

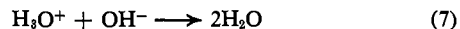
Figure 7. Conductivity change as a function of time in a pulse-irradiated $2 \times 10^{-4} M$ aqueous SF_6 solution at pH 8; dose, 200 rads; (a) time scale, $50 \mu\text{sec/cm}$; (b) time scale, $10 \mu\text{sec/cm}$.

base.¹² Hydronium ions can therefore coordinate with the electron pair, thereby assisting sulfur-fluorine bond breaking (acid catalysis). Since the rate constant for the base-catalyzed reaction is much greater than that for the acid-catalyzed hydrolysis, the most likely reaction mechanism in basic solution is the nucleophilic attack of the hydroxide ion on the sulfur.

(12) H. J. Emeleus, "The Chemistry of Fluorine and Its Compounds," Academic Press, New York, N. Y., 1969.

Likewise, the relatively slow neutral hydrolysis could occur by nucleophilic attack of water on sulfur.

Combination of H_3O^+ and OH^- Ions. Figure 7 shows the change in conductivity of a solution at pH 8.0 which was irradiated with a dose that produces as many hydronium ions in the fast reactions 1 and 4 as there are OH^- ions present. Immediately after the pulse the conductivity increases due to the formation of $2H_3O^+$ and $2F^-$ per e_{aq}^- scavenged by SF_6 . Then the neutralization



leads to a decrease in conductivity. Subsequently the hydrolysis of SF_4 is responsible for the second increase. From the first half-life $ca. t_{1/2} = 7 \mu\text{sec}$ of the second-order decrease of the conductivity after the pulse and the known concentration of $[H_3O^+] = [OH^-] = 10^{-6} M$, the rate constant for the neutralization reaction can be calculated as $k_7 = 1/(10^{-6} \times 7 \times 10^{-6}) = (1.4 \pm 0.3) \times 10^{11} M^{-1} \text{sec}^{-1}$, which is in good agreement with the results of other authors.¹³

Acknowledgment. It is a pleasure to acknowledge the benefit of helpful discussions with Professors A. Henglein and R. H. Schuler and Dr. E. J. Fendler.

(13) M. Eigen and L. deMaeyer, *Z. Elektrochem.*, **59**, 986 (1955); G. Ertl and H. Gerischer, *ibid.*, **65**, 629 (1961); K. H. Schmidt and S. M. Ander, *J. Phys. Chem.*, **73**, 2846 (1969).

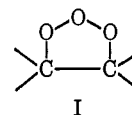
A Quantitative Investigation of the Ozonolysis Reaction. XII. Quantum Chemical Conformational Analysis of Primary Ozonides

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Contribution from the Department of Chemistry, University of Montreal, Montreal, Quebec, Canada. Received October 21, 1969

Abstract: Extended Hückel LCAO-MO calculations indicate that the half-chair conformation of the five membered 1,2,3-trioxolane ring is more stable than the envelope form. The equatorial conformation is preferred by all substituents in the primary ozonides of monosubstituted ethylenes. In the primary ozonides of *trans*-1,2-disubstituted ethylenes, the equatorial, equatorial conformation is preferred by small substituents (methyl, ethyl *n*-propyl), whereas the bulkier isopropyl and *t*-butyl groups prefer the axial, axial conformation. In the primary ozonides of *cis*-1,2-disubstituted ethylenes, the largest group prefers the equatorial conformation when both substituents are small, and the axial conformation when one of the substituents is at least as large as the *n*-propyl group. When one of the substituents is as large as the *t*-butyl group, the primary ozonide does not appear to possess a "stable" conformation.

The very unstable 1,2,3-trioxolanes (primary ozonides) I, which results from the electrophilic 1,3-dipolar cycloaddition¹ of ozone to a carbon-carbon double bond, have been the object of recent studies. Because of the great instability of the primary ozonides, any experimental study with these intermediates in the ozonolysis reaction must be performed at low temperatures (-78 to -130°).



Criegee and Schröder,² and Greenwood³ have isolated α -diols by the treatment of ozonized solutions of olefins (-115°) in ether by an isopropyl Grignard reagent. The configurations of the α -diols obtained

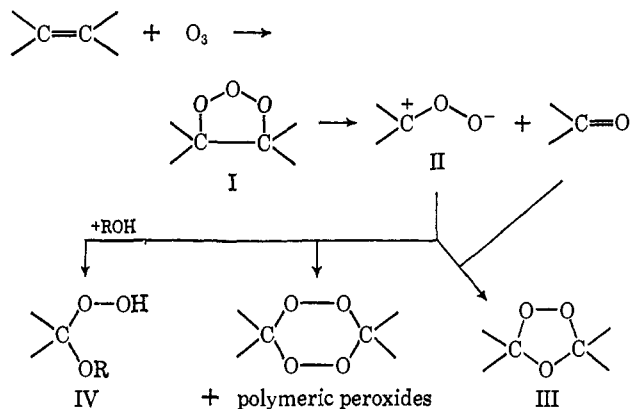
(1) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565, 633 (1963); A. J. Whitworth, R. Ayoub, Y. Rousseau, and S. Fliszár, *J. Amer. Chem. Soc.*, **91**, 7128 (1969); D. G. Williamson and R. J. Cvetanović, *ibid.*, **90**, 4248, 3668 (1968).

(2) R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960).
(3) F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964); **30**, 3108 (1965).

suggest the 1,2,3-trioxolane structure I, which is the structure previously favored by Criegee⁴ for the ozone-olefin transitory adduct.⁴ Subsequent low-temperature (-110°) nmr experiments by Bailey, *et al.*,⁵ and by Greenwood, *et al.*⁶ (-130°), confirm structure I, and provide data on the relative "stabilities" of initial ozonides from *cis* and *trans* olefins. The evidence for a 1,2,3-trioxolane structure is not unambiguous for the *cis* primary ozonides, which are reported to be even more unstable than the *trans* isomers⁶ at temperatures as low as -110° , but an analogous structure to the *trans* primary ozonide is suggested.

