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The Mechanism of the Ene Reaction of Singlet Oxygen with Olefins[1a]

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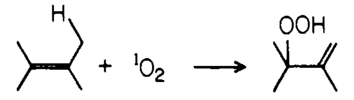
Abstract: Ab initio calculations (correlated wave functions using double ζ basis plus polarization functions) on the reaction of $^1O_2$ with ethylene are combined with thermochemical methods of estimating substituent effects to predict the energetics for proposed intermediates in the addition of $^1O_2$ to substituted olefins. The results include estimates of peroxy biradical, open 1,4-zwitterion, and perepoxide intermediates. It is concluded that the major reaction pathway involves the biradical intermediate, although certain solvents and substituents can greatly enhance the zwitterion character of this state. Detailed comparisons of the theoretical predictions to experimental results show that many aspects of the stereospecificity and regiospecificity can be understood in terms of the biradical intermediate or transition state.

I. Introduction

The ene reaction of singlet oxygen with olefins is of synthetic,[2] environmental,[3,4] and biochemical[5-8] significance. As such, it has been the focus of intensive experimental and theoretical studies extending over the last 20 years. The mechanism of this reaction has become an increasingly controversial question with numerous conflicting results and interpretations appearing in the literature (vide infra).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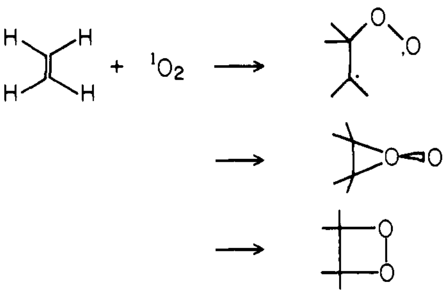
We have previously reported[9] extensive ab initio studies (large basis set, generalized valence bond, and configuration interaction wave functions) on key intermediates in proposed $^1O_2$-olefin reaction mechanisms. Analogous theoretical calculations on the bond energies of simple molecules [e.g., D(Me-Me), D(Me-OH), D(HO-OH)] were shown to lead to an accuracy of ±5% (0-4 kcal). However, the level of calculation necessary for this accuracy is such that it is currently impractical for applications to a large number of substituted olefins.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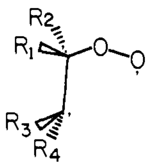
In this paper we report an extrapolation of our theoretical work to reactions of $^1O_2$ with substituted olefins. To do this, we combine the ab initio results with thermochemical estimates of substituent effects in a manner similar to that developed by Benson.[10] Using this procedure, the key energetic quantities for such possible intermediates as **1-3** are estimated. These energetics lead to a number of intriguing interpretations and predictions for both gas-phase and solution-phase $^1O_2$-olefin chemistry.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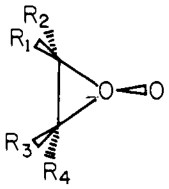
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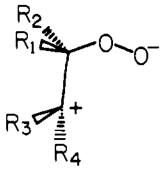
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From this analysis, we conclude that the gas-phase mechanism involves a biradical **1** with (at most) a small barrier for decomposition to reactants and (at most) a small barrier to hydrogen abstraction forming the ene product. Depending upon the substituents, the gas-phase biradical, **1**, will incorporate varying degrees of zwitterionic character. Furthermore, in a sufficiently polar solvent, the zwitterionic character can dominate.

The organization of this paper is as follows. Section II contains a summary of the key experimental and theoretical results. In section III, we present a description of the procedure used for the thermochemical estimates together with derivations of the necessary parameters. In section IV we use these theoretical methods to examine the addition of $^1O_2$ to alkyl- and methoxy-substituted olefins and to compare these results with the relevant experimental studies.

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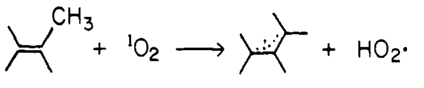
II. Summary of Previous Results

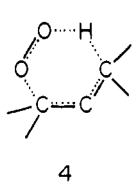
A. Experimental Studies. In this section we briefly summarize some of the important experimental results on the $^1O_2$-olefin ene reaction.

Early work by Foote,[11] Schenck,[12] and Nickon[13] showed that the double bond in the product hydroperoxide is invariably shifted to a position adjacent to the original double bond, as shown in (1). These results eliminated mechanisms such as (5),



(5)

involving an initial hydrogen abstraction, to form an allyl radical, followed by radical recombination. Thus, Nickon et al.[13] concluded that the mechanism must be of a cyclic nature **4.** They noted, however, that these results do not yield any information concerning the timing of the formation of C–O and O–H bonds, and therefore could not exclude a nonconcerted mechanism involving any of several intermediates.



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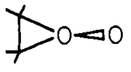
Later, Litt and Nickon[14] analyzed the rates and product distributions of several photooxidations in terms of six possible intermediates, **5–10.**



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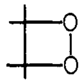

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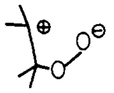

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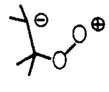

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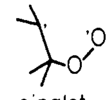

singlet

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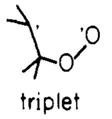


triplet

10

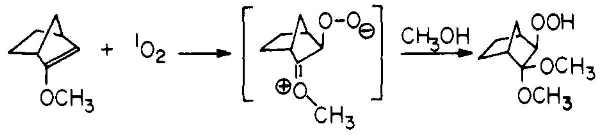
The perepoxide **5** was first proposed as an intermediate by Sharp.[15] Nickon, however, argued against the intermediacy of perepoxides, citing as evidence the product distributions from photooxidation of trimethylethylene.[14] Studies on the photooxidation of norbornene showed a lack of the carbonyl products expected from a dioxetane intermediate, **6**, and no evidence of carbonium-ion-like rearrangements. Thus, Nickon[14] concluded that neither **6** nor **7** is a likely intermediate. In addition, the higher reactivity of tri- and tetraalkyl-substituted olefins relative to mono- and disubstituted olefins was cited as evidence against the intermediacy of **8**. Foote[16] has also concluded that the zwitterionic intermediates, **5, 7,** and **8**, are not plausible owing to the lack of a correlation between the reaction rates and solvent polarity.

Nickon[14] and later Foote[16] and Kearns[17] have considered and ruled out the possibility of diradical intermediates. Nickon cited the lack of a detectable cis–trans isomerization of starting olefin as evidence against reversible formation of biradicals. Nickon also presented a detailed thermochemical and kinetic argument against irreversible diradical formation.

Foote[16a] and others[17] have cited the lack of Markownikoff and other substituent directing effects as evidence against a biradical intermediate. Foote[16b] has also interpreted the unusually low reactivity of 1-methylcyclohexene toward $^1O_2$ as evidence for participation of the C–H bond in the transition state. He concludes, however, that the degree of C–H bond breaking in the transition state is small.

Jefford[18–20] has recently reported an analysis of the reaction of $^1O_2$ with a series of substituted norbornenes and methylidenenorbornanes, the objective being to probe the nature of the transition state for hydroperoxidation. By comparing exo–endo rate constants of compounds with varying degrees of steric impedance, Jefford[18] concluded that $^1O_2$ does not simultaneously form C–O bonds with both ends of the double bond. Consequently, Jefford considers the intermediacy of a perepoxide as unlikely. He further noted that the steric evidence is most consistent with a one-step process in which significant dipolar character is developed in the early stages. Jefford also cites the small intermolecular deuterium isotope effects $(K_H/K_D = 1.14)$[18b] as evidence against significant participation of the C–H bond in the transition state and the dependence of product composition[21,22] on solvent as evidence *for* a dipolar transition state. The latter conflicts with the observations of Foote[12] and others[13] who have cited the lack of a solvent polarity dependence as evidence *against* a strongly dipolar transition state.

In their most recent work, Jefford et al.[20] cite the isolation of products incorporating methanol (solvent) as evidence for a zwitterionic intermediate (either a perepoxide or an open 1,4 zwitterion) in the addition of $^1O_2$ to 2-methoxynorborn-2-ene (eq 6).



