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Ab Initio and Experimental Studies on the Hetero-Diels−Alder and Cheletropic Additions of Sulfur Dioxide to (*E*)-1-Methoxybutadiene: A Mechanism Involving Three Molecules of SO_2

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Kinetics on the cheletropic addition of sulfur dioxide to (*E*)-1-methoxybutadiene (**1**) to give the corresponding sulfolene **2** (2-methoxy-2,5-dihydrothiophene-1,1-dioxide) gave the rate law $d[\mathbf{2}]/dt = k[\mathbf{1}][SO_2]^x$ with $x = 2.6 \pm 0.2$ at 198 K. Under these conditions, no sultine **3** [(2*RS*,6*RS*)-6-methoxy-3,6-dihydro-1,2-oxathiin-2-oxide] resulting from a hetero-Diels−Alder addition was observed, and the cheletropic elimination $\mathbf{2} \rightarrow \mathbf{1} + SO_2$ did not occur. Ab initio and DFT *quantum* calculations confirmed that the cheletropic addition $\mathbf{1} + SO_2 \rightarrow \mathbf{2}$ follows two parallel mechanisms, one involving two molecules of SO_2 and the transition structure with $\Delta G^‡ = 18.2 \pm 0.2$ kcal/mol at 198 K (exptl); 22.5−22.7 kcal/mol [B3LYP/6-31G(d,p)], the other one involving three molecules of SO_2 with $\Delta G^‡ = 18.9 \pm 0.1$ kcal/mol at 198 K (exptl); 19.7 kcal/mol [B3LYP/6-31G(d,p)]. The mechanism involving only one molecule of SO_2 in the transition structure requires a higher activation energy, $\Delta G^‡ = 25.2$ kcal/mol [B3LYP/6-31G(d,p)]. Comparison of the geometries and energetics of the structures involved into the $\mathbf{1} + SO_2 \rightarrow \mathbf{2}, \mathbf{3}$ and $\mathbf{1} + 2SO_2 \rightarrow \mathbf{2}, \mathbf{3} + SO_2$ reactions obtained by ab initio and DFT methods suggest that the latter calculation techniques can be used to study the cycloadditions of sulfur dioxide. The calculations predict that the hetero-Diels−Alder addition $\mathbf{1} + SO_2 \rightarrow \mathbf{3}$ also prefers a mechanism in which three molecules of SO_2 are involved in the cycloaddition transition structure. At 198 K and in SO_2 solutions, the entropy cost ($T\Delta S^‡$) is overcompensated by the specific solvation by SO_2 in the transition structures of both the cheletropic and hetero-Diels−Alder reactions of (*E*)-1-methoxybutadiene with SO_2.

Introduction

Conjugated dienes have been known since 1914[1] to undergo cheletropic additions[2] with sulfur dioxide, generating the corresponding 2,5-dihydrothiophene-1,1-dioxide (sulfolenes). Homoconjugated dienes can be rearranged into conjugated 1,3-dienes in the presence of SO_2 via ene reactions[3] or undergo homocheletropic additions.[4−7] At low temperature and in the presence of a protic or Lewis acid catalyst, simple 1,3-dienes add reversibly to SO_2 via suprafacial hetero-Diels−Alder addition to generate 3,6-dihydro-1,2-oxathiin-2-oxides (sultines).[8] They are usually unstable above −50 °C and undergo fast cycloreversion liberating the starting dienes and SO_2 that can undergo the expected cheletropic addition at higher temperature. These observations led us to invent a new carbon−carbon bond-forming reaction in which electron-rich dienes are condensed with electron-rich alkenes and SO_2 giving sulfinic derivatives that can undergo stereoselective retro-ene elimination of SO_2 providing polypropionate fragments containing up to three new stereogenic centers and a (*E*)-alkenic unit, on one hand,[9] or that can react with electrophiles giving the corresponding sulfones, on the other hand.[10,11] An asymmetric version of this one-pot four-component synthesis of sulfones has been presented recently.[12] In these applications of SO_2 chemistry, substituted 1-alkyloxybutadienes generate sultine intermediates, these later being able to explain the stereoselectivity observed in the products,[11] even though 1-alkyloxybutadienes such as **1** does not form stable sultines to be observed in solution (see Scheme 1).[13]

The mechanism of the Diels−Alder reactions between dienes and SO_2 has been analyzed theoretically by means of ab initio calculations. Aspects such as the regioselectivity and stereoselectivity,[14] the role played by Lewis acid catalysts,[15] solvent effects,[16] or the substituent

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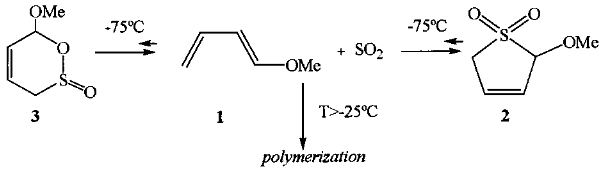
Scheme 1



effects[17] have been extensively discussed in terms of the molecular orbital theory, showing how the theoretical models helped to rationalize the experimental facts. Particularly interesting was the interpretation of the exo/endo stereoselectivity in terms of CH···O hydrogen bonding.[14,18] On the other hand, the theoretical analysis of the corresponding cheletropic cycloaddition reactions[19−21] has allowed us to interpret the kinetic and thermodynamic factors controlling the two competitive processes (Diels−Alder and cheletropic additions).

As reported in a previous work,[22] sulfur dioxide promotes its hetero-Diels−Alder and cheletropic additions to 1,2-dimethylidenecyclohexane. High-level ab initio calculations [G2(MP2,SVP)] on the model reaction butadiene + SO_2 have shown that a second molecule of SO_2 stabilizes the transition structures in such a way that the reduction of the energy barrier overwhelms the loss of entropy due to condensation. Two different mechanisms are possible: (a) formation of the $(SO_2)_2$ dimer and further reaction with the diene, or (b) formation of a diene•SO_2 van der Waals prereactive complex with further evolution to the product (sultine or sulfolene) passing through a transition structure stabilized by the second molecule of SO_2. The $(SO_2)_2$ and diene•SO_2 species involved in these mechanisms are known to exist in the gas phase, with stabilization energies of ca. 3 kcal/mol[23] and 3.2 kcal/mol (butadiene•SO_2),[24] respectively.

(*E*)-1-Methoxybutadiene possesses, in principle, two favorable sites for the SO_2 molecule to interact forming van der Waals complexes, namely, the diene π-electron cloud and the MeO group. Therefore, it is reasonable to speculate that the transition structure for the (*E*)-1-methoxybutadiene + SO_2 reactions could involve more SO_2 molecules than that of butadiene + SO_2 as butadiene has only one site (the diene π-electron cloud) to form diene•SO_2 van der Waals complexes. In other words, it is expected that the primary solvation shell (i.e., the number of solvent molecules that surrender their own translational freedom and remain with the solute when it moves relative to the surrounding solvent)[25] of the (*E*)-1-methoxybutadiene + SO_2 transition structure contains a greater number of SO_2 molecules than in the case of the butadiene + SO_2 reaction.

