The Thermal Sulfenate−Sulfoxide Rearrangement: A Radical Pair Mechanism

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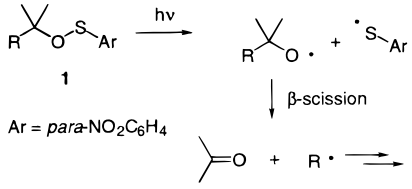
Abstract: The thermal reaction of sulfenates (RS−OR), yielding their corresponding sulfoxides (RS(=O)R), was studied experimentally. The first step of the reaction was found to be the formation a radical pair by homolytic cleavage of the carbon−oxygen bond of the sulfenate. The two transient radicals formed then recombine to form the carbon−sulfur bond of the sulfoxide. The thermolysis of cinnamyl-4-nitrobenzenesulfenate has a positive entropy of activation ($\Delta S^{\ddagger} = 6.4 \pm 2.0$ eu in toluene), characteristic of a dissociative pathway. A normal secondary kinetic isotope effect ($k_H/k_D = 1.19 \pm 0.04$) was also measured with this substrate. Finally, a trapping experiment allowed the isolation and characterization of a product coming from the coupling of the cinnamyl radical and TEMPO. These studies confirm a mechanism that was proposed earlier based on computational studies. The experimentally determined bond dissociation energy of the carbon−oxygen bond of ∼28 kcal·mol^{-1} is in good agreement with the computed value of ∼26 kcal·mol^{-1}. These studies confirm a unique structural feature of the sulfenate moiety, where the weakest bond of the molecule in the ground state is not the heteroatom−heteroatom bond intuitively considered to be the weakest based on the analogy to peroxides or disulfides. Radical stabilizing substituents are expected to have a large effect on the thermal reactivity of sulfenates. Evidence for a competing acid-catalyzed mechanism has also been observed.

Introduction

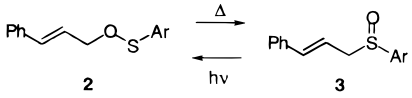
Alkyl-4-nitrobenzenesulfenates **1** are useful reagents for the generation of both alkoxy and alkyl radicals.[1,2] Their structure is related to the one of peroxide, where an oxygen atom would have been replaced by the next higher homologous element: sulfur. The *p*-nitrobenzene group confers to the sulfenate both stability, owing to its electrowithdrawing properties, and UV absorbance in the 350 nm region. Light of that wavelength cleaves the oxygen−sulfur bond homolytically, forming an alkoxy radical as well as a sulfenyl radical as shown in Scheme 1. When the alkoxy radical is tertiary, it will undergo a β-scission, losing a molecule of acetone, and give an alkyl radical. This versatile method for the generation of both alkoxy and alkyl radicals have been used to study the mode of ring opening of substituted oxiranyl methyl radicals.[3]

Observations in our laboratories suggested that these compounds are also sensitive to heat. Cinnamyl-4-nitrobenzenesulfenate **2** in refluxed benzene overnight yielded the corresponding sulfoxide **3** as the only product according to ^{1}H NMR analysis, as shown in Scheme 2. This reactivity was observed before, but the mechanism is still unclear.[4] Recently, this sulfenate−sulfoxide chemistry has attracted interest because the reverse reaction, that is, the rearrangement of a sulfoxide to a sulfenate has been observed under photochemical conditions.[5−8]

Scheme 1: Sulfenates as Precursors of Alkyl and Alkoxy Radicals by Photolysis



Scheme 2: The Thermolysis of Sulfenates Is the Reverse Reaction of the Photolysis of Sulfoxides



UV light induces an α-cleavage of the carbon−sulfur bond of aryl benzyl sulfoxides, and the two transient radicals formed recombine in the solvent cage to form the corresponding sulfenate in the first two steps of the reaction.[6] This product can then undergo further reactions under photolysis conditions.

Computational studies performed by us[9] and others[10] predicted a diradical pathway, shown in Scheme 3, to be favored over a concerted [1,2]-sigmatropic shift mechanism for the thermolysis of sulfenates. Here, we present experimental results on the thermolysis of cinnamyl-4-nitrobenzenesulfenate supporting the radical pair mechanism suggested there. This

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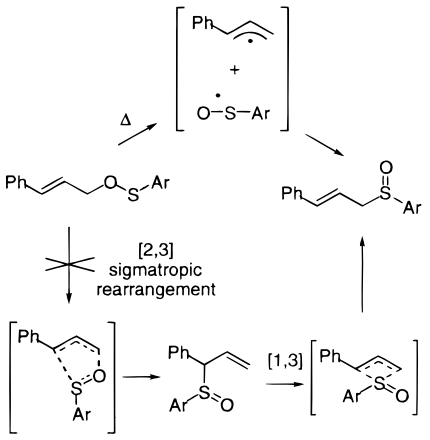
Scheme 3: Possible Mechanisms for the Thermolysis of Cinnamyl-4-nitrobenzenesulfenate



substrate was chosen for the study because the cinnamyl group stabilizes a possible radical intermediate, making the reaction faster at lower temperatures and therefore easier to perform in the laboratory. Moreover, the cinnamyl group is not prone to undergo the [2,3]-sigmatropic rearrangement (also called Evans−Mislow rearrangement) that is usually observed with allyl sulfenates.[11−13] The equilibrium between the sulfenate and the sulfoxide corresponding to a [2,3]-sigmatropic rearrangement shown in Scheme 3 was not observed in our early studies of the thermolysis of **2** when monitoring the reaction by NMR. Even though such a rearrangement involves lowering the energy by ∼5 kcal·mol^{-1} by going from a sulfenate to a sulfoxide moiety, as estimated by G2 calculations on CH_3SOCH_3 and DMSO,[10] it also involves breaking the conjugation between the allyl and the phenyl groups as well as going from a disubstituted to monosubstituted alkene, which would increase the energy by ∼6 kcal·mol^{-1}.[14] Therefore this rearrangement is likely to be energetically unfavorable. The possibility of a [2,3]-sigmatropic rearrangement as the first step of the mechanism of thermolysis of cinnamyl-4-nitrobenzensulfenate, followed by a [1,3]-shift to form the observed product has also been evaluated. However, the results presented in this paper refute this hypothesis. In addition, the thermolysis of benzyl-*p*-toluenesulfenate reported earlier cannot undergo such a reaction.[4]

