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Mechanisms of *Front-Side* Substitutions. The Transition States for the S_Ni Decomposition of Methyl and Ethyl Chlorosulfite in the Gas Phase and in Solution

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We examined the front (S_Ni)- and back (S_N2)-side substitutions of methyl and ethyl chlorosulfite in isolated and in simulated solution conditions using *ab initio* MO methods. All methyl chlorosulfite structures were optimized up to the MP2(fc)/6-31+G* level, but the changes are small with increased sophistication of the computational method. Consequently, we optimized ethyl chlorosulfite structures at HF/6-31G* and computed single point energies at MP2(fc)/6-31+G*//HF/6-31G*. Solution effects were simulated by means of single point energies on the HF/6-31G* optimized geometries using the self consistent reaction field (SCRF) model. Dielectric constants ϵ of hexane, carbon tetrachloride, sulfur dioxide, methanol, and water were employed. While the front-side substitution of methyl chlorosulfite is favored in the gas phase and in nonpolar solvents, back-side attack is preferred in polar solvents due to a more favorable stabilization of the back-side transition state. The S_Ni mode is preferred for ethyl chlorosulfite, in the gas phase and in all solvents; the cationic center is stabilized more by hyperconjugation than by solvent interaction.

Introduction

While nucleophilic displacement reactions are generally characterized by back-side nucleophilic attack, *front-side* attack is often found in internal nucleophilic displacement reactions (S_Ni) of, e.g., a primary alkyl chlorosulfite. The "classical" S_Ni (eq 1) reaction involves the formation and decomposition of an intermediate chlorosulfite (ROSOCl) from the reaction of an alcohol with thionyl chloride ($SOCl_2$).

$$ROH + SOCl_2 \rightarrow ROSOCl \rightarrow RCl + SO_2 \tag{1}$$

The retention of configuration of the decomposition products, alkyl chlorides, was attributed to a front-side substitution mechanism. In our recent experimental and theoretical investigation,[2] we concluded that ionization in polar solvents, e.g., acetonitrile, yields $ROSO^+ + Cl^-$ for R = primary alkyl group, and $R^+ + OSOCl^-$ for R = secondary or tertiary alkyl group. The decomposition of apocamphanyl chlorosulfite (7,7-dimethylbicyclo[2.2.1]-heptyl 1-chlorosulfite) and neopentyl chlorosulfite [$(H_3C)_3CCH_2OSOCl$] proceeds without rearrangement to give alkyl chlorides. This provided evidence for nucleophilic *front-side* attack of $ROSO^+$ by Cl^-, and this reaction pathway was designated S_N2i.[3] We also confirmed experimentally that the rates of decomposition of chlorosulfites, which follow first order kinetics, are accelerated in polar solvents.

We have now computed the reaction paths for the front- and back-side attack of $ROSO^+$ by Cl^- for methyl and ethyl chlorosulfite. Furthermore, we examined the effect of different solvent polarities upon the energies of stationary structures by employing the self-consistent reaction field model (SCRF).[4]

Methods

The *ab initio* program Gaussian 92,[5] running on an Indigo Iris XS-24 workstation, was employed to fully optimize geometries within the designated symmetry constraints at the restricted Hartree–Fock (HF)[6] level using gradient optimization techniques[7] and standard basis sets (3-21G(*), 6-31G*, and 6-31+G*). Electron correlation was incorporated by applying second-order Møller–Plesset theory (MP2)[6,8] keeping the core electrons frozen (MP2-fc). Analytic vibrational frequencies were obtained up to the HF/6-31G* level of theory to determine the number of imaginary frequencies (NIMAG) which characterize each stationary point (where minima have NIMAG = 0 and transition structures have NIMAG = 1).[9]

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[1] (a) University of Georgia. (b) Universität Erlangen—Nürnberg.

[2] Schreiner, P. R.; Schleyer, P. v. R.; Hill, R. K. *J. Org. Chem.* **1993,** *58,* 2822, and references cited therein.

[3] The term S_N2i does not refer to second-order kinetics, but rather to a description of the nature of the transition state, which is S_N2-like. The reaction is still first-order.

[4] Ming, W. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991,** *113,* 4776 and references cited therein.

[5] GAUSSIAN 92, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M, A.; Replogle, E. S.; Gomperts, R.; Andres, J. L; Raghavachari, K.; Binkley, J. S.; Gonzales, G.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1992.

[6] Hehre, W. J.; Radom, L.; Pople, J. A.; Schleyer, P. v. R. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons, Inc., New York, 1986.