In this paper, we explore the possibility that the (*E*)-1-methoxybutadiene + SO_2 cycloadditions proceed through mechanisms involving more than two molecules of SO_2. Theoretical (post Hartree−Fock and Kohn−Sham) calculations and experimental work have been coordinated in order to accumulate evidence to validate such an hypothesis.

Theoretical Methods

Ab initio calculations have been carried out to evaluate the thermodynamic and activation parameters of the Diels−Alder and cheletropic addition of (*E*)-1-methoxybutadiene to sulfur dioxide. Moller−Plesset (MP2)[26] perturbation method and density functional theory (DFT)[27] with Becke's three-parameter exchange functional[28] and the correlation functional of Lee−Yang−Parr[29] (B3LYP) were employed to explore the corresponding potential energy surfaces (PESs). Pople and co-worker's standard 6-31G(d,p) basis sets were used in both MP2 and DFT-(B3LYP) calculations.

The MP2/6-31G(d,p) methodology has been extensively employed as a standard level to study chemical reactivity.[30] Particularly, it has proved to produce reliable predictions when studying pericyclic reactions proceeding through a one-step mechanism.[31] On the other hand, the DFT method is a very efficient computational tool when the size of the chemical systems under consideration becomes a critical factor.[32] In this context, Houk and coworkers have shown that the DFT method makes correct predictions for the activation energies and isotope effects of Diels−Alder additions following either concerted or stepwise mechanisms.[33]

In the present work, we will perform optimizations of cycloaddition transition structures involving up to 142 electrons and 277 basis functions which in order to keep the computational cost within practical limits we used the DFT method. In addition to these mechanistic studies, our purpose was also to compare the performance of the MP2 and DFT methodologies, thus complementing in some aspects previous studies.[32−34] On one hand, we were interested in analyzing how the geometrical and energetic data vary between the MP2 and DFT(B3LYP) calculations for transition structures of cycloadditions involving one molecule of diene and one molecule of SO_2 (1:1 complexes). On the other hand, we explored other transition structures with stoichiometries diene•$(SO_2)_2$ and diene•$(SO_2)_3$, involving π-electron cloud···SO_2, MeO···SO_2, and SO_2···SO_2 noncovalent interactions. It is well-known[35−37] that the present DFT functionals such

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as B3LYP do not represent properly the London dispersion (attractive) component of the interaction energy. Consequently, the DFT methodology was not expected to be appropriate to carry out studies on systems where the dispersion forces are expected to play a relevant role. The superiority of MP2 over DFT for studying nonbonded interactions has been stressed in a recent feature article by Rappé and Bernstein.[37] Nevertheless, we will show that in cases such as the Diels−Alder and cheletropic addition of SO_2 to (*E*)-1-methoxybutadiene the nature of the interactions involved in the structures considered is such that DFT provides predictions that are consistent with those given by the ab initio MP2 approach. This was encouraging and permitted the rationalization of our experimental observations. We are dealing with weakly bound molecules in which the "binding" is mainly derived from the electrostatic interactions between molecules.[38]

The basis set superposition error (BSSE) is expected to make non-negligible contributions to the stabilization energies of the weakly bound complexes analyzed in the present work. However, its consideration, by means of the counterpoise procedure (CP), [39] rarely varies the relative stabilities in a family of related complexes.[40−42] Thus, bearing in mind that the application of the CP algorithm is not straightforward in the cases of trimers or larger clusters,[43] we estimated the BSSE only for the prereactive (dimer) van der Waals complexes.

The location of the minima and transition structures on the PESs was performed by means of standard algorithms as implemented in the GAUSSIAN 98 package of programs.[44] All the stationary points located were characterized by computing the Hessian matrix and by checking the number of negative eigenvalues (zero for the minima and one for the transition structures). This allowed us to perform the thermochemistry analysis using the ideal gas, rigid-rotor, and harmonic oscillator approximations.[45] To take into account the effects of the condensed phase[46] we have also computed the Gibbs free energies changing the ideal gas standard state ($p = 1$ atm, 0.041 M) to a new state defined in accordance with the condensed phase experimental contitions ($p = 261$ atm, 16.1 M).

Results and Discussion

Experimental Results. The cheletropic addition **1** + $SO_2 \rightarrow$ **2** has been studied by ^{1}H NMR at 198 K, the temperature at which the reverse reaction (cheletropic elimination) is not observed. Pseudo-first-order rate constants were determined for various excesses of SO_2 by following both the formation of sulfolene **2** and the disappearance of diene **1**. The rate follows the law d[**2**]/d$t = k_{obs}$[**1**] with k_{obs}: $(0.26 \pm 0.12) \times 10^{-6}$, $(1.23 \pm 0.66) \times 10^{-6}$, $(1.17 \pm 0.14) \times 10^{-6}$, $(3.52 \pm 0.06) \times 10^{-6}$, $(4.40 \pm 0.07) \times 10^{-6}$, $(8.4 \pm 0.4) \times 10^{-6}$, $(11.9 \pm 0.07) \times 10^{-6}$, $(11.6 \pm 1.3) \times 10^{-6}$, $(13.0 \pm 0.06) \times 10^{-6}$, $(18.7 \pm 0.2) \times 10^{-6}$ dm^3 mol^{-1} s^{-1} for $[SO_2] = 2.21$, 3.88, 4.30, 7.42, 7.86, 10.15, 10.87, 11.13, 11.66, and 13.39 molar (error < 2%), respectively. These data allow one to measure the partial order for SO_2, by fitting the experimental data with $k_{obs} = k[SO_2]^x$, yielding a partial order of $x = 2.6 \pm 0.2$ with $k = (1.9 \pm 0.6) \times 10^{-8}$. Such a partial order can be seen as a combination of different pathways involving either two or three more molecules of SO_2 in the transition structure than in the reactant. Fitting $k_{obs} = k_2[SO_2]^2 + k_3[SO_2]^3$ to the experimental data gives $k_2 = (3.0 \pm 1.2) \times 10^{-8}$ dm^6 mol^{-2} s^{-1} and $k_3 = (5.6 \pm 1.0) \times 10^{-9}$ dm^9 mol^{-3} s^{-1}. These rate constants can be converted into Gibbs activation energies $\Delta G^{\ddagger}{}_2 = 18.2 \pm 0.2$ and $\Delta G^{\ddagger}{}_3 = 18.9 \pm 0.1$ kcal/mol at 198 K, respectively.

