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### Theoretical Determination of Molecular Structure and Conformation. 7. Stereoselectivity of the Ozonolysis Reaction

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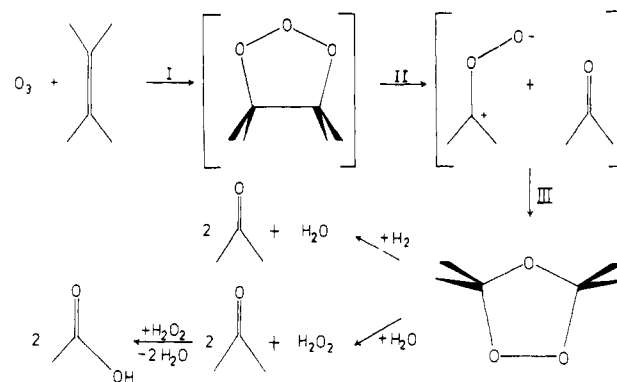
**Abstract:** Restricted Hartree-Fock calculations with an augmented split-valence basis have been used to determine the electronic properties of alkyl substituted primary and final ozonides (PO's and FO's). The PO's are found to possess stable envelope conformations while the FO's are more stable in their twist forms. Barriers to pseudorotation range from 3 to 4 kcal/mol. Conformers which are expected to resemble the transition states (TS's) of the ozonolysis reaction are stabilized by equatorially positioned alkyl groups. This is due to favorable orbital interactions between the substituent and the ring ( $\pi$  effect). As for the stereochemistry of the ozonolysis, predictions can be made when characterizing the reacting molecules by substituent-substituent, substituent-ring, and dipole-dipole interactions. In this way, ab initio results verify conclusions drawn from heuristic reaction models in the case of the ozonolysis of bulky alkenes. They show also that the nature of the TS's changes when small alkenes are ozonolyzed.

The reaction of ozone with alkenes in solution is known to proceed via the formation of a primary ozonide (PO), its cleavage to aldehyde and carbonyl oxide (CO), and the recombination of these molecules to final ozonide (FO) (Scheme I). This reaction sequence was first suggested by R. Criegee.<sup>1,2</sup> Since then ample evidence has been gathered in support of the Criegee mechanism of ozonolysis.<sup>2</sup>

One experimental observation not covered by Scheme I is the stereoselectivity of the reaction. It has been found that *cis*-(*trans*-) alkenes tend to produce more *cis* (*trans*) FO.<sup>2</sup> Thus, the stereochemical relationship of substituents located at the alkene double bond is preserved in some way through the various reaction steps. The Criegee mechanism, however, implies a *cis*-*trans* ratio of FO's equal to unity irrespective of the configuration of the inserted alkene.

In order to rationalize the stereoselectivity of the ozonolysis, heuristic reaction models have been developed. Particularly noteworthy in this connection is the work of Bailey<sup>3,4</sup> and Kuczkowski.<sup>5</sup> Assuming certain nonplanar forms of both PO and FO to be more important than others for the reaction course, these authors were able to explain many of the observed *cis*-*trans* FO

Scheme I



ratios. At the same time, however, it became obvious that the ozonolysis of small alkenes, which shows a different stereochemistry, is difficult to rationalize. For example, both isomers of 2-butene or 2-pentene lead to *cis*-*trans* ratios lower than unity.<sup>2</sup>

In the work reported here, we will make an attempt to elucidate the stereochemistry of the ozonolysis by applying an ab initio theoretical approach. Actually, such a venture would imply a calculation of ground and transition states (GS's and TS's) of Scheme I for a series of alkenes. Although first steps to an ab initio investigation of the TS's of reactions I and II have been undertaken,<sup>6</sup> it is still too costly to monitor, e.g., the decomposition

(1) (a) Criegee, R.; Wenner, G. *Liebigs Ann. Chem.* **1949**, 564, 9-15. (b) Criegee, R. *Ibid.* **1953**, 583, 1-36.

(2) For recent reviews, see: (a) Criegee, R. *Angew. Chem.* **1975**, 87, 765-771. (b) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. I.

(3) Bauld, L.; Thompson, J. A.; Hudson, C. E.; Bailey, P. S. *J. Am. Chem. Soc.* **1968**, 90, 1822-1830.

(4) (a) Bailey, P. S.; Ferrell, T. M.; Rustaiyan, A.; Seyhan, S.; Unruh, L. E. *J. Am. Chem. Soc.* **1978**, 100, 894-898. (b) Bailey, P. S.; Ferrell, T. M. *Ibid.* **1978**, 100, 899-905.

(5) Lattimer, R. P.; Kuczkowski, R. L.; Gillies, C. W. *J. Am. Chem. Soc.* **1974**, 96, 348-358.

(6) (a) Leroy, G.; Sana, M. *Tetrahedron* **1976**, 32, 1379-1382. (b) Hiberty, P. C. *J. Am. Chem. Soc.* **1976**, 98, 6088-6092. (c) Hiberty, P. C.; Devidal, J. P. *Tetrahedron* **1979**, 35, 1015-1017.

Table I. Conformational Data of Puckered Primary Ozonides Calculated with Basis C<sup>a</sup>

$\phi^b$	rel energy <sup>c</sup>	$\pi$ -effect <sup>d</sup> subst	$\alpha_X^e$	$\alpha_Y, \alpha_Z^e$	interaction energy <sup>f</sup>	$\tau(\text{XCOO})$	$\tau(\text{YCOO}),$ $\tau(\text{ZCOO})$	R in RCHOO
Propene PO (2) (X = CH <sub>3</sub> , Y = H)								
0	0.09	0.6	26.8		-0.9	92.5	92.5	X or Y
36	2.05	3.1	12.7		-3.2	78.5	119.9	X
90	3.28	3.3	7.6		-4.7	85.7	153.6	X or Y
144	1.51	1.6	25.0		-2.1	120.0	161.2	Y
180	0	-1.0	43.7		-0.9	147.6	147.6	X or Y
216	1.27	-2.8	57.8		-2.6	161.2	120.0	X
270	2.92	-1.4	61.2		-3.7	153.6	85.7	X or Y
324	1.29	-0.4	44.8		-2.2	119.9	78.5	Y
<i>cis</i> -2-Butene (3) (X = CH <sub>3</sub> , Y = CH <sub>3</sub> )								
0	0.88	1.9	32.5	32.5	-1.4	97.0	97.0	X or Y
36 (324)	1.52	1.8	18.3	50.9	-6.0	84.4	126.1	X (Y)
90 (270)	2.31	0.1	10.3	68.2	-13.2	88.3	160.5	X or Y
144 (216)	0.90	-2.3	29.3	63.4	-7.9	124.9	170.0	Y (X)
180	0	-3.2	49.2	49.2	-2.6	154.9	154.9	X or Y
<i>trans</i> -2-Butene PO (4) (X = CH <sub>3</sub> , Z = CH <sub>3</sub> )								
0 (180)	0	-0.1	26.8	136.3	-1.9	92.5	147.6	X or Z
36 (144)	1.84	4.4	12.7	155.0	-7.3	78.5	120.0	X (Z)
90	3.47	5.8	7.6	172.4	-12.6	85.7	85.7	X or Z
216 (324)	1.14	-3.7	57.8	135.2	-4.5	161.2	119.9	X (Z)
270	2.72	-3.0	61.2	118.8	-9.2	153.6	153.6	Y or Z

