PHYSICAL AND CHEMICAL PROPERTIES OF SINGLET MOLECULAR OXYGEN

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Received December 23, 1970 (Revised Manuscript Received March 31, 1971)

Contents

I. Introduction

The possibility that electronically excited, metastable singlet oxygen molecules might be involved as the reactive intermediate in dye-sensitized photooxygenation reactions was first suggested by Kautsky over 30 years ago.[1] In support of this proposal he demonstrated that excitation of sensitizer molecules which were adsorbed on silica gel caused the oxygenation of acceptor molecules which absorbed on a different set of silica gel particles physically separated from the dye-coated ones. He concluded from this that the oxygenation must have involved formation of some metastable species which was capable of migrating in the gas phase from the sensitizer to the acceptor, and suggested that this species was excited singlet oxygen molecules. A recent version of the Kautsky experiment has now been carried out using a system where the sensitizer and oxidizable acceptor were applied to opposite sides of a stearate film.[2,3] Even though the sensitizer molecules were physically located as far as 500 Å from the acceptor, significant photosensitized oxygenation was observed owing to diffusion of singlet oxygen molecules through the film. In spite of his ingenuous experiments, Kautsky's proposal that singlet oxygen molecules were the reactive intermediates in sensitized photooxygenation reactions was rejected by so many noted scientists that it was never accepted during his lifetime.[4]

Until about 5 years ago interest in the properties of singlet oxygen was primarily the concern of astrophysicists, small-molecule spectroscopists, and some gas-phase kineticists. This situation was changed dramatically in 1963–1964, largely as the result of studies by Khan and Kasha,[5,6] Foote and Wexler,[7] and Corey and Taylor.[8] In 1963 Khan and Kasha[5,6] carried out a spectroscopic investigation of the red chemiluminescence which accompanies the decomposition of hydrogen peroxide in the presence of sodium hypochlorite and observed two emission bands centered at 6334 Å (15,788 cm^{-1}) and 7032 Å (14,221 cm^{-1}). Since the spacing between these bands (1567 cm^{-1}) closely matched the spacing between vibrational levels of ground state molecular oxygen (1556 cm^{-1}), they correctly suggested that the emission was from electronically excited oxygen molecules, but incorrectly assigned the 6334-Å band to a solvent-induced displacement of the origin of the 7620-Å $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$ transition observed with gaseous oxygen. Subsequently, Arnold, Ogryzlo, and Witzke[9] correctly assigned the emission to a simultaneous transition involving a *pair* of singlet oxygen molecules, both

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* John Simon Guggenheim Fellow, 1969–1970.

[1] H. Kautsky, *Trans. Faraday Soc.*, **35**, 216 (1939).

[2] B. Schnuriger and J. Bourdon, *Photochem. Photobiol.*, **8**, 361 (1968).

[3] J. Bourdon and B. Schnuriger in "Physics and Chemistry of the Organic State," Vol. III, D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience, New York, N. Y., 1967, pp 59–131.

[4] See, for example, *Trans. Faraday Soc.*, **35**, 2241 (1939).

[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] E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3881 (1964).

[9] S. J. Arnold, E. A. Ogryzlo, and H. Witzke, *J. Chem. Phys.*, **40**, 1769 (1964).

in their $^1\Delta_g$ state [$2O_2(^1\Delta) \rightarrow 2O_2O^3\Sigma_g) + h\nu$]. In spite of the initial uncertainty in the exact assignment, it was clear from these early studies that the decomposition of the H_2O_2 provided a good source of singlet molecular oxygen. The important connection between these spectroscopic observations and the entire field of sensitized photoxygenation was provided by Foote and Wexler[7] who showed that the H_2O_2 + NaOCl system is an effective reagent for oxygenating a number of different organic acceptors, and, most importantly, that the oxygenation products and product distributions which they obtained using H_2O_2–NaOCl as the reagent were the same as those obtained by sensitized photooxygenation of these same acceptors. At the same time, Corey and Taylor demonstrated that excited oxygen molecules generated in a radiofrequency (rf) discharge reacted with various substituted anthracenes and olefins to yield oxygenation products that were identical with those formed in the sensitized photooxygenation of these same acceptors.[8] On the basis of these comparisons it was concluded that singlet oxygen was probably the reactive intermediate in the sensitized photooxygenation reactions, as Kautsky had suggested.[1] With these important discoveries singlet oxygen was drawn back into the mainstream of chemical research, and the field has developed at a rapid pace since then.

The range of phenomena, reactions, and systems in which singlet oxygen is now believed to be directly or indirectly involved is indeed remarkable. Singlet oxygen is clearly involved in numerous dye-sensitized photooxygenation reaction of olefins, dienes, and aromatic hydrocarbons, and in the quenching of the excited singlet and triplet state molecules. There is reason to suspect that singlet oxygen may also be involved in chemiluminescent phenomena, photodynamic action, photocarcinogenicity, ozonolysis reactions, peroxide decompositions and in the decomposition of other oxygen rich species, photosynthesis, and perhaps even in metal-catalyzed oxygenation reactions.

From a chemical standpoint the recent appreciation of the importance of singlet oxygen has opened up many new areas of research and raised a number of new questions regarding (i) mechanism of formation of singlet oxygen, (ii) chemical and physical methods for detecting singlet oxygen, (iii) physical properties of singlet oxygen in the gas and condensed phases, (iv) scope of singlet oxygen reactions, (v) mechanisms of singlet oxygen reactions, (vi) quantum chemical basis of reactivity, (vii) new chemical sources of singlet oxygen, and (viii) role of singlet oxygen in certain chemiluminescent reactions.

During the past few years several review articles have appeared which discuss various aspects of the singlet molecular oxygen including its formation, deactivation, chemical reactions, and other special properties.[10–19] Since much of the earlier work in the field is summarized in these articles, this permits us to concentrate on topics which have not previously been reviewed, to examine in detail those areas where new experimental findings appear to require reevaluation of some of the current "established" notions, and to assess our current understanding of the chemical and physical properties of singlet oxygen. Many of the topics chosen for discussion are either directly or indirectly concerned with the role of singlet oxygen in photosensitized oxygenation reactions, and this represents a bias of the author. In reviewing this material one of the notions which we have tried to develop is that many of the unique properties of singlet oxygen can be understood, at least qualitatively, in terms of relatively simple quantum chemical considerations. For this reason appropriate quantum mechanical concepts have been introduced and used wherever possible to unify our discussion of this rather diverse set of topics.

We begin with a brief discussion of the electronic structure of molecular oxygen and some of the spectroscopic properties of singlet oxygen. With this background information, we then consider the various methods which have been used to generate singlet oxygen, giving particular attention to the formation of singlet oxygen by energy transfer from electronically excited singlet or triplet state molecules. A brief review of the different techniques which have been used to detect singlet oxygen will also be given. Because of its importance to the interpretation of both chemical and spectroscopic studies, the quenching of singlet oxygen both in the gas phase and in solutions will be discussed in some detail. As a preface to a discussion of the reactions of singlet oxygen with different types of organic acceptors, we outline some quantum chemical procedures which have been useful in interpreting singlet oxygen reactions. These results are then used in a reexamination of singlet oxygen reaction mechanisms. Singlet oxygen has been implicated in various chemiluminescence reactions, and we shall examine some of the evidence bearing on this topic in the last section.

II. Electronic States of Molecular Oxygen

In order to facilitate discussion of the spectral properties of singlet oxygen, the mechanism of energy transfer from electronically excited molecules to oxygen, and the formation, quenching, and reactions of singlet oxygen, a simplified description of the electronic structure of ground state and electronically excited molecular oxygen will be presented first.

A. ELECTRONIC STRUCTURE

Molecular oxygen is somewhat unique among molecules with an even number of electrons in that the highest energy occupied orbitals are a pair of doubly degenerate antibonding orbitals which hold only two electrons.[20] For free molecular oxygen where orbital angular momentum about the O–O axis is quantized, these two orbitals are denoted as π^*_+ and π^*_-, where the plus and minus denote respectively $\pm\hbar$ units of angular momentum. According to Hund's rule a triplet $^3\Sigma_g^-$ (hereafter denoted $^3\Sigma$) is the state of lowest energy and will have electronic configuration[21,22]

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(10) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, 9, 507 (1964).

(11) K. Gollnick and G. O. Schenck in "1–4 Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 255.

(12) C. S. Foote, *Science*, 162, 963 (1968).

(13) C. S. Foote, *Accounts Chem. Res.*, 1, 104 (1968).

(14) K. Gollnick, *Advan. Chem. Ser.*, 77, 78 (1968).

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(22) J. S. Griffith in "Oxygen in Animal Organisms," F. Dickens and E. Niel, Ed., Pergamon Press, Oxford, 1964, p 481.

$$\underset{M_z=0}{{}^3\psi({}^3\Sigma)} = \frac{1}{\sqrt{2}}\{|\pi^*_+(1)\bar{\pi}^*_-(2)| + |\bar{\pi}^*_+(1)\pi^*_-(2)|\}$$

Other possible electronic configurations correspond to the three different singlet states which have the electronic configurations and energies,[23,24] E, relative to the ground state indicated below.

$$^1\psi_+(^1\Delta) = |\pi^*_+(1)\bar{\pi}^*_+(2)| \qquad E = 22 \text{ kcal}$$

$$^1\psi_-(^1\Delta) = |\pi^*_-(1)\bar{\pi}^*_-(2)| \qquad E = 22 \text{ kcal}$$

$$^1\psi(^1\Sigma) = \frac{1}{\sqrt{2}}\{|\pi^*_+(1)\bar{\pi}^*_-(2)| - |\bar{\pi}^*_+(1)\pi^*_-(2)|\}$$

$$E = 38 \text{ kcal}$$

The two delta states, $^1\Delta_g$ (hereafter denoted $^1\Delta$), are degenerate in energy and both have components of angular momentum $\pm 2\hbar$ about the O–O axis.[23] The singlet sigma state (hereafter denoted $^1\Sigma$) lies higher in energy (1.6 eV) above the ground state and is diamagnetic since the orbital angular moment associated with an electron in the π^*_+ orbital is exactly canceled by the angular momentum of the electron in the π^*_- orbital. If we make use of the relations[25]

$$\pi^*_+ = -\frac{1}{\sqrt{2}}(\pi^*_x + i\pi^*_y)$$

$$\pi^*_- = \frac{1}{\sqrt{2}}(\pi^*_x - i\pi^*_y)$$

we can rewrite the above functions in terms of real orbitals, $\pi_{x,y}^*$ (the usual x and y directed π orbitals), and these functions are given below.

$$\underset{M_z=0}{{}^3\psi({}^3\Sigma)} = \frac{1}{\sqrt{2}}\{|\pi^*_x(1)\bar{\pi}^*_y(2)| + |\bar{\pi}^*_x(1)\pi^*_y(2)|\}$$

$$^1\psi(^1\Delta_g) = \frac{1}{\sqrt{2}}[|\pi^*_x(3)\bar{\pi}^*_y(4)| - |\bar{\pi}^*_x(3)\pi^*_y(4)|]$$

$$^1\psi(^1\Delta_g) = \frac{1}{\sqrt{2}}[|\pi^*_x(3)\bar{\pi}^*_x(4)| - |\pi^*_y(3)\bar{\pi}^*_y(4)|]$$

$$^1\psi(^1\Sigma) = \frac{1}{\sqrt{2}}[|\pi^*_x(3)\bar{\pi}^*_x(4)| + |\pi^*_y(3)\bar{\pi}^*_y(4)|]$$

These functions are appropriate only to free oxygen molecules. If the molecule suffers collisions with other molecules in the gas phase, or is perturbed by placing it in a condensed medium, then the $^1\Sigma$ state can be mixed with one of the $^1\Delta$ states because the π^*_+ and π^*_- orbitals are mixed.[26] For example, application of a small one-electron perturbation $\mathcal{H}'$ of the form such that

$$V' = V_{xx} - V_{yy}$$

where $V_{xx} = \langle\pi^*_x|\mathcal{H}'|\pi^*_x\rangle$, $V_{yy} = \langle\pi^*_y|\mathcal{H}'|\pi^*_y\rangle$, and $V_{xx} \neq V_{yy}$, mixes $^1\psi(^1\Sigma)$ and one of the $^1\psi(^1\Delta)$ states, yielding the following new wavefunctions which are no longer eigenfunctions of the operator for orbital angular momentum.

$$^1\psi^{(1)}(^1\Delta) = {}^1\psi^0(^1\Delta) + \frac{V'}{\Delta E}\,{}^1\psi^0(^1\Sigma)$$

$$^1\psi^{(1)}(^1\Sigma) = {}^1\psi^0(^1\Sigma) - \frac{V'}{\Delta E}\,{}^1\psi(^1\Delta)$$

As long as the perturbation is small, $V'/\Delta E$ is small so that there is no substantial change in the form of the $^1\psi(^1\Delta)$ and $^1\psi(^1\Sigma)$ functions, but, as we shall see later, the small mixing of $^1\psi(^1\Delta)$ and $^1\psi(^1\Sigma)$ has very important consequences on the lifetime of $^1\Sigma$ in condensed media.

B. ELECTRONIC TRANSITIONS

1. Single Molecule Transitions

For a free molecular oxygen, the following electronic transitions can be observed both in absorption and in emission in the upper atmosphere.

$$^1\Delta \longleftarrow {}^3\Sigma, \quad \Delta E = 7882 \text{ cm}^{-1} \text{ (22 kcal)}$$

$$^1\Sigma \longleftarrow {}^3\Sigma, \quad \Delta E = 13{,}121 \text{ cm}^{-1} \text{ (38 kcal)}$$

Measurements of the integrated absorption coefficients for these transitions yield *radiative* lifetimes of 45 min[27,28] for $^1\Delta$ and between 7 to 12 sec for $^1\Sigma$.[29,30] The observed lifetimes are usually considerably shorter because of collisions with other molecules, and in the condensed phases they are very short indeed ($\tau_{^1\Sigma} \sim 10^{-9}$ sec, $\tau_{^1\Delta} \sim 10^{-3}$ sec; estimates).[16]

2. Simultaneous Transitions

At low altitudes where the oxygen pressure is higher and oxygen–oxygen collisions are more probable or in liquid oxygen (see Figure 1a), additional absorption bands are observed at 630 and 477 nm.[31,32] Energetically these bands are seen to correspond to various combinations of pairs of single molecule transitions and therefore can be assigned as simultaneous transitions in which a single photon is responsible for excitation of two molecules.[33,34] The assignments and energies of the simultaneous transitions are summarized in Table I along with the single molecule transitions. The intensities of these transitions vary with the square of the oxygen pressure and are most conveniently observed

Table I

Single molecule transitions	*Energy, cm^{-1} (nm)*
$^1\Delta \leftarrow {}^3\Sigma$	7,882 (1269)
$^1\Sigma \leftarrow {}^3\Sigma$	13,120 (762)
Simultaneous transitions	
$2(^1\Delta) \leftarrow 2(^3\Sigma)$	15,765 (634)
$^1\Sigma + {}^1\Delta \leftarrow 2(^3\Sigma)$	21,003 (476)
$2(^1\Sigma) \leftarrow 2(^3\Sigma)$	26,242 (381)

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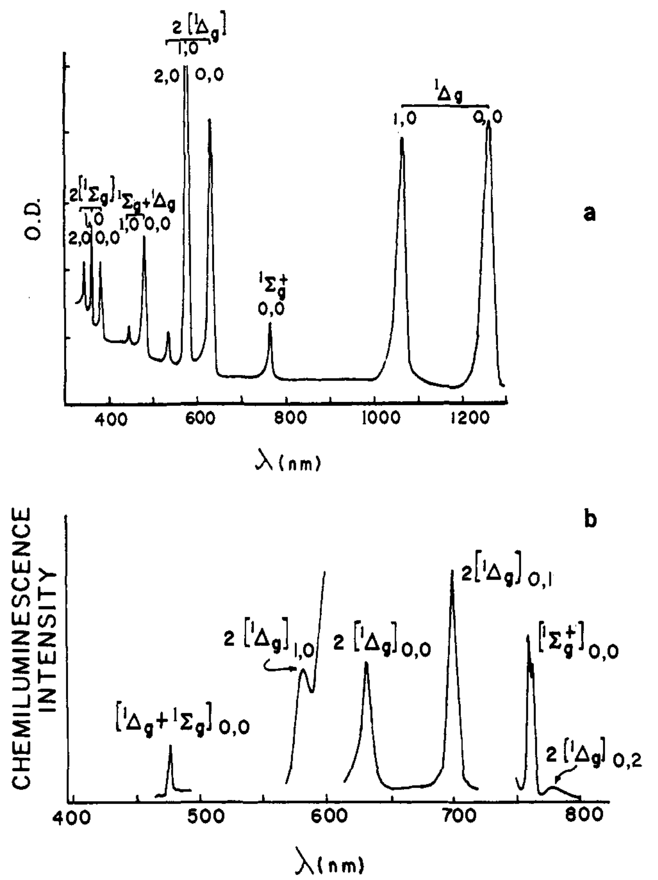

Figure 1. A comparison of the absorption spectrum of liquid oxygen (a) with portions of the chemiluminescence from the H_2O_2 + NaOCl reaction (b),[142] illustrating the mirror-image relationship of the absorption and emission bands. In both figures the bands have been labeled by upper-state symbols.

in the spectrum of liquid oxygen.[33,34] The single molecule transitions $^1\Delta \leftarrow {}^3\Sigma$ and $^1\Sigma \leftarrow {}^3\Sigma$ are also enhanced in the high-pressure gas and liquid.

Cooperative transitions have also been observed in emission in gas-phase laboratory systems where excited oxygen molecules are generated by an electrical discharge (radiofrequency or microwave)[35-39] or chemically,[5,6] and a comparison of the oxygen emission and absorption spectra is presented in Figure 1.

3. *Theoretical Studies*

A theoretical analysis of the source of the intensity in the collision induced single molecule transitions and the simultaneous transitions observed in liquid oxygen has been given by Rettschnick and Hoytink,[40] Robinson,[41] and Krishna.[42-44]

In a qualitative way the significant intensification of the $^1\Delta \leftarrow {}^3\Sigma$ and $^1\Sigma \leftarrow {}^3\Sigma$ transitions and the appearance of the collision-induced simultaneous transitions can be explained in much the same way as oxygen enhancement of singlet → triplet transitions in aromatic hydrocarbons.[41,45] Most authors agree that the intensity for some of the transitions is borrowed from the strongly allowed transition

$$B^3\Sigma_u^- \longleftarrow X^3\Sigma_g^- \; (f = 0.2,\ \nu = 68{,}000\ \mathrm{cm}^{-1})$$

known as the Schumann-Runge system.[46] Using first-order perturbation theory, the intensity of transition from a ground state, 0, to some excited state i of the collision complex is given by[41]

$$f_{i\leftarrow 0} \simeq \left[\frac{\langle i|\mathcal{H}|{}^3\Sigma_u^-\rangle}{E({}^3\Sigma_u^-) - E(i)}\right]^2 \times 0.2$$

In order to account for the observed intensities of the collision-induced transitions in liquid oxygen, the exchange integral responsible for mixing a state i with the Schumann-Runge state would only have to be on the order of 5–10 cm^{-1}.[41] Both Robinson[41] and Hoytink[40] have suggested that the same sort of exchange integrals are probably involved in mixing of all these low-lying pair states with the higher energy Schumann-Runge system, and therefore concluded that both the enhanced single molecule transitions and the simultaneous transitions should all be of comparable intensity in liquid oxygen. While this is approximately true, there are interesting variations in intensity of these different transitions. This problem has been examined in some detail by Krishna and Cassen,[43] who find in agreement with experiment and the suggestion of Robinson[41] and Hoytink,[40] that the transitions $({}^1\Delta + {}^3\Sigma) \leftarrow 2({}^3\Sigma)$ and $2({}^1\Delta) \leftarrow 2({}^3\Sigma)$ should be of comparable intensity. Transitions to the $({}^1\Sigma + {}^3\Sigma)$, $({}^1\Sigma + {}^1\Delta)$, and $2({}^1\Sigma)$ states are predicted to be weaker than the $({}^1\Delta + {}^3\Sigma) \leftarrow 2({}^3\Sigma)$ and $2({}^1\Delta) \leftarrow 2({}^3\Sigma)$ transitions because these latter transitions can borrow intensity from several allowed transitions, including the strongly allowed π–π transition, whereas the former ones borrow only from weaker transitions involving π–σ excitations which are expected to be at higher energy. The lack of mixing with the Schumann-Runge system results from extensive cancellation of matrix elements such that all interactions with states resulting from π–π promotions vanish for all geometries of the $O_2 \cdots O_2$ pairs. Consequently, the $({}^1\Sigma + {}^3\Sigma) \leftarrow 2({}^3\Sigma)$, $({}^1\Delta + {}^1\Sigma) \leftarrow 2({}^3\Sigma)$, and $2({}^1\Sigma) \leftarrow 2({}^3\Sigma)$ transitions cannot steal from the Schumann-Runge bands and must obtain intensity by mixing with states resulting from allowed π–σ transitions. Thus, the more detailed evaluation of the relevant matrix elements[43] has indicated that the first-order interpretation of the intensity of the various transitions is not strictly correct.

While these theoretical studies give us a good qualitative understanding of the factors responsible for the intensities of the collision-induced absorption bands of molecular oxygen, there are still interesting details of the spectra which remain to be explained. For example, the 0–0 band of the $^1\Delta \leftarrow {}^3\Sigma$ transition in liquid oxygen is stronger than the 0–1 vibronic band. This is to be contrasted with the prediction of simple Franck-Condon theory which gives the opposite result. Tsai and Robinson have suggested that this apparent

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discrepancy may be attributed to intermolecular vibronic effects.[44] There are important changes in the relative intensities of the different electronic transitions in going from liquid oxygen to solid oxygen which remain to be explained.[42,47] A good theoretical interpretation of the band widths for the different types of simultaneous transitions is yet to be developed, although the careful gas-phase absorption study of Blickensderfer and Ewing[48] indicates some of the important factors which must be involved. Perhaps the success of the qualitative theoretical investigations of the properties of electronically excited singlet oxygen molecules will stimulate further detailed computations on some of the problems which we noted above.

4. Oxygen Dimers

The question of whether oxygen exists as a stable dimer in its ground state or in its excited state is a long standing one,[49] and renewed interest in this problem has been considerably stimulated by other studies of the chemical and physical properties of singlet oxygen. It would appear that the matter has largely been settled by the recent work of Blickensderfer and Ewing.[48] They studied the collision-induced absorptions of oxygen in the gas phase and the effect of temperature on the absorption coefficients for the various transitions. Although shifts of the simultaneous transitions from the position calculated using free-molecule electron and vibrational constants ranged from $+125$ to -30 cm^{-1}, they inferred that the O_2–O_2 binding energies between *pairs* of excited state molecules were on the order of the 100 cm^{-1} or less. Gray and Ogryzlo[38] examined the temperature dependence of the emission from singlet oxygen at 4800 Å. This emission is assigned by Khan and Kasha[50] to the cooperative transition $(^1\Delta + {}^1\Sigma) \rightarrow 2(^3\Sigma) + h\nu_{4800}$, and over a range of temperatures from 120 to 300°K the intensity of the 4800-Å band was directly proportional to the products of the concentrations of $^1\Sigma$ and $^1\Delta$.[38] The conclusion to be drawn from these studies is that there is no evidence for anything which could reasonably be called an oxygen dimer, either in the ground state or in the excited state.

