

# Theoretical Determination of Molecular Structure and Conformation. 6. The Criegee Intermediate. Evidence for a Stabilization of Its Syn Form by Alkyl Substituents

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**Abstract:** Rayleigh–Schrödinger–Møller–Plesset (RSMP) perturbation calculations using a split-valence basis augmented by d-type polarization functions have been carried out on peroxyethylene, the so-called Criegee intermediate of the ozonolysis reaction. Accurate equilibrium structures for the bent, linear, and perpendicular molecule as well as its cyclic isomer, dioxirane, have been determined. With these structures, the barriers to rotation and inversion have been found to be 32 and 41 kcal/mol, respectively. Methyl substitution enhances these barriers. Thus, an equilibration of syn and anti alkylperoxyethylenes in solution-phase ozonolysis has to be excluded. In nonpolar solvents, the syn form of methylperoxyethylene is more stable by 3–4 kcal/mol than the anti form.

## I. Introduction

Ever since Criegee<sup>1</sup> proposed a general mechanism for the reaction of ozone with olefins in solution, the ozonolysis reaction has been the subject of many experimental and theoretical studies.<sup>2</sup> Today some of the key questions about the ozonolysis mechanism center around the nature of the so-called Criegee intermediate,  $RR'CO_2$ , a compound which should be referred to as a peroxyethylene.<sup>3</sup> There are three questions which have to be answered in connection with the role of peroxyethylene in the ozonolysis reaction. First, does the ground state of peroxyethylene in solution resemble a zwitterion or a singlet diradical? Second, does an alkylperoxyethylene exist in a syn and anti form separated by a large interconversional barrier or is there the possibility of an equilibration of the two forms? Finally, which of the two forms is more stable, the syn or the anti form?

The first question has recently led to a controversy between experimentalists and theoreticians,<sup>4</sup> which we believe to be more or less academic. The true ground state of planar peroxyethylene in the gas phase certainly is a superposition of a 1,3-singlet diradical and a zwitterion where the diradical character prevails.<sup>5,6</sup> On the other hand, substituents as well as solvent effects can lead to a dominance of the zwitterion character. At least, this is suggested by a heuristic theoretical approach to this problem carried through by Goddard et al.<sup>5b</sup> At the present time, however, it is very difficult to describe the electronic nature of a solvated alkylperoxyethylene by rigorous theoretical methods. Therefore we refrain from a discussion of this question and refer to the work of Goddard.<sup>5</sup>

The second question is rather a substantial one since it is closely connected with an elucidation of the experimentally observed stereochemical peculiarities of the ozonolysis.<sup>7</sup> The reported mechanistic explanations of the stereochemistry of the ozonolysis reaction rely heavily on the premise of nonequilibration of syn and anti alkylperoxyethylenes.<sup>8a,9</sup> This assumption gains support from the configurational stability of related compounds, e.g., oximes, as well as by the results of some of the relevant theoretical calculations.<sup>5</sup> On the other hand, Bailey et al. have recently suggested that there is an equilibration of syn and anti peroxyethylene stereoisomers which is steered by the solvent, the temperature, and the presence or absence of a complexing agent.<sup>8b,10</sup> Their suggestion is in agreement with Hiberty's calculation of the barrier to rotation of  $CH_2O_2$ . With a 4-31G basis and limited con-

figuration interaction (CI) he finds a barrier of just 12 kcal/mol.<sup>6a</sup>

No direct experimental clues reveal whether the syn or anti form of alkylated peroxyethylenes is more stable. For steric reasons one tends to attribute higher stability to the anti form. But there do exist in some molecules electronic forces which cause a reversion of the expected configurational stabilities.<sup>11</sup> Such a case is assumed for peroxyethylene by Bailey et al., who suggest that steric repulsion in the syn form is counterbalanced by hydrogen bonding between an alkyl substituent and the terminal oxygen atom.<sup>10</sup>

From a theoretical point of view, questions two and three have only been dealt with insufficiently in published ab initio studies. The first ab initio investigation of peroxyethylene by Ha et al.<sup>12</sup> was based completely on single-determinant, restricted Hartree–Fock (RHF) theory with assumed bond lengths taken from reported alkyl peroxide structures. From all that is known about the electronic nature of ozone,<sup>13</sup> which is isoelectronic with  $CH_2O_2$ , such an approach is hardly appropriate to give a realistic quantum-chemical description of peroxyethylene. That is why Hiberty included in his study of peroxyethylene limited CI and optimized three out of seven structural parameters.<sup>6</sup> One weakness of his work, however, lay in the basis set employed, which was of split valence shell quality. It is well established that the inclusion of polarization functions is necessary in order to obtain a reliable description of peroxo compounds.<sup>14</sup> Therefore, the accuracy of Hiberty's results has to be doubted. The importance of a flexible basis was correctly considered only by Harding and Goddard.<sup>5b</sup> Unfortunately, these authors also refrained from a complete geometry optimization.

