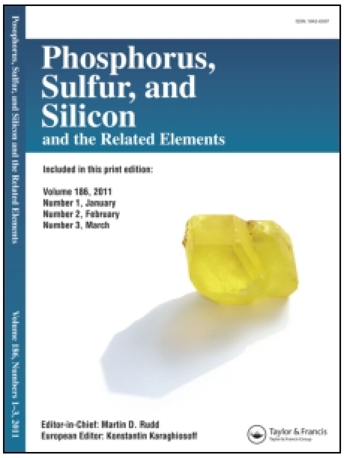

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PHOTOOXIDATION OF AROMATIC SULFIDES

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PHOTOOXIDATION OF AROMATIC SULFIDES

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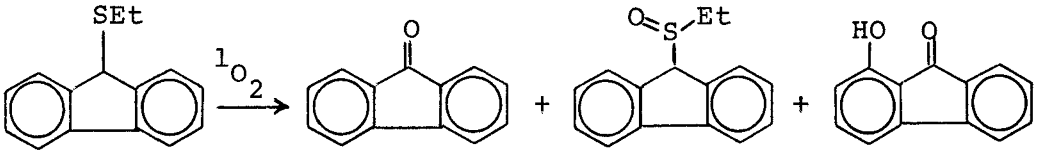
Dye sensitized photooxidation of sulfides proceeds by way of singlet oxygen to give sulfoxides and sulfones, and the evidence for several intermediates has been reported. We now report that photooxidation of aromatic sulfides gives the product of an unusual type; and the reaction may proceed by either superoxide or hydroperoxysulfurane. 9-Ethylthiofluorene was photooxidized in dichloromethane or acetone with methylene blue as sensitizer. Three main products were isolated and identified as fluorenone (15%), 9-fluorenyl ethyl sulfoxide (19%) and 1-hydroxyl-9-fluorenone(23%).



Addition of β-carotene and DABCO did not result formation of the products. The formation of sulfoxide and ketone presumably involves the intermediates which formulated by Foote[1].

The formation of 1-hydroxyl-9-fluorenone might involve the hydroperoxysulfurane or superoxide by electron transfer from sulfur to singlet oxygen. The product distributions from dicyanoanthracene(DCA) sensitized oxygenation of the fluorenyl sulfide in CH_3CN are shown to be similar with those of dye sensitized oxidation. Addition of β-carotene did not quench the formation of the products.

Dye and DCA sensitized reactions of aromatic vinyl sulfides will described.