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PHOTOOXIDATION OF ALIPHATIC SULFIDES

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Sulfides are known to undergo photosensitized oxidation to their corresponding sulfoxides. This oxidation was found to be induced by singlet oxygen1).

We wish to report on the direct photooxidation of aliphatic sulfides in hydrocarbon solution and as solids. To the best of our knowledge this represents the first example of a photooxidation occuring in the crystalline state.

$$\mathrm{RSR} \xrightarrow[\lambda > 300\mathrm{nm}]{h\nu,\ O_2} \mathrm{RSOR}$$

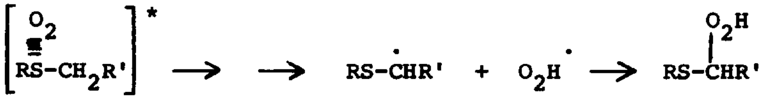
$R = n\text{-}C_4H_9(I),\ C_{12}H_{25}(II),\ C_{14}H_{29}(III),\ CH_2CO_2C_{12}H_{25}(IV),$
$CH_2CH_2CO_2C_{12}H_{25}(V),\ t\text{-}C_4H_9(VI)$

Thus, clean conversions to sulfoxides were observed upon irradiation2) of solid crystalline samples of sulfides (II - V) in air. Similar_ly, by irradiation of hexane solutions of sulfides I - V, the corresponding sulfoxides were obtained quantitatively. In the cases II - V sulfoxides separated as white powders during irradiation. Di-t-butylsulfide (VI) was not oxidized under these conditions.

In the absence of sensitizers and with no direct light absorption possible a mechanism for these oxidations is not immediately obvious. Further, these oxidations cannot be thermal processes since it has been demonstrated that aliphatic sulfides in hydrocarbon solution do not oxidize at temperatures below 100°C3).

We have noted the appearance of an intense absorption band ($\lambda_{max.}$ = 300nm) on saturating liquid di-n-butylsulfide (I) and liquid di-t-butylsuldide (VI) with oxygen. These new absorptions can be annihilated by purging with nitrogen. Such reversibility ascertains the presence of charge-transfer (C.T.) complexes which are formed by interaction between oxygen as an electron acceptor and sulfur as an electron donor. Absorption of the di-t-butylsulfide C.T. complex was found to be more intense than that of the di-n-butylsulfide C.T. complex as expected from the respective electron donating groups, inducing accumulation of negative charge at the sulfur atom.

Our results are in agreement with C.T. absorption as a primary step in the photooxidation of sulfides, similar to C.T. complexes found in the photooxidation of ethers$^{4)}$ and amines$^{5)}$. It can be assumed that excited C.T. complex chemistry leads to an α- alkyl-thioalkyl radical (VII) capable of combining with a hydroperoxide radical. Sulfide peroxides (VIII) have been suggested as common intermediates in thermal autoxidation of sulfides$^{6)}$.



$$\left[\overset{O_2}{\overset{\vdots}{RS}}-CH_2R'\right]^* \longrightarrow \longrightarrow RS-\dot{C}HR' + O_2\dot{H} \longrightarrow RS-\overset{O_2H}{\overset{|}{C}}HR'$$

VII VIII

The proposed mechanism can account for the photooxidative inertness of di-t-butylsulfide (VI) where, due to the absence of necessary α-hydrogen atoms, the formation of peroxide VIII is not possible.

References and Footnotes

1) V.D. Foote and J.W. Peters, J. Amer. Chem. Soc. 93, 3795(1971).

2) Irradiations at ambient temperature through Pyrex glass using a medium-pressure mercury-lamp (2000 Watt) and a Philips-HPK-125 immersion lamp for solids and solutions, respectively.

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6) D. Barnard, L. Bateman and J.I. Cunneen in "The Chemistry of Organic Sulfur Compounds", Ed. V. Kharash and C.Y. Meyers, Pergamon Press, vol. 1, 229(1966).