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RATES OF ADDITION OF SULPHUR DIOXIDE TO SOME 1,3-DIENES

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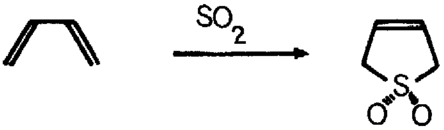
The formation of Δ^3-sulpholenes by the cycloaddition of sulphur dioxide to dienes is a well-known reaction which has been widely interpreted as a concerted (4+2) cheletropic process[1-3]. While a few qualitative observations concerning the ease of addition of various dienes have been made [4,5], no kinetic measurements have been made which could attempt to evaluate the importance of structural changes on reactivity and compare these with the more familiar Diels-Alder reaction. We now report rates of addition of SO_2 to 14 butadiene derivatives.



Rates of addition were carried out in benzene solution at 30° and with initial diene:SO_2 ratio greater than 20:1, following the disappearance of SO_2 spectrophotometrically at 320 nm . Pseudo first-order kinetics were observed , the rate constants being given in Table 1. Rates at four temperatures were measured for seven of the dienes permitting the determination of activation parameters for these cases.

The electronic effects of the substituents clearly affect the rates, an electron-withdrawing group reducing the activity of the diene:R=Me$>$$CH_2Br$$>$ Cl. From rates of addition to the limited series of 2-arylbutadienes a value of $\rho \sim -1.1$ is indicated. This may be understood as an increase in the attractive interactions between the reagents the more nucleophilic the diene. The earlier qualitative observation, p-NO_2 $>$ H in this series we believe due to the reaction between p-nitrophenylbutadiene and SO_2 taking a different course than the formation of a sulpholene [5] . The rates of reactions in Table 1 show them to be influenced to a considerable degree by the steric effects of 2-substituents. The rate order ; 2-Me $<$ 2-Et $<$ 2-isoPr $<$ 2-tertBu probably is a result of the tendency of the more bulky groups to favour the cisoid conformation of the diene which must be essential to reaction. Little is known of the activation barriers involved in this series of dienes though isoprene,unlike butadiene, is known to favour the s-cis conformation [6] . In support of this, the rigid cisoid diene,14, is considerably more reactive than the non-rigid but electronically similar 11.

Table 1

	-Butadiene	$10^4 k/min^{-1}$(30) (± 1-2%)		E_A/kcal mol^{-1}	log A	ΔH/kcal mol^{-1}	ΔS/cal mol^1K^1
		absolute	relative				
1	2-methyl	1.83	1.00	15.6	5.76	14.9	-15
2	2-ethyl	4.76	2.60	11.2	3.0	10.6	-20
3	2-isopropyl	13.0	7.38	13.1	4.8	12.5	-17
4	2-tert.butyl	38.2	20.8	10.6	3.4	10.0	-19
5	2-neopentyl	17.2	9.4	12.2	4.2	11.6	-18
6	2-chloro	0.24	0.13				
7	2-bromomethyl	0.72	0.39				
8	2-*p*-tolyl	24.7	13.5	11.0	3.4	10.4	-19
9	2-phenyl	17.3	9.45				
10	2-(*p*-bromophenyl)	9.07	4.96				
11	2,3-dimethyl	3.54	1.93	12.9	4.14	12.3	-18
12	*cis*-1-methyl	0.18	0.10				
13	*trans*-1-methyl	0.69	0.38				
14	1,2-dimethylene-cyclohexane	24.7	13.5	12.0	5.3	11.4	-16
15	2-methyl-1,1,4,4-d_4	1.96					

There is little data available by which to compare these rates with those of Diels-Alder reactions of the dienes. However the additions of tetracyanoethylene to 1,6,10,11 and 12 occur at relative rates 1:0.045:1.47:1.53:49. There are qualitative similarities here but the 1-substituent appears to be slightly activating whereas with SO_2 additions it is deactivating. The secondary isotope effect (7.5%) is less than that found in the Diels-Alder reaction (19%) which should indicate the latter has the tighter transition state with greater bond reorganisation. The greater steric effect of 1-substituents with SO_2 addition is likely to be due to the more planar transition state and the eclipsing interactions developing between α-substituents and the sulphone oxygens, a feature absent in the former case.

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