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Mechanism of the Diphenyldisulfone-Catalyzed Isomerization of Alkenes. Origin of the Chemoselectivity: Experimental and Quantum Chemistry Studies

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Abstract: Polysulfone- and diphenyldisulfone-catalyzed alkene isomerizations are much faster for 2-alkyl-1-alkenes than for linear, terminal alkenes. The mechanism of these reactions has been investigated experimentally for the isomerization of methylidenecyclopentane into 1-methylcyclopentene, and theoretically [CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p) calculations] for the reactions of propene and 2-methylpropene with a methanesulfonyl radical, $MeSO_2^{\bullet}$. On heating, polysulfones and $(PhSO_2)_2$ equilibrate with sulfonyl radicals, $RSO_2^{\bullet}$. The latter abstract allylic hydrogen atoms in one-step processes giving allylic radical/RSO_2H pairs that recombine within the solvent cage producing the corresponding isomerized alkene and $RSO_2^{\bullet}$. The sulfinic acid, RSO_2H, can diffuse out from the solvent cage (H/D exchange with MeOD,D_2O) and reduce an allyl radical. Calculations did not support other possible mechanisms such as hydrogen exchange between alkenes, electron transfer, or addition/elimination process. Kinetic deuterium isotopic effects measured for the $(PhSO_2)_2$-catalyzed isomerization of methylidenecyclopentane and deuterated analogues and calculated for the H abstraction from 2-methylpropene and deuterated analogues by $CH_3SO_2^{\bullet}$ are consistent also with the one-step hydrogen transfer mechanism. The high chemoselectivity for this reaction is not governed by an exothermicity difference but by a difference in ionization energies of the alkenes. Calculations for $CH_3SO_2^{\bullet}$ + propene and $CH_3SO_2^{\bullet}$ + 2-methylpropene show a charge transfer of 0.34 and 0.38 electron, respectively, from the alkenes to the sulfonyl radical in the transition states of these hydrogen abstractions.

Introduction

Double bond migration in alkenes can be induced by SO_2. The process is generally explained by invoking an ene reaction between an SO_2 molecule and the alkene **1** to give a β,γ-unsaturated sulfinic acid intermediate **2** which then undergoes a [1,3]-sigmatropic shift to form an isomeric β,γ-unsaturated sulfinic acid **3** followed by a retro-ene reaction that eliminates SO_2 (Scheme 1) and produces the isomeric alkene **4**.[1]

In the case of methylidenecyclopentane and related alkenes we found that their isomerization was inhibited by radical-scavenging agents such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical) and Bu_3SnH. Kinetic measurements showed an induction period followed by a zeroth-order reaction. During the induction period a white precipitate of a 1:1 copolymer of the alkene **1** and SO_2, a polysulfone, was formed.[2] When pure alkenes **1** were exposed to pure polysulfones arising from various olefins, isomerizations **1** → **4** occurred in the absence of SO_2.[3] The ESR spectrum of the polysulfone showed typical signals for carbon-centered and sulfonyl radicals.[4] Alkene isomerizations **1** → **4** were also induced upon UV irradiation or heating (80−120 °C) of **1** in the presence of a catalytic amount of $(PhSO_2)_2$ (diphenyldisulfone).[5] Both the polysulfone- and diphenyldisulfone-catalyzed alkene isomerizations followed zeroth-order rate laws and were inhibited by radical scavenging agents. Importantly, these reactions were much better yielded than the SO_2-induced isomerizations, the latter being ac-

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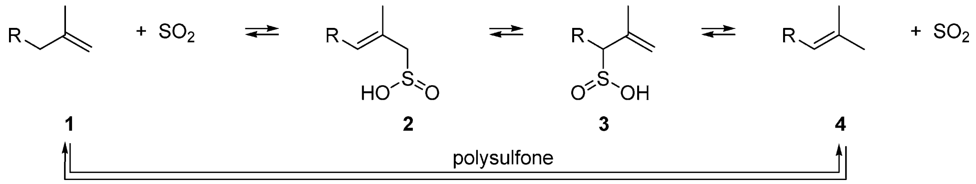
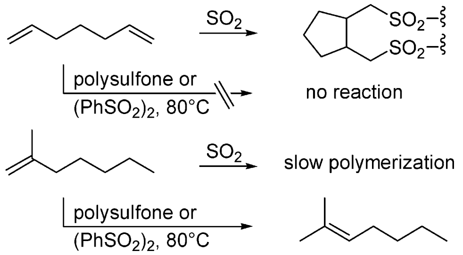
10.1021/ja0579210 CCC: $33.50

Scheme 1



Scheme 2. Selectivity of SO_2 and Polysulfone-Catalyzed Alkene Isomerizations



companied by polymer formation.[3] Furthermore, the polysulfone- and diphenyldisulfone-catalyzed alkene isomerization were chemoselective in the sense that linear, terminal alkenes (1-substituted ethylenes) and 1,2-dialkylethylenes were not isomerized at all, whereas 2-alkyl substituted alk-1-enes were isomerized (Scheme 2). This discovery led us to invent new strategies for the protection and deprotection of alcohols and the semiprotection of polyols. Methallyl, prenyl, and methylprenyl ethers undergo selective cleavages catalyzed either by diphenyldisulfone[6] or by the solid polysulfone **PS** (generated from the copolymerization of SO_2 with methylidenecyclopentane) under neutral conditions (Scheme 3). Allyl ethers and other alcohol protective groups were not cleaved under these conditions.[7,8] In a preliminary communication[3] we proposed that the **PS**- and $(PhSO_2)_2$-catalyzed isomerization of methylidenecyclopentane (**5**) imply the generation of allyl radical intermediate **6** which can diffuse out of the polymer or from the solvent cage and react with another molecule of **5** to generate product **7** (1-methylcyclopentene) and another allyl radical **6** (chain process, mechanism A + B of Scheme 4). This hypothesis was consistent with the observation that a 1:1.06 mixture of **5** and hexadeuterated derivative **8** led, in the presence of **PS**, to a mixture of 1-methylcyclopentenes with CH_3, CH_2D, CHD_2, and CD_3 groups.

We present here new experiments that refute this hypothesis and shall show that the alternative mechanism A + C of Scheme 4 interprets the data better. Instead of direct hydrogen (deuterium) atom transfer from **5** (**8**) to the allyl radical **6** (**9**), the hydrogen (deuterium) atom is transferred via the sulfinic acid, $RSO_2H(D)$, generated by the reaction of the alkene with sulfonyl radicals. It is the intermediate allyl radicals **6** (**9**) that can diffuse away from the polysulfone (or the solvent cage in the case of $(PhSO_2)_2$-catalyzed isomerization) and encounter another sulfinic acid moiety (mechanism C of Scheme 4). As it is known that sulfonyl radicals, in particular $PhSO_2^{\bullet}$, can combine[9] into a sulfinyl−sulfonyl anhydride, PhS(O)−OSO_2Ph,[10] a trace of water could generate sulfinic and sulfonic acids (RSO_2H, RSO_3H) capable of catalyzing the alkene isomerization by protonation and deprotonation or acid addition and elimination (mechanism D, Scheme 5).[11]

The benzenesulfonyl radical engendered by thermal decomposition of diphenyldisulfone is capable of abstracting a hydrogen atom from diphenylmethane as demonstrated by the formation of 1,1,2,2-tetraphenylethane.[12] Sulfonyl radicals are electrophilic[13] and able to be added to alkenes, a key reaction during polymerization of alkenes promoted by sulfonyl radicals and during the copolymerization of alkenes and sulfur dioxide.[2] In mechanism E of Scheme 5, we envision that the formation of allyl radicals (e.g., **6**) and sulfinic acids (e.g., $PhSO_2H$) is not a one-step hydrogen atom transfer as involved in mechanism A and C of Scheme 4 but a two-step process involving first the addition of sulfonyl radical $RSO_2^{\bullet}$ onto the alkene with generation of the alkyl radicals of types **10** and **11**. In a second step, which can be fast because of the radical-assisted heterolysis[14] elimination of RSO_2H and formation of the allyl radical, intermediate **12** occurs.[15] This mechanism would explain the chemoselectivity of our alkene isomerizations as secondary radicals **10** would form less readily than the corresponding tertiary alkyl radicals **11**.

Alternatively, and as found for polar radicals,[16,17] the hydrogen atom transfer is a two-step process starting by an electron transfer to generate radical cations of type **13** and **14**, followed by proton transfer to the sulfinate anion (mechanism F, Scheme 5). This mechanism would also explain the chemoselectivity of our alkene isomerizations. Quantum calculations, kinetic deuterium isotopic effects, and other experiments presented in this work favor mechanism A + C; i.e., they support one-step hydrogen transfer from the allylic C−H of alkene to the sulfonyl radical. The hydrogen/deuterium scram-

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(11) This mechanism is also compatible with inhibition by radical scavenging agents; the latter inhibit the combination of two sulfinyl radicals.