<sup>a</sup> Energies in kcal/mol; angles in deg. <sup>b</sup> Angles in parentheses indicate enantiomeric conformers. For these X and Y or Z have to be exchanged as indicated in the last column. <sup>c</sup> Absolute energies of most stable forms are -341.46296 (propene PO), -380.50082 (*cis*-2-butene PO), -380.5307 hartree (*trans*-2-butene PO). <sup>d</sup> Evaluated from  $\Delta = [\epsilon(\text{X-PO})_{q>0} - \epsilon(\text{X-PO})_{q=0}] - [\epsilon(\text{PO})_{q>0} - \epsilon(\text{PO})_{q=0}]$  where  $\Delta$  defines the  $\pi$  effect and  $\epsilon$  stands for the sum of the energies of the two HOMO's. See ref 7b. <sup>e</sup> Substituent orientation angle, see ref 7b and 13. <sup>f</sup> Interaction energies are given relative to the planar PO forms. They have been calculated from the rotational potentials of ethyl peroxide, 1-propanol, and butane. See ref 7b.

of a substituted PO or the formation of a FO by nonempirical methods at the required level of theoretical accuracy. The necessity of employing (a) large augmented basis sets and (b) flexible conformational models has already become obvious when calculating the GS energies of PO's and FO's.<sup>7</sup> In addition, a quantum chemical description of the TS's requires a multi determinant approach in order to obtain reliable estimates of activation energies. Any simplifying assumption with regard to these basic requirements will impede a straightforward analysis of the ozonolysis mechanism.<sup>8</sup>

Facing these difficulties we have pursued a different way to describe TS's I, II, and III. This involved (a) location of those ozonide conformers which are closest to TS's I-III, (b) computation of their relative energies for various substituents, and (c) analysis of their stabilities in terms of substituent-ring and substituent-substituent interactions. Since the ozonolysis reaction has been found to be irreversible and exothermic,<sup>9</sup> we assume early TS's for all three reaction steps (this assumption is discussed in more detail in paper 8).<sup>10</sup> For our analysis it means that TS's I and III are more influenced by reactant rather than product properties. Accordingly, we have to consider orbital and electrostatic interactions between two approaching molecules, namely, ozone and alkene in I and CO and aldehyde in III. Again, this task will be facilitated by utilizing computed GS properties of the molecules in question.

Describing the various TS's in this way it will be possible to distinguish between reaction routes leading to *cis* or *trans* FO. If for a given alkene one route is energetically more favorable than the others, a prediction with regard to the *cis*-*trans* ratio of FO can be made. We will compare these predictions with the mea-

sured ratios in order to estimate the reliability of our approach. Finally, the Bailey<sup>3,4</sup> and Kuczkowski reaction models<sup>5</sup> are examined on the basis of our theoretical results.

#### Numerical Techniques

Standard restricted Hartree-Fock (RHF) theory<sup>11</sup> has been used throughout. As in paper 3<sup>7a</sup> three basis sets, A, B, and C, have been employed. They correspond to Pople's minimal STO-3G, split valence 4-31G, and augmented split valence 6-31G\* basis.<sup>12</sup>

In previous work<sup>7</sup> we have demonstrated that conformations of five-membered ozonides are preferentially described by two ring puckering coordinates,<sup>13</sup> i.e., a puckering amplitude  $q$  reflecting the degree of nonplanarity and a pseudorotation phase angle  $\phi$  defining the mode of puckering.  $\phi$  values of 0 and 180° correspond to the C<sub>s</sub> symmetrical envelope (*E*) and inverted *E* forms of ethylene ozonide and those of 90 and 270° to the C<sub>2</sub> symmetrical twist (*T*) and inverted *T* form (see Figure 1 in ref 7b,c).

Our method to evaluate the relative conformational energies of PO's and FO's is as follows: (1) For given values of  $\phi$  we optimize the amplitude  $q$ , ring bond lengths, and internal and external ring bond angles of ethylene PO and ethylene FO using basis B. All external ring bond lengths are kept at standard values.<sup>14</sup> (2) Then the puckering amplitude and internal ring angles are reoptimized with basis C which is better suited for a description of puckered ozonide forms.<sup>7a</sup> (3) The geometries thus found serve as geometrical models in the case of *trans*-alkene ozonides. As for *cis*-alkene ozonides it turned out to be necessary to recalculate all external ring angles. This has been done for *cis*-2-butene PO at  $\phi = 0, 36, 90, 144, 180^\circ$  and for *cis*-2-butene FO at  $\phi = 180^\circ$ . Thus a semirigid pseudorotator model of PO's and FO's is established. (4) This conformational model serves

(7) (a) Cremer, D. *J. Chem. Phys.* **1979**, *70*, 1898-1910. (b) *Ibid.* **1979**, *70*, 1911-1927. (c) *Ibid.* **1979**, *70*, 1928-1938.

(8) We note that Hiberty<sup>6b</sup> calculates an  $E_a(\text{II})$  value of 33.1 kcal/mol employing basis B and 3X3 CI. The large error of about 20 kcal/mol is probably caused by neglect of polarization functions and the limited CI applied. Obviously, these calculations do not provide a basis to analyze product distributions resulting from energy differences less than 1 kcal/mol.

(9) For the reaction of stilbene and ozone Briner and Dallwigk (Briner, E.; Dallwigk, E. *Helv. Chim. Acta* **1957**, *40*, 1978-1982) reported an enthalpy of 103 kcal/mol. Criegee and Schröder (Criegee, R.; Schröder, G. *Chem. Ber.* **1960**, *93*, 689-700) found an enthalpy of 39 kcal/mol for the decomposition of the PO of *trans*-di-*tert*-butylethylene.

(10) Cremer, D. *J. Am. Chem. Soc.*, following paper in this issue.

(11) Rootaan, C. C. *J. Rev. Mod. Phys.* **1951**, *23*, 69-89. (b) Hall, G. *Proc. R. Soc. London, Ser. A* **1951**, *A205*, 541-552.

(12) (a) STO-3G: Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657-2664. 4-31G: Ditchfield, R.; Hehre, W. J.; Pople, J. A. *Ibid.* **1971**, *54*, 724-728. (c) 6-31G\*: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213-222.

(13) (a) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354-1357. (b) Cremer, D. *Israel J. Chem.* **1980**, *20*, 12-19.

(14) Pople, J. A.; Gordon, M. S. *J. Am. Chem. Soc.* **1967**, *89*, 4253-4261.

Table II. Absolute and Relative Energies of 2-Pentene and 3-Hexene Primary Ozonides Calculated with Basis A<sup>a</sup>

pseudorotation parameters		2-pentene PO				3-hexene PO			
$\phi$ , deg	$q$ , pm	5 (cis)		6 (trans)		7 (cis)		8 (trans)	
		abs	rel	abs	rel	abs	rel	abs	rel
0	47.0	-414.34522	0.48	-414.34761	0	-452.92498	0.38	-452.92711	0
36	44.1	-414.34236	2.27	-414.34320	2.77	-452.92207	2.20	-452.92781	2.70
90	41.6	-414.33537	6.66	-414.33555	7.57	-452.91497	6.66	-452.91516	7.50
144	44.1	-414.34265	2.09	-414.34381	2.38	-452.92226	2.20		
180	47.0	-414.34599	0	-414.34751	0.06	-452.92558	0		
216	44.1	-414.34256	2.15	-414.34371	2.45			-452.92325	2.42
270	41.6	-414.33522	6.75	-414.33572	3.23			-452.91514	7.51
324	44.1	-414.34233	2.29	-414.34324	2.74				
planar	0	-414.33241	8.52	-414.33480	8.04	-452.91217	8.42	-452.91445	7.94

<sup>a</sup> Absolute energies in hartree; relative energies in kcal/mol. Geometries are taken from RHF/C calculations on 3 (cis) and 1 (trans), see ref 7.