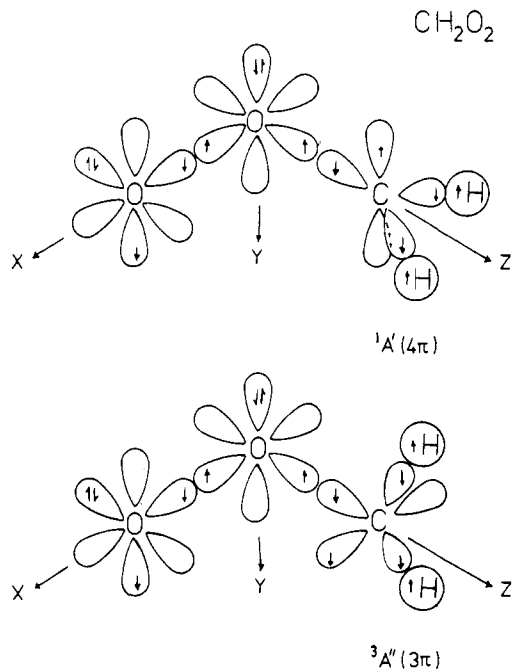
Apart from the technical limitations of the reported ab initio studies on  $CH_2O_2$  none of these works primarily investigated the question of a possible equilibration of syn and anti alkylperoxyethylenes. Only  $CH_2O_2$  has been studied and only the first of the two possible interconversional modes, namely, rotation around the CO bond and inversion at the central oxygen atom, has been considered explicitly. Thus, the rotational transition state of  $H_2CO_2$  has been calculated<sup>5,6a</sup> but not the linear  $C_{2v}$  form of peroxyethylene which corresponds to the inversional transition state.

The purpose of the present work is twofold. First, the configurational stability of peroxyethylene with regard to rotation and inversion is studied in a rigorous way by (1)

**Table I.** Total Molecular RSMP Energies, Second-Order Correlation Energies, and Relative Molecular Energies of Various States of O<sub>3</sub> and CH<sub>2</sub>O<sub>2</sub>

molecule <sup>a</sup>	state <sup>b</sup>	basis B <sup>c</sup>	basis C	basis D
A. Absolute Energies (hartree)				
ozone	<sup>1</sup> A <sub>1</sub> (4π)	-224.399 14	-224.876 83	-225.053 09
trioxirane	<sup>1</sup> A <sub>1</sub> (6π)	-224.369 12	-224.820 51	-224.991 58
peroxymethylene, I	<sup>1</sup> A' (4π)	-188.627 19	-189.052 83	
	II	<sup>3</sup> A'' (3π)	-188.588 57	-189.001 66
	III	<sup>1</sup> A <sub>1</sub> (4π)	-188.572 71	-188.987 89
dioxirane	<sup>1</sup> A <sub>1</sub> (4π)	-188.681 78	-189.107 81	
B. Second-Order Correlation Energies (hartree)				
ozone	<sup>1</sup> A <sub>1</sub> (4π)	-0.506 72	-0.639 61	-0.749 04
trioxirane	<sup>1</sup> A <sub>1</sub> (6π)	-0.499 86	-0.596 84	-0.696 87
peroxymethylene, I	<sup>1</sup> A' (4π)	-0.363 31	-0.512 49	
	II	<sup>3</sup> A'' (3π)	-0.290 62	-0.436 94
	III	<sup>1</sup> A <sub>1</sub> (4π)	-0.337 88	-0.491 39
dioxirane	<sup>1</sup> A <sub>1</sub> (4π)	-0.378 26	-0.507 90	
C. Relative Energies (kcal/mol) <sup>d</sup>				
ozone	<sup>1</sup> A <sub>1</sub> (4π)	0	0	0
trioxirane	<sup>1</sup> A <sub>1</sub> (6π)	18.8 (14.5)	35.3 (8.5)	38.6 (5.9)
peroxymethylene, I	<sup>1</sup> A' (4π)	0	0	
	II	<sup>3</sup> A'' (3π)	24.2 (-21.4)	32.1 (-15.3)
	III	<sup>1</sup> A <sub>1</sub> (4π)	34.2 (18.2)	40.7 (27.5)
dioxirane	<sup>1</sup> A <sub>1</sub> (4π)	-34.3 (-24.9)	-34.5 (-37.4)	

<sup>a</sup> Structures I, II, and III correspond to the planar, perpendicular, and linear forms of peroxymethylene. See Figure 3. <sup>b</sup> Number of π electrons is given in parentheses. See discussion in the text. <sup>c</sup> Basis B energies of forms I, II, and III have been obtained with RSMP/basis C structures. <sup>d</sup> Number in parentheses refers to the corresponding HF energies.



**Figure 1.** Qualitative orbital pictures of the ground states of planar (above) and perpendicular (below) peroxymethylene.

considering basis set effects, (2) correcting the HF results for correlation errors, and (3) optimizing all geometrical parameters of the planar form and the two interconversional transition states. Also, a possible rearrangement of peroxymethylene to dioxirane is investigated.

Secondly, these calculations are repeated in part for methylperoxymethylene. So far no ab initio study on this molecule has been reported in the literature, although the determination of its configurational and conformational stability is important for a theoretical elucidation of the stereochemistry of the ozonolysis reaction. Methylperoxymethylene is formed during the ozonolysis of propene and 2-butene (or other 2-alkenes).

We have investigated cyclic intermediates of these reactions previously.<sup>15</sup> Thus, with the present paper we continue the theoretical investigation of the ozonolysis mechanism for small alkenes that was begun in part 3.<sup>16</sup>

## II. Numerical Procedures

As already indicated in the Introduction, molecules like ozone or peroxymethylene cannot satisfactorily be treated by single-determinant HF theory since correlation effects turn out to be extremely important in these electronic systems.<sup>5,6</sup> It has been shown by Goddard and co-workers<sup>13</sup> that HF calculations on ozone lead to drastic failures. Therefore, only correlation-corrected wave functions provide a reliable description of molecules like O<sub>3</sub> and CH<sub>2</sub>O<sub>2</sub>. To this purpose we have used second-order Rayleigh-Schrödinger-Møller-Plesset (RSMP) perturbation theory<sup>17</sup> which is known to give reasonable estimates of the correlation energy.<sup>14</sup> In this method the RHF wave function and energy are inserted as  $\Phi^{(0)}$  and  $E^{(0)}$  in the case of a closed-shell species. For the triplet states calculated in this work, the zeroth-order wave function and energy are obtained by unrestricted HF (UHF) theory according to Pople and Nesbet.<sup>18</sup> The RSMP total energy is determined by

$$E = E^{(0)} + E^{(2)} \quad (1)$$

where  $E^{(2)}$  represents the second-order correlation energy.

