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The Electronic Structure of the Criegee Intermediate. Ramifications for the Mechanism of Ozonolysis

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Abstract: Generalized valence bond (GVB) and configuration interaction (CI) calculations using a double ζ basis set have been carried out on methylene peroxide (H_2COO), the reactive intermediate in the Criegee mechanism for ozonolysis of olefins. The ground state of methylene peroxide (using an open geometry) is shown to be a singlet biradical rather than a zwitterion. A strong analogy between methylene peroxide and its isoelectronic counterpart, ozone, is developed. The calculations also show that the ring state of methylene peroxide is 1 eV lower than the open form. Moreover, the ring state may reopen to give the dioxymethane biradical. The ab initio results are combined with thermochemical data in order to analyze the stability of the Criegee intermediate as well as the possible modes of reaction in ozonolysis. With regard to ozonolysis in solution, the mechanism for epoxide formation is elucidated and the possible role of methylene peroxide rearrangement to dioxymethane is considered in interpreting the ^{18}O isotope experiments. With regard to ozonolysis in the gas phase, the production of many of the chemiluminescent species observed by Pitts and coworkers is explained. The production of reactive radicals such as OH and HO_2 in the course of ozonolysis, which may have important consequences for understanding the generation of photochemical air pollution, is also delineated.

I. Introduction

The reaction of ozone and olefins (in solution) with its puzzling set of products has intrigued chemists for years.[2-4] More recently, the corresponding gas phase reaction has come under scrutiny as an important link in the chain of photochemical smog production.[5] The isolation in solution of 1,2,4-trioxolanes rather than 1,2,3-trioxolanes from ozone–olefin reaction mixtures and the incorporation of foreign aldehydes in the 1,2,4-trioxolanes led Criegee[6] 25 years ago to propose the following mechanism
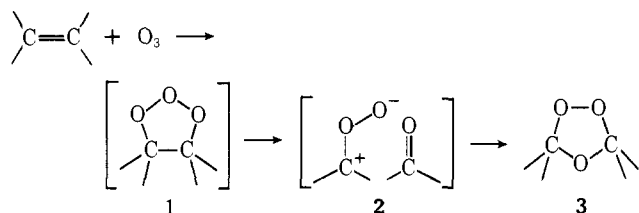

Since then a great deal of experimental work has substantiated the Criegee mechanism as either the predominant or at least a major pathway for ozonolysis in solution.[3,4,7-9] However, no definitive mechanistic studies have as yet been performed on gas phase ozonolysis.

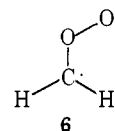Recent extensive ab initio calculations[10,11] have shown that ground state ozone is basically a singlet biradical (4)

rather than the resonance of two VB zwitterions (5)
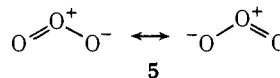
as often proposed. In fact, the state that corresponds most closely to **5** is about 5 eV higher than the ground state![10] Since the Criegee intermediate, methylene peroxide (2), is isoelectronic to ozone, we expected it to have an analogous ground state and hence to correspond essentially to a singlet biradical (6) rather than a zwitterion (2) as is normally assumed. In order to establish the electronic structure of methylene peroxide (2 or 6) and to investigate the role of

this intermediate in the mechanism of ozonolysis, we carried out extensive generalized valence bond (GVB) and configuration interaction (CI) studies which are reported herein.

The first section (II) presents the qualitative GVB model for the electronic structure of methylene peroxide. This section illustrates the types of arguments that can be (and were) made on the basis of general principles, without appeal to actual calculations. The next section (III) provides the details concerning how the calculations were carried out, and section IV summarizes the numerical results. Section V contains a detailed description of the orbitals obtained from GVB calculations at various geometries of the Criegee intermediate. In section VI we use both the theoretical calculations and thermochemical considerations to estimate the heats of formation for the various intermediates involved in ozonolysis, and in section VII we use these results to examine the experimental results for both gas phase and solution ozonolysis studies.

II. The Qualitative GVB Description of H$_2$COO

We have found that a good picture of the ground and low-lying excited states for a molecule can be obtained *prior* to any calculations by building up the molecule from its component atoms in their ground atomic configuration and using simple ideas concerning formation of chemical bonds and of the role of the Pauli principle.[11] Higher lying states may be found by considering excited atomic configurations. The basic idea here is that the energy involved in the atomic excitation carries over to the molecular system.

Methylene peroxide (6) may be formed by bonding a methylene molecule to one end of an oxygen molecule, both molecules being in their ground states ($^3B_1$ and $^3\Sigma_g^-$, respectively). As has been shown previously, the electronic wave functions for the ground states of methylene[12] and dioxygen[10c,11,13] lead to the following diagrams


$$CH_2(^3B_1) \qquad O_2(^3\Sigma_g^-)$$
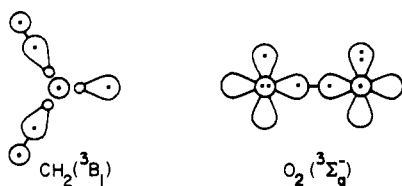
Here, we have ignored the core orbitals, 1s for carbon, 1s and 2s for oxygen, which are tightly bound and remain relatively unchanged as the atoms are brought together to form the molecules. Each hydrogen 1s orbital is represented by O, the carbon and oxygen 2p orbitals are each represented by

if in the plane of the paper and by O if perpendicular to the plane of the paper, and the carbon sp hybrids are represented by

Dots indicate the number of electrons in each orbital and tie lines indicate the coupling of two singly occupied orbitals into a bonding pair. We will often simplify these diagrams by using a line connecting two atoms to represent the pairing of two singly occupied orbitals into a bonding pair.
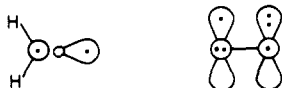
It is important to keep in mind that these diagrams represent the entire molecular wave function and do *not* just describe the shape of the molecular orbitals.

Before describing methylene peroxide, a few comments about the π system of the oxygen molecule are warranted. GVB calculations on $O_2(^3\Sigma_g^-)$ have shown that the two sets of three-electron π bonds contribute a total of ~60 kcal to the O$_2$ bond.[10c,11] The origin of the bonding may be understood in terms of two effects that occur as the two atoms are brought together. Because of the Pauli principle, the singly occupied p$_\pi$ orbital on one center must become orthogonal to the doubly occupied p$_\pi$ orbital on the other center. This leads to antibonding character in the singly occupied orbital.


However, the doubly occupied orbital finds the other nucleus to be only partially shielded and can delocalize onto the other center leading to a significant bonding effect.


The resulting delocalization of these two orbitals would normally introduce ionic character into the wave function; however, the doubly occupied π orbitals in the x and y planes delocalize in opposite directions so that the total wave function remains neutral. When a bond is made to one of the π orbitals, as in HO$_2$, it prevents delocalization of the O$_2$ π orbitals in the HOO plane. In addition, the delocalization of the O$_2$ π orbitals in the other plane decreases since the resulting ionic character is no longer compensated.[10c] As a result, this three-electron π bond is much weaker (~13 kcal/mol[14] instead of 30 kcal/mol[10c,11]).

The two reasonable geometries for bonding $CH_2(^3B_1)$ to $O_2(^3\Sigma_g^-)$ have the CH$_2$ and COO planes either perpendicular or coplanar

planar   perpendicular
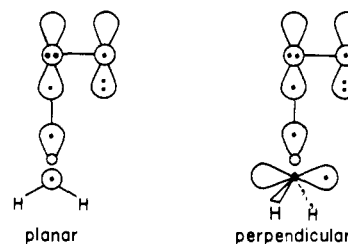
In the perpendicular form, there is a repulsive interaction (arising from the Pauli principle) between the central oxygen π pair and the CH bonds. In the planar form, the central π pair may delocalize onto the carbon, while the carbon p$_\pi$ orbital becomes orthogonal to the π pair (building in antibonding character). Such delocalization of the π pair was found to be quite important for bonding in ozone.[10c,11] However, in methylene peroxide the delocalization onto the carbon will be much less because of its lower electronegativity. Nevertheless, these simple considerations suggest the planar form to be more favorable than the perpendicular.

The planar structure for methylene peroxide (7) gives

$$7$$
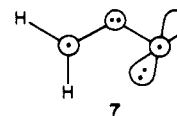
rise to both a singlet and a triplet state. In our discussion we will refer to the left, center, and right π orbitals as π$_l$, π$_c$, and π$_r$, respectively, even though the GVB orbitals are not

localized entirely on one center. The relative energy of the singlet and triplet states is governed by the size of the overlap (S) of the two singly occupied π orbitals, π_1 and π_r.[15] For atomic π orbitals the overlap is quite small ($S \sim 0.01$), so that the singlet and triplet states should be nearly degenerate. However, because of the (bonding) delocalization of the π_c pair and the concomitant (antibonding) delocalization of the π_l and π_r orbitals, the overlap between the self-consistent π_1 and π_r GVB orbitals is much greater ($S = 0.25$). Consequently, the singlet state is expected to be significantly lower than the triplet. In ozone, the corresponding overlap is $S = 0.28$ and the comparable singlet–triplet splitting is 1.47 eV![10bc,11] The splitting in methylene peroxide should be smaller than in ozone (we find $\Delta E = 0.84$ eV), since the central oxygen π pair will not delocalize as much onto the less electronegative carbon. As a result, both the overlap of the terminal p_π orbitals and the splitting energy are smaller.

To facilitate the discussion of the various methylene peroxide states, we will label each state according to the number of π electrons. For example, the states obtained from **7** are $^1A'$ (4π) and $^3A'$ (4π).

Other low-lying states that are formed from ground atomic configurations may be found by rotating either end of methylene peroxide by 90° giving rise to **8** and **9**. Config-


8　　　　　**9**
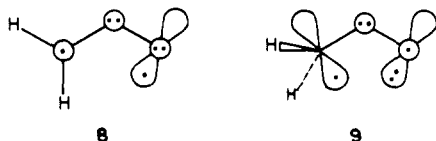
urations **8** and **9** lead to $^{1,3}A''(5\pi)$ and $^{1,3}A''(3\pi)$ states, respectively. For **8** and **9** the triplet states are expected to be slightly lower in energy since the singly occupied orbitals are orthogonal. The analogous singlet and triplet states in ozone are $\sim$2 eV above the ground state.[10,11] Since the π bonds in methylene peroxide are weaker than in ozone, one would expect the energies of the A'' 3π and 5π states to be significantly less than 2 eV. Moreover, the 3π states should be lower than the 5π states, since the COπ bond lost in rotating the methylene group to give **9** is weaker than the OO π bond lost in rotating the terminal oxygen orbitals to give **8**. Also, the oxygen π pair oxygen π pair interaction (of **8**) is worse than the oxygen π pair–CH bond interaction (of **9**), since the CH bonds are bent back away from the π pair.

Finally, rotation of both terminal groups by 90° leads to **10** and two more higher lying states, $^{1,3}A'(4\pi)$. Since the


10
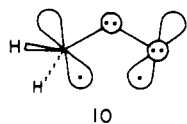
two singly occupied orbitals have small overlap, the singlet state is expected to be slightly lower than the triplet. The analogous states in ozone appear near 4 eV.[10,11] To distinguish the $^{1,3}A'(4\pi)$ states obtained from **7** and **10**, we denote them as planar (**7**) or perpendicular (**10**) according to the orientation of the hydrogens with respect to the COO plane. The perpendicular $^1A'(4\pi)$ state is particularly interesting in that it should lead to a ring-like equilibrium geometry.

11
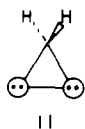
(All other states discussed above involve repulsive interac-

tions between the terminal atoms and should have equilibrium bond angles >100°.) In ozone, the ring state is calculated to lie 1.5 eV above the ground state.[10,11] The ring state in methylene peroxide is even more interesting from a mechanistic point of view than its ozone counterpart since it may reopen by breaking the OO σ bond to give the dioxymethane biradical

12
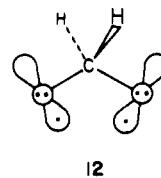
Depending on the energetics of this rearrangement, this pathway may have important implications for the isotope (^{18}O) studies of ozonolysis (cf. section VII).

Configuration **12** leads to $^{1,3}A_1(4\pi)$ states [the molecular symmetry is now C_{2v} instead of C_s] with the singlet expected to be slightly lower in energy. Rotating either of the oxygens by 90° leads to $^{1,3}A_2(3\pi)$ and $^{1,3}B_1(3\pi)$ states, the triplets being lower in energy. Rotating both the oxygens leads to $^1A_1(2\pi)$ and $^3B_2(2\pi)$ states, with the singlet expected to be only slightly lower (since the singly occupied orbitals have small overlap). Here the central CH bond will not delocalize as the central oxygen π pair did in methylene peroxide.

All of the states discussed thus far are covalent in character; none correspond to the zwitterionic structure (**2**) normally used for the Criegee intermediate. For ozone the lowest ionic states arise from charge transfer of a π electron from the central to the terminal oxygen.[10,11,16]

13
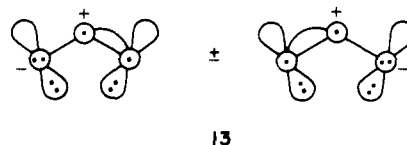
The minus combination leads to the lower state (1 $^1B_2$), which is the upper state of the well-known Hartley band at 4–6 eV.[17] Note that these configurations (**13**) are just the VB zwitterionic structures (**5**) often written for the ground state of ozone. The zwitterionic structures actually describe an excited state about 5 eV above the ground state.

One would expect the lowest ionic structures for the methylene peroxide to be analogous to those of ozone, i.e.