Table III. Semirigid Pseudorotor Model for Final Ozonides: RHF/Basis C Geometries and Energies of Compounds 9 and 11<sup>a</sup>

PO	X = Y = H			X = Y = CH <sub>3</sub>
$\phi$	0	72	90	180
$q$	36.2	41.7	45.6	18.5
$r(\text{O}_E\text{C})$	141.5	142.2 (142.8)	142.6	141.5
$r(\text{CO}_P)$	143.9	142.3 (143.8)	143.3	143.9
$r(\text{OO})$	147.6	146.7	146.7	147.6
$\angle\text{CO}_E\text{C}$	103.8	100.2	106.5	108.6
$\angle\text{O}_E\text{CO}_P$	104.9	103.7 (103.5)	104.6	107.0
$\angle\text{COO}$	105.1	107.3 (104.7)	100.1	106.6
$\angle\text{O}_E\text{CX}(\text{Y})$	109.6	109.9 (109.7)	110.8	113.2
$\angle\text{O}_E\text{CH}(\text{Z})$	111.9	111.4 (111.6)	110.5	106.8
$\angle\text{O}_P\text{CX}(\text{Y})$	109.3	112.1 (109.0)	111.7	111.5
$\angle\text{O}_P\text{CH}(\text{Z})$	110.5	108.5 (112.1)	108.7	107.4
abs energy	-302.51087	-302.51527	-302.51623	-380.59448
rel energy	3.36	0.60	0	

<sup>a</sup> Distances in pm; angles in deg. Bond lengths and external ring angles have been calculated with basis B, the remaining parameters with basis C. The designations O<sub>E</sub> and O<sub>P</sub> stand for epoxide and peroxide oxygen. Numbers in parentheses refer to distances or angles involving ring atoms 5 and 4.

Table IV. Conformational Data of Puckered Final Ozonides Calculated with Basis C<sup>a,b</sup>

$\phi$	rel energy <sup>c</sup>	$\pi$ -effect subst	$\alpha_X$	$\alpha_Y, \alpha_Z$	interaction energy	$\tau(\text{XCOO})$	$\tau(\text{YCOO}), \tau(\text{ZCOO})$	$\mu, \text{D}$
Propene FO (10) (X = CH <sub>3</sub> , Y = H)								
0	3.16	-0.5	56.0		-2.0	141.1	141.1	2.36
72	0.49	1.3	26.8		-0.9	92.8	159.6	1.55
90	0.62	2.9	16.9		-1.3	80.3	157.6	1.40
108	1.49	3.4	11.7		-1.3	77.7	145.4	1.65
180	6.03	4.2	14.1		-0.7	97.1	97.1	2.51
252	0.45	-0.6	43.9		-0.8	145.4	77.7	1.74
270	0	-1.2	54.1		-1.8	157.6	80.3	1.52
288	0.38	-1.9	58.7		-2.5	159.6	92.8	1.66
<i>cis</i> -2-Butene FO (11) (X = CH <sub>3</sub> , Y = CH <sub>3</sub> )								
0	2.40	-1.2	56.0	56.0	-4.0	141.1	141.1	2.30
72 (288)	0	-0.4	26.8	58.7	-3.4	92.8	159.6	1.63
90 (270)	0.31	1.5	16.9	54.1	-3.1	80.3	157.6	1.53
108 (252)	1.67	2.8	11.7	43.9	-2.1	77.7	145.4	1.80
180	6.20	12.6	14.1	14.1	-1.4	97.1	97.1	2.24
<i>trans</i> -2-Butene FO (12) (X = CH <sub>3</sub> , Z = CH <sub>3</sub> )								
0 (180)	5.70	2.6	56.0	165.9	-2.7	141.1	97.1	2.44
72 (108)	1.47	4.5	26.8	168.3	-2.2	92.8	77.7	1.57
90	1.21	5.3	16.9	163.1	-2.6	80.3	80.3	1.36
252 (288)	0.34	-2.3	43.9	121.3	-3.3	145.4	159.6	1.76
270	0	-2.9	54.1	125.9	-3.6	157.6	157.6	1.60

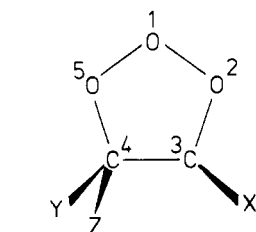
<sup>a</sup> Energies in kcal/mol; angles in deg. <sup>b</sup> See footnotes b and d-f of Table I. <sup>c</sup> Absolute energies of most stable forms are -341.56057 (propene FO), -380.60437 (*cis*-2-butene FO), -380.60502 hartree (*trans*-2-butene FO).

as the basis to compute RHF/basis C energies of various small alkene PO's and FO's. Some higher alkene PO's have also been examined at the RHF/A level. The actual calculations have been carried out as has been described in papers 3 and 4.<sup>7</sup>

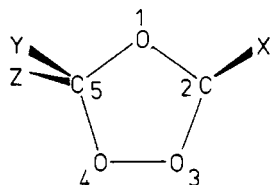
## Results and Discussions

Since the computed data for the semirigid PO model have already been published elsewhere,<sup>7a-b</sup> only those results from the

RHF/C calculations on compounds 2-4 which are relevant to the following discussion are summarized in Table I. Absolute and relative RHF/A energies of compounds 5-8 are shown in Table II. A semirigid FO model has been established by determining theoretical structures and energies of compounds 9 and 11. These are recorded in Table III. The RHF/C results of Table IV provide a similar summary for the FO's 10-12 as shown for the corresponding PO's in Table I.



- 1, X = Y = Z = H
- 2, X = CH<sub>3</sub>; Y = Z = H
- 3, X = Y = CH<sub>3</sub>; Z = H
- 4, X = Z = CH<sub>3</sub>; Y = H
- 5, X = CH<sub>3</sub>; Y = C<sub>2</sub>H<sub>5</sub>; Z = H
- 6, X = CH<sub>3</sub>; Z = C<sub>2</sub>H<sub>5</sub>; Y = H
- 7, X = Y = C<sub>2</sub>H<sub>5</sub>; Z = H
- 8, X = Z = C<sub>2</sub>H<sub>5</sub>; Y = H



- 9, X = Y = Z = H
- 10, X = CH<sub>3</sub>; Y = Z = H
- 11, X = Y = CH<sub>3</sub>; Z = H
- 12, X = Z = CH<sub>3</sub>; Y = H

**Formation of the Primary Ozonide (Step I).** Experimental evidence gathered so far indicates that the initial reaction of ozone with alkene can be considered as a symmetry-allowed concerted [ $\pi_4s + \pi_2s$ ] cycloaddition.<sup>2b,5</sup> Accordingly, reaction I should proceed via a TS which is characterized by an alignment of the  $\pi$  orbitals in parallel planes. As can be seen from Figure 1 both TS Ia and Ib guarantee maximum  $\pi$  overlap. For X and Z being alkyl groups (*trans*-alkenes), the two TS's can hardly be distinguished. For *cis*-alkenes, however, we encounter three effects which should stabilize TS Ib somewhat more than TS Ia. These are (1) reduced steric repulsion, (2) reduced dipole-dipole repulsion, and (3) an enhanced stability of the PO formed (see Table I,  $\phi = 0$  and  $180^\circ$ ). We note that the first effect only counts if X and Y are bulky groups. As for the interactions of two dipoles  $\mu_a$  and  $\mu_b$  being approximately (anti-) parallel oriented in TS I, their energy may be estimated by eq 1 where  $r_{ab}$  is the distance

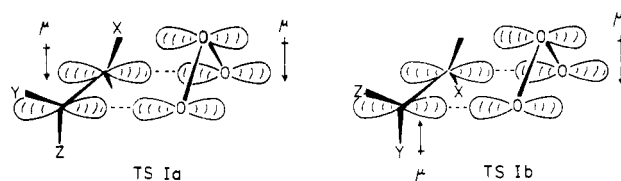
$$E_{a,b} = (\mu_a \mu_b / r_{ab}^3) \cos(\tau_b - \tau_a) \quad (1)$$

between the two dipoles. The angles  $\tau$  serve to distinguish between a parallel ( $\tau_a = \tau_b = 0^\circ$ ;  $E_{a,b} > 0$ ; repulsion) and an antiparallel ( $\tau_a = 0^\circ$ ,  $\tau_b = 180^\circ$ ;  $E_{a,b} < 0$ ; attraction) alignment of the two dipoles. Since both  $\mu(\text{O}_3)$  (0.5 D) and  $\mu(\text{alkene})$  [ $\mu(\text{cis-2-butene}) = 0.3$  D] are small,<sup>15</sup> the dipole-dipole effect should be negligible.

