

THE VOLUME PROFILE FOR A CHELETROPIC REACTION

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The volumes of activation and of reaction were measured for the reaction between sulphur dioxide and 2,3-dimethylbuta-1,3-diene to form 3,4-dimethylsulpholene. Values of ΔV and ΔV^* are -33 and -35 $\text{cm}^3 \text{mol}^{-1}$, respectively in accordance with a concerted reaction having a very product-like transition state.

INTRODUCTION

The volume profile for a reaction, the change in partial molar volumes for both activation and reaction, gives useful information concerning the nature of the transition state and its relationship with reagents and products.^{1,2} Although a large number of volume profiles for Diels–Alder reactions have been reported, those for chelotropic reactions, cycloadditions between dienes and a single atom 2π component, have not. Accordingly, we report here data for the best known reaction of this type, that between a 1,3-diene (2,3-dimethylbuta-1,3-diene) and sulphur dioxide, which leads quantitatively to the sulpholene, **1**.³ 2,3-Dimethylbuta-1,3-diene is fairly reactive towards SO_2 since it prefers a cisoid diene conformation.⁴ The disrotatory course of this reaction has previously been demonstrated and the pericyclic nature justified theoretically by Woodward and Hoffmann,⁵ so that prior expectations for the volume profile would be for large, negative values for both ΔV and ΔV^* , parallel to those for Diels–Alder reactions (around -35 $\text{cm}^3 \text{mol}^{-1}$). These volumes of activation are frequently even more negative than are the corresponding volumes of reaction, which is usually attributed to non-bonding interactions between the diene and substituents such as carbonyl groups on the dienophile in the transition state. Since it is difficult to see how such ‘secondary orbital interactions’ could be possible in a chelotropic reaction for steric reasons, the present measurements were undertaken in part to test the hypothesis.

EXPERIMENTAL AND RESULTS

A 1 cm path length spectrophotometer cell (Spectrociil) was filled with redistilled dimethylbutadiene and sulphur dioxide was passed in slowly through a capillary until the absorbance at 320 nm rose to around 1.5. A stopper having an open top connecting the cell by a capillary (Figure 1) was then inserted, filled to above the capillary with dimethylbutadiene- SO_2 and a quantity of mercury inserted in the top. In this way, pressure could be transmitted without damage to the cell while the reacting solution remained isolated from the surrounding medium. The apparatus was then placed inside a thermostated pressure vessel fitted with sapphire windows which was mounted inside the spectrometer. The vessel was filled with hexane as pressure-transmitting medium. After attaching the threaded closure, the apparatus was raised to the desired pressure by a hand pump. Progress of reaction was then monitored at 320 nm and first-order rate constants were obtained using the Guggenheim procedure.⁶

The volume of activation was obtained from equation (1) and a plot of $\ln k$ against p was found to be linear over the experimental range (Figure 2).

$$\Delta V^* = -RT \text{d}(\ln k)/\text{d}p \quad (1)$$

The volume of reaction, V , was determined by measurement of separate partial molar volumes for the reactants and product in hexane solution at concentrations, c , between 0.02 and 0.05 M. A Paar high-precision densitometer was used to measure densities of solutions (ρ) and solvent (ρ_0), obtaining values of V

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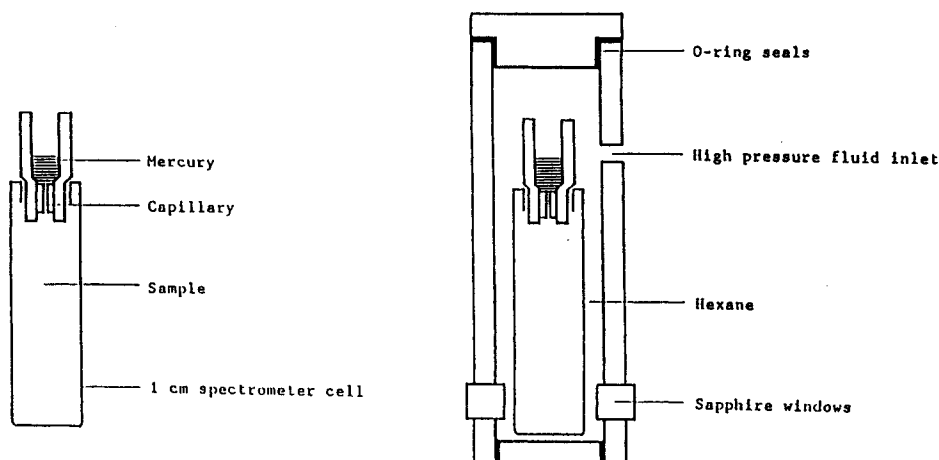


Figure 1. Pressure-equalizing spectrometer cuvette and arrangement in high-pressure cell

from the equation

$$V = \frac{1000(\rho_0 - \rho)}{\rho_0 C} + \frac{M}{\rho} \quad (2)$$

The results are given in Table 1.

