Gas Phase Reactions of Methyloxirane with HO^- and Methylthiirane with HO^- and HS^-. An *Ab Initio* Study of Addition and Elimination

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For the title reactions, high-level *ab initio* calculations (MP2/6-31+G**//MP2/6-31+G*) were used to characterize the potential energy surfaces for nucleophilic addition at carbon (C_1 or C_2) and E2 elimination (anti or syn). In accord with gas phase experiments, elimination is slightly favored over addition when HO^- is the nucleophile. In all the HO^--induced eliminations, the constraints of the 3-membered ring do not allow for periplanar transition states. When HS^- is used, the barrier to elimination is high and addition is the only viable pathway. Attack at the sulfur of thiirane (desulfurization) was also investigated for HO^- and HS^-. Asynchronous reactions with relatively large barriers are observed, and surprisingly, a stable, hypervalent sulfur intermediate is present in the reaction of HO^- with thiirane. To assess the effects of ring strain, calculations were also completed on the corresponding reactions of acyclic analogs ($CH_3CH_2OCH_3$ and $CH_3CH_2SCH_3$). Although the additions of HO^- involve early transition states, the calculations suggest that ~75% of the ring strain is released at the transition state. Because the HO^--induced eliminations are E1cb-like, much less ring strain (~30%) is released at the transition state. In contrast, the HS^--induced eliminations have relatively late transition states and a larger portion of the ring strain is released.

Introduction

Small ring heterocycles display more diverse reactivity than their acyclic analogs because the inherent strain weakens bonds and opens new reaction pathways.[1] For example, although ethers rarely undergo S_N2 reactions, nucleophilic addition to oxiranes is well-known and has been exploited in a number of synthetic schemes;[2] the ~25 kcal/mol of strain in the three-membered ring overcomes the disadvantage of a highly basic leaving group. When strong, non-nucleophilic bases are used, alkyl substituted oxiranes instead undergo elimination reactions to yield allylic alcohols.[3,4] Work by Rickborn[4] and co-workers suggests that the eliminations are stereo-, and regioselective, and have a preference for forming trans alkenes by deprotonation of the least substituted carbon. In addition, deuterium-labeling experiments indicate that the transition state adopts a syn conformation.[4b,c]

The sulfur analog, thiirane, has ~20 kcal/mol of ring strain and also undergoes a wide variety of reactions with nucleophiles.[1,2] The most common one is nucleophilic attack at a ring carbon to give an addition product; however, alkyllithiums are known to attack thiiranes at sulfur to yield an alkene and the lithium salt of an alkyl thiolate.[5] Little work has been reported on the reactivity of alkylthiiranes with strong, non-nucleophilic bases, but elimination has been observed in systems activated at a β-carbon.[3c,6]

In recent years, gas phase studies have played an important role in investigating the mechanisms of eliminations, substitutions, and other nucleophilic processes. In the absence of solvation and ion pairing effects, the potential energy surface is only dependent on the reaction partners. As a result, it is possible to generate definitive structure–reactivity relationships and therefore gain important insights into reaction mechanisms. Although many studies have focused on S_N2 reactions,[7] relatively little work has been reported on the reactivity of small ring heterocycles. In an early flowing-afterglow study,

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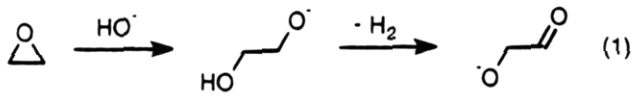
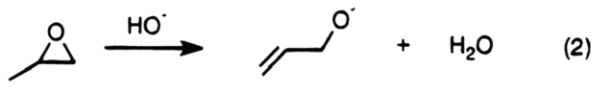
Bierbaum and DePuy[8] observed a relatively efficient reaction of HO^- with oxirane to give a product whose mass was consistent with addition followed by loss of molecular hydrogen. A recent computational study of this reaction confirmed DePuy's assumption that it involves the formation of a vibrationally excited, ring-opened intermediate that sheds its excess energy by expelling H_2 (eq 1).[9] In contrast, when HO^- is allowed to



(1)



(2)

react with alkyloxiranes in the gas phase, elimination to give an allylic alkoxide is the exclusive pathway (eq 2); no products of addition were observed in the reactions of HO^- with methyl or 1,2-dimethyloxirane.[10] Thiiranes have been somewhat ignored in gas phase studies, but the reaction of HS^- with thiirane has been investigated, and the only observed product is $HSCH_2CH_2S^-$.[11] Computational studies of this reaction have been completed and they indicate that there is a large barrier to H_2 expulsion and therefore the initial addition product survives.[9]

In a series of recent computational studies of gas phase substitutions and eliminations, we have investigated a number of the factors that affect the relative activation barriers.[12-15] Calculations[12] as well as gas phase experiments[16] suggest that elimination and substitution can be competitive for localized, first-row nucleophiles, but that, for second-row nucleophiles, eliminations face large barriers and substitution dominates. In addition, *ab initio* calculations have confirmed that eliminations generally prefer antiperiplanar transition states;[12-15,17,18] however, they also indicate that syn eliminations have greater conformational freedom and can readily adopt twisted (syn-clinal) transition states.[13,14]

Although several studies have addressed the electrophilic ring-opening of oxiranes,[19-20] there has been less work on the reactions of nucleophiles with small heterocycles. In addition to our previous study of the reactions

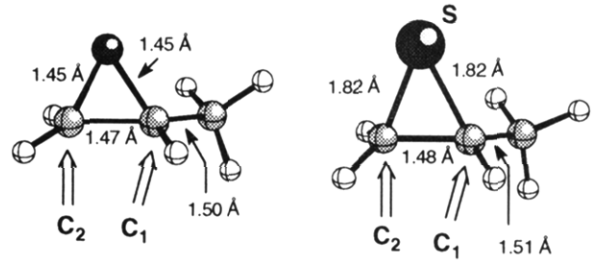


Figure 1. Structures of methyloxirane and methylthiirane optimized at the MP2/6-31+G* level (hydrogen, white; carbon. Light grey; oxygen (sulfur), dark grey).

of HO^- with oxirane and HS^- with thiirane,[9] Glad and Jensen[21] have completed high-level calculations on the reactions of oxirane with a series of nucleophiles, and Fujimato[22,23] *et al.* have investigated the reaction of F^- with oxirane. In the present study, we have investigated the gas phase, nucleophilic reactivity of methyloxirane with HO^- and methylthiirane with HO^- and HS^-. These systems allow us to evaluate the relative importance of ring strain relief in lowering the barriers of substitutions and eliminations. Transition states for addition (at C_1 and C_2) as well as elimination (anti and syn) were located for both substrates (Figure 1). In addition, attack at sulfur was investigated for thiirane.[24] Finally, the structures of several ion–dipole complexes were characterized. To put this work in perspective, acyclic analogs were considered and transition states were located for the corresponding S_N2 and E2 (anti and syn) reactions of $CH_3CH_2OCH_3$ and $CH_3CH_2SCH_3$. In addition, our earlier studies of oxirane and thiirane were updated with optimizations at the MP2 level.

