

Table II. Correlation Matrix $\times 100$ for Geometrical Parameters of Tetrabromoformaldazine^a

	$r(\text{N-N})$	$r(\text{C=N})$	$r(\text{C-Br})$	$\angle \text{CNN}$	$\langle \angle \text{NCBr} \rangle$	$\Delta(\angle \text{NCBr})$	$\angle \text{CNNC}$	$\angle \text{NNCBr}$
σ^b	0.0063	0.0027	0.0015	0.57	0.08	0.35	1.82	1.37
	100	45	-16	-71	-16	45	-15	24
		100	-20	-47	-31	47	-3	12
			100	9	80	15	25	-14
				100	5	-63	53	-55
					100	-7	21	-23
						100	-8	15
							100	-87
								100

^a Distances (r) and root-mean-square amplitudes (l) in ångströms; angles in degrees. ^b Standard deviations from least squares.

are meaningless because of possible nonplanarity of the trigonally bonded groups comprising the ends of the molecules, the values are not inconsistent with the qualitative ideas outlined above. Calculation based on the reported geometries and on van der Waals radii shows, for example, that nonbond repulsions for a given value of central bond torsion angle have for the three molecules the relative magnitudes $\text{C}_2\text{N}_2\text{Br}_4 > \text{C}_4\text{Cl}_6 > \text{C}_4\text{F}_6$ assuming, of course, that the unshared electron pair in $\text{C}_2\text{N}_2\text{Br}_4$ plays an important repulsive role. If the gauche and anti conformations in conjugated systems of this type are taken to be ones for which *bond-bond* repulsions are minimal as we have argued in the cases of the oxalyl halides,^{5,12} then the relative values of the torsion angles in the three molecules may be understood as follows. The anti forms are unstable because of the dominant effect of atom-atom steric repulsion. At the gauche conformation (torsion angle equal to 120° relative to anti at 0°) the effect of conjugation tending to stabilize the syn forms is opposed by the steric effects, least for the fluorine and greatest for the bromine compound, so as to result in the observed relative magnitudes of torsion angle.

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Foundation for support of this work under Grant GP 27763X.

Supplementary Material Available: Experimental intensity curves (eight) after removal of backgrounds and complete correlation matrix (5 pages). Ordering information is given on any current masthead page.

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Mechanisms of Gas-Phase and Liquid-Phase Ozonolysis

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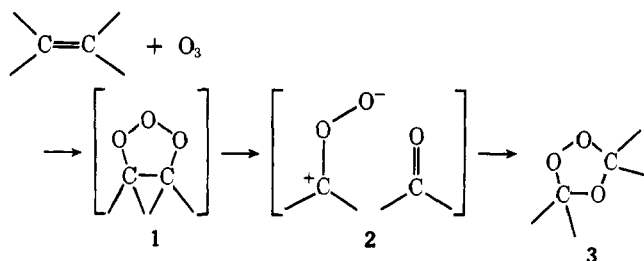
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Abstract: Generalized valence bond (GVB) and configuration interaction (CI) calculations using an extensive basis [double ζ plus polarization functions (DZd)] have been carried out on peroxyethylene (H_2COO , often referred to as carbonyl oxide or as the Criegee intermediate), dioxirane, and dioxymethylene (OCH_2O). The *ab initio* thermochemical results are combined with existing thermochemical data to analyze possible modes of ozonolysis. The predicted heat of formation of peroxyethylene is 29.1 kcal, indicating that the dissociation of the primary ozonide to form peroxyethylene biradical and formaldehyde is 9 kcal endothermic. The ring state, dioxirane, is predicted to be 36 kcal below peroxyethylene with dioxymethylene lying 15 kcal above the ring state. Gas-phase experimental results are shown to be consistent with the predicted thermochemistry. In addition, solution-phase results on the stereospecificity of ozonolysis are shown to be consistent with a biradical intermediate.

I. Introduction

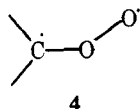
The reaction of ozone and olefins has been of continuing interest to chemists for over 100 years. Most recently the gas-phase reaction has received considerable attention due to

its importance in photochemical smog formation.² Nearly 30 years ago Criegee proposed³ the mechanism in order to explain the isolation of 1,2,4-trioxolanes (3) from ozone-olefin reaction mixtures and to explain the incorporation of foreign aldehydes into these products. Since then a great deal of experimental

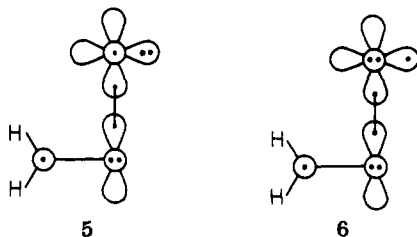


evidence (solution phase) has been reported, supporting the Criegee mechanism⁴ with only minor modifications.⁵

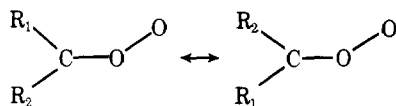
Recent *ab initio* calculations¹ on the peroxymethylene intermediate (CH_2OO) have established the electronic structure of the planar gas-phase species to be that of a singlet biradical (4) similar to ozone. As discussed in the earlier paper,¹ the π



system of the planar ground state consists of a doubly occupied p orbital on the central oxygen and singly occupied p orbitals on both of the terminal atoms, 5. The terminal p orbitals are found to overlap considerably ($S = 0.346$), leading to a ground-state singlet, $^1A'$ (4π), and a low-lying excited-state triplet, $^3A'$ (4π) (corresponding to triplet coupling the two singly occupied orbitals). Two other low-lying excited states of the planar molecule, $^1A''$ (5π) and $^3A''$ (5π), derive from configuration 6, in which the $p\pi$ orbital of the terminal oxygen is doubly occupied.

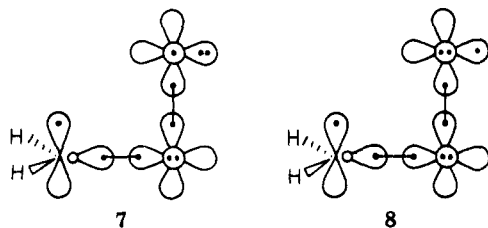


Of considerable importance in understanding the mechanism of ozonolysis is the barrier to interconversion of the syn and anti peroxymethylene intermediates:



The transition state for this interconversion is expected to be a peroxymethylene species in which the plane of the carbon has been rotated 90° (making the R_2CR_1 plane perpendicular to the COO plane).⁶

Rotating the CH_2 group of 5 and 6, we obtain 7 and 8, re-



spectively. Of these we expect the singlet and triplet states corresponding to 7, $^1A''$ (3π) and $^3A''$ (3π), to be lower in energy due to the three-electron O-O π bond.