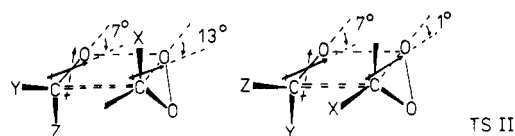
If an early TS is assumed, the stability of the PO formed should also be of minor importance. Hence, we expect only in the case of bulky groups X and Y a marked preference of TS Ib leading to a PO with  $\phi = 180^\circ$  (inverted *E* form). Whether this preference will be of any consequence is discussed below.

**Decomposition of the Primary Ozonide (Step II).** Even at low temperatures PO's 1-8 can undergo pseudorotation as the barriers are just 3-4 kcal/mol (Table I). This is also true for 2-pentene and 3-hexene PO's (Table II). Calculations on 3 with both basis sets A and C have indicated that the minimal basis overestimates the barrier by about 4.5 (cis) and 4 kcal/mol (trans).<sup>16</sup>

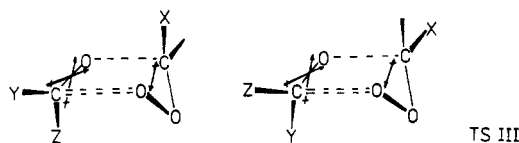
In all cases so far investigated the *E* forms turn out to be the most stable ones. This is a result of a favorable stabilization of the two PO HOMO's at  $\phi = 0$  or  $180^\circ$ . The HOMO's are both



**Figure 1.** Possible TS's of a concerted cycloaddition of ozone and alkene (*cis*-alkene, X = Y = alkyl, Z = H; *trans*-alkene, X = Z = alkyl, Y = H).



- CIS :  $\Delta \approx 6^\circ$                        $\Delta \approx 8^\circ$   
 TRANS :  $\Delta = 20^\circ$                        $\Delta = 6^\circ$



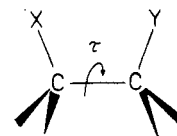
- CIS : (a)  $\Delta = 200^\circ$                       (c)  $\Delta = 174^\circ$   
 TRANS : (b)  $\Delta = 186^\circ$                       (d)  $\Delta = 188^\circ$

**Figure 2.** Interaction of molecular dipole moments in TS's II and III. Orientation angles  $\tau_a$  and  $\tau_b$  ( $\Delta = \tau_b - \tau_a$ ) are given for acetaldehyde and methyl CO.

antibonding and  $\pi$  type in the planar PO ring. The antibonding character is decreased due to  $\sigma$ - $\pi$  mixing in the puckered forms. Taking the flip-flop rotor  $\text{H}_2\text{O}_3$  as a model compound, we have shown that for 1, the *E* form should be more stable by 6-7 kcal/mol,<sup>17</sup> which is about equal to the stabilization of the HOMO's when going from the *T* to the *E* form.<sup>7b</sup>

This energy difference is, of course, counterbalanced by unfavorable bond eclipsing in the *E* forms. As long as there are only small groups attached to the ring, the *E* forms are located at or close to the pseudorotation minima. This will also hold for bulky substituents X and Z. For *cis*-alkene PO's with large alkyl groups, however, substituent-substituent (X-Y) interactions will outweigh the higher " $\pi$  effect" in the *E* forms.<sup>7b</sup> Accordingly, the conformational minima are shifted to  $\phi = 90$  or  $270^\circ$ .

In assessing which *cis*-alkene PO's possess stable *T* conformers we have calculated substituent-substituent interactions in ethanes 13-18.<sup>18</sup> This was done with basis A at  $\tau$  values found for the



- 13, X = Y = H
- 14, X = CH<sub>3</sub>; Y = H
- 15, X = Y = CH<sub>3</sub>
- 16, X = CH<sub>3</sub>; Y = C<sub>2</sub>H<sub>5</sub>
- 17, X = Y = C<sub>2</sub>H<sub>5</sub>
- 18, X = Y = CH(CH<sub>3</sub>)<sub>2</sub>

2-butene PO's 3 and 4 (see Table V). Employing a standard geometry model<sup>14</sup> with all bond angles kept fixed during rotation (rigid rotor model of Table V), we find large destabilizing interactions at low  $\tau$  values already for pentane. The calculated

(15) Nelson, R. D., Jr.; Lide, D. R., Jr.; Maryott, A. A. "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase", *Natl. Bur. Stand.* 1967, 10.

(16) See ref 7b. For a discussion of basis set effects in calculations on puckered PO forms see ref 7a.

(17) Cremer, D. *J. Chem. Phys.* 1978, 69, 4456-4471.

(18) The RHF/A rotational potentials of 13-15 have been taken from published data: Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* 1970, 92, 4786-4795.

**Table V.** Conformational Energies of Alkanes: Substituent-Substituent Interactions X-Y for Dihedral Angles Resembling the Situation in Key Conformers of Alkylated Primary Ozonides (RHF/A Calculations for Flexible Rotor Models)<sup>a</sup>

molecule	X	Y	$\tau = 0^\circ$ (cis PO, $\phi = 0^\circ$ )	$\tau = 40^\circ$ (cis PO, $\phi = 90^\circ$ )	$\tau = 120^\circ$ (trans PO, $\phi = 0^\circ$ )	$\tau = 160^\circ$ (trans PO, $\phi = 90^\circ$ )	$\tau = 90^\circ$ (trans PO, $\phi = 270^\circ$ )
ethane <sup>b</sup> (13)	H	H	2.9			0.2	
propane <sup>b</sup> (14)	H	CH <sub>3</sub>	3.5	0.9	3.5	0.2	1.7
butane <sup>b</sup> (15)	CH <sub>3</sub>	CH <sub>3</sub>	6.9	3.3	3.3	0.4	1.5
pentane (16)	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	6.9 (14.5)	3.2 (6.6)	3.5 (3.9)	0.8	1.9 (2.3)
hexane (17)	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	7.0 (14.5)	3.2 (6.6)	3.4 (3.9)	0.8	1.9 (2.2)
2,5-dimethyl- hexane <sup>c</sup> (18)	CH(CH <sub>3</sub> ) <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	19.2 (>47)	2.8	3.0	0.9	3.0

<sup>a</sup> Energies in kcal/mol relative to the energy of the trans form with  $\tau = 180^\circ$ ; numbers in parentheses are calculated for rigid rotor models.

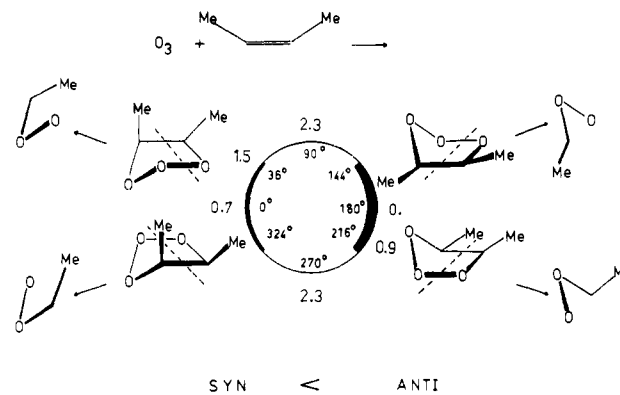
<sup>b</sup> From ref 18. <sup>c</sup> At  $\tau = 25$  and  $28^\circ$  (cis PO,  $\phi = 36$  and  $144^\circ$ ) the relative energies are 6.0 and 5.2 kcal/mol. More complete geometry optimizations suggest that the relative energy of 18 at  $\tau = 0^\circ$  is still overestimated: Cremer, D.; Pachter, R., unpublished results.

energy difference of 7.9 kcal/mol for a rotation from  $\tau = 0^\circ$  to  $\tau = 40^\circ$  suggests that the *T* form of **5** is more stable than the *E* form contrary to what has been found in direct calculations of **5** (Table II).