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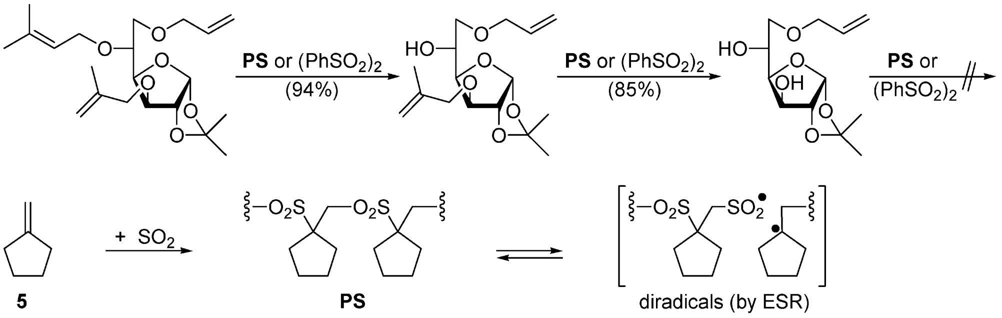
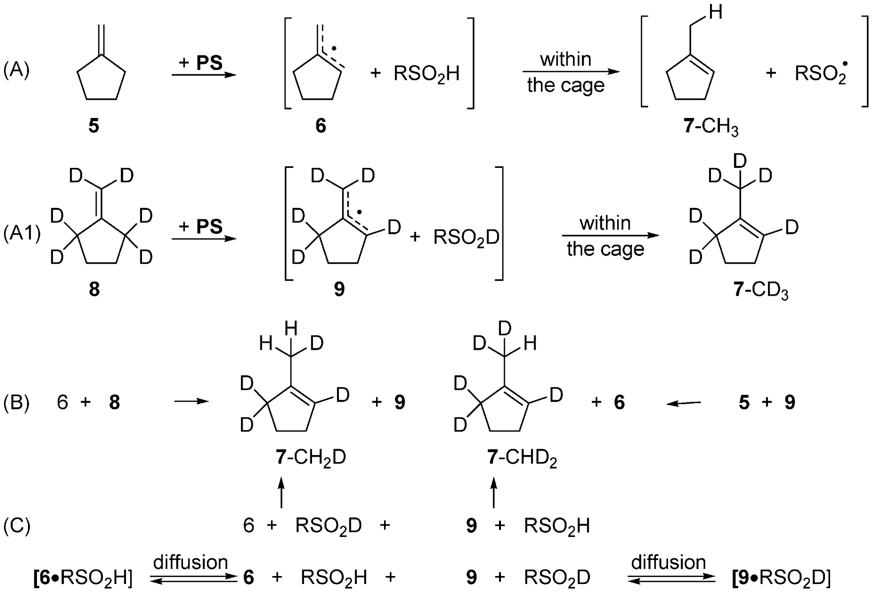
(15) The elimination of RSO_2H from the alkyl radical might be concerted or become a radical-cation/RSO_2^- pair.

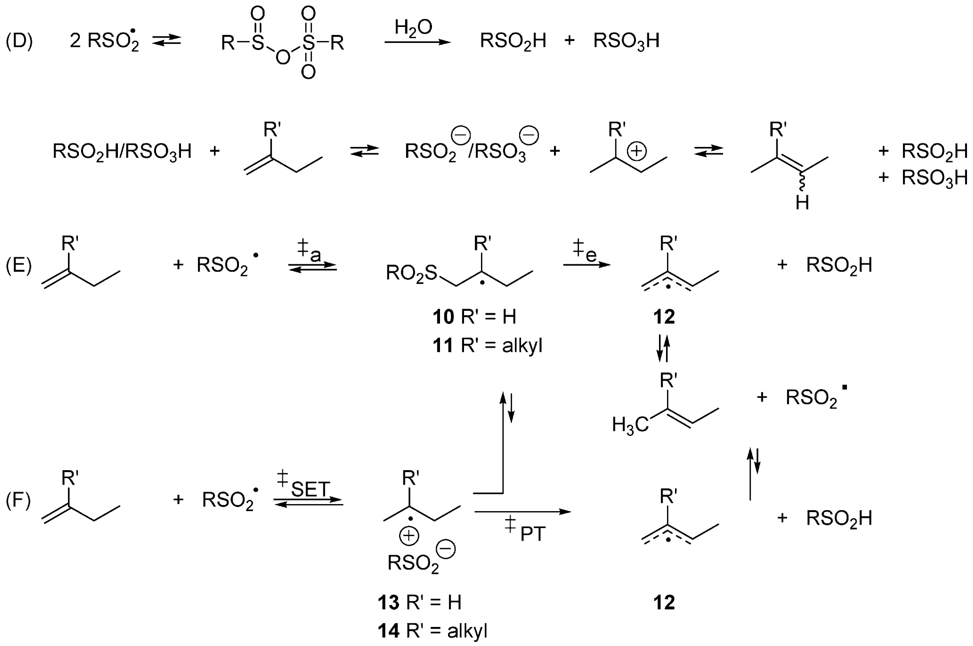
Scheme 3. Chemoselective Cleavage of Alkyl Substituted Allyl Ethers under Neutral Conditions and without Metal Catalyst



Scheme 4. Possible Mechanisms for the Scrambling of H/D



Scheme 5. Other Possible Mechanisms for the Alkene Isomerizations Catalyzed by Polysulfones and Diphenyldisulfone



bling presented in Scheme 4 is not due to allyl radical/alkene reactions but to diffusion of the allyl radical and/or sulfinic acid intermediates out of the solvent cage, a process that competes with the transfer of a hydrogen atom from it to the allyl radical intermediate within the initial solvent cage.

Theoretical Methods

Propene, 2-methylpropene, and a methanesulfonyl radical were chosen as model systems to carry out a theoretical mechanistic analysis on the sulfonyl radical-catalyzed alkene isomerization.

Geometry optimizations were carried out using Density Functional Theory (DFT)[18] with the Becke three-parameter Lee−Yang−Parr[19,20] (B3LYP) hybrid functional and Pople's valence triple-ζ 6-311++G(d,p) basis set.[21] All the geometrical parameters were fully optimized, and all the structures located on the potential energy surfaces (PESs) were characterized as minima or transition structures by computing the corresponding Hessian matrices and examining the number of imaginary frequencies from them.

The energy predictions were improved in the case of the abstraction reactions of propene and 2-methylpropene with the methanesulfonyl radical by performing single-point CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p) calculations. As shown below, the chemoselectivity observed experimentally for these reactions (no isomerization was detected when using 1-substituted ethylenes and 1,2-dialkylethylenes) will arise from the comparison between the substantially similar energy profiles for the propene and 2-methylpropene reactions. Therefore, a high level of accuracy is required to ensure the validity of the conclusions.

Graphical analyses of the imaginary frequencies of the transition structures as well as intrinsic reaction coordinate (IRC) calculations in the mass-weighted internal coordinates[22] allowed us to interconnect the different structures located on the PESs and then construct the corresponding energy profiles.

Solvation effects were estimated by using a continuum solvent description: the so-called polarized continuum model (PCM).[23] Calculations were carried out for dichloromethane with a dielectric constant, ϵ, of 8.93. The atomic radii were taken from the universal force field (UFF).[24] The ion convention standard state (1M)[25] was used to compute the changes in Gibbs free energies (ΔG).

The thermodynamic functions (ΔH, ΔS, and ΔG) were estimated within the ideal gas, rigid rotor, and harmonic oscillator approximations.[26] A temperature of 298 K was assumed.

The Gaussian98 and Gaussian03 packages of programs[27] were used to carry out all these calculations. Isotope effects were computed by means of the QUIVER program,[28] which employs the Bigeleisen−Mayer formulation[29] within the transition-state-theory approximation.

Experimental Results and Discussion

A. Mechanism of the Hydrogen Exchange between Alkenes. Isomerization of methylidenecyclopentane (**5**) into 1-methylcyclopentene (**7**) catalyzed by the solid polysulfone **PS** generated by copolymerization of **5** and SO_2 occurs already at 0 °C. The rate of the isomerization does not depend on the mode of preparation of **PS** and upon the amount of aqueous NaOH used to neutralize the free SO_2H groups it contains. The **PS** as well as the diphenyldisulfone-catalyzed isomerizations **5** → **7** have similar rates (at a given temperature) in CH_2Cl_2 or heptane. The **PS**-catalyzed isomerization **5** → **7** is strongly retarded in polar solvents such acetone, EtOAc, or DMF. This is not the case for the disulfone-catalyzed isomerization. We attribute this different behavior between the **PS** and disulfone catalyst to the swelling properties of the polar solid polysulfone catalyst. Polar solvent diffuse with greater difficulty out of the polymer and do not leave a chance for the alkene to get into the active site of the solid catalyst.[30] When THF/H_2O mixtures were used as solvent, the isomerization **5** → **7** catalyzed by $(PhSO_2)_2$ at 80 °C was not stopped on adding $NaHCO_3$. The reaction was slowed, however, due to decomposition of diphenyldisulfone under those conditions. Finally, benzenesulfinic acid (10 mol %) was not capable of inducing isomerization of methylidenecyclopentane (**5**) into 1-methylcyclopentene (**7**) during 3 h at room temperature. These observations demonstrate that it cannot be neither protonation/deprotonation nor sulfinic acid addition/elimination that is responsible for the alkene isomerization. Thus mechanism D of Scheme 5 can be ruled out. These results also demonstrate that the sulfinic acid intermediate RSO_2H, formed by abstraction of a hydrogen atom from the alkene, does not have to diffuse out of the solvent cage (in the case of the disulfone-catalyzed isomerization) to deliver an

