tronic principle, familiar to chemists. We have made no separation of core and valence electrons, but it may be argued that ΔV_{ee} is largely due to the valence electrons.

Note that if $\partial(\mathrm{BE})/\partial Z_B$ were exactly zero, the binding energy calculated by assuming eq 1 to be valid would be too high by a factor of 3. As $\partial(\mathrm{BE})/\partial Z_B$ is probably positive, the binding energy will be somewhat less, and in fact Boer, *et al.*,[12] suggest correcting the calculated binding energy by dividing by 2. In concluding, we must agree with Boer, *et al.*, that, since the cancellation of V_{NN} and ΔV_{ee} is good only to a few tenths of an atomic unit, a true SCF calculation cannot be expected to yield correct binding energies by this procedure, but that trends within a series of related molecules may be predicted.

Selection Rules for Singlet-Oxygen Reactions. Concerted Addition Reactions

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Abstract: In this paper we have used molecular orbital and state correlation diagrams to predict the reactions of molecular oxygen with monoolefins and conjugated dienes. From this analysis the following selection rules are obtained. (1) The concerted addition of ground-state ($^3\Sigma$) oxygen to olefins and dienes is forbidden unless the π-ionization potential of the acceptor is unusually low. (2) The reaction of excited singlet oxygen in its $^1\Delta$ state with *cis*-dienes is predicted to be allowed. The addition of $^1\Delta$ oxygen to olefins may be forbidden unless the olefin has a low π-ionization potential. (3) $^1\Sigma$ oxygen is expected to be unreactive toward olefins and dienes in concerted addition reactions. The thermochemical and photochemical properties of the diene and olefin oxygenation products have been examined, and selection rules for their thermal and photodecomposition have also been derived. The selection rules for the oxygen reactions are compared with those for the corresponding reactions of ethylene and their relation to the Woodward–Hoffmann selection rules is discussed.

During the past 4–5 years a large body of data has been collected which indicates that electronically excited singlet-state oxygen molecules (presumably $^1\Delta$) are the reactive intermediates in numerous photooxygenation reactions.[1-11] With the recent spectroscopic detection of the photosensitized formation of singlet ($^1\Delta$) oxygen,[12-14] and the demonstration that the quantum yield for this process is high (perhaps 100%),[12] the evidence for the involvement of singlet oxygen in many photooxygenation reactions is now virtually unassailable.

In previous papers we presented a relatively simple theoretical procedure for predicting the relative reactivity of ground-state and electronically excited oxygen molecules toward various organic acceptors.[15,16] In the present paper this approach is further refined and used to investigate the various factors which control the reactivity of oxygen toward different types of acceptors. Since the 1,4 addition of oxygen to dienes appears to be one of the simpler reactions which singlet oxygen undergoes,[7,8,11] this reaction is considered first. The addition of oxygen to isolated olefins and polyenes is also examined and useful conclusions regarding the reactivity of oxygen with these acceptors are drawn.

Inasmuch as the products of some of the singlet-oxygen reactions appear to have unusual chemical and photochemical properties, as in chemiluminescent systems,[17-19] the properties of some of the oxygenation products are also examined theoretically.

Finally, since there are interesting parallels between the reactions of oxygen and olefins with conjugated dienes,[1,9,11,20] we have carried out a comparison of these two types of reactions. This comparison also allows us to investigate the extent to which the Woodward–Hoffmann selection rules for concerted cycloaddition reactions are applicable to cycloaddition reactions of singlet oxygen.[21-23]

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Theoretical Investigation of the Reactions of Oxygen with Organic Acceptors

In view of the outstanding success which Woodward and Hoffmann have had using molecular orbital correlation diagrams to predict the stereochemical course of thermochemical and photochemical electrocyclic reactions,[21-23] we initially hoped that the same approach would be similarly useful in treating the reactions of oxygen. It soon became evident, however, that because of the degeneracy of antibonding π^* orbitals of molecular oxygen, it is not possible to adequately treat the reactions of oxygen simply at the molecular orbital level.[15,16] The difficulty is obvious when we realize that if electron–electron interactions were neglected, the ground $^3\Sigma$ state, the $^1\Delta$ states, and the $^1\Sigma$ state of oxygen would all be degenerate in energy. Therefore, in order to understand why these different states of oxygen exhibit different chemical reactivities it is necessary to explicitly consider the electron–electron interactions which are responsible for removing this degeneracy. This, of course, complicates the problem since the information contained in an orbital correlation diagram cannot be directly used to follow the reactions of oxygen with an acceptor unless careful attention is given to including the effects of electron–electron interaction. Before treating the general problem of the reactions of oxygen, we first examine the electronic structure of oxygen and consider how perturbation of the oxygen orbitals affects the ground triplet and the low-lying excited singlet states of oxygen. With this information in hand, we then go on to a consideration of the reactions of oxygen.

1. Description of the Low-Lying States of Molecular Oxygen. If we use the real form for the molecular orbitals for molecular oxygen (π_x^*, π_y^*) instead of angular momentum eigenfunctions ($\pi_\pm^*$) which are appropriate for the free molecule, then the following set of zero-order singlet- and triplet-state wave functions can be constructed.

$$^3\psi_{xy} = \frac{1}{\sqrt{2}}\{|\pi_x^*(1)\bar{\pi}_y^*(2)| + |\pi_x^*(1)\pi_y^*(2)|\}$$

$$^1\psi_{xy} = \frac{1}{\sqrt{2}}\{|\pi_x^*(1)\bar{\pi}_y^*(2)| - |\bar{\pi}_x^*(1)\pi_y^*(2)|\}$$

$$^1\psi_{xx} = |\bar{\pi}_x^*(1)\pi_x^*(2)|$$

$$^1\psi_{yy} = |\bar{\pi}_y^*(1)\pi_y^*(2)|$$

If electron–electron interaction is neglected, these states are all degenerate in energy; however, when it is included, the states described by $^3\psi_{xy}$ and $^1\psi_{xy}$ are shifted, and the states described by $^1\psi_{xx}$ and $^1\psi_{yy}$ are not only shifted in energy, but they are mixed with one another as a result of an exchange interaction

$$K = \langle \pi_x^*(1)\pi_y^*(1)|e^2/r_{12}|\pi_x^*(2)\pi_y^*(2)\rangle$$

The appropriate new functions and their energies relative to the ground triplet state are [24]

$$^3\psi_0(^3\Sigma) = {}^3\psi_{xy} \qquad E = 0$$

$$^1\psi_1(^1\Delta^*) = {}^1\psi_{xy} \qquad E = 22 \text{ kcal}$$

$$^1\psi_2(^1\Delta) = \frac{1}{\sqrt{2}}(^1\psi_{xx} - {}^1\psi_{yy}) \qquad E = 22 \text{ kcal}$$

$$^1\psi_3(^1\Sigma) = \frac{1}{\sqrt{2}}(^1\psi_{xx} + {}^1\psi_{yy}) \qquad E = 38 \text{ kcal}$$

The above discussion applies to free oxygen molecules, where the π_x^* and π_y^* orbitals are degenerate in energy. If oxygen interacts with some appropriate organic acceptor, then the degeneracy between the π_x^* and π_y^* orbitals can be lifted. To see how removal of the $\pi_{x,y}^*$ degeneracy affects the behavior of the oxygen states, let us assume that the interaction changes the π_x^* orbital energy by an amount ΔE_x, and the π_y^* orbital by an amount ΔE_y, but that there is no change in the *form* of the orbital wave functions. With these assumptions we are essentially treating the oxygen–acceptor interaction as a "crystal field" problem much in the manner discussed by Griffith.[25] If we now return to the zero-order wave functions, we find that, within the above approximations, the states associated with $^3\psi_{xy}$ and $^1\psi_{xy}$ are unchanged in form, but they have new energies.

$$^3\psi_0(^3\Sigma) = {}^3\psi_{xy} \qquad E(^3\Sigma) = \Delta E_x + \Delta E_y$$

$$^1\psi_1(^1\Delta^*) = {}^1\psi_{xy} \qquad E(^1\Delta^*) = 22 + \Delta E_x + \Delta E_y$$

The contribution from closed-shell electrons to the total energy has not been included in the above expression since it is the same for all states, and may simply be calculated by summing orbital energies over all of the doubly occupied orbital.

