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A Comparative Analysis of the Mechanisms of Cheletropic and Diels–Alder Reactions of 1,3-Dienes with Sulfur Dioxide: Kinetic and Thermodynamic Controls

D. Suárez, T. L. Sordo, and J. A. Sordo*

Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, Julián Clavería 8, 33006 Oviedo, Principado de Asturias, Spain

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Ab initio calculations at the MP2/6-31G*//HF/6-31G* level have been carried out to study both thermal and Lewis acid-catalyzed $[_{\omega}2_s + _{\pi}4_s]$-cheletropic and $[_{\pi}4_s + _{\pi}2_s]$-cycloaddition reactions of sulfur dioxide with 1,3-dienes (1,3-butadiene and isoprene). The ab initio results have been analyzed by means of a theoretical method based on the expansion of the MOs of the supermolecule in terms of those of the fragments and the performance of the configuration analysis. While the thermal cheletropic reaction proceeds in a way which closely resembles a σ donation/π back-donation mechanism, the alternative Diels–Alder cycloaddition mostly involves charge transfer in one direction, HOMO(diene) → LUMO(dienophile). Although a Diels–Alder adduct is the kinetic product of reactions of sulfur dioxide with conjugated dienes, the cheletropic reaction gives rise to a thermodynamically more stable five-membered ring adduct, in agreement with the experimental facts.

Introduction

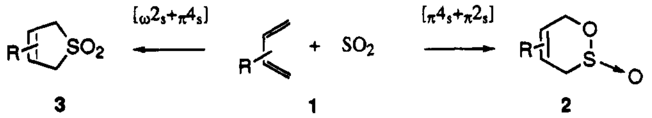
It has been recently reported that sulfur dioxide reacts with isoprene and piperilene to give the corresponding Diels–Alder adducts (Scheme 1).[1] This behavior contrasts with previous findings indicating that the conjugated dienes react with sulfur dioxide to give 2,5-dihydrothiophene derivatives via a $[_{\omega}2_s + _{\pi}4_s]$-cheletropic reaction (Scheme 1).[2]

Cheletropic reactions were defined by Woodward and Hoffmann as pericyclic reactions in which two σ bonds are made or broken in a single atom.[3] Some authors consider these reactions to be a subclass of cycloadditions.[4] Other representative examples of these reactions are the addition of carbenes to olefines, the thermal loss of N_2 from diazenes, and the pyrolytic decarbonilation of cyclic ketones.[5]

Experimental work has shown that a Diels–Alder adduct is the kinetic product of reactions of sulfur dioxide with conjugated dienes but that the adduct is thermally unstable and readily undergoes a retro-Diels–Alder reaction to 1,3-butadiene and sulfur dioxide.[6] A thermodynamically more favorable addition then ensues, producing a stable five-membered ring adduct. Thus, the apparent inability of sulfur dioxide to form Diels–Alder adducts is not derived from reactivity but from product instability.[2]

We have previously studied theoretically thermal and Lewis acid-catalyzed Diels–Alder reactions of 1,3-butadiene and isoprene with sulfur dioxide using ab initio methodology.[7,8] In this paper, we present the results of a MP2/6-31G*//HF/6-31G* ab initio study of $[_{\omega}2_s + _{\pi}4_s]$-cheletropic and $[_{\pi}4_s + _{\pi}2_s]$-cycloaddition reactions of 1,3-butadiene and isoprene with sulfur dioxide. We will show that our calculations are in good agreement with the experimental facts; namely, when sulfur dioxide reacts with **1** in the presence of a Lewis acid catalyst, the kinetically controlled formation of the sultine **2** by a $[_{\pi}4_s + _{\pi}2_s]$-cycloaddition takes place faster than the concurrent and more exothermic $[_{\omega}2_s + _{\pi}4_s]$-cheletropic reaction leading to the sulfolene **3**. As in our previous work,[7,8] a nonconcerted mechanism for the Diels–Alder reaction, involving a biradical intermediate, has not been considered through UHF, MCSCF, or QCl calculations because there is both experimental[1,9,10] and theoretical[11] evidence suggesting a concerted mechanism for that type of reactions. Furthermore, the good agreement found between the present (and previous[7,8]) results and experiments on reactivity, regioselectivity, and stereoselectivity[1,9,12] represents an additional support for the concerted mechanism. On the other hand, the analysis of the wave functions of the transition structures by means of a theoretical method based on the expansion of the MOs of a complex system in terms of the MOs of its fragments, using the geometry each fragment has in the corresponding transition structures, and the performance of the configurational analysis[13] allows us to throw some light