14

15
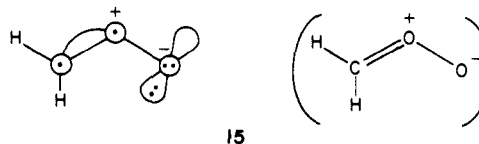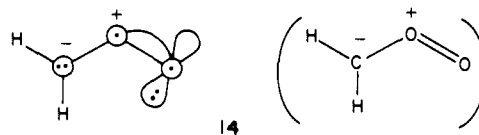
Using simple electronegativity arguments, **15** is expected to be lower in energy than **14**. In fact, the Criegee intermediate is often written as **15**, but it still should be 3–4 eV above the singlet biradical configuration (**7**). The structure (**2**) usually given for the Criegee intermediate corresponds to **16** and is actually just a poor representation of the state that is well described by **15**. The very bad pair–pair interaction between the doubly occupied oxygen p_π orbitals will cause the central π pair to delocalize onto carbon, giving

16   2
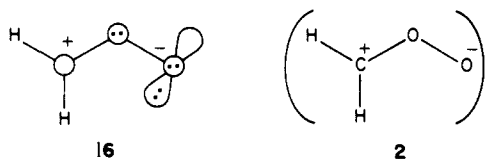
rise to **15**. Therefore, even before any calculations it is evident that **2** is an inappropriate representation of the Criegee intermediate. Moreover, the foregoing argument demonstrates the importance of associating electrons with orbitals, when thinking about molecules. Structure **2** may appear reasonable, but **16** certainly does not!

III. Calculational Details

A. Geometries. In this initial investigation of the Criegee intermediate, calculations were performed at the equilibrium geometries for the states of interest. (More extensive potential curves will be generated later.) Since the Criegee intermediate is a highly reactive species, experimental geometries are not available. Nevertheless, reasonable geometries may be developed by referring to experimental and theoretical results on related systems.

The various geometric parameters employed in this study are listed in Table I. In every case, the CH bond distance was assumed to be 1.08 Å and the HCH bond angle to be 120°. A slightly smaller bond angle (113–116°) may be more appropriate for the configurations in which the carbon is bonded to both oxygens.[18-20] However, the effect of a small change in this bond angle should be negligible for our considerations.

Configurations **7–10** involve either three or four π electrons on the oxygens. The OO bond distance is expected to be shorter for the states with three oxygen π electrons. In fact, experimental results on the hydroperoxyl radical, HOO, suggest an OO bond distance of 1.34 Å for the 3π states and 1.41 Å for the 4π states,[21,22] and theoretical cal-


3π   4π

culations on ozone indicate a difference in bond lengths of 0.06 Å. Recent ab initio GVB-CI calculations[14] on HO$_2$ yield $R_{OO} = 1.34a_0$ for the 3π state and $R = 1.42a_0$ for the 4π; in both cases the bond angle is 102°. In order not to bias the geometry in favor of either the states with three oxygen π electrons or those with four, we took the OO bond distance to be 1.37 Å for configurations **7–10**. It should be mentioned that one would expect the OO bond distance in methylene peroxide to be generally larger than that in the hydroperoxyl radical because of the repulsive interactions with the larger methylene group.

The COO bond angle was taken to be 103° for configurations **7–10**. This bond angle is intermediate with respect to the experimental COO angle of 105° in dimethyl peroxide and the experimental HOO angle of 100° in hydrogen peroxide.[23] The COO angle in 1,2,4-trioxolane is 99.2°.[20] Using the same reasoning as for the OO bond distance, the CO bond distance is expected to be shorter for the planar configuration than for the perpendicular. For the perpendicular configurations (**9** and **10**), the CO bond distance was assumed to be the same as in dimethyl ether, namely, 1.41 Å.[17] This is a normal length for a CO single bond. The CO bond distance in the planar configurations (**7** and **8**) is expected to be shorter than 1.41 Å but longer than the CO bond distances in the $^3n\pi^*$ (1.31 Å) and the $^1n\pi^*$ (1.32 Å) states of formaldehyde.[17] Therefore, we took the CO bond distance to be 1.35 Å. This reduction of 0.06 Å in bond

Table I. Geometric Parameters Used for the Theoretical Studies

Configuration	R_{OO}, Å	R_{CO}, Å	∠COO, deg
7, 8	1.37	1.35	103
9, 10	1.37	1.41	103
			∠OCO, deg
11	1.45	1.436	60.6
12		1.41	106

H$_2$CO(nπ*)
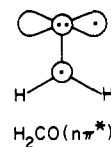
length for a three-electron π bond is the same as found in the hydroperoxyl radical.

The reason why we took into account the effect of the three-electron CO π bond and not the three-electron OO π bond when determining geometries is that describing the perpendicular states necessitated a geometry change relative to the planar case, while the number of oxygen π electrons did not.

For the ring state (**11**), the CO bond distance was assumed to be 1.436 Å as in ethylene oxide[19] and the OO bond distance to be 1.45 Å, as in the analogous ring state of ozone.[10b] Finally, for the dioxymethane biradical (**12**), the CO bond distance was assumed to be 1.41 Å, while the OCO bond angle was chosen to be 106° in analogy to 1,2,4-trioxolane. A slightly shorter CO bond distance would be more appropriate for the dioxymethane 3π and 2π states.

B. Basis Set and Wave Functions. All the calculations were performed with the Dunning[24] double ζ [4s, 2p/2s] contraction of the Huzinaga[25] (9s, 5p/4s) set of primitive Gaussian basis functions. The hydrogen exponents were scaled to 1.2.

Earlier calculations on ozone have shown that the Hartree-Fock (HF) wave function provides a very poor description of many of the low-lying states, leading, for example, to a triplet ground state![10bc,11] A much better description[10,11] is obtained with the GVB wave function,[13,26] which allows singlet-paired orbitals to be singly occupied and overlapping rather than forcing the orbitals to be doubly occupied or orthogonal as in HF. Specifically, the doubly occupied HF orbitals are replaced in the GVB wave function by a pair of nonorthogonal singlet-coupled orbitals.

$$HF: \; \varphi(1)\varphi(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$GVB: \; [\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Allowing the HF doubly occupied orbital to be described as a GVB pair increases in importance as the overlap of φ_a and φ_b decreases. For example, the ground state of H$_2$ is fairly well described by an HF wave function near the equilibrium bond distance, but as the molecule is pulled apart the description becomes increasingly worse.[11,26,27] The electrons are not allowed to localize on the separating atoms; ionic character is introduced, and the HF wave function does not dissociate properly.

Turning to the planar $^1A'(4\pi)$ state of methylene peroxide (**7**), it should be recalled that the π orbitals on the outer carbon and oxygen have relatively low overlap and will not be well described by an HF wave function. In fact, for the analogous state of ozone forcing these two electrons into one orbital introduces an error of >3 eV.[10c] As a consequence in the HF description the $^3B_2(4\pi)$ state of ozone is 2.2 eV lower than the $^1A_1(4\pi)$ state![10c] We will want to consider the dissociation of the Criegee intermediate into

CH$_2$ + O$_2$ or CH$_2$O + O. At the dissociation limits the orbitals involved in the CO or OO bonds are singly occupied. Therefore, to obtain a consistent description the CO and OO bonding orbitals are allowed to split into GVB pairs. The remaining orbitals are doubly occupied at both the equilibrium geometry and the dissociation limits. Since no significant differential effects are expected here, these orbitals will not be allowed to split into GVB pairs. Therefore, a wave function with three GVB pairs will be employed for the planar $^1A'(4\pi)$ state. To simplify the solution for the above wave function, two approximations are made:[13] (1) orbitals from different pairs are taken to be orthogonal (strong orthogonality) and (2) the orbitals in each pair are assumed to be singlet coupled (perfect pairing).[28] The resulting wave function, designated GVB(3/PP), has the form

$$\Psi = A[\phi_1^2 \ldots \phi_n^2(\phi_a\phi_b + \phi_b\phi_a)(\phi_c\phi_d +$$
$$\phi_d\phi_c)(\phi_e\phi_f + \phi_f\phi_e)\alpha\beta \ldots \alpha\beta]$$

When solving for the wave function, the equivalent representation of the GVB pairs in terms of two natural orbitals is used.[29]

$$\phi_a\phi_b + \phi_b\phi_a = c_1\phi_1^2 - c_2\phi_2^2$$

For the corresponding planar $^3A'(4\pi)$ state, the same GVB(3/PP) wave function is employed except that the terminal π orbitals are triplet coupled and are taken to be orthogonal. (For triplet-paired orbitals, orthogonalization is not a restriction on the wave function.) Similarly, GVB(3/PP) wave functions are employed for the planar $^{1,3}A''(5\pi)$ and perpendicular $^{1,3}A''(3\pi)$ states (8 and 9), taking the orthogonal singly occupied orbitals on the terminal atoms to be singlet or triplet coupled. In the GVB(3/PP) wave function for the perpendicular $^1A'(4\pi)$ state, the singly occupied orbitals on the terminal atoms form a nonorthogonal GVB pair, while for the perpendicular $^3A'(4\pi)$ state they are taken to be orthogonal. The GVB(3/PP) wave function correctly describes the forming of the ring state (11) and the reopening to give 12. GVB(3/PP) wave functions were used for both the $^1A_1(4\pi)$ and $^1A_1(2\pi)$ states arising from 12.

Earlier we mentioned two restrictions imposed on the GVB(3/PP) wave function, namely, strong orthogonality and perfect pairing. Past experience has shown that these restrictions, in general, do not alter the qualitative orbital picture of the system in question.[10-13] However, to obtain quantitatively accurate excitation energies ($\sim$0.1 eV) relaxation of these restrictions is necessary. The restrictions are removed in a CI calculation by allowing excitations among the six orbitals from the three GVB pairs and the two oxygen lone pair orbitals.

Three types of CI wave functions were employed.

1. GVB(3): a limited intrapair CI involving only the six orbitals from the three GVB pairs; this allows relaxation of the perfect-pairing spin-coupling restriction.

2. GVB–CI: a limited CI involving the six orbitals of (1) and the two oxygen long pairs; this relaxes both the perfect pairing and strong orthogonality restrictions. (This calculation provides the best energies for quantitative use.)

3. SD–CI: from each dominant configuration all single and double excitations are allowed among the eight orbitals of (2). There are two dominant configurations for the planar and perpendicular $^1A'(4\pi)$ states as well as for the $^1A_1(2\pi)$ and $^1A_1(4\pi)$ states of 13. The remaining states have only one dominant configuration.

Previous calculations have shown that the ionic charge-transfer states of ozone are not well described by CI calculations within the GVB space.[10b] The calculated vertical ex-

citation energies are 1–2 eV too high. This result is not at all surprising since ionic charge-transfer states are known to involve diffuse orbitals.[30] We have performed a more extensive CI calculation to remedy this problem.

4. π POL(2)–CI: the GVB–CI configurations are augmented by allowing from each dominant configuration all single and double excitations among the eight orbitals of (2) and the three remaining virtual π orbitals with the restriction that only single excitations were allowed into the three double ζ (DZ) virtual π orbitals.

We performed π POL(2)–CI calculations on the ionic planar 4π and 5π states as well as on the ionic perpendicular 3π states of methylene peroxide. To check the description of the ionic charge-transfer states provided by the DZ basis set, the basis was augmented with one diffuse p_π primitive Gaussian on each oxygen and the carbon. The exponents (0.028 for oxygen and 0.021 for carbon) were optimized to describe 3p Rydberg states for the respective atoms.[31] Using the augmented basis set, we performed more extensive POL(2)–CI calculations on the ionic planar 4π states.

5. R(π) POL(2)–CI: same as the π POL(2)–CI except single excitations are allowed into the larger six orbital (DZ + R) virtual π space.

IV. Results

The results of the GVB(3/PP) and CI calculations are shown in Table II. In general, the CI calculations were based on the GVB(3/PP) wave function optimized for the state in question. The exceptions to this procedure are the higher roots [e.g., planar 2 $^1A'(4\pi)$] for which the vectors of the lowest root are used, the 1 $^3A_1(4\pi)$ state for which 1 $^1A_1(4\pi)$ vectors were used, and the 1 $^3A_1(2\pi)$, 1 $^{1,3}A_2(3\pi)$, and 1 $^{1,3}B_1(3\pi)$ states for which 1 $^1A_1(2\pi)$ vectors were used. In Table III, we compare the energies of the planar 4π and 5π states with their ozone analogs. The parallel between the spectrum of states for the Criegee intermediate and ozone is manifest.

The basic ordering of states turns out to be in excellent agreement with what we predicted from the qualitative GVB description in section II. The $^1A'(4\pi)$ state is the lowest in energy for planar methylene peroxide. However, the ring state is calculated to be $\sim$1 eV lower than the planar $^1A'(4\pi)$ state. The interpretation and ramifications of this result will be discussed later in section VII.

Comparing the GVB(3/PP) energies with the various CI calculations, it is clear that relaxation of the spin coupling [GVB(3)] and relaxation of the strong orthogonality between the GVB pairs and the oxygen lone pairs [GVB–CI] are both very important. As in ozone, the GVB(3/PP) wave function underestimates the strength of the π bonds in the planar $^1A'(4\pi)$ state, leading to excitation energies that are too small. Relaxing the spin coupling, in general, decreases the energy of the planar $^1A'(4\pi)$ state by 0.2 eV relative to the other states. Relaxing the strong orthogonality restriction is even more important, lowering the energy of the planar $^1A'(4\pi)$ state by 0.1 to 0.4 eV relative to the other states. Finally, we see that the SD–CI and the GVB–CI involve approximately the same number of spin eigenfunctions (SEF's) and lead to qualitatively similar results.

