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Theoretical Studies of the Sulfenate−Sulfoxide Rearrangement

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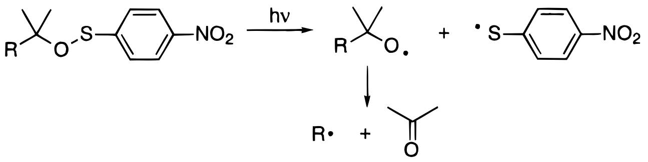
Introduction

Alkyl 4-nitrobenzenesulfenates are useful reagents for the generation of alkyl and alkoxy radicals.[1,2] Irradiation of these compounds with light of a wavelength of 350 nm induces the homolytic cleavage of the oxygen−sulfur bond and the formation of an alkoxy radical and the corresponding arylthyl radical. When the alkoxy radical is tertiary, it undergoes a β-scission to form an alkyl radical and a carbonyl compound, as shown in Scheme 1. When the alkoxy radical is primary or secondary, disproportionation and β-scission are observed. This versatile method for the generation of alkoxy and alkyl radicals has been employed to study the mode of ring opening of oxiranylmethyl radicals.[3]

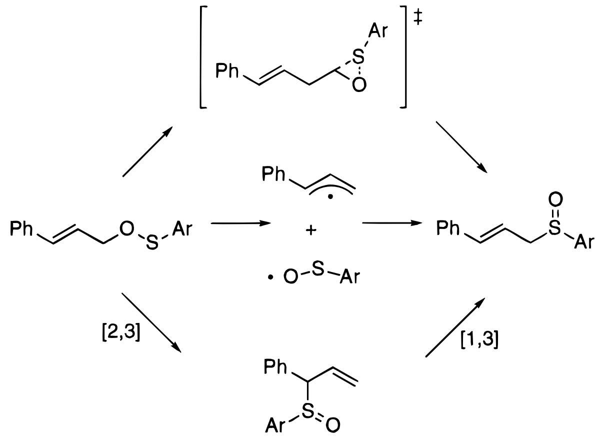
The thermal reactivity of alkyl 4-nitrobenzenesulfenates has also been explored. A solution of cinnamyl 4-nitrobenzenesulfenate in benzene refluxed for several hours yields cinnamyl 4-nitrobenzenesulfoxide as the only product. This type of reaction has precedents in the literature, but the mechanism has yet to be elucidated.[4] More recently, the sulfenate−sulfoxide chemistry has attracted considerable interest, in part because the opposite reaction, i.e., the rearrangement of a sulfoxide to a sulfenate, has been observed under photochemical conditions.[5] Upon photolysis, aryl benzyl sulfoxides are proposed to undergo α-cleavage to form a radical pair which upon recombination in the solvent cage yields the corresponding sulfenate as the first step in the rearrangement reaction.[5b]

We present the results of theoretical studies on the rearrangement of alkyl aryl sulfenates to alkyl aryl sulfoxides. Three possible mechanisms, shown in Scheme 2, have been taken into consideration: two concerted pathways involving a $[1_s,2_s]$ alkyl shift and a $[1_a,2_s]$ alkyl shift and a stepwise pathway involving the homolytic cleavage of the carbon−oxygen bond producing a radical pair intermediate. The two-step mechanism consisting of a $[2_s,3_s]$ sigmatropic shift[6] followed by a $[1_a,3_s]$ shift of the sulfoxide group was not considered because the symmetry allowed $[1_a,3_s]$ shift involves a contorted geometry and is expected to be slower than the $[2_s,3_s]$ sigmatropic shift. This should lead to a buildup of the $[2_s,3_s]$ rearrangement product. In the experimental studies, however, no intermediate could be detected when the reaction was monitored by NMR. Moreover, the same type of thermal rearrangement involving benzyl *p*-toluenesulfenate has been studied by Mislow and coworkers and does not allow a [2,3] shift to occur as the first step of the reaction.[4] This reaction sequence is therefore not likely to occur.