Scheme 1



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on the different mechanisms through which Diels–Alder and cheletropic reactions proceed.

Methods

Ab initio calculations have been carried out at the Hartree–Fock (HF) level of theory using the Gaussian 92 package of programs.[14] Structures were fully optimized with the 6-31G* basis set,[15] followed by vibrational frequency calculations which confirmed that reactants (and products) and transition structures (located by means of Schlegel's algorithm)[16] have zero and one imaginary frequency, respectively. In addition, single-point MP2/6-31G* calculations were carried out on all the HF/6-31G* geometries.

The HF/6-31G* wave functions of the transition structures located in the present work were analyzed by means of a theoretical method based on the expansion of the MOs of a complex system in terms of the MOs of its fragments, using the geometry each fragment has in the corresponding transition structures, and the performance of the configurational analysis. Such a method has been developed by Fukui's group for bimolecular interactions[17] and extended by us to three-molecule interactions.[13] The basic ideas of the method can be summarized as follows: Let us consider three species A, B, and C, which have closed-shell structures, and their composite system A–B–C. We represent the MOs of A–B–C, ψ_g (g = 1, 2, ..., occ), by linear combinations of the MOs of A, B, and C as

$$\psi_g(1) = \sum_x \sum_i D_{i,x}(g)\chi_i(1) \qquad (1)$$

where x runs over all fragments and i runs over all MOs of each fragment (occupied and unoccupied).

A calculation on the composite system A–B–C and on A, B, and C separately renders the MOs ψ and χ_i in terms of the atomic basis functions used to compute A, B, and C. Then the coefficients $D_{i,x}(g)$ in eq 1 can be obtained by solving linear simultaneous equations to fit the basis functions coefficients with respect to each MO of A–B–C.

To express the wave function of the complex, Ψ, in a chemically graspable form, we rewrite it by combination of various electronic configurations as

$$\Psi = c_o\Psi_o + \sum_q c_q\Psi_q \qquad (2)$$

where Ψ_o is the state in which neither electron transfer nor electron excitation takes place and Ψ_q stands for monotransferred configurations (one electron in an occupied MO in any of the three fragments A, B, and C is transferred to an unoccupied MO of a different fragment), monoexcited configurations (one electron in an occupied MO of any of the three fragments A, B, and C is excited to an unoccupied MO of the same fragment), etc. The coefficients c_o and c_q in eq 2 are computed by means of mathematical expressions previously derived.[13] The level of accuracy of this type of analysis is directly related to the basis set used to compute the different wave functions (see ref 13 for more details). This method has proven useful for understanding the chemical features of complex formation from two or three chemically interacting systems.[18]

Results and Discussion

Figure 1 shows the transition structures located for the thermal and Lewis acid-catalyzed (BH_3 was used as a model for the Lewis acid catalyst) cheletropic reactions of 1,3-butadiene (**TS1**, **TS2**) and isoprene (**TS3**, **TS4**) with sulfur dioxide, and Table 1 collects the corresponding activation energies and exothermicities, as computed at the different theoretical levels used in this work. The HF geometries of the transition structures, activation energies, and exothermicities for the corresponding Diels–Alder cycloadditions can be found elsewhere,[7] and the correlation contributions have been computed to the MP2/6-31G*//HF/6-31G* level (the activation energies and exothermicities, at the different theory levels, are collected in parentheses in Table 1 for convenience). It is worthwhile to mention that, during the extensive exploration carried out on the potential energy hypersurface, we were unable to locate any transition structure corresponding to the C_s approach of the SO_2–BH_3 complex to 1,3-butadiene (three third-order and one second-order C_s saddle points involving different relative orientations of the three hydrogen atoms in BH_3, with activation energies of 35.6, 35.7, 37.1, and 37.0 kcal/mol at the HF/6-31G* level, respectively, were located).

