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THE ACID-CATALYSED HYDROLYSIS OF ETHYLENE EPISULPHOXIDE

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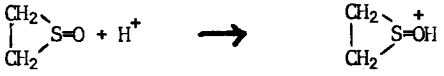
The formation of episulphones from the corresponding episulphides by oxidation with hydrogen peroxide is well documented (1). Only recently, however, has a successful partial oxidation procedure been reported (2) for the preparation of a number of episulphoxides.

Ethylene episulphoxide was found to undergo acid-catalysed nucleophilic attack with opening of the ring. Haskell and Paige suggested (2) that protonation occurs, followed by attack of the nucleophile on the conjugate acid to form a sulphenic acid (I). Due to the instability of alkyl sulphenic acids (3) the products obtained are a disulphide (II) and a thiolsulphonate (III), i.e.,


.......(1)


.......(2)

(I)

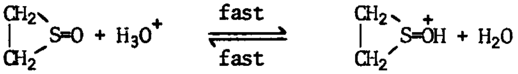
(I) $\longrightarrow (Y.CH_2.CH_2.S\text{-})_2 + Y.CH_2.CH_2.SO_2.S.CH_2.CH_2.Y$

(II) (III)

(where Y = HO^- or Cl^-)

In an attempt to determine the detailed mechanism of this reaction we now report preliminary kinetic studies of the perchloric acid catalysed reaction.

The value obtained for the kinetic deuterium solvent effect on the hydrolysis of ethylene episulphoxide ($\underline{k}_1^{D_2O}/\underline{k}_1^{H_2O} = 2.4$) is characteristic (4) of reactions which proceed by pre-equilibrium proton transfer, i.e. specific hydrogen ion catalysis occurs



The variation of rate of hydrolysis with concentration of perchloric acid is shown in the Figure.

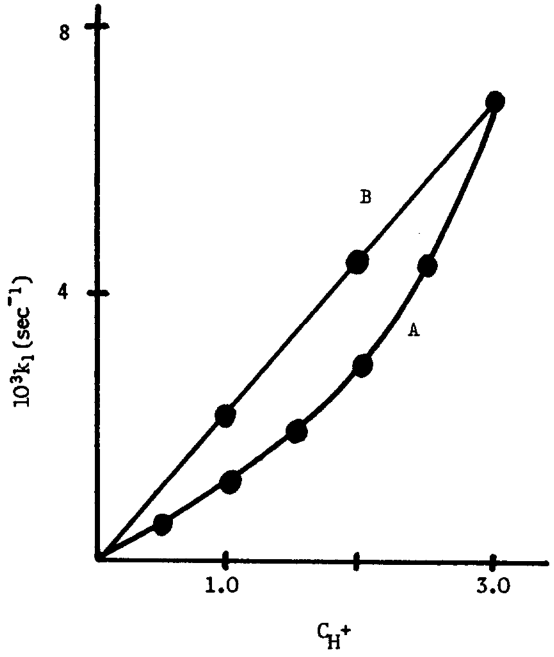
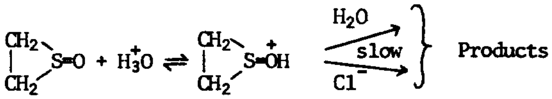


Figure. First-order rate coefficients, k_1 (5), for the acid-catalysed hydrolysis of ethylene episulphoxide in water at 25°. A, $HClO_4$; B, $HClO_4$ + $LiClO_4$ (3.0 molar)

The rate at first increases linearly with acid concentration but above ca 1.5 molar acid, increases more rapidly than does acid concentration.(A) Such positive deviations from linearity could be attributed to the superposition of a primary salt effect on the linear stoicheiometric acid dependence expected for a bimolecular (A-2) reaction on the basis of the Zucker-Hammett hypothesis (6). That this is indeed the case for ethylene episulphoxide is shown by the fact that, in mixtures of perchloric acid and lithium perchlorate at constant perchlorate ion concentration, the rate is directly proportional to stoicheiometric acidity.(B) The rate-determining step therefore involves nucleophilic attack on the conjugate acid by a water molecule. When hydrochloric acid is used as the catalysing acid, chloride ions compete with water as the nucleophile.



Another criterion of mechanism which can be used is the generalisation that for substrates of similar type a rather more positive entropy of activation would be expected for a unimolecular reaction, whereas the corresponding bimolecular reaction will show a relatively large negative entropy (7,8). The value for ethylene episulphoxide is $\Delta S^{\ddagger} = -8.20$ e.u. It is of interest to compare this value with those obtained for the hydrolysis of other three-membered rings e.g.

ethylene oxide (9) (-6.1 e.u.) and ethylene imine (10) (-9.4 e.u.). The mechanisms of hydrolysis of these other substrates have been the subject of much discussion but it is now thought that both hydrolyse by the A-2 mechanism (11) despite the relatively low $\Delta S^{\ddagger}$ values.

Examination of the pH-rate data according to Bunnett's treatment (12) of the function of water in rate-determining processes leads to a $\underline{w}$ value of 3.4. This falls into the range of $\underline{w}$ values associated with water acting as a nucleophile and provides further confirmation that the hydrolysis proceeds by an A-2 mechanism.

The hydrolysis of ethylene episulphoxide in the presence of acids as first reported by Haskell and Paige (2) is unexpected. Although the acid-catalysed equilibration and racemisation of five- and six-membered cyclic sulphoxides is well known (13), the hydrolysis of the sulphoxide group in such compounds has not been observed. In accord with this, trimethylene and tetramethylene sulphoxides showed no perceptible hydrolysis under the conditions used to follow the hydrolysis of ethylene episulphoxide or at much higher temperatures and concentrations of acid.

The rate of hydrolysis of the three-membered ring sulphoxide is therefore considerably greater than that of the corresponding five- and six-membered ring analogues. Such differences in rate towards acid-catalysed hydrolysis could be due to differences in basicity. Clearly, under catalysis by acids, greater basicity will favour increased protonation and hence increase the rate of reaction.

Tamres and Searles (14) showed that the basicity of cyclic sulphoxides varied with ring size in the order 6- $\geqslant$ 5- > 4-membered ring. The relative basicity of the three-membered cyclic sulphoxide has not previously been measured. Our results for the hydrogen-bonding ability (15) of cyclic sulphoxides are in qualitative agreement with those of Tamres and Searles and show furthermore that ethylene episulphoxide and trimethylene sulphoxide have approximately equal basicity.

The enormous reactivity of the three-membered ring relative to that of other cyclic sulphoxides is not due therefore to the relative basicity of its exocyclic oxygen atom but must arise from the relief of angular strain on ring opening.

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