

Oxygenation and de-oxygenation of organic compounds on irradiated semiconductor catalyst, TiO_2

C. Srinivasan

Department of Materials Science, Madurai Kamaraj University, Madurai 625 021, India

Though photo-oxidation of organic compounds on semiconductor (SC) catalysts has been extensively studied, there are only a few examples of direct oxygenation and de-oxygenation of organic compounds on SC catalysts. The oxygenation of organic sulphur compounds to the corresponding sulphoxides and sulphones, Ar_3M ($\text{M} = \text{P, As, Sb, or Bi}$) to the corresponding Ar_3MO and aldimines to nitrones on irradiated TiO_2 are some of the important reactions. This photocatalyst also brings about effective de-oxygenation of sulphones, Ar_3MO and nitrones. The mechanisms of oxygenation and de-oxygenation on bandgap irradiation of TiO_2 are discussed.

THOUGH photo-oxidation of organic compounds on semiconductor (SC) catalysts has been extensively studied¹, there are only a few examples of direct oxygenation of organic compounds on SC catalysts¹⁻⁴. Because of ubiquitous oxygen, direct oxygenation of organic compounds will be of great importance to chemists. The direct removal of oxygen from an organic substrate without affecting other parts of the molecule, will be a good synthetic strategy. In an organic molecule, irradiation of light promotes an electron from a filled (HOMO) to unfilled (LUMO) molecular orbitals. Analogous to an organic molecule, in SC the filled (valence band, VB) and empty (conduction band, CB) molecular orbitals are separated by bandgap energy. Electromagnetic radiation of energy equal to or greater than the bandgap energy is required to promote an electron from VB to CB resulting in the creation of electron deficiency or hole in the VB. The electrons promoted to the CB are mobile. TiO_2 is widely used as the SC photocatalyst in many organic reactions due to its nontoxic nature, chemical stability, availability and capability of repeated use without substantial loss of catalytic activity². The result of irradiation of TiO_2 using low energy UV radiation ($\lambda > 350 \text{ nm}$) is the formation of electron-hole pair ($e^- - h^+$). The electron promoted from the VB to CB is readily available for transference and the positive equivalent, the hole in the VB is ready to accept the electron from the substrate⁵ (Figure 1). A substrate that

receives an electron from the SC would be reduced whereas one which donates an electron to the SC is oxidized. Therefore it is not surprising that one of the most active areas of research in recent years has been the study of redox reactions employing SCs as photocatalysts^{5,6}. The use of TiO_2 as a photocatalyst in the redox reactions of several organic substrates is well documented. Thus SC-photoinduced organic reactions like geometrical isomerization, valence isomerization, dimerization, cycloreversion, [1,3]-sigmatropic shift, oxidation, reduction, condensation, polymerization and other types of reactions have been discussed in several review articles¹⁻³. In this account, only reactions involving direct oxygenation and de-oxygenation of organic compounds on TiO_2 will be discussed. Though this type of reactions may fall under the category of oxidation and reduction reactions, it will be of interest to know the results of direct oxygenation and de-oxygenation.

The electron promoted to the CB in TiO_2 reacts with oxygen (if it is present) to form a superoxide radical ion (Figure 1) which can oxidize the organic molecule. In most of the oxygenation reactions, the superoxide radical ion plays an important role. One of the earliest examples of direct oxygenation is the conversion of diphenylethylenes into benzophenones and epoxides⁷⁻⁹

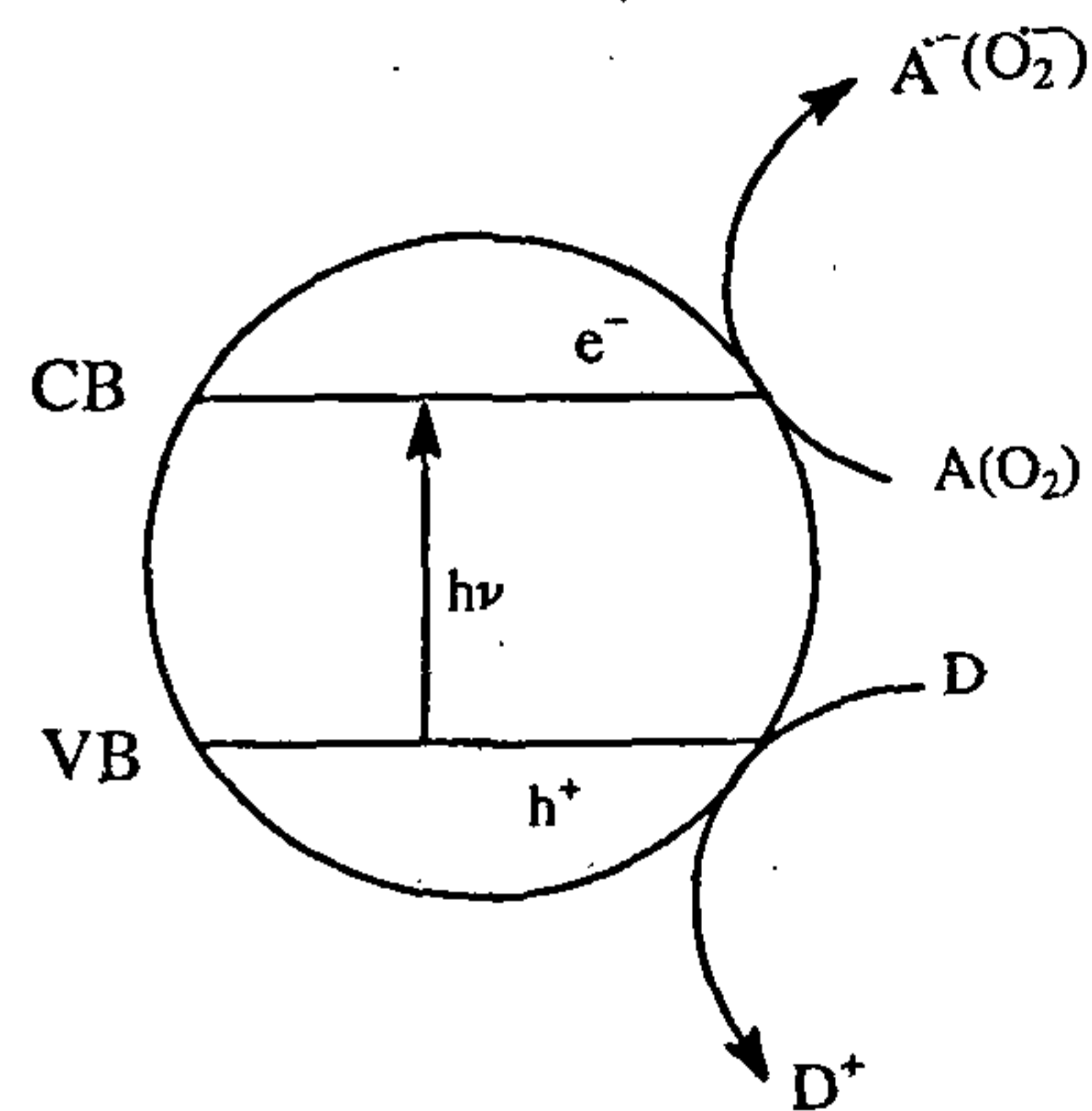
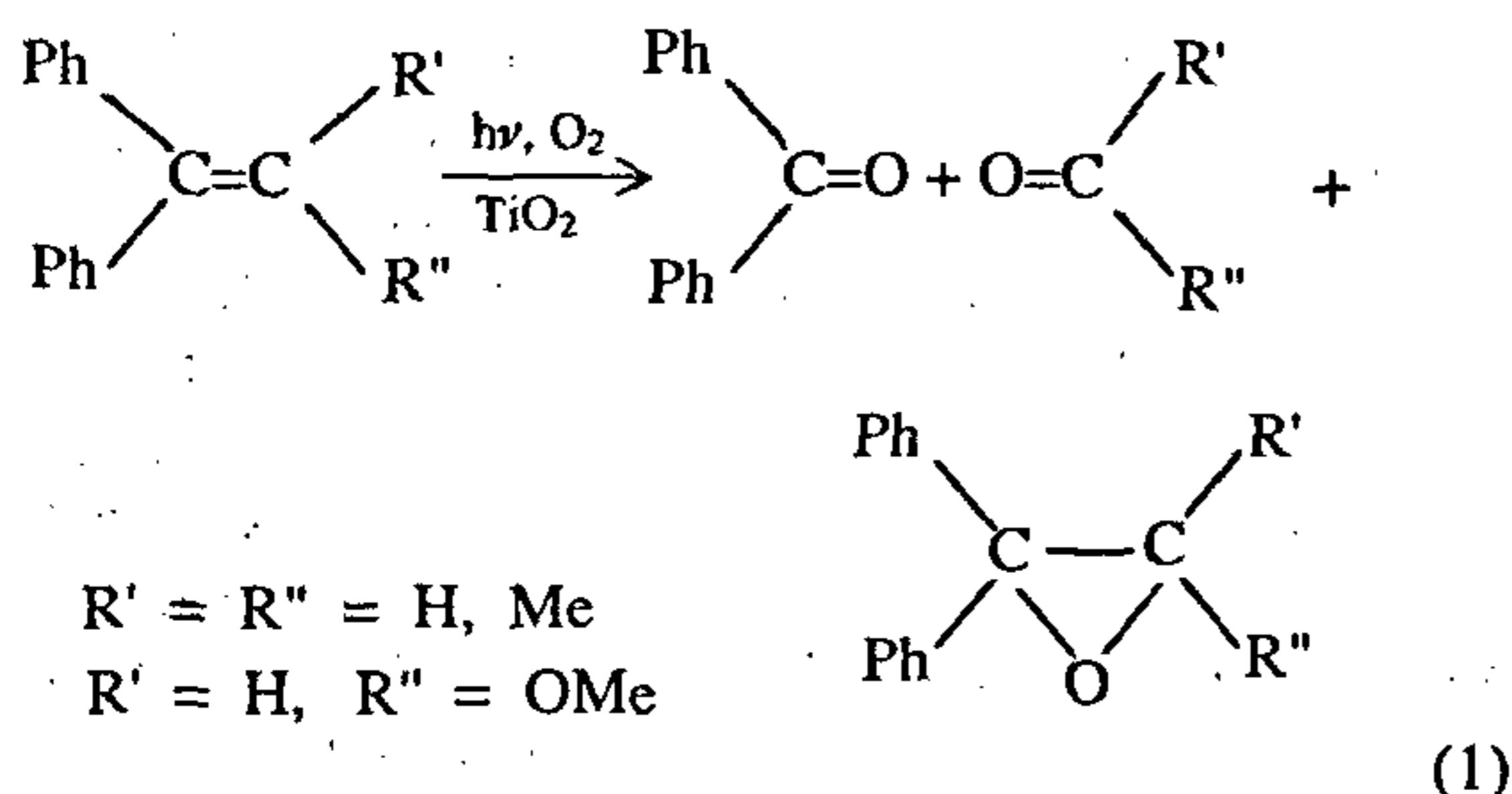