From Table II we see that performing the π POL(2)–CI, which allows the ionic states to become more diffuse, lowers the excitation energies to these states by $\sim$0.6 eV on the average. This is in agreement with the results on the analogous ionic states of ozone.[10b] In Table IVA, we compare the π POL(2)–CI results for the planar $^1A'(4\pi)$ states with and without the diffuse functions. Augmenting the DZ basis set with diffuse functions lowers the excitation energies by

Table II. Calculated Excitation Energies for Methylene Peroxide and Dioxymethane (eV)

State	GVB(3/PP)	GVB(3)	SD–CI	GVB–CI	π POL(2)–CI
		(A) Open Planar COO			
4π 1 ^{1}A'	0.0^a [8]^b	0.0^a [37]^b	0.0^a [119]^b	0.0^a [180]	0.0^a [475]^b
1 ^{3}A'	0.21 [4]	0.45 [39]	0.78 [148]	0.84 [234]	0.80 [673]
2 ^{1}A'		5.87 [37]	5.18 [119]	4.60 [180]	3.66 [475]
2 ^{3}A'		12.25 [39]	8.47 [148]	7.96 [234]	7.64 [673]
3 ^{1}A'		13.10 [37]		9.46 [180]	8.68 [475]
3 ^{3}A'		14.23 [39]		11.09 [234]	
5π 1 ^{3}A''	0.60 [4]	0.83 [25]	1.33 [145]	1.43 [135]	1.24 [627]
1 ^{1}A''	0.65 [4]	0.88 [17]	1.40 [109]	1.50 [99]	1.30 [423]
2 ^{3}A''		12.78 [25]		8.68 [135]	8.20 [627]
2 ^{1}A''		14.90 [17]	10.29 [109]	9.47 [99]	9.11 [423]
		(B) Open Perpendicular COO			
3π 1 ^{3}A''	0.13 [4]	0.31 [25]	0.60 [161]	0.71 [216]	0.64 [750]
1 ^{1}A''	0.22 [4]	0.44 [17]	0.74 [117]	0.83 [150]	0.76 [503]
2 ^{3}A''		13.16 [25]	7.88 [161]	7.47 [216]	6.68 [750]
2 ^{1}A''		15.08 [17]	8.01 [117]	7.53 [150]	6.76 [503]
4π 1 ^{1}A'	0.35 [8]	0.43 [37]	1.14 [169]	1.39 [37]	
1 ^{3}A'	0.65 [4]	0.81 [39]	1.42 [207]	1.78 [39]	
2 ^{1}A'		7.58 [37]	6.67 [169]	8.54 [37]	
2 ^{3}A'		13.20 [39]	10.31 [207]	14.17 [39]	
		(C) Ring			
4π ^{1}A'	−1.59 [8]	−1.88 [37]	−1.12 [169]	−0.91 [37]	
		(D) Open Perpendicular OCO			
4π 1 ^{1}A$_1$	−1.67 [8]	−1.34 [37]	−0.61 [169]	−0.37 [37]	
1 ^{3}A$_1$		−1.20 [39]	−0.58 [207]	−0.24 [39]	
3π 1 ^{3}A$_2$		−1.03 [100]	−0.18 [220]	−0.65 [432]	
1 ^{1}A$_2$		−0.97 [68]	0.02 [160]	−0.48 [300]	
1 ^{3}B$_1$		−0.88 [100]	0.19 [220]	−0.52 [432]	
1 ^{1}B$_1$		−0.78 [68]	0.38 [160]	−0.31 [300]	
2π 1 ^{1}A$_1$	−2.14 [8]	−1.79 [37]	−1.06 [120]	−0.96 [180]	
1 ^{3}B$_2$		−1.76 [34]	−1.03 [158]	−0.93 [234]	

^{a} Energies for the 1 ^{1}A' state are −188.59319, −188.61073, −188.64223, −188.64617, and −188.67240 for columns 1–5, respectively (energies in hartrees). ^{b} Number of spin eigenfunctions used in CI listed in brackets.

Table III. Comparison of the Excitation Energies for Ozone and Planar Methylene Peroxide

Methylene peroxide	ΔE	Ozone	ΔE
1 ^{1}A'(4π)	0.0	1 ^{1}A$_1$ (4π)	0.0^a
1 ^{3}A'(4π)	0.84	1 ^{3}B$_2$(4π)	1.47^a
1 ^{3}A''(5π)	1.43	1 ^{3}B$_1$(5π)	(1.45)^b
		1 ^{3}A$_2$(5π)	(1.73)^b
1 ^{1}A''(5π)	1.50	1 ^{1}B$_1$(5π)	1.98^a
		1 ^{1}A$_2$(5π)	2.06^a

^{a} Reference 10b. ^{b} T. H. Dunning, Jr., P. J. Hay, and W. A. Goddard III, to be published.

Table IV. Properties of the ^{1}A'(4π) Ionic States of Methylene Peroxide

	π POL(2) CI	
	DZ(π)^a	DZ(π) + R(π)^b
(A) Vertical Excitation Energies (eV)		
1 ^{1}A'(4π) → 2 ^{1}A'(4π)	3.66 (0.100)^c	3.64
1 ^{1}A'(4π) → 3 ^{1}A'(4π)	8.68 (0.058)	8.65

(B) Dipole Moments (D)^d

	μ_i
1 ^{1}A'(4π)	3.03
2 ^{1}A'(4π)	4.84
3 ^{1}A'(4π)	3.02

(C) Transition Moments (au)^d

	$|M_{ij}|$
1 ^{1}A'(4π) → 2 ^{1}A'(4π)	1.06
1 ^{1}A'(4π) → 3 ^{1}A'(4π)	0.52

^{a} 475 spin eigenfunctions. ^{b} 697 spin eigenfunctions. ^{c} Oscillator strength. ^{d} Calculated using DZ(π) POL(2)–CI wave function. The central oxygen was used as the origin.

≤0.03 eV. Therefore, we may conclude that introduction of diffuse functions is not necessary.

In Table IV we also list the calculated dipole moments for the three ^{1}A'(4π) states as well as the transition moments and oscillator strengths for the excitations 1 ^{1}A'(4π) → 2 ^{1}A'(4π) and 1 ^{1}A'(4π) → 3 ^{1}A'(4π). The dipole moment of the 1 ^{1}A'(4π) state (3.03 D) is much greater than that for ground state ozone (0.53 D^{32}). The significant increase in the dipole moment is a manifestation of the polarization of the CO bond toward the oxygen, as is evident from the direction of the dipole moment vector (cf. Table IVB). The size and direction of the dipole and transition moments for the 2 ^{1}A'(4π) and 3 ^{1}A'(4π) are in agreement with our simple picture that these states involve charge transfer from the central oxygen π pair to the terminal oxygen [2 ^{1}A'(4π)] or the carbon [3 ^{1}A'(4π)]. Both charge-transfer transitions are strong with calculated oscillator strengths of 0.100 and 0.058 for the 2 ^{1}A'(4π) and 3 ^{1}A'(4π) states, respectively. These oscillator strengths are comparable to that for the analogous transition in the Hartley band of ozone ($f = 0.085$).^{10c} Since the 1 ^{1}A'(4π) → 2 ^{1}A'(4π) transition is strong and relatively low lying (the

band maximum should be at 3.64 eV or 3410 Å), it may be seen in spectroscopic experiments on olefin ozonolyses if methylene peroxide is present in reasonable concentrations.

Before discussing the implications of our results, we should compare our results with the only previous ab initio calculations of methylene peroxide. Ha et al.^{33} employed a closed shell HF wave function with a DZ basis. A modest geometry search was carried out with the conclusion that the ring state is 1.59 eV lower than the open planar form. However, the poor description of planar ^{1}A'(4π) states provided by the HF wave functions vitiates the quantitative as-
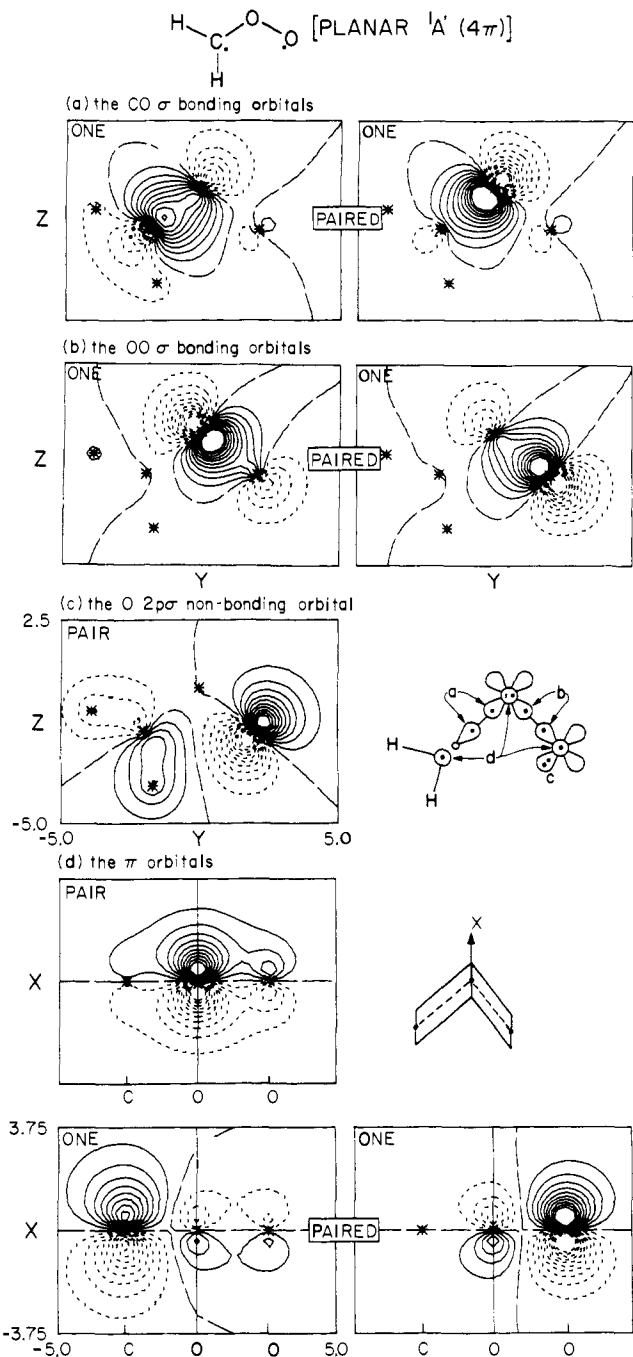
Figure 1. Contour plots of the GVB(3/PP) orbitals for the $^1A'(4\pi)$ state of planar methylene peroxide. Long dashes indicate zero amplitude; the contour increment is 0.05 au. The ONE or PAIR in upper left corner of each plot indicates whether the orbital is singly or doubly occupied. GVB pairs are indicated with the symbol PAIRED connecting them. The same conventions are used in all subsequent plots.

pects of their geometry optimization. Had they carried out calculations on the triplet states, they would have found the planar $^3A'(4\pi)$ state to be nearly 3 eV below the planar $^1A'(4\pi)$ state and 1.5 eV below the ring state! We find the planar $^3A'(4\pi)$ state to be 0.84 eV above the $^1A'(4\pi)$ state and 1.75 eV above the ring state.

V. The Quantitative GVB Description of H₂COO

A. Planar Methylene Peroxide. As expected from section II, the ground state of the planar Criegee intermediate is a singlet biradical. The overlap of the terminal π orbitals is 0.25, slightly smaller in magnitude than the overlap in ozone (0.28).[10c,11] This indicates that there is still signifi-

cant delocalization of the central oxygen π pair onto the outer atoms with the concomitant (Pauli principle induced) increase in the antibonding character of the terminal π orbitals.

Contour plots for the six GVB orbitals and two oxygen lone pairs from the planar $^1A'(4\pi)$ state are given in Figure 1, while plots of the analogous orbitals for the ground state of ozone are given in Figure 2. The (bonding) delocalization of the central π pair onto the outer oxygen in H₂COO is comparable to that in O₃, but the delocalization onto the less electronegative carbon is much less, as expected. Consequently, the three-electron CO π bond is much weaker than the three-electron OO π bond. Also, we note that the (antibonding) delocalization of the carbon singly occupied orbital is much greater than that of the oxygen singly occupied orbital.

The OO σ bonding orbitals in H₂COO are nearly identical to those in O₃. However, for the CO σ bond, the oxygen 2p orbital is much less delocalized than for the OO σ bond, while the carbon sp hybrid is significantly delocalized onto the oxygen. Again this is what one would expect from simple electronegativity arguments. Figure 1 shows that the oxygen lone pair in H₂COO possesses a significant amount of the CH bond character. However, since this orbital was doubly occupied (not described as a GVB pair), it is not uniquely defined, leading to a mixture of what would have been the localized O bond pair and the CH bond pairs.[34]

The plots in Figures 1 and 2 substantiate the qualitative GVB description of H₂COO and O₃ obtained by building these molecules from ground state atoms. The atomic character of all the orbitals is manifest. It is interesting to note that the σ bond orbitals on each oxygen are basically 2p orbitals set at an atomic angle of 90°, so that the 2p orbitals do not, in general, point toward the atom to which they are bonded.

The splitting of the planar $^{1,3}A'(4\pi)$ states (0.84 eV) is 40% smaller than the comparable splitting in ozone (1.47 eV). This is a manifestation of the weaker π bonds in the Criegee intermediate. Similarly, the excitation energies to the planar $^{1,3}A''(5\pi)$ states are 40% smaller than the analogous excitation energies in ozone.

Except for minor differences in the singly occupied π orbitals, the orbital plots for the $^3A'(4\pi)$ state are superimposable on those for the $^1A'(4\pi)$ state. Plots for the three π orbitals and the singly occupied σ orbital from the $^1A''(5\pi)$ state are given in Figure 3. [The plots for the $^3A''(5\pi)$ are superimposable.] The σ bonding orbitals in the $^1A''(5\pi)$ have barely changed from the $^1A'(4\pi)$ state.

Comparing the π orbitals in Figures 1 and 3, we see that the central oxygen π pair delocalizes more onto the carbon for the 5π states; this is expected since it cannot delocalize in a bonding fashion onto the outer oxygen. Therefore, the three-electron CO π bond is expected to be slightly stronger in the 5π states. The central π pair also builds in antibonding character to become orthogonal to the pair localized on the outer oxygen. Finally, we see that the singly occupied nonbonding orbital, now uniquely defined, is localized on the outer oxygen. This reinforces the conclusion that the delocalization of this nonbonding orbital in the $^1A'(4\pi)$ state was solely an artifact of the computational method.