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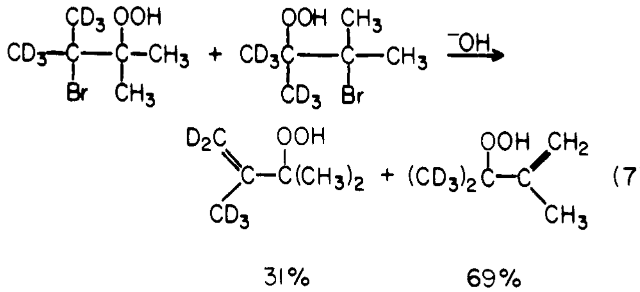
Kopecky[23,24] has recently reported the results of a novel approach to the question of perepoxide intermediates. In these experiments, a perepoxide is generated by treatment of a β-halo hydroperoxide with base and the resulting product distribution, (7) is shown to be different from the photooxidation results, (8). Thus, it was concluded that the perepoxide is not an intermediate in the latter process.



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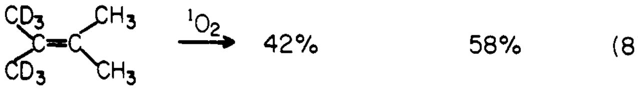

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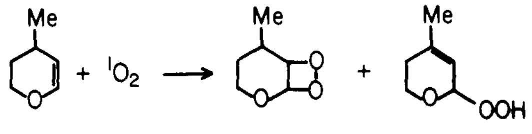
Several experimental studies have been interpreted to support the intermediacy of perepoxides. Recent experiments by McCapra[25] are in apparent conflict with the earlier work of both Nickon[14] and Jefford.[18] In reactions of camphenylidene–adamantane and adamantylidene–camphene with $^1O_2$, McCapra reports the isolation of products resulting from carbonium ion rearrangements. These results are interpreted to support the intermediacy of a perepoxide, or zwitterionic species.

Further evidence comes from an extensive study by Bartlett et al.[26] of tritium isotope effects on the reaction of $^1O_2$ with methyl dihydropyrans, **11.** In this work, the primary and secondary isotope effects are used to probe the interactions between various centers in the transition state(s) leading to both dioxetane, **12**, and allylic hydroperoxide, **13**, products. They conclude that the transition state leading to ene product, **13**,



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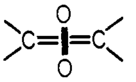
11 **12** **13**

is not a simple six-centered cyclic structure, **4**, and that the observed isotope effects are more consistent with the criss-cross transition state **14** of a classic $2_s + 2_a$ concerted cycloaddition.



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They further note that this probably leads to a perepoxide intermediate.

B. Theoretical Studies. In addition to the above experimental studies, a few theoretical efforts directed at elucidating the $^1O_2$-olefin reaction mechanisms have been reported. In 1971, Kearns[17] analyzed the various proposed modes of addition using orbital correlation diagrams. He concluded the preferred mode leads to formation of a perepoxide, **5**.

Fukui[27] has reported the results of semiempirical calculations, CNDO/2-CI, on these reactions from which he concluded that addition to form perepoxides is the favored mode. He notes, however, that the calculations indicate that the perepoxide is not a true minimum on the reaction path and, therefore, terms the perepoxide a quasi-intermediate. In addition, Fukui[28] has reported a HOMO-LUMO analysis (assuming a perepoxide-like transition state and incorporating intermolecular nonbonded attractions) which rationalizes the observed direction of addition of $^1O_2$ to unsymmetrical olefins.

Paquette[29] has noted a strong correlation between the reactivity of an olefin toward $^1O_2$ and the ionization potential of the olefin, the most reactive olefins being those with the lowest ionization potential. This trend was also rationalized using a HOMO-LUMO analysis with a perepoxide-like transition state. We note, however, that the assumption of a perepoxide is not crucial to this analysis.

The most extensive theoretical study published to date is that of Dewar and Thiel.[30] Using the semiempirical MINDO/3 method on the reaction of $^1O_2$ with ethylene and with several substituted olefins, Dewar concluded that in most cases this reaction proceeds through a discrete perepoxide intermediate. The only exceptions found were certain electron-rich olefins which were predicted to form the open zwitterionic intermediate, **7**, upon adding $^1O_2$. In the addition of $^1O_2$ to propene, the MINDO/3 calculations predict that addition to form the perepoxide is 16 kcal *exothermic* with a barrier to addition of 11 kcal. Subsequent rearrangement to propene hydroperoxide is predicted to proceed with a barrier of 21 kcal.

Ab initio calculations (GVB-CI) by Harding and Goddard[9] are in disagreement with both the CNDO and the MINDO results. The GVB-CI calculations place the perepoxide **5** 17 kcal *endo*thermic from ethylene plus $^1O_2$, well above the observed gas-phase activation energies for allylic hydroperoxidation (2-10 kcal).[31] The ab initio calculations also indicate the biradical species **9** to be 8 kcal below the perepoxide (or 9 kcal above the reactants). According to the ab initio GVB-CI results then, the biradical is an energetically permissible intermediate while the perepoxide is not. Finally, Harding and Goddard[32] have shown that certain unusual aspects of the stereochemistry of $^1O_2$ hydroperoxidation can be understood on this basis of a biradical mechanism and that the observed stereochemistry is *not* consistent with the perepoxide mechanism as suggested by Fukui.[28]

Table I. Carbon-Centered Radical Group Functions

bond energies[a]		group functions[b]	
$MeCH_2$-H	98.8	$C\cdot(H)_2(C)$	36.5
$(Me)_2CH$-H	94.5	$C\cdot(H)(C)_2$	37.5
$(Me)_3C$-H	92.7	$C\cdot(C)_3$	38.7
$MeOCH_2$-H	94.1	$C\cdot(O)(H)_2$	31.9
(MeO)(Me)CH-H	(89.8)[c]	$C\cdot(O)(C)(H)$	29.6
$(MeO)(Me)_2C$-H	(88.0)[c]	$C\cdot(O)(C)_2$	28.7

[a] From ref 10 except where noted. [b] Obtained using $G[C\cdot(X)(Y)(Z)] = G[C(H)(X)(Y)(Z)] + D_0 - 52.1$. [c] Estimated assuming bond energy lowering on methyl substitution identical with that for corresponding hydrocarbon.

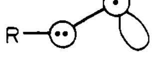
III. Energetic Estimates

As indicated in the Introduction, the approach here is to combine the results of the ab initio theoretical studies on the addition of $^1O_2$ to ethylene with standard thermochemical methods of estimating substituent effects to predict the energetics for reactions involving substituted olefins. In order to avoid ambiguities, we present here a detailed discussion of the methods and parameters used in this work.

A. Group Additivity Parameters. The method of group additivities (GA) has been developed and extensively tested by Benson and co-workers.[10] Benson has shown that for most compounds the GA method leads to $\Delta H_f°$ estimates with an accuracy of ±1 kcal/mol. Similar estimates for free radicals give heats of formation with a comparable accuracy. In the present work, we use the parameters of ref 10a, augmented (vide infra) with parameters from the ab initio calculations (for perepoxides) and from experiment (for radical centers).

The perepoxide parameters are derived using the calculated (GVB-CI) heat of formation of the parent perepoxide (51.6 kcal).[9] This gives an O-O bond energy of 40.6 kcal (relative to $O(^1D)$ and ethylene oxide) for the parent perepoxide which is assumed to be unchanged by substitution on the carbons. Thus, the heat of formation of a substituted perepoxide is obtained by adding 64.2 kcal to the estimated $\Delta H_f°$ of the corresponding epoxide. No corrections for nonbonded repulsions are made, although these are expected to favor placing the terminal oxygen on the least hindered side of the olefin.