This thermal sulfenate−sulfoxide rearrangement is of considerable importance because of its possible involvement in the synthetically useful [2,3]-sigmatropic rearrangement of allylic sulfoxides.[13] An allylic sulfenate is generated as an intermediate and is prone to homolytic cleavage and the formation of the corresponding sulfoxide. The net result would correspond to a [1,3]-shift of the sulfoxide moiety. Another interest resides in the fact that one can choose which bond to cleave homolytically in the sulfenate moiety, either S−O or O−C, by applying either light or heat. To our knowledge, this kind of versatile reactivity is unprecedented. The nature of the mechanism corresponding to the thermal sulfenate−sulfoxide rearrangement shown in Scheme 2 remains unclear as contradictory observations have been reported on this thermolysis.[4] A negative entropy of activation as well as a partial retention of configuration on the carbon α to the oxygen were reported and are consistent with a concerted pathway. However, a strong ESR signal was recorded and is congruous with the formation of a radical pair.[4] To tackle this question, we performed kinetic studies in toluene and acetonitrile, and the activation parameters of the reaction were determined. A normal secondary kinetic isotope effect (i.e., $k_H/k_D > 1$) was measured when the methylene group of **2** was deuterated. Finally, trapping experiments were carried out with a radical scavenger. Our experimental results strongly support the mechanism that was proposed earlier with our computational studies.

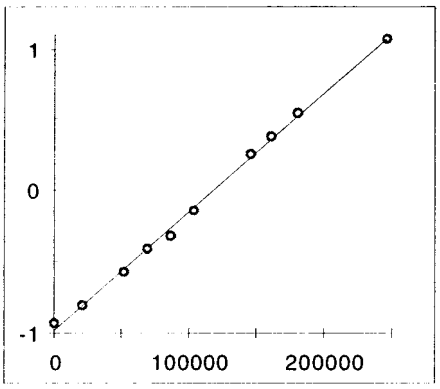


Figure 1. Plot of ln(1/[**2**]) vs time (s), in toluene at 40 °C.

Table 1. Kinetic Studies in Toluene

temperature (°C)	rate (s^{-1})	r^2
40.0	8.2×10^{-6}	0.996
40.0	8.3×10^{-6}	0.997
65.6	2.7×10^{-4}	0.997
76.5	1.0×10^{-3}	0.999
76.5	9.1×10^{-4}	0.999

Results

Kinetic Studies. Cinnamyl-4-nitrobenzenesulfenate was prepared from commercially available cinnamyl alcohol by reaction with 4-nitrobenzenesulfenyl chloride in the presence of triethylamine in methylene chloride at dry ice temperature. After purification, this product was subjected to thermolysis in toluene, and the reaction was monitored by HPLC analysis. The reaction was performed at 40, 66, and 76 °C. In all cases, the reaction was found to be first order in disappearance of the starting material with good correlation coefficients. Details on the method are presented in the experimental part. Figure 1 shows the plot of ln(1/[**2**]) vs time at 40 °C in toluene, and is a typical example of the kind of graph that was obtained with these studies. The determined rates and the corresponding correlation coefficients are displayed in Table 1.

Determination of the activation parameters for the reaction was done accordingly to the Eyring transition state theory. Details on the estimation of the errors made on the values of the activation parameters are presented in the Supporting Information. The activation enthalpy was estimated to be 27.6 ± 0.6 kcal·mol^{-1}, the activation entropy is 6.4 ± 2.0 eu. This positive value for activation entropy is congruous with a dissociative mechanism where the order within the molecule would decrease going from the reactant to the transition state. This observation, as well as the fact that the reaction follows a first-order rate law, agrees well with a mechanism where the sulfenate would undergo a cleavage of a bond, forming two molecules in the rate-determining step. To investigate the potential role of the solvent polarity on the reaction, the thermolysis was then performed in a much more polar solvent, acetonitrile, as shown in Table 2.

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Table 2. Kinetic Studies in Acetonitrile

temperature (°C)	rate (s^{-1})	r^2
40.0[a]	8.5×10^{-6}	0.990
40.0[b]	7.7×10^{-6}	0.993
40.0[b]	7.3×10^{-6}	0.994
55.8[a]	1.2×10^{-4}	0.979
66.4[a]	9.0×10^{-4}	0.989
65.7	6.5×10^{-4}	0.995
66.0	1.1×10^{-3}	0.994
75.4[a]	6.8×10^{-3}	0.981
76.0[a]	5.5×10^{-3}	0.992
77.2	8.0×10^{-3}	0.998
76.8[b]	5.5×10^{-3}	0.998
76.65[b]	5.9×10^{-3}	0.999

[a] Measurements performed on a different solution of sulfenate. [b] Values used for the calculation of the activation parameters.

Table 3. Kinetic Studies by 1H NMR with/without Base/Acid

solvent	time	added	% completion[c]
CD_3CN	20 min	0.17% base[a]	22.7 ± 1.9
CD_3CN	20 min	-	60.7 ± 3.9
CD_3CN	15 min	0.44% acid[b]	60.4 ± 0.8
CD_3CN	15 min	-	52.0 ± 0.3
toluene-d_8	1 hour	16% base	54.9 ± 1.0
toluene-d_8	1 hour	-	57.1 ± 1.3

[a] Base is 2,6-Di-*tert*-butylpyridine. [b] Acid is *p*-Toluenesulfonic acid monohydrate. [c] Measured on the average of three experiments.