Cheletropic reactions of 1,3-dienes with sulfur dioxide turn out to be synchronous processes in the case of the thermal reaction of 1,3-butadiene (**TS1**) and with a certain degree of asynchronicity (two-stage reaction) for the rest of the cases considered in this work (**TS2**–**TS4**).

From the energy viewpoint, Table 1 shows that the presence of an electron-releasing methyl group in 1,3-butadiene has a smaller effect upon the activation barrier of cheletropic reactions (compare **TS1** with **TS3** and **TS2** with **TS4**) than in the case of the corresponding Diels–Alder cycloadditions. The effect of the catalyst, although less important than for Diels–Alder processes, still remains significant, causing a certain lowering in the activation energies of cheletropic reactions (compare **TS1** with **TS2** and **TS3** with **TS4**). This result is consistent with very recent experimental findings[9] showing that the effect of Lewis acid catalysts is stronger for hetero-Diels–Alder additions of sulfur dioxide to 1,3-dienes than for cheletropic reactions of sulfur dioxide with polyenes containing 1,4-diene moieties. In both types of processes (Diels–Alder and cheletropic), the most favorable reaction from a kinetic viewpoint is that involving isoprene and the SO_2–BH_3 complex.

On the other hand, Table 1 shows that, in agreement with experimental findings,[1,2,12] the Diels–Alder adducts should be the kinetic products of reactions of sulfur dioxide with conjugated dienes. Indeed, at the MP2/6-31G*//HF/6-31G* level, the activation barriers leading to the Diels–Alder adducts are 1.1 (6.2) and 2.9 (6.3) kcal/mol lower than those leading to the corresponding sulfolenes for the reactions of sulfur dioxide (or SO_2–BH_3) with 1,3-butadiene and isoprene, respectively. The exothermicities (**P1**, **P2**) computed at the Hartree–Fock level indicate that, contrary to expectations,[1,2,12] Diels–Alder cycloadditions should also be, in general, thermo-

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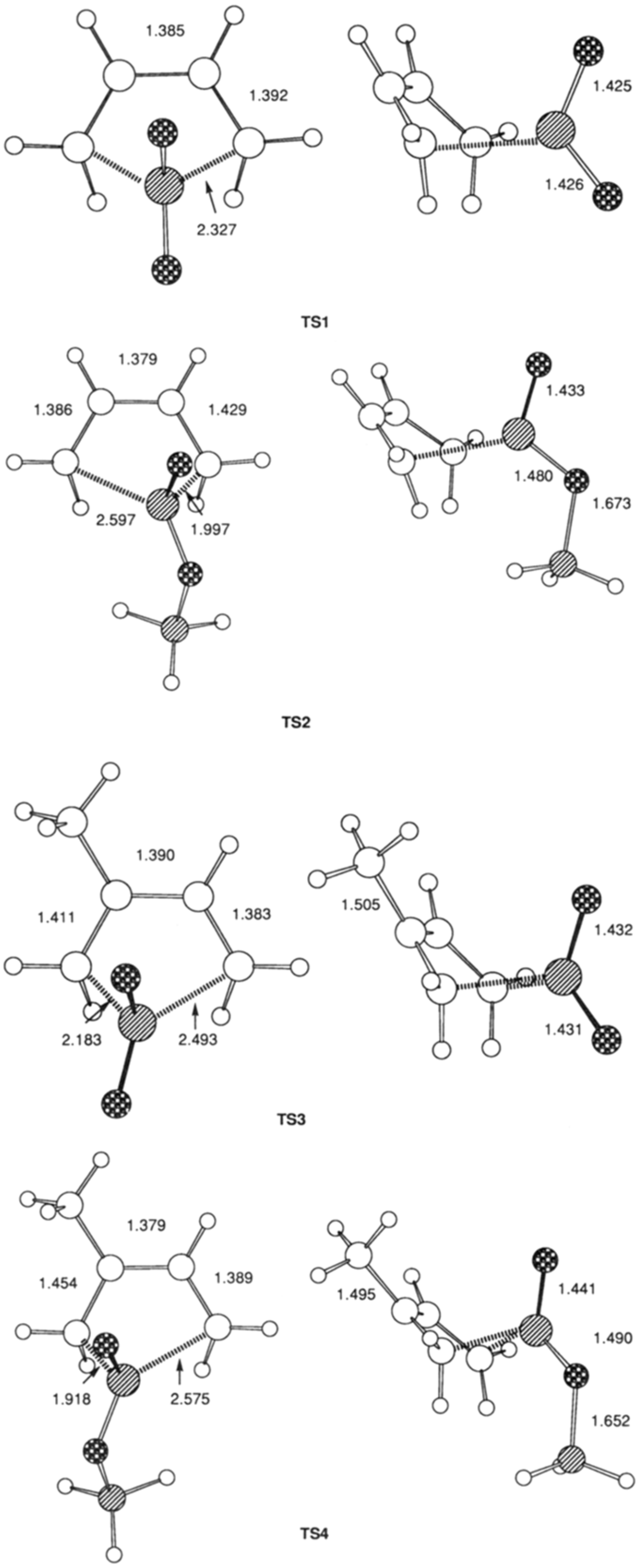

