

## Relative Reactivity Studies for Olefin Sulphonation with Sulphur Trioxide in Dichloromethane: Evidence for Concerted $[2_s + 2_s]$ Cycloaddition

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Relative rate studies are described for the sulphonation by sulphur trioxide in dichloromethane at  $-50^\circ\text{C}$  of nine alkenes bearing one, two, or three alkyl substituents on the olefinic carbon atoms. There is remarkably little variation of reactivity with alkene structure, the most reactive alkene studied, 3-methylpent-2-ene, combining with sulphur trioxide only 3.4 times faster than the least reactive, non-1-ene. The findings are interpreted in terms of a concerted  $[2_s + 2_s]$  cycloaddition mechanism, which is shown by orbital correlation analysis to be allowed thermally.

Reactions of olefins with sulphur trioxide give rise to various products, depending on the nature of the olefin and on the reaction conditions. In the case of fluoro-olefins,  $\beta$ -sultones can often be isolated.<sup>1</sup> There is evidence from spectroscopy and trapping experiments that  $\beta$ -sultones are formed as the major products in the sulphonation of simple alkenes such as dodec-1-ene and dodec-2-ene, but under most reaction conditions they are short-lived and too unstable to be isolated.<sup>2</sup>

It is widely assumed, both for fluoro-olefins<sup>1,3</sup> and simple alkenes,<sup>4-7</sup> that the initial step in the reaction with sulphur trioxide consists of an electrophilic attack, in accordance with Markownikov's rule, to give a zwitterionic intermediate that can undergo a variety of reactions, including reversible cyclisation to a  $\beta$ -sultone (Mechanism 1). An alternative mechanism, in which the initial step is a concerted cycloaddition reaction, forming the  $\beta$ -sultone directly (Mechanism 2), was proposed in 1974,<sup>8</sup> but has not so far been considered in detail. Both mechanisms are consistent with the observed kinetic form of the reaction:<sup>8</sup> rate =  $k[\text{alkene}][\text{SO}_3]$ .

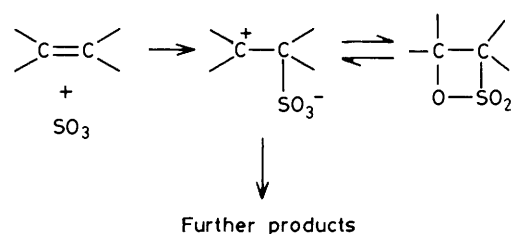
Evidence in favour of Mechanism 2 is provided by the observation of complete stereospecificity in the formation of  $\beta$ -sultones from reactions of the *cis* and *trans* isomers of but-2-ene and pent-2-ene with sulphur trioxide (both uncomplexed and as its 1:1 dioxane complex) in chloroform at  $0^\circ\text{C}$ .<sup>8</sup> However, this evidence does not completely rule out the stepwise mechanism (Mechanism 1), since it could be argued that ring closure of the zwitterionic intermediate is much faster than rotation about the bond between the carbon atoms  $\alpha$  and  $\beta$  to the sulphur atom.

In this paper we describe a relative rate study aimed at determining which of these two mechanisms is most applicable for the sulphonation of a range of simple olefins, and consider the orbital correlations relevant to Mechanism 2.

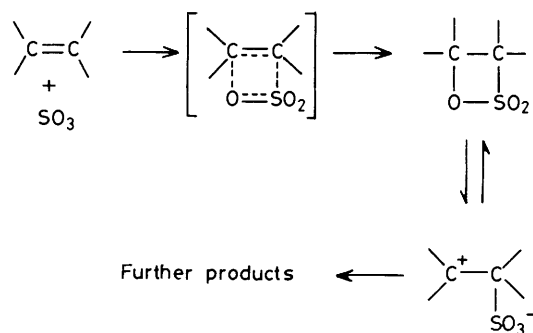
### Discussion

**Relative Rate Data.**—Competition experiments were carried out in which equimolar amounts of two olefins were treated with 0.5 molar equivalents of sulphur trioxide in dichloromethane at  $-50^\circ\text{C}$ . The conditions were chosen to ensure kinetic rather than thermodynamic control, and to avoid acid-catalysed isomerisation of the olefins. From the concentrations of unreacted olefins A and B, measured by gas-liquid chromatography, relative rate constants were calculated as in equation (1), where the subscripts o and f refer to initial and

$$\frac{k(\text{A})}{k(\text{B})} = \frac{\log([A]_f/[A]_o)}{\log([B]_f/[B]_o)} \quad (1)$$



Mechanism 1. Electrophilic addition



Mechanism 2. Concerted cycloaddition

final concentrations, respectively. This equation assumes that the kinetic form of the reaction is the same for both olefins A and B. In no case was there any evidence found for isomerisation of the unsulphonated olefins. The olefins studied are listed in Table 1.

