# Ei Elimination: An Unprecedented Facet of Sulfone Chemistry

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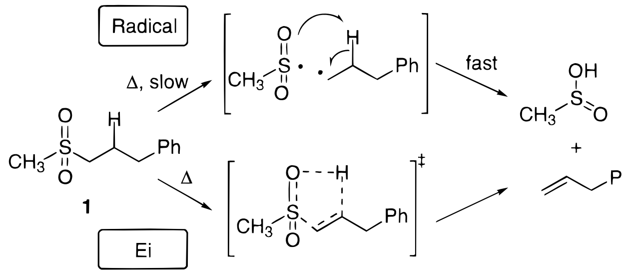
**Abstract:** Thermolysis of methyl 3-phenylpropyl sulfone in the gas phase results in formation of allylbenzene. Activation parameters of $\Delta H^{\ddagger} = 53.5 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -0.7 \pm 1.4$ cal/(mol·K) were obtained over the range of 490−550 °C. Similar measurements with a deuterated analogue show a substantial isotope effect, and a lower activation enthalpy is observed for the formation of styrene from methyl 2-phenylethyl sulfone. Along with high-quality ab initio calculations of activation parameters and kinetic isotope effects, these results indicate that this is the first reported Ei reaction of a simple sulfone.

## Introduction

The thermolytic behavior of both structurally simple and complex sulfones has been studied for a number of years. Progress was reviewed as early as 1966.[1] Pyrolysis of sulfones usually results in the loss of $SO_2$ and the reactions are generally understood to be homolytic, electrocyclic, or chelotropic, though ionic mechanisms have been suggested on occasion.[2−4] We report here a new reaction pathway for sulfones, the Ei elimination. Though familiar from sulfoxide chemistry,[3,5−8] this reaction does not appear to have ever been suggested or demonstrated for the more highly oxidized cousin.

Two limiting mechanisms for the formation of allylbenzene from sulfone **1**, homolytic and Ei, may be envisioned, as illustrated in Scheme 1. Ei elimination postulates that the sulfone group acts simultaneously as base and leaving group.[9] Sulfinates are well-known leaving groups in E2 and $E1_{cb}$ reactions.[10−15] However, sulfones are considerably less basic than sulfoxides. The proton affinity of dimethyl sulfone is a full 17 kcal/mol less than that of dimethyl sulfoxide.[16] It is thus imperative to demonstrate the plausibility of the sulfone Ei reaction by means other than analogy. Below are presented results from gas-phase activation data, kinetic isotope effects, and ab initio computations that all strongly support the concerted elimination of sulfinic acids from unactivated alkanes to give olefins.

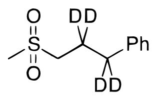
**Scheme 1**



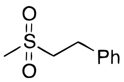
## Results

**Experimental Results.** Pyrolysis of sulfones **1**−**3** was carried out in a temperature-controlled pulsed stirred-flow reactor (SFR) with He carrier gas that feeds into a GC.[17] Allylbenzene was observed from **1** and **2**, and styrene from **3**. Methanesulfinic acid was not detected directly; its presence was inferred. Activation parameters for the formation of olefins from sulfones **1**, **2**, and **3** are given in Table 1.

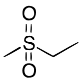
The residence time in the hot zone of the quartz reactor is individually calibrated and is of the order of a few seconds. Temperature regions for data collection are limited to where both starting material and product can be accurately quantified from the GC run of a single reaction on that time scale. Thus the data for **1** and **2** were collected over the range of 490−550 °C. Data for **3** were collected over the range of 450−500 °C.