The above results are particularly useful in the treatment of the oxygen reactions since they indicate that the behavior of both the $^3\Sigma$ and $^1\Delta^*$ states during the *initial* stages of a reaction can immediately be deduced from a consideration of orbital energies. This simplification arises, of course, from the fact that when π_x^* and π_y^* are degenerate, the $^3\Sigma$ and $^1\Delta^*$ states can be described by single configuration wave functions, and this holds true even when the orbital degeneracy is removed. The behavior of the $^1\Sigma$ and $^1\Delta$ states, on the other hand, is more complicated.

When π_x^* and π_y^* are no longer degenerate, the exchange integral K still causes $^1\psi_{xx}$ and $^1\psi_{yy}$ to mix, but the resulting functions are no longer 50:50 mixtures of $^1\psi_{xx}$ and $^1\psi_{yy}$, and the energy expressions for these states are also changed. Without having to solve for the wave functions, we can write down the new energies $E'(^1\Sigma)$ and $E'(^1\Delta)$ for the two states which correlate with the $^1\Sigma$, and the $^1\Delta$ state of free oxygen, respectively, and these are

$$E'(^1\Sigma) = 30 + {}^1/_2[(\Delta E_x + \Delta E_y) + \sqrt{4K^2 + (\Delta E_x - \Delta E_y)^2}]$$

$$E'(^1\Delta) = 30 + {}^1/_2[(\Delta E_x + \Delta E_y) - \sqrt{4K^2 + (\Delta E_x - \Delta E_y)^2}]$$

To facilitate the later discussion, the effect of the orbital

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[24] In order to see how these functions are related to the functions for the $^3\Sigma$, $^1\Delta$, and $^1\Sigma$ states of a free oxygen, we made use of the relation $\pi_x^* = (^1/_2)(\pi_+^* + \pi_-^*)$; $\pi_y^* = (^1/_{2i})(\pi_+^* + \pi_-^*)$.

[25] J. S. Griffith in "Oxygen in Animal Organisms," F. Dickens and E. Niel, Ed., Pergamon Press, Ltd., Oxford, England, 1964, p 481.

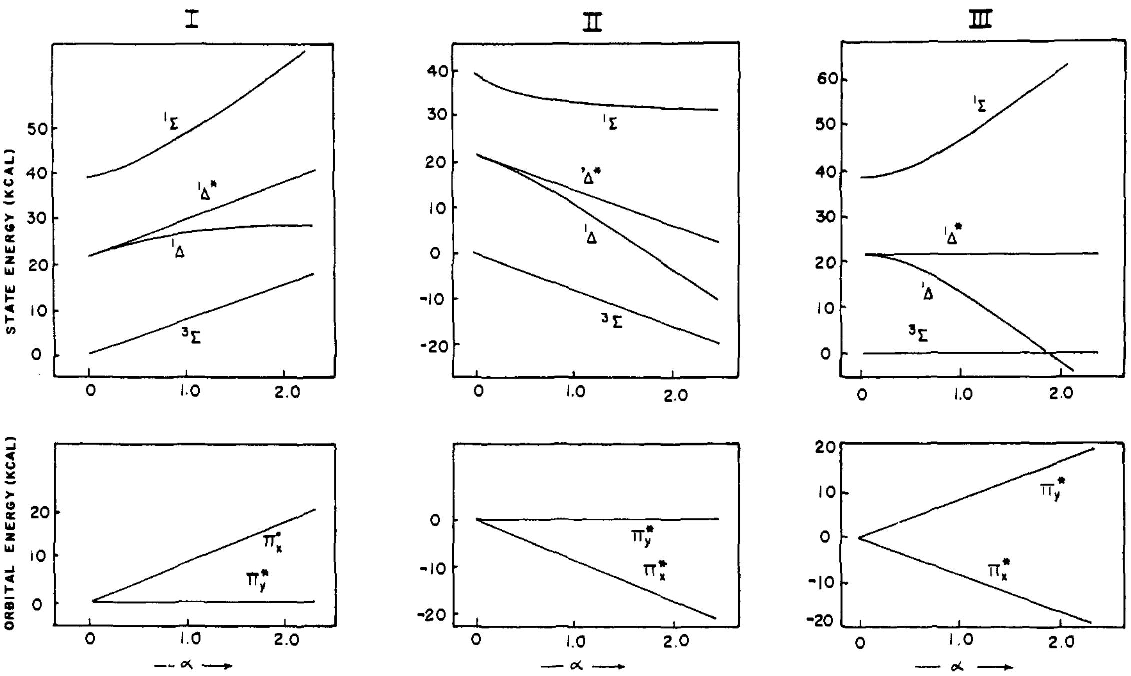

Figure 1. Behavior of the orbitals and states of molecular oxygen subjected to a perturbation which lifts the degeneracy of the π_x* and π_y* orbitals: case I, $\Delta E_x = \alpha K$, $\Delta E_y = 0$; case II, $\Delta E_x = -\alpha K$, $\Delta E_y = 0$; case III, $\Delta E_x = -\Delta E_y = -\alpha K$.

perturbation on the oxygen states is shown graphically in Figure 1 for the following three cases.

$$\Delta E_x = +\,\alpha K \qquad \Delta E_y = 0 \tag{I}$$

$$\Delta E_x = -\,\alpha K \qquad \Delta E_y = 0 \tag{II}$$

$$\Delta E_x = \Delta E_y = \alpha K \tag{III}$$

For mathematical convenience we have expressed the change in the orbital energies in terms of the dimensionless parameter $\alpha = \Delta E_{x,y}/K$, where K is the exchange integral which mixes $^1\psi_{xx}$ and $^1\psi_{yy}$. Once simple orbital considerations have been used to establish the behavior of the $^3\Sigma$ and $^1\Delta^*$ states, the curves of Figure 1 can then be used to deduce the behavior of the $^1\Delta$ state and the higher energy $^1\Sigma$ state.

The results presented in Figure 1 can be summarized as follows.

(1) The behavior of $^3\Sigma$ state can be immediately determined by calculating the total orbital energy for an electronic configuration in which one electron is placed in each of the two orbitals which correlate with the π^*-antibonding orbitals of free oxygen.

(2) The behavior of the $^1\Delta^*$ state parallels the behavior of the ground $^3\Sigma$ state, except that it lies 22 kcal higher in energy.

(3) The $^1\Delta$ state starts out degenerate with the $^1\Delta^*$ state, but as the degeneracy between the two π^* orbitals is lifted, it behaves as if its outer two electrons were placed in whichever π^* orbital lies lower in energy.

(4) The $^1\Sigma$ state behaves as if both of the outer electrons of oxygen were placed in the higher energy π^* orbital.