Six different mechanisms for the cheletropic addition of SO_2 to (*E*)-1-methoxybutadiene involving either two or three molecules of SO_2 can be envisaged (see Scheme 2 where $K_{\alpha i} = k_{\alpha i}/k_{-\alpha i}$ and ‡ denotes the rate determining step). Mechanisms A and B correspond to processes involving two molecules of SO_2 and are similar to those previously proposed for the hetero-Diels−Alder and cheletropic reactions of SO_2 with 1,2-dimethylidenecyclohexane.[22] The first one (A) implies the formation of a prereactive van der Waals complex between the diene and one molecule of SO_2, **1**•SO_2, whereas in the second one (B), (*E*)-1-methoxybutadiene adds to $(SO_2)_2$ present in liquid SO_2.[47] The remaining four mechanisms (C−F) involve three molecules of SO_2. In mechanisms C and D, it is considered that sulfur dioxide can exists as monomer (SO_2) or dimer [$(SO_2)_2$] units in solution.[47] In a second step, the diene forms a prereactive van der Waals complex either with SO_2 (C) or with $(SO_2)_2$ (D) and finally the sulfolene **2** is formed by liberating two molecules of SO_2 (since the experimental condictions are chosen in such a way that k_{-c3} and k_{-d3} in Scheme 2 are negligible, it does not matter whether $2SO_2$ or $(SO_2)_2$ are released). Mechanisms E and F contemplate the consecutive formation of two prereactive van der Waals complexes, **1**•SO_2 and **1**•$2SO_2$, the latter leading to the final product **2** with liberation of two molecules of SO_2 [$2SO_2$ or $(SO_2)_2$; Scheme 2 assumes $2SO_2$].

According to our calculations (see below), the **1**•SO_2 prereactive complex is more stable than $(SO_2)_2$ [the MP2/6-31G(d,p) stabilization energies are 5.6 and 3.1 kcal/mol, respectively]. This result agrees with the experimental observation that electron rich dienes such as **1** form a yellow colored complex on disolving in SO_2/CH_2Cl_2 solutions. This coloration disappears at the end of the cheletropic addition. IR absorption spectra did not provide conclusive evidence for the formation of **1**•SO_2 complexes as the main SO_2 absorption (1336 and 1145

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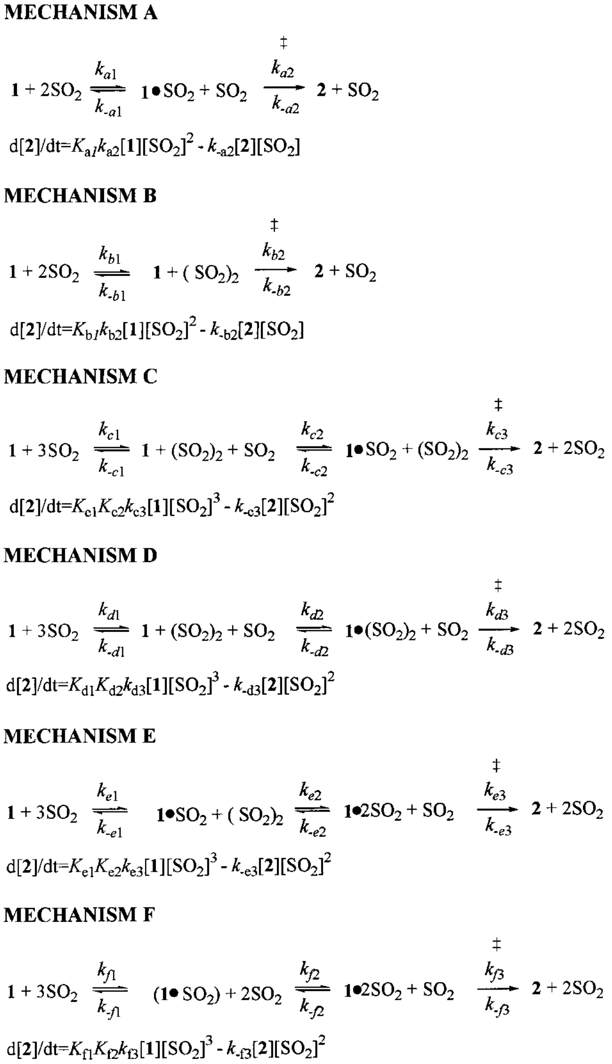
Scheme 2



MECHANISM A

$$\mathbf{1} + 2SO_2 \underset{k_{-a1}}{\overset{k_{a1}}{\rightleftharpoons}} \mathbf{1}{\bullet}SO_2 + SO_2 \underset{k_{-a2}}{\overset{\overset{\ddagger}{k_{a2}}}{\longrightarrow}} \mathbf{2} + SO_2$$

$$d[\mathbf{2}]/dt = K_{a1}k_{a2}[\mathbf{1}][SO_2]^2 - k_{-a2}[\mathbf{2}][SO_2]$$

MECHANISM B

$$\mathbf{1} + 2SO_2 \underset{k_{-b1}}{\overset{k_{b1}}{\rightleftharpoons}} \mathbf{1} + (SO_2)_2 \underset{k_{-b2}}{\overset{\overset{\ddagger}{k_{b2}}}{\longrightarrow}} \mathbf{2} + SO_2$$

$$d[\mathbf{2}]/dt = K_{b1}k_{b2}[\mathbf{1}][SO_2]^2 - k_{-b2}[\mathbf{2}][SO_2]$$

MECHANISM C

$$\mathbf{1} + 3SO_2 \underset{k_{-c1}}{\overset{k_{c1}}{\rightleftharpoons}} \mathbf{1} + (SO_2)_2 + SO_2 \underset{k_{-c2}}{\overset{k_{c2}}{\rightleftharpoons}} \mathbf{1}{\bullet}SO_2 + (SO_2)_2 \underset{k_{-c3}}{\overset{\overset{\ddagger}{k_{c3}}}{\longrightarrow}} \mathbf{2} + 2SO_2$$

$$d[\mathbf{2}]/dt = K_{c1}K_{c2}k_{c3}[\mathbf{1}][SO_2]^3 - k_{-c3}[\mathbf{2}][SO_2]^2$$

MECHANISM D

$$\mathbf{1} + 3SO_2 \underset{k_{-d1}}{\overset{k_{d1}}{\rightleftharpoons}} \mathbf{1} + (SO_2)_2 + SO_2 \underset{k_{-d2}}{\overset{k_{d2}}{\rightleftharpoons}} \mathbf{1}{\bullet}(SO_2)_2 + SO_2 \underset{k_{-d3}}{\overset{\overset{\ddagger}{k_{d3}}}{\longrightarrow}} \mathbf{2} + 2SO_2$$

$$d[\mathbf{2}]/dt = K_{d1}K_{d2}k_{d3}[\mathbf{1}][SO_2]^3 - k_{-d3}[\mathbf{2}][SO_2]^2$$