[7] Broyden, C. G. *J. Math. Appl.* **1970,** *6,* 222. Fletcher, R. *Comp. J.* **1970,** *13,* 317. Goldfarb, D. *Math. Comput.* **1970,** *24,* 647. Shanno, D. F. *J. Optim. Theory Appl.* **1985,** *46,* 87.

[8] Møller, C.; Plesset, M. S. *Phys. Rev.* **1934,** *46,* 618. Binkley, J. S.; Pople, J. A. *Int. J. Quant. Chem.* **1975,** *9,* 229. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quant. Chem.* **1976,** *S10,* 1.

[9] The normal coordinates of the imaginary vectors of the transition structures have been carefully examined to ensure that they actually do point in the direction of the minimum energy structures for the forward and backward reaction. We have no reason to assume other minima along the course of the reaction. A more detailed analysis of the reaction path (in form of, e.g., an intrinsic reaction coordinate calculation) therefore seems to be unnecessary.

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Table 1. Absolute Energies (in au) of Ground and Transition States of Methyl and Ethyl Chlorosulfite. Zero-Point Vibrational Energies (ZPVE) in Brackets. MP2 in Frozen Core Approximation (MP2-fc)

species	HF/3-21G(*)	HF/6-31G*	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
MeOSOCl^{a} (**1**, C_1)	1041.29323 (32.7)	1046.24469 (32.9)	1046.25413 (32.8)	1047.00830	1047.03081
MeOSO$^{+\,a}$ (**2**, C_s)	583.61153 (31.2)	586.47721 (31.6)	586.48087 (31.5)	587.10924	587.11945
$\mathbf{TS_{1f}}^{a}$ (C_1)	1041.20487 (29.9)	1046.15229 (29.6)	1046.16218 (29.6)	1046.91303	1046.93753
$\mathbf{TS_{1b}}^{a}$ (C_s)	1041.19950 (30.7)	1046.14021 (30.7)	1046.15690 (30.7)	1046.90494	1046.92755
EtOSOCl^{b} (**3**, C_1)	1080.11904 (51.8)	1085.28576 (52.0)	1085.29555	1086.17472	1086.19852
EtOSO$^{+\,b}$ (**4**, C_s)	622.44336 (50.3)	625.52459 (50.4)	625.52876	625.27775	626.28919
$\mathbf{TS_{3f}}^{b}$ (C_1)	1080.04238 (48.8)	1085.21027 (48.4)	1085.22078	1086.08542	1086.11206
$\mathbf{TS_{3b}}^{b}$ (C_s)	1080.02928 (49.7)	1085.19548 (48.4)	1085.20669	1086.07025	1086.09574
Cl^-	457.44412	459.52510	459.53966	459.65210	459.67115

^{a} Structures fully optimized at all levels. ^{b} Structures fully optimized at the HF/3-21G(*) and HF/6-31G* levels. Higher levels are single-point energy calculations on the optimized HF/6-31G* geometries.

Table 2. Relative Energies (in kcal mol^{-1}, including ZPVE) of the Transition States for the Methyl and Ethyl Chlorosulfite Decomposition versus the Ground States. MP2 in Frozen Core Approximation (MP2-fc). ZPVE's at the MP2 Levels Taken from the Frequency Calculations at HF/6-31+G* for Methyl Chlorosultie and at HF/6-31G* for Ethyl Chlorosulfite

species	HF/ 3-21G(*)	HF/ 6-31G*	HF/ 6-31+G*	MP2/ 6-31G*	MP2/ 6-31+G*
$\mathbf{TS_{1f}}^{a}$	52.6	54.7	54.5	56.6	55.6
$\mathbf{TS_{1b}}^{a}$	59.3	63.3	58.9	62.7	62.7
$\mathbf{TS_{1f}}$ vs $\mathbf{TS_{1b}}$	−7.5	−9.8	−5.5	−7.3	−8.5
$\mathbf{TS_{3f}}^{b}$	45.1	43.8	43.3	52.4	50.6
$\mathbf{TS_{3b}}^{b}$	54.2	53.0	52.1	61.9	60.9
$\mathbf{TS_{3f}}$ vs $\mathbf{TS_{3b}}$	−9.1	−9.2	−8.8	−9.5	−10.3

^{a} Structures fully optimized at all levels. ^{b} Structures fully optimized at the HF/3-21G(*) and HF/6-31G* levels. Higher levels are single-point energy calculations on the optimized HF/6-31G* geometries.