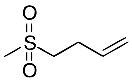
**2**



**3**



**4**



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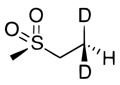

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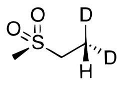
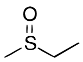


**7**



**8**

The temperature-dependent kinetic isotope effect (KIE) for **1** vs **2** was evaluated by successive injections of **1** and **2** into the SFR on the same day using the same reactor cell to ensure

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10.1021/ja994150p CCC: $19.00

**Table 1.** Experimental Activation Parameters[a]

| compd | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | $E_a$ | log *A* |
|---|---|---|---|---|
| **1** | 53.5 ± 1.0 | −0.7 ± 1.4 | 55.0 ± 1.0 | 13.5 ± 0.4 |
| **2** | 52.5 ± 1.6 | −3.2 ± 2.0 | 54.0 ± 1.6 | 12.9 ± 0.4 |
| **3** | 47.0 ± 1.8 | −6.8 ± 2.4 | 48.5 ± 1.8 | 12.2 ± 0.6 |

[a] $\Delta H^{\ddagger}$ and $E_a$ values expressed in kcal/mol; $\Delta S$ in cal/(mol·K); log A in $s^{-1}$. Errors are expressed as the 95% confidence limits.

accuracy. A $k_H/k_D$ of 2.0 ± 0.2 was observed over the whole range, as shown in Figure 1.

**Computational Results.** Model compounds **4** and **5** were examined using ab initio methods. Activation enthalpies and heats of reaction including zero-point energies are shown in Table 2. In a similar detailed experimental and computational study to be published separately,[18] it was determined that MP2/6-311+(3df,2p)//MP2/6-31G(d,p) calculations accurately reproduced activation parameters of sulfinyl Ei reactions, and this level of theory was applied here. The transition state (TS) for **4** is illustrated in Figure 2. CASSSF/6-31G(d,p) calculations were also carried out on the TS of **4**, and were consistent with a single-configuration closed-shell TS. The active space for these calculations consisted of 6 electrons in 5 orbitals. The input orbitals in the transition state correlated to the C−S $\sigma$ and $\sigma^*$ orbitals, the C−H $\sigma$ and $\sigma^*$ orbitals, and a lone pair on O in the starting material. The correlation to the product was to the C−C $\pi$ and $\pi^*$ orbitals, OH $\sigma$ and $\sigma^*$ orbitals, and a lone pair on sulfur.

The temperature-dependent KIE for the Ei reaction was calculated[19] using the program ISOEFF98,[20,21] which uses vibrational frequencies from the substrate and its respective TS to solve for the KIE using the Bigeleisen equations.[22−24] The KIE was calculated for conformers **6** and **7** of dideuterated **4** at 298 K (5.02 and 4.74, unscaled and scaled vibrational frequencies, respectively) and in the temperature range of the experiments, 763−823 K (1.95−1.86 and 1.90−1.82, unscaled and scaled vibrational frequencies, respectively). The calculated KIE is in agreement with the experimental KIE (2.0 ± 0.2).

## Discussion

The compounds used in this experimental and computational study were chosen to distinguish between homolytic and Ei mechanisms. The homolytic path does not predict a significant activation enthalpy difference between **1** and **3** because C−S cleavage is certainly rate limiting. Yet, a 6.5 kcal/mol difference is observed (Table 1), consistent with partial formation of the olefin TS. Further, the observed $\Delta S^{\ddagger}$ values do not appear consistent with a homolysis reaction.

Computational models **4** and **5** were used to gauge expectations for the difference in activation enthalpies for **1** and **3**. The calculated $\Delta H^{\ddagger}$ values for **4** and **5** are within reasonable expectations of the experimental values for **1** and **3**. The 4 kcal/mol deviation for **3**/**5** is the largest we have observed using this level of theory and similar molecular simplification on sulfonyl and sulfinyl elimination reactions.[18] Nonetheless, the experimentally observed change of about 6.5 kcal/mol is consistent with expectations for the Ei reaction, borne out by the 3.9 kcal/mol difference in the model compound calculations.