The singlet state of 8, $^1A''$ (4π), can undergo ring closure forming dioxirane, 9. The weakest bond of dioxirane is the

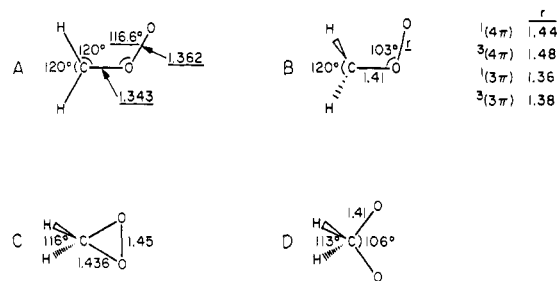
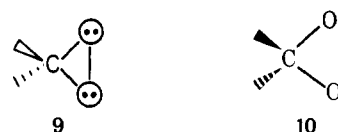
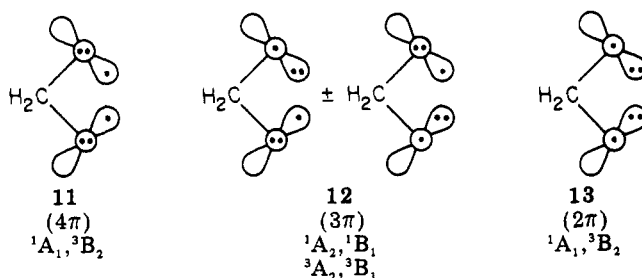


Figure 1. Geometric parameters used in calculations. All bond lengths are in angstroms. All C-H bond lengths were taken to be 1.08 Å. Underlined parameters are the optimum values from GVB-Cl calculations.

O-O bond, and cleaving this bond leads to the reactive intermediate dioxymethylene (10). There are altogether eight



biradical states corresponding to 10, four singlets and four triplets 11-13, all of which are expected to lie fairly close (10 kcal) in energy.



It is the purpose of this paper to examine with accurate *ab initio* calculations (large basis set, correlated wave functions) the electronic structure and relative energies of configurations 5-13 and to discuss the implications of these results on the mechanism of ozonolysis. In section II, details concerning the geometries, basis set, and wave functions are presented. The results of the calculations are presented in section III and discussed in section IV.

II. Computational Details

A. Basis Set and Geometries. All calculations used the valence double- ζ (DZ) basis of Huzinaga and Dunning⁷ [(9s,5p/4s) primitive Gaussians contracted to (3s,2p/2s)] augmented with d-polarization functions ($\alpha_C = 0.6760$, $\alpha_O = 0.8853$) centered on each heavy atom. The hydrogen exponents were scaled by 1.44 (corresponding to a Slater function with $\zeta = 1.2$).

The geometries employed in these calculations are shown in Figure 1. In all configurations C-H bonds were assumed to be 1.08 Å and all trivalent carbon bond angles were taken to be 120° . Optimized parameters are indicated by an underline in Figure 1.

For the planar ground state of peroxymethylene [configuration 5], the three remaining parameters, $r(\text{C}-\text{O})$, $r(\text{O}-\text{O})$, and $\angle\text{COO}$ were optimized. The results are shown in Figure 1A.

For perpendicular peroxymethylene [configurations 7 and 8 and Figure 1B], the C-O bond length was assumed to be that of dimethyl ether,⁸ 1.41 Å, and the COO bond angle was taken to be 103° , intermediate between that of dimethyl peroxide (105°) and hydrogen peroxide (100°).⁹ The O-O bond length was optimized for each of the four valence states.

Table I. Calculated Excitation Energies for Peroxymethylene Biradical and Dioxymethane (eV)

state	GVB(3/PP)	GVB(3)-CI	GVB(7/17)-CI
(A) Open Planar COO; see 5 and 6			
4 π 1 $^1A'$	1.86	1.29	
1 $^3A'$	2.45	2.49	
2 $^1A'$		5.28	
2 $^3A'$		9.58	
5 π 1 $^3A'$	2.86	2.92	
1 $^1A''$	2.92	3.00	
2 $^3A''$		9.27	
2 $^1A''$		9.51	
(B) Open Perpendicular COO; see 7 and 8			
3 π 1 $^3A''$	2.40	2.37	
1 $^1A''$	2.50	2.55	
4 π 1 $^1A'$	2.50	2.70	3.13
1 $^3A'$	2.81	2.95	
(C) Open Perpendicular OCO; see 11, 12, and 13			
2 π 1 1A_1	0.05	0.48	
1 3B_2	0.05	0.52	
3 π 1 3A_2		0.60	
1 1A_2		0.78	
1 3B_1		0.94	
1 1B_1		1.14	
4 π 2 1A_1	0.45	0.97	1.33
2 3B_2	0.55	1.04	
(D) Ring; see 9 ^a			
4 π 1 A_1	0.00	0.00	0.00

^a Total energy (hartrees): GVB(3/PP), -188.74026; GVB(3)-CI, -188.80355.

For the ring state [configuration 9 or Figure 1C], the C-O bond length and the HCH angle were taken to be 1.436 Å and 116°, as in ethylene oxide.¹⁰ The O-O bond distance was taken as 1.45 Å, as is found in the ring state of ozone.¹¹

Finally, for dioxymethylene, the C-O distance was assumed to be 1.41 Å (from dimethyl ether)⁸ and the OCO and HCH angles were chosen to be 106° and 113°, respectively (from 1,2,4-trioxolane¹²). We optimized the bond lengths of a closely related diradical, CH₂CH₂O, obtaining a C-O bond length of 1.411 Å; this supports the choice of 1.41 Å chosen for dioxymethylene.

B. GVB(3) Calculations. Previous calculations on ozone have shown the Hartree-Fock (HF) wave function to lead to a qualitatively inaccurate description of the low-lying states (for example, HF predicts the ground state of ozone to be a triplet).¹¹ The cause of this failure is the orbital occupancy restrictions placed on the HF wave function which leads to a poor description of states with considerable singlet biradical character [such as 5].

The GVB method corrects the major deficiencies in the HF wave functions by allowing singlet-paired electrons to split or correlate with singly occupied nonorthogonal orbitals. This corresponds to the replacement

$$\phi_{\text{HF}}(1)\phi_{\text{HF}}(2) \rightarrow \phi_1(1)\phi_r(2) + \phi_r(1)\phi_l(2) = \lambda_1\phi_a^2 - \lambda_2\phi_b^2$$

where ϕ_l and ϕ_r are the nonorthogonal valence bond-like orbitals and ϕ_a and ϕ_b form the equivalent natural-orbital representation. Calculations on a large number of well-characterized small molecules¹³⁻¹⁶ have shown that for the purpose of calculating excitation energies of valence states it is necessary to have a consistent level of correlation in the ground- and excited-state wavefunctions. [Hartree-Fock calculations in which the ground and excited states usually have differing numbers of open-shell orbitals are *not* consistent.]