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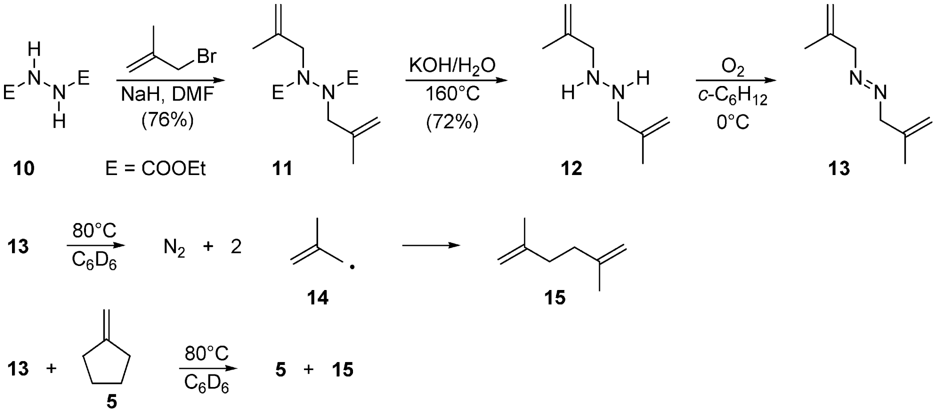
(30) One referee suggested that the mechanism of the $(PhSO_2)_2$-induced alkene isomerization might not be the same as that of the polysulfone-induced reaction. If sulfonyl-centered radicals should equilibrate with the polysulfone already at room temperature, the C−S bond energy in sulfones of type (dialkyl)C−SO_2−alkyl is too high for such a homolysis. He calculates (CBS-QB3) bond dissociation energies of 71.8 and 67.2 kcal/mol for the C−S bonds in Me_2SO_2 and $MeSO_2$−C(Me)$_2$, respectively. Experimental thermochemical data allow one to estimate to ca. 63 kcal/mol the C−S bond energy of $MeSO_2C(Me)_3$ considering the C−S bond dissociation energy in $MeSO_2Me$ of 73.5 kcal/mol[31] and the difference in C−H bond energies between Me−H and Me_3C−H.[31] The existence of the sulfonyl-centered radical in our polysulfone **PS** derived from the copolymerization of SO_2 and methylidenecyclopentane is demonstrated by ESR.[3] Polysulfones are known to equilibrate with SO_2 and alkenes on heating: the ceiling temperature depends on the nature of the alkene used for the copolymerization with SO_2. It can be lower than 273 K with 2-alkylalk-1-enes,[32] and sulfonyl-centered radicals have been detected by ESR during the depolymerization of polysulfones.[33] During the copolymerization of alkenes and SO_2, sulfite moieties (CH_2−S(O)−OC(R)$_2$−) are formed concurrently with sulfone moieties (CH_2−SO_2−C(R)$_2$). The former undergo homolysis into alkyl and sulfonyl radicals much more readily than the latter as the sulfones are significantly more stable than their isomeric sulfinates.[31b,c] The sulfinate impurities are the most probable source of the radicals formed in the initial step of the polysulfone depolymerization process.[34] With our solid polysulfone **PS** Front-strain and Back-strain are expected to lower the barriers of the C−S(sulfone) and C−O(sulfinate) homolyses, and highly positive entropies of dissociation are expected for the C−O bond leakage of sulfinates with high molecular mass.

Scheme 6



hydrogen atom to another allyl radical; the isomerization can occur within the solvent cage or polymer active site.

On heating **5** (sealed tube, CD_2Cl_2) in the presence of AIBN (2,2′-azobisisobutyronitrile, 10−50 mol %), no isomerization **5** → **7** could be observed after complete destruction of AIBN. This shows that the 2-cyanoisopropyl radical is not capable of abstracting a hydrogen atom from alkene **5**, or if it can do it, it does not lead to the isomerization **5** → **7**. As reaction $Me_2(C(CN)^\bullet + \mathbf{5} \rightarrow \mathbf{6} + Me_2(CN)CH$ is endergonic[31] we reasoned that the 2-methylallyl radical would be a better initiator for the isomerization **5** → **7** as reaction $CH_2{=}C(Me)CH_2^\bullet + \mathbf{5} \rightarrow \mathbf{6} +$ isobutylene is estimated to be exergonic by −1 to −2 kcal/mol.[31] If this equilibrium should occur, it could lead to isomerization **5** → **7** via the radical chain process **5** + **6** → **7** + **6** (mechanism A + B, Scheme 4). To test this hypothesis we prepared 1,1′-azobis(2-methylpropene) (**13**) following a procedure analogous to that reported for the preparation of 1,1′-azo(propene).[35]

N,*N*-Bis(ethoxycarbonyl)hydrazine (**10**)[36] was reacted with methallyl bromide in the presence of NaH in DMF giving **11** in 76% yield. Treatment of **11** with aqueous KOH at 100 °C led to a poor yield (12%) in hydrazine **12**. However, when heated to 160 °C in an autoclave, 87% of **12** was obtained. Known methods[35] for the oxidation of **12** into the azo compound **13** such as treatment with $HgO/HgSO_4$ in ether at 0 °C led to the exclusive formation of 2,5-dimethylhexa-1,5-diene (**15**). Finally we found that simple bubbling of air in a solution of **12** in cyclohexane at 0 °C led to its clean oxidation into **13** that was isolated pure in 73% yield (Scheme 6). On heating **13** in C_6D_6 at 80 °C, 2,5-dimethylhexa-1,5-diene (**15**) and N_2 were formed quantitatively, a reaction believed to imply the formation of a 2-methylallyl radical intermediate (**14**).[37]

To our surprise, when solutions of methylidenecyclopentane (**5**) in C_6D_6 containing 5−50 mol % of azo compound **13** were heated to 60−80 °C, only **15** was formed[38] and **5** was recovered unrearranged quantitatively (^1H NMR analysis). These observations demonstrate that the hydrogen atom transfer from **5** to the methallyl radical (**14**) is a very slow reaction that does not compete with the dimerization of **14** into **15**. This suggests that the hydrogen atom transfer from **5** to the allyl radical **6** might also be a very slow process that cannot be taken to be responsible for isomerization **5** → **7** and for the hydrogen/deuterium scrambling presented in Scheme 4. Mechanism A + B cannot be retained, isomerization occurs, in part, within the solvent cage of the $allyl^\bullet RSO_2H$ species, and the D/H scrambling between **5** and **8** (Scheme 4) is due to competitive diffusion of the allyl radical or/and the sulfinic acid species outside the solvent cage (mechanism A + C of Scheme 4). This latter hypothesis was confirmed by the following experiments.

On heating **5** (0.2 molar) in cyclohexane containing 4 to 10 equiv of MeOD in the presence of 10 mol % of $(PhSO_2)_2$, isomerization **5** → **7** occurred and **7** was partially deuterated at its methyl group. The proportion of **7**:**7**-d_1 (Scheme 7) varied between 45:55 and 55:45. The incomplete monodeuteration, although MeOD was used in excess, indicates that about 50% of the isomerization **5** → **7** occurs within the solvent cage and that about 50% occurs with concurrent diffusion of the allyl radical or/and $PhSO_2H$ outside the solvent cage (assuming fast deuterium hydrogen exchange once $PhSO_2H$ gets in contact with MeOD). Similar results were obtained on treating **5** with 5 mol % I_2 in THF-d_8/MeOD at 80 °C (Scheme 7). In this latter experiment, the yield in **7** + **7**-d_1 was mediocre due to concurrent formation of several other products. To confirm the above hypothesis we ran an isomerization **5** → **7** in THF/D_2O and another one in THF-d_8/D_2O, both catalyzed by 10 mol % diphenyldisulfone (80 °C). This generated pure **7** + **7**-d_1 in the proportion 55:45 (10 to 30 equiv of D_2O).[39] On adding 20 mol % of $NaHCO_3$ to these solutions, the diphenyldisulfone-

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(33) See e.g.: Zutty, N. L.; Wilson, C. W.; Potter, G. H.; Priest, D. C.; Whitworth, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **1965**, *3*, 2781−2799 and ref 4.

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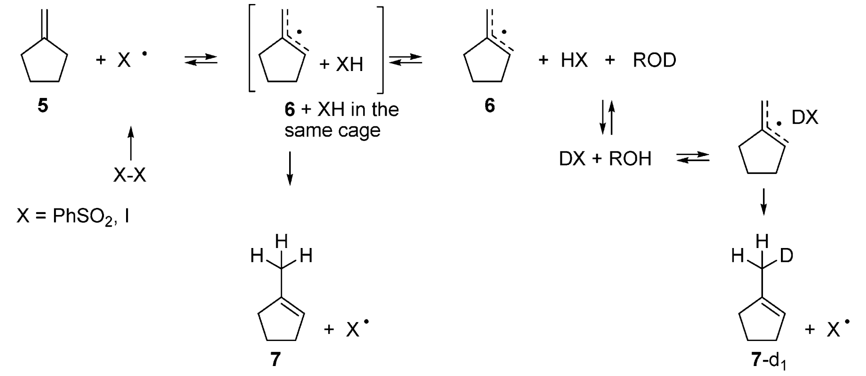
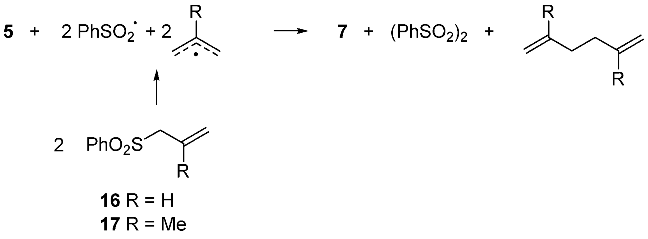
(38) (a) Hefter, H. J.; Wu, C.-H. S.; Hammond, G. S. *J. Am. Chem. Soc.* **1973**, *95*, 851−855. (b) Roth, W. R.; Bauer, F.; Beitat, A.; Ebbrecht, T.; Wüstefeld, M. *Chem. Ber.* **1991**, *124*, 1453−1460.

(39) Concurrent hydrolysis of diphenyldisulfone occurred under these conditions, thus leading to incomplete isomerization of the alkene, unless more diphenyldisulfone would be added to the reaction mixture. For the hydrolysis of diphenyldisulfone, see: Kice, J. L.; Margolis, H. C.; Johnson, W. C.; Wulff, C. A. *J. Org. Chem.* **1977**, *43*, 2933−2935.

Scheme 7. Deuterium Incorporation Implies Migration of the Allyl Radical or/and RSO_2H outside the Solvent Cage of Allyl Radical + RSO_2H



Scheme 8. $PhSO_2^\bullet$-Induced Isomerizations



catalyzed (80 °C) isomerization **5** → **7** led only to the formation of nondeuterated isomerized alkene **7**. By ^{2}D-NMR analysis (toluene-d_8 as internal reference), less than 3% of **7**-d_1 was formed under the latter conditions.