The Criegee mechanism of ozonolysis⁴ (Scheme I)

Scheme I

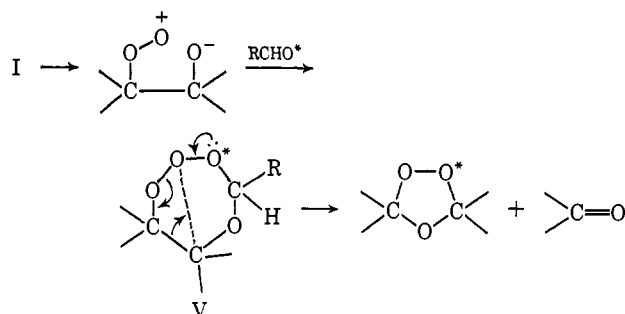


provided a satisfactory explanation for the formation of carbonyl compounds, ozonides (III), and peroxidic compounds which are observed during the course of the "normal" ozonolysis in inert solvents and of the alkoxy hydroperoxides (IV) formed in the presence of alcohols. The formation of all these products is explained by reactions involving the zwitterions (II) and the carbonyl compounds which are formed from the decomposition of the primary ozonide I.^{7,8}

The first inconsistencies of the Criegee mechanism were revealed¹⁰ by the fact that *cis* and *trans* isomers of 1-arylpropenes did not give the same proportions of ozonolysis products, *i.e.*, ozonides, aldehydes, and peroxides. Subsequent studies indicated that the *cis-trans* ozonide ratios for the normal ozonides, as well as for the cross ozonides obtained from unsymmetrical olefins, depend on the olefin geometry.¹¹ In order to explain the stereospecific dependence of ozonide *cis-trans* ratios on olefin geometry, Murray, Youssefyeh,

and Story¹² suggested the mechanism depicted in Scheme II, which involves the attack of an aldehyde

Scheme II



molecule on the primary ozonide to give the seven-membered ring intermediate V. This pathway, which is considered as a competitive pathway to Criegee's mechanism, can be discussed in terms of the fate of the ¹⁸O incorporation from participating ¹⁸O-labeled aldehyde (O* = ¹⁸O). While the Criegee mechanism would demand an exclusive ¹⁸O incorporation of the aldehyde in the ether position of the ozonide, the participation of the seven-membered ring intermediate (Scheme II) would lead to an ¹⁸O labeling in the peroxidic oxygen of the resulting ozonide. In the ozonolysis of *trans*-1,2-diisopropylethylene in the presence of acetaldehyde-¹⁸O, Story, *et al.*,¹³ reported a substantial ¹⁸O incorporation in the peroxidic oxygen of the resulting ozonide, but the ozonization of a series of phenylethylenes in the presence of benzaldehyde-¹⁸O revealed that, in agreement with Criegee's mechanism, the incorporation of ¹⁸O takes place exclusively in the ether position of the ozonides formed.^{14,15}

Recently Bailey, *et al.*,¹⁶ have proposed a refinement of Criegee's mechanism which takes into account and is capable of explaining all the available data concerning the stereospecificity of ozonide formation. This proposal, in which the conformation of the primary ozonide is crucial, is based on the following assumptions: (i) the primary ozonide is represented in a half-chair conformation in which the substituents can be either equatorial or axial, and (ii) the zwitterion resulting from the cleavage of the primary ozonide can possess *syn* or *anti* configuration, as already suggested by Criegee.¹⁷



The mechanism of Bailey and Bauld can be summarized in three general rules. Rule 1: The equatorial substituents are preferentially converted into

(4) R. Criegee and G. Wenner, *Justus Liebigs Ann. Chem.*, **564**, 9 (1949); R. Criegee, *ibid.*, **583**, 1 (1953); R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957).

(5) P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Amer. Chem. Soc.*, **88**, 4098 (1966).

(6) L. J. Durham and F. L. Greenwood, *Chem. Commun.*, 24 (1968); *J. Org. Chem.*, **33**, 1629 (1968).

(7) For a review, see P. S. Bailey, *Chem. Rev.*, **58**, 926 (1958).

(8) Recent studies⁹ have dealt with the direction of cleavage of unsymmetrical primary ozonides following the two possible paths.

(9) S. Fliszár and M. Granger, *J. Amer. Chem. Soc.*, **91**, 3330 (1969), and references contained therein.

(10) E. Briner, E. Dallwigk, and M. Ricca, *Helv. Chim. Acta*, **41**, 1390 (1958); E. Briner and M. Ricca, *ibid.*, **41**, 2178 (1958); E. Briner and S. Fliszár, *ibid.*, **42**, 1310, 2063 (1959).

(11) (a) R. Criegee, S. S. Bath, and B. von Bornhaupt, *Chem. Ber.*, **93**, 2891 (1960); (b) G. Schröder, *ibid.*, **95**, 733 (1962); (c) P. Kolsaker, *Acta Chem. Scand.*, **19**, 223 (1965); (d) F. L. Greenwood and B. J. Haske, *Tetrahedron Lett.*, 631 (1965); (e) O. Lorenz and C. R. Parks, *J. Org. Chem.*, **30**, 1976 (1965); (f) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **88**, 3143 (1966); (g) F. L. Greenwood, *ibid.*, **88**, 3146 (1966).

(12) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **88**, 3144 (1966); R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **89**, 2429 (1967).

(13) P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **90**, 1907 (1968).

(14) S. Fliszár, J. Carles, and J. Renard, *ibid.*, **90**, 1364 (1968).

(15) S. Fliszár and J. Carles, *ibid.*, **91**, 2637 (1969).

(16) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *ibid.*, **90**, 1822 (1968).

(17) R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, New York, N. Y., 1962, p 29.

anti, and the axial substituents into *syn* zwitterions. Rule 2: An equatorial substituent is incorporated into a zwitterion moiety in preference to an axial substituent. Rule 3: Aldehydes interact preferentially with *anti* zwitterions so as to orient bulky substituents diequatorially (*cis*) and with *syn* zwitterions to orient bulky substituents into an equatorial,axial (*trans*) conformation.