The group additivity parameters for peroxy radicals are derived, assuming $D_0(ROO\text{-}H) = D_0(HOO\text{-}H) = 89.7$ kcal, for all saturated groups, R. In terms of group functions this can be expressed as $G[C(O_2\cdot)(X)(Y)(Z)] = G[C(O)(X)(Y)] + 16.8$. It is important at this point to note that there are two low-lying states of peroxy radicals (see section VB), a π^3 ground state, **15**, and a π^4 excited state, **16**. The above estimates apply to the π^3 ground state. Ab initio calculations[33] and experiments[34] on HO_2 indicate that the π^4 state is 20 kcal higher. For the processes addressed in this paper, then, the π^4 state of the peroxy radical should not play an important role.



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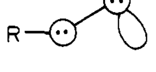

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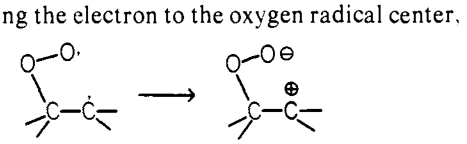
Finally, group functions for carbon-centered radicals are summarized in Table I. These are based on C-H bond energies (also listed in Table I) derived from the radical heats of formation of ref 10a. In these derivations, the value of $G[C\text{-}(C\cdot)(X)(Y)(Z)]$ is assigned to be equal to $G[C(C)(X)(Y)(Z)]$. Thus, the parameters in Table I together with the peroxy radical group functions are sufficient to estimate the heats of formation of the relevant biradicals.

Table II. Biradical–Zwitterion Separations (kcal/mol) for $R_1R_2CCH_2OO$[e]

R_1	R_2	biradical ΔH_f[a]	 IP	positive ion ΔH_f	ΔE $E_{zwit} - E_{birad}$
H	H	26.5	193[c]	220[b]	49
CH_3	H	17.6	170[c]	187	26
CH_3	CH_3	8.4	154[c]	162	10
HO	H	−18.5	155	136[d]	11
HO	CH_3	−29.3	145	115[d]	1

[a] Obtained from the heats of formation of ref 10 and the C–H bond energies of Table I. [b] From ref 36. [c] F. A. Houle and J L. Beauchamp, 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978; F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, to be submitted. [d] From J. F. Wolfe, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977). [e] Positive ΔE indicates that the biradical is lower.

B. Zwitterion Estimates. The 1,4 zwitterion **7** is an important proposed intermediate of $^1O_2$–olefin reactions. In order to estimate the energy of this species, we consider the process starting with the biradical, ionizing the carbon radical electron, and attaching the electron to the oxygen radical center, (10).

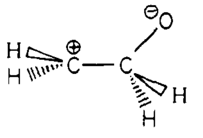

(10)

The energy for this process is then approximated with the equation

$$\Delta E(\text{kcal}) = \text{IP}(\text{C}\cdot) - \text{EA}(\text{O}\cdot) - 332.1/R \qquad (11)$$

where ΔE is the zwitterion–biradical energy separation (kcal/mol), IP(C·) is the estimated ionization potential (kcal/mol) of the carbon-centered radical (see Table II), EA(O·) is the estimated electron affinity (kcal/mol) of the oxygen-centered radical (18.5 kcal),[35] and R is the distance (Å) between the two radical centers (2.65 Å). The resulting zwitterion–biradical energy separations are given in Table II.

To test the validity of this relationship, we carried out a model calculation on the energy of a 1,3 zwitterion **17** relative to the corresponding biradical.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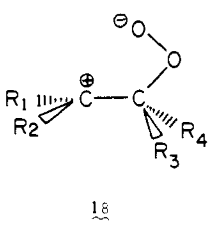
In this calculation (Appendix A) the ionization potential, electron affinity, and biradical–zwitterion separation are all calculated with the same quality GVB wave function.[37,38] The results are as follows: IP(C·) = 208.2 kcal, EA(O·) = 1.9 kcal, and $332.1/R$ = 139.5 kcal. Therefore, using (11), we obtain an excitation energy of ΔE = 66.8 kcal for the zwitterion state relative to the biradical state. For comparison, the calculated GVB excitation energy is 61.8 kcal, indicating an error, in the estimate, of 5 kcal. Thus, the estimated zwitterion energies are considerably less accurate than the biradical estimates; however, the error is sufficiently small that the predicted trends should be reliable. In particular, predictions concerning the preferred *direction* of addition to unsymmetrical olefins are expected to be quite accurate. The key assumption in this is that the relative energies of two zwitterions, for example, **18** and **19**, are dominated by the stability of the carbonium ion fragment.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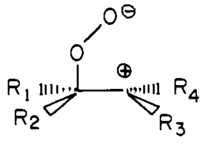
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Estimates of this kind indicate that the $^+CCOO^-$ zwitterions, **7**, are much more stable (~100 kcal) than $^-CCOO^+$ zwitterions, **8**. Therefore, the latter is not a likely intermediate and will not be considered further.

IV. Results and Comparison with Experiment

A. Electronic Structure of $^1O_2$. Before discussing the character of the O$_2$–olefin adducts, it is important to review the character of the states of O_2, particularly the $^1\Delta_g$ state. Letting π_{g+} and π_{g-} indicate (antibonding) π_g orbitals with angular momentum +1 and −1 with respect to the molecular axis, the simple MO descriptions of the low-lying states of O_2 are

$$\begin{aligned}
{}^3\Sigma_g{}^-&: \mathcal{A}\{\pi_{g+}(1)\pi_{g-}(2)\alpha(1)\alpha(2)\}\\
&= [\pi_{g+}(1)\pi_{g-}(2) - \pi_{g-}(1)\pi_{g+}(2)]\alpha(1)\alpha(2)\\
{}^1\Delta_{g+}&: \mathcal{A}\{\pi_{g+}(1)\pi_{g+}(2)\alpha(1)\beta(2)\}\\
&= \pi_{g+}(1)\pi_{g+}(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \qquad (12)\\
{}^1\Delta_{g-}&: \mathcal{A}\{\pi_{g-}(1)\pi_{g-}(2)\alpha(1)\beta(2)\}\\
&= \pi_{g-}(1)\pi_{g-}(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\\
{}^1\Sigma_{g+}&: \mathcal{A}\{\pi_{g+}(1)\pi_{g-}(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\}\\
&= [\pi_{g+}(1)\pi_{g-}(2) + \pi_{g-}(1)\pi_{g+}(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]
\end{aligned}$$

where $\mathcal{A}$ is the antisymmetrizer, the numbers in parentheses refer to electrons, the seven doubly occupied orbitals common to all states ($1\sigma_g$, $1\sigma_u$, $2\sigma_g$, $2\sigma_u$, $3\sigma_g$, $1\pi_{u+}$, and $1\pi_{u-}$) have been deleted, and normalization of the total wave function has been neglected.

The dependence of the orbitals π_{g+} and π_{g-} upon the rotation angle, ϕ, about the molecular axis is given by

$$\pi_{g+}(\pi, \phi, z) = f(\rho, z)e^{+i\phi}$$

$$\pi_{g-}(\rho, \phi, z) = f(\rho, z)e^{-i\phi}$$

where z is the distance along the axis and ρ is the distance perpendicular to the axis. An alternative choice of orbitals is to use cos ϕ and sin ϕ as the angular terms:

$$\pi_{gx}(\pi, \phi, z) = f(\rho, z)\cos\phi$$

$$\pi_{gy}(\rho, \phi, z) = f(\rho, z)\sin\phi$$

In terms of these orbitals, we can construct four wave functions

$$\begin{aligned}
{}^2\Sigma_g{}^-&: \mathcal{A}\{\pi_{gx}\pi_{gy}\alpha\alpha\} = (\pi_{gx}\pi_{gy} - \pi_{gy}\pi_{gx})\alpha\alpha\\
{}^1\Delta_{ga}&: \mathcal{A}\{\pi_{gx}\pi_{gy}(\alpha\beta - \beta\alpha)\}\\
&= (\pi_{gx}\pi_{gy} + \pi_{gy}\pi_{gx})(\alpha\beta - \beta\alpha)\\
{}^1\Delta_{gs}&: \mathcal{A}\{(\pi_{gx}\pi_{gx} - \pi_{gy}\pi_{gy})\alpha\beta\}\\
&= (\pi_{gx}\pi_{gx} - \pi_{gy}\pi_{gy})(\alpha\beta - \beta\alpha) \qquad (13)\\
{}^1\Sigma_g{}^+&: \mathcal{A}\{(\pi_{gx}\pi_{gx} + \pi_{gy}\pi_{gy})\alpha\beta\}\\
&= (\pi_{gx}\pi_{gx} + \pi_{gy}\pi_{gy})(\alpha\beta - \beta\alpha)
\end{aligned}$$

where the electron numbers have been dropped and the subscript s and a indicate wave functions that are symmetric and antisymmetric (respectively) with respect to the xz plane.

