. *J. Am. Chem. Soc.* **1998**, *120*, 10863−10870.

(36) The cis ion (**2c**) also might exchange if the $\mathbf{4} \rightarrow \mathbf{4'}$ and $\mathbf{2d}\cdot HX \rightarrow \mathbf{2c}\cdot HX$ barriers are not too large. In addition, protonation of I may lead to $\mathbf{4}\cdot X^-$ but the transoid structure in III ($\mathbf{4c}\cdot HX$) is required for isomerization to IV.

(37) (a) Squires, R. R.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 4256−4258. (b) DePuy, C. H.; Bierbaum, V. M. In *NATO ASI Ser., Ser. C., Structure/Reactivity and Thermochemistry of Ions;* Ausloos, P., Lias, S. G., Eds.; D. Reidel Publishing Co.: Boston, 1987; pp 293−303.

MP2(fc)/6-31+G(d,p) structures for thiirane *S*-oxide, its anions and transition structures, and related species are presented in Figures 5 and 6. Comparison of the calculated and experimental structures for thiirane *S*-oxide (**2**) again shows the two to be in good accord with one another.[38] Here, the largest differences are found for the S−O bond (0.031 Å) and C−S−C angle (0.9°). Owing to the presence of two pairs of chemically unique hydrogens, deprotonation of thiirane *S*-oxide leads to two anions: one with the nascent charge cis (**2a**) and the other trans (**2b**) to the sulfoxide group. The cis species shows a 0.060 Å contraction of the CH−S bond, while the S−O bond undergoes a 0.033 Å expansion. The degree to which the sulfoxide group is bent out of the plane in the cis species also decreases by 5.6°. Similar structural changes are seen for the trans anion, although the CH−S and S−O bonds have contracted and expanded to lesser and greater extents, respectively; the sulfoxide group also has flattened out less. Examination of the Mulliken charges (see Figure S2 in the Supporting Information) shows that, while more negative charge is localized at the methine carbon atom in the trans anion, both species have shifted significant electron density to the sulfoxide group, specifically the sulfur atom. Negative charge has also been transferred to a lesser degree to the methylene carbon atom in both anions. These changes in charge density result in ylidic ($S^+ \rightarrow O^-$) structures for the anions that are less pronounced than for their neutral precursor.

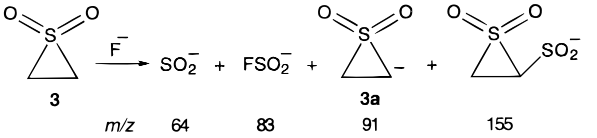
Interconversion between the cis and trans anions is accomplished via a C_1 transition structure (**2g**). The structure possesses a vibrational frequency along the reaction coordinate (corresponding to movement of the methine proton through the plane of the ring) of 415i cm^{-1}. Interestingly, this structure is quite similar to those found for the ring openings; the CH−S bond has contracted to 1.683 Å, while the CH_2−S bond has expanded to 2.027 Å. The anion appears to undergo a partial ring opening so as to facilitate inversion at the methine position. Appreciable negative charge remains localized at the methine carbon atom, the balance having been transferred to the sulfur and carbon atoms of the sulfoxide and methylene groups. Interconversion of the two thiirane *S*-oxide anions could also occur through inversion of the sulfoxyl group. This is unlikely given that a 73.6 kcal/mol (MP2/6-31+G(d)//HF/6-31+G(d)) barrier to inversion via the sulfoxide group exists for thiirane *S*-oxide.

Actual ring opening proceeds through two conrotatory transition structures. The reader should be aware that, given the C_1 symmetry of the two anions, four conrotatory transition structures are possible. Protracted attempts to locate the other two transition structures were unsuccessful. This result is consistent with previous findings by Maccagnani et al.[14] and may represent an extreme case of torqoselectivity[39] (see the Discussion section below). The anti TS is tighter by 261i cm^{-1} than the corresponding syn TS and shows greater lysis of the CH_2−S bond. The largest structural differences between the anti (**2e**) and syn (**2f**) transition structures can be seen for the CH−S and C−C bonds. Greater contraction of the CH−S bond has occurred in the syn transition structure (−0.054 Å (**2e**) vs −0.017 Å (**2f**)), while the situation is reversed for the C−C bond (−0.086 Å (**2e**) vs −0.046 Å (**2f**)). These features serve to highlight the highly asynchronous nature of these ring-opening processes. In both transition structures, negative charge is shifted to the sulfur atom of the sulfoxide group, the transfer being slightly more advanced in the syn TS. Analysis of the Mulliken charges for the *cis*- (**2c**) and *trans*-vinyl sulfenates (**2d**) reveals that well over two-thirds of the negative charge ends up localized on the sulfur atom and less than one-tenth on the oxygen atom of the sulfoxyl group.