Following the Bailey-Bauld conformational analysis of the primary ozonides, the stereochemical course of ozonide formation with olefins possessing bulky substituents can be described as indicated in Table I.

Table I. Stereochemical Course of Ozonide Formation

Olefin configuration	Primary ozonide Configuration	Conformation ^a	Zwitterion configuration ^b	Final ozonide configuration ^b
<i>cis</i>	<i>cis</i>	a, e	<i>anti</i>	<i>cis</i>
<i>trans</i>	<i>trans</i>	a, a	<i>syn</i>	<i>trans</i>
<i>trans</i>	<i>trans</i>	e, e	<i>anti</i>	<i>cis</i>

^a a = axial, e = equatorial. ^b Predominant.

The conformational study of the primary ozonides is, at present, impossible with conventional experimental methods. Quantum chemical calculations seem to be the most suitable way of gaining information about the shape of the primary ozonides.

The object of the present paper is to determine the preferential shape of the 1,2,3-trioxolane ring and the conformation of the substituents for a series of primary ozonides from a comparison of total electronic energies calculated by LCAO-EHMO methods for different geometries of the primary ozonides. Such a study will permit a discussion of the rules of the stereochemical course of ozonide formation.

Method of Calculation

The calculations were made with the aid of a CDC-6400 computer using the extended Hückel molecular orbital (EHMO) program developed by Hoffmann.¹⁸ This is known to be a reliable method for predicting the shape of molecules. This point has been discussed by Allen¹⁹ in a comparison with the *ab initio* LC (Hartree-Fock) AO-SCF-MO method of calculation. A typical example for the applicability of the method of Hoffmann can be found in the work of Kier²⁰ who calculated for the 3-phenyl sydnone an energy minimum for a dihedral angle of 27°, which is in excellent agreement with the experimental value of 27° 16' found by X-ray analysis. Hoffmann's EHMO calculations have also given satisfactory explanations for several reactivity problems.²¹ In a more general theoretical study, Coulson²² concluded that this method gives "reasonably satisfactory results for molecules that cannot, at present, be handled with facility by standard LCAO molecular Hartree-Fock methods."

(18) (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3487 (1962); (b) *ibid.*, **37**, 2872 (1962); (c) R. Hoffmann, *ibid.*, **39**, 1397 (1963).

(19) L. C. Allen and J. D. Russel, *ibid.*, **46**, 1029 (1967).

(20) L. B. Kier, *Tetrahedron Lett.*, 1233, 1236 (1967).

(21) K. Fukui, H. Hao, and H. Fujimoto, *Bull. Chem. Soc. Jap.*, **40**, 2787 (1967), and references therein; K. Fukui and H. Fujimoto, *ibid.*, **42**, 348 (1969); A. G. Hopkinson, R. A. McClelland, K. Yates, and I. G. Csizmadia, *Theor. Chim. Acta*, **13**, 65 (1969).

(22) G. Blyholder and C. A. Coulson, *ibid.*, **10**, 316 (1968).

In the present EHMO calculations, each MO is assumed to be of the form

$$\Phi_j = \sum_k \sum_r C_{jrk} \chi_{rk}$$

where the C_{jrk} 's are LCAO coefficients and χ_{rk} 's are normalized atomic orbitals of Slater's type. The overlap integrals

$$S_{rks_i} = \int \chi_{rk} \chi_{s_i} d\tau$$

are computed according to Mulliken's formulas.²³ The secular determinant is then constructed and solved using the approximations $H_{ii} =$ valence-state ionization potential, $H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij}$.²⁴ The Wolfsberg-Helmholz proportionality coefficient K has been taken as 1.75.¹⁸ The valence-state ionization potentials are taken according to Pritchard and Skinner²⁵ and Slater's exponential parameter μ according to Mulliken,²⁶ as indicated in Table II.

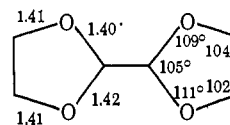
Table II

Valence shell	μ	H_{ii} , eV
H (1s)	1.000	-13.6
C (2s)	1.625	-20.78
C (2p)	1.625	-11.31
O (2s)	2.275	-34.35
O (2p)	2.275	-17.86

The energy levels ϵ_j and the LCAO coefficients C_{jrk} are calculated and the total energy of the ground state computed. The resulting wave function is subjected to a Mulliken population analysis,²⁶ which yields overlap populations and gross atomic populations.

Geometry of the 1,2,3-Trioxolane Ring

The Hoffmann LCAO-EHMO calculation is known to have given unreliable results for interatomic distances.¹⁸ No attempt was made therefore to determine the interatomic distances in the primary ozonide ring by minimizing their total energy. The interatomic distances were chosen by analogy with data available for similar bonds. The following values are taken from the "Table of Interatomic Distances":²⁷ $\text{CH}_3\text{O}-\text{OCH}_3$, C-O = 1.44 Å, $\angle \text{COO} = 105 \pm 3^\circ$; $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$, C-O = 1.43 Å; $\text{CH}_3\text{OCH}_2\text{OCH}_3$, C-O = 1.42 Å. For bis-1,3-dioxo-2-cyclopentyl, values are given as follows



Furthermore, in his X-ray study of the structure of organic peroxides, Silbert²⁸ gives an average value of

(23) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(24) M. Wolfsberg and L. Helmholz, *ibid.*, **20**, 837 (1952).

(25) G. Pritchard and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

(26) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

(27) "Tables of Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958.

(28) L. S. Silbert, L. P. Witnauer, D. Swern, and C. Ricciuti, *J. Amer. Chem. Soc.*, **81**, 3244 (1959).

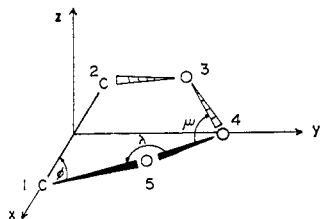


Figure 1. Geometry of the half-chair conformation.

1.44 Å for d_{O-O} . In the present study, the geometry which has been adopted after taking into consideration all the above values is $d_{O-O} = d_{C-O} = d_{C-C} = 1.44$ Å.