To confirm that $PhSO_2^\bullet$ is indeed the species responsible for the diphenyldisulfone-catalyzed alkene isomerization we generated it from other sources than $(PhSO_2)_2$. For instance, on heating **5** in cyclohexane-d_{12} (sealed tube, ^{1}H NMR analysis) to 110 °C in the presence of 10 mol % of sulfones **16**[40] and **17**,[41] **7** was formed quantitatively together with a few percents of hexa-1,5-diene and 2,5-dimethylhexa-1,5-diene, respectively. The above isomerizations **5** → **7** were inhibited on adding small amounts (2−10 mol %) of $(Bu_3Sn)_2$ to the reaction mixture (Scheme 8).

We also verified that $PhSO_2H$ is capable of reducing allyl radical intermediates by hydrogen transfer.[1f] Thus, on heating the azo compound **13** with 2 equiv of $PhSO_2H$ in cyclohexane-d_{12} at 40 °C (sealed tube, ^{1}H NMR analysis), quantitative formation of isobutylene (2-methylpropene) was observed (Scheme 9).

Furthermore, we found that 4-bromoheptane can be reduced smoothly into heptane on heating it to 120 °C in cyclohexane-d_{12} in the presence of 1.3 equiv of $PhSO_2H$ and a 1 equiv of $(Bu_3Sn)_2$.

B. Mechanism of the Formation of Allyl Radical Intermediates. To address the question of the mechanism of formation of allyl radicals by reaction of sulfonyl radicals, $RSO_2^\bullet$, with alkenes (distinction between mechanisms A (direct one-step hydrogen transfer), E ($RSO_2^\bullet$ radical addition and subsequent 1,3-elimination of RSO_2H), and F (single electron transfer and subsequent proton transfer of Scheme 5)) we have measured the kinetic deuterium isotopic effects defined in Scheme 10. The results will be compared with related kinetic isotopic effects calculated (see below) for model reactions. As we shall see, quantum calculations as well as our experimental results support mechanism A for the formation of allyl radical intermediates.

Next the hexadeuterated methylidenecyclopentane **8** was prepared along with the tetradeuterated derivative **19** and the dideuterated derivative **20** (Scheme 10).[42]

The degree(s) of deuterium incorporation at C(2,5) and at the olefinic center were measured by ^{1}H NMR (residual ^{1}H signal compared with a ^{13}C−H satellite) and by mass spectrometry. The rate constants for the diphenyldisulfone-catalyzed isomerization (10 mol %) were measured by ^{1}H NMR and ^{2}D-NMR in benzene-d_6 at 80 °C for each compound **5**, **8**, **19**, and **20** and for pairs of alkenes (1:1 mixtures of **5** + **8**, **5** + **19**, **5** + **20**, **19** + **20**, **8** + **19**, and **8** + **20**). Internal reference was 10 mol % of toluene-d_8; initial concentration of alkenes: 0.1−0.15 M. The kinetic data so-obtained (all zeroth-order rate laws) are shown in Table 1.

We notice that deuteration of **5** at C-2 and C-5 retards the isomerization much more than deuteration at the terminal center of the alkene.

If a single electron transfer should be the rate-determining step, much smaller k_H/k_{6D} and k_H/k_{4D} values would be observed.[43] Similarly, if the rate determination step of the isomerization **5** → **7** should be the addition of $PhSO_2^\bullet$ onto the alkene to generate the tertiary radical **11** (R′ = Me) (see Scheme 5) smaller k_H/k_{6D} and k_H/k_{4D} values would have been expected. If mechanisms E or/and F of Scheme 5 should be followed for the formation of the allyl radical **6** and $PhSO_2H$, our kinetic deuterium isotopic effects would imply that the second step of these mechanisms would be rate-determining; i.e., either the 1,3-elimination **11** (R′ = Me) → **6** + $PhSO_2H$ or the proton transfer **14** (R′ = Me) → **6** + $PhSO_2H$ is the slow step.[43] When the latter mechanism is followed (rate-determining proton

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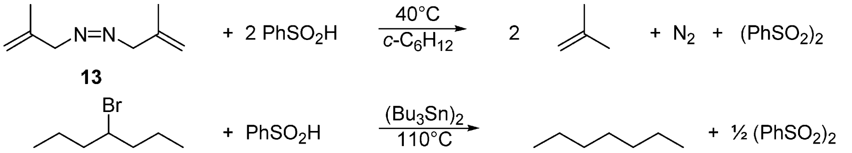
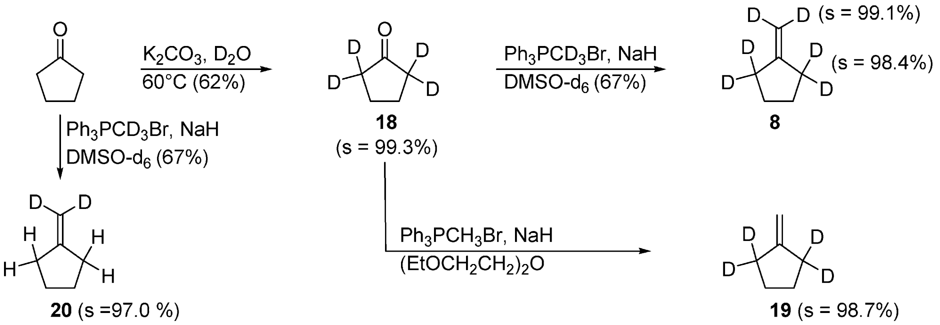
Scheme 9. Reduction with $PhSO_2H$



Scheme 10. Preparation of Deuterated Methylidenecyclopentanes (s = deuteration degree at the marked positions)



Scheme 11

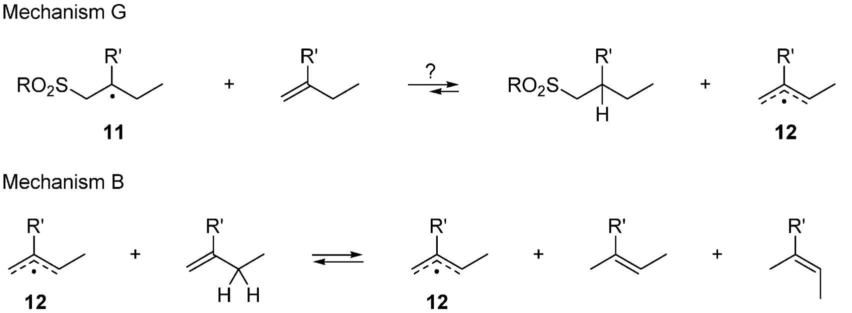


Table 1. Zeroth-Order Rate Constants (mol kg^{-1} min^{-1}, benzene-d_6, 80 °C, 10 mol % $(PhSO_2)_2$, 10 mol % toluene-d_8) of the Disulfone-Catalyzed Isomerizations of **5**, **8**, **19**, **20** (Average of 3 Measurements at least)[a]

5 → **7**-CH_3	$k_H = 0.001\,43 \pm 0.000\,02$
8 → **7**−CD_3	$k_{6D} = 0.000\,39 \pm 0.000\,01$
19 → **7**−CH_2D	$k_{4D} = 0.000\,48 \pm 0.000\,01$
20 → **7**−CD_2H	$k_{2D} = 0.001\,27 \pm 0.000\,03$

Kinetic Deuterium Isotopic Effects (80 °C)

k_H/k_{6D}	k_H/k_{4D}	k_H/k_{2D}	k_{2D}/k_{4D}	k_{2D}/k_{6D}	k_{4D}/k_{6D}
3.67 ± 4% (4.21−4.57)	2.97 ± 3.5% (4.08−4.43)	1.12 ± 3.8% (1.02−1.03)	2.64 ± 4.5%	3.25 ± 5%	1.23 ± 4.8%

[a] The theoretical estimates of the kinetic isotopic effects (in parentheses) were obtained by employing the zero- and small-curvature tunneling models, respectively (see the text for further details).

transfer), usually higher primary kinetic deuterium isotopic effects are reported.[44]

As we shall show below, our ab initio calculations do confirm that the sulfonyl radical addition to an alkene is a fast process at room temperature. This suggested, apart from the possible intervention of mechanism B, the operation of mechanism G shown in Scheme 11. As additions of $RSO_2^•$ to alkenes are relatively facile, the intermediate tertiary alkyl radicals **11** so-obtained might abstract a hydrogen atom from the alkenes and generate the corresponding allyl radicals **12** in exergonic processes, and thus start a chain process (mechanism B) responsible for the alkene isomerization. As we have found that the 2-cyanoprop-2-yl radical and methallyl radical are not capable of catalyzing the isomerization of methylidenecyclopentane into 1-methylpentane; this pathway (mechanisms E + G + B) can be ruled out. Indeed, as we shall see here below, our quantum calculations predict a high barrier for the hydrogen atom transfer between isobutylene and the methallyl radical, and consequently such a pathway can also be discarded based on theoretical considerations.

Theoretical Analysis of the Mechanism

A. Mechanism of the Hydrogen Exchange between the Alkene and Sulfonyl Radicals. Figures 1 and 2 contain the B3LYP/6-311++G(d,p) geometries for the species involved in the abstraction reactions between propene and 2-methylpropene, respectively, with the methanesulfonyl radical. Table 2 collects their corresponding CCSD(T)/6-311++G(d,p)// B3LYP/6-311++G(d,p) ΔU, ΔH, ΔS, ΔG(gas phase), and ΔG_{sol}(CH_2Cl_2 solution) values, and Figure 3 shows the associated energy profiles.