MECHANISM E

$$\mathbf{1} + 3SO_2 \underset{k_{-e1}}{\overset{k_{e1}}{\rightleftharpoons}} \mathbf{1}{\bullet}SO_2 + (SO_2)_2 \underset{k_{-e2}}{\overset{k_{e2}}{\rightleftharpoons}} \mathbf{1}{\bullet}2SO_2 + SO_2 \underset{k_{-e3}}{\overset{\overset{\ddagger}{k_{e3}}}{\longrightarrow}} \mathbf{2} + 2SO_2$$

$$d[\mathbf{2}]/dt = K_{e1}K_{e2}k_{e3}[\mathbf{1}][SO_2]^3 - k_{-e3}[\mathbf{2}][SO_2]^2$$

MECHANISM F

$$\mathbf{1} + 3SO_2 \underset{k_{-f1}}{\overset{k_{f1}}{\rightleftharpoons}} (\mathbf{1}{\bullet}SO_2) + 2SO_2 \underset{k_{-f2}}{\overset{k_{f2}}{\rightleftharpoons}} \mathbf{1}{\bullet}2SO_2 + SO_2 \underset{k_{-f3}}{\overset{\overset{\ddagger}{k_{f3}}}{\longrightarrow}} \mathbf{2} + 2SO_2$$

$$d[\mathbf{2}]/dt = K_{f1}K_{f2}k_{f3}[\mathbf{1}][SO_2]^3 - k_{-f3}[\mathbf{2}][SO_2]^2$$

cm^{-1}) coincides with that of the diene. Alternatively, the relative concentration of complexes **1**•SO_2 in equilibrium with **1** + SO_2 might be too low to be detected by IR spectroscopy (see below). UV/vis measurements were not found useful as our experimental device did not allow us to cool the system at temperatures lower than −25 °C (above this temperature, sulfur dioxide initiates diene polymerization,[48,49] see Scheme 1). Ab initio calculations have been applied to determine the structures of these complexes.

All the rate laws given in Scheme 2 are consistent with the pseudo-first-order rate law $d[\mathbf{2}]/dt = k_{obs}[\mathbf{1}]$ with $k_{obs} = K_{\alpha1}k_{\alpha2}[SO_2]^2$ (α = a, b; mechanisms A and B) and $k_{obs} = K_{\alpha1}K_{\alpha2}k_{\alpha3}[SO_2]^3$ (α = c, f; mechanisms C−F), derived experimentally under conditions where the cheletropic elimination is not observed [$k_{-\alpha2}$ (α = a,b) = $k_{-\alpha3}$ (α = c−f) = 0].

Calculations and Discussion

Prereactive van der Waals Complexes. Sulfur dioxide has been known for some time to form van der Waals complexes in the gas phase and solution with small unsaturated hydrocarbons.[50,51] Several of these complexes have been studied in the past decade by means of microwave spectroscopy by Kuczkowski and co-workers.[52] Their work has provided general patterns and trends for these systems. For example, all of them showed a stacked near parallel plane configuration in which the sulfur end of SO_2 is usually closer to the π-electron cloud and the distances between the centers of mass of the two moieties are about 3.5 Å. SO_2 complexes with nitrogen or oxygen Lewis base donors (for example, methanol•SO_2)[53] have been studied as well. They show the same structural pattern described above but are characterized by shorter distances (below 3 Å).

Some recent theoretical work on SO_2 containing van der Waals complexes from our laboratory[40−42] has shown that high-level ab initio studies nicely complements the spectroscopic results, providing structural and energetic information in good agreement with the experimental data. To the best of our knowledge, no spectroscopic studies on the of 1:1 van der Waals complexes between (*E*)-1-methoxybutadiene and SO_2 have been reported yet. Our theoretical results (geometrical parameters, rotational constants and dipole moments for all the structures located in the present work are available upon request) may be useful to plan future experimental work on these systems (e.g., rotational spectra).[54]

Figure S1 (Supporting Information) shows the 10 1:1 van der Waals structures located on the PES for the reaction of diene **1** and SO_2. Table 1 collects the corresponding interaction energies. Five of them involve the s-trans conformer of (*E*)-1-methoxybutadiene (**T1**−**T5**) and the other five the s-cis conformers (**C1**−**C5**). Three favorable regions in the diene are expected to give rise to molecular associations with a Lewis acid such as SO_2: (a) the lone pair at the oxygen atom in the MeO group (see **T1** and **C1**). This type of interaction is similar to that reported for the $CH_3OH{\bullet}SO_2$ van der Waals complex, an *outer* complex with methanol acting as a donor and sulfur dioxide as an acceptor,[40] (b) the π-electron cloud (see **T2**, **T3, T4** and **C2**, **C3, C4**). In particular, the relative orientation of SO_2 in structure **T2** is quite similar to that found experimentally for the butadiene•SO_2 complex.[55] In this case, the SO_2 is sitting above the center of the diene plane (approximately over the C−C single bond) with the SO_2 and hydrocarbon planes very nearly coplanar, and (c) the hydrogen atoms in the MeO group (see **T5** and **C5**), give rise to a side-long structure quite similar to that reported for the $CH_3OH{\bullet}SO_2$ system in which sulfur dioxide acts as a donor and methanol as an acceptor.[40]

Inspection of Figure S1 shows that the relative orientations adopted by the two subunits (diene and SO_2) are rather similar at the MP2 and DFT(B3LYP) levels. The discrepancies in some of the distances are a direct consequence of the flatness of the PES inherent to this

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Table 1. MP2, B3LYP and MP2//B3LYP Stabilization (D_0 and Gibbs Free (ΔG)) Energies (Related to Reactants: *s-trans*-(*E*)-1-MeO-butadiene and SO_2, in kcal/mol) Corresponding to the van der Waals Complexes Located on the Potential Energy Surface for the (*E*)-1-MeO-butadiene (*s-trans* and *s-cis*) + SO_2 Reaction[a]