III. Methods for Generating Singlet Oxygen Molecules

A. PHOTOPROCESSES LEADING TO THE FORMATION OF SINGLET OXYGEN

One of the major conclusions derived from studies of dye-sensitized photooxygenation reactions is that singlet oxygen molecules may be generated with high efficiency by energy transfer from excited triplet state sensitizer molecules, and possibly from excited singlet state sensitizers.[12-15] Because of the important role which energy transfer plays in photosensitized oxygenation reactions, in this section we shall examine both theoretically and experimentally the mechanisms by which oxygen quenches excited singlet and triplet state molecules.

1. Oxygen Quenching of Fluorescence

It has been known for some time that oxygen efficiently quenches the fluorescence of many organic molecules,[51-56] but the mechanism by which the quenching occurs has remained obscure until recently. Because of its direct relevance to the field of sensitized photooxygenation, there has been a renewed interest in the details of this quenching process, and a number of recent experimental studies have been carried out with the goal of distinguishing between various possible quenching mechanisms.

a. Theoretical Considerations

To discuss the oxygen quenching of excited singlet and triplet state molecules, we first consider the various types of pair states which are associated with a weak collision complex of oxygen and some organic molecule, M. Enumeration of these various pair states and their relative energies indicated in Figure 2 immediately suggests the following energetically feasible mechanisms for the oxygen quenching of excited singlet state molecules

$$^1M_1 + {}^3O_2 \longrightarrow (M^+ + O_2^-) \tag{I}$$
$$\longrightarrow {}^3M_2 + {}^3O_2(^3\Sigma) \tag{II}$$
$$\longrightarrow {}^3M_1 + O_2(^1\Delta) \tag{III}$$
$$\longrightarrow {}^3M_1 + O_2(^3\Sigma) \tag{IV}$$
$$\longrightarrow {}^1M_0 + O_2(^3\Sigma) \tag{V}$$

where $^1M_1$, $^3M_2$, and $^3M_1$ denote excited singlet and triplet states, and $^1M_0$ denotes the ground state of M. In each case we have indicated the states of the molecule and of oxygen which are formed initially in the quenching of ^1M, recognizing that they may rapidly decay into still lower energy electronic states.

Other possible mechanisms such as quenching by electron transfer,[57,58] or through an inhomogeneous field effect,[59] do not appear to be generally important, although special cases may be found where electron transfer does occur.[60]

The general problem of calculating radiationless transition rates has been discussed in some detail by Robinson and Frosch.[61] This theory can only be considered approximate,[62] but it provides a useful starting point for indicating which molecular parameters are important in the quenching process and permits one to decide which of several processes might be more important. According to the Robinson–Frosch theory, the rate, k_{if}, at which a system initially in some

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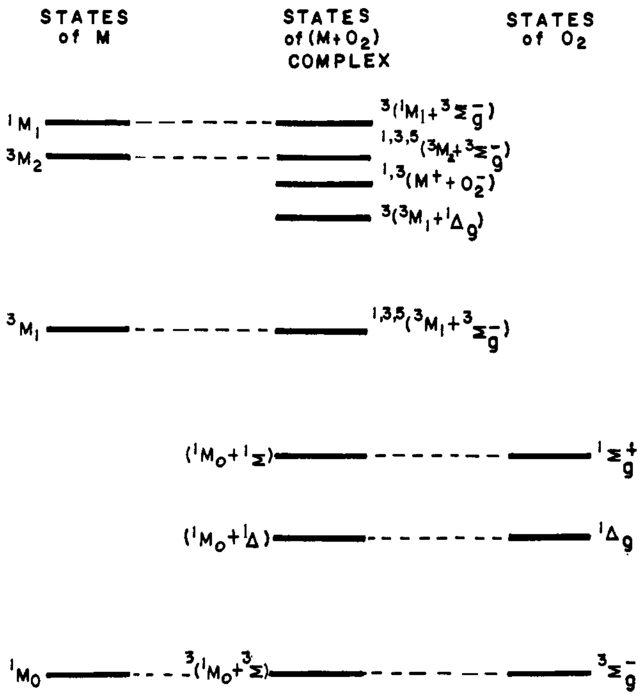

Figure 2. The low-lying electronic states of a 1:1 complex [M $\cdots$ O$_2$] between an organic molecule, M, and O$_2$, showing the relation between the electronic states of the free molecules M and O$_2$ and those of the complex.

state specified by Ψ_i makes a transition to some final state Ψ_f will be given by the expression

$$k = (2\pi\rho/\hbar N)\sum_n|\langle\Psi_f{}^n|\mathcal{H}|\Psi_i\rangle|^2 = (2\pi/\hbar\alpha)\sum_n|\beta n|^2 \quad (1)$$

where N is the number of final vibronic states degenerate with the initial state, $\alpha = \rho/N$ is the energy of interaction between these final vibronic states, ρ is the density of final states, and $\mathcal{H}$ is the complete Hamiltonian for the system. The complete wavefunctions, Ψ, will be functions of both electronic and nuclear coordinates, but in the Born–Oppenheimer approximation we can write

$$\Psi_{i(r,q)} = \psi_{i(r,q)}\chi_{i(q)} \quad (2)$$

where $\psi_{i(r,q)}$ is a function of all electronic coordinates, r, and depends parametrically on the nuclear coordinates, q, and $\chi_{(q)}$ depends only on the nuclear coordinates, q. Incorporation of these approximations into eq 1 yields the following expression for k.[61]

$$k \cong (2\pi\rho/\hbar N)|\langle\psi_f|\mathcal{H}|\psi_i\rangle|^2\sum_n\langle\chi_f{}^n|\chi_i\rangle^2 = (2\pi\rho/\hbar N)\beta_{el}{}^2F_{if} \quad (3)$$

where β_{el} is a matrix element integrated over all electronic coordinates and F is a Franck–Condon factor. An approximate expression which relates the variation of F with ΔE, the amount of electronic energy, converted into vibrational excitation has been derived by Siebrand,[63,64] and this is

$$F \simeq 0.15 \times 10^{-[(\Delta E-4000)/5000]} \quad (4)$$

This expression is applicable only to aromatic hydrocarbons and only when $\Delta E > 4000$ cm^{-1}. These theoretical expressions provide a framework then for comparing the various processes by which molecular oxygen quenches excited state molecules both in singlet and triplet states.[65]

If we accept Hoytink's[66] estimate that $\alpha = 10$ cm^{-1}, then with the evaluation of β_{el} eq 1 can actually be used to calculate values for k_q. In connection with an investigation of the intensity of charge transfer absorption bands resulting from collisions between oxygen and aromatic hydrocarbons, Tsubomura and Mulliken[67] and Murrell[68,69] estimated that β_{el}, the matrix element coupling the initial excited state with the charge transfer state, had a magnitude on the order of 0.1 eV = 800 cm^{-1}. The β_{el}'s for the remaining quenching mechanisms, on the other hand, are all expected to be orders of magnitude smaller since they depend upon intermolecular exchange integrals.[70,71] Judging from recent studies of exciton splittings of S–T transitions in molecular crystals and previous theoretical estimates,[72] these intermolecular exchange integrals are expected to have values in the range of 10 cm^{-1}, or about two orders smaller than the β_{el} for coupling with the charge transfer state.

Since we expect the Franck–Condon factor for a transition to the CT state to be reasonably large, relaxation to a lower lying charge transfer state is expected to occur with a rate constant that could approach 10^{13}–10^{14}/sec. Because of the smaller β_{el} factors, and the fact that the Franck–Condon factor becomes much smaller when large amounts of electronic excitation are converted into vibrational excitation, the other mechanisms (II–V) are expected to be much less important. For a relatively small ΔE, a $\beta_{el} \simeq 10$ cm^{-1} will still lead to a rate constant of order of 10^{11}–10^{12}/sec. From these theoretical considerations we conclude the following.

(1) Relaxation to the charge transfer state is expected to be the dominant mechanism by which oxygen quenches excited singlet state molecules, provided the CT state lies below the excited singlet state of M.

(2) If the charge transfer state lies above $^1M_1$, then quenching to the lowest excited triplet state, $^3M_1$, or possibly second triplet state, could occur with a rate constant in the range of 10^{11} sec^{-1}.

(3) Quenching directly to the ground state is expected to be the least important process because of the relatively smaller β_{el} and very small Franck–Condon factor ($\sim10^{-5}$).

b. Experimental Observations

The oxygen quenching of fluorescence of aromatic hydrocarbons both in solution and in the vapor phase appears to be nearly diffusion controlled.[73-82] Some of these data are pre-

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Table II

Rate Constants for the Oxygen Quenching of Excited Singlet and Triplet State Molecules[a]

Compound	$\Delta E(S_1-T_1)^b$	*Singlet quenching constant,* $k_q^S \times 10^{10}$, *l.* M^{-1} *sec*$^{-1}$	*Triplet quenching constant,* $k_q^T \times 10^9$, *l.* M^{-1} *sec*$^{-1}$
Benzene	8,700	16.0 (80, v)	12.0 (82, v)
		12.0 (82, v)	
		14.0 (78, v)	
		2.4 (81, l)	
Naphthalene	10,500	2.8 (81, l)	2.1 (105, v)
Anthracene	12,000	2.6 (81, l)	2.1 (105, v)
		3.5 (74, l)	2.9 (*c*, l)
		2.5 (74, l)	4.0 (105, v)
		3.9 (74, l)	
		3.1 (*c*, l)	
9,10-Dichloroanthracene		2.2 (74, l)	
9,10-Diphenylanthracene		2.6 (74, l)	
9,10-Dimethylanthracene	~11,000	3.1 (91, l)	3.3 (91, l)
Naphthacene	10,850	2.0 (81, l)	
Pyrene	10,000	2.5 (*c*, l)	1.6 (*c*, l)
Chrysene	7,700	2.9 (*c*, l)	1.0 (*c*, l)
		2.4 (*c*, l)	
Perylene	9,900	2.3 (*c*, l)	
		3.1 (74, l)	
Phenanthrene	7,200	2.5 (81, l)	
1,2-Benzanthracene		3.0 (*c*, l)	1.9 (*c*, l)
1,2,5,6-Dibenzanthracene	7,000	2.9 (*c*, l)	1.3 (*c*, l)
1,2,3,4-Dibenzanthracene	7,100	2.6 (*c*, l)	1.5 (*c*, l)
Triphenylene	5,300	2.0 (81, l)	
Coronene	4,500		
3,4-Benzpyrene	8,500[c,d]	2.9 (*c*, l)	2.6 (*c*, l)
3,4-Benzphenanthrene	6,400[c,d]		1.2 (*c*, l)
3,4,9,10-Dibenzpyrene	6,000[c,d]	2.9 (*c*, l)	1.0 (*c*, l)
β-Carotene	~12,000 (est)		~2.0 (112, l)
Hexafluoroacetone		7.6×10^{-3} (75, v)	0.4 (75, v)
Biacetyl	2,400[e]		5.0 (111, l)
SO_2		0.51 (108, v)	0.01 (108, v)

[a] The numbers in parentheses refer to references, and the letters v or l indicate that the measurements were carried out in the vapor phase or in some liquid. [b] Splitting, in cm^{-1}, between the lowest excited singlet and triplet states of the molecule (quoted in ref 81). [c] L. K. Patterson, G. Porter, and M. R. Tropp, *Chem. Phys. Lett.*, 7, 612 (1970). [d] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, N. Y., 1951. [e] J. W. Sidman and D. S. McClure, *J. Amer. Chem. Soc.*, 77, 6461, 6471 (1955).

sented in Table II. In addition to confirming the expectation that the quenching rate constant should be large, these data taken collectively also provide some insight into the quenching mechanism.

For example, as Parmenter and Rau[81] have pointed out, all of the aromatic hydrocarbons appear to be quenched by O_2 at the same rate regardless of the S_1–T_1 gap, suggesting that mechanism III is probably not involved. The data in Table II further demonstrate that a high quenching rate does not depend upon whether T_2 is located above or below S_1. From these observations we may conclude that quenching of S_1 to T_2 or to T_1 with concomitant production of singlet Δ oxygen is not *necessary* for efficient quenching. However, as the quenching is diffusion controlled, these data alone do not rule out the possibility that $^1\Delta$ might be generated in those cases where it is energetically possible. All that would be required is that $k_{\rm I}$, $k_{\rm II}$, $k_{\rm III} > 1/\tau_c$, where τ_c is the lifetime of the collision complex.

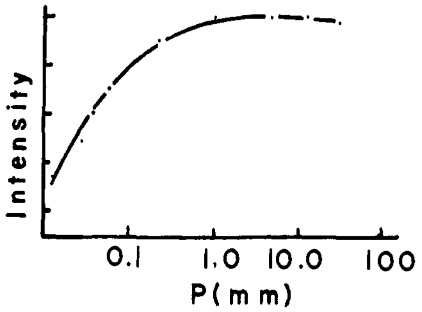

Figure 3. Variation in the intensity of the $O_2(^1\Delta)$ emission at 12,700 Å with the oxygen pressure for benzene–oxygen mixtures containing 20 Torr of benzene.[83]

Direct evidence on the role of energy transfer to singlet oxygen in the quenching of excited singlet state molecules is provided by Snelling's study of the benzene photosensitized generation of singlet Δ oxygen.[83] The essential results of his study are presented in Figure 3 which displays the varia-

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tion in the concentration of $^1\Delta$ (as monitored by the intensity of emission at 12,600 Å; $^1\Delta \rightarrow {}^3\Sigma$) as a function of the oxygen pressure. At low pressure the $^1\Delta$ oxygen is produced entirely by energy transfer from *triplet* state benzene molecules, since quenching of the short-lived excited singlet is negligible. When the pressure of O_2 is raised above 1 Torr, quenching of the singlet becomes important but, significantly, the concentration of $^1\Delta$ continues to increase monotonically to a limit. Since the fluorescence yield of benzene in the vapor phase is $\sim$0.3[78,84–87] and since the benzene fluorescence intensity at 50 Torr is reduced to 4% of the oxygen-free value, these observations show that direct quenching of S_1 to its ground state (process V) is unimportant compared to processes which ultimately lead to formation of $^1\Delta$. Since the singlet–triplet splitting in benzene[88] is larger than 8000 cm^{-1}, oxygen quenching of benzene singlets could occur by energy transfer (process III) in which case each excited singlet benzene could ultimately be responsible for the formation of two $^1\Delta$ molecules. This possibility also appears to be excluded by Snelling's observations on the pressure dependences of the $^1\Delta$ concentration.[83] The experiments indicate than that quenching occurs either *via* a charge transfer state which relaxes to ^{3}M + $^3O_2$, or by relation of S_1 to T_1 (or T_2) directly.

Further proof that the quenching of excited singlet states does not involve energy transfer to $^1\Delta$ or direct relaxation of S_1 to S_0 is provided by a recent series of studies of the kinetics of the direct and sensitized photooxygenation of various anthracene derivatives.[89–92] From an analysis of results obtained at various oxygen concentrations, with or without triplet quenchers, it was shown that oxygen quenching of the excited state sensitizer molecules is entirely due to the diffusion limited enhanced intersystem crossing (processes II or IV). No evidence for the direct formation of $^1\Delta$ as the result of oxygen quenching of $^1M_1$ was found, and direct quenching to the ground singlet state was eliminated.[89–92]

Recently Birks[93] has reanalyzed some of the earlier quenching data using the expression

$$k_q = k_c(R/R_c)$$

where k_c is the diffusion-controlled encounter rate constant, R_c is the collisional van der Waals separation, and R is the distance over which the quenching occurs. For anthracene[74] a value of R = 11 Å is obtained. This is considerably larger than the value of <7 Å which Jones and Siegel[94] obtained from their study of the static quenching of naphthalene fluorescence in 3-methylpentane solutions at 77°K. Further comparisons of the fluid and rigid glass solutions will be required to resolve this discrepancy.

The possibility that long-lived complexes might be formed as the result of the interaction of oxygen with electronically excited molecules was suggested some years ago by Schenck, who proposed that an excited dye–oxygen complex (moloxide) might be the oxygen-transferring species in dye-sensitized photooxygenation reactions.[95] At that time it was kinetically impossible to distinguish between such a metastable complex and other metastable intermediates such as singlet oxygen. When it was conclusively shown that $^1\Delta$ is the reactive intermediate in many sensitized photooxygenation reactions,[7,8] interest in the Schenck mechanism diminished, but still there was no proof that a long-lived moloxide complex was not the precurser to the formation of free singlet molecular oxygen. Resolution of this important problem was finally accomplished by comparing the efficiency of the oxygen quenching of pyrene excimer fluorescence under conditions of low- and high-intensity irradiation using light from a N_2 laser.[96] Under high-intensity conditions 200 excited pyrene excimers are initially produced for each oxygen molecule in the thin layer where most of the absorption occurs, yet the fluorescence quenching was found to be comparable ($\sim$91%) to that observed under much lower intensity illumination (93% quenching under conditions employed). In order to account for the high-intensity observations, each O_2 molecule has to be free to quench approximately 100–200 pyrene molecules so that the lifetime of any pyrene–oxygen complex would have to be less than about 2×10^{-10} sec in order to permit a single oxygen molecule to quench the necessary number of excited pyrene excimers. These experiments conclusively rule out the formation of an excited pyrene–oxygen complex and at the same time rule out the existence of any excited state species involving oxygen which was a lifetime greater than 2×10^{-10} sec. On this basis the authors further concluded that oxygen quenching of excited pyrene molecules does not lead to the formation of $^1\Delta$ (lifetime in solution $\simeq 10^{-5}$ sec) and that pyrene was either directly or indirectly quenched to its ground singlet state without intersystem crossing to the triplet state and without energy transfer to oxygen.[96] Since this contradicts conclusions reached by other workers,[31,83,88–93] it requires careful analysis. The key feature involved in ruling out any quenching processes which might lead to the formation of $^1\Delta$ is the implied assumption that $^1\Delta$ or $^1\Sigma$ will not quench excited state pyrene molecules. This ignores, however, the possibility that singlet oxygen molecules might themselves be very efficient quenchers of excited singlet state molecules by any one of the three following mechanisms.

$$^1M_1 + {}^1\Delta \longrightarrow {}^1(M^+ + O_2^-) \longrightarrow {}^1({}^3M + {}^3O_2) \qquad \text{(VI)}$$

$$^1M_1 + {}^1\Delta \longrightarrow {}^1({}^3M + {}^3O_2) \qquad \text{(VII)}$$

$$^1M_1 + {}^1\Delta \longrightarrow {}^1M_0 + {}^1\Delta \qquad \text{(VIII)}$$

Since there is good experimental and theoretical evidence that matrix elements coupling the charge transfer state with other excited pair states of M of the ($M\cdots O_2$) complex are large,[67–69,97,98] process VI is expected to have a very large rate constant. Similarly, the quenching of triplet state pyrene molecules by $^1\Delta$ or $^1\Sigma$ is also expected to be rapid, and experimental evidence for this will be presented in section V. Thus, under the high-intensity excitation conditions used in these

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(98) C. Dijkgraaf, R. Sitters, and G. J. Hoytink, *Mol. Phys.*, **5**, 643 (1962).

experiments we suggest it is likely that excited singlet and triplet state pyrene molecules are rapidly quenched *both* by ground triplet state oxygen molecules as well as excited singlet oxygen molecules (presumably $^1\Delta$, but perhaps $^1\Sigma$). It should be possible to test for the presence of $^1\Delta$ in this system by carrying out similar laser experiments,[96] but in the presence of organic acceptors which would react with any free singlet oxygen molecules that might be produced without quenching the excited singlet state of the sensitizer.

It is interesting to note that whereas the quenching of excited state molecules by molecular oxygen is diffusion controlled with all aromatic hydrocarbon molecules, the quenching of some excited ketones is less efficient. For example, the rate constant (k_q) for the O_2 quenching of fluorescence of hexafluoroacetone (HFA) in the vapor phase is only 7.6×10^7 l. M^{-1} sec^{-1},[75] or 5×10^3 times smaller than the theoretical collision-controlled value. Because of the small singlet–triplet splitting, quenching to a second triplet state is ruled out, as is quenching to the lowest triplet with transfer of energy to oxygen. The fact that the ionization of potential of HFA is 11.68 eV[99] would appear to rule out the participation of charge transfer states in the quenching process. By process of elimination enhanced intersystem crossing to the lowest triplet state would appear to be the mechanism responsible for the quenching, and the only surprising aspect of these observations is that the rate constant for this process should be so small. There are several features of HFA which might be contributed to the small value of k_q. First of all, the density of vibronic states associated with the manifold of triplet states which are nearly degenerate with the first singlet state may be small. Secondly, the intermolecular exchange integral which is responsible for the oxygen-enhanced intersystem crossing is expected to be much smaller than for a similar situation where charge transfer states are involved. The importance of charge transfer states to rapid quenching is further suggested by the fact that NO, which has a higher electronic affinity than oxygen,[100] is approximately 100 times better in quenching the singlet state of HFA than is oxygen.[75] Another obvious difference between acetone and the aromatic hydrocarbons is that the lowest excited singlet state is an (n,π) state, rather than a (π,π) state.

The inefficient quenching of HFA singlet states by oxygen suggests that an investigation of the oxygen quenching of other molecules which have low-lying (n,π) singlet states would be interesting, and could provide information that would further help to identify those molecular properties which are important in controlling quenching rates.

2. *Oxygen Quenching of Triplets*

The oxygen quenching of triplet state molecules has a long and interesting history.[51,54–56] Although this phenomenon was well known to spectroscopists,[51–54] more wide spread interest in the quenching mechanism has resulted from the discovery of the important role of excited oxygen molecules in photosensitized oxygenation reactions.[7,8] Historically, a number of different mechanisms have been proposed to account for the oxygen quenching of triplet state molecules.[1,57,59] To indicate the rationale behind some of these suggestions, we again refer to the energy level diagram in Figure 2 which depicts various excited pair states arising from the interaction of molecular oxygen with an aromatic hydrocarbon.

On the basis of this diagram, the following process could reasonably be expected to be involved in the quenching of triplet state molecules.

$$^1(^3M_1 + {}^3O_2) \longrightarrow {}^1M_0 + {}^1\Sigma \qquad \text{(IX)}$$

$$^1(^3M_1 + {}^3O_2) \longrightarrow {}^1M_0 + {}^1\Delta \qquad \text{(X)}$$

$$^3(^3M_1 + {}^3O_2) \longrightarrow {}^1M_0 + {}^3O_2 \qquad \text{(XI)}$$

The first two quenching mechanisms appear to have been first suggested by Kautsky in connection with his discussion of sensitized photooxygenation reactions.[1] The third process is in effect an enhancement of intersystem crossing in M resulting from interaction with a paramagnetic oxygen molecule. Although such a transition can be facilitated by the inhomogeneous magnetic field generated at ^3M by the paramagnetic perturber,[59] Tsubomura and Mulliken demonstrated that the fields were not of sufficient magnitude to account for the experimental observations.[67] Furthermore, Porter and Wright in their studies of the quenching of triplet state molecules by paramagnetic ions found no correlation between quenching efficiency and the magnetic moment of the paramagnetic ions.[101]

Another mechanism, which was suggested by Weiss,[57] is quenching by electron transfer to oxygen. While this mechanism may be important in the quenching of triplet state molecules which have particularly low ionization potentials (amines) in polar solvents, this mechanism cannot be of general importance simply from energetic consideration. Direct reaction of the triplet state molecule with ground state molecular oxygen represents another possible quenching mechanism, but even for those molecules which undergo photooxygenation, the experimental evidence indicates that the actual quenching of triplet state molecules occurs without reaction.

a. Theoretical Considerations

The theoretical framework which we discussed in connection with the oxygen quenching of singlet states may also be used to compute rate constants for the quenching of triplet state molecules, and the details of these calculations have been presented previously.[65] An essential finding of this study is that β_{el} is the same for processes IX, X, and XI, and therefore the relative importance of the three processes is determined by the spin statistical factors ($^1/_3$ for process XI and $^1/_9$ for processes X and IX) and the Franck–Condon factors. The results which are presented in Table III were for calculations on an $M \cdots O_2$ collision complex with an intermolecular separation on the order of 4 Å. These results clearly indicate that energy transfer to triplet oxygen, generating either $^1\Sigma$ or $^1\Delta$, should be considerably more effective than quenching to the ground state without energy transfer. This difference, according to theory, arises almost entirely from differences in Franck–Condon factor. Although the absolute magnitudes of the rate constants are not expected to be particularly accurate, the relative values should be much better.

