Tetrahedron Letters No. 46, pp 4603 - 4606, 1973. Pergamon Press. Printed in Great Britain.

PREPARATION OF SINGLET OXYGEN BY HETEROGENEOUS PHOTOSENSITISATION

John R. Williams, Graham Orton and Larry R. Unger
Department of Chemistry, Temple University, Philadelphia, Pa. 19122

(Received in USA 6 September 1973; received in UK for publication 5 October 1973)

With the dramatic increase in the interest in the properties of singlet oxygen since 1963,[1] a wide variety of methods have been developed for its synthesis. The physical methods used include the sensitisation of oxygen in radiofrequency discharge tubes,[2] incandescent tungsten lamps,[3] and photolysis of ozone.[4] Chemical methods involve sensitisation by energy transfer,[1] use of aqueous hypochlorite-hydrogen peroxide solutions,[5-7] decomposition of ozonides,[8] and of endoperoxides,[9] the reaction of peroxyacetyl nitrate with base[10] and the treatment of potassium perchromate with water.[11] Unfortunately there are a number of disadvantages with these techniques. The physical gas-phase methods usually lead to low (less than 10^{-5} M) concentrations of singlet oxygen and the chemical methods can be complicated by unwanted side reactions. Furthermore, with chemical methods the reaction products have to be separated from the reagent products.

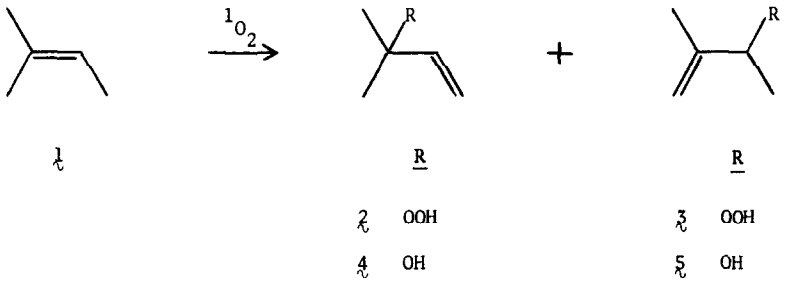
The method still most widely used for the generation of singlet oxygen in the laboratory is dye-sensitised excitation of oxygen. This method has the disadvantage that the dye is present throughout the reaction and must be removed from the reaction product. Secondly, most of the dyes used are not readily soluble in organic solvents. Thirdly, depending upon the nature of the solvent, temperature and concentration, the photosensitising dyes form dimers and higher aggregates thereby reducing their efficiencies as photosensitisers.[12]

With these problems in mind we wish to report a method using polymers for heterogeneous photosensitisation of oxygen. This method avoids contamination of the reaction product with the dye and allows a very easy and simple workup.

Since most of the common photosensitising dyes are charged it was found that they formed very strong complexes with the appropriate ion exchange resin. The anionic photosensitising dyes such as Rose Bengal, and Eosin were attached to a strongly basic anion exchange resin Amberlite IRA-400, (Rohm & Haas, Philadelphia, Pa.). The cationic photosensitising dye Methylene Blue was attached to a strongly acidic cation exchange resin Amberlite IRC-200.

To prepare the photosensitising polymer the ion exchange resin was added to an excess of the photosensitising dye in methanol solution and stirred for 10 min. For greater efficiency the ion exchange resin may be ground in a mortar and pestle to increase the number of dye molecule attached to the resin. The resulting colored resin was filtered off, washed thoroughly with water and methanol to remove the excess dye, dried and stored ready for use. The stirred photosensitising resin was then used as in normal dye-sensitised photooxygenations. However, using the photosensitizing polymer the product was simply obtained by filtering off the resin. Furthermore the resin may be washed and reused.