In nearly all calculations we have used a direct energy minimization technique based on an univariate search in the space of pseudocanonical molecular orbitals (MO).<sup>19</sup> In this way, an oscillation between different states of peroxymethylene which we frequently encountered in the conventional Roothaan-Hall procedure<sup>20</sup> was avoided. In order to achieve accurate  $E^{(2)}$  values the convergence criterion on the density matrix had to be set to  $10^{-6}$ .

As in the preceding papers 3-5,<sup>15,16</sup> two augmented basis sets have been primarily employed. We call these basis sets C and D where basis C<sup>21</sup> represents an augmented split-valence (10s4p1d/4s)[3s2p1d/2s] basis of Gaussian-type functions (GTF) and basis D<sup>22</sup> corresponds to Dunning's augmented double- $\zeta$  (9s5p1d/4s1p)[4s3p1d/2s1p] basis which we have

Table II. Comparison of Various Theoretical Structures Obtained for CH<sub>2</sub>O<sub>2</sub><sup>a</sup>

author	Ha et al.	Hiberty	Klopman et al.	Hull	Goddard et al.	this work	this work	this work
ref	12	6a	29	30	5b			
method	HF	6 × 6 CI	MINDO/3	MINDO/3	GVD-CI	RSMP	RSMP	RSMP
basis	[3s2p/2s] <sup>c</sup>	[3s2p/2s]		2 × 2 CI	[3s2p/d/2s2s]	STO-3G	[3s2p/2s]	[3s2p/d/2s]
Planar Form I <sup>f</sup>								
R(OO)	(1.48)	1.269	1.303	1.268	1.362	1.316	1.659	1.295
R(CO)	(1.44)	1.367	1.247	1.252	1.343	1.418	1.212	1.297
R(CH <sub>2</sub> )	(1.09)	(1.08)	1.113	1.110	(1.08)	1.096	1.073	1.083
R(CH <sub>1</sub> )	(1.09)	(1.08)	1.113	1.110	(1.08)	1.095	1.074	1.079
COO	115	117.5	124.0	125.7	116.6	118.1	114.2	120.3
H <sub>2</sub> CO	116 <sup>d</sup>	(120)	128.0	129.5	(120)	119.0	120.6	118.0
H <sub>1</sub> CO	116 <sup>d</sup>	(120)	118.4	116.1	(120)	113.8	119.9	114.3
HCH	128	(120)	113.6	114.4	(120)	127.2	119.5	127.7
Perpendicular Form II								
R(OO)	(1.48)	1.269			1.38	1.382		1.339
R(CO)	(1.44)	1.433			(1.41)	1.435		1.388
R(CH)	(1.09)	(1.08)			(1.08)	1.101		1.076
COO	115 <sup>e</sup>	117.2			(103)	107.5		110.1
HCO	116 <sup>e</sup>	(120)			(120)	119.3		116.9
HCH	128 <sup>e</sup>	(120)			(120)	121.4		125.2
ΔE <sup>b</sup>	30.3	12.4			24.9	5.3		32.1
Linear Form III								
R(OO)	(1.48)			1.237		1.374	1.654	1.345
R(CO)	(1.44)			1.176		1.287	1.254	1.239
R(CH)	(1.09)			1.109		1.113	(1.08)	1.098
HCH	128 <sup>e</sup>			115.5		118.8	(120)	120.8
ΔE <sup>b</sup>	24.9			25.3		45.7	24.7	40.7
Ring Form								
R(OO)	(1.48)			1.456	(1.45)	1.490	1.645	1.529
R(CO)	(1.44)			1.342	(1.436)	1.463	1.469	1.398
R(CH)	(1.09)			1.123	(1.09)	1.112	1.086	1.089
HCH	116			107.4	(116)	115.1	117.4	116.6
OCO	61.8			65.7	60.6	61.2	68.1	66.3
ΔE <sup>b</sup>	-36.7			-33.7	-29.7	-44.3	-35.4	-34.5

<sup>a</sup> Bond lengths in ångströms, angles in degrees. Numbers in parentheses are assumed structural parameters. <sup>b</sup> Relative energy with regard to the planar form I. The absolute energies (hartrees) of I are -188.4378 (ref 12), -188.271 81 (ref 6a), -188.756 14 (ref 5b), -186.246 21 (RSMP/basis A), -188.625 38 (RSMP/basis B). <sup>c</sup> Contracted Gaussian lobe functions. <sup>d</sup> Assumed to be equal. <sup>e</sup> Angles taken from structure I. <sup>f</sup> For the designations of the CH bonds, see Figure 3.

completely rescaled for RSMP studies on polyoxides.<sup>14</sup> First estimates of energy and structure have been obtained with Pople's minimal STO-3G<sup>23</sup> and split valence (8s4p/4s)-[3s2p/2s] basis sets,<sup>24</sup> henceforth called basis A and basis B, respectively.<sup>25,26</sup>

