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Pyrolytic elimination reactions of sulfinate and sulfonate esters

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ABSTRACT: The barriers to pyrolytic unimolecular elimination by ethyl methanesulfonate and ethyl methanesulfinate were calculated for both five-membered ring eliminations that yield acetaldehyde and six-membered ring eliminations that yield ethylene. The experimental observation that related sulfinates undergo the five-centered elimination and sulfonates the six-centered elimination is reproduced by the calculations and rationalized in terms of a nucleophilicity/electrophilicity matching issue in the former and a charge-separated transition state in the latter. Copyright © 2001 John Wiley & Sons, Ltd.
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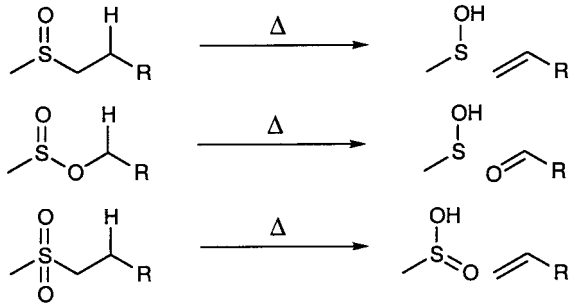
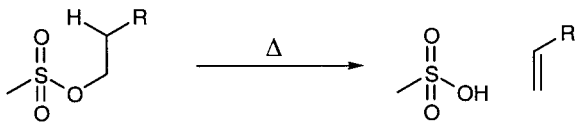
KEYWORDS: sulfinic ester; sulfonic ester; pyrolysis; internal elimination

INTRODUCTION

We have recently studied the β-elimination reaction of sulfoxides by means of gas-phase experimental kinetics and computational methods.[1] We showed experimentally that it could be extended to some new functional derivatives, including sulfinic esters[1] and sulfones.[2] All of these reactions proceed through planar, cyclic five-membered ring transition states. The reactions are concerted and relatively synchronous.



During the course of that study, our attention was naturally drawn to the case of the corresponding sulfonate ester, which can formally undergo an analogous reaction to form a sulfinic ester and a carbonyl compound. However, the gas-phase pyrolysis of alkyl sulfonates has been well studied and the universal result is an elimination by way of a six-membered ring transition state to give olefin and sulfonic acid.[3–10] We prefer the ylide notation to the double bond notation for the sulfoxide because we fell that it better represents the electronic nature of the compounds; however, because for sulfonic derivatives the ylide notation is even less commonly used and more difficult to read, we use the S=O notation consistently in this paper.



Early work in the field led to the conclusion that the members of this class of six-membered ring eliminations, which includes esters, xanthates, etc., are highly concerted, with little charge separation in the respective transition states.[11] Chuchani *et al.*,[6] however, picture the reaction proceeding 'in terms of an intimate ion pair intermediate.' This conclusion is based on the relative ease of the reaction compared to its analogs,[4] various anchimeric effects,[5,7,8,10] and substituent effects.[6] It is further bolstered by the observation that the gas-phase pyrolysis of neopentyl mesylate, which cannot undergo the classical six-membered ring transition state, forms methanesulfonic acid and mainly 2-methyl-2-butene and 2-methyl-1-butene with an Arrhenius activation energy only a few kcal mol^{-1} (1 kcal = 4.184 kJ) higher than for the benchmark sulfonic esters.