No attempt was made to identify the final products from the competitive sulphonation reactions. Olefins of the types represented by I, III, IV, and V are known to give  $\beta$ -sultones under conditions of low-temperature sulphonation such as we have used; these sultones isomerise on warming to mixtures of alkenesulphonic acids and  $\gamma$ - and  $\delta$ -sultones.<sup>2,8-10</sup> The remaining olefins are all 2,2-dialkyl or 1,2,2-trialkyl derivatives of ethylene: there are no data on the low-temperature stability of the corresponding  $\beta$ -sultones, but sulphonation at room temperature and above of olefins of these types is known to give alkenesulphonic acids.<sup>2,9,10</sup> Table 1 shows the over-all relative reactivity data for the olefins studied. It can be seen that the most reactive olefin IX studied reacts only 3.4 times as fast as the least reactive olefin I, although the corresponding

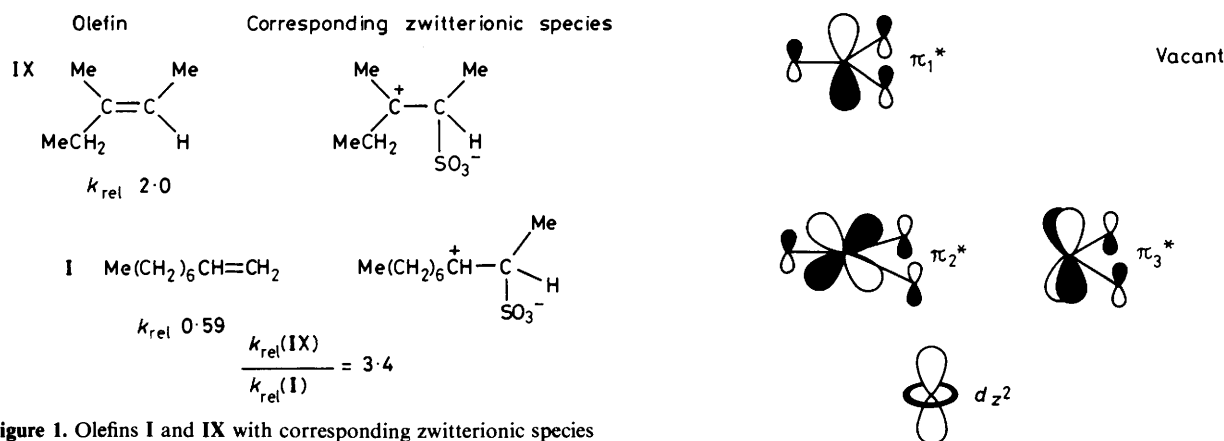
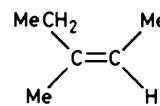
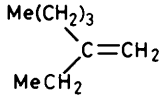
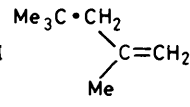
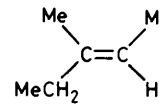


Figure 1. Olefins I and IX with corresponding zwitterionic species

Table 1. Relative rate constants ( $k_{rel}$ ) for reactions of olefins with sulphur trioxide in dichloromethane at  $-50^\circ\text{C}$

Olefin structure	$k_{rel}$
I $\text{Me}(\text{CH}_2)_6\text{CH}=\text{CH}_2$	0.59
II $\text{Me}_3\text{CCH}=\text{CMe}_2$	0.65
III $\text{Me}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{Me}$ <i>cis</i>	0.71
IV $\text{Me}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{Me}$ <i>trans</i>	0.71
V $\text{Me}(\text{CH}_2)_4\text{CH}=\text{CHMe}$ <i>trans</i>	0.71
VI 	0.88
VII 	1.00
VIII 	1.00
IX 	2.00

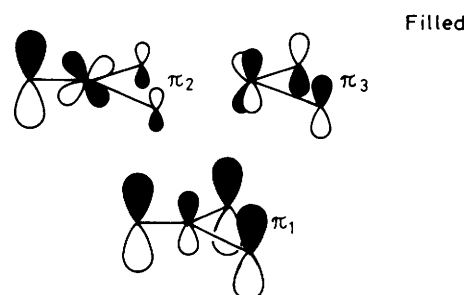


Figure 2. Sulphur trioxide orbitals perpendicular to the plane of the molecule

zwitterionic intermediates of Mechanism 1 have tertiary and secondary carbocation centres, respectively (Figure 1).