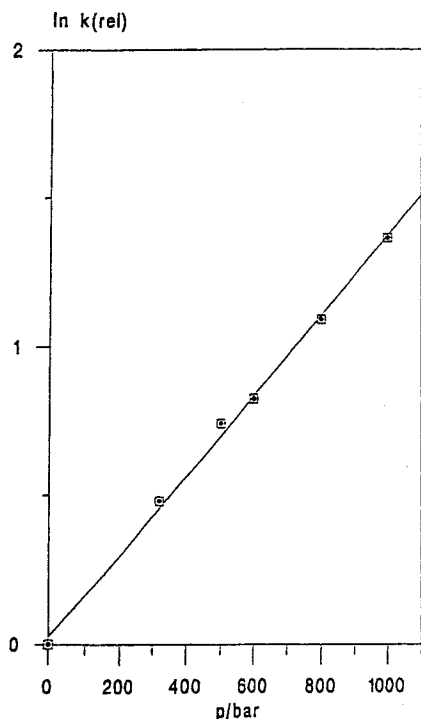


Figure 2. Plot of \ln (relative rate) for the reaction between 2,3-dimethylbuta-1,3-diene and sulphur dioxide versus pressure

Table 1. Reaction rates as a function of pressure

p (bar)	$10^5 k_1$ (s^{-1})	$\ln k_{rel}$
1	3.46	0.0
320	5.60	0.481
500	6.96	0.742
600	7.49	0.824
800	10.3	1.090
1000	13.5	1.365

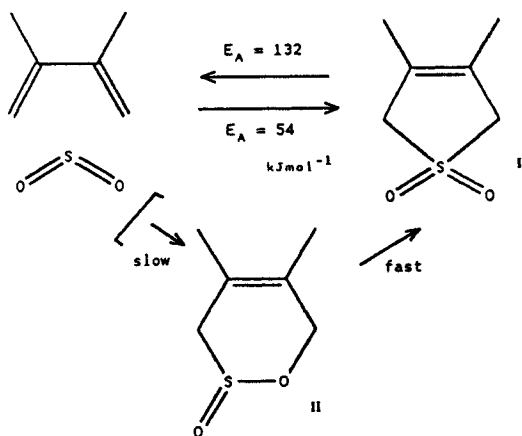
The linear least-squares gradient was $(1.347 \pm 0.02) \times 10^{-7}$ with a correlation coefficient of 0.9988. The volume of activation was $-35.0 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$. Partial molar volumes were as follows: dimethylbutadiene, $117 \text{ cm}^3 \text{ mol}^{-1}$; dimethylsulpholene, $122 \text{ cm}^3 \text{ mol}^{-1}$; and sulphur dioxide, $38 \text{ cm}^3 \text{ mol}^{-1}$. The volume of reaction was $-33 \text{ cm}^3 \text{ mol}^{-1}$.

DISCUSSION

The results show that the transition state for this reaction is very close in volume to that of the product sulpholene. The almost negligible effect of solvent polarity on the rate of the reverse reaction, the thermal decomposition of the sulpholene,⁷ shows that there is no significant polar character in the transition state and hence it must lie very close in structure to the product and with bond reorganization almost complete. Values are both within the range common to Diels-Alder reactions.⁸ This can best be accommodated by a chelotropic mechanism. Further, similarly to observations on the Diels-Alder reaction, the volume of activation appears to be slightly more negative than the volume of

reaction with $\theta = 1.06$, where $\theta = \Delta V^*/\Delta V$. A value of >1 is frequently observed for Diels–Alder reactions⁹ and is interpreted as being due to ‘secondary orbital interactions,’¹⁰ attractive forces between the diene structure and *endo* substituent components in the dienophile. The magnitude of θ can reach values as high as 1.6 and in general increases with electron donor substituents on the diene and solvents of low polarity. The chelotropic addition of sulphur dioxide, however, would appear to be unsuited to interactions of this type since only a four-atom relationship exists between an oxygen and C-2 of the diene. If the measurements do indicate the presence of such intra-molecular attractive forces, they must operate over a considerable range of distance.

Alternatively, the rigidity and loss of freedom and the preference for an *endo* configuration of the transition state might originate elsewhere. In considering



the mechanism of this reaction, one cannot rule out a (4 + 2) cycloaddition at the S=O bond as the slow step, with rapid rearrangement of the resultant sulpheno-lactone, II. This has been demonstrated for a very few examples with II isolable and thermally convertible to I¹¹. The present measurements could not distinguish a process of this type but similar steric constraints on a value of $\theta > 1$ would seem to be present. One can say with confidence, however, that the reaction being observed is kinetically controlled since the activation energies for the forward and back reactions are 54 and 132 kJ mol⁻¹ respectively,^{4,7} but it is possible that the rate-determining step is the formation of II which subsequently undergoes rearrangement.

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