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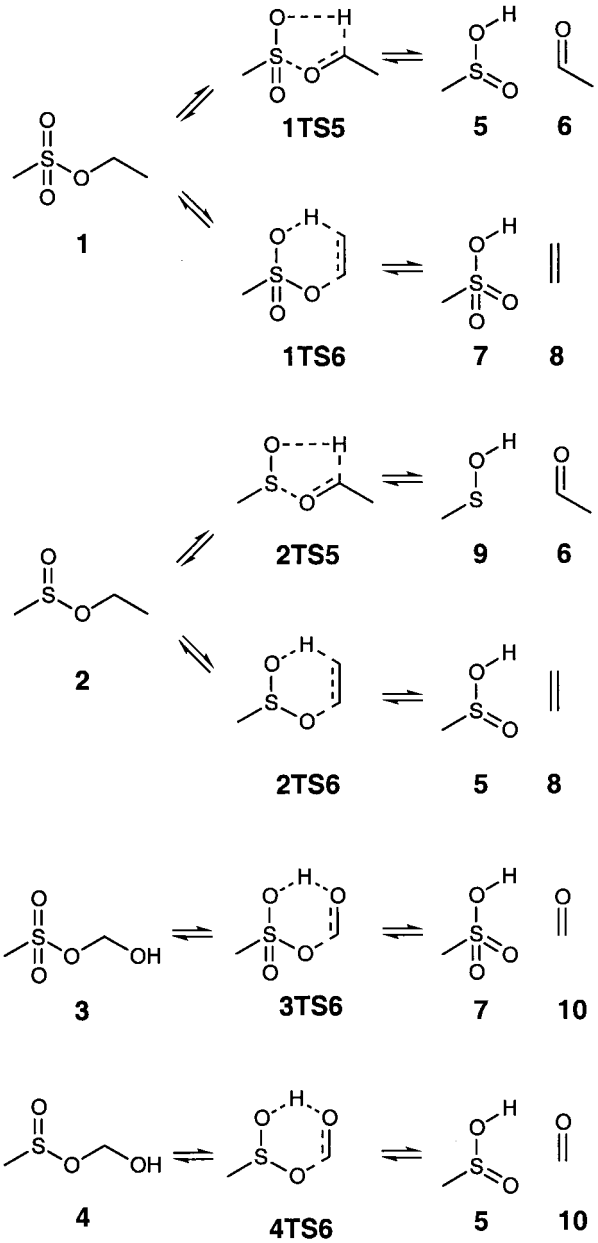
In this study, we attempted to provide further insight into the essence of the sulfinate and sulfonate elimination reactions through computational methods and to understand the experimentally observed selectivity. We compared the five- and six-centered cyclic transition states for sulfinic and sulfonic esters and report here the $\Delta H^{\ddagger}_{elim}$, ΔH_{rxn} and $\Delta H^{\ddagger}_{addn}$ values. We also examined charge distributions in transition states and show that, although we see no evidence for an intermediate in the benchmark six-centered eliminations, the Chuchani description of the transition state as being highly charge separated is borne out by the computations.

COMPUTATIONAL METHODS

To find the low-energy conformations of the starting materials and products, conformational searches were performed using the PM3 semiempirical method as implemented in Spartan.[12] Initial guess transition states were also found at this level of theory. All subsequent calculations were performed using the GAMESS suite of programs,[13] and the results were visualized using MacMolPlt.[14]

Geometries were optimized at HF/6–31G(d,p) and then refined at MP2/6–31G(d,p). Final energies reported here result from single-point calculations at the MP2/6–311 + G(3df,2p)//MP2/6–31G(d,p) level. Hessians were also obtained at the MP2/6–31G(d,p) level to confirm the nature of the stationary points and to determine zero-point energy corrections. The Gonzales–Schlegel second-order method[15] was used for determining intrinsic reaction coordinate (IRC) paths. The reported ΔH values are obtained from the absolute energies of the substrates and the unscaled ZPEs. This level of theory was shown to reproduce experimental activation enthalpies very well for sulfoxide eliminations [see Ref. 1 for further discussion on this point, in particular for a discussion of the alternatives of B3LYP, CASSCF with MRMP2, and CCSD(T)]. Products were calculated as isolated molecules.