Contrasting this relative reactivity value with that for the limiting  $S_N1$  solvolysis of tertiary and secondary halides, which is thought<sup>11</sup> to be of the order  $k_{tert}/k_{sec} = 10^8$ , it seems clear that in the transition state for olefin sulphonation the  $\beta$  carbon atom of the incipient  $\beta$ -sulfone bears much less positive charge than would be expected on the basis of Mechanism 1.

An alternative explanation, that the narrow range of relative rates which we observe results from the reactions being partly diffusion controlled, can be dismissed. Kinetic data of Miyachi *et al.*<sup>12</sup> allow us to calculate that the rate for the homogeneous olefin sulphonation reaction is some three orders of magnitude slower than the limiting value for diffusion control.

In Table 2 the relative rate data for olefin sulphonation are presented in a different format and compared with published data for reactions of olefins with dihalogenocarbenes,<sup>13</sup> bromine,<sup>14</sup> chlorine,<sup>15</sup> peracetic acid,<sup>16</sup> and aqueous acid.<sup>17</sup> For these reactions the spread of olefin reactivities ranges from *ca.* 40 in the case of dibromocyclopropanation which, like

Table 2. Relative rate data for addition reaction of olefins. Rate constants relative to isobutene or 2-ethylhex-1-ene (for  $\text{SO}_3$  reaction)

Olefin	Reagent						
	$\text{CCl}_2$ , $25^\circ\text{C}$ , ref. 13	$\text{CBr}_2$ , $25^\circ\text{C}$ , ref. 13	$\text{Br}_2$ , $25^\circ\text{C}$ , ref. 14	$\text{Cl}_2$ , $25^\circ\text{C}$ or $-9^\circ\text{C}$ , ref. 15	$\text{MeCO}_3\text{H}$ , $25.8^\circ\text{C}$ , ref. 16	$\text{H}^+ - \text{H}_2\text{O}$ , ref. 17	$\text{SO}_3$ , $-50^\circ\text{C}$
$\text{R}-\text{CH}=\text{CH}_2$	0.03 <sup>a</sup>	0.07	0.01	0.02	0.05	$10^{-4}-10^{-3}$ ( $1.0^b$ )	0.59(I)
$\text{R}^1\text{CH}=\text{CHR}^2$ <i>trans</i>	0.18	0.35	0.31-0.68	0.87	1.01-1.40	$10^{-4}-10^{-3}$ ( $0.71^b$ )	0.71(IV,V)
$\text{R}^1\text{CH}=\text{CHR}^2$ <i>cis</i>	0.27	0.44	0.48-1.19	1.09		$10^{-4}-10^{-3}$ ( $1.68^b$ )	0.71(III)
$\text{R}^1\text{R}^2\text{C}=\text{CH}_2$	1.0	1.0	0.99-1.63	1.0-2.76	1.0	1.0	1.0(VII,VIII)
$\text{R}^1\text{R}^2\text{C}=\text{CHR}^3$	3.12	2.6	16.8-22.0	190	13.5	0.67	2.0(IX), 0.88(VI), 0.65(II)

<sup>a</sup> Based on data of P. S. Skell and M. S. Cholod, *J. Am. Chem. Soc.*, 1969, **91**, 7131. <sup>b</sup> Relative to propene.