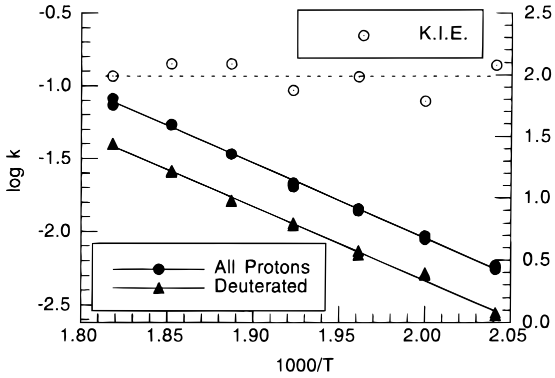

**Figure 1.** Kinetic data for the elimination reaction of 1 and 2a. The dotted line is arbitrarily drawn at the average $k_H/k_D = 2.0$. All reactions were run in triplicate.

**Table 2.** Calculated Activation Barriers and Heats of Reaction[a]

| compd | $\Delta H^{\ddagger}$ | $\Delta H$ | $\Delta H_{est}$[b] |
|---|---|---|---|
| **4** | 54.5 | 35.7 | 35.3 |
| **5** | 50.6 | 28.3 | 28.6 |
| **8** | 32.3 | 22.6 | |

[a] Calculated enthalpies at MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) include appropriately scaled zero-point energies. All enthalpies are in kcal/mol. [b] $\Delta H_{est}$ is estimated from Benson-type values of $\Delta H_f$ for **4** and **5**, experimental values for ethylene and butadiene, and a G2 calculation for $CH_3SO_2H$.[35−37]

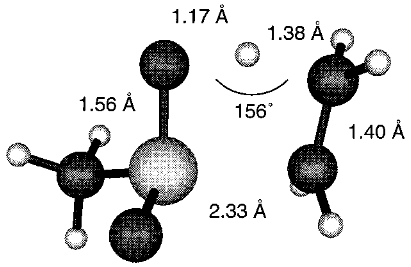

**Figure 2.** Calculated transition state for conversion of **4** to ethylene and methanesulfinic acid.

Compounds **1** and **2** also support the Ei mechanism in that a significant KIE is not predicted for the radical pathway. Both primary and secondary KIEs are expected for the Ei reaction, and the large primary KIE should be observable even at elevated temperatures.

An isotope effect is indeed observed, as illustrated in Figure 1. Table 1 illustrates the limits of the precision of the current data, obtained under a fairly narrow temperature region. The activation enthalpy for **2** is not expected to be lower than that of **1**, and it should be noted that there is significant overlap of the ranges within the reported error bars. (Based on ZPE differences for the isotopomers, the dideuterated compound should have a 0.9 kcal/mol higher $\Delta H^{\ddagger}$.) Over the entire range of data, a $k_H/k_D$ of 2.0 ± 0.2 was observed experimentally for **1** vs **2** (Figure 1). The KIEs calculated for Ei elimination of **6** and **7** vs **4** to give deuterioethylene are from 1.90 to 1.82 over this same temperature range. Inspection of Figure 1 reveals that the data scatter does not allow observation of a KIE change of <5% over the temperature region, and the dotted line is

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arbitrarily plotted at the average value, 2.0. Given the limitations of the experimental data and the necessity to reduce the size of the molecule for computations, the calculated and experimental KIEs are taken to be in excellent agreement.

A final experimental consideration is the observed value of $\Delta H^{\ddagger}$, which is inconsistent with the radical mechanism. The C−S bond dissociation energies (BDEs) of sulfones **1**−**3** are expected to be approximately 68 kcal/mol,[25,26] significantly higher than the observed $\Delta H^{\ddagger}$ of 53.5 kcal/mol.

The magnitude of $\Delta H^{\ddagger}$ for the sulfone Ei reaction is significantly greater than that for the corresponding sulfoxide elimination. The activation entropies in Table 1, however, are in line with literature reports and our observations for the sulfoxide reaction.[18] The calculated $\Delta H$ and $\Delta H^{\ddagger}$ for sulfoxide **8** are included in Table 2 for comparison. Neither the sulfoxide nor the sulfone reaction has a transition state that can be described as particularly early or late. The computed transition state geometries are substantially similar, save that both the C−H and H−O distances are 0.02−0.03 Å shorter at the expense of a 0.05 Å longer C−C distance for **4**, compared to the sulfoxide **8**. Both have all 5 key atoms in a nearly coplanar arrangement.