The carbon-carbon distance $d_{C-C} = 1.44$ Å in the five-membered ring has been chosen for simplicity, as this is the mean distance between 1.54 Å for a single C-C bond and 1.34 Å for a carbon-carbon double bond.²⁹ This mean distance seems justified, after consideration of Bailey's suggestion⁵ of a partial double-bond character for C-C in the primary ozonide, which was invoked to explain the unusually large shift to a lower field of the nmr peaks of the methine protons when the Freon 11 solvent is replaced by the more polar acetone- d_6 . Using this C-C distance, all bond angles are of 108° in the planar form of the 1,2,3-trioxolane ring. The C-H distance for the methine hydrogens of the primary ozonides has been assumed to be 1.08 Å. For the substituents, the bond distances of 1.54 Å for C-C and of 1.09 Å for C-H have been assumed. All the sp^3 angles, other than those of the primary ozonide ring, have been taken as $109^\circ 47'$.

Two conformations of the primary ozonide ring have been studied, the half-chair and the envelope conformation. The geometry of the half-chair conformation has been calculated as follows.

All the interatomic distances of the ring are fixed at 1.44 Å. $C_2C_1O_4$ is chosen as reference plane (Figure 1). The dihedral angle θ between this reference plane

Table III. Half-Chair Conformation of the Primary Ozonide Ring

θ	$\angle C_2C_1O_5$	$\angle C_1O_5O_4$	$\angle O_5O_4O_3$	z , Å
0	108°	108°	108°	0.0000
5	$107^\circ 40'$		$107^\circ 44'$	0.1156
10	$106^\circ 42'$		107°	0.2335
15	105°		$105^\circ 40'$	0.3500
20	$102^\circ 25'$		$103^\circ 20'$	0.4699
25	$98^\circ 40'$		$100^\circ 10'$	0.5911
30	$93^\circ 02'$		$95^\circ 56'$	0.7112

(29) The "true" value for the C-C distance in the trioxolane ring is not known, nor is it necessarily the same in all the primary ozonides. By assuming a too-low d_{C-C} value with respect to the true one, the interactions between the 1,2 substituents are overestimated and, hence, the ring deformation (indicated in the following by the angle θ) required for reducing these nonbonded interactions is equally overestimated. Conversely, a too large d_{C-C} value would result in an underestimation of the ring deformation θ . A comparison of the calculations made with 1,2-di-*n*-butylethylene (*cis* and *trans*) assuming $d_{C-C} = 1.54$ and 1.44 Å indicates that the conclusions that can be drawn are not significantly affected by the uncertainty on the C-C distance. For the *trans* isomer, the calculated ring deformations are 15° ($d_{C-C} = 1.44$ Å) and 10 – 12° ($d_{C-C} = 1.54$ Å). The calculated distance z from O_5 to the reference plane (Figure 1) is 0.35 Å in the former case, and 0.38–0.42 Å for the longer C-C distance. For the *cis* isomer, the same conclusions are drawn from the results calculated with $d_{C-C} = 1.44$ or 1.54 Å. Finally, the gross electron densities and the Mulliken overlap populations calculated with $d_{C-C} = 1.54$ Å are very similar to those calculated assuming $d_{C-C} = 1.44$ Å, both for the *cis* and the *trans* isomer.

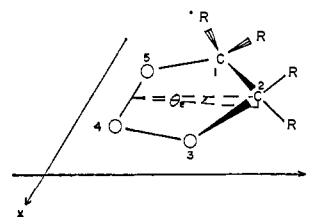


Figure 2. Geometry of the envelope conformation.

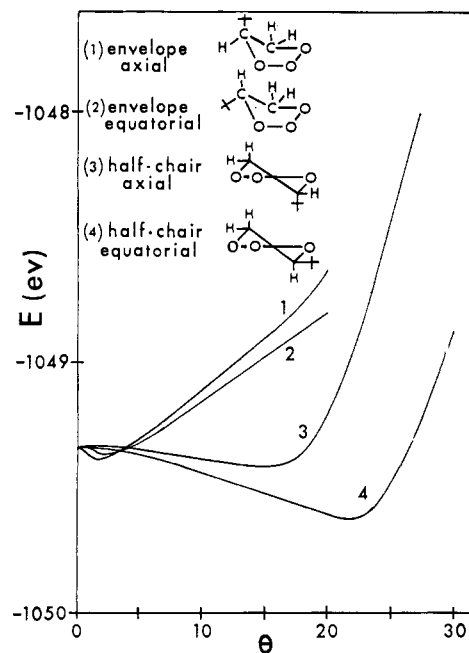


Figure 3. Comparison between the half-chair and envelope conformations of 3,3-dimethyl-1-butene primary ozonide.

$C_2C_1O_4$ and the plane $C_1C_2O_5$ (or $C_1C_2O_3$) was chosen as variable and was allowed to vary between 0 and 30° . The resulting bond angles of the five-membered ring have been computed by trigonometric methods and are displayed in Table III, as well as the distance (z) from O_5 to the reference plane. The Cartesian coordinates of the complete molecules were calculated using Kutnezov's xyz program.

Only the envelope conformation with one of the carbon atoms out of the plane of the other four atoms has been investigated, because only such a conformation can significantly change the interactions between the substituents and, hence, modify the total energy of the molecule. The dihedral angle θ_e between the planes $O_4O_5C_2$ and $O_3O_4O_5C_1$ (Figure 2) has been chosen as variable and was allowed to vary between -20 and $+20^\circ$. Subsequently the Cartesian coordinates of the complete molecule were computed by means of Kutnezov's xyz program.

Results

Comparison between the Half-Chair and the Envelope Conformations. This comparison has been carried out with the primary ozonides of ethylene, propene, 3,3-dimethyl-1-butene, and 2-butene. In all cases the calculated values for the total energy indicate the envelope conformation to be far less stable than the half-chair form. Figure 3 shows a typical example which

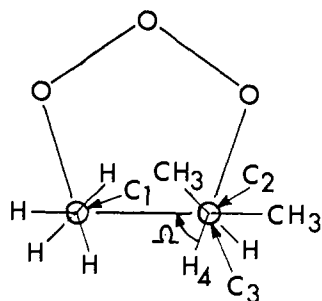


Figure 4. Conformation of the substituents in 4-methyl-2-pentene primary ozonide.