Figure 1. Oxidation and reduction processes at the illuminated SC surface.

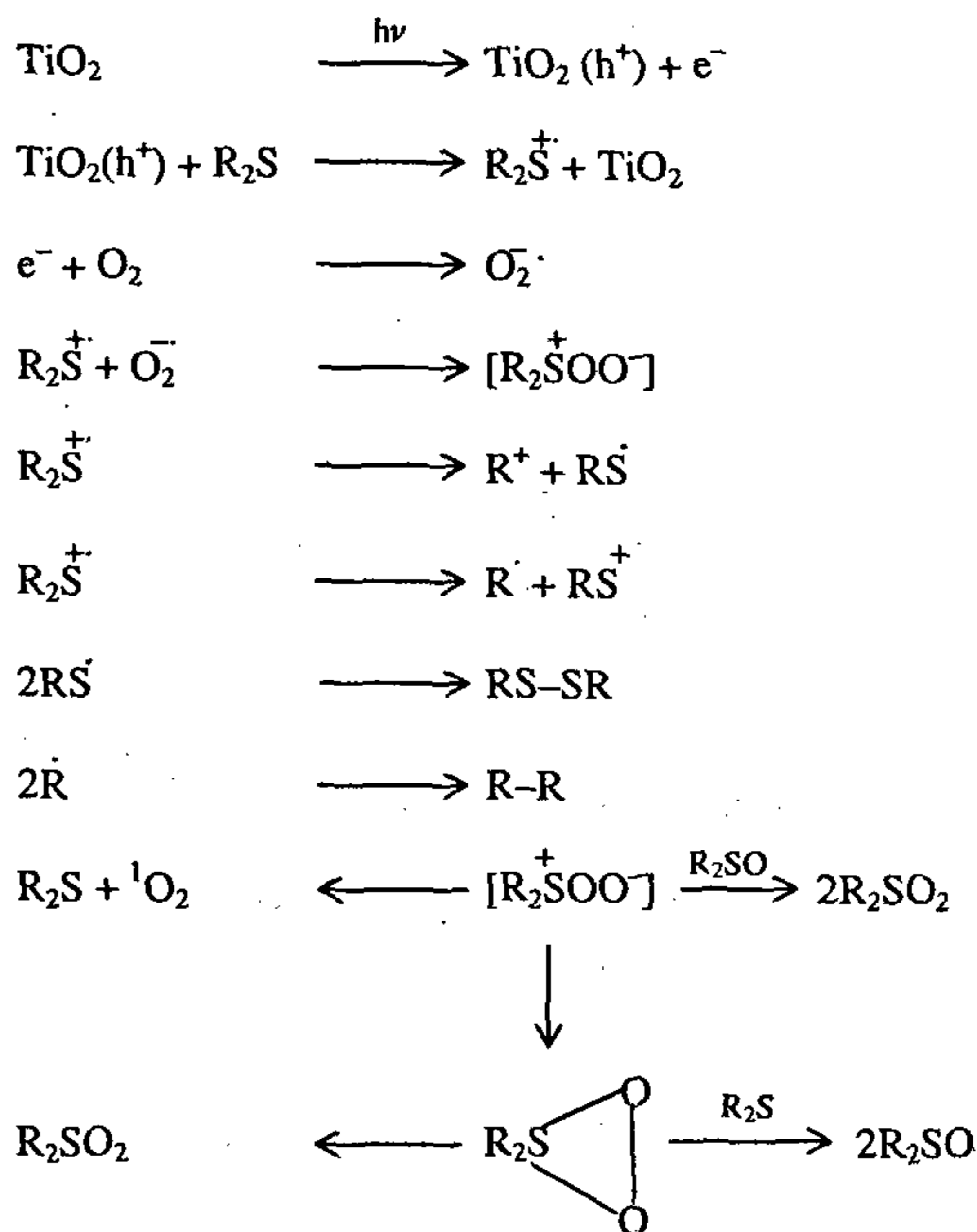
(eq. (1)) in the irradiation of TiO_2 suspended in oxygenated acetonitrile.



On excitation of the SC the olefins transfer initially an electron to the photogenerated positive hole to give the olefin cation radical as evidenced by the observation of transient absorption spectra⁸ corresponding to the radical cation upon laser excitation of powdered SC in the presence of olefin. Concurrently the electron promoted to the CB is transferred to oxygen to give superoxide anion. These resulting species subsequently undergo free radical chain reactions to yield the products. It has also been observed that generally the reactive olefins are those with lower oxidation potentials. In the photocatalytic oxygenation, the formation of cation radical of diphenylethylenes has also been demonstrated by studying the photocatalytic oxidation of a series of 4-substituted diphenylethylenes and by invoking the Hammett relationship. The negative slope ($\rho^+ = -0.56$) found in the plot of the relative rates of the reaction and σ^+ substantiates the formation of the radical cation⁹. Though the reaction involves the photocatalytic cleavage, there is also the direct oxygenation of the olefins which results in the formation of epoxides. The epoxides may further undergo decomposition.

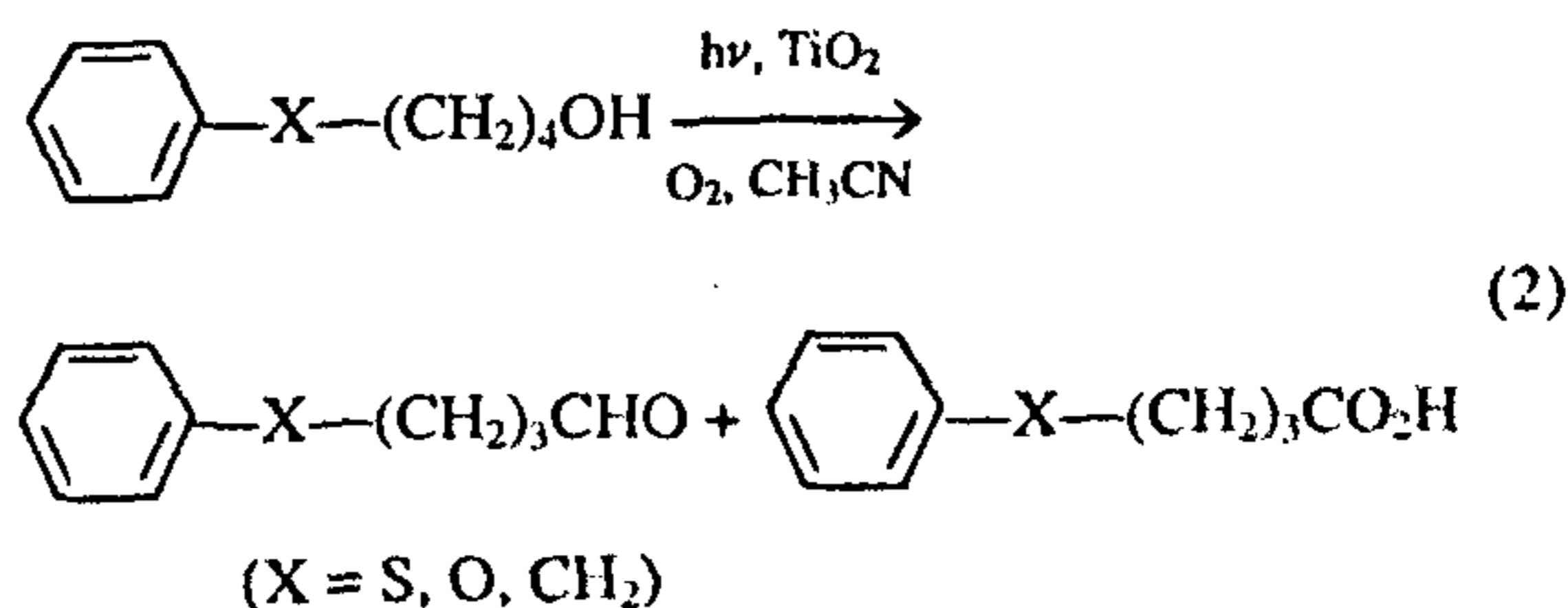
Organic compounds containing functional group bearing a nonbonded lone pair may readily undergo photocatalysed oxygenation. Therefore the direct oxygenation of organic sulphur compounds has been extensively studied by three groups – Davidson¹⁰, Fox^{11,12} and Srinivasan^{13,14}. TiO_2 has been shown to photosensitize the oxidation of dialkyl sulphides and diphenyl sulphide to give sulfoxides and sulphones by Davidson and Pratt¹⁰. The authors have ruled out the oxidation by singlet oxygen as the rates of formation of oxidation products do not correlate with the relative rate constants¹⁰ reported for the oxidation of the same sulphides with singlet oxygen. They have proposed a mechanism (Scheme 1) in which the sulphide radical cation reacts with the superoxide radical.

