Flash Thermolysis: Evidence for Sulphene Formation in the Fission of Thietan Derivatives

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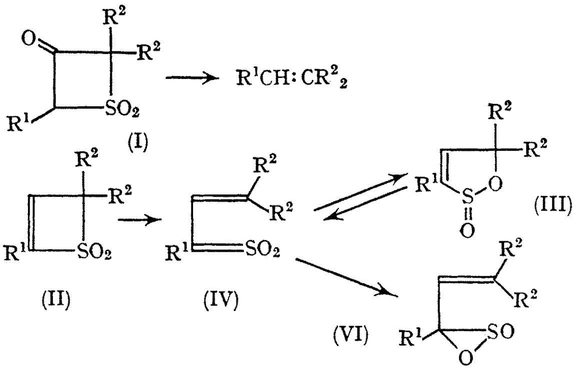
IN continuation of our efforts to generate sulphenes[1,2] by physical methods we have subjected a number of thietan derivatives to flash thermolysis.† We suggest that sulphenes are produced in certain instances, but that, under the conditions of formation, they rearrange.

Th thermolysis of the ketones (I; $R^1 = H$, $R^2 = H$), (I; $R^1 = Ph$, $R^2 = H$), and (I; $R^1 = H$, $R^2 = Me$) (at 930—950°) failed to provide evidence for sulphene intermediacy, the overall reaction in three cases being loss of carbon monoxide and sulphur dioxide and formation of the corresponding alkene (96—98%). There is ample analogy for carbon monoxide loss by thermal and photolytic means.[3]



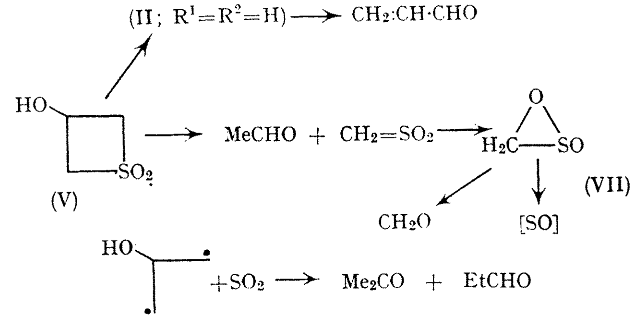
The low-temperature (600°) thermolysis of the thiet 1,1-dioxides (II; $R^1 = H$ or Ph, $R^2 = H$) gave different results in that fragmentation was not observed, but rather, the formation of the cyclic sulphinates (III; $R^1 = H$ or Ph) as described in the accompanying Communication[4] possibly *via* the vinyl sulphene (IV; $R^1 = H$ or Ph, $R^2 = H$).

The flash thermolysis of the alcohol (V) (930—960°) gave results of greater direct significance. With methanol as a trapping agent, acetaldehyde and its dimethyl acetal were found (Table), which suggested that the desired fission had occurred. No methyl methanesulphonate could, however, be detected. Amongst the other products acetone and propanal may be considered as being derived by loss of sulphur dioxide and rearrangement within the diradical, or closure to cyclopropanol.

The fate of the sulphene moiety, the formation of formaldehyde, the low yield of sulphur dioxide, and the formation of acrolein were rationalised when high-temperature (*ca.* 1000°) flash thermolyses of the thiet dioxides (II) were investigated.

The thermolysis at 950° has been shown to give acrolein (84%). In like manner from the phenyl derivative (II; $R^1 = Ph$, $R^2 = H$) phenyl vinyl ketone was obtained (85%) as was 3-methylbut-2-enal (72%) from (II; $R^1 = H$, $R^2 = Me$). In two cases (II; $R^1 = H$, $R^2 = H$; and $R^1 = Ph$, $R^2 = H$) no sulphur dioxide was detected and in the third *ca.* 15%: it was the latter which gave the lowest yield of carbonyl compound. The extruded moiety 'sulphur monoxide' was observed as a red material on the Dewar surface which was transformed into a yellow polymer on being warmed to room temperature. This behaviour is compatible with disproportionation of sulphur monoxide to disulphur monoxide and polymerisation of the latter to poly(sulphur oxide).[5]