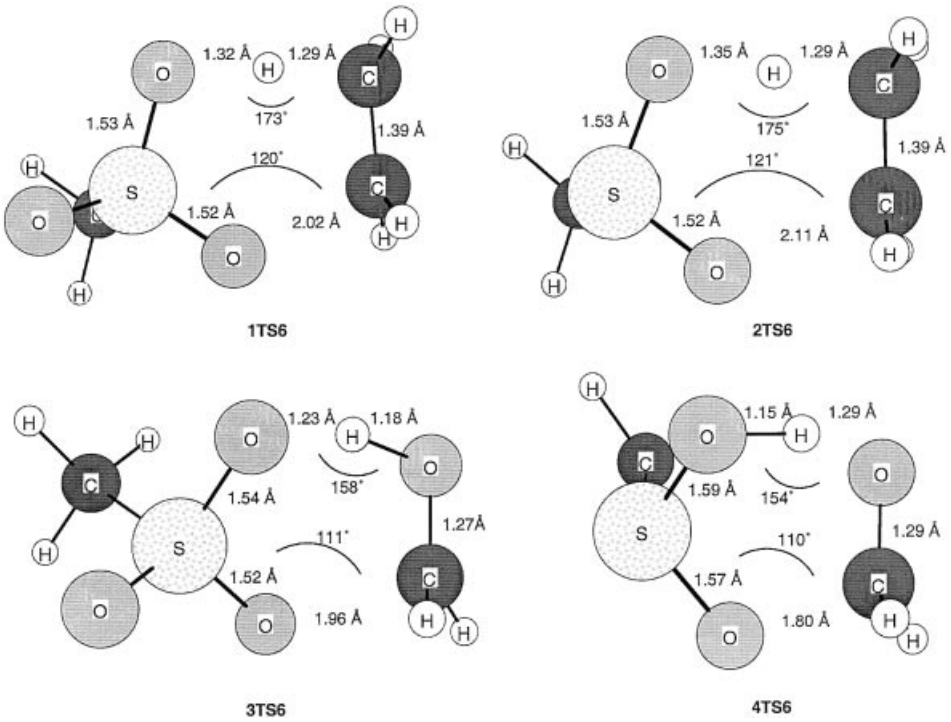
The experimental geometry of dimethyl sulfoxide is reproduced very well at the HF/6–31G(d,p) level of theory, better than when either the basis set or theoretical model is improved in isolation,[16] as we have done here by using MP2/6–31G(d,p). We have attributed this to a fortuitous cancellation of errors. Geometries at the MP2/6–31G(d,p) level have bond lengths that are slightly too long. Nonetheless, we use these for the single-point calculations with the larger basis set. First, since we are primarily interested in the relationship between the reactants and transition states, we must calculate the transition states reliably. We have seen at least one instance where the geometry of the transition state of a sulfoxide elimination reaction calculated at HF/6-31G(d,p) differed dramatically from that calculated at any other of several correlated levels of theory.[1] As a result, at least MP2 calculations are required across the board. Although large basis sets are required to obtain relative energies of isomers correct in these systems,[17] MP2 optimizations with those basis sets remain extremely time consuming. Fortunately, in all but the most sensitive cases among the sulfoxide eliminations, such optimizations lead to changes in $\Delta H^{\ddagger}$ and ΔH of <1 kcal mol^{-1},[1] so such refinements were not performed here. Atomic charges and bond order indices were obtained from the generalized MP2 density matrix.



Scheme 1

RESULTS AND DISCUSSION

The compounds examined, schematic transition states



Scheme 2

and products are shown in Scheme 1. The calculated geometries of **1TS6**, **2TS6**, **3TS6** and **4TS6** are shown in Scheme 2. The calculated activation enthalpies ($\Delta H^{\ddagger}_{elim}$), reaction enthalpies ($\Delta H_{rxn}$) and activation enthalpies for the reverse reaction ($\Delta H^{\ddagger}_{addn}$, i.e. the addition of the sulfur oxyacid to the π-system), all at 0 K, are given in Table 1. The *syn* and *anti* designations for the five-membered ring eliminations depend on the relative stereochemistry of the two methyl groups. Given that the calculated activation enthalpies are approximately equal, all further discussion will be restricted to the *anti* transition states, which are slightly lower in energy. For the six-centered elimination, no intermediates were found. Instead, a single transition state was obtained, which was shown to connect the starting materials and products by running intrinsic reaction coordinate (IRC) calculations, the results of which are shown in the supplementary material, available at the epoc website at http://www.wiley.com/epoc.