A large part of the difference in $\Delta H^{\ddagger}$ may lie simply in the fact that the sulfone reaction is substantially more endothermic. It is also attractive to speculate that the decreased basicity of the sulfonyl group relative to the sulfinyl group outweighs the increased nucleofugacity in the transition state. While studies that compare nucleofugacity are generally system dependent, we have been unable to find any cases in which sulfones are any more than modestly better leaving groups than the corresponding sulfoxide.[13−15]

Finally, given the strong evidence for the Ei reaction of sulfones, one must ask why this simple thermolytic reaction has escaped the attention of the chemical community until now. First, the activation enthalpy is not insubstantial. Many sulfones that have been pyrolyzed at sufficiently high temperatures for the Ei reaction to be observed are not physically capable of the reaction or have substituents that lower a C−S bond dissociation energy such that it is in the range of the $\Delta H^{\ddagger}$ reported here. Not only are the BDEs for benzyl− and allyl−$SO_2R$ bonds low (55−56 kcal/mol), but the $CH_3$−$SO_2Ph$ BDE is reported to be 54−57 kcal/mol.[25,26] Such weak bonds would probably make homolytic reactions very competitive, especially considering the favorable $\Delta S^{\ddagger}$ values for the homolyses. Cyclic compounds may not have revealed Ei reactivity because the reverse reaction is likely to be very rapid, with sulfone being overwhelmingly favored thermodynamically.

## Conclusions

In summary, a new unimolecular reaction of sulfones, Ei elimination to form alkenes, has been observed. Its activation enthalpy, though high, is below what is to be expected for C−S bond rupture. The radical mechanism further is ruled out on grounds of substituent effects and computations of an Ei transition state that well reproduces the absolute $\Delta H^{\ddagger}$ and KIE.

## Experimental Section

**Instrument.** The stirred-flow reactor has a temperature-controlled furnace and is modeled very closely after the one that has been previously described.[17] It uses He as a carrier gas to bring the sample into a reactor whose volume controls the residence time, which is a few seconds. Samples were injected as concentrated solutions in acetonitrile. After the furnace section, the gases are sent to a GC that operates at lower temperatures, where starting materials and products are separated and quantified. Rate constants are extracted from each run, and multiple injections were made at each temperature. For the isotope effect measurements, the samples **1** and **2** were measured alternately at each temperature to ensure accurate measurements of $k_H/k_D$. All sulfones thermalized were greater than 99% purity, as determined by the observation of a single peak by GC without thermolysis.

**Compound Preparation: General.** Unless otherwise noted, starting materials were obtained from Aldrich and used as received. Characterization was carried out on a Bruker Avance DXR NMR operating at 400 MHz for proton and 100 MHz for carbon. The $^{13}C$ signals for $CD_2$ carbons were generally not observed due to the low signal-to-noise and high multiplicity. MS were obtained on a Finnigan TSQ 700 operating in the EI mode. IR spectra were obtained on a Mattson Galaxy Series FTIR 3000. Dry THF was freshly distilled from benzophenone ketyl. Both compounds **1** and **3** are known;[27−29] the isotopomer **2** is a new compound. Modern spectroscopic data for **1** and **2**, both prepared by oxidation sulfoxides already on hand,[30] are given in the Supporting Information.

**General Procedure for Preparation of Sulfone from Sulfide (or Sulfoxide).** To an ice-cooled solution of 2−3 mmol of the sulfoxide (sulfide) in methylene chloride (15 mL) was added 2.2 (1.1) equiv of *m*-chloroperbenzoic acid dissolved in 25 mL of methylene chloride dropwise by means of a dropping funnel. After 2 h, the mixture was poured into aqueous NaOH (5%, 50 mL) and the layers were separated. The organic layer was washed with another portion of aqueous NaOH, then dried with $MgSO_4$ and concentrated in vacuo. Yields were nearly quantitative and products clean by NMR. Further purification was carried out as noted.

