I

time the reaction mixture was allowed to warm slowly to 25 °C and was stirred for 16 h. The mixture was then cooled to 0 °C and $(CH_3)_2CHOH$ (10 mL) was added carefully. After the evolution of gas had ceased, removal of the solvent in vacuo and sublimation of the residue (0.1 mmHg, 120 °C) gave I (3.2 g, 76%) as air- and moisture-sensitive white crystals.

The structure of I was established from the following data. The proton decoupled ^{31}P NMR spectrum[4] showed a simple AB_2 pattern with peaks at 18.6 ppm[5] (a doublet with J_{PNP} = 12 Hz) and 12.1 ppm (a triplet with J_{PNP} = 12 Hz). The peak at 12.1 ppm was significantly larger than expected because of the nuclear Overhauser influence by the hydrogen atom bound to this phosphorus. In the proton-undecoupled ^{31}P NMR spectrum, the peak at 12.1 ppm was split into a doublet (J_{PH} = 560–570 Hz). The ^1H NMR spectrum[6] showed the methyl protons at 1.77 ppm (as a doublet, J_{PCH} = 16 Hz, of multiplets, J_{HPCH} = 3.4 Hz, J_{PNPCH} = 4 Hz). The hydride resonance appeared at 7.44 ppm (as a doublet, J_{PH} = 568 Hz, of triplets, J_{PNPH} = 11 Hz, of multiplets, J_{HCPH} = 3.4 Hz). The coupling constants were confirmed by ^1H homo-decoupled NMR experiments.

The infrared spectrum showed bands for the CH_3 group at 3000 (w) and 2910 (w), PH units at 2409 (m) and 2399 (m), and PN bonds at 1220 (s), 1180 (s) and 1160 (s) cm^{-1}. The mass spectrum showed a parent ion at m/e 291, with a characteristic Cl_4 isotope pattern. Correct microanalytical data were also obtained.[7]

The only other example of a hydridophosphazene was synthesized by Schmidpeter et al.[8,9] by rearrangement of a proton from skeletal nitrogen during the condensation of a linear aryl–phosphorus–nitrogen species with a phosphine. Compound I is the first example of a hydridophosphazene formed as the result of the reaction of an organometallic reagent with a preformed cyclic phosphazene. It is also the only example of a cyclophosphazene with both halogen and hydrogen atoms as substituent groups. Thus, it is a valuable synthetic intermediate. For example, the reaction of I with chlorine in carbon tetrachloride led to the formation in high yields of $N_3P_3Cl_5CH_3$, a compound not readily available by other routes. The P–H bond also generates intriguing possibilities for insertion-type reactions.

The reactions of Grignard reagents with organic substrates in the presence of *catalytic* amounts of copper are well documented, and these reactions are thought to proceed via organocopper intermediates.[10] However, in the reaction reported here, the yield of I *depended* on the copper concentration, and the maximum yield was obtained with copper:phosphazene ratios of $\geq 0.5:1$. Vapor phase chromatography experiments showed that the concentration of $(NPCl_2)_3$ decreased in proportion to the amount of Grignard added, *but* I was not formed until 2-propanol was added to the mixture.

The 2-propanol was added initially as a Grignard deactivation agent. However, isotope-labeling studies using $(CH_3)_2CHOD$ indicated that the alcohol was the source of the hydrogen atom bound to phosphorus in I. This suggests that I is generated via the intermediate formation of a metallophosphazene species where two phosphazene molecules are associated with one copper atom, and this possibility is being investigated.

Acknowledgment. We thank the Office of Naval Research for the support of this work.

References and Notes

(1) M. Biddlestone and R. A. Shaw, *J. Chem. Soc. A*, 178 (1968); 1750 (1970).
(2) C. W. Allen and T. Moeller, *Inorg. Chem.*, **7**, 2178 (1968).
(3) T. N. Ranganathan, S. M. Todd, and N. L. Paddock, *Inorg. Chem.*, **12**, 316 (1973).
(4) ^{31}P NMR spectra were obtained in $CDCl_3$ solution.
(5) Positive ^{31}P shifts are downfield from external phosphoric acid.
(6) ^1H NMR spectra were obtained in $CDCl_3$. The peak positions are downfield from internal Me_4Si.
(7) Anal. Calcd for $CH_4N_3P_3Cl_4$: C, 4.13; H, 1.37; N, 14.33; P, 31.74; Cl, 48.45. Found: C, 3.98; H, 1.40; N, 14.23; P, 31.65; Cl, 47.45.
(8) A. Schmidpeter and J. Ebeling, *Angew. Chem.*, **80**, 197 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 209 (1968).
(9) A. Schmidpeter, J. Hogel, and F. R. Ahmed, *Chem. Ber.*, **109**, 1911 (1976).
(10) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).