Scheme 1



Scheme 2



We report here rigorous calculations of the parent reaction, the rearrangement of methylsulfenate to methylsulfoxide using high-level quantum mechanical methods and large basis sets to evaluate the energies of reactant, product, transition structures, and intermediates. G2(MP2)[7] and complete basis set CBS-Q[8] calculations have been carried out in order to provide a reference since these methods have been proven to be highly accurate (within ∼1 kcal/mol).[9]

Computational Methodology

The GAUSSIAN94 package of programs[10] has been used for all of the calculations. Geometries were fully optimized at the UHF/6-31G* level, the MP2/cc-pVDZ, and the B3LYP/cc-pVDZ[11] levels of theory. All stationary points have been characterized by harmonic frequency analysis and possess the correct number of imaginary frequencies. Zero point energy (ZPE) corrections have been taken from the frequency analysis at the appropriate levels of theory. All UHF, MP2, and B3LYP energies are reported in kcal/mol relative to the starting material **1** and are corrected for zero-point energies. Basis set effects have been studied by single-point energy calculations on optimized geometries using the cc-pVTZ and cc-pVQZ basis sets. G2(MP2) and

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† Dr. Daniel J. Pasto deceased on March 25, 1998.

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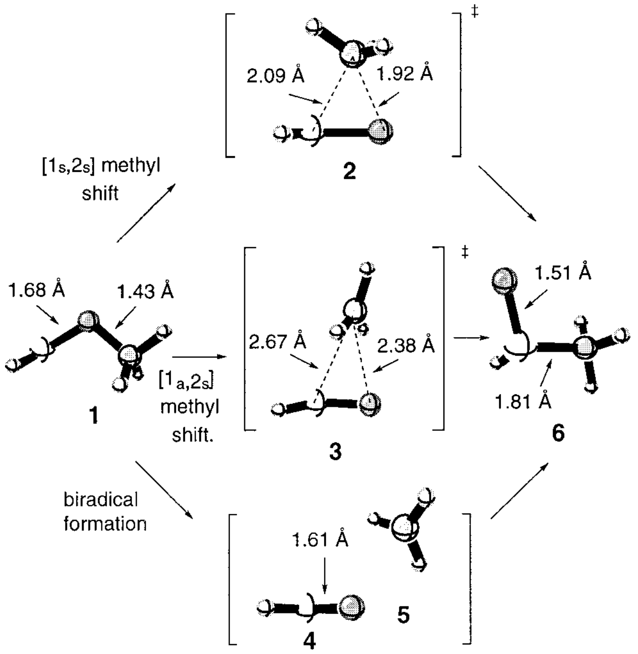

Figure 1. MP2/6-31G* geometries of the reactants, transition structures, intermediates and products of the parent sulfenate–sulfoxide rearrangement.

CBS-Q calculations have been performed to provide a reference for the other calculations since no experimental data are available on the thermochemistry of the reaction under study. Both methods have been shown to give reliable thermochemical data for a number of open-shell species, as well as for thiols, sulfides, and sulfoxides.[12]

Results and Discussion

Theoretical calculations have been carried out on the reactant **1**, the product **6**, and two concerted transition structures corresponding to the supra-suprafacial pathway, **2**, and the supra-antarafacial pathway, **3**. The stepwise pathway involving the radical pair **4** and **5** was also calculated. The geometries obtained for structures **1**, **2**, and **6** were found to be similar to the ones obtained by Schlegel in a study of the electronic structure of dimethyl sulfoxide.[13] The structures obtained in our study are shown in Figure 1.

Thermochemistry. The initial calculations involved the investigation of the thermochemistry of the overall reaction. The results for these calculations are summarized in Table 1. At the best levels of theory used in this study, the reaction of the methylsulfenate model system is found to be essentially thermoneutral. However, the calculated reaction energies are found to be surprisingly sensitive to basis set effects. The relatively small double-ζ basis set is clearly not capable of describing the thermochemistry of the reaction adequately and predicts the reaction to be endothermic by approximately 16 kcal/mol. This large heat of reaction was already observed on previous calculations with a similar system and level of theory.[13] Increasing the basis set size with the B3LYP and MP2 methods lowers the energy difference between the product and the reactant. For both methods, a difference of ~10 kcal/mol is found on going from a cc-pVDZ basis set to a cc-pVTZ basis set. The same trend is observed to a smaller extent (~3 kcal/mol) when the size of the basis set is increased to cc-pVQZ. Very interestingly, the energies of activation for the different mechanisms do not reveal any significant basis set size dependency. It appears that the structure of the product and the nonconventional sulfur–oxygen double bond requires that large diffuse functions must be included for an accurate energy calculation.[14]