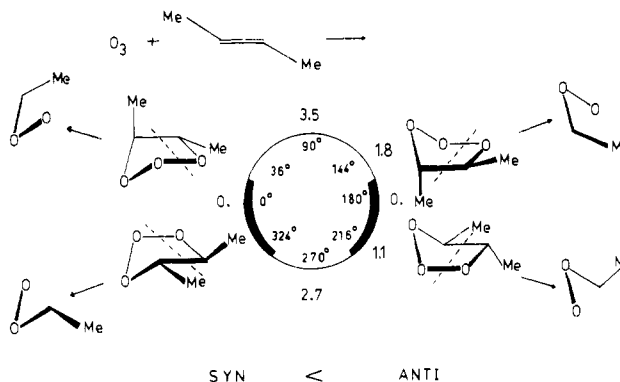
Adopting, however, a more flexible rotor model where the bond angles between heavy atoms are optimized (Tables V and VI), all relevant energy differences computed for compounds **13**–**17** stay below 4 kcal/mol. That means that for X and Y being either methyl or ethyl, the substituted PO's always prefer the *E* forms. Only if both X and Y are isopropyl, do the *T* forms become more stable as is indicated by the results of Table V. For X and Y being larger than isopropyl the pseudorotation barriers are likely to be increased to 10 kcal/mol. Thus two groups of PO's can be distinguished: first, all *trans*-alkene PO's and those *cis*-alkene PO's with small groups X and Y and, second, *cis*-alkene PO's with bulky substituents. For the first group all possible conformers along the most favorable pseudorotation itinerary will be populated once the PO has been formed. A larger population, of course, should be found in the neighborhood of  $\phi = 0^\circ$  and  $180^\circ$ . According to the Curtin-Hammett principle<sup>19</sup> this will be only of relevance for the decomposition reaction if the activation energy of step II is lower or of the same size as the pseudorotational barriers.

Actually, for the cleavage of 1-hexene and *trans*-3-hexene PO (**8**) at  $-100^\circ\text{C}$  activation energies  $E_a$  of 7<sup>20</sup> and 8 kcal/mol,<sup>21</sup> respectively, have been reported. These values, however, imply *A* factors of 6.3 and  $6.8 \times 10^6 \text{ s}^{-1}$  which are quite unlikely for an unimolecular reaction. Assuming an *A* factor of  $10^{13} \text{ s}^{-1}$ , the  $E_a$  values increase to 12–13 kcal/mol.<sup>22</sup> A similar value can be derived in the following way. The  $E_a$  value of step I has been reported to be about 5 kcal/mol,<sup>23</sup> an energy which can be used as a lower limit of  $E_a(\text{II})$ . TS II will be destabilized relative to TS I due to unfavorable dipole-dipole interactions as illustrated in Figure 2. On the basis of the known dipole moments of aldehydes (2.3–2.7 D<sup>15</sup>) and CO's (4–5 D<sup>24</sup>), one gets dipole-dipole repulsion energies of 5–20 kcal/mol for  $r_{ab}$  values ranging from 270 to 210 pm. For an early TS the repulsion energy is certainly lower than 20 kcal/mol, since charges have not fully developed in that situation. An activation energy  $E_a(\text{II}) \geq 10$  kcal/mol with an upper limit of 15 kcal/mol seems to be reasonable.

As far as the first group of PO's is concerned, the varying molecular population along the pseudorotation path is immaterial. The decomposition mode is solely determined by the relative energy levels of the possible TS's. For the second group of PO's one might expect pseudorotation to compete with decomposition. If this is so, conformers with  $90^\circ < \phi < 270^\circ$  are more often among the



**Figure 3.** Decomposition of *cis*-2-butene PO (**3**). Most probable PO precursors to the TS's of the cleavage reaction are shown.



**Figure 4.** Decomposition of *trans*-2-butene PO (**4**). Most probable PO precursors to the TS's of the cleavage reaction are shown.

decomposing molecules than those with  $270^\circ < \phi < 90^\circ$ . This is a result of the higher stability of the former already indicated by the relative energies of Tables I and II. If, however, both pseudorotation and inversion are hindered by barriers being considerably higher than  $E_a(\text{II})$ , a situation occurs where the higher stability of TS Ib is of consequence. Then, more PO molecules decompose via the conformer at  $\phi = 180^\circ$  than that at  $\phi = 0^\circ$ .

Since the majority of PO's will follow the path with the lowest  $E_a(\text{II})$  barrier, those conformers have to be found which are best suited to O–O and C–C bond cleavage. In Table VII computed Mulliken overlap populations  $\rho$  of compounds **1**–**4** are listed for various  $\phi$ . Although  $\rho$  values of different bonds cannot be used to obtain estimates of bond energies, it is possible to monitor by  $\rho$  changes in bond strength during a conformational process. Thus, lowest values of  $\rho_{\text{OO}}$  are evaluated at  $\phi = 36, 144, 216,$  and  $324^\circ$ . PO forms with these puckering modes have one relatively weak and one relatively strong O–O bond. We conclude that these conformers are most prone to decomposition. This is in accord with the rules of conservation of orbital symmetry when assuming step II to proceed as a concerted cycloreversion.<sup>5</sup> The forms shown

(19) For a discussion of the Curtin-Hammett principle, see: Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Interscience: New York, 1965; p 28 and references cited therein.

(20) Razumovskiy, S. D.; Berezova, L. V.; *Izv. Akad. Nauk SSSR., Ser. Khim.* **1968**, *1*, 207–208.

(21) Greenwood, F. L.; Durham, L. J. *J. Org. Chem.* **1969**, *34*, 3363–3366.

(22) A similar value has been suggested by Nangia, P. S.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 3105–3115.

(23) DeMore, W. B.; *Int. J. Chem. Kinet.* **1969**, *1*, 209–220. See also ref 6a and 22.

(24) Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199–7205 and references cited therein.

**Table VI.** RHF/Basis A Geometries and Energies of Alkanes XCH<sub>2</sub>CH<sub>2</sub>Y (16–18) Computed for Various Dihedral Angles<sup>a</sup>

parameter <sup>b</sup>	$\tau = 0$	40	60	90	120	180
Pentane (16)						
$\angle \text{CCC}_X$	115.4	114.3	113.6	112.6	112.7	112.1
$\angle \text{CC}_X\text{C}_X$	111.6	111.8	112.0	112.2	112.2	112.2
$\angle \text{CC}_Y$	115.4	114.4	113.6	112.6	112.7	112.2
rel energy <sup>c</sup>	6.93	3.15	1.46	1.95	3.50	0
Hexane (17)						
$\angle \text{CCC}_X$	115.6	114.4	113.7	112.6	112.7	112.2
$\angle \text{CC}_X\text{C}_X$	111.6	111.8	112.0	112.3	112.2	112.2
rel energy <sup>c</sup>	7.02	3.24	1.52	1.92	3.42	0
2,5-Dimethylhexane (18)						
$\angle \text{CCC}_X$	120.8	115.5	114.7	114.7	114.0	113.6
$\angle \text{CC}_X\text{C}_t$	108.2	109.6	109.5	109.5	109.8	109.6
$\angle \text{CC}_X\text{C}_g$	115.6	111.6	112.0	112.8	112.0	112.5
$\angle \text{C}_t\text{C}_X\text{C}_g$	107.0	108.3	108.1	107.8	108.0	107.0
rel energy <sup>c</sup>	19.21	2.79	0.71	2.99	3.01	0

<sup>a</sup> Relative energies in kcal/mol; angles in deg. <sup>b</sup> Group X and Y carbons are indicated by appropriate subscripts. For 18 C<sub>2</sub> symmetry has been retained during rotation; carbon atoms trans and gauche to the central CC bond have been distinguished by subscripts t and g. <sup>c</sup> Absolute energies of most stable conformations are -194.04606 (16), -232.62622 (17), and -309.77973 hartree (18).