Before going on to the perpendicular states, the 4π and 5π ionic states will be discussed. Analysis of the CI wave functions for the $2\ ^{1,3}A'(4\pi)$, $3\ ^{1,3}A'(4\pi)$, and $2\ ^{1,3}A''(5\pi)$ allows one to conclude that these states are ionic. Moreover, the $2\ A'(4\pi)$ states correspond to charge transfer of a π electron from the central oxygen to the terminal oxygen [configuration **15**], while the $3\ A'(4\pi)$ states involve charge transfer to the carbon [configuration **14**]. Referring to the π POL(2)–CI results we see that the lower electronegativity
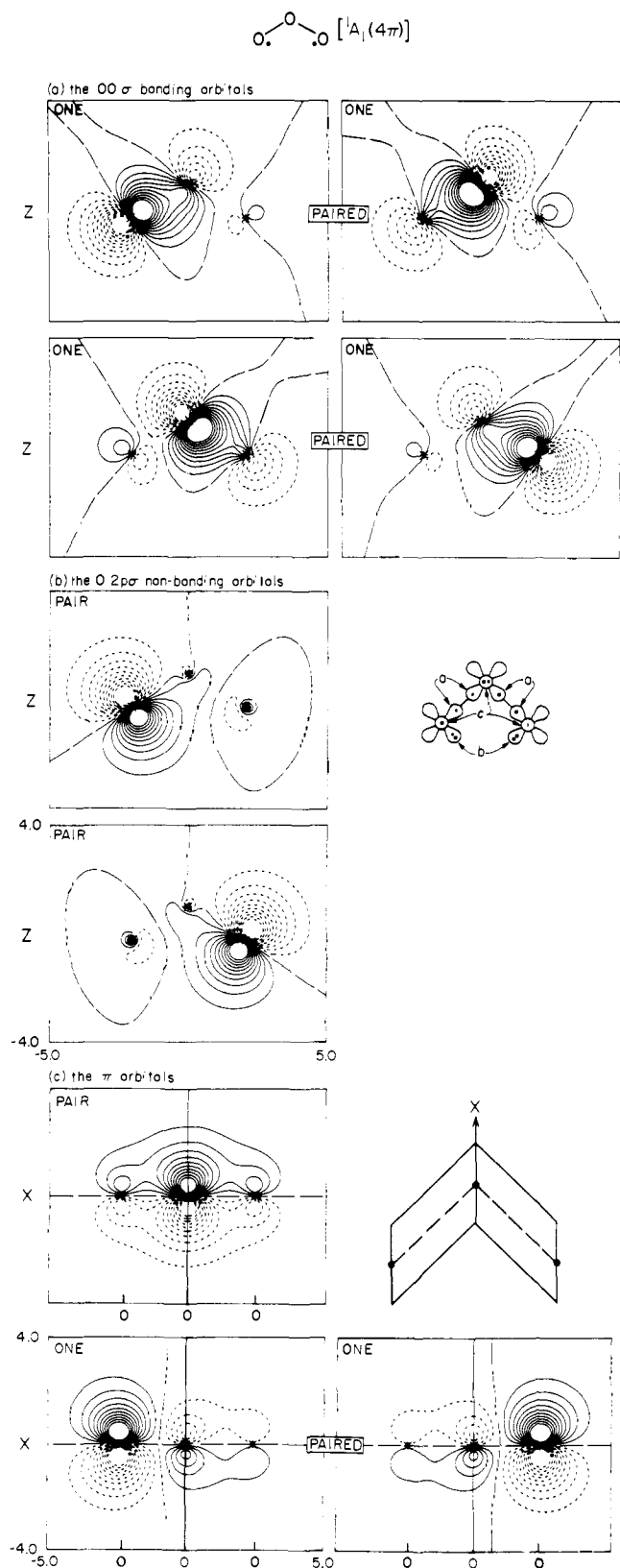
$O \cdot \overset{O}{\diagdown} \cdot O \quad [^1A_1(4\pi)]$

(a) the OO σ bonding orbitals

(b) the O 2pσ non-bonding orbitals

(c) the π orbitals

Figure 2. Contour plots of the GVB(3/PP) orbitals for the ground state $[^1A_1(4\pi)]$ of ozone.

$H-\overset{H}{\underset{H}{C}}-\overset{O}{\diagdown}O \quad [\text{PLANAR } ^1A''(5\pi)]$

(a) the O 2pσ non-bonding orbital

(b) the π orbitals

Figure 3. Contour plots of the GVB(3/PP) orbitals for the $^1A''(5\pi)$ state of planar methylene peroxide.

17

of the carbon leads to a splitting of 5 eV between the two types of charge-transfer states. As expected from the analogy to ozone, the configuration (**15**) usually written for the Criegee intermediate is 3.64 eV [vertical excitation] above the true singlet biradical ground state!

Finally, the ionic 5π states correspond to configuration **17**. The outer π pair on the oxygen delocalizes onto the cen-
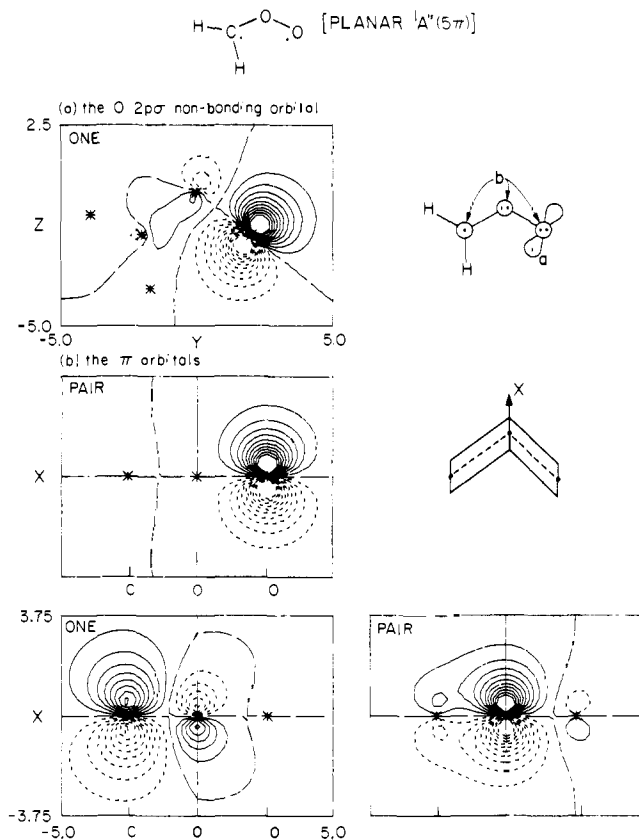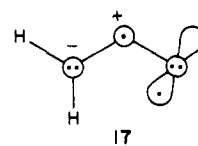
tral oxygen, so that the ionic 5π states are expected to occur at energies comparable to the 3 $A''(5\pi)$ states. The results in Table II confirm this.

B. Perpendicular Methylene Peroxide. The excitation energies to the perpendicular $^{1,3}A''(3\pi)$ states are one-half the energies to the planar $^{1,3}A''(5\pi)$. This is to be expected for two reasons: (1) as discussed previously, the CO π bond is weaker than the OO π bond and, thus, easier to break, and (2) the interaction of the central π pair with the CH bonding pair is not as bad as with the terminal oxygen π pair, since the CH pairs are bent away from the central oxygen. However, it should be pointed out that the difference in the energies of the 3π and 5π states is exaggerated, since the CO bond length was allowed to increase in the (perpendicular) 3π states, while the OO bond length in the planar 5π states was forced to be the same as in the 4π states.

Plots of the π orbitals and σ nonbonding orbitals for the $^1A''(3\pi)$ state are given in Figure 4. [The plots for the $^3A''(3\pi)$ are superimposable.] As expected, the central π pair delocalizes onto the outer oxygen even more than in the planar $^1A'(4\pi)$ state. The singly occupied carbon σ nonbonding orbital builds in antibonding character to become orthogonal to the oxygen lone pair. The other σ-bonding orbitals are nearly identical to those of the $^1A'(4\pi)$ state. We point out here that the carbon 2p orbital is more diffuse than the oxygen 2p orbital, as expected.

When both ends of the Criegee intermediate are rotated to give the perpendicular $^1A'(4\pi)$ state, there is a signifi-
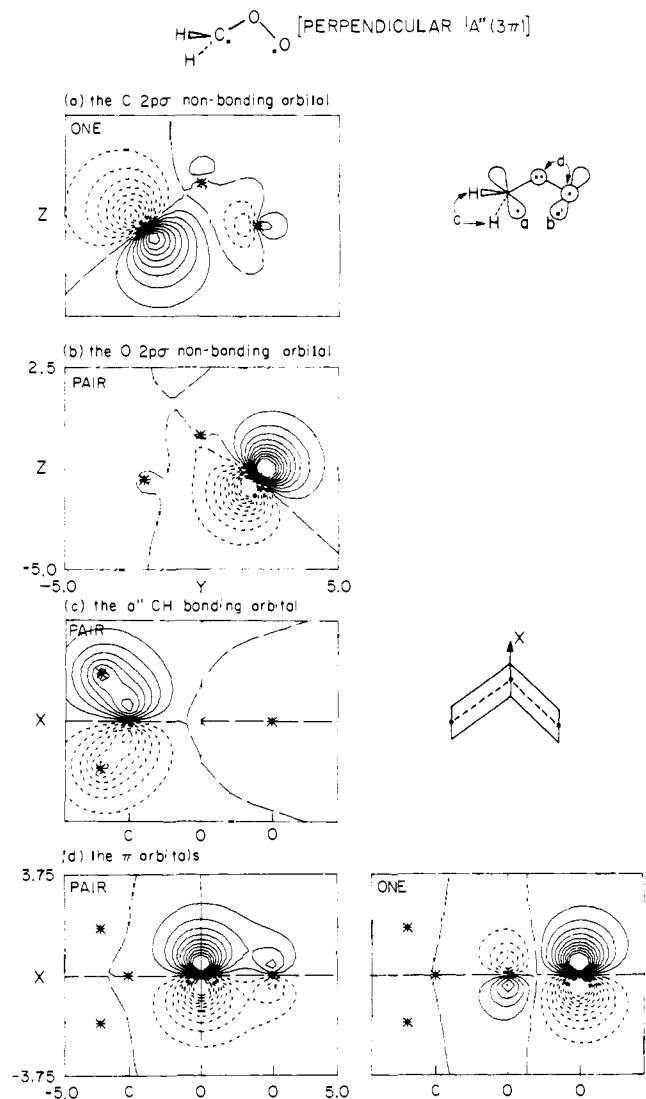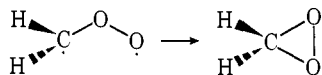
Figure 4. Contour plots of the GVB(3/PP) orbitals for the $^1A''(3\pi)$ state of perpendicular methylene peroxide.

Figure 5. Contour plots of the GVB(3/PP) orbitals for the $^1A'(4\pi)$ state of perpendicular methylene peroxide.

cant amount of bonding between the singly occupied orbitals on the terminal carbon and oxygen even with the bond angle of 103°! The presence of this bonding is manifest in that the perpendicular $^3A'(4\pi)$ state is 0.39 eV = 9.0 kcal/mol higher than the singlet. (The singlet and triplet states would be nearly degenerate in the absence of the 1–3 bonding effect.) This is very similar to the situation encountered in the trimethylene biradical (with a bonding of 5 kcal/mol for a CCC angle of 112°[35]).

The six GVB σ bonding orbitals for the $^1A'(4\pi)$ state are plotted in Figure 5. One can see that the terminal carbon and oxygen 2p orbitals are already beginning to overlap one another. The calculated overlap is 0.23.

C. The Ring State. Closing the COO bond angle to obtain the ring state lowers the energy of the perpendicular

$^1A'(4\pi)$ state by 2.30 eV. Thus, the ring state in methylene peroxide is 0.9 eV lower than the planar $^1A'(4\pi)$ state, while in ozone the ring state is 1.5 eV higher than the ground state.[10] The difference in the two cases (2.4 eV) is too large to be accounted for solely by the weaker CO π bond in methylene peroxide. This judgment is supported by the fact that the $1\,^1A_1(2\pi)$ state of the dioxymethane birad-
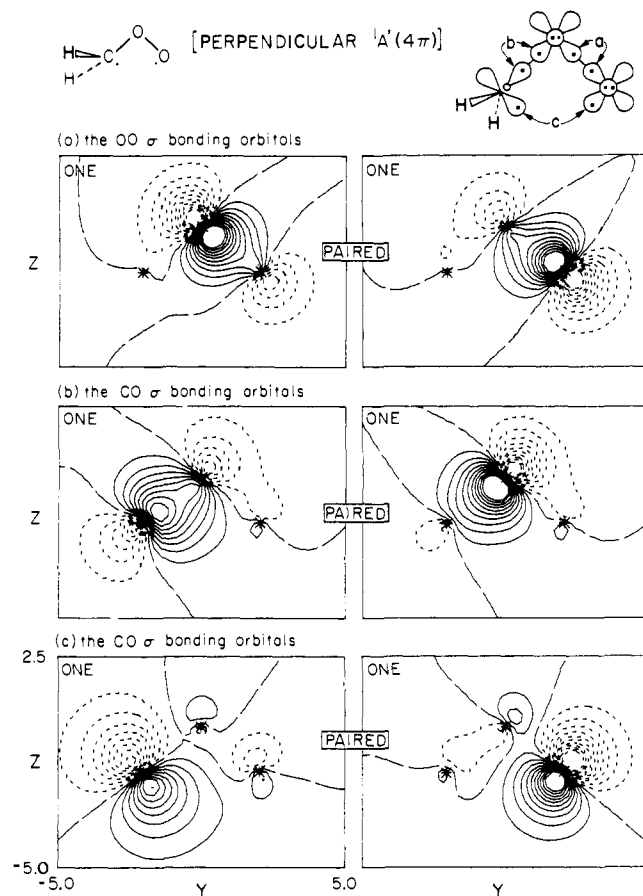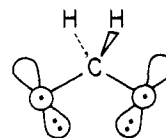
ical shown below

is slightly lower in energy than the ring state (vide infra). The π bond in the $1\,^1A_1(2\pi)$ state is negligible since the $1\,^3A_1(2\pi)$ state is only 0.03 eV higher. Therefore, we conclude that losing the π bond is responsible for reducing the splitting of the ring and the open biradical state by 1.5 eV from what it was in ozone. This is reasonable since the singlet–triplet splitting of the open biradical in ozone was also 1.5 eV.[10] Similarly, the splitting of the planar $^{1,3}A'(4\pi)$ states (7) in methylene peroxide is 0.8 eV, so that the weaker π bond can account for only 1.5 − 0.8 = 0.7 eV of the destabilization of the planar state relative to the ring state.

The remaining 1.7 eV of destabilization must arise from the σ system. Here we note that the OO σ bond formed in the ozone ring state is worth ~12 kcal/mol,[10c] while the CO σ bond formed in the methylene peroxide ring state is worth ~56 kcal/mol (vide infra). The differential effect, 44 kcal/mol = 1.9 eV, nicely accounts for the stability of the methylene peroxide ring state.