Determination of the activation parameters according to the Eyring transition state theory for the reaction in acetonitrile gave an entropy of activation of 41.3 ± 2.4 eu. Even though the reaction is still clearly first order and the linear Eyring plot have excellent correlation coefficients, this value is unusually large and is difficult to explain even when solvent reorganization is taken into consideration. Rather, we considered the possibility of a competing pathway that could be catalyzed by traces of acid. To test this hypothesis, the reaction was repeated in the presence of the non-nucleophilic base 2,6-di-*tert*-butylpyridine. This sterically crowded weak base is not likely to intervene in the reaction in any other way than trapping acid traces in the solvent. The result of those studies is shown in Table 3. The presence of base decreased the rate of reaction by about a factor of 2, while adding a small amount of *p*-toluenesulfonic acid monohydrate to the reaction mixture increased the rate of the reaction by about 10%. Clearly, the traces of acid contained in the solvent as impurities were sufficient to promote a competing reaction pathway when the reaction was performed in acetonitrile. Addition of base to the reaction mixture when the reaction was performed in toluene did not change the rate significantly.

These results can be explained by considering the solvent effects on a radical pair and proton catalyzed mechanism. The charged intermediate obtained by adding a proton to the sulfenate is expected to be stabilized by the polar acetonitrile, while the apolar toluene would destabilize it. The kinetic studies in acetonitrile were therefore repeated with ~25% base added to suppress the competing acid-catalyzed pathway. The results are shown in Table 4.

The activation parameters were calculated, and the entropy of activation of 7.9 ± 1.8 eu in the presence of base was found to be very similar to the value of 6.4 ± 2.0 eu obtained in toluene. The rates themselves are similar for both solvents, and no dramatic effect was observed. Therefore, no large charge separation in the transition state is expected. This is consistent with the formation of a radical pair. If the rate-determining step would be the formation of an ion pair, an increase in the rate would be expected when going from toluene to acetonitrile as the solvent. Our results for the activation parameters in toluene and acetonitrile with and without base are summarized in Table 5. The positive values of the entropy of activation determined in each case is in contrast to the value $\Delta S^{\ddagger} = -2$ eu determined earlier for the thermolysis of benzyl-*p*-toluenesulfenate in benzene.[4] However this study was performed over the relatively small temperature range of 110−130 °C. This and the fact that the reaction deviates from a first-order behavior, indicating a slow competing pathway for the decomposition of the sulfenate, could explain the difference in the values obtained.

Table 4. Kinetic Studies in Acetonitrile with Base

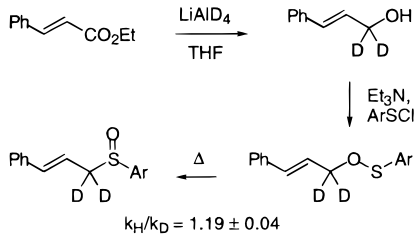
temperature (°C)	rate (s^{-1})	r^2
40.0	9.2×10^{-6}	0.997
40.0	9.0×10^{-6}	0.996
66.3	4.2×10^{-4}	0.999
66.3	4.0×10^{-4}	0.998
76.5	1.2×10^{-3}	0.994
76.5	1.1×10^{-3}	0.997

Table 5. Summary of the Activation Parameters of the Thermolysis of Cinnamyl-4-nitrobenzenesulfenate

conditions	$\Delta H^{\ddagger}$ (kcal·mol^{-1})	$\Delta S^{\ddagger}$ (eu)
In toluene	27.6 ± 0.6	6.4 ± 2.0
In acetonitrile, with base	28.0 ± 0.6	7.9 ± 1.8
In acetonitrile, without base[a]	38.6 ± 0.8	41.3 ± 2.4

[a] These values have to be considered with caution since evidence of a competing acidic catalysis has been found.

Scheme 4: Preparation of a Deuterium-Labeled Sulfenate and Measurement of a Kinetic Isotope Effect



Kinetic Isotope Effects. To obtain further information on the reaction mechanism, we determined the secondary kinetic isotope effect of the reaction. Deuterium-labeled sulfenate **2**-d_2 was prepared by reduction of *trans*-ethyl cinnamate using lithium aluminum deuteride[15] as shown in Scheme 4. The kinetic isotope effect was then determined to be $k_H/k_D = 1.19 \pm 0.04$ via an intermolecular competition experiment at low conversion. This normal (i.e., $k_H/k_D > 1$) isotope effect indicates a lowering of the force constants of the normal modes in the transition state.[16] This is consistent with the sp^3 to sp^2 rehybridization during the formation of the radical pair of a homolytic cleavage as well as the formation of an allyl cation in a heterolytic cleavage reaction. An inverse (i.e., $k_H/k_D < 1$) isotope effect would have been expected in the case of a concerted reaction.[16]

Trapping Experiment. The thermolysis of cinnamyl-4-nitrobenzenesulfenate was performed in the presence of a high concentration (~1.9 mol·L^{-1}) of tetramethylpiperidine-*N*-oxyl (TEMPO). The trapping of a radical intermediate with TEMPO is a well-established procedure for the detection of radical mechanisms.[17,18] Separation of the products by flash chromatography allowed the isolation of cinnamyloxy-2,2,6,6-tetramethylpiperidine, as shown in Scheme 5. This compound is

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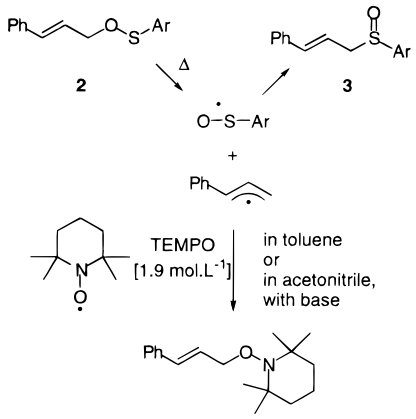
Scheme 5: Trapping of an Intermediate Using a Radical Scavenger



presumably formed by the coupling of TEMPO and the cinnamyl radical along the reaction pathway. The experiment was performed in toluene and in acetonitrile in the presence of base. In both cases the amount of radical scavenger used was similar and the yield of the trapping product was ∼ 20%.