Substitution of the expression

$$\pi_{g\pm} = \frac{1}{\sqrt{2}}(\pi_{gx} \pm i\pi_{gy})$$

into the $^3\Sigma_g{}^-$ and $^1\Sigma_g{}^+$ wave functions of (12) leads directly to (13). The same substitution into the $^1\Delta_g$ states leads to

$$^1\Delta_{g+} = \frac{1}{\sqrt{2}}(^1\Delta_{gs} + i\,^1\Delta_{ga})$$
$$^1\Delta_{g-} = \frac{1}{\sqrt{2}}(^1\Delta_{gs} - i\,^1\Delta_{ga}) \qquad (14)$$

Since the two components of the $^1\Delta_g$ state are degenerate, either form ($^1\Delta_{g+}$ and $^1\Delta_{g-}$ or $^1\Delta_{gs}$ and $^1\Delta_{ga}$) is valid for the free unperturbed molecule.

Suppose now that the molecule is perturbed by the presence of another atom, for example, in the xz plane. The introduction of the third center splits the degeneracy of the $^1\Delta_g$ components and the choice of component wave functions is no longer arbitrary. In this case, the perturbed system still possesses a plane of symmetry (the xz plane) and, therefore, the eigenfunctions of this system must also be eigenfunctions of reflection through the xz plane. With this constraint, the only choice of component wave functions is $^1\Delta_{gs}$ and $^1\Delta_{ga}$, (13).

The $^1\Delta_{ga}$ and $^3\Sigma_g^-$ wave functions of (13) contain a singly occupied π_{gx} orbital and a singly occupied π_{gy} orbital (appropriately antisymmetrized). These wave functions both describe 1,2 biradicals, the difference being only in the spin pairing. Since these orbitals have zero overlap, the energy separation is twice the K_{xy} exchange integral with the triplet lower.

In order to analyze the character of the $^1\Delta_{gs}$ wave function, we first rotate the coordinate system 45° about the z axis and express the $^1\Delta_{gs}$ wave function in terms of the new coordinates, $\bar{x}$ and $\bar{y}$. Thus

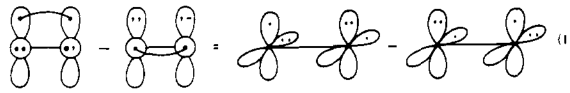
$$x = (\bar{x} + \bar{y})/\sqrt{2}$$
$$y = (\bar{y} - \bar{x})/\sqrt{2}$$

and in these coordinates the $^1\Delta_{gs}$ wave function becomes

$$^1\Delta_{gs}: = \mathcal{A}\{\pi_{g\bar{x}}\pi_{g\bar{y}}(\alpha\beta - \beta\alpha)\}$$
$$= (\pi_{g\bar{x}}\pi_{g\bar{y}} + \pi_{g\bar{y}}\pi_{g\bar{x}})(\alpha\beta - \beta\alpha) \qquad (15)$$

Comparing the $^1\Delta_{ga}$ wave function (13) and the $^1\Delta_{gs}$ wave function (15), it is clear that the $^1\Delta_{gs}$ is simply at 45° rotation of the $^1\Delta_{ga}$ and, therefore, both are singlet 1,2 biradicals.

In a valence bond wave function, the $^1\Delta_{gs}$ and $^1\Delta_{ga}$ states may be written schematically as (16) and (17) where in the left

$^1\Delta_{gs}$:

(16)

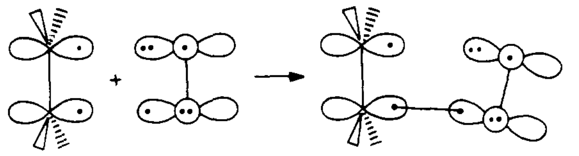
$^1\Delta_{ga}$:

(17)

drawing a circle represents a p orbital perpendicular to the plane and the right drawing is a three-dimensional perspective representation of the same wave function in the rotated coordinate system. In (16) and (17) the biradical character of the two wave functions is readily apparent.[39]

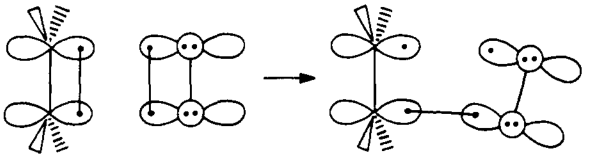
This biradical character of the $^1\Delta_g$ state invalidates the orbital correlation analysis[17] that led to the prediction of perepoxide intermediates. Implicit in the correlation analysis is the assumption of a reactant electronic structure involving only doubly occupied orbitals (analogous to one of the two resonance structures in the $^1\Delta_s$ wave function). The analysis presented here shows that such wave functions are not correct representations of the reactant $O_2(^1\Delta_g)$. Similarly, the orbital phase continuity analysis[41] of Yamaguchi et al.[42] does not apply since the overlap of the relevant reactant orbitals is zero, and therefore the relative phase is indeterminate.

B. Electronic Structure of the $^1O_2$–Olefin Adduct. Coupling one of the singly occupied orbitals of the $^1\Delta_{ga}$ state, (17), with a pπ orbital of an olefin leads to the π^3 state of the peroxy biradical, (18). In this olefin–oxygen adduct, the oxygen orbital


(18)

directed toward the carbon radical center is doubly occupied. Consequently (18) is prevented from closing directly to the [2 + 2] cycloaddition product, dioxetane. In order to ring close, it is necessary to orient (18) in such a way as to develop overlap between the two radical orbitals, leading to an additional barrier (~12 kcal for ethylene plus $^1O_2$) to dioxetane formation.

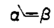
Addition of the $^1\Delta_s$ state of O_2 to an olefin leads to the π^4 state of the peroxy biradical, (19). The orbital phase continuity


(19)

arguments of Yamaguchi[42] *do apply* to this state and indicate that the concerted [$2_s + 2_s$] cycloaddition (without a diradical intermediate) is a forbidden process. However, as noted earlier, the π^4 state of peroxy radicals lies 0.88 eV (20 kcal) above the π^3 state (owing to repulsions between the four π electrons) and therefore this state is not expected to play a role in $^1O_2$–olefin ene reactions (where E_a = 2–10 kcal).