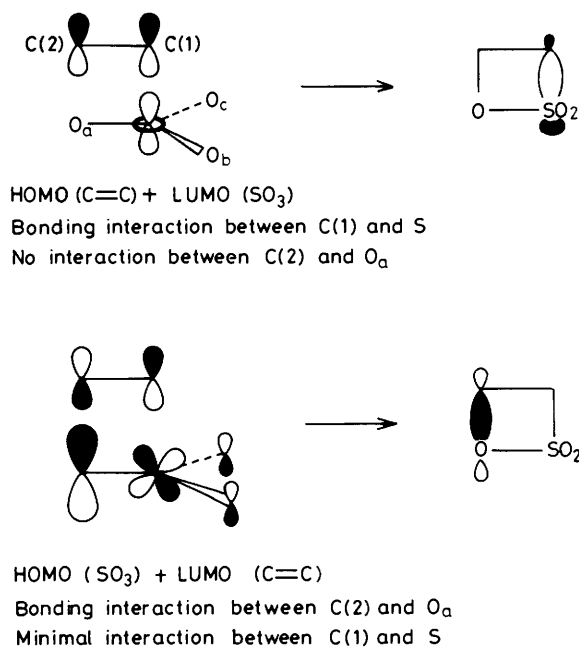


Figure 3. HOMO-LUMO interactions for [2<sub>s</sub> + 2<sub>s</sub>], direct

dichlorocyclopropanation (spread *ca.* 100), is known to proceed by a concerted mechanism<sup>13</sup> to about 10<sup>4</sup> for acid-catalysed hydration, which is believed to proceed *via* an intermediate carbenium ion.<sup>17</sup> It can be seen from Table 2 that the sulphonation reaction has a reactivity spread (3.4) smaller even than that of dibromocyclopropanation. The pattern of reactivity, with varying degrees and positions of alkyl substitution of the double bond, is roughly parallel for the dihalogenocyclopropanation and sulphonation reactions. Thus the relative rate data for sulphonation are consistent with Mechanism 2 but not with Mechanism 1.

**Orbital Correlations for Concerted Cycloaddition Reactions of Sulphur Trioxide with Olefins.**—The sulphur trioxide orbitals, excluding those in the plane of the nuclei, may be drawn as in Figure 2. On the basis of the He<sup>I</sup> photoelectron spectrum of sulphur trioxide,<sup>18</sup>  $\pi_2$  and  $\pi_3$  are taken as the HOMOs. We have found no data on the relative energies of the nonbonding and antibonding orbitals of sulphur trioxide: it seems reasonable to assume that  $\pi_2^*$  and  $\pi_3^*$  will be of higher energy than  $d_{z^2}$ , but the energy of  $\pi_1^*$  is more difficult to assign. In the following discussion it is assumed that  $d_{z^2}$  is the LUMO of sulphur trioxide. Since the  $3p_z$  orbital on sulphur is the major contributor to  $\pi_1^*$ , the properties of  $\pi_1^*$  as regards bonding-antibonding interactions with olefinic  $\pi$  orbitals are analogous to those of  $d_{z^2}$ , so that the same conclusions are reached irrespective of whether  $\pi_1^*$  or  $d_{z^2}$  is taken as the LUMO.†

The HOMOs and LUMO of sulphur trioxide are non-symmetrical, in a non-trivial sense, through the plane bisecting the S-O bond involved in cycloaddition. Thus it is not appropriate to represent the cycloaddition in conventional orbital symmetry formalism. Instead we consider the interactions of the HOMO and LUMO of sulphur trioxide with the

† If  $\pi_1^*$  is the LUMO then the net C-S bonding interaction between HOMO (olefin) and LUMO (sulphur trioxide) will be partly offset by an antibonding C-O interaction. However, since the coefficient of the sulphur  $3p$  orbital will be larger than that for the oxygen  $2p$  orbitals in the wave function for  $\pi_1^*$ , the C-S bonding interaction is predominant.

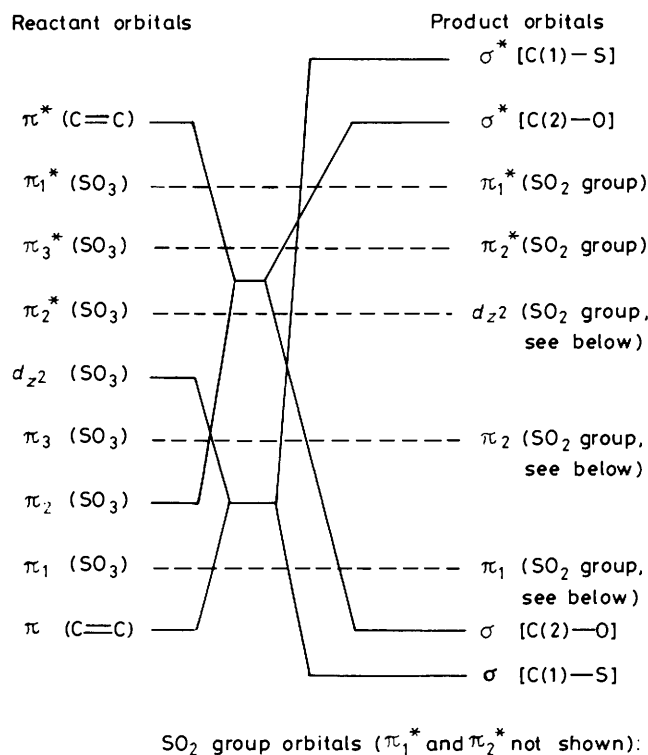


Figure 4. Correlations between reactant and product orbitals for [2<sub>s</sub> + 2<sub>s</sub>], direct

LUMO and HOMO of an olefin, and examine how these interactions correlate with the formation of new, *localised*, C-O and C-S  $\sigma$  and  $\sigma^*$  orbitals.

