# Reaction of Some Sulphur Heterocycles with Methyl Fluorosulphonate

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*Summary* The enhanced reactivity of cyclic disulphides is related to the dihedral angle and the energy of orbital splitting as measured by photoionisation spectra.

IN a previous communication,[1] we suggested that the influence of lone pairs on reactivity may depend on the conformation of the nucleophile. We present here a quantitative demonstration of this effect for the reaction of disulphides with methyl fluorosulphonate in dimethyl sulphate. (Table 1).

The reactivities of the cyclic thio-ethers are similar to that of diethyl sulphide, but the rate of alkylation of the disulphides increases with decreasing ring size. This we attribute to increasing lone-pair–lone-pair repulsion with decreasing C–S–S–C dihedral angle ($\theta$). Each sulphur atom is largely unhybridised,[2] and hence the highest occupied orbital is mainly $p$-non-bonding. Combination of the adjacent lone-pair orbitals leads to orbital splitting measured by photoionisation spectra.[2]

In a simple treatment, the energies of the two orbitals, $E_+$ and $E_-$ are given by

$$E_+ = \frac{\alpha + \beta}{1 + S}; \quad E_- = \frac{\alpha - \beta}{1 - S}$$

where $\alpha$ and $\beta$ are Coulomb and resonance integrals respectively and $S$ is the overlap integral for $p_\pi p_\pi$ bonds. Using the Mulliken approximation, $\beta = \kappa S$, we have for the orbital splitting $(E_+ - E_-)$

$$\Delta E_\pi \simeq 2(\kappa - \alpha)S$$

Now for adjacent $p_\pi$ orbitals, the overlap integral, $S$ is proportional to cos $\theta$, so that

$$\Delta E_\pi \simeq 2(\kappa - \alpha)S_\pi \cos\theta \qquad (1)$$

The orbital splitting thus increases with cos $\theta$ (Table 2).

The repulsion energy, $\Delta E_r$ is given by

$$\Delta E_r = \frac{2(\alpha + \beta)}{1 + S} + \frac{2(\alpha - \beta)}{1 - S} - 4\alpha = \frac{4\alpha S^2 - 4\beta S}{1 - S^2}$$

$$\text{Thus, } \Delta E_r \simeq -4(\kappa - \alpha)S_\pi{}^2\cos^2\theta \qquad (2)$$

Table 1. *Rate of reaction of some sulphides and disulphides with methyl fluorosulphonate in dimethyl sulphate at* 25 °C

| Compound | $k_2{}^a$/l mol$^{-1}$ min$^{-1}$ | Compound | $k_2{}^a$/l mol$^{-1}$ min$^{-1}$ |
|---|---|---|---|
| Et·S·S·Et (**1**) .. .. .. .. .. .. | $6.05 \times 10^{-2}$ | Et·S·Et | 10·65 |
| 4*H*-2,3-dithianaphthalene .. .. .. .. | $1.04 \times 10^{-1}$ | thian | 10·45 |
| 1,2-dithian (**2**) .. .. .. .. .. | $2.00 \times 10^{-1}$ | thiolan | 8·05 |
| 5-[3-(1,2-dithiolanyl)]valeric acid (**3**) .. .. | 2·27 | | |

[a] The rate constant is corrected for the limited reaction with the solvent.

This gives a measure of the destabilisation of the nucleophile due to $p_\pi$–$p_\pi$ repulsion, which should produce an increase in reactivity. Table 2 shows that the relative reactivity of cyclic and acyclic compounds, $k_{Me}$ does increase with $\cos^2\theta$ as required by equation (2). Although at present the data are limited, the agreement is remarkably good (approx. ± 5% for the 3 rate values given in Table 2).

The photoionisation and kinetic data may be correlated in the following way. If the changes in reactivity, given by $k_{Me}$ (Table 2), are produced mainly by orbital splitting, the difference in the free energy of activation of cyclic and acyclic disulphides is given approximately by the following equation,

$$-RT \ln k_{Me} \simeq \beta^* \Delta E_r$$

The proportionality constant $\beta^*$ is expected to increase with the extent of bond formation in the transition state, as measured by the Brönsted coefficient or some other linear free energy parameter.

$$\text{Then } \frac{-RT \ln k_{Me}}{\cos^2\theta} \simeq 2\beta^* \; S_\pi\left(\frac{\Delta E_\pi}{\cos\theta}\right)$$

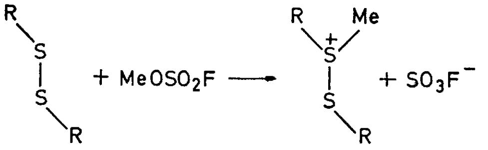

Table 2. *Comparison of reactivity and photoionisation data with the dihedral angle* ($\theta$)

| Compound | $\theta$° | $\Delta E_\pi$(eV)[2] | log $k_{Me}{}^a$ | $\cos^2\theta$ |
|---|---|---|---|---|
| (**1**) | 84·7[b] | 0·24 | 0 | 0·01 |
| (**2**) | 60[c] | 0·95 | 0·52 | 0·25 |
| (**3**) | 35[d] | — | 1·57 | 0·67 |

[a] $k_{Me}$ is the ratio of $k_2$ for the cyclic compound to $k_2$ for Et·S·S·Et. [b] D. Sutter, *Z. Naturforsch.*, 1965, **20a**, 1676. [c] O. Foss, K. Johnson, and T. Reistad, *Acta Chem. Scand.*, 1964, **18**, 2345. [d] R. M. Stroud and C. H. Carlisle, *Acta Cryst.*, 1972 **B28**, 304.

From the data of Table 2, taking $S_\pi$ for the –S–S– bond to be 0·16 as recommended by Mulliken[3] for Slater orbitals, $\beta^*$ is 0·21. This value is close to $\beta$ normally obtained for alkylation (values of 0·22—0·30 are reported[4]).

Although other factors, *e.g.* hybridisation changes and ring strain, will also affect the reactivity, the above analysis suggests that orbital splitting is the main factor to be considered.

One of us (F.F.) wishes to thank the Fondo Nazionale Svizzero per le Ricerche Scientifiche and the Stiftung für Stipendien auf dem Gebiete der Chemie for a research fellowship.

(*Received*, 24*th March* 1972; *Com.* 493.)

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