C. Alkyl-Substituted Olefins. Theory and Experiment. The results of the energetic estimates on the addition of $^1O_2$ to alkyl-substituted olefins are shown in Table III. Of the three

Table III. Energetics (kcal/mol) for Addition of $^1O_2$ to Alkyl-Substituted Olefins[b]

		Olefin Dioxygen Adducts					
Olefin	Olefin ΔH_f	Zwitterion $\Delta H(\alpha)$	Zwitterion $\Delta H(\beta)$	Perepoxide ΔH	Birodical $\Delta H(\alpha)$	Birodical $\Delta H(\beta)$	Exper.[a] E_a
	+12.5	+59		+16.1	+10.1		--
	+4.6	+58	+39	+15.2	+8.7	+8.8	--
	-2.2	32		+13.7	+6.3		6.5
	-3.2	33		+13.7	7.3		7.3
	-3.8	56	18	+14.0	7.5	8.2	--
	-10.7	31	16	+12.6	5.2	5.8	4.9
	-17.1	13		+10.4	2.6		3.2
	+37.5	36			5.6		
	+29.0	31	15		4.5	5.1	
	+20.6	14			3.9		4.0
	8.6	33			7.2		7.4
	0.2	32	17		6.0	6.6	6.0
	-7.3	14			4.5		4.0
	-0.8	31			5.5		>8.2
	-9.2	30	15		4.3	5.0	7.5
	-17.0	13			2.8		4.0

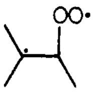
[a] Reference 31. [b] The enthalpy of forming the olefin–dioxygen adducts from olefin and $^1O_2$ is listed for the zwitterion, perepoxide, and biradical intermediates. $\Delta H_f(\alpha)$ and $\Delta H(\beta)$ are the estimated enthalpies (kcal/mol) of addition to the α and β sides of olefin, respectively.

proposed intermediates considered (**5**, **7**, and **9**) the one of lowest energy is the peroxy biradical. In fact, *the peroxy biradical is the only intermediate calculated to have a sufficiently low energy to be consistent with the observed activation energies* (also shown in Table III). The perepoxides are on the average ~10 kcal above the observed activation energy while the open zwitterions are too high by 15–50 kcal.

Comparing the energies necessary to form the peroxy biradical to the observed activation energies, it is found that within the uncertainty of the estimates (±2 kcal) the two are equal. Thus, if the biradical is an intermediate, there must be very low barriers (~0.5 kcal) both to the initial addition forming the biradical and to the subsequent hydrogen abstraction. Such a low barrier is consistent with the form of the wave functions; there are no orbital phase restrictions or nonbonded interactions which would lead to large barriers. Indeed, the H-abstraction process is analogous to bimolecular radical disproportionation reactions, processes which are known to proceed with near zero activation energies.[10]

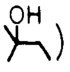
An important result in Table III is the predicted direction of $^1O_2$ attack on unsymmetrically substituted olefins. Taking as an example trimethylethylene, the estimates predict that addition of $^1O_2$ to the disubstituted end of the double bond, **20**,


20


21

is 0.6 kcal *lower* energy than addition at the monosubstituted end, **21**. However, in the literature it is often assumed that addition of a radical to a double bond leads to the most highly substituted radical center. For the case of radical HX addition, this is the explanation of the well-known Markownikoff directing effect. For this reason, and because the energy difference between **20** and **21** is smaller than the expected error limits of these estimates, it is important to consider carefully whether or not the predicted *ordering* is correct.

In fact, we believe that the predicted ordering is correct and note the following experimental results in support of this prediction. Starting with the experimentally determined heats of formation of the two analogous alcohols[43] and assuming (see

ΔH_f () $= -79.07 \pm 0.35$ kcal

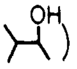
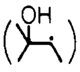
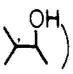
ΔH_f () $= -75.35 \pm 0.36$ kcal

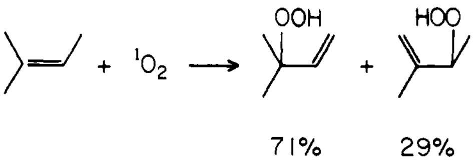
Table I) a secondary C–H bond energy of 94.5 kcal and a tertiary C–H bond energy of 92.7 kcal leads to

ΔH_f () $= -36.7$ kcal

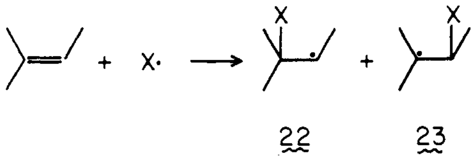
ΔH_f () $= -34.8$ kcal

Again, the *less* substituted radical is predicted to be *more* stable (by 1.9 kcal in this instance). This estimate made use of standard C–H bond energies to secondary and tertiary carbons. In order to reverse the predicted radical ordering, it would be necessary to assume that the tertiary C–H bond is ~3.5 kcal weaker than the secondary C–H bond. This is approximately twice the accepted difference (1.8 kcal)[10] and, hence, it is concluded that the predicted radical order is correct.

The experimental product distribution from the reaction of $^1O_2$ with trimethylethylene in the gas phase is[44] completely consistent with a biradical intermediate. However, these and similar solution-phase results, showing a lack of Markownikoff directing effects, have often been interpreted as evidence against a biradical.[16,17] The key assumption was that the tertiary radical must be more stable than the secondary radical [i.e., $\Delta H_f(\mathbf{21}) < \Delta H_f(\mathbf{20})$]. In fact, our energetic estimates indicate that this assumption is incorrect; the secondary biradical is *more* stable than the tertiary.



In order to make clear the origin of the Markownikoff effect and why it does not apply here, consider the more general addition of a radical X· to trimethylethylene. Again, there are two possible radicals, a tertiary radical, **23**, and a secondary radical, **22**. In order to compare the energies of these two radicals, we must use a common reference point, for example, the heat of formation of the reactants. The relative radical energies are then given by the C–X bond energies,[45] one involving a tertiary carbon and the second a secondary carbon. For many radicals (for example, X· = Br·, I·, R_3Si·, R_3C·, H·, RS., etc.), the bond energy to a secondary carbon is larger than that to a tertiary carbon. Thus, for these radicals the most stable adduct is the tertiary radical (in agreement with the Markownikoff effect). However, for highly electronegative radicals (X· = Cl·, F·, or RO·) the bond to a tertiary carbon is *stronger* than that to a secondary carbon.[46] The conclusion, then, is that *normal Markownikoff directing effects are not expected in the addition of $^1O_2$ to unsymmetrical olefins* whether or not a biradical is involved at the product-determining step. Furthermore, the results of gas-phase $^1O_2$ additions are consistent with a biradical or biradical-like species being product determining.

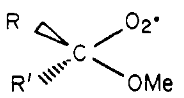


Note that the preferred direction of addition of $^1O_2$ to form a zwitterion is the opposite of that to form a biradical. These estimates clearly show that, if a zwitterion is involved in the product-determining step, addition of $^1O_2$ should invariably occur at the least substituted carbon.

The thermochemical estimates for additions to six-membered cyclic olefins exhibit an interesting trend. For both cyclohexene and methylcyclohexene the observed activation energies are significantly above the energy necessary to form the biradical. This could indicate an additional conformational barrier to either the initial addition or to H abstraction. This effect is most pronounced for cyclohexene where the H abstraction must be endocyclic.

D. Methoxy-Substituted Olefins. Theory and Experiment. The results for the addition of $^1O_2$ to methoxy olefins are shown in Table IV. Although not shown, estimates of the perepoxide energetics give results comparable to those found for alkyl olefins (i.e., the perepoxides are typically ~10 kcal above the biradical).

Before discussing these results in more detail, it is necessary to consider an important factor governing the conformation



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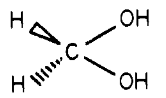

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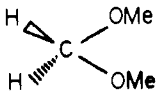
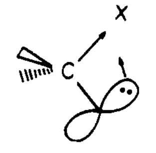


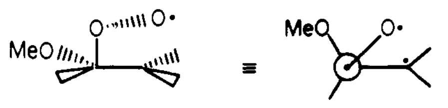
26

of these olefin-O_2 adducts. Addition of $^1O_2$ to the carbon α to the methoxy group leads to structure **24.** This structure is analogous to methanediol (**25**) and dimethoxymethane (**26**) in that all possess an O-C-O linkage. It is now well established[47] that the preferred OCOX dihedral angle in such compounds is ~90°. That such geometries are preferred is often referred to as the anomeric effect.

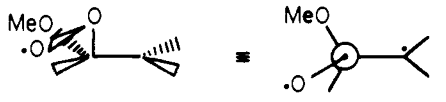
The origin of this effect can be described as follows.[32,48-51] The CO σ bonds, being highly polarized toward the oxygen, can effectively stabilize an adjacent lone pair lying in the same plane. In effect, the oxygen lone pair delocalizes into the region of the adjacent polar $\cdot\sigma$ bond as shown below. The result is an increased stability (2-6 kcal, see Appendix B) of conformations in which the oxygen lone pair is in the same plane as the adjacent ionic bond.



