A Novel Unimolecular Heterolytic Scission of the Sulphur–Sulphur Bond in a Symmetrical Disulphide

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Summary The thermal heterolytic scission of two symmetrical disulphides to give the parent thiol and a mesoionic compound containing two fewer hydrogen atoms is shown to follow first-order kinetics in a variety of solvents; there is a linear correlation between log *k* and the polarity parameters *Y* and *Z*.

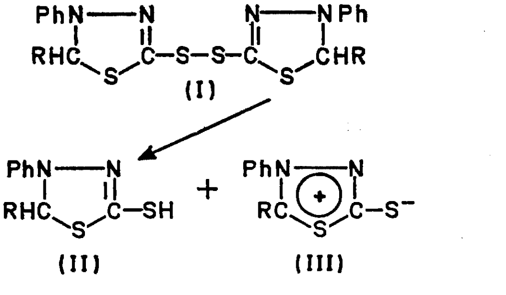
ALTHOUGH there have been many studies of bimolecular heterolytic scission of sulphur–sulphur bonds in organic disulphides, R^1–S–S–R^2, by both nucleophilic[1,2] and electrophilic reagents[3] no unambiguous example of a unimolecular heterolytic scission in this class of compounds appears to have been reported. Heterolytic bond cleavage does not occur in the gas phase: in solution the possibility of heterolysis would be favoured by the participation of the solvent, more especially if this is polar.

In 1895 Busch[4] observed that the disulphide (I; R = H) obtained by the oxidation of the thiol (II; R = H) underwent spontaneous fission on melting or on standing in chloroform solution to give equal amounts of the parent thiol and a compound containing two fewer hydrogen atoms which was later formulated by Baker as the mesoionic compound (III; R = H).

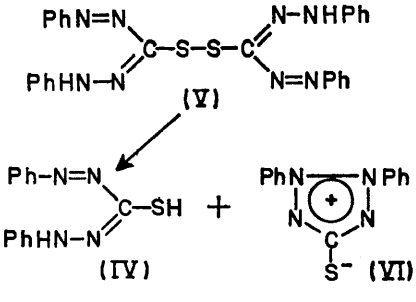
Qualitative observations showed that the ease of scission was much reduced when R = Me or Ph.

We have studied the reaction for R = H in a number of solvents and find it to be first order with respect to the bis-thiadiazoline (I; R = H) in every case. The rate of reaction, *k*, was found to increase as the polarity of the solvent increases and there is a good linear correlation between log *k* and the polarity parameter *Z* of the solvent[6] (Figure 1). Values of ΔH are found to lie within the range 3·3—4·2 kJ mol^{-1}. Values of ΔS within the range 4·0—7·5 J deg^{-1} are consistent with some interaction between the solvent and a charge-separated species in the transition state. The addition of protons [*e.g.* by adding trichloroacetic acid to the chloroform solution of (I)] considerably accelerated the reaction: pyridine had no effect.

The reaction between dithizone (IV) and an oxidant such as iodine in neutral conditions or Se^{IV} in acidic conditions has been shown to yield bis-(3-mercapto-1,5-diphenylformazan) and this disulphide (V) which gives


(I)

(II) (III)


(V)

(IV) (VI)

orange-yellow solutions in a variety of solvents undergoes spontaneous scission at room temperature to give the green thiol (IV) and an orange mesoionic compound (VI) containing two fewer hydrogen atoms.[7] Here again the reaction has been found to be first order with respect to (V) and the rate increases with the polarity of the solvent (Figure 1). When the reaction is conducted in ethanol-water mixture log k is found to be a linear function of the solvent polarity parameter[8] Y (Figure 2).

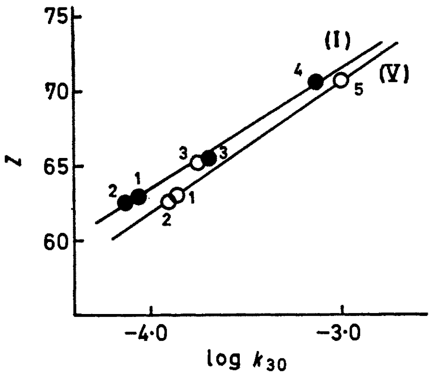


FIGURE 1. *Correlation with* Z *values of the rates of decomposition of bis-*(2-*mercapto*-4-*phenyl*-Δ^2-1,3,4-*thiadiazoline*) (I) (*black circles*), *and bis-*(3-*mercapto*-1-5-*diphenylformazan*) (V) (*open circles*) *in organic solvents at* 30°. 1. $CHCl_3$; 2. $ClH_2C.CH_2Cl$; 3. Me_2CO; 4. Me_2SO; 5. MeCN.

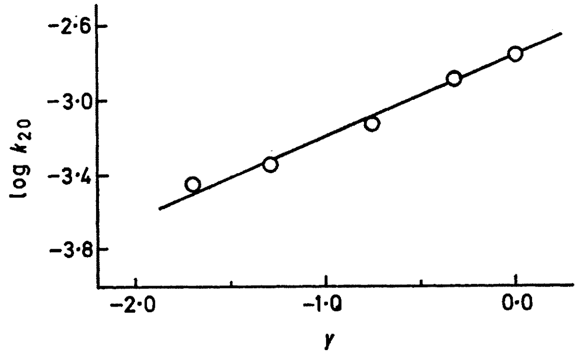


FIGURE 2. *Correlation with* Y *values of the rate of decomposition of bis-*(3-*mercapto*-1,5-*diphenylformazan*) (V) *in ethanol-water mixtures.*

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