Methods

All calculations were carried out on HP-720 or HP-735 computers using the GAUSSIAN92[25] quantum mechanical package developed by Pople and co-workers. All structures were fully optimized using a 6-31+G* basis set.[26] The curvature of the potential energy surface at all minima and transition states was confirmed with analytical second-derivatives at the Hartree–Fock level. When appropriate, the possibility of multiple rotamers was investigated. Earlier work has shown that the

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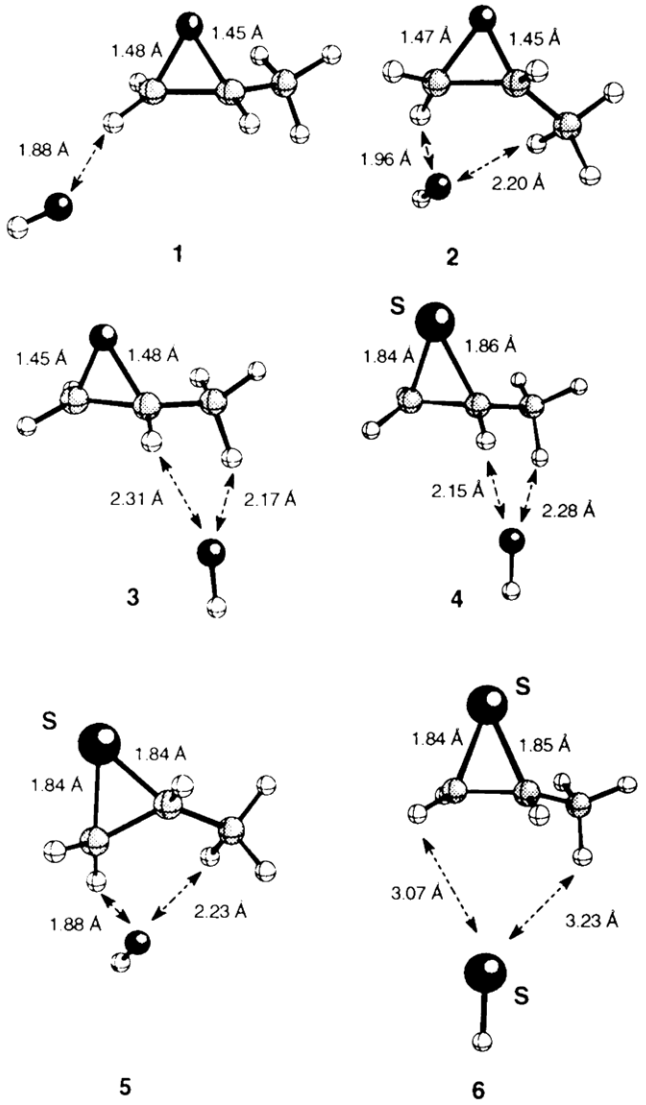

Figure 2. Structures of complexes optimized at the MP2/6-31+G* level (hydrogen, white; carbon, light grey; oxygen (sulfur), dark grey).

Hartree–Fock level overestimates the degree of E1-character in concerted eliminations;[14] consequently, geometries were reoptimized at the MP2/6-31+G* level and final energy calculations were completed with a more polarized basis set (MP2/6-31+G** level).[27] Using the Hartree–Fock frequencies, corrections were made for zero-point energy differences (scaled by 0.9).[28]

Results and Discussion

Ion–Dipole Complexes. The first intermediate in ion–molecule reactions is generally a loosely-bound, ion–dipole complex. For polyatomic neutrals such as methyloxirane and methylthiirane, there are usually several, energetically similar orientations for the complex. In Figure 2, a sample of three ion–dipole complexes is shown for the reaction of HO^- with methyloxirane. They vary in energy by 2.3 kcal/mol (Table 1) and the most stable complex, **2**, exhibits an interaction between the HO^- and a hydrogen on C_2 as well as one on the methyl group. This complex is 16.0 kcal/mol more stable than the separated reactants at the MP2/6-31+G**//MP2/6-31G* level. Complex **3** has interactions with hydrogens on C_1 and the methyl group, whereas complex **1**, the least stable, lacks an interaction with the CH_3 group.

Two ion–dipole complexes for the reaction of HO^- with methylthiirane are shown in Figure 2. Complex **5** is preferred by 1.1 kcal/mol (Table 2) and exhibits the same interactions as in complex **2** (*i.e.*, with hydrogens on C_2 and the methyl group). In complex **4**, the interactions involve hydrogens on C_1 and the methyl group. Overall, the complexes with methylthiirane are about 2 kcal/mol more stable than those with methyloxirane. This is clearly a result of the greater polarizability of the C–S bonds. A complex of HS^- with methylthiirane (**6**) is also shown in Figure 2. The diffuse nature of the HS^- anion leads to a weakly bound complex that lies on a very flat potential energy surface. Complex **6** is only ~11 kcal/mol more stable than the separated reactants and does not display any strong hydrogen-bonding interactions.

Nucleophilic Attack at Carbon. The transition states for the addition of HO^- to C_2 (**7**) and C_1 (**8**) of methyloxirane are shown in Figure 3. In **7**, the breaking C–O bond has stretched to 1.75 Å (24%), but the forming C–O bond is still long (2.14 Å, 49% longer than normal). The geometry is similar in the alternative transition state, **8**, with the major difference being a greater extension of the breaking C–O bond (1.78 Å). As expected for a nucleophilic attack, there is a preference for addition at the least-substituted carbon. The added crowding in transition state **8** (secondary vs primary carbon) makes it 2.6 kcal/mol less stable than **7** (Table 1). For comparison, the calculated barrier difference in the reactions of fluoride with 1- and 2-chloropropane is ~3 kcal/mol.[14]

Transition state **7** is 9.4 kcal/mol less stable than complex **2**, but 6.6 kcal/mol more stable than the separated reactants. This is a common result in ion–molecule reactions and implies a negative activation energy.[29] As Brauman[7h,i,30] has pointed out, negative activation energies do not necessarily lead to collision-controlled rates because severe entropic bottlenecks are possible, particularly for a highly-ordered, S_N2-like transition state. For example, our calculations suggest that the barrier to addition in HO^- + oxirane is −4.9 kcal/mol (Table 1), yet experimentally an efficiency of only 10% is observed.[8] Comparing the calculated activation barriers for HO^- addition to oxirane and methyloxirane, it can be seen that the addition of a methyl group to the carbon adjacent to the reaction center reduces the barrier by about 1.5 kcal/mol. This effect has been seen in other examples and is the result of the methyl group using its polarizability to stabilize the charged transition state.[7m,14] When the methyl group is at the α-carbon (**8**), the polarizability effect is canceled by increased crowding and the transition state is destabilized. In the addition of H_2O to protonated methyloxirane, Ford *et al.*[19b] have completed calculations at the MNDO level and found a preference of 7.7 kcal/mol for attack at C_1. The transition states in the protonated system are much looser (the forming C–O distance is ~3 Å) and as expected, there is a strong