In considering the addition of $^1O_2$ to a methoxy olefin, then, the anomeric effect dictates a preference for conformations in which the O-O bond is gauche to the methoxy, C-O bond, as shown in **27** and **28** (the left drawing is a side view, the right a top view).



27



28

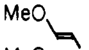
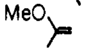
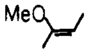
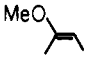
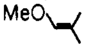
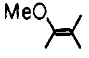
In conformation **28,** the oxygen radical center is not adjacent to an abstractable hydrogen and, therefore, this conformation cannot go directly to product. As the barrier to dissociation to olefin + $^1O_2$ is small (~0.5 kcal) compared to rotational barriers (~3 kcal),[10] if conformation **28** is formed, it will simply dissociate.

In conformation **27** the oxygen radical center is adjacent to the substituent cis with respect to the MeO group. Since the barriers to product formation (~0.5 kcal) are small relative to the rotational barriers, conformation **27,** if formed, will lead to a product hydroperoxide resulting from hydrogen abstraction cis to the MeO group.

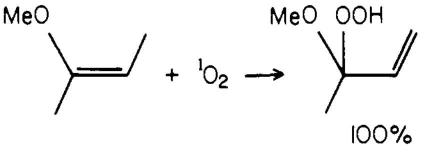
In summary, the assumption of a biradical mechanism and consideration of the implications of the anomeric effect lead to a clear prediction for a directing influence of an alkoxy group (or other highly electronegative substituent). The conclusion is that product formation will be biased toward attack of the $^1O_2$ on the α carbon (adjacent to the alkoxy group) and, furthermore, toward abstraction of an hydrogen from the β substituent cis with respect to the alkoxy group. Similar conformational effects are expected for dimethoxy-substituted olefins,[52] fluoro olefins,[52] and amino olefins.[52,53] However, the parameters necessary to predict whether α or β addition is preferred are not available for these olefins.

In order to test these predictions, Hammond[54] recently carried out gas-phase experiments yielding the following results. In reaction 20 the only observed product results from initial α addition followed by cis abstraction, consistent with both predictions (1) and (2). In reaction 20 there are no abstractable hydrogens cis to the methoxy group and, therefore, the preferred mode is not available. The result is that now two competing modes are detectable, one being α addition (followed by trans abstraction) and the second being β addition.

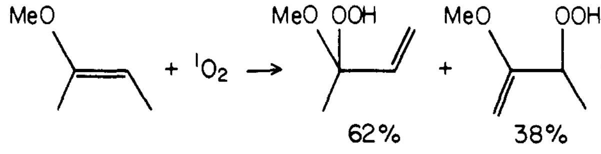
Table IV. Energetics (kcal/mol) of Addition of $^1O_2$ to Methoxy-Substituted Olefins[b]

Olefin	Olefin ΔH_f	Zwitterion $\Delta H(\alpha)$	Zwitterion $\Delta H(\beta)$	Biradical $\Delta H(\alpha)^a$	Biradical $\Delta H(\beta)$
	-25.7	56	19	6.8	8.1
	-33.6	31	17	5.5	5.7
	-33.6	31	17	5.5	5.7
	-11.6	52	6	2.8	5.5
	-42.1	27	5	1.5	4.1
	-41.1	26	4	0.5	3.1
	-42.1	15	17	5.0	5.6
	-49.6	10	3	0.0	2.0

[a] Assumes a conformation consistent with the anomeric effect (see text). [b] The enthalpy of forming the olefin-dioxygen adducts from olefin and $^1O_2$ is listed for the zwitterion and biradical intermediates (energies in kcal/mol).

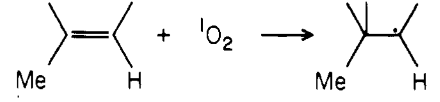


(20)



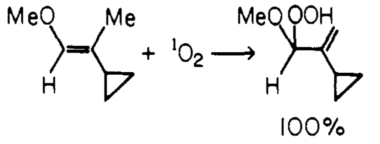
(21)

Related work by Cross,[55] using crossed molecular beams, has shown that gas-phase addition of $^1O_2$ to 2-methoxypropene leads to luminescence, presumably from decomposition of a dioxetane. Cross notes that this is an unexpected result since activation energies for [2 + 2] cycloaddition (forming dioxetane) are typically much larger than those for the ene process. However, the results in Table IV indicate that the preferred biradical is the α adduct, which cannot undergo the ene reaction.

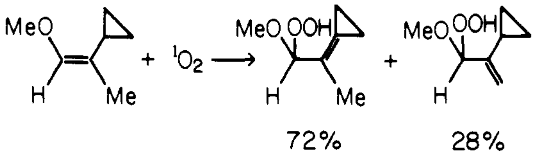


(22)

Additional support for this interpretation comes from work by Conia et al.[56] Conia's results are summarized in eq 23 and



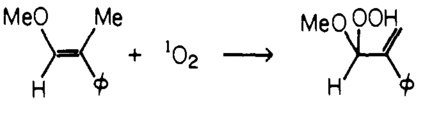
(23)



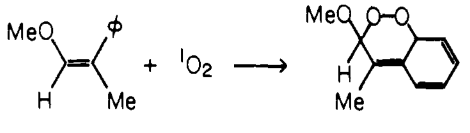
(24)

24. Again the products show a clear bias toward H abstraction from the substituent cis to the methoxy group. In the latter reaction, (24), the dominant (cis abstraction) product is 9 kcal *less* stable than the minor product (trans abstraction), indicating that the effect is indeed an important one. Conia also notes that replacement of the methoxy group by methyl removes the directing effect. In this case products resulting from abstraction of the cyclopropyl hydrogen are *not* observed (from either isomer).

Finally, recent studies by Foote et al.[57] also show the importance of this directing effect. In this work, the observed reactions are (25) and (26). In both cases, the only observed products are those resulting from attack of the oxygen radical center on the group cis to the methoxy.



(25)



(26)

Recently Jefford[58] has suggested an alternative explanation for the observed cis-directing effect of methoxy groups. Noting a number of experiments[59,60] where it was found that H abstraction takes place preferentially from the sterically more hindered side of the olefin, Jefford suggested that these results can be explained by assuming an open zwitterionic (or biradical) intermediate in which rotation about the C–C bond is both product determining and controlled by the steric bulk of adjacent groups. Jefford further suggested that the methoxy results are simply a special case of this. This mechanism does not, however, explain the lack of cyclopropyl H abstraction products found by Conia[56] when the methoxy groups in (24) are replaced with methyl. The effect pointed out by Jefford may be important in alkyl olefins, but it is not sufficient to explain the polar-group directing effect.

E. Solution-Phase Mechanism. In the previous sections we presented and discussed estimates for the energies of gas-phase 1,4 biradicals and 1,4 zwitterions relative to the $^1O_2$-olefin reactants. In this section we will consider the effects of solvation on these relative energies and on the mechanism of $^1O_2$-olefin reactions.

As a simple model for solvation, assume the intermediate to be in a spherical cavity of radius R(Å), surrounded by a dielectric medium with dielectric constant ϵ. The stabilization of the zwitterion relative to the biradical can then be estimated using the formula[61,62]

$$\Delta E(\text{kcal}) = 14.4 \frac{(\epsilon - 1)}{(2\epsilon + 1)} \frac{[\mu_{\text{zwit}}^2 - \mu_{\text{birad}}^2]}{R^3} \qquad (27)$$

where μ_{zwit} is the dipole moment (D) of the zwitterionic state and μ_{birad} is the dipole moment of the biradical. It is further assumed that $\mu_{\text{zwit}}^2 \gg \mu_{\text{birad}}^2$ and that μ_{zwit} can be approximated with the dipole resulting from two point charges separated by a distance of 2.65 Å, the approximate distance between the carbon and oxygen radical centers of a gauche 1,4 biradical (see Appendix A).