To demonstrate that singlet oxygen was generated by these photosensitising resins, the photosensitised oxidation of 2-methyl-2-butene 1 and anthracene 6 were investigated. These two substrates undergo characteristic reactions with singlet oxygen: 1 reacts via the "ene" reaction to form a mixture of hydroperoxides 2 and 3[13] which may be reduced with $NaBH_4$ and characterised as their alcohols 4 and 5, and 6 is known to react via the Diels-Alder reaction to yield 7.[14]



1

R

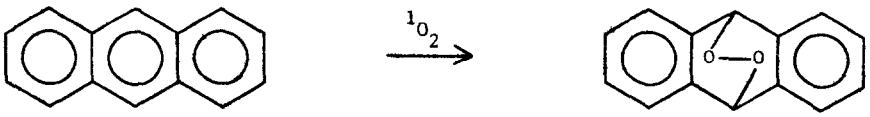
2 OOH

4 OH

R

3 OOH

5 OH



6

7

Photolyses were carried out in a water cooled immersion irradiation apparatus similar to the one described by Gollnick and Schenck [15] A solution of 1.5 g of 1 or 6 in 100 ml. of MeOH containing 5.0 g of dye saturated resin, was irradiated with a Sylvania "Sungun" Type DWY 625-W tungsten-iodine lamp. The resin was stirred and the volume of oxygen uptake measured (usually slightly less than one mole). The peroxides 2 and 3 were reduced with $NaBH_4$ and the products analysed and characterised by gas chromatography and spectroscopic methods. The results are summarised in Table I.

Table I.

Photooxygenation of 1 and 6 using Photosensitising Polymers

Photosensitising Polymer	Products		
	Percent in Reaction Mixture		Yield(%)
	4	5	7
Rose Bengal in soln[13]	51	49	30[14]
Rose Bengal in IRA 400	55	45	41
Eosin Y on IRA 400	56	44	40
Methylene Blue on IRC 200	53	47	27

The ratio of the two alcohols 4 and 5 is characteristic of the reaction of 1 with singlet oxygen.[13] Furthermore the formation of 7 from 6 is also a characteristic reaction of singlet oxygen.[14] These results therefore prove that the photosensitising polymers in Table I react by energy transfer to generate singlet oxygen.[16]

Recently a similar polymer-based photosensitiser for singlet oxygen generation was reported.[17]

Heterogeneous photosensitised oxidation should find wide application because of its ease of operation especially in the photooxygenation of biological molecules.

References

1. For leading references see D. R. Kearns, Chem. Revs., 71, 395 (1971).
2. J. F. Noxon, Can. J. Phys., 39, 1110 (1961).
3. A. U. Khan, Chem. Phys. Lett., 4, 567 (1970).
4. I. T. N. Jones and R. P. Wayne, J. Chem. Phys., 51, 3617 (1969).
5. A. U. Khan and M. Kasha, J. Chem. Phys., 39, 2105 (1963); 40, 605 (1964).
6. A. U. Khan and M. Kasha, Nature, 204, 241 (1964).
7. C. S. Foote and S. Wexler, J. Amer. Chem. Soc., 86, 3879 (1964).
8. R. W. Murray and M. L. Kaplan, ibid., 90, 537 (1968).
9. H. H. Wasserman and J. R. Schaeffer, ibid., 89, 3073 (1967).
10. R. P. Steer, K. R. Karnall and J. N. Pitts, Tetrahedron Letters, 3765 (1969).
11. J. W. Peters, J. N. Pitts, Jr., I. Rosenthal and H. Fuhr, J. Amer. Chem. Soc., 94, 4348 (1972).
12. R. W. Chambers and D. R. Kearns, Photochemistry and Photobiology, 10, 215 (1969).
13. C. S. Foote, S. Wexler, W. Ando, Tetrahedron Letters, 4111 (1965).
14. C. S. Foote, S. Wexler, W. Ando and R. Higgins, J. Amer. Chem. Soc., 90, 975 (1968).
15. K. Gollnick and G. O. Schenck in "1,4-Cycloaddition Reactions" J. Hamer, ed., Academic Press, New York, N.Y. 1967, p.255.
16. Careful checks were made to verify the dye needed to be present for the reaction to occur and that the dye had not been leached out of the photosensitising resin.
17. E. C. Blossey, D. C. Neckers, A. L. Thayer and A. P. Schaap, J. Amer. Chem. Soc., 95, 5820 (1973).