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Table 1. Energies of Reactants, Complexes, Transition States, Products, and Related Species from the Reaction of HO^- + Methyloxirane[a]

reactants	HF/6-31+G*	MP2/6-31+G**	ZPE	relative energies HF	relative energies MP2
reactants					
HO^-	−75.37642	−75.60206	5.1		
methyloxirane	−191.91448	−192.53755	52.0		
complexes					
1	−267.30995	−268.16251	57.8	−11.2	−13.7
2	−267.31197	−268.16664	58.1	−12.3	−16.0
3	−267.31127	−268.16473	58.0	−11.9	−14.9
transition states					
7	−267.28912	−268.15115	57.7	1.7	−6.6
8	−267.28470	−268.14702	57.8	4.6	−4.0
19	−267.28451	−268.15017	54.6	1.5	−9.2
20	−267.27936	−268.14346	54.7	4.8	−4.8
products					
16	−267.37186	−268.21957	60.4	−47.5	−46.9
21	−191.30705	−191.93394	42.6	−22.9	−18.5
analogs					
oxirane	−152.87183	−153.34624	35.1		
HO^- + oxirane	−228.24553	−228.95740	41.0	2.5	−4.9
ethyl methyl ether	−193.10981	−193.75050	65.7		
13	−268.44493	−269.32895	70.3	25.4	14.3
E2(anti)		−269.35209	68.2		−2.2
E2(syn)		−269.34503	68.2		2.2

[a] Geometries optimized at the HF/6-31+G* and MP2/6-31+G* levels. Relative energies are comparisons to the appropriate isolated reactants. ZPE is scaled by 0.9, see text.

Table 2. Energies of Reactants, Complexes, Transition States, Products, and Related Species from the reaction of HO^- + Methylthiirane[a]

	HF/6-31+G*	MP2/6-31+G**	ZPE	relative energies HF	relative energies MP2
reactants					
HO^-	−75.37642	−75.60206	5.1		
methylthiirane	−514.58759	−515.15611	50.5		
complexes					
4	−589.98882	−590.78621	56.5	−14.7	−16.7
5	−589.98881	−590.78804	56.5	−14.7	−17.8
transition states					
9	−589.98260	−590.77831	56.4	−10.8	−11.8
10	−589.98135	−590.77415	56.6	−9.9	−9.0
22	−589.96791	−590.77426	53.2	−4.8	−12.5
23	−589.95691	−590.76458	53.3	2.1	−6.3
27		−551.57687	41.4[b]		−2.6
28		−551.56639	40.9[b]		3.4
products					
17	−590.07012	−590.84663	60.1	−62.1	−51.0
24	−514.01553	−514.57047	42.5	−43.6	−28.6
analogs					
thiirane	−475.54832	−475.96614	33.5		
HO^- + thiirane	−550.94208	−551.58498	39.3	−10.1	−9.8
ethyl methyl sulfide	−515.77215	−516.35822	63.3		
14	−591.13070	−591.94563	68.9	11.8	9.8
E2(anti)	−591.13836	−591.96345	65.7	3.7	−4.7
E2(syn)	−591.13183	−591.95652	65.7	7.9	−0.3

[a] Geometries optimized at the HF/6-31+G* and MP2/6-31+G* levels. Relative energies are comparisons to the appropriate isolated reactants. ZPE is scaled by 0.9, see text. [b] Frequencies calculated at the MP2/6-31+G* level. No scaling factor was used.

preference for addition at the substituted carbon because it can better stabilize the carbocation character of the transition state.

The transition states for addition of HO^- to methylthiirane are shown in Figure 4. As expected for more exothermic reactions, the transition states are earlier on the reaction coordinate than those found for methyloxirane. The C−OH distance is long (~2.2 Å), and the breaking C−S bond is stretched by only ~15%. The transition state for addition at C_2, **9**, is 2.8 kcal/mol more stable than the one for addition at C_1, **10** (Table 2). As in methyloxirane, the two transition states have similar structures except for an elongation of the breaking C−S bond in **10**. The activation energy for addition (via **9**) is −11.8 kcal/mol with respect to the separated reactants; **9** lies ~6 kcal/mol above complex **5**. Therefore, along with earlier transition states, the HO^- additions to methylthiirane have smaller barriers (with respect to the reactants or the encounter complex) than the corresponding additions to methyloxirane.

The transition states for the addition of HS^- to methylthiirane (**11** and **12**) are shown in Figure 5. Since HS^- is a weaker gas phase nucleophile than HO^-, the transition states occur later on the reaction coordinate and exhibit greater C−S cleavage. For example, the breaking C−S bonding in **11** is stretched by almost 20% (2.18 Å)

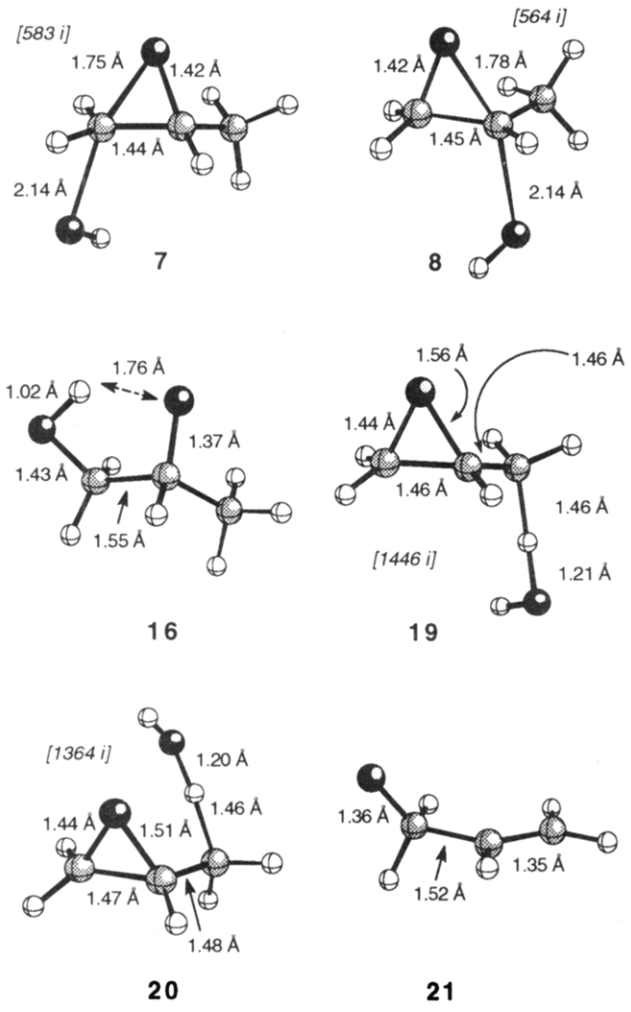


Figure 3. Structures related to the reaction of HO^- + methyloxirane. Optimizations at the MP2/6-31+G* level. For transition states, imaginary frequency given in italics (cm^{-1}) (hydrogen, white; carbon, light grey; oxygen, dark grey).