With this examination of how removal of the π_x*, π_y* orbital degeneracy affects the states of oxygen, we can now discuss the approach which we have used to predict the course of reactions involving the addition of molecular oxygen to various organic acceptors.

2. Reactions of Excited Oxygen with Organic Acceptors. Outline of Theory.

In order to follow the reaction of oxygen with an acceptor, a state correlation diagram must be constructed showing how different possible states of the reactants adiabatically go over into (correlate with) the various states of the product during the course of a reaction. While this can be approached in different ways,[15,16,21–23,26–33] in our approach we have attempted to build into our calculations as much experimental information on energy levels as possible. In this way only minimal reliance is placed on what we know to be rather inadequate theoretical calculations.

The construction of the state correlation diagrams involves the following steps.[15,16]

(i) Thermochemical data (bond strengths, resonance energies, strain energies, heats of formation) are used to locate the ground state of the reactants (a weak complex between O_2 and the acceptor) relative to the ground state of the product.

(ii) Spectroscopic data are used to locate the excited states of the reactants relative to their ground state, and likewise for the product. The problem of deciding which initial state of the reactants ultimately correlates with a particular state of the product, and more importantly, determining how this correlation will occur, requires the introduction of the sort of information which can be obtained from an orbital correlation diagram.

(26) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, 87, 2045 (1965).

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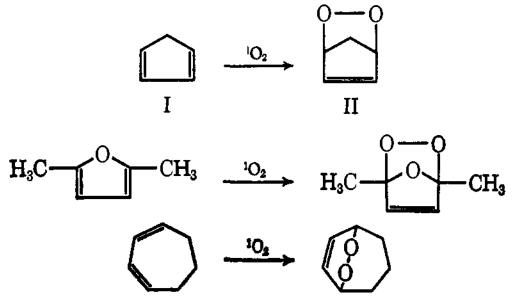
Table I. Thermochemical Data

Reaction	ΔH, kcal
$R{-}CH{=}CH{-}\underset{H}{\overset{R}{C}}{-}H \rightarrow R{-}CH{=}CH{-}\underset{H}{\overset{R}{C}}\cdot + H\cdot$	$+81^a$
$CH_2{=}CH{-}\underset{H}{\overset{H}{C}}{-}O_2\cdot \rightarrow CH_2{=}CH{-}C\cdot H_2 + O_2$	$+12^a$
$R{-}O{-}O{-}H \rightarrow R{-}O{-}O\cdot + H\cdot$	
$R{-}O{-}O{-}H \rightarrow R{-}O{-}O\cdot + H\cdot$	$+90^{a,b}$
$CH_3{-}CH_2{-}O{-}O{-}C_2H_5 \rightarrow CH_3{-}CH_2{-}O{-}O\cdot + \cdot C_2H_5$	$+72^b$
$C_2H_5{-}O{-}O\cdot \rightarrow C_2H_5\cdot + O_2$	$+25^a$
$C\cdot H_2{-}CH_2{-}O_2 \rightarrow \underset{H}{\overset{H}{C}}{=}\underset{H}{\overset{H}{C}} + O_2$	-40
$R{-}O{-}O{-}R \rightarrow 2RO\cdot$	$+35^a$

[a] J. C. Calvert and J. N. Pitts, "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1964. [b] S. W. Benson, *J. Chem. Educ.*, **42,** 502 (1965).

(iii) A reasonable geometry for the transition state in the reaction is chosen, and an orbital correlation diagram for the reaction is then constructed, using procedures that have been discussed in detail elsewhere.[21–23] From the orbital correlation diagram symmetries can be assigned to the various possible reactant and product states, and from a knowledge of how the *orbitals* of the reactants and products correlate with one another, one can determine how the *states* of the reactants and products correlate with one another. The emphasis, then, is on the behavior of the *states* rather than orbitals although we do, of course, make use of information obtained from orbital calculations. By use of "experimental" data for the initial and final state energies, hopefully we avoid some of the uncertainty which is associated with dependence on orbital correlation diagrams, not only for symmetry and behavior of states, but also for the location of states. As a first example, we examine the application of this procedure to the addition of oxygen to *cis*-dienes.

3. 1,4 Addition of Oxygen to *cis*-Dienes. The cycloaddition of singlet oxygen to *cis*-dienes to form transannular peroxides is one of the more well-studied singlet-oxygen reactions,[7,9,11,20,34] and some examples of this type of reaction are indicated. We now consider the addition of oxygen to, say, cyclopentadiene (I).[9,11] To construct the state correlation diagram for this reaction, we first need to specify the ground-state energy of the endoperoxide (II) relative to the ground state of the reactants ($^1O_2$ + I). The thermochemical data used in this calculation are given in Table I. If strain energy is negligible we calculate that the over-all ΔH for this reaction is -29 kcal, assuming that the resonance energy associated with I is about 3 kcal.[35] This serves to locate the ground state of the reactants relative to the product, and we next need to arrange in energy excited states relative to the ground states. The three lowest lying excited states of the reactants are all singlet states associated with excitation of oxygen to one of its $^1\Delta$ states (~22 kcal) or to its $^1\Sigma$ state (~38 kcal).[36] The next higher excited state is undoubtedly associated with excitation of the diene to its lowest triplet state, which is probably located about 55 kcal above the ground state.[37] Interaction of a triplet-state diene molecule with $^3\Sigma$ oxygen then gives rise to singlet, triplet, and quintet states, depending upon how the spins of the oxygen and diene are coupled. Little is known about the spectroscopic properties of the endoperoxide product (II), but we expect that it will have an electronic structure somewhat similar to simple alkyl peroxides. On this basis II should have low-lying excited singlet and triplet states located between 75 and 85 kcal (vertical energies) above the ground state.[38]



To determine how the various possible reactant and product states just mentioned correlate with each other, an orbital correlation diagram must be constructed. If we assume that there is a plane of symmetry in the transition state, then construction of the orbital correla-

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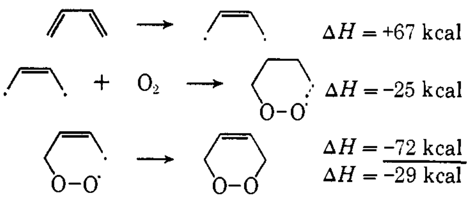
[35] J. D. Roberts and M. Casario, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964. ΔH for this reaction was calculated using the following cycle.



[36] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1950.

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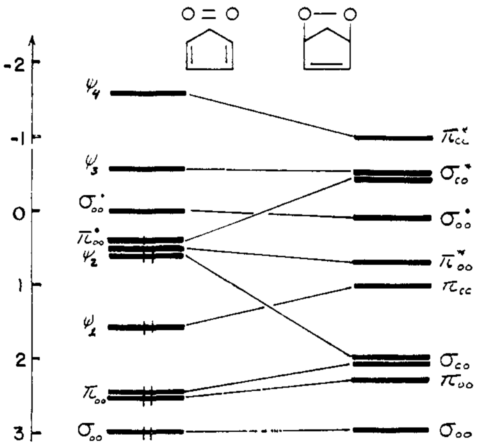


Figure 2. Orbital correlation diagram for the concerted addition of molecular oxygen to cyclopentadiene. $\psi_1 \cdots \psi_4$ are molecular orbitals of cyclopentadiene, π_{OO}, π_{OO}^*, σ_{OO}, σ_{OO}^* are oxygen orbitals, and σ_{CO}'s are linear combinations of two interacting σ_{CO} orbitals. Orbital energies are in units of β.

tion diagram for the addition of O_2 to cyclopentadiene is entirely straightforward and the results are given in Figure 2. The parameters which we used in this and subsequent orbital correlation diagrams are given in Table II.