**Ethyl 2,2,3,3-Tetradeuterio-3-phenylpropionate.** In a 250 mL round-bottom flask, ethyl phenylpropiolate (10.0 g, 57.4 mmol) was dissolved in diethyl ether (10 mL) and Pd/C (2.0 g) was added. The mixture was stirred rapidly and $D_2$ was introduced into the chamber as follows: a three-way valve was attached to the deuterium source, the reaction flask, and a calibrated U-shaped tube (1.4 L) filled with mineral oil. The reaction was run until completion as monitored by GC. The mixture was filtered and concentrated to give the product in 86% yield. The product was clean by NMR and used for subsequent steps. $^1H$ NMR ($CDCl_3$) $\delta$ 7.3−7.18 (m, 5H), 4.13 (q, $J = 7.2$ Hz, 3H), 1.23 (t, $J = 7.2$ Hz, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 173.2, 140.7, 128.7, 126.4, 60.6, 14.4; IR (thin film) 3026, 2981, 2222, 2101, 1732, 1268, 1026, 735, 699 $cm^{-1}$.

**2,2,3,3-Tetradeuterio-3-phenyl-1-propanol.** To a suspension of lithium aluminum hydride (0.63 g, 16.5 mmol) in dry THF (25 mL) under Ar at O °C was added ethyl 2,2,3,3-tetradeuterio-3-phenylpropionate (1.0 g, 5.49 mmol). The suspension was allowed to warm to room temperature. After being stirred 1 h the reaction mixture was heated to reflux for 5 h. The reaction was quenched by slow, successive addition of $H_2O$ (0.6 mL), aqueous NaOH (0.6 mL), and $H_2O$ (1.8 mL). The solution was filtered then poured into ether (30 mL) and washed with brine (3 × 25 mL). The organic layer was dried ($MgSO_4$) and concentrated to give 2,2,3,3-tetradeuterio-3-phenyl-1-propanol in 98% yield. The material was clean by NMR and used in the next step without further purification. $^1H$ NMR ($CDCl_3$) $\delta$ 7.29−7.16 (m, 5H) 3.65 (s, 2H), 1.64 (s, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 141.8, 128.5, 128.5, 125.9, 62.2; IR (thin film) 3346, 3024, 2918, 2876, 2206, 2112, 1604, 1043, 699 $cm^{-1}$.

**2,2,3,3-Tetradeuterio-3-phenylpropyl *p*-Toluenesulfonate.** In a

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round-bottom flask (50 mL), 2,2,3,3-tetradeuterio-3-phenyl-1-propanol (0.7 g, 5.0 mmol) was dissolved in chloroform (10 mL) and cooled in an ice bath (0 °C). To the solution was added pyridine (0.8 g, 10.0 mmol), followed by *p*-toluenesulfonyl chloride (1.4 g, 7.5 mmol). The reaction was monitored by TLC and completed after being stirred for 2.5 h. To the mixture were added ether (30 mL) and water (15 mL) and the layers were separated. The organic layer was washed successively with HCl (2N, 20 mL), NaHCO$_3$ (5%, 20 mL), and water (25 mL). The solution was dried (MgSO$_4$) and concentrated. Flash chromatography (75/25 hexane/EtOAc) was use to obtain a clean sample in 71% isolated yield. $^1$H NMR (CDCl$_3$) $\delta$ 7.77 (d, $J$ = 8.4 Hz, 2H), 7.33 (d, $J$ = 8.4 Hz, 2H), 7.22 (t, $J$ = 7.2 Hz, 2H), 7.15 (t, $J$ = 7.2 Hz, 1H), 7.05 (d, $J$ = 7.2 Hz, 2H), 4.01 (s, 2H), 2.43 (s, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 144.8, 140.3, 133.1,129.9, 128.5, 128.5, 128.0, 126.2, 69.6, 21.7; IR (thin film) 3060, 2985, 2209, 2118, 1598, 1356, 1177, 919, 663 cm$^{-1}$.