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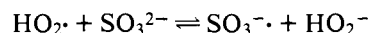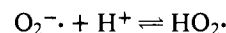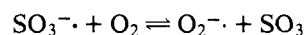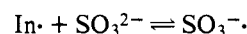*University Park, Pennsylvania 16802*
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Photochemical Generation of O_2^- by Rose Bengal and $Ru(bpy)_3^{2+}$

Sir:

The photochemical formation of singlet oxygen from dye sensitizers[1a] has been assumed since Foote and Wexler's[1b] classic experiments reconfirmed Kautsky's original proposals. Yet there is another possibility when an excited dye, or other excited molecule, encounters molecular oxygen—namely electron transfer.[2] This latter reaction would produce superoxide and the radical cation from the sensitizer. We report our results regarding this latter possibility herein.

The aerobic oxygenation of sulfite is a sensitive detector of *superoxide* ion (O_2^-).[3] Superoxide enhances the autoxidation of sulfite, SO_3^{2-}, according to the following mechanistic scheme:

$$In\cdot + SO_3^{2-} \rightleftharpoons SO_3^-\cdot$$

$$SO_3^-\cdot + O_2 \rightleftharpoons O_2^-\cdot + SO_3$$

$$O_2^-\cdot + H^+ \rightleftharpoons HO_2\cdot$$

$$HO_2\cdot + SO_3^{2-} \rightleftharpoons SO_3^-\cdot + HO_2^-$$

In this scheme $In\cdot$ is an initiator. In now classic studies, SO_3^{2-} oxidation was used by Fridovich and Handler in a number of ways—to prove the one-electron reduction using xanthine oxidase,[4] to demonstrate the inhibiting actions of carbonic anhydrase and myoglobin on the reduction of cytochrome c by xanthine oxidase,[5] and to detect superoxide anion in illuminated dye solutions containing sulfite.[6,7]

Recently several groups have become concerned with (a) the mechanism of singlet oxygen formation from certain dyes, in particular rose bengal, and (b) the role of superoxide (O_2^-) in reactions attributed to singlet oxygen.[8]

To study the role that superoxide may play in sensitized photooxidation reactions, we have studied oxygen uptake, with a Clark oxygen electrode, of a solution of sulfite dyes, and the superoxide inhibiting enzyme, superoxide dismutase.

Dark solutions of sulfite and rose bengal were saturated with oxygen at 35 °C buffered at 7.8 pH with phosphate and the oxygen uptake measured. When a solution of sulfite and rose bengal was irradiated at 562 nm with a monochromator, the rate of sulfite oxidation increased severalfold over that of the oxidation in the dark for the same solution. According to the
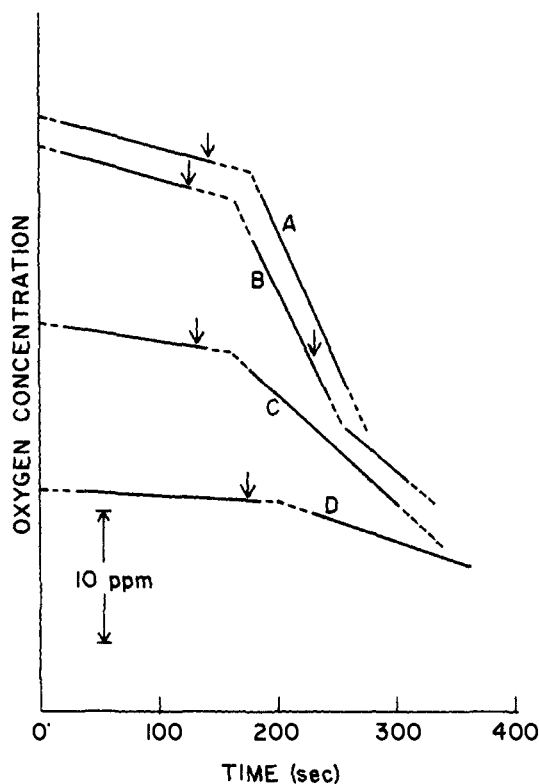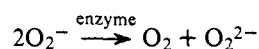
Figure 1. Initiation of the oxidation of sulfite by rose bengal. A and B: reaction solutions with rose bengal (6.9×10^{-5} M), sodium sulfite (3.2×10^{-2} M), and EDTA (1.8×10^{-4} M) in pH 7.8 phosphate buffer. The first arrow on each plot points to the time at which the irradiation at 562 nm was started. The second arrow on B points to the time at which the enzyme superoxide dismutase was introduced. C is same solution as above with the enzyme added at the beginning. All solutions were saturated with O_2 at 35 °C. D is the same solution as A, with Dabco (0.14 M) added at the beginning.