In the cases of CH<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> all structural parameters have been optimized using an improved version of the complementary Davidson-Fletcher-Powell (DFP) method.<sup>27</sup> Since test calculations with basis A indicated only minor structural changes for CH<sub>2</sub>O<sub>2</sub> in the case of methyl substitution, a geometrical model for methylperoxymethylene was derived from the relevant RSMP/basis C structures of CH<sub>2</sub>O<sub>2</sub>. Bond lengths and bond angles of the methyl group have been taken from a tabulation of standard values.<sup>28</sup> All calculations have been performed with the program package COLOGNE '76.<sup>14</sup>

### III. Results and Discussion

RSMP total energies and second-order correlation energies obtained for various forms of CH<sub>2</sub>O<sub>2</sub> are listed in Table I. Basis B energies of peroxymethylene have been calculated with RSMP/basis C structures since only the latter provide realistic equilibrium geometries. All other energies refer to optimized structures. Molecular energies of ozone and trioxirane are included in Table I for comparison. Table II contains a summary of computed ab initio geometries of CH<sub>2</sub>O<sub>2</sub>.<sup>5,6,12</sup> The results of two recent MINDO/3 studies, one at the single-determinant level<sup>29</sup> and one using 2 × 2 CI,<sup>30</sup> have been in-

cluded. Since it is difficult to assess the reliability of these calculations (the "parametrization-configuration" paradox<sup>31</sup> of empirically adjusted quantum-chemical methods has to be mentioned in this connection), we refrain from an explicit analysis of these data. In Table III, the computed energies of methylperoxymethylene are listed.

**Peroxymethylene.** In Figure 1, the main electronic features of the <sup>1</sup>A' (4π) ground state of planar CH<sub>2</sub>O<sub>2</sub> are sketched.<sup>32</sup> In order to minimize pair-pair repulsion effects the two single electrons at the carbon atom and the terminal oxygen atom occupy the pπ orbitals. Owing to a finite overlap of these orbitals and a delocalization of the π electrons, the singlet state has a lower energy than the corresponding triplet state. The 4π-electron interaction stabilizes the ground state of the planar form. This becomes obvious when considering the relevant π MOs of ozone (Figure 2), which resemble those of peroxymethylene. In ozone the HOMO (1a<sub>2</sub>) is 1,2 nonbonding and 1,3 antibonding. Accordingly, one expects partial double-bond character for the heavy-atom bonds of ozone as well as peroxymethylene. The actual OOX angle (X = C, O) should be considerably larger than the 90° angle depicted in the molecular model of Figure 1.

In the case of ozone these predictions are confirmed by the spectroscopically observed equilibrium structure (R<sub>c</sub>(OO) = 1.2716 (2) Å and α<sub>c</sub>(OOO) = 117.79 (3)°).<sup>33</sup> No experimental data have been reported for peroxymethylene. Therefore, any knowledge about this molecule depends exclusively

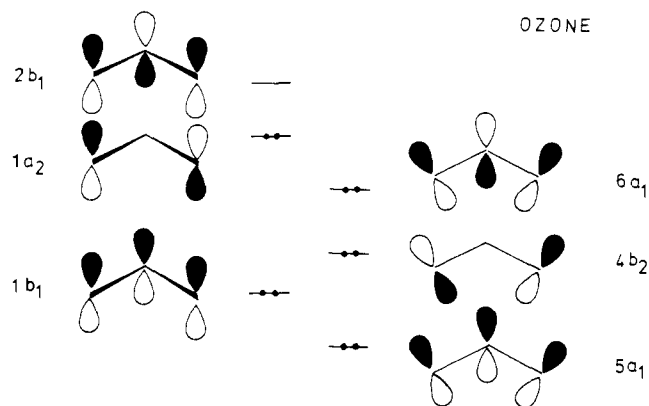


Figure 2.  $\pi$ - and  $n$ -type MOs of ozone formed by the  $p\pi$  atomic orbitals. In the complete MO set, the  $3b_2$  MO has to be inserted between the  $5a_1$  and the  $1b_1$  MO.

on the reliability of quantum-chemical descriptions which in turn can be best rated by their accuracy in reproducing known ozone data. Test calculations show that the theoretical equilibrium structure of  $O_3$  is strongly basis set and correlation dependent.<sup>34</sup> Thus, one encounters changes between 1.19 and 1.37 Å in the OO bond length and between 113 and 120° in the OOO bond angle when the basis set and the method are varied. A short OO length and a large bond angle are found with large augmented basis sets at the HF level of theory while a large bond length and a relatively small bond angle result from a correlation-corrected *ab initio* calculation with a small, rigid basis set. A fortuitous coincidence with experimental data can be achieved with minimal basis set HF calculations since at this level of theory basis set and correlation errors largely cancel. A realistic account of the structural data, however, can only be obtained with correlation-corrected wave functions constructed from extended basis sets augmented by polarization functions. Only in that case is a correct description of charge-transfer and charge-repulsion effects guaranteed.<sup>34</sup>

For a quantum-chemical study of  $CH_2O_2$  similar arguments hold, although the situation is somewhat more complicated. The HOMO ( $\pi_2$ , corresponding to the  $1a_2$  MO of  $O_3$ ) is now partially CO bonding and partially OO antibonding while the LUMO of peroxymethylene ( $\pi_3$ , corresponding to the  $2b_1$  MO of  $O_3$ ) exhibits stronger antibonding character in the CO than the OO part. Accordingly, one finds at the HF level  $R_e(CO) < R_e(OO)$  (RHF/basis A:  $R_e(CO) = 1.257$ ,  $R_e(OO) = 1.429$  Å; see also ref 29 and column 4 of Table II). Since the HOMO-LUMO difference is small, a major contribution to the correlation energy can be attributed to the double excitation (DE)  $(\pi_2)^2 \rightarrow (\pi_3)^2$  which primarily describes left-right correlation of the bond electrons. Consequently, correlation-corrected calculations should lead to a reduction of the bond-length difference  $R_e(OO) - R_e(CO)$ . This, for example, is confirmed by the  $2 \times 2$  CI study of Hull<sup>30</sup> performed with the MINDO/3 method. Minimal basis set RSMP calculations or limited CI with basis B involving two HOMOs and the LUMO of  $CH_2O_2$  reverse the bond-length ordering (see columns 7 and 3 of Table II).