Table II. Parameters Used in Molecular Orbital Calculations

$\alpha_O = \alpha_C + 1.5\beta$	
$\alpha_C = 0$	
$\beta_{CO}(\pi) = 1.5\beta$	$\beta_{CC}(\sigma) = 1.5\beta$
$\beta_{CC}(\pi) = \beta$	$\beta_{CO,CO} = 0.3\beta$ (dioxetane)
$\beta_{OO}(\pi) = \beta$ (0.8β in dioxetane)	$\beta_{CO}(\sigma) = \beta$
	$\beta_{OO}(\sigma) = 1.5\beta$ (1.4 in dioxetane)

Depending upon the type of calculation carried out, a wide range of values for parameters have been used in MO calculations.[33] We chose the values α_O, β_{CO}, and β_{OO} so that they would approximately reproduce the results obtained from extended Hückel calculations on ethylene and oxygen and formaldehyde.[16] Other parameters were chosen so that the relative stabilities of the various species would be in agreement with thermochemical data. Some of the β values for the dioxetane were reduced in order to take into account ring strain. Since the choice of parameters in our work, as in others,[33] is somewhat arbitrary, we should point out that any conclusions which depend delicately upon the exact values assigned to the MO parameters must be regarded with some suspicion. Correspondingly, results which are relatively insensitive variations in the parameter values may be accepted with considerably more confidence.

Using the orbital correlation diagram, symmetries can be assigned to the reactant and product state of interest. The ground state of the acceptor–oxygen complex [$^3O_2$ + diene] and the three low-lying excited states [$^1O_2$ ($^1\Delta$ or $^1\Sigma$) + diene] are all symmetric with respect to the assumed plane of symmetry in the transition state. The ground singlet state of the product and its lower excited singlet and triplet states [electronic configuration ($\cdots\pi_{OO}^{*1}\sigma_{OO}^{*1}$)] are also symmetric states, as is the ex-

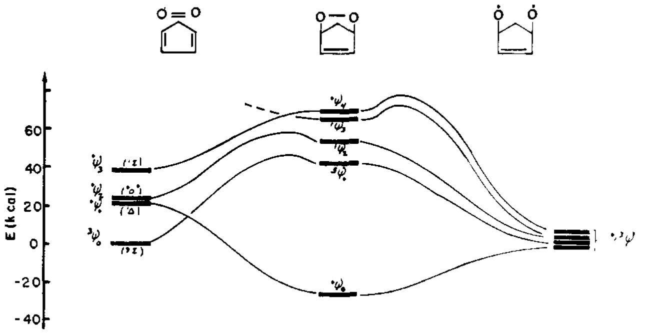


Figure 3. Left side: State correlation diagram for the concerted addition of molecular oxygen to cyclopentadiene. The states of molecular oxygen in the oxygen–diene complex have been indicated in parentheses. Right side: State correlation diagram depicting the decomposition of the endoperoxide II by cleavage of the O–O bond.

cited singlet state arising from a $\pi_{OO}^* \rightarrow \sigma_{CO}^*$ promotion. With the assignment of spin and symmetry, application of the noncrossing rule immediately allows us to decide which reactant and product states correlate with one another. To determine *how* these states correlate with one another, however, requires some care in using the orbital correlation diagram.

Our initial consideration of the effect of removing the degeneracy of the π_x^* and π_y^* orbitals on the states of oxygen revealed that the behavior of those reactant states of the oxygen–acceptor complex which arise from the interaction of the acceptor with the $^3\Sigma$ state, or one of the $^1\Delta$ states of oxygen could be obtained simply by assigning one electron to each of the π_x^* and π_y^* orbitals of oxygen and adding up orbital energies for all occupied orbitals.

According to the orbital correlation diagram given in Figure 2 then, the ground state ($^3\Psi_0$) of the [O_2–acceptor] complex has an electronic configuration ($\cdots\psi_1^2\psi_2^2\pi_x^{*1}\pi_y^{*1}$). As molecular oxygen is forced to cycloadd to the diene, this initial state will attempt to correlate with an excited triplet state of the product which has an electronic configuration ($\cdots\sigma_{CO}^2\pi_{CC}^{*2}\pi_{OO}^{*1}\sigma_{CO}^{*1}$). As a result of the crossing of the σ_{OO}^* and π_{OO}^* orbitals, however, the correlation will ultimately be with the lower triplet state of the product ($^3\psi_1$) which has an electronic configuration ($\cdots\sigma_{CO}^2\pi_{CC}^2\pi_{OO}^{*1}\sigma_{OO}^{*1}$) as shown in Figure 3. The reactant state arising from the interaction with $^1\Delta^*$ oxygen behaves like the ground state, and it too passes through a maximum in energy before correlating with the first excited singlet state of the product ($^1\psi_2$). To predict how the $^1\psi_1$ (Δ) state of the reactant (complex between $^1\Delta$ state of oxygen and ground state diene) behaves, we note that the behavior of the π_x^* and π_y^* orbitals appears to be similar to case I shown in Figure 1. Judging from this, and the behavior of the $^3\psi_0$ state, we anticipate that initially the $^1\psi_1$ (Δ) state of the reactants will be little changed in energy by small displacements along the reaction coordinate, but ultimately it will be stabilized and correlate exothermically with the ground state of the product as shown in Figure 3. It should be noted that this conclusion is insensitive to wide variations in the choice of MO parameters and may therefore be taken as a strong prediction of the theory. Finally, the $^1\psi_3$($^1\Sigma$) state of the reactant formed by the interaction of $^1\Sigma$ with the ground-state diene correlates endothermically with a relatively energetic excited state of the product.

The information contained in the state correlation diagram allows us to make the following predictions regarding the cycloaddition of oxygen to dienes.

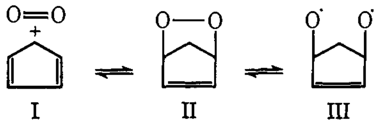
(i) Under normal conditions $^3\Sigma$ is not expected to cycloadd to dienes since interaction of $^3\Sigma$ oxygen with a ground-state diene with $^3\Sigma$ oxygen leads to a triplet state complex which correlates endothermically with an *excited* triplet state of the product.

(ii) $^1\Delta$ is expected to cycloadd since this leads to a reactant state which correlates exothermically with the *ground* state of product. From a simplified point of view, the cycloaddition of $^1\Delta$ is allowed because the electron that initially starts out in the $\pi_{OO}{}^*$ orbital which becomes destabilized in the course of product formation can be transferred to the other $\pi_{OO}{}^*$ orbital which is actually stabilized by product formation.

(iii) The low-lying excited states $^1\psi_2(\Delta^*)$ and $^1\psi_3(^1\Sigma)$, which arise from the interaction of $^1\Delta^*$ and $^1\Sigma$ oxygen with a ground-state diene, correlate endothermically with high-energy excited states of the product; hence, $^1\Delta^*$ and $^1\Sigma$ are not expected to react in concerted addition reactions.