results of Fridovich and Handler,[3] this implicates the formation of superoxide, Figure 1A.

We were able to confirm the presence of superoxide in the reaction mixture by the addition of the enzyme superoxide dismutase, which dismutates the superoxide ion.[9,10]

$$2O_2^- \xrightarrow{\text{enzyme}} O_2 + O_2^{2-}$$

Since superoxide dismutase (SOD) competes for O_2^- one can expect the light sensitized oxidation of SO_3^{2-} to be affected if O_2^- is involved in the process.

That the oxidation of sulfite is affected by SOD is indicated by the results in Figure 1B. The arrow points to the time at which the enzyme was injected. In Figure 1C, studies of oxygen uptake for a solution of dye, enzyme, and sulfite are shown. During irradiation the rate of oxygen uptake is similar to that of the third segment of Figure 1B.

The conclusion of the experiments is obvious—illuminated rose bengal produces superoxide ion.[11]

To answer the question whether the singlet oxygen and SO_3^{2-} give rise to O_2^- via a chain reaction, quenching experiments with 1,4-diazabicyclo[2.2.2]octane [Dabco] were performed with various amounts of Dabco.[12] The slope attributed to O_2^- became constant above 0.1 M for Dabco, indicating that the singlet oxygen oxidation is completely inhibited above this concentration. If the singlet oxygen is the only source of O_2^- in the chain reaction, the oxidation of SO_3^{2-} should be completely quenched by the action Dabco. As one can see in Figure 1D however, the photooxidation of SO_3^{2-} occurs even in the presence of 0.14 M Dabco. Thus singlet oxygen cannot be the sole reason for SO_3^{2-} oxidation in dye-
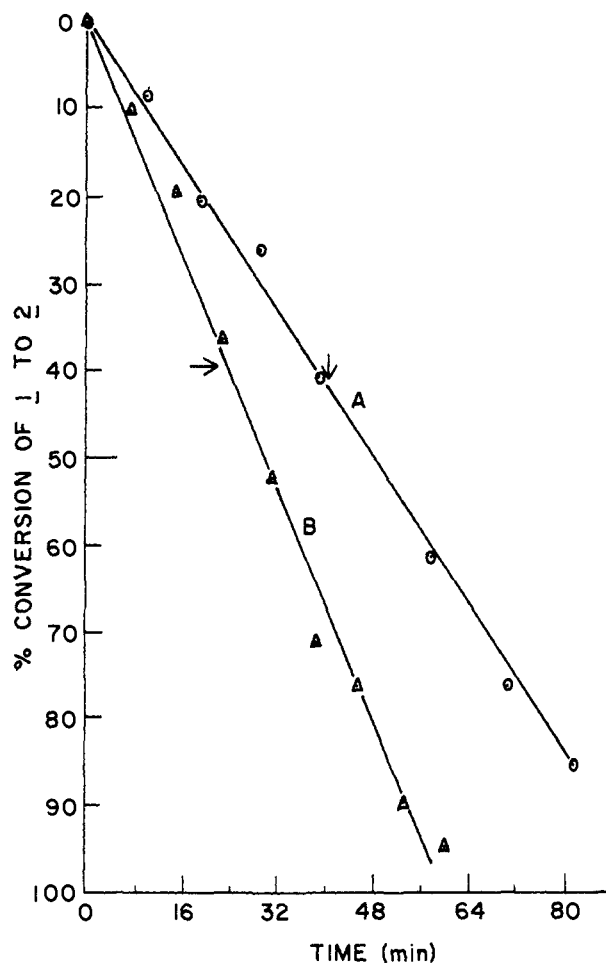

Figure 2. Singlet oxygen trapping studies with rose bengal and 2,3-diphenyl-*p*-dioxene (**1**). A: the reaction solution contains 2 μmol of rose bengal, 210 μmol of **1**, and 8.3 μmol of Tris in 8 mL of methanol; the arrow points to the time at which 0.6 mg of superoxide dismutase was introduced. B: a reaction solution containing 1.2 μmol of rose bengal and 126 μmol of **1** in a mixture of 5 mL of THF and 5 mL of pH 7.8 phosphate buffer; the arrow points to the time at which the enzyme was introduced.

illuminated solutions. Superoxide (O_2^-) is also independently generated. This is further indicated by the difference in the slopes of the second segment of 1B and 1D. We also conclude that $^1O_2$ reacts with sulfite, by a different pathway.