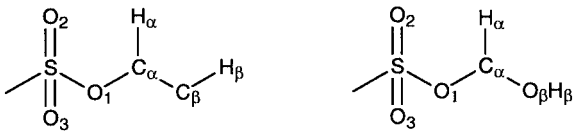
The atoms involved in bond making and breaking in structures **1TS5** and **2TS5** are aligned in a plane. We have reported extensively on transition states closely analogous to these elsewhere.[1] The key atoms in **1TS6** and **2TS6** are also in a planar arrangement. As illustrated in Scheme 2, the O—H—C angle is nearly 180°. In their planarity, these transition states are consistent with those recently discussed by Birney and co-workers[18,19] in the context of pseudopericyclic six-membered ring reactions of carbonyl-containing compounds, but the reactions are not pseudopericyclic in that the sulfur atom is not directly involved.

The calculated activation enthalpies may only be

Table 1. Calculated reaction and activation enthalpies[a]

Compound	$\Delta H^{\ddagger}_{elim}$(kcal mol^{-1})	ΔH_{rxn}(kcal mol^{-1})	$\Delta H^{\ddagger}_{addn}$(kcal mol^{-1})
Six-centered elimination —			
1	42.6	21.4	21.2
2	50.6	20.9	29.7
3	16.7	12.4	4.3
4	18.3	12.3	6.0
Five-centered elimination —			
1 *syn*	63.4	17.9	45.5
1 *anti*	63.2	17.9	45.3
2 *syn*	30.6	7.2	23.4
2 *anti*	29.8	7.2	22.6

[a] MP2/6–311 + G(3df,2p)//MP2/6–31G(d,p) + ZPE. Enthalpies are thus calculated for 0 K.



Scheme 3

compared with experimental data in two cases. No data are available for **3** or **4** (or models thereof), and only the lower energy reaction is experimentally observed for **1** and **2**. The five-centered elimination is characteristic of sulfinyl derivatives, and the calculated value of 30 kcal mol^{-1} can be compared with the experimental value of 35 kcal mol^{-1} for 3-phenylpropyl methanesulfinate.[1] This deviation of 5 kcal mol^{-1} compared with the best experimental model is larger than any of the others previously calculated for these reactions, most of which are within 2 kcal mol^{-1}.[1,2] The experimental Arrhenius activation energy for the six-membered ring elimination of ethyl methanesulfonate to give ethylene and methanesulfonic acid is 41.0 ± 0.3 kcal mol^{-1}.[4] This corresponds to an activation enthalpy of $\sim$ 39.9 kcal mol^{-1}, and compares well with the calculated value of 42.6 kcal mol^{-1}.

In Tables 2, 3 and 4 are given the calculated atomic charges and bond order indices[21–23] for compounds **1**–**4**, the respective transition states and products. The atom numbering system for the tables is given in Scheme 3. There are a number of different approaches to computing atomic charge, each of which has its advantages and disadvantages; we use the ubiquitous Mulliken charges with the 6–31G(d,p) basis set, where it is known to perform well.[20]

The surprising reversal of selectivity for thermolysis of sulfinates and sulfonates can be rationalized with help from the present data. First we consider the Chuchani conclusion that the six-centered reactions are interpretable as going by way of ion pairs. Although we see no evidence for intermediates, there is evidence for charge separation in the transition state. In particular, O_1 and O_2 (and in fact, the SO_2 or SO_3 functionality when summed) go through maxima in negative charge in the six-membered ring eliminations at the transition state. For **1TS6**, in which the reaction is actually observed, the O_1—C_α bond breaking is the most advanced process. This is consistent with an asynchronous concerted reaction that may be described as *E*1-like. Chuchani *et al.* experimental results are consistent with this and also drive our further interpretation of the six-membered ring elimination of **2**.

