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MECHANISM OF CHELETROPIC REACTIONS OF 1,3-DIENES WITH SULFUR DIOXIDE

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In a recent paper [N.S. Isaacs and A. Laila, *J. Phys. Org. Chem.* 7, 178 (1994)2] the volume profile for the cheletropic addition of sulphur dioxide to a 1,3-diene (2,3-dimethylbuta-1,3-diene) indicated that a two-step mechanism for this reaction, with a (4 + 2) cycloaddition at the S═O bond as the slow step followed by a rapid rearrangement of the resultant sulpheno-lactone, cannot be ruled out. However, *ab initio* calculations, at the MP2(FC)/6-31G*//RHF/6-31G* level, show that such a mechanism can be conclusively discarded.

Experimental work[1] has shown that a Diels–Alder adduct is the kinetic product of reactions of sulphur dioxide with 1,3-dienes, but is thermally unstable and readily undergoes a retro-Diels–Alder reaction to the 1,3-diene and sulphur dioxide. A thermodynamically more favourable addition (cheletropic reaction) then ensues, producing a stable five-membered ring adduct (see Scheme 1).

In a series of recent papers,[2] *ab initio* methodologies and configurational analysis 3 were used to rationalize the reactivity, regioselectivity and stereoselectivity of both thermal and Lewis acid-catalysed Diels–Alder reactions between 1,3-dienes and sulfur dioxide. In particular, a comparative analysis of the mechanism of cheletropic and Diels–Alder reactions of 1,3-dienes and sulphur dioxide was carried out.[4] The results were shown to be in full agreement with the above-mentioned experimental facts regarding kinetic and thermodynamic control.

As a result of new experimental work, based on measurements of the volume profile for the cheletropic reaction between 2,3-dimethylbuta-1,3-diene and sulphur dioxide, Isaacs and Laila[5] concluded that a mechanism for the formation of sulpholenes from the corresponding sultines involving a rapid rearrangement cannot be ruled out (see Scheme 2). In this paper, we present the results of an *ab initio* study to analyse the plausibility of a mechanism such as that presented in Scheme 2.

MP2(FC)/6-31G*//RHF/6-31G* calculations were carried out to study the Diels–Alder and cheletropic reactions of buta-1,3-diene and sulphur dioxide using the Gaussian 92[6] package of programs, as this level of theory has proved appropriate to provide reliable information on this type of reaction.[2,4] {Previous MP2(FC)/6-31G*//RHF/3-21G* calculations on 2,3-dimethyl-buta-1,3-diene showed that its behaviour is similar to that exhibited by buta-1,3-diene in Diels–Alder and cheletropic reactions with sulphur dioxide (see Refs 2 and 4), namely, while the Diels–Alder adduct is the kinetic product [$\Delta H\ddagger$(Diels–Alder) = 10·7 kcal mol^{-1}, $\Delta H\ddagger$(cheletropic) = 15·1 kcal mol (1 kcal = 4·184 kJ); the latter value is in reasonable agreement with the experimental value mentioned in Ref. 5, 12·9 kcal mol^{-1}, the cheletropic reaction gives rise to a thermodynamically more stable five-membered ring adduct [ΔH_{rxn}(Diels–Alder) = −7·7 kcal mol^{-1}, ΔH_{rxn}(cheletropic) = −12·4 kcal mol^{-1}]. Buta-1,3-diene is less reactive [$\Delta H\ddagger$(Diels–Alder) = 14·6 kcal mol^{-1}, $\Delta H\ddagger$(cheletropic) = 17·5 kcal mol^{-1}) and the corresponding sultine and sulpholene are less stable ΔH_{rxn}(Diels–Alder) = −6·5 kcal mol^{-1}, ΔH_{rxn} (cheletropic) = −8·4 kcal mol^{-1}]. Therefore, the simpler buta-1,3-diene was chosen to carry out the present MP2(FC)/6-31G*//RHF/31G* study.} Structures were fully optimized (at the RHF/6-31G* level), followed by vibrational frequency calculations which confirmed that the reactants and transition structures (located by means of Schlegel's algorithm)[7] have zero and one imaginary frequency, respectively. Figure 1 depicts the RHF/6-31G* structures of the two sultine conformers: axial (**P1**, COSO angle = 43·5°) and equatorial (**P2**, COSO angle = 180·3°), the transition structure connecting such conformers (**TS1**, COSO angle = 131·2°), the corresponding sulpholene (**P3**),