From the valence bond diagrams, 5-8, we conclude that a consistent level of description for peroxymethylene biradical is one in which three pairs are allowed to correlate, the C-O

and O-O σ bonds and the π pair. We will denote these wave functions as GVB(3/PP) indicating three pairs have been correlated and the perfect pairing restriction has been applied.^{17,18}

In order to obtain accurate excitation energies, it is necessary to relax the perfect pairing restriction and to include the important interpair correlation terms neglected in the GVB(3/PP) wave function. By using the self-consistent GVB(3/PP) orbitals this can be accomplished with a relatively small configuration interaction (CI) calculation¹⁹ [the CI calculations also included four additional virtual p orbitals, one corresponding to each occupied p orbital; thus, for example, the CI basis for the states of planar peroxymethylene would include three p- π virtuals (one on each oxygen and carbon) and a p- σ virtual centered on the terminal oxygen]. In all cases the GVB(3/PP) orbitals used in the CI calculations were solved self-consistently for the lowest states of each appropriate symmetry.

C. The GVB(7) Calculations. Although the GVB(3)-CI calculations are sufficiently accurate for the purposes of calculating valence excitation energies or one-electron properties (e.g., dipole moments), they do not lead to sufficiently accurate bond energies. For example, the equivalent calculations on the A-B bond energies of CH₃-CH₃, CH₃-OH, and HO-OH lead to results that are consistently low, the errors being 10, 22, and 21 kcal, respectively.²⁰ There are primarily two sources of error in these calculations; the neglect of all but the dominant intrapair correlation and the neglect of interpair correlations between the bond pair being broken and other adjacent bond pairs and lone pairs.

In order to include the intrapair terms it is necessary to optimize additional correlating natural orbitals for the bond pair to describe the radial and angular correlations in addition to the dominant (left-right) correlation. Calculations on simple molecules have shown three additional natural orbitals to be sufficient.

In order to include the interpair terms it is necessary to correlate not only the bond being broken but also all of the adjacent bond pairs and lone pairs. An extensive CI calculation within the resulting set of orbitals serves to include the important intra- and interpair terms.²¹ The equivalent calculations on the bond energies of CH₃-CH₃, CH₃-OH, and HO-OH lead to errors of 3, 1, and -4 kcal, respectively.

Calculations of this level of accuracy are essential for comparing energies of species with differing numbers (or types) of bond pairs (for example, to obtain the relative energy of the ring state to any of the open states).

III. Results

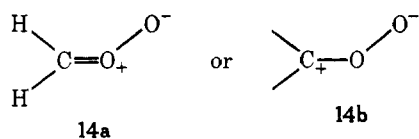
A. Peroxymethylene. As noted earlier, the ground state of gas-phase peroxymethylene is a planar singlet biradical, $^1A'$ - (4 π). The π electronic structure of this state is very similar to that of ozone, consisting of a doubly occupied p- π orbital on the central oxygen and two singly occupied, singlet-coupled p- π orbitals on the terminal atoms. The calculated geometry is found to be very close to that predicted earlier.^{1,22}

The lowest *vertical* excited state of peroxymethylene, $^3A'$ - (4 π), arises from triplet coupling of the terminal p- π orbitals and is calculated to lie 1.20 eV above the ground state (see Table I). This is slightly lower than the corresponding state of ozone, 1.59 eV,^{11,23} indicating a smaller degree of π delocalization (smaller overlap between the terminal p- π orbitals). By analogy to ozone we expect the triplet state to lead to longer bond lengths, a smaller angle, and an adiabatic excitation energy considerably below the vertical value (for ozone the adiabatic excitation energy is ~0.9 eV; thus, the value for peroxymethylene may be as low as 0.5 eV).

The remaining two low-lying biradical states, $^3A''$ (5 π) and $^1A''$ (5 π), are calculated to be 1.63 and 1.71 eV, respectively,

above the ground state. These also are slightly lower than the corresponding states of ozone.

Of particular interest is the energy of the zwitterionic state, **14**, commonly assumed to be the ground state. The GVB-CI calculations lead to a vertical excitation energy of 3.99 eV for this state, $2^1A'(4\pi)$ considerably below that of the analogous state of ozone, 5.81 eV.^{23,24} Apparently the lower electronegativity of carbon stabilizes the zwitterionic structure **14b**



relative to the corresponding state of ozone. [See section IVD, for further discussion of the zwitterion-biradical character.]

In the case of substituted peroxymethylene, the planar ground state can exist as either of two isomers, syn or anti, depending on which side the substituent is placed. In order to determine the stereochemical consequences of this, it is necessary to know the barrier to interconversion of these two isomers, i.e., the barrier to rotation about the C-O bond.⁶ The GVB-CI calculations lead to a barrier for this process of 29.1 kcal, indicating that in solution-phase reactions, at least, the isomers will not interconvert. However, this will not necessarily be true in gas-phase reactions where the Criegee intermediate may be formed with sufficient vibrational energy to surmount this barrier (we estimate that the reaction leading to the Criegee intermediate is exothermic by >40 kcal/mol).

The calculated energies of the other states of perpendicular peroxymethylene are summarized in Table I.

B. Dioxymethylene. The calculated GVB-CI energies of the eight biradical states of dioxymethylene (open geometry) are shown in Table I. Averaging over spin states, the relative energies are 2π (**13**) = 0.0 kcal, 3π (**12**) = 8.9 kcal, and 4π (**11**) = 11.8 kcal. There are two surprising aspects of these results. First, we would normally expect the singlet 4π state to be lowest since in this state the p_σ orbitals can overlap, leading to increased bonding (decreasing the OCO angle of the singlet 4π state leads directly to the ground state of dioxirane). Second, the total separation, 12 kcal, between the 2π and 4π states is much too large for normal 1,3-biradical couplings.

The explanation for these effects lies in the interaction of a doubly occupied oxygen σ lone pair with an adjacent C-O bond; see **11-13**. The C-O bond, being highly polarized toward the oxygen, effectively stabilizes adjacent lone pairs lying in the same plane as the C-O bond. Thus the 2π states, having two stabilized lone pairs, are lowest in energy and the 4π states, having no stabilized lone pairs, are highest.

