

Mechanism of Ozonolysis. (a) Microwave Spectra, Structures, and Dipole Moments of Propylene and *trans*-2-Butene Ozonides. (b) Orbital Symmetry Analysis

Robert P. Lattimer, Robert L. Kuczkowski,* and Charles W. Gillies

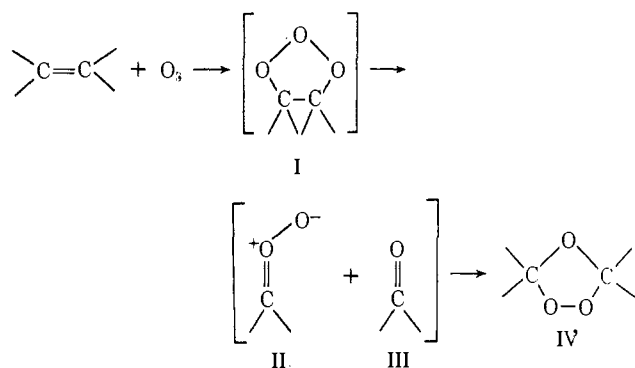
Contribution from the Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104. Received July 13, 1973

Abstract: The microwave spectra of 11 isotopic species of propylene ozonide and the normal isotopic species of *trans*-2-butene ozonide were assigned. Both compounds were found to have an oxygen–oxygen half-chair conformation with equatorial methyl groups. No effects from pseudorotation or internal rotation were observed. The detailed structure of propylene ozonide was determined. The dipole moments of both compounds were measured. The *cis*–*trans* ratio of 2-butene ozonide obtained as a cross ozonide from propylene was found to be 81:19 in contrast to the ~40:60 ratio obtained from 2-butene. The *syn*–*anti* zwitterion mechanism for ozonolysis was reviewed; a mechanistic scheme consistent with orbital symmetry arguments was presented to elucidate the pathway of *syn*–*anti* zwitterion formation and the formation of *cis* and *trans* final ozonides.

The mechanism of the reaction of ozone with alkenes in solution has been of recent experimental and theoretical interest. Three mechanistic proposals for the reaction have received prominent attention: the Criegee mechanism,¹ the aldehyde interchange (SMY) mechanism,² and the *syn*–*anti* zwitterion (Bauld–Bailey) mechanism.³ It is generally accepted that the first step in ozonolysis is the formation of an alkene–ozone adduct which is called either the molozonide, the initial ozonide, or the primary ozonide. This adduct is not well characterized, but experimental evidence supports the 1,2,3-trioxacyclopentane structure.^{4,5} All of the above named mechanisms start with this primary ozonide.⁶

The Criegee mechanism (Scheme I) proposes that the

Scheme I



primary ozonide (I) breaks into a zwitterion (II) and a carbonyl compound (III).¹ These then recombine to give the final ozonide (IV). The zwitterion–carbonyl

scheme received strong support originally from the fact that the addition of a foreign aldehyde to the reaction mixture finds this aldehyde also incorporated into the ozonide ring.¹ Other experimental data have accumulated, however, which cannot be rationalized on the basis of the simple Criegee mechanism.^{2c} In particular, the discovery that the *cis*–*trans* ratios of cross ozonides prepared by the ozonolysis of unsymmetrical olefins depend on alkene geometry⁷ led Story and co-workers to propose a competing “aldehyde interchange” mechanism.² In brief, this additional pathway involves the incorporation of an aldehyde into the primary ozonide ring, followed by the ejection of a different aldehyde to give the final ozonide. Bauld, Bailey, *et al.*,³ later proposed a revision of the original Criegee mechanism to account for the new data. The Bauld–Bailey mechanism retains the zwitterion intermediate, but this moiety is capable of existing in *syn* and *anti* forms which determine the stereochemistry of the overall reaction. Inherent also in this mechanism are assumed conformations of both initial and final ozonides.

Both the Criegee mechanism and the Bauld–Bailey revision predict that a foreign aldehyde will incorporate its oxygen atom only in the epoxy position of the final ozonide, while the aldehyde interchange scheme predicts incorporation only in the peroxy bridge. Labeled foreign aldehyde experiments have been used as tests for the various proposals. ¹⁸O-Labeled aldehyde appears to incorporate only in the epoxy position for ethylene⁸ and phenyl ethylenes,⁹ but in some other cases peroxy incorporation is also observed.¹⁰ The aldehyde interchange proposal can be used to explain this peroxy ¹⁸O incorporation, although Fliszár and Carles¹¹ have suggested an alternate way in which peroxy incorporation can be justified within the Criegee scheme.