Maccagnani et al.[14] have previously reported results from an ab initio investigation of the potential energy surface associated with the thiirane *S*-oxide anion. Structures were determined at the HF/3-21+G(d[S]) level, and MP2/3-21+G(d[S]) single-point energies were subsequently computed.[40] These structures differ, at times significantly, from those presented in the current study at the MP2(fc)/6-31+G(d,p) level, the largest discrepancies involving C−S bonds. Comparison of **2a** and **2b** from the two levels of theory reveals a mean absolute difference of 0.058 Å, the CH−S and CH_2−S bonds being too long and short, respectively, in the Hartree−Fock (HF) structures. These differences in C−S bond lengths widen to 0.078 and 0.085 Å for the ring opening and inversion transition structures, respectively. The C−S bonds in the former structures are too long at the HF level; the C−C bonds are, moreover, too short. The CH_2−S bond in the HF/3-21+G(d[S]) transition structure for inversion is appreciably shorter (0.161 Å) than that found for the MP2(fc)/6-31+G(d,p) structure. The HF and MP2 structures for the vinyl sulfenates are in much better agreement with one another in that none of the bond lengths vary by more the 0.029 Å.

The MP2/3-21+G(d[S]) and G2+ potential energy surfaces share the same gross topological features. The most notable differences between the two surfaces are as follows. (1) The MP2 TSs for ring opening from the cis and trans anions (0.8 and 8.1 kcal/mol, respectively) are lower in energy than their G2+ counterparts (syn TS = 3.7 and anti TS = 13.1 kcal/mol). (2) The MP2 barriers to ring opening and inversion from the trans anion are of comparable heights (8.1 and 7.6 kcal/mol, respectively). A 6.0 kcal/mol differential (E_a(ring opening) > E_a(inversion)) exists at the G2+ level. (3) The MP2 enthalpies for the ring-opening reactions (syn pathway = −48.9 and anti pathway = −52.0 kcal/mol) are appreciably more exothermic than the G2+ values (syn pathway = −32.3 and anti pathway = −40.0 kcal/mol).

Thiirane *S*,*S*-Dioxide. Due to its nonvolatile nature, all of the gas-phase experiments upon thiirane *S*,*S*-dioxide (**3**) were carried out with our FT-MS. Reaction of F$^-$ with thiirane *S*,*S*-dioxide affords the conjugate base of **3** (**3a**, *m/z* 91) along with small amounts (<5%) of SO_2^- (*m/z* 64), FSO_2^- (*m/z* 83), and $C_2H_3S_2O_4^-$ ([adduct − C_2H_4]$^-$, *m/z* 155, eq 16). Carbon disulfide reacts with **3a** to generate [adduct − SO_2]$^-$ (*m/z* 103), HC≡CS$^-$, and a



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[38] Saito, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 663−666.

[39] Houk, K. N. In *Strain and Its Implications in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; Kluwer Academic Publishers: Boston, 1989; pp 25−37.

[40] The 3-21+G(d[S]) basis set possesses a single set of d-polarization functions on only the S atoms.

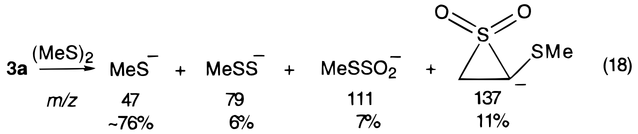
Table 4. Summary of Proton-Transfer Reactions with the M − 1 Anion (3a) of Thiirane *S,S*-Dioxide[a]

ref acid (HX)	ΔH°_{acid} (kcal/mol)	proton transfer[b]	
		forward	reverse
t-BuOD	374.6 ± 2.1	−[c]	na
HF	370.9 ± 0.2	na	+
Et_2NOH	370.6 ± 2.1	−	na
$C_6H_5NH_2$	366.4 ± 2.1	+ (slow)	+
p-$FC_6H_4NH_2$	364.3 ± 2.1	+	+ (slow)
CF_3CH_2OD	361.8 ± 2.5	+	−