	$D_0 = \Delta H$ (0 K)			ΔG (1 atm)			ΔG (261 atm)		
structure	MP2	DFT	MP2//DFT	MP2	DFT	MP2//DFT	MP2	DFT	MP2//DFT
T1	−4.9 (−1.5)	−3.6 (−1.2)	−4.8 (−1.7)	+0.8 (+4.2)	+1.9 (+4.3)	+0.6 (+3.7)	−1.4 (+2.0)	−0.3 (+2.1)	−1.6 (+1.5)
T2	−4.7 (−1.0)	−3.6 (−1.3)	−3.8 (−0.6)	+1.4 (+5.0)	+2.6 (+4.9)	+2.3 (+5.6)	−0.8 (+2.8)	+0.4 (+2.7)	+0.2 (+3.4)
T3	−4.3 (−1.3)	−3.5 (−1.0)	−4.0 (−0.3)	+1.1 (+4.1)	+2.6 (+5.1)	+2.5 (+5.7)	−1.1 (+1.9)	+0.5 (+2.9)	+0.3 (+3.6)
T4	−3.7 (−0.9)	−2.9 (−1.0)	−2.7 (−0.2)	+1.8 (+4.5)	+2.5 (+4.4)	+2.7 (+5.2)	−0.4 (+2.4)	+0.3 (+2.2)	+0.5 (+3.0)
T5	−2.2 (−0.4)	−1.1 (+0.1)	−2.1 (−0.5)	+2.8 (+4.5)	+3.4 (+4.6)	+2.5 (+4.0)	+0.6 (+2.3)	+1.2 (+2.4)	+0.4 (+1.8)
C1	−3.2 (+0.9)	−0.3 (+2.0)	−2.3 (+0.7)	+3.2 (+7.2)	+5.2 (+7.5)	+3.1 (+6.2)	+1.0 (+5.0)	+3.0 (+5.3)	+0.9 (+4.0)
C2	−2.5 (+1.5)	−0.1 (+2.5)	−0.9 (+2.9)	+3.8 (+7.8)	+5.9 (+8.5)	+5.2 (+9.0)	+1.6 (+5.6)	+3.7 (+6.4)	+3.0 (+6.8)
C3	−2.0 (+1.4)	+0.1 (+2.4)	−1.7 (+1.5)	+3.8 (+7.1)	+6.0 (+8.3)	+4.2 (+7.3)	+1.6 (+5.0)	+3.8 (+6.1)	+2.0 (+5.2)
C4	−1.6 (+1.6)	+0.9 (+3.0)	−1.2 (+1.8)	+4.5 (+7.7)	+6.6 (+8.7)	+4.6 (+7.4)	+2.3 (+5.5)	+4.4 (+6.5)	+2.4 (+5.3)
C5	+0.3 (+2.1)	+2.3 (+3.5)	+0.5 (+2.1)	+5.3 (+7.0)	+7.1 (+8.3)	+5.4 (+6.8)	+3.1 (+4.8)	+4.9 (+6.1)	+3.2 (+4.7)

[a] According to the experimental conditions (see the text) a temperature of 198 K was assumed. ΔG (261 atm) includes the correction factor for changing the standard state from 1 to 261 atm (see the text). BSSE corrected values in parentheses. All calculations were carried out with the 6-31G(d,p) basis set. See Figure S1 (Supporting Information) for notation.

type of molecular complexes. Nevertheless, the geometrical discrepancies do not exert appreciable influences on the computed interaction energies. Indeed, Table 1 shows that the MP2//DFT stabilization energies coincide in most of the cases with those obtained at the MP2 level. The DFT energies are consistently lower (absolute values; i.e., less stabilizing) than the MP2 ones. This can be interpreted in terms of the dispersion contributions that are not accounted for in the former calculation method (the fact that the lowering is greater in the case of the more "compact" cis structures supports this hypothesis). The most stable structures are the **T1**/**C1** complexes with interaction energies (D_0) of −4.9/-3.2 kcal/mol [(MP2/6-31G(d,p)] or −3.6/-0.3 kcal/mol [B3LYP/6-31G(d,p)], although the interaction of SO_2 with the π-system is strong enough to give rather similar stabilization energies for the complexes **T2**/**C2**: −4.7/-2.5 [MP2/6-31G(d,p)] and −3.6/-0.1 [B3LYP/6-31G(d,p)]. **T3**/**C3** and **T4**/**C4** structures are somewhat less stable and **T5/C5** are clearly the least stable structures. The calculated binding energies obtained for the complexes of s-trans and s-cis butadiene at the same levels of theory are −3.2 (s-trans)/-0.6 (s-cis) kcal/mol [MP2/6-31G(d,p)] and −1.9 (s-trans)/+1.3 (s-cis) kcal/mol [B3LYP/6-31G(d,p)], respectively. An experimental stabilization energy of -3.24 ± 0.48 kcal/mol was estimated for the s-trans complex in a photoionization study by Grover et al.[24] Comparison between the binding energies calculated above suggests that $\mathbf{1}{\bullet}SO_2$ complexes are, in general, more stable than butadiene$\bullet SO_2$ complexes.

Since (*E*)-1-methoxybutadiene has more "binding sites" than butadiene, mechanisms C−F (Scheme 2) that involve one additional molecule of SO_2 are theoretically plausible.

It is important to stress that the small magnitude of the above binding energies suggests that they cannot overwhelm the cost of the entropy of condensation. Indeed, the formation of the most stable prereactive complex (**T1**) in Table 1 ($\mathbf{1} + SO_2 \leftrightarrows \mathbf{1}{\bullet}SO_2$) becomes an endergonic process at 198 K when BSSE is taken into account [ΔG(198 K, 261 atm) = 1.5−2.1 kcal/mol], and consequently, the above equilibrium is expected to shift toward reactants ($\mathbf{1} + SO_2$).

Transition Structures of Diels−Alder and Cheletropic Additions with 1:1 Stoichiometry. Figures S2 and S3 (Supporting Information) represent the transition structures resulting from the Diels−Alder addition $\mathbf{1} + SO_2 \rightarrow \mathbf{(DA)_1}^{\ddagger} \rightarrow \mathbf{3}$ and the cheletropic addition $\mathbf{1} + SO_2 \rightarrow \mathbf{(Che)_1}^{\ddagger} \rightarrow \mathbf{2}$ as computed at the MP2/6-31G(d,p) and B3LYP/6-31G(d,p) levels of theory. The formation of the two new bonds, C−S and C−O in $\mathbf{(DA)_1}^{\ddagger}$ (with MP2 Pauling bond orders[56] 0.28 and 0.20, respectively), and C−S and C−S in $\mathbf{(Che)_1}^{\ddagger}$ (with MP2 Pauling bond orders[56] 0.28 and 0.21) is asynchronous. Systematically, the DFT(B3LYP) structures result more asynchronous than the corresponding MP2 ones. The discrepancies between the MP2 and B3LYPT distances for the forming bonds in the Diels−Alder cycloaddition is larger than that reported for the standard cycloaddition reactions,[32,33] in agreement with previous findings.[34] In the case of the cheletropic reaction the discrepancies become larger. The MP2 methodology predicts structures where the distance between one of the SO_2 oxygen atoms and one of the MeO hydrogen atoms in the diene is significantly shorter than that predicted by the DFT(B3LYP) method. This suggests that the MP2 calculations are more likely to favor the C−H···O hydrogen bonding interactions.

The calculated energies collected in Table 2 show that at both levels [MP2 and DFT(B3LYP)] the Diels−Alder cycloaddition is faster than the cheletropic reaction. The B3LYP barrier heights (9.2 and 18.4 kcal/mol, respectively) are 3−5 kcal/mol lower than the MP2 ones and compare rather well with the barriers predicted by the G2(MP2, SVP) method (11.5 and 16.0 kcal/mol, respectively),[21] thus suggesting a good performance of nonlocal DFT methods in estimating reaction barriers, in agreement with previous studies on different systems.[32−34] The energy lowering when passing from MP2 to B3LYP has also been observed when studying other Diels−Alder and cheletropic reactions between dienes and SO_2.[57] The three levels of theory [MP2, DFT(B3LYP) and G2(MP2, SVP)] agree predicting **3** as the kinetic product for the (*E*)-1-methoxybutadiene + SO_2 reaction (although **3** is not experimentally detected, there are experimental[11−13] and theoretical[21] evidences supporting its formation).