(1) R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957).

(2) (a) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *J. Amer. Chem. Soc.*, **88**, 3144 (1966); (b) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **89**, 2429 (1967); (c) R. W. Murray, *Accounts Chem. Res.*, **1**, 313 (1968).

(3) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *J. Amer. Chem. Soc.*, **90**, 1822 (1968).

(4) (a) F. L. Greenwood, *J. Org. Chem.*, **30**, 3108 (1965); (b) L. J. Durham and F. L. Greenwood, *Chem. Commun.*, 843 (1967); (c) *ibid.*, 24 (1968); (d) *J. Org. Chem.*, **33**, 1629 (1968); (e) P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Amer. Chem. Soc.*, **88**, 4098 (1966).

(5) L. A. Hull, I. C. Hisatsune, and J. Hecklen, *J. Amer. Chem. Soc.*, **94**, 4856 (1972).

(6) It should be mentioned that the SMY proposal (ref 2) prefers a tricyclic (epoxide) primary ozonide for sterically hindered *cis* olefins.

(7) (a) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **88**, 3143 (1966); (b) F. L. Greenwood, *ibid.*, **88**, 3146 (1966).

(8) C. W. Gillies and R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **94**, 7609 (1972).

(9) S. Fliszár and J. Carles, *J. Amer. Chem. Soc.*, **91**, 2637 (1969).

(10) (a) P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *J. Amer. Chem. Soc.*, **90**, 1907 (1968); (b) R. W. Murray and R. Hagen, *J. Org. Chem.*, **36**, 1103 (1971); (c) P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, *J. Amer. Chem. Soc.*, **93**, 3042 (1971).

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

A microwave study of ethylene ozonide was recently initiated to further elucidate the mechanism of the ozonolysis reaction.^{8,12} This work concluded that the ozonolysis of ethylene was consistent with the original Criegee mechanism, but serious objections were raised to the two more recent proposals. In particular, no peroxy incorporation of ¹⁸O-labeled formaldehyde was observed in the ozonolysis of ethylene,⁸ and it was concluded that the aldehyde interchange mechanism was not very important for ethylene at -78° . Furthermore, the observed conformation of ethylene ozonide (the O-O half-chair with C_2 symmetry)¹² was found to be inconsistent with the final ozonide conformation proposed by Bauld-Bailey (the C-O half-chair). It was recognized, however, that since steric effects were unimportant in the ozonolysis of ethylene, it would be unwise to attempt an extension of these results to olefins possessing substituents other than hydrogen. The SMY and Bauld-Bailey mechanisms had been proposed, after all, to account for the ozonolysis of substituted alkenes.

In the present work, we report results relevant to the mechanism of the ozonolysis of propylene and 2-butene.¹³ The conformations of propylene and *trans*-2-butene ozonides determined by microwave spectroscopy are reported, and in addition a detailed structure for propylene ozonide is presented. This structure is important in its own right since little information is available in the literature on the structure of ozonides or on other five-membered saturated heterocycles, particularly those with substituents.

In this investigation both propylene and *trans*-2-butene ozonides are found to possess the same O-O half-chair conformation as ethylene ozonide. (This conformation is different from that proposed by the Bauld-Bailey mechanism.³) It was also found that the *cis*-*trans* ratio for 2-butene ozonide obtained as a cross ozonide from propylene differs significantly from that obtained as a normal ozonide from *cis*- or *trans*-2-butene. The Bauld-Bailey mechanism³ is reviewed in the light of these data and possible revisions are considered.

Experimental Section

Synthesis. Propylene ozonide was prepared by ozonizing $\sim 1.0 M$ propylene (C. P. grade, Matheson Co.) in isobutane at -95° , with fast warm-up.¹⁴ 2-Butene ozonide was prepared in a similar manner, using either *cis*- or *trans*-2-butene (C. P. grade, Matheson Co.). Ozone (~ 0.15 mmol/min) from the sample outlet of a Welsbach Model T-408 ozonator was used for the ozonolyses, which were carried out to $\sim 70\%$ completion. The ozonides were separated from the solvent by low-temperature fractional condensation, using a series of traps at -45° , -95° , and -196° . High-boiling impurities were trapped at -45° , the ozonides at -95° , and the solvent at -196° .

