Asian Journal of Chemistry Vol. 6, No. 4 (1994), 796–800

Photochemical Oxidation of Dimethyl Sulphoxide by Singlet Oxygen

S.L. MALI, VEENA VAIDYA, R.L. PITLIYA, V.K. VAIDYA
and SURESH C. AMETA*
Department of Chemistry
M.L.V. Government (Autonomous) College
Bhilwara-311 001, India

Reaction of dimethyl sulphoxide with singlet oxygen was carried out using methanol as a solvent in presence of a sensitizer rose bengal. A white solid product was isolated and characterized as dimethyl sulphone by physical, chemical and spectral methods. A quantitative mechanism has been proposed for this reaction.

INTRODUCTION

There seems to be no doubt that the results on the photochemical behaviour of dyes in solution can be transferred in principle to more complex systems. In many cases, the reaction taking place on light absorption by the dye should be similar both in model systems and in dyed fibres. Therefore, the results of model system can give valuable hints for many photochemical reactions. It is important that an understanding of the mechanism of photochemical reaction results principally from studies of the photochemistry of dyes in solution. The reactions of singlet molecular oxygen with diethyl sulphides have been investigated[1–3]. The efficiency of their conversion into sulphone has been observed to be solvent dependent. The use of aprotic solvents and high temperature results in very low yields. Many photo-reactions have been reported for sulphur containing compounds and results were interpreted in terms of homolytic fission of carbon-sulphur bond[4]. The oxidation of dimethyl sulphoxide by potassium dichromate[5] and of methionine by U(VI)[6] have been reported while no attention has been paid on dye-sensitized photo-oxidation of dimethyl sulphoxide by singlet oxygen in the visible range. In view of this, it was considered of interest to undertake the title investigation.

EXPERIMENTAL

Dimethyl sulphoxide (E. Merk, b.p. 189°C), 1,4-diazo-bicyclo-(2,2,2)-octane (DABCO), rose bengal (CI 45440, Aldrich), methylene blue (CI 52015, Aldrich),

---

*Head, Department of Chemistry, Patan University, Patan (Gujarat), India.

crystal violet (CI 42555, E. Merk), eosin-Y (CI 45380, BDH), thionine (CI 52000, Ridel), riboflavin (LC) and methanol (BDH) were used. Solutions for the experiment were prepared by dissolving purified DMSO in methanol to a concentration of about 1 ml per 100 ml (V/V). The solutions were filtered through a fine cellulose fibre pad (4 mm thick). In this way, gel particles over 20 μm were removed. The dyes were dissolved in methanol at concentration 10^{-3} to 10^{-4} M and 1 ml of dye was added to 100 ml of the reaction mixture. The reaction mixture containing these dyes rapidly consumed oxygen on irradiation with 200 w tungsten lamp in visible light. The progress of reaction was followed by TLC. After 12 h. of irradiation TLC plate shown two spots; one corresponding to parent DMSO ($R_f = 0.93$) and other corresponding to the product ($R_f = 0.58$). The reaction was allowed to go for completion and the photoproduct was isolated from the reaction solution.

Rose bengal was used in the dye-sensitized photo-oxidation as it was found to be more competible with polysulphide and sulphoxide than other dyes as shown in Table 1.

TABLE 1

EFFECT OF TRIPLET ENERGIES ON THE YIELD OF PHOTO PRODUCT

Sensitizer	Triplet energy[7–9] KJ/mol.	Yield of product %
Rose bengal	157.0–176.6	20.0*
Eosin-Y	181.3–192.6	12.0
Methylene blue	142.3	14.0
Thionine	200.9	10.0
Riboflavin	242.0	08.0

Sensitizer = 8×10^{-5} M, Time of irradiation = 20 h

*In presence of monochromatic light the yield decreases.

Dye sensitized photo-oxidation of DMSO has also been carried out in presence of different sensitizers as shown in Table 1. The effect of triplet energy of sensitizers on the yield of photo-product has also been observed. As the triplet energy of the sensitizer was increased, the yield of the photo-product decreased. All these triplet energies are sufficient for the formation of singlet oxygen $^1O_2(\Delta g)$ while rose bengal, eosinY, thionine, riboflavin have enough triplet energies for the transfer, forming the singlet oxygen $^1O_2(\Sigma g^+)$. The sigma singlet oxygen is rapidly quenched in solution, so $^1O_2(\Delta g)$ is responsible for the oxidation.[10] The participation of singlet oxygen was confirmed by using different singlet oxygen scavengers in the reaction mixture where the yield was considerably reduced in presence of these scavengers and the results are summarized in Table 2. The spectral data obtained are summarized in Table 3

TABLE 2
EFFECT OF SINGLET OXYGEN SCAVENGERS

Scavengers[11-13]	Yield of Product
	20.0
Nickel chloride	Nil
Cobalt chloride	Nil
β-Carotene	Nil
DABCO	Nil
α-Tocopherol	Nil

(Rose Bengal) = 8×10^{-5} M, Time of irradiation = 20 h, (Scavengers) = 1.0×10^{-6} M

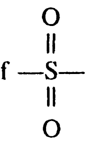
TABLE 3
ABSORPTION CHARACTERISTICS OF DIMETHYL SULPHOXIDE AND DIMETHYL SULPHONE[14-15]

Dimethyl Sulphoxide	Dimethyl Sulphone	Assignment
3020	3020	C–H stretching
2930	2930	C–H stretching
1460	1450	C–H bending
1410	1390	C–H bending
—	1330	S=O stretching
—	1150	S=O stretching
1100	—	S=O stretching
690	700	C–S stretching
680	680	C–S stretching

(B) Mass Spectroscopic Data

m/e = 94, 79, 64, 48, 32, 15.