Figure 1. Transition structures, computed at the HF/6-31G* level, for the (uncatalyzed and Lewis acid-catalyzed) cheletropic reactions of 1,3-butadiene (**TS1**, **TS2**) and isoprene (**TS3**, **TS4**) with sulfur dioxide.

Table 1. Calculated Energies (kcal/mol) of the HF/6-31G*-Optimized Transition Structures and Products Relative to Reactants for the Cheletropic and Diels–Alder (in parentheses) Reactions

transition structures[a]		HF/6-31G*	HF/6-31G* (ZPE)[b]	MP2/6-31G*[c]
1,3-butadiene + SO_2	**TS1**	38.6 (32.3)	40.7 (34.6)	17.1 (16.0)
1,3-butadiene + SO_2–BH_3	**TS2**	33.6 (20.6)	37.9 (24.9)	10.7 (4.5)
isoprene + SO_2	**TS3**	37.5 (28.2)	39.2 (30.0)	16.7 (13.8)
isoprene + SO_2–BH_3	**TS4**	28.8 (15.7)	32.7 (19.4)	9.4 (3.1)

products		HF/6-31G*	HF/6-31G* (ZPE)[b]	MP2/6-31G*[c]
1,3-butadiene + SO_2	**P1**	−10.6 (−12.7)	−5.9 (−7.9)	−9.5 (−7.6)
isoprene + SO_2	**P2**	−13.0 (−13.9)	−8.7 (−9.5)	−11.7 (−9.1)

[a] Diels–Alder values correspond to the "endo" and "meta-endo" (see ref 7 for details). [b] HF/6-31G* energies including zero-point energy correction. [c] MP2/6-31G*//HF/6-31G* energies.

Table 2. Relative Weights of the Most Important Fragment Electronic Configurations in the HF/6-31G* TSs for the Chelotropic and Diels–Alder (in parentheses) Reactions

configurations[a]	TS1	TS3
AB	1.0000 (1.0000)	1.0000 (1.0000)
A^+B^- (HOMO → LUMO)	0.2459 (0.4433)	0.2692 (0.4818)
A^-B^+ (HOMO → LUMO)	0.1598 (0.0294)	0.1472 (0.0268)
AB^* (HOMO → LUMO)	0.0419 (0.1264)	0.0391 (0.1265)
A^*B^* (HOMO → LUMO/HOMO → LUMO)	0.0313 (0.0176)	0.0401 (0.0191)

configurations[b]	TS2	TS4
AB	1.0000 (1.0000)	1.0000 (1.0000)
A^+B^- (HOMO → LUMO)	0.4304 (0.5903)	0.5362 (0.7063)
A^-B^+ (HOMO → LUMO)	0.0872 (0.0204)	0.0856 (0.0168)
AB^* (HOMO → LUMO)	0.0964 (0.1647)	0.1228 (0.1941)
A^*B^* (HOMO → LUMO/HOMO → LUMO)	0.0421 (0.0177)	0.0533 (0.0145)