From the magnitude of the 2π - 3π - 4π splittings, we conclude that this *lone-pair stabilization effect* is worth ~6 kcal/lone pair. An experimental estimate of the energy involved in lone-pair stabilization can be obtained by comparing the C-O bond energy of methanediol with that of ethanol. First though, consider the effect of an adjacent oxygen on typical C-H bond energies:^{25,26} $D_0(\text{CH}_3\text{CH}_2\text{CH}_2-\text{H}) = 97.9$ kcal and $D_0(\text{CH}_3\text{OCH}_2-\text{H}) = 94.1$ kcal. We conclude that an oxygen lone pair adjacent to a carbon radical center stabilizes the radical by 3.8 kcal. Now, consider the analogous C-O bond energies:²⁵ $D_0(\text{CH}_3\text{CH}_2-\text{OH}) = 92.1$ kcal and $D_0(\text{HOCH}_2-\text{OH}) = 96.9$ kcal. Thus replacement of CH_3 by OH *strengthens* the adjacent C-O bond by 4.8 kcal. Since the OH stabilizes the radical center by 3.8 kcal, the lone-pair stabilization of the diol must be 8.6 kcal, in reasonable agreement with that estimated for dioxymethylene (12 kcal). Because of the large magnitude of the lone-pair stabilization effect, it plays an important role in the mechanisms of many reactions, including the ozonolysis of olefins (e.g., see section

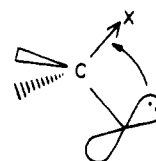
Table II. Calculated Bond Dissociation Energies (kcal/mol) of Dioxirane^{a,b}

bond	calcd D_e	estd zero-point correction	estd error in theoretd D_e	estd D_0
	72.1 ^d	-5.6	+0.8	67.3
	30.7 ^e	-0.5	-4.2	26.0

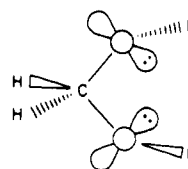
^a These calculated energies assume 4π states for the dissociation species; since this is not the lowest state, the adiabatic bond energies are smaller (see Table III). ^b Based on GVB(7/17)-CI wave functions for dioxirane and for the $^1(4\pi)$ state of the biradicals. ^c Taken from equivalent calculations on the bond energies of CH_3-OH and $\text{HO}-\text{OH}$. ^d Total energy of ring state, -188.8437 hartrees. ^e Total energy of ring state, -188.8515 hartrees.

IVB), the ozonolysis of acetals,²⁷ and the $^1\text{O}_2$ -olefin ene reaction.²⁸

This lone pair stabilization is a very general phenomenon, often referred to in the literature as the *anomeric effect*.²⁹⁻³¹ As noted here and elsewhere^{28,29,31,32} the effect results from a delocalization of a heteroatom lone pair into the region of an adjacent polar bond:



The result is an increased stability (~5 kcal each) of configurations in which a lone pair is in the same plane as an adjacent heteroatom. As an example, consider methanediol. The O-H bonds are roughly perpendicular to the oxygen lone pairs and thus orienting the lone pairs in the OCO plane (to maximize lone-pair stabilization) forces the O-H bonds to be perpendicular to this plane. In fact, it is found³² that the most stable configuration of methanediol is one in which both O-H bonds are perpendicular to the OCO plane:



C. Thermochemistry. The C-O and O-O bond energies of the ring state from GVB(7/17)-CI calculations are shown in Table II. These results together with the GVB(3)-CI energies, Table I, accurately determine (± 4 kcal) the relative heats of formation of all of the states corresponding to configurations **5-13**. In order to obtain absolute heats of formation it is necessary to estimate independently the heat of formation of one of these states. As a starting point, consider methanediol, $\Delta H_f = -93.5$ kcal (all ΔH_f will be for 298 K).²⁶ The O-H bond energies of methanediol are expected to be nearly independent of each other and approximately equal to the O-H bond energy of methanol, 103.6 kcal.²⁶ Therefore we estimate as follows:

$$\Delta H_f \left(\text{H}_2\text{C} \begin{array}{c} \diagup \text{O} \cdot \\ \diagdown \text{O} \cdot \end{array} \right) = -93.5 + 2(103.6) - 2(52.1) = 9.5 \text{ kcal}$$

Now, methanediol is stabilized by the lone-pair C-O bond interaction discussed in section IIIB. Therefore the estimated ΔH_f corresponds to an average over those biradical states with

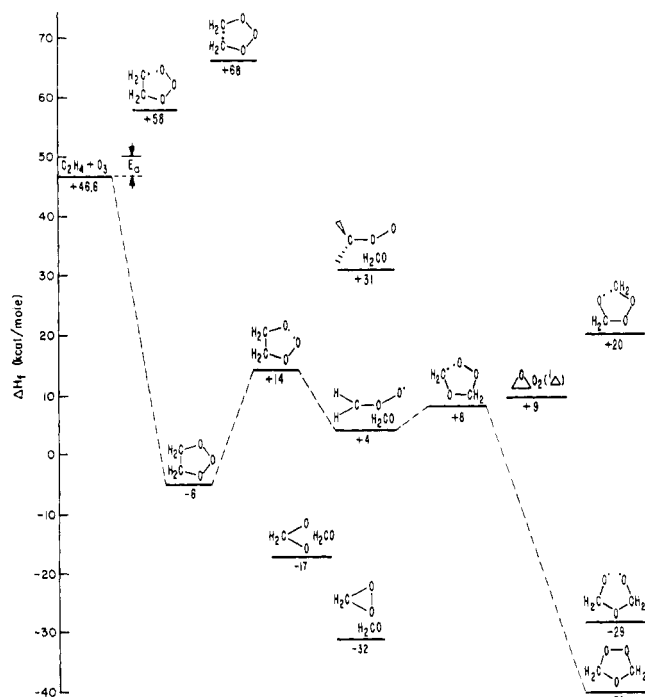
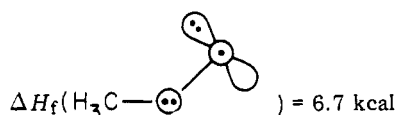


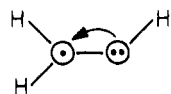
Figure 2. Thermochemistry of ozonolysis. The calculated heats of formation (kcal/mol) are shown below each set of molecules. The dashed lines trace out the Criegee mechanism.

similar stabilizing interactions, i.e., an average of the $^1(2\pi)$ and $^3(2\pi)$ states. Using this estimate and the results of the GVB-CI leads to the heats of formation shown in Table III.

As a check on the consistency of the calculations, we can independently estimate the heat of formation of one of the COO biradical states. For example, starting with the peroxy-methane radical²⁶ we first estimate the C-H bond energy. In



order to minimize any 1,3-diradical interaction, we break a C-H bond in the COO plane, forming the (3π) biradical states of perpendicular peroxy-methylene. The C-H bond strength of methanol is 94 kcal, 4 kcal less than that of ethane. The decrease is due to a three-electron bonding interaction in the biradical



an effect that is not present in the perpendicular geometry of peroxy-methylene biradical. Therefore we use a C-H bond energy of 98 kcal leading to the following expression for the biradical heat of formation:

$$\Delta H_f(\text{H}_2\text{COO}) = 6.7 + 98 - 52.1 = 52.6 \text{ kcal}$$

This represents the average of the singlet and triplet (3π) biradical states of perpendicular peroxy-methylene. Excitation energies from GVB-CI calculations lead to $\Delta H_f[{}^1A''(3\pi) \text{ perpendicular peroxy-methylene}] = 54.7 \text{ kcal}$, in good agreement with the previous estimate of 58.2 kcal (Table III).

Using the group-additivity method of Benson²⁶ together with the GVB-CI heat of formation for the ring state (-5.7 kcal) leads to a predicted ring strain, for **9**, of 21 kcal/mol. This is slightly less than the strain energy for other three-membered rings (27.6 kcal for cyclopropane and 26.9 kcal for ethylene oxide).