[2<sub>s</sub> + 2<sub>s</sub>] *Cycloaddition, direct.* For this mechanism, we assume the two reagents to approach each other as indicated in Figure 3. Figure 3 shows how a HOMO ( $\pi_2$ ) of sulphur trioxide can interact with the olefin LUMO to give  $\sigma$  C-O and how the sulphur trioxide LUMO interacts with the olefin HOMO to give  $\sigma$  C-S of the  $\beta$ -sultone. In each case, an analogous interaction in which one of the reagent orbitals is inverted gives the corresponding  $\sigma^*$  orbital. We conclude, from the orbital correlations shown in Figure 3, that the concerted [2<sub>s</sub> + 2<sub>s</sub>] cycloaddition is thermally allowed. Figure 4 shows how the other sulphur trioxide orbitals shown in Figure 2 can be correlated with orbitals in the  $\beta$ -sultone.

[2<sub>s</sub> + 2<sub>s</sub>], *via a  $\pi$ -complex.* A mechanism for the reaction of sulphur trioxide with alkenes can be envisaged whereby the sulphur atom approaches the olefin in the plane of its  $\pi$  orbital and along the bisector of the olefinic double bond. Figure 5(a) shows the bonding in the resulting  $\pi$  complex,  $\pi_2$  being used as the sulphur trioxide HOMO. Alternatively,  $\pi_3$  could be used as the sulphur trioxide HOMO, in which case the -SO<sub>3</sub> group would be rotated by 90° around the  $z$ -axis from the position shown. Since all linear combinations of the two degenerate

