

REACTION OF SINGLET OXYGEN WITH SULFIDE: A SIMILARITY OF SINGLET OXYGENATION  
AND COUPLING REACTION OF CATION RADICAL AND SUPEROXIDE ION

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Summary: Photosensitized oxygenation of 5H,7H-dibenzo[b,g][1,5]dithiocin afforded the sulfoxides. The reaction of its cation radical derived from oxidation by nitrosyl tetrafluoroborate with superoxide ion gave the same products.

Much attention has been focused on an electron-transfer process in singlet oxygenation.<sup>1</sup> Reaction of several electron-rich substrates such as amines<sup>2</sup> and sulfides<sup>3-8</sup> with singlet oxygen may proceed by electron-transfer from the electron-rich substrate (D) to singlet oxygen to give a cation radical-superoxide ion pair or charge-transfer complex. Coupling reaction of the ion pair would give the product (DO<sub>2</sub>); back-electron transfer would produce triplet oxygen and the compound D.<sup>1</sup>



We have already reported an example in which the reaction of thianthrene cation radical and superoxide ion gave the sulfoxide via direct coupling.<sup>7</sup> Thianthrene itself is, however, unreactive toward singlet oxygen. We here report a detailed comparison of the oxidized products in oxidations of 5H,7H-dibenzo[b,g][1,5]dithiocin<sup>9</sup> (1) by singlet oxygen, and its cation radical by superoxide ion, and show that, both apparently proceed through the same intermediate.

Photosensitized Oxygenation of Dithiocin.<sup>10</sup>

The results obtained are summarized in Table 1. The reaction did not

proceed at all without a sensitizer and in the presence of DABCO, a singlet oxygen quencher<sup>11</sup> (Entry 2). The product ratios of sulfoxides, 2 and 3, are moderately independent of the solvent and the sensitizer used. In the presence of methyl phenyl sulfoxide as a nucleophilic-oxygen atom acceptor,<sup>12</sup> sulfoxides, 2 and 3, were obtained by accompanying with formation of methyl phenyl sulfone (Entry 6). Meanwhile, diphenyl sulfide as an electrophilic-oxygen atom acceptor<sup>13</sup> was oxidized to the sulfoxide under similar conditions (Entry 7). One plausible rationale for these observations might seem that the present reaction is a singlet oxygen one. The mechanism is outlined in Scheme.<sup>13</sup> Photosensitized oxygenation of sulfides having acidic  $\alpha$ -hydrogen atom as dibenzyl sulfide has been known to give the fragmentation products (aldehyde and sulfenic acid) by C-S bond cleavage, besides sulfoxides and sulfones as the usual S-oxidation products.<sup>6,14</sup> It is, however, noteworthy that photooxygenation of 1 yielded none of the fragmentation products. These results may have some relations with conformation of a persulfoxide intermediate 4.<sup>15</sup> DCA-sensitized oxygenation<sup>5</sup> under similar conditions also afforded 2 and 3 (Entry 8). The following results, however, indicate that singlet oxygen is the reactive intermediate.<sup>16</sup> This photooxygenation was completely inhibited by addition of DABCO<sup>11</sup> (Entry 9). The solvent deuterium isotope effect<sup>17</sup> for this reaction in acetonitrile ( $\Phi(D)/\Phi(H) = 1.6$ ) is in good agreement with the value ( $\Phi(D)/\Phi(H) = 1.8$ ) calculated assuming a singlet oxygen mechanism.<sup>18</sup>

Table 1. Photosensitized Oxygenation of Dithiocin.

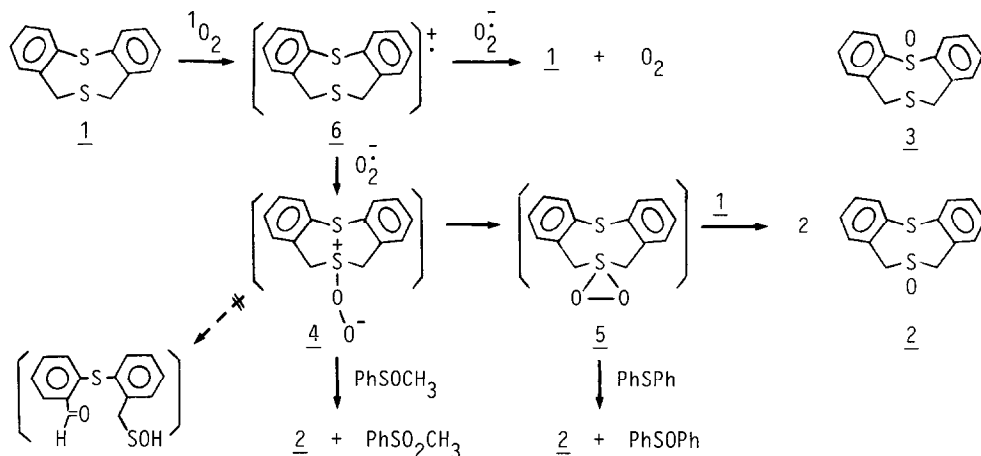
Entry	System	Products and Yields(%) <sup>a</sup>		
		<u>2</u>	<u>3</u>	
1	MB <sup>b</sup> /CH <sub>2</sub> Cl <sub>2</sub>	98	2	
2	MB/CHCl <sub>3</sub> /DABCO(1eq)	0	0	
3	Ⓢ -RB <sup>c</sup> /CHCl <sub>3</sub>	96	4	
4	RB <sup>d</sup> /THF	91	9	
5	RB/CH <sub>3</sub> COCH <sub>3</sub>	96	4	
6	MB/CH <sub>2</sub> Cl <sub>2</sub> /PhSOCH <sub>3</sub> (2eq)	99	1	PhSO <sub>2</sub> CH <sub>3</sub> 17
7	MB/CH <sub>2</sub> Cl <sub>2</sub> /PhSPh(10eq)	99	1	PhSOPh 47
8	DCA/CH <sub>3</sub> CN	94	6	
9	DCA/CH <sub>3</sub> CN/DABCO(1eq)	0	0	

a) Conversion yields. b) Methylene blue. c) Polymer-bound rose bengal. d) Rose bengal.

