

ON DIRECT PHOTO-OXIDATION OF SULFIDES
 IN THE PRESENCE OF OXYGEN

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Recently Sinnreich et al. reported a novel photo-oxidation reaction of sulfides, mentioning that only aliphatic sulfides possessing α -hydrogen were oxidized to give sulfoxides by direct photolysis in the presence of oxygen¹. They proposed a mechanism in which radical (1) and hydroperoxide (2) were implicated as intermediates. We wish to report new evidence which rules out the mechanism suggested by the previous authors.

When a methanol solution of diphenyl sulfide (10^{-2} M) was irradiated with a high pressure mercury lamp through Pyrex filter with bubbling oxygen for 7 hours, diphenyl sulfoxide was formed in 25% yield. Methyl phenyl sulfide, pentamethylene sulfide, and di-n-butyl sulfide were also photo oxidized under the similar condition to give the corresponding sulfoxides in good yield (Table 1). The direct photo-oxidation did not show so profound solvent dependency. For example, diphenyl sulfoxide was also formed, when diphenyl sulfide was photolyzed in methylene chloride or in benzene as a solvent (Table 1).

The mechanism of this photo-oxidation reaction is of considerable interest. The fact that diphenyl sulfide was photo oxidized implies that

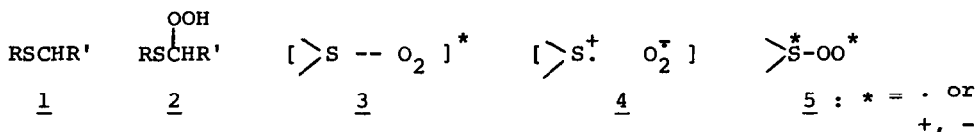


Table 1. The yield of sulfoxides after irradiation of 5 hours.

Sulfides	Sulfoxides	Solvents	Yield
PhSPh	PhSOPh	MeOH	17%
"	"	CH ₂ Cl ₂	13%
"	"	C ₆ H ₆	9%
PhSMe	PhSOMe	MeOH	71%
"	"	CH ₂ Cl ₂	72%
(CH ₂) ₅ S	(CH ₂) ₅ SO	MeOH	40%
"	"	CH ₂ Cl ₂	42%
n-Bu ₂ S	n-Bu ₂ SO	MeOH	100%
"	"	CH ₂ Cl ₂	67%

δ-hydrogen is not a necessary factor for the formation of sulfoxides. The excited complex between sulfide and oxygen (3)¹ will be a role for this oxidation reaction, since the oxygen saturated diphenyl sulfide showed U.V. absorption band around 350mμ². A possible reactive intermediate species arising subsequently from 3 would be either singlet oxygen, a pair of superoxide anion radical and cation radical of sulfide (4), or zwitterionic and/or biradical species such as 5. However the singlet oxygen may not concern to this reaction, because it is known to be inert to the oxidation of diphenyl sulfide in benzene³. The relatively low solvent dependency of the direct photo-oxidation of sulfides seems to suggest an intermediacy of the surperoxide anion radical⁴. However the definite conclusion must be awaited for the trapping of such species, which is currently investigated.

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References and Notes

- 1) D. Sinnreich, H. Lind, and H. Batzen, Tet. Letters, 1976, 3541.
- 2) This absorption band disappeared when oxygen was purged by Argon gas.
- 3) C. S. Foote, J. W. Peters, J. Amer. Chem. Soc., 93, 3795 (1971); J. Goollnik, Advan. Photochem., 6, 1 (1968).
- 4) J. Eriksen, C. S. Foote, and T. L. Parker, J. Amer. Chem. Soc., 99, 6455 (1977).