They have also observed products derived from C-S bond cleavage and their formation can be explained on the basis of dissociation of R_2S^+ radical cations as outlined in Scheme 1. The alpha cleavage of thioether

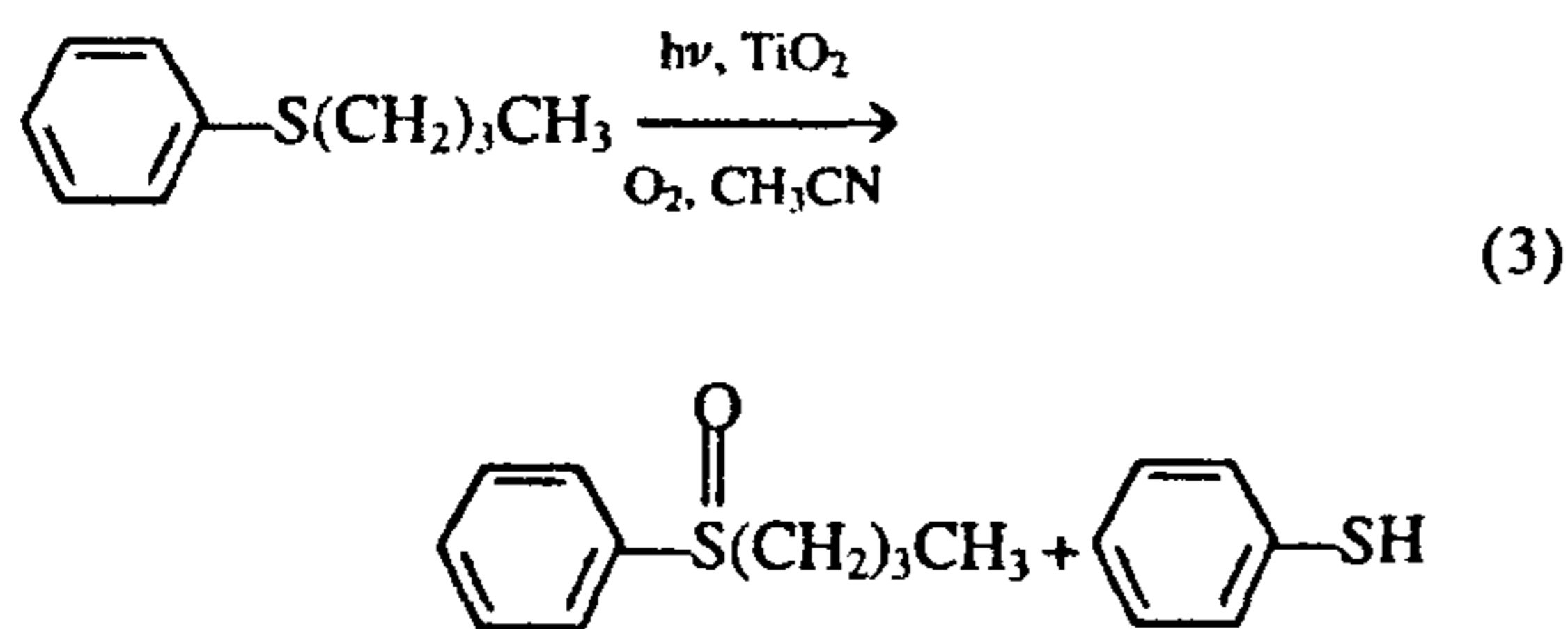


Scheme 1.

cation radical¹⁵ leading to oxidative cleavage is well known. Fox¹² has shown that irradiated SC surfaces to be promising vehicles for controlling photocatalytic oxidations of organic molecules containing multifunctional groups. If more than one oxidizable group is present, oxidative selectivity can be influenced by adsorption effects, band-edge redox energetics, light flux effects, the kinetics of electron-hole recombination and back electron transfer from adsorbed redox reagents¹⁶. Upon bandgap irradiation of a solution of 4-thiophenyl-1-butanol in acetonitrile in the presence of suspended TiO_2 and its non-sulphur-containing analogs (eq. (2)), a mixture of aldehydes and acids are formed in high chemical yield. Thus the photocatalytic oxidation of sulphur containing aliphatic alcohols occurs mainly at the alcohol group, presumably because the primary interfacial electron transfer at the OH, by virtue of the possibility of proton exchange, is significantly less reversible than at the thioether site.



On the other hand, the non-alcoholic analog, phenyl *n*-butyl sulphide was converted to the corresponding sulfoxide in a lower yield process with the C–S bond cleavage representing the major competing route (eq. (3)).



It has also been demonstrated by Fox¹² that on photo-oxygenation of diaryl sulphides in the presence of the photocatalyst, the corresponding sulfoxides are formed and on continued irradiation the sulfoxides are converted into their sulphones (eq. (4)). The relative rates of