No product originating from the coupling the sulfinyl radical (RS•O) and TEMPO has been observed. It is known in the literature that TEMPO reacts preferentially with carbon centered radicals. With alkyl radicals the coupling is very fast ($k \cong 1.0 \times 10^9$ L·mol^{-1}·s^{-1}),[19,20] but TEMPO is inert toward alkylperoxy radicals ($RO_2^•$)[21] and reacts only slowly with alkoxy radicals (RO•): the reaction of *tert*-butoxy with nitroxyl radicals has a bimolecular rate constant of $\sim 10^3$ L·mol^{-1}·K^{-1}.[22] The reaction of arylsulfinyl radicals with stable nitroxide radicals is also reported to have a rate constant of 10^9 M^{-1}·s^{-1}, but the product of such a reaction has not been isolated.[23] The sulfinyl radical is also expected to dimerize to form the corresponding thiosulfonate ($ArSO_2SAr$) as the final product. It is suggested that it forms first a sulfenyl sulfinate (ArS(═O)OSAr) which then rearranges to the thiosulfonate.[24−26] However, no product indicating the fate of the sulfinyl radical could be detected in our studies.

Discussion

The Radical Pair Formation. The observations of a positive SKIE and a positive entropy of activation associated with the rate-determining step strongly support a dissociative mechanism. A concerted pathway is expected to have a negative entropy of activation. Concerted mechanisms such as pericyclic reactions have typically a negative entropy of activation that is due to a necessary pre-orientation of the functional groups prior to reaction. For example, for the Cope and Claisen rearrangements, $\Delta S^‡$ is -13.8 ± 1 eu[27] and ~ -8 eu,[28] respectively. The entropy of activation of the sigmatropic [1,5]-hydrogen shift was estimated at ~ -8 eu,[29,30] while the one of the [1,3]-shift of the sulfides varies from -1.3 ± 0.4 eu to -11.4 ± 0.5 eu, depending on the solvent.[31] The possibility of a [2,3]-sigmatropic rearrangement as the rate-determining step of this reaction is very unlikely since such a reaction was shown to have an entropy of activation between −0.7 and −10 eu.[12] If the reaction would be initiated with such a rearrangement as a fast step followed by a slower, rate-determining step with a positive entropy of activation, a build-up of the sulfoxide formed by a [2,3]-sigmatropic rearrangement of cinnamyl-4-nitrobenzenesulfenate would be expected. The presence of a terminal alkene in this compound would make it easily recognizable in ^{1}H NMR, but no peak corresponding to this moiety was detected during the runs. Therefore, it appears that cinnamyl-4-nitrobenzenesulfenate does not undergo a [2,3]-sigmatropic rearrangement under thermolysis. Isolation of a product coming from the trapping of an intermediate with TEMPO also strongly suggests that a homolytic cleavage of the carbon−oxygen bond occurs in the rate-determining step.

The Recombination Step. The trapping experiment does not allow the estimate of the rate of recombination between the two transient radicals to form the sulfoxide. The cinnamyl radical has to escape from the solvent cage before coupling to TEMPO. Therefore, knowledge of the rate of cage escape is necessary to calculate the rate constant for recombination from the amount of coupling product observed. Our studies do not allow the prediction of the ratio between "cage" and "out-of-cage" products and only an approximation can be formulated. It is a reasonable assumption that the coupling reaction of the cinnamyl radical with TEMPO is faster than the escape of the cinnamyl radical from the solvent cage. TEMPO is in high concentration (∼1.9 mol·L^{-1}), and the rate of coupling with alkyl radical is $k \cong 1.0 \times 10^9$ L·mol^{-1}·s^{-1}. Under these conditions, a cinnamyl radical leaving the solvent cage would recombine instantaneously with TEMPO. The ratio between the amounts of trapping product and sulfoxide then represents the ratio between the number of radicals breaking loose of the solvent cage over the ones recombining inside the cage. Since the yield of trapped product was determined to be ∼20%, approximately one-fourth of the generated radicals pairs escaped the cage before recombining to the sulfoxide. Numerous factors are known to influence the so-called "cage effect", a non-exhaustive list includes the viscosity of the medium, the size of the radicals, and the interactions with the solvent.[32−34] Further experiments would have to be performed to estimate this rate of recombination.

Comparison with Theoretical Results. Our computational studies[9] investigated the homolytic cleavage of cinnamyl phenylsulfenate at the B3LYP/6-31G* level.[35,36] This substrate differs from the one studied experimentally only by the *p*-nitro group on the aryl moiety. As stated earlier, this group confers UV absorbance and makes the sulfenate light reactive, but it is

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Table 6. Comparison between Theoretical and Experimental Activation Parameters

	gas phase B3LYP 6-31G*	toluene experimental
$\Delta G^{\ddagger}$ (kcal·mol^{-1}) at rt	13.9	25.7
$\Delta H^{\ddagger}$ (kcal·mol^{-1})	25.9	27.6
$\Delta S^{\ddagger}$ (eu)	40.2	6.4

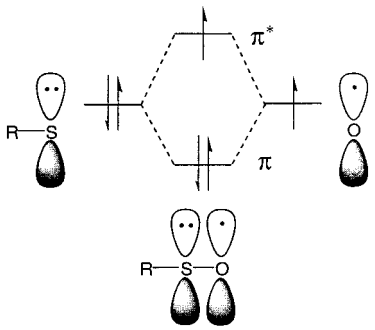
expected to have a relatively small effect on the thermolysis reaction. The agreement between the computational and experimental enthalpies of activation $\Delta H^{\ddagger}$, shown in Table 6, is good, both values are within 1 kcal·mol^{-1} from each other. In comparison, the theoretical entropy of activation $\Delta S^{\ddagger}$ is significantly higher than the experimental one with a difference of 33.8 eu. This accounts for the large difference between calculated and observed $\Delta G^{\ddagger}$, as $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$.

There are several reasons for the large discrepancy between the experimental and computed entropy of activation that can be traced back to the effects of the solvent cage, which are not included in our gas phase calculation. First, the computed entropy is the one of two radicals infinitely separated, and is larger than for a pair radical still close together in a solvent cage. Second, while the two radicals are forming, the cage size increases, more solvent molecules become involved in the ordered first solvent layer and the entropy of the solvent decreases, making the observed entropy lower than the calculated one. Third, the tight environment in the solvent cage shortens the amplitude of the vibrations inside the radicals, decreases the number of vibrational levels available at a given temperature and therefore lowers their intrinsic entropy compared to the gas phase where the vibrations stand no external constraints. These factors can reasonably explain the large difference observed in the theoretical and experimental entropies of activation.