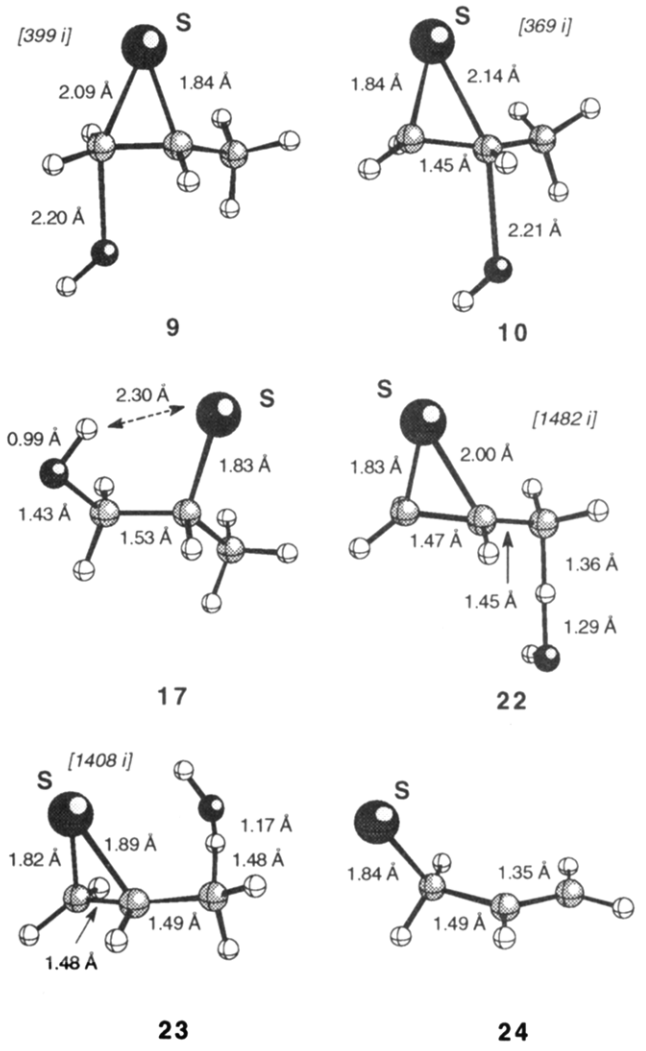


Figure 4. Structures related to the reaction of HO^- + methylthiirane. Optimizations at the MP2/6-31+G* level. For transition states, imaginary frequency given in italics (cm^{-1}) (hydrogen, white; carbon, light grey; oxygen (sulfur), dark grey).

and the forming C–S bond is about 40% longer than normal. In addition, the preference for attack at the least substituted carbon (5.6 kcal/mol) is greater than in the previous examples because the larger size of the nucleophile combined with the later transition state amplifies the effects of crowding in **12**. The preferred transition state, **11**, is ~10 kcal/mol less stable than complex **6**, and therefore the activation energy for attack at C_2 is −1.2 kcal/mol. The addition reactions of HS^- are much less exothermic than those of HO^-, so it is not surprising that higher barriers are observed. Nonetheless, a negative activation energy suggests an observable gas phase reaction.

To assess the importance of ring strain relief, comparisons must be made to acyclic analogs. For this purpose, we have chosen the S_N2 reactions of HO^- with ethyl methyl ether (**13**) and ethyl methyl sulfide (**14**) as well as the reaction of HS^- with ethyl methyl sulfide (**15**). The transition states for these reactions are shown in Figure 6 and the energies of important species are listed in Tables 1–3. As expected, transition state **13** occurs much later on the reaction coordinate than **7** or **8**. The forming C–O bond is shorter (1.94 Å vs. 2.14 Å), and the breaking C–O bond is longer (1.90 Å vs. 1.75 Å). Transition state **13** is 14.3 kcal/mol less stable than the separated reactants and therefore the barrier to nucleophilic addition is 20.8 kcal/mol larger than in methyloxirane. In other words, of the ~27 kcal/mol of strain energy in the oxirane ring,[1] almost 75% is released even though the transition state is early on the reaction coordinate. This effect was noted in our earlier study of oxirane and is also observed in the reaction of HO^- with ethyl methyl sulfide (**14**). Transition state **14** is 9.8 kcal/mol less stable than the separated reactants yielding a barrier that is ~20 kcal/mol larger than for attack at C_2 of methylthiirane. Again, the majority of the ring strain is released at the transition state in spite of the fact that it occurs early on the reaction coordinate. The effect is most dramatic when comparing the reactions of HS^- with ethyl methyl sulfide (**15**) and methylthiirane. Here, the activation energy in the ring system is over 25 kcal/mol smaller than in the acyclic system even though the strain energy of thiirane is only ~20 kcal/mol.[1] The lack of ring strain in transition states of this type has been investigated in detail in a recent study of the ring closures of $HSCH_2CH_2S^-$, $HSCH_2CH_2CH_2S^-$, and $HSCH_2CH_2CH_2CH_2S^-$ to give thiirane, thietan, and tetrahydrothiophene.[31] This study suggests two important factors. First, Bader[32]

(31) Gronert, S.; Lee, J. M. Submitted.
(32) (a) Bader, R. F. W.; Duke, A. J.; Messer, R. R. *J. Am. Chem. Soc.* **1973**, *95*, 7715.

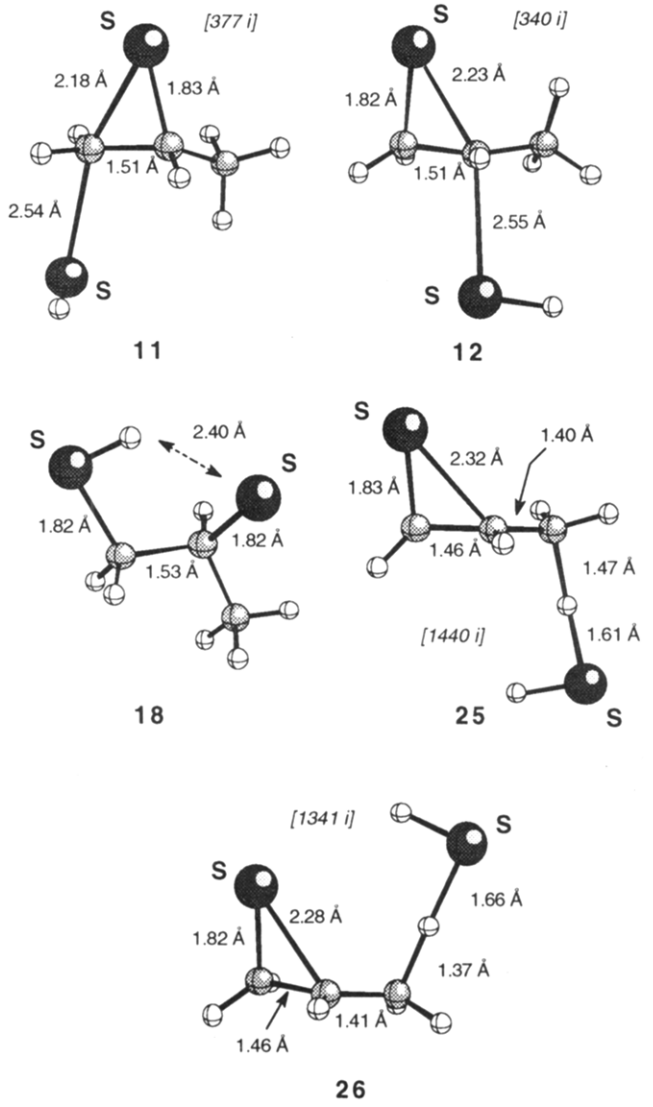
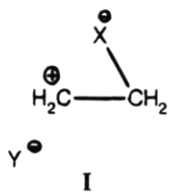