Plots of the six GVB σ bonding orbitals for the methylene peroxide ring state are given in Figure 6. The orbitals still retain their basic atomic character and so are not directed toward the atom with which they form a bond. As before, the carbon orbitals delocalize more than the oxygen orbitals.

D. Dioxymethane. Comparing the low-lying states of the dioxymethane biradical with their counterparts in ozone, we
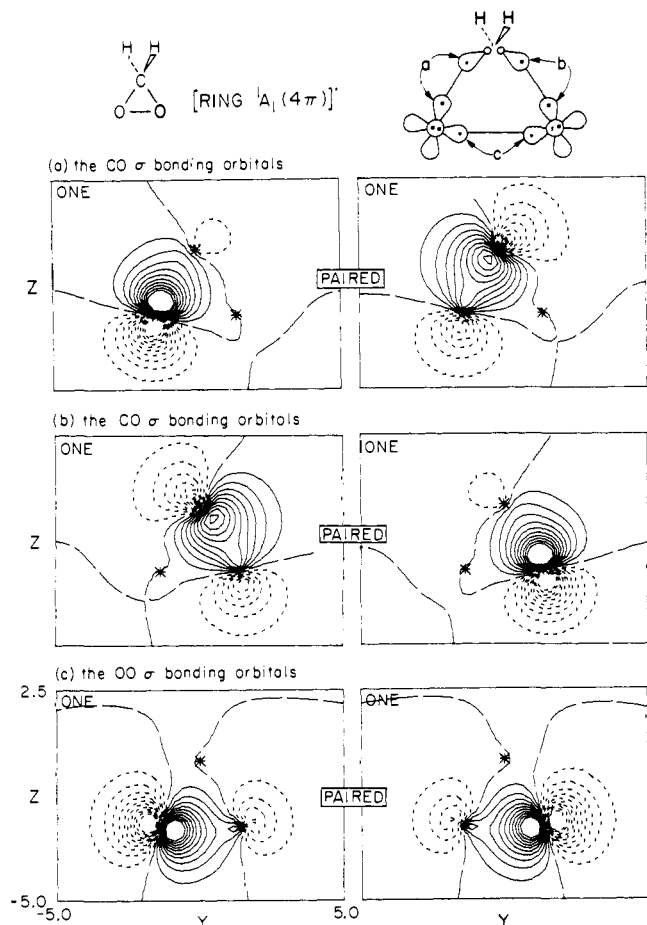
Figure 6. Contour plots of the GVB(3/PP) orbitals for the $^1A_1(4\pi)$ state of ring methylene peroxide.

see that the width of the spectrum has been drastically decreased. The smaller excitation energies in dioxymethane demonstrate the loss of bonding in the π system. The central CH bonds cannot delocalize as the central oxygen π pair did in ozone or methylene peroxide. The excitations to the 3π states (analogous to the 5π states of ozone) occur in the range 0.3–0.6 eV instead of 1.8–2.1 eV.[10]

In Figure 7 the plots of the six GVB σ bonding orbitals for the $^1A'(4\pi)$ state of dioxymethane are given. They are exactly what one would expect to get upon opening the ring state by breaking the OO σ bond. In Figure 8 the π and oxygen long pairs for the $^1A'(2\pi)$ state are plotted. As mentioned above, the CH bond does not delocalize significantly and the singly occupied orbitals are localized on the oxygens. The overlap of the singly occupied π orbitals is 0.05 instead of 0.25 as in methylene peroxide.

VI. Stability of the Criegee Intermediate

A. GVB Calculations. For methylene peroxide to play an important role as an intermediate in the ozonolysis mechanism, it must have a reasonable lifetime. One might imagine that methylene peroxide, if formed, would rapidly fall apart into $CH_2 + O_2$ or $H_2CO + O$. This possibility can be checked by calculating the dissociation energies of the states of methylene peroxide.

1. Planar Methylene Peroxide. First consider the planar $^1A'(4\pi)$ state [or $^3A'(4\pi)$]. Breaking the CO bond leads to $CH_2(^3B_1) + O_2(^3\Sigma_g^-)$
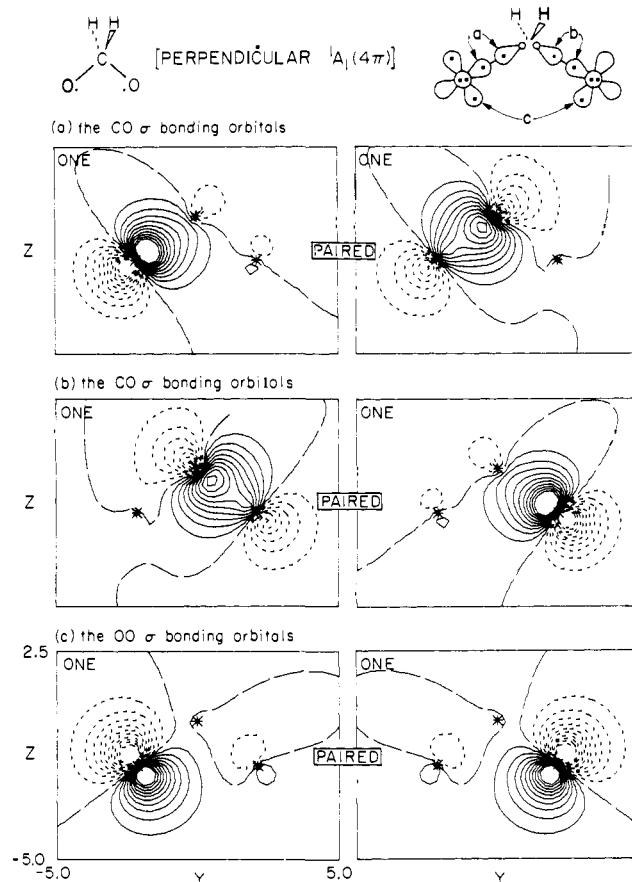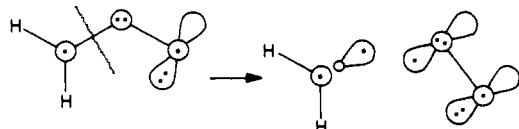
Figure 7. Contour plots of the GVB(3/PP) orbitals for the $^1A_1(4\pi)$ state of dioxymethane.

Table V. Calculated Bond Strengths (kcal/mol) and Total Energies (hartree) for Methylene Peroxide[e]

	GVB–CI, au	
$H_2COO[\text{plan } 1\ ^1A'(4\pi)] \rightarrow H_2CO(^3A'') + O(^3P)$	43.5	
$H_2COO[\text{plan } 1\ ^1A'(4\pi)] \rightarrow CH_2(^3B_1) + O_2(^3\Sigma_g^-)$	55.9	
$H_2COO[\text{perp } 1\ ^3A''(4\pi)] \rightarrow H_2CO(^1A_1) + O(^3P)$	−53.8	
$H_2COO[\text{perp } 1\ ^3A''(4\pi)] \rightarrow CH_2(^3B_1) + O_2(^3\Sigma_g^-)$	39.7	
	GVB(PP), au	
$H_2COO[\text{plan } 1\ ^1A'(4\pi)]$	−188.59319	−188.64617
$H_2COO[\text{perp } 1\ ^3A''(3\pi)]$	−188.58844	−188.62025
$H_2CO(^3A'')$	−113.77798[a]	−113.77798[a]
$H_2CO(^1A_1)$	−113.88504[a]	−113.90722[a]
$O(^3P)$	−74.79884[b]	−74.79884[b]
$CH_2(^3B_1)$	−38.9119[c]	−38.9119[c]
$O_2(^3\Sigma_g^-)$	−149.60125[d]	−149.64510[d]

[a] L. B. Harding and W. A. Goddard III, J. Am. Chem. Soc., submitted for publication. [b] Reference 24. [c] Reference 12a. [d] W. A. Goddard III and W. R. Wadt, unpublished results. [e] All calculations are for the double ζ basis.

while breaking the OO bond leads to $H_2CO(^3A'') + O(^3P)$

The calculated dissociation energies using consistent GVB–CI wave functions are listed in Tables V and VI. The OO and CO bond strengths are calculated to be 43.5 and 55.9 kcal/mol, respectively, so that the planar $^1A'(4\pi)$ state is stable with respect to dissociation.[36] The planar $^3A'(4\pi)$ state is only 19.4 kcal/mol above the $^1A'(4\pi)$ state and so it is also bound with respect to dissociation. Even the planar

[PERPENDICULAR $^1A_1(2\pi)$]

(a) the CO σ bonding orbital

(b) the CO σ bonding orbitals

(c) the O 2pσ non-bonding orbitals

(d) the a'' CH bonding orbitals
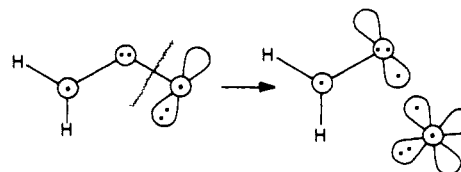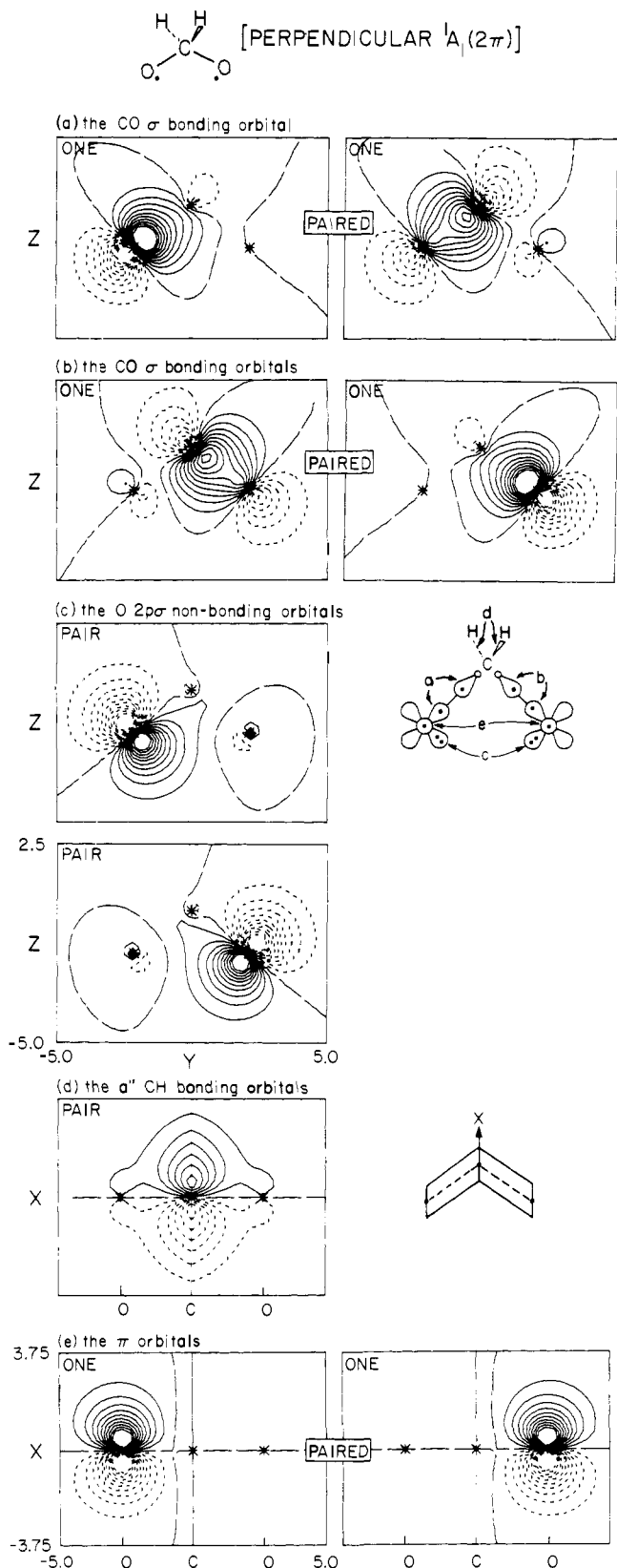

(e) the π orbitals

Figure 8. Contour plots of the GVB(3/PP) orbitals for the $^1A_1(2\pi)$ state of dioxymethane.

Table VI. Calculated Dissociation Energies (kcal/mol)

State	Geometry	Dissociation products	ΔE
1 $^1A'(4\pi)$	COO plan	$H_2CO(^3A'') + O(^3P)$	−43.5
1 $^3A'(4\pi)$	COO plan	$H_2CO(^3A'') + O(^3P)$	−24.1
1 $^3A''(5\pi)$	COO plan	$H_2CO(^3A'') + O(^3P)$	−10.5
1 $^1A''(5\pi)$	COO plan	$H_2CO(^3A'') + O(^3P)$	−8.9
1 $^3A''(3\pi)$	COO perp	$H_2CO(^1A_1) + O(^3P)$	53.8
1 $^1A''(3\pi)$	COO perp	$H_2CO(^1A_1) + O(^1D)$	5.6
1 $^1A'(4\pi)$	COO perp	$H_2CO(^1A_1) + O(^1D)$	24.1
1 $^3A'(4\pi)$	COO perp	$H_2CO(^1A_1) + O(^3P)$	78.5
1 $^1A_1(4\pi)$	Ring	$H_2CO(^1A_1) + O(^3P)$ [spin change]	16.5
1 $^1A_1(4\pi)$	OCO perp	$H_2CO(^1A_1) + O(^3P)$ [spin change]	28.9
1 $^3A_1(4\pi)$	OCO perp	$H_2CO(^1A_1) + O(^3P)$	31.9
1 $^3A_2(3\pi)$	OCO perp	$H_2CO(^1A_1) + O(^3P)$	22.4
1 $^1A_2(3\pi)$	OCO perp	$H_2CO(^1A_1) + O(^3P)$ [spin change]	26.4
1 $^3B_1(3\pi)$	OCO perp	$H_2CO(^1A_1) + O(^3P)$	26.4
1 $^1B_1(3\pi)$	OCO perp	$H_2CO(^1A_1) + O(^3P)$ [spin change]	30.3
1 $^1A_1(2\pi)$	OCO perp	$H_2CO(^3A'') + O(^3P)$	−65.6
1 $^3B_2(2\pi)$	OCO perp	$H_2CO(^3A'') + O(^3P)$	−64.9
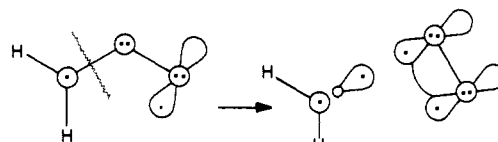
bond strength in the 5π states is 45.4 kcal/mol for the triplet and 88.5 kcal/mol for the singlet.