Transition Structures of Diels−Alder and Cheletropic Additions with 1:2 Stoichiometry. In a previous study on the butadiene + SO_2 reaction,[22] we found that a second molecule of SO_2 has a notable effect on the Diels−Alder and cheletropic mechanisms producing a considerable lowering of the energy barriers. It was shown that the stabilization of the transition structure is more important than the loss of entropy due to

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Table 2. MP2/6-31G(d,p) and B3LYP/6-31G(d,p) (in Parentheses) Electronic Energies, Enthalpies, and Gibbs Activation Energies (Related to Reactants in kcal/mol) Corresponding to the Transition Structures Located on the Potential Energy Surface for the (*E*)-1-MeO-butadiene + SO_2 Reaction (DA: Diels−Alder, Che: Cheletropic)[a]

	$\Delta U^‡$		$\Delta H^‡$		$T\Delta S^‡$ (1 atm)		$\Delta G^‡$ (1 atm)		$T\Delta S^‡$ (261 atm)		$\Delta G^‡$ (261 atm)	
$(DA)_1^‡$	12.5	(8.2)	14.0	(9.2)	−9.2	(−9.1)	23.2	(18.3)	−7.0	(−6.9)	21.0	(16.1)
$(DA)_{2a}^‡$	6.7		9.0		−15.2		24.2		−10.8		19.8	
$(DA)_{2b}^‡$	5.2	(2.0)	7.6	(4.0)	−15.2	(−15.2)	22.7	(19.2)	−10.8	(−10.8)	18.3	(14.8)
$(DA)_{2c}^‡$	1.6	(−3.4)	4.2	(−1.2)	−15.8	(−16.3)	20.1	(15.1)	−11.4	(−11.9)	15.7	(10.7)
$(DA)_3^‡$		(−9.1)		(−6.0)		(−22.2)		(16.2)		(−15.6)		(9.6)
$(Che)_1^‡$	20.2	(17.4)	21.5	(18.4)	−8.8	(−9.0)	30.3	(27.4)	−6.6	(−6.8)	28.1	(25.2)
$(Che)_{2a}^‡$	13.7	(13.8)	15.9	(15.7)	−15.0	(−14.4)	30.9	(30.1)	−10.6	(−10.0)	26.5	(25.7)
$(Che)_{2b}^‡$	12.1	(9.2)	14.5	(11.3)	−15.1	(−15.6)	29.6	(26.9)	−10.7	(−11.2)	25.2	(22.5)
$(Che)_{2c}^‡$	11.2	(9.3)	13.6	(11.5)	−15.2	(−15.6)	28.8	(27.1)	−10.8	(−11.2)	24.4	(22.7)
$(Che)_3^‡$		(1.3)		(4.4)		(−22.1)		(26.5)		(−15.3)		(19.7)

[a] According to the experimental conditions (see text), a temperature of 198 K was assumed. ΔG(261 atm) includes the correction factor for changing the standard state from 1 to 261 atm (see the text).

condensation, consistently with kinetics of pseudo-first order with a partial order 2 in SO_2 (i.e., d[product]/dt = k_{obs}[butadiene] with $k_{obs} = k[SO_2]^2$). We analyze now the kinetic effects of a second molecule of SO_2 in the **1** + $2SO_2$ → **2** + SO_2 and **1** + $2SO_2$ → **3** + SO_2 additions.

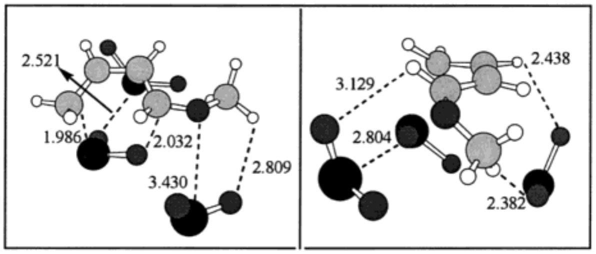
After an exhaustive search on the PES, three 1:2 transition structures were located at the MP2/6-31G(d,p) level for both Diels−Alder [see **$(DA)_{2a}^‡$**, **$(DA)_{2b}^‡$**, and **$(DA)_{2c}^‡$** in Figure S2] and cheletropic [see **$(Che)_{2a}^‡$**, **$(Che)_{2b}^‡$**, and **$(Che)_{2c}^‡$** in Figure S3] additions. In all cases, one of the SO_2 molecules exhibits a geometrical disposition rather similar to that adopted by the SO_2 molecule in the 1:1 transition structures **$(DA)_1^‡$** and **$(Che)_1^‡$** (with similar values of the C−S and C−O bond forming distances). It is the reacting molecule that becomes part of the resulting sultine (**3**) or sulfolene (**2**). In the case of the **$(DA)_{2a}^‡$** and **$(Che)_{2a}^‡$** structures, the second SO_2 molecule clearly interacts with the MeO group staying far away from the other SO_2 molecule. In the remaining four transition structures [**$(DA)_{2b}^‡$**, **$(DA)_{2c}^‡$**, **$(Che)_{2b}^‡$**, and **$(Che)_{2c}^‡$**], besides the diene•SO_2 interaction, the two SO_2 molecules interact each other (O−S−O···SO_2) adopting geometrical dispositions closely resembling those found for the butadiene + SO_2 cycloaddition reaction.[22]

Table 2 shows that **$(DA)_{2a}^‡$** and **$(DA)_{2b}^‡$** are about 5−6 kcal/mol lower in energy than **$(DA)_1^‡$** and that the **$(DA)_{2c}^‡$** transition structure is about 10 kcal/mol more stable than the corresponding 1:1 transition structure **$(DA)_1^‡$**. In the case of the cheletropic addition, the three structures **$(Che)_{2a}^‡$**, **$(Che)_{2b}^‡$**, and **$(Che)_{2c}^‡$** do not differ too much in energy, representing a stabilization of 6−8 kcal/mol with respect to the 1:1 transition structure **$(Che)_1^‡$**. The entropy contributions ($T\Delta S^‡$) predict an energy cost of about 4 kcal/mol for both cycloaddition reactions at 198 K (once the appropriate corrections for the reference state are considered).[46] As a global result, the Gibbs activation energies for the transition structures involving two molecules of SO_2, **$(DA)_{2c}^‡$** and **$(Che)_{2c}^‡$**, become about 3−5 kcal/mol smaller than the $\Delta G^‡$ values for the 1:1 transition structures. These results are consistent with the mechanisms A and B in Scheme 2.