Table III. Calculated Heats of Formation ($T = 298 \text{ K}$) of Peroxymethylene Biradical, Dioxirane, and Dioxymethylene (kcal)

geometry	state	$\Delta H_f^\circ_{298}$
planar COO (Figure 1A)	${}^1A' (4\pi)$	29.1
	${}^3A' (4\pi)$	56.8
	${}^1A'' (5\pi)$	68.5
	${}^3A'' (5\pi)$	66.7
perpendicular COO (Figure 1B)	${}^1A' (3\pi)$	58.2
	${}^3A' (3\pi)$	54.0
	${}^1A'' (4\pi)$	61.6
	${}^3A'' (4\pi)$	67.4
ring (Figure 1C)	${}^1A' (4\pi)$	-5.7
perpendicular OCO (Figure 1D)	$1 {}^1A_1 (2\pi)$	9.0
	$1 {}^3B_2 (2\pi)$	10.0
	${}^1A_2 (3\pi)$	16.0
	${}^3A_2 (3\pi)$	11.8
	${}^1B_1 (3\pi)$	24.3
	${}^3B_1 (3\pi)$	19.6
	$2 {}^1A_1 (4\pi)$	20.3
	$2 {}^3B_2 (4\pi)$	21.9

Using a combination of experimental, group additivity, and GVB-CI heats of formation leads to the ozonolysis thermochemistry shown in Figure 2. The heats of formation of the four $\text{C}_2\text{H}_4\text{O}_3$ biradicals were calculated using the following radical group functions: $\cdot\text{C}(\text{C})(\text{H})_2 = 36.1$, $\cdot\text{C}(\text{O})(\text{H})_2 = 31.9$, $\cdot\text{O}(\text{C}) = 13.6$, $\cdot\text{O}_2(\text{C}) = 16.7$, and $\cdot\text{O}_2(\text{O}) = 35.2 \text{ kcal}$. The ring strain of the 1,2,3-trioxalane structure was assumed to be 6 kcal (based on cyclopentane), while that of the 1,2,4-trioxalane was assumed to be $\sim 16 \text{ kcal}$ due to the loss of lone-pair stabilizations upon ring formation. Finally, the group function for $\text{O}(\text{O})_2$ was taken to be 14 kcal, from an extrapolation of the heats of formation of CH_3OCH_3 and CH_3OOCH_3 rather than the value suggested by Benson (19 kcal), which is an average of the $\text{CH}_3\text{O}_n\text{CH}_3$ and HO_nH extrapolations.

IV. Discussion

A. Gas-Phase Mechanism. From Figure 2 we see that the steps in the Criegee mechanism are energetically plausible. Note, however, that the step leading to epoxide and O_2 (${}^1\Delta_g$) is also energetically acceptable as are the steps leading to dioxymethane in the open or closed forms. Epoxide is a well-known product; however, there is apparently no strong evidence in favor of intermediacy of dioxymethane.

In gas-phase ozonolysis the slower quenching of vibrationally excited intermediates allows several additional reaction pathways and a number of additional products have been observed experimentally.^{33,34} For example, Pitts has reported the formaldehyde ${}^1A''(n\pi^*) \rightarrow {}^1A_1$ and $\text{OH } {}^2\Sigma^+ \rightarrow {}^2\Pi$ chemiluminescence from ozonolysis of ethylene. Emission from 3A_u glyoxal has been observed from the ozonolysis of *cis*- and *trans*-2-butene. O'Neal and Blumstein³⁵ have proposed a competing pathway for the gas-phase ozonolysis of ethylene involving H abstraction by the primary ozonide biradical (pathway D of Figure 3) leading directly to an α -hydroperoxyaldehyde intermediate. The Pitts' experiments have been interpreted to support this mechanism.

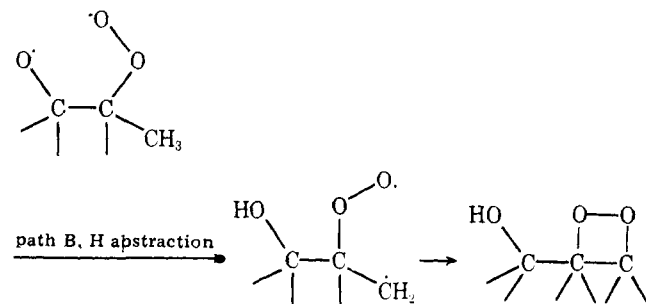
In Figure 3 we show four possible pathways for decomposition of the primary ozonide biradical. Pathway B involves a splitting of the form proposed by Criegee, while pathway D is the H abstraction of O'Neal and Blumstein. We suggest a third possibility, pathway A, consisting of a 1,2-hydrogen shift leading to a biradical which can then undergo ring closure, forming a dioxetane. The dioxetane intermediate would then be expected to cleave, forming an electronically excited formaldehyde (${}^1A''$) and a ground-state formic acid. The key step in pathway A is the initial 1,2 H migration. The activation energy for this process is expected to be only slightly less than

the C-H bond strength (~ 16 kcal), unless the H migration and ring closure are concerted. While significantly larger than previous estimates for the H-abstraction pathway (~ 9 kcal),³⁵ this is still well below the available vibrational energy of the biradical (~ 33 kcal).

The activation energy for the Criegee splitting process, B, is in considerably greater doubt. O'Neal and Blumstein³⁵ have suggested an activation energy of 16.5 kcal based on the experimental activation energy for decomposition of the *t*-BuO radical. They note, however, that this does not include any "polarization" stabilization of peroxyethylene. The GVB-CI calculations indicate this stabilization to be >20 kcal (comparing with the perpendicular biradical states). Assuming then that the transition state is stabilized by half this amount leads to a predicted activation energy of <6.5 kcal, well below that estimated for any of the competing mechanisms.

We also note in Figure 3 a pathway, C, leading to the formation of $O_2(^1\Delta_g)$. It has been shown³⁶ that $O_2(^1\Delta_g)$ reacts with ethylene in the gas phase leading to $^1A''$ formaldehyde chemiluminescence. Thus pathway C provides an alternative explanation for the observed excited-state formaldehyde.

A number of additional products can be formed from bimolecular reactions involving some of the proposed intermediates; however, in Figure 3 we have restricted ourselves to unimolecular processes. In addition, excitation energy transfer may lead to some of the observed chemiluminescence. O'Neal and Blumstein have suggested that the observed $^1A''$ formaldehyde chemiluminescence may result from a dioxetane intermediate formed as follows:



This mechanism requires a substituted ethylene and hence does not explain the observed chemiluminescence of $^1A''$ CH_2O in the ozonolysis of ethylene.³⁴ However, this chemiluminescence can be understood on the basis of the 1,2 H-migration mechanism as shown in Figure 3 (Path A).