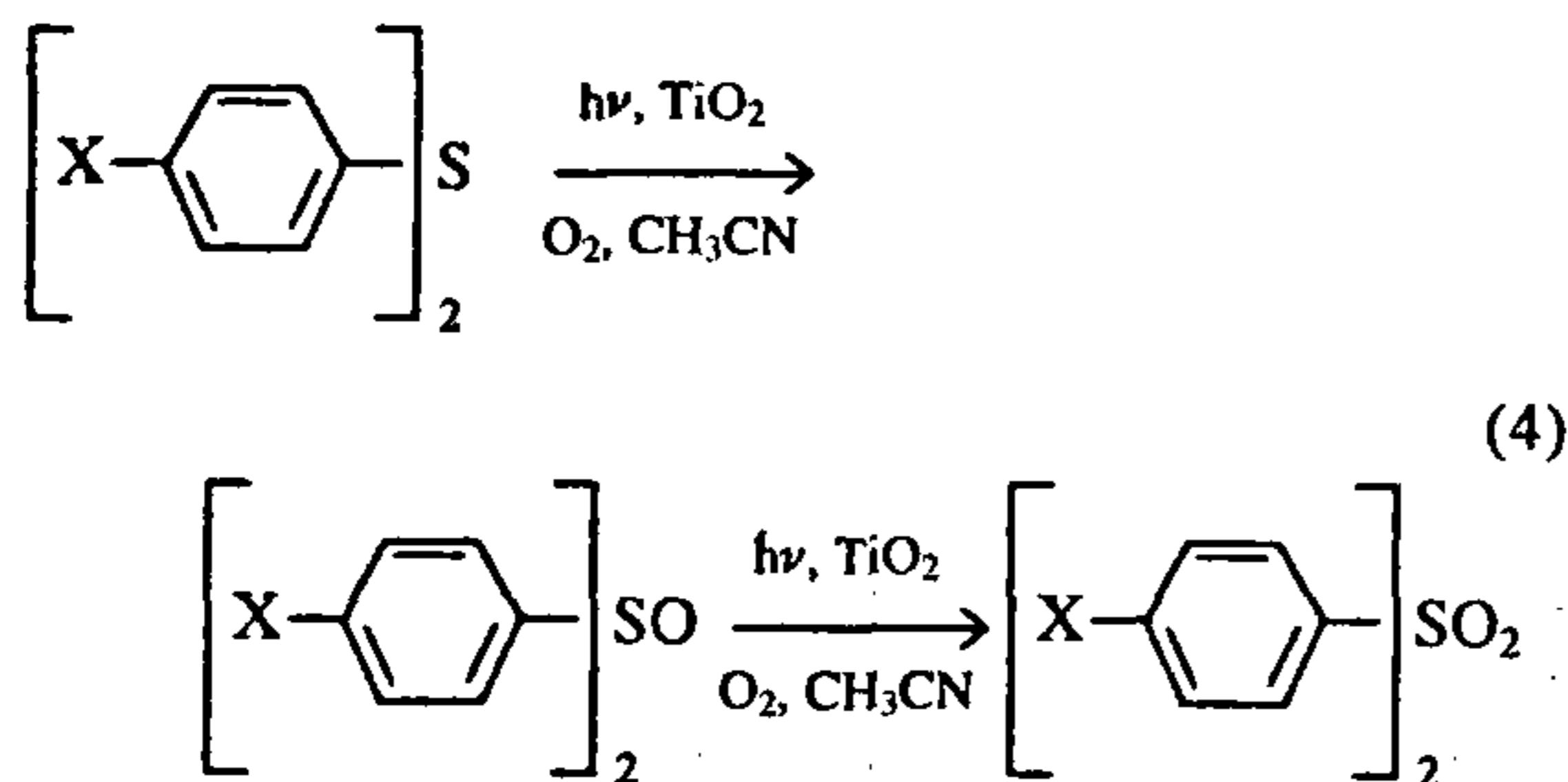
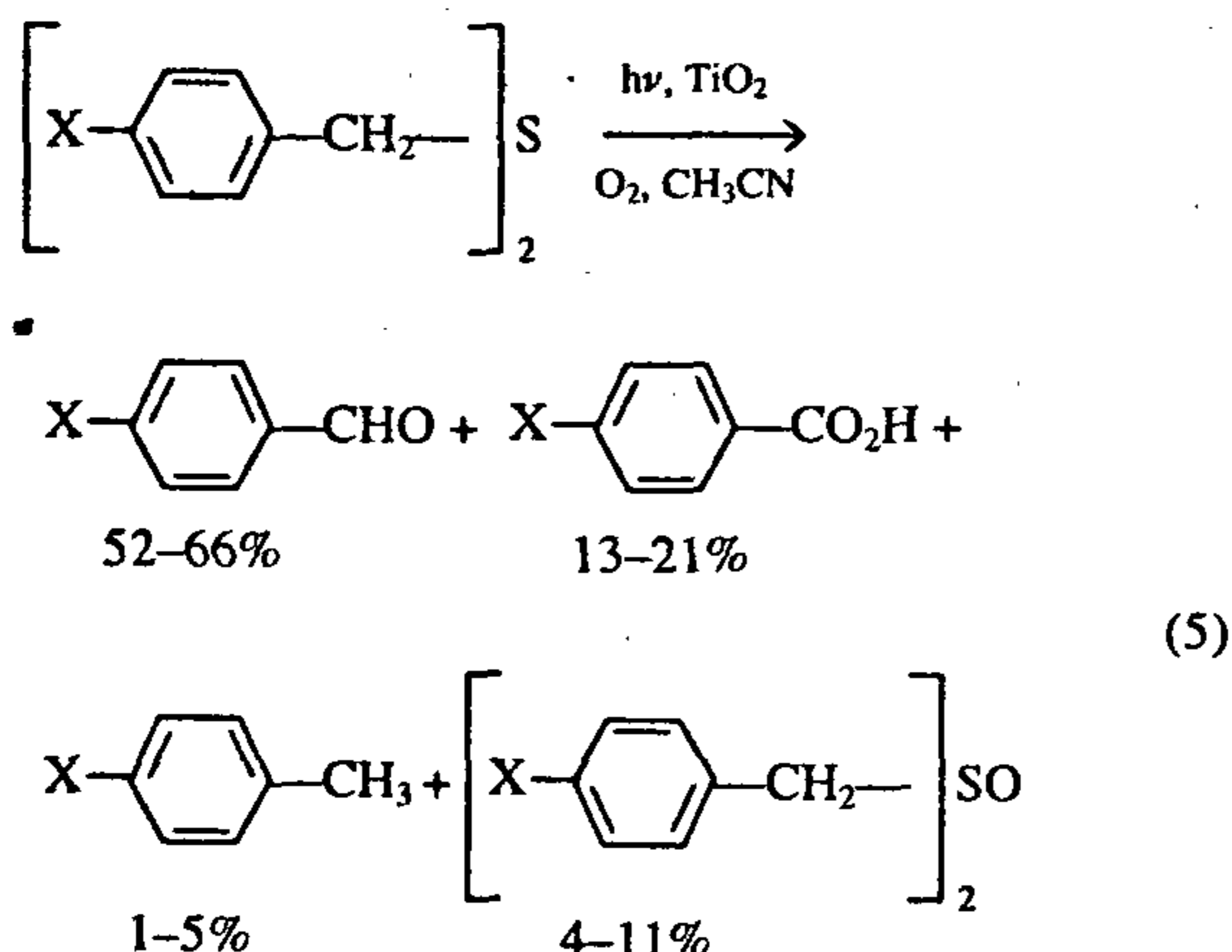
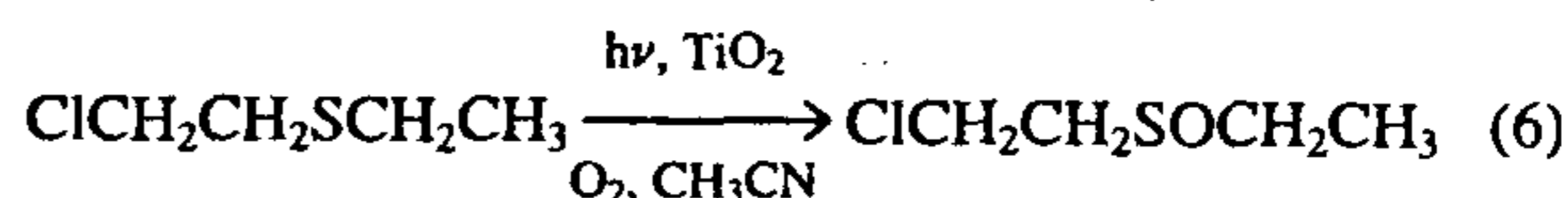


photo-oxygenation of substituted diphenyl sulphides correlate linearly with σ^+ with a ρ^+ value of -0.7 , indicating the formation of a surface bound cation radical in the primary photoprocess. In contrast, substituted dibenzyl sulphides suffer C–S bond cleavage upon photocatalysed oxidation (eq. (5)).



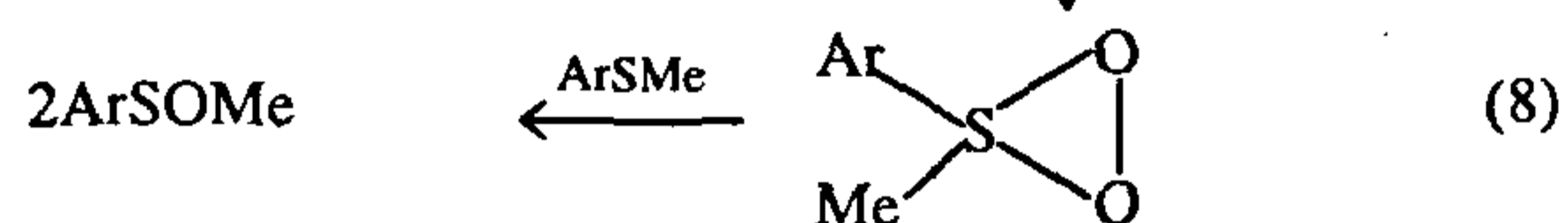
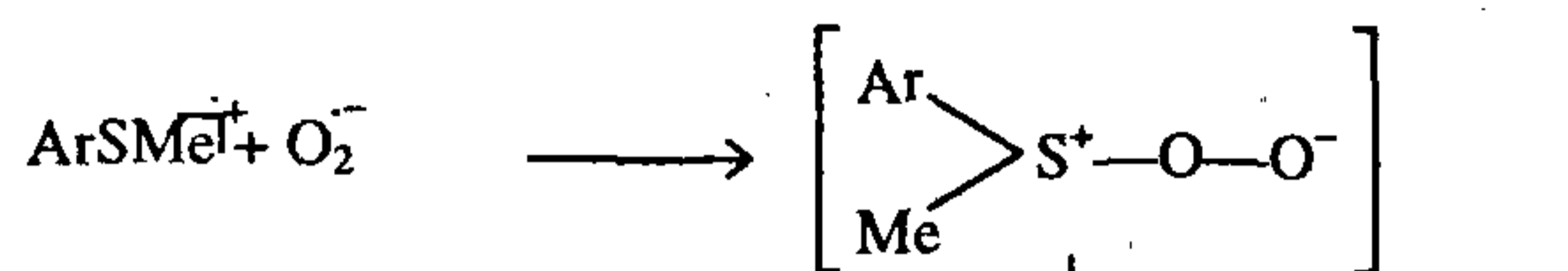
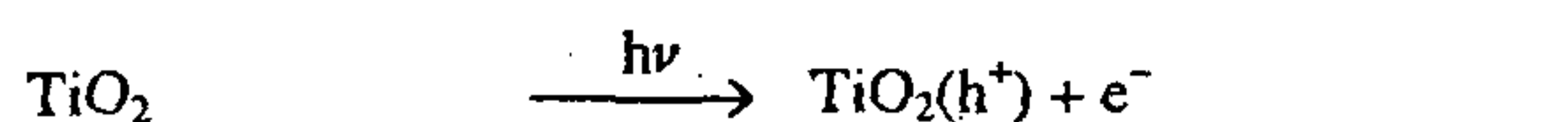
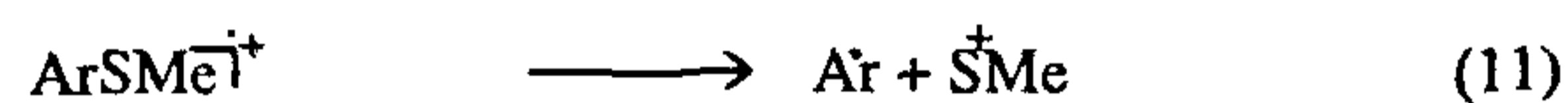
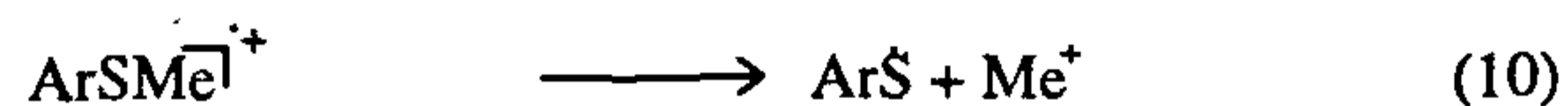
The competition between C–S bond cleavage (as observed in dibenzyl sulphide) and oxygenation (noticed with diaryl sulphides) is controlled by the stability of the possible fragments and by access of a nucleophile¹⁷ to the developing cation center. Presumably, the ratio of the rates of deprotonation and O₂ trapping of the adsorbed cation radical is mediated by the SC surface, bringing together both the photogenerated cation radical and either O₂ or superoxide¹⁸.