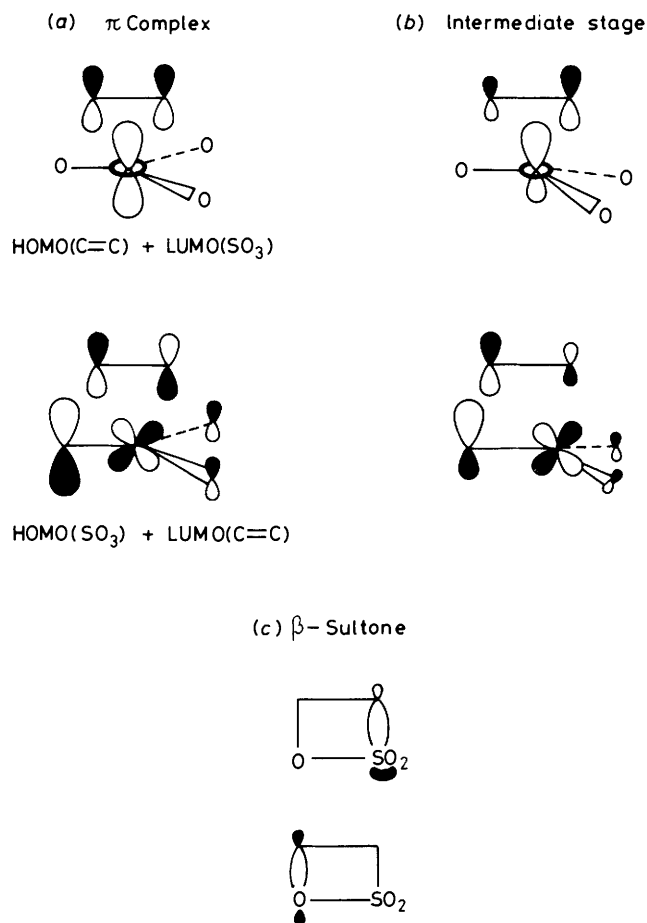


Figure 5. HOMO-LUMO interactions for  $[2_s + 2_s]$ , via a  $\pi$  complex

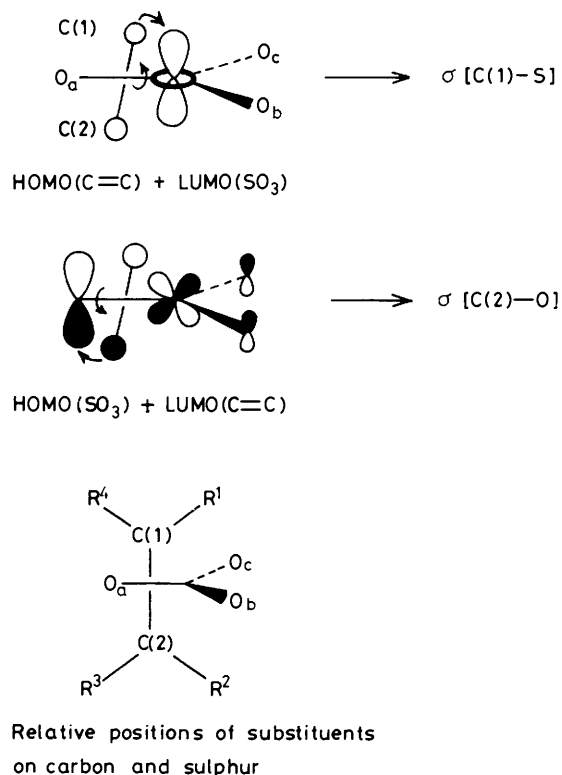


Figure 6. HOMO-LUMO interactions for  $[2_s + 2_s]$

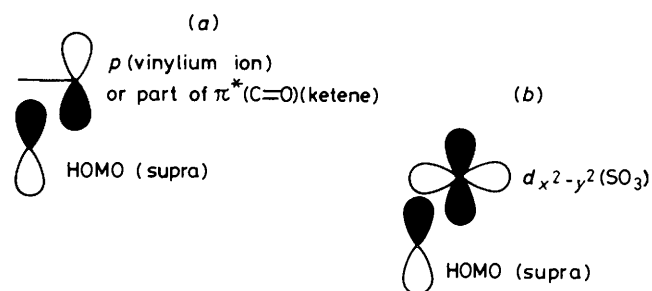


Figure 7. Secondary interactions for  $[2_s + 2_s]$  cycloadditions. Views along the double bond of the suprafacial component. (a) Ketene or vinylium ion as antarafacial component. (b) Sulphur trioxide as antarafacial component

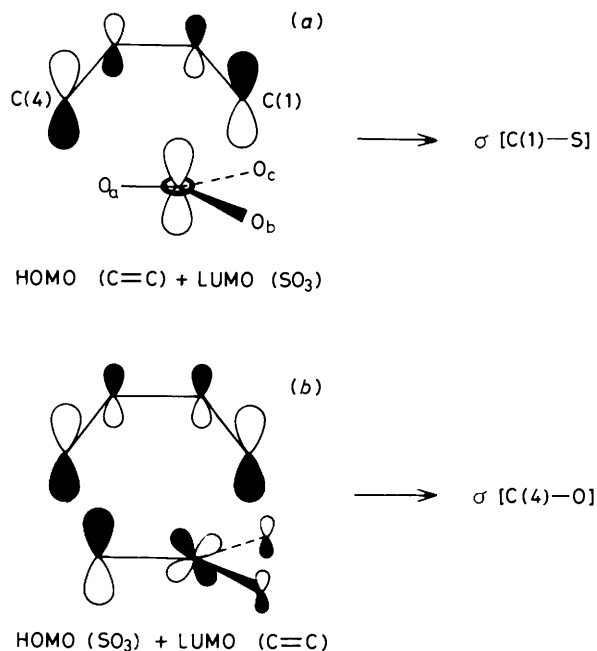


Figure 8. HOMO-LUMO interactions for  $[4_s + 2_s]$ . (a) Bonding interaction between C(1) and S; no interaction between C(4) and  $O_a$ . (b) Bonding interaction between C(4) and O; weak antibonding interaction between C(1) and S

HOMOs  $\pi_2$  and  $\pi_3$  are equally valid, it follows that rotation of the  $-\text{SO}_3$  group about the  $z$ -axis is allowed in the complex. Figure 5(b and c) shows how, by movement of the  $-\text{SO}_3$  group in the  $\pi$  plane, the bonding orbitals in the  $\pi$ -complex are transformed without discontinuity into the  $\sigma$  C-O and  $\sigma$  C-S orbitals of the  $\beta$ -sultone. Similarly, the antibonding combinations between the sulphur trioxide and olefin HOMOs and LUMOs are transformed into  $\sigma^*$  C-O and  $\sigma^*$  C-S of the  $\beta$ -sultone. Clearly, this mechanism is thermally allowed.

$[2_s + 2_s]$  Cycloaddition. If the  $[2_s + 2_s]$  mechanism applies to the sulphur trioxide-olefin reaction, the olefin must be the suprafacial component, to account for the observed retention of configuration in sulphonation of *cis* and *trans* olefins.<sup>8</sup> Figure 6 shows the interactions of the HOMOs and LUMOs, and shows how combinations of these orbitals can be correlated with the  $\sigma$  C-O and  $\sigma$  C-S bonds of the  $\beta$ -sultone.