The utility of GVB diagrams is evident, since without them one might naively assume that planar methylene peroxide would dissociate into ground state H_2CO, rather than the $n\pi^*$ state. The $n\pi^*$ state of H_2CO is about 3 eV or 70 kcal/mol above the ground state,[17] so that methylene peroxide is actually higher in energy than $H_2CO(^1A_1)$ + $O(^3P)$. Therefore, one could have been mislead concerning the stability of planar methylene peroxide.

2. Perpendicular Methylene Peroxide. Turning to the perpendicular form of methylene peroxide, we find a totally different situation. For the perpendicular $^3A''(3\pi)$ state breaking the CO bond leads to $CH_2(^3B_1) + O_2(^3\Sigma_g^-)$ and a
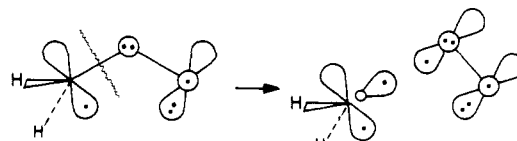
calculated bond strength of 39.7 kcal/mol (note that this process is *not* spin forbidden). However, breaking the OO bond leads to $H_2CO(^1A_1) + O(^3P)$ and a calculated bond
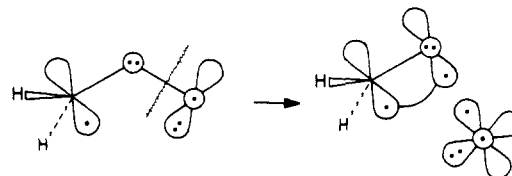
strength of −53.8 kcal/mol, i.e., the perpendicular $^3A''(3\pi)$ state should fall apart, since a significant barrier for scission of the OO bond is not expected. Breaking the OO bond in the $^1A''(3\pi)$ state leads to $H_2CO(^1A_1) + O(^1D)$. Since $O(^1D)$ is 45.4 kcal/mol above $O(^3P)$[39] and the $^1A''(3\pi)$ state is 2.8 kcal/mol above the $^3A''(3\pi)$ state, the $^1A''$ (3π) state is unbound by only 5.6 kcal/mol. Dissociation to $H_2CO(^1A_1) + O(^3P)$ is 45.4 kcal/mol further downhill, but is a much slower process as it requires a change in multiplicity, i.e., intersystem crossing. Finally, the perpendicular $^3A'(4\pi)$ state will fall apart into $H_2CO(^1A_1) + O(^3P)$ [downhill by 78.5 kcal/mol], while the perpendicular $^1A'(4\pi)$ state will collapse into the ring state [downhill by

$^3A''(5\pi)$ and $^1A''(5\pi)$ states are bound states as they are 33.0 and 34.6 kcal/mol above the $^1A'(4\pi)$ state.[37] Breaking the CO bond in the 5π states leads to $CH_2(^3B_1) + O_2(^1\Delta_g)$ for the triplet state and $CH_2(^1B_1) + O_2(^1\Delta_g)$ for the singlet state. Since $O_2(^1\Delta_g)$ is 22.5 kcal/mol above $O_2(^3\Sigma_g^-)$[38] and $CH_2(^1B_1)$ is 44.7 kcal/mol above $CH_2(^3B_1)$,[12a] the CO

53.0 kcal/mol]. The $^1A'(4\pi)$ state is unbound with respect to $H_2CO(^1A_1)$ + $O(^1D)$, but this is downhill by only 24.1 kcal/mol.

The 3π and 4π triplet states of dioxymethane readily dissociate into $H_2CO(^1A_1)$ + $O(^3P)$. The 3π and 4π singlet states, however, are bound by 15–20 kcal/mol with respect to dissociation into $H_2CO(^1A_1)$ + $O(^1D)$, but may dissociate *slowly* by intersystem crossing into $H_2CO(^1A_1)$ + $O(^3P)$. The singlet and triplet 2π states dissociate into $H_2CO(^3A'')$ + $O(^3P)$ and so have CO bond strengths on the order of 65 kcal/mol.

B. Thermochemical Calculations. 1. Methylene Peroxide. As a check of our quantum mechanical dissociation energies, we recalculated them using thermochemical arguments.[40] The experimental heats of formation for the various dissociation products were obtained for the most part from Benson.[40-42] The heat of formation of methylene peroxide is, of course, not known experimentally, so it must be estimated by constructing it from related molecules for which there are experimental data.

Methylene peroxide may be formed from methyl peroxide by pulling off one of the hydrogens

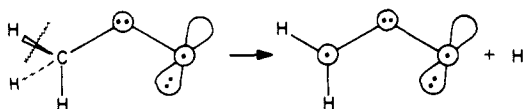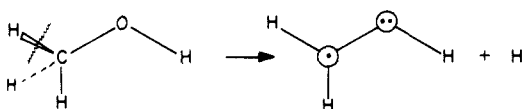so that $\Delta H_f°(\dot{C}H_2OO\cdot) = D(H\text{-}CH_2OO) - \Delta H_f°(H) + \Delta H_f°(CH_3OO\cdot)$. The CH bond strength in methyl peroxide should be comparable to that in methanol, $D(H\text{-}\dot{C}H_2OH)$

= 94 kcal/mol,[40,43,44] since in both cases the resulting state is stabilized by a three-electron $CO\pi$ bond. Moreover, since $D(H\text{-}CH_2CH_3)$ = 98 kcal/mol, the three-electron CO π bond is worth 4 kcal/mol. By analogy, $D(H\text{-}CH_2OO)$ is assumed to be 94 kcal/mol.

To estimate $\Delta H_f°(CH_3OO\cdot)$, we use

$$\Delta H_f°(CH_3OO\cdot) = \Delta H_f°(CH_3O) + \Delta H_f°(O) -$$

$$D(CH_3O\text{-}O) = 3.5 + 59.6 - D(CH_3O\text{-}O) =$$

$$63.1 - D(CH_3O\text{-}O)$$

inserting the experimental values for $\Delta H_f°(CH_3O)$ and $\Delta H_f°(O)$. To estimate $D(CH_3O\text{-}O)$, we consider

$$D(HO\text{-}O) = \Delta H_f°(OH) + \Delta H_f°(O) - \Delta H_f°(HOO\cdot) =$$

$$9.4 + 59.6 - 5 = 64$$

In addition, it is known experimentally that $D(HO\text{-}OH)$ = 51.3 kcal/mol, while $D(RO\text{-}OR)$ = 38 kcal/mol. From this, we conclude that each R group destabilizes an OO σ bond by 7 kcal/mol through repulsive interactions with the oxygen lone pairs. Therefore, we assume $D(CH_3O\text{-}O)$ = 64 – 7 = 57, so that $\Delta H_f°(CH_3OO\cdot)$ = 63 – 57 = 6 kcal/mol (in agreement with the tentative experimental value of 6.7 kcal/mol[40]). Finally, we obtain

$$\Delta H_f°(\dot{C}H_2OO\cdot) = 94 - 52 + 6 = 48 \text{ kcal/mol}$$

Using this value, we find

$$D(CH_2O\text{-}O) = \Delta H_f°(CH_2O^*) + \Delta H_f°(O) -$$

$$\Delta H_f°(\dot{C}H_2OO\cdot) = 46 + 59\tfrac{1}{2} - 48 = 57\tfrac{1}{2} \text{ kcal/mol}$$

This result is in excellent agreement with our previous estimate, $D(O\text{-}OR)$ = 57 kcal/mol. Therefore, we will assume

$\Delta H_f°(CH_2OO\cdot)$ = 48 kcal/mol. Using this value, we calculate the OO and CO bond strengths to be

$$D(CH_2O\text{-}O) = 46 + 59\tfrac{1}{2} - 48 \cong 57\tfrac{1}{2} \text{ kcal/mol}$$

$$D(CH_2\text{-}OO) = \Delta H_f°(CH_2) + \Delta H_f°(O_2) -$$

$$\Delta H_f°(CH_2OO) = 93 + 0 - 48 = 45 \text{ kcal/mol}$$

Comparing with the ab initio results, we see that there is a discrepancy of ~10 kcal/mol in each bond strength. Since both the thermochemical and ab initio results are expected to have errors of ±5 kcal/mol, the agreement between the two approaches is reasonable.

2. Dioxymethane. Thermochemical estimates of the heat of formation for dioxymethane are also readily made. Dioxymethane may be formed by breaking both OH bonds in dihydroxymethane
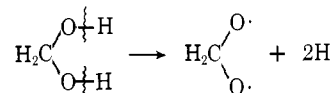
or $\Delta H_f°(CH_2O_2) = D(H_2C(OH)O\text{-}H) + D(H_2C(\dot{O})O\text{-}H) + \Delta H_f°(H_2C(OH)_2) - 2\Delta H_f°(H)$. Experiment gives $D(RO\text{-}H)$ = 104 kcal/mol so that

$$\Delta H_f°(CH_2O_2) = 104 + 104 + \Delta H_f°(H_2C(OH)_2) -$$

$$2(52) = 104 + \Delta H_f°(H_2C(OH)_2)$$

To estimate $\Delta H_f°(H_2C(OH)_2)$, we consider

$$\Delta H_f°(H_2C(OH)_2) = \Delta H_f°(OH) + \Delta H_f°(H_2\dot{C}OH) -$$

$$D(H_2C(OH)\text{-}OH) = 9.4 - 6 - D(H_2C(OH)\text{-}OH) =$$

$$3.4 - D(H_2C(OH)\text{-}OH)$$

But, from our previous calculations we would expect

$$D(H_2C(OH)\text{-}OH) = D(R\text{-}OH) - (\text{stabilization of three-}$$

$$\text{electron CO } \pi \text{ bond}) = 92 - 4 = 88$$

Therefore, we have $\Delta H_f°(H_2C(OH)_2)$ = –84.5 kcal/mol. The experimental value[44] of $\Delta H_f°(H_2C(OH)_2)$ = –93.5 kcal/mol seems to us to be too low since it leads to $D(H_2C(OH)\text{-}OH)$ = 97, an unrealistically large value.

Using $\Delta H_f°(H_2C(OH)_2)$ = –84.5 kcal/mol, we have $\Delta H_f°(H_2C\dot{O}_2)$ = 19.5 kcal/mol. It is important to note that this calculation of the heat of formation assumes there is no interaction between two radical electrons. There are in fact three possible configurations (2π, 3π, and 4π), each leading to both singlet and triplet states. Significant splittings are expected between some of these states. Thus the $\Delta H_f°$ = 19.5 kcal/mol does not refer to any specific state of dioxymethane. A firmer reference point for comparison with the ab initio results is obtained by forming the ring state
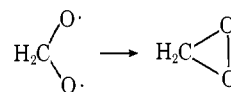
The energy drops by just the strength of the new OO σ bond. Normally, $D(RO\text{-}OR)$ = 38, but a correction must be made for strain. Using Benson's[40] estimate of 26 kcal/mol strain energy for a three-membered ring, the heat of formation of the ring state becomes 19.5 – 12 = 7.5 kcal/mol.

As a check of our previous estimate of $\Delta H_f°(\dot{C}H_2OO\cdot)$, we recalculate it using the heat of formation of the ring state. Breaking one of the CO σ bonds in the ring state costs $D(R\text{-}OR) - 26 = 82 - 26 = 56$ kcal/mol, so that the heat of formation for the perpendicular $A'(4\pi)$ state with no interaction between the radical electrons is 63.5 kcal/mol.
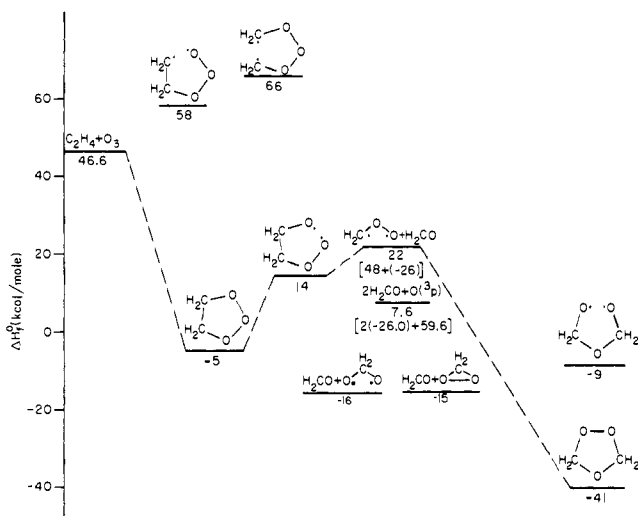
Figure 9. The thermochemistry of ozonolysis. The calculated heats of formation are shown below each molecule or set of molecules.

Table VII. Calculated Heats of Formation, ΔH_f° (kcal/mol)

		Thermo-chemical	GVB–CI	SD–CI
(structure)	$^1A'(4\pi)$	48	28.5	33.3
(structure)	$A'(4\pi)$	63.5	65.0	62.8
(structure)	$^1A_1(4\pi)$	7.5	7.5[a]	7.5[a]
(structure)	$A_1(4\pi)$	19.5	21.4	19.6

[a] The thermochemical heat of formation for the ring state has been used as the reference point for converting the results of the CI calculations into standard heats of formation.

Rotating both terminal groups and forming three-electron CO and OO π bonds gives the planar $^1A'(4\pi)$ state. As before, the three-electron CO π bond is worth 4 kcal/mol, while the OO π bond is worth 13 kcal/mol. The latter result was obtained from heats of formation of HOO· and ROO·. Therefore, the calculated heat of formation of the planar $^1A'(4\pi)$ state is 46.5 kcal/mol, which is in good agreement with our previous result of 48 kcal/mol.

C. Comparison of GVB and Thermochemical Calculations. In Table VII we compare the relative energies of the ring state with the open methylene peroxide and dioxymethane states as calculated by thermochemical and ab initio techniques. The thermochemical energies for the perpendicular biradical species are based on the assumption of no interaction between the radical orbitals. There is, in fact, some interaction (1–9 kcal/mol separation of the singlet and triplet states), and hence we have averaged the ab initio energies in order to compare with the thermochemical values. (Consequently reference to spin multiplicity in the state designation is dropped.)

