EFFECT OF RING SIZE ON THE OXIDATION OF SOME CYCLIC SULPHOXIDES WITH CHROMIUM(VI) IN AQUEOUS ACETIC ACID

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THE effect of ring size on reaction rates has proved to be useful to investigate the characteristics and magnitude of hybridization changes occurring at the reaction centre on going from the ground state to the transition state[1]. It is generally observed that reactions in organosulphur compounds are known to proceed with very little variation of co-ordination at sulphur or with the intervention of reactive intermediates with expanded co-ordination. The effect of ring size on various reactions of organosulphur compounds has been studied extensively[2-5].

Scorrano *et al*[5] reported the oxidation of some cyclic sulphoxides to sulphones with peroxybenzoic acid. The relative rates in the oxidation of four-, five- and six-membered ring sulphoxides in acidic medium are 1.43, 1.00 and 2.74, whereas in the alkaline medium the relative rates are 1.54, 1.00 and 1.50. These rates indicate only a slight variation in the rate with ring size. In both the acidic and alkaline medium the five-membered ring sulphoxide reacts at a slower rate.

It was therefore considered worthwhile to investigate the changes in the rates brought about by varying the ring size in the oxidation of some cyclic sulphoxides with chromium(VI). The four-, five- and six-membered ring sulphoxides [$(CH_2)_n SO$, $n = 3, 4, 5$] are chosen as the model substrates, since the variation in reaction rates in these systems should arise as a result of changes in angle strain and steric compression effects.

In the present study the rate constants for the oxidation of four-, five- and six-membered sulphoxides with chromium(VI) were measured at 30° and 40°. The experimental details are given elsewhere[6]. Second-order rate constants are calculated and presented in table 1.

A high rate for the oxidation of thietan-1-oxide is observed. This is possibly due to the partial oxidation of the highly strained four-membered ring with chromium(VI). An analysis of the oxidation product (TLC) showed that it contained not only sulphone but also other unidentified products. The oxidation products could not be isolated and hence the interpretation of the rate constant for the oxidation of thietan-1-oxide is somewhat misleading; of the remaining two, the six-membered ring sulphoxide reacts faster than the five-membered ring sulphoxide.

Table 1 *Data on the oxidation of cyclic sulphoxides with chromium(VI)*

Compound	$k_2 \times 10^4$ at 30° l.mol^{-1} sec^{-1}	$k_2 \times 10^4$ at 40° l mol^{-1} sec^{-1}	Relative rate at 30
Thietan-1-oxide	78.7	141.0	4.35
Tetrahydrothiopen-1-oxide	18 1	39.1	1 00
Tetrahydrothiopyran-1-oxide	26.3	53.3	1.45

The relative rates found for the oxidation of four-, five- and six-membered cyclic sulphoxides are respectively 4.35, 1.00, 1.45. In other systems, *e. g.* the borohydride reduction of cycloalkanones, large variations in rates occur on going from cyclobutanone to cyclohexanone, the relative rates being 38:1:23[7]. In this reaction $sp^2 \rightarrow sp^3$ rehybridisation at the reaction centre occurs on going from the ground state to the transition state, and the observed trend in relative rates results from changes in relief of strain angle and steric compression effects. No such large difference in rates is observed for the oxidation of cyclic sulphoxides; some rehybridization change at the reaction centre should occur on going from the ground state to the transition state but the rate constants suggest that they are very small.

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