The abstraction of an allylic hydrogen from propene by $CH_3SO_2^•$ proceeds through a transition structure (see $\mathbf{TS1_{abs}}$ in Figure 1) that implies a substantial barrier height ($\Delta G_{sol} = 27.8$ kcal/mol). The abstracted hydrogen remains at the midway between the methyl group in propene (C···H = 1.315 Å) and the oxygen atom of the $CH_3SO_2^•$ radical (H···O = 1.267 Å). $\mathbf{TS1_{abs}}$ evolves toward a weakly bound structure, $\mathbf{wbc_{post}}$, in which the methanesulfinic acid formed weakly interacts with

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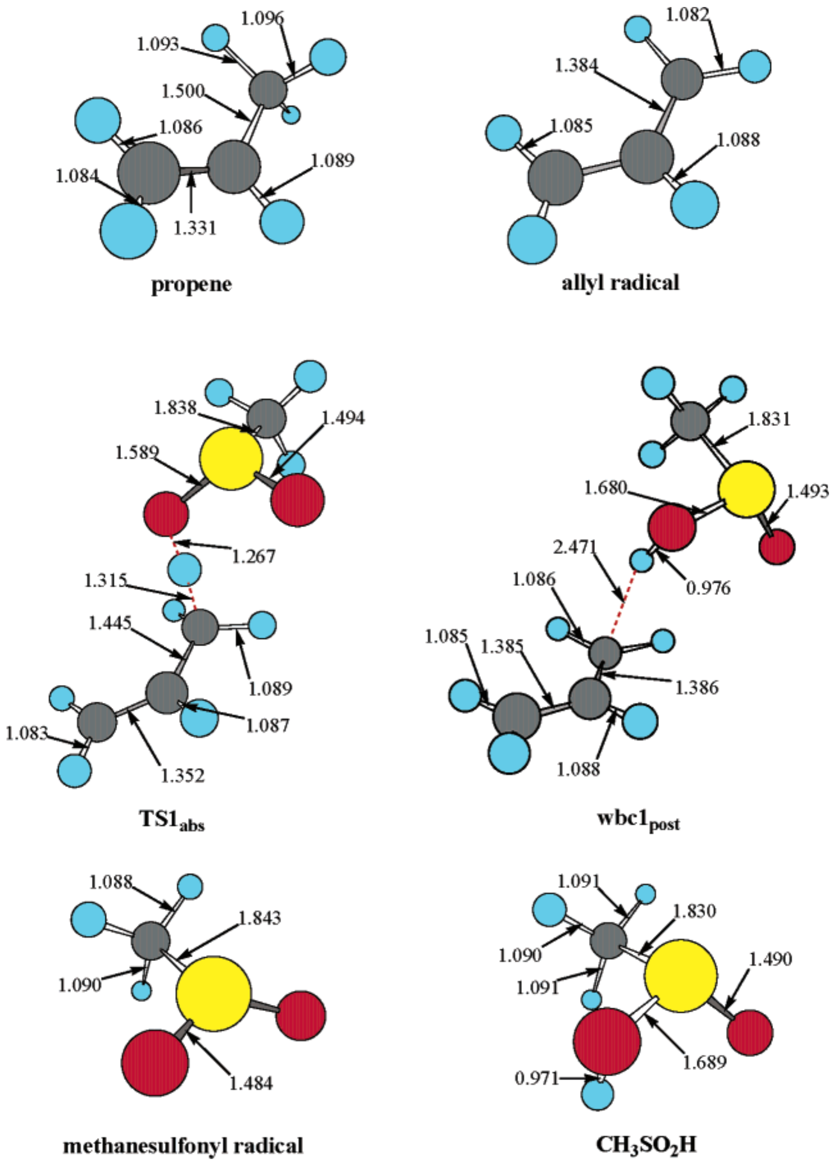
[44] See e.g.: (a) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265−273. (b) Fraser, R. R.; Champagne, P. J. *Can. J. Chem.* **1980**, *58*, 72−78. (c) Jarczewski, A.; Schroeder, G.; Leffek, K. T. *Can. J. Chem.* **1991**, *69*, 468−473. (d) Grzeskowiak, I.; Galezowski, W.; Jarczewski, A. *Can. J. Chem.* **2001**, *79*, 1128−1134. (e) Jarczewski, A.; Hubbard, C. D. *J. Mol. Struct.* **2003**, *649*, 287−307.


propene

allyl radical

TS1$_{\mathbf{abs}}$

wbc1$_{\mathbf{post}}$

methanesulfonyl radical

CH_3SO_2H

Figure 1. B3LYP/6-311++G(d,p) structures for the species involved in the abstraction reaction between propene and the methanesulfonyl radical to give the allyl radical and methanesulfinic acid. Distances are given in Å.

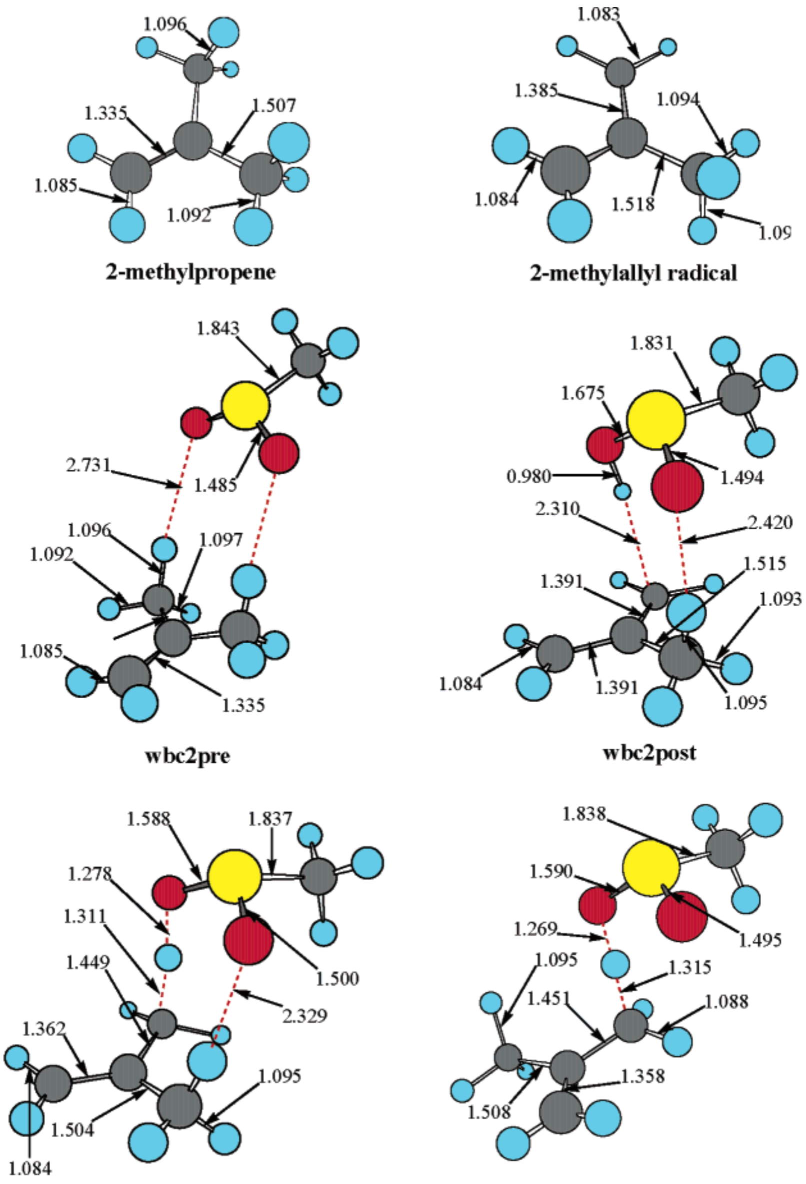
the allyl radical (OH···C = 2.471 Å). The formation of this weakly bound complex ($\Delta H = -0.8$ kcal/mol) is entropically disfavored ($\Delta G = +7.4$ kcal/mol) and consequently disappears from the Gibbs free energy profile (see Figure 3).

As can be seen in Figure 3, the propene + $CH_3SO_2^\bullet$ abstraction reaction is a slightly endergonic process ($\Delta G_{\text{sol}} = 2.7$ kcal/mol). The allyl radical formed can react, either within the solvent cage or after diffusing out from it, with a second molecule of CH_3SO_2H giving rise to the isomerized alkene (similar to the reactant because of the particular model alkene employed in our calculations, namely, propene) through an exergonic process ($\Delta G_{\text{sol}} = -2.7$ kcal/mol) involving the reverse pathway defined by a transition structure equivalent to **TS1**$_{\mathbf{abs}}$.

In the case of the 2-methylpropene + $CH_3SO_2^\bullet$ reaction, a new structure, **wbc**$_{\mathbf{pre}}$, appears on the PES. It is a molecular association formed through a weak interaction between reactants. The formation of **wbc**$_{\mathbf{pre}}$ is a slightly more exothermic ($\Delta H = -1.5$ kcal/mol) process than the formation of **wbc**$_{\mathbf{post}}$ ($\Delta H = -1.0$ kcal/mol), but both structures are strongly disfavored entropically, thus disappearing from the Gibbs free energy profile (see Figure 3). The 2-methylpropene + $CH_3SO_2^\bullet$ reaction is an endergonic process involving a change in Gibbs free energy quite similar to that for propene + $CH_3SO_2^\bullet$ (2.6 vs 2.7 kcal/mol). However, the energy barrier **TS2**$_{\mathbf{abs}}$ is 1.1 kcal/mol lower. This theoretical prediction supports the experimentally observed chemoselectivity that favors the reactivity of the 2-allyl substituted alkenes over that of the 1-susbtituted ethylenes (see the Experimental Section).

We have also considered transition structures involving hydrogen abstractions through the sulfur atom. However, they are about 8 kcal/mol higher in energy than the corresponding reactions at oxygen.

It is interesting to note that the structures of the two transition structures **TS1**$_{\mathbf{abs}}$ and **TS2**$_{\mathbf{abs}}$ involved in the abstraction reactions of propene and 2-methylpropene with $CH_3SO_2^\bullet$ are substantially different (see Figures 1 and 2). While the abstraction process is quite similar in both cases (the C···H and H···O distances in **TS2**$_{\mathbf{abs}}$ are 1.311 and 1.278 Å, respectively, which agree rather well with the abovementioned values for **TS1**$_{\mathbf{abs}}$), a hydrogen bonded interaction involving the second oxygen



2-methylpropene **2-methylallyl radical**

wbc2pre **wbc2post**

TS2abs **TS2'abs**

Figure 2. B3LYP/6-311++G(d,p) structures for the species involved in the abstraction reaction between 2-methylpropene and the methanesulfonyl radical to give the 2-methylallyl radical and methanesulfinic acid. Distances are given in Å.

atom in $CH_3SO_2^{\bullet}$ and one of the hydrogen atoms of the second methyl group in 2-methylpropene (the S−O···H−CH_2 distance is 2.329 Å) is only present in $\mathbf{TS2_{abs}}$.