These theoretical predictions are in good accord with the experimental observations that *cis*-dienes (i) are relatively unreactive toward ground-state oxygen at room temperature,[7,9] (ii) readily cycloadd to $^1\Delta$ even at low temperatures,[9,11] and (iii) appear to be unreactive toward $^1\Sigma$, although the experimental evidence is difficult to obtain in view of the fact that $^1\Sigma$ is apparently easily deactivated to $^1\Delta$ by intermolecular collision with even inert acceptors.[39]

4. Thermochemical and Photochemical Properties of Endoperoxides. Before considering other reactions of oxygen we digress at this point to examine the photochemical and thermochemical properties of endoperoxides which are formed by cycloaddition of molecular oxygen to dienes. At least two different decomposition modes must be considered: (i) loss of molecular oxygen in a process which is similar to the reverse of the formation process, and (ii) cleavage of the O–O bond.[40,41] The state correlation diagram which we used to discuss the cycloaddition reaction of oxygen to the diene to form the endoperoxide can also be used to treat the reverse reaction.



I II III

The orbital diagram for the cleavage reaction is shown in Figure 4 and this was then used to construct the state correlation diagram for the O–O cleavage reaction depicted on the right-hand side of Figure 3. The ground-state electronic configuration of the diradical III was taken to be $(\cdots\pi_{CC}{}^2P_O{}^6)$ in order to maintain all atoms neutral. As a consequence of this choice, the ground state of the diradical (probably a triplet state) is nearly degenerate in energy with a number of low-lying excited singlet and triplet states as indicated in the right-hand side of Figure 3.

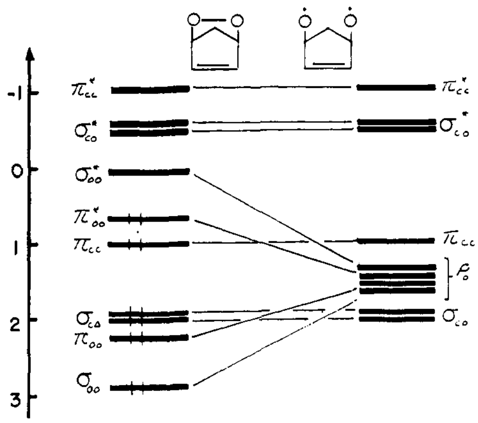
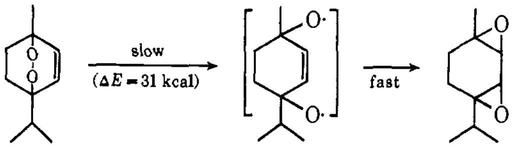


Figure 4. Orbital correlation depicting the decomposition of the endoperoxide II by cleavage of the O–O bond. Orbital energies are in units of β.

Based on the completed state correlation diagram given in Figure 3, the following predictions regarding the thermochemical and photochemical properties of the endoperoxide II can be made.

Thermochemical Properties. Thermal dissociation leading to diradical formation will probably be favored over thermal dissociation into parent hydrocarbon and molecular oxygen simply because the activation energy for the O–O cleavage ($\Delta E \simeq 32$ kcal) appears to be lower than for the dissociation reaction ($\sim$38 kcal) judging from Figure 3. The uncertainty in this prediction is due to the problem of accurately predicting where the curves for $^1\psi_1(^1\Delta)$ and $^3\psi_0(^3\Sigma)$ states cross and estimating the stability of the endoperoxide relative to initial reactants.

In agreement with these predictions, Boche and Runquist recently found in their examination of the kinetics of the homolytic cleavage of the O–O bond in ascaridole (IV) that the activation energy was $\sim$31 kcal.[41] Although homolytic cleavage of the O–O band is the major pathway for thermal decomposition of ascaridole ($\sim$80%), some regeneration of parent hydrocarbon and molecular oxygen might be expected to occur, but this was not mentioned. Loss of molecular oxygen is expected to be more important in those endoperoxides which, upon loss of molecular oxygen, gain significant resonance stabilization. As we have discussed elsewhere,[15,16] resonance stabilization of the parent hydrocarbon is presumably the reason why endoperoxides of many polycyclic aromatic hydrocarbons are observed to thermally decompose by loss of molecular oxygen, rather than by O–O bond cleavage.[9]



IV V

Photochemical Properties. The first excited singlet and triplet states [electronic configuration $(\cdots\pi_{CC}{}^2\text{-}\pi_{OO}{}^{*1}\sigma_{OO}{}^{*1})$] of II are expected to decompose by cleavage of the O–O bond since these states correlate smoothly and exothermically with low-lying states of the diradical. Decomposition into parent hydrocarbon and molecular oxygen is prevented by the appearance

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(39) E. A. Ogryzlo, ref 15, p 133.
(40) E. K. Nelson, *J. Am. Chem. Soc.*, 33, 1404 (1911); 35, 84 (1913).
(41) J. Boche and O. Runquist, *J. Org. Chem.*, 33, 4285 (1968).

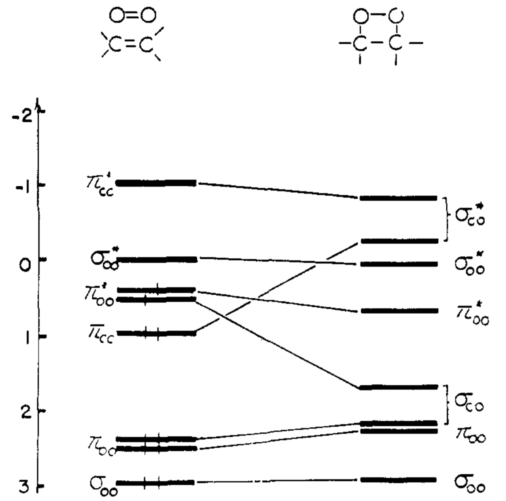
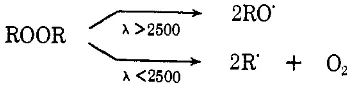


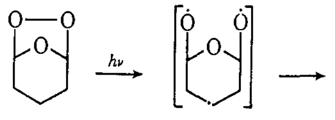
Figure 5. Orbital correlation diagram for the concerted addition of molecular oxygen to an olefin to form a dioxetane. Orbital energies are in units of β.

of energy barriers in the excited-state potential energy curves. As examination of Figures 2–4 reveals, this energy barrier arises from the fact that promotion of an electron from a π_{OO}^* to a σ_{OO}^* orbital weakens the O–O bond, but not the relatively strong C–O bond.

Promotion from a π_{OO}^* to a σ_{CO}^* orbital, however, has the opposite effect, in that the C–O bond is weakened and the O–O bond is actually strengthened. Consequently, excitation to the excited singlet state ${}^1\psi_4$ with electronic configuration $(\cdots\pi_{OO}{}^{*1}\sigma_{CO}{}^{*1})$ is expected to cause dissociation into parent hydrocarbon and ${}^1\Sigma$ oxygen.

While we have little information of the photochemical properties of II, or similar endoperoxides, there are fragmentary data on the properties of some simple alkyl peroxides and the ozonide (VI).[42,43]





VI VII

Insofar as low-lying excited states are concerned, the state correlation diagrams for cyclic and linear peroxides, and even ozonides, should be rather similar, and it is interesting to note that excitation of either VI or alkyl peroxides, with light of wavelength longer than about 3000 Å, produces homolytic cleavage of the O–O bond.[42,43] Perhaps more interesting is the observation that with very short wavelength excitation (λ 1900–2300 Å) the alkyl peroxides lose molecular oxygen.[42]

While our theoretical predictions regarding the behavior of the simple endoperoxides have not been fully tested, the properties of these closely related compounds appear to provide at least a partial confirmation of our predictions. Comprehensive testing of the theory will have to await an investigation of the wavelength dependence of the photodecomposition of compounds such as ascaridole or the endoperoxides of other cyclic dienes.