[a] The + and − signs correspond to the occurrence and nonoccurrence, respectively, of the given reaction; na signifies that the reaction is not applicable. [b] HX + **3a** corresponds to the forward direction, and X^- + **3** represents the reverse pathway. [c] Three H/D exchanges were observed.

little HS^- (eq 17). Dimethyl disulfide also reacts with the thiirane *S,S*-dioxide anion to give MeS^- (*m*/*z* 47), $MeSS^-$ (*m*/*z* 79), $MeSSO_2^-$ (*m*/*z* 111), and [adduct − MeSH]$^-$ (*m*/*z* 137, eq 18). Both of these transformations are consistent with the carbanionic structure of **3a**. Moreover, **3a** undergoes 3 hydrogen−deuterium exchanges with *t*-BuOD as expected for the conjugate base of an acid with 4 chemically equivalent hydrogens.

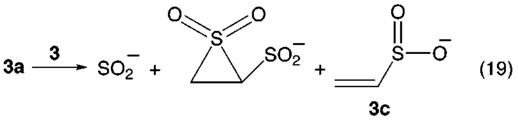
$$\begin{array}{lccccc} \mathbf{3a} \xrightarrow{CS_2} & HS^- & + & HC{\equiv}CS^- & + & CH_2{=}CHCS_2^- \\ m/z & 33 & & 57 & & 103 \\ & \sim5\% & & 12\% & & 83\% \end{array} \qquad (17)$$



(18)

To determine the PA of the conjugate base of thiirane *S,S*-dioxide, a number of acids of varying strength were allowed to react with it. The results of these reactions are summarized in Table 4. Likewise, the reverse direction in which a series of anions interact with thiirane *S,S*-dioxide also was examined. Since proton transfer takes place in both the forward and reverse directions with aniline and *p*-fluoroaniline and the endothermic (slow reaction) direction was determined, we can assign PA(**3a**) = 365 ± 2 kcal/mol; it is interesting to note that in the forward (HX + **3a**) and reverse (**3** + X^-) directions of the acid−base reactions, products of the form XSO_2^- are observed.[41] The intensity of these species track with the thermicity of the proton-transfer reaction, that is, XSO_2^- is more abundant in the energetically less favorable (forward or reverse) direction. This serves as a check of our assigned proton affinity as does the calculated value (367.2 kcal/mol, Table 2).

Thiirane *S,S*-dioxide (**3**) undergoes a secondary reaction with **3a** to afford SO_2^- and [adduct − C_2H_4]$^-$, but these products appear to be minor compared to **3c**, the ring opened isomer of **3a** (eq 19). Formation of **3c** is easily



(19)

detected since it does not react with any of the reference acids or probe reagents used. From our very limited data, PA(**3c**) ≤ 362 kcal/mol can be assigned, which is consistent with the predicted value of 332.1 kcal/mol at the G2+ level. The formation of this ion can be stopped by transferring **3a** immediately after it is formed to the second cell in the FT-MS where **3** is not present.

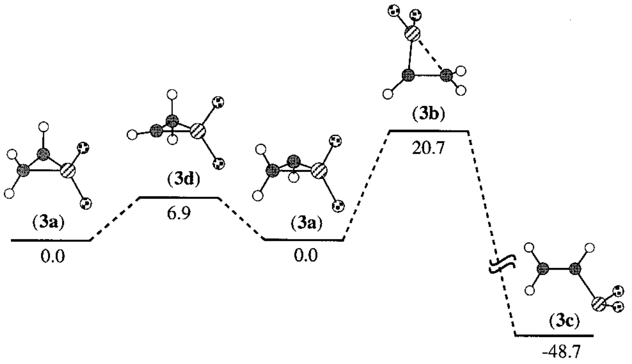


Figure 7. G2+ potential energy surface for the thiirane *S,S*-dioxide system. All energies are in kcal/mol.