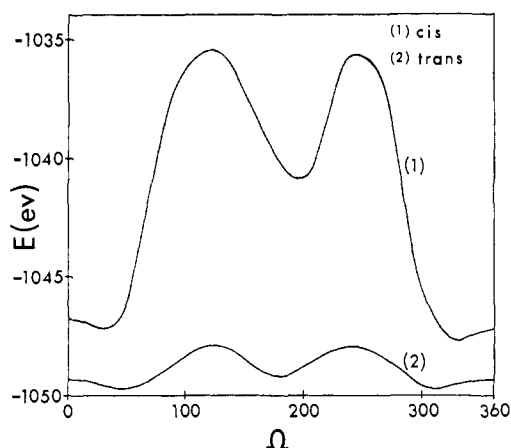


Figure 5. Energy vs. the dihedral angle Ω for *cis*- and *trans*-4-methyl-2-pentene primary ozonide.

facilitates a comparison between envelope and half-chair forms in the case of the primary ozonide of neohexene. The results are in agreement with those reported by Eliel³⁰ for cyclopentanone, tetrahydrofuran, pyrrolidine, and tetrahydrothiophene, compounds for which the half-chair conformation is the most stable.

In order to obtain the most stable half-chair conformation of the primary ozonides, the following procedure has been adopted throughout this work: (i) the preferential arrangement of the substituents is determined with the assumption that the 1,2,3-trioxolane ring is planar and (ii) the arrangement of the substituents in their preferential positions having been determined, the most stable half-chair conformation of the primary ozonide can be calculated by varying the geometry of the ring.

To illustrate this method of calculation, let us consider the following examples, *i.e.*, the primary ozonides of *cis*- and *trans*-4-methyl-2-pentene.

(i) The most stable arrangements for the isopropyl and the methyl groups are determined assuming a planar five-membered ring. All the C-H bonds of the methyl group are arranged so that they will achieve a staggered conformation with respect to their neighboring groups. The dihedral angle Ω between the planes $C_1C_2C_3$ and $C_2C_3C_4$ is varied in this study (see Figure 4).

The results are represented in Figure 5. The *trans* primary ozonide exhibits a minimum total energy for the dihedral angle $\Omega = 50^\circ$, whereas the *cis* primary ozonide exhibits a minimum energy for $\Omega = 330^\circ$.

(30) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 251.

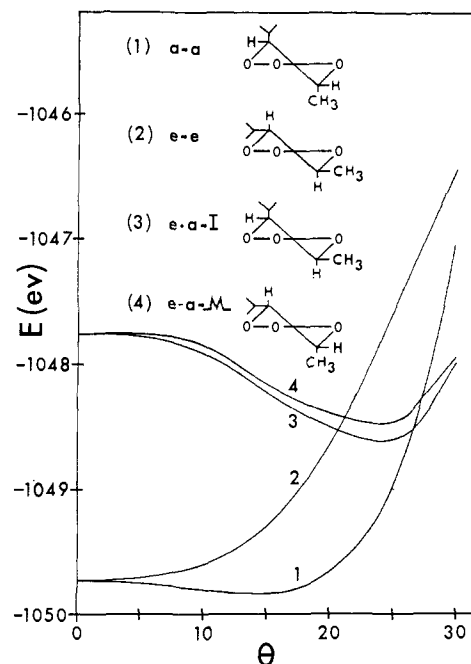


Figure 6. Comparison of different half-chair conformations of *cis*- and *trans*-4-methyl-2-pentene primary ozonide.

(ii) Using the dihedral angle Ω determined above, the energies for the different half-chair conformations are computed. The results are illustrated in Figure 6. The axial-axial (a-a) conformation of the substituents in the *trans* primary ozonide exhibits an energy minimum for the dihedral angle $\Theta = 15^\circ$, whereas the equatorial-equatorial (e-e) conformation exhibits no such minimum. The two conformations of the *cis* primary ozonide, *i.e.*, e-aM (methyl axial) and e-aI (isopropyl axial), both possess an energy minimum for the dihedral angle $\Theta = 25^\circ$. The e-aI conformation appears to be more stable than the e-aM conformation. Hence the bulky isopropyl group prefers the axial conformation to the equatorial.

This calculation procedure has been applied to selected primary ozonides in order to investigate the influence of the substituents on the conformation of the primary ozonide ring.

Primary Ozonides of Ethylene and Monosubstituted Ethylenes. The half-chair conformation of the primary ozonide of ethylene has been found to possess an energy minimum for a dihedral angle of $\Theta = 22^\circ$. This corresponds to a distance $z = 0.5 \text{ \AA}$ from O_5 to the reference plane (Figure 1). For the cyclopentane, an energy minimum corresponding to the out-of-plane distance of 0.5 \AA was reported.³¹

When a hydrogen atom is replaced by a methyl, ethyl, *n*-propyl, isopropyl, or *t*-butyl group, an energy minimum is calculated corresponding to a certain value of Θ , both for the equatorial and axial conformations of the substituents. Figure 3 shows the primary ozonide of 3,3-dimethyl-1-butene as an example. As indicated by the values reported in Table IV, the dihedral angle Θ (for the most stable conformation of the equatorial substituent) is constant (22°) at the same value calculated for ethylene. For the bulky isopropyl and *t*-butyl groups, however, this angle decreases to

(31) K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, **81**, 3214 (1959).

