face of the CdSe. At −0.15 V a photocurrent of 0.047 mA (a quantum yield for electron flow of 0.046) was observed corresponding to a power output of at least 7×10^{-3} mW. The power conversion efficiency is then $(7 \times 10^{-3})/2$ or 0.35%. Efficiency has not been optimized, but these experiments establish the importance of chemical stabilization of the photoelectrode. The details of these studies, along with results of attempts to increase efficiency, will be reported subsequently.

Note Added in Proof. We have now found that etching the CdS and CdSe leads to significantly improved efficiencies: ~5% for CdS at 500 nm and up to ~9% for CdSe at 633 nm in a 1 M Na_2S, 1 M S, 1 M NaOH aqueous electrolyte. Stability is still maintained at these high power conversion efficiencies.

Acknowledgment. We thank the National Aeronautics and Space Administration for support of this research.

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Ground and Excited State Correlations in the Rupture of Oxygen–Oxygen Bonds in Peroxides

Sir:

The ground state rupture of peroxide bonds is known to be involved in a number of condensed phase chemi- and bioluminescence reactions.[1] In addition, the photodecomposition of the peroxide linkage is used as a method of generating a number of radical species.[2] There is, however, some question about the photochemical nature of the states reached by photoexcitation. In particular, it is not generally recognized[3] that besides the ground state of hydrogen peroxide a number of singlet and triplet excited states are adiabatically correlated with the two ground state hydroxyl radicals. However, in a recent review article[4] Dauben, Salem, and Turro classified the rupture of a peroxide bond as being of the $(\sigma\pi)(\sigma\pi)$ type showing that a total of four pairs of diradical states are possible. This paper will show that this is computationally correct. We will also propose a simple bonding argument to show why it is correct.

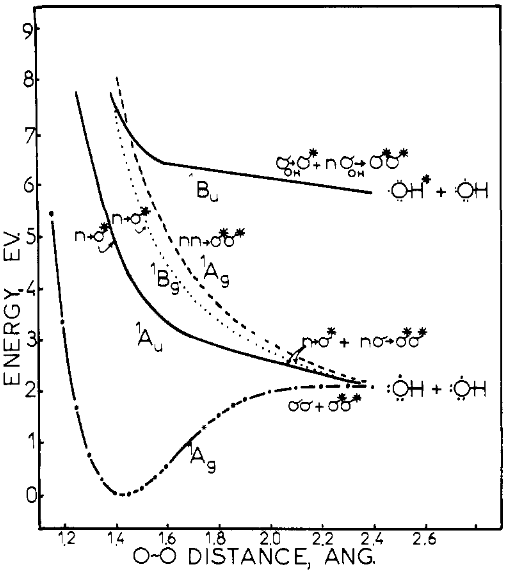
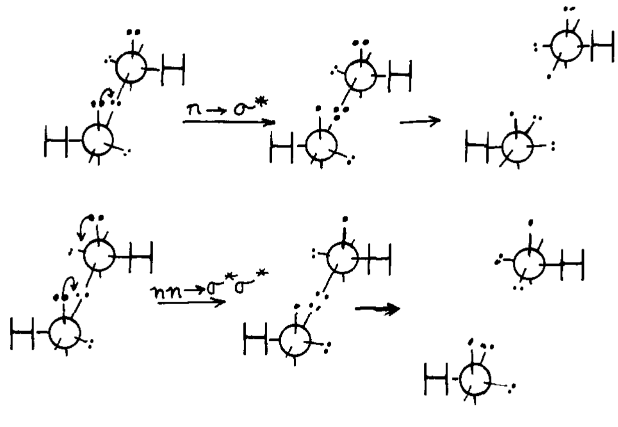


Figure 1. Ground and excited singlet correlations in *trans*-H_2O_2. The n orbital is either n_1 or n_2 (see text), while the σ or σ^* refers to the oxygen bonding and antibonding orbitals. Also shown are the principal configurations at short (1.4 Å) and long distances (2.0 Å).

Shown in Figure 1 is the cross section of a semiempirically computed potential energy surface for the rupture of the O-O bond in trans (C_{2h}) hydrogen peroxide. This computation was achieved using a combination of the Eaker–Hinze[5] and DasGupta–Huzinaga[6] modifications of the CNDO/2 parameterization. The latter modification was used to approximate the experimental bond dissociation energy[7] of H_2O_2 (ca. 2 eV). This modified CNDO technique was used to generate the wave functions necessary for a configuration interaction estimate of the ground and excited single and triplet states. Approximately 80 configurations of the single and double excitation type were used for the singlet surfaces. Detailed analysis of the configurational wave functions showed no unexpected features. In addition, test calculations indicated that triple excitations were not of relative importance for correlating the states in question. Although the calculations were only calibrated to reproduce the approximate O-O bond energy, reasonable estimates were obtained for the excitation energies of peroxides[2] and the hydroxyl radical,[8] the ground state heat of atomization, and the O–O bond distance at the energy minimum.[9] The O–O force constant is too high, but better than previous semiempirical calculations.[9] Although all semiempirical calculations suffer from being parameter dependent, the imposition of configuration interaction at a modest level assures that the curves shown have utility as semiquantitative state correlation diagrams, provided that Rydberg type transitions are not important.