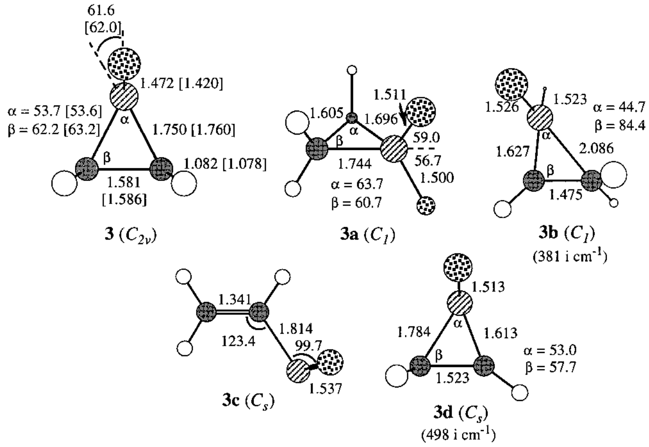


Figure 8. MP2(fc)/6-31+G(d,p) structures for the thiirane *S,S*-dioxide system. Bracketed values are from experiment. All structures are minima unless noted (e.g., 381i cm^{-1}). Bond distances and angles are in angstroms and degrees.

The G2+ potential energy surface for the thiirane *S,S*-dioxide anion is illustrated in Figure 7. While the enthalpy associated with the ring opening process is exothermic by 48.7 kcal/mol, a sizable barrier (20.7 kcal/mol) is present. Once again, attempts to locate a second conrotatory transition structure proved fruitless. The height of this barrier helps to explain the structural stability of **3a**. A modest barrier of 6.9 kcal/mol for inversion at the methine position is also found.

MP2(fc)/6-31+G(d,p) structures for the neutral, anions, and transition structures are given in Figure 8. While generally good agreement is still found between the experimental and computed structures for thiirane *S,S*-dioxide (**3**), an appreciable discrepancy (0.052 Å) has arisen in the S−O bond.[42] Upon deprotonation of the C_{2v} neutral, a C_1 anion (**3a**) results. With the exception of minor changes in the CH−S and S−O bonds, the neutral and anion structures are geometrically quite similar. Over half of the nascent negative charge remains at the methine center, the remainder having been partitioned nearly equally between the methylene and sulfonyl groups (see Figure S3 in the Supporting Information).

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[41] In the reaction of **3a** with Et_2NOH, SO_2^- is the major product, presumably because of the extra stability of Et_2NO.

[42] Kim, H, *J. Chem. Phys.* **1972**, *57*, 1075−1077.

Table 5. Physical and Thermodynamic Properties Associated with Thiirane, Thiirane *S*-Oxide, and Thiirane *S*,*S*-Dioxide[a]

	compd			
	1	**2** (cis)	**2** (trans)	**3**
$\Delta H°_f$[b]	19.6	−7.0	−7.0	−60.0
$\Delta H°_{acid}$	394.4	377.7	379.3	367.2
$q(S)_{neutral}$	−0.13	0.73	0.73	1.26
$q(S)_{anion}$	−0.45	0.39	0.54	1.15
$\mu_{neutral}$	2.34	5.07	5.07	5.58
μ_{anion}	3.45	2.42	4.80	3.26

[a] The heats of formation ($\Delta H°_f$) and acidities ($\Delta H°_{acid}$) are in kcal/mol, charges (q) are in electrons, and dipole moments (μ) are in debye. With the exception of the heats of formation, all values were obtained via calculations at the modified G2+ level of theory (see text for details). [b] Reference 30.

The transition structure for ring opening (**3b**) shows noticeable contractions in the C−C and CH−S bonds; appreciable expansion of the CH_2−S bond is also seen. As dramatic as these geometric changes are, reorganization of the charge distribution at the TS is even more striking. About two-thirds of the negative charge has been transferred to the sulfonyl group. Interconversion of identical thiirane *S*,*S*-dioxide anions is once again accomplished via inversion of the methine proton. A C_s transition structure (**3d**) has been located that differs widely from the geometries of the anions it connects. Significant contractions of the C−C and CH−S bonds (0.082 and 0.083 Å, respectively) are registered at the TS to inversion which is itself a little more than 100i cm^{-1} tighter than that determined for ring opening. The transition structure for inversion also differs from that for ring opening in that little in the way of reorganization of the charge distribution has occurred.