To relate the calculated rate constants to the experimental quenching rate constant, it is necessary to take account

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Table III

Franck–Condon Factors and Quenching Rate Constants for Oxygen Quenching of Excited Triplet State Molecules

Energy of triplet state molecule, kcal	*Franck–Condon factor* *Energy transfer to* $^1\Sigma$			*Quenching rate constant*[a] *Energy transfer to* $^1\Sigma$		
		$^1\Delta$	*Enhanced intersystem crossing*		$^1\Delta$	*Enhanced intersystem crossing*
72	0.01	0.001	0.00001	10^{11}	10^{10}	10^{8}
56	0.1	0.01	0.0001	10^{12}	10^{11}	10^{9}
42	~1.0	0.1	0.001	10^{13}	10^{12}	10^{10}

[a] Units of l. M^{-1} sec^{-1}.

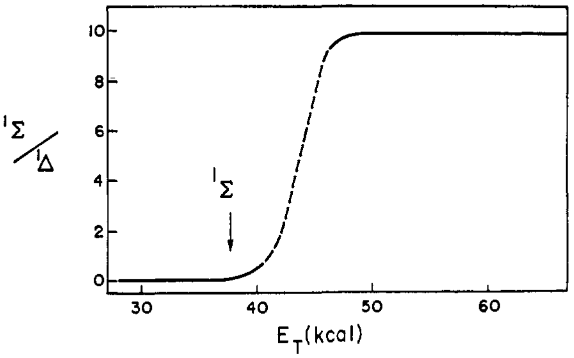

Figure 4. Predicted variation in the $^1\Sigma/^1\Delta$ ratio with the triplet state energy, E_T, of the sensitizer.

of the fact that the lifetime of the collision complex, $\tau_c = 1/k_{-d}$, is quite short, and that all encounters between ^3M and $^3O_2$ may not lead to the formation of a collision complex in the required spin state. The details of the kinetics of the quenching process can be analyzed according to the scheme outlined below

$$\begin{array}{lll} {}^3M + {}^3O_2 \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} {}^{1,3,5}(M\cdots O_2)_i & \xrightarrow{k^i{}_{1\Sigma}} & {}^1\Sigma + {}^1M_0 \\ & \xrightarrow{k^i{}_{1\Delta}} & {}^1\Delta + {}^1M_0 \\ & \xrightarrow{k^i{}_{3\Sigma}} & {}^3\Sigma + {}^1M_0 \end{array}$$

where $(M\cdots O_2)_i$ denotes a collision complex in some spin state i, k_d is the diffusion-controlled collision rate constant, k_{-d} is the unimolecular rate constant for dissociation of the collision complex, $k^i{}_{1\Sigma}$ is the unimolecular rate constant for a transition from state i of the collision complex to a final state in which $^1\Sigma$ is generated, and similarly for $k^i{}_{1\Delta}$ and $k^i{}_{3\Sigma}$.

In terms of these quantities, k_Q, the quenching constant, measured experimentally is[102]

$$k_Q = \left(\frac{k_d}{9}\right)\left[\left(\frac{k_{1\Sigma} + k_{1\Delta}}{k_{1\Sigma} + k_{1\Delta} + k_{-d}}\right) + 3\left(\frac{k_{3\Sigma}}{k_{3\Sigma} + k_{-d}}\right)\right] \quad (5)$$

where the $^1/_9$ factor occurs as a result of the fact that nine different spin states may be generated from the combination of two triplet state molecules.[102] There is only one singlet combination, but three triplet combinations and hence the presence of the factor of 3 in the second term of eq 5.

Since the calculations indicate that $k_{1\Sigma}$ and $k_{1\Delta} > k_{-d}$ in solution, we anticipate that $k_Q = k_d/9$, and that energy transfer to oxygen will be the major mechanism for quenching of ^3M.[65] Because of the much smaller Franck–Condon factor, enhanced intersystem crossing (process XI) is expected to be relatively unimportant. A second consequence of these theoretical calculations is shown in Figure 4 where the variation in the relative amounts of $^1\Sigma$ and $^1\Delta$ generated with the triplet state energy of the sensitizer is depicted.[103,104] The 10:1 $^1\Sigma$:$^1\Delta$ ratio predicted for high-energy sensitizers (triplet state energy greater than 40 kcal) is a consequence of the more favorable Franck–Condon factor for energy transfer to $^1\Sigma$, and the drop in the $^1\Sigma/^1\Delta$ ratio below 38 kcal simply takes account of the conservation of energy.

b. Experimental Observations

The oxygen quenching of triplet state molecules has been studied in the vapor,[105–108] liquid,[109–112] and solid phases,[2,91,113–116] and some of these results are presented in Table II. In the liquid phase the quenching constants consistently appear to be about one order of magnitude smaller than k_d, but this was expected because of the $^1/_9$ spin statistical factor associated with energy transfer to oxygen. If enhanced intersystem crossing were the major quenching mechanism, large variations in the quenching rate with triplet state energy might be expected, and the limited experimental data do not indicate such a variation. These observations further imply that $k_{1\Sigma}$, $k_{1\Delta} > k_{-d}$, consistent with the theoretical estimates. In the vapor phase the quenching constants for triplet state anthracene and naphthalene are about *two* orders smaller than the collision controlled value. This indicates that $k_{1\Sigma}$, $k_{1\Delta} \sim (k_d/10)$ or that the value of either $k_{1\Sigma}$ or $k_{1\Delta}$ is about 3×10^{10}, which is close to the theoretical estimate. The very small rate constant for the O_2 quenching of $^3SO_2$ is perhaps suggestive of a very poor Franck–Condon factor, but this deserves further study.[108]

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Until recently there was no proof that energy transfer is the major mechanism by which oxygen quenches triplet state molecules, but this has now been independently demonstrated by three groups[83,117,118] and reconfirmed by another.[119] Snelling studied the intensity of the 12,700-Å emission characteristics of $^1\Delta$, resulting from irradiation of a benzene–oxygen mixture at 2537 Å, and these results are shown in Figure 3.[83] The first point to note is that the reaction producing $^1\Delta$ is essentially complete at oxygen pressures slightly below 1 Torr, and there is no further increase in $^1\Delta$ with increasing O_2 pressure. Since the fluorescence of benzene is only 30% quenched at 1 Torr, Snelling concluded that $^1\Delta$ is produced by quenching of triplet benzene rather than singlet benzene.[83] Although he was unable to detect emission from $^1\Sigma$ at 7620 Å, he suggested that this might be attributed to rapid deactivation, thus leaving unanswered the question of whether $^1\Sigma$ was generated first and then subsequently decays to $^1\Delta$. The rate constant for the quenching of benzene triplets calculated from the observed pressure dependence and an assumed benzene triplet lifetime of 2.6×10^{-5} sec was 3×10^{10} l. M^{-1} sec^{-1}, which is in reasonable agreement with the value of 2×10^{10} l. M^{-1} sec^{-1} found by Morikawa and Cvetanović.[82] Proof that energy transfer to oxygen is the *principal* mechanism by which oxygen quenches triplet state molecules was obtained by epr experiments where it was shown that the quantum yield for formation of singlet oxygen (based on the number of triplet state molecules formed) is of the order unity.[117,120] While these experiments confirm a major feature of the theoretical predictions,[65] unfortunately, they provide no information on the relative amounts of $^1\Sigma$ and $^1\Delta$ molecules that were *initially* generated in the quenching process. Thus, the theoretical expectation that molecules which have relatively high-energy triplet states will generate more $^1\Sigma$ than $^1\Delta$ remains untested.[104]

The spectroscopic techniques which have been so useful for studying the photosensitized generation of singlet oxygen in the gas phase are not applicable to solution-phase studies. Consequently, studies in this area have depended upon indirect chemical methods to follow the formation of singlet oxygen. On the assumption that the photooxygenation of various substituted anthracenes involves singlet oxygen as an intermediate, Stevens and his coworkers have shown in a series of studies that sensitizer triplet state molecules are the sole precursers to the formation of singlet oxygen molecules, and that the quenching rate constant is approximately $k_d/9$.[89,91,92] An attempt was made to determine whether or not $^1\Sigma$ oxygen is involved in the quenching of triplet state sensitizers, but all that could be established was that, if $^1\Sigma$ is formed, it must be quantitatively relaxed to $^1\Delta$. This is strongly supported by the observation that the limiting quantum yield for product formation in dye-sensitized photooxygenations is equal to the intersystem crossing quantum yield of the sensitizer.[10] For those molecules which have fluorescence yields approaching unity the limiting quantum yield for sensitized photooxygenation varies directly with the fractional quenching of the fluorescence,[89,91,92] indicating that oxygen enhances the $S_1 \rightarrow T_1$ conversion.

c. O_2 Quenching of β-Carotene

It has recently been shown that oxygen quenches the triplet state of β-carotene at a rate which is comparable to the oxygen quenching of the naphthalene triplet.[112] In view of our discussion of the oxygen quenching of other triplet state molecules, this would not be unusual were it not for the fact that β-carotene is believed to have a triplet state which lies *below* that of singlet Δ.[121] Consequently, triplet β-carotene cannot be quenched by energy transfer, but it still may be quenched by an oxygen enhanced intersystem crossing according to the following (spin-allowed) mechanism.

$$^3(\beta\text{-carotene}) + {}^3O_2 \longrightarrow {}^1(\beta\text{-carotene}) + {}^3O_2$$

A relatively large rate constant is expected for this process because a large Franck–Condon factor is associated with a T_1–S_0 splitting of less than 8000 cm^{-1} and the spin statistical factor associated with this mechanism is $^1/_3$ rather than $^1/_9$. Thus, the suggestion[112] that there is a contradiction between the fact that ground state β-carotene can quench $^1\Delta$ oxygen (presumably by energy transfer to β-carotene) while at the same time ground state oxygen can quench *triplet* β-carotene is probably not valid.

d. Complexes between O_2 and Triplet State Molecules

In connection with an earlier interpretation of sensitized photooxygenation reactions, Schenck[95] suggested that the oxygen-transferring species is a metastable complex (moloxide) between ^3M and $^3O_2$. A theoretical study of the energies of the various states of the $(M\cdots O_2)$ complex has been carried out, and the results are shown in Figure 5.[122] Although a

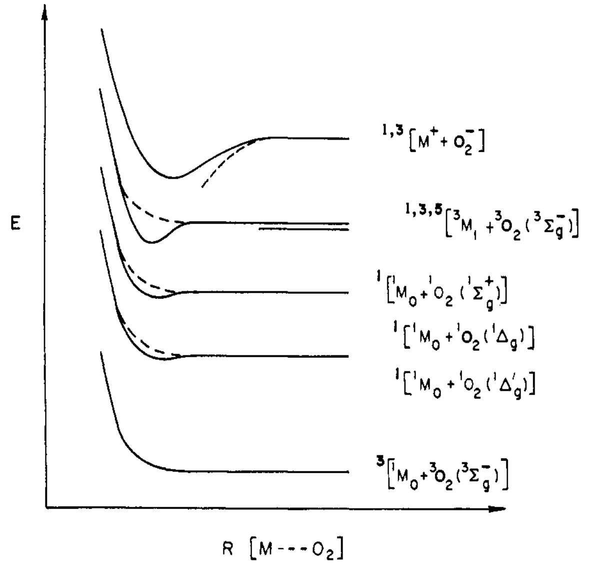

Figure 5. A schematic representation of the potential energy curves for the states of an $[M\cdots O_2]$ complex. The free molecule states into which the states of the complex dissociate at large intermolecular separation are indicated on the right-hand side of the diagram. The dashed curves indicate how the states of the complex would behave in the absence of configuration interaction. The solid curves are drawn to include the effects of configuration interaction. The "binding" energies are calculated to be ~200 cm^{-1} or less.[122]

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small minimum ($\lesssim$ 300 cm^{-1}) is found for the ($^3M + {}^3O_2$) complex, this state is expected to have an exceedingly short lifetime ($<10^{-10}$ sec) because of rapid relaxation to lower lying dissociative states of the complex [($^1M_0 \cdots {}^1\Delta$) and ($^1M_0 \cdots {}^1\Sigma$)]. The moloxide would obviously be too short lived to be identified as the oxygen-transferring intermediate in sensitized photooxygenation reactions.[122]

The high-intensity pulsed laser experiments on the O_2 quenching of pyrene excimers appear to confirm this conclusion.[96] As discussed in the previous section these experiments demonstrated that oxygen-pyrene complexes (if they are formed) have lifetimes less than 10^{-10} sec. Since the fluorescence quenching undoubtedly involves formation of triplet state pyrene molecules, and hence $^1\Delta$, these results also rule out the existence of a long-lived complex between $^3M_0$ and $^1\Delta$. It would be premature, however, to conclude from the pyrene experiments that there are no sensitizers capable of forming metastable moloxides with oxygen, and a study of a variety of the common types of sensitizers analogous, to the pyrene study, would be interesting.

e. Comparison of NO and O_2 Quenching of Triplets

The theory used to treat the oxygen quenching of triplet state molecules[65] may also be applied to other paramagnetic quenchers, such as NO.[102] In this case there is no possibility for electronic energy transfer, and quenching occurs only through an enhancement of intersystem crossing. If the electrostatic matrix elements are comparable to those obtained with oxygen quenching, we find that NO should be a much poorer quencher of triplets than O_2 because the Franck-Condon factor is so much smaller. Contrary to this expectation, Siegel and Judeikis[114] concluded from an investigation of the O_2 and NO quenching of triplet state molecules in rigid 3-methylpentane glasses that NO is a *better* triplet state quencher than is O_2. They further concluded that enhancement of intersystem crossing in naphthalene is probably the dominant quenching process for *both* O_2 and NO, an interpretation which disagrees with solution[89,91,92] and gas-phase[83,117,118] studies which prove that the oxygen quenching of triplet state molecules proceeds almost exclusively *via* energy transfer to oxygen.

A possible resolution of this discrepancy was provided by Birks[93] who reinterpreted the data of Siegel and Judeikis[114] and suggested that the quenching which they observed probably occurred at the *singlet* state level, rather than at the *triplet* level. This possibility has now been reexamined experimentally[94] and, as Birks suggests, the quenching is at the excited singlet state level where NO is in fact a more effective quencher than O_2. The revised range of interaction values for the singlet quenching are $R^{\text{singlet}}(\text{NO}) = 12.3$ Å, $R^{\text{singlet}}(O_2) \leq 7.1$ Å, and the new value for triplet quenching is $R \simeq 10.0$ Å. Unfortunately, the corresponding value for NO could not be obtained.

With the resolution of this apparent discrepancy it would appear that there are no important disagreements between the major predictions of the quenching theory[65] and experiment observations.

3. *Direct Optical Excitation of Singlet Oxygen Molecules*

Liquid oxygen and oxygen gas under high pressure exhibit a set of absorption bands in the visible region corresponding to various simultaneous transitions.[30,31] Fortunately, the light from a He-Ne laser (6238 Å) almost exactly coincides with the absorption band associated with the $2(^3\Sigma) \rightarrow 2(^1\Delta)$ transition, and Evans[123] found that when a solution of 9,10-dimethylanthracene was placed under 2000 psi of oxygen pressure and excited with the He-Ne laser, he was able to effect the photooxygenation of the anthracene. The quantum yield for the reaction was only 0.13, but when he used the more reactive singlet oxygen acceptor 1,3-diphenylisobenzofuran under similar conditions, the quantum yield for the photooxygenation was about 0.6.[123] Through the use of a series of different light sources Evans was also able to obtain a crude "action spectrum" for photooxygenation and show that only light of wavelengths corresponding to known absorption bands of oxygen was effective in promoting the oxygenation reactions. While this technique may not have great synthetic utility, it should be valuable in mechanistic studies where it is important to know that singlet oxygen molecules are the only excited state molecular species present in solution.

A particularly important observation which Evans made was that the effectiveness of excitation at 7600 Å ($^3\Sigma \rightarrow {}^1\Sigma$) relative to 12,700 Å ($^3\Sigma \rightarrow {}^1\Delta$) was commensurate with the relative intensities of the oxygen absorption bands at these two different wavelengths. From this observation we conclude that either the efficiencies with which $^1\Sigma$ and $^1\Delta$ react with acceptors are identical, or the $^1\Sigma$ molecules initially generated by excitation at 7600 Å rapidly decay to $^1\Delta$ which then reacts. Since the quenching of $^1\Sigma$ by the solvent ($k_q > 10^9$ l. M^{-1} sec^{-1})[16] is known to be much faster than by reaction with the acceptor (acceptor concentrations on the order of 10^{-4}–10^{-5} M), the Evans experiments prove that the quenching of $^1\Sigma$ in these systems leads primarily to the formation of $^1\Delta$ and not ground state triplet oxygen. This appears to be the only clear experimental evidence that $^1\Delta$ is the product of quenching $^1\Sigma$.

4. *Photolytic Generation of Singlet Oxygen*

The photolysis of ozone provides still another method for generating both $^1\Sigma$ and $^1\Delta$ oxygen in a gas-phase system[124–129] *via* the reaction

$$O_3 \xrightarrow{h\nu} O_2(^1\Sigma \text{ or } ^1\Delta) + O$$

From strictly energetic considerations the limiting wavelengths required for the direct production of $^1\Sigma$ and $^1\Delta$ from the photolysis of ozone can be set. Photolysis of ozone with λ 2537 Å could generate either $^1\Sigma$ or $^1\Delta$ and leave the oxygen atom in an excited ^1D state in a spin conserving process, but experimentally it appears that only $^1\Delta$ is produced.[125] The $^1\Sigma$ which is observed in this system apparently arises from the following secondary reaction involving energy

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transfer from excited oxygen *atoms* to ground state molecular oxygen[124,126,127,130]

$$O(^1D) + O_2(^3\Sigma) \longrightarrow O(^3P) + O_2(^1\Sigma)$$

Although the reported rate constants for this reaction vary from about 10^6 to 10^{11} l. M^{-1} sec^{-1}, the evidence favors the higher values.[130]

The reactions

$$O(^1D) + O_2(^3\Sigma) \longrightarrow O_2(^1\Delta) + O(^3P)$$

and

$$O_3 + h\nu_{2537} \longrightarrow O_2(^1\Sigma) + O(^1D)$$

are found to be only minor sources of $^1\Delta$ and $^1\Sigma$ in this system.[125]

$^1\Sigma$ can also be produced from the photolysis of molecular oxygen,[131,132] and the following scheme has been suggested[131]

$$O_2 + h\nu_{1470} \longrightarrow O(^1D) + O(^3P)$$
$$O(^1D) + O_2(^3\Sigma) \longrightarrow O_2(^1\Sigma) + O(^3P)$$

While the photolysis of ozone and oxygen may not be generally useful methods for generating large amounts of singlet oxygen, they suggest that it might be worthwhile to examine the photolysis of other small oxides.[133]

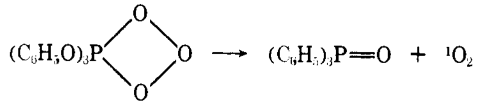
B. CHEMICAL SOURCES OF SINGLET OXYGEN

1. Decomposition of Hydrogen Peroxide

The decomposition of hydrogen peroxide has played an important role in the field of singlet oxygen chemistry since this system was used to provide the first definitive evidence for the participation of singlet oxygen in sensitized photooxygenation reactions.[5–7,134] It had been known for some time that peroxide decompositions yielding molecular oxygen are often accompanied by a visible chemiluminescence,[135–139] and there had even been suggestions that this emission arose from excited singlet oxygen molecules.[139] It was not, however, until the studies of Khan and Kasha[5] in 1963 and those of Arnold, Ogryzlo, and Witzke[35] in 1965 that this was confirmed. In the original studies of the chemiluminescence of hydrogen peroxide only a single band at 6348 Å was reported,[138] but Khan and Kasha observed an additional band at 7032 Å.[5] In a subsequent study Browne and Ogryzlo reported weak bands at 10,700 and 12,700 Å as well as weak bands in the 7600–8700-Å region.[140–142] From a comparison of the bands observed in chemiluminescence with emission bands which appear in electrically discharged gaseous oxygen, and with absorption bands observed in liquid oxygen,[32,33] it was unequivocally established that large quantities of singlet oxygen molecules are generated by the decomposition of hydrogen peroxide.[5,6,35,36,38,142] The chemiluminescence was due to double molecule transitions $2(^1\Delta) \rightarrow {}^3\Sigma + 6340$ Å; $^1\Sigma + {}^1\Delta \rightarrow 2(^3\Sigma) + 4800$ Å as well as single molecule transitions $^1\Sigma \rightarrow {}^3\Sigma + 7600$ Å and $^1\Delta \rightarrow {}^3\Sigma + 12{,}600$ Å. In addition to demonstrating that the decomposition of hydrogen peroxide is a source of singlet molecular oxygen, the chemiluminescence studies[5,35,142] provided some other rather surprising results. First of all, the fact that the strongest band in the chemiluminescence spectrum, the band at 7032 Å, arises from a cooperative transition involving a *pair* of $^1\Delta$ molecules indicated that significant concentrations of excited singlet oxygen were generated by the decomposition. Secondly, the 7600-Å $^1\Sigma \rightarrow {}^3\Sigma$ "solution" chemiluminescence band exhibits rotational structure which indicates that the emission is from singlet oxygen molecules in gas bubbles,[6] rather than from dissolved oxygen. Rotational structure was not observed on other bands, but it is likely that all the emission is from oxygen molecules in the gas phase since it has not been possible to sensitize the luminescence from oxygen molecules which are actually dissolved in solution. Furthermore, studies of the decay of singlet oxygen in the gas phase and in solution suggest that the lifetime of singlet oxygen in solution is quite short compared with the gas phase (see section V).