The agreement between the thermochemical and ab initio results for the perpendicular states is excellent. However, the relative energies of the planar and perpendicular states appear to be underestimated by the GVB calculations. There are two apparent reasons for this discrepancy. (1) The GVB–CI may be biased in favor of the planar state as many more configurations or spin eigenfunctions are used for the planar state. The fact that the SD–CI leads to energy separations (between the planar and perpendicular states) about 5 kcal/mol closer to the thermochemical results supports this argument. (Note, however, that the relative energies of the perpendicular states are the same in both CI calculations, reaffirming that the smaller GVB–CI has all the important configurations required for a consistent description.) (2) The energies of the perpendicular states are too high relative to the planar state because of the particular geometry and basis set used in the calculations. Double-ζ bases are known to favor states with open geometries versus those with ring geometries.[45] [Introduction of polarization functions (d basis functions) leads to a more consistent description.] Finally, the geometry employed for the perpendicular $^{1,3}A'(4\pi)$ states is not optimal. As mentioned previously, a longer OO bond should have been used to account for the repulsive interaction of the oxygen π pairs.

One important observation drawn from the data in Table

VII is that Benson's[40] estimate of 26 kcal/mol for the strain energy of a three-membered ring *is* consistent with our ab initio calculations.

VII. Implications for the Mechanism of Ozonolysis

A. Solution Phase. 1. Formation of the Primary Ozonide. Figure 9 shows an energy level diagram for the ozonolysis of ethylene.[46-48] The overall pathway assumed by the Criegee mechanism, shown by the dotted line in Figure 9, is certainly feasible from a thermochemical standpoint. However, interesting facets of ozonolysis will become evident if we pursue the Criegee mechanism step by step.

Ozonolysis of ethylene is known to have a very low activation energy (4–5 kcal/mol).[49-51] Nonconcerted addition of ozone to ethylene would lead to an activation energy of >10 kcal/mol (cf. Figure 9), so that the primary ozonide must be formed in a concerted manner. Bailey[52] has proposed a loosely bound π complex (18) between the ozone and olefin as a precursor to the primary ozonide. The only

18
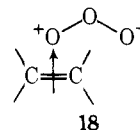
experimental evidence for such a π complex relates to complexes (presumably charge transfer in nature) between ozone and aromatic π systems.[7,53] Since we now know that the ozone is a singlet biradical rather than a zwitterion, the possibility of a π complex as envisioned by Bailey becomes very remote.

There is some experimental evidence for pathways other than the Criegee mechanism. For example, the production in some systems of epoxides and concomitant evolution of O_2 rather than production of secondary ozonides has been interpreted as evidence for a σ complex (19).[54] It is easy to

19
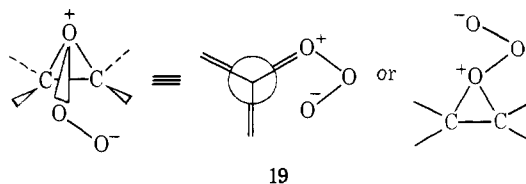
see how 19 can lose O_2 to form an epoxide or proceed directly to a secondary ozonide. However, the GVB diagram (20) corresponding to 19 shows that too many electrons are crammed into the same region of space, so that the σ complex is actually an unreasonable (high energy) structure.

20
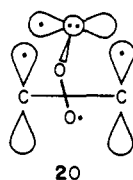
The production of epoxides is greatest in 1-olefins with the 1 position disubstituted with bulky groups (**21**).[52] Bailey has performed extensive studies on **21** varying R and R′

21
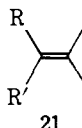
with the conclusion that the production of epoxides and evolution of O_2 is directly correlated with steric hindrance.[52] To explain these results, Bailey proposed that the ozone addition was not concerted but rather proceeded through an open σ complex (**22**), which could give off O_2 and close to

22
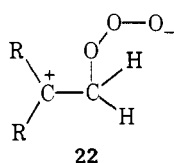
the epoxide.[6b,55] This approach is much more reasonable although we believe that **22** is a poor representation of the intermediate. The appropriate GVB diagram is given by **23**. The dotted line in **23** indicates crudely the space excluded

23
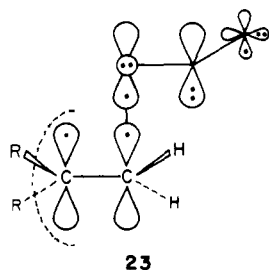
by the bulky R groups [arising from the pair–pair repulsion (Pauli principle) between the bonding pairs of R and those of ozone]. As a result a bidentate attack by the ozone is energetically unfavorable. From **23** we see that as the OO σ bond breaks to yield a free $O_2(^3\Sigma_g^-)$, the remaining O is in perfect position to close to the epoxide.
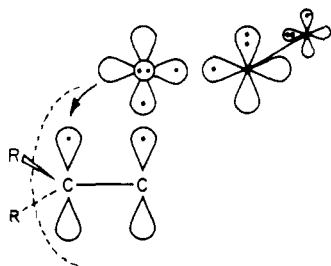
2. Decomposition of the Primary Ozonide. Decomposition of the primary ozonide into methylene peroxide and formaldehyde is likely to proceed via the biradical intermediate shown in Figure 9, in which only a weak OO σ bond is broken. Formation of the Criegee intermediate from the equilibrium conformation of either the primary ozonide or the higher energy intermediate leads preferentially to the planar $^1A'(4\pi)$ state. The perpendicular $^1A''(3\pi)$ state may also be formed. Use of molecular models is necessary to see this result for the concerted reaction, while the state produced by the biradical intermediate may be seen as follows.
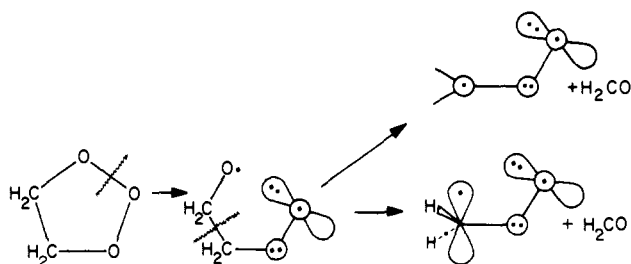
The fast rotation about the CC bond together with the orientation of the oxygens to give a three-electron π bond in the intermediate determines the states of methylene peroxide that are produced. Since the energy of the perpendicular $^1A''(3\pi)$ state is 19.1 kcal/mol above that of the planar $^1A'(4\pi)$ state assumed in Figure 2, formation of the $^1A''(4\pi)$ state is expected to be the primary decomposition pathway in solution.

At this point it seems obvious that decomposition of the primary ozonide leads to a singlet biradical state of methylene peroxide. How then did the Criegee zwitterion gain such a broad acceptance among chemists? As previously stated, simple VB structures indicated that ozone was a zwitterion and hence it was natural to conclude that methylene peroxide was also. Moreover, Criegee[6b] found that ozonolysis of styrene does not produce any detectable amounts of polystyrene. From this result, he concluded that no radicals were present, confirming his postulate of the zwitterion intermediate.

We now know that both ozone and methylene peroxide are singlet biradicals. The key conceptual problem that led to the misinterpretation of the styrene experiment was the failure to recognize that singlet biradicals may behave very differently from simple radicals. The persistence of this misconception is evident in the analysis of some very illuminating mechanistic work on ozonolysis by Murray and Suzui.[9] They photolyzed diazo compounds in the presence of O_2 and aldehyde. Secondary ozonides were produced, which were interpreted as confirmation of the Criegee zwitterion as an intermediate in ozonide formation. The following reaction scheme was proposed[9]
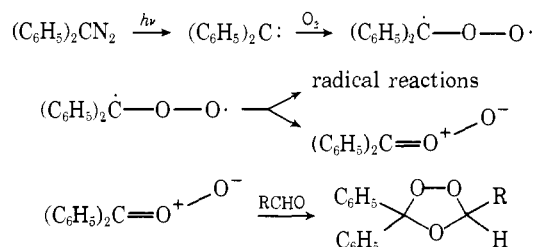
The diphenyl methylene peroxide is assumed to lead to reactions characteristic of free radicals while only the zwitterionic form produces the secondary ozonides.[56]

The intermediacy of the zwitterion in forming secondary ozonides is not only unnecessary, as shown in Figure 9, but it is also incorrect since the zwitterionic state is too energetic (~75 kcal/mol) to be populated. Therefore, replacing the zwitterion model with the biradical model will not cause any major conflict with experiment, although it should have important consequences for interpretation of experiment.

3. The Role of Dioxymethane. The planar $^1A'(4\pi)$ state produced by the decomposition of the primary ozonide has enough excess energy to deform into the more stable ring state. The ring state, if formed, may reopen and attack either an aldehyde to give the secondary ozonide or an olefin to give a 1,3-dioxolane

(4π)
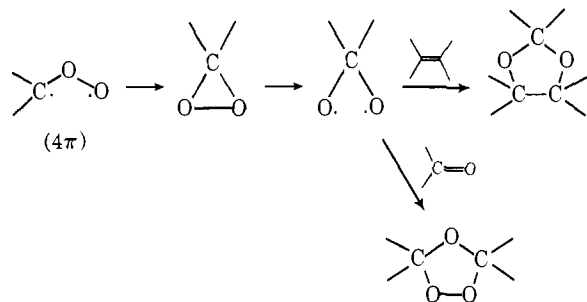
The reaction of dioxymethane with formaldehyde is downhill by some 35 kcal/mol, while the reaction with ethylene is downhill nearly 100 kcal/mol! However, there is no experimental evidence for production of 1,3-dioxolanes and trapping experiments were interpreted to rule out the possibility of dioxymethane as an intermediate.[57]

A few comments about the latter experiments are in order. It is clear that formation of dioxymethane would have important ramifications for the oxygen isotope labeling work. Attack of aldehyde labeled with ^{18}O by dioxymethane would lead to a statistical distribution of the labeled oxygen in the secondary ozonide. Attack of labeled aldehyde, on the other hand, by methylene peroxide would lead to secondary ozonide with the labeled oxygen exclusively in the ether position. This fact stirred Fliszar and coworkers[57] to investigate the possibility of dioxymethane as an intermediate. They ran ozonolyses in the presence of alcohols in order to trap the Criegee intermediate. Trapping of methylene peroxide with alcohol was assumed to lead exclusively to alkoxy hydroperoxides, which is in agreement with the thermochemistry of the reaction.

$\Delta H = -54$ kcal/mol

$\Delta H = -8$ kcal/mol
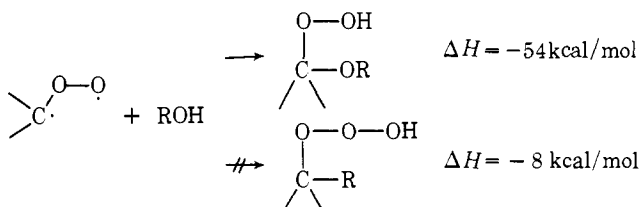
Trapping of dioxymethane with alcohol was assumed to lead exclusively to hydroxyperoxides, which is not, however, supported by the thermochemistry

$\Delta H = -35$ kcal/mol

$\Delta H = -38$ kcal/mol
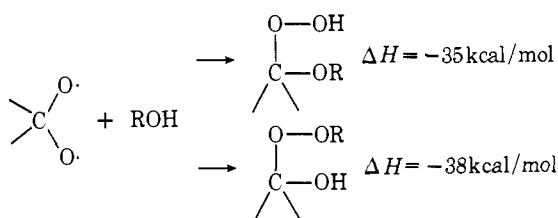
More dynamic data are necessary to be able to distinguish between these two reaction pathways. In any case, Fliszar[57] could not detect any hydroxyperoxides. However, this result is *not* conclusive proof against dioxymethane, as previously thought.

B. Gas Phase. 1. Decomposition of the Primary Ozonide.
The thermochemical scheme for ozonolysis outlined in Figure 9 applies in the gas phase. However, there is no solvent present to soak up excess energy rapidly, so that production of highly excited and/or reactive species ensues. Some of these may be important in carrying the chain reactions that occur in atmospheric air pollution.

The decomposition of the primary ozonide into methylene peroxide and formaldehyde proceeds via a biradical intermediate in which a weak OO σ bond is severed. Recently, O'Neal and Blumstein[47] proposed an alternative reaction sequence involving the biradical intermediate, namely, α-H abstraction to produce a hydroperoxide.

$\Delta H = -74$ kcal/mole
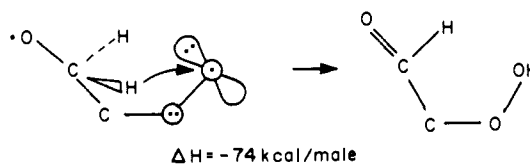
In light of the great exothermicity, it is not surprising that simple theoretical calculations show hydroperoxide formation dominating decomposition into methylene peroxide and formaldehyde.[47] In addition, α-H abstraction, along with β- and γ-H abstraction for alkylated ethylenes, has been used to explain many of the products observed in gas phase ozonolyses, as well as the chemiluminescent species.[47,58] However, it is not clear why H abstraction appears to be a negligible decomposition mode for the primary ozonide in solution. Hydroperoxides would be expected as a major product in solution phase ozonolyses, if the α-H abstraction reaction scheme were operative. Further theoretical and experimental work is warranted to determine the relative importance of H abstraction and decomposition into methylene peroxide and formaldehyde.

As intimated in section VII.A.2, the planar $^1A'(4\pi)$ state of methylene peroxide is expected to be formed preferentially in the decomposition of the primary ozonide. One would expect the planar $^1A''(4\pi)$ state to react with H_2CO (to give the secondary ozonide), O_3 (*vide infra*), and O_2 (if present).[59]

$\Delta H = -24$ kcal/mole

$\Delta H = -18$ kcal/mole $\Delta H = -6$ kcal/mole
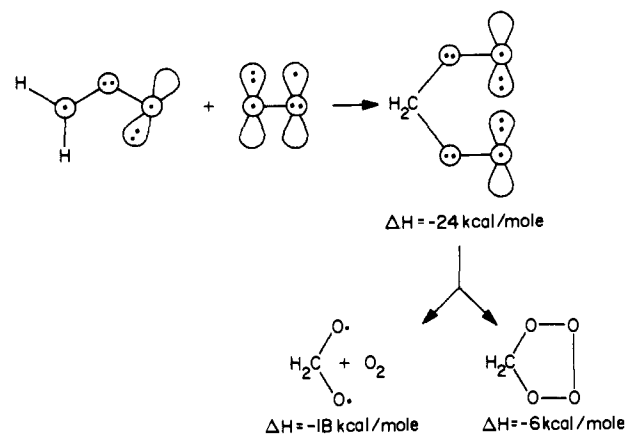
The diperoxy compound should lose oxygen to give dioxymethane.