The assumptions then are as follows.

(1) The primary effect of the solvent can be approximated by a structureless dielectric medium.

(2) The dominant term in the dielectric interactions is the dipole term (the effects of the quadruple and higher moments are neglected).

(3) The dipole moments of the two states can be approximated as noted above. Although these assumptions are only partially correct, this procedure should yield valid predictions of the general trends in the solvent effects.

Using a cavity of radius 3.0 Å and the above approximations, expression 27 reduces to

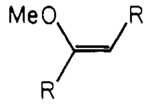
$$\Delta E(\text{kcal}) = \frac{\epsilon - 1}{2\epsilon + 1} \times 86.4 \qquad (28)$$

or, in the limit of high dielectric constant, $\Delta E \approx 40$ kcal. Since this is larger than most of the estimated zwitterion–biradical energy separations (Table II), it is concluded that high dielectric solvents or low dielectric solvents with electron-donating olefin substituents can stabilize the zwitterion with respect to the biradical. Under these conditions the intermediate will have the character of a 1,4 zwitterion with a smaller biradical component. In solvents of lower polarity the intermediate can have a character intermediate between that of a biradical and a zwitterion.

Similar solvent effects on the energy of the perepoxide are also to be expected. However, the dipole moment of the perepoxide, 5.6 D (see Appendix A), is much smaller than that expected for the open 1,4 zwitterion (~12 D). Since the solvent stabilization is proportional to μ^2, the stabilization of the open 1,4 zwitterion will be ca. three times that of the perepoxide. Thus, in extreme cases solvent stabilization may lower both the zwitterion and the perepoxide below the biradical; however, the ground state would most likely be an open zwitterion, not a perepoxide.

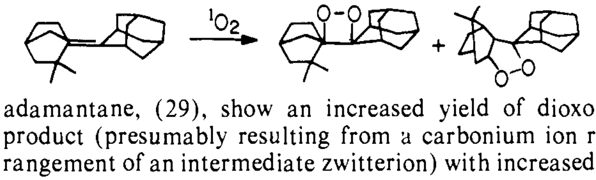
Although there are large uncertainties in the estimates of both the zwitterion energies and the solvation effects, some useful trends can be extracted. Consider first the addition of $^1O_2$ to an unsymmetrical alkyl olefin. Biradical energetics indicate that the preferred direction of addition is to the *most* substituted carbon in agreement with gas-phase experiments. The zwitterion estimates indicate that the preferred direction is to the *least* substituted carbon. Thus, if a solvent-stabilized zwitterionic character is important, the product distribution should shift to larger yields of the less substituted peroxide.[63]

Similarly in the addition of $^1O_2$ to an olefin of the form



estimates of gas-phase biradical energies show a clear preference for addition α to the methoxy group (in agreement with results of gas-phase experiments[54]). Zwitterion energetics, however, indicate that addition to the β carbon is 22 kcal lower energy than addition to the α carbon. Therefore, if solvent-stabilized open zwitterions play an important role in this reaction, there should be a large shift in the product distribution as a function of the dielectric constant.[64]

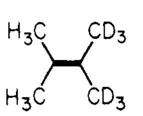
Several intriguing features of solution-phase $^1O_2$-olefin chemistry can be understood by assuming a solvent-dependent intermediate of varying degrees of biradical and zwitterion character. For example, McCapra's results[25] on the product ratios resulting from photooxidation of camphenylidene–adamantane, (29), show an increased yield of dioxolane product (presumably resulting from a carbonium ion rearrangement of an intermediate zwitterion) with increased solvent dielectric.



(29)

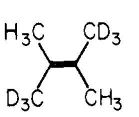
It has also been reported that increased solvent polarity increases the amount of [2 + 2] cycloaddition product (dioxetanes) at the expense of alkylic hydroperoxides.[26] This is understandable since the zwitterionic structure should exhibit a greater tendency toward ring closure than the biradical (see section IVB).

F. Isotope Effects. Studies of isotope effects on a number of $^1O_2$-olefin reactions have been reported and have often been interpreted as being inconsistent with a biradical intermediate. However, the observed rate ratios resulting from deuterium substitution at allylic positions can be explained either as primary, product-determining isotope effects (not rate determining) or, in some cases, as secondary β deuterium isotope effects. For example, the intramolecular isotope effects reported by Nickon[66] are as follows, where no correction for the number of deuteriums has been made (no correction need be made if, and only if, these are primary isotope effects). Of these, the results for **30** and **31** can be attributed to a primary, product-determining effect in the hydrogen abstraction step of the biradical mechanism. The observed ratio for **29**, however, must be attributed to a β secondary isotope effect. In this case it is necessary to correct the observed effect to a per deuterium basis:



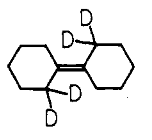
29

k_H/k_D = 1.78-2.24



30

k_H/k_D = 1.28-1.77

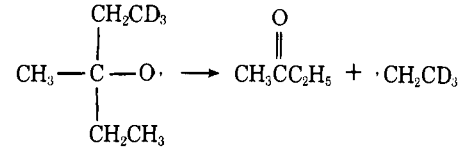


31

k_H/k_D = 1.18-1.20

$$k_H/k_D = \sqrt[n]{K_{Hn}/K_{Dn}}$$

leading to a value of 1.10-1.16. More recent work by Kopecky et al.[23] on **29** and **30** led to somewhat smaller isotope effects, 1.31-1.65 and 1.21-1.46, respectively. Converting again to a per deuterium ratio for **29** leads to a range of 1.05-1.09. For comparison, the secondary β deuterium isotope effect for the formation of ethyl radical from decomposition of methylethylethyl-*2,2,2-d*$_3$-carbonyloxy radical is reported to be 1.08[67]



$$CH_3-\underset{CH_2CH_3}{\overset{CH_2CD_3}{C}}-O\cdot \longrightarrow CH_3\overset{O}{\overset{\|}{C}}C_2H_5 + \cdot CH_2CD_3$$

(again on a per deuterium basis). Thus the observed isotope effects imply no C-H bond cleavage in forming the transition state.

Kopecky's results[23] and related work by Bartlett[26] indicate the magnitude of these isotope effects to be dependent on the solvent. For example, Bartlett[26] reports kinetic isotope effects (k_H/k_D) of 1.1 in acetonitrile and 1.2 in benzene. Apparently then, the nature of the transition state is dependent on the solvent.

Recently, Stephenson[68] has reported isotope effects for *cis*- and *trans*-tetramethylethylene-d_6 in a relatively polar solvent. The cis compound exhibits a small isotope effect, $k_H/k_D \approx 1.05$, while the trans isomer exhibits a much larger effect, ~1.4. Stephenson concludes that these results support the intermediacy of a perepoxide or, at least, a perepoxide-like structure. Before the significance of these results with regard to the mechanism proposed here can be analyzed, it will be necessary to determine if this cis-trans difference persists in nonpolar solvents. We note, however, that the observed difference might be explained by steric effects in a manner analogous to that suggested by Jefford,[58] within the concept of an open (biradical or zwitterionic) intermediate.

Bartlett[26] has measured tritium isotope effects for the vinylic positions of several 2,3-dihydro-γ-pyrans. These results indicate that attack of O_2 on the double bond is nonsymmetrical and is also not consistent with a simple concerted mechanism. Unfortunately these reactions lead to both dioxetanes and ene products. Since it is not possible to separate out the isotope effects for the ene path alone, a detailed analysis of these results is not yet feasible.