Table 1. Energy Difference[a] between the Reactant and the Product

method	ΔE (in kcal/mol)
UHF/6-31G*	17.7
UMP2/6-31G*	10.0
QCISD(T)/6-311G(d,p)//UMP2/6-31G*	11.9
MP2/6-311+G(3df, 2p)//UMP2/6-31G*	−0.6
G2/MP2 enthalpy	1.0
CBS-Q	0.1
B3LYP/cc-pVDZ	16.4
B3LYP/cc-pVTZ//B3LYP/cc-pVDZ	6.2
B3LYP/cc-pVQZ//B3LYP/cc-pVDZ	3.4
MP2/cc-pVDZ	16.8
MP2/cc-pVTZ//MP2/cc-pVDZ	4.3
MP2/cc-pVQZ//MP2/cc-pVDZ	0.4

Activation Energies. The homolytic cleavage of the carbon–oxygen bond of the sulfenate was studied by comparing the sum of the energies of the two radicals formed (methyl and sulfinyl) with the energy of the starting material. To investigate the existence of a transition structure for the formation of this pair of radicals, the C–O bond length was increased from 1.43 to 3.13 Å while optimizing all other parameters at the UQCISD/6-31G* level of theory. Single-point energy calculations were then performed at the UQCISD(T)/6-311G(d,p) level of theory on these optimized structures. When the O–S bond length was greater than 2.53 Å, the geometry could no longer be optimized using the UQCISD method, mainly because of the lack of analytic gradients in this method. A similar scan was then performed, and the geometries were optimized at the UMP2/6-31G* level of theory. Again, single-point energy calculations were performed at the UQCISD(T)/6-311G(d,p) level of theory on these optimized geometries. The two energy curves thus obtained are displayed in Figure 2. The UQCISD(T)/6-311G(d,p) energies on the two different geometry scans are within 2 kcal/mol, and it can be assumed that

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Table 2. Energies of Activation for the $[1_s,2_s]$ and the $[1_a,2_s]$ Methyl Shifts, Energy of Dissociation for the Formation of a Radical Pair with Different Methods of Calculation (Given in kcal/mol)

method	$E_a([1_s,2_s]$ TS)[a]	$E_a([1_a,2_s]$ TS)[b]	E (dissociation)[c]
UHF/6-31G*	96.0	103.0	32.3
UMP2/6-31G*	93.3	80.0	57.2
QCISD(T)/6-311G(d,p)//UMP2/6-31G*	84.3	67.3	61.2
MP2/6-311+G(3df, 2p)//UMP2/6-31G*	73.3	70.5	54.5
G2/MP2 enthalpy	71.6	56.7	53.7
CBS-Q	72.1	57.8	50.5
B3LYP/cc-pVDZ	78.2	71.2	53.0
B3LYP/cc-pVTZ//B3LYP/cc-pVDZ	74.1	65.3	47.1
B3LYP/cc-pVQZ//B3LYP/cc-pVDZ	73.0	64.2	45.8

[a] Calculated as $E(\mathbf{2}) - E(\mathbf{1})$. [b] Calculated as $E(\mathbf{3}) - E(\mathbf{1})$. [c] Calculated as $E(\mathbf{4}) + E(\mathbf{5}) - E(\mathbf{1})$.

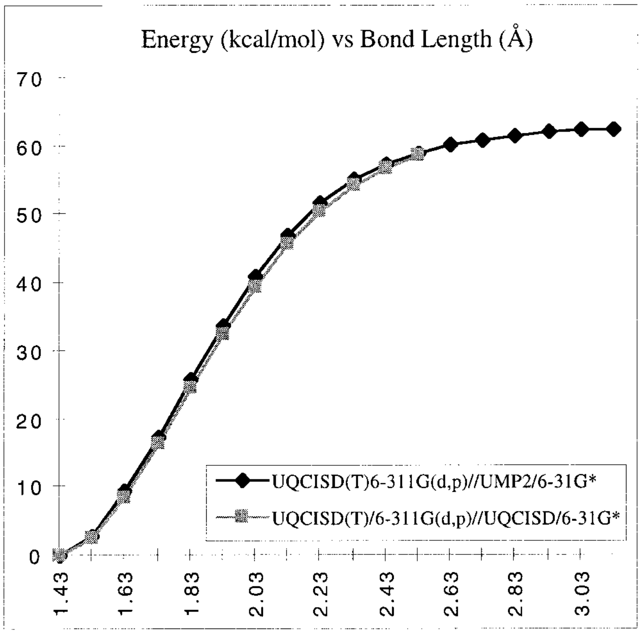

Figure 2. Potential energy surface scan along the C−O bond in methyl sulfenate.

the UMP2/6-31G* calculations yield very similar geometries compared with those obtained by the UQCISD/6-31G* level of theory. No transition structure could be found in these potential energy surface scans, and the energy levels off at approximately 62 kcal/mol above the reactants when the carbon−oxygen bond length reaches 2.5 Å. The difference in energy between the radical pair and the reactant corresponds to the energy of activation for the homolytic cleavage of the carbon−oxygen bond.