The unusual nature of the singlet surfaces shown in Figure 1 is that a total of four molecular states, 2 ^1A_g, ^1A_u, and ^1B_g, correlate with two ground state hydroxyl radicals. Corresponding calculations also showed four triplet states, all

Scheme I Photoexcitation and Adiabatic Dissociation of H_2O_2



repulsive (^3A_u, ^3B_g, 2 ^3B_u), correlating with the same two ground state radicals. In total, this gives one bonding state and seven repulsive excited states correlating with the two hydroxyl ground state radicals. The general behavior of Figure 1 can be predicted from symmetry considerations alone.[4] The origin lies in the doubly degenerate character of the ground state hydroxyl radical ($^2\pi$).[8] Each radical fragment is characterized by two ground state wave functions which in double combination will yield four singlet states and four triplet states. In a nondegenerate radical pair system, such as two ground state methyl radicals, only one singlet and one triplet state correlation can result. In water,[10] where one of the fragments is degenerate, the combination of the ground state of hydroxyl radical and ground state hydrogen atom will yield a correlation with both the ground state and excited state singlet. The excited state singlet, in the C_{1h} approach of the two radical fragments, corresponds to the lowest $^1B_1$ excited state of water, which in the crudest valence orbital terms results from the promotion of a nonbonding electron into an OH antibonding orbital. The excited states in H_2O_2 can be viewed in much the same way. At short O-O distances the ^1A_u state results from an electron promotion from the nonbonding orbital n_1 (b_g) to the O-O antibonding orbital σ_{O-O}^* (b_u), while the ^1B_g state is the same kind of transition but from the n_2 (a_u) nonbonding orbital.[11] The ^1A_g excited state results from a double excitation $n_1n_1 \rightarrow \sigma_{O-O}^*\sigma_{O-O}^*$. At large O-O distances the ground and excited states have large doubly excited components of the type shown in the figure. Diagramatically, these states can be analyzed using state symmetry arguments.[4] Promotion of electrons from the nonbond regions into the O-O bond region yields either three electron (A_u and B_g) or four electron "bonds" (A_g). Separation of the two radical fragments in a nonionic manner after excitation gives a pictorial view of why two $^2\pi$ hydroxyl fragments are formed. Separation of the two systems in the ground state of H_2O_2 also yields the same two hydroxyl radicals (see Scheme I).

In organic oxygen radicals resulting from peroxide bond ruptures the degeneracies present in OH may (methoxy, *tert*-butoxy)[12] or may not remain (phenoxy, carboxy)[13] depending on the symmetries of the fragments. It is expected that the molecularly-induced splittings will not be large (1 eV).[13] Because of the adiabatic nature of the surfaces shown in Figure 1 the photodecomposition of peroxides should be singlet as well as triplet sensitized.[14]

Although it is apparent in the much studied dioxetane thermal decomposition that the major partitioning of the reaction is into triplet products,[1,11] the reasons for the chemiluminescence are less-well rationalized theoretically. Although a number of investigators[15] have theoretically proposed ground-triplet state surface crossing to rationalize the triplet product formation and even ground-excited singlet state crossing[15b] to rationalize excited singlet formation, we are struck with the eightfold energetic degeneracy encountered in the O-O bond rupture in H_2O_2. Even with appropriate molecularly induced splittings of these degeneracies in a more complex system one can readily envisage an extreme complexity of surfaces in the regions at or near the possible transition state. Since there exists the acceptable possibility that the processes generating chemiluminescence need not be restricted to pathways along surfaces it is difficult to limit consideration to simple two state crossings[15] when other isoenergetic states may exist at geometries not far from the one under consideration.[16] With regard to the controversy between concerted and nonconcerted pathways, it is difficult to reject well-developed kinetic and thermochemical arguments[17] in favor of evolving theoretical treatments.[15d] Finally, the calculations shown here indicate that a moderately large configuration interaction treatment is necessary to describe the degenerate or near degenerate character of any developing oxygen radical, a conclusion valid for ab initio as well as semiempirical treatments.

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Book Reviews

The Hydrogen Bond and Other Intermolecular Forces. By J. CLARE SPEAKMAN. The Chemical Society, London. 1975. 33 pp. 60 pence.

A booklet of only 33 pages for such a vast subject as The Hydrogen Bond obviously must be intended for an audience other than the research worker. This publication is one in a series of Monographs for Teachers begun in 1959 by the Royal Institute of Chemistry. As such, its objective is a concise, understandable, introductory presentation of the topic given in the title. This the author has succeeded in doing. Teachers, and students too, should find this monograph easy to read and quite helpful.