Final purification and separation of the ozonides was accomplished using gas chromatography. An 18 ft 15% Dow 710 silicone (on Chromosorb W) column was used in a Varian Model 920 chromatograph. The following conditions were used: column temperature 40 – 50° , injector 70 – 80° , detector 70 – 80° , helium flow rate 140 – 160 ml/min. These conditions were adequate to separate ethylene and 2-butene cross ozonides from propylene ozonide. The relative ozonide yields (from the ozonolysis of propylene) were as follows: ethylene 11%, propylene 85%, 2-butene 4%. Slower

flow rates were employed (60 – 80 ml/min) to separate the *cis* and *trans* isomers of 2-butene ozonide. It was not possible to obtain complete separation of the *cis*-*trans* isomers with just one pass through the column; consequently, two or more passes were generally made in order to obtain nearly pure *cis* or *trans* ozonide samples. The *trans* isomer had the shorter retention time and was the one used in the microwave study.¹⁵ While the *cis*-*trans* ratio of 2-butene ozonide obtained as the normal ozonide from either *cis*- or *trans*-2-butene was less than unity ($\sim 40:60$) as reported previously,^{2b,7b} this ratio obtained as a cross ozonide from propylene was rather surprisingly greater than unity ($81:19$).¹⁶ The desired ozonide samples were collected from the chromatograph using a series of U-tube traps cooled to -196° . Gaseous infrared spectra of the ozonides agreed well with those reported previously.^{5,17} All ozonide samples were stored at liquid nitrogen temperature to avoid decomposition with time.¹⁸

Isotopes. Isotopically enriched samples of propylene ozonide were prepared as follows. Singly deuterated ozonide, $\text{CH}_3\text{CDOOCH}_2\text{O}$, was prepared by ozonizing propylene-2- d_1 (98% enriched, Merck Sharp and Dohme). A mixture of two additional singly deuterated species, $\text{CH}_3\text{CHOOCHD}_{ax}\text{O}$ and

$\text{CH}_3\text{CHOOCHD}_{ax}\text{O}$, was prepared by ozonizing ethylene-1,2- d_2 (98% enriched, Isomet Corp.) in the presence of excess added acetaldehyde (Reagent grade, Matheson Coleman and Bell).

Carbon-13 enriched ozonide, $\text{CH}_3\text{CHOO}^{13}\text{CH}_2\text{O}$, was prepared by ozonizing excess *trans*-2-butene in the presence of added formaldehyde-¹³C. Formaldehyde-¹³C had been prepared by oxidizing methanol-¹³C (90% enriched, Miles-Yeda) over a hot metal oxide catalyst.¹⁹ A mixture of three ¹³C-enriched species (CH_2 -

$^{13}\text{CHOOCH}_2\text{O}$, $^{13}\text{CH}_3\text{CHOOCH}_2\text{O}$, and $^{13}\text{CH}_3\text{CHOOCH}_2\text{O}$) was prepared by ozonizing excess ethylene (C. P. grade, Matheson Co.) in the presence of acetaldehyde-1,2-¹³C (50% enriched, ¹³C randomly distributed, Isomet Corp.). A mixture of singly, doubly, and triply ¹⁸O-substituted ozonides was prepared by ozonizing propylene in a stream of ¹⁸O-enriched ozone. The ozone had been prepared by an electrical discharge through oxygen-18 gas (54% enriched, Bio-Rad Laboratories).²⁰

Spectrometers. Microwave spectra were obtained on a 80-kHz square-wave modulated spectrometer of conventional design.²¹ Most spectra were acquired using klystron sources, but some spectra were obtained using a Hewlett-Packard Model E40-8400B microwave spectroscopy source (K band). In general, frequency measurements had an accuracy of better than ± 0.10 MHz. Most spectra were obtained with the sample cell cooled between room and Dry Ice temperatures and at pressures of several microns. At the higher temperature the samples tended to decompose in the waveguide, while at the lower temperature they condensed rather strongly on the cell walls.

Spectra. The initial phases of the microwave spectral study of propylene ozonide were aided by the earlier work on ethylene ozonide.¹² That molecule was found to possess only one stable conformation, a half-chair in which the two adjacent oxygen atoms are twisted out of the C-O-C plane. No nonrigid rotor effects from ring pseudorotation were observed. Using the conformational and structural parameters from ethylene ozonide and adding a methyl group, the transitions arising from propylene ozonide were predicted and assigned fairly readily. In careful searches only one conformation of the molecule has been observed, that possessing the same O-O half-chair conformation as ethylene

(15) Our microwave conformational analysis provides an unequivocal ozonide stereoisomer assignment. This assignment correlates with earlier work which indicated, using a combination of infrared, nmr, vpc, chemical reactivity, and kinetic resolution data, that the *trans* isomer is the one having the shorter vpc retention time; see R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **88**, 3655 (1966).