[a] A: diene. B: SO_2. [b] A: diene. B: SO_2–BH_3.

dynamically more favorable. However, consideration of correlation effects, even though in a very approximate fashion (MP2/6-31G*//HF/6-31G*),[19] shows the sulfolenes to be more stable than sultines, in agreement with experimental facts.[1,2,12]

The counterpoise correction for basis set superposition error[20] modifies the total energies of the structures considered in the present work in about 3–5 kcal/mol, but the changes in relative energies are completely negligible.

It is also noteworthy that in a recent experimental work[10] the activation energy for the cheletropic reaction between 2,3-dimethylbuta-1,3-diene and sulfur dioxide is mentioned to be 12.9 kcal/mol (31.6 kcal/mol for the back-reaction). Such a result is consistent with the MP2/6-31G*//HF/6-31G* activation energy for the cheletropic reaction of isoprene with sulfur dioxide (see Table 1), 16.7 kcal/mol (28.4 kcal/mol for the back-reaction).

Table 2 collects the relative weights (from coefficients c_o and c_q in eq 2) of the most important fragment electronic configurations in **TS1–TS4** (the relative weights of the corresponding Diels–Alder cycloadditions are also given in parentheses). A two-fragment analysis[13] has been carried out in all cases to allow for a direct interpretation in terms of orbitals depicted in Figure 2.

As can be seen, there is a significant difference between the composition of the wave function of the transition structures located for the thermal cheletropic reactions and that for the corresponding thermal Diels–Alder cycloadditions. In fact, while for the former, the A^+B^- and A^-B^+ (A = diene, B = SO_2) fragment electronic configurations contribute more or less the same to the

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(19) MP2/6-31G* calculations confirmed this finding. In fact, MP2/6-31G* exothermicities are in kilocalories per mole: −5.4 (cheletropic, butadiene + SO_2), −3.8 (Diels–Alder, butadiene + SO_2), −7.6 (cheletropic, isoprene + SO_2), and −5.3 (Diels–Alder, isoprene + SO_2).