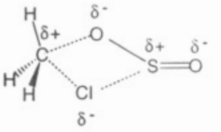
The self-consistent reaction field (SCRF)[4] method, as implemented in the Gaussian 92 program,[5] is based on the Onsager model.[10] The solute is surrounded by a spherical cavity that represents a continuous medium with a dielectric constant ϵ. The radius of the cavity is determined by the molecular volume of the molecule, i.e., its van der Waals volume. Thus, the dielectric constant of the solvent and the radius of the spherical cavity are the only additional parameters required for a SCRF calculation. Standard notation[6] is used; "//" means "at the geometry of ".

Results and Discussion

Gas Phase. Methyl Chlorosulfite. We fully optimized all structures involved in the decomposition of methyl chlorosulfite (1) up to the MP2/6-31+G* level (Tables 1 and 2, Figure 1). Surprisingly, the effects of basis set and theoretical method upon the relative energies of the front- and back-side transition states are not large, and range only between 5.5 and 9.8 kcal mol^{-1}. Front side attack ($\mathbf{TS_{1f}}$) is favored in all cases over back-side displacement ($\mathbf{TS_{1b}}$), by 8.5 kcal mol^{-1} at our best level (including ZPVE, Table 2). Nevertheless, the absolute activation energies are large, 55.6 ($\mathbf{TS_{1f}}$) and 62.7 ($\mathbf{TS_{1b}}$) kcal mol^{-1}, and this can generally be attributed to the instability of the methyl cation which was found to be nearly planarized for both transition structures. If one uses the degree of planarization as an indication for the cation character of the methyl cation moiety in both transition states, we found that they are very similar, as the H–C–H angles are 116.8° ($\mathbf{TS_{1f}}$) and 116.2° ($\mathbf{TS_{1b}}$). Consequently, ion pair stabilization must play the dominant role in determining the mechanism, as we will discuss below. On the other hand, the methyl sulfinyl cation (CH_3OSO^+) is quite stable, and has been observed in solution[12] and in the solid state.[13]

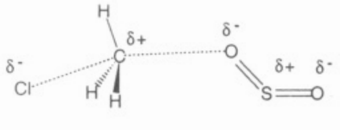
Two suggestions may be offered for the 6.3 kcal mol^{-1} (this is the absolute energy difference between the two transition structures, Table 2) preference of front- over back-side attack in nonpolar environments:

(a) Electrostatic attraction (mainly the sulfur–chlorine interaction) is maximized in $\mathbf{TS_{1f}}$, where we found a quadrupole interaction instead of the simple dipole interactions in $\mathbf{TS_{1b}}$.



TS$_{1f}$

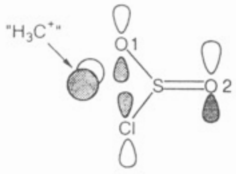
vs.



TS$_{1b}$

Since the sulfur dioxide and methyl cation moieties in both transition structures are quite comparable, the main difference between $\mathbf{TS_{1f}}$ and $\mathbf{TS_{1b}}$ appears to be electrostatic interactions. The stabilization provided by the sulfur–chlorine interaction in $\mathbf{TS_{1f}}$ is the principal electrostatic attraction favoring front-side attack.

(b) The [1,3]-methyl shift from oxygen to chlorine is a symmetry allowed concerted process, due to Y-conjugation with another p-orbital on oxygen(2). An idealized (by constraining $\mathbf{TS_{1f}}$ to C_s symmetry) representation of one of the p-orbitals depicted below shows that the suprafacial shift of the methyl cation involving inversion is an allowed concerted process.



Even though a concerted reaction is not necessarily favored over a stepwise process, a lower barrier for the concerted reaction could be justified because the reorganization of atoms is significantly less, as no ionization has

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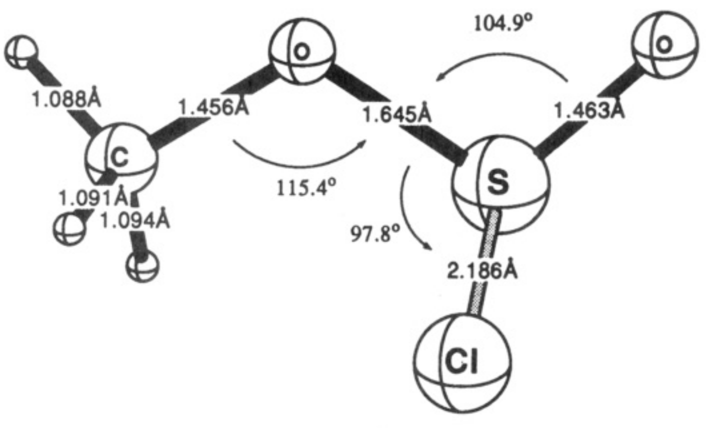
(10) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.