2. Decomposition of Ozonides

The discovery that the decomposition of hydrogen peroxide produces singlet oxygen molecules has stimulated the search for other chemical systems which might be capable of generating excited oxygen. Murray and Kaplan presented the first chemical evidence that adducts between aryl phosphites and ozone, prepared at −70°, when heated above −35° release singlet molecular oxygen according to the reaction[143–147]



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In these studies evidence for singlet oxygen formation was based on the observation that the phosphite–ozone adduct is capable of oxidizing various oxygen acceptors to give the same products as those formed in the reaction of singlet oxygen with the same acceptors. In subsequent studies epr spectroscopy was used to demonstrate unambiguously that the decomposition of the phosphite–ozone adduct generates $^1\Delta$ which was detected in the gas phase after escaping from solution.[148] Although these studies prove that ozone–phosphites generate singlet oxygen, Bartlett and Mendenhall have shown

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that there can be complicating side reactions and that "chemical tests" for singlet oxygen should only be accepted with caution.[149] They found that tetramethylethylene, a very good singlet oxygen acceptor, reacts with the triphenyl phosphite ozonide (**1**) at temperatures (−60°) far below those where **1** yields free oxygen at an appreciable rate. Furthermore, competitive reactions between tetramethylethylene and 2,5-dimethylfuran, another good singlet oxygen acceptor, show that tetramethylethylene is the more reactive acceptor with **1**, whereas the reverse is true in sensitized photooxygenation reactions. On the basis of this study it was concluded that there is a second mechanism of direct O_2 donation from triphenyl phosphite ozonide which yields the *same* products as free singlet oxygen, but has very different selectivities toward different types of substrates. These studies have been extended to other olefins where again evidence for direct oxygen donation from **1** the acceptor is found.[150] In this regard, these ozonides have properties very much like those which Schenck proposed for the moloxide intermediates.

3. Decomposition of Endoperoxides

It has been known for some time that various aromatic hydrocarbons, particularly the linear polyacenes, react with singlet oxygen in sensitized photooxygenation reactions to produce endoperoxides which, upon heating, dissociate and regenerate the parent hydrocarbon and free molecular oxygen.[15,151] Elementary theoretical considerations suggest that the oxygen regenerated by the decomposition may be formed in an excited singlet state (see section VI).[104] This theoretical possibility receives experimental support from the observations of Wasserman and Scheffer, who demonstrated that the decomposition of 9,10-diphenylanthracene peroxide in the presence of suitable singlet oxygen acceptors can be used to promote reactions which are typical of singlet oxygen reaction.[152] In view of the complications which have been found in the ozonide studies,[149,150] it would be desirable to have independent spectroscopic confirmation that singlet oxygen molecules are generated during the decompositions of these endoperoxides.[152]

4. Decomposition of Superoxide Ion

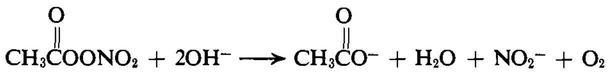
The superoxide ion O_2^- is another potential source of singlet oxygen since loss of an electron of appropriate spin could produce either ground state molecular oxygen or singlet excited oxygen according to the following scheme.

$$^2O_2^- \longrightarrow {}^{1,3}O_2 + e^-$$

Khan[153] recently has provided chemical and chemiluminescence data to support this notion. He found that upon the addition of various fluorescent dyes to a saturated solution of potassium superoxide in dimethyl sulfoxide sensitized fluorescence characteristic of the dye could be observed. On the *assumption* that singlet oxygen molecules are responsible for sensitizing the dye luminescence (see section VIII), this was taken as evidence for the formation of singlet oxygen, but other mechanisms for the chemiluminescence were not ruled out. In parallel chemical studies, it was found that superoxide reacts with 2,5-dimethylfuran to form a product which gives a positive peroxide test. Since hydrogen peroxide is also generated during the decomposition of the superoxide, this could account for the positive peroxide test. While these two experimental indications of the formation of singlet oxygen are not conclusive, they are suggestive, and superoxides certainly deserve further study. Conceivably superoxide ions may provide an unsuspected source for singlet oxygen molecules in certain enzyme systems where they have recently been discovered.[154–157]

5. Other Chemical Sources of Singlet Oxygen

Peroxyacetyl nitrate (PAN) is an important component of smog which is highly reactive and decomposes in the presence of base according to the reaction



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}ONO_2 + 2OH^- \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}O^- + H_2O + NO_2^- + O_2$$

Steer, Darnall, and Pitts[158] have examined this reaction for near-infrared emission and find that accompanying the decomposition there is a weak emission band centered at 12,700 Å due to the $^1\Delta \rightarrow {}^1\Sigma$ transition. They suggest that the ability of PAN to generate singlet oxygen may be involved in its high reactivity in chemical and biological systems.

Some other compounds which might prove interesting with regard to generation of singlet oxygen are the monomeric oxygen adducts of various transition metals[159–162] and clathrate compounds of oxygen,[163] and perhaps even hemoglobin.[164] All of these oxygen-containing systems have the common property that they reversibly release the bound oxygen, and the presence of a paramagnetic atom in some of the complexes could facilitate the release of oxygen as excited singlet oxygen. The photodecomposition of certain peroxides might provide another source of singlet oxygen (see section VI).[104]

Evidence that singlet oxygen can be "reversibly" trapped at low temperatures by a variety of different sensitizers (rhodamine B, eosin, erythrosin, rose bengal, acridine orange, methylene blue, pyrene, 1,2-benzopyrene, anthracene, perylene) was recently presented by Balny, *et al.*[165] Presumably the sensitizer–oxygen complex would be similar to the moloxide complex which Schenck[95] proposed as an intermediate

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in dye-sensitized photooxygenation reactions. As a result of a more detailed reexamination of these systems, however, the authors have now retracted this interesting possibility.[166]

In spite of the variety of techniques which are available for generating singlet oxygen [rf discharge, photolysis of O_2 or O_3, sensitization by energy transfer, direct optical excitation, decomposition of hydrogen peroxide, ozone-phosphites, PAN, and O_2^- (?)] there are occasions when it would be useful to have additional methods. For example, the chemical methods for generating singlet oxygen and the dye-sensitized formation of singlet oxygen may be complicated by unwanted side reactions. The gas-phase methods on the other hand suffer from the fact that the $^1\Delta$ concentrations are rather low (less than 10^{-5} *M*). Although the difficulties of using a gas-phase source of singlet oxygen have somewhat been overcome through the use of special reactors,[167] a continued search for efficient and clean sources of singlet oxygen in condensed phases would be desirable.

C. OTHER SINGLET OXYGEN SOURCES

1. *Gaseous Discharges*

Radiofrequency discharge tubes have been one of the most convenient sources of singlet oxygen for spectroscopic studies since it is possible to excite approximately 10% of the oxygen in a flow discharge to the $^1\Delta$ state. Noxon first demonstrated the presence of $^1\Delta$ in a flow discharge system,[168] and Foner and Hudson[169] utilized mass spectroscopy to show that the $^1\Delta$ survived outside the discharge. Some $^1\Sigma$ oxygen is also produced in the discharge,[170] but is relaxed (presumably to $^1\Delta$) so rapidly that its steady state concentration in the flow would be quite low if this were the only source.[16] Because of the presence of substantial concentration of $^1\Delta$, most of the $^1\Sigma$ down stream from the discharge is formed by the following energy pooling process first suggested by Young and Black.[170]

$$O_2(^1\Delta) + O_2(^1\Delta) \longrightarrow O_2(^1\Sigma) + O_2(^3\Sigma)$$

Microwave or rf discharges also produce substantial concentrations of oxygen atoms; however, this may be suppressed by interposing a film of mercuric oxide between the discharge and position of observation.[171] Ozone is another component of the discharge which can react with $^1\Sigma$ according to the reaction[172]

$$O_2(^1\Sigma) + O_3 \longrightarrow O_2 + O_2 + O$$

The oxygen atoms generated by this reaction are then scavenged by reaction with other ozone molecules.

$$O + O_3 \longrightarrow 2O_2$$

In the absence of ozone and other added gases the decay of both $^1\Delta$ and $^1\Sigma$ is primarily due to collisions with the walls of the flow system.[173] Although the efficiency with which the walls deactivate $^1\Sigma$ and $^1\Delta$ can vary significantly depending upon the history of the wall, clean Pyrex surfaces all appear to behave similarly, with deactivation efficiencies of 10^{-5} for $^1\Delta$ and 2×10^{-3} for $^1\Sigma$.[16,174,175] For a more detailed discussion of some other aspects of the formation of $^1\Delta$ and $^1\Sigma$ in electric discharges, the recent review articles by Wayne[18] and by Ogryzlo[173] should be consulted.

2. *Tungsten Lamps*

Khan recently presented evidence for the generation of electronically excited molecular oxygen in ordinary incandescent tungsten filament lamps.[176] He observed that the spectral output from tungsten filament lamps exhibits a series of pronounced peaks superimposed on the smooth blackbody emission of the lamp, and noted that the positions of these peaks correspond well with bands which have been assigned as simultaneous transitions of oxygen pairs. Conceivably electronically excited oxygen molecules are generated on the surface of the tungsten and then emit after leaving it.[177] Khan's[176] spectroscopic observations suggest that the weak luminescence in the 520–620-nm region which McCarroll[178] observed when oxygen was chemi-absorbed on clean tungsten surfaces may also be due to emission from excited oxygen molecules. Perhaps the weak luminescence which Rufov, *et al.*,[179] observed in the 600–800-nm region when they exposed oxygen molecules to the solid surfaces of a number of metal oxides also involves singlet oxygen molecules.

IV. Methods for Detecting Singlet Oxygen

One factor which has slowed research on singlet oxygen has been the lack of convenient methods for detecting singlet oxygen in the gas phase and particularly in condensed phases. The situation has been substantially improved, insofar as gas-phase work is concerned, through the development and application of a number of techniques (microwave spectroscopy, emission spectroscopy, photoionization spectroscopy, mass spectrometry, and calorimetry), but detection of singlet oxygen in condensed phases is restricted almost entirely to chemical techniques which may be misleading.

A. GAS-PHASE TECHNIQUES

There have recently been several reviews which discuss the techniques which have been used to detect singlet oxygen in the gas phase,[18,19] so that it will be necessary here only to mention these methods and comment on their range of applicability.

1. *Paramagnetic Resonance*

Oxygen in the $^1\Delta$ state is paramagnetic by virtue of its orbital angular momentum, and Falick, Mahan, and Myers[180] and Falick and Mahan[181] have detected and analyzed the para-

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(166) C. Balny, J. Canva, P. Douzou, and J. Bourdon, private communication.

(167) J. R. Scheffer and M. D. Ouchi, *Tetrahedron Lett.*, 223 (1970).

(168) J. F. Noxon, *Can. J. Phys.*, **39**, 1110 (1961).

(169) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **25**, 601 (1956).

(170) R. A. Young and G. T. Black, *ibid.*, **44**, 3741 (1966).

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

(172) R. E. March, S. G. Furnival, and H. I. Schiff, *Photochem. Photobiol.*, **4**, 971 (1965).

(173) K. Furukowa, E. W. Gray, and E. A. Ogryzlo, *Ann. N. Y. Acad. Sci.*, **171**, 175 (1970).

(174) I. D. Clark and R. P. Wayne, *Chem. Phys. Lett.*, **3**, 93 (1969).

(175) R. P. Steer, R. A. Ackerman, and J. N. Pitts, *J. Chem. Phys.*, **51**, 843 (1969).

(176) A. U. Khan, *Chem. Phys. Lett.*, **4**, 567 (1970); see also ref 310.

(177) G. Mannella and P. Harteck, *J. Chem. Phys.*, 34, 2177 (1961).

(178) B. McCarroll, *ibid.*, **50**, 4758 (1969).

(179) Yu. N. Rufov, A. A. Kadushin, and S. Z. Roginskii, *Proc. Acad. Sci. USSR, Phys. Chem. Soc.*, **171**, 777 (1966).

(180) A. M. Falick, B. H. Mahan, and R. J. Myers, *J. Chem. Phys.*, **42**, 1837 (1965).

(181) A. M. Falick and B. H. Mahan, *ibid.*, **47**, 4778 (1967).

magnetic resonance spectrum of $^1\Delta$ in discharged oxygen. In their experiments they observed the $\Delta M = 1$ transitions for the $J = 2$ total angular momentum state associated with the $^1\Delta$ molecule. They were also able to observe resonances from ground state $^3\Sigma$ and in this way estimated that under their conditions the $^1\Delta$ concentration constituted 10% of the total oxygen concentration. The epr method was subsequently used to detect the formation of $^1\Delta$ in the gaseous products from decomposition of the triphenyl phosphite–ozone adduct,[148] and the formation of $^1\Delta$ by energy transfer from triplet state sensitizers (naphthalene, quinoxaline, and perfluoronaphthalene).[117,118]

2. *Emission Spectroscopy*

The optical emission from $^1\Delta$ and $^1\Sigma$ provides another method by which excited oxygen molecules may be detected in the gas phase.[16,35,37,39,83,168,182–185] Single molecule emission bands occur at 7620 and 12,700 Å,[83,168] and when high concentrations of $^1\Delta$ are present, as in rf discharges, cooperative emission bands at 6340 and 7030 Å can easily be detected.[35,36,37,184,185] With appropriate sensitivity additional weaker bands at ~4770 and ~3810 Å resulting from cooperative transitions from the $(^1\Sigma + {}^1\Delta)$ and $2(^1\Sigma)$ pair states, respectively, may also be observed. Some important advantages of emission spectroscopy are that it permits both $^1\Sigma$ and $^1\Delta$ to be detected over a wide range of gas pressures, and can be used in many systems where organic molecules also are present in the gas phase. This overcomes important limitations of the epr experiments which only permit detection of $^1\Delta$ at pressures less than a few Torr, and the photoionization method described below which cannot be used if organic molecules are present in the system. The sensitivity of this method has recently been improved by Ness and Hercules through the use of an image intensifier to detect the emission.[186]

The bright chemiluminescence which results from the addition of molecular iodine to a flow discharge of oxygen may provide a useful way of monitoring singlet oxygen molecules in gas-phase systems, particularly since it depends on the presence of both $^1\Sigma$ and $^1\Delta$ molecules.[37,187]

3. *Photoionization*

The photoionization technique for detecting excited oxygen was first used by Cairns and Samson,[188] and subsequently by McNeal and Cook,[189,190] who found that with monochromatic excitation they could detect ionization of singlet oxygen molecules which have ionization potentials about 1 or 1.6 eV lower than that of ground state oxygen (12.5 eV).[191] The sensitivity of the method was greatly improved by Clark and Wayne[192] who eliminated the use of a monochromator by employing rare gas resonance lines to ionize the excited oxygen molecules. The 1165-Å line of krypton, for example, ionizes only $^1\Sigma$, whereas the argon 1067- and 1048-Å resonance lines ionize both $^1\Delta$ and $^1\Sigma$ but not ground state oxygen. Using this technique they have been able to obtain valuable information about the rate constants for various reactions of singlet oxygen molecules in the gas phase. Although the photoionization technique is very sensitive, it is limited in that it cannot be applied to systems which contain organic molecules, oxides of nitrogen, or other molecular species which have ionization potentials less than about 11 eV.

Foner and Hudson[169] have used mass spectrometry to detect the formation of $^1\Delta$ oxygen in an electrical discharge by taking advantage of the lower ionization potential of $^1\Delta$. This detection method has had only limited application in singlet oxygen studies because it requires a relatively large $^1\Delta/^3\Sigma$ ratio, and it is difficult to introduce the stream of excited oxygen molecules into the spectrometer without collisionally deactivating them. Because of these limitations, it has not yet been possible to use mass spectrometry to detect $^1\Sigma$.[18]

4. *Calorimetry*

Calorimetric methods have also been used to detect the presence of singlet oxygen molecules in the gas phase.[16,35,36,71] In this method, a heated wire is introduced into the gas flow, and the excited oxygen molecules can be detected by the amount of heat which they release when they are deactivated. Arnold has shown that cobalt-coated wires deactivate more than 95% of the $^1\Delta$ oxygen in a gas stream and that with proper calibration this can be a very convenient method for measuring concentrations of excited molecules. The disadvantage of this method lies in the fact that it is not selective and there may be contributions from $^1\Sigma$ molecules, oxygen atoms, and any other excited state species that are present in the gas.

B. CONDENSED-PHASE METHODS

Most of the methods used to detect singlet oxygen in the gas phase cannot be applied to solution-phase studies, unless the oxygen molecules are swept out of solution into the gas. Emission spectroscopy might occasionally be useful in solution studies (as it has in "chemiluminescence" spectroscopy of singlet oxygen[5,6,35,142]), but this may in particular cases prove to be impracticable because $^1\Sigma$ and $^1\Delta$ oxygen are rapidly quenched and consequently have low emission quantum yields (less than 10^{-8} for $^1\Delta$) in condensed media. Because of the difficulties associated with the spectroscopic methods, it has been necessary to resort to chemical methods for detecting singlet oxygen in solution. Since the mechanism of singlet oxygen reactions will be discussed in detail later (section VII), we will make only a few general comments about the chemical detection of singlet oxygen.

If chemical detection methods are to be reliable and useful, then the reaction should be reasonably rapid, completely specific for singlet oxygen, free of complicating side reactions, and easily analyzed for products. In practice, all of these requirements are usually not satisfied. For example, the reaction of tetramethylethylene (**2**) with singlet oxygen leads to the rearranged allylic hydroperoxide (**3**),[7,12,13] and it is often assumed that the formation of **3** is diagnostic for the

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

(183) M. A. A. Clyne, B. A. Thrush, and R. P. Wayne, *Photochem. Photobiol.*, **4**, 957 (1965).

(184) S. J. Arnold and E. A. Ogryzlo, *Can. J. Phys.*, **45**, 2053 (1967).

(185) E. A. Ogryzlo and A. E. Pearson, *J. Phys. Chem.*, **72**, 2913 (1968).

(186) S. Ness and D. M. Hercules, *Anal. Chem.*, **41**, 1467 (1969).

(187) R. G. Derwent, D. R. Kearns, and B. A. Thrush, *Chem. Phys. Lett.*, **6**, 115 (1970).

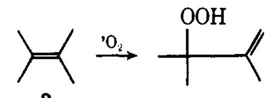
(188) R. B. Cairns and J. A. R. Samson, *Phys. Rev.*, **139**, A1403 (1965).

(189) R. J. McNeal and G. R. Cook, *J. Chem. Phys.*, **45**, 3469 (1966).

(190) R. J. McNeal and G. R. Cook, *ibid.*, **47**, 5385 (1967).

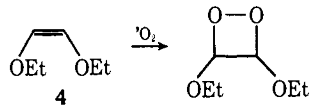
(191) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1953, p 2340.

(192) I. D. Clark and R. P. Wayne, *Mol. Phys.*, **18**, 523 (1970).



2 3

formation of $^{1}O_2$.[153,193] Bartlett and Mendenhall have pointed out, however, that the same allylic hydroperoxide product may be produced from ground state oxygen in a chain reaction involving free radical intermediates.[149,194,195] Singlet oxygen reacts with vinylene diethers to form dioxetanes as indicated below.



4 5

While this reaction might be useful as a singlet oxygen trap, Schaap and Bartlett[196] have also shown that entirely similar products can be obtained by nonsinglet oxygenation reactions, so that one must be very careful about the choice of acceptor molecules and carry out necessary tests to demonstrate that other nonsinglet oxygen mechanisms are not involved. Of all the types of reactions which have been studied, it would appear that 1,4-cycloaddition to conjugated dienes has the requisite properties, since no other reagent is capable of giving the same product.[194]

There is experimental evidence that singlet oxygen molecules are able to sensitize the fluorescence of aromatic hydrocarbons, and it has been suggested that this could be used as a method for detecting singlet oxygen in solutions. The entire question of involvement of singlet oxygen in chemiluminescence phenomena is sufficiently important to warrant a separate discussion and this will be examined in section VIII.

V. Quenching of Singlet Oxygen

A. QUENCHING IN THE GAS PHASE

Because of their long radiative lifetimes (~7 sec for $^{1}\Sigma$ and 45 min for $^{1}\Delta$), the actual lifetime of a singlet oxygen in most systems is determined by nonradiative quenching mechanisms, and consequently considerable effort has been put into determining these quenching rate constants. Since spectroscopic observations on singlet oxygen cannot be conveniently made in condensed phases, most of the data are from gas-phase measurements. A variety of different techniques have been used to generate singlet oxygen ($^{1}\Sigma$ and $^{1}\Delta$)[15,128,197-205] including photolysis of oxygen or ozone,[127,128,132,197] benzene-photosensitized production of $^{1}\Delta$,[198] and rf discharge.[16,199-201] Concentrations of singlet oxygen were determined by monitoring singlet oxygen emission bands at 7620 or 12,700 Å,[16,127,128,197-199] or through the use of the photoionization method.[201,202]

1. Inert Quenchers

The results of studies with inert quenchers are compiled in Table IV, and one feature which is immediately apparent from these data is that the rate constants for the quenching of $^{1}\Sigma$ are often three to four orders of magnitude larger than for quenching of $^{1}\Delta$. This greater sensitivity of $^{1}\Sigma$ to collisional deactivation is perhaps understandable in terms

Table IV

Rate Constants for the Deactivation of $^{1}\Sigma$ and $^{1}\Delta$ Oxygen

Quencher	$k_Q(^{1}\Sigma)$, *l. M^{-1} sec^{-1}*	*Ref*	$k_Q(^{1}\Delta)$, *l. M^{-1} sec^{-1}*	*Ref*
O_2	9.0×10^4	128	1.4×10^3	201
	6.0×10^4	127		
	6.0×10^4	203		
	2.7×10^5	132		
N_2	1.2×10^6	128	$<6.0 \times 10$	201
	1.3×10^6	127		
	1.3×10^6	203		
	1.1×10^6	132		
	2.1×10^5	199		
CO_2	1.8×10^8	128	2.3×10^3	201
	1.2×10^8	203		
	2.6×10^8	132		
	2.3×10^7	199		
CO	1.8×10^6	128		
	1.9×10^6	203		
	2.6×10^6	132		
	1.5×10^6	199		
H_2O	5.3×10^8	199	9.0×10^3	201
	2.0×10^9	132		
	3.2×10^9	204		
D_2O	4.1×10^8	199		
	2.2×10^9	204		
H_2	6.6×10^8	132		
	6.6×10^8	204		
HD	$<2.5 \times 10^8$	204		
D_2	1.1×10^7	204		
NH_3	5.2×10^7	132		
	1.5×10^8	199		
C_2H_2	2.7×10^8	204		
C_2D_2	5.0×10^7	204		
CH_4	6.6×10^6	199		
	6.6×10^7	132		
C_2H_4	2.6×10^8	204		
	1.9×10^8	132		
C_2D_4	8.5×10^7	204		
He	$\sim 6.0 \times 10^4$	132		
	6.0×10^5	199		
Ar	1.9×10^6	199	$<1.2 \times 10^2$	201
	3.5×10^3	132		
Cyclopentadiene			8.8×10^6	173
2,5-Dimethylfuran			2.8×10^6	173
cis-Butene-2			2.5×10^4	173
Hexene-2			6.7×10^3	173

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(193) H. W. Coomber and J. N. Pitts, *Environ. Sci. Technol.*, 506 (1970).

(194) P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. N. Y. Acad. Sci.*, 171, 79 (1970).

(195) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 45, 798 (1967).

(196) A. P. Schaap and P. D. Bartlett, *J. Amer. Chem. Soc.*, 92, 6055 (1970).

(197) S. V. Filseth and K. H. Welge, *Ann. N. Y. Acad. Sci.*, 171, 226 (1970).

(198) F. D. Findlay, C. J. Fortin, and D. R. Snelling, *Chem. Phys. Lett.*, 3, 204 (1969).

(199) S. J. Arnold, Ph.D. Thesis, University of British Columbia, 1966.

(200) A. M. Winer and K. D. Bayes, *J. Phys. Chem.*, 70, 302 (1966).

(201) I. D. Clark and R. P. Wayne, *Chem. Phys. Lett.*, 3, 405 (1969).

(202) I. D. Clark and R. P. Wayne, *Proc. Roy. Soc., Ser. A*, 314, 111 (1969).