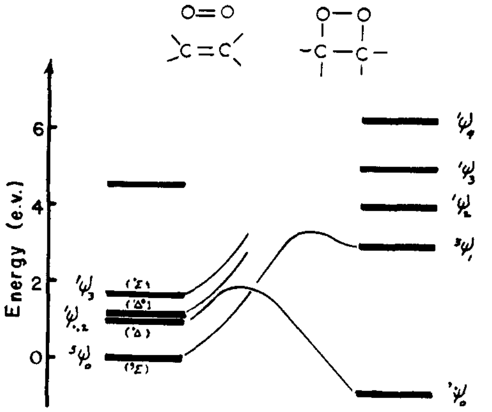
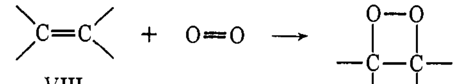


Figure 6. State correlation diagram for the concerted addition of molecular oxygen to an olefin to form a dioxetane.

With this discussion of the 1,4 cycloaddition of oxygen to dienes, we now turn to an examination of another type of reaction which we believe to be characteristic of singlet oxygen, namely 1,2 cycloaddition to olefins.

5. 1,2 Cycloaddition of Oxygen to Olefins. If molecular oxygen were to cycloadd to an isolated olefin (VIII), one possible product would be a dioxide or a dioxetane (IX). Dioxetanes have often been proposed as intermediates in chemiluminescent reactions,[17–19] but their involvement in singlet-oxygen reactions seems to have been taken less seriously.[1,7,10,11,44] In recent work, however, we have obtained chemical evidence that dioxetanes are indeed intermediates in the reaction of singlet oxygen with olefins.[45] To explore this reaction we have constructed the orbital and state correlation diagrams for the concerted addition of oxygen to an olefin, and these results are presented in Figures 5 and 6. In constructing the state correlation diagram, we assumed that the strain energy associated with the formation of the dioxetane ring is on the order of 20 kcal, in which case the dioxetane is stable by only 12 kcal with respect to ground-state oxygen and parent olefin.



VIII IX

From the state correlation diagram it is evident that there are certain parallels between the reaction of oxygen with olefins and dienes, in the following respect. Those reactant states which arise from the interaction of the olefin with ${}^3\Sigma$, ${}^1\Delta^*$, and ${}^1\Sigma$ oxygen correlate endothermically with excited states of the product dioxetane. Hence oxygen in any of these three states is not expected to undergo concerted addition to an olefin. The same results were obtained in the case of oxygen addition to a diene.

The selection rules governing the reaction of ${}^1\Delta$ oxygen with an olefin are less certain since they depend rather sensitively on the relative energies of the π_{CC} and

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[42] See, for example, J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley & Sons. Inc., New York, N. Y., 1966, Chapter 5.

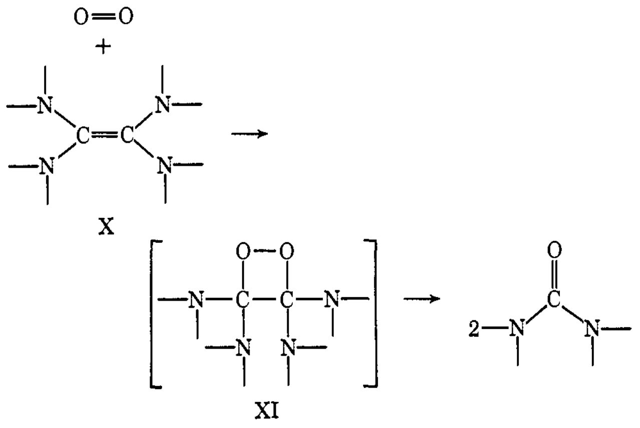
[43] P. R. Story, W. H. Morrison, T. K. Hall, J. C. Farine, and C. E. Bishop, *Tetrahedron Letters*, **29**, 3291 (1968).

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

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

π_{OO}^* orbitals. The initial complex between $^1\Delta$ oxygen and ground-state olefin would have an electronic configuration $(\cdots\pi_{CC}{}^2\pi_{OO}{}^{*2})$, and this state attempts to correlate with a highly excited state of the dioxetane product with an electronic configuration $(\cdots\sigma_{CO}{}^2\sigma_{CO}{}^{*2})$. As a result of the crossing of the π_{CC} and π_{OO}^* orbitals, however, there will be a change in the electronic configuration, somewhere during the course of the reaction from the initial $(\cdots\pi_{CC}{}^2\pi_{OO}{}^{*2})$ configuration to $(\cdots\sigma_{CO}{}^2\pi_{OO}{}^{*2})$ which is the ground-state configuration of the dioxetane. Whether or not there is an activation energy for the 1,2 addition of $^1\Delta$ to an olefin depends upon the relative energies of the π_{CC} and π_{OO}^* orbitals in the free molecule, and this in turn is directly related to the π-ionization potential of the olefin. While it would be difficult at this point to predict the absolute magnitude of the activation energies, we can predict that molecules which have lower π-ionization potentials, *i.e.*, higher energy occupied π_{CC} orbitals, should be more reactive with singlet ($^1\Delta$) oxygen. In fact, if the π_{CC} orbital could be raised above the π_{OO}^* orbitals, by appropriate substitution of electron-donating substituents, then the cycloaddition reaction with $^1\Delta$ oxygen would be thermally allowed. To test these notions we have plotted in Figure 7 the relative rates of photooxidation of substituted olefins and cyclohexenes as a function of their π-ionization potentials. Within a series of related molecules we find that there is indeed a good correlation between ionization potential and reactivity toward singlet oxygen. While we take this as evidence in support of the intermediacy of dioxetanes in the reaction of singlet oxygen with olefins, these data alone do not exclude other possible reaction mechanisms.

Although $^3\Sigma$ oxygen is generally not expected to cycloadd to olefins, conceivably, through addition of appropriate substituents, it would be possible to destabilize the π_{CC} orbital to such an extent that even the reaction with $^3\Sigma$ oxygen could take place. This, apparently, is what happens in the autooxidation of tetrakis(dimethylamino)ethylene (X) which is believed to occur *via* formation of a dioxetane intermediate (XI) as indicated below.[46]


X

XI

There is one final point in connection with the role of dioxetane intermediates in singlet-oxygen reactions which needs to be mentioned. In many of the reactions of singlet oxygen with olefins which have been studied so far, carbonyl products, which we suggest arise from formation of dioxetanes, are not the major oxygenation products.[7,11,20] Instead, with olefins which have allylic hydrogens the products are often allylic hydroperoxides, and these are generally believed to be formed by an "ene" mechanism as indicated below.[2,7,11,20,44]

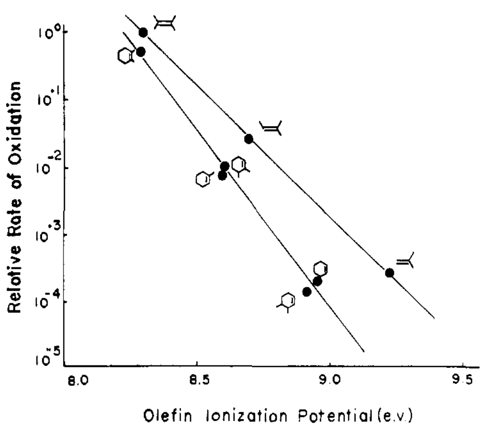
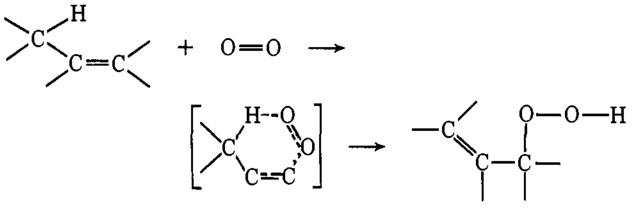
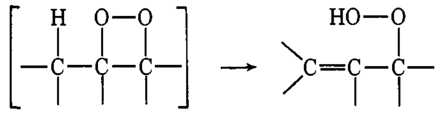


Figure 7. Semilog plot of the relative rate of photooxidation of olefins as a function of their ionization potential. Rate data taken from ref 4 and 11. Ionization potential data taken from K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1962).