Discussion

One measure of an anion's stability is its proton affinity. That α-substitution by a sulfur atom confers additional stability upon carbanions is well-documented.[8,16] For example, on the basis of the results from gas-phase experiments, a PA of 415.6 ± 2.0 kcal/mol has been estimated for *n*-propyl anion ($CH_3CH_2CH_2^-$),[43] whereas the corresponding value for the conjugate base of dimethyl sulfide is 390.2 ± 1.5 kcal/mol. Sulfur substitution thus leads to a 25.4 kcal/mol stabilization. Similar substitution by an oxygen atom drops the PA by only 8.6 kcal/mol (PA($CH_3OCH_2^-$) = 407.0 ± 2.0 kcal/mol), but in this case the effect is quite variable and stabilization does not always result.

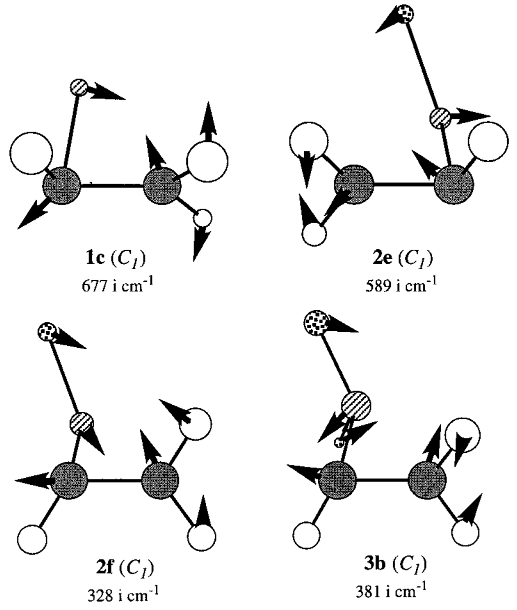
1c (C_1) 677 i cm^{-1} **2e** (C_1) 589 i cm^{-1} **2f** (C_1) 328 i cm^{-1} **3b** (C_1) 381 i cm^{-1}

Figure 9. Graphical representation of the displacement vectors for the ring-opening transition structures **1c**, **2e**, **2f**, and **3b**. Vibrational frequencies were determined at the MP2-(fc)/6-31+G(d,p) level of theory.

In the present context, a monotonic decrease in PA is seen with increasing oxidation of the sulfur atom of thiirane. This increase in anion stability, as reflected in lower PA values, can be largely attributed to electrostatic effects (Table 5). The ability of the anions to delocalize negative charge to the more electronegative sulfur atom is inductively stabilizing. This becomes more important as the oxidation state of sulfur increases since the sulfur becomes more electron deficient. Likewise, there is an increase in the dipole moment, and thus, charge-dipole interactions (field effects) are enhanced. When these two factors are coupled with an increased potential for polarization of the substituent (SO_2 > SO > S), the observed trend in PAs is easily explained. It is interesting to note that the experimental PAs for the acyclic analogues of the anions of thiirane, thiirane *S*-oxide, and thiirane *S*,*S*-dioxide are only lower by 1.4−4.2 kcal/mol (PA($CH_3SCH_2^-$) = 390.2, PA($CH_3SOCH_2^-$) = 373.5, and PA($CH_3SO_2CH_2^-$) = 365.8 kcal/mol). The implication is that arguments involving ring strain or rehybridization are not particularly important to the explanation of the calculated PAs for the cyclic anions.

Anion stability may also be gauged in terms of the ease with which they undergo unimolecular isomerizations. On the basis of the above experimental results, the M − 1 anion of thiirane *S*-oxide is least stable with respect to ring opening; no evidence for a cyclic anion was obtained, and the results are entirely consistent with those of a sulfenate anion. Deprotonation of thiirane leads to both cyclic and acyclic anions. The conclusion to be drawn is that the thiirane anion lies at the margin of anion stability. Finally, the M − 1 anion of thiirane *S*,*S*-dioxide exhibits the greatest degree of stability in that no evidence for unimolecular ring opening was uncovered.