**Table VII.** Overlap Populations and Dipole Moments of Ethylene, Propene, and 2-Butene Primary Ozonides Calculated with Basis C

$\phi$ , deg	overlap populations					$\mu$ , D
	O(1)- O(2)	O(2)- C(3)	C(3)- C(4)	C(4)- O(5)	O(5)- O(1)	
Ethylene PO (1)						
0	0.1674	0.3592	0.6388	0.3592	0.1674	4.11
36	0.1712	0.3584	0.6598	0.3568	0.1498	4.18
90	0.1592	0.3604	0.6776	0.3604	0.1592	4.16
planar	0.1428	0.3562	0.6382	0.3562	0.1428	4.26
Propene PO (2)						
0	0.1704	0.3404	0.6546	0.3534	0.1638	4.09
36	0.1728	0.3472	0.6759	0.3548	0.1462	4.10
90	0.1592	0.3432	0.6928	0.3554	0.1564	4.03
144	0.1482	0.3216	0.6722	0.3520	0.1686	4.09
180	0.1650	0.3272	0.6534	0.3499	0.1668	4.13
216	0.1674	0.3282	0.6848	0.3524	0.1504	4.30
270	0.1538	0.3316	0.7062	0.3586	0.1602	4.27
324	0.1452	0.3268	0.6814	0.3556	0.1708	4.22
planar	0.1424	0.3250	0.6510	0.3512	0.1422	4.25
<i>cis</i> -2-Butene PO (3)						
0	0.1652	0.3280	0.6833	0.3280	0.1652	4.13
36	0.1698	0.3484	0.7018	0.3244	0.1442	4.20
90	0.1566	0.3510	0.7158	0.3328	0.1560	4.19
144	0.1473	0.3236	0.6927	0.3290	0.1692	4.25
180	0.1662	0.3232	0.6668	0.3232	0.1662	4.19
planar	0.1418	0.3180	0.6746	0.3180	0.1418	4.29
<i>trans</i> -2-Butene PO (4)						
0	0.1702	0.3300	0.6732	0.3194	0.1610	4.08
36	0.1704	0.3430	0.6822	0.3202	0.1444	3.99
90	0.1566	0.3394	0.7020	0.3394	0.1566	3.90
216	0.1670	0.3224	0.7056	0.3188	0.1462	4.30
270	0.1546	0.3268	0.7322	0.3268	0.1546	4.34
planar	0.1418	0.3186	0.6596	0.3186	0.1418	4.21

in Figures 3 and 4 guarantee maximal  $\pi$  overlap in the developing  $\pi$  systems. For example, the smaller of the two ring dihedral angles  $\theta(\text{CCOO})$  is just 0.3°.

In assessing which of the four PO forms most easily undergo decomposition, we utilize the computed substituent–ring interactions (Table I). The stability of a PO is affected by the  $\pi$  acceptor ability of its substituents. In the case of a methyl group this ability was found to vary smoothly when the substituent position changes from axial to equatorial and vice versa during pseudorotation. An equatorially located methyl group can depopulate the two antibonding ring HOMO's thus causing an

overall stabilization of the ring. This has been called the “ $\pi$  effect” of the substituent.<sup>7b</sup> An axially positioned methyl group only weakly interacts with the  $\pi$ -type HOMO's, since its pseudo  $\pi$  orbitals are nearly orthogonal. It acts essentially as a  $\sigma$  donor, thus leading to destabilization of the ring. This is reflected by the relevant data of Table I.

Assuming that the  $\pi$  effect of the substituent is also active in TS II, we expect the relative energies of the four conformers in question to reflect those of the corresponding TS's. This is illustrated by Figures 3 and 4 where for the cycloreversion of 3 and 4 the most likely PO precursors to TS II are depicted. The dotted lines indicate which bonds will be broken. The circles symbolize the pseudorotation paths in  $q, \phi$  space.  $\phi$  areas with higher molecular populations are displayed by black bars.

Applying the principle of least motion (PLM),<sup>25</sup> one can determine from the dihedral angles  $\tau(\text{XCOO})$  and  $\tau(\text{YCOO})$  listed in Table I which of the conformers of Figures 3 and 4 should lead to syn or anti CO. A  $\tau$  value  $< 90^\circ$  should cause cleavage to syn CO and  $\tau > 90^\circ$  cleavage to anti CO. This is also indicated in Figures 3 and 4.

When the calculated relative energies and  $\pi$  effects of Table I are compared, it becomes obvious that all small alkene PO's should cleave to anti CO irrespective of their configuration. In the case of bulky alkyl groups the  $\pi$  effect will be outweighed by substituent–substituent interactions. These affect conformers of *trans*-alkene PO's with relatively low  $\tau(\text{XCCZ})$  dihedral angles ( $\phi$  close to 270°). Comparison of the relevant data of Tables I, II, and V reveals that for  $X = Z \geq \text{CH}(\text{CH}_3)_2$  the conformers at  $\phi = 90^\circ$  become more stable than those at 270°. Due to lower X–Z steric repulsion the TS's with PO precursors at 36 or 144° should be more favorable for *trans*-alkene PO decomposition. It follows that syn CO is predominantly formed for these *trans* PO's. Bulky *cis*-alkene PO's, on the other hand, will most probably decompose via TS's associated with  $\phi$  values of 144 and 216°. The conformational energies of 18 (Table V) suggest that steric hinderance resulting from alkyl–alkyl interactions is considerably lower at these  $\phi$  values than at  $\phi = 0^\circ(180^\circ)$ . According to Table I and Figure 3, an enhanced formation of anti CO has to be expected.

So far we have not considered those effects which should influence a late TS II. These are the dipole–dipole interactions between aldehyde and CO and the “syn effect” first found for methyl CO.<sup>24,26</sup> If TS II would be affected in any way by the properties of CO, those routes would more frequently be traversed which lead to syn CO's. As has been shown in paper 6, syn CO experiences stabilizing orbital and electrostatic interactions between the terminal oxygen and the alkyl group.<sup>24</sup> This holds for  $X = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2$ , and even  $\text{C}(\text{CH}_3)_3$ .<sup>27</sup>

As for dipole–dipole interactions we expect that a late TS is most destabilized if the aldehyde dipole is oriented parallel to the CO one ( $\tau_a = \tau_b = 0^\circ$  in eq 1). For the decomposition of compounds 3 and 4 the actual dipole moments of acetaldehyde and methyl CO have to be considered. According to RHF/C calculations the axis of the aldehyde dipole is inclined by 7° with regard to the C–O bond and the axis of the CO dipole by 13 (syn CO) and 1° (anti CO), respectively, with regard to the line connecting the methylene carbon and the terminal oxygen atom. In TS II (Figure 2) the dipoles are distorted by 6 and 8° (decomposition of 3) and 20 and 6° (4) from a parallel alignment, provided maximum overlap is preserved. Thus, only in the case of *trans*-2-butene PO does the consideration of the dipole–dipole interactions lead to a clear distinction of the possible TS's. We note that the reaction path leading to syn CO should be the more favorable one, provided step II proceeds via a late TS. These predictions are summarized in Table VIII.