There is an increase in the activation barrier from 43 to 51 kcal mol^{-1} for the six-membered ring elimination on going from the sulfonate (i.e. **1**) to the sulfinate (**2**). This is not simply a reflection of the endothermicity of the reaction, since ΔH_{rxn} is about the same for **1** and **2**. Given an *E*1-type mechanism, however, this is understood by considering the sulfonate's increased ability to support a negative charge over the sulfinate. It is well known from bimolecular reactions, for example, that sulfonates are better leaving groups than sulfinates. This is, of course, related to the basicity of the methanesulfonate and methanesulfinate anions, which are 315 and 321 kcal mol^{-1} (ΔG), respectively.[24,25] In other words, we can interpret the higher activation barrier for **2**, along with the somewhat smaller advancement of the O_1—C_α bond breaking as a pair of coupled indicators that reflect the poorer leaving group ability of the sulfinate over sulfonate ion. If the sulfinate were a better leaving group, the reaction would, like the sulfonate case, be more asynchronous.

The five-center elimination results deviate from the pattern set by the six-membered case for **1** and **2**. The Mulliken charges on sulfur and O_1, for example, change smoothly, without a maximum or minimum at the

Table 2. Atomic charges[a]

	S	O_1	C_α	H_α	X_β	H_β	O_2	O_3
1	1.31	−0.60	0.01	0.15	−0.36	0.14	−0.53	−0.53
ITS5	1.09	−0.49	−0.01	0.29	−0.34	0.11	−0.55	−0.51
5 + 6	0.92	−0.36	0.28	0.35	−0.42	0.14	−0.64	−0.58
1TS6	1.30	−0.63	−0.02	0.19	−0.50	0.37	−0.65	−0.51
7 + 8	1.28	−0.50	−0.22	0.11	−0.22	0.37	−0.61	−0.50
2	0.95	−0.61	0.02	0.13	−0.35	0.12	−0.59	—
2TS5	0.65	−0.48	0.00	0.28	−0.34	0.13	−0.56	—
9 + 6	0.33	−0.36	0.28	0.35	−0.42	0.14	−0.62	—
2TS6	1.03	−0.66	−0.02	0.16	−0.54	0.38	−0.69	—
5 + 8	0.92	−0.58	−0.22	0.11	−0.22	0.35	−0.64	—
3	1.31	−0.60	0.25	0.14	−0.54	0.34	−0.58	−0.50
3TS6	1.32	−0.64	0.21	0.16	−0.48	0.47	−0.69	−0.50
7 + 10	1.28	−0.50	0.16	0.08	−0.33	0.37	−0.61	−0.50
4	0.99	−0.61	0.25	0.12	−0.55	0.35	−0.63	—
4TS6	1.06	−0.66	0.23	0.13	−0.59	0.44	−0.70	—
5 + 10	0.92	−0.58	0.16	0.08	−0.33	0.35	−0.64	—

[a] Mulliken, MP2/6–31G(d,p).

Table 3. Bond order indices for five-centered transition states

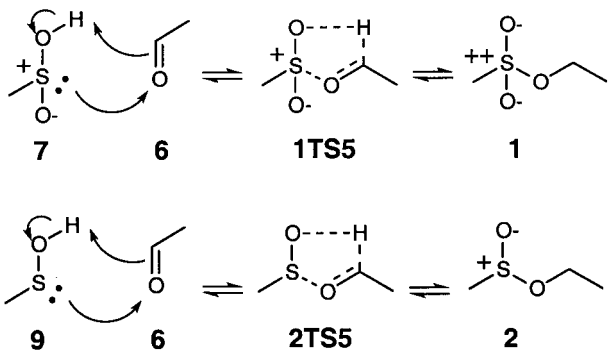
	$S—O_1$	$O_1—C_\alpha$	$C_\alpha—H_\alpha$	$H_\alpha—O_2$	$O_2—S$	$S—O_3$
1	0.82	0.77	0.91	—	1.62	1.62
1TS5	0.32	1.21	0.45	0.34	1.14	1.57
5 + 6	—	1.84	—	0.83	0.77	1.58
2	0.74	0.81	0.93	—	1.56	—
2TS5	0.31	1.24	0.43	0.38	1.12	—
6 + 9	—	1.84	—	0.83	0.82	—