**Methyl 2,2,3,3-Tetradeuterio-3-phenylpropyl Sulfide.** To a solution of sodium thiomethoxide (0.3 g, 4.0 mmol) in dry ethanol (15 mL) under Ar was added 2,2,3,3-tetradeuterio-3-phenylpropyl *p*-toluenesulfonate (0.39 g, 1.3 mmol) dissolved in dry THF (20 mL). The mixture was stirred for 3 h and poured into water (25 mL), and the aqueous layer was extracted with ether (3 × 25 mL). The combined organic layers were washed successively with brine (2 × 25 mL) and water (2 × 25 mL). The mixture was dried (MgSO$_4$) and concentrated to yield methyl 2,2,3,3-tetradeuterio-3-phenylpropyl sulfide in quantitative yield. $^1$H NMR (CDCl$_3$) $\delta$ 7.29−7.24 (m, 2H), 7.20−7.15 (m, 3H), 2.48 (s, 2H), 2.08 (s, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 140.8, 128.5, 128.4, 125.9, 33.4, 15.5; IR (thin film) 3059, 3024, 2914, 2205, 2101, 1603, 909, 733, 700 cm$^{-1}$.

**Methyl 2,2,3,3-tetradeuterio-3-phenylpropyl sulfone** (**2**) was prepared from methyl 2,2,3,3-tetradeuterio-3-phenylpropyl sulfide (0.2 g, 1.2 mmol) as described above in quantitative yield. It was further purified by recrystallization from ether at low temperature. $^1$H NMR (CDCl$_3$) $\delta$ 7.31−7.15 (m, 5H), 2.95 (s, 2H), 2.84 (s, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 139.7, 128.8, 128.5, 126.6, 53.7, 40.6; EI-MS ($m/e$, rel abundance) 202 (26), 120 (100), 93 (48); IR (thin film) 3019, 2198, 2160, 2102, 1305, 1133, 744, 704 cm$^{-1}$. Anal. Calcd for $C_{10}H_{12}D_2O_2S$: C, 59.37; H, 6.98; S, 15.85. Found: C, 59.21; H, 7.12; S, 15.81, assuming D analyzes as H.

**Computational Details.** All computations, except the G2 calculation on methanesulfinic acid and a few semiempirical conformational searches, were carried out with the GAMESS suite of programs.[31] Results were visualized with MacMolPlt.[32] The G2 calculation was carried out using GAUSSIAN 94,[33] in which the default 6-311 basis set was made to conform with those in GAMESS, as developed by McLean and Chandler.[34] Low-energy conformations of **4**, **5**, **8**, and methanesulfinic acid were determined using the PM3 model, and subsequent optimizations used those conformations as starting geometries. Hessians were obtained to confirm the nature of the stationary points. For each molecule below, the coordinates, absolute energy in hartrees, and zero-point energies are given in the Supporting Information.

CASSCF/6-31G(d,p) calculations were carried out on the transition state for **4**. The active space consisted of 5 orbitals with 6 electrons as described in the main text. Optimization was begun from the MP2/6-31G(d,p) geometry and did not result in substantial changes. The natural orbital occupations were very close to 2 or 0. The Supporting Information contains the final coordinates and the precise occupations of the natural active space orbitals.

The temperature-dependent KIE for the Ei reaction was calculated[19] using the program ISOEFF98,[20,21] which uses vibrational frequencies from the substrate and TS to solve for the KIE using the Bigeleisen equation.[22−24] The ISOEFF98 program uses Hessian matrices obtained from GAMESS output. The Supporting Information contains the calculated KIE for both unscaled and scaled vibrational frequencies for **6** and **7**. The numbers reported in the text are averages of the KIE calculated for **6** and **7**.

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**Supporting Information Available:** Compound preparation and further computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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