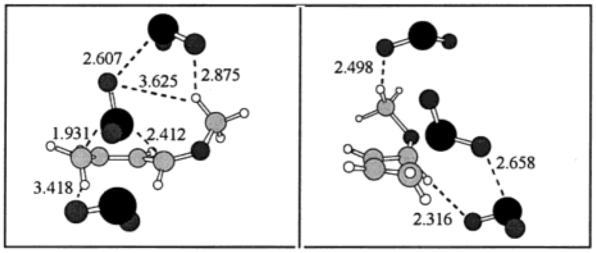
In Figures S2 and S3, the corresponding B3LYP/6-31G-(d,p) transition structures (**2a**, **2b**, and **2c**) are presented. The DFT(B3LYP) methodology failed to locate the weakest complex **$(DA)_{2a}^‡$** arising from the MP2 exploration of the PES. This result suggests that for that weakly bound structure the dispersion forces, which as mentioned above are not properly represented by today's DFT potentials,[35−37] might play a relevant role. The remaining five transition structures [**$(DA)_{2b}^‡$** and **$(DA)_{2c}^‡$** for the Diels−Alder reaction and **$(Che)_{2a}^‡$**, **$(Che)_{2b}^‡$**, and **$(Che)_{2c}^‡$** for the cheletropic addition] show geometries quite similar to those obtained at the MP2 level with the exception of **$(Che)_{2c}^‡$** for which the second molecule of SO_2 tends to adopt an orientation slightly more favorable for the interaction with the MeO group at the B3LYP level. As demonstrated in the case of the prereactive van der Waals complexes (**T1**−**T5** and **C1**−**C5**), the discrepancies between the B3LYP and MP2 distances in the transition structures **2a**−**c** must be ascribed to the flatness of the PESs for those regions corresponding to long-distance interactions and have little effect on the energetics (small variations in some dihedral angles give rise to appreciable changes in the distances between some atoms separated by long distances, producing negligible variations in the electronic energies). The B3LYP energy barriers for the 1:2 transition structures are about 2−5 kcal/mol lower than the MP2 ones in agreement with the trends found for the 1:1 transition structures (see above).

The analysis carried out in the previous subsections leads us to conclude that the DFT(B3LYP) methodology seems to be appropriate to investigate the way in which the SO_2 promotes its hetero-Diels−Alder and cheletropic additions to dienes as it makes predictions that basically agree with those from other ab initio methods shown to reproduce experimental data.[22] The small stabilizing contribution of the dispersion forces corresponding to the van der Waals interactions underestimated at the DFT-(B3LYP) level mentioned when analyzing the **T1**−**T5** and **C1**−**C5** van der Waals complexes, is more than counterbalanced by the greater stabilizing tendency observed for the DFT(B3LYP) 1:1 and 1:2 transition structures. In the next subsection we will use the B3LYP/6-31G(d,p) level to explore the PESs of reactions of **1** with three molecules of SO_2. Both the size of the system considered (142 electrons and 277 basis functions) and the extreme flatness of these PESs, implicating trimer molecular associations [**1**•$(SO_2)_2$, $(SO_2)_3$], make the MP2/6-31G(d,p) exploration impractical from the computational viewpoint.

Transition Structures of Diels−Alder and Cheletropic Additions with 1:3 Stoichiometry. Figure 1 depicts the transition structures for the Diels−Alder [**$(DA)_3^‡$**] addition **1** + $3SO_2$ → **3** + $2SO_2$ and cheletropic [**$(Che)_3^‡$**] addition **1** + $2SO_2$ → **2** + SO_2, as computed at the B3LYP/6-31G(d,p) level. One of the SO_2 molecules adopts a geometrical disposition similar to that observed in the **$(DA)_1^‡$** and **$(Che)_1^‡$** transition structures. It is the reacting molecule forming two new bonds and giving rise



$(\mathbf{DA})_3^{\neq}$



$(\mathbf{Che})_3^{\neq}$

Figure 1. MP2/6-31G(d,p) and B3LYP/6-31G(d,p) transition structures with 1:3 stoichiometries located on the potential energy surfaces for the Diels−Alder $(\mathbf{DA})_3^{\ddagger}$ and cheletropic $(\mathbf{Che})_3^{\ddagger}$ reactions between (*E*)-1-methoxybutadiene and SO_2. All distances are given in angstroms.

to the final sultine (**3**) and sulfolene (**2**), respectively. The remaining two SO_2 molecules choose geometrical arrangements that closely resemble those in the **2b** and **2c** 1:2 transition structures (those lower in energy), thus fully confirming expectations based on energy criteria.

From an energy viewpoint, Table 2 shows that $(\mathbf{DA})_3^{\ddagger}$ is 15.2 kcal/mol lower in enthalpy than $(\mathbf{DA})_1^{\ddagger}$ whereas the predicted entropy contribution ($T\Delta S^{\ddagger}$) is only 13.1 kcal/mol (taking $p = 1$ atm as the reference state) or 8.7 kcal/mol (taking as the reference state $p = 261$ atm which reproduces closer the experimental conditions)[41] It means that the change in Gibbs activation energy ($\Delta G^{\ddagger}$) is smaller for the transition structure involving three molecules of SO_2 than for the transition structures involving one or two SO_2 molecules (when the $T\Delta S^{\ddagger}$ values corresponding to the $p = 1$ atm reference state are used, the resulting $\Delta G^{\ddagger}$ value is slightly greater than the corresponding value for the $(\mathbf{DA})_{2c}^{\ddagger}$ transition structure). In the case of the cheletropic cycloaddition, the $\Delta G^{\ddagger}$ value for $(\mathbf{Che})_3^{\ddagger}$ is somewhat smaller than those for the $(\mathbf{Che})_1^{\ddagger}$ and $(\mathbf{Che})_{2a-c}^{\ddagger}$ transition structures, no matter the reference state considered (see Table 2). These results are consistent with the mechanisms C−F in Scheme 2.

The above theoretical results can be summarized as follows: the B3LYP/6-31G(d,p) $\Delta G^{\ddagger}$ values (1 atm/ 261 atm reference states) for the transition structure involving three molecules of SO_2 (26.5/19.7 kcal/mol) are smaller than those for the standard mechanism involving a single molecule (27.4/25.2 kcal/mol) and similar in magnitude to those corresponding to a mechanism implicating two SO_2 molecules (26.9/22.5 kcal/mol). Therefore, the present theoretical results suggest that the mechanisms A and B (involving two molecules of SO_2) and C−F (involving three molecules of SO_2) are equally probable and consequently a rate law with a partial order in SO_2 between 2 and 3 should be found. As mentioned in the Experimental Section, the kinetic experiments carried out lead to the rate law d[**2**]/dt = k[**1**]$[SO_2]^{2,6}$, in full agreement with our theoretical predictions. On the other hand, the B3LYP/6-31G(d,p) $\Delta G^{\ddagger}$ values computed according to the $p = 261$ atm reference state for $(\mathbf{Che})_{2b}^{\ddagger}$, $(\mathbf{Che})_{2c}^{\ddagger}$, and $(\mathbf{Che})_3^{\ddagger}$ are 22.5, 22.7, and 19.7 kcal/mol, respectively. These values are not far away from the Gibbs activation energies measured experimentally at 198 K for the pathways involving two (18.2 ± 0.2 kcal/mol) and three (18.9 ± 0.1 kcal/mol) molecules of SO_2 and can be considered a reasonable approach bearing in mind the limitations inherent in our calculations, namely: (a) the level of theory (method + basis set) employed,[21] (b) the underestimation of the stabilization energies for the nonbonded interactions as a consequence of using the DFT methodology,[35−37] and (c) the errors in estimating the thermodynamic functions as a consequence of the anharmonicity of the intermolecular vibrations associated with weakly bound interactions.[58,59]