Further insight into these experimental observations can be gained from the ab initio calculations. The E_a's computed for the ring-opening processes support the above experimental trend. At the G2+ level of theory, barriers of 3.7, 10.8, and 20.7 kcal/mol were calculated for the *cis*-thiirane *S*-oxide, thiirane, and thiirane *S*,*S*-dioxide anions, respectively. All three isomerizations share the same driving force: the lysis of the CH_2−S bond (Figure 9). The energy required to break this bond is offset by the relief of ring strain, formation of a C−C double bond, and the transfer of the formal negative charge from the relatively electropositive methine group to that of the substituent.[44] The net result is an enthalpy of reaction that is highly exothermic (−40 to −50 kcal/mol at the G2+ level). In specific terms of relief of ring strain and delocalization of negative charge, the pathway associated with the thiirane *S*-oxide anion should be most

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(43) (a) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968−1973. (b) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051−4053.

preferred enthalpically. In actuality, the isomerization energy of the thiirane anion is computed to be as favorable because it is destabilized relative to the thiirane S,S-dioxide anion. All three ring openings also are entropically favored, but examination of the vibrational frequencies along the reaction coordinates (Figure 9) reveals that the TS corresponding to the thiirane S-oxide anion is loosest and thus should be preferred in this regard. All three pathways are clearly conrotatory in nature, and yet they show varying degrees of asynchronicity. This asynchronous behavior is revealed by the extent to which breakage of the CH_2-S bond foreshadows actual conrotation and in the differential rates of rotation for the methylene and sulfoxyl/sulfonyl groups.

The computed E_a's can be rationalized by examining the changes in structure and charge distribution of the transition structures. In a general sense, the barriers to ring opening can be explained via an appeal to the "principle of least motion";[45] i.e., those processes exhibiting the smallest changes in nuclear position and electronic configuration should be kinetically favored. On the basis of these criteria, the closest similarity between an anion and a transition structure is seen for the thiirane S-oxide system. Only a 0.167 Å elongation of the CH_2-S bond is required at the TS, compared with 0.337 and 0.342 Å increases at the thiirane and thiirane S,S-dioxide TSs, respectively. While roughly comparable changes in the CH$-$S bonds are seen in the three TSs, larger differences exist with respect to contraction of the C$-$C bond: 0.046, 0.088, and 0.130 Å for the thiirane S-oxide, thiirane, and thiirane S,S-dioxide transition structures, respectively.

Similar trends with respect to charge distributions are also seen (see Figures S1$-$S3 in the Supporting Information). In particular, the Mulliken charges indicate that reorganization of the charge density is greatest at the TS for the thiirane S,S-dioxide anion and least for the *cis*-thiirane S-oxide anion. Increases in the negative charge of 0.09, 0.25, and 0.32 electrons on the sulfur substituent (SO, S, and SO_2) have occurred in the thiirane S-oxide, thiirane, and thiirane S,S-dioxide TSs, respectively. Likewise, 0.10, 0.22, and 0.29 electron decreases are observed on the methine groups in the thiirane S-oxide, thiirane, and thiirane S,S-dioxide transition structures.

The careful reader will no doubt have noticed that the foregoing discussion has carefully avoided the barrier to ring opening associated with the *trans*-thiirane S-oxide anion. At the G2+ level of theory, a barrier of 13.1 kcal/mol was found, a value intermediate to those determined for the thiirane (10.8 kcal/mol) and thiirane S,S-dioxide (20.7 kcal/mol) anions. This result would appear at first glance to be inconsistent with experiment (i.e., given that the thiiranyl anion is observed and that its TS lies 2.3 kcal/mol below that predicted for the trans anion of thiirane S-oxide, why is **2b** not observed in the gas phase?) The answer rests with the relatively low (5.5 kcal/mol) and loose (415i cm^{-1}) TS to interconversion of the *trans*- to the *cis*-thiirane S-oxide anion via inversion of the methine center. Given that the calculated G2+ PAs for the two species are within 2 kcal/mol of one another, deprotonation of the neutral precursor at both sites is likely to occur. The cis isomer readily ring opens to the sulfenate, while the trans anion presumably first undergoes inversion, followed by ring opening.

Examination of the required changes in structure and charge distribution for the *trans*-thiirane S-oxide anion at its respective TS for ring opening reveals that it occupies a position intermediate to those of the thiirane and thiirane S,S-dioxide anions. While reorganization of the charge density is clearly greatest for this species (+0.33, $-$0.20, and $-$0.14 electron at the sulfoxyl, methine, and methylene positions, respectively), the structural changes (+0.359 and $-$0.086 Å in the CH_2-S and C$-$C bonds, respectively) closely approximate those found for the thiirane system.