Table 4. Bond order indices for six-centered transition states

	$S—O_1$	$O_1—C_\alpha$	$C_\alpha—X_\beta$	$X_\beta—H_\beta$	$H_\beta—O_2$	$O_2—S$	$S—O_3$
1	0.82	0.77	0.94	0.93	—	1.62	1.62
1TS6	1.27	0.26	1.28	0.48	0.29	1.22	1.69
7 + 8	1.65	—	1.85	—	0.80	0.83	1.65
2	0.74	0.81	0.93	0.93	—	1.56	—
2TS6	1.12	0.34	1.27	0.39	0.39	1.06	—
5 + 8	1.58	—	1.85	—	0.83	0.77	—
3	0.84	0.74	0.98	0.80	—	1.54	1.69
3TS6	1.25	0.27	1.42	0.42	0.34	1.15	1.70
7 + 10	1.65	—	1.85	—	0.80	0.83	1.65
4	0.75	0.80	0.96	0.80	—	1.47	—
4TS6	1.07	0.40	1.33	0.33	0.46	1.03	—
5 + 10	1.58	—	1.85	—	0.83	0.77	—

transition state. Similarly, there is no charge maximum at the transition state, considering the sum of the sulfur and oxygen atoms combined. The difference in the thermochemistry between five- and six-centered eliminations is dramatic. The five-membered ring elimination, preferred for sulfinic esters, is endothermic for both substrates (by 18 and 7 kcal mol^{-1} for **1** and **2**, respectively). More dramatic, however, are the $\Delta H^{\ddagger}_{\mathrm{elim}}$ values of 63 kcal mol^{-1} for **1** and 30 kcal mol^{-1} for **2**, a difference of more than 30 kcal mol^{-1}, and in the opposite direction than for the six-centered elimination.

Sulfoxides are more basic than sulfones;[26] recent experiments and computations indicate that this trend also manifests itself for sulfinic esters compared with sulfonic esters.[27] However, while there is certainly a component of acid–base chemistry to the five-membered ring eliminations, the 30 kcal mol^{-1} difference in activation enthalpies between **1** and **2**, we believe, has more to do with unfavorable charge interactions in the transition state. This difference is best rationalized by examining the back (addition) reaction,[1] as illustrated in Scheme 4, in which we have for purposes of emphasis used the ylide notation for the sulfur center. The values of $\Delta H^{\ddagger}_{\mathrm{addn}}$ are 45 and 23 kcal mol^{-1} for the formation of **1** and **2**, respectively. The salient point is that in the five-membered ring addition, the sulfur is acting as a *nucleophilic* center. The polarity of the carbonyl is reversed from what would be the favorable form in the addition reactions to form **1** and **2**; the addition reaction between **6** and **9** proceeds virtually without barrier with the carbonyl in the other orientation.[1] Here, however, we can view **2** as a structural modification of **1** in which the sulfur atom has been made even less nucleophilic. This leads to the worst possible nucleophilic–electrophilic mismatch within this set of compounds and a tremendously high barrier for an exothermic reaction. In other words, for the five-centered elimination to have a low barrier, the product sulfur should be relatively nucleophilic, in addition to the reaction being less endothermic overall.



Scheme 4

In essence, the experimental selectivity of **2** for the five-membered ring elimination and that of **1** for the other boils down to a coincidence. The structural requirements on the sulfur group for the five- and six-membered ring eliminations, although not exactly opposite, are at least complementary. The sulfonic ester is a good substrate for

olefin formation and a bad substrate for carbonyl formation, while the sulfinic ester is mediocre for both.