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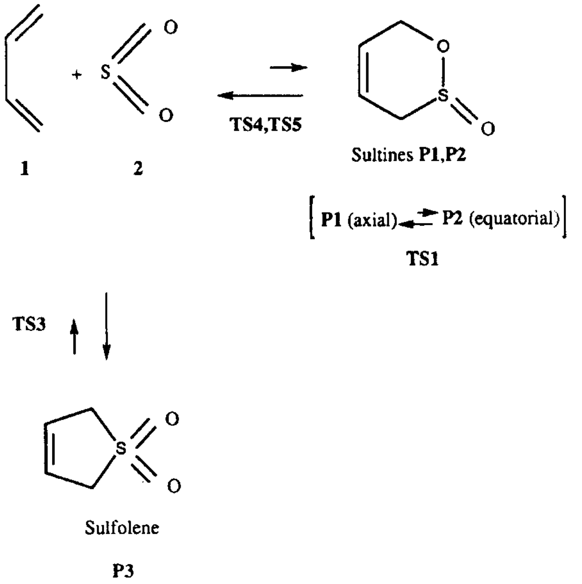

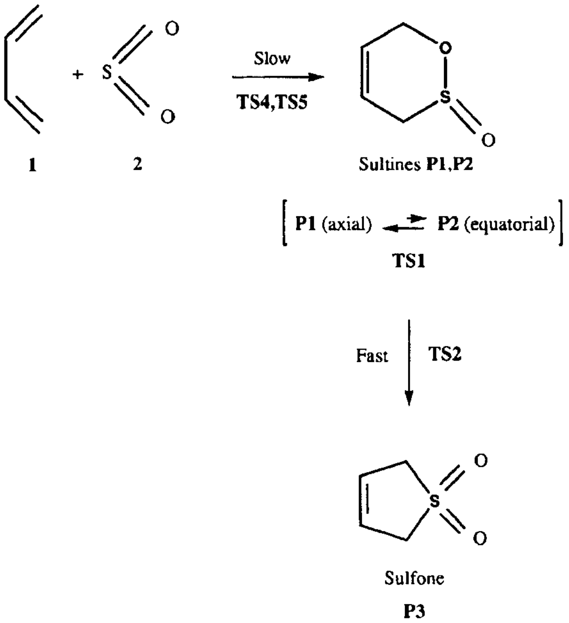

and the transition structure (**TS2**) connecting the equatorial sultine and the sulpholene (an extensive search on the RHF/6-31G* potential hypersurface showed that a transition structure connecting the axial sultine and the sulpholene does not exist). The transition structures of the one-step cheletropic (**TS3**) and Diels–Alder (**TS4**, **TS5**) reactions[2,4] have also been included in Figure 1 for completeness. Table 1 owes the relative energies for all the structures considered.

According to experimental data,[1] the axial sultine (**P1**) is the most stable Diels–Alder cycloadduct and the sulpholene (**P3**) is more stable than both sultines (**P1**, **P2**). As reported elsewhere,[4] correlation effects are important to predict theoretically such a behaviour (see results for **P3** in Table 1). On the other hand, Table 1 clearly shows that the one-step mechanism (see Scheme 1) is definitely much more favourable than the two-step mechanism shown in Scheme 2. In fact, the assumed 'rapid rearrangement' from the sultine to the sulpholene suggested by Isaacs and Laila[5] really involves a transition structure (**TS2**) much higher in energy than the transition structure involved in the one-step mechanism

Table 1. Relative energies[a] (kcal mol^{-1}) of the structures considered in this work (see Figure 1) for the reaction between buta-1,3-diene (**1**) and sulphur dioxide(**2**)

Structure		RHF/6-31G*[c]	MP2(FC)/6-31G*[d]
Sultine (axial)	**P1**	0·0	0·0
Sultine (equatorial)	**P2**	3·3	3·3
Sulfolene	**P3**	2·0	−1·8
P1 $\rightleftharpoons$ **P2**	**TS1**	7·3	7·2
P2 $\rightleftharpoons$ **P3**	**TS2**	83·6	73·3
1+**2** $\rightleftharpoons$ **P3**	**TD3**[b]	48·6	24·7
1+**2** $\rightleftharpoons$ **P1**	**TS4**[b]	42·5	23·6
1+**2** $\rightleftharpoons$ **P2**	**TS5**[b]	44·1	23·7

[a] The RHF/6-31G* total energies (au) for structures **P1**, **P2**, **P3**, **TS1**, **TS2**, **TS3**, **TS4** and **TS5** are: −702·108831, −702·103306, −702·105565, −702·096240, −701·971347, −702·027171, −702·037148 and −702·034388, respectively, and the corresponding MP2(FC)/6-31G*//RHF/6-31G* total energies (au) are −703·106159, −703·100832, −703·109082, −703·094736, −702·989332, −703·066796, −703·068503 and −703·068424, respectively.