G. Concerted vs. Biradical Mechanisms. In the preceding sections we have presented a thermochemical analysis of $^1O_2$-olefin additions in terms of biradical and zwitterionic intermediates. This analysis, of course, does not deny the possibility of a concerted mechanism; it simply shows that the biradical is an energetically accessible intermediate and that it leads to regiospecificity in agreement with experiment. The possibility of a slightly lower energy, concerted pathway cannot be discarded solely on the basis of these estimates. We stress, however, that these estimates indicate the biradical to be roughly degenerate with the gas-phase transition state. This is in contrast to the situation for such clearly concerted reactions as the Cope rearrangement, [2 + 4] cycloadditions, or the cycloaddition of ozone to olefins. For example, in the latter case formation of a biradical requires 11 kcal while the observed activation energy is 4 kcal.[69]

In summary, the theory and experiment are consistent with the saddle point for the reaction being of biradical structure with no bonding between the radical centers. Whether this state is a true saddle point or whether there are very small (~0.5 kcal) barriers to cleavage and abstraction has not been determined. Without such small barriers one might consider the reaction mechanism to be concerted but highly asynchronous (initial C-O bond formation followed by H abstraction) as suggested by Nickon[14] and Foote.[16]

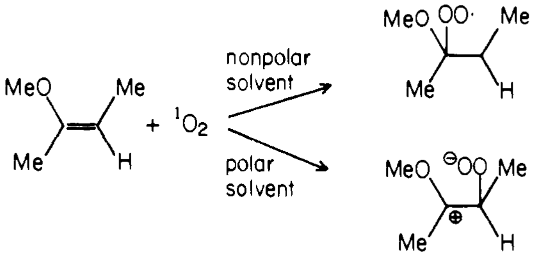
Finally, we note that whether the reaction is nonconcerted, involving a true biradical intermediate, or concerted, involving a biradical quasi-intermediate does not affect the predictions of regioselectivity discussed here. In either case, the factors (anomeric effect, etc.) which govern the biradical conformations will be of similar importance in determining the conformation of a biradical-like transition state.

VI. Summary

An analysis of the $^1O_2$-olefin ene reaction in terms of ab initio energies and thermochemical estimates has been presented. The results indicate that the energetics and regioselectivity of the gas-phase reaction can be understood in terms of the peroxy biradical intermediate or quasi-intermediate. It is shown that the often cited lack of Markownikoff directing effects is *not* inconsistent with a biradical intermediate.

Energetic estimates indicate that both biradical and solvent stabilized zwitterions are energetically accessible intermediates in many solution-phase reactions. The precise nature of the intermediate is critically dependent upon the nature of its environment (both solvent and substituent). It is shown that many of the solvent-dependent features of this reaction can be understood assuming an (quasi) intermediate of varying biradical-zwitterion character.

The results of this analysis also lead to a number of verifiable predictions. The solvent-dependent balance between zwitterionic and biradical character indicates that in many cases a marked shift in product distribution should occur as solvent polarity is increased. A particularly appropriate test for this



(30)

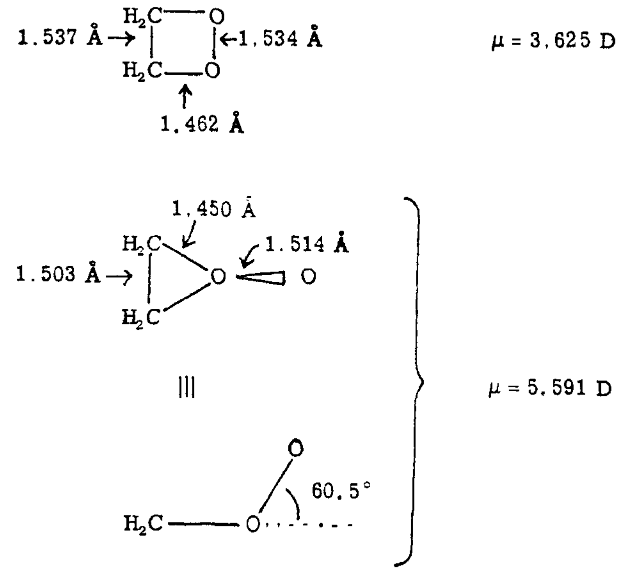


Figure 1. Calculated geometries and dipole moments of dioxetane and perepoxide.

prediction would be 1-methoxybut-2-ene, (30), since the biradical and zwitterionic energetics lead to clearly different predictions.

Finally, it is predicted that the observed directing influence of a MeO substituent should be a quite general effect. In particular, F or Cl substitution should lead to a similar directing effect.

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Appendix A. Ab Initio Calculations

The ab initio calculations on $\cdot CH_2CH_2O\cdot$ used the valence double ζ (DZ) basis of Huzinaga and Dunning[38] [(9s, 5p/4s) primitive Gaussians contracted to (3s, 2p/2s)] augmented with d polarization functions (α_C = 0.6760 and α_O = 0.8853) centered on each heavy atom. In addition, a set of diffuse oxygen-centered s and p functions (α = 0.059) was included to describe the negative ion character correctly.

The geometry used for all states was R_{CC} = 1.51 Å, R_{CO} = 1.41 Å, R_{CH} = 1.08 Å; all bond angles about the saturated carbon were tetrahedral and all those about the C radical center were 120°. The CO and CC bond lengths were optimized for the biradical state using the DZd-GVB wave functions. The remaining geometric parameters are all standard values

Using this basis and geometry, GVB wave functions[37] were optimized in which all valence electron pairs were correlated, each with one correlating natural orbital. These calculations were carried out for each of four states: biradical, positive ion, negative ion, and zwitterion. The latter is the same symmetry as the ground-state biradical. For this reason, it was necessary to place a restriction (the tighter of the two carbon radical pπ atomic orbitals was required to have a zero coefficient in all orbitals) on the wave function of this state. The resulting total energies (hartrees) follow: biradical, −152.962 78; positive ion, −152.631 00; negative ion, −152.965 74; zwitterion, −152.864 25. With these wave functions, the calculated dipole moments of the biradical and zwitterionic states are 2.36 and 10.14 D, respectively. For comparison, the two radical centers are 2.39 Å apart; thus, the simple model of two point charges (see text) leads to a zwitterion dipole moment of 11.46 D. For a 1,3 zwitterion then this model overestimates the dipole moment by ~10%. For a 1,4 zwitterion the errors are expected to be smaller.

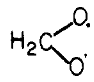
We stress that the ab initio calculations reported here serve only to test the assumptions implicit in the thermochemical estimates. In particular, the calculations indicate that the point-charge model gives a reasonable dipole moment for the zwitterionic states, and eq 11 gives a reasonable estimate of the biradical-zwitterion energy separation. These calculations are *not* sufficiently extensive to yield accurate biradical-zwitterion energy separations and are not used here for that purpose.

Comparable calculations on the unsubstituted dioxetane and perepoxide reported earlier[9] led to the geometries and dipole moments shown in Figure 1.

Appendix B. Anomeric Effect

The exact magnitude of the anomeric effect depends on the nature of the substituents. Thus, for example, calculations[43] on methanediol indicate an anomeric effect (V_2) of ~0.5 kcal while similar studies on dimethoxymethane lead to a value of ~1.5 kcal. The calculated preference for gauche over anti, however, was considerably larger for both of these molecules (3.7 and 2.6 kcal, respectively).

Calculations on dioxymethylene,[69] in which the anomeric effect is exhibited in the separations between the eight possible biradical states, lead to a value of 6 kcal. Although no experimental barriers are available for methanediol or dimethoxymethylene, recent NMR studies[70] of rotational barriers of chloromethyl methyl ether and fluoromethyl methyl ether have led to an anomeric effect of 2–3 kcal.



Thus, both experimental and theoretical studies indicate a clear anomeric preference for gauche conformations over anti in molecules of the form **24–26.** The magnitude of this effect is variable, 2–6 kcal, depending on the particular molecule and the method of analysis. Finally, we note that the product distribution from the gas-phase reaction of $^1O_2$ with 2-methoxybut-2-ene has been found[54] to be consistent with an anomeric interaction of 3 kcal, in good agreement with the values from both theory and experiment on related molecules.

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(63) Solution-phase hydroperoxidations of trimethylethylene[14] do show a small shift toward the secondary hydroperoxide relative to the gas-phase result.[44] It is not known if this shift is dependent on solvent polarity.

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