Although the thiet 1,1-dioxides at lower temperatures give cyclic sulphinate[4] (III) it seems unlikely that these substances are intermediates in the formation of the aldehydes. Loss of sulphur monoxide from (III; $R^1 = Ph$, $R^2 = H$) would be expected to give β-phenylacrolein, but, in fact, the thermolysis of that substance at 930° gives phenyl vinyl ketone (83%). A reasonable explanation is that, as suggested,[4] (III) itself is formed through the vinyl sulphene (IV) with which, at 400—600°, it is in equilibrium. At the higher temperatures the equilibrium is disturbed irreversibly, the sulphene undergoing an "abnormal" attack[4] upon itself, *i.e.* a nucleophilic addition of oxygen on



The products of the flash thermolysis of (V)

Product	MeCHO	MeCH(OMe)$_2$	CH$_2$(OMe)$_2$	EtCHO	Me$_2$CO	CH$_2$=CH·CHO	C$_2$H$_4$	SO$_2$
Yield*	3·7	23·7	6·3	22	25	3	8·5	42

* The organic compounds were estimated by g.l.c. with methyl formate as calibrating compound. The yields of aldehydes are probably low because of polymerisation and incomplete acetal formation. Sulphur dioxide was estimated volumetrically (I_2–$Na_2S_2O_3$).

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† By the term 'flash thermolysis' we imply high temperature gas phase conditions in which the contact time is of the order of msec. or less. The present apparatus consists of a heated ceramic tube operating in a flow system in the micron pressure range. The pyrolysate, after emergence from the hot zone is immediately condensed on the surface of a liquid nitrogen Dewar. A similar apparatus has been described very recently (E. Hedaya and D. McNeil, *J. Amer. Chem. Soc.*, 1967, **89**, 4213). We thank Dr. Hedaya for several useful discussions. The thermolyses were carried out at about 1—5 microns pressure at the temperature indicated with a contact time of approximately 1 msec.

the sulphene carbon. The resulting cyclic isomer (VI), on loss of sulphur monoxide, then yields the observed products. The literature provides some analogy[6] for loss of sulphur monoxide,[7] although it has been but rarely observed and in a recent compilation received but one reference.[3]

The acrolein obtained in the thermolysis of the alcohol (V) may then be understood if prior dehydration to (II; $R^1 = R^2 = H$) is assumed. The formaldehyde may be formed from sulphene *via* (VII) itself by an equivalent rearrangement to that of the vinyl sulphene. Under these circumstances sulphur dioxide would derive only from the processes leading to acetone and propanal. It will be noted that these combined yields (47%) are near that of sulphur dioxide.

These results suggest that sulphenes are indeed intermediates in the thermolysis of certain thietan derivatives, but that their conversion in the gas phase to carbonyl compounds is a general reaction.

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[1] C. L. McIntosh, and P. de Mayo, *Tetrahedron Letters*, 1967, **1**, 37.

[2] P. de Mayo, E. Morkved, J. F. King and A. Stoessl, *Canad. J. Chem.*, 1963, **41**, 100; J. L. Charlton and P. de Mayo, *ibid.*, 1968, **46**, 55.

[3] For a review, see B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press, 1967.

[4] J. F. King, K. Piers, D. J. H. Smith, C. L. McIntosh, and P. de Mayo, preceding Communication.

[5] P. W. Schenk and R. Steudel, *Angew. Chem. Internat. Edn.*, 1965, **4**, 402.

[6] E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, 1966, **88**, 2836; R. D. Chambers and J. A. Cunningham, *Chem. Comm.*, 1967, 583; G. E. Hartzwell and J. N. Paige, *J. Amer. Chem. Soc.*, 1966, **88**, 2616.

[7] The most recent work (S. Saito, *Tetrahedron Letters*, 1968, 4961) suggests that the sulphur monoxide formed in the pyrolysis of ethylene episulphoxide, a close model for the present elimination, is in the triplet (ground) state.