Irradiation of β -chlorodiethyl sulphide suspended in aerated aqueous, nonaqueous or mixed solvents in the presence of suspended TiO₂ leads to the formation of the corresponding sulfoxide in high yield and subsequently the sulphone (eq. (6)) (ref. 2).



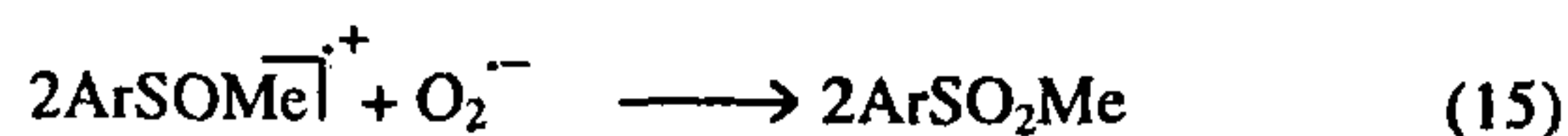
Despite the studies on the photocatalysed oxygenation of dialkyl, dibenzyl and diaryl sulphides, there are no reports of such studies with aryl methyl sulphides. Our continued interest in the rates of oxygenation of organic sulphur compounds by several oxidants^{19–30} prompted us to study the photocatalysed oxidation of aryl methyl sulphides and sulfoxides. Irradiation of solutions of aryl methyl sulphides in acetonitrile in the presence of suspended TiO₂ results in the formation of aryl methyl sulfoxides as the major product along with aryl methyl sulphones and small amounts of products formed due to C–S bond cleavage¹⁴. With the objective of increasing the yield of the two-step oxidation product, sulphone, the irradiation time was increased; though the formation of sulphone was slightly increased, the products contained more of the starting material which has been attributed to disproportionation reaction (eq. (9)). In the proposed mechanism (Scheme 2), the photogenerated hole readily accepts an electron from the sulphide adsorbed on the surface of the photocatalyst to give the sulphide radical cation ArSMe⁺ which then reacts with the superoxide to yield the sulfoxide as the major product via persulphoxide (eq. (8)).

Photoelectrochemical measurements also provide evidence for the electron transfer from sulphide¹⁴. At a constant applied potential, on illumination of TiO₂ electrode in the presence of O₂, aryl methyl sulphides exhibited photocurrent which increased with decreasing oxidation potential and no photocurrent was observed in the absence of ArSMe. Further, a fairly good Hammett correlation observed between percentage of conversion and substituent constants with a negative slope (-0.28) supports the formation of sulphur radical cation¹⁴. There are a few reports on the formation of such cations. In the 9,10-dicyanoanthracene sensitized photo-oxidation of sulphides, the formation of such a radical cation has

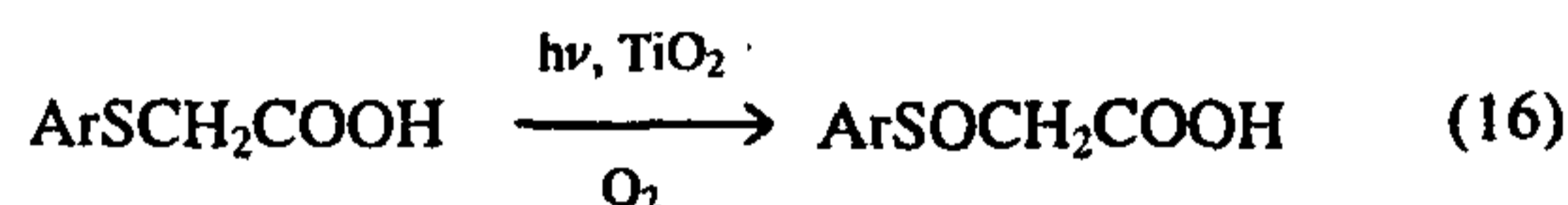
**Disproportionation****C-S bond cleavage**

Scheme 2.

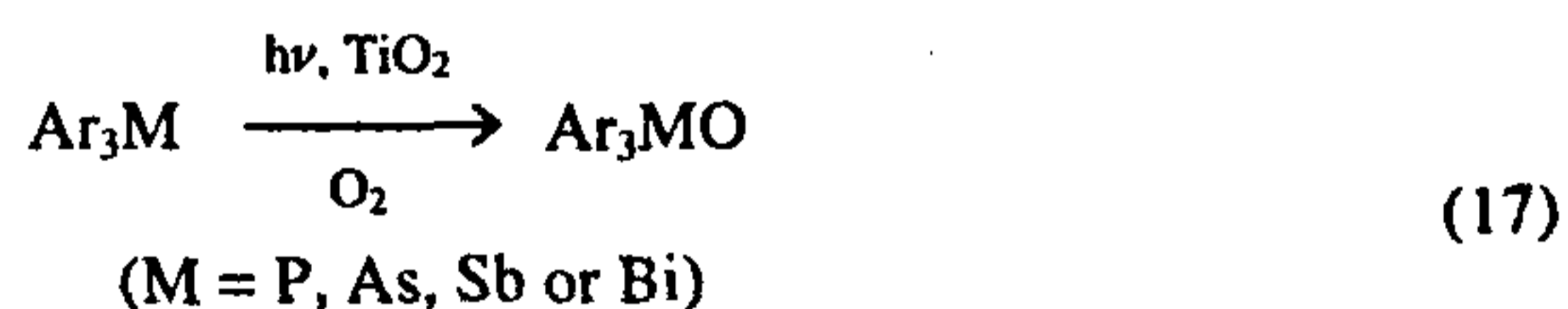
been postulated³¹. Employing SO_4^- and Ti^{2+} as the oxidizing species, the cations of aryl methyl sulphides were also produced by pulse radiolysis³². Recently it has been reported that sulphur cations produced by one-electron photo-oxidation through triplet 4-carboxybenzophenone can react with superoxide to yield two equivalents of sulphoxide per equivalent of one-electron oxidized sulphur³³ as we have postulated in eq. (8). Though it has been shown that methyl group is affected in the SC photocatalysed oxidation of toluene^{2,34,35}, analysis of the products in the oxidation of ArSMe reveals the absence of products due to the oxidation of methyl group and only the sulphur moiety is affected. TiO_2 also functions as an effective photocatalyst in the quantitative oxygenation of aryl methyl sulphoxides to the corresponding sulphones¹⁴; (eqs (14), (15)). As sulphonyl group is a powerful electron-withdrawing group, it will be difficult to produce ArSO_2Me^+ and therefore no disproportionation product has been observed in the oxidation of sulphoxide.



During photosensitized oxidation of organic acids in the presence of TiO_2 or diaryl ketones, decarboxylation is the most favoured process^{34,36}. As it is an interesting challenge to achieve site selectivity in photocatalytic reactions of multifunctional organic molecules, we studied in general redox reactions of ArXCOOH ($\text{X}=\text{CH}_2, \text{OCH}_2, \text{SCH}_2, \text{SOCH}_2, \text{or SO}_2\text{CH}_2$) and in particular photo-oxidation of arylthioacetic acids¹³. Solutions of phenylacetic acid and phenoxyacetic acid in the presence of oxygen undergo decarboxylation quantitatively in the presence of TiO_2 to give toluene and anisole respectively. This is analogous to the photo-oxidation of acetic acid to methane and carbon dioxide as reported by Kraeutler and Bard³⁷ and also to that of other aliphatic acids and benzoic acid³⁸ on TiO_2 . However, under similar conditions phenylthioacetic acid and *p*-substituted phenylthioacetic acids yield about 70% of arylsulphinylacetic acids (eq. 16) with no further oxidation to sulphonylacetic acids. The photocatalysed oxygenation of arylthioacetic acids follow a mechanism similar to that proposed for the oxidation of sulphides. At high concentration of the catalyst, decarboxylation occurs with phenylthioacetic acids and it is presumed that the carboxyl group also is adsorbed and that may promote decarboxylation.

