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Sulfur Dioxide Promotes Its Hetero-Diels−Alder and Cheletropic Additions to 1,2-Dimethylidenecyclohexane

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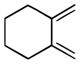
Simple 1,3-dienes add to SO_2 in the presence of acid catalysts to generate the corresponding 3,6-dihydro-1,2-oxathiin-2-oxides (sultines)[1] at low temperature. This observation led us to invent a new carbon−carbon bond forming reaction in which electron-rich dienes are condensed with electron-rich alkenes giving sulfinic acids that undergo stereoselective retro-ene elimination of SO_2. Polypropionate fragments containing three contiguous stereogenic centers and one (*E*)-alkenic unit can be generated in a one-pot procedure.[2] We now report that both the well-known cheletropic addition[3] (giving sulfolenes) and the hetero-Diels−Alder addition of SO_2 to 1,3-dienes are promoted by SO_2 itself as suggested by ab initio quantum calculations and demonstrated by the order of the rate-laws of these reactions.

Although the dipole moment of SO_2 ($\mu = 1.63$ D)[4] is relatively small, it is a good Lewis acid that associates strongly with anions and, therefore, promotes heterolysis.[5] The binding enthalpy of the charge-transfer complex $Me_3N^{\bullet+}SO_2^{\bullet-}$ ($\mu = 4.95$ D) amounts to ca. 12 kcal/mol in heptane.[6] It is therefore possible that a second molecule of SO_2 can intervene in the transition states of the hetero-Diels−Alder additions and stabilize them in such a way that compensates for the unfavorable entropy term. On comparing rate constants of the additions of ethylenetetracarbonitrile to various dienes,[7] 1,2-dimethylidenecyclohexane (**1**) was expected to be one of the most reactive 2,3-dialkyldiene in a Diels−Alder cycloaddition.[8] Indeed, **1**[9] added to SO_2 readily at 187 K without catalyst, generating sultine **2** nearly quantitatively, the structure of which was given by its ^{1}H and ^{13}C NMR spectra. At this temperature and below 223 K, the sulfolene **3** was not observed. Above 253 K, only **3**[10] was formed, with sultine **2** undergoing complete cycloreversion to **1** and SO_2. Rates of formation of **2** and of the disappearance of diene **1** were measured at different temperatures and for various concentrations and excesses of SO_2. They follow the law $d[\mathbf{2}]/dt = k_2^{obs}[\mathbf{1}][SO_2]^2 - k_{-2}^{obs}[\mathbf{2}][SO_2]$ at 198 K for concentrations of SO_2 varying between 0.92 and 11.2 molar.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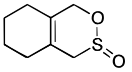
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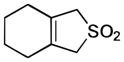
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Under conditions where $k_{-2}^{obs}[\mathbf{2}][SO_2]$ is negligible, $k_2^{obs}[SO_2]^x$: $(5.05 \pm 1.0)10^{-5}$, $(5.7 \pm 0.5)10^{-4}$, $(1.38 \pm 0.12)10^{-3}$, $(3.33 \pm 0.20)10^{-3}$, and $(9.4 \pm 0.1)10^{-3}$ min^{-1} for $[SO_2] = 0.92$, 2.97, 4.3, 7.1, and 11.2 molar (error <2%), respectively, were obtained. In the gas phase, SO_2 generates a dimer with a binding energy amounting to ca. 3 kcal/mol.[11] One can thus admit mechanism (a)

$$\mathbf{1} + 2SO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{1} + (SO_2)_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathbf{2} + SO_2 \qquad \text{(a)}$$

Alternatively, since butadiene is known to form a van der Waals complex with SO_2 with a binding energy of 3.24 ± 0.48 kcal/mol[12] we cannot exclude mechanism (b)

$$\mathbf{1} + 2SO_2 \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} (\mathbf{1}\cdot SO_2) + SO_2 \underset{k'_{-2}}{\overset{k'_2}{\rightleftharpoons}} \mathbf{2} + SO_2 \qquad \text{(b)}$$

The rate law for (a) is $d[\mathbf{2}]/dt = k_2K[SO_2]^2[\mathbf{1}] - k_{-2}[SO_2][\mathbf{2}]$ and for (b) $d[\mathbf{2}]/dt = k'_2K'[SO_2]^2[\mathbf{1}] - k'_{-2}[SO_2][\mathbf{2}]$ with $K = k_1/k_{-1}$, $K' = k'_1/k'_{-1}$, k_1, k_{-1}, k'_1 and k'_{-1} larger than k_2 or k'_2 (rate-determining steps). Our data are consistent with both mechanisms (a) and (b).