**Formation of Final Ozonide (Step III).** Again our analysis is based on the assumption of a symmetry-allowed concerted reaction

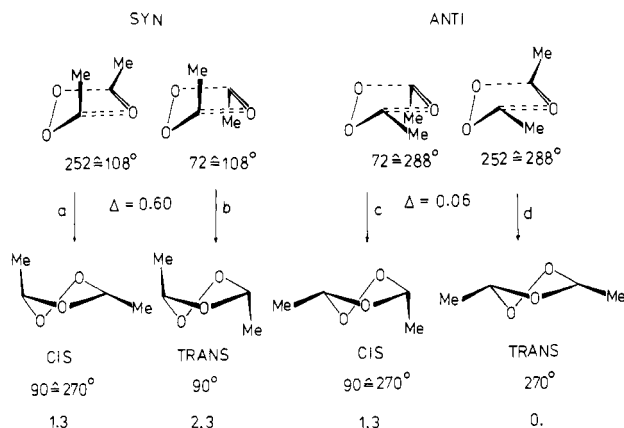
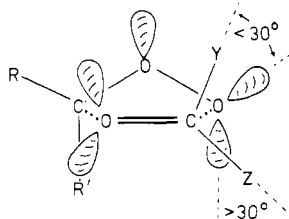
(25) Rice, F. O.; Teller, E. *J. Chem. Phys.* **1938**, *6*, 489–496. See also: Hine, J. *Adv. Phys. Org. Chem.* **1978**, *15*, 1–61.

(26) Block, E.; Penn, R. E.; Bazzi, A. A.; Cremer, D. *Tetrahedron Lett.* **1981**, *22*, 29–32.

(27) Cremer, D., unpublished results.

**Table VIII.** Theoretical Predictions Concerning the Stereochemical Course of the Ozonolysis Reaction<sup>a</sup>

config of alkene	bulk of alkene	config of CO		config of FO	
		TS II		(A)	(B)
		(A) early	(B) late		
cis	small	anti	syn	cis	trans
trans	small	anti	syn	cis	trans
cis	large	anti	anti	cis	cis
trans	large	syn	syn	trans	trans

<sup>a</sup> Predominant configuration of CO and FO is given.**Figure 5.** Reaction of syn and anti-methyl CO with acetaldehyde. TS's III a-d are shown together with phase angles  $\phi$  and relative energies of the corresponding FO conformers.**Figure 6.** Lone pair-substituent interactions as expected by Kuczkowski<sup>5</sup> for TS III.

step.<sup>2,5</sup> Maximum overlap between the  $\pi$  orbitals of aldehyde and CO can be expected for those molecular arrangements which correspond to FO conformers at  $\phi = 72, 108, 252,$  and  $288^\circ$  as reflected by the data of Table IV (see also Figure 5).

Kuczkowski has examined the four TS's of Figure 5 by comparing the interactions of the aldehyde substituents (Y and Z in Figure 6) with the lone pair electrons on the terminal oxygen in CO.<sup>5</sup> Assuming the lone pairs to be localized in  $sp^2$  hybrid orbitals, he expected stronger repulsive interactions with a bulky group Z. Although the stereochemical rules derived from that argument seem to be quite useful,<sup>5</sup> we doubt that substituent-lone pair repulsion is a decisive factor. Both groups Y and Z are almost eclipsed with the O lone pairs, the appropriate dihedral angles being about  $30^\circ$  in both cases.<sup>28</sup> Thus, the lone pair-aldehyde interactions should be of similar magnitude when both Y and Z are alkyl groups.

It seems more reasonable to characterize TS III by (a) the steric 1,3 interactions between aldehyde and CO substituents, (b) the

**Table IX.** Theoretical Cis-Trans Final Ozonide Ratios Based on the Conformational Energies of Compounds 3, 4, 11, and 12<sup>a</sup>

reaction	product	<i>cis</i> -2-butene		<i>trans</i> -2-butene	
		$T = 120$ K	$T = 200$ K	$T = 120$ K	$T = 200$ K
		II	syn CO (A)	6.9	17.4
	anti CO (B)	93.1	82.6	95.0	85.3
III	cis FO (A)	0.5	3.1	0.4	2.7
	(B)	40.7	38.2	41.6	39.4
	(A + B)	41.2	41.3	42.0	42.1
	trans FO (A)	6.4	14.3	4.6	12.0
	(B)	52.4	44.4	53.4	45.9
	(A + B)	58.8	58.7	58.0	57.9
expt <sup>b</sup>	cis FO	37	38	40	37
	trans FO	63	62	60	63

<sup>a</sup> CO and FO yields in %. <sup>b</sup> From ref 4.

dipole-dipole interactions, and (c) the  $\pi$  effect of the substituents that possibly develops in the TS and reaches its full magnitude in the FO.

If syn CO and aldehyde recombine, either R-R (TS IIIa, Figure 5) or R-H interactions (TS IIIb) are encountered. The two TS's IIIc and IIId which involve anti CO lead to H-H or R-H interactions. With increasing bulk of the alkyl group R cycloaddition routes passing through IIIa and d will become less favorable, i.e., syn CO will preferentially lead to trans FO and anti CO to cis FO.

TS III requires an almost antiparallel arrangement of dipole axes. Accordingly, its activation energy should be lower than that of TS I due to dipole-dipole attraction. For an early TS ( $r_{ab} \leq 300$  pm) the  $E_a$  value should be considerably lower than 5 kcal/mol.<sup>30</sup> We expect those TS's to be most stabilized that offer maximum dipole-dipole attraction and maximum overlap at the same time. In the TS's IIIa-d (Figure 2) the molecules must rotate by 20, 6, 6, and  $8^\circ$  in order to fulfill the first condition. When inserting the corresponding differences  $\tau_b - \tau_a$  (200, 186, 174,  $188^\circ$ ) in eq 1, it becomes obvious that again TS's IIIb and c are somewhat more favored than a and d.

As for the  $\pi$  effect, we utilize what has been calculated for the puckered FO's at the relevant  $\phi$  values (Table IV). The relative energies and  $\pi$  effects of the FO's 10-12 suggest that  $\pi$  stabilization—if at all an important factor—should occur preferentially in TS's IIIc and d. The RHF/C energies of 11 and 12 indicate that the conformers corresponding to TS IIIc and d are of equal stability and more stable by 1-2 kcal/mol than those corresponding to a and b. The latter differ by 0.6 kcal/mol.

Considering all possible effects we conclude that the energy of the four possible TS's III should increase in the order  $c \leq d < b < a$  where the equal sign applies to the ozonolysis of small alkenes. This result is in accord with that of Kuczkowski.<sup>5</sup> It implies the formation of either cis or trans FO as shown in Table VIII.<sup>31</sup>

Obviously, the situation is clear in the case of bulky alkenes [X, Y, or Z > CH(CH<sub>3</sub>)<sub>2</sub>]. *Cis*- (*trans*-) alkenes should lead to more cis (*trans*) FO. This prediction agrees with both experimental results<sup>2</sup> and those of the heuristic reaction models of Bailey<sup>3,4</sup> and Kuczkowski.<sup>5</sup> Quite different is the situation for alkenes like 2-butene or 2-pentene. Irrespective of the alkene isomer to be inserted into the reaction, only one FO configuration seems to be preferred. This may be either cis or trans depending on whether an early or a late TS is traversed in step II. Experimental observations suggest that the latter is true. We will investigate this question in paper 8.<sup>10</sup>

It is interesting to note that direct use of relative conformational energies of ozonides 3, 4, 11, and 12 in eq 2 [C, concentration

(28) If the lone pair (lp) directions in methyl CO are calculated with the Boys localization procedure,<sup>29</sup> OO lp angles of 102 and  $105^\circ$  result. With a CCO angle of  $124^\circ$  computed for acetaldehyde with basis C, this leads to YCO lp and ZCO lp angles in TS III of 8 and  $49^\circ$ . Thus lone pair-aldehyde interactions should be even somewhat more favorable for Z being an alkyl group.