The energies of activation for the three mechanistic pathways are given in Table 2. The biradical pathway is found to be favored independent of the method used. The two most accurate methods, G2(MP2) and CBS-Q, both predict that the antarafacial concerted rearrangement is disfavored over the diradical pathway by 3 and 7 kcal/mol, respectively. According to the principle of conservation of orbital symmetry,[15] the $[1_s,2_s]$ shift is forbidden while the $[1_a,2_s]$ shift is allowed (Figure 3). In agreement with this qualitative picture, the energy of activation is calculated to be 14−15 kcal/mol higher for the $[1_s,2_s]$ methyl shift than for the $[1_a,2_s]$ pathway. It is important to note that the combined energy of the pair of radicals was calculated without taking the basis set superposition error (BSSE) into account. It is known that this error depends on the basis set size, and given the large basis set used in G2(MP2) and CBS-Q methods, the BSSE is expected to be small. The energies found at the UHF/6-31G* level are found to be quite inaccurate when compared to the values calculated with the G2(MP2) and CBS-Q methods. Unrestricted Hartree−Fock methods are known to give poor energy values for radical species due to spin contamination and an inappropriate description of electron correlation. The relative energies of the radical pair obtained by the B3LYP/cc-pVDZ method are very close to the ones obtained by the G2(MP2) method and only 2.5 kcal/mol higher than the value from the CBS-Q method. The energy difference of the $[1_s,2_a]$ pathway obtained at this level is 18.4 kcal/mol which is substantially higher than the 7.3 kcal/mol obtained by the CBS-Q reference method.

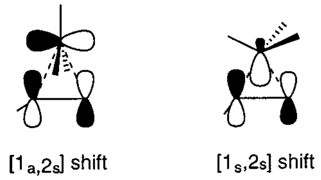

Figure 3. Orbital interactions in the transition states of the $[1_a,2_s]$ and the $[1_s,2_s]$ shift.

Performance of the Density Functional Theory (DFT) Methods. Calculations using hybrid DFT have also been carried out in order to evaluate the performance of this approach for the study of the sulfenate−sulfoxide rearrangement. Larger systems that cannot be studied with time-consuming conventional post-Hartree−Fock methods become accessible to calculation by the use of hybrid DFT methods. These methods are computationally much more effective and are easily applicable to more realistic chemical systems. In the attempt to evaluate the performance of the B3LYP method, it was found that, as with the other methods, the biradical pathway is favored over the concerted pathways. It should be noted, however, that the $[1_s,2_s]$ shift is found to be disfavored by only 8−9 kcal/mol compared to the $[1_a,2_s]$ shift, while this difference is 14−15 kcal/mol with the G2(MP2) and CBS-Q methods. To further analyze this deviation from the reference calculations, a charge analysis using CHelPG[16] was performed on both transition structures at the B3LYP/cc-pVDZ and MP2/6-31G* levels of theory. The results are given in Table 3.

The charge separation observed for the $[1_s,2_s]$ transition structure is small, and both methods give similar values (0.24 for B3LYP/cc-pVDZ and 0.31 for MP2/6-31G*). However, the MP2/6-31G* calculation finds a

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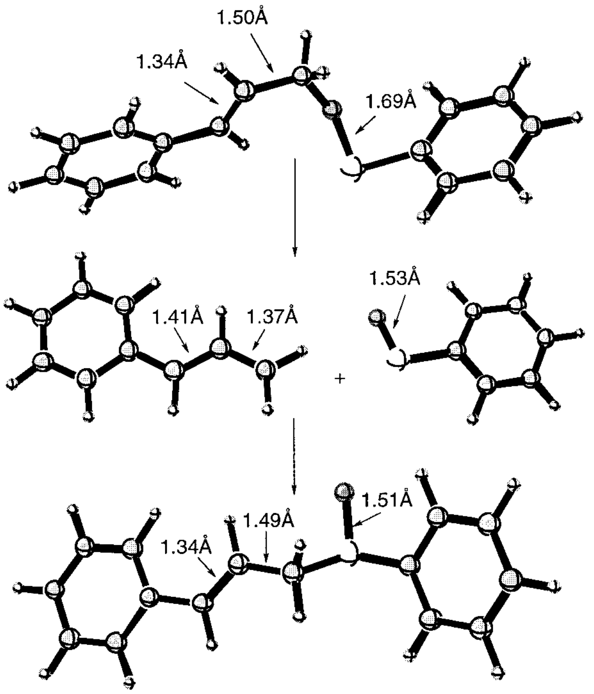

Figure 4. Optimized geometries (Becke3LYP/6-31G*) for the dissociation of cinnamyl phenylsulfenate.