Included in the presentation are attractive and repulsive forces, methods of studying hydrogen bonding, geometrical aspects and location of the proton, and examples of hydrogen-bonded systems. Greater emphasis is given to crystallographic aspects and reflect the author's interest. Obviously much is omitted or mentioned only briefly, but there is provided a bibliography of texts and review articles enabling one to delve deeper into the subject if so desired. One pertinent reference, too new to make the list, is "Hydrogen Bonding" by M. D. Joesten and L. J. Schaad, Marcel Dekker, Inc., New York, 1974.

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Carbenes. Volume II. Edited by R. A. MOSS and M. JONES, JR. John Wiley & Sons, Inc., New York, N.Y. 1975. xiii + 373 pp. $24.95.

This volume begins with the less well-known segment of organic chemistry, the reactions of free carbon atoms. Their generation, as for instance from graphite at 2200°, does not give a single species, but a variable mixture of not only C_3, C_2, and C_1 but also indications of different states of C_1. Their chemistry is complex, characterized by electron deficiency, but showing C-H insertion to some extent. The reactions may be carbene-like but differ somewhat. The second chapter is devoted to unsaturated carbenes about which considerable knowledge has been accumulated. Not only has the Newman nitrosooxazolidine synthesis been discussed, but also α-elimination. Acetylenes tend to form; otherwise typical carbene products are obtained as described in an impressive list of reactions. In the third chapter, the Seyferth organometallic precursors for carbenes are discussed. Phenyltrifluoromethylmercury with sodium iodide is given prominence as precursor for difluorocarbene, as is to be expected if it is one's own discovery. But the questions that arise are not answered here: what is the most economical, quickest, safest, and most convenient method of making difluorocarbene? Sodium chlorodifluoroacetate has been sloughed off as being a poor transfer reagent, yet it has been used recently to make difluorocyclopropanes in the steroid family (*J. Org. Chem.*, **38**, 289 (1973)). Triphenyltrifluoromethylphosphonium bromide has been dismissed by emphasis on the lower yield (21%) in difluorocyclopropanation when in fact a yield of 79% was obtained with the proper catalyst (this volume, p 154, Addendum No. 6). In another example, the phase-transfer method was found to be superior in every respect to the Seyferth method in dichlorocyclopropanation (*Syn. Commun.*, **4**, 341 (1974)).

The fourth chapter discusses the application of CIDNP, ESR, and flash photolysis in the study of carbene intermediates. The discussion of recent CIDNP results is especially useful.

The fifth chapter is devoted to a rather special type of carbenes, those in conjugation with one or more aromatic rings.

The sixth, last, and longest chapter is devoted to an extensive coverage of both theoretical and experimental work dealing with the spin states of carbenes. The first section provides an excellent chronological development of the theoretical treatment of carbenes. The section on experiments dealing with the singlet-triplet question is quite complete and blends the theoretical results nicely into the discussion of the experimental findings.

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Foundations of Quantum Dynamics. By S. M. BLINDER (University of Michigan). Academic Press, London. 1974. ix + 226 pp. $17.25.

The student of modern physical chemistry, and particularly the aspiring theorist, must now master a formidable amount of quantum mechanics in order to read the current literature with understanding. "Foundations of Quantum Dynamics" by S. M. Blinder provides a clear and concise account of the principles of the quantum theory at a level designed to aid the student in bridging the gap between elementary aspects and the advanced techniques of current applications. Professor Blinder's book can be conveniently divided into four sections. The first gives a survey of classical dynamics (Chapter 1) and electrodynamics (Chapter 2) written at levels corresponding to those found in Goldstein and Panofsky and Phillips, respectively. The survey of quantum-mechanical formalism (Chapter 3) and the description of the principles of quantum dynamics (Chapter 4) which comprise the second section, written at a level similar to that found in Schiff, is in my view superior in many respects to the presentations found in many of the standard textbooks currently used in both physics and chemistry departments. The time evolution of the wave function is treated here with particular clarity. A lengthy but appropriate discussion of the free particle (Chapter 5) à la Bohm, and a very useful introductory treatment of Green's functions (Chapter 6) à la Blinder comprise the third section. Finally, the applications to transition phenomena (Chapter 7) and the interactions between radiation and matter (Chapter 8) given in the last section provide a sound basis for further reading in this area. Students who master Professor Blinder's book, which should be appropriate both for self-study and for an expanded semesters course work, will be well equipped to tackle more specialized and advanced developments in the quantum theory.

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Polymer Chemistry: An Introduction. By MALCOLM P. STEVENS (University of Hartford). Addison-Wesley/W. A. Benjamin, Inc., Reading, Mass. 1975. xv + 458 pp. $25.00 (cloth); $17.50 (paper).

This book is intended by the author to "serve as an introductory text for a course in polymer chemistry at the advanced undergraduate or graduate level." What the author means by polymer chem-