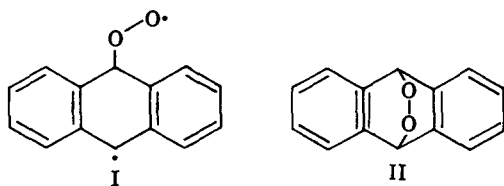


Kautsky⁶; the reactive intermediate is an excited singlet state of molecular oxygen.

The evidence which supports mechanism a is as follows. (1) Gaffron found that with one sensitizer, at least, light of 8200 Å. is effective. Since this wavelength is of insufficient energy to excite the $^1\Sigma_g^+$ state of O₂, Gaffron concluded that singlet oxygen could not be intermediate.⁶ Kautsky, however, pointed out that there was ample energy in Gaffron's system to excite oxygen to the lower-lying $^1\Delta_g$ state.^{5c} (2) Livingston's kinetic studies indicate that the active intermediate has somewhat different kinetic behavior when formed with anthracene or with diphenylanthracene as sensitizer.⁷ The rates were measured indirectly, and with a fairly high probable error, making this conclusion somewhat questionable. In other cases, Schenck has found that the rate of disappearance of the active intermediate does not depend on sensitizer.^{2d}

Until now, the singlet oxygen mechanism has been generally disregarded despite the following observations. (1) Kautsky observed that reaction occurs even when sensitizer and acceptor are adsorbed on separate granules of silica gel, which would indicate that a reactive intermediate is formed which is capable of diffusion under vacuum.^{5a,b} Similar phenomena were noted by Rosenberg and Shombert.⁸ *No satisfactory explanation of these observations in terms of mechanism a has yet been made.* (2) The "moloxide" would have to have an unexpected property; for example, in the reaction with anthracene, which is both sensitizer and acceptor, the kinetics require that the intermediate (which, if it is a moloxide, is presumably of structure I) cannot collapse to product II itself, but must transfer oxygen to a second anthracene molecule.^{3,9}



Since singlet oxygen has now been shown to be effective in carrying out reactions identical with the photosensitized autoxidations,¹⁰ the weight of the evidence favors the intermediacy of singlet oxygen. Further experiments are in progress.

- (5) (a) H. Kautsky and H. de Bruijn, *Naturwiss.*, **19**, 1043 (1931); (b) H. Kautsky, H. de Bruijn, R. Neuwirth, and W. Baumeister, *Ber. deut. chem. Ges.*, **66**, 1588 (1933); (c) H. Kautsky, *Biochem. Z.*, **291**, 271 (1937).
 (6) H. Gaffron, *ibid.*, **287**, 130 (1936), and references cited therein.
 (7) R. Livingston and V. Subba Rao, *J. Phys. Chem.*, **63**, 794 (1959).
 (8) J. L. Rosenberg and D. J. Shombert, *J. Am. Chem. Soc.*, **82**, 3527 (1960).
 (9) G. O. Schenck, *Naturwiss.*, **41**, 452 (1954).
 (10) (a) C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3879 (1964); (b) E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3881 (1964).

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A Study of the Peroxidation of Organic Compounds by Externally Generated Singlet Oxygen Molecules

Sir:

The existence of two low-lying metastable singlet states of diatomic oxygen ($^1\Delta_g$ and $^1\Sigma_g$ which are 0.977

and 1.63 e.v. above the ground state)¹ and the "forbiddenness" of radiative return to the ground state suggested the possibility that singlet O₂ might be a useful and selective reagent in organic chemistry. We were further interested in this case as a result of our previous experience with another highly reactive small molecule, diimide² (N₂H₂), and because of the possible importance of metastable O₂ in photosensitized peroxidations.^{3,4} It seemed to us that the O₂ molecule, raised above its ground state by *ca.* 22.5 or 37.5 kcal./mole and converted to a singlet state (removing spin-conservation difficulties in forming singlet products from reactants of singlet multiplicity), could reasonably be expected to afford the same reactions as observed in sensitized photooxidation.³

Our initial studies have been conducted using gaseous oxygen subjected to electrodeless discharge at 6.7 Mc., a method for producing singlet O₂ first described by Foner and Hudson.⁵ The radiofrequency unit was a T21/ARC-5 U. S. surplus aircraft transmitter (modified to permit resonant coupling to the discharge tube) with the output leads attached (by platinum wire) to two aluminum foil bands (2 cm. apart) fitted around quartz tubing (12-mm. o.d.). Oxygen was passed through the quartz tube at *ca.* 20 mm. with the discharge operating to produce a definite glow in the tube between the aluminum terminals, and the emerging gas was bubbled into a solution of the reactant (usually stirred). The reactor was located downstream from the discharge zone by 20–30 cm.; the exact distance did not appear to be a critical variable, however. A water aspirator was employed at the end of the system to pull gas through. The vessel containing the organic reactant was shielded from light by a covering of aluminum foil.

Using this apparatus and bromobenzene as solvent at 0°, anthracene, 9,10-diphenylanthracene, and 9,10-dimethylanthracene were cleanly converted to the corresponding 9,10-endoperoxides, identical with authentic samples prepared by the photooxidation route. *No other product could be detected.* In control experiments in the same apparatus, under the same conditions *but with the radiofrequency unit and discharge off*, no more than trace quantities of peroxide were formed (analysis by chromatography). Therefore, the zero level of the $^3\Sigma_g$ ground state of O₂ is not responsible for endoperoxide formation. It also seems improbable that vibrationally excited $^3\Sigma_g$ molecules could persist long enough to effect oxidation in solution. Ozone and monatomic oxygen can also be excluded since these would lead to other types of products.^{6–8} The species

- (1) See G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., New York, N. Y., p. 560, for example.
 (2) E. J. Corey and W. L. Mock, *J. Am. Chem. Soc.*, **84**, 865 (1962), and previous papers; see also S. Hunig, H. Muller, and W. Thier, *Tetrahedron Letters*, No. 11, 353 (1961); E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *J. Am. Chem. Soc.*, **83**, 3725 (1961).
 (3) For a recent review see G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957).
 (4) This possibility appears to have been suggested first by H. Kautsky and H. deBruijn, *Naturwiss.*, **19**, 1043 (1931).
 (5) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **25**, 601 (1956); **23**, 1974 (1955).
 (6) R. J. Cvetanovic, "Advances in Photochemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, p. 115.
 (7) R. E. Erickson, P. S. Bailey, and J. C. Davis, Jr., *Tetrahedron*, **18**, 389 (1962).
 (8) P. S. Bailey, *Chem. Rev.*, **58**, 926 (1958); P. S. Bailey, P. Kolsaker, B. Sinha, J. B. Ashton, F. Dobinson, and J. E. Batterbee, *J. Org. Chem.*, **29**, 1400 (1964).