While the principle of least motion yields a phenomenological rationalization of the computed barrier heights, it fails, nevertheless, to provide the kind of insight into their origin offered by an orbital argument. Stabilization of the ring opening TSs is promoted through formation of the C$-$C π bond. In principle, this bond can be formed via rotation of the methylene group in one of two directions (clockwise or counterclockwise) as shown in Figure 10. As illustrated, counterclockwise rotation initially decreases overlap between the lone pair π orbital and the rear lobe of the CH_2-S σ^* orbital and is thus destabilizing. Clockwise rotation, on the other hand, steadily increases overlap and results in a stabilizing interaction. As a consequence, TSs that show clockwise rotation of the methylene group are predicted to be lower in energy than their counterclockwise partners. For the thiirane S-oxide (cis and trans) and thiirane S,S-dioxide systems, only TSs characterized by clockwise rotation were located. Attempts to find the corresponding TSs with counterclockwise rotation were unsuccessful as the methine group typically inverted. While a TS with counterclockwise rotation for the thiirane system was found, it proved to be 12.4 kcal/mol higher in energy at the MP2//HF level than its clockwise analogue.[46] It is also interesting to observe that the barrier to inversion at this same level of theory (23.3 kcal/mol) is higher in energy than both ring opening TSs. The barriers to inversion for the thiirane S-oxide and thiirane S,S-dioxide systems are significantly lower in energy than that of the thiirane. These differences in relative energy may help to explain why searches for the second conrotatory transition structures for the thiirane S-oxide and thiirane S,S-dioxide systems proved fruitless.

Orbital symmetry arguments dictate that the ring-opening processes occur in a conrotatory fashion. It is this demand for conservation of orbital symmetry that yields an explanation of the relative ordering of the E_a's. Maccagnani et al.[14] have noted that the conrotatory ring opening of the *cis*-thiirane S-oxide anion (**2a**) results in the rotation of the sulfoxyl group *away* from the thiiranyl ring (Figure 10). Consequently, a number of antibonding

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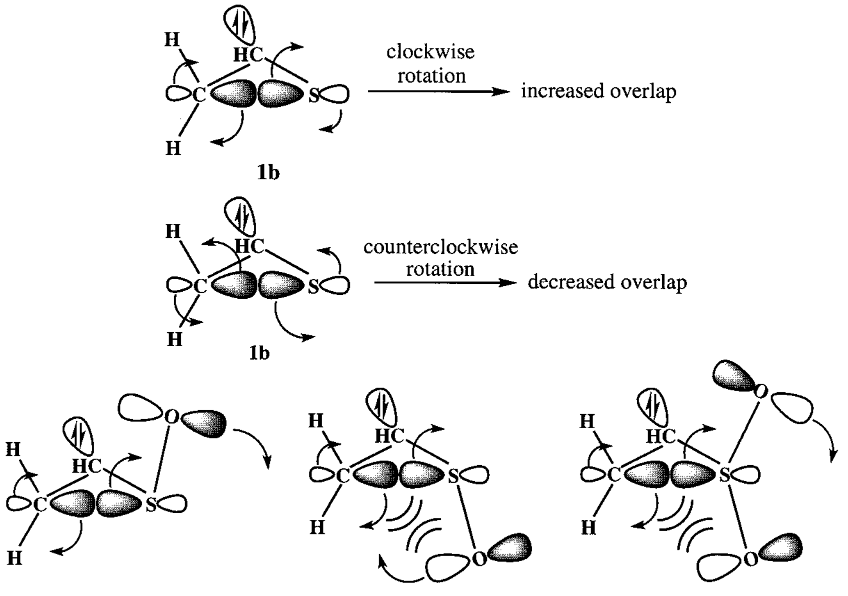
[44] As the experimental heats of formation for thiirane, thiirane S-oxide, and thiirane S,S-dioxide are known, it is possible to estimate their ring strain via a group equivalency scheme. Using the system of Benson, ring strains of 19.4, 22.8, and 25.1 kcal/mol are derived for thiirane, thiirane S-oxide, and thiirane S,S-dioxide, respectively. See: Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279$-$324.