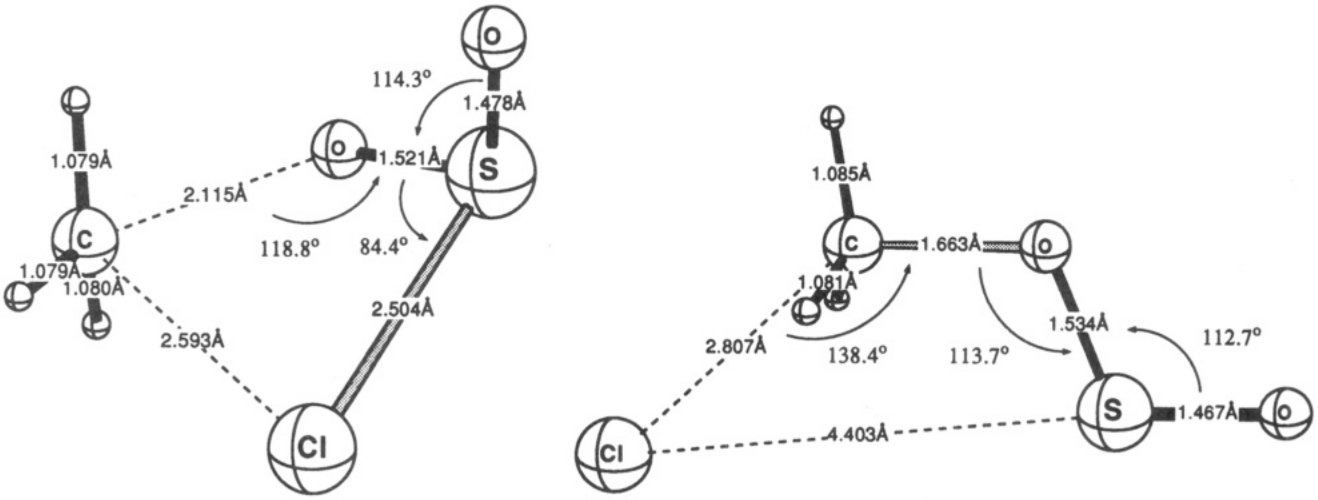
(11) Olah, G. A.; Schilling, P.; Bollinger, M. J.; Nishimura, J. *J. Am. Chem. Soc.* **1974**, *96*, 2221.

(12) Gillespie, R. J.; Riddell, F. G.; Shim, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 8069.

(13) *Handbook of Chemistry and Physics*, 1st student ed.; CRC Press Inc.; Boca Raton, Florida, 1987.



Methyl chlorosulfite (**1**), C_1, [0]



$\mathbf{TS_{1f}}$, C_1, [1] $\mathbf{TS_{1b}}$, C_s, [1]

Figure 1. All stationary points on the methyl chlorosulfite decomposition energy hypersurface at the MP2/6-31+G* level. The number of imaginary frequencies (HF/6-31+G*) is given in square brackets.

to precede front-side displacement (see discussion on the entropy of the reaction below).

The 8.5 kcal mol^{-1} difference in activation energies corresponds to a ca. 10^5 faster front-side than back-side decomposition. Thus, in the gas phase, or in a nonpolar solvent (see below), only *front-side* substitution should occur.

Ethyl Chlorosulfite. Since the changes in geometries at various levels of theory are not large, we optimized ethyl chlorosulfite (**3**), the simplest chain alkyl chlorosulfite, at HF/3-21G(*) and at HF/6-31G*. The latter geometries were used for single point energy computations at higher levels. As for methyl chlorosulfite, the range in relative activation energies (8.8–10.3 kcal mol^{-1}) favoring front-side attack (Tables 1 and 2, Figure 2) is small. The differences in the activation barriers are somewhat larger than for the methyl case. More importantly, the absolute activation barriers are lower for the decomposition of **3**, due to the more stable ethyl cation moiety in the transition states ($\mathbf{TS_{3f}}$ and $\mathbf{TS_{3b}}$).

$$\mathbf{1} \rightarrow \mathbf{TS_{1f}} \quad (2) \quad \Delta H^{\ddagger} = 54.7 \text{ kcal mol}^{-1}$$

$$\mathbf{3} \rightarrow \mathbf{TS_{3f}} \quad (3) \quad \Delta H^{\ddagger} = 43.8 \text{ kcal mol}^{-1}$$

$$\Delta\Delta H^{\ddagger} \text{ (eq 3–eq 2)} = 10.9 \text{ kcal mol}^{-1}$$

$$\mathbf{1} \rightarrow \mathbf{TS_{1b}} \quad (4) \quad \Delta H^{\ddagger} = 63.3 \text{ kcal mol}^{-1}$$

$$\mathbf{3} \rightarrow \mathbf{TS_{3b}} \quad (5) \quad \Delta H^{\ddagger} = 53.3 \text{ kcal mol}^{-1}$$