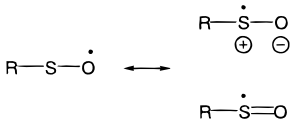
To conclude, B3LYP/6-31G* is a reliable method for the prediction of the enthalpy of activation. This method's precision for this kind of system has been established previously by comparison with the highly accurate[37] G2(MP2)[38] and CBS-Q[39] computational methods. Experimental data confirms the adequacy of the B3LYP method. Its predicted bond dissociation energy falls within 2 kcal·mol^{-1} of the experimental value.

The S−O and O−C Bond Dissociation Energies. Sulfenates are structurally similar to peroxides but behave differently.[10] In peroxides, the repulsion between the lone pairs of the oxygen atoms is believed to be the cause of the relative weakness of the RO−OR bond. In disulfides, these lone pairs are more diffuse and therefore the repulsion is smaller and the bond stronger. In a sulfenate, the lone pair repulsion is approximately halfway between the value for peroxides and disulfides. Our estimate[40] from experimental values of the bond dissociation energy (BDE) of CH_3S-OCH_3 is 53 ± 10 kcal·mol^{-1}, while the respective DBEs for CH_3O-OCH_3 and CH_3S-SCH_3 are 38 ± 2 kcal·mol^{-1} [41] and 65 ± 1 kcal·mol^{-1}.[42] Unlike the RS−OR bond, the relative weakness of the RSO−R relies on the stability of the formed radicals RSO$^{\bullet}$ and R$^{\bullet}$. In the sulfinyl radical (RSO$^{\bullet}$), the unpaired electron previously involved in the σ orbital of the O−C bond, now in a π orbital, overlaps one of the sulfur lone pair.[10,24] Overall, the three-electron π system is stabilized: two electrons occupy the π orbital, and only one, the π^* orbital, as shown in Scheme 6.

Scheme 6: Energy Levels in the Sulfinyl Radical



Scheme 7: Mesomeric Forms of the Sulfinyl Radical



The extend of this stabilization relies on the difference of electronegativity between sulfur and oxygen. This can be rationalized considering the mesomeric structures where the charge ends up on the most electronegative atom, oxygen, and the spin density on sulfur, as shown in Scheme 7.

More quantitative theoretical studies have been published by Gregory and Jenks[10] and the order of stability for related radicals is: RSO$^{\bullet}$ > RSS$^{\bullet}$ > ROO$^{\bullet}$ > ROS$^{\bullet}$. Our estimates of the respective BDEs of CH_3SO-CH_3, CH_3OO-CH_3 and CH_3SS-CH_3 are 48 ± 4 kcal·mol^{-1}, 66 ± 5 kcal·mol^{-1}, and 57 ± 4 kcal·mol^{-1}.[40] The stability of the sulfinyl radical compared to the peroxyl and perthiyl radicals lowers the BDE of the carbon-heteroatom bond of sulfenates by ∼20 kcal compared to peroxides and ∼10 kcal compared to disulfides.

Interestingly, both S−O and O−C bonds are relatively weak and their BDEs are relatively close in CH_3SOCH_3. This peculiarity makes the bond-cleaving of sulfenates a versatile process. By varying its substituents in their ability to stabilize a radical and to confer UV absorbance, one can induce the cleavage of the S−O bond by photolysis while the cleavage of the O−C bond can be induced by thermolysis. The flipside of this two-faced reactivity is that special care has to be taken to exclude light and/or heat while manipulating sulfenates to avoid side reactions.

The Acid Catalysis of the Reaction. A competing mechanism is observed when the thermolysis of cinnamyl-4-nitrobenzene sulfenate is performed in acetonitrile where traces of acid present in the solvent can protonate the sulfenate. The charged intermediate is stabilized in the polar solvent and therefore plays an important role in the competing pathway. Analysis by NMR showed that cinnamyl alcohol is formed in small amounts when the reaction is performed in the presence of acid in acetonitrile. This product, which is not detected when base is present, is proposed to be formed during the hydrolysis of the protonated sulfenate intermediate, along with the corresponding sulfenic acid as shown in Scheme 8. The sulfenic acid is then expected to undergo further reactions, including the formation of the corresponding thiosulfinic ester. However, we did not identify any product to provide us information on the further fate of the

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(40) Details on the calculations and approximations we made in this study are available in the Supporting Information.
(41) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493−532.
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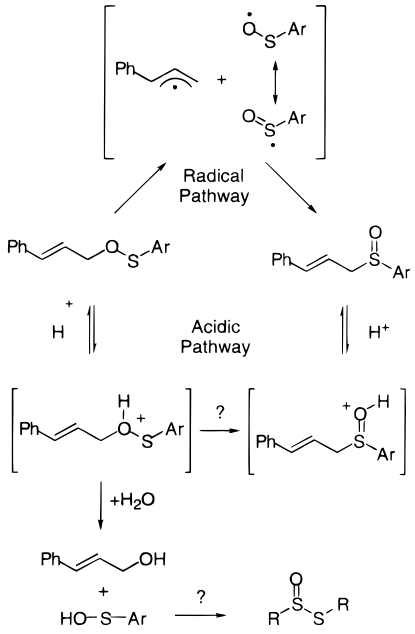
Scheme 8: Thermolysis of Cinnamyl-4-nitrobenzenesulfenate in Acetonitrile, Two Competing Mechanisms



sulfur derivatives after hydrolysis. This is presumably due to the large number of possible follow-up reactions leading to a complex mixture rather than a single product.[43]

The details of the mechanism of the rearrangement of the protonated intermediate to form the sulfoxide remain unclear. Our kinetic experiments do not allow us to elaborate on the activation parameters of this step. After making a steady-state approximation on the protonated sulfenate, an equation of the rate constant involves the concentration in acid in its denominator. Since the reaction was observed in solvents where only traces of acid are present, the error made in the calculus of the rate constant would be enormous. Further studies are necessary to be able to propose a mechanism for this competing pathway.