If the number of correlation orbitals is increased by enlarging the basis and considering all virtual orbitals in the CI or RSMP approximation, the role of  $\pi_3$  is diminished. Besides left-right correlation effects, in-out and angular correlation of electrons gain importance. This is demonstrated by RSMP/basis B results (column 8 of Table II). Since basis B tends to overestimate bond polarities, a relatively large charge transfer from C to O is computed at the HF level.<sup>14</sup> This charge resides in the outer valence-shell regions of the O atoms. At the RSMP level additional charge is brought into these atomic

Table III. HF and RSMP Energies of Various Configurations and Conformations of  $CH_3CHO_2^a$

		CH <sub>3</sub> group confor- mation <sup>b</sup>	HF basis B	HF basis C	RSMP basis B
A. Absolute Energies (hartree)					
I	syn	ecl	-227.260 12	-227.592 45	-227.712 07
		stag	-227.257 69	-227.589 70	-227.708 01
	anti	ecl	-227.254 82	-227.587 03	-227.705 51
		stag	-227.256 12	-227.588 73	-227.706 79
II		ecl	-227.284 25		-227.667 89
		stag	-227.283 10		-227.666 89
III		ecl	-227.227 32		-227.655 10
		stag	-227.227 89		-227.655 21
ring		ecl	-227.299 99	-227.643 62	-227.752 72
		stag	-227.303 43	-227.647 56	-227.756 78
B. Relative Energies (kcal/mol)					
I	syn	ecl	0	0	0
		stag	1.5	1.7	2.5
	anti	ecl	3.3	3.4	4.1
		stag	2.5	2.3	3.3
II		ecl	-15.1		27.7
		stag	-14.4		28.4
III		ecl	20.6		35.8
		stag	20.2		35.7
ring		ecl	-25.0	-32.1	-25.5
		stag	-27.2	-34.6	-28.1

<sup>a</sup> RSMP/basis C structures of  $CH_2O_2$  have been used. <sup>b</sup> The designations ecl (eclipsed) and stag (staggered) refer to the conformation of adjacent CH bonds (see Figure 4).

areas, thus causing enhanced repulsion between the O atoms. As a direct consequence of a better description of in-out correlation of electrons, an unrealistically long OO bond length results. When the deficiencies of basis B are compensated by using more GTFs of the s type and by introducing d functions on the heavy atoms, charge-repulsion effects are decreased. Hence, with RSMP/basis C calculations one finds an adjustment of the CO bond distance to the OO value (last column of Table II).

The data of Table II show that the theoretically determined equilibrium structure of the  $^1A'(4\pi)$  state of  $CH_2O_2$  is highly sensitive to basis set and correlation effects. Since both effects strongly couple, it is difficult to assess the reliability of our results as compared to Goddard's findings.<sup>5b</sup> Judging from related studies on ozone,<sup>13,34</sup> we tend to prefer our RSMP/basis C calculations because of the following three reasons. First, our final energy for peroxymethylene (see Table I, basis C) is almost 0.3 hartree or 190 kcal/mol lower than the best energy of ref 5b. Secondly, we note that the better calculation leads to the shorter heavy-atom bond distances.<sup>34</sup> Finally, the structural parameters of Table II indicate a coupling between all bond lengths and angles of peroxymethylene. Hence, a complete optimization as performed in this work should lead to the more reliable equilibrium structure. Further indication for this conclusion is the fact that both the CO and OO bond length are similar to the OO bond distance of ozone, thus stressing the relationship of the two molecules. The computed bond lengths of about 1.30 Å are somewhat shorter than the average of the corresponding single and double bond lengths. This is in line with the expected double-bond character of each bond.

**Interconversional Transition States of Peroxymethylene.** With the aid of Figures 1 and 2 the electronic changes due to rotation around the CO bond or inversion at the central O atom can be discussed. The computed equilibrium structures of the interconversional transition states (RSMP/basis C structures)

**Table IV.** Theoretical Barrier Values (kcal/mol) for Rotation around a CO Bond and Inversion at an Oxygen Atom Compared for Various Molecules

molecule	method/ basis	rotational barrier	inversional barrier	ref
HOH	RSMP/C		37.2	<i>a</i>
CH <sub>3</sub> OH	RHF/[42/2]	1.4	32.5	<i>b</i>
H <sub>2</sub> C(O)OH	RHF/A	9.6	53.8	<i>c</i>
H <sub>2</sub> C=O <sup>+</sup> H	RSMP/C	31.5	24.3	<i>a</i>
CH <sub>3</sub> CH=O <sup>+</sup> H	RSMP/C	31.6	25.5	<i>a</i>
H <sub>2</sub> COO	RSMP/C	32.1	40.7	this work
CH <sub>3</sub> CHOO	RSMP/C	35.6 <sup>d</sup>	42.2 <sup>d</sup>	this work