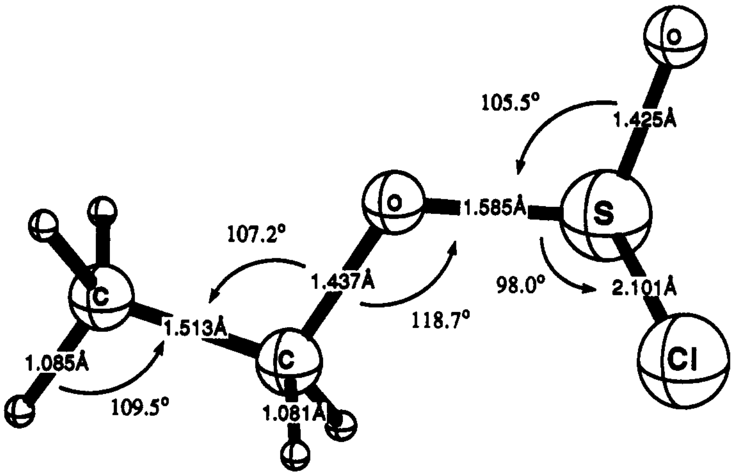
$$\Delta\Delta H^{\ddagger} \text{ (eq 5–eq 4)} = 10.0 \text{ kcal mol}^{-1}$$

$$CH_3^+(D_{3h}) + H_2 \rightarrow CH_4(T_d) + H^+ \quad (6) \quad \Delta H = 101.8 \text{ kcal mol}^{-1}$$

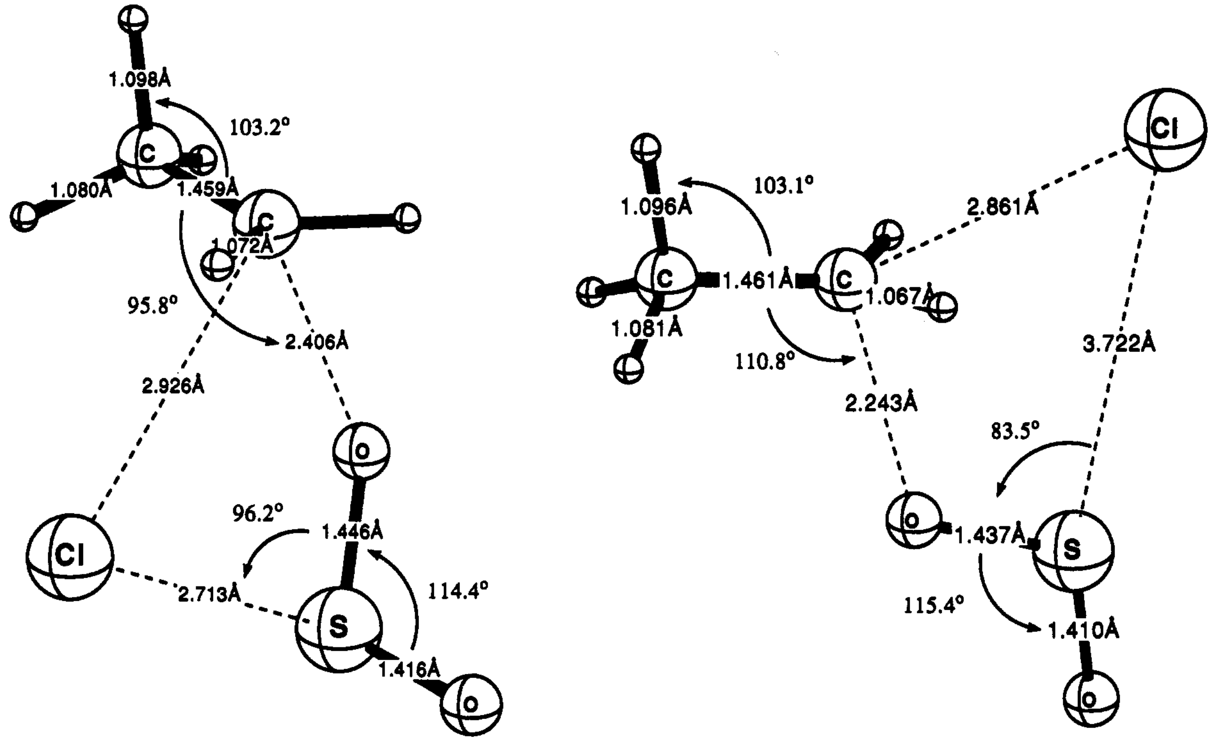
$$C_2H_5^+(C_{2v}) + H_2 \rightarrow C_2H_6(D_{3d}) + H^+ \quad (7) \quad \Delta H = 130.2 \text{ kcal mol}^{-1}$$