(16) The *cis*-*trans* ratios of 2-butene ozonide reported previously (see ref 3, Tables II and III) have always been less than or close to unity.

(17) D. Garvin and C. Schubert, *J. Phys. Chem.*, **60**, 807 (1956).

(18) L. A. Hull, I. C. Hisatsune, and J. Hecklen, *J. Phys. Chem.*, **76**, 2659 (1972).

(19) C. W. Gillies, Doctoral Dissertation, University of Michigan, 1972.

(20) C. W. Gillies, R. P. Lattimer, and R. L. Kuczowski, *J. Amer. Chem. Soc.*, in press.

(21) R. L. Kuczowski, *J. Amer. Chem. Soc.*, **90**, 1705 (1968).

(12) C. W. Gillies and R. L. Kuczowski, *J. Amer. Chem. Soc.*, **94**, 6337 (1972).

(13) For a preliminary report of this work, see R. P. Lattimer, C. W. Gillies, and R. L. Kuczowski, *J. Amer. Chem. Soc.*, **95**, 1348 (1973).

(14) R. W. Murray and R. Hagen, *J. Org. Chem.*, **36**, 1098 (1971).

Table I. Ground-State Transition Frequencies of the Equatorial Isomer of Propylene Ozonide (MHz)

Transition	ν_{obsd}	$\nu_{\text{obsd}} - \nu_{\text{calcd}}$
1 ₁₀ -2 ₁₁	13073.83	0.05
2 ₁₂ -3 ₁₃	17049.06	0.06
2 ₀₂ -3 ₀₃	17920.29	0.02
3 ₁₃ -4 ₁₄	22619.73	-0.06
3 ₀₃ -4 ₀₄	23452.49	0.00
4 ₁₄ -5 ₁₅	28119.23	-0.10
4 ₀₄ -5 ₀₅	28774.67	-0.09
4 ₂₃ -5 ₂₄	30352.25	-0.06
4 ₃₂ -5 ₃₃	30905.04	-0.05
4 ₃₁ -5 ₃₂	31104.86	-0.14
4 ₁₃ -5 ₁₄	32077.30	0.20
4 ₂₂ -5 ₂₃	32177.45	-0.04
5 ₁₅ -6 ₁₆	33553.80	-0.20
5 ₀₅ -6 ₀₆	33996.20	-0.27
1 ₁₀ -2 ₂₁	25367.88	0.00
1 ₁₁ -2 ₂₀	26313.67	0.08
2 ₁₂ -3 ₀₃	14539.70	0.09
2 ₀₂ -3 ₁₃	20429.70	0.04
2 ₁₁ -3 ₂₂	30657.42	-0.04
3 ₁₃ -4 ₀₄	20942.94	-0.16
3 ₀₃ -4 ₁₄	25129.16	-0.02
4 ₁₄ -5 ₀₅	27097.99	-0.09
4 ₀₄ -5 ₁₅	29795.91	-0.11
5 ₁₅ -6 ₀₆	32975.00	-0.21
5 ₀₅ -6 ₁₆	34575.10	-0.16

Table II. Excited Vibrational State Transitions of Equatorial Propylene Ozonide (MHz)

Transition	$\nu = 1$		$\nu = 2$	
	ν_{obsd}	$\Delta\nu^a$	ν_{obsd}	$\Delta\nu$
4 ₁₄ -5 ₁₅	28171.56	0.03	28220.72	0.08
4 ₀₄ -5 ₀₅	28819.25	0.01		
4 ₂₃ -5 ₂₄	30403.33	0.22	30451.48	-0.08
4 ₃₂ -5 ₃₃	30959.44	0.15	31011.20	0.06
4 ₃₁ -5 ₃₂	31162.20	-0.04	31217.03	-0.06
2 ₁₁ -3 ₂₂	30565.28	-0.05	30482.52	0.04
2 ₁₂ -3 ₂₁	33618.94	0.07	33538.46	-0.07
4 ₁₄ -5 ₀₅	27172.27	0.05	27241.73	0.16
4 ₀₄ -5 ₁₅	29818.55	0.00	29840.27	-0.04

