The Thermal Decomposition of Allylic Sulfinic Acids: A Study of a Retro-ene Transition State

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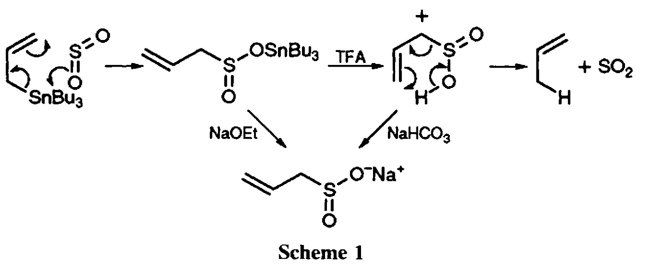
The thermal desulfination of allylsulfinic acid proceeds with a negative activation volume, solvent independence and a relatively small deuterium isotope effect which, together with the results of a previous stereochemical study, confirm a concerted retro-ene mechanism and suggest a relatively compact, early transition state.

Allylic sulfinic acids undergo a facile desulfination at ambient temperatures to yield the corresponding alkene with allylic transposition of the double bond.[1-7] Although this method has been employed synthetically, the instability of the substrate has hindered a detailed mechanistic study of this transformation. We recently reported that trialkyltin allylic sulfinates are convenient precursors to allylic sulfinic acids and their alkali metal salts (Scheme 1).[8] Acidolysis of the tin sulfinates rapidly yields the corresponding sulfinic acid, the decomposition of which can be conveniently monitored spectroscopically. Desulfination is first order with γ-*syn* hydrogen migration and a large negative entropy of activation ($\Delta S^{\ddagger} = -146 \pm 17$ J K^{-1} mol^{-1}) which is consistent with a concerted retro-ene mechanism (Scheme 1).[8]

To distinguish between a concerted and stepwise process and to provide additional transition-state information we have now conducted a study of the volume change and solvent and isotope effects which accompany desulfination. An activation volume was determined for the thermal decomposition of allysulfinic acid (prepared by trifluoacetolysis of tributyltin allylsulfinate) in dichloromethane by monitoring the appearance of SO_2 (315 nm) at elevated pressures. The spectrophotometer cell was capped with a mercury seal to allow pressure equalisation and placed in a thermostatted, high-pressure optical cell as previously described.[9] Two or three experiments were performed at each pressure and each obeyed a first-order rate law to completion. The plot of ln *k* against pressure (Fig. 1) was linear within experimental error.

An activation volume of -5.5 ± 1.0 cm^3 mol^{-1} was calculated according to the equation $\Delta V^{\ddagger} = -RT\cdot \mathrm{d/dp}(\ln k)$.[10] By monitoring the change in density during the course of the reaction it was possible to estimate a reaction volume of *ca.* 20 cm^3 mol^{-1}. The difficulty associated with determining the partial molar volume of the unstable allylsulfinic acid precludes a more precise figure. Nevertheless, a positive reaction volume together with a negative activation volume indicates a 'retro Diels–Alder like' volume profile[11] (Fig. 2) in which the transition state is more compact than the reactant (or the products). This result strongly supports a concerted rather than sequential pathway.

The value of -5.5 cm^3 mol^{-1} for the activation volume is also of comparable magnitude to that of a retro Diels–Alder reaction[11] and is consistent with a compact transition state by virtue of concertedness rather than charge development with electrorestriction of solvent.[10] The independence of rate on solvent (Table 1) supports this hypothesis.



Scheme 1

A deuterium kinetic isotope effect of 2.5 ± 0.1 at 297 K was determined by cleavage of tributyltin allylsulfinate with [^{2}H]-TFA in toluene and monitoring of the first-order desulfination by ^{1}H NMR spectroscopy. This relatively small k_H/k_D value

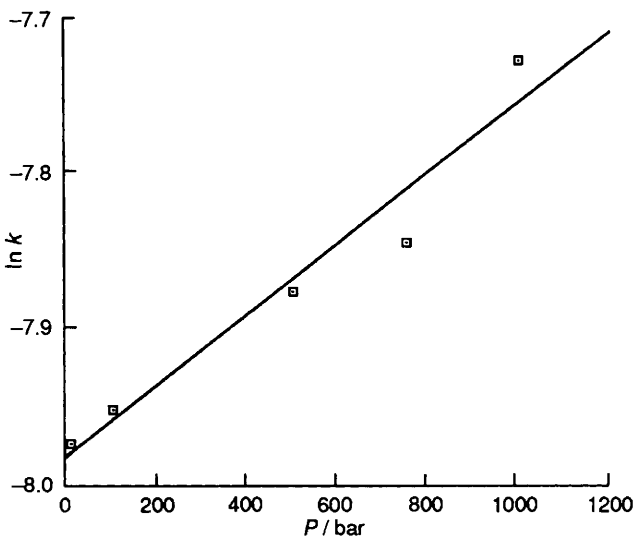


Fig. 1 Effect of pressure on decomposition of allylsulfinic acid

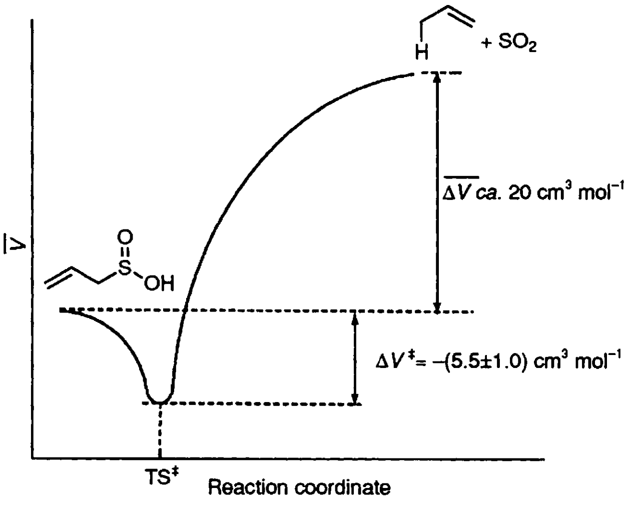


Fig. 2 Volume profile for decomposition of allylsulfinic acid

Table 1 Solvent dependence of decomposition

Solvent	Relative rate
Toluene	1.00
CH_2Cl_2	0.96
Acetone	1.05

indicates an unsymmetrical transition state which the values of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ suggest is rigid, compact and 'reactant like'. Together with our previous report of regio- and stereo-specific γ-*syn* hydrogen migration these results fulfill the criteria necessary for a concerted retro-ene mechanism.

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