$$\Delta\Delta H \text{ (eq 7–eq 6)} = 28.4 \text{ kcal mol}^{-1}$$

The energies of the transition states (eqs 2–5, HF/6-31G*) generally do not reflect the 28.4 kcal mol^{-1} stabilization of $C_2H_5^+$ vs CH_3^+ (eqs 6 and 7, evaluated, for uniformity, at HF/6-31G*). We find much smaller values, 10.9 and 10.0 kcal mol^{-1}. The difference in stabilization is compensated by a larger ion pair stabilization in the methyl case through a stronger interaction with sulfur dioxide and the chloride ion. This is demonstrated in Figures 1 and 2: the C–O and C–Cl bonds, which provide



Ethyl Chlorosulfite (3), C_1, [0]



TS$_{3f}$, C_1, [1]

TS$_{3b}$, C_s, [1]

Figure 2. All stationary points on the ethyl chlorosulfite decomposition energy hypersurface at the HF/6-31G* level. The number of imaginary frequencies (HF/6-31G*) is given in square brackets.

an estimate of the ion pair interactions, are considerably shorter in **TS$_{1b}$** and **TS$_{1f}$** vs **TS$_{3b}$** and **TS$_{3f}$**.

Solution Simulation. We chose five different dielectric constants ϵ between 2.02[13] (hexane) and 78.54[13] (water) as solvent parameters to cover the usual range of solvent polarities. From our experimental experience,[2] we know that chlorosulfite decomposition reactions can actually be carried out in hexane, carbon tetrachloride, and sulfur dioxide, whereas methanol and water would attack either sulfur or carbon. Thus, the latter solvent parameters serve to model trends. The dielectric constant is only a rough guide to solvent properties and does not correlate linearly with directly measured effects of solvents on reaction rates.[14] For instance, water is represented through a large dielectric constant, but hydrogen bonding is neglected. Nevertheless, ϵ distinguishes nonpolar solvents, where ionic substances will remain associated, from polar solvents which facilitate ionic bond cleavages.

Methyl Chlorosulfite. We used the HF/6-31G* optimized gas phase geometries for all our SCRF/6-31G* single point energy computations. A full optimization of 1 in water at SCRF/3-21G(*) compared to the isolated structure HF/3-21G(*) (Figure 3) shows that the geometry does not change significantly, even in the most-polar solvent. The changes in, e.g., the bond lengths, are only in the 0.02-Å range.

Our results are summarized in Tables 3 and 4. **TS$_{1b}$** benefits more from solvent stabilization than **TS$_{1f}$** because of the larger charge separation in **TS$_{1b}$**. While the activation energies in all solvents are smaller than in the

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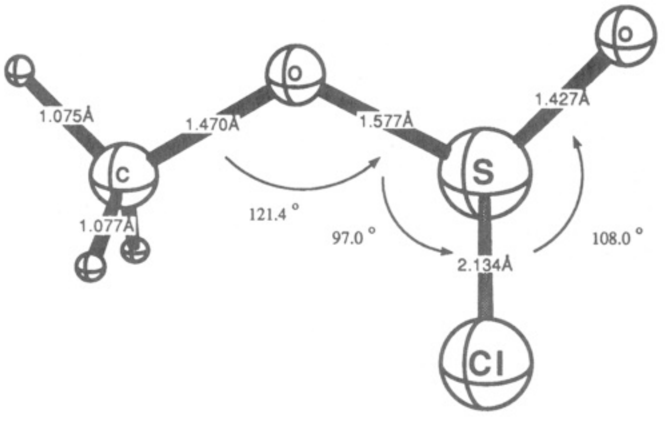
[14] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987, p 177.