Table 3. Partial Charges on Methyl Group in the Two Transition Structures

method	[1_s,2_s] TS	[1_a,2_s] TS
UB3LYP/cc-pVDZ	0.23	0.14
UMP2/6-31G*	0.31	0.38

charge separation of 0.38 for the [1_a,2_s] transition structure which is much higher than the 0.14 obtained with the B3LYP/cc-pVDZ method. Given the relatively "loose" [1_a,2_s] transition structure, it appears that the B3LYP method is unable to correctly describe the charge. This problem is less pronounced in the tighter [1_s,2_s] transition structure. There have already been several reports of the problems of DFT calculations on weakly bonded systems in the literature.[17] The DFT results for the [1_a,2_s] transition structure should therefore be considered with caution.

It should be noted that the calculated activation energies are very high when compared with the experimental conditions under which the reaction takes place. This is due to the lack of radical stabilization in our methyl sulfenate model system. Since the B3LYP/cc-pVTZ//B3LYP/cc-pVDZ method allows a fairly accurate description of the lowest energy diradical pathway, we decided to use the hybrid DFT method for the calculation of a chemically more realistic system. The dissociation of cinnamyl phenylsulfenate into the cinnamyl radical and the corresponding sulfuranyl radical to form cinnamyl phenyl sulfoxide was evaluated with a calculation at the B3LYP/cc-pVTZ//B3LYP/6-31G* level. The optimized geometries are shown in Figure 4. It can be seen from these structures that the unpaired electron is completely delocalized in the cinnamyl moiety. At the same time, the highest spin density in the phenyl sulfuranyl radical resides on the sulfur, making the observed recombination to cinnamyl phenyl sulfoxide the predominant process. An energy difference of 19.6 kcal/mol was computed between the radical pair and the sulfenate. Taking into account that the B3LYP/cc-pVTZ method overstabilizes the dissociative pathway by 3−7 kcal/mol for the model system as shown in Table 2, the dissociation energy of cinnamyl phenylsulfenate can be corrected to 23−27 kcal/mol. This value is consistent with the temperature (~80 °C) at which the reaction of cinnamyl 4-nitrobenzenesulfenate was observed experimentally. The reaction was found to be endothermic by 1.8 kcal/mol, compared to 3.4 kcal/mol for the reaction of **1**. The cinnamyl and phenyl groups stabilize the sulfoxide compared to the sulfenate by ~2 kcal/mol. Considering that the B3LYP/cc-pVTZ method overestimates the endothermicity compared to G2(MP2) and CBS-Q on the small system as shown in Table 1 by 2−3.5 kcal/mol, the thermolysis of cinnamyl phenylsulfenate becomes thermoneutral or slightly exothermic (−2 to 0 kcal/mol) after correction.

Conclusions

Three different pathways have been considered in this theoretical study to account for the thermal reaction of alkyl arylsulfenates: a supra-suprafacial [1,2] alkyl shift, an antara-suprafacial [1,2] alkyl shift, and a homolytic scission giving a radical pair. The formation of the radical pair was found to occur without going through a transition structure. The biradical mechanism was predicted to be the lowest energy pathway by both the G2(MP2) and CBS-Q methods, with the radical pair being 53.7 and 50.5 kcal/mol higher in energy than the reactants, respectively. The energy of activation for the [1_a,2_s] methyl shift was calculated to be ~3 and ~7 kcal/mol, respectively, higher than the diradical pathway. Therefore, a [1_a,2_s] mechanism cannot be definitively excluded for the model system. The transition structure corresponding to this concerted pathway displays a large charge separation. The hybrid DFT method B3LYP was found to display some degree of inaccuracy due to its inability to separate the charges present in the [1_a,2_s] methyl-shift transition structure. The heat of formation of the radical pair derived from the chemically more significant cinnamyl phenylsulfenate is, however, only 23−27 kcal/mol, making a diradical process the most likely mechanism for the observed rearrangement. A strong basis set size effect was obtained when calculating the energy of the sulfoxide, the product of the reaction. The thermal rearrangement reaction is currently under further investigation. The results of these experimental studies will be published in due course.

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Supporting Information Available: Cartesian coordinates and energies of all structures reported (14 pages). This material is contained 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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