^a $\Delta\nu = \nu_{\text{obsd}} - \nu_{\text{calcd}}$.**Table III.** Ground-State Transitions of Isotopically Substituted Species of Equatorial Propylene Ozonide (MHz)

Transition	CH ₃ CDOOCH ₂ O	CH ₃ CHOOCHD _{eq} O	CH ₃ CHOOCHD _{ax} O	CH ₃ CH ¹⁸ OCH ₂ O	CH ₃ CHO ¹⁸ OCH ₂ O
4 ₁₄ -5 ₁₅	27929.84 (0.08) ^a	27289.75 (0.05)	27667.15 (0.07)	27832.18 (0.17)	27458.75 (0.18)
4 ₀₄ -5 ₀₅	28558.75 (-0.03)	27937.56 (0.02)	28928.25 (0.04)	28431.48 (0.02)	28115.80 (0.06)
4 ₂₃ -5 ₂₄	30006.88 (-0.12)	29451.57 (0.07)	29753.19 (0.05)	30153.36 (-0.12)	29618.79 (0.00)
4 ₁₃ -5 ₁₄	31622.61 (0.01)	31129.07 (0.06)	31375.28 (0.00)	31895.60 (0.39)	
4 ₂₂ -5 ₂₃	31680.73 (0.03)		31434.69 (0.03)	32155.27 (0.13)	
5 ₁₅ -6 ₁₆		32565.78 (0.00)	33025.53 (-0.06)		
5 ₀₅ -6 ₀₆		33007.12 (0.18)	33457.05 (-0.05)		
1 ₁₀ -2 ₂₁	24616.04 (0.03)	24798.08 (-0.05)	24558.93 (-0.05)	24553.26 (0.00)	25013.13 (-0.17)
1 ₁₁ -2 ₂₀		25712.50 (0.02)	25440.77 (0.02)		25926.24 (0.15)
2 ₀₂ -3 ₁₃	20165.61 (0.15)	19885.58 (-0.01)		20001.76 (0.12)	
3 ₀₃ -4 ₁₄	24884.24 (-0.06)	24443.55 (-0.09)	24682.35 (0.07)	24639.52 (0.02)	24623.16 (0.02)
4 ₁₄ -5 ₀₅			26656.71 (0.06)	26993.82 (-0.07)	26401.11 (-0.11)
4 ₀₄ -5 ₁₅	29566.61 (-0.03)	28965.84 (-0.01)	29308.75 (0.11)	29269.46 (-0.12)	29173.03 (-0.06)
5 ₁₅ -6 ₀₆	32763.99 (0.02)	31978.63 (-0.01)	32446.59 (-0.08)		32162.46 (-0.06)
5 ₀₅ -6 ₁₆		33593.97 (-0.11)	34035.93 (-0.09)		32769.54 (0.02)

^a Number in parentheses is $\nu_{\text{obsd}} - \nu_{\text{calcd}}$.

ozonide and having the single methyl substituent in an equatorial position. The presence of an axial isomer or other conformers is not ruled out, but these apparently are much less abundant.

The rotational spectrum of propylene ozonide consists primarily of several moderately intense b-type R-branch transitions, and a much greater number of weaker a-type R-branch lines. Each

transition is accompanied by a series of rather strong regularly spaced vibrational satellites; the two strongest satellites (which are successive excitations of the same mode) have been assigned. Ground-state transitions are given in Table I and excited-state transitions in Table II. In addition, the spectra from ten isotopically substituted species have been assigned; these frequencies are given in Tables III and IV. Rotational constants (determined by a least-squares fit) and moments of inertia for all the propylene ozonide species observed are given in Table V. The assignments of transitions were confirmed by (1) the agreement with the calculated spectra (including isotope shifts), (2) the observation of correct second-order Stark splittings, and (3) the agreement of intensities with those expected.

Based on the study of propylene ozonide, it was expected that the addition of a second methyl group to the ozonide ring would not grossly affect the ring conformation. Therefore, using the ethylene ozonide structural parameters and adding two methyl groups, the transitions arising from one species of 2-butene ozonide were predicted and assigned fairly readily. This species was the trans isomer possessing two equatorial methyl groups and a C₂ symmetry axis (see the Dipole Moment Components section). The assigned transitions for this molecule were observed only in the 2-butene ozonide isomer having the shorter VPC retention time.¹⁵ The microwave spectrum of the cis isomer has also been investigated; however, we have not yet been able to make a spectral assignment for this isomer.