Dioxymethane may also be formed directly by rearrangement of methylene peroxide as discussed earlier. In either case, our calculations show that the most stable form of dioxymethane is the $^1A_1(2\pi)$ state (even lower than the ring state). Examining the GVB diagram for the $^1A_1(2\pi)$ state shows that it is in a perfect conformation for a simple H migration, leading to formic acid. This process is downhill by 95 kcal/mol!

$\Delta H \cong -95$ kcal/mole

Formic acid is one of the products found in the gas phase ozonolyses.[5,60,61]

The CH bond strength in formic acid is 92.5 kcal/mol, so that it may decompose, producing an H atom

$$\left(\begin{matrix} O \\ \| \\ HCOH \end{matrix} \right)^* \longrightarrow \begin{matrix} O \\ \| \\ \cdot COH \end{matrix} + H \qquad (1)$$

The H atom would be expected to react as follows[5]

$$H + O_3 \longrightarrow HO + O_2 \qquad \Delta H = -76.5 \text{ kcal/mol}$$

$$H + C_2H_4 \longrightarrow C_2H_5 \qquad \Delta H = -38.5 \text{ kcal/mol}$$

and if O_2 is present

$$H + O_2 \xrightarrow{M} HO_2 \qquad \Delta H = -47 \text{ kcal/mol}$$

We see that the most favorable reaction is with ozone, leading to highly vibrationally excited products. In fact, experimental studies of the $H + O_3$ reaction show that up to the $v = 9$ vibrational level of OH is populated corresponding to 75 kcal/mol (all the exothermicity in the newly formed OH bond).[62] Subsequent emission (the Meinel bands[63]) from the nine lowest vibrational levels has been observed by Pitts and coworkers[5,64] in low-pressure ozonolysis studies, indicating the production of H atoms. However, they observed the same chemiluminescence for ozonolysis of tetramethylene and concluded that there must be another pathway for production of either H or excited OH.

The ·C(O)OH radical from (1) would be expected to react with O_3 to give

$$\overset{O}{\underset{||}{\cdot COH}} + O_3 \longrightarrow \overset{O}{\underset{||}{C}}-\overset{\cdot}{O} + O_2 + OH \quad \Delta H = -34 \text{ kcal/mol}$$
$$\searrow CO_2 \qquad\qquad \Delta H = -51 \text{ kcal/mol}$$

In addition, the dioxymethane may itself react with O_3 or O_2

$$\underset{H_2C}{\overset{O\cdot}{\diagdown}}\overset{/}{\underset{O\cdot}{}} + O_2 \longrightarrow \overset{O}{\underset{||}{HCO\cdot}} + HO_2 \quad \Delta H = -39 \text{ kcal/mol}$$

$$+ O_3 \longrightarrow \overset{O}{\underset{||}{HCO\cdot}} + OH \quad \Delta H = -69 \text{ kcal/mol}$$
$$+ O_2$$

Subsequent reaction of HCO_2 with O_2 or O_3 gives

$$HCO_2 + O_2 \longrightarrow \overset{O}{\underset{||}{C}}-\overset{\cdot}{O} + HO_2 \qquad \Delta H = -12 \text{ kcal/mol}$$

$$HCO_2 + O_3 \longrightarrow \overset{O}{\underset{||}{C}}-\overset{\cdot}{O} + OH + O_2 \quad \Delta H = -32 \text{ kcal/mol}$$

The reactions of OH (and HO_2) expected for low pressure gas phase ozonolyses have previously been outlined by Pitts.[5]

If any methylene peroxide in the perpendicular $^3A''(3\pi)$ state is formed by the decomposition of the primary ozonide, it should decompose into $H_2CO(^1A_1) + O(^1D)$ according to Table VI. The $O(^1D)$ will react rapidly with almost anything that is around, e.g.[65]

$$O(^1D) + O_3 \longrightarrow 2O_2(^1\Sigma_g^+) \qquad (2)$$

$$O(^1D) + C_2H_4 \longrightarrow OH + C_2H_3 \qquad (3)$$

$$O(^1D) + H_2CO \longrightarrow OH + HCO \qquad (4)$$

The production of the hydroxyl radical in (3) and (4) is potentially important because of its central role in chain processes of photochemical smog.[66]

The perpendicular $^1A''(3\pi)$ state may also dissociate into HCO + OH

$$\rightarrow HCO + OH \qquad \Delta H = -48 \text{ kcal/mole}$$

This is not the appropriate place to pursue the myriad of reactions possible for reactive species such as the formyl

and hydroxyl radicals. However, to show what is involved, consider just the reactions of the formyl radical expected in the presence of O_3 or O_2.

$$HCO + O_2 \longrightarrow H_{O2} + CO \qquad \Delta H = -31.2 \text{ kcal/mol}$$

$$HCO + O_2 \xrightarrow{M} \overset{O}{\underset{||}{HCOO}} \qquad \Delta H = -43 \text{ kcal/mol}$$

$$HCO + O_3 \longrightarrow \overset{O}{\underset{||}{HCO}} + O_2 \qquad \Delta H = -77 \text{ kcal/mol}$$

$$HCO + O_3 \longrightarrow CO + OH + O_2 \qquad \Delta H = -61 \text{ kcal/mol}$$

2. Chemiluminescent Products. Although reasonable reaction pathways exist for forming almost every possible combination of H, C, and O atoms, there are still certain important experimental results that have not yet been explained with our calculations. First, chemiluminescence has been detected from $H_2CO(^1A'')$ and $OH(^2\Sigma^+)$.[5,64,67] The planar $^1A'(4\pi)$ state of methylene peroxide dissociates smoothly to $H_2CO(^3A'') + O(^3P)$, but both ab initio and thermochemical calculations indicate that the reaction of $O_3 + C_2H_4$ is not exothermic enough to provide the $^1A'(4\pi)$ state with enough vibrational energy to dissociate to these products. The most likely mechanism for production of $H_2CO(^1A'')$ is attack by ozone on the planar $^1A'(4\pi)$ state of methylene peroxide.

$$\Delta H = -27 \text{ kcal/mole}$$

Although both the $^3A''$ and $^1A''$ states of formaldehyde may be produced by this reaction, emission is seen only from the $^1A''$ state. (The $^3A''$ state is known not to emit.[68]) Finally, the formaldehyde chemiluminescence is not affected by the presence of O_2,[58] which is consistent with the above scheme.

Formation of $OH(^2\Sigma^+)$ is not as easy to rationalize. Energy transfer from H_2CO ($^1A''$ or $^3A''$) is not possible since the electronic excitation energy in OH is ~ 1 eV greater than in H_2CO.[17,38] Earlier, we showed that the perpendicular $^1A''(3\pi)$ state of methylene peroxide decomposed into $H_2CO(^1A_1) + O(^1D)$. However, the subsequent reaction of $O(^1D) + H_2CO(^1A_1)$ to give $HCO + OH(^2\Sigma^+)$ is endothermic by 29 kcal/mol. Therefore, we do not understand for formation of $OH(^2\Sigma^+)$ in Pitts' experiments.[58,69]

Chemiluminescence from vibrationally excited $OH(^2\Pi)$, the Meinel bands, has also been seen in low-pressure ozonolysis of a variety of methylated ethylenes.[5,64] The emission from OH corresponds closely to that produced by the reaction $H + O_3 \rightarrow OH^*_{\nu\leq9} + O_2$, which is exothermic by 77 kcal/mol. For ozonolysis of ethylene, we outlined one mechanism for production of H atoms and, thence, the Meinel bands, namely

$$\underset{H_2C}{\overset{O\cdot}{\diagdown}}\overset{/}{\underset{O\cdot}{}} \longrightarrow \overset{O}{\underset{||}{HC}}-OH \longrightarrow H + \overset{O}{\underset{||}{\cdot COH}}$$

Another mechanism for producing H atoms is decomposition of the vibrationally excited $H_2CO(^1A_1)$, $H_2CO(^3A'')$, or $H_2CO(^1A'')$ into H + HCO, requiring 88, 16, and 7 kcal/mol of vibrational energy, respectively.[70,71] The needed vibrational energy can be supplied by the reaction of methylene peroxide with O_3, e.g., as shown below. Therefore, the observation of the Meinel bands from the ozonolysis of ethylene is quite reasonable. On the other

$\Delta H = -127 \, \text{kcal/mole}$

$+ \, 2O_2$

$+ \, 2O(^3P) \, + \, O_2$

$\Delta H = -8 \, \text{kcal/mole}$

hand, the Meinel bands are also seen when tetramethylethylene reacts with ozone.

Ozonolysis of tetramethylethene should lead to dimethylmethylene peroxide, which might undergo a hydrogen migration to form an α-unsaturated hydroperoxide.

$\Delta H = -52 \, \text{kcal/mole}$

The hydroperoxide may decompose (losing an OH group) or be attacked by O_3. Subsequent decomposition of the resulting adduct might lead to production of H atoms. This scheme is very cumbersome and tenuous. However, it is evident how multiple reactions with ozone may break the tetramethylethylene into molecules similar to those obtained in ethylene ozonolysis and, hence, some of the same chemiluminescent species may be produced.

VIII. Conclusion

By performing high quality ab initio calculations we have shown that the ground state of methylene peroxide (the Criegee intermediate) is a singlet biradical rather than a zwitterion. The zwitterionic description in actuality corresponds to a state 3.5 eV above the singlet biradical ground state. A strong analogy between the ground and low-lying excited states of methylene peroxide and its isoelectronic counterpart, ozone, was demonstrated. The excitation energies in methylene peroxide are, in general, smaller than the comparable energies in ozone. This is reasonable in light of the weaker π bonds expected for methylene peroxide. The ring state of methylene peroxide is found to lie nearly 1 eV lower than the planar open state, while the analogous ring state in ozone is 1.5 eV higher than the open ground state.[10] The ring state can reopen, breaking the weak OO bond, to form dioxymethane. The $^1A_1(2\pi)$ state of dioxymethane was found to lie even lower than the ring state.

Combining our ab initio results with thermochemical data, we analyzed the stability of the Criegee intermediate as well as the possible modes of reaction in ozonolysis. We were able to explain the production of many of the chemiluminescent species observed by Pitts and coworkers[5,58,64] in their low-pressure ozonolysis studies. However, the mechanism for formation of $OH(^2\Sigma^+)$ was not evident in our scheme. Our calculations also predict the production of reactive radicals such as OH and HO_2 in the course of ozonolysis, which may have important consequences for understanding the generation of photochemical air pollution. Further calculations and experiments are warranted in this area.

With regard to ozonolysis in solution, the mechanism whereby epoxides are produced by ozonolysis of 1-olefins disubstituted at the 1 position with bulky groups was elucidated. Also, the possible role of methylene peroxide rearrangement to dioxymethane in interpreting the ^{18}O isotope experiments was reexamined and shown to be plausible.

Finally, it is clear that more calculations are needed on the initial phases of ozonolysis, the formation of the primary ozonide, and its subsequent decomposition. As indicated by the gas phase work, the decomposition of the primary ozonide into an aldehyde and the Criegee intermediate may only be telling part of the story.

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$$\psi_S = \mathfrak{a}[\langle \text{core}\rangle(\pi_1\pi_r + \pi_r\pi_1)\alpha\beta \ldots \alpha\beta]$$

$$\psi_T = \mathfrak{a}[\langle \text{core}\rangle(\pi_1\pi_r - \pi_r\pi_1)\alpha\beta \ldots \alpha\beta]$$

Using the same orbitals for both states, the energies are

$$E_S = E_{core} + \frac{E_0 + E_x}{1 + S^2}$$

$$E_T = E_{core} + \frac{E_0 - E_x}{1 - S^2}$$

where

$$E_0 = \langle \pi_1\pi_r | \mathcal{H}(1,2) | \pi_1\pi_r \rangle$$

$$E_x = \langle \pi_1\pi_r | \mathcal{H} | \pi_r\pi_1 \rangle = $$
$$2\langle \pi_1 | \pi_r \rangle\langle \pi_1 | h | \pi_r \rangle + \langle \pi_1\pi_r | 1/r_{12} | \pi_r\pi_1 \rangle = 2Sh_{1r} + K_{1r}$$

Thus $E_x > 0$ favors the triplet state while $E_x < 0$ favors the singlet state. Since $S \geq 0$, $K_{1r} \geq 0$, $h_{1r} \leq 0$, and normally $S|h_{1r}| > K_{1r}$, we see that the singlet state is usually lower when the orbitals are nonorthogonal, while the triplet state is always lower when the orbitals are orthogonal.
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Stereochemistry of Complex Inorganic Compounds. XXXV. A Complex Containing a Ligand That Spans Trans Positions

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Abstract: By chlorination of *trans*-[Pt(NH₃)₂Cl₂] to *trans*-[Pt(NH₃)₂Cl₄] and replacement of three of the coordinated chlorine atoms with RN(CH₂CH₂NH₂)₂ (R = H or CH₃), a compound, chloro-2,4-diammine-3,5,6-RN(CH₂CH₂NH₂)₂platinum(IV), is formed. Reduction of the platinum atom to the platinum(II) state converts the compound to a four-covalent, planar molecule again, with the two ammonia molecules trans to each other and the two primary nitrogen atoms of the RN(CH₂CH₂NH₂) molecule trans to each other. In this compound, the central nitrogen atom of the triamine is not attached to the platinum.

One of the postulates of Werner's coordination theory is that a chelating ligand will attach itself only to cis positions in the coordination complex. Werner used this postulate in much of his stereochemical work, and it has become almost universally accepted by coordination chemists. Werner²ᵃ assumed it, for example, when he compared the stability of chelate rings of coordination compounds with those of five- and six-membered organic rings and Grinberg²ᵇ used it in