(29) Boys, S. F. In "Quantum Theory of Atoms, Molecules and the Solid State"; Löwdin, P. O., Ed.; Academic Press: New York, 1966; pp 253-262.

(30) A low  $E_a$ (III) value is in line with the fact that CO can only be detected by indirect methods, e.g., by interception in the presence of proton active compounds.<sup>2</sup>

(31) The correlation of syn (anti) CO with *trans* (*cis*) FO is explained by Harding and Goddard<sup>35</sup> by invoking the anomeric effect for an assumed biradical intermediate.

$$C_1/C_2 = e^{-\Delta E_s/RT} \quad (2)$$

of ozonide conformer either decomposed to (step II) or formed from (step III) CO] leads to FO cis-trans ratios lower than unity in agreement with experiment. Investigation of the quantitative data summarized in Table IX reveals that the higher trans FO yield is caused by the small portions of syn CO which are transformed almost exclusively to trans FO. The theoretical ratios are higher than the experimental ones, thus indicating that the amount of syn CO is indeed underestimated by a reaction model based on an early TS II.

**Comparison with the Bauld-Bailey and Kuczkowski Schemes.**<sup>3-5</sup> Our analysis indicates that most of the rationales and principles previously used to elucidate the stereochemistry of the ozonolysis reaction are quite reasonable. These are (a) the consideration of step I-III as one-step, concerted, symmetry-allowed [ $\pi 4_s + \pi 2_s$ ] reactions,<sup>5,4</sup> (b) the assumption of nonplanar ozonide conformers as well as syn-anti isomers of CO's,<sup>3,4</sup> (c) the application of the PLM to the PO decomposition reaction,<sup>3,4</sup> and (d) the analysis of the reaction steps in terms of substituent-ring and substituent-substituent interactions.<sup>5,4</sup>

Since the heuristic reaction models of Bailey and Kuczkowski have been developed at a time when almost no molecular data on the key intermediates, namely, PO and CO, were available, it is not surprising that some of their details do not agree with our ab initio results. For example, it is not correct to expect stable *T* conformers for *trans*-alkene PO's or *cis*-alkene PO's with small alkyl groups. We have shown that the *E* forms are more stable due to favorable  $\sigma$ - $\pi$  mixing which lowers the antibonding character of the two PO HOMO's. Bond eclipsing in the *E* forms is only of minor importance as log as substituent-substituent interactions do not exceed 7 kcal/mol.<sup>7</sup>

Interactions between the  $\pi$ -type orbitals of the ozonide ring and the substituent lead to a preference of equatorial positions in alkyl ozonides. This is in line with the experimental observations made by Kuczkowski et al. in the case of propene and *trans*-2-butene FO.<sup>5</sup> We note that Fliszar was the first to point out the higher stability of PO's with equatorial alkyl groups.<sup>32</sup> This was indicated by EHT calculations. The EHT method (as well as other semiempirical methods), however, is inappropriate for the quantum chemical description of PO's.<sup>7</sup> It falsely predicts the *T* forms to be more stable than the *E* forms and exaggerates the relative energies of conformers with similar puckering modes, as has been discussed in more detail in paper 4.<sup>7b</sup>

Most of the conclusions drawn from the EHT results cannot be confirmed by our analysis. In particular, it is necessary to note that propene and *cis*- and *trans*-2-butene PO show identical conformational behavior, i.e., the conformers with equatorial methyl groups are clearly more stable than the corresponding axially substituted forms. This also holds for the *T* conformers of *trans*-2-butene PO which have incorrectly been described by EHT as being equally stable.<sup>32</sup>

If we follow the Bauld-Bailey mode of predicting cis-trans FO ratios for propene and 2-butene, ratios greater than unity have to be expected: Cis FO should be formed preferentially via an anti CO for both alkenes, irrespective of their configuration.<sup>3</sup> This, however, does not comply with experimental findings for 2-butenes and other small alkenes. It is obvious that the Bauld-Bailey model is not able to explain the stereochemical results found in the ozonolysis of small alkenes.

Actually, this is not surprising, since the Bauld-Bailey scheme was originally intended only for alkenes with bulky groups at the double bond. In these cases, substituent-substituent interactions, which are easily estimated utilizing what is known for other ring compounds, outweigh the  $\pi$  effect which is more difficult to foresee without any reliable quantum chemical calculations. Certainly,

this also applies to the Kuczkowski scheme which does stress the importance of substituent-ring interactions in the decomposing PO but fails to rate them correctly in the case of PO's with small alkyl groups. Again this is due to the lack of sufficient stereochemical data on peroxides, especially on ozonides.

In a revised version of the original Bauld-Bailey model, Bailey et al.<sup>4</sup> have considered the possibility that CO rather than PO properties determine the nature of TS II. Thus the experimental cis-trans FO ratios observed for small alkenes could be explained as resulting from a preferred formation of syn CO which in turn leads to a preponderance of trans rather than cis FO. This, of course, is one of the conclusions of the present work where the factors leading from an early to a late TS II are still unclear.

Certainly, one of the merits of the Bauld-Bailey analysis is the application of the PLM to the ozonolysis reaction. While this had to be done in the past by using crude molecular models, we are now able to base our analysis on quantitative data describing the exact position of the alkyl group. These data reveal that as far as the decomposition of PO's is concerned, it is most critical which conformers are considered—the most stable ones or those close to the TS. Bailey et al. have chosen the former possibility but stress that their stereochemical analysis can also be applied to any other set of conformers.<sup>3,4</sup> Kuczkowski, on the other hand, discusses conformers which resemble a concerted TS with optimal  $\pi$  orbital alignment.<sup>5</sup>

In view of the preceding analysis it is evident that the actual choice of the PO conformers has to comply with the Curtin-Hammett principle.<sup>19</sup> Only for *cis*-alkene PO's with bulky substituents should the more stable conformer decide the course of step II. In all other cases it is immaterial, since pseudorotation will be much faster than decomposition. If the more stable *E* conformers would play any role, cleavage to anti CO and cis-trans ratios greater than unity for all group 1 PO's would be the consequence (Table I). Again, this is contrary to what has been expected by Bailey on the basis of qualitative molecular models.<sup>4</sup>

Both Bailey and Kuczkowski have expected step II to be an exothermic reaction with its TS resembling the PO rather than the cleavage products. Following this assumption we do find a similar stereochemistry for the ozonolyses of *cis*- and *trans*-2-butene, but our predictions are not in accord with experimental observations. Theoretical predictions and experimental results can only be reconciled if the assumption of an early TS II is abandoned for small alkenes. According to the Hammond postulate,<sup>33</sup> step II should be endothermic in these cases.<sup>34</sup> Then the syn effect active in alkyl CO's may play a decisive role in TS II.

Although the physical basis of Kuczkowski's approach to step III is not confirmed by our analysis, our predictions agree with those reported in ref 5. This is somewhat fortuitous, since the 1,3 steric and dipole-dipole interactions considered here as being active in TS III are not related to the effects assumed by Kuczkowski et al.<sup>5</sup>

Bailey has analyzed step III referring to product rather than reactant properties. This, of course, does not comply with the Hammond postulate.<sup>33</sup> Consideration of this question, however, should await an investigation of the energetics of the ozonolysis, which will be presented in paper 8.

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(33) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334-338. For a mathematically based discussion of the Hammond postulate, see: Miller, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 1984-1992.

(34) In fact, endothermicity is predicted for step II by our ab initio calculations.<sup>10</sup> See also ref 35.

(35) Harding, L. B.; Goddard, W. A. *J. Am. Chem. Soc.* **1978**, *100*, 7180-7188.

(32) Renard, J.; Fliszar, S. *J. Am. Chem. Soc.* **1970**, *92*, 2628-2635.