In considering what makes a good substrate for these reactions, the acidity of the abstracted hydrogen has been a structural consideration, at least in the extensive literature on the *syn* elimination of sulfoxides. The effect of a carbomethoxy group, substituted at the α- or β-position, is a dramatic increase in the rate over the unsubstituted case, but the effect is of similar magnitude, regardless of which position the substitution is made on.[28,29] Hence the effect has been attributed to conjugation in the transition state more than on the acidity of the proton. However, we have shown that when an NH_3^+ substituent is placed in the β-position, thus increasing the acidity without adding conjugation, the activation enthalpy is also lowered.[1] α-Hydroxysulfoxides, which have acidic protons in the β-position, have been proposed as reactive intermediates.[30,31]

They are not generally observed as stable compounds and are calculated to have low barriers to the five-centered elimination.[1] We therefore considered the six-membered ring eliminations of compounds **3** and **4** for comparison with **1** and **2**. Transition state **3TS6** (Scheme 2) is less planar than those of compounds **1** and **2**, assuming a half-chair conformation. The O and C are on opposite sides of the plane defined by the SO_2H group. In **3TS6**, the 'protonated formaldehyde' moiety has an H—O—C—H dihedral angle of about 45°, where 90° would represent the maximum overlap between the breaking HO bond and the forming π-bond. The analogous angle in **1TS6** and **2TS6** is much closer to the ideal. The transition-state geometry for **4TS6** is more boat-like. In both **3TS6** and **4TS6**, there is a greater deviation in linearity for the O_2—H_β—X_β angle than in the parent structures. As can be seen from Table 4, **4TS6** is more asymmetric with respect to bond making and breaking. It is earlier than **3TS6** with respect to O_1—C_α cleavage and C_α—O_β π-bond formation and later with respect to O_2—H_β bond formation.

For these molecules, the following differences can be noted from the parent compounds: (1) the transferred proton, viewed from the starting ester, is much more acidic; (2) the oxygen, viewed from the product aldehyde, is more basic than the carbon of ethylene; and (3) the carbonyl π-bond is stronger than an ethylene π-bond. Because of the last of these considerations, ΔH_{rxn} is smaller than for **1** or **2** by about 9 kcal mol^{-1}. The activation barriers are also very low. Very eye-catching, however, is the real *similarity* in the calculated barriers for **3** and **4**, smaller than the difference between **1** and **2**. That for **3**, the sulfonate derivative, is only about 1.6 kcal mol^{-1} lower than that for **4**, the sulfinate.

The negative charge build-up on O_1 in the transition states is now similar between the sulfinate and sulfonate derivatives. Most of the corresponding positive charge build-up appears on H_β. There are not large changes in the BOI trends in comparing the parallel systems. To the extent that the atomic charges continue to behave non-monotonically, the elimination reactions of **3** and **4** should also be thought of as *E*1-like. In this context, the lack of dependence of the activation enthalpy on the sulfur 'leaving group' is surprising. We suggest that this dependence may be mitigated by the oxygen atom in the β-position, which greatly stabilizes the 'cation' that one would write if construing the reaction formally as two steps. Interestingly, the transition states for **3TS6** and **4TS6** are both earlier than their respective analogs **1TS6** and **2TS6** with respect to O_1—C_α bond cleavage. Considering the reaction from the addition standpoint, the complementary barrier lowering is easily understood in chemical terms by considering the greater electrophilicity of the formaldehyde carbon than ethylene toward protonation of O_1.

CONCLUSIONS

The sulfoxide-like five-membered ring internal elimination reaction of sulfinates is closely related to the six-membered internal elimination of sulfonates. However, the six-membered ring elimination traverses a transition state that involves an increase of charge separation, relative to the starting materials or products. As a result, the activation barrier is about 8 kcal mol^{-1} higher for sulfinates than for sulfonates because of the latter's greater ability to support negative charge. A complementary selectivity of larger magnitude (about 32 kcal mol^{-1}) for sulfinates over sulfonates arises in the five-centered elimination, which does not involve a highly charge-separated transition state. We attribute the large barrier difference between **1** and **2** in the five-centered elimination to a nucleophilic–electrophilic mismatch in the transition state that is made worse when the sulfur atom is more positively charged, as in the sulfonate.