Figure 5. Structures related to the reaction of HS^- + methylthiirane. Optimizations at the MP2/6-31+G* level. For transition states, imaginary frequency given in italics (cm^{-1}) (hydrogen, white; carbon, light grey; sulfur, dark grey).

and others[12,14,33] have noted that S_N2 transition states can be dominated by an ionic resonance form (**I**).



I

If covalency plays only a small role in the breaking C–X bond, then neither of the bonding partners suffers significantly from angle strain (bond angle distortions are only meaningful if there is shared density). In addition, rehybridization of the inverting carbon significantly reduces the eclipsing interactions characteristic of three-membered rings. As a result, the only major component of ring strain remaining at the transition state is the C_α–C_β–X angle distortion. Given that this distortion should account for a few kcal/mol of strain, it is not unreasonable that much of the ring strain could be released early on the reaction coordinate. The second factor is less straightforward, but explains why the transition state could be stabilized by more than the total strain energy. Wiberg[34] has pointed out that although three-membered rings have tremendous angular strain, they benefit from the absence of unfavorable 1,3-interactions. This implies that the angular strain of a three-membered ring actually is *larger* than the total strain energy because the latter term contains a stabilizing contribution to account for the lack of 1,3-interactions. Careful analysis of the reaction pathway for the ring opening of thiirane indicates that these terms manifest themselves at different points on the reaction coordinate. That is, the angular strain is released early whereas the destabilization from the development (relative to an acyclic analog) of unfa-

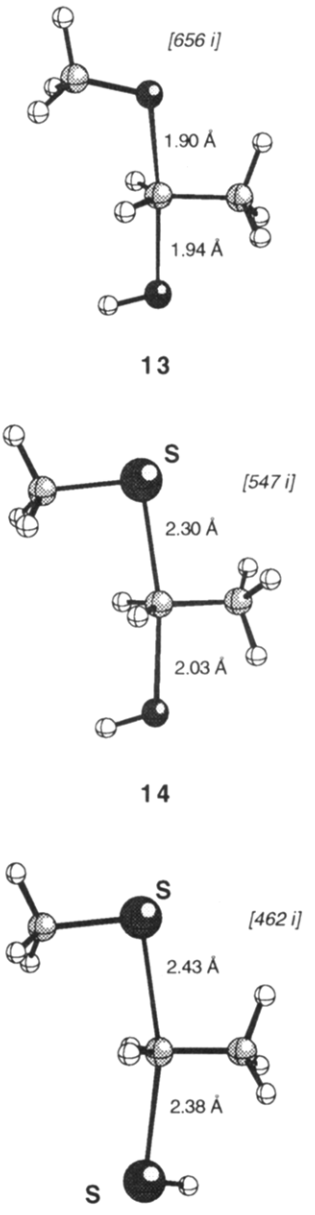


Figure 6. Structures of the S_N2 transition states of the acyclic analogs. Optimizations at the MP2/6-31+G* level. Imaginary frequency given in italics (cm^{-1}) (hydrogen, white; carbon, light grey; oxygen (sulfur), dark grey).

(33) Shi, Z.; Boyd, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 1072.

(34) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

Table 3. Energies of Reactants, Complexes, Transition States, Products, and Related Species from the Reaction of HS^- + Methylthiirane[a]

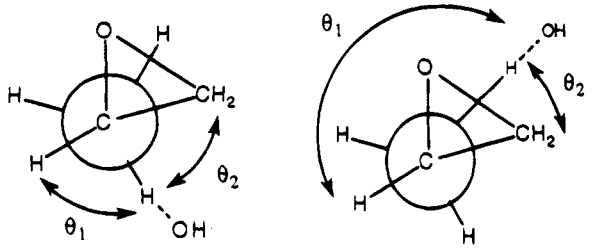
reactants	HF/6-31+G*	MP2/6-31+G**	ZPE	relative energies HF	relative energies MP2
reactants					
HS^-	−398.10689	−398.24135	3.6		
methylthiirane	−514.58759	−515.15611	50.5		
complex					
6	−912.70773	−913.41604	54.6	−7.7	−11.1
transition states					
11	−912.68740	−913.40036	54.7	5.1	−1.2
12	−912.68158	−913.39117	54.5	8.6	4.4
25	−912.64968	−913.37121	51.0	25.1	13.4
26	−912.63700	−913.36269	51.1	33.1	18.9
29	−873.60997	−874.18109	36.9	28.3	16.4
products					
18	−912.72137	−913.43812	56.7	−14.3	−22.9
24	−514.01553	−514.57047	42.5	4.6	7.2
analogs					
thiirane	−475.54832	−475.96614	33.5		
HS^- + thiirane	−873.64844	−874.20750	37.7	4.9	0.6
ethyl methyl sulfide	−515.77215	−516.35822	63.3		
15	−913.82549	−914.55848	66.5	33.3	25.4
E2(anti)	−913.79088	−914.54165	62.1	50.6	31.6
E2(syn)	−913.78019	−914.53566	62.7	57.9	36.0

[a] Geometries optimized at the HF/6-31+G* and MP2/6-31+G* levels. Relative energies are comparisons to the appropriate isolated reactants. ZPE is scaled by 0.9, see text.

vorable 1,3-interactions occurs late (after the transition state).[35] Because the angular strain is greater than the total strain energy, this course of events allows for a situation in which the transition state is stabilized by more than the total strain energy. Evidence to support this analysis has been presented in detail elsewhere.[31]

The products of the additions to C_2 of methyloxirane and methylthiirane are shown in Figures 3–5. In accord with our earlier work on the unsubstituted systems, the anions prefer structures with intramolecular hydrogen bonds. The additions of HO^- are very exothermic, so the products are formed in vibrationally excited states and a variety of conformations should be possible: each reaction has a ΔE of approximately −50 kcal/mol. The reaction of HS^- with methylthiirane is less exothermic (ΔE = ∼−23 kcal/mol), but the product still should have considerable conformational freedom.