The rates of formation of sulfolene **3** were measured at 261.2 K as a function of SO_2 concentration. They followed the rate law $d[\mathbf{3}]/dt = k_3^{obs}[\mathbf{1}][SO_2]^2$ with $k_3^{obs}[SO_2]^x = (11.67 \pm 0.12)10^{-3}$, $(14.07 \pm 0.07)10^{-3}$, $(18.53 \pm 0.34)10^{-3}$, $(70.9 \pm 1.4)10^{-3}$, $(110.7 \pm 2.9)10^{-3}$, $(110.1 \pm 3.3)10^{-3}$, and $(174.9 \pm 3.8)10^{-3}$ min^{-1} for $[SO_2] = 2.66$, 3.19, 4.68, 9.55, 12.64, 13.02, and 15.16 M (error <2%), respectively. Thus, mechanisms analogous to (a) and (b) can be retained for the cheletropic addition $\mathbf{1} + SO_2 \rightleftarrows \mathbf{3}$.

Ab initio calculations were carried out to explore the model reactions between 1,3-butadiene and SO_2 to give the corresponding sultine and sulfolene. Geometry optimizations were performed at the MP2/6-31G* level of theory followed by single-point MP2/6-311+G(3df,2p) and QCISD(T)/6-31G* calculations which allowed a G2(MP2,SVP)[13] estimate of the barriers involved in the cycloaddition reactions studied. Thermochemistry (1 atm, 298.15 K) was computed at the HF/6-31G* level using the ideal gas, rigid-rotor, and harmonic oscillator approximations.[14] The GAUSSIAN 94 package of programs[15] was employed to carry out all reported calculations. Solvent effects were analyzed by

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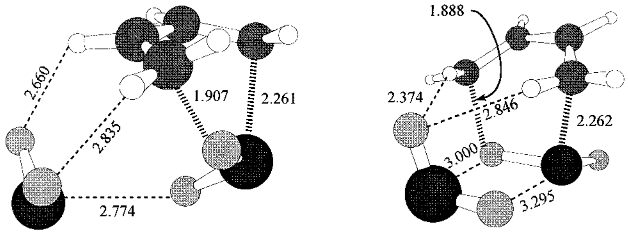
Table 1. Energies (Related to Reactants in kcal/mol) Corresponding to the Transition Structure for (**1**) Butadiene + SO_2 and (2) Butadiene + $2SO_2$ Reactions (DA: Diels−Alder, Che: Cheletropic)

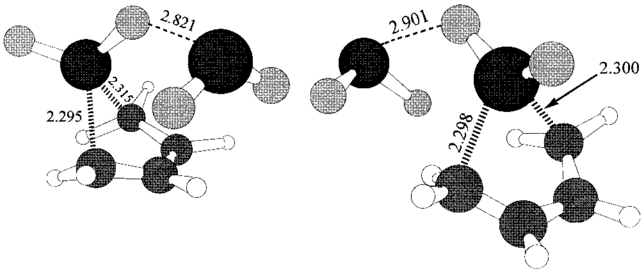
reaction	ZPVE[a]	MP2/6-31G*	MP2/6-31G* SCFR ($\epsilon = 13.3$)	MP2/6-311+G(3df,2p)	QCISD(T)/6-31G*	G2(MP2,SVP)[b]
(1)‡**(DA)$_1$**	2.3	17.8	17.7	14.5	20.6	19.2
‡**(Che)$_1$**	2.2	19.6	19.0	11.7	25.0	19.0
(2)‡**(DA)$_{2a}$**	2.7	11.8	13.1	8.4	14.4	13.4 (7.8)[c]
‡**(DA)$_{2b}$**	2.6	14.0	15.4			
‡**(Che)$_{2a}$**	2.4	14.8	16.3	6.4	20.1	13.8 (12.2)[c]
‡**(Che)$_{2b}$**	2.4	15.1	16.3			

