# Evidence for a Linear Sulphurane Intermediate in the Oxidation of Sulphoxide by Persulphoxide

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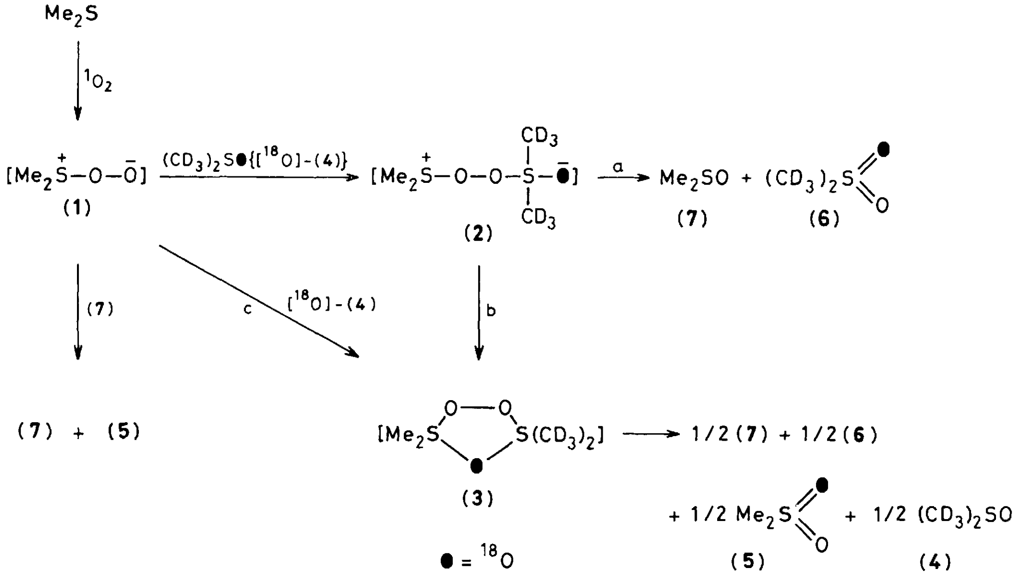
Oxidation of $^{18}$O-labelled [$^2H_6$]dimethyl sulphoxide by dimethyl persulphoxide produced by photosensitised oxygenation of dimethyl sulphide proceeded *via* a linear sulphurane intermediate.

Recently, oxygen atom transfer reactions of a persulphoxide intermediate $[R_2\overset{+}{S}{-}O{-}\overset{-}{O}]$ have been demonstrated in photosensitised oxygenation of sulphides.[1] Ogata[2] and Foote[3] suggested that a persulphoxide intermediate can oxidise a sulphoxide to a sulphone nucleophilically though the reaction mechanism was not fully clarified. We report here on a mechanistic investigation of this reaction using a tracer technique.

There are several possible mechanisms for nucleophilic oxidation of sulphoxide by a persulphoxide intermediate. One involves an initial nucleophilic attack of the outer oxygen atom of the persulphoxide (**1**) on the sulphur atom of a sulphoxide to form a linear sulphurane intermediate (**2**) which by elimination of the sulphoxide gives the sulphone (path a, Scheme 1) for which there is literature precedent in the reactions of peroxide anion.[4] An alternative route involves cyclisation of (**2**) to (**3**) followed by collapse to give the sulphoxide and sulphone (path b). The persulphoxide (**1**) may also add to the sulphoxide as a 1,3-dipole to form (**3**) (path c). We used labelled dimethyl sulphoxide to show which of paths a—c was operative in the oxidation.

$^{18}$O-Labelled [$^2H_6$]dimethyl sulphoxide {[$^{18}$O]-(**4**), $^2$H content 99.8 atom%; $^{18}$O content 54.2 atom%} was prepared from [$^2H_6$]dimethyl sulphoxide by literature methods.[5,6] Dimethyl sulphide (0.05 M) and the labelled sulphoxide (0.25 M) with methylene blue (0.05 mM) as a sensitiser were dissolved in $CD_3CN$ and the resulting solution was irradiated with a



Scheme 1

**Table 1.** Yields and $^{16}O/^{18}O$ ratios for compounds (**4**)—(**7**).

| | | Theoretical | | |
|---|---|---|---|---|
| Product | Yield (%) | *via* (**2**) $^{16}O:^{18}O$ | *via* (**3**) $^{16}O:^{18}O$ | Experimental $^{16}O:^{18}O$ |
| (**7**) | 77.5[a] | 100:0 | 100:0 | 100:0 |
| (**4**) | 95.6[b] | 45.8:54.2 | >45.8:<54.2 | 45.3:54.7 |
| (**5**) | 7.5[a] | 100:0 | 72.9:27.1 | 100:0 |
| (**6**) | 4.0[c] | 72.9:27.1 | 72.9:27.1 | 73.0:27.0 |

[a] Based on dimethyl sulphide (0.05 M) used. [b] Recovered; $^{16}O/^{18}O$ ratio of starting (**4**) is 45.8:54.2. [c] Based on (**4**) (0.25 M) used.

500 W Xe lamp under an oxygen flow for 10 min. The dimethyl sulphoxide and dimethyl sulphone produced were determined by g.l.c. and the yields of the non-deuteriated sulphoxide and sulphone were determined by $^1H$ n.m.r. spectroscopy. Control experiments showed that (**4**) was unreactive toward $^1O_2$ under the same conditions. The $^{16}O/^{18}O$ ratios of the sulphoxide and the sulphone were determined by a comparison of the peak heights of their molecular ions in their mass spectra. The results are shown in Table 1.

Since no incorporation of $^{18}O$ in $Me_2SO_2$ (**5**) was observed, path b and path c could be ruled out. In path a, the $^{18}O$ should be contained solely in (**6**) with none in (**5**) while in both path b and path c 50% of the original $^{18}O$ would be found in (**6**) and the same in the non-deuteriated sulphone (**5**), since the cyclic sulphurane (**3**) should collapse to give equal amounts of (**5**) and (**6**) (Scheme 1). Based on this rationale and the results in Table 1, we infer that nucleophilic oxidation of (**4**) by (**1**) proceeds *via* path a. The sulphone (**5**) could arise from the oxidation by (**1**)[2,3] of the non-deuteriated sulphoxide (**7**) formed during the reaction and/or by intramolecular rearrangement of (**1**) itself.[7] A decrease in solvent polarity would be expected to favour the formation of the non-ionic intermediate (**3**) rather than the dipolar intermediate (**2**), however, a change of solvent from $CD_3CN$ to $[^2H_6]$benzene–$CD_2Cl_2$–$CDCl_3$ did not alter the $^{18}O$ distribution in the product sulphones.

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