Attack at the Methyl Group. The transition states for the anti and syn E2 reactions of HO^- with methyloxirane are shown in Figure 3. The geometry of the transition state for anti elimination (**19**) suggests significant E1cb-character; the C−H distance is long (1.46 Å, 34% extension) and the C_1−O distance (1.56 Å, 11% extension) is relatively short. The transition state is not periplanar and an O−C_1−C_β−H dihedral angle of ∼160° is observed. In this ring system, an antiperiplanar transition state would result in an eclipsing interaction between one of the methyl hydrogens and the C_1−C_2 bond of the ring. Given that the ring structure requires a distorted expulsion pathway for the heteroatom (it is highly unsymmetric with respect to the other groups at C_1), it is useful to analyze the conformation in terms of the substituent groups at the α-carbon (*i.e.*, the twist of the forming alkene). The twist angle should give a better gauge of the extent of π-overlap than the corresponding O−C_1−C_β−H dihedral angle. Looking at the difference in dihedral angles to the breaking C−H bond (see definition below), a twist angle of ∼−13° is observed in this system. In our studies of syn eliminations, we noted



$$\text{Twist Angle} = \frac{(\theta_1 - \theta_2)}{2}$$

that the need for periplanarity is reduced in E1cb-like reactions[13] and that eclipsing interactions can force the transition state to be twisted (syn-clinal).[14] Transition state **19** is the first computational example of an anti elimination that adopts a twisted conformation to avoid eclipsing interactions. In the acyclic analog, HO^- + $CH_3CH_2OCH_3$, torsional strain is minimized in an antiperiplanar conformation and a twist angle of 0° is observed (Figure 7a). In comparison to this acyclic analog, transition **19** has less E1cb-character. The breaking C−O bond is longer (1.56 Å vs 1.50 Å) and the C−H distance is shorter (1.46 Å vs 1.58 Å) in **19**. Obviously, the advantage of ring strain relief is enhancing the C−O cleavage component of transition state **19** and a more synchronous elimination results. The activation energy for anti elimination is −9.2 kcal/mol with respect to the separated reactants. The E2 (anti) reaction of HO^- with $CH_3CH_2OCH_3$ has an activation energy of −2.2 kcal/mol; therefore, of the approximately 27 kcal/mol of strain energy found in the substrate, 7 kcal/mol (∼25%) is released at the transition state.

The syn transition state, **20**, is also shown in Figure 3. The shorter C_1−O distance in **20** indicates that the syn elimination has more E1cb-character than the anti.

(35) In the reaction of HS^- with thiirane, two, new heavy-atom 1,3-interactions are developed, whereas in the reaction of HS^- with CH_3SCH_2CH, one is lost.

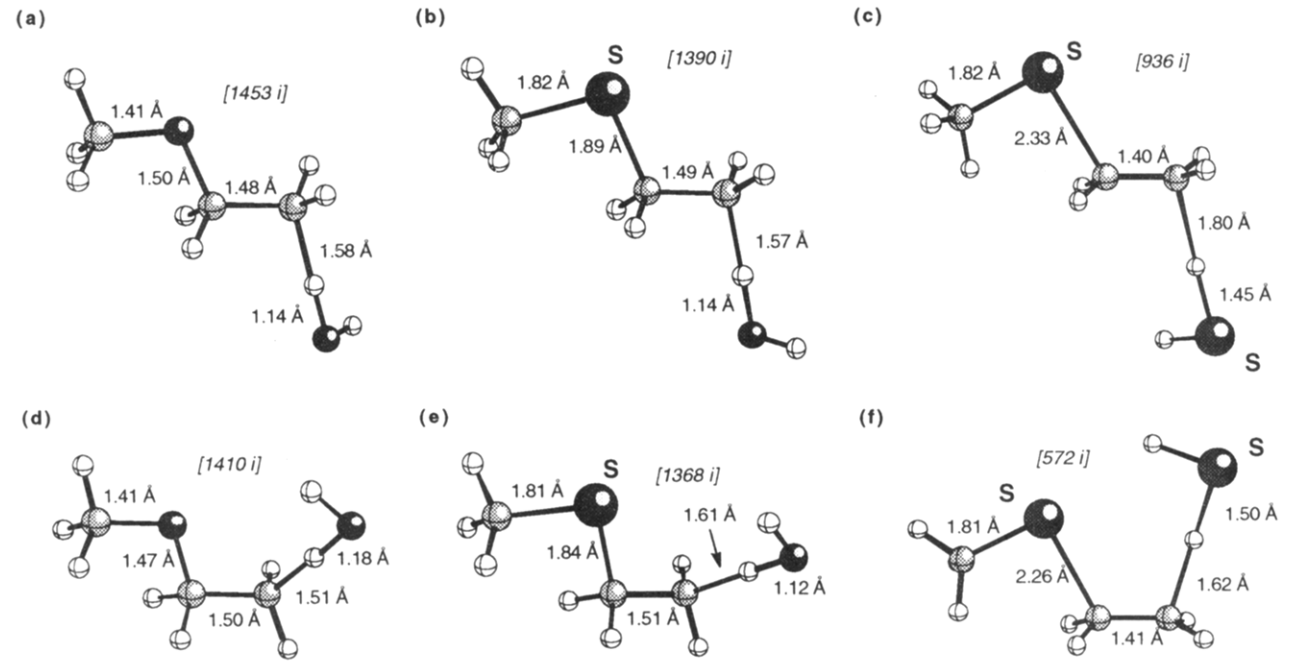


Figure 7. Structures of the E2 transition states of the acyclic analogs. Optimizations at the MP2/6-31+G* level. Imaginary frequency given in italics (cm^{-1}); (a) anti HO^- + ethyl methyl ether (EME), (b) anti HO^- + ethyl methyl sulfide (EMS), (c) anti HS^- + EMS, (d) syn HO^- + EME, (e) syn HO^- + EMS, and (f) syn HS^- + EMS (hydrogen, white; carbon, light grey; oxygen (sulfur), dark grey).

As expected for a syn elimination, the transition state is not periplanar, but adopts a syn-clinal conformation ($<O-C_1-C_\beta-H$ = 28°, twist angle = 58°) to avoid eclipsing interactions. In **20**, the small dihedral angle (~60°) between the groups on C_1 causes torsional strain to be minimized with an $O-C_1-C_\beta-H$ dihedral angle of approximately 30°. For comparison, a dihedral angle of ~40° is found in the syn elimination of HO^- + $CH_3CH_2OCH_3$ (Figure 7d). It is tempting to suggest that **20** could be stabilized by an intramolecular hydrogen-bond between the forming oxyanion and the hydrogen of the hydroxide (six-membered ring). In earlier gas phase work, Nibbering[36] postulated such an interaction in the hydroxide-induced eliminations of diethyl ether. However, strong hydrogen-bonding interactions are not possible in these transition states because there is little charge development on the departing oxygen and the need for a nearly linear proton transfer alignment prevents a close approach.[13] Transition state **20** is 4.4 kcal/mol less stable than **19** and the activation energy for the syn elimination is −4.8 kcal/mol with respect to the reactants. For comparison, anti elimination is favored over syn by 4.4 kcal/mol in the reaction of hydroxide with $CH_3CH_2OCH_3$; therefore, it appears as if anti and syn conformations gain approximately the same advantage from ring strain relief. However, ring cleavage has progressed to a greater extent in the anti conformation. This apparent contradiction can be resolved by assuming that in addition to ring strain relief in the oxirane system, the syn transition state is preferentially stabilized by an enhanced interaction between the developing carbon lone pair and the σ^* orbital of the strained C−O bond (the $C_\beta-C_\alpha-O$ angle is naturally larger in methyloxirane (116°) and some of the repulsive interactions found in syn transition states[17a] are reduced).