One could be tempted to conclude that the main factor responsible for the lower energy barrier of $\mathbf{TS2_{abs}}$ should be this S−O···H−CH_2 hydrogen bonding stabilizing interaction which does not exist in $\mathbf{TS1_{abs}}$. However, a more detailed analysis showed that this is not the case. Indeed, an extensive exploration of the PES for the 2-methylpropene + $CH_3SO_2^{\bullet}$ abstraction reaction led to the location and characterization of a second pathway which involved the transition structure $\mathbf{TS2'_{abs}}$ in Figure 2. This transition structure does not involve any hydrogen bonding, and therefore it is very similar to the situation found in the propene + $CH_3SO_2^{\bullet}$ abstraction reaction ($\mathbf{TS1_{abs}}$). Indeed, the C···H and H···O distances (1.315 and 1.269 Å) in $\mathbf{TS2'_{abs}}$ are virtually identical to the corresponding ones in the case of $\mathbf{TS1_{abs}}$ (1.315 and 1.267 Å). Table 2 shows that, as a consequence of the extra stabilization due to the hydrogen

Table 2. ΔU, ΔH, ΔG (kcal/mol), and ΔS (cal/K·mol) Values (Relative to Reactants), as Computed at the CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p) Level, for the Abstraction of an Allylic Hydrogen in the Reactions between Propene or 2-Methylpropene and the Methanesulfonyl Radical[a]

structure	ΔU	ΔH	ΔS	ΔG	ΔG_{sol}
R1[a]	0.0	0.0	0.0	0.0	0.0
$\mathbf{TS1_{abs}}$	22.2	19.0	−32.3	26.7	27.8
$\mathbf{wbc1_{post}}$	−0.6	−0.8	−24.4	4.6	7.4
P1	4.4	2.8	−1.2	3.2	2.7
R2[b]	0.0	0.0	0.0	0.0	0.0
$\mathbf{wbc2_{pre}}$	−2.7	−1.5	−18.7	2.2	4.7
$\mathbf{TS2_{abs}}$	19.3	16.1	−36.4	25.0	26.7
$\mathbf{TS2'_{abs}}$	21.2	18.0	−30.6	25.2	26.9
$\mathbf{wbc2_{post}}$	−0.7	−1.0	−27.3	5.2	8.5
P2	6.1	4.5	4.7	3.1	2.6

[a] The standard state 1 M at 298.15 K was assumed. ΔG_{sol} represents the increment in Gibbs free energy in dichloromethane (ϵ = 8.93). [a] **R1** stands for the reactants (propene + $CH_3SO_2^{\bullet}$), and **P1**, for the products (CH_3SO_2H + allyl radical). [b] **R2** stands for the reactants (2-methylpropene + $CH_3SO_2^{\bullet}$), and **P2**, for the products (CH_3SO_2H + 2-methylallyl radical).

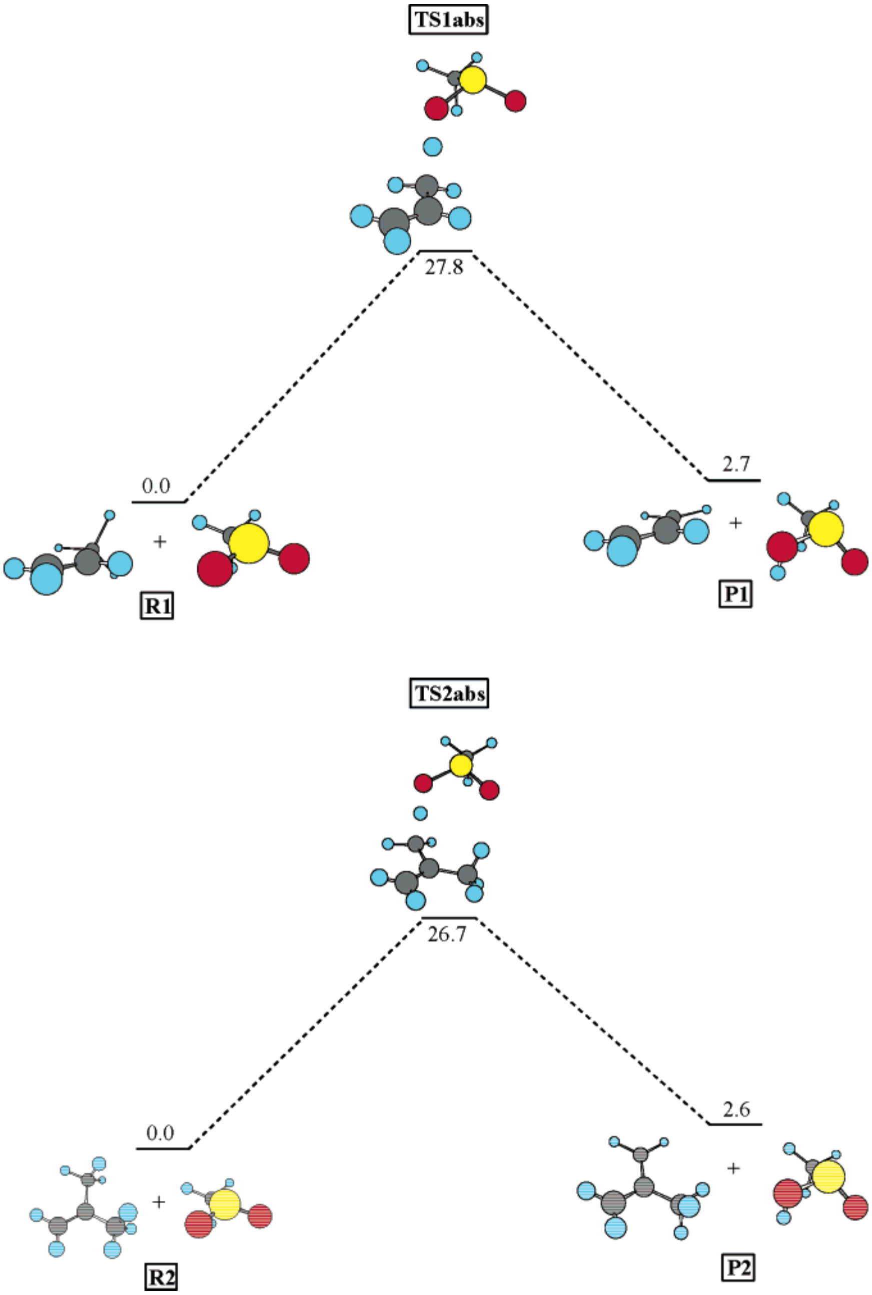


Figure 3. CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p) Gibbs free energy (ΔG_{solv}) energy profile for the abstraction reactions between propene (2-methylpropene) and the methanesulfonyl radical to give the allyl (2-methylallyl) radical and methanesulfinic acid.

bonding interaction, the activation enthalpy associated with $\mathbf{TS2_{abs}}$ is almost 2 kcal/mol lower than that of $\mathbf{TS2'_{abs}}$. However, the entropy contribution disfavors $\mathbf{TS2'_{abs}}$ in about the same amount. Consequently, as shown in Table 2, the activation Gibbs free energies for $\mathbf{TS2_{abs}}$ and $\mathbf{TS2'_{abs}}$ are quite similar, the former being slightly lower by 0.2 kcal/mol.

The above analysis makes clear that the hydrogen bonding interaction present in $\mathbf{TS2_{abs}}$ cannot be responsible for rendering the hydrogen abstraction from 2-methylpropene easier than that from propene. As the two reactions exhibit virtually the same endergonicities (see Table 2), the thermodynamic driving forces[45] will be similar and we must conclude that the intrinsic barrier should be governed by the differences in ionization energies between propene (IE = 9.73 eV)[31] and 2-methylpropene (IE = 9.22 eV).[31] The expression derived by Shaik and Schlegel for the energy barrier of reactions in which a radical abstracts an hydrogen atom from a molecule, within the framework of the state correlation diagrams (SCD) model,[46] shows that the lower the ionization potential the lower the energy barrier, in full agreement with the experimentally observed and theoretically predicted chemoselectivity for the reactions studied. A natural bond orbital (NBO) analysis[47] (see Figure 4) shows that the charge transfer from the alkene to the $CH_3SO_2^{\bullet}$ radical is 0.34 and 0.38 e for $\mathbf{TS1_{abs}}$ and $\mathbf{TS2_{abs}}$, respectively. The

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[45] Shaik, S. S.; Schlegel, H. B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry*; Wiley: New York, 1992.

[46] (a) Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692−3701. (b) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363. (c) Shaik, S. S. In *New Theoretical Concepts for Understanding Organic Reactions*; Bertrán, J.; Csizmadia, I. G. Eds.; NATO ASI Series, Kluwer Academic Publishers: Dordrecht, 1988.

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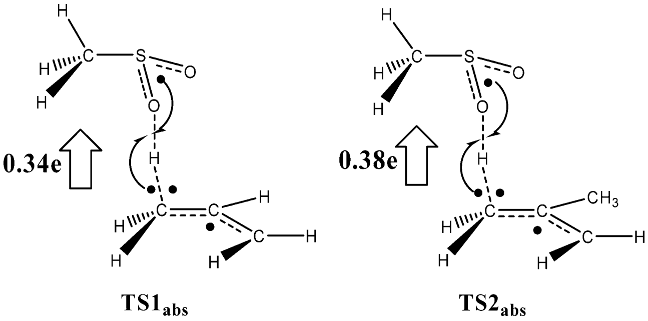


Figure 4. Lewis representations of the **TS1**$_{\mathbf{abs}}$ and **TS2**$_{\mathbf{abs}}$ transition structures as arising from a natural bond orbital (NBO) analysis.