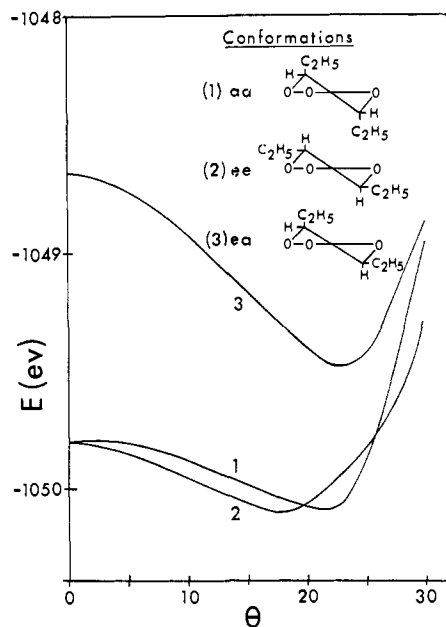


Figure 7. Most stable conformations of *cis*- and *trans*-3-hexene primary ozonides.

15° for the substituent in the axial position. Inspection of the E_e and E_a values in Table IV reveals that in all cases the equatorial conformation is more stable than the axial conformation.

Table IV. Total Electronic Energies of Equatorial and Axial Monosubstituted Primary Ozonides of Ethylene

R	θ , deg	$-E_e$, eV	θ , deg	$-E_a$, eV	$-E_{\text{planar}}$, eV
CH ₃	22	741.13	22	741.075	740.725
C ₂ H ₅	22	844.055	22	843.980	843.668
<i>n</i> -C ₃ H ₇	22	947.035	22	946.952	946.635
<i>i</i> -C ₃ H ₇	22	946.97	15	946.66	946.55
<i>t</i> -C ₄ H ₉	22	1049.62	15	1049.41	1049.33

Primary Ozonides of *trans*-1,2-Disubstituted Ethylenes. Two classes of primary ozonides have been studied, *i.e.*, symmetrical primary ozonides, arising from the ozonolysis of 2-butene, 3-hexene, 2,5-dimethyl-3-hexene, and di-*t*-butylethylene, and unsymmetrical primary ozonides corresponding to 2-pentene, 2-hexene, 4-methyl-2-pentene, 4,4-dimethyl-2-pentene, and 5,5-dimethyl-3-hexene.

The results are reported in Table V. These results show that, depending upon the size of the substituents, two different types must be considered. Primary ozonides with small substituents, such as CH₃, C₂H₅, and *n*-C₃H₇, display similar behavior, in that the *e-e* conformation, with an energy minimum for $\theta_{ee} = 18^\circ$, is more stable than the most stable *a-a* conformation with an energy minimum for the dihedral angle $\theta_{aa} = 22^\circ$ (Figure 7). The other primary ozonides, which possess at least one bulky group, do not exhibit an energy minimum for the *e-e* conformation but an energy minimum for the *a-a* conformation (compare with Figure 6) at angles of 10–15° for the bulky groups.

Primary Ozonides of *cis*-1,2-Disubstituted Ethylenes. Table VI summarizes the results obtained for the primary ozonides from the *cis* isomeric olefins.

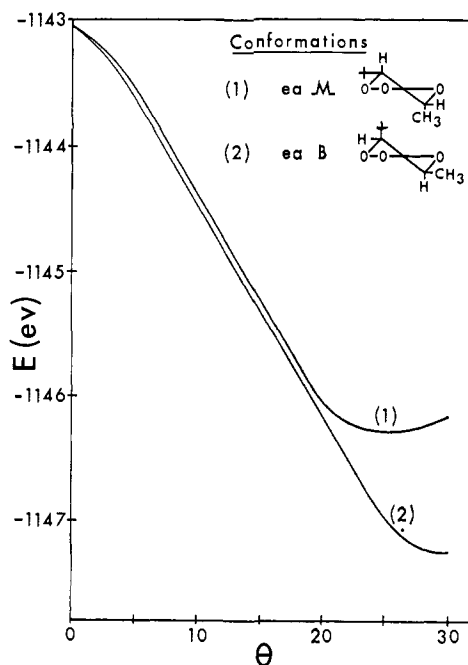


Figure 8. Comparison of different conformations of *cis*-4,4-dimethyl-2-pentene primary ozonide.

As shown in Figure 7 for 3-hexene, the three symmetrical *cis* primary ozonides display the same behavior in that they possess an energy minimum for the dihedral angle of 23°. The behavior of the un-

Table V. Total Electronic Energies of Primary Ozonides of *trans*-1,2-Disubstituted Ethylenes

Parent olefin	θ_{aa} , deg	θ_{ee} , deg	$-E_{aa}$, eV	$-E_{ee}$, eV	$-E_{\text{pl}}$, eV
2-Butene	22	18	844.220	844.220	843.907
2-Pentene	22	18	947.145	947.170	946.852
3-Hexene	22	18	1050.085	1050.108	1049.795
2-Hexene	22	18	1050.120	1050.160	1049.819
4-Methyl-2-pentene	15	0	1049.828		1049.731
2,5-Dimethyl-3-hexene	10	0	1255.599		1255.555
4,4-Dimethyl-2-pentene	15	0	1152.555		1252.480
5,5-Dimethyl-3-hexene	15	0	1255.492		1255.400
Di- <i>t</i> -butylethylene	15	0	1460.994		1460.190

Table VI. Total Electronic Energies of Primary Ozonides of *cis*-1,2-Disubstituted Ethylenes^a

Parent olefin	θ_{eas} , deg	θ_{eab} , deg	$-E_{eas}$, eV	$-E_{eab}$, eV	$-E_{\text{planar}}$, eV
2-Butene	23		843.630		842.763
2-Pentene	23	23	946.565	946.550	945.745
3-Hexene	23		1049.482		1048.655
4-Methyl-2-pentene	24	23	1049.510	1049.580	1048.680
2-Hexene	25	25	1048.463	1048.587	1047.789
2,5-Dimethyl-3-hexene	23		1253.685		1252.865
4,4-Dimethyl-2-pentene	30	25	1147.234	1146.286	1143.065
5,5-Dimethyl-3-hexene	30	28	1250.362	1249.378	1246.005
Di- <i>t</i> -butylethylene	25		1442.265		1434.986

^a θ_{eas} and E_{eas} refer to the configuration with the smaller substituent in axial position, and θ_{eab} and E_{eab} to the configuration with the bulky group in axial position.

symmetrical primary ozonides is, however, more complex. There are two conformations, *i.e.*, the *eas* conformation, which has the small substituent in the axial position, and the *eab* conformation, where the