Thus far we have considered primarily the mechanism of ethylene ozonolysis. The effect of alkyl substituents on the C-C double bond will be threefold: (i) additional pathways for decomposition of the primary ozonide biradical will become available (β and γ H abstraction),³³ (ii) excess vibrational energy will be dissipated to some extent, leading to an increased importance of processes with smaller activation energies (regardless of the A factors involved), and (iii) the C-C bond strength will be decreased, leading to a decrease in the activation energy for Criegee splitting.

B. Solution-Phase Mechanism. In solution the ozonolysis intermediates, although formed vibrationally "hot", will be rapidly quenched, leading to a decrease in the number of competing pathways and to an increase in stereospecificity. Indeed, solution-phase ozonolysis of olefins is known to proceed to high yields of secondary ozonide, in some cases stereospecifically.^{5,37}

Conformational analysis of the primary ozonide⁵ (see Figure 4) indicates that axial substituents should exhibit a preference for forming the *syn* peroxymethylene conformation, while equatorial substituents should be preferentially incorporated into the anti position. Furthermore, the anti peroxymethylene conformation is the more stable one (by 1–2 kcal) and hence

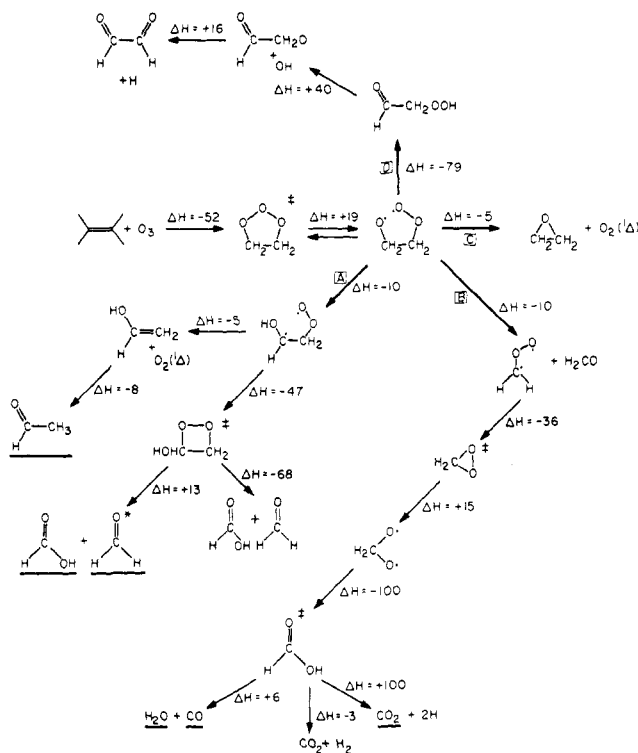


Figure 3. Possible mechanisms for gas-phase ozonolysis of ethylene. Species formed with a large excess of vibrational energy are marked with ‡; those formed in excited electronic states are denoted by *. Pathways A and C are new mechanisms, pathway B involves an initial Criegee-like splitting, and pathway D was proposed by O'Neal and Blumstein (ref 35).

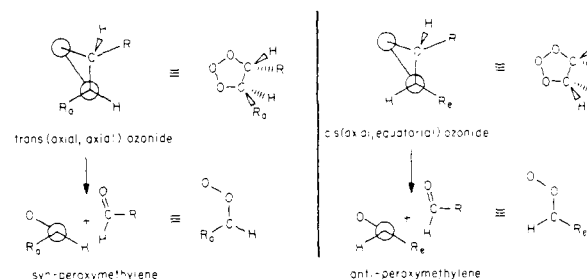
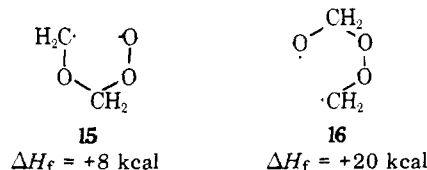


Figure 4. Stereoselective decomposition of cis and trans disubstituted primary ozonides. This analysis is based on the C(O-O) envelope conformation, which is most appropriate for very large substituents (e.g., *tert*-butyl). A similar analysis leads to the same result for all six envelope and half-chair conformations, with the exception of the trans O(C-C) envelope. This latter conformation is not expected to be low energy (ref 42).

should be formed with some preference, other factors being equal. For sizable substituents, the trans disubstituted primary ozonide will prefer a diaxial conformation, while the cis ozonide will prefer an axial-equatorial conformation.⁵ Thus we expect trans-disubstituted olefins to preferentially form *syn*-peroxymethylene, while cis olefins should form *anti*-peroxymethylene.

The final step in the ozonolysis reaction involves the addition of peroxymethylene to an aldehyde. The estimated thermochemistry of this addition is shown in Figure 2. Assuming the addition to involve a biradical intermediate, there are two possible biradicals to consider, **15** and **16**. However, since the



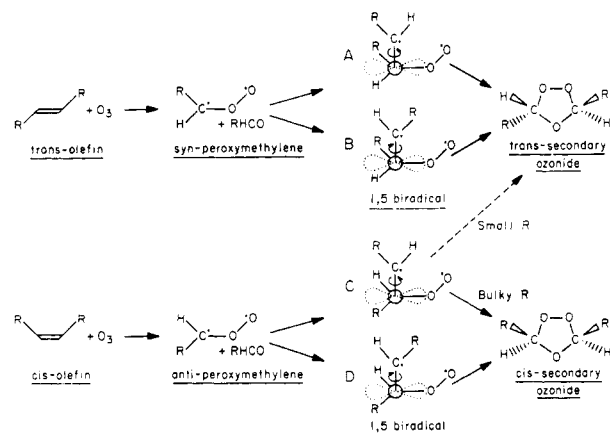
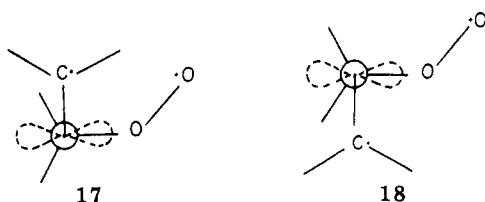


Figure 5. Proposed biradical mechanism for the stereospecific ozonolysis of cis and trans disubstituted olefins. In the drawings A, B, C, and D, the carbonyl oxygen is directly above the peroxymethylene carbon and the conformations are such that the dotted p orbital has a lone-pair stabilization (anomeric interaction) with the peroxymethylene CO bond. Arrows around the biradical C–O bonds indicate the sterically preferred direction of rotation to closure (such that the bulky R group will move away from all neighboring groups). Orbital phase considerations predict suprafacial addition and hence lead to the same closure direction for biradicals B and D but the opposite direction for A and C. For large groups (e.g., R = *t*-Bu) the steric effects dominate for all four cases. For small groups (e.g., R = CH₃), C is expected to follow the orbitally allowed (suprafacial) addition as indicated with dotted lines; even here, the other three cases should follow the steric pathways.