RESULTS AND DISCUSSION

The photo-product was recrystallized (m.p. 109°C) and characterized as dimethyl sulphone by physical, chemical and spectral methods. When the solution of photo-product was evaporated to dryness and the mouth of the test tube was covered with a disk of nickel hydroxide paper and heated on micro flame, a black fleck appears on the green paper indicating the presence of  $—\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}—$ group in the photo-product[16].

The control experiments were preformed as:

(1) In presence of dye and light (no oxygen was passed)
(2) In presence of oxygen and dye (no exposure to light)
(3) In presence of oxygen and light (no dye was added)

It was observed that no product has been obtained in all the above three cases indicating the necessity of all the three components (light, dye and oxygen) in the photo-oxidation.

The photo-oxidation of neat DMSO was also carried out in absence of methanol. By keeping all other factors identical, it was observed that photo-oxidation takes place with the formation of photo-product which confirms the life time of singlet oxygen in DMSO.[10] The following scheme can be considered as describing the course of a singlet oxygen reaction.

$$\begin{aligned} D &\xrightarrow{h\nu} {}^1D^* \quad K_a \\ {}^1D^* &\longrightarrow {}^3D^* \quad K_i \\ {}^3D^* + {}^3O_2 &\longrightarrow D + {}^1O_2 \quad K_{O_2} \\ {}^1O_2 + S &\longrightarrow P \quad K_r \\ {}^1O_2 + Q &\longrightarrow {}^3O_2 + Q \quad K_Q \\ {}^1O_2 &\longrightarrow {}^3O_2 \quad K_d \end{aligned}$$

where D = dye, S = substrate, Q = quencher and P = product.

Application of the steady state assumption to the concentration of ${}^1O_2$ will provide an expression for the rate of consumption of oxygen:

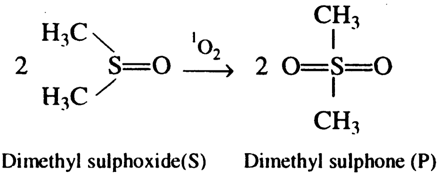


Fig. 1 Mechanism of photochemical oxidation of dimethyl sulphoxide.

$$-\frac{d[{}^3O_2]}{dt} = \frac{\beta K_r[s][{}^3O_2]}{K_r[s] + K_Q[Q] + K_d}$$

where β incoporates the quantum yield for production of ${}^3O_2$ (ground state oxygen).

The above mechanism for the reaction is in confirmation with the mechanism reported earlier[5, 17, 18]

REFERENCES

1. J.C. Bailar, H.I. Ir. Emeleus, R. Nyholm and A.F.T. Dickenson, Comprehensive Inorganic Chemistry, Pergamon, New York (1973).
2. G.O. Schenck and C.H. Kranch, *Chem. Berr*, **96**, 517 (1963).
3. C.S. Foote, R.W. Denny, L. Weaver, Y. Chang and J.W. Petters, *Ann. N.Y. Acad. Sci.*, **171**, 139 (1970).
4. S. Rao Vnkateswara and V. Jagannathan, *Indian, J. Chem.*, **27A**, 252 (1988).

5. K. Ganpathy and K. Iyangar, *Indian J. Chem.*, **27A**, 436 (1988).
6. R. Bhatt, Ph.D. thesis, Vikram University, Ujjain (1985).
7. D.R. Kearns, *J. Photochem. Photobiol., A: Chem.*, **10**, 215 (1969).
8. K. Eskins, *J. Photochem Photobiol., A: Chem.*, **29**, 609 (1979).
9. W. Adams, *Chem Ztg.*, **99**, 144 (1975).
10. B. Ranby and J.F. Rabek, Singlet Oxygen Reactions with Organic Compounds and Polymers, John Wiley & Sons, Chichester (1978).
11. D.J. Carlson, G.D. Medenhall, T. Sprunchuk and D.M. Wiles, *J. Am. Chem. Soc.*, **94**, 8960 (1972).
12. D.J. Carlson, T. Sprunchuk and D.M. Wiles, *Can. J. Chem.*, **52**, 3728 (1974).
13. C.S. Foote and R.W. Denny, *J. Chem. Soc.*, **52**, 6233 (1968).
14. D.H. Williams and I. Fleming, Spectroscopic Methods in Organic Chemistry, 4th Edn. (1990).
15. R.M. Silverstein, G.C. Bassler and T.C. Moroill, Spectroscopic Identification of Organic Compounds, 4th Edn. (1981).
16. F. Feigl, Spot Test in Organic Analysis, Elsevier Publishing Company, Amsterdam London-New York (1966).
17. V.K. Vaidya, R.L. Pitliya, H.S. Sharma and S.C. Ameta, *Curr. Sci.* (India), **58**, 17 (1989).
18. S.C. Ameta, P.B. Punjabi, C.S. Chobisa, N. Mangal and R. Bhardwaj, *Asian J. Chem. Rev.*, **1**, 106 (1990).

(*Received*: 6 July 1993; *Accepted*: 15 January 1994) AJC-752