However rose bengal has been used for many years as a source of singlet oxygen. It occurred to us therefore that illuminated rose bengal might produce either superoxide exclusively in lieu of singlet oxygen, that superoxide might precede singlet oxygen on the reaction coordinate, or the superoxide might be produced competitively with singlet oxygen from illuminated rose bengal.

To test, again, for the presence of singlet oxygen we carried out the following experiments.

Singlet oxygen undergoes a cycloaddition reaction with 2,3-diphenyl-*p*-dioxene (**1**) yielding carbonyl containing products (**2**). This reaction has been used effectively to study
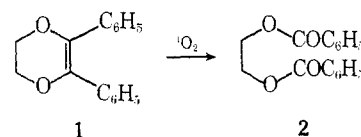
the generation of singlet oxygen from irradiated polymer-bound rose bengal.[13]

We followed the oxidation of **1** by irradiating a buffered rose bengal solution in methanol, both in the absence and the

presence of SOD. We also carried out the experiments in a well-dispersed heterogenous mixture of tetrahydrofuran and aqueous phosphate buffer (pH 7.8) containing rose bengal. Both the reactant and the product were monitored by gas chromatography. The solutions did not contain any free-radical inhibitor.[13]

The results are shown in Figure 2. The reaction was zero order with respect to **1** as expected,[13] but was unaffected by the presence of the enzyme SOD within the limits of experimental detection. Even after the injection of the enzyme the rate of conversion of **1** to **2** remained the same. This indicates that there is a parallel mechanism for the generation of $^1O_2$ from rose bengal as compared to the production of O_2^- reported earlier.[14]

We performed similar experiments in the presence of SO_3^{2-}, to study the quenching effects of SO_3^{2-} on the $^1O_2$. The half-life of SO_3^{2-} in such solutions was quite short; yet for the first 10 min we were able to confirm that, indeed, $^1O_2$ is quenched by sulfite ions.

We conclude therefore that both the generation of O_2^- and of $^1O_2$ are possible from irradiated rose bengal in the presence of oxygen.

The quantum efficiency for the removal of oxygen by both the singlet oxygen path and the superoxide path can be calculated from the measured oxygen uptake in the presence and the absence of SOD, as well as with Dabco. If one writes the reactions, the relative efficiency of formation of singlet oxygen and superoxide can be calculated. Comparison of the slopes of 1B and 1D indicates that relative amounts are 77 to 23 in favor of $^1O_2$. This compares favorably with the values reported earlier by Schade and Gollnick.[15] In accompanying studies, we have studied the photochemical reaction of $Ru(bpy)_3^{2+}$ with SO_3^{2-} and oxygen.

We followed the oxygen uptake rate in $Ru(bpy)^{2+}$, phosphate buffered sulfite solution both in the dark and with illumination (453 nm) as above. Similar studies with SOD and Dabco indicated the generation of O_2^-.