The rotational spectrum of *trans*-2-butene ozonide consists of several quite weak b-type R-branch transitions. The spectral assignment was supported by the rigid rotor frequency fit and the Stark effect for a number of transitions. The observed transitions and rotational constants are listed in Table VI. No vibrational satellites were observed due to the overall weak intensity of the spectrum. No effects from pseudorotation or methyl internal rotation were observed. As stated previously only one isomer has been observed; in particular there is no evidence for a biaxial trans isomer which might be expected to be in equilibrium with the observed biequatorial trans isomer. The presence of a second isomer or another conformer cannot be ruled out, however, since the overall observed spectrum is not very intense.

Dipole Moment Components. Dipole components for both propylene and *trans*-2-butene ozonides were determined by observations and analysis of the second-order Stark effect.²² The observed and calculated Stark coefficients are listed in Table VII, and the dipole moment components (determined by least-squares fits of the observed coefficients) are given in Table VIII. Propylene ozonide, lacking molecular symmetry, was found to possess three nonzero dipole components (although μ_c is very small). *trans*-2-Butene ozonide, on the other hand, was found to have only one nonzero component, μ_b , indicating that the molecule has a twofold

symmetry axis. The total dipole moments for both molecules are somewhat larger than the total moment of 1.09 D found for ethylene ozonide.¹² Apparently, the addition of methyl substituents intro-

(22) S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).

Table IV. Ground-State Transition Frequencies of Isotopically Substituted Species of Equatorial Propylene Ozonide (MHz)

Transition	$\text{CH}_3\text{CHOOCH}_2^{18}\text{O}$	$\text{CH}_3\text{CHOO}^{13}\text{CH}_2\text{O}$	$\text{CH}_3^{13}\text{CHOOCH}_2\text{O}$	$^{13}\text{CH}_3\text{CHOOCH}_2\text{O}$	$^{13}\text{CH}_3^{13}\text{CHOOCH}_2\text{O}$
4 ₁₄ -5 ₁₅	27804.79 (0.15) ^a	27804.09 (-0.01)	28034.18 (0.02)		27388.18 (0.14)
4 ₀₄ -5 ₀₅	28398.79 (-0.07)	28458.01 (-0.13)	28690.34 (-0.08)		28066.37 (-0.11)
4 ₂₃ -5 ₂₄	30137.36 (-0.21)	30002.46 (-0.05)	30242.02 (-0.09)	29571.07 (0.01)	29477.70 (-0.16)
4 ₁₃ -5 ₁₄	31882.67 (0.31)	31705.65 (-0.01)			31128.39 (0.21)
4 ₂₂ -5 ₂₃	32159.68 (0.04)	31788.48 (0.03)			31105.03 (0.00)
1 ₁₀ -2 ₂₁	24486.95 (0.00)	25162.45 (0.00)		25296.39 (0.10)	25233.36 (0.00)
1 ₁₁ -2 ₂₀	25484.43 (0.10)	26092.78 (0.07)	26239.93 (0.02)		26112.96 (0.17)
2 ₀₂ -3 ₁₃	19963.51 (0.13)	20229.46 (-0.03)	20379.81 (0.01)	20146.51 (0.08)	20099.90 (-0.03)
2 ₁₁ -3 ₂₂	29706.58 (-0.12)	30393.30 (-0.11)	30581.17 (0.02)	30467.62 (-0.12)	30392.42 (-0.20)
3 ₀₃ -4 ₁₄	24594.66 (0.07)	24877.18 (0.21)	25069.57 (0.01)	24743.54 (-0.02)	24688.67 (0.04)
4 ₁₄ -5 ₀₅			27000.27 (0.12)		
4 ₀₄ -5 ₁₅	29220.52 (-0.08)	29489.53 (0.01)		29291.12 (0.00)	29226.43 (0.06)

^a Number in parentheses is $\nu_{\text{obsd}} - \nu_{\text{calcd}}$.**Table V.** Rotational Constants (MHz) and Moments of Inertia ($\text{amu } \text{Å}^2$) for Equatorial Propylene Ozonide

