Kautsky[6]; 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 wave length is of insufficient energy to excite the $^1\Sigma_g{}^+$ state of O_2, 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]

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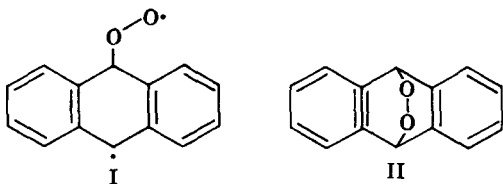
Since singlet oxygen has now been shown to be effective in carrying out reactions identical with the photosensitized autoxidations,[10] the weight of the evidence favors the intermediacy of singlet oxygen. Further experiments are in progress.

(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 O_2 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, diimide[2] (N_2H_2), and because of the possible importance of metastable O_2 in photosensitized peroxidations.[3,4] It seemed to us that the O_2 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 O_2 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 O_2 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).

which can account most reasonably for the observed results are $^1\Delta_g$ or $^1\Sigma_g$ forms of O_2. Both of these are known to be produced by the technique used in the present work,[5,9,10] the former in greater amount by at least 10^2.

The relative rates of peroxidation of the three anthracenes studied were 9,10-dimethylanthracene > 9,10-diphenylanthracene > anthracene. With the particular apparatus used in the present work, 19 hr. was required for complete conversion of 100 mg. of 9,10-dimethylanthracene to the 9,10-peroxide. Even in the case of this relatively reactive substrate there does not seem to be a highly efficient capture of reactive oxygen, based on the supposition that 10% of the oxygen molecules are converted to the $^1\Delta_g$ state[5] and the estimated flow rate. The considerable difference in reactivity of 9,10-dimethylanthracene and anthracene (roughly 100-fold) indicates that this reactive O_2 is rather selective.

An interesting effect of solvent on the rate of peroxidation of 9,10-diphenylanthracene was noted. Chlorobenzene, bromobenzene, and nitrobenzene gave faster reaction rates than anisole, dimethyl sulfoxide, or iodobenzene (which were all about the same), and these in turn led to faster oxidation than p-cymene or decalin. The rate factor from the most effective solvent chlorobenzene to decalin, the poorest, was over twenty (at $0°$).

Reactive 1,3-dienes are also susceptible to endoperoxidation. For example, and in analogy with the classical case of photooxidation,[3] exposure of α-terpinene to singlet oxygen afforded ascaridol. 2,5-Diphenyl-3,4-isobenzofuran afforded 1,2-dibenzoylbenzene[3] in high yield. On the other hand, attempts to convert olefins to allylic hydroperoxides have so far not succeeded in the case of α-pinene, 1-phenylcyclohexene, tetramethylethylene (gas phase), or cholest-4-en-3β-ol. Work is in progress to ascertain the significance of these preliminary results.

Although the instrumentation and techniques used in the present work are quite simple (comparable to those conventionally employed for ozonolysis), they are satisfactory only on a limited scale; with quantities greater than several millimoles, inconveniently long reaction times are required for complete conversion. Improvements in the metastable oxygen generator are clearly desirable.

We have followed with interest several recent publications on the chemical generation of singlet oxygen by the oxidation of hydrogen peroxide,[11-14] but we have done no work on the application of these systems to peroxidation of organic substrates. We have been informed by Professor Christopher Foote[15] that he has succeeded in effecting a number of peroxidation reactions by the oxidation of hydrogen peroxide in the presence of various substrates.

(9) L. Elias, E. A. Ogryzlo, and H. I. Schiff, *Can. J. Chem.*, **37**, 1680 (1959).

(10) M. A. A. Clyne, B. A. Thrush, and R. P. Wayne, *Nature*, **199**, 1057 (1963).

(11) A. U. Khan and M. Kaska, *J. Chem. Phys.*, **39**, 2105 (1963).

(12) S. J. Arnold, E. A. Ogryzlo, and H. Witzke, *ibid.*, **40**, 1769 (1964).

(13) E. J. Bowen and R. A. Lloyd, *Proc. Chem. Soc.*, 305 (1963).

(14) R. J. Browne and E. A. Ogryzlo, *ibid.*, 117 (1964).

(15) C. S. Foote, personal communication, June 22, 1964; see C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3879, 3880 (1964). Professor Foote has also indicated that Professor K. Bayes of U.C.L.A. is also engaged in the study of singlet O_2.

It is possible that singlet O_2 might also be a product of other types of chemical processes, *e.g.*, the reaction of hydrogen peroxide with oxalyl chloride,[16] which yields both molecular oxygen and luminescence, and the reactions of ozone with phosphines, phosphite esters, sulfides, etc.[17]

Work on the chemistry of externally generated metastable oxygen is being continued along the lines suggested by the results described above.

(16) E. A. Chandross, *Tetrahedron Letters*, **No. 12**, 761 (1963).

(17) See Q. E. Thompson, *J. Am. Chem. Soc.*, **83**, 845 (1961), and references cited therein.

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Amineborane Reductions in Aqueous Acid Media

Sir:

Recent solvolysis studies[1,2] have shown that certain amineboranes have a high degree of kinetic stability in water and mixed aqueous solvents. Their slow rates of hydrolysis permit studies of their reactions in highly acidic media, conditions which preclude the study of many other hydridic compounds such as the alkali metal borohydrides. The present communication describes an investigation of reactions of amineboranes with specific carbonyl compounds under such conditions. The amineboranes employed were effective reducing agents in strong aqueous acid, and *their rates of reaction with carbonyl compounds were found to increase with increasing acidity of the medium*.

The use of amineboranes for the reduction of aldehydes and ketones to the corresponding alcohols is well known.[3-7] In the present investigation, the rate of disappearance of each amineborane in a buffered solution containing a large excess of the carbonyl compound was followed iodometrically[8] and found to be first order in amineborane. Variations in rate with changes in the concentration of the carbonyl component revealed a first-order dependence on the concentration of aldehyde or ketone. For a given system, above a certain concentration of hydrogen ion, the observed rate varied linearly with $[\mathrm{H^+}]$ as shown in Fig. 1 for the reaction of acetone with morpholineborane in water at $25°$. The data lead to the following rate equation.

$$\frac{-d(\text{amineborane})}{dt} = (\text{amineborane})(R\overset{\overset{\displaystyle O}{\|}}{-}C-R')(k_1 + k_2[\mathrm{H^+}])$$

(1) H. C. Kelly, F. R. Marchelli, and M. B. Giusto, *Inorg. Chem.*, **3**, 431 (1964).

(2) G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **82**, 3290 (1960).

(3) Callery Chemical Co., Technical Bulletin C-200, April, 1958.

(4) R. P. Barnes, J. H. Graham, and M. D. Taylor, *J. Org. Chem.*, **23**, 1561 (1958).

(5) H. Nöth and H. Beyer, *Ber.*, **93**, 1078 (1960).

(6) W. M. Jones, *J. Am. Chem. Soc.*, **82**, 2528 (1960).

(7) H. C. Kelly and J. O. Edwards, *ibid.*, **82**, 4842 (1960).

(8) D. A. Lyttle, E. H. Jensen, and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).