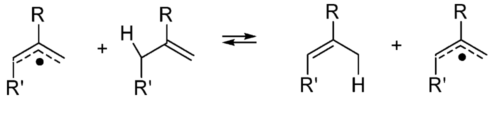
greater efficiency of the charge-transfer mechanism in the case of 2-methylpropene is consistent with its greater chemoselectivity.

It should be stressed at this point that the above considerations agree rather well with one of the empirical rules governing the free-radical substitution reactions;[48] namely, electron donor substituents (like CH_3 in 2-methylpropene) will enhance transfer reactions by electronegative radicals (like $CH_3SO_2^{\bullet}$). Sometimes, however, the competing addition reaction is more favorable than hydrogen transfer as shown by Schöneich and co-workers in the case of polyunsaturated fatty acids.[49]

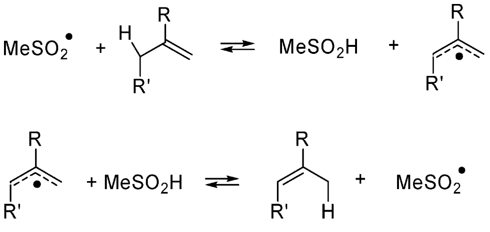
The so-called polar effect ($R{:}H{\cdot}X \rightleftarrows R{\cdot}^{+}H{:}X^{-}$) has been invoked to explain numerous directive effects observed in aliphatic systems,[50] but scarce theoretical work has been developed to rationalize the experimental findings. In a recent article,[51] some theoretical analysis on reactions involving thiyl radical-mediated cleavage of allylic C−N bonds is presented. The authors focus on the thermodynamical analysis of the hydrogen abstraction mechanism and mention that other alternative pathways like, for example, electron transfer, were not considered.

Addition, electron transfer, and other a priori suitable mechanisms have been theoretically explored by us, and the corresponding results are presented and discussed in the next sections.

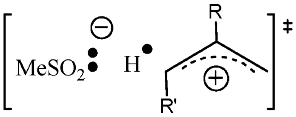
Particularly interesting is the connection between Shaik-type analysis, based on Marcus treatment of hydrogen-atom transfer reactions,[45,46] and the so-called polarity-reversal catalysis introduced by Roberts and co-workers.[52] According to these latter authors, a notable reduction in the activation energy for the hydrogen-atom transfer reaction



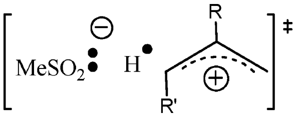
occurs when this process is carried out through a two-step pathway according to,



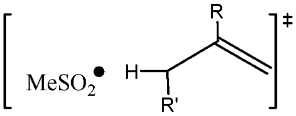
where $MeSO_2$ is said to act as a polarity-reversal catalyst.[52] The charge-transfer configuration



will stabilize the transition structures of the two-step mechanism as a consequence of the electrophilic character of the methanesulfonyl radical. The diabatic curves of the low-lying charge-transfer



and zero (ground-state) configurations



will interact strongly, thus giving rise to a notable reduction in the activation energy.[46,53] The calculations presented in the next sections fully confirmed such expectations.

From the Shaik treatment's view, one can conclude that the high electron affinity of the methanesulfonyl radical and the lower ionization energy of 2-methylpropene versus propene will favor the hydrogen-transfer reaction.

B. Alternative Pathways. The initially proposed mechanism[3] involved the reaction between the allyl radical and the alkene (see Scheme 4). We carried out an extensive exploration of the B3LYP/6-311++G(d,p) PESs for the propene and 2-methylpropene reactions, and the results are collected in Table 3. Geometries of the transition structures defining the different pathways explored, which correspond to different relative orientations of the two reactants, can be found in Figure S1 of the Supporting Information. One important point clearly emerges from inspection of Table 3.

The energy barriers are much higher than those for the reactions with the methanesulfonyl radical. Indeed, Table 3 shows that for the latter the B3LYP/6-311++G(d,p) barriers are 5−6 kcal/mol lower. This theoretical prediction reinforces the arguments based on the experimental facts, presented in the previous section, in favor of mechanism A + C in Scheme 4, in which the hydrogen atom is transferred via the sulfinic acid.

On the other hand, both mechanism E in Scheme 5 and mechanism E + G + B also mentioned in the Experimental Section imply addition of the methanesulfonyl radical to the

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Table 3. ΔU, ΔH, ΔG (kcal/mol), and ΔS (cal/K·mol) Values (Relative to Reactants), as Computed at the B3LYP/6-311++G(d,p) Level, for the Two Transition Structures Corresponding to the Abstraction of an Allylic Hydrogen in the Reactions between Propene (2-Methylpropene) and the Methanesulfonyl Radical, **TS1$_{abs}$** (**TS2$_{abs}$, TS2′$_{abs}$**), and for the Three Possible Transition Structures Corresponding to the Abstraction of an Allylic Hydrogen in the Reaction between Propene (2-Methylpropene) and the Allylic Radical (2-Methyl Allylic Radical), **TS3A-C** (**TS4A-C**)[a]

structure	ΔU	ΔH	ΔS	ΔG	ΔG_{sol}
TS1abs	17.0	13.8	−32.3	21.6	22.7
TS3A	20.9	19.0	−31.1	26.4	27.2
TS3B	20.9	19.0	−31.1	26.4	27.3
TS3C	20.8	18.9	−31.7	26.4	27.4
TS2abs	15.4	12.1	−36.4	21.1	22.8
TS2′abs	16.8	13.6	−30.6	20.8	22.5
TS4A	20.5	18.6	−33.9	26.8	28.0
TS4B	20.5	18.5	−34.9	27.1	28.4
TS4C	20.6	18.7	−35.2	27.3	29.0

[a] The standard state 1 M at 298.15 K was employed. ΔG_{sol} represents the increment in Gibbs free energy in dichloromethane ($\epsilon = 8.93$).

Table 4. ΔU, ΔH, ΔG (kcal/mol), and ΔS (cal/K·mol) Values (Relative to Reactants), as Computed at the B3LYP/6-311++G(d,p) Level, for Some Selected Addition Pathways of the Methanesulfonyl Radical on Propene or 2-Methylpropene[a]

		structure	ΔU	ΔH	ΔS	ΔG	ΔG_{sol}
propene	O-addition	**TS5Aadd**	16.7	16.8	−34.7	25.2	25.3
		P5Aadd	3.3	4.3	−34.3	12.6	14.7
		TS5_6Arot	4.0	4.5	−39.2	14.3	16.1
		P6Aadd	3.1	4.3	−33.6	12.4	14.3
	S-addition	**TS7Aadd**	6.5	7.0	−38.0	16.4	16.6
		P7Aadd	2.8	4.2	−39.3	14.0	13.5
2-methylpropene	O-addition	**TS5Badd**	13.7	13.8	−35.6	22.5	23.5
		P5Badd	2.3	3.6	−34.4	12.0	14.8
		TS5_6Brot	2.7	3.4	−37.6	12.7	15.5
		P6Badd	2.0	3.4	−32.2	11.1	13.6
	S-addition	**TS7Badd**	5.5	6.1	−35.9	14.9	15.1
		P7Badd	2.6	4.2	−36.8	13.2	12.7

[a] The standard state 1 M at 298.15 K was assumed. ΔG_{sol} represents the increment in Gibbs free energy in dichloromethane ($\epsilon = 8.93$).

alkene. We explored the B3LYP/6-311++G(d,p) PESs corresponding to the addition reactions of $CH_3SO_2^{\bullet}$ to propene and 2-methylpropene, respectively. Table 4 collects the results for the addition pathways (Figures S2 and S3 in the Supporting Information show the geometries for the transition structures and products present in these routes).

Additions of the methanesulfonyl radical (see Figures S2 and S3 in the Supporting Information where drawings for structures **TS5**−**TS7**, **P5**−**P7** are presented) can be carried out either through an oxygen atom (**TS5A$_{add}$**, **TS5B$_{add}$**) or through the sulfur atom (**TS7A$_{add}$**, **TS7B$_{add}$**) giving rise to the final products: **P5A$_{add}$**, **P5B$_{add}$** and **P7A$_{add}$**, **P7B$_{add}$**, respectively. Appropriate rotations (**TS5_6A$_{rot}$**, **TS5_6B$_{rot}$**) lead to slightly more stable addition products (**P6A$_{add}$**, **P6B$_{add}$**) in the case of the O-addition. From data in Table 4 we learn that the most stable addition products are obtained when the reaction proceeds through the sulfur atom (**P7A$_{add}$ P7B$_{add}$**). From the kinetic viewpoint, the energy barriers are substantially lower in the case of the addition through the sulfur atom (**TS7A$_{add}$**,**TS7B$_{add}$**). In any case, we can conclude that the sulfonyl radical addition to an alkene is a fast process at room temperature ($\Delta G^{\ddagger} = 16.6$ and 15.1 kcal/mol for the reactions of propene and 2-methylpropene, respectively).

Although this theoretical prediction would support the plausibility of the E + G + B mechanism, the analysis carried out above on the allyl/2-methallyl radical + propene/2-methylpropene reactions (mechanism B in Scheme 4) allows us to safely discard such an alternative.

However, the addition−elimination mechanism E in Scheme 5 could be, according to the data in Table 4, a much more favorable pathway when compared with the abstraction channel which involves much higher energy barriers [about 23 kcal/mol at the B3LYP/6-311++G(d,p) level; see Table 3].