(203) F. Stuhl and K. H. Welge, *Can. J. Chem.*, 47, 1870 (1969).

(204) F. Stuhl and H. Niki, *Chem. Phys. Lett.*, 7, 473 (1970).

(205) E. A. Ogryzlo and C. W. Tang, *J. Amer. Chem. Soc.*, 92, 5034 (1970).

of the following considerations. If we limit our considerations to physical quenchers with ground singlet states and no low-lying excited states, then there are two mechanisms by which $^1\Sigma$ may be quenched.

$$O_2(^1\Sigma) + {}^1M \longrightarrow O_2(^1\Delta) + {}^1M \qquad (XII)$$

$$O_2(^1\Sigma) + {}^1M \longrightarrow O_2(^3\Sigma) + {}^1M \qquad (XIII)$$

The first process is a spin-allowed process, and, according to time-dependent perturbation theory,[62] the rate constant for this process will depend upon the extent to which the perturber molecule, ^1M, induces mixing of wavefunctions for the $^1\Sigma$ and $^1\Delta$ states. In section II.A we showed how a noncylindrical perturbation causes mixing of $^1\Sigma$ and $^1\Delta$ through the introduction of off-diagonal matrix elements of the form

$$V' = \langle \psi(^1M,{}^1\Sigma)|\mathcal{H}'|\psi(^1M,{}^1\Delta)\rangle = \frac{1}{2}\{\langle \pi_x|\mathcal{H}'|\pi_x\rangle - \langle \pi_y|\mathcal{H}'|\pi_y\rangle\} = V_{xx} - V_{yy}$$

where $\mathcal{H}'$ is some one-electron operator representing the effect of the perturber. Since V_{xx} and V_{yy} will not in general be equal, this perturbation can induce rapid transitions between $^1\Sigma$ and $^1\Delta$.

The variations in the rate constants for the quenching of $^1\Sigma$ appear to be most closely related to the magnitude of the intermolecular interaction between oxygen and the quencher as deduced from Lennard-Jones potential parameters for the interaction of two nonpolar molecules, or from Stockmayer potentials for the interaction with polar molecules.[199] The magnitude of the intermolecular potential between oxygen and the quencher appears, therefore, to be the major factor in determining the magnitude of V' and hence the quenching efficiency. The high efficiency of the polar molecules is consistent with the expectation that molecules with dipole moments could exert a "long-range" perturbing effect *via* the interaction of the dipole moment of the perturber with the electrons of oxygen. This in general would lead to nonequal values of V_{xx} and V_{yy} and hence to nonvanishing values of V'.

In reaction XIII $^1\Sigma$ is quenched to a ground triplet state and this is spin forbidden unless the perturber is paramagnetic, and hence this mechanism is not expected to be effective for diamagnetic perturbers. Consequently, we expect that the quenching of $^1\Sigma$ by diamagnetic perturbers will lead to the production of $^1\Delta$. While this is usually assumed to be the case,[16,18] Evan's direct photoexcitation experiments are the only ones which provide independent support for this assumption.[123]

The quenching of $^1\Delta$ by inert quenchers must involve the following reaction.

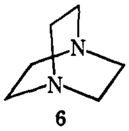
$$O_2(^1\Delta) + {}^1M \longrightarrow O_2(^3\Sigma) + {}^1M \qquad (XIV)$$

Because this is a spin-forbidden reaction, $^1\Delta$ is expected to be much more resistant to quenching than $^1\Sigma$, except perhaps when paramagnetic quenchers are involved. As we noted above, the rate constants for the quenching of $^1\Sigma$ are typically three to four orders of magnitude larger than for the quenching of $^1\Delta$, and interestingly enough, paramagnetic ground state oxygen is a much better quencher of $^1\Delta$ than is, say, N_2. The reverse was true in the case of quenching of $^1\Sigma$.

If the gas-phase results are extrapolated to the condensed phase, $^1\Delta$ and $^1\Sigma$ are expected to be rapidly quenched in solution. In aqueous solutions, the gas-phase quenching values lead to a lifetime of 10^{-11} sec for $^1\Sigma$ and 2×10^{-5} sec for $^1\Delta$. This latter value is probably correct since Wilkinson[206] has recently obtained evidence from flash photolysis studies that the lifetime in $^1\Delta$ in solution is about 10^{-5} sec, and Foote obtains a similar value assuming diffusion-controlled β-carotene quenching of singlet oxygen reactions.[207] Emission from $^1\Delta$ molecules trapped on a cold finger at 4.2°K was recently reported, and it appears from these measurements that the lifetime of $^1\Delta$ in the oxygen matrix is about 10^{-6} sec.[208]

2. Amines

Although amines might have been included with the inert quenchers, since they generally do not appear to react with singlet oxygen, experimentally they constitute a separate class because they are very efficient quenchers of $^1\Delta$. Typically, the rate constants, k_q, for quenching of $^1\Delta$ by amines range from 10^5 to 10^7 l. M^{-1} sec^{-1} or 10^2–10^4 larger than other singlet oxygen quenchers of comparable size.[205] The high quenching efficiency of amines was first discovered by Quannès and Wilson, who found that the diamine 1,4-diazobicyclo[2.2.2]-octane (**6**) is a powerful inhibitor of singlet oxygen reactions in solution and then demonstrated that **6** also quenches $^1\Delta$ in the gas phase.[209] The mechanism by which amines quench $^1\Delta$ is not known, but there is a remarkably good correlation between log k_q and the ionization energy of the amine.[205] This suggests that charge-transfer-type states are somehow involved in the quenching process, and the fact that amines do exhibit charge transfer absorption bands in the presence of oxygen certainly makes this suggestion quite plausible.[67,97] Since these charge transfer states lie much higher in energy than the $^1\Delta$ state, the exact manner in which the CT states are involved remains to be resolved.



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3. Excited Triplet State Quenchers

In a recent study of the photosensitized generation of $^1\Delta$ we introduced the sensitizers (naphthalene or quinoxaline) into the oxygen flow downstream from a microwave discharge and used epr spectroscopy to monitor the $^1\Delta$ concentration even further downstream.[120] A schematic diagram of the apparatus is shown in Figure 6, and with this setup it was possible to separately measure the concentration of $^1\Delta$ formed by energy transfer from the photoexcited sensitizer, or by the microwave discharge, or by both sources together. Surprisingly, we found that when both the discharge and the lamp were on, the $^1\Delta$ concentration was *smaller* than when just the microwave discharge was on (see Figure 7). Ground state sensitizer (quinoxaline) had no effect on $^1\Delta$ generated by the microwave discharge, and in the combined microwave–photo experiment, the $^1\Delta$ concentration immediately returned

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[206] F. Wilkinson, private communication.

[207] C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, 90, 6233 (1968).

[208] H. Akimoto and J. N. Pitts, *J. Chem. Phys.*, 53, 1312 (1970).

[209] C. Quannès and T. Wilson, *J. Amer. Chem. Soc.*, 90, 6527 (1968).

to the steady state dark value when the lamp was turned off. Because of the short lifetime of the excited singlet state of quinoxaline (probably less than 10^{-9} sec),[210] the quinoxaline quenching of $^1\Delta$ cannot be due to interaction of excited singlet state quinoxaline with $^1\Delta$ oxygen. The quenching must therefore involve the interaction of triplet state quinoxaline molecules and $^1\Delta$ which is present in concentrations as high as 10% in the flow discharge. An investigation of the variation of the $^1\Delta$ concentration with light intensity and with oxygen pressure also supports this interpretation. An analysis of the kinetic data indicates that the quenching mechanism is

$$^3\text{quinoxaline} + {}^1\Delta \xrightarrow{k} [\text{quinoxaline}\cdots O_2] \longrightarrow ?$$

and that the rate constant for this process must be on the order of 10^{11} sec^{-1}, which is very nearly the theoretical value for a collisionally controlled reaction.

Energetically, the product of the interaction of triplet quinoxaline and $^1\Delta$ could be a collision complex with quinoxaline in its *second* excited triplet state and oxygen in its ground triplet oxygen, or a charge transfer state ($Q^{+}\cdots O_2^{-}$). Transitions to both of these states are spin allowed and would be expected to be rapid for the same reasons that quenching of excited singlet state molecules by ground state is rapid.

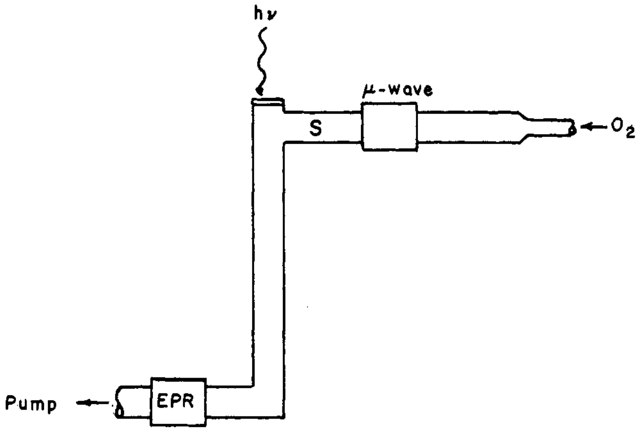

Figure 6. Schematic diagram of the experimental setup used to investigate the generation of $^1\Delta$ oxygen by energy transfer from triplet sensitizers, and by a microwave discharge.[120] The sensitizer, S, was introduced downstream from the microwave discharge.

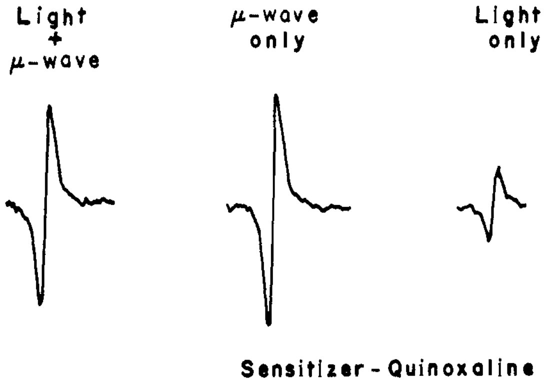

Figure 7. A comparison of the epr signals from $^1\Delta$ oxygen in experiments where $^1\Delta$ was generated either by a microwave discharge or by photosensitized energy transfer with that generated by both sources together.[120] For these experiments, only one of the four lines in the epr spectrum of $^1\Delta$ was monitored.

B. QUENCHING IN SOLUTION

Of all ground state diamagnetic molecules that have been studied so far, β-carotene is uniquely effective as a singlet oxygen quencher.[207,211,212] Foote and Denny[207] found that extremely low concentrations of β-carotene (order of 10^{-4} *M*) effectively quenched sensitized photooxygenation reactions as well as oxygenation reactions involving singlet oxygen generated by the decomposition of hydrogen peroxide, and from their data calculated that one β-carotene molecule could quench as many as 250–1000 singlet oxygen molecules. To account for this extraordinarily high quenching efficiency ($\beta = 10^{-4}$),[14] they proposed the following mechanism in which energy is transferred *from* singlet oxygen *to* the β-carotene generating triplet state β-carotene and ground state $^3\Sigma$ oxygen.[207]

$$^1O_2(^1\Delta) + {}^1\beta\text{-carotene} \longrightarrow {}^3O_2(^3\Sigma) + {}^3\beta\text{-carotene}$$

This process is essentially the reverse of the triplet-sensitized generation of singlet oxygen discussed in section III.A.2. Assuming that the β-carotene quenching is diffusion controlled (3×10^{10} M^{-1} sec^{-1}), the lifetime of $^1\Delta$ was estimated to be about 10^{-5} sec in solution.[212] This mechanism is feasible if, and only if, the triplet state of β-carotene lies below 22 kcal. The exact location of the triplet state of β-carotene is still unknown, but from the fact that β-carotene quenches the triplet state of chlorophyll (triplet state at 29 kcal),[213] naphthacene (E_T = 29 kcal),[214] and pentacene[215,112] ($E_T \cong$ 24 kcal)[88] at a diffusion-controlled rate[216] and from extrapolation of triplet state energies of other polyenes,[217,218] it may be inferred that the triplet of β-carotene lies well below 25 kcal. Additional support for this quenching mechanism is provided by the observation that other long-chain polyenes (with 9 or 11 double bonds in conjugation) are also efficient quenchers, whereas the shorter polyenes (seven, five, or fewer double bonds) which have higher energy triplet states are much poorer quenchers of singlet oxygen reactions.[212,219] Perhaps the most compelling evidence for the energy-transfer mechanism is provided by the observation that $^1\Delta$ generated from NaOCl-H_2O_2 induces the isomerization of 15,15′-*cis*-β-carotene to all *trans*-β-carotene and that approximately one β-carotene is isomerized for each singlet oxygen molecule quenched.[219] Since the cis → trans, but not the trans → cis, isomerization of β-carotene can be sensitized by triplet state

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(210) P. Loustauneau, G. Nouchi, and A. Rousset, *C. R. Acad. Sci.*, 257, 2928 (1963).

(211) S. Mazur and C. S. Foote, *J. Amer. Chem. Soc.*, **92**, 3225 (1970).

(212) C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters, *Ann. N. Y. Acad. Sci.*, **171**, 139 (1970).

(213) R. Becker and M. Kasha, *J. Amer. Chem. Soc.*, **77**, 3669 (1955).

(214) M. Chessin, R. Livingston, and T. G. Truscott, *Trans. Faraday Soc.*, **62**, 1519 (1966).

(215) A. Sykes and T. G. Truscott, unpublished results quoted in ref 112.

(216) E. Fujimori and R. Livingston, *Nature*, 180, 1036 (1957).

(217) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(218) R. E. Kellog, and W. T. Simpson, *J. Amer. Chem. Soc.*, **87**, 4230 (1965).

(219) C. S. Foote, Y. C. Chang, and R. Denny, *ibid.*, **92**, 5216, 5218 (1970).

sensitizers such as chlorophyll,[220] these observations strongly support the energy-transfer mechanism for the β-carotene quenching of $^1\Delta$.

Recently several authors[112,221] have questioned Foote's mechanism for the quenching of $^1\Delta$. Using pulsed radiolysis, Land, Sykes, and Truscott examined the decay of triplet state β-carotene in solution and found that *ground* state oxygen quenches triplet β-carotene at a rate which is comparable to the oxygen quenching of naphthalene triplets.[112] They suggest that these observations are difficult to reconcile with the Foote and Denny's[207] observation that β-carotene quenches $^1\Delta$. The apparent implication is that the triplet state of β-carotene must lie above $^1\Delta$ since it is rather efficiently quenched by ground state oxygen. As noted above there is good reason to believe that the triplet state of β-carotene lies below 22 kcal. The rapid oxygen quenching of β-carotene is undoubtedly due to oxygen-enhanced intersystem crossing in the β-carotene. Although such a process is slow (10^9 l. M^{-1} sec^{-1}) for molecules with high-energy triplet states the quenching is expected to be much faster with β-carotene because less electronic excitation must be converted into vibrational excitation of the products. Thus, the fact that ground state β-carotene efficiently quenches $^1\Delta$ is quite compatible with the fact that ground state oxygen rapidly quenches triplet state β-carotene.

Schenck and Schade[221] have suggested that the β-carotene quenching appears to be associated with the oxygenation of β-carotene. Although β-carotene can, under certain circumstances, react with $^1O_2$,[222] chemical reaction does not appear to be the major mechanism for quenching since a single β-carotene molecule is capable of quenching as many as 1000 $^1\Delta$ molecules.[207]

The observation that β-carotene quenches singlet oxygen molecules appears to have very important photobiological implications. Chlorophyll is one of the most effective sensitizers for the photooxygenation of organic substrates, and it has been recognized for some time that naturally occurring carotenoids protect photosynthetic organisms from the potentially lethal effects of their own chlorophyll. Foote's work clearly suggests that the mechanism of this protection involves the β-carotene quenching of singlet oxygen.[207] This possibility is further supported by their recent observations that the protective action of various naturally occurring polyenes closely parallel their ability of quench singlet oxygen.[219]

VI. Theoretical Studies of Singlet Oxygen Reactions

The successful use of orbital correlation diagrams to predict the course of concerted electrocyclic reactions involving ground state hydrocarbons[223] has stimulated attempts to extend these methods to the reactions of the singlet oxygen.[104,224–229] In one approach orbital and state correlation diagrams were used to examine the concerted addition of oxygen (ground triplet state or excited singlet state) to both olefins and dienes.[104,224–226] The second approach relies more on numerical computation of various reactivity indexes to account for the effect of substituents on the formation of endoperoxides of various aromatic hydrocarbons.[227–229]

Since it will be useful in our discussion of singlet oxygen reaction mechanisms, we first outline the correlation diagram approach to the addition of oxygen to dienes and olefins.

A. ADDITION TO DIENES

The construction of *state* correlation diagram for the concerted addition of oxygen to an acceptor begins with construction of an orbital correlation diagram for the reaction using well-known procedures.[223] The orbital correlation diagram for the concerted addition of oxygen to a conjugated diene is depicted in Figure 8a. Because of the degeneracy of the "antibonding" orbitals of O_2, care must be exercised in using the orbital correlation diagram to construct a state correlation diagram, without including the effects of electron–electron interaction. This problem has been examined in some detail,[225] and fortunately it is possible to enumerate a set of simple rules which make it possible to use *orbital* correlation diagrams to construct *state* correlation diagrams.

(1) The behavior of the ground state $^3\Sigma$ oxygen as it adds to the acceptor is obtained by calculating the total *orbital* energy for an electronic configuration in which one electron is placed in each of the two orbitals of the oxygen-acceptor complex which correlate with the two π^*_{OO} antibonding orbitals of free oxygen.

(2) The behavior of one of the $^1\Delta$ states of oxygen exactly parallels the behavior of the ground state, except that it is displaced by 22 kcal above the ground state.

(3) The second $^1\Delta$ state starts out degenerate with the first $^1\Delta$ state; however, when the degeneracy between the two π^*_{OO} orbitals is removed, this state behaves as if the outer two electrons of O_2 were transferred to whichever of the two π^*_{OO} orbitals is more stabilized (or least destabilized) during the course of reaction.

(4) The $^1\Sigma$ state behaves as if it had an electronic configuration in which the outer pair of electrons initially associated with the oxygen were placed in the *higher* energy of the two π^*_{OO} orbitals.

Using these qualitative rules along with spectroscopic and thermochemical data to obtain the relative energies of the ground and excited states of the reactants and products, it is a relatively simple matter to construct the *state* correlation diagram presented in Figure 8b. From the orbital and state correlation diagrams, several conclusions may be drawn. First of all, there is the strong prediction that ground state oxygen will not add in a concerted fashion to a diene, because this state of the oxygen–diene complex correlates endothermically with an excited triplet state of the product. One of the $^1\Delta$ states is, however, expected to react smoothly with the diene, since it is evident that the state of the complex formed by interaction of $^1\Delta$ and ground state diene correlates smoothly

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[220] L. Zechmeister, "Cis-trans-Isomeric Carotenoids, Vitamins A and Arylpolyenes," Academic Press, New York, N. Y., 1962, pp 46–57.

[221] G. O. Schenck and G. Schade, *Chimia*, 24, 13 (1970).

[222] S. Isoe, S. B. Hyeon, and T. Sakan, *Tetrahedron Lett.*, 279 (1969).

[223] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Academic Press, N. Y., 1970, and references contained therein.

[224] A. U. Khan and D. R. Kearns, *Advan. Chem. Ser.*, 77, 143 (1968).

[225] D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

[226] D. R. Kearns, W. Fenical, and P. Radlick, *Ann. N. Y. Acad. Sci.*, **171**, 32 (1970).

[227] O. Chalvet, R. Daudel, C. Ponce, and J. Rigaudy, *Int. J. Quantum Chem.*, **2**, 521 (1968).

[228] O. Chalvet and R. Daudel, *C. R. Acad. Sci.*, **265**, 301 (1967).

[229] O. Chalvet, R. Daudel, and G. H. Schmid, *Tetrahedron Lett.*, 26, 365 (1970).

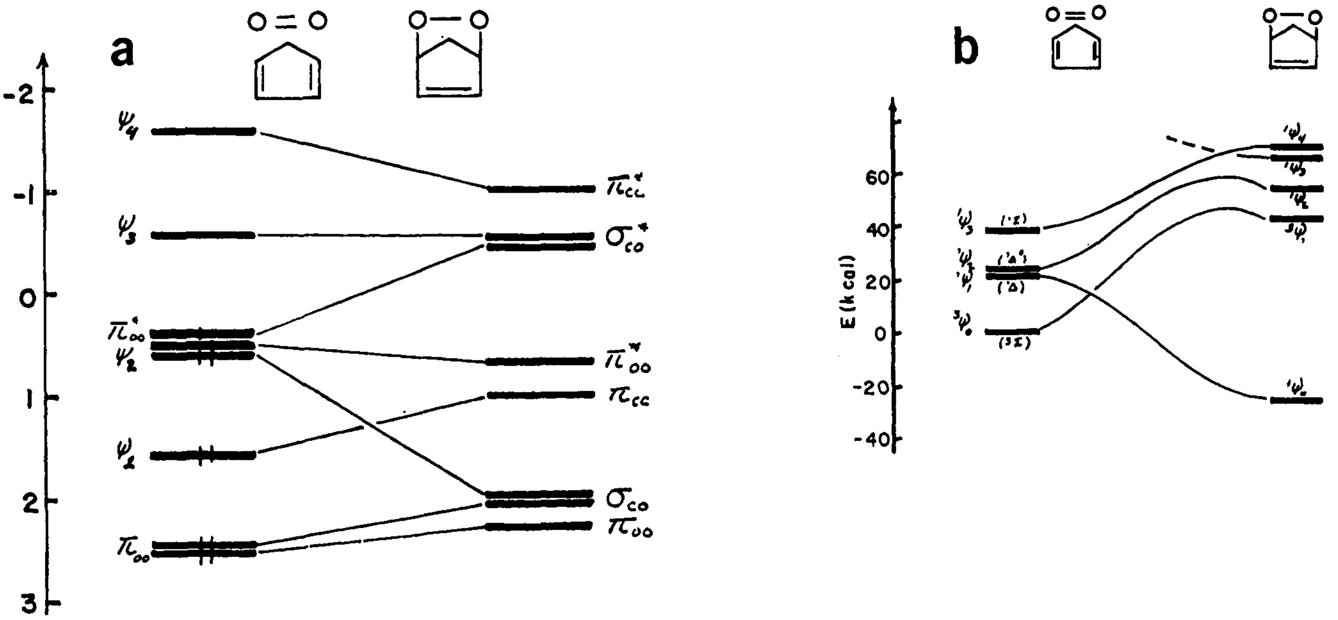
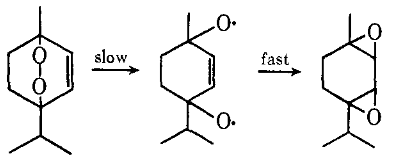


Figure 8. Orbital (a) and state (b) correlation diagrams for the concerted addition of molecular oxygen to cyclopentadiene. In the orbital correlation diagram (a), $\psi_1, \ldots, \psi_4$ are π molecular orbitals of cyclopentadiene. In the state correlation diagram (b), the states of molecular oxygen in the initial oxygen–diene complex are indicated in parentheses.

and exothermically with the product *ground* state. $^1\Sigma$ is not expected to react because it forms a state which correlates with an excited state of the product.