[a] Zero point vibrational energies (ZPVE) were computed at the HF/6-31G* level of theory. [b] ZPVE calculated, were scaled by 0.8509 (DeFees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 333) to compute G2(MP2,SVP) values. [c] Computed activation energies using BH_3 as a Lewis acid catalyst in parentheses (butadiene + SO_2 + BH_3).



‡(DA)$_{2a}$ ‡(DA)$_{2b}$

Figure 1. MP2/6-31G* optimized structures corresponding to two transition structures [‡**(DA)$_{2a}$**, ‡**(DA)$_{2b}$**] for the hetero-Diels−Alder reaction of 1,3-butadiene + $2SO_2$.



‡(Che)$_{2a}$ ‡(Che)$_{2b}$

Figure 2. MP2/6-31G* optimized structures corresponding to two transition structures [‡**(Che)$_{2a}$**, ‡**(Che)$_{2b}$**] for the cheletropic reaction of 1,3-butadiene + $2SO_2$.

means of Onsager model reaction field calculations as implemented in GAUSSIAN 94.[15]

Since the thermodynamic aspects of this reaction have been discussed elsewhere,[16] we focus here on the kinetic aspects. Besides the transition structures corresponding to the addition of one molecule of sulfur dioxide [‡**(DA)$_1$**: Diels−Alder, ‡**(Che)$_1$**: cheletropic][16] two new transition structures for the hetero-Diels−Alder reaction [‡(**DA**)$_{2a}$, ‡(**DA**)$_{2b}$, see Figure 1)] and two new transition structures for the related cheletropic addition [‡(**Che**)$_{2a}$, ‡(**Che**)$_{2b}$; see Figure 2)], both involving two molecules of SO_2, were located and characterized. Table 1 collects the energetic results [G2(MP2,SV) energies were only computed for transition structures exhibiting lower barriers: ‡(**DA**)$_{2a}$ and ‡(**Che**)$_{2a}$].

Our calculations estimate (MP2/6-31G*) dipole moments of 3.04 and 3.68 D for the transition structures ‡(**DA**)$_1$ and ‡(**Che**)$_1$ involving one molecule of SO_2. It might be therefore expected that a second molecule of SO_2 can stabilize both transition structures in such a way that the reduction of the energetic barrier may overwhelm the loss of entropy due to condensation. Our calculations support this hypothesis. Indeed, transition structures ‡(**DA**)$_{2a}$ and ‡(**Che**)$_{2a}$ are more than 5 kcal/mol lower in energy than the corresponding ‡(**DA**)$_1$ and ‡(**Che**)$_1$ transition structures (Table 1), whereas the entropy contributions ($T\Delta S^{\ddagger}$), as computed at 200 K (Diels−Alder) and 261.2 K (cheletropic) predict an additional enthalpy cost of 2.5 and 2.6 kcal/mol, respectively, for the Diels−Alder and cheletropic reactions with transition structures involving two molecules of SO_2. According to expectations, the (MP2/6-31G*) dipole moments of such transition structures reduce to 2.37 D [‡(**DA**)$_{2a}$] and 2.25 D [‡(**Che**)$_{2a}$] as a consequence of the presence of a second molecule of SO_2. Solvation calculations predict a moderate destabilization consistent with such a reduction.[17]

As it can be seen in Table 1, the lowering of energy barriers due to the presence of a second molecule of SO_2 in transition structures is remarkable when compared with the catalytic action of a Lewis acid catalyst.[18]

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Supporting Information Available: Experimental procedures and spectral data for **2**, **3**, kinetic measurement examples, total energies for all of the structures located as computed at the different levels of theory, and two views of each structure in Figures 1 and 2 (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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