References and Notes

(1) (a) H. Kautsky and H. de Bruijn, *Naturwissenschaften*, **19**, 1043 (1931); (b) C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3876 (1964).
(2) (a) R. Livingston, *J. Phys. Chem.*, **46**, 233 (1942); (b) C. S. Foote, "Photosensitized Oxidation and Singlet Oxygen: Consequences in Biological System", in Free Radicals in Biology, Vol. II, Academic Press, New York, N.Y., 1976.
(3) I. Fridovich and P. Handler, *J. Biol. Chem.*, **236**, 1836 (1961).
(4) I. Fridovich, *J. Biol. Chem.*, **245**, 4053 (1970).
(5) J. M. McCord and I. Fridovich, *J. Biol. Chem.*, **243**, 5753 (1968).
(6) I. Fridovich and P. Handler, *J. Biol. Chem.*, **235**, 1835 (1968).
(7) I. Fridovich and P. Handler, *Biochim. Biophys. Acta*, **35**, 546 (1959).
(8) C. W. Jefford and A. F. Boschung, *Tetrahedron Lett.*, 4771 (1976).
(9) I. Fridovich, *Acc. Chem. Res.*, **5**, 321 (1972).
(10) A. U. Khan and M. Kasha, *J. Am. Chem. Soc.*, **88**, 1574 (1966).
(11) We were also able to confirm the presence of O_2^- in reactions sensitized by polymer-bound rose bengal, though we had to use much more intense light source for this work.
(12) C. Ouannes and T. Wilson, *J. Am. Chem. Soc.*, **90**, 6528 (1968).
(13) A. P. Schaap, A. L. Thayer, E. C. Blossey, and D. C. Neckers, *J. Am. Chem. Soc.*, **97**, 3741 (1975).
(14) Of significance is that the reaction attributed to singlet oxygen required a much lighter lamp intensity than that of superoxide.
(15) K. Gollnick, T. Franken, G. Schade, and G. Dorhafer, *Ann. N.Y. Acad. Sci.*, **171**, 89 (1970).

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Reaction of Singlet Oxygen with a Norbornadienol Ether. Intramolecular Interception of a Zwitterionic Peroxide

Sir:

Whether perepoxides are intermediates in the reaction of singlet oxygen with monoolefins still remains problematic,[1] However, for electron-rich olefins, such as enamines[2] and enol ethers,[3] evidence has been steadily accumulating that dioxetanes are formed in a two-step process.[4,5] A pertinent example is provided by the photooxygenation of 2-methoxynorbornene (**1**) in the presence of methanol as an external nucleophile.[6] The hydroperoxy ketal (**5**) is formed, whose origin is the short-lived zwitterionic peroxide **2** or its perepoxide tautomer **3** which are intercepted by methanol before they collapse to the end product, the *exo*-dioxetane **4**. We now report that, by
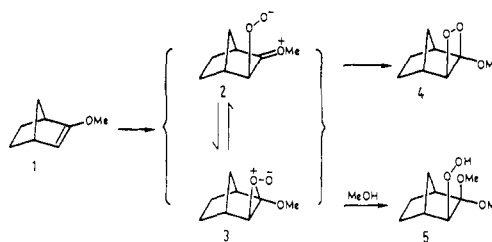

appropriately modifying the skeleton of **1**, the zwitterionic peroxide can be trapped intramolecularly. The molecules chosen are 2-trimethylsiloxy-2,5-norbornadiene (**6**) and its 7,7-dimethyl derivative (**7**).[7] Their particular advantage is that a cationic center engendered by reaction with singlet oxygen should be captured by the norbornenyl double bond to produce nortricyclyl products.[9] Not only is this expectation realized, but all three possible modes of internal interception of the initially formed zwitterionic peroxide are exhibited.

Photooxygenation of the norbornadiene **6** in deuteriochloroform using *meso*-tetraphenylporphin as sensitizer at −20 °C gave mostly the *exo*-α-silylperoxy ketone **8** (~80%), traces of its endo isomer **9** (<5%), and substantial amounts of the *exo*-dioxetane **10** (20%).[10] The total yield was low (15–20%), as much polymeric material was formed. Reaction of the
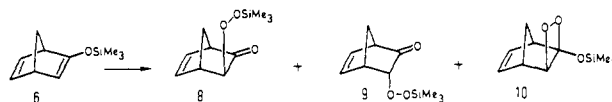
7,7-dimethyl derivative **7**, under the same conditions, provided a dramatically different result. A clean, polymer-free, mixture of the expected *endo*-α-silylperoxy ketone **11** (64%) and a new tetracyclic peroxide **12** (36%) was formed. Careful scrutiny of the mixture by NMR spectroscopy at low temperature revealed traces of the *endo*-dioxetane **13** (<5%). Both **11** and
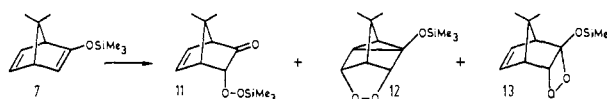
12 were isolated by column chromatography at low temperature and were readily identified by their NMR spectra.[11]

These results are convincingly rationalized in terms of the formation of ionic intermediates as the primary event. Attack by singlet oxygen on the parent norbornadiene **6** takes place preferentially on the less hindered exo face of the molecule to give the zwitterionic peroxide **14** or its tautomer **15**. Subse-