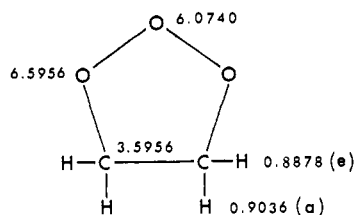


Figure 9. Charge distribution in the ethylene primary ozonide.

bulkier substituent is axial. Whereas the *eas* conformation appears to be slightly more stable than *eab* in 2-pentene, the calculations reveal that in 2-hexene and 4-methyl-2-pentene the *eab* conformation is preferred to *eas*. This result confirms the trend observed with the *trans* primary ozonides indicating that the bulky group is more stable in the axial than in equatorial configuration. A different situation is encountered with 4,4-dimethyl-2-pentene, 5,5-dimethyl-3-hexene, and di-*t*-butyl-ethylene. As shown in Figure 8, the deforma-

Table VII. Gross Electron Densities of the 1,2,3-Trioxolane Ring

Con-figuration	R ₁	R ₂	C-1	C-2	O-3	O-4	O-5
	C ₂ H ₅	H	3.4483	3.5894	6.6046	6.5970	6.0781
	<i>t</i> -C ₄ H ₉	H	3.4727	3.6274	6.6039	6.5976	6.0818
<i>trans</i>	<i>i</i> -C ₃ H ₇	CH ₃	3.4790	3.4416	6.5891	6.5916	6.0823
<i>cis</i>	<i>i</i> -C ₃ H ₇	CH ₃	3.4786	3.4346	6.6082	6.6094	6.0730
<i>trans</i>	<i>t</i> -C ₄ H ₉	CH ₃	3.4891	3.4727	6.5899	6.5949	6.0854
<i>trans</i>	<i>t</i> -C ₄ H ₉	C ₂ H ₅	3.4881	3.4907	6.5901	6.5929	6.0851
<i>cis</i>	<i>t</i> -C ₄ H ₉	CH ₃	3.4815	3.4680	6.6633	6.7755	6.2779
<i>cis</i>	<i>t</i> -C ₄ H ₉	C ₂ H ₅	3.4693	3.4641	7.0140	7.0480	7.1561
<i>trans</i>	<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉	3.5190	3.5190	6.5888	6.5888	6.0909
<i>cis</i>	<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉	3.3028	3.2930	7.0539	7.0447	7.1823

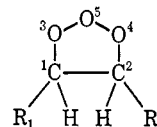
Table VIII. Mulliken Overlap Populations

Configuration	R ₁	R ₂	C ₁ -C ₂	C ₁ -O ₃	C ₂ -O ₄	O ₃ -O ₅	O ₄ -O ₅
	C ₂ H ₅	H	0.7854	0.4748	0.4673	0.4043	0.4089
	<i>t</i> -C ₄ H ₉	H	0.7880	0.4767	0.4649	0.4021	0.4079
<i>trans</i>	<i>i</i> -C ₃ H ₇	CH ₃	0.8090	0.4734	0.4745	0.4069	0.4060
<i>cis</i>	<i>i</i> -C ₃ H ₇	CH ₃	0.8052	0.4754	0.4746	0.4051	0.4074
<i>trans</i>	<i>t</i> -C ₄ H ₉	CH ₃	0.8140	0.4717	0.4771	0.4069	0.4021
<i>trans</i>	<i>t</i> -C ₄ H ₉	C ₂ H ₅	0.8125	0.4717	0.4763	0.4067	0.4026
<i>cis</i>	<i>t</i> -C ₄ H ₉	CH ₃	0.7837	0.4672	0.4631	0.3557	0.2636
<i>cis</i>	<i>t</i> -C ₄ H ₉	C ₂ H ₅	0.7923	0.4657	0.4696	-0.0575	-0.0946
<i>trans</i>	<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉	0.8143	0.4724	0.4724	0.4027	0.4027
<i>cis</i>	<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉	0.4849	0.4733	0.4786	-0.0866	-0.0832

tion of the 1,2,3-trioxolane ring results in an unusually large decrease of the energy. The lowest energy that was calculated corresponds to a dihedral angle of 30°, *i.e.*, in a situation where the deformation is so important as to cause the cleavage of the primary ozonide. This anomalous behavior in the "stability" of the primary ozonides is also revealed by the unusual charge distributions and bond orders which (as explained below) are exhibited for these *cis* primary ozonides. The results of these calculations thus agree with the experimental observations which indicate the greatly reduced stability of *cis* primary ozonides compared to their *trans* isomers.

Charge Distributions in the Primary Ozonides. With three exceptions, the charge densities localized on the atoms of the 1,2,3-trioxolane ring do not vary greatly in all of the primary ozonides which have been calculated. A typical example is represented by Figure 9, which indicates the electron densities calculated for the primary ozonide of ethylene.

Most of the primary ozonides which have been examined exhibit charge densities very similar to those indicated in Figure 9. The extreme deviations from these values are about 0.02 electron for the oxygen atoms and 0.2 electron for the carbon atoms of the trioxolane ring, depending on the substituents. Exceptional charge distributions are, however, found for the *cis* primary ozonides of 4,4-dimethyl-2-pentene, 2,2-dimethyl-3-hexene, and di-*t*-butylethylene. Table VII gives the charge densities for selected primary ozonides. The atoms are numbered as follows.



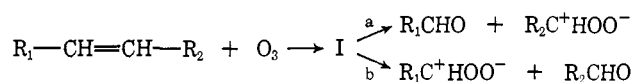
The Mulliken overlap populations which were calculated for the most stable conformations of the primary ozonides are summarized in Table VIII.

The overlap populations obtained for the primary ozonides of *cis*-4,4-dimethyl-2-pentene, 2,2-dimethyl-3-hexene, and di-*t*-butylethylene confirm their anomalous behavior, which has been stressed above in connection with their conformational study and with their unusual charge densities.

Discussion

In this discussion only the primary ozonides of symmetrical olefins are considered since, for unsymmetrical olefins, any comparison with the Bailey-Bauld rules

on the stereochemical course of ozonide formation requires a knowledge of the proportions of cleavage of the unsymmetrical primary ozonides following the two possible paths (a and b).