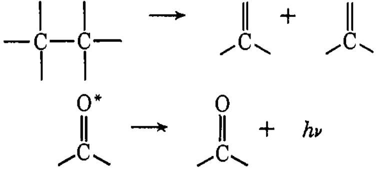


Our work[45] and the recent work of Kopecky[47] suggest an alternative mechanism for the formation of allylic hydroperoxides, namely, by a stereospecific intramolecular hydrogen abstraction from an intermediate dioxetane.



Because of the lack of symmetry, theoretical exploration of these two different pathways for formation of allylic hydroperoxides is difficult and will have to await computer calculations. The available experimental data do not allow us to distinguish between these two mechanisms.[45]

6. Thermochemical Properties of Dioxetanes. In many chemiluminescent systems it is believed that dioxetane intermediates are involved, and that chemiluminescence arises from formation of electronically excited carbonyl products during the decomposition of the dioxetane.[17-19,48-50] The experimental observations suggest the following mechanism.



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

(47) K. K. Kopecky, unpublished results.

(48) F. McCapra, D. G. Richardson, and Y. C. Chang, *Photochem. Photobiol.*, **4**, 1111 (1965).

(49) J. P. Paris, *ibid.*, 4, 1059 (1965).

(50) W. H. Urry and J. Sheeto, *ibid.*, **4**, 1067 (1965).

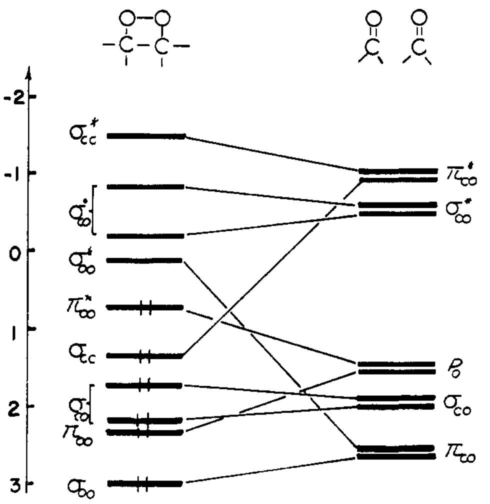


Figure 8. Orbital correlation diagram depicting cleavage of dioxetane IX.

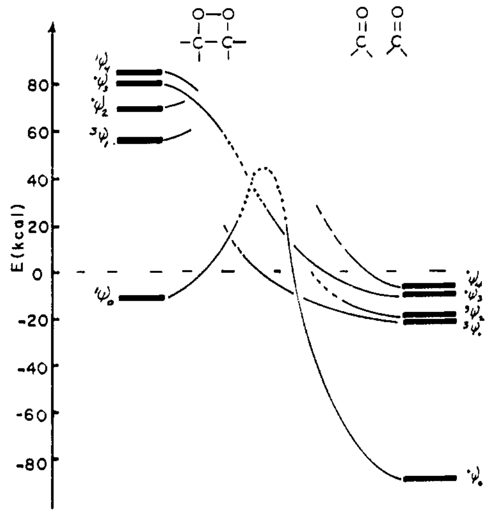


Figure 9. State correlation diagram depicting cleavage of dioxetane IX.

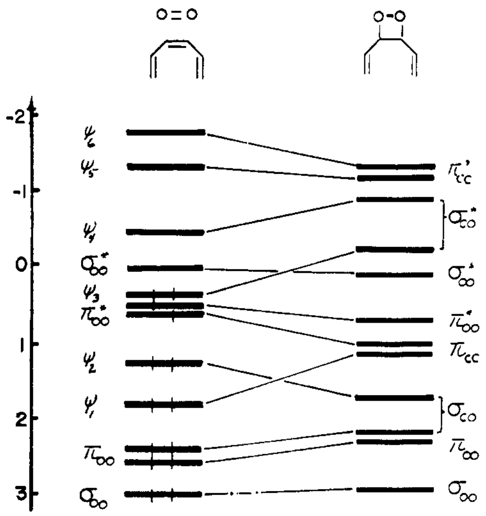
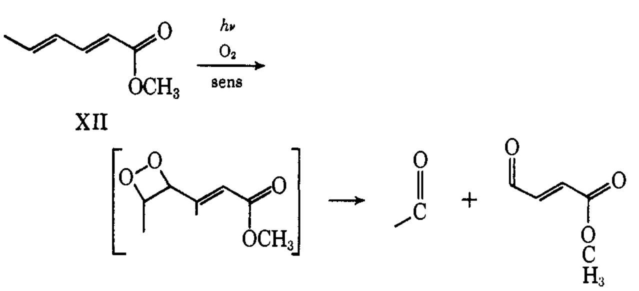


Figure 10. Orbital correlation diagram for the 3,4 addition of oxygen to a triene.

To explore this interesting possibility we have constructed the orbital and state correlation diagrams for the cleavage reaction, and these results are presented in Figures 8 and 9. According to the orbital correlation diagram, the ground-state electronic configuration of the dioxetane ($\cdots\sigma_{CC}{}^2\pi_{OO}{}^{*2}$) correlates with a highly excited electronic state of the carbonyl products. (This was first suggested in a communication by McCapra.[19]) Some of the lowest excited states of the dioxetane, on the other hand, are stabilized by ring cleavage, and as a consequence of this, there is a crossing of curves in the state correlation diagram which might allow the dioxetane to go over to an excited singlet state of the product. While the details of the curve crossings are uncertain, it is clear that the state correlation diagram for this reaction offers an interesting possible explanation of how chemiluminescence might occur.

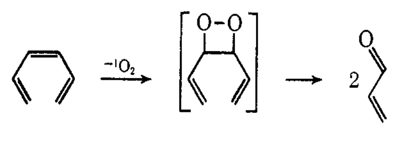
7. 1,2 *vs.* 1,4 Cycloaddition of Oxygen to Conjugated Dienes. With *cis*-dienes 1,4 addition is favored over 1,2 addition because of the possibility of activation energy for the latter reaction. With *trans*-dienes and polyenes where 1,4 addition is sterically not possible, 1,2 or 3,4 addition may become possible. It is interesting to note that the sensitized photooxygenation of the diene methyl sorbate (XII) does lead to the products expected from the cleavage of the dioxetane intermediate.[11]



XII

In other singlet-oxygen reactions with dienes, allylic hydroperoxides are the major products, but as we mentioned above, it is not clear at present whether these arise from an ene mechanism or from intramolecular hydrogen abstraction from a dioxetane intermediate.

With trienes, $^1O_2$ might react by a 3,4 cycloaddition as indicated below.