Acknowledgments

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REFERENCES

1. Cubbage JW, Guo Y, McCulla RD, Jenks WS. *J. Org. Chem.* 2002; in press.
2. Cubbage JW, Vos BW, Jenks WS. *J. Am. Chem. Soc.* 2000; **122**: 4968–4971.
3. Alvarez GJ, Chuchani G. *J. Phys. Org. Chem.* 1990; **3**: 456–458.
4. Chuchani G, Pekerar S, Dominguez RM, Rotinov A, Martin I. *J. Phys. Chem.* 1989; **93**: 201–202.
5. Chuchani G, Dominguez RM, Rotinov A, Martin I, Alvarez GJ. *J. Phys. Chem.* 1990; **94**: 3341–3343.

6. Chuchani G, Alvarez GJ, Martin I. *J. Phys. Org. Chem.* 1991; **4**: 399–403.
7. Martin I, Chuchani G, Dominguez R, Rotinov A. *J. Phys. Org. Chem.* 1992; **5**: 725–730.
8. Chuchani G, Dominguez RM. *J. Chem. Soc., Perkin Trans. 2* 1993; 1295–1298.
9. Chuchani G, Martin I, Dominguez RM, Rotinov A, Pekerar S, Gomez M. *J. Phys. Org. Chem.* 1993; **6**: 85–94.
10. Chuchani G, Martin I, Dominguez RM. *Int. J. Chem. Kinet.* 1995; **27**: 657–661.
11. DePuy CH, Bishop CA. *Tetrahedron Lett.* 1963; 239–241.
12. Hehre W. *Spartan*. Wavefunction: Irvine, CA, 1994.
13. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS *et al.*, *J. Comput. Chem.* 1993; **14**: 1347–1363.
14. Bode BM, Gordon MS. *J. Mol. Graphics. Mod.* 1998; **16**: 133–138.
15. Gonzales C, Schlegel HB. *J. Chem. Phys.* 1989; **90**: 2154–2161.
16. Cubbage JW, Jenks WS. *J. Phys. Chem. A.* 2001; **105**: 10588–10595.
17. Turecek F. *J. Phys. Chem. A* 1998; **102**: 4703–4713.
18. Birney DM, Xu S, Ham S. *Angew. Chem., Int. Ed. Engl.* 1999; **38**: 189–193.
19. Birney DM, Ham S, Unruh GR. *J. Am. Chem. Soc.* 1997; **119**: 4509–4517.
20. Wiberg KB, Rablen PR. *J. Comput. Chem.* 1993; **14**: 1504–1518.
21. Giambiagi M, Giambiagi M, Grempel DR, Heymann CD. *J. Chim. Phys. Phys.-Chim. Biol.* 1975; **72**: 15–22.
22. Mayer I. *Chem. Phys. Lett.* 1983; **97**: 270–274.
23. Mayer I. *Chem. Phys. Lett.* 1985; **117**: 396.
24. Sorensen DN. *Three Studies in Ion Thermodynamics*. University of Tennessee: Knoxville, TN, 1994.
25. Koppel IA, Taft RW, Anvia R, Zhu SZ, Hu LQ *et al.*, *J. Am. Chem. Soc.* 1994; **116**: 3047–3057.
26. Buncel E, Decouzon M, Formento A, Gal J-F, Herreros M *et al.*, *J. Am. Soc. Mass Spectrom.* 1997; **8**: 262–269.
27. Borrajo AMP, Gal J-F, Maria P-C, Decouzon M, Ripley D *et al.*, *J. Org. Chem.* 1997; **62**: 9203–9209.
28. Tsukurimichi E, Yoshimura T, Yoshizawa M, Itakura H, Shimasaki C. *Phosphorus Sulfur Silicon* 1989; **1989**: 113–120.
29. Crich D, Lim BL. *J. Chem. Res. (S)* 1987; **11**: 353.
30. Clennan EL, Toutchkine A. *J. Am. Chem. Soc.* 2000; **122**: 1834–1835.
31. Toutchkine A, Aebisher D, Clennan EL. *J. Am. Chem. Soc.* 2001; **123**: 4966–4973.