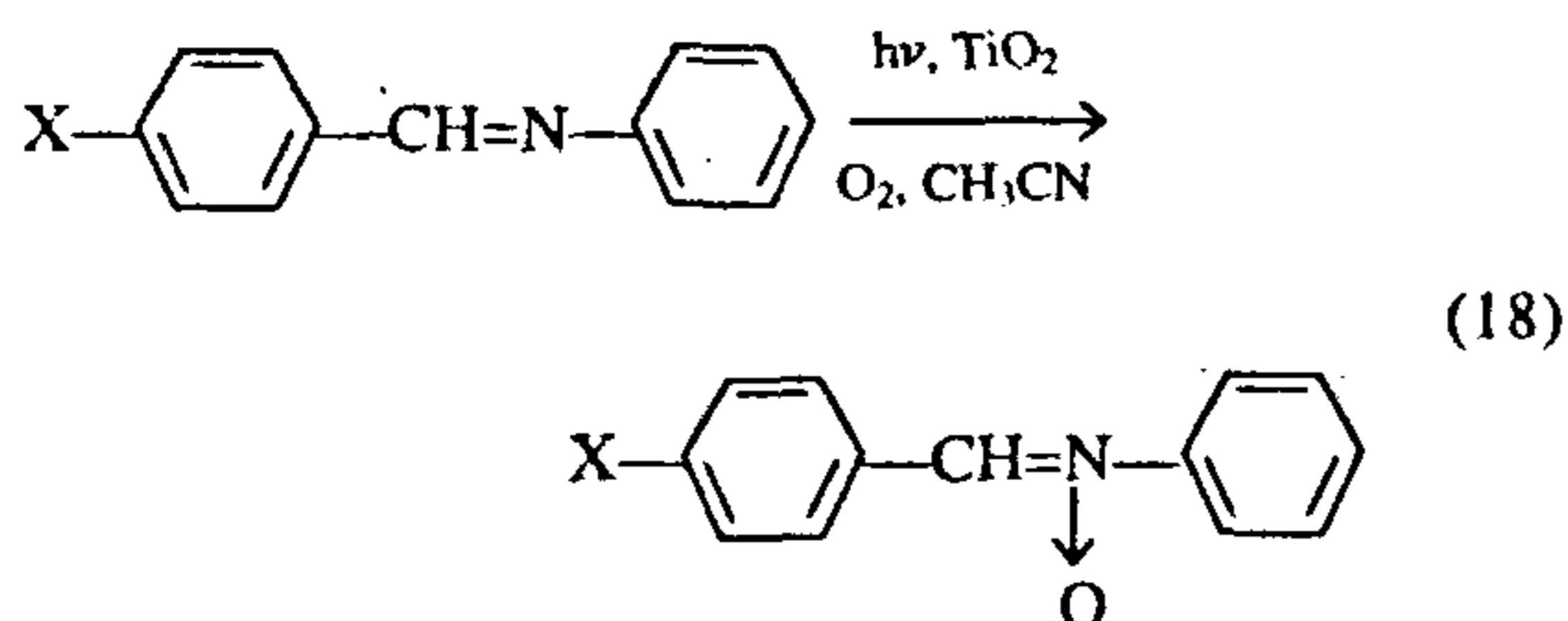


Triphenyl derivatives of P, As, Sb and Bi (Ar_3M) readily undergo photo-oxygenation in the presence of TiO_2 to give the corresponding oxides³⁹, Ar_3MO (eq. (17)). The relative order of reactivity is found to be $\text{Ph}_3\text{P} > \text{Ph}_3\text{Sb} > (p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As} > \text{Ph}_3\text{Bi}$ and the same order of reactivity was observed by us during the oxidation of Ar_3M by isostructural and iso-electronic oxidants peroxodisulphate⁴⁰ and peroxodiphosphate⁴¹.



When an acetonitrile solution of aldimine is irradiated in the presence of TiO_2 and oxygen, the corresponding nitrene (eq. (18)) is formed in $\geq 70\%$ without affecting the $\text{C}=\text{N}$ bond along with small amounts of aldehydes, hydroxylamines, amines, carboxylic acids and diazo compounds⁴². The mechanism involves the donation of an electron from the aldimine to the hole with the formation of the cation radical which subsequently reacts with superoxide to furnish the nitrene. The formation of the cation radical is also supported by the fact that the

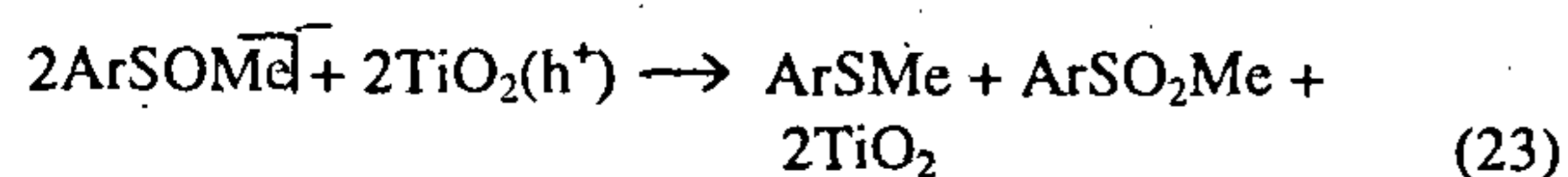
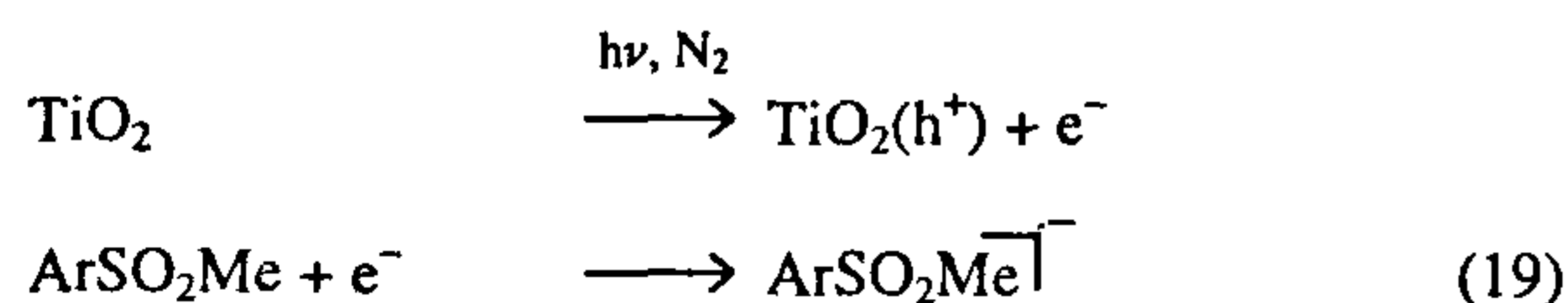
yield of nitron is more with 4-methoxybenzylideneaniline (88%) than with 4-chlorobenzylideneaniline (69%).



De-oxygenation reactions on irradiated TiO₂

Compared to the extensive studies on the SC photoinduced oxidation of organic compounds, there are only a few reports of photosensitized reductions such as reduction of aldehydes and ketones⁴³, nitroaromatics⁴⁴ and the reports from our laboratory. The modestly negative potential of electrons at the CB of the SC and the ready abstraction of electrons by oxygen may be responsible for the limited success of reductions of organic compounds on SC surfaces. In the absence of oxygen and in the presence of nitrogen, the electron promoted from the VB to the CB of TiO₂ will be available for the acceptance of organic molecules. Herein we cite examples of direct de-oxygenation of organic compounds on irradiated SC surfaces.