It can be concluded that the  $[2_s + 2_s]$  mechanism is thermally allowed. However, it may be contrasted with the cycloaddition reactions of ketenes and vinylium ions.

For these reagents, which are believed to react as antarafacial components in  $[2_s + 2_s]$  cycloaddition reactions, it has been

argued that the presence of a low lying unoccupied  $\pi^*$  (for ketenes) or  $p$  (for vinylion ions) orbital orthogonal to the double bond involved in the cycloaddition is a special feature favouring the  $[2_s + 2_a]$  mechanism, since it gives rise to a strong secondary bonding interaction with the suprafacial component<sup>19,20</sup> [Figure 7(a)]. In the case of the sulphur trioxide-olefin  $[2_s + 2_a]$  mechanism, the unoccupied orbital orthogonal to the S-O  $\pi$  bond is the  $d_{x^2-y^2}$  orbital, or a low lying  $\pi^*$  orbital corresponding to interaction between  $d_{x^2-y^2}$  and  $p_x$  or  $p_y$  orbitals of oxygen. This orbital, as shown in Figure 7(b), has little if any net interaction with the suprafacial component. Thus we conclude that the  $[2_s + 2_a]$  mechanism is not favoured for sulphur trioxide cycloaddition reactions. The same arguments would apply to reactions of sulphenes.

If the  $[2_s + 2_a]$  mechanism did apply for the sulphur trioxide-olefin reaction, substantial steric effects would be expected. As shown in Figure 6, one of the oxygen atoms, destined to become part of the  $-\text{SO}_2-$  group of the  $\beta$ -sultone, is very close to two of the substituents,  $\text{R}^1$  and  $\text{R}^2$ , on the double bond. It follows that an olefin whose smaller substituent on C(1) is *cis* to the smaller substituent on C(2) would be expected to react faster than its *trans* isomer, since in the former case the two smaller groups could occupy the positions of  $\text{R}^1$  and  $\text{R}^2$ , in Figure 6. A similar argument applies to cycloaddition reactions of ketenes, for which the observations that *cis*-1,2-disubstituted ethylenes react more readily than their *trans* isomers have been cited as evidence for the  $[2_s + 2_a]$  pathway.<sup>21</sup> For sulphonation of the olefins shown in Table 1, III should be more reactive than IV or V, and VI should be more reactive than IX, on the basis of the  $[2_s + 2_a]$  mechanism. In fact III, IV, and V are all equally reactive and VI is less reactive than IX. Thus our relative rate findings do not support the  $[2_s + 2_a]$  mechanism.

$[4 + 2]$  for reactions with conjugated dienes. Interactions between the HOMOs and LUMOs for the  $[4_s + 2_s]$  reaction between sulphur trioxide and a conjugated diene are shown in Figure 8. It can be seen that the  $[4 + 2]$  reaction is thermally allowed but, since the distance between the terminal carbon atoms [C(1) and C(4)] of the diene (2.84 Å) is significantly greater than the S-O bond length in sulphur trioxide (1.43 Å<sup>22</sup>), the HOMO-LUMO interactions are probably weaker than in the  $[2_s + 2_s]$  case. Thus we conclude that the  $[2_s + 2_s]$  reaction is likely to be preferred.

In keeping with this conclusion, very few cases of formation of unsaturated  $\delta$ -sultones by sulphonation of conjugated dienes are known. Isoprene and 2,3-dimethylbutadiene are reported to give 2-methyl- and 2,3-dimethyl-but-2-ene sultones, respectively, in 48 and 18% yields, respectively, on sulphonation with a sulphur trioxide-dimethylformamide ( $\text{SO}_3$ -DMF) complex.<sup>23</sup> The latter sultone is also reported as being obtained in 16% yield from sulphonation of 2,3-dimethylbutadiene with a sulphur trioxide-dioxane complex.<sup>10</sup> No evidence has been presented as to whether these unsaturated  $\delta$ -sultones are formed directly or by a stepwise reaction pathway. Unsaturated  $\delta$ -sultones were not obtained in sulphonation of buta-1,3-diene, penta-1,3-diene, and cyclohexa-1,3-diene with  $\text{SO}_3$ -DMF.<sup>23</sup>

## Conclusions

Taken as a whole, the evidence for Mechanism 2 is quite compelling. Mechanism 2 is thermally allowed, it correctly predicts the stereospecificity of the sulphonation reaction, and unlike Mechanism 1 it is consistent with the relative reactivity data presented here. We therefore conclude that the initial step in sulphonation of aliphatic hydrocarbon olefins is a concerted cycloaddition to form a  $\beta$ -sultone. Orbital correlation analysis leads us to favour the  $[2_s + 2_s]$  pathway for the cycloaddition,

but on the basis of the present data it is not possible to decide whether the  $\beta$ -sultone is formed directly or *via* an intermediate  $\pi$  complex. It remains to be established whether Mechanism 2 also applies to other olefin types, such as fluoro-olefins.