Conclusions

The sulfenate−sulfoxide rearrangement of cinnamyl-4-nitrobenzenesulfenate occurs via the homolytic cleavage of the carbon−oxygen bond (RSO−R) followed by the recombination of the two transient radicals. The activation parameters for the radical-forming rate-limiting step are measured to be $\Delta H^{\ddagger} = 27.6 \pm 0.6$ kcal·mol^{-1}, $\Delta S^{\ddagger} = 6.4 \pm 2.0$ eu in toluene and $\Delta H^{\ddagger} = 28.0 \pm 0.6$ kcal·mol^{-1}, $\Delta S^{\ddagger} = 7.9 \pm 1.8$ eu in acetonitrile. A normal secondary kinetic isotope effect of $k_H/k_D = 1.19 \pm 0.04$ was measured in toluene. The cinnamyl radical formed by the dissociation was trapped with TEMPO. The rate of recombination of the two radicals could not be determined but is shown to be in the same order of magnitude as the rate of escape from the solvent cage. When the reaction was performed in the very polar solvent acetonitrile, a competing acid-catalyzed mechanism was detected. This pathway also yields the sulfoxide, and is accompanied by hydrolysis of the sulfenate.

The BDE of the carbon−oxygen bond of cinnamyl-4-nitrobenzenesulfenate is found of ∼28 kcal·mol^{-1}, in good agreement with the theoretical value, ∼26 kcal·mol^{-1} calculated at the B3LYP/6-31G* level. The weakness of this bond is due to the stability of the cinnamyl and sulfinyl radicals. Estimates of BDE for simpler sulfenates based on known experimental data give ∼48 kcal·mol^{-1} for the CH_3SO-CH_3 bond and ∼53 kcal·mol^{-1} for the CH_3S-OCH_3 bond. These BDEs are consistent with the observed reactivity of sulfenates to light, which cleaves the S−O bond. In the excited state, the sulfenate's weakest bond becomes the sulfur−oxygen one instead of the carbon−oxygen one.

Considering the relative BDEs of R_1S-OR_2 and R_1SO-R_2, substitution of the R_1 and R_2 group has a large effect on the reactivity of sulfenates. Radical stabilizing group such as cyano or *tert*-butyl will lower the energy of $R_2^{\bullet}$ compared to that of $R_2O^{\bullet}$, as well as the BDE of the O−C bond compared to that of the S−O bond, and the overall effect will be an increased sensitivity to thermolysis of the sulfenate.

Experimental Section

General. All final ^{1}H and ^{13}C NMR (300 and 600 MHz) spectra were obtained on either a General Electric GN 300 connected to a General Electric 1280 station, a Varian Unity Plus 300, or a Varian Unity Plus 600. Deuterochloroform (99.98% in $CDCl_3$), deuterotoluene (99+% in C_7D_8) and deuteroacetonitrile (99.6% in CD_3CN) were used as solvents and the chemical shifts were assigned using tetramethylsilane, $CHCl_3$, $C_5D_5CD_2H$, or CD_2HCN as internal references.

The mass spectral analyses were carried out on a Finningan-Mat 8430 mass spectrometer equipped with a Varian 3400 gas chromatograph. TLC analyses were carried out on a commercially available 0.2 mm thick silica gel 60 PF_{254} containing gypsum as a binder. Column chromatographic separations were carried out using 230−400 mesh silica gel purchased from Aldrich company.

High Performance Liquid Chromatography was performed on a Waters 600 pump connected to a Waters Photodiode Array Detector 960. HPLC grade solvents were used and were degassed prior to use.

Synthesis. General Synthesis of Alkyl of 4-Nitrobenzenesulfenates. To a 50 mL three-neck flask containing the alcohol (5 mmol) and 15 mL of anhydrous methylene chloride under an argon atmosphere in a darkened hood was added at −30 °C 1.6 mL (11.5 mmol) of freshly distilled triethylamine. After the addition, the mixture was stirred for 10 min. 10 mL of a methylene chloride solution of 4-nitrobenzenesulfenyl chloride was then added slowly via a dropping funnel. After the reaction, the mixture was stirred for 15 min and was then allowed to warm to room temperature for 30 min. The reaction mixture was washed with cold 5% hydrochloric acid (2 × 10 mL) and cold water (3 × 10 mL), and the extract was dried over magnesium sulfate, keeping the light exposure to a minimum. The solvent was removed under reduced pressure in an aluminum-wrapped flask giving the sulfenates in a crude form. Analysis of the crude products by ^{1}H NMR showed the presence of unreacted alcohol, 4-nitrobenzene disulfide and the corresponding sulfinate, presumably formed by air/light oxidation of the sulfenate during the workup, as the major side products. The sulfenates were purified by flash chromatography with silica gel using a eluent system composed of hexanes and methylene chloride in a 3:1 ratio.

Cinnamyl-4-nitrobenzenesulfenate. The compound was prepared in 28% yield after purification from cinnamyl alcohol. This compound was found to be sensitive to air oxidation in the presence of light. Pale yellow solid, forming flakes: mp (uncorrected) 64−66 °C. ^{1}H NMR ($CDCl_3$) δ 8.22 (d, $J = 9$ Hz, 2 H), 7.34 (m, 5 H), 7.3 (d, $J = 9.2$ Hz, 2 H), 6.7 (d, $J = 15.9$ Hz, 1H), 6.33 (dt, $J = 15.9$, 6.8 Hz, 1 H), 4.54 (d, 6.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$) δ 79.6, 120.4, 123.5, 124.5, 127.0 (2 CH), 128.8, 128.9, 136.0, 136.4, 151.7. IR (neat): 1577, 1509, 1333, 1084, 921, 837, 740. MS (CI, $[M + H]^+$) calcd: 288.0694, obsd: 288.0714.