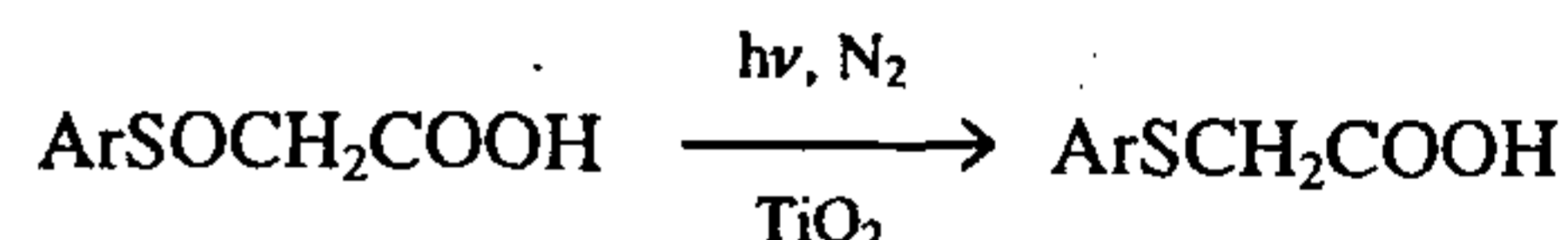
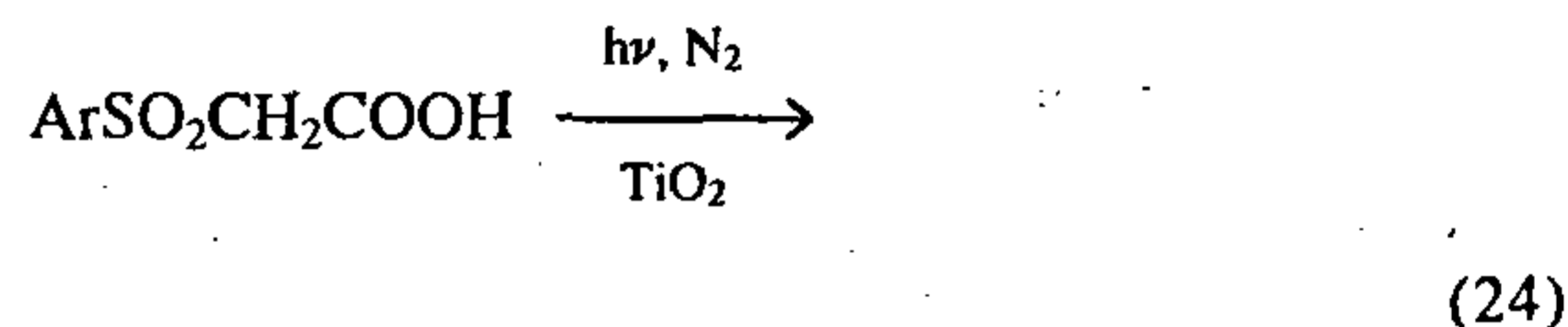
The difficult reduction of the S–O bond of the sulphone group to the corresponding sulfoxide and sulphide may generally be achieved by the reaction with metal hydrides such as LiAlH₄ and (*iso*-Bu)₂AlH^{45,46} and also by the treatment with SmI₂-THF-HMPA⁴⁷. As the sulphonyl group is electron-withdrawing, sulphone is likely to accept electrons from the CB of an irradiated SC. Indeed it has been shown that TiO₂ acts as an effective photocatalyst in the reduction of dialkyl and aryl methyl sulphones to give the de-oxygenated products⁴⁸. While the reduction of aryl methyl sulphones furnishes sulfoxides as the major product along with the sulphides, dialkyl sulphones yield more of sulphides. The mechanism of the reaction is shown in Scheme 3.



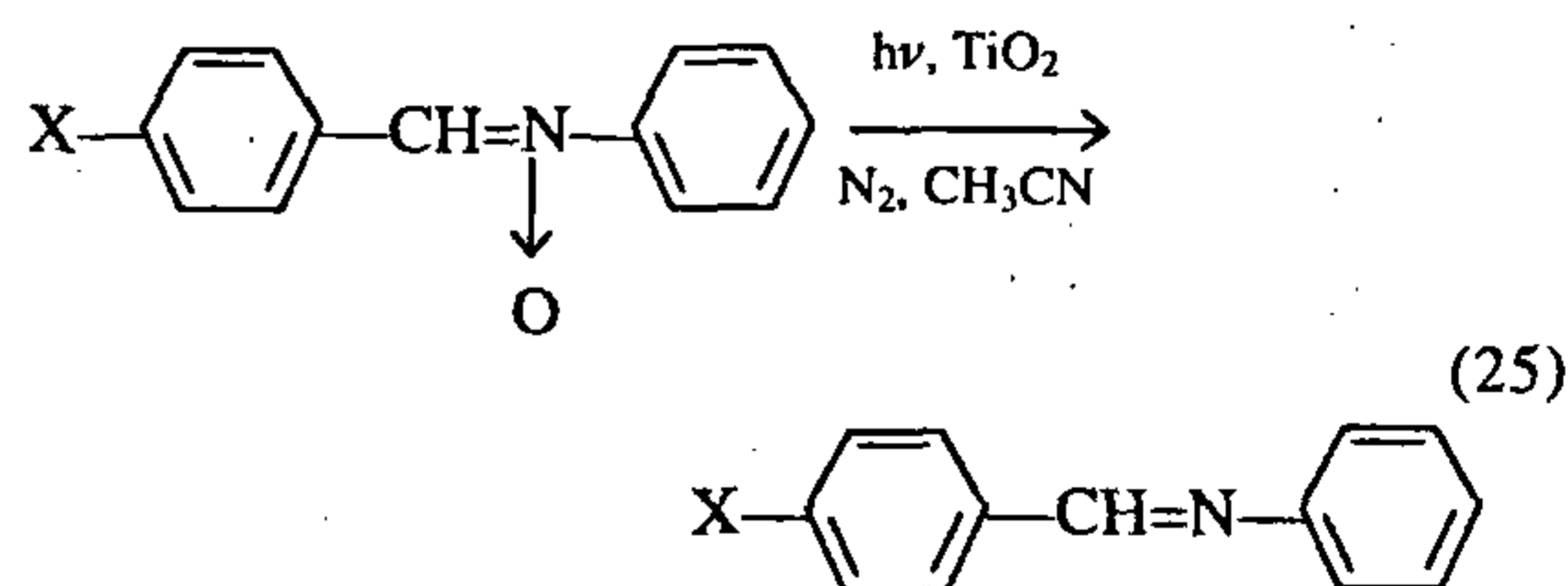
Scheme 3.

The following experimental observations support the above mechanism: (i) the product mixture obtained from the photocatalysed reduction of aryl methyl sulphones in the presence of nitrogen contained aryl methyl sulfoxides and separate experiments with aryl methyl sulfoxides under the same experimental conditions as employed for aryl methyl sulphones furnished the de-oxygenated product, i.e. sulphides; (ii) in the case of *p*-methoxyphenyl methyl sulphone more of unreacted sulphone was recovered after the reaction and this is not surprising as a strong electron-donating group will not favour electron transfer to the sulphone (eq. (19)) and (iii) increase of irradiation time instead of increasing the de-oxygenated products, results in the recovery of the unreacted sulphone and this supports the disproportionation step (eq. (23)) in the mechanism.

On bandgap irradiation of TiO₂ suspended in methanol in nitrogen atmosphere, arylsulphonylacetic acids are de-oxygenated to a mixture of sulphinyl and sulphenyl acids with the former as the major product (eq. (24)) (ref. 13).

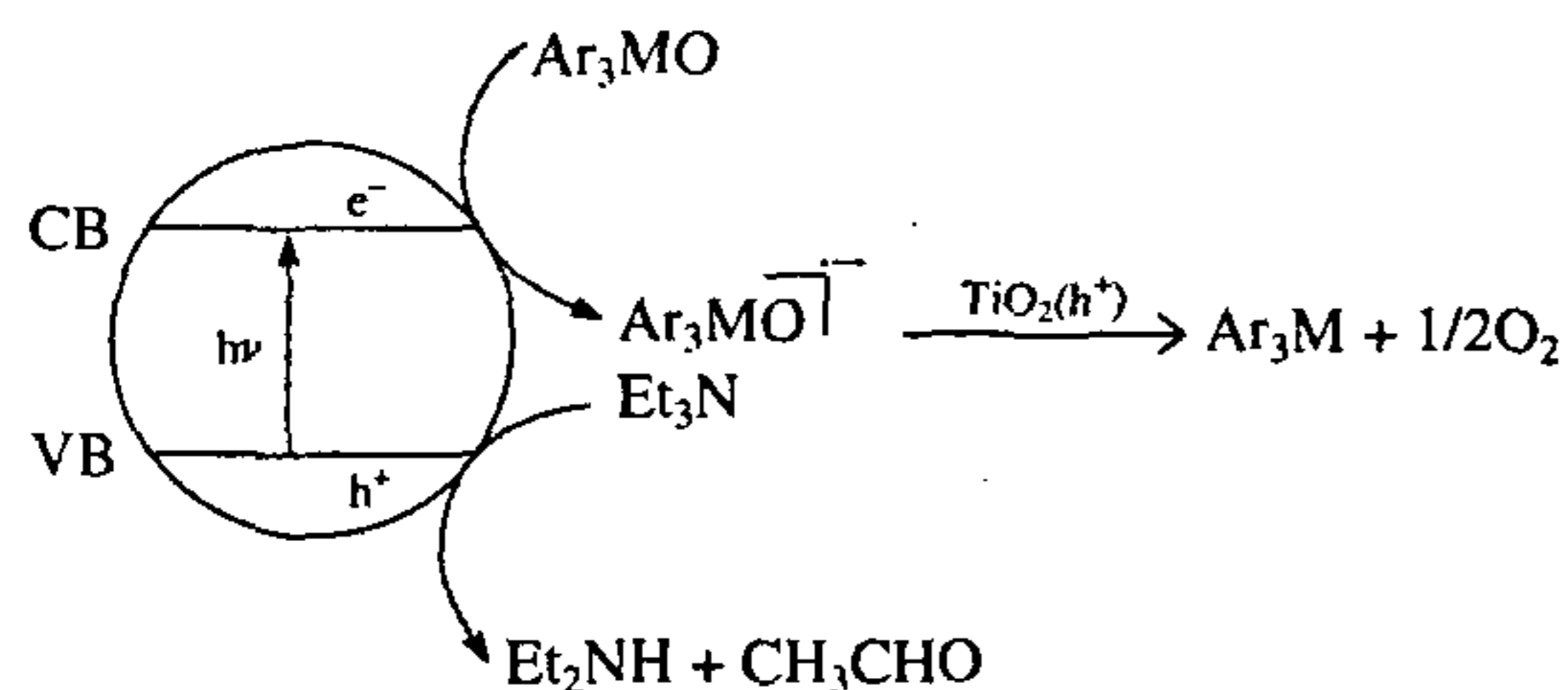


TiO₂ photocatalysed reduction of acetonitrile solutions of α -aryl-*N*-phenyl nitrones in the presence of nitrogen resulted in the formation of aldimines⁴² in good yields ($\geq 79\%$) without affecting C=N bond (eq. (25)). The reaction occurs only with low light intensity probably due to the fact that the electron-hole recombination process is negligible in that light intensity range.