This same state correlation diagram may also be used to discuss the thermal decomposition of endoperoxides.[224,225] Because of the weakness of the O–O bond in the endoperoxide (clearly expected on the basis of the orbital diagram which places a pair of electrons in an antibonding π^*_{OO} orbital) cleavage of the O–O bond is generally expected and found to be the favored pathway for thermal decomposition of many endoperoxides. The decomposition of ascaridole, for example, proceeds by this mechanism.[230]



In the specific case of aromatic hydrocarbon endoperoxides resonance energies can play a very important role in determining the pathway for decomposition. For a related series of endoperoxides the ΔH for the rupture of the O–O bond remains roughly constant at about 30–35 kcal, but the gain in resonance energy accompanying loss of molecular oxygen and regeneration of the parent hydrocarbon can vary considerably. If this resonance energy gain is large enough, then the overall ΔH for loss of molecular oxygen may become lower than for rupture of the O–O bond, and the state correlation diagram indicates that oxygen could be released as $^1\Delta$.[104,224] The observation by Wasserman and Scheffer[152] that the oxygen released from the thermal decomposition of 9,10-diphenylanthracene peroxide exhibits singlet-oxygen type reactivity supports these theoretical expectations. Luminescence often accompanies the thermal decomposition of endoperoxides, and this too suggests that the oxygen may have been released as singlet oxygen.[142]

The magnitude of the resonance energy is apparently an important factor in determining whether or not an aromatic hydrocarbon will form an endoperoxide in the first place. Phenanthrene, for example, would lose about 40 kcal in resonance energy if it formed a peroxide, and experimentally it does not appear to react with singlet oxygen at room temperature.[225] Conceivably, it might be possible to trap the phenanthrene peroxide at low temperatures. Anthracene, on the other hand, reacts rapidly with singlet oxygen, but in this case the loss of resonance energy is only about 28 kcal.

The state correlation diagrams can also be used to make predictions about the photochemical properties of various endoperoxides.[104,224,225] While the experimental studies of the photochemical properties of the photoperoxides are scarce, interesting variations in product distribution with the wavelength of excitation have been observed.[231] Studies of the photochemical properties of the photoperoxides would appear to be an interesting area for further study.

B. ADDITION TO OLEFINS

In Figures 9 and 10 three different modes for the concerted addition of oxygen to an olefin are depicted. In the first mode of addition (C_s transition state), a three-membered ring compound, a peroxirane, is formed. As in all concerted additions, reaction with triplet state oxygen is expected to be unfavorable because it attempts to form an excited state of the product. The doubly occupied bonding π_{CC} orbital of the reacting olefin is involved in a reasonably favorable correlation with a partially bonding orbital of the product, and the state correlation diagram indicates that the addition of $^1\Delta$ to form the peroxirane is probably smooth and exothermic.[226]

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(230) J. Boche and O. Runquist, *J. Org. Chem.*, 33, 4285 (1968).

(231) See, for example, J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, Chapter 5.

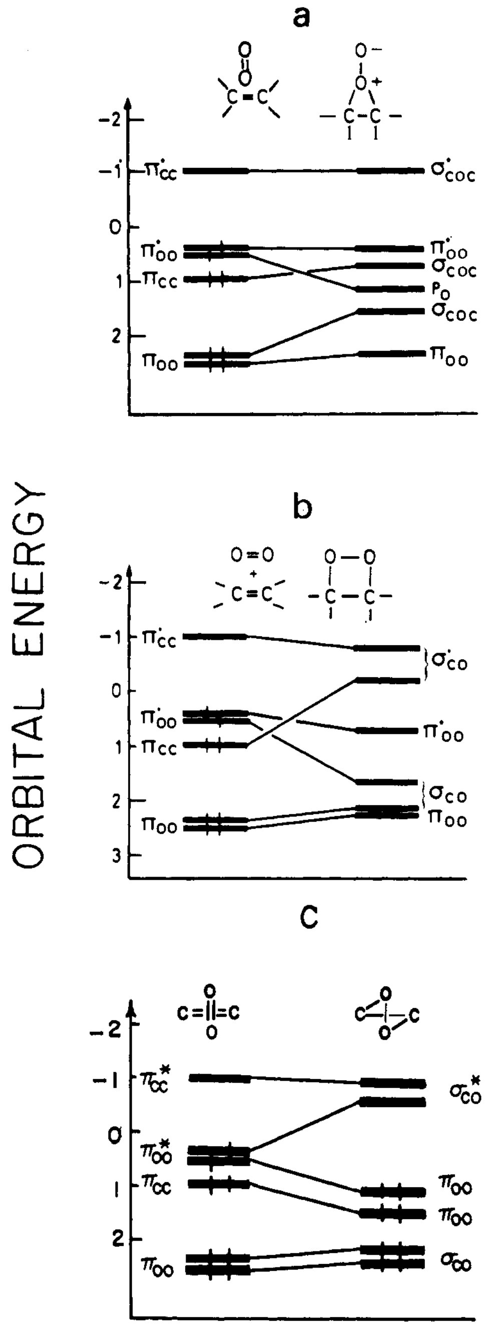

Figure 9. Orbital correlation diagrams for the concerted addition of molecular oxygen to an olefin. Three different modes of addition are depicted with transition states which are assumed to have C_s (a), C_{2v} (b), and C_2 (c) symmetries, respectively.

In the second mode of addition, a four-membered ring compound, a dioxetane, is formed.[232] If the transition state is assumed to have C_{2v} symmetry, then this is essentially a $[_\pi 2_s + _\pi 2_s]$ addition,[223] and the orbital and state correlation diagrams shown in Figures 9b and 10b, respectively, are obtained. Addition of triplet state oxygen is again forbidden, and the state correlation diagram indicates that there may even be a barrier for the addition of $^1\Delta$. Examination of the orbital correlation diagram indicates that this barrier arises from the unfavorable behavior of the π_{CC} orbital of the reacting olefin. The height of the barrier depends upon the relative energies of the π^*_{OO} and π_{CC} orbitals and therefore upon the π ionization potential of the olefin.[104,224,225] With electron-rich olefins which have particularly low π ionization potentials, it is possible that the ordering of the π_{CC} and π^*_{OO} orbitals could be inverted from that shown in Figure 9b, in which case addition of $^1\Delta$ to form a dioxetane might become allowed. Should such a reaction take place, the transition state would be very polar owing to transfer of electrons from the π_{CC} to the π^*_{OO} orbital in the transition state.

A dioxetane could also be formed through a transition state with C_2 symmetry. This is essentially a $[_\pi 2_a + _\pi 2_s]$ addition and, in contrast to the C_{2v} symmetry case, this mode of addition appears to have the characteristics of an allowed reaction insofar as addition of $^1\Delta$ is concerned.[233] Since singlet oxygen is an electrophilic species, one would again expect the electron-rich olefins to be more reactive if this were the mode of addition. At present we have no method for distinguishing between a $[_\pi 2_s + _\pi 2_s]$ and a $[_\pi 2_a + _\pi 2_s]$ addition of oxygen to olefins.

If we accept these results literally, it would appear that peroxirane formation will generally be favored over dioxetane formation, although in special cases dioxetane formation may also occur. Both dioxetanes and peroxiranes would be expected to be rather unstable intermediates, and, depending upon nature of substituents, they could easily rearrange to form more stable products. In the case of dioxetanes, cleavage to carbonyl fragments is to be expected and found to be a major pathway for decomposition.[232] Peroxiranes, on the other hand, might undergo an intramolecular rearrangement to an allylic hydroperoxide, as suggested by Sharp.[234] It is also possible that dioxetanes and peroxiranes might be interconvertible, in which case it might be difficult to find out which of the two is actually first formed. Because of the lack of symmetry it unfortunately is not possible to simply construct orbital and state correlation diagrams for this interconversion, and the results of more detailed CNDO/2 calculations were inconclusive.[226]

It is interesting to note that the involvement of dioxetanes and peroxiranes as intermediates in singlet oxygen reactions with olefins was considered some time ago and that both possibilities were rejected in favor of the so-called "ene" mechanism.[235] Within the past 2 years, however, new experimental evidence for the involvement of these intermediates in singlet oxygen reactions has been obtained. Through the use of low-temperature photolysis, dioxetanes have now been isolated in good yields from the reaction of singlet oxygen with several different substituted olefins.[194,233] The involvement of peroxiranes in singlet oxygen reactions is still a subject for active investigation, so that some of the other predictions will have to await final confirmation.[226,236]

C. CORRELATION OF $^1O_2$ REACTIONS AND REACTIVITY INDEXES

Chalvet, *et al.*,[227-229] have examined the reactivity of singlet

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(232) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, 47, 709 (1969).

(233) P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, 92, 3223 (1970).

(234) D. B. Sharp, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, Abstract 79P.

(235) See, for example, papers in "Oxidation of Organic Compounds—III," Advances in Chemistry Series, No. 77, American Chemical Society, Washington, D. C., 1968.

(236) W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, 91, 7771 (1969).

oxygen toward aromatic hydrocarbons using a somewhat different approach. In their initial work three different mechanisms for the addition of singlet oxygen to substituted aromatic hydrocarbons were considered in which (1) oxygen forms an intermediate complex which leads to a reduction in the extent of delocalization of the π system; (2) oxygen acts as an electrophilic agent and the electronic structure of the intermediate complex is similar to that of the initial molecules; (3) oxygen forms an intermediate complex which extends the size of the delocalized π system. If the π systems were reduced in the formation of intermediate complex, then the relative reactivity of different compounds should correlate with paralocalization energies. According to this assumption the presence of 1,4-dimethoxy substituents on anthracene should decrease the possibility of reaction at the 1 and 4 positions, whereas experimentally the opposite is true. If oxygen reacts primarily as an electrophilic agent without substantially altering the π electronic system of the acceptor in the transition state, then there should be a correlation between reactivity and charge density. Again, calculations indicate that in 1,4-dimethoxyanthracene the 9,10 positions are more negative than the 1,4 positions, and hence reaction should take place at the 9,10 positions rather than at the 1,4 positions. Again, this is opposite to experimental observations. If it is assumed that the π system is more delocalized in the transition state, then a good correlation between the delocalization energy and position of reaction is expected. The fact that such a correlation exists strongly implies that the ability of the oxygen to form a π complex with the acceptor is important in controlling the relative reactivity of different acceptors, and positions of reaction within a given acceptor. The orbital correlation diagrams which we discussed earlier provide additional insight into the nature of these addition reactions and complement the numerical computations which do not distinguish between the different types of singlet oxygen.

With this discussion of the theoretical aspects of the different types of concerted addition reactions that singlet oxygen might undergo and the factors which influence each mode of reactivity, we now turn to an examination of the experimental data on singlet oxygen reactions and reaction mechanisms.

VII. Experimental Studies of Singlet Oxygen Reactions

A. EVIDENCE FOR SINGLET OXYGEN INTERMEDIATES

During the past 5 years a compelling case has been made for identifying singlet oxygen molecules as the reactive intermediates in dye-sensitized photooxygenation reactions.[10-19,237] The bulk of the evidence rests largely on demonstrating that reagents which are known to produce singlet oxygen (microwave discharge, decomposition of H_2O_2) are able to effect the same reactions as the dye-sensitized photooxygenation reactions.[12-19,237] These comparisons show that not only are the products of these oxygenation reactions the same for a given acceptor, but that the relative rates of oxygenation of different acceptors are the same regardless of how the singlet oxygen is generated. Some of these comparisons, which are shown in Table V, provide convincing evidence that free singlet oxygen molecules are indeed the reactive intermediate in many dye-sensitized photooxygenation reactions. So far no evidence for the existence of a Schenck-type moloxide[95] has been found, and the possibility that free radical intermediates are involved has been specifically eliminated in a number of cases.[13,15] It should not be concluded, however, that all dye-sensitized photooxygenation reactions necessarily involve singlet oxygen. In fact, it is clear that there are many dye-sensitized photooxidation reactions which do not involve singlet oxygen as a reactive intermediate.[238] Therefore, to be confident that a particular dye-sensitized photooxygenation reaction is actually a singlet oxygen reaction, a number of tests should be applied. If possible this should include a comparison of the dye-sensitized oxygenation with chemical oxygenation using the hydrogen peroxide system, and a gas-phase oxygenation using singlet oxygen generated by a microwave discharge, or by photosensitizers such as quinoxaline[117] or hexafluoronaphthalene.[118] Competitive oxygenation experiments using a well-studied acceptor and several different oxygenation techniques would also be useful. Quenching experiments using molecules such as β-carotene and amines, which are specific quenchers of singlet oxygen, and an examination of the effect of radical scavengers should be carried out.

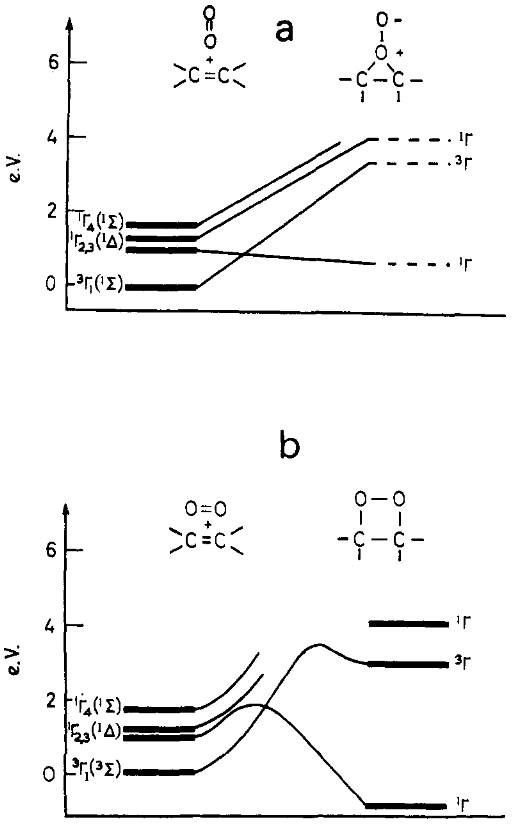

Figure 10. State correlation diagram depicting the concerted addition of oxygen to an olefin leading to the formation of a peroxirane (a) or a dioxetane (b). The relative energies of various states of the reactants and products are estimated from spectroscopic and thermochemical data. The curves connecting various states of the reactants and products are deduced from information contained in the orbital correlation diagrams.

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(237) C. S. Foote, *Pure Appl. Chem.*, in press.

(238) L. I. Grossweiner in "Physical Processes in Radiation Biology," Academic Press, 1964, p 287.

Table V

Relative Reactivity of Olefins toward Various Reagents[a]

Olefin	*Photooxidation*	*H_2O_2/OCl^-*	*Peracetic acid*	*Deactivation of $^1\Delta$, l. M^{-1} $sec^{-1} \times 10^{-4}$*	*Trifluoromethyl radical*
Alkylethylene	0.1		0.032		1.4
2-Methylpropene	1.7		0.71		3.8
cis-2-Butene			0.71	2.5	1.3
trans-4-Methyl-2-pentene	2.5	0.4			
2-Hexene	9		0.76	67	
Cyclohexene	1	2.4	1		
Cyclopentene	16		1.51		
1-Methylcyclohexene	45	56		1	
2-Methyl-2-butene	~1000	280	9.61	23	
1-Methylcyclopentene	390	300	17.2	40	
1,2-Dimethylcyclohexene	2900				
2,3-Dimethyl-2-butene	5500	10,000	3000	95	1.2

[a] Data taken from ref 14, 173, and 261.

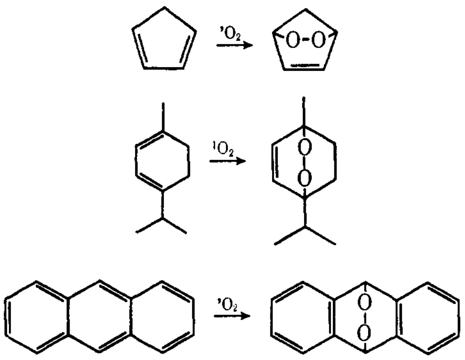
If all of these tests are positive, then one could be confident in concluding that the reaction is a singlet oxygen reaction. Unfortunately, photooxygenation reactions are beginning to appear in the literature which are claimed to be singlet oxygen reactions without supporting data of this kind. This may be dangerous in the case of unreactive acceptors and with heterocyclic acceptors.

In most cases it would appear that $^1\Delta$ rather than $^1\Sigma$ is the reacting species. This is to be expected on the basis of the physical quenching studies discussed earlier which show that $^1\Sigma$ is readily collisionally deactivated, whereas $^1\Delta$ is relatively immune to collisional quenching.[197–199] Therefore, simply on the basis of lifetimes, $^1\Sigma$ is not expected to survive long enough to react in a condensed phase (lifetime estimated to be on the order of 10^{-10} sec). Additional experimental evidence against the involvement of $^1\Sigma$ has been provided by Gollnick's study.[14] He used a wide range of photosensitizers to effect singlet oxygen reactions with acceptors which formed more than one type of oxygenation product and in this way hoped to see whether or not there was a change in product distribution when sensitizers of varying triplet energy were used. For a given acceptor, he found that there was no variation in product distribution regardless of whether the triplet state energy of the sensitizer was above or below the minimum energy required to produce $^1\Sigma$ (see Figure 4). He concluded that there was no evidence for the involvement of $^1\Sigma$ oxygen. Another reason for believing that $^1\Sigma$ is not involved in most photooxygenation reactions is that it cannot, for theoretical reasons, enter into a concerted addition reaction, and yet most singlet oxygen reactions do appear to be concerted.[104,224,225]

Since much of the early experimental work on the chemistry of singlet oxygen has already been summarized in recent review articles,[10–15,18,237] the discussion in this section will be devoted to a reexamination of the three major types of singlet oxygen reactions with respect to reaction mechanism and their relation to the theoretical studies discussed in section VI.

B. REACTION WITH DIENES AND AROMATIC HYDROCARBONS

With acceptors such as cis dienes or aromatic hydrocarbons singlet oxygen appears to behave as a good dienophile as some of the following examples depict. The similarity between



these reactions and the more familiar Diels–Alder reactions is obvious, and, in fact, the parallels between the two are quite good.[11–13,15,239–243] In general, those molecules which are more reactive in Diels–Alder reactions are also more reactive toward singlet oxygen. Thus, while anthracene reacts well, both with singlet oxygen and other good dienophiles, naphthalene appears to be unreactive toward singlet oxygen and all but the most potent dienophiles.[11,15] Not unexpectedly, the parallel even extends to a theoretical comparison between singlet oxygen addition to dienes and the thermal Diels–Alder reactions.[225] Proof that the cyclic peroxide products are in fact the result of the addition of singlet molecular oxygen was first obtained by Corey and Taylor[8] who showed that $^1\Delta$ produced by an rf discharge reacts with anthracenes to produce the same peroxides that are observed from sensitized photooxygenation experiments. Foote and Wexler[7] used singlet oxygen from the decomposition of hydrogen peroxide to react with 1,3-cyclohexadiene and 2,5-dimethylfuran to obtain the same products previously found in the photooxygenation reactions. On the basis of these and subsequent experiments, there can be no doubt that the reactive intermediate in these reactions is singlet oxygen.

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(239) Yu. A. Arbuzov, *Russ. Chem. Rev.*, 34, 8, 558 (1965).

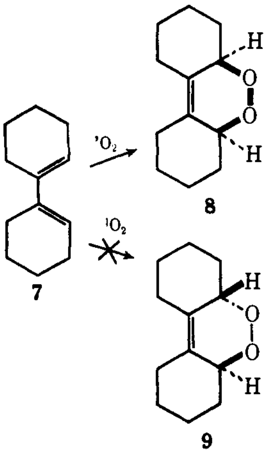
(240) E. J. Bowen, *Discuss. Faraday Soc.*, **14**, 143 (1953).

(241) E. J. Bowen and D. E. Tanner, *Trans. Faraday Soc.*, **51**, 475 (1955).

(242) N. Sugiyama, M. Iwata, M. Yoshioka, K. Yamada, and H. Aoyama, *Chem. Commun.*, 1563 (1968).

(243) N. Sugiyama, M. Iwata, M. Yoshioka, K. Yamada, and H. Aoyama, *Bull. Chem. Soc. Jap.*, **42**, 1377 (1969).

The concerted character of the addition reaction is indicated by examination of the addition reaction of oxygen to the cisoid conformation of 1,1′-bicyclohexenyl (7). The reaction leads exclusively to the cis peroxide **8** as the only product. The trans product could be formed in a nonconcerted two-step reaction involving formation of an intermediate diradical, but this is ruled out experimentally.[244] To account for these

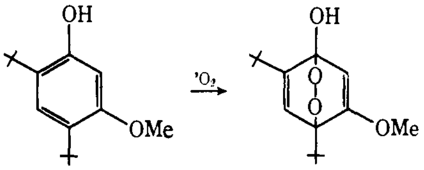


and other experimental observations, it is suggested that the addition of singlet oxygen proceeds through a six-membered ring transition state, analogous to the Diels–Alder reaction.[14,15]

Koch[245] has carried out a systematic investigation of the effect of temperature on the rate of reaction of singlet oxygen with a variety of acceptors including a number of dienes. In general, the activation energies are reasonably small, ranging from essentially 0 for some of the more reactive dienes to about 6 kcal/mol for relatively inert dienes.

The concerted character and low activation energy for the addition of singlet oxygen to dienes are in accord with the theoretical results which indicated that the concerted addition of $^1\Delta$ to dienes and to certain aromatic hydrocarbons is an allowed reaction. The recent observations that substituted naphthalenes and 1,4-disubstituted anthracenes may also react with singlet oxygen to form endoperoxides is also in accord with theoretical expectations.[227,229]

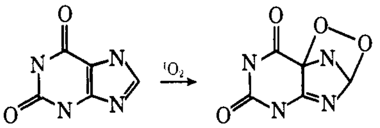
Finally, we note that there is a recent preliminary report in which it is suggested that singlet oxygen may even undergo a concerted addition reaction with substituted benzenes as indicated below.[246]



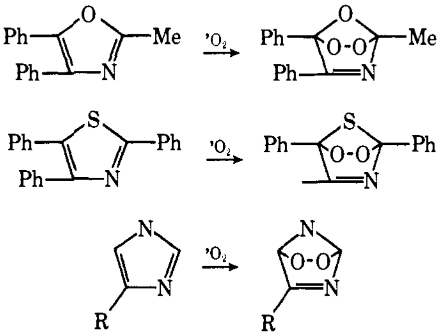
Confirmation of this suggestion will have to wait upon proof of the structure of the product and additional evidence that the reaction involves singlet oxygen.

In contrast to other modes of reactivity, the addition of singlet oxygen to aromatic hydrocarbons appears to be a uniquely characteristic reaction, and therefore this reaction should be useful as a diagnostic test for the presence of singlet oxygen.

The photooxygenation of various purine derivatives is also presumed to be analogous to the addition of singlet oxygen to dienes, and a number of examples of this type of reactivity have been presented.[247,248]



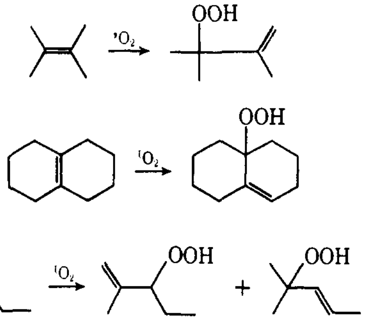
It has been suggested that cyclic peroxides are intermediates in the photosensitized oxygenation of certain five-membered heteroaromatics such as pyrroles,[249] oxazoles,[250,251] thiazoles,[252] imidazoles,[253] isobenzothiophenes,[254] and thiophenes.[255] Recently, this list has been extended to include



silicon heteroaromatics.[256]

C. REACTION WITH OLEFINS. FORMATION OF ALLYLIC HYDROPEROXIDES

The second and perhaps most thoroughly studied type of singlet oxygen reaction is the "ene" reaction in which oxygen adds to olefins to form allylic hydroperoxides.[95] Some examples of this mode of reaction are summarized below, and many



other examples are discussed in detail in earlier review articles on singlet oxygen chemistry.[9,12–15] Until a few years ago

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(244) K. H. Schulte-Elte, Dissertation, University Gottingen, 1961; cited by K. Gollnick and G. O. Schenck, ref 11.