An investigation on the direction of ozone cleavage of a series of unsymmetrical *cis*-1,2-disubstituted ethylenes revealed that in all cases the equatorial substituent (as determined by the present calculations) is incorporated into the zwitterion moiety in preference to the

axial substituent. This is in agreement with Bailey and Bauld's 2nd rule, which is discussed in isolation in a forthcoming paper.³²

The experimental evidence for the stereochemical course of ozonide formation is in the final ozonide *cis-trans* ratios that are observed for different *cis* and *trans* olefins (Table IX). The ozonide *cis-trans* ratios

Table IX. Ozonide *cis-trans* Ratios from Symmetrical Olefins

Olefin	<i>cis-trans</i> ratio
<i>cis</i> -2-Butene	39/61 ^a
<i>trans</i> -2-Butene	38/62 ^a
<i>cis</i> -3-Hexene	53/47 ^a
<i>trans</i> -3-Hexene	53/47 ^a
<i>trans</i> -2,5-Dimethyl-3-hexene	53/47 ^a
<i>cis</i> -2,5-Dimethyl-3-hexene	66/34 ^a
<i>trans</i> -Di- <i>t</i> -butylethylene	28/72 ^b
<i>cis</i> -Di- <i>t</i> -butylethylene	70/30 ^b

^a From ref 12, 1.0 *M* solution in pentane, temperature of ozonolysis -70°. ^b From ref 16, 0.3 *M* solution in pentane, temperature of ozonolysis -75°.

depend, however, on a number of conditions^{16, 33, 34} (e.g., solvent, temperature of ozonolysis, olefin concentration). Hence only results obtained under identical experimental conditions should be compared.

Inspection of the results for the *cis* olefins (Table IX) reveals that the ozonide *cis-trans* ratio increases with increasing bulk of the substituents. For discussion of any *cis-trans* olefin isomer pair, the *cis* primary ozonide is considered as the reference term to which the *trans* isomer is compared. Stated in a different way, the behavior of expected a-a and e-e primary ozonide mixtures (from *trans* olefins) are compared to a-e primary ozonides from *cis* olefins.

For the *trans* olefins with small substituents (CH₃ and C₂H₅), the results in Table V indicate that both a-a and e-e conformations are possible and have similar energies (E_{ee} and E_{aa}), which are both significantly lower than the energy of the planar form of the primary ozonide. From the results of the calculations, the a-a and e-e conformations for 2-butene and 3-hexene are expected to be approximately of equal importance. The experimental *cis-trans* ratios observed with these olefins indicate the similarity of the results obtained from the *trans* olefins to those observed from the a-e *cis* isomers. However, for the bulkier isopropyl group, a predominance of axial,axial conformation of the primary ozonide is expected from the calculated results (Table V). This agrees with Bailey and Bauld's prediction, on the basis that, with very bulky substituents, the axial,axial conformation should be preferred since interference between the *gauche* substituents in the equatorial,axial conformer should be greater than interference between the *trans* substituents and the relevant oxygen lone pairs in the axial,axial conformer. As the axial,axial conformation is preferred by the primary ozonide of *trans* diisopropylethylene,

(32) J. Renard and S. Fliszár, in preparation.

(33) R. W. Murray, R. D. Youssefeyeh, G. J. Williams, and P. R. Story, *Tetrahedron*, **24**, 4353 (1968).

(34) S. Fliszár and J. Carles, *Can. J. Chem.*, **47**, 3921 (1969).

the production of *syn* zwitterion is favored (rule 1) and, hence, the production of *trans* ozonide. This agrees with the experimental results which indicate a proportion of 47% *trans* ozonide from *trans* olefin, as compared with 34% *trans* ozonide from *cis* olefin. In the case of *trans* di-*t*-butylethylene, this trend is more pronounced and the axial,axial conformation of this olefin appears to be more favored with respect to any other form (e.g., the planar form) of primary ozonide than is found with diisopropylethylene. It is thus predicted that the formation of *syn* zwitterion is enhanced and, consequently, that the *trans* olefin will produce considerably more *trans* ozonide (72%) than the *cis* isomer (30%).

The present calculations therefore confirm the prediction that bulkier substituents will promote axial,axial conformation of primary ozonides from *trans* olefins, resulting in an enhanced formation of *trans* ozonide, as compared with the results for the isomeric *cis* olefins.

Conclusions

A comparison of the total energies calculated for the envelope and half-chair conformations of the primary ozonides indicates the envelope conformation to be far less stable than the half-chair form.

The primary ozonides of monosubstituted ethylenes and *trans*-1,2-disubstituted ethylenes possess an energy minimum in correspondence to a particular ring conformation. The corresponding *cis* primary ozonides possess the same property, except those bearing a *t*-butyl group. This observation agrees with the experimental results of Greenwood⁶ and Bailey,⁵ which show that all *trans* primary ozonides can be observed, including the one of *trans*-1,2-di-*t*-butylethylene, whereas only the *cis* primary ozonides bearing small substituents (e.g., those of 2-hexene and 2-pentene) can be observed. All attempts to observe the *cis*-1,2-di-*t*-butylethylene primary ozonide have failed.

The equatorial conformation is preferred by all substituents in the primary ozonides of monosubstituted ethylenes.

The equatorial,axial conformation is preferred by small substituents (methyl, ethyl, *n*-propyl) in *trans*-1,2-disubstituted ethylene primary ozonides, whereas the bulkier isopropyl and *t*-butyl groups prefer the axial,axial conformation, as suggested by Bailey.¹⁶

In the primary ozonides of *cis*-1,2-disubstituted ethylenes, the largest substituent prefers the equatorial conformation when both groups are small, and the axial conformation when one of the substituents is at least as large as the *n*-propyl group. When one of the substituents is as large as the *t*-butyl group, the primary ozonide does not appear to possess a "stable" conformation. It would rather appear that the attempt to assume a stable form is accompanied by the cleavage of the "primary ozonide."

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