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

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Oxidation of <sup>18</sup>O-labelled [<sup>2</sup>H<sub>6</sub>]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  $[R_2S-O-O]$  have been demonstrated in photosensitised oxygenation of sulphides.<sup>1</sup> Ogata<sup>2</sup> and Foote<sup>3</sup> 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.<sup>4</sup> 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.

<sup>18</sup>O-Labelled [<sup>2</sup>H<sub>6</sub>]dimethyl sulphoxide {[<sup>18</sup>O]-(4), <sup>2</sup>H content 99.8 atom %; <sup>18</sup>O content 54.2 atom %} was prepared from [<sup>2</sup>H<sub>6</sub>]dimethyl sulphoxide by literature methods.<sup>5,6</sup> 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<sub>3</sub>CN and the resulting solution was irradiated with a



Table 1. Yields and <sup>16</sup>O/<sup>18</sup>O ratios for compounds (4)-(7).

	Theoretical			
Product	Yield (%)	via (2) <sup>16</sup> O: <sup>18</sup> O	<i>via</i> (3) <sup>16</sup> O: <sup>18</sup> O	Experimental <sup>16</sup> O: <sup>18</sup> O
(7) (4) (5) (6)	77.5ª 95.6 <sup>b</sup> 7.5ª 4.0°	100:0 45.8:54.2 100:0 72.9:27.1	$\begin{array}{c} 100:0 \\ > 45.8: < 54.2 \\ 72.9:27.1 \\ 72.9:27.1 \end{array}$	100:0 45.3:54.7 100:0 73.0:27.0

<sup>a</sup> Based on dimethyl sulphide (0.05 M) used. <sup>b</sup> Recovered;  ${}^{16}O/{}^{18}O$  ratio of starting (4) is 45.8: 54.2. <sup>c</sup> 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 <sup>1</sup>H n.m.r. spectroscopy. Control experiments showed that (4) was unreactive toward <sup>1</sup>O<sub>2</sub> under the same conditions. The <sup>16</sup>O/<sup>18</sup>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 <sup>18</sup>O in Me<sub>2</sub>SO<sub>2</sub> (5) was observed, path b and path c could be ruled out. In path a, the <sup>18</sup>O should be contained solely in (6) with none in (5) while in both path b and path c 50% of the original <sup>18</sup>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.<sup>7</sup> 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<sub>3</sub>CN to  $[^{2}H_{6}]$ benzene-CD<sub>2</sub>Cl<sub>2</sub>-CDCl<sub>3</sub> did not alter the <sup>18</sup>O distribution in the product sulphones.

We are grateful for financial support from the Ministry of Education, Science, and Culture of Japan.

Received, 1st June 1983; Com. 703

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