(245) E. Koch, *Tetrahedron Lett.*, 24, 6295 (1968).

(246) I. Saito, S. Kato, and T. Matsuura, *ibid.*, 239 (1970).

(247) T. Matsuura and I. Saito, *Chem. Commun.*, 1247 (1967).

(248) T. Matsuura and I. Saito, *Tetrahedron Lett.*, 24, 6609 (1968).

(249) P. de Mayo and S. T. Reid, *Chem. Ind. (London)*, 1576 (1962).

(250) H. W. Kurtz and H. Schecter, *Chem. Commun.*, 689 (1966).

(251) H. H. Wasserman and M. B. Floyd, *Tetrahedron Suppl.*, No. 7, 441 (1966).

(252) T. Matsuura and I. Saito, *Bull. Chem. Soc. Jap.*, 42, 2973 (1969).

(253) H. H. Wasserman, K. Stiller, and M. B. Floyd, *Tetrahedron Lett.*, 3277 (1968).

(254) C. Dufraisse and S. Ecary, *C. R. Acad. Sci.*, 223, 735 (1946).

(255) H. H. Wasserman and W. Strehlow, *Tetrahedron Lett.*, 7951 (1970).

(256) T. Sato, I. Moritani, and M. Matsuyama, *ibid.*, 5113 (1969).

the mechanism for this reaction appeared to be reasonably well established.[12-15] Recently, however, there are new experimental observations which suggest that the mechanism currently accepted by many workers in the field may not be the correct one.[226,236] We shall therefore devote this section to a reexamination of the mechanism by which singlet oxygen reacts with olefins to form allylic hydroperoxides.

The salient experimental observations which must be accounted for by any mechanism are summarized below.

(1) The oxygen is always introduced on the same face of the molecule from which the hydrogen is removed and the double bond always shifts.[10,12-15,257]

(2) The reactions cannot be quenched by addition of radical traps, and this includes both the photooxygenation experiments and chemical (H_2O_2) reactions.[257]

(3) With substituted olefins, the ratio of secondary to tertiary hydroperoxides is about 1 : 1.[10,12-15,258]

(4) Substituent groups which hinder the double bond prevent attack of singlet oxygen.[259]

(5) When optically active olefins are oxidized, there is no loss of optical activity.[257,260] Furthermore, comparison of the photooxygenation of cis-trans olefin pairs reveals that no cis-trans isomerization is induced during the oxygenation reaction.[258]

(6) The reactivity of a related series of olefins is enhanced by alkyl substitution (factor of ~10 per CH_3 group).[261]

(7) For most olefins there is very little solvent effect on either product distribution or on rate of reaction with singlet oxygen.[10,12-15]

(8) Isotope effect studies to date are rather inconclusive; however, they appear to be small.[237,258]

(9) In the photooxygenation of substituted trimethylstyrenes, the product distribution is essentially unaffected by the nature of the substituent in the meta or para positions of the benzene ring.[13]

(10) Norbornene is unreactive toward singlet oxygen, whereas other olefins such as cyclohexene are reactive.[258]

(11) The dioxetane of tetramethylethylene is relatively stable at room temperature, but at higher temperatures decays exclusively to carbonyl products, not allylic hydroperoxides.[232,262]

(12) There is an excellent correlation between the relative rates of reaction of olefins with peracids and with singlet oxygen.[261]

(13) There is a very poor correlation between the rates of reaction of substituted olefins with free radicals and with singlet oxygen.[261] Relative reactivities toward singlet oxygen span a factor of 10^4 whereas reactivity toward the trifluoromethyl radicals varies by only a factor of 2.

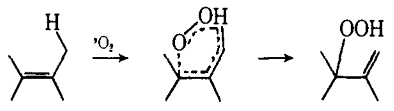
(14) The addition of NaN_3 to oxygenation systems (both chemical and dye photosensitized) causes a reduction in the normal oxygenation products and the appearance of *trans*-azido hydroperoxides in their place.[226,236]

In order to account for the products which are observed in "ene"-type singlet oxygen reactions a variety of mechanisms, each one involving a different intermediate or transition state, have been proposed and these are summarized in Chart I. We now want to reexamine each of these mechanisms in light of the 14 different experimental observations noted above. Most of the arguments previously used to rule out certain of the mechanisms are of course still valid. Some of the new experimental observations require revision of several earlier conclusions.

Chart I

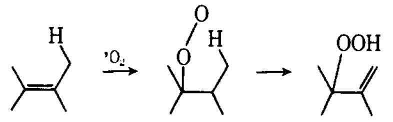
Possible Mechanisms for the Concerted Addition of Singlet Oxygen to Olefins

"Ene" Mechanism



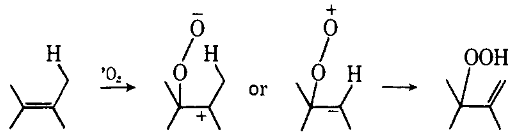
10

Radical Intermediate



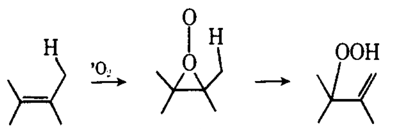
11

Ionic Intermediates



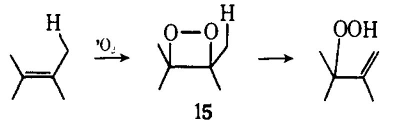
12 13

Peroxirane Intermediate



14

Dioxetane Intermediate



15

1. The "Ene" Mechanism

The one mechanism which currently seems to be favored by most authors[10,12-15,263,264] is a concerted addition of oxygen to the olefin exactly analogous to the mechanism proposed for the "ene" reaction. The transition state for this reaction is sketched below.

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(257) C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Lett.*, 4111 (1965).

(258) F. A. Litt and A. Nickon in ref 235, pp 118–132.

(259) K. Gollnick, S. Schroeter, G. Ohloff, G. Schade, and G. O. Schenck, *Justus Liebigs Ann. Chem.*, **687**, 14 (1965).

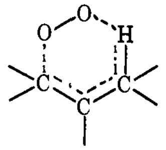
(260) G. O. Schenck, K. Gollnick, G. Buchwald, S. Schroeter, and G. Ohloff, *ibid.*, **674**, 93 (1964).

(261) K. R. Kopecky and H. H. Reich, *Can. J. Chem.*, **43**, 2265 (1965).

(262) K. R. Kopecky, J. H. Van de Sande, and C. Mumford, *Can. J. Chem.*, **46**, 25 (1968).

(263) A. Nickon and W. L. Mendelson, *J. Amer. Chem. Soc.*, **87**, 3921 (1965).

(264) A. Nickon and J. F. Bagli, *ibid.*, **83**, 1498 (1961).



10

This mechanism is attractive since it accounts for the stereochemistry of the reaction, the absence of any evidence for radical intermediates, and the lack of solvent and substituent effects, and is consistent with the secondary-tertiary hydroperoxide product ratios and the effect of alkyl group substituents. The nonreactivity of norbornene is, of course, required by the ene mechanism.[234] It is not obvious, however, that the excellent correlation between rates of peracid oxidation and photooxidation follows straightforwardly from the ene mechanism.[261]

The azide quenching studies are definitely not consistent with the "ene" mechanism.[226,236] Since this mechanism does not involve a real chemical intermediate, as do some of the other mechanisms, it is difficult to see why azide should quench the normal products of a single oxygen reaction and lead to the formation azidohydroperoxides instead. While it is possible that azide radicals could be formed in a dye-sensitized photoprocess, no photoreaction is possible in the chemical oxygenation systems. Furthermore, the azidohydroperoxides which are formed in the azide trapping studies have a trans stereochemistry, whereas both *cis*- and *trans*-azidohydroperoxides would be expected from the addition of an azide radical to an olefin.[236] We conclude, therefore, that the azide trapping studies provide strong evidence against the "ene" mechanism, and suggest that quenching studies with other nucleophilic reagents would be useful.

2. *Radical Intermediates*

Of all the mechanisms which have been proposed, it would appear that the experimental evidence is perhaps strongest in ruling out mechanisms which involve radical intermediates. These observations include the fact that radical traps do not quench singlet oxygen reactions, the reaction is in fact concerted, there are no Markovnikov-type directing effects, and there is no correlation between relative rates of photooxygenation and rates of reaction with radicals.[261]

3. *Ionic Intermediates*

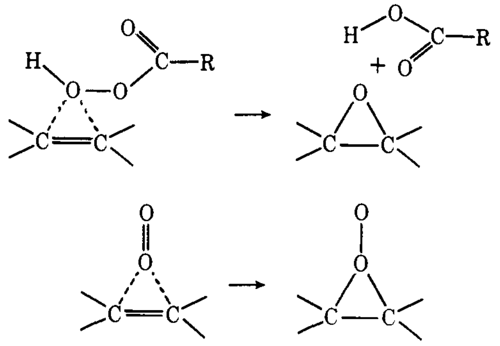
The involvement of ionic intermediates such as **12** and **13** in singlet oxygen reactions can generally be ruled out since one would expect to find significant solvent effects on the rates of reaction. Experimentally, the solvent effects are small and the variations do not correlate at all with the polarity of solvent.[12–15] The lack of substituent effects in the oxygenation of substituted stilbenes provides additional strong evidence against the participation of ionic intermediates.[13]

4. *Dioxetane Intermediates*

Although we[236,265] and others[194,207,233] have recently shown that dioxetanes are formed in the reaction of singlet oxygen with certain olefins, it is quite clear that dioxetanes are not intermediates in the formation of allylic hydroperoxides. The evidence on this point comes from Kopecky's[232,262] observation that the dioxetane of tetramethylethylene thermally decomposes to yield only acetone, but no allylic hydroperoxide. With the exception of this sole observation, virtually all of the observations on the reaction of singlet oxygen with olefins could be accommodated by a mechanism involving rearrangement of a dioxetane intermediate as indicated in Chart I.

5. *Peroxirane Intermediates*

The mechanism which still appears to be consistent with all the experimental observations listed above is one involving a peroxirane or perepoxide intermediate. The excellent correlation between rates of peracid oxidation of olefins and their rates of reaction with singlet oxygen is to be anticipated in terms of the similarities of the two mechanisms, as illustrated below.[234] It was, in fact, this correlation which Kopecky and Reich first used to support the involvement of peroxirane in singlet oxygen reactions.[261] Other experimental observations such as the lack of substituent effects,[264] the evidence for a concerted mechanism, the stereochemistry, and the absence of Markovnikov directing effects[12–15] are all consistent with this mechanism. The nonreactivity of norbornene can be accounted for in terms of the lack of any abstractable allylic hydrogens and presumed instability of a peroxirane intermediate with respect to regeneration of parent hydrocarbon and oxygen. While it had been argued that the lack of solvent and substituent effects rule out the involvement of peroxirane intermediates, these arguments are based on the assumption that the transition state for this reaction is highly polar and that different peroxirane intermediates of the same acceptor are not interconvertible.[258] Contrary to the structure usually drawn, [14,258] we find by CNDO/2 calculations[70,226] that the oxygen atoms of the peroxirane bear relatively little charge (~0.4 e), and therefore the transition state would be even less polar than the peroxirane itself. Solvent effects obviously cannot be used to rigorously rule out this mode of reactivity. Studies of the effect of sodium azide appear to provide strong support for the involvement of a peroxirane intermediate in the reaction of singlet oxygen with olefins.[226,236] With tetramethylethylene, for example, the normal product from reaction with singlet oxygen is the allylic hydroperoxide **3** indicated below.



In the presence of sodium azide, however, only 3% of the normal product is obtained; 97% of the mixture consists of the azidohydroperoxide **16**. When a chemical oxygenation of TME was carried out in the presence of 1 M N_3^-, approximately half of the oxygenation product consisted of the azide **16**. (The failure of the azide to completely quench the normal course of this latter reaction is probably due to the hetero-

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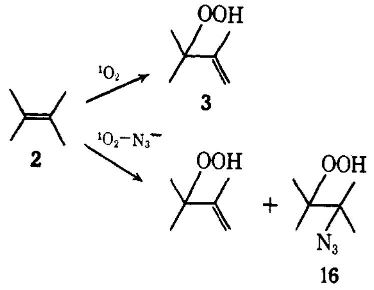
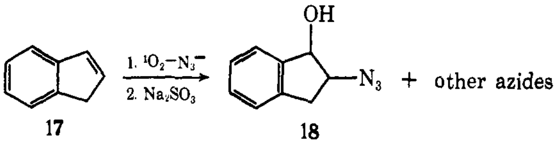
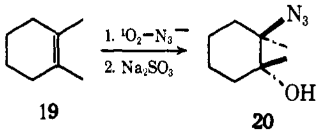
[265] W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 3396 (1969).

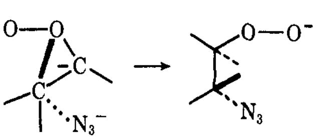


geneous character of the reaction conditions.) Control experiments demonstrate that the azide incorporation products are not due to attack of N_3^- on the normal oxygenation products, and photoreactions of the azide ion are also discounted since TME was completely inert when the photolysis was conducted under anaerobic conditions. Azide also diverts the normal course of photooxygenation of other olefins as the examples listed below indicate.[226,236]





The azide incorporation studies demonstrate that trappable chemical intermediates are present in the reaction of singlet oxygen with olefins. The nature of the azide incorporation products which are formed and their stereochemistry are consistent with formation of an intermediate peroxirane which is trapped by nucleophilic attack of N_3^- according to the scheme

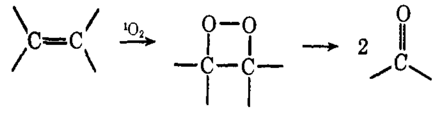


Dioxetanes might also react with azide to give the same products but their involvement in the formation of the allylic hydroperoxides is ruled out by Kopecky's[232,262] observations on the decomposition of the dioxetane of TME. The weight of experimental evidence strongly points to the involvement of peroxiranes in the reaction of singlet oxygen with olefins to form allylic hydroperoxides. It should be emphasized, however, that the azide trapping studies appear to be the only ones which permit the ene mechanism to be distinguished from all other mechanisms which involve intermediates such as dioxetanes or peroxiranes. Consequently, effort should be made to determine whether or not azide ions are functioning in the simple manner indicated by experiments to date. In particular, some effort should be made to demonstrate that azide ions do not react directly with singlet oxygen or the excited dye molecules.

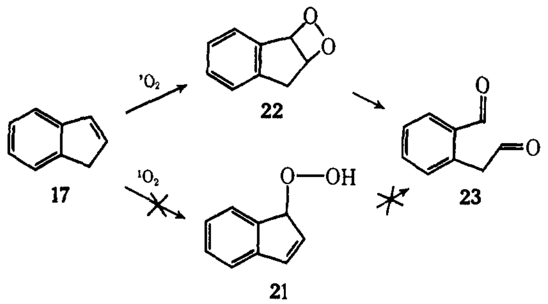
In closing this section we should point out that the theoretical considerations discussed in section VI indicated that the addition of singlet oxygen to olefins to form peroxiranes is an allowed reaction. Unfortunately, the simple theory did not permit us to examine the "ene" mechanism, so that we cannot compare these two modes of reactivity theoretically.

D. REACTION WITH OLEFINS. DIOXETANE FORMATION

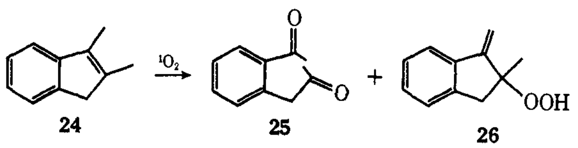
A third mode of reaction exhibited by singlet oxygen with olefins is 1,2 cycloaddition to form relatively unstable dioxetanes which may cleave to yield carbonyl fragments.



Although this possibility was suggested some years ago,[13] most of the literature examples of this mode of reactivity were neglected for several reasons. First of all, before 1968 no dioxetane had ever been isolated.[266] Secondly, it was assumed that the carbonyl fragments which frequently appeared in photooxygenation reactions arose from secondary reactions of initially formed unstable allylic hydroperoxides,[15] rather than cleavage of an intermediate dioxetane. The situation was significantly changed in 1968 when the first successful preparation of a stable dioxetane was reported.[232,262] During that same year, Foote and Lin[267] suggested a dioxetane as one of three possible intermediates in the reaction of singlet oxygen with enamines. Huber[268] also proposed that a dioxetane intermediate might be involved in the reaction of singlet oxygen with enamines. The general significance of dioxetane as intermediate in singlet oxygen reactions with electron-rich olefins became clear when it was shown that a dialdehyde (**23**), the sole product from the sensitized photooxygenation of indene (**17**), does not arise from rearrangement of an unstable allylic hydroperoxide (**21**).[265]



Additional evidence against the earlier suggestion that the carbonyl products were simply rearrangement products of initially formed allylic hydroperoxides was provided by the photooxygenation of dimethylindene (**24**) which afforded significant amounts of *both* the allylic hydroperoxide **26** as well as the diketone **25**. Further evidence for the importance of dioxetane intermediates in the addition of singlet oxygen to electron-rich olefins is provided by the numerous examples of



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(266) H. A. O'Neal and W. H. Richardson, *J. Amer. Chem. Soc.*, **92**, 6553 (1970).

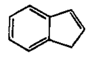
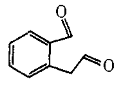
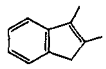
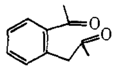
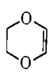
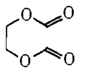
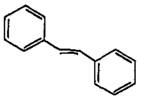
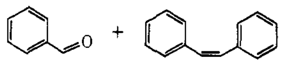
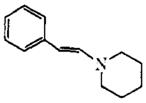
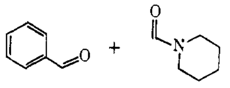
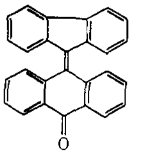
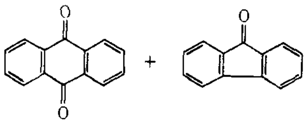
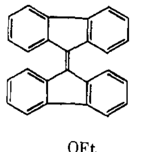
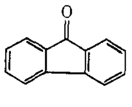
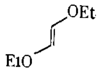
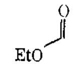
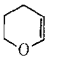
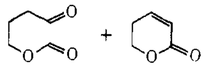
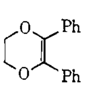
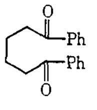
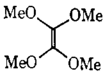
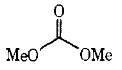
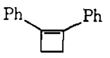
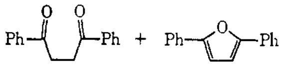
(267) C. S. Foote and J. W.-P. Lin, *Tetrahedron Lett.*, 3267 (1968).

(268) J. Huber, *ibid.*, 3271 (1968).

olefins which react rapidly with singlet oxygen in spite of the fact that they lack abstractable hydrogen atoms in allylic positions. Some of these examples are indicated in Table VI.[226]

Table VI

Examples of Electron-Rich Olefins Which React with Singlet Oxygen to Form Carbonyl Products

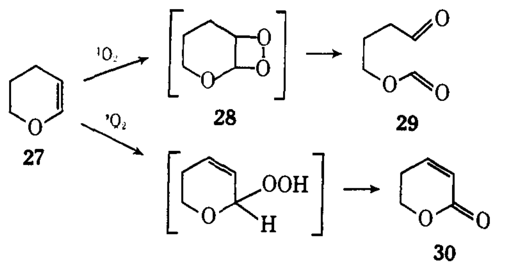
Acceptor	*Product (S)*	*Ref*
		226, 265
		226, 265
		194, 226
		226, *a*
		267
		307
		*b*
		233
		194
		194
		207
		270

[a] G. Rio and J. Berthelot, *Bull. Soc. Chim. Fr.*, 3609 (1969). [b] W. H. Richardson and V. Hodge, *J. Org. Chem.*, **35**, 1216 (1970).

In each case the carbonyl products expected from cleavage of an intermediate 1,2-dioxetane are obtained, and any involvement of an "ene" mechanism and allylic hydroperoxide intermediates is clearly ruled out.

Indisputable evidence for the intermediacy of dioxetanes in the reaction of singlet oxygen with certain olefins was finally obtained when a dioxetane was isolated from the photooxygenation of *cis*-diethoxyethylene.[194,269] In subsequent work the addition of the singlet oxygen to both isomers of diethoxyethylene[233] was shown to be stereospecific 1,2-cis, thus eliminating a stepwise biradical addition of the singlet oxygen which would have led to loss of configuration. Mazur and Foote have also been successful in isolating the dioxetane from photooxygenation of tetramethoxyethylene.[217] A concerted 1,2 addition of singlet oxygen to these activated olefins is consistent with theoretical expectations,[225] but the present data are insufficient to rule out the possibility that peroxirane formation precedes the formation of a more stable dioxetane.

The photooxygenation of dihydropyran (**27**) may help to shed some light on the nature of the transition state involved in formation of dioxetanes. As with the photooxygenation of dimethylindene,[265] photooxygenation of this compound yields two products: an aldehydoformate (**29**), the product expected from cleavage of the dioxetane (**28**), and dihydropyrone (**30**), the probable dehydration product from the hydroperoxide. The product ratio (**29**/**30**) varies over a 58-fold range as the solvent is changed from benzene to acetonitrile, with polar solvents favoring the 1,2 cycloaddition over hydroperoxide formation.[194,269] If we accept the notion that peroxiranes are the intermediates in the formation of allylic hydroperoxides, then one possible interpretation of these results is that the transition state for dioxetane formation is more polar than for peroxirane formation. This is consistent with the theoretical studies which indicate that a $[_{\pi}2_s + _{\pi}2_s]$ addition of singlet oxygen requires substantial charge transfer from the olefin to oxygen in the transition state (but not in the final product), whereas peroxirane formation does not involve such a polar transition state, even though the final product may be more polar.[235] Alternatively, it is possible that a peroxirane is the common intermediate in the formation of *both* dioxetanes and allylic hydroperoxides and that the solvent dependence simply reflects the manner in which partition between the two products depends upon solvent.[233]



In contrast to the above results, Schultz and Schlessinger find essentially the opposite solvent dependence of product distribution from the photooxygenation of 1,2-diphenylcyclobutene.[270] In this case polar solvents favored formation of the allylic hydroperoxide, and nonpolar solvents favored formation of the diketone expected from decomposition of a dioxetane intermediate. These contrasting examples clearly indicate the need for more experimental data on solvent effects on product distribution and leave open the question of

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(269) P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, paper presented at International Symposium on Singlet Oxygen, New York Academy of Sciences, New York, N. Y., Oct 23, 1969.