To further assess the viability of mechanism E, we focused on the elimination part leading to the isomerized alkene as shown in Scheme 5. We carried out an exhaustive exploration on the B3LYP/6-311++G(d,p) PESs, and no saddle point for a reaction eliminating CH_3SO_2H from $CH_3SO_2CH_2C^{\bullet}(CH_3)_2$, the product of addition of $CH_3SO_2^{\bullet}$ to 2-methylpropene, could be located. The lack of an elimination pathway has also been reported recently for the abstraction of an allylic hydrogen in the chlorine atom reactions with alkenes.[54] For these processes, Ragains and Fynlayson-Pitts[55] speculated about the possibility that the formation of HCl was not a direct bimolecular abstraction reaction but a rather involved addition of the chlorine atom followed by elimination of HCl. However, ab initio calculations failed to locate any transition structure for the elimination channel.[54]

Therefore, the lack of an elimination pathway for CH_3SO_2H from the addition product allows us to rule out the alternative mechanism E in Scheme 5.

Finally, we also checked the viability of the two-step mechanism F which implies the formation of an intermediate between a radical cation of the type **13** and **14** and the sulfinate anion (see Scheme 5). An exhaustive analysis showed that the only existing intermediates on the PESs are those arising from the weak interaction between the methallyl radical and sulfinic acid (**wbc$_{post}$**) or, in the case of the reaction of 2-methylpropene, a weakly bound complex formed by the interaction between the alkene and $CH_3SO_2^{\bullet}$ (**wbc$_{pre}$**). However, as pointed out previously the formation of these weakly bound complexes are endergonic processes. Furthermore, no charge separation (electron transfer) is observed. Therefore, no moieties of the type **13** or **14** are present on the PESs, and consequently, mechanism F can be discarded.

It has been pointed out recently[56] that the PCM model could produce relatively important errors when applied to anions and cations. On the other hand, it is also well-known[57,58] the important role played sometimes by the explicit consideration of solvent molecules on the reaction coordinate.

To show that our conclusions above on the unsuitability of mechanism F are not biased by a poor treatment of solvent effects, we performed additional calculations where the explicit influence of solvent molecules on the stabilization of species **13** and **14** and their associated transition structures was taken into account. Furthermore, we have chosen a highly polar solvent (water) to enhance the potential effects of the very first solvation shell.[58] PCM-UFF and PCM-UAKS models[56] were employed to estimate solvation effects on the explicitly solvated

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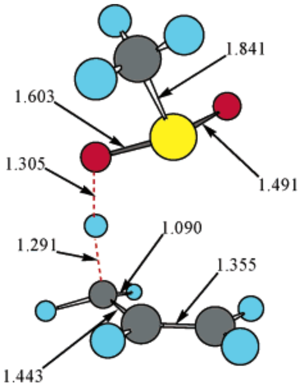

TS1'$_{abs}$

Figure 5. Structure for another abstraction pathway (**TS1′$_{abs}$**) for the reaction between propene and the methanesulfonyl radical.

systems (2-methylpropene ··· H_2O, $CH_3SO_2^•$ ··· H_2O, 2-methylpropene$^{•+}$ ··· H_2O, $CH_3SO_2^-$ ··· H_2O; see Figure S4 in the Supporting Information). From the thermodynamic viewpoint, it is clear that formation of radical cations and sulfinate anions is disfavored by more than 40 kcal/mol with respect to the neutral alkene and sulfonyl radical species, according to B3LYP/6-3111++G(d,p) calculations (both geometries as well as energetic data are provided as Supporting Information; see Figure S4 and Table S8). From the kinetic viewpoint, an ionic mechanism should be accompanied by a transition structure in which the explicit presence of solvent molecules is expected to favor charge separation. However, the transition structures located on the B3LYP/6−3111++G(d,p) PES (see Figure S5 in Supporting Information section), including one and two solvent molecules, showed only a slight increase in charge separation (less than 0.01 e) between the alkene and sulfinyl radical, as compared with **TS1$_{abs}$** (see Figure S5).

It is interesting to stress at this point that a possible pathway avoiding the stabilization problems of the charged species involved in the two-step process F (see Scheme 5) mentioned above is the so-called proton-coupled electron-transfer (PCET) mechanism.[17] We were able to locate a new transition structure on the PES (see **TS1′$_{abs}$** in Figure 5), similar to those reported by Olivella and co-workers[17b] representing a pathway where the proton transfer is coupled to an electron transfer. Examination of the spin populations shows that the corresponding values for the carbon and oxygen atoms involved in the hydrogen atom transfer (0.26 and 0.29, respectively) are quite similar to those found in **TS1$_{abs}$** (0.30 and 0.25, respectively). Consequently, the argument that the triplet repulsion between the unpaired electrons at these atoms becomes negligible, thus facilitating the PCET mechanism,[17e] does not apply in the present case. Furthermore, an electron localization function (ELF) analysis[59] confirmed that a greater steric hindrance in **TS1′$_{abs}$** clearly disfavors this transition structure (see Figure S6 in Supporting Information) which, according to B3LYP/6-311++G(d,p) calculations, resulted in higher energy than **TS1$_{abs}$** by 3.1 kcal/mol. As a conclusion, no PCET mechanism operates in the diphenyldisulfone-catalyzed isomerization of alkenes.

Another possible mechanism involves sulfinyl radical addition to the alkene, followed by heterolytic fragmentation giving rise to a radical cation and sulfinate anion: A combination of E + F mechanisms (see Scheme 5). Radical-induced polar substitution and elimination reactions in polar media such as water have long been known.[60] Giese and co-workers[61] have pointed out that the analysis of solvent effects in β-phosphate radical chemistry plainly shows that a heterolytic β-C,O bond cleavage mechanism, with formation of charged species (phosphate anion and radical cation), operates. The low polarity of the solvent employed in our study (CD_2Cl_2) strongly suggests that such a mechanism involving formation of ionic intermediates should be highly unlikely. Furthermore, the kinetic and thermodynamic arguments given above when discussing the explicit consideration of solvent molecules allow us to safely discard such a mechanism.

C. Kinetic Isotope Effects. Table 1 collects the kinetic isotope effects for the 2-methylpropene + $CH_3SO_2^•$ reaction at different degrees of deuteration as computed with QUIVER[28] at the B3LYP/6-311++G(d,p) level. Tunneling effects were estimated by using the zero- and small-curvature tunneling models.[62] We employed different intervals along the reaction coordinate and various step sizes until converged values for the transmission coefficients were obtained. Values reported in Table 1 were computed using the interval from $s = -1.65$ to $s = +1.65$ bohr on the reaction path, with a step size of 0.025 bohr. A temperature of 353.15 K, the one at which the rate constants were obtained experimentally for the isomerization of methylidenecyclopentane into 1-methylcyclopentene, was assumed.

The theoretical values reproduce qualitatively well the experimental observation that deuteration of the allylic positions retards the isomerization much more than deuteration at the terminal center sp^2(C) of the alkene. The k_H/k_{6D} and k_H/k_{4D} theoretical values for the 2-methylpropene model reaction (4.21−4.57 and 4.08−4.43, respectively) are slightly larger than the k_H/k_{4D} experimental measurements (3.67 and 2.97) for the **5** + $PhSO_2^•$ reaction, but the k_H/k_{2D} theoretical prediction (1.02−1.03) is in excellent agreement with its corresponding experimental value (1.12). This good agreement constitutes additional theoretical support to the fact that the diphenyldisulfone-catalyzed isomerizations of alkenes studied in this work proceed through the mechanism A + C in Scheme 4.

Conclusions

The PESs for the model reactions between propene and 2-methylpropene with methanesulfonyl radicals were explored at the B3LYP/6-311++G(d,p) level. The energy predictions were further improved by carrying out CCSD(T)/6-311++G-(d,p)// B3LYP/6-311++G(d,p) single-point calculations.

Calculations show that the isomerizations of the 2-alkylalk-1-enes are kinetically favored over those of 1-alkylethylenes. The difference in ionization energies between propene and 2-methylpropene seems to be the main factor responsible for that preference, according to Shaik's SCD model for reactions

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in which a radical abstracts a hydrogen atom from a molecule. The theoretically predicted kinetic deuterium isotope effects for the model reactions were in good agreement with the experimental measurements, thus supporting a mechanism in which the hydrogen is transferred via the sulfinic acid, $RSO_2H(D)$, generated by the reaction of the alkene with either diradicals arising from polysulfone or sulfonyl radicals from diphenyldisulfone.

An alternative mechanism based on the hydrogen exchange between alkenes involves energy barriers 5−6 kcal/mol higher and can be ruled out. Furthermore, the lack of an elimination pathway for a sulfinic acid (RSO_2H) from the product of the alkene + $RSO_2^{\bullet}$ addition reaction represents theoretical evidence for discarding other potentially plausible mechanisms for the polysulfone- and diphenyldisulfone-catalyzed isomerization reactions of alkenes. On the other hand, another potentially suitable two-step mechanism based on electron transfer to generate radical cations, followed by proton transfer to the sulfinate anion, can be discarded as the only intermediates located on the potential energy surface correspond to weakly bound complexes formed through slightly exothermic but endergonic processes with no separation of charge between the alkene and sulfonyl radical.

The predictions based on the quantum calculations for model reactions with the methanesulfonyl radical, propene, and 2-methylpropene are in perfect agreement with experimental studies on the diphenyldisulfone-catalyzed isomerization of methylidenecyclopentane into 1-methylcyclopentene and deuterated analogues.

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Supporting Information Available: Procedures for the preparation of **11**, **12**, **13** for the reduction of **13** into 2-methylpropene, for the reduction of 4-bromoheptane into heptane, for the formation of hexa-1,5-diene and 2,5-dimethylhexa-1,5-diene by heating sulfones **16** and **17**, respectively, for the deuterium incorporation in 1-methylcyclopentane (**7-*d*$_1$**), for the preparation of **8**, **19**, **20**. Examples of kinetic measurements and description of the spectrometers used. Cartesian coordinates and absolute energy values for all the structures located on the ab initio potential energy surfaces. Geometric and energetic data for additional pathways, not included in the main body of the article, located on the potential energy surfaces of the reactions theoretically studied. Complete ref 27. This material is available free of charge via the Internet at http://pubs.acs.org.

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