It should be stressed that the present calculations show that the primary solvation shell of the transition structure for the reactions between (*E*)-1-methoxybutadiene and SO_2 is formed ***at least*** by three molecules (one of them being reacting with the diene and giving rise to the final sultine or sulfolene). The possibility that more than three molecules of SO_2 are involved in the transition structures of the cheletropic addition cannot be ruled out on the basis of the experimental and theoretical results reported in this work. The experimental data and calculations are consistent with (E)-1-methoxybutadiene (**1**) equilibrating partially only with complex **1•**SO_2. Going from reactants to the transition structure of the cheletropic addition immobilizes at least two further molecules of sulfur dioxide.

Conclusions

The mechanisms of the hetero-Diels−Alder and cheletropic cycloaddition reactions of (*E*)-1-methoxybutadiene and SO_2 have been investigated in a combined experimental−theoretical study. While the Diels−Alder reaction does not form stable sultines to be observed in solution, the formation of the corresponding sulfolene has been studied by ^{1}H NMR at 198 K. The cheletropic addition follows the pseudo-first-order rate law d[**2**]/dt = k_{obs}[**1**] with $k_{obs} = [SO_2]^{2.6\pm0.2}$. The partial order in SO_2 can be seen as a combination of different routes involving either two ($\Delta G^{\ddagger} = 18.2 \pm 0.2$ kcal/mol) or three ($\Delta G^{\ddagger} = 18.9 \pm 0.1$ kcal/mol) molecules of SO_2 in the corresponding transition structures.

Ab initio [MP2/6-31G(d,p)] and DFT [B3LYP/6-31G-(d,p)] calculations were carried out to explore the potential energy surfaces of these reactions, considering transition structures involving one (1:1), two (1:2) and three (1:3) molecules of SO_2 (the latter system could only be explored at the DFT level due to computational limitations). It is shown that even with some discrepancies in the geometrical parameters, mainly arising from the extreme flatness shown by the potential energy surfaces at those regions corresponding to weakly bound interactions, both methods provide similar pictures and energy values for the 1:1 and 1:2 transition structures.

The B3LYP/6-31G(d,p) calculations suggest that the Diels−Alder and cheletropic reactions proceed through

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a combination of mechanisms involving transition structures with two and three molecules of SO_2. The B3LYP/6-31G(d,p) $\Delta G^{\ddagger}$ computed values for the mechanisms involving two (22.5−22.7 kcal/mol) and three (19.7 kcal/mol) molecules of SO_2 in the cheletropic addition represent a reasonable approach to the experimentally estimated Gibbs activation energies, bearing in mind the limitations inherent in the computational level employed. The results can be physically interpreted by invoking the well-known concept of primary solvation shell. The experimental facts and the B3LYP/6-31G(d,p) calculations suggest that the solvation number of the transition structures for the reactions between (*E*)-1-methoxybutadiene and SO_2 is at least 3, although the kinetic data do not allow one to exclude the possibility of a more crowded primary solvation sheath. Our study demonstrates that specific solvation effects must be expected for organic reactions occurring in sulfur dioxide solutions.

Experimental Section

NMR Sample Preparation. Methoxybutadiene, CD_2Cl_2, and toluene were distilled, SO_2 was filtered through a column of alkaline aluminum oxide 90 (activity I, Merck) before use. In a weighed, dry 5-mm NMR Pyrex tube, dienes (0.23−0.91 mmol), toluene (internal reference, 9−13 mg), CD_2Cl_2 (0.16−0.48 g) and $CFCl_3$ (0.13−0.39 g) were mixed at 20 °C. The solution was degassed by several freeze−thaw cycles at 10^{-2} Torr. Degassed SO_2 (0.1−0.4 mL) was transferred to the above mixture on the vacuum line. The NMR tube was sealed under vacuum. The NMR tube, frozen in liquid N_2, was transferred into the Bruker ARX-400 spectrometer probe cooled to 198 ± 1 K. When the kinetic measurements were terminated, the NMR tube was allowed to reach room temperature and was weighed together with the piece of tube left over after sealing: this allowed verification of the exact amount of SO_2 introduced in the diene solution.

The kinetic measurements use 5 mm NMR tubes prepared as above. ^1H NMR (400 MHz) spectra were recorded with 90° pulses and delay of 30 s, according full relaxation for the toluene aromatic signals, used as internal reference for the concentration determination. Pseudo-first-order kinetic constants were calculated by fitting the experimental concentration evolution for both diene and sulfolene with an irreversible kinetic model (see Table 3)

Table 3. Details of Different Assays and Measured Pseudo-First-Order Rate Constants

run	diene **1** (mmol)	SO_2 (mmol)	$CFCl_3$ (mg)	$CDCl_2$ (mg)	toluene (mg)	volume (mL)	k_{obs} (s^{-1})
1	0.25(9)	1.31	392	369	10.6	0.59	0.26 ± 0.12
2	0.27(0)	2.46	273	361	11.0	0.57	1.17 ± 0.14
3	0.25(4)	2.61	318	477	11.4	0.67	1.23 ± 0.66
4	0.51(1)	4.19	191	300	10.1	0.57	3.52 ± 0.06
5	0.28(4)	4.73	265	284	10.9	0.60	4.40 ± 0.07
6	0.23(4)	6.41	199	295	12.9	0.63	8.4 ± 0.4
7	0.91(2)	7.25	148	241	9.0	0.65	11.6 ± 1.3
8	0.25(2)	6.72	297	162	11.2	0.62	11.9 ± 0.07
9	0.25(1)	6.02	131	187	11.4	0.52	13.0 ± 0.06
10	0.24(0)	9.49	196	228	11.0	0.71	18.7 ± 0.2

NMR characterization of 2-methoxy-2,5-dihydrothiophene-1,1-dioxide **2** has already been published.[13,60]

Preliminary IR measurements have been realized with a FT-IR Perkin spectrometer with a high-pressure cell,[61] with a 1 molar solution of methoxybutadiene and further condensation of sulfur dioxide in the cooled (−30 °C) cell.

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Supporting Information Available: Cartesian coordinates, total energies, and two views of all the structures (MP2 and B3LYP). This material is available free of charge via the Internet at http://pubs.acs.org.

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