Our orbital correlation analysis also leads us to conclude that for concerted cycloaddition reactions of sulphur trioxide, none of the possible pathways are thermally disallowed in any absolute sense. However, by considering in a simple qualitative manner the relative magnitudes of the HOMO-LUMO interactions, some pathways can be seen to be more favoured than others. In a further paper we will consider whether this is a general feature of cycloaddition reactions involving non-symmetrical reagents.

## Experimental

**Materials.**—Sulphur trioxide was obtained by distillation of a stabilised commercial sample of liquid sulphur trioxide (Sulfan).

Olefins I, II, IV, V, VI, VIII, IX (Fluka), and VII (Pfalz and Bauer) were purchased and used as supplied. Olefin III (*cis*-oct-4-ene) was prepared by a Wittig procedure based on a literature method for *cis*-unsaturated carboxylic acids,<sup>24</sup> as described below.

**Preparation of *cis*-oct-4-ene.** n-Butyl iodide (92 g, 0.5 mol) and triphenylphosphine (162 g, 0.6 mol) were heated together in refluxing toluene (700 ml) for 8 h. The reaction mixture was left to stand overnight, then filtered to give n-butyltriphenylphosphonium iodide as a white solid (200 g, 88% yield).

Dry dimethylformamide (350 ml) was added to a solution of sodium ethoxide (27 g, 0.4 mol) in absolute ethanol (75 ml), under a nitrogen atmosphere, with cooling (ice). The n-butyltriphenylphosphonium iodide was then added.

The mixture was stirred for 1 h at room temperature, then a solution of butyraldehyde (18 g, 0.25 mol) in dimethylformamide (20 ml) was added over a period of 2 h. After standing at room temperature overnight the reaction mixture was diluted with water and extracted with pentane. The pentane extract was distilled at atmospheric pressure, discarding early and late fractions, to give a product (b.p. 120 °C) found by g.l.c. to consist of *cis*-oct-4-ene, 89%, and *trans*-oct-4-ene, 11%. This material was used as *cis*-oct-4-ene in the competition experiments described below, allowance being made for its *trans* isomer content.

**G.l.c. Analysis.**—A Perkin-Elmer Sigma 3B dual f.i.d. gas chromatograph was used for g.l.c. analysis of olefin mixtures; 2 m columns were used, packed for all but the final 22 cm with 25% w/w ethylene glycol saturated with silver nitrate on Chromosorb (80–100)W. The final 22 cm were packed with 3% OV1 on 100–120 Gas-Chrom Q. The temperature programme was varied slightly from experiment to experiment in order to achieve optimum separation of peaks: a typical programme was 25 °C for 4 min, 25 to 70 °C at 2.5 °C min<sup>-1</sup>, 2 min at 70 °C.

**Competition Experiments.**—Solutions of pairs of olefins in dry dichloromethane were made up so as to be 0.1M in each olefin. The solutions were examined by g.l.c. to determine the relative peak areas for the two olefins and thereby determine response factors.

Each olefin solution (10 ml aliquots, 1 mmol of each olefin) was stirred under dry nitrogen and cooled to -50 °C, then a solution of sulphur trioxide (0.08 g, 1 mmol) in dry dichloromethane (1 ml) was introduced over a period of ca. 5 min by injection through a septum cap, with vigorous stirring. The resulting solutions were examined by g.l.c. to determine the relative amounts of the unreacted olefins, from which the ratio

of rate constants,  $k_A/k_B$ , was calculated using equation (1), and expressions (2) and (3),  $[B_f]$  being calculated similarly to  $[A_f]$ .

$$[A]_0 = [B]_0 = 0.1 = \text{initial concentrations of olefins A and B} \quad (2)$$

$$[A_f] = 0.1 \left( \frac{\text{corrected peak area for A}}{\text{combined corrected peak areas for A and B}} \right) \quad (3)$$

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