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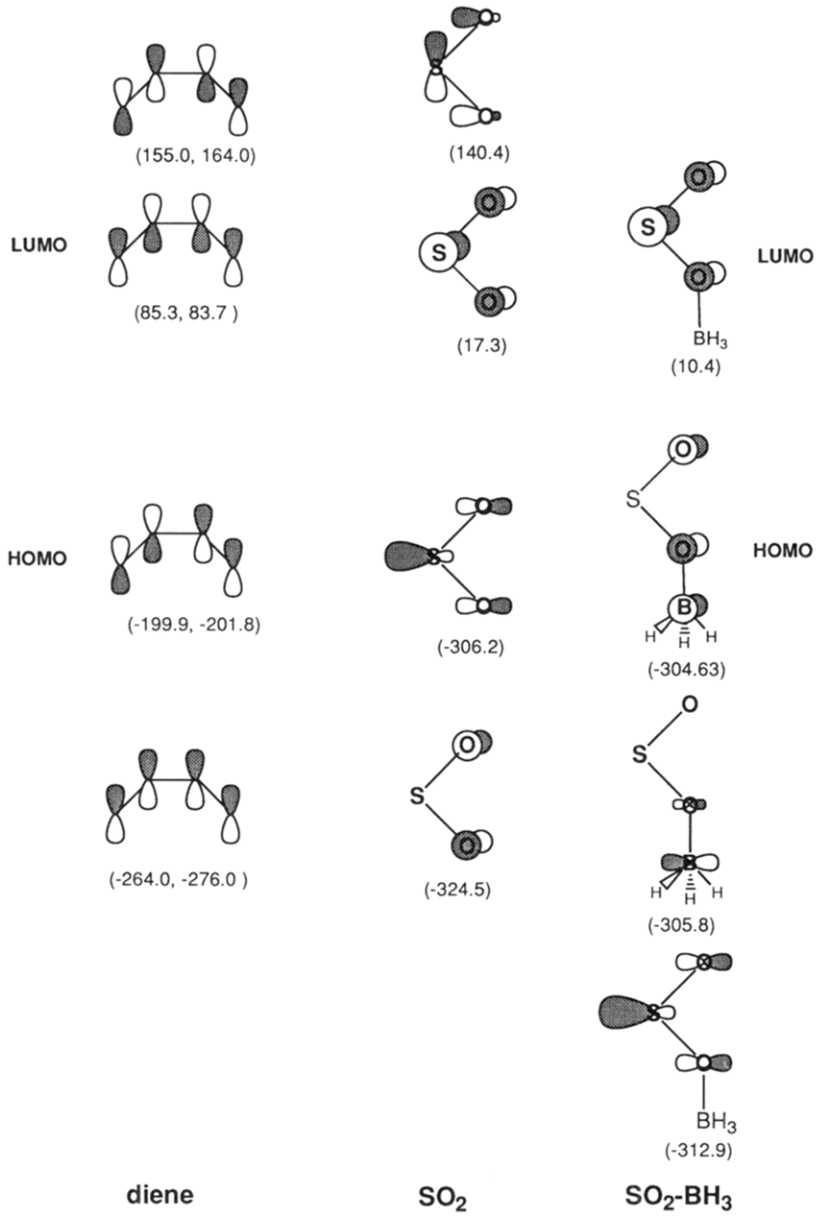

Figure 2. Molecular orbitals of the different reactants involved in the studied reactions (diene stands for both 1,3-butadiene and isoprene). The molecular orbital energies (kcal/mol) are given in parentheses (in the case of the diene, the two molecular orbital energies correspond to 1,3-butadiene and isoprene, respectively).

supermolecule wave function, for the latter, only the A^+B^- configuration makes an appreciable contribution. Thus, the cheletropic reaction seems to proceed in a way which closely resembles the σ donation/π back-donation mechanism operating in the metal–ligand bonding in transition metal complexes;[21] in other words, electron density from the filled HOMO level of the diene is transferred to the empty LUMO of sulfur dioxide. Likewise, electron density from the filled HOMO of sulfur dioxide is transferred to the empty diene's LUMO. As a consequence, the two cheletropic C–S-forming bonds turn out to be synergistic and the net charge transfer diene ↔ sulfur dioxide is negligible, in sharp contrast with what happens in the corresponding Diels–Alder cycloaddition where a considerably large net charge transfer from diene to dienophile occurs[7] (0.28 and 0.32 electrons for the Diels–Alder reactions of sulfur dioxide with 1,3-butadiene and isoprene, respectively). In this latter case, the very small relative weight of the A^-B^+ fragment electronic configuration indicates that a neutralization of the HOMO(diene) → LUMO(SO_2) charge transfer through the corresponding HOMO(SO_2) → LUMO(diene) back-donation is unlikely.

Figure 2 helps us to understand the nature of the interactions leading to the sultine **2** (via a [${}_\pi 4_s + {}_\pi 2_s$]-cycloaddition) or to the sulfolene **3** (via a [${}_\omega 2_s + {}_\pi 4_s$]-cheletropic reaction). Indeed, this figure shows that the orbital symmetries of the diene and sulfur dioxide MOs allow for both HOMO(diene)–LUMO(SO_2) and HOMO(SO_2)–LUMO(diene) interactions in order to form the two C–S bonds of sulfolene **3**. However, the latter gives rise to an antibonding interaction for one of the forming bonds (C–S, C–O) of the corresponding Diels–Alder adduct. These symmetry considerations do explain why the two configurations A^+B^- (HOMO(diene) → LUMO(SO_2)) and A^-B^+ (HOMO(SO_2) → LUMO(diene)) are important in the case of cheletropic reactions while only one configuraion, A^+B^- (HOMO(diene) → LUMO(SO_2)), has an important

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relative weight in the corresponding Diels–Alder cycloadditions.