[b] See Ref. 4.

[c] Including zero-point energy correction.

[d] MP2(FC)/6-31G*//RHF/6-31G*.

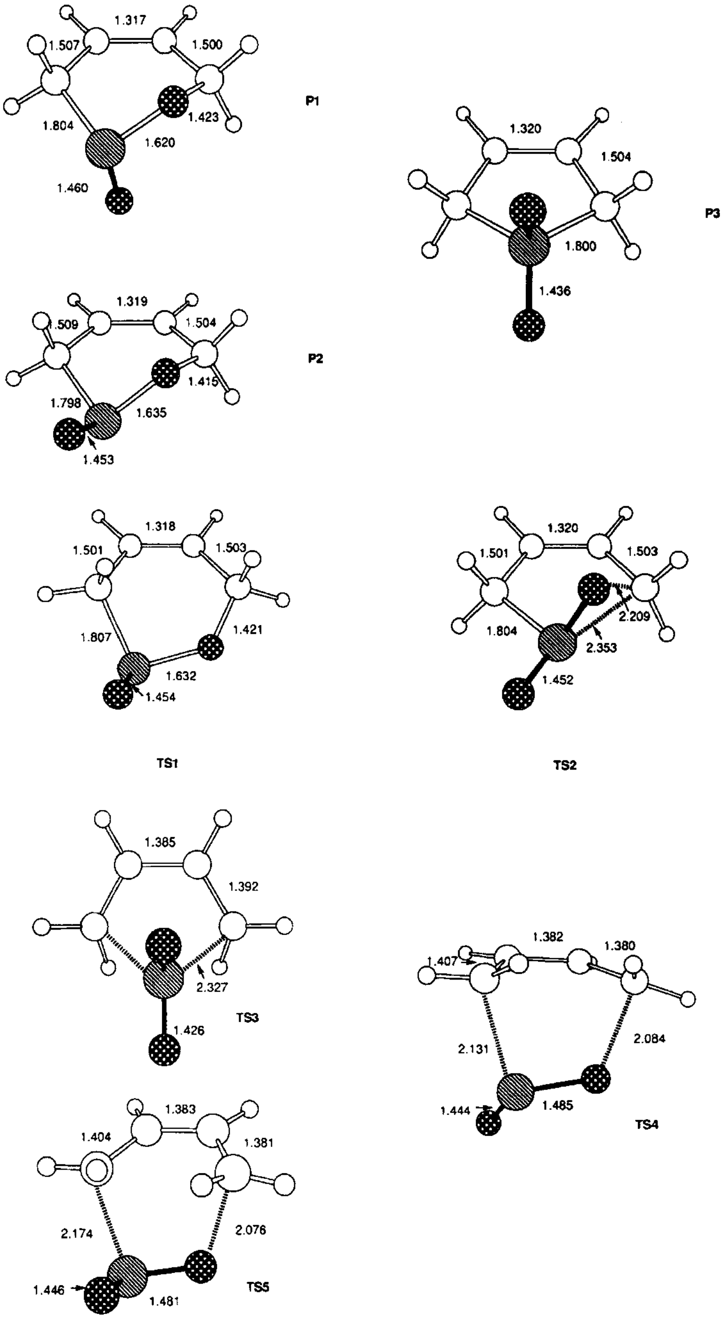

Figure 1. RHF/6–31G* structures of the two sultine conformers (axial, **P1**; and equatorial, **P2**), the transition structure connecting such conformers (**TS1**), the corresponding sulfolene (**P3**), the transition structure connecting the equatorial sultine and the sulpholene (**TS2**), and the transition structures of the one-step cheletropic (**TS3**) and Diels–Alder (**TS4**, **TS5**) reactions between buta-1,3-diene and sulphur dioxide

(**TS3**). Therefore, when 1,3-dienes react with sulphur dioxide, MP2(FC)/6–31G*//RHF/6–31G* calculations predict the formation of a sultine which undergoes a fast cycloreversion to give finally a thermodynamically more stable sulpholene. While a two-step mechanism involving the formation of a sultine followed by a rapid rearrangement to give a sulpholene cannot be excluded in the light of experimental data on the volume profile for this type of reaction, *ab initio* calculations show that such a mechanism can be conclusively ruled out.

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