	$\nu = 0$	$\text{CH}_3\text{CHOOCH}_2\text{O}$ $\nu = 1$	$\nu = 2$	$\text{CH}_3\text{CDOOCH}_2\text{O}$	$\text{CH}_3\text{CHOOCHD}_{\text{eq}}\text{O}$
<i>A</i>	7574.36 ± 0.03	7538.01 ± 0.03	7505.13 ± 0.06	7326.45 ± 0.03	7410.52 ± 0.04
<i>B</i>	3476.33 ± 0.02	3481.22 ± 0.02	3486.02 ± 0.03	3410.82 ± 0.02	3372.04 ± 0.02
<i>C</i>	2644.79 ± 0.02	2650.43 ± 0.02	2655.69 ± 0.02	2636.66 ± 0.02	2566.58 ± 0.02
κ	-0.662632	-0.660039	-0.657556	-0.669856	-0.667438
<i>I_a</i>	66.7218	67.0435	67.3372	68.9795	68.1970
<i>I_b</i>	145.3760	145.1716	144.9718	148.1684	149.8724
<i>I_c</i>	191.0832	190.6766	190.2987	191.6722	196.9058

	$\text{CH}_3\text{CHOOCHD}_{\text{ax}}\text{O}$	$\text{CH}_3\text{CHOO}^{13}\text{CH}_2\text{O}$	$\text{CH}_3^{13}\text{CHOOCH}_2\text{O}$	$^{13}\text{CH}_3\text{CHOOCH}_2\text{O}$	$^{13}\text{CH}_3^{13}\text{CHOOCH}_2\text{O}$
<i>A</i>	7316.41 ± 0.03	7515.66 ± 0.04	7555.92 ± 0.05	7570.19 ± 0.05	7551.24 ± 0.05
<i>B</i>	3387.18 ± 0.02	3434.42 ± 0.02	3460.27 ± 0.03	3373.21 ± 0.04	3359.94 ± 0.02
<i>C</i>	2609.76 ± 0.02	2615.48 ± 0.02	2637.80 ± 0.01	2585.72 ± 0.02	2579.64 ± 0.02
κ	-0.669650	-0.665751	-0.665533	-0.684026	-0.686097
<i>I_a</i>	69.0742	67.2429	66.8846	66.7586	66.9251
<i>I_b</i>	149.2024	147.1501	146.0507	149.8204	150.4121
<i>I_c</i>	193.6484	193.2246	191.5899	195.4481	195.9095

	$\text{CH}_3\text{CHOOCH}_2^{18}\text{O}$	$\text{CH}_3\text{CH}^{18}\text{OOCH}_2\text{O}$	$\text{CH}_3\text{CHO}^{18}\text{OCH}_2\text{O}$
<i>A</i>	7292.36 ± 0.04	7313.40 ± 0.05	7476.71 ± 0.06
<i>B</i>	3475.90 ± 0.02	3475.09 ± 0.02	3388.34 ± 0.06
<i>C</i>	2609.88 ± 0.02	2613.08 ± 0.02	2583.17 ± 0.02
κ	-0.630100	-0.633213	-0.670924
<i>I_a</i>	69.3020	69.1028	67.5934
<i>I_b</i>	145.3940	145.4283	149.1513
<i>I_c</i>	193.6395	193.4026	195.6416

Table VI. Ground-State Transition Frequencies and Rotational Constants for the Biequatorial Trans Isomer of 2-Butene Ozonide (MHz)

Transition	ν_{obsd}	$\nu_{\text{obsd}} - \nu_{\text{calcd}}$
1 ₁₀ -2 ₂₁	19761.81	0.01
1 ₁₁ -2 ₂₀	20199.35	-0.01
2 ₁₁ -3 ₂₂	32029.20	0.01
3 ₁₃ -4 ₂₄	26336.70	-0.16
3 ₂₃ -4 ₃₄	35892.75	0.14
4 ₀₄ -5 ₁₅	20310.01	0.18
4 ₁₃ -5 ₂₄	29318.54	0.06
4 ₁₄ -5 ₂₃	34382.67	-0.03
5 ₁₄ -6 ₂₅	32110.49	-0.15

A = 6022.05 ± 0.03 MHz *I_a* = 83.9208 amu Å²
B = 2103.08 ± 0.03 MHz *I_b* = 240.302 amu Å²
C = 1695.66 ± 0.02 MHz *I_c* = 298.040 amu Å²
 κ = -0.811658 MHz

Table VII. Stark Coefficients [(MHz cm²)/V²] for Propylene and *trans*-2-Butene Ozonides