With regard to the catalyzed reactions, the above analysis mostly applies, the only difference being that, in this case, the relative weight of the A^-B^+ (A = diene, B = SO_2–BH_3) fragment electronic configuration for cheletropic reactions is smaller. Even so, it is much larger than that for the corresponding Diels–Alder cycloadditions. Consequently, the net charge transfer for the catalyzed cheletropic reactions, although notably lower than the one for the corresponding catalyzed Diels–Alder reactions (about 0.50 electrons),[7] increases with respect to the thermal cheletropic reactions (0.29 and 0.36 electrons from diene to the SO_2–BH_3 complex for 1,3-butadiene and isoprene, respectively). Therefore, it is clear that the catalyst hinders the back-donation mechanism. It has been shown elsewhere[7,8,18] that, for quite different reactions, the presence of a Lewis acid catalyst makes the weight of one of the present configurations increase remarkably so that the diabatic curve representing such a configuration will interact strongly with that of the zero configuration, thus causing an important lowering in the activation energy.[22] Tables 1 and 2 show that cheletropic reactions are not exceptions to this general behavior.

Let us now make a comment on the diminution of the relative weights of the A^-B^+ configuration and the augment of those of the A^+B^- configuration observed in the case of Lewis acid-catalyzed cheletropic reactions when compared with the corresponding thermal reactions (compare **TS1** → **TS2** and **TS3** → **TS4** in Table 2). Figure 2 shows that the sulfur dioxide's LUMO remains the LUMO of the SO_2–BH_3 complex, the only difference being that its energy becomes lower, thus favoring the HOMO(diene)–LUMO(SO_2–BH_3) interaction and, consequently, increasing the importance of the A^+B^- configuration. On the other hand, the sulfur dioxide's HOMO undergoes a considerable stabilization when the SO_2–BH_3 complex is formed. Such a stabilization disfavors the interaction between this orbital and the diene's LUMO, thus decreasing the importance of the A^-B^+ configuration.

Finally, it is noteworthy that, in all cases, Table 2 shows that the relative weights of the A^+B^- fragment electronic configurations for Diels–Alder cycloadditions are larger than any other configuration for the corresponding cheletropic reactions; accordingly, a stronger interaction between its diabatic curve and that of the zero configuration is expected, and, consequently, a more important lowering in the activation barrier should be observed,[22] in agreement with data collected in Table 1. This result allows for a rationalization of the abovementioned experimental fact that a Diels–Alder adduct is the kinetic product of reactions of sulfur dioxide with conjugated dienes.

Conclusions

The $[_\omega 2_s + {}_\pi 4_s]$-cheletropic and $[_\pi 4_s + {}_\pi 2_s]$-cycloaddition reactions of 1,3-butadiene and isoprene with sulfur dioxide have been studied ab initio at the MP2/6-31G*//HF/6-31G* level of theory.

It has been shown that, according to experimental evidence, a Diels–Alder adduct is the kinetic product of reactions of sulfur dioxide with conjugated dienes, but the cheletropic addition gives rise to a thermodynamically more favorable product. Correlation energy seems to be important in order to get this result.

A configurational analysis shows that the two fragment electronic configurations A^+B^- (HOMO(diene) → LUMO(SO_2)) and A^-B^+ (HOMO(SO_2) → LUMO(diene)) are important in the case of cheletropic reactions (the latter somewhat less important in the case of the Lewis acid-catalyzed reactions), while only the former cofiguration, A^+B^-, has an important relative weight in the Diels–Alder cycloadditions. All these facts have been shown to be consistent with predictions from the analysis of the frontier orbital symmetry.

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