In contrast to our computational studies, condensed-phase experiments by Rickborn and co-workers[4b,c] indicate that the elimination occurs through a syn pathway. The only explanation for this discrepancy is that in solution, ion pairing effects stabilize the syn transition state. In the reactions of electrophiles with lithium amides, precoordination to an electronegative center is a common first step. In fact, precoordination has been implicated in experimental studies of the reactions of lithium amides with epoxides.[3b,37] Of course, coordination of lithium with the oxirane oxygen would predispose the system to a syn pathway. Moreover, coordination to lithium would stabilize the forming oxyanion in the transition state. Schleyer *et al.* recently have used *ab initio* calculations to explore this effect in the additions of organolithiums to oxirane.[23a]

The elimination product from methyloxirane, 2-propenoxide (**21**), is shown in Figure 3 and its energy is given in Table 1. The elimination reactions are much less exothermic than the additions and have a ΔE of −18.5 kcal/mol at this level of theory.

The transition states for the anti (**22**) and syn (**23**) eliminations of HO^- + methylthiirane are shown in Figure 4 and energies are listed in Table 2. The geometry of **22** indicates an early transition state with some E1cb-character. The $C_\beta-H_\beta$ distance is stretched by 25% (1.36 Å) and the C_1-S bond is stretched by ~11% (2.00 Å). The eliminations of methylthiirane produce **24** and are 10 kcal/mol more exothermic than those of methyloxirane so earlier transitions state are anticipated. The anti transition state is not periplanar, and a small twist angle of ~−7° is observed ($\angle S-C_1-C_\beta-H = 160°$). The barrier to the anti elimination (−12.5 kcal/mol) is 3.3 kcal/mol lower than that of methyloxirane. For comparison, the reaction of HO^- with ethyl methyl sulfide (Figure 7b) has a periplanar transition state and an activation energy of −4.7 kcal/mol; therefore, ring strain relief provides

(36) deKoning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1987**, *109*, 1715.

(37) Harder, S.; Boersma, J.; Brandsma, L.; Kanters, J. A.; Duisenberg, J. M.; van Lenthe, J. H. *Organometallics*, **1990**, 9511.

about 8 kcal/mol of stabilization to transition state **23**. As in the ether, less than 50% of the ring strain relief is realized in the elimination transition state.

The syn transition state, **23**, is truly E1cb-like and exhibits only a small extension of the breaking C−S bond. The transition state is significantly twisted, and a dihedral angle (∠H−C_β−C_1−S) of 38° is observed (twist angle = 68°). In fact, the breaking C−H bond almost perfectly bisects the S−C_1−C_2 angle of the ring. The activation energy for syn elimination (−6.3 kcal/mol) is 6.2 kcal/mol greater than that of anti elimination. For comparison, the anti preference in HO^- + $CH_3CH_2SCH_3$ is 4.4 kcal/mol. In this case, it appears that the anti transition state is better able to take advantage of ring strain release (greater C−S cleavage), and an enhanced anti preference results.

The transition states for the HS^--induced eliminations of methylthiirane are shown in Figure 5. The geometries of the anti (**25**) and syn (**26**) transition states suggest more synchronous reactions and are characterized by significant cleavage of the ring C−S bond. In **25**, the C−S bond is stretched by ~25% (2.32 Å) and the C−H bond is stretched by ~33% (1.47 Å). Given that these eliminations have later transition states with significant π-bonding, it is not surprising that they involve nearly periplanar conformations. Transition states **25** and **26** have twist angles of −6° and 2°, respectively.

The barriers to elimination are large in the HS^- + methylthiirane system and transition states **25** and **26** are 13.4 and 18.9 kcal/mol less stable than the separated reactants. This is in accord with experimental studies that indicate that sulfur bases are surprisingly ineffective for eliminations.[16a,b] Ring strain relief does play an important role and in comparison to an acyclic analog (HS^- + $CH_3CH_2SCH_3$, Figure 7c,f), the barrier to anti elimination is reduced by 18.2 kcal/mol. The bond lengths in the syn transition state, **26**, are somewhat unusual. Although it is less stable than the anti transition state, the C−H and C−S distances suggest that it occurs earlier on the reaction coordinate and has less E1cb-character. This type of "anti-Hammond" behavior has been noted in computational studies of nucleophilic addition to powerful electrophiles such protonated oxiranes and diazonium ions. In these additions, Ford *et al.* suggested that the unusual behavior was the result of S_N1 character in the transition state.[19c] By analogy, it would imply E1 character in the present system. Unlike the HO^--induced eliminations, the reactions with HS^- have large barriers and are only slightly exothermic. As the proton is removed by HS^-, the energy of the system rises sharply (HS^- is a poor base kinetically and thermodynamically) and C−S bond cleavage (ring opening) is required earlier on the reaction coordinate to stabilize the incipient carbanion. In the syn elimination, the poor orbital overlap between the α- and β-carbons[17a] makes proton transfer very unfavorable and the ring opening becomes significant (*i.e.*, the transition state is reached) after only a minor extension of the C−H bond. In the anti elimination, better overlap allows for greater C−H cleavage before the ring begins to open. The key difference between the HO^-- and HS^--induced eliminations is that the former are dominated by the proton transfer component and the latter by the ring-opening component of the reaction.

Attack at the Sulfur of Thiirane. As noted in the introduction, alkyllithiums are known to undergo nucleophilic addition to the sulfur of thiiranes.[5] When HO^- attacks the sulfur of thiirane, a stable addition product (**27**) is formed (Figure 8). Correlation is required to characterize this minimum, and it does not appear at the Hartree−Fock level.[38] The complex is 2.6 kcal/mol more stable than the separated reactants. From **27**, the system passes through transition state **28** and over a barrier of 6.0 kcal/mol (3.4 kcal/mol with respect to the separated reactants) to yield ethene and HOS^-.[39] The geometry of **28** indicates as asynchronous, yet concerted process in which one C−S bond cleaves before the other. C−S distances of 2.12 and 2.40 Å are observed. The C−C distance is relatively short (1.40 Å), and the carbon associated with the long C−S distance is almost planar. In fact, it is slightly pyramidalized away from the sulfur. The geometry is probably best described as a carbanion that is stabilized by a polarizable group (−SOH) at the adjacent carbon. Bordwell used a similar description of the transition state when discussing the condensed phase reaction of thiiranes with alkyllithiums.[5] The reaction is exothermic by 6.5 kcal/mol at this level of theory.