[45] Rice, F. O.; Teller, E. *J. Chem. Phys.* **1938**, *6*, 489$-$496.

[46] At the MP2/6-31+G(d)//HF/6-31+G(d) (ZPE and finite-temperature corrected) level, the other conrotatory ring opening TS lies 21.3 kcal/mol in energy above the thiirane anion and 10.8 kcal/mol above structure **4**. The associated vibrational frequency along the reaction coordinate is 1236 i cm^{-1}. Structural parameters are as follows. Bond lengths (Å): $CH_2-S = 2.210$; $CH-S = 1.800$; $C-C = 1.409$; bond angles (degrees): $C-S-C = 39.5°$; $S-CH-CH_2 = 86.2°$; $S-CH_2-CH = 54.3°$.



1b

1b

2a 2b 3a

Figure 10. Principal orbitals associated with the conrotatory ring-opening transition states (**1b**, **2a**, **2b**, and **3a**). The G2+ barriers are 10.8 (**1b**), 3.7 (**2a**), 13.1 (**2b**), and 20.7 (**3a**) kcal/mol.

interactions between the $CH_2{-}S$ σ orbital and π orbitals on the oxygen atom of the sulfoxyl group are avoided. The analogous conrotatory process for the *trans*-thiirane *S*-oxide (**2b**) forces the sulfoxyl group to rotate *toward* the thiiranyl ring (in order to maximize the carbon lone-pair/$CH_2{-}S$ σ^* overlap), and the above antibonding interactions are thus enhanced. An identical situation exists for the thiirane *S*,*S*-dioxide system only in this case one of the oxygen atoms must rotate toward the ring in either conrotatory process. The origin of the barrier to ring opening for the thiirane anion arises from the unfavorable interaction between the lone-pair electrons on the sulfur atom and the $CH_2{-}S$ σ bond. While this overlap is not as unfavorable as that associated with the p-orbitals of the sulfoxyl and sulfonyl groups, it is, nonetheless, greater than that for the lone-pair electrons on the sulfur atom of the sulfoxyl group. This leads to a barrier for ring opening of the thiirane anion that is intermediate to those of the *cis*- and *trans*-thiirane *S*-oxide anions.

The magnitude of these unfavorable orbital interactions determines in part the relative ordering of the barriers along the ring-opening reaction coordinates. A larger destabilizing contribution is made to the $CH_2{-}S$ σ molecular orbital by the π atomic orbitals of the sulfonyl group than by those of the sulfoxyl group. As oxidation of the thiiranyl anion appears to be intrinsically destabilizing vis-à-vis conrotatory ring opening (i.e., the E_a corresponding to ring opening increases with increasing oxidation), the extent of the unfavorable antibonding interactions offers an explanation of the experimental observations and the computed barrier heights. A great deal of the asynchronicity associated with these ring openings can also be understood in terms of these antibonding interactions. The degree to which breakage of the $CH_2{-}S$ bond foreshadows the conrotatory process is directly related to the potential for antibonding interactions in the system (see the above discussion regarding the TS to ring opening for the *trans*-thiirane *S*-oxide anion).

Conclusions

Thiirane, thiirane *S*-oxide, and thiirane *S*,*S*-dioxide were deprotonated in the gas phase, and the reactivity and thermochemistry of the resulting anions studied. The results indicate that a facile isomerization via a ring-opening mechanism occurs for the $M - 1$ anion of thiirane *S*-oxide, while the analogous process for the anion of thiirane *S*,*S*-dioxide was not detected. Evidence for the existence of vinyl thiolate and thiiranyl anion was also obtained. As such, PAs for the thiirane, thiirane *S*,*S*-dioxide, and vinyl sulfenate anions were determined. High-level ab initio calculations were carried out and compared with the experimental observations. Computed structures and PAs were offered in support of the gas-phase results. Estimates of E_a's for the ring-opening and inversion processes were made, and arguments based upon the principle of least motion and conservation of orbital symmetry were advanced to explain the calculated barriers along the various reaction coordinates.

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Supporting Information Available: Mulliken charges for the thiirane, thiirane *S*-oxide, and thiirane *S*,*S*-dioxide systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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