#### Reaction of Dithiocin Cation Radical and Superoxide Ion.<sup>19</sup>

Dithiocin cation radical tetrafluoroborate (6) was prepared, similar to the case of 1,5-dithiacyclooctane,<sup>20</sup> by mixing solutions of nitrosyl tetrafluoroborate and 1 in dry acetonitrile. A pale-yellow colored solution with  $\lambda_{\max}$  of 414 nm was formed instantly.<sup>21</sup> This cation radical was readily hydrolyzed to afford sulfoxide 2 ( 55% ) and 1 ( 45% )<sup>22</sup> (Entry 1).

Scheme



The results are summarized in Table 2. In entry II, two products, 1 and 2, were obtained in comparable yields accompanied with small amount of 3, but none of the sulfone and fragmentation products was detected.<sup>6,14</sup> In the presence of methyl phenyl sulfoxide and diphenyl sulfide, the formation of 2 is apparently suppressed (Entry III and IV), and the yield of 1 is concomitantly increased. Under these conditions, 1, methyl phenyl sulfoxide, and diphenyl sulfide are not oxidized with  $\text{KO}_2$ . These results could be explained in terms of interception of reactive intermediates 4 and 5 by methyl phenyl sulfoxide<sup>12</sup> and diphenyl sulfide,<sup>13</sup> respectively. Consequently, dithiocin cation radical 6 and superoxide ion underwent, in addition to the annihilation reaction to produce 1, the direct coupling reaction to afford a persulfoxide intermediate 4 outlined in Scheme.<sup>7</sup>

Thus, the reaction of the cation radical and superoxide ion may show similarity in possible reaction modes with singlet oxygenation.

Table 2. Reaction of Dithiocin Cation Radical and Superoxide Ion.

Entry	System	Products and Yields(%) <sup>a</sup>			$\text{O}_2$
		<u>1</u>	<u>2</u>	<u>3</u>	
I	$\text{H}_2\text{O}$	45	55	0	-
II	$\text{KO}_2$	13	82	3	22
III	$\text{KO}_2$ + $\text{PhSOCH}_3$ (5eq)	38	58	2	$\text{PhSO}_2\text{CH}_3$ 25 34
IV	$\text{KO}_2$ + $\text{PhSPh}$ (10eq)	30	60	2	$\text{PhSOPh}$ 11 22

a) Average values for two experiments.

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- 10) In a typical experiment, 1 ( 0.01 M ) with methylene blue ( 0.1 mM ) as a sensitizer was dissolved in methylene chloride and the resulting solution was irradiated with two 500W halogen lamps under an oxygen flow for 1 hr. Dithiocin 6-oxide 2; <sup>13</sup> mp 178-180°C; m/e 260(M<sup>+</sup>); IR(KBr)  $\nu$  1040, 1075 cm<sup>-1</sup>; NMR(CDCl<sub>3</sub>)  $\delta$  7.16-8.04(m,8H), BC-form(24%); 5.67(d,2H, J=12Hz), 4.20(d,2H,J=12Hz), TB-form(76%); 3.83(d,2H,J=14Hz), 4.03(d,2H,J=14Hz) ppm; Anal. Calcd for C<sub>14</sub>H<sub>12</sub>S<sub>2</sub>O<sub>1</sub>: C,64.58; H,4.64. Found: C,64.51; H,4.65. Dithiocin 12-oxide 3; mp 195-196°C; m/e 260(M<sup>+</sup>); IR(KBr)  $\nu$  1040, 1078 cm<sup>-1</sup>; NMR(CDCl<sub>3</sub>)  $\delta$  8.08-8.37(m,2H), 7.10-7.74 (m,6H), 4.68(d,2H,J=14.6Hz), 3.96(d,2H,J=14.6Hz) ppm; Anal. Calcd for C<sub>14</sub>H<sub>12</sub>S<sub>2</sub>O<sub>1</sub>: C,64.58; H,4.64. Found: C,64.50; H,4.61.
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- 18) Calculated from the eq.3 in ref. 17); k<sub>9</sub> was taken to be 1.9 x 10<sup>5</sup> M<sup>-1</sup>s<sup>-1</sup>. The relative rate of 1 with <sup>1</sup>O<sub>2</sub> to diethyl sulfide ( k<sub>r</sub> = 7.6 x 10<sup>6</sup> M<sup>-1</sup>s<sup>-1</sup>; Wilkinson, F.; Brummer, J. G., *J. Phys. Chem., Ref. Data*, 1981, 10, 809 ) is estimated to be 1/40.
- 19) The reaction on the vacuum line was carried out by the same manner mentioned in ref. 7.
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