Cinnamyl-4-nitrobenzenesulfenate-d_2. The compound was prepared in 12% yield after purification from cinnamyl alcohol-d_2. This compound was found to be sensitive to air oxidation in the presence of light. Pale yellow solid, forming flakes: mp (uncorrected) 61−65 °C. ^{1}H NMR ($CDCl_3$) δ 8.22 (d, $J = 9$ Hz, 2 H), 7.3−7.5 (m, 5 H),

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7.31 (d, $J = 9.1$ Hz, 2 H), 6.69 (d, $J = 15.8$ Hz, 1H), 6.33 (d, $J = 15.9$ Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 78.5, 120.1, 123.1, 124.3, 126.8, 128.5, 128.7, 135.7, 136.2, 151.6. IR (neat): 1577, 1509, 1335, 1085, 1052, 966 (C−D bend), 910, 836, 740. MS (CI, $[M + H]^+$) calcd: 290.8020, obsd: 290.8020.

Kinetic Studies, Monitoring of the Reaction, Determination of the Activation Parameters. Preparation of the Stock Solutions. Four stock solutions of sulfenate were prepared with about the same concentration: $c = 10^{-3}$ mol/L. In acetonitrile without base, 24.8 mg of cinnamyl-4-nitrobenzenesulfenate and 6 mg of naphthalene were dissolved in 89 mL of acetonitrile. Another stock solution was prepared with 71 mg of cinnamyl-4-nitrobenzenesulfenate, 21 mg of naphthalene and 250 mL of acetonitrile. In acetonitrile with base, 100 mg of cinnamyl-4-nitrobenzenesulfenate, 63 mg of naphthalene and 20 μL of 2,6-Di-*tert*-butylpyridine were dissolved in 250 mL of acetonitrile. In toluene, 78 mg of cinnamyl-4-nitrobenzene sulfenate and 50 mg of anthracene were dissolved in 250 mL of toluene. All solutions were degassed upon preparation by sonication/vacuum to remove any potential oxygen from the solution and avoid an oxidation of the sulfenate into sulfinate during storage.

Experimental Procedure for Thermolysis. The solution is placed in a 13 × 100 mm test tube containing a small magnetic stirrer. The tube is closed with a septum (fits in the inner ring of the septum). The solution is degassed with ultrasounds/vacuum for 10 min then the test tube is placed under nitrogen. A 500 mL three necks round-bottom flask is filled almost to the top with solvent (depending on the desired temperature, the nature of the solvent varies) and a thermometer is placed on one neck with an adapter. A condenser is placed on the second neck of the flask. The third neck of the flask is closed with a glass stopper hat can be easily removed and replaced by the 13 × 100 mL test tube with the septum. The 19/32 glass neck fits tightly with the outer ring of the septum. The liquid is refluxed in the round-bottom flask and is stirred with a large magnetic stirrer at a fast speed to ensure homogeneity of the temperature in the liquid. When the temperature is stable, the glass stopper is removed and the solution of sulfenate in the test tube is placed in the refluxing liquid. The stirring plate is moved in a way that the small magnetic stirrer in the test tube can rotate and maintain homogeneity of the temperature inside the test tube. Some solution of sulfenate is taken out of the test tube via a syringe (~0.05 mL) regularly and is immediately cooled to dry ice temperature in a small vial. The vial is then placed and stored in dry ice until the solution can be used for injection in HPLC. Typically, the first collection via a syringe was performed at least one minute after the test tube was placed in the refluxing solvent to allow the contents to reach a constant and homogeneous temperature. The liquids used in the round-bottom flask were chosen for their boiling points and were: methylene chloride (bp 40 °C), acetone (bp 56 °C), tetrahydrofuran (bp 66 °C) and ethyl acetate (bp 77.1 °C).

Separation and Quantification with HPLC and Photodiode Array Detector. The separation and quantification of the sulfenate and the products of thermolysis in acetonitrile was performed by HPLC with a reversed phase column (Nova Pak C18, 60 Å, 4 μm, 39 × 150 mm). The injection volume was 20 μL; the eluent is a gradient of water and acetonitrile. First minute: isocratic mixture of 30% acetonitrile/70% water, then a linear gradient for 1 min to reach 60% acetonitrile/40% water, then a linear gradient for 8 min to reach 100% acetonitrile, then 2 min of 100% acetonitrile. Under these conditions, retention times were ~6.7 min for the sulfoxide, ~8.2 min for naphthalene, and ~9.4 min for the sulfenate, determined by comparison with authentic samples. The amounts of sulfenates and sulfoxide were calculated as the ratio between the area of their respective absorption peaks at 254 nm and the area of the naphthalene peak. This ratio is then considered as a measure of the concentration of the different products.

For the study of the thermolysis in acetonitrile in the presence of base a LiChrospher C18, 5 μm, 4.6 × 250 mm column was used with a gradient of water and acetonitrile. First minute: isocratic mixture of 30% acetonitrile/70% water, then a linear gradient for 1 min to reach 50% acetonitrile/50% water, then a linear gradient for 16 min to reach 100% acetonitrile, and finally 5 min of 100% acetonitrile. Under these conditions, retention times were ~11 min for the sulfoxide, ~15 min for naphthalene, and ~17 min for the sulfenate.

The separation and quantification of the sulfenate and its products of thermolysis in toluene was performed by HPLC with a normal phase column (LiChrosphere, 100 Å silica 5 μm, 4.6 × 250 mm). The injection volume was 20 μL; the eluent is a gradient of hexanes and ethyl acetate. First 5 min: isocratic mixture of 8% ethyl acetate/92% hexanes, then a linear gradient for 3 min to reach 90% ethyl acetate/10% hexanes, and finally an isocratic mixture of 90% ethyl acetate/10% hexanes for 2 min. Under these conditions, retention times were ~11.5 min for the sulfoxide, ~2.2 min for anthracene and ~3.6 min for the sulfenate. The amounts of sulfenates and sulfoxide were calculated as the ratio between the area of their respective absorption peaks at 340 nm and the area of the anthracene peak.