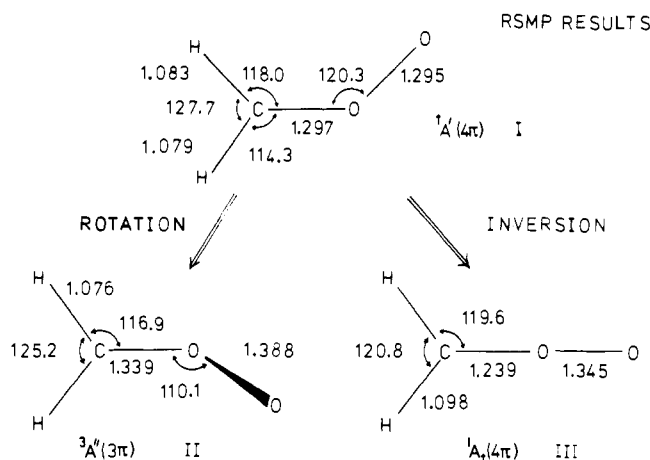
<sup>a</sup> D. Cremer, unpublished results. <sup>b</sup> L. M. Tel, S. Wolfe, and I. G. Csizmadia, *J. Chem. Phys.*, **59**, 4047 (1973). <sup>c</sup> M. R. Peterson and I. G. Csizmadia, *J. Am. Chem. Soc.*, **101**, 1076 (1979); barriers measured relative to the syn form. <sup>d</sup> Estimated from the increase of RSMP/basis B barriers and the RSMP/basis C barriers of CH<sub>2</sub>OO.

are summarized in Figure 3 together with the corresponding barrier values.

From Figure 1 it can be seen that a 90° rotation of the CH<sub>2</sub> group causes a decoupling of the two single electrons. In the perpendicular form of CH<sub>2</sub>O<sub>2</sub>, the overlap between the corresponding p orbitals vanishes, thus leading to a triplet rather than a singlet ground state. The three remaining π electrons interact with two electrons occupying the pseudo-π orbital of the methylene group. As a consequence, the antibonding π<sub>3</sub> MO is now singly occupied. In terms of the MOs of Figure 2, the rotational process may be thought of as causing a single excitation (6a<sub>1</sub>)<sup>2</sup> → 6a<sub>1</sub>2b<sub>1</sub>. Since π<sub>3</sub> is stronger CO than OO antibonding, the CO bond lengthening is more pronounced. Furthermore, the 1,3-bonding character of π<sub>3</sub> is responsible for the decrease of the COO bond angle. The reduction of the angle, of course, is also due to the loss of the 4π stabilization energy which causes sp<sup>2</sup> hybridization at the central O atom of planar peroxymethylene. Our optimized parameters reflect these geometrical changes.

The simple orbital picture of Figure 1 tells us that inversion at the central O atom requires sp hybridization. The 2s(O) lone pair is forced into a p orbital lying in the xz plane. Therefore, lone pair-lone pair repulsion between the O atoms is enhanced. A longer OO bond length than the one found for the planar form should be the consequence. On the other hand, the overlap between the pseudo-π-orbital of the CH<sub>2</sub> group and the p<sub>x</sub>(O) orbital increases and a shorter CO bond length results. All theoretical parameters of Table II are in accord with these predictions, obeying the relationship R<sub>c</sub>(CO) < R<sub>c</sub>(OO). With RSMP/basis C calculations one gets essentially a slightly lengthened CO double bond (1.24 Å) and a distinctly reduced OO single bond of 1.35 Å, which corresponds to changes of 0.05 Å with regard to the planar form I.

The reliability of these structural predictions can be judged by comparing the relevant parameters of dioxirane (ring form of CH<sub>2</sub>O<sub>2</sub>, see Table II) with the reported experimental data, namely, R(OO) = 1.516 Å, R(CO) = 1.388 Å, R(CH) = 1.090 Å, ∠HCH = 117.3°, and ∠OCO = 66.2°. The later values have been taken from the recent microwave study of Suenram and Lovas.<sup>35</sup> The RSMP/basis C structure is in reasonable agreement with these data, although the theoretical ring bond lengths are somewhat too long, 0.013 Å in the case of the OO bond and 0.010 Å in the case of the CO bond. This discrepancy could result from the fact that a r<sub>e</sub> structure is compared with a r<sub>s</sub> structure. However, from what we know about the dependence of the RSMP bond lengths on the basis it is more likely that a basis D calculation would result in shorter ring bonds. Thus, we have found for H<sub>2</sub>O<sub>2</sub> an OO bond



**Figure 3.** RSMP/basis C structures of planar (I), perpendicular (II), and linear (III) peroxymethylene. Note that a rotation of the O<sub>2</sub> group is equivalent to a rotation of the CH<sub>2</sub> group.

length reduction of 0.015 Å when going from C to D.<sup>14</sup> A similar decrease in the case of dioxirane would bring the theoretical and experimental ring bonds to coincidence.

As can be seen from Table II, neither basis A nor basis B gives a reasonable set of structural parameters for dioxirane. This is also true for calculations at the HF level<sup>36</sup> or at the semiempirical MINDO/3 level.<sup>30</sup> Thus, this discussion of the structure of dioxirane provides further evidence that the best set of structural parameters for peroxymethylene is obtained from RSMP/basis C calculations. Similarly, this level of theory is necessary to find the energy changes during an interconversional process. It is demonstrated by the basis A and B energies of the perpendicular form as well as by the corresponding result of Hiberty<sup>6a</sup> that small basis set calculations lead to an underestimation of the barrier to rotation of peroxymethylene. This has to do with the fact that at the HF level the <sup>3</sup>A''(3π) state lies 15–20 kcal/mol below the <sup>1</sup>A'(4π) state of CH<sub>2</sub>O<sub>2</sub>. When correlation corrections are included, the HF-energy difference is reversed due to the higher correlation energy of the planar form (there are 12 electron pairs in I as compared to only 11 in II). If correlation is badly described as in small basis set calculations, the rotational barrier comes out too low.

