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MECHANISM OF SULFUR EXTRUSION FROM THIIRANE

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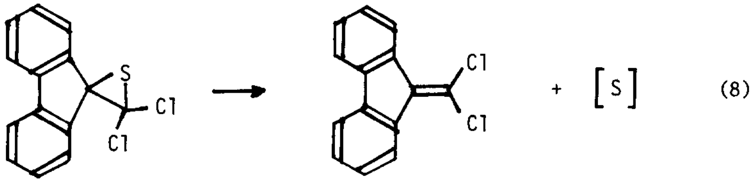
Summary: The thermal decomposition of thiirane 1 to olefin 2 is not a first order reaction, and is therefore not a simple chelotropic process.

There is a formal loss of one sulfur atom (molecular sulfur S°) in a number of reactions involving sulfur-containing compounds such as in chelotropic reactions (1) like decomposition of thiirane to olefin (2) and decomposition of thiosulfoxide to thioether (3). The absence of reaction products which could be attributed to the reaction of S° singlet or triplet, in the decomposition of dimethyl thiosulfoxide generated *in situ* and of a thionosulfite (4) raised the question of the nature of the sulfur atom lost in these and related reactions (5). Photochemical decomposition of carbon oxide sulfide has been shown to give S° in singlet and triplet state whose reactivity has been studied (6). The instability of thiosulfoxide and the large number of decomposition products of thionosulfite (5) excluded a kinetic study. The competition between the sigmatropic [2,3] shift of aryl allyl thiosulfoxide to disulfide and the sulfur extrusion to give a thioether has been studied (7). In 1920, STAUDINGER and SIEGWART prepared thiiranes and described their clean decomposition to olefins and sulfur in high yield (8). This reaction is very suitable for a kinetic study whose results are reported and discussed here. Indeed if the reaction 1 → 2 gives rise to one atom of sulfur, the process should be monomolecular.



1 2

The decomposition rate of 1 was determined in decalin at 100°±3°C in the absence of light. The results are presented in Fig. 1 and Table 1.

TABLE 1

Concentration of thiirane 1 mM	Added compounds	Rate constant [(a)] (sec^{-1})
1.0		$(9.0 \pm 0.3)\ 10^{-5}$
0.275		$(5.5 \pm 0.25)\ 10^{-5}$
0.10		$(5.0 \pm 0.4)\ 10^{-5}$ [(b)]
0.275	0.31 mM $n\text{-}C_{18}H_{37}SCH_3$	$(5.3 \pm 0.2)\ 10^{-5}$ [(c)]
0.275	3.05 mM $n\text{-}C_{18}H_{37}SCH_3$	$(13.5 \pm 0.7)\ 10^{-5}$ [(c)]
0.66	0.09 mM S_8	$(6.0 \pm 0.6)\ 10^{-5}$
0.275	0.87 mM $(nC_8H_{17})_3P$	(d)

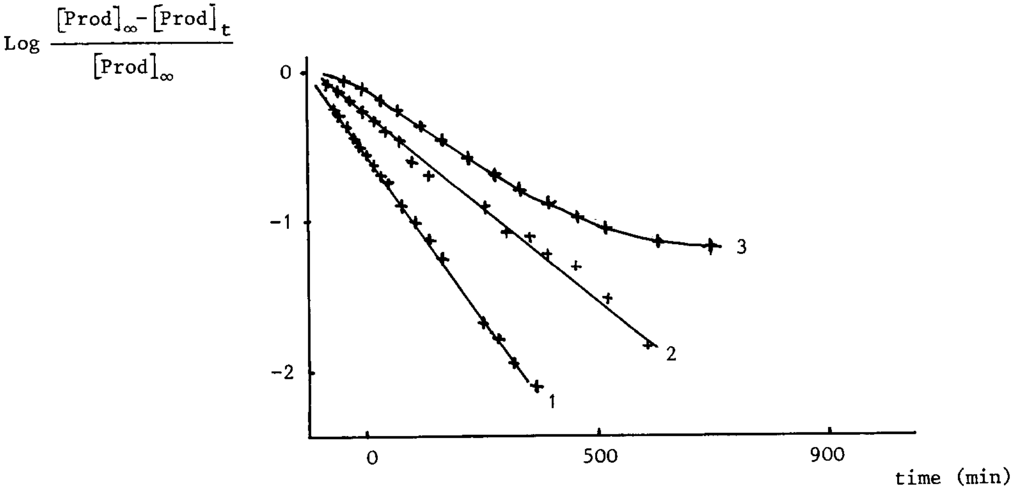
(a) determined by following the absorption changes at 318 nm and 260 nm. Exclusion of oxygen did not influence the kinetics.

(b) calculated from 130 to 430 minutes.

(c) with reaction vessel washed with piperidine (measurement at 318 nm).

(d) after 15 min, the reaction was found to be over.

FIGURE 1

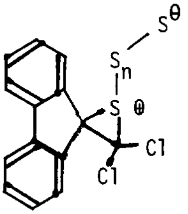


Dependance of Log of the ratio of indicated concentrations of olefin 2 with time t (minutes) during the decomposition of thiirane 1 to olefin 2 at 102±2°C in decalin at initial concentration of thiirane 1
1: 1.0 mM ; 2: 0.275 mM ; 3: 0.10 mM.

The thiirane decomposition is not of first order and an induction period noticeable at higher concentration extends beyond 100 min at 0.1 mM concentration. Addition of octadecyl methyl thioether (0.31 mM) or sulfur S_8 (0.09 mM) showed only minor effects on the rate. With trioctylphosphine, a tremendous increase of the decomposition rate was found, due to the direct attack of the phosphine on the thiirane.

In repeating the decomposition of thiirane in presence of thioether in the same reaction vessel washed with acetone, it was found that the decomposition rate was reduced. When the reaction vessel was cleaned with piperidine, the reaction rate was reproducible. Such an effect was not found in the absence of thioether.

$$1 + A \rightarrow 2 + AS$$



3 (n=0,1,2...)

In conclusion, the decomposition of thiirane 1 to the olefin 2 is not first order and is thus not a simple chelotropic reaction (9). A more complex reaction scheme is involved. Likely the thiirane 1 reacts with a species A which accepts the sulfur atom to give the olefin 2 and AS species which reacts further with another molecule of thiirane. The induction period is due to the pre-steady state and the linear period (in Figure 1) due to a steady state (10). A structure like 3 (11) for 1 seems excluded by the experiment where a thioether was added. Indeed, the thioether could also act as a sulfur acceptor (12). The reaction of 1 with sulfur S_n ($n < 8$) generated during the induction period is not to be rejected. S_8 is known to be less reactive than S_6 and S_7 (13). The nature of A remains unknown and a surface effect is not excluded. However the present experiments do not exclude that the atomic sulfur is slowly extruded during the induction period. Other sulfur extrusion reactions should be examined in this respect.

The conversion of thiiranes to olefins with phosphines and other phosphorus derivatives occurs in syn manner (14) and likely involves attack of phosphor on the sulfur (2a). As expected, the reaction rate $1 \rightarrow 2$ is greatly increased in presence of trioctylphosphine. Is this chelotropic reaction concerted ?

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