To examine this possibility, we have constructed the orbital correlation diagram for the 3,4 addition reaction, and these results are presented in Figure 10. Because of the location of the ψ_8 orbital slightly above the antibonding $\pi_{OO}{}^*$ orbitals of oxygen, it appears from this diagram that the reaction with $^1\Delta$ could be thermally allowed. Because of the low symmetry of the transition state the 1,2 addition to a triene has not yet been treated so that we are unable at this time to compare 1,2 with 3,4 addition.

8. Comparison between Singlet-Oxygen Reactions and Olefin Reactions. The Woodward-Hoffmann Rules. In earlier review articles on the chemistry of singlet oxygen it has been noted that there are interesting parallels between the 1,4 cycloaddition of singlet oxygen to *cis*-dienes and Diels-Alder reactions in which an olefin acts as the dieneophile.[9,11,20] In view of these

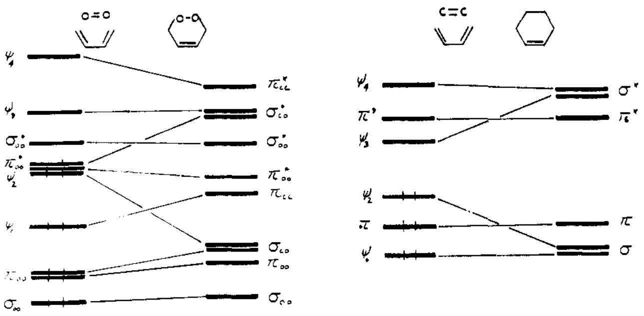


Figure 11. A comparison of the orbital correlation diagrams for the addition of oxygen to a *cis*-diene and ethylene to a *cis*-diene.

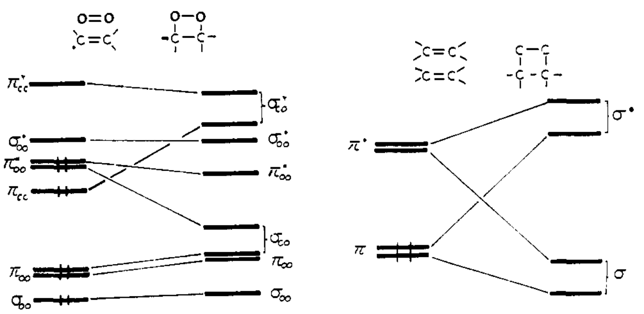


Figure 12. A comparison of the orbital correlation diagrams for the addition of oxygen to an olefin, and of ethylene to an olefin.

parallels it was further suggested that the Woodward–Hoffmann selection rules which had been developed to treat thermal cycloaddition reactions should also be applicable to the analogous singlet-oxygen reactions.[11]

In order to explore this latter point, we have compared, in Figure 11, the orbital correlation diagrams for the cycloaddition of oxygen to a 1,3 *cis*-diene with the corresponding diagram for the ethylene + diene reaction. This latter reaction is clearly expected to be thermally allowed, and so is the corresponding singlet-oxygen reaction. The orbital correlation diagrams for the oxygen + ethylene and the ethylene + ethylene cycloaddition reactions are compared in Figure 12.[11] While it is obvious that the thermal ethylene + ethylene reaction requires a very large thermal activation energy, the selection rule on the addition of singlet oxygen to olefins is less obvious. As our earlier discussion indicated, the O_2 + olefin reaction may or may not be thermally forbidden depending upon just where the highest π_{CC} orbital of the olefin lies with respect to the $\pi_{OO}{}^*$ antibonding orbitals of oxygen. Olefins which have low ionization potentials may cycloadd to singlet oxygen with essentially no thermal activation energy being required, whereas reaction with olefins which have higher ionization potentials (IP) will be thermally forbidden.

Thus, although the correlation diagrams for reactions involving oxygen and those involving ethylene are somewhat different, there is a rough parallelism in the selection rules in that 1,4 cycloaddition of oxygen to *cis*-dienes is expected to be thermally allowed, but 1,2 addition to isolated olefins may or may not be thermally forbidden depending upon the IP of the olefin.

Summary

We can summarize the results of our theoretical investigation of oxygen reactions as follows.

$^3\Sigma$ and $^1\Sigma$ oxygen are both expected to be unreactive in cycloaddition reactions with olefins, dienes, and polyenes. This selection rule arises from the fact that the reactant states formed by interaction of oxygen in one of these states with the acceptor correlates exothermically with excited states of the product. Exceptions to this rule are expected in those cases where the oxygenation product is exceptionally stable with respect to the reactants. The autooxidation of tetrakis(dimethyl)ethylene is cited as a possible example of this latter case.

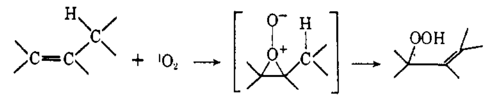
$^1\Delta$ oxygen is expected to undergo an allowed 1,4 addition to *cis*-dienes. The 1,2 addition of $^1\Delta$ oxygen to olefins may or may not be allowed, depending upon whether the olefin has a low, or high π-ionization potential. It appears, on theoretical grounds, that formation of 1,2 dioxides (dioxetanes) may be involved in the addition of singlet oxygen to olefins, and this is supported by recent experimental observations.[45,47]

A comparison of the oxygen reactions with the corresponding reactions of ethylene allows us to examine the relation between the Woodward–Hoffmann selection rules for the olefin reactions and the selection rules for the singlet oxygen reactions. While there are interesting parallels there are differences which depend upon the relative energies of the olefin and oxygen orbitals, and the fact that oxygen brings to the reaction partially filled antibonding π^* orbitals.

Examination of the cycloaddition products of the oxygen reactions reveals the following. 1,4 endoperoxides are expected to be thermally unstable with respect to cleavage of the O–O bond and possibly with respect to loss of molecular oxygen and re-formation of the parent hydrocarbon. The photodecomposition of endoperoxides is predicted to be wavelength dependent. The lower lying excited states are predicted to decompose by cleavage of the O–O bond, whereas the higher lying excited states are expected to lose molecular oxygen. Dioxetanes are shown to be metastable with respect to cleavage into carbonyl products, and the correlation diagram suggests that it may be possible to generate the carbonyl products in excited states.[51]

Acknowledgments. I am indebted to Professor Phillip Radlick and to Dr. William Fenical of this Chemistry Department for numerous helpful discussions and suggestions. The support of the American Cancer Society (California Division) and the U. S. Army Research Office is most gratefully acknowledged.

(51) Note Added in Proof. Recently[52] we have examined the concerted addition of singlet oxygen to olefins to form perepoxides (XII).



XII

In contrast to the 1,2-cycloaddition reactions in which dioxetanes are formed, the formation of perepoxides by the concerted addition of singlet oxygen to olefins appears to be an allowed reaction. With olefins that have a high ionization potential perepoxide formation may effectively compete with dioxetane formation. These considerations coupled with Kopecky's recent observation that the dioxetane of tetramethylethylene decomposes to carbonyl fragments, and not to the rearranged allylic hydroperoxide,[53] suggest that perepoxides rather than dioxetanes are intermediates in the formation of allylic hydroperoxides. Additional chemical evidence for this suggestion will appear shortly.[54]

(52) D. R. Kearns, W. Fenical, and P. Radlick, *Trans. N. Y. Acad. Sci.*, in press.

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

(54) W. Fenical, D. R. Kearns, and P. Radlick, *J. Am. Chem. Soc.*, **91**, 3396 (1969).