Table 3. Absolute Energies (in au) Determined by Self-Consistent Reaction Field (SCRF/6-31G*, ϵ = dielectric constant at 298 K) Energy Computations in Different Solvents (geometries taken from the fully optimized HF/6-31G* gas-phase geometries)

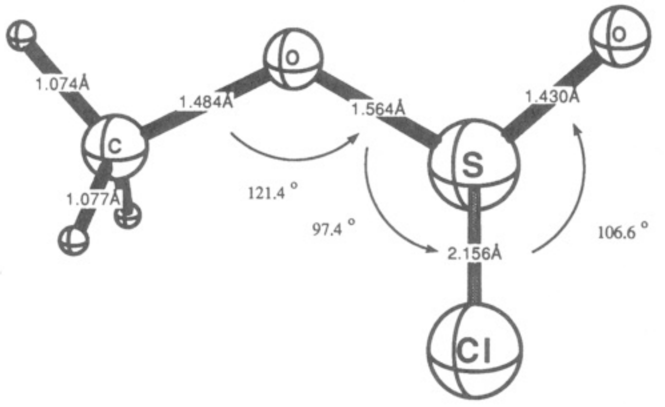
species (diameter, Å)	hexane ($\epsilon = 2.02$)	carbon tetrachloride ($\epsilon = 2.23$)	sulfur dioxide ($\epsilon = 14.10$)	methanol ($\epsilon = 32.68$)	water ($\epsilon = 78.54$)
1 (3.77)	1046.24674	1046.24699	1046.24953	1046.24988	1046.25004
2 (3.42)	586.47756	586.47760	586.47804	586.47811	586.47513
$\mathbf{TS_{1f}}$ (3.84)	1046.15645	1046.15696	1046.16225	1046.16299	1046.16333
$\mathbf{TS_{1b}}$ (3.87)	1046.15239	1046.15390	1046.16953	1046.17170	1046.17271
3 (3.99)	1085.28764	1085.28787	1085.29023	1085.29056	1085.29071
4 (3.68)	625.52464	625.52465	625.52471	625.52472	625.52472
$\mathbf{TS_{3f}}$ (4.05)	1085.21586	1085.21655	1085.22365	1085.22463	1085.22509
$\mathbf{TS_{3b}}$ (4.09)	1085.20196	1085.20276	1085.21096	1085.21209	1085.21261
Cl^- (2.94)	459.52600	459.52600	459.52600	459.52600	459.52600

Table 4. Relative Energies (in kcal mol^{-1} + ZPVE(HF/6-31G*) versus the Parent Chlorosulfite in Different Solvents at the SCRF/6-31G* Level (geometries taken from the fully optimized HF/6-31* gas-phase geometries)

species	hexane ($\epsilon = 2.02$)	carbon tetrachloride ($\epsilon = 2.23$)	sulfur dioxide ($\epsilon = 14.10$)	methanol ($\epsilon = 32.68$)	water ($\epsilon = 78.54$)
1	0.0	0.0	0.0	0.0	0.0
$\mathbf{TS_{1f}}$	53.3	53.2	51.5	51.2	51.1
$\mathbf{TS_{1b}}$	57.2	56.4	48.2	47.0	46.5
2 + Cl^-	151.4	151.3	152.7	152.9	153.0
3	0.0	0.0	0.0	0.0	0.0
$\mathbf{TS_{3f}}$	41.4	41.1	38.2	37.8	37.6
$\mathbf{TS_{3b}}$	50.2	49.8	46.1	45.6	45.4
4 + Cl^-	147.1	147.2	148.7	148.5	149.0



Methyl chlorosulfite (**3**), gas phase



Methyl chlorosulfite (**3**), in water

Figure 3. The structures of methyl chlorosulfite (**3**) in the gas phase and in water (SCRF calculation using a dielectric constant of $\epsilon = 78.54$) using the 3-21(*) basis set.

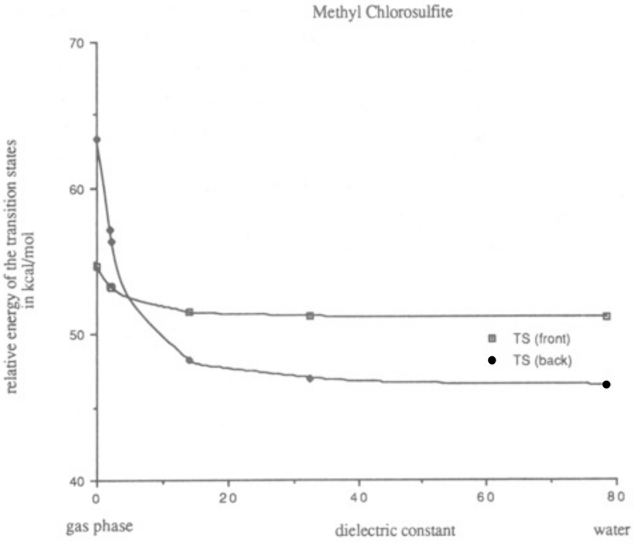


Figure 4. The relative energies of $\mathbf{TS_{1f}}$ versus $\mathbf{TS_{1b}}$ in the gas phase and in different solvents, determined at the SCRF/6-31G*//HF/6-31G* level.

gas phase, increase in ϵ favors $\mathbf{TS_{1b}}$ increasingly over $\mathbf{TS_{1f}}$. Back-side attack is preferred in a solvent of intermediate polarity (in sulfur dioxide by 3.3 kcal mol^{-1}), but does not increase very much in polar solvents (in water: 4.6 kcal mol^{-1}). The situation is shown in Figure 4.