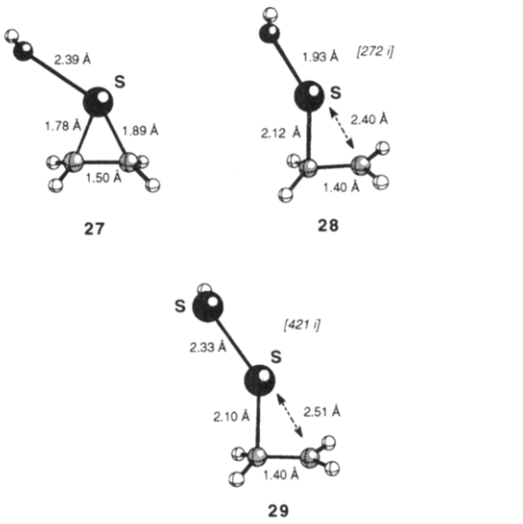


Figure 8. Structures related to attack at the sulfur of thiirane. Optimizations at the MP2/6-31+G* level. For transition states, imaginary frequency given in italics (cm^{-1}) (hydrogen, white; carbon, light grey; oxygen (sulfur), dark grey).

The addition of HS^- to the sulfur of thiirane (**29**) is also shown in Figure 8. Here, at the Hartree−Fock and MP2 levels, a single-step process is observed. A barrier of 16.4 kcal/mol is calculated, and again the transition state geometry suggests an asynchronous process (C−S bond lengths of 2.51 and 2.10 Å). In this case, the relative weakness of S−S bonds prevents the formation of a stable addition product. HS^--promoted desulfurization is endothermic by 3.1 kcal/mol at this level of theory.

Addition vs Elimination. Experimentally, DePuy and co-workers have studied the reactions of HO^- with oxirane[8] and methyloxirane.[10] In oxirane, addition is the only pathway and an efficiency (reaction rate divided by collision rate) of 0.10 was reported. In contrast, the reaction of HO^- with methyloxirane leads exclusively to

(38) At the Hartree−Fock level, the sulfur abstraction is a single-step process with no intermediate. By gradually extending the O−S distance in **27** at the MP2/6-31+G* level, it appears that a barrier of ~0.5 kcal/mol prevents it from dissociating to an ion−dipole complex such as **4** or **5**.

(39) The reactions of this ion have been studied previously, see: O'Hair, R. A. J.; DePuy, C. H.; Bierbaum, V. M. *J. Phys. Chem.* **1993**, *97*, 7955.

elimination (formation of CH_2=$CHCH_2O^-$) and an efficiency of 0.71 has been reported. Our computational work on methyloxirane suggests that the barrier to elimination is 2.6 kcal/mol below that of addition and therefore elimination should dominate. Moreover the highly-ordered addition transition state will be disfavored entropically. Therefore, it is not surprising that the addition products are not observed experimentally; however, it is interesting to point out that gas phase reactions with negative activation energies can exhibit high selectivity between exothermic channels. The calculations predict that both pathways should be relatively facile, yet only one is active. As for the stereoselectivity of the elimination, the barriers suggest that the anti pathway should dominate in the gas phase.

In the reaction of HO^- with methylthiirane, the elimination (anti) is favored over addition (at C_2) by only 0.7 kcal/mol. In addition, the elimination transition state is favored by entropy. Although it would be dangerous to use calculations at this level to predict product ratios, these calculations suggest that addition should be more competitive than in the reaction of HO^- with methyloxirane. Desulfurization *via* HO^- attack at sulfur has a relatively large barrier and should not compete effectively with addition or elimination. Unfortunately, there have been no gas phase experiments reported for the reaction of HO^- with alkylthiiranes.

In going from HO^- to HS^- as the nucleophile, the barrier to addition at C_2 of methylthiirane rises by about 10 kcal/mol; however, the activation energy for HS^- addition is still negative (−1.2 kcal/mol) so an observable gas phase reaction is expected. In contrast, the barrier to elimination rises by about 25 kcal/mol and consequently HS^--induced elimination is not possible under typical gas phase conditions. Attack at the sulfur of thiirane has a high activation energy and desulfurization should not compete with the additions to carbon.

The difference in reactivity between first and second row nucleophiles is nicely illustrated in the data for the S_N2 and E2 reactions of the acyclic analogs in this study (Tables 1 and 3). The S_N2 reaction of HO^- with $CH_3CH_2OCH_3$ is ~15 kcal/mol more exothermic than the corresponding reaction of HS^- with $CH_3CH_2SCH_3$,[40] and a somewhat smaller activation energy is observed (14.3 vs 25.4 kcal/mol). For the E2 (anti) mechanism, the reaction of HO^- + $CH_3CH_2OCH_3$ is also about 15 kcal/mol more exothermic than the reaction of HS^- with $CH_3CH_2SCH_3$, but there is an enormous difference in the activation barriers (−2.2 vs 31.6 kcal/mol). Obviously, HS^- is an exceptionally poor bases for eliminations. In an earlier comparison of the E2 reactions of F^- and PH_2^- with CH_3CH_2Cl (both reactions are almost equally exothermic), we also found a strong bias against the second-row nucleophile.[12] In that work, we explained the bias by pointing out that the lower effective electronegativity of second-row centers destabilizes the ionic component of the proton transfer process. The effect of electronegativity on simple proton transfers has been analyzed in detail elsewhere.[41]

Conclusions

Ring strain effects stabilize the transition states for addition and elimination, but generally are most significant for the former. Ring strain relief occurs early on the reaction coordinate and even in additions with early transition states, much of the ring strain can be released. The HO^--induced eliminations in this study have E1cb-like transition states and therefore gain less from ring strain relief; consequently, in these small heterocycles, the bias toward elimination is smaller than in acyclic analogs. This may explain why addition rather elimination is observed experimentally when alkyloxiranes are treated with strong, nucleophilic bases such as alkyllithiums. With a weak gas phase nucleophile, HS^-, the reactions have later transition states and the activation energies suggest that most of the ring strain is released. However, the poor kinetic basicity of HS^- leads to a large barrier to elimination. Although addition at the sulfur of thiirane is possible, the activation energy is too large in these systems to be competitive with addition at carbon.

It is hoped that these results will encourage further gas phase studies of the nucleophilic reactivity of small heterocycles. In particular, it appears that investigations of the competition between addition and elimination are warranted in the reactions of alkylthiiranes.

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Supporting Information Available: Tables of Cartesian coordinates for all species (11 pages). This material is available in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(40) This difference is mainly driven by the fact that CH_3SH is less acidic than H_2S whereas CH_3OH is more acidic than H_2O, see: (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1. (b) Stull, D. R.; Westrun, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons, Inc.: New York, 1969.

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