The dependence of the correlation corrections on the basis set is also responsible for the strong variation of the relative energies of the cyclic isomers trioxirane and dioxirane as compared to ozone and peroxymethylene (see Tables I and II). While the inclusion of polarization functions leads to the well-known improvement of the cyclic state energies at the HF level, its impact on the correlation energies of ozone and peroxymethylene is almost twice as large. Therefore, the energy difference between the cyclic and bent form of O<sub>3</sub> and CH<sub>2</sub>O<sub>2</sub>, respectively, is considerably underestimated both with large basis set HF and small basis set correlation-corrected calculations.

The RSMP/basis C interconversional barriers of CH<sub>2</sub>O<sub>2</sub> fit well into a tabulation of relevant barrier values computed for molecules with a CO bond (Table IV). Thus, the rotational barrier of peroxymethylene is of the same size as that evaluated for protonated formaldehyde. In both compounds the double-bond character of the CO bond is responsible for the high barrier. As for the inversional barrier, the value of CH<sub>2</sub>O<sub>2</sub> lies between those found for an alcohol and an acid.

**Methylperoxymethylene.** The incorporation of a methyl group into peroxymethylene leads to an overall stabilization of the molecule. This can be seen when calculating the bond

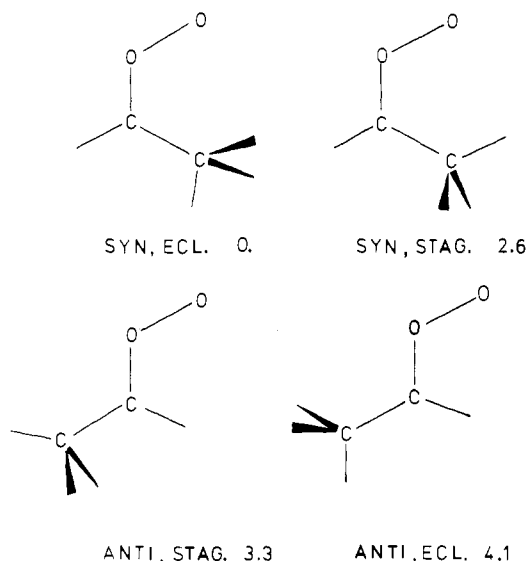
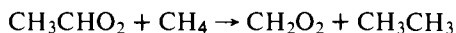


Figure 4. Possible conformations of syn and anti methylperoxymethylene. Their relative stabilities are given in kcal/mol.

separation energy of the formal reaction



which is 11.4 kcal/mol (RSMP/basis B) for the most stable conformation of the planar molecule.

In Figure 4, four steric forms of methylperoxymethylene are depicted, namely, two syn and two anti forms. For each configuration, two conformations of the methyl group can be distinguished, one with a methyl hydrogen being eclipsed with the adjacent methylene hydrogen and one with staggered CH bonds, but the CO bond and a CH bond being eclipsed.

According to Table III, the syn forms are more stable than the anti forms, contrary to what one expects on the basis of steric repulsion. The reasons for this extra stability of the syn forms become obvious when examining Figure 5. There, it is shown that in the syn form with eclipsed CH bonds a pseudo- $\pi$  orbital of the methyl group can overlap with the  $p\pi$  orbital of the terminal O atom. If we consider the four  $2p\pi$  orbitals of the heavy atoms and the  $\pi$ -type combination of the hydrogen orbitals, these will constitute five  $\pi$  MOs, three low-lying, primarily bonding, and two antibonding MOs. Six electrons, namely, four from the peroxymethylene system and two from the  $\text{CH}_3$  group, can be assigned to these MOs. This suggests an "aromatic" stabilization of the syn form similar to the one encountered in double rotors with geminal methyl groups.<sup>37</sup> Evidence for the  $\pi$  stabilization mechanism is provided by the positive overlap populations between the hydrogen atoms and the terminal oxygen atom.

If the  $\text{CH}_3$  group rotates to the staggered conformation (lower half of Figure 5),  $\pi$  stabilization is no longer possible. However, the overlap population between the in-plane hydrogen atom of the  $\text{CH}_3$  group and the terminal oxygen atoms reveals a stabilization of the staggered conformation which is due to  $\sigma$ -electron attraction. As shown in Figure 5, a ring of six atomic orbitals involving the  $\sigma$ -type lone pair orbitals of the O atoms and the orbitals of the in-plane CH bonds can be observed. A detailed analysis of the resulting MOs shows that their interaction leads to some stabilization, especially because the two highest occupied MOs of this set are 1,5 bonding.