COCOO• form (**15**) is expected to be 9 kcal more stable than the alternative •OCOOC• form and since the addition of aldehyde to peroxymethylene forming the •COCOO• biradical (**15**) is only 4 kcal endothermic, we expect that the addition will proceed through the •COCOO• biradical intermediate.

Considering in more detail the 1,5-•COCOO• biradical (**15**), the lone-pair stabilization (anomeric) effect (section IIIB) implies that this biradical will exist in either of two preferred conformations, **17** and **18**, with a ~5 kcal barrier to intercon-



version. Furthermore, rotation about the O–C–OO• bond will be hindered due to the lone-pair stabilization. Thus conformation **18** will have an additional 5 kcal barrier to ring closure and should either dissociate or generate free-radical products. We predict therefore that the secondary ozonides are formed via the •COCOO• biradical with the conformation shown in **17** and that the stereochemistry of this reaction can be understood on the basis of this intermediate.

Considering now the specific case of a symmetrical, disubstituted olefin, we show the predicted reaction pathways in Figure 5. We have assumed here that the dominant factor in determining the course of the reaction for bulky substituents will be nonbonded, steric repulsions. Thus, for large substituents, biradicals A–D will ring-close in such a way that the bulky carbonyl substituent is rotated away from all neighboring group interactions. The result is that these steric interactions cause the *syn* peroxymethylene to favor production of *trans* product, while the *anti* form should lead to *cis* product. Hence, for bulky substituents, *cis* and *trans* olefins are expected to lead stereospecifically to *cis* and *trans* secondary ozonides, respectively.

An additional effect on the biradical closure should be

considered. Since the peroxymethylene biradical is isoelectronic with ozone, orbital-phase arguments³⁸ indicate that it will exhibit a preference for suprafacial $4\pi_s + 2\pi_s$ addition. For biradicals B and D (Figure 5) the steric and orbital-phase considerations lead to the same prediction. However, for biradicals A and C, opposite results are predicted (steric considerations imply antarafacial addition). Of these two biradicals the steric repulsions will be much larger for A (R...R interaction) than for C (R...H interaction). Thus, orbital-phase considerations are expected to be more important (relative to the steric effects) for the ring closure of C, and hence for small substituents (e.g., R = CH₃) orbital-phase effects could dominate this ring closure. In fact, ozonolysis of both *cis*- and *trans*-2-butenes is observed to produce primarily *trans* secondary ozonide,⁵ as expected on the basis of orbital-phase considerations.

Several additional features of solution-phase ozonolysis reactions can be understood on the basis of this mechanism. For example, steric considerations predict that addition of a carbonyl to a peroxymethylene having a bulky group in the *syn* position will lead preferentially to biradical **18**. This biradical will have large rotational barriers preventing ring closure, and thus formation of **18** is expected to lead to an increase in radical reactions (polymeric products) and a decrease in ozonide yield. In fact, ozonolysis of *trans* olefins (via *syn*-peroxymethylene) is observed to proceed with much lower yields of secondary ozonide than the corresponding *cis* olefins.^{5,37}

A second conclusion from the biradical mechanism is that the *cis*-secondary ozonides result from the thermodynamically more stable peroxymethylene intermediate (*anti*). Thus *syn*–*anti* equilibration of the peroxymethylene species will lead to an increase of *cis* product. Recently, Bailey et al.³⁹ reported the results of experiments on the effect of complexing agents on the stereospecificity of ozonolysis reactions. They found that complexing agents lead to an increase in the relative yield of *cis*-secondary ozonide from both *cis* and *trans* olefins. Furthermore, at increased temperatures (or increased solvent polarities), in the absence of a complexing agent, they found a decrease in the stereospecificity of the reaction. On the basis of the proposed biradical mechanism, we interpret these results as follows:

1. In the absence of complexing agent, little or no *syn*–*anti* equilibration occurs (the calculated barrier to interconversion is 29 kcal).
2. The complexing agent greatly increases the rate of *syn*–*anti* equilibration (probably by reversibly binding to one end of the peroxymethylene), leading to an increased concentration of the more stable (*anti*) peroxymethylene and thus to an increase in *cis* ozonide product.⁴⁰
3. At higher temperatures the final ring-closure step is less stereospecific (due to increased rates of bond rotation relative to the rate of ring closure). It is expected that this would favor the more stable product (*trans*) as observed.
4. An increase in the solvent polarity may increase the lifetime of the 1,5-biradical, again leading to a loss of stereospecificity.

In conclusion, the biradical mechanism proposed here explains a large body of experimental results on solution-phase ozonolysis.

C. Comparison with Previous Calculations. Recently, Hiberty⁴¹ has reported the results of calculations on the mechanism of ozonolysis. These calculations employed a double ζ basis set and Hartree–Fock wave functions, augmented in some cases with limited CI calculations. The present calculations involve a much more flexible basis set (double ζ plus d-polarization functions) and extensive CI calculations. Comparison of the present DZd–GVB results with earlier DZ–GVB calculations¹ indicates that d functions have large effects (10–20 kcal) on the relative energies of various intermediates. For example,

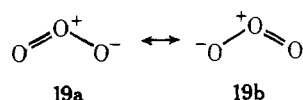
Table IV. Substituent Effects on the Energy, ΔE , of the Zwitterionic State of Peroxymethylene (R_1R_2COO) Relative to the Biradical State^a

R_1	R_2	$\Delta H_f(R_1R_2COH^+)$, kcal	$\Delta H_f(R_1R_2\dot{C}OH)$, kcal	IP(C \cdot) eV	ΔE , kcal
H	H	160, ^b 172 ^c	-6.0	7.5	23
CH ₃	H	136, ^b 145 ^c	-18.5	7.0	12
CH ₃	CH ₃	115, ^b 125 ^c	-29.3	6.5	0

^a See section IVD, for explanation of parameters. ^b From ref 44b, assuming the proton affinity of NH₃ is 205 kcal. ^c From ref 44a.

without d functions the barrier to syn-anti interconversion is predicted to be 19 kcal, while comparable DZd calculations predict a barrier of 29 kcal (Hiberty predicts a barrier of 12 kcal). In addition, the DZ calculations predict some states of the open $\cdot OCO\cdot$ biradical to be below the ring state, while the DZd calculations predict the ring state to be at least 10 kcal below *all* of the biradical states. In light of these differences, we conclude that calculations employing DZ basis sets, while adequate for predicting the qualitative nature of the intermediates, are not sufficiently accurate to predict relative energies of key intermediates.

D. Singlet Biradicals vs. Zwitterions. Calculations reported here and elsewhere^{1,14} indicate that peroxymethylene and ozone are most accurately described as 1,3 singlet biradicals. In the past, the observed reactivity of these species has been interpreted to indicate a zwitterionic mode of bonding. For example, ozone has most often been described as a resonance of structures **19a** and **19b**. The zwitterion model of ozone has



received indirect support from experiments implying an electrophilic nature for ozone. For example, the relative reactivities of substituted aromatic compounds with ozone fit the trends expected of an electrophilic agent.⁴² Similar studies on the ozonolysis of chlorinated olefins have also been interpreted to support the electrophilic character of ozone and the zwitterionic model of bonding in ozone.⁴³ Similarly, it has been shown that addition of peroxymethylene to carbonyls occurs in a manner consistent with the zwitterion model.