As in the gas phase (see above), the ionization of **1** in the different simulated solvents is endothermic by around 152 kcal mol^{-1}, which is surprisingly high and not in agreement with our experiments,[2] where we observed that an ionization occurs easily in polar solvents. Consequently, we must either attribute this observation to a large entropy effect or to a drawback of the employed method in describing an ionization process properly. The experimental free energy of activation for ionization of neopentyl chlorosulfite indeed has a small enthalpy and a large entropy component ($\Delta H^a = 1.1$ kcal mol^{-1} and $\Delta S^a = -53.7$ cal K^{-1} mol^{-1}). We computed the entropy and ΔG, but the discrepancies did not improve significantly. We assume that the reorganization of the solvent and the increase of the number of species resulting from ionization are the largest entropy contributors, and those quantities are difficult to estimate.

Nevertheless, an ionization step to yield H_3COSO^+ and Cl^- must precede the back-side mode, but is not necessary for the front-side pathway.

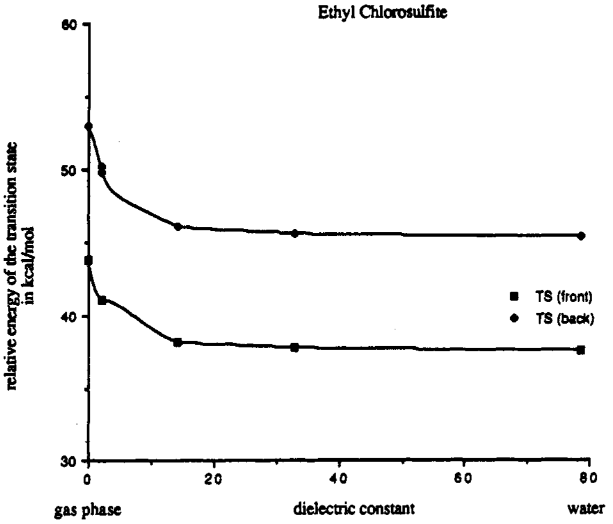


Figure 5. The relative energies of $\mathbf{TS_{3f}}$ versus $\mathbf{TS_{3b}}$ in the gas phase and in different solvents, determined at the SCRF/6-31G*//HF/6-31G* level.

Ethyl Chlorosulfite. The ethyl derivative is a more appropriate representative for primary alkyl chlorosulfites, and we found it to behave quite differently from methyl chlorosulfite. While the transition states $\mathbf{TS_{1f}}$ and $\mathbf{TS_{1b}}$ were stabilized to different degrees in different solvents, $\mathbf{TS_{3f}}$ and $\mathbf{TS_{3b}}$ benefit equally well from solvent stabilization. Consequently, the absolute activation barriers decrease with increasing polarity of the solvent, but the difference in relative energies of the two transition states remains approximately constant (Table 4 and Figure 5). The *front-side* attack is favored in *all* solvents, regardless of the polarity. This result is surprising at first, and the only reasonable explanation for this observation is that internal stabilization through hyperconjugation of a carbenium ion-like structure must be larger than the stabilization through the interaction with the solvent. It is known that the relative stability order of carbenium ions in the gas phase is the same as in the liquid phase.[14]

Conclusions

Front-side substitution ($\mathrm{S_N}$i) of methyl chlorosulfite is favored over back-side substitution ($\mathrm{S_N}2$) in the gas phase and in nonpolar solvents. In polar solvents, the back-side mode becomes more favorable due to a better stabilization of the back-side transition state by the solvent. For primary alkyl chlorosulfites, such as ethyl chlorosulfite, we find that the *front-side* attack is *always preferred*, in the gas phase and in solution.

The implications of our findings should be quite general for cases where the reacting carbon is an unstable cationic center or where a back-side substitution is impossible, e.g., at strained bridgehead positions.[15]

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(15) Olah, G. A., Lee, C. S.; Prakash, G. K. S. 205th American Chemical Society National Meeting, Denver, CO, Mar 28–Apr 2, 1993, ORGN 35. The authors found that 1-chloronorbornane readily alkylates substituted benzenes in the presence of aluminum chloride even at room temperature; as no long-lived 1-norbornyl cation was observed, a front-side mechanism was attributed to this reaction.