Kinetic Studies with/without Base. Thermolysis of Cinnamyl-4-nitrobenzene Sulfenate in Acetonitrile-d_3, with ~0.17% of Base Added. Cinnamyl-4-nitrobenzene sulfenate (74 mg) and 2-naphthyl acetonitrile (28 mg) were dissolved in 4.0 mL of acetonitrile-d_3, and three tubes each containing 0.6 mL of this solution were prepared. (Concentration of sulfenate: ~6.44 10^{-2} mol·L^{-1}). A solution of 2,6-di-*tert*-butylpyridine (20 μL, ~0.12 M) in acetonitrile-d_3 was added to the remaining solution and mixed, and three other NMR tubes were filled with 0.6 mL of the basic solution. ^{1}H NMR was taken before and after thermolysis for each tube. The thermolysis itself was realized by putting the NMR tube at 66 °C (the tip of the tube containing the sample is placed in refluxing THF, in these conditions, it is assumed that the sample is placed at constant temperature) for 20 min. Special care was taken to ensure that tubes were stored at a dry ice temperature and away from light during the course of the experiment.

Thermolysis of Cinnamyl-4-nitrobenzene Sulfenate in Acetonitrile-d_3, with ~0.44% of Acid Added. Cinnamyl-4-nitrobenzene sulfenate (70 mg) and 2-naphthyl acetonitrile (25 mg) were dissolved in 4.0 mL of acetonitrile-d_3, and three tubes each containing 0.6 mL of this solution were prepared. A solution of *p*-toluenesulfonic acid in acetonitrile-d_3 (50 μL, ~0.12 M) was added to the remaining solution and mixed, and three other NMR tubes were filled with 0.6 mL of the acidic solution. ^{1}H NMR was taken before and after thermolysis for each tube. The thermolysis itself was realized by putting the NMR tube at 66 °C (the tip of the tube containing the sample is placed in refluxing THF; in these conditions, it is assumed that the sample is placed at constant temperature) for 15 min. Special care was taken to ensure that tubes were stored at dry ice temperature and away from light during the course of the experiment.

Thermolysis of Cinnamyl-4-nitrobenzene Sulfenate in Toluene-d_8, with ~0.16 Equiv of Base Added. Cinnamyl-4-nitrobenzene sulfenate (77 mg) and 2-naphthyl acetonitrile (23 mg) were dissolved in 3.0 mL of toluene-d_8 and three tubes each containing 0.5 mL of this solution were prepared. (Concentration of sulfenate: ~8.9 10^{-2} mol·L^{-1}). 2,6-Di-*tert*-butylpyridine (5 μL) was added to the remaining solution and mixed, and three other NMR tubes were filled with 0.6 mL of the basic solution. ^{1}H NMR was taken before and after thermolysis for each tube. The thermolysis itself was realized by putting the NMR tube at 66 °C (the tip of the tube containing the sample is placed in refluxing THF, in these conditions, it is assumed that the sample is placed at constant temperature) for 1 h. Special care was taken to ensure that tubes were stored at dry ice temperature and away from light during the course of the experiment.

Kinetic Isotope Effect Measurement. The measurement of k_H/k_D was realized in deuterotoluene. NMR was used to determine the ratio of cinnamyl-4-nitrobenzenesulfenate and cinnamyl-4-nitrobenzene-sulfenate-d_2 before the reaction and at 10−20% completion. Five identical samples were prepared by dissolving 78 mg of cinnamyl-4-nitrobenzenesulfenate-d_2, 63 mg of cinnamyl-4-nitrobenzenesulfenate, and 41 mg of 2-naphthylacetonitrile in 3.5 mL of toluene-d_8. 2-Naphthylacetonitrile was used as reference. The solution was degassed using vacuum/sonication for ~10 min and was transferred in five different NMR tubes (5 mm). The ^{1}H NMR spectrum was obtained for each tube. The solution in the NMR tube was then transferred to a small test tube containing a small stirring bar and was placed for 4 min at ~76 °C (in a refluxing ethyl acetate bath). The solution in the test tube was then cooled by putting the test tube in an ice bath. The cold

solution was then transferred to a clean NMR tube, and the ^{1}H NMR spectrum was taken again.

Trapping Experiment. In a 13 × 100 mm test tube, 46 mg (0.16 mmol) of cinnamyl-4-nitrobenzenesulfenate and 300 mg of 2,2,6,6-tetramethylpiperidine-*N*-oxyl, (TEMPO, $c = 1.9$ mol·L^{-1}) were dissolved in ∼1 mL of toluene. The solution was degassed by sonication /vacuum for ∼10 min. The test tube was flushed with argon, sealed with a septum, and placed at 76 °C under stirring for 90 min. The tube was then cooled to room temperature in a water bath. The crude product was deposited on silica gel and a flash chromatography was performed using a mixture of 92% hexanes/8% diethyl ether as the eluent. This allowed the separation of the product from the unreacted TEMPO, which prevents any characterization attempts by NMR. A second flash chromatography was performed to further purify the isolated product using an eluent composed of hexanes and methylene chloride in a 1:1 ratio. Cinnamyloxy-2,2,6,6-tetramethylpiperinide (10 mg, 23% yield) was isolated as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.2−7.4 (m, 5H), 6.6 (d, $J = 16$ Hz, 1H), 6.3 (dt, $J = 16$ Hz, 5.9 Hz, 1 H),4.45 (dd, $J = 5.9$ Hz, 1.5 Hz, 2H), 1.47 (m, 4H), 1.22 (s, 6H), 1.14 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 17.4, 20.4, 33.2, 39.9, 60.0, 78.3, 125.8, 126.6, 127.7, 128.7, 131.6. IR (neat) 1469, 1449, 1374, 1359, 1133, 1030, 963, 742, 691. MS (CI, $[M + H]^+$) calcd: 274.2171, obsd: 274.2184. MS (FAB, $[M + H]^+$) calcd: 274.2171, obsd: 274.2158.

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Supporting Information Available: Complete graphs and details of the calculations concerning the monitoring of the thermolysis of sulfenates, the measurement of the kinetic isotope effect, and estimations of the bond dissociation energies from experimental data are reported. Cartesian coordinates and energies of structures discussed in the comparison with experimental results are reported. NMR and IR spectra are included as well as the description of an independent synthesis of cinnamyl-4-nitrobenzenesulfoxide. Preparation of cinnamyl alcohol-d_2 is also reported (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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