A key misconception in the interpretation of these experiments is in the assumed behavior of 1,3 biradicals. The electrophilic nature of oxygen-centered radical species is well-established and is consistent with the large electron affinities observed for oxygen-centered radicals [$EA(C_2H_5O\cdot) = 1.68$ eV, $EA(O_3) = 1.92$ eV].⁴⁴ For example, the electronic structure of $O_2(^1\Delta)$ involves two perpendicular, singly occupied "radical" orbitals and yet 1O_2 exhibits electrophilic character in reactions with olefins.⁴⁵ Thus the chemistry of ozone and of peroxymethylene is quite consistent with the 1,3-biradical character derived from the ab initio wave functions, and there is no need to postulate zwitterionic structures.

There are two important qualifications to the preceding discussion. The calculations reported here describe an unsubstituted, gas-phase (i.e., not solvated) peroxymethylene molecule. Both solvation and substitution should alter the relative energies of the biradical and zwitterionic states and may alter the character of the ground state.

In section IIIA it was noted that the present ab initio calculations place the zwitterionic state of peroxymethylene 3.99 eV above the biradical ground state. However, in these calculations the excited zwitterionic state is forced to be orthogonal to the lower biradical state. In order to discuss the effects of solvation and substitution, it is more relevant to consider the energy of a zwitterionic state that is not constrained to be orthogonal to the biradical state. The actual optimum wave

function will, of course, be a combination of both states, emphasizing whichever state is of lower energy.

To estimate the energy of a nonorthogonalized zwitterion state, we will start with the 1,3 biradical and construct the 1,3 zwitterion by ionizing the electron of the carbon radical center and attaching this electron to the oxygen radical center. The energy change for this process is given approximately by the relationship

$$\Delta E(\text{eV}) = IP(C\cdot) - EA(O\cdot) - 14.40/R_{CO} \quad (1)$$

where $IP(C\cdot)$ is the ionization potential (eV) of the carbon radical center, $EA(O\cdot)$ is the electron affinity (eV) of the oxygen radical center, and R_{CO} is the distance (\AA) between the carbon and oxygen radical centers (2.23 \AA). In order to account accurately for the effect of coupling between the radical centers, the energy of the zwitterionic state is calculated relative to that of the $^1(5\pi)$ biradical state in which the radical orbitals are rigorously orthogonal. The energy of the zwitterionic state relative to the $^1(4\pi)$ biradical state can then be obtained using the GVB-CI $^1(4\pi) \rightarrow ^1(5\pi)$ excitation energy.

In order to evaluate the zwitterionic energy from (1), we must estimate appropriate "local" radical center ionization potentials and electron affinities. In the calculations reported here, $EA(O\cdot) = 1.68$ eV = $EA(CH_3CH_2O\cdot)$ and $IP(C\cdot) = IP(R_1R_2\dot{C}OH)$ are assumed,^{44,46} and the results are given in Table IV.⁴⁷ These calculations indicate, as expected, that alkyl substituents significantly stabilize the zwitterionic state relative to the biradical state. In fact, the calculations predict that the biradical and zwitterionic states of gas-phase dimethyl-substituted peroxymethylene are approximately degenerate. Thus, the ground state of this species will have a large degree of both biradical and zwitterionic character. Stronger π -donating substituents (amino, alkoxy, etc.) are expected to swing this balance even further toward the zwitterionic state.

Consider now the effect of solvation on the electronic structure of peroxymethylene. As a model, assume the molecule to be in a spherical cavity of radius $R(\text{\AA})$ surrounded by a dielectric medium with dielectric constant ϵ . The stabilization of the zwitterion relative to the biradical can then be estimated using the formula^{48,49}

$$\Delta E(\text{kcal}) = \left(\frac{\epsilon - 1}{2\epsilon + 1} \right) \frac{\mu_Z^2 - \mu_B^2}{R^3} \times 14.4$$

where μ_Z is the dipole moment (debye) of the zwitterionic state and μ_B is the dipole moment of the biradical state. Taking $\mu_B = 3.50$ D (from the GVB-CI wave function), $\mu_Z = 10.7$ D (unit charges separated by a distance of 2.23 \AA), and $R = 2.5$ \AA , we obtain

$$\Delta E = \frac{\epsilon - 1}{2\epsilon + 1} \times 94.2 \text{ kcal/mol}$$

Therefore, for unsubstituted peroxymethylene, a solvent dielectric constant of ≥ 2.5 will bring the zwitterionic state below the biradical.

We conclude then that the ground state of gas-phase peroxymethylene is most accurately described as a 1,3-singlet biradical. However, the energy separation between the

nonorthogonalized biradical and zwitterionic states is small and can be significantly affected by substituents or solvation. Thus the electronic structure of Criegee intermediates will depend critically on the nature of their environment. However, since the chemistry of the two species [singlet biradical and zwitterion] is expected to be very similar (vide supra), the distinction may well be unimportant for mechanistic considerations.

V. Conclusion

The qualitative model of ozonolysis previously suggested¹ involving a singlet peroxyethylene biradical intermediate has been confirmed with more accurate calculations (larger basis set, more extensively correlated wave functions). In addition, the calculations reported here are of sufficient quality to determine accurately the relative heats of formation of the various proposed intermediates in ozonolysis. It was found that formation of the Criegee intermediate (peroxyethylene) is 10 kcal endothermic from the primary ozonide (1,2,3-trioxolane) or ~10 kcal exothermic from a postulated 1,5-biradical intermediate. Peroxyethylene calculated to have a 29 kcal barrier to rotation about the C–O bond, indicating that syn and anti isomers will be configurationally stable in solution. In addition, it is found that the ring state of methylene peroxide (dioxirane) is 36 kcal below the open peroxyethylene form.

These results are used to propose a mechanism for the gas-phase ozonolysis of ethylene involving four pathways to decomposition of the postulated 1,5- $\text{OCCOO}\cdot$ biradical intermediate. One pathway, 1,2 H migration, is found to lead to a dioxetane intermediate, the cleavage of which would lead to chemiluminescence from $^1A'' \text{CH}_2\text{O}$ (as recently observed).

In addition, it is shown that many facets of solution-phase ozonolysis (including stereospecificity, relative yields, and effects of complexing agents) can be understood on the basis of the biradical mechanism.

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- Note that the energy of the zwitterionic state of peroxyethylene from these calculations (23 kcal) is much lower than the GVB–CI energy (92 kcal). This difference is primarily due to the removal of orthogonality constraints and differences in geometries; however, the GVB–CI calculation was not designed to accurately describe the zwitterionic state, and up to 30 kcal of this difference may be due to inaccuracies in the calculations.²⁴
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