Though triphenylphosphine has been extensively employed as a de-oxygenating agent⁴⁹, not much attention has been paid to the de-oxygenation of the oxide. Handa *et al.*⁴⁷ reduced Ph₃PO to Ph₃P using the SmI₂-THF-HMPA system. In our laboratory the de-oxygenation of Ar₃MO to Ar₃M (M = P, As, Sb or Bi) has been achieved on the surface of illuminated TiO₂ in an organic solvent purged with nitrogen and also in the presence of triethylamine (TEA). In the absence of TEA no de-oxygenated product could be obtained. TEA func-

tions as a sacrificial electron donor which prevents electron-hole recombination process by trapping the hole effectively^{2,3}. TEA has been converted to diethylamine and acetaldehyde as observed in the reduction of organic substrates by illuminated CdS in the presence of TEA⁵⁰. The proposed mechanism is shown in Scheme 4.



Scheme 4.

- Al-Ekabi, H., in *Photochemistry in Organized and Constrained Media* (ed Ramamurthy, V.), VCH Publications, Weinheim, 1991, p. 495.
- Fox, M. A., Chen, C. C., Park, K. and Younathan, J. N., in *Organic Transformations in Non-homogeneous Media* (ed. Fox, M. A.), ACS Symposium Series, 1985, p. 278; Fox, M. A. and Dulay, M. T., *Chem. Rev.*, 1993, **93**, 341; Fox, M. A., *Acc. Chem. Res.*, 1982, **16**, 314.
- Kamat, P. V., *Chem. Rev.*, 1993, **93**, 267.
- Rao, N. N. and Natarajan, P., *Curr. Sci.*, 1994, **66**, 742.
- Linsebigler, A. L., Lu, G. and Yates, Jr, J. T., *Chem. Rev.*, 1995, **95**, 735.
- Staffor, U., Gray, K. A. and Kamat, P. V., *Het. Chem. Rev.*, 1996, **3**, 77.
- Kanno, T., Oguchi, T., Sakuragi, H. and Tokumuru, K., *Tetrahedron Lett.*, 1980, **21**, 467.
- Fox, M. A., Lindig, B. A. and Chen, C. C., *J. Am. Chem. Soc.*, 1982, **104**, 5828.
- Fox, M. A. and Chen, C. C., *Tetrahedron Lett.*, 1983, **24**, 547.
- Davidson, R. S. and Pratt, J. E., *Tetrahedron Lett.*, 1983, **24**, 5903.
- Fox, M. A. and Abdel-Wahab, A. A., *Tetrahedron Lett.*, 1990, **31**, 4533.
- Fox, M. A. and Abdel-Wahab, A. A., *J. Catal.*, 1990, **126**, 683.
- Somasundaram, N. and Srinivasan, C., *J. Photochem. Photobiol.*, 1996, **A99**, 67.
- Somasundaram, N. and Srinivasan, C., *J. Photochem. Photobiol.*, in press.
- von Sonntag, C. and Schuchmann, H. P., in *Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulfur Analogs* (ed. Patai, S.), Wiley, New York, 1980, p. 721.
- Fox, M. A., Ogawa, H. and Muzyka, J., *Proc. Electrochem. Soc.*, 1988, **88-14**, 9.
- Dinnocenzo, J. P., Farid, S., Goodman, L., Gould, I. R., Todd, W. P. and Mattes, S. L., *J. Am. Chem. Soc.*, 1989, **111**, 8973.
- Fox, M. A., Chen, C. C. and Younathan, J. N., *J. Org. Chem.*, 1984, **49**, 1969.
- Srinivasan, C., Kuthalingam, P. and Arumugam, N., *Can. J. Chem.*, 1978, **56**, 3043.
- Srinivasan, C., Kuthalingam, P. and Arumugam, N., *J. Chem. Soc., Perkin Trans. II*, 1980, 170.
- Srinivasan, C. and Rajagopal, S., *React. Kinet. Catal. Lett.*, 1979, **12**, 45.
- Srinivasan, C. and Pitchumani, K., *Int. J. Chem. Kinet.*, 1982, **14**, 789.
- Srinivasan, C., Kuthalingam, P. and Arumugam, N., *Int. J. Chem. Kinet.*, 1982, **14**, 1139.
- Srinivasan, C. and Pitchumani, K., *Bull. Chem. Soc. Jpn.*, 1982, **55**, 289.
- Srinivasan, C., Chellamani, A. and Kuthalingam, P., *J. Org. Chem.*, 1982, **47**, 428.
- Srinivasan, C., Perumal, S. and Arumugam, N., *J. Chem. Soc., Perkin Trans. II*, 1985, 17.
- Srinivasan, C., Chellamani, A. and Rajagopal, S., *J. Org. Chem.*, 1985, **50**, 1201.
- Srinivasan, C., Rajagopal, S. and Chellamani, A., *J. Chem. Soc., Perkin Trans. 2*, 1990, 1839.
- Srinivasan, C. and Subramaniam, P., *J. Chem. Soc., Perkin Trans 2*, 1990, 1061.
- Chellamani, A., Alhaji, N. M. I., Rajagopal, S., Sevel, R. and Srinivasan, C., *Tetrahedron*, 1995, **51**, 12677.
- Eriksen, J., Foote, C. S. and Parker, T. L., *J. Am. Chem. Soc.*, 1977, **101**, 2979.
- Ioele, M., Steenken, E. and Bacilicchi, E., *J. Phys. Chem.*, 1997, **101**, 2979.
- Miller, B. L., Williams, T. D. and Schoneich, C., *J. Am. Chem. Soc.*, 1996, **118**, 11014.
- Fox, M. A., *Top. Curr. Chem.*, 1987, **142**, 71.
- Pelizzetti, E. and Serpone, N. (eds), *Homogeneous and Heterogeneous Photocatalysis*, Riedel, Dordrecht, 1986.
- Davidson, R. S., Harrison, K. and Steiner, P. R., *J. Chem. Soc.*, 1970, 3480.
- Kraeutler, B. and Bard, A. J., *J. Am. Chem. Soc.*, 1978, **100**, 2239.
- Harada, H., Veda, T. and Sakata, T., *J. Phys. Chem.*, 1989, **93**, 1542; Sakata, T., Kawai, T. and Hashimoto, *J. Phys. Chem.*, 1984, **88**, 2344; Izumi, I., Fan, F. R. F. and Bard, A. J., *J. Phys. Chem.*, 1981, **85**, 218; Sato, S., *J. Chem. Soc., Chem. Commun.*, 1986, 26.
- Somasundaram, N. and Srinivasan, C., *J. Org. Chem.*, 1996, **61**, 2895.
- Srinivasan, C. and Pitchumani, K., *Int. J. Chem. Kinet.*, 1982, **14**, 1315.
- Srinivasan, C. and Pitchumani, K., *Can. J. Chem.*, 1985, **63**, 2285.
- Somasundaram, N. and Srinivasan, C., *Tetrahedron Lett.*, 1998, **39**, 3547.
- Pruden, C. J., Pross, J. K. and Li, Y., *J. Org. Chem.*, 1992, **57**, 5087.
- Mahdavi, F., Bruton, T. C. and Li, Y., *J. Org. Chem.*, 1993, **58**, 744.
- Oae, S. and Doi, J. T. (eds), *Organic Sulfur Chemistry: Structure and Mechanism*, CRC Press, London, 1991, pp. 321-326 and references cited therein.
- Patai, S., Rappoport, Z. and Stirling, C. J. M. (eds), *The Chemistry of Sulphones and Sulfoxides*, Wiley, 1988, 1001 and references cited therein.
- Handa, Y., Inanaga, J. and Yamaguchi, M., *J. Chem. Soc., Chem. Commun.*, 1989, 298.
- Somasundaram, N., Pitchumani, K. and Srinivasan, C., *J. Chem. Soc., Chem. Commun.*, 1994, 1473.
- Amose, R. A., *J. Org. Chem.*, 1985, **50**, 1311.
- Shiramugi, T., Fukami, S., Wada, Y. and Yanagida, S., *J. Phys. Chem.*, 1993, **97**, 12882.

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