The energies of the anti forms lie 3.3 and 4.1 kcal/mol (RSMP/basis B) above the eclipsed syn form of methylperoxymethylene. The computed preference of the staggered conformation is indicative of the marked tendency of methyl hydrogens to eclipse rather than to stagger an unsaturated linkage.<sup>38</sup> The 0.7 kcal/mol barrier to rotation of the methyl

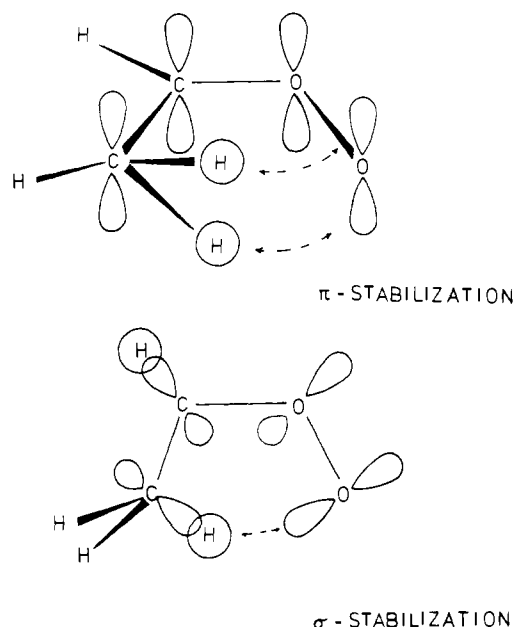


Figure 5.  $\pi$  stabilization and  $\sigma$  stabilization in the syn form of methylperoxymethylene.

group in the anti form compares well with the corresponding barrier value of acetaldehyde, which is 1.16 kcal/mol.<sup>39</sup>

In view of the computed stabilities of methylperoxymethylene we expect a preponderance of syn alkylperoxymethylenes over the corresponding anti forms in nonpolar solvents. In polar solvents, the anti form will gain some stability because its dipole moment is 0.5 D larger, thus guaranteeing a higher solvation energy. This effect, however, is unlikely to reverse the relative stabilities shown in Figure 4.<sup>40-42</sup>

As can be seen from the energies of Table III, the methyl substituent impedes an equilibration of the syn and anti form rather than facilitating it. Applying the same level of basis set sophistication (RSMP/basis B), a 4 kcal/mol increase of the barrier to rotation and a 1.5 kcal/mol increase of the barrier to inversion can be observed. If we assume similar increases at the RSMP/basis C level, the barrier values of Table IV result. They are nearly independent of the conformation of the methyl group.

The destabilizing effect of the  $\text{CH}_3$  group in forms II and III has to do with the electron-donating ability of an alkyl substituent. In the case of peroxomethylene, charge transfer to the peroxy group increases by 0.02 (II) and 0.06 e (III), respectively, when methyl is incorporated into the molecule. Accordingly, the electron population of the antibonding MO  $\pi_3$  of perpendicular peroxymethylene is increased thus leading to its destabilization. Similarly, the charge repulsion between the O atoms of the linear form is enhanced and a higher barrier to inversion results.

In view of the computed interconversional barriers it can be concluded that an equilibration of syn and anti forms of alkylperoxymethylene does not take place in solution-phase ozonolysis. According to the theoretical dipole moments of forms I, II, and III, solvent effects are unlikely to change this picture.<sup>43</sup> In gas-phase ozonolysis, however, the high exothermicity of the formation of the peroxymethylene from ozone and alkene<sup>44</sup> can cause rotation as well as inversion of the molecule. An excitation to the  $^1A''(4\pi)$  state of II which lies slightly above the triplet state<sup>5</sup> is possible. This state can undergo ring closure to form dioxirane. Since the ring structure of  $\text{CH}_2\text{O}_2$  and  $\text{CH}_3\text{CHO}_2$  is about 35 (Table I) and 28 kcal/mol (Table III), respectively, more stable than the corresponding open form I, dioxirane and methyl dioxirane are more likely to be detected in the gas phase.<sup>35</sup>

#### IV. Conclusions

Several important points should be noted from this study.

(1) A reliable ab initio study of peroxyethylene requires a large basis set augmented by polarization functions, extensive correlation corrections, and a complete optimization of structural parameters. If these basic requirements are fulfilled, realistic structures for the various  $\text{CH}_2\text{O}_2$  forms I, II, and III are calculated. This is confirmed by the agreement of the RSMP/basis C structure of dioxirane with the spectroscopically observed  $r_s$  structure of this compound.<sup>35</sup>

(2) In view of the computed interconversional barriers of 32 (rotation) and 41 kcal/mol (inversion) an equilibration of syn and anti forms of alkylperoxymethylenes under the conditions of the solution-phase ozonolysis can be excluded.<sup>43</sup> During the gas-phase ozonolysis planar peroxyethylene can form dioxirane via the  ${}^1A''(4\pi)$  state of the perpendicular form II. The ring isomer is 35 kcal/mol more stable than the  ${}^1A'(4\pi)$  state of  $\text{CH}_2\text{O}_2$ .

(3) Methyl substitution enhances the stability of peroxyethylene considerably. On the other hand, the rotational and inversional barriers are increased owing to the electron-donating ability of the  $\text{CH}_3$  group.

(4) In agreement with Bailey's suggestion,<sup>10</sup> the syn form of methylperoxymethylene is found to be more stable than the anti form. However, it turns out that the syn form prefers to eclipse rather than to stagger its CH bonds in order to gain "aromatic"  $\pi$  stabilization. The conformation considered by Bailey et al.<sup>10</sup> is less stable by 2.6 kcal/mol.

(5) The computed dipole moments indicate that the energy difference between the syn and anti stereoisomers is reduced in polar solvents. In this case the syn form is estimated to be more stable by at least 2.7 kcal/mol than the anti form.<sup>40</sup>

**Note Added in Proof.** Recently, it has been reported that the principal component of the lachrymatory factor of the onion corresponds to (*Z*)-propanethial *S*-oxide,  $\text{C}_2\text{H}_5\text{CHSO}$ .<sup>45</sup> The observation of a syn CCSO arrangement confirms our theoretical results for  $\text{CH}_3\text{CHOO}$  and can be explained along the same lines represented above.

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