(270) A. G. Schultz and R. H. Schlessinger, *Tetrahedron Lett.*, 2731 (1970).

whether dioxetane formation is in competition with peroxirane formation, or whether peroxiranes can rearrange to dioxetanes, or both. This latter possibility is suggested by the experimental observation that the intermediate in the photooxygenation of indene can be intercepted by azide.[226]

The discovery that dioxetanes are indeed intermediates in the reaction of singlet oxygen with electron-rich olefins has been one of the more interesting developments that has taken place in the chemistry of singlet oxygen during the last few years. These findings are all the more interesting in view of the fact that dioxetanes have been proposed for years as intermediates in a number of chemiluminescent reaction.[271] The isolation of dioxetanes and demonstration that they are chemiluminescent have now provided the compelling support for this proposal which had been lacking until now. We shall have more to say about the thermochemical properties of dioxetanes in the next section where we discuss the role of singlet oxygen in chemiluminescence phenomena.

E. REACTIONS OF $^1\Sigma$

Studies of the photosensitized production of singlet oxygen molecules suggest that significant amounts of $^1\Sigma$ may be generated if the sensitizer molecule has a triplet state above ~40 kcal (see Figure 4).[65] Since $^1\Sigma$ and $^1\Delta$ are expected both on energetic and theoretical grounds to exhibit different chemical reactivities, this could have interesting chemical consequences. With the appropriate acceptor molecule it might be possible to find a variation in distribution of oxygenation products which correlates with the triplet state energy of the sensitizer. Such a variation in product distribution is found in the dye-sensitized photooxygenation of cholest-4-en-3β-ol.[263] Photooxygenation of this compound yields only two products, an enone and an epoxy ketone, and depending upon the triplet state energy of the sensitizer the enone:epoxy ketone ratio varies from 30:1 to 1:5. Since a dramatic change in the product ratio occurs when the triplet state energy of the sensitizer falls below ~45 kcal, it was proposed that both the $^1\Sigma$ and $^1\Delta$ are involved as reaction intermediates, and that the variation in the product distribution with sensitizer resulted from a variation in the relative amounts of $^1\Sigma$ and $^1\Delta$ generated.[103,272] Serious doubt was cast upon this proposal by Ogryzlo's[16] observations on the quenching of $^1\Sigma$ oxygen, which indicated that the lifetime of $^1\Sigma$ in solution would probably be less than 10^{-10} sec. This is much too short to allow it to react with acceptors which were present in concentrations of only 10^{-3} *M*. More recently Foote and Wong[273] have provided convincing kinetic evidence against a *simple* reaction scheme in which the enone product arises from reaction of $^1\Sigma$ and epoxy ketone arises from $^1\Delta$. These observations, coupled with the studies of the quenching of $^1\Sigma$, appear to rule out $^1\Sigma$ as a reactive intermediate in the sensitized photooxygenation of cholestenol. In retrospect it is obvious that if evidence for $^1\Sigma$ reactions is to be found, it will undoubtedly come from gas-phase experiments where $^1\Sigma$ will have a much longer lifetime.

Following the initial suggestion that $^1\Sigma$ might be involved in sensitized photooxygenation reactions, several other authors have presented examples of abstraction reactions which they suggest might involve reactions of $^1\Sigma$,[274,275] but the evidence for a $^1\Sigma$ reaction was not particularly strong. In fact, Bartholomew and Davidson[276] have shown that in the photosensitized oxidation of amines the reaction occurs by abstraction of a hydrogen atom from the amine by the excited sensitizer, followed by reaction of the amine radical with ground state molecular oxygen.

VIII. Chemiluminescence

Chemiluminescence and its various biological manifestations have intrigued people for centuries, but our understanding of the mechanisms involved in generating electronically excited molecules has not progressed until recently.[271,277-282] Studies of the mechanism of chemiluminescence have been hampered by the fact that the luminescence is usually very weak, the species emitting the luminescence may have been excited by energy transfer from some other initially formed excited molecule, and the structures of the excited intermediates in general have not been determined. Furthermore, a variety of different chemiluminescence mechanisms,[282-289] including radical-radical recombination,[282-284] anion-cation recombination,[285-287] energy transfer from other electronically excited species,[232] and thermal decomposition of certain cyclic peroxides (dioxetanes, dioxetanediones)[232,281,290-292] may be involved.

A. ROLE OF SINGLET OXYGEN IN CHEMILUMINESCENCE PHENOMENA

Shortly after it was discovered that the reaction of H_2O_2 with either Cl_2 or OCl^- generates substantial quantities of $^1\Sigma$ and $^1\Delta$ oxygen molecules,[5,6,35,36,140] Khan and Kasha[50] suggested that singlet oxygen molecules might also be responsible for the chemiluminescence in other oxygen producing systems. Taking account of their spectroscopic observations on the chemical generation of singlet oxygen, they proposed that "in systems generating excited singlet molecular oxygen, luminescence of any energetically favorable species may be produced and observed as a 'chemiluminescence' by direct

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(271) J. W. Hastings, *Ann. Rev. Biochem.*, 37, 597 (1968).

(272) D. R. Kearns, R. A. Hollins, A. U. Khan, and P. Radlick, *J. Amer. Chem. Soc.*, 89, 5456 (1967).

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(274) M. H. Fisch, J. C. Gramain, and J. A. Oleson, *Chem. Commun.*, 13 (1970).

(275) T. Matsuura, N. Yoshimura, A. Nishinaga, and I. Saito, *Tetrahedron Lett.*, 1669 (1969).

(276) R. F. Bartholomew and R. S. Davidson, *Chem. Commun.*, 1174 (1970).

(277) See, for example, E. N. Harvey, "Bioluminescence," Academic Press, New York, N. Y., 1952.

(278) F. McCapra, *Quart. Rev., Chem. Soc.*, 20, 485 (1966).

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(280) E. J. Bowen, *Pure Appl. Chem.*, 9, 473 (1964).

(281) M. M. Rauhut, *Accounts Chem., Res.*, 2, 80 (1969).

(282) R. F. Vassil'ev, *Progr. Reaction Kinetics*, 4, 305 (1967).

(283) E. A. Chandross and F. I. Sonntag, *J. Amer. Chem. Soc.*, **88**, 1089 (1966).

(284) R. E. Kellogg, *ibid.*, **91**, 5433 (1969).

(285) D. M. Hercules, *Accounts Chem. Res.*, 2, 301 (1969).

(286) A. Weller and K. Zachariasse, *J. Chem. Phys.*, **46**, 4984 (1967).

(287) A. Weller, *Pure Appl. Chem.*, 16, 115 (1968).

(288) R. L. Bardsley and D. M. Hercules, *J. Amer. Chem. Soc.*, 90, 4545 (1968).

(289) V. A. Belyakov and R. F. Vassil'ev, *Photochem. Photobiol.*, **11**, 179 (1970).

(290) E. H. White and M. J. C. Harding, *J. Amer. Chem. Soc.*, **86**, 5686 (1964).

(291) A. W. Berger, J. N. Driscoll, J. S. Driscoll, J. A. Pirog, and H. Linschitz, *Photochem. Photobiol.*, 7, 415 (1968).

(292) A. V. Kariakin, *Opt. Spectrosc. (USSR)*, 7, 75 (1959).

energy transfer from excited oxygen molecular *pairs*."[250] With this mechanism, pairs of excited singlet oxygen molecules could be utilized to excite organic molecules with excited singlet states as high as 26,000 cm^{-1}, depending upon which excited oxygen pair states are utilized. So far there have been no careful estimates of the rate constants for the various processes which would be required in order to account for the observed luminescence yields. Recently, Khan and Kasha[142] extended their initial proposal by suggesting that while the sensitization of the luminescence requires an actual collision between a pair of metastable singlet oxygen molecules, energy may be transferred from the oxygen molecules to an acceptor molecule which is located some distance (unspecified) away. They did not discuss the mechanism, but long-range energy transfer from one electronically excited species (donor) to another acceptor molecule (acceptor) is of course well known and well understood through the work of Förster.[293-296] In order for transfer distances to be large, however, two important criteria must be satisfied. The emission spectrum of the excited donor must overlap strongly with the absorption spectrum of the acceptor, and the lifetime of the excited donor species (a collision complex between a pair of excited oxygen molecules) should approach its radiative lifetime. Now the oscillator strengths for the various cooperative transitions observed in liquid oxygen are on the order of 10^{-8} so that the *radiative lifetime* of a collision complex is on the order of ~0.5 sec.[297] Since this is about ten orders of magnitude longer than the lifetime of a collision complex in solution, long-range transfer from oxygen pairs seems unlikely. Wilson has studied the sensitization of rubrene fluorescence by energy transfer from singlet oxygen molecules,[298] and as required by the Khan-Kasha mechanism she found that the intensity of the rubrene luminescence varied with the square of the $^1\Delta$ concentration. Addition of the amine **6**, a molecule known to selectively and efficiently quench singlet oxygen, drastically reduced the rubrene luminescence. Transfer of energy from excited oxygen pairs involving $^1\Sigma$ is virtually excluded in solution by the fact that $^1\Sigma$ is so readily deactivated, and Wilson concluded that the rubrene fluorescence was sensitized by energy transfer from pairs of $^1\Delta$ molecules.[298] Since the lowest excited singlet state of rubrene is ~53 kcal, the energy transfer process requires an activation energy of 8 kcal, and indeed Wilson finds that the oxygen-sensitized rubrene chemiluminescence is temperature dependent (apparent activation energy of about 6.5 kcal).

While these data are consistent with the Khan-Kasha mechanism, there is an alternative scheme proposed by Ogryzlo and Pearson[185] which also accounts for Wilson's results.[298] According to this mechanism, the sensitization of the excited singlet state of the fluorescer involves two consecutive spin-allowed energy transfers from singlet oxygen monomers as indicated below.

$$^1O^*_2 + {}^1M_0 \longrightarrow {}^3M^*_1 + {}^3O_2$$

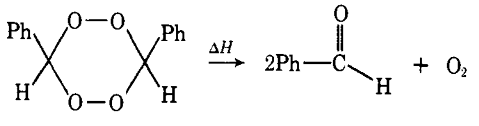
$$^1O^*_2 + {}^3M_1 \longrightarrow {}^1M^*_1 + {}^3O_2$$

Since the triplet state of rubrene probably lies slightly below 28 kcal, the energy of the lowest triplet state of naphthacene,[88] the first transfer step is expected to be endothermic by about 6 kcal. In this way the temperature dependence observed by Wilson could be accounted for.

Substantial evidence for an energy pooling mechanism which involves the triplet state of the luminescing molecule as an intermediate has been provided by Ogryzlo and Pearson's study of the singlet oxygen induced chemiluminescence of violanthrone.[185] From an examination of the variation of the violanthrone emission intensity with the concentration of both $^1\Sigma$ and $^1\Delta$ oxygen, it was shown that $^1\Sigma$ plays no significant role in the excitation mechanism and that the sensitizer luminescence varied linearly with the *square* of the $^1\Delta$ concentration. From the variation in the sensitized luminescence intensity with the oxygen pressure, energy transfer from a pair of $^1\Delta$ molecules was ruled out.[185]

Through the controlled generation of singlet oxygen in the gas-phase Wilson[298] and Ogryzlo[185] have provided convincing experimental evidence that energy transfer from singlet oxygen molecules can excite the fluorescence of rubrene and violanthrone. It is going to be much more difficult, however, to establish the role of singlet oxygen in solution-phase chemiluminescence phenomena which involve the decomposition of peroxides and other oxygen-rich compounds, because of problems in detecting singlet oxygen in solution and because of the multiplicity of other mechanisms which may be involved. For example, tetrakisdimethylaminoethylene reacts with *ground* state oxygen to form an intermediate which is strongly chemiluminescent.[299-302] Singlet oxygen also reacts with ketenes to produce dioxetanones[303] which are chemiluminescent,[281] and it is quite clear from energetic considerations that the excited state products could not have been sensitized by energy transfer from singlet oxygen.

The chemiluminescence resulting from the decomposition of dibenzoyl diperoxide may involve singlet oxygen.[304] A pair of benzaldehyde molecules and molecular oxygen are produced by decomposition of this molecule, and, if spin is conserved during the decomposition, then excited singlet oxygen is generated and the two benzaldehyde molecules are formed in their ground states. If one of the benzaldehydes is formed in an excited triplet state, then singlet oxygen could be formed by energy transfer from triplet state benzaldehyde molecules. The intensity of the chemiluminescence in these systems varies with the square of the initial concentration of peroxide as required for a mechanism involving energy transfer from singlet oxygen molecules, but additional experimental evidence is required before it can be concluded that singlet oxygen was necessarily involved.



Because of the high sensitivity with which it is possible to detect weak light emission, it would be very useful to have a

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(293) Th. Förster, *Ann. Phys.*, **2**, 55 (1948).

(294) Th. Förster, *Z. Elektrochem.*, **53**, 93 (1949).

(295) Th. Förster in "Comparative Effects of Radiation," M. Burton, J. S. Kirby-Smith, and J. L. Magee, Ed., Wiley, New York, N. Y., 1960, pp 300–319.

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(298) T. Wilson, *J. Amer. Chem. Soc.*, **91**, 2387 (1969).

(299) J. P. Paris, *Photochem. Photobiol.*, **4**, 1059 (1965).

(300) A. N. Fletcher and C. A. Heller, *ibid.*, **4**, 1051 (1965).

(301) R. E. Preutt, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, *J. Amer. Chem. Soc.*, **72**, 3646 (1950).

(302) W. H. Urry and J. Sheeto, *Photochem. Photobiol.*, **4**, 1067 (1965).

(303) L. J. Bollyky, *J. Amer. Chem. Soc.*, **92**, 3230 (1970).

(304) S. R. Abbott, S. Ness, and D. M. Hercules, *ibid.*, **92**, 1128 (1970).

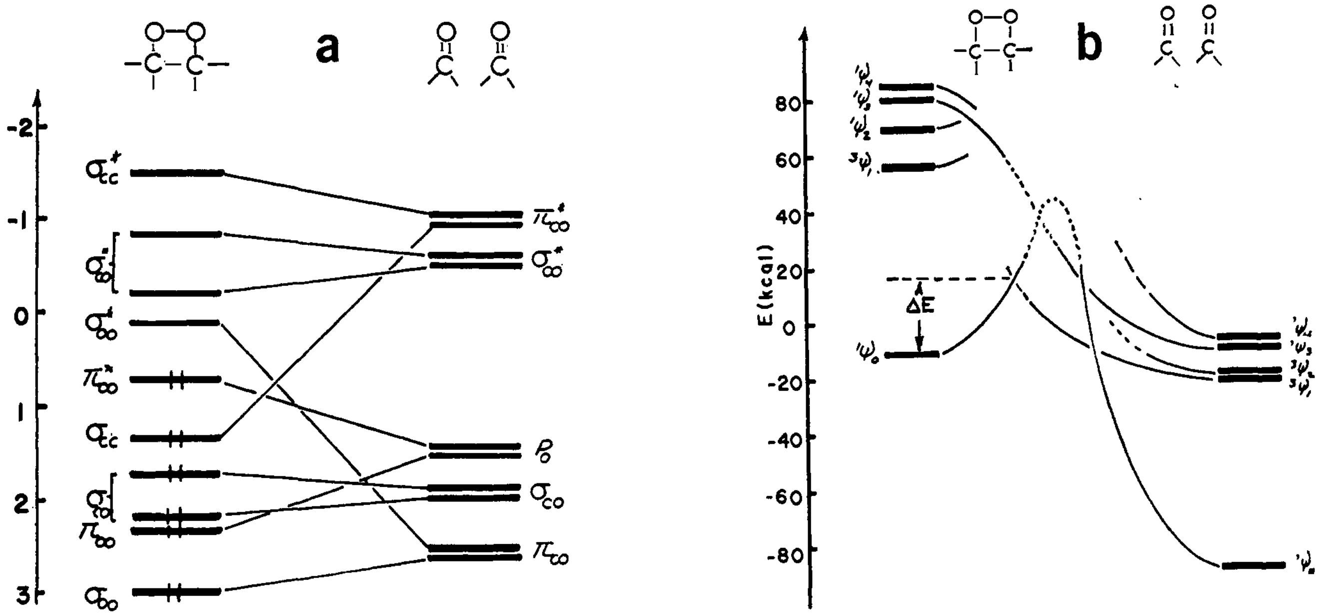
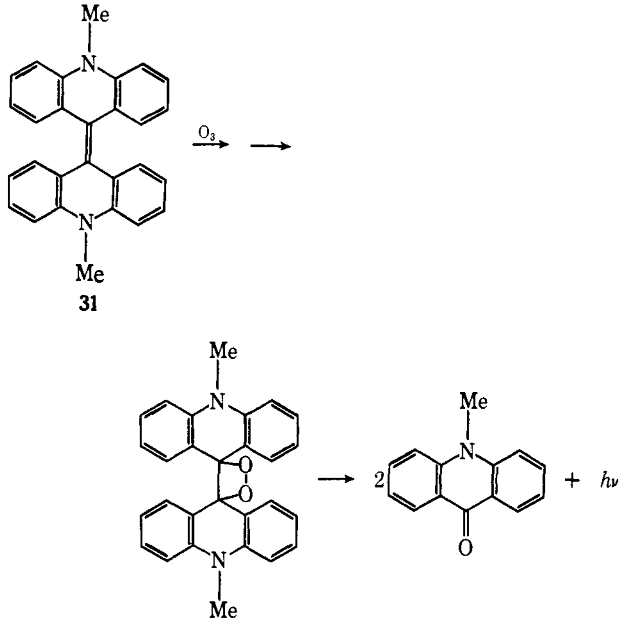


Figure 11. Orbital (a) and state (b) correlation diagrams depicting the cleavage of a dioxetane into two carbonyl fragments.

chemiluminescent system where the luminescence was produced only by energy transfer from singlet oxygen molecules. From the above discussion, however, it is obviously going to be difficult to find such a system because of the problems of ruling out other mechanisms which do not involve singlet oxygen. Additional fundamental studies in this interesting area are obviously required before chemiluminescence can be used as a diagnostic test for singlet oxygen.

B. OZONE-INDUCED CHEMILUMINESCENCE

There are reports that ozone induces luminescence with a number of fluorescent organic substrates, and a survey of this phenomenon was reported some time ago by Bowman and Alexander.[305] From their description it would appear that the chemiluminescence yields can be very high since an acetone solution of safranin exposed to ozone was bright enough to read by.[305] The reaction of ozone with 10,10′-dimethyl-9,9′-biacridylidene (**31**) is also chemiluminescent, but in this case the suggested mechanism involves formation of a dioxetane intermediate which decomposes to yield an electronically excited product.[306]



C. DIOXETANES AND CHEMILUMINESCENCE

As noted earlier (section VII.D), the discovery of dioxetane intermediates in reactions of singlet oxygen with electron-rich olefins is particularly interesting from several standpoints. First of all, the impression was given in some of the earlier literature that dioxetanes had been eliminated from consideration as important intermediates in singlet oxygen reactions.[235] Secondly, they have often been proposed as intermediates in many chemiluminescence and bioluminescence reactions.[271,278] Kopecky achieved an important breakthrough in this area when he synthesized several different dioxetanes and demonstrated that they chemiluminesced upon decomposition.[232,262] Shortly after Kopecky's work, convincing evidence for the formation of dioxetanes in singlet oxygen reactions was presented,[194,207] and this added a new dimension to the role of singlet oxygen in chemiluminescence phenomena. In a previous section we discussed some theoretical considerations relating to the concerted addition of singlet oxygen to olefins to form dioxetanes. In this section we shall use this same theoretical approach to comment on the mechanism of the thermal decomposition of dioxetanes and the possible origin of their chemiluminescence. The orbital and state correlation diagrams for the thermal decomposition of a dioxetane are depicted in Figures 11a and 11b. According to the orbital correlation diagram, the ground state electronic configuration attempts to correlate with a highly excited

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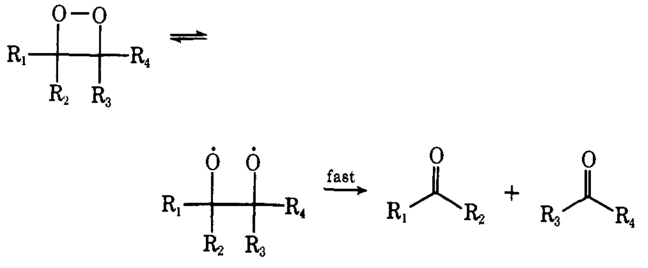
(305) R. L. Bowman and N. Alexander, *Science*, **154**, 1454 (1966).

(306) E. G. Janzen, I. G. Lopp, and J. W. Happ, *Chem. Commun.*, 1140 (1970).

electronic state of the dicarbonyl product.[105,225,307,308] The lowest excited singlet and triplet states with electronic configuration ---$\pi^{*1}_{OO}\sigma^{*1}_{OO}$ are, however, stabilized by cleavage of the O–O bond. As a result of this opposite behavior on cleavage there may be a crossing of the potential energy curves for excited states and the ground state. While small distortions from C_{2v} symmetry would prevent crossing of the ground state curve with an excited *singlet* state curve, crossing of an excited triplet state curve could occur (neglecting mixing due to spin-orbit coupling). These results suggest that there should be a barrier to the thermal decomposition (ΔE in Figure 11b), that one of the carbonyl ketones could be left in an excited triplet state as a result of the expected curve crossing shown in Figure 11b, and that dioxetanes should be photochemically unstable with respect to cleavage.

Experimentally, the barrier to the thermal decomposition of the dioxetane of trimethylethylene is about 24 kcal, and the decomposition is accompanied by chemiluminescence from the acetone product.[232,262] White has shown that the excited state products from the dioxetane decomposition are capable of sensitizing chemical reactions that ordinarily are photosensitized.[309] Although both excited singlet and triplet state acetone is present, it remains to be demonstrated whether one or both states are initial products of the decomposition. Evidence supporting the expected photosensitivity of dioxetanes is contained in Bartlett's[194] report of the synthesis of dioxetane where it was noted that the dioxetane decomposition was photosensitized by the sensitizer. Direct photolysis of the dioxetane would obviously be of interest.

Although we assumed in the above discussion that the decomposition occurs by a concerted, one-step mechanism, this remains to be proven. It is interesting to note that O'Neal and Richardson[266] have been able to accurately predict the observed activation energy and rate constant for the decomposition of the trymethylethylene–dioxetane decomposition by assuming that the decomposition mechanism involves a two-step biradical sequence.



While these thermochemical results make this alternative look attractive, it is not clear then why the decomposition should be accompanied by electronic excitation of one of the product molecules.[310]

Acknowledgments. I am indebted to Professor A. U. Khan for stimulating much of my initial interest in the singlet oxygen field, and to Professor P. Radlick for his collaborative efforts and insights into the chemistry of singlet oxygen. I also wish to thank Dr. Errett Turner (Bell Telephone Laboratories) for his aid in compiling the literature references, and Professor Michael Kasha for carefully reading the manuscript and for his helpful suggestions. This work was supported by grants from the U. S. Public Health Service (CA11459) and the National Science Foundation (GP 12050).

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(307) F. McCapra and R. A. Hann, *Chem. Commun.*, 442 (1969).

(308) F. McCapra, *ibid.*, 155 (1968).

(309) E. H. White, J. Wiecko, and D. F. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969).

(310) NOTE ADDED IN PROOF. The data referred to in ref 176 have been found to be in error as a result of an instrumental artifact (A. K. E. Hogopian, J. Marrs, and A. U. Khan, submitted for publication). J. T. Richards, G. West, and J. K. Thomas (*J. Phys. Chem.*, **74**, 4137 (1970)) have shown by triplet–triplet absorption measurements that the oxygen quenching of pyrene fluorescence occurs primarily by enhancing intersystem crossing to the triplet state. Quenching directly to the ground state was found to be negligible.