Transition	<i>M</i>	$\Delta\nu/E^2 \times 10^4$	
		Obsd	Calcd
Propylene Ozonide			
1 ₁₀ -2 ₂₁	0	3.47	3.33
1 ₁₁ -2 ₂₀	0	-3.58	-3.65
2 ₀₂ -3 ₁₃	1	3.95	3.92
2 ₁₁ -3 ₂₂	1	-10.79	-10.36
2 ₁₁ -3 ₂₂	2	-42.51	-42.94
3 ₁₃ -4 ₂₄	2	-2.87	-2.80
<i>trans</i> -2-Butene Ozonide			
1 ₁₁ -2 ₂₀	1	0.146	0.144
2 ₁₁ -3 ₂₂	1	-0.0548	-0.0565
1 ₁₀ -2 ₂₁	1	-0.519	-0.511

duces an appreciable bond-moment contribution to the ring which tends to increase the molecular dipole moment to some extent.

Vibrational Satellites. Propylene ozonide is expected to possess

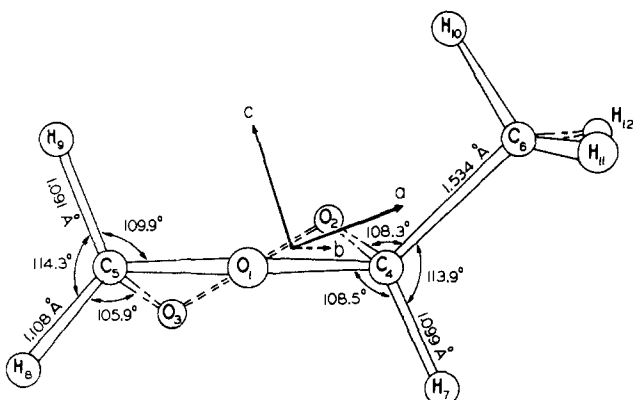


Figure 1. Structure of equatorial propylene ozonide, O-O half-chair conformation.

Table VIII. Dipole Moment Components (D) for Propylene and *trans*-2-Butene Ozonides^a

Propylene Ozonide	
μ_a	0.74 ± 0.01
μ_b	1.06 ± 0.02
μ_c	0.10 ± 0.08
μ_t	1.29 ± 0.02
<i>trans</i> -2-Butene Ozonide	
$\mu_b = \mu_t$	1.34 ± 0.03

^a Stark cell calibrated using $\mu(\text{OCS}) = 0.71521 \text{ D}$.

three low-frequency vibrations: two ring-puckering modes (a twist and a bend) and one methyl torsional mode. The two assigned series of propylene ozonide vibrational satellite transitions must arise from one or more of the above modes. The linear variation of rotational constants with vibrational state and the regular decrease in intensities of the observed satellites indicates that both assigned species arise from a single normal mode. Since no E-A splittings were observed in either the $v = 1$ or $v = 2$ states, it is believed that the excited mode is not the methyl torsion. The vibration observed is probably the bending mode, since this mode was found to be of much lower energy than the twisting vibration in ethylene ozonide.^{8,23} Relative intensity measurements²⁴ have been utilized to give the following estimates for the energy difference from the ground state for the observed vibrational modes: $100 \pm 15 \text{ cm}^{-1}$ ($v = 1$) and $201 \pm 25 \text{ cm}^{-1}$ ($v = 2$).

Results and Discussion

Structure of Equatorial Propylene Ozonide. Atoms numbered 1 through 9 (Figures 1 and 2) have each been isotopically substituted, so it is possible to obtain the r_s coordinates of these nuclei with the use of Kraitchman's equations.²⁵ These principal axis coordinates are given in Table IX. Kraitchman's equations are known to give the most reliable results for coordinates larger than about 0.15 \AA .^{25b} For coordinates smaller than this, fairly large uncertainties may result, and as a coordinate approaches zero, its Kraitchman value may even appear to be imaginary.^{25b} Four substitution coordinates were found to possess imaginary values in propylene ozonide: the b coordinates of atoms 4 and 6, and the a coordinates of atoms 1 and 2. Values for these coordinates were derived in the following manner. The two small b coordinates were found using the first moment (center of mass) equation for the b and c principal axes. By assuming that the methyl hydrogen

(23) The twisting mode fundamental in ethylene ozonide is $388 \pm 35 \text{ cm}^{-1}$; see ref 19.

(24) A. S. Esbitt and E. B. Wilson, Jr., *Rev. Sci. Instrum.*, **34**, 701 (1963).

(25) (a) J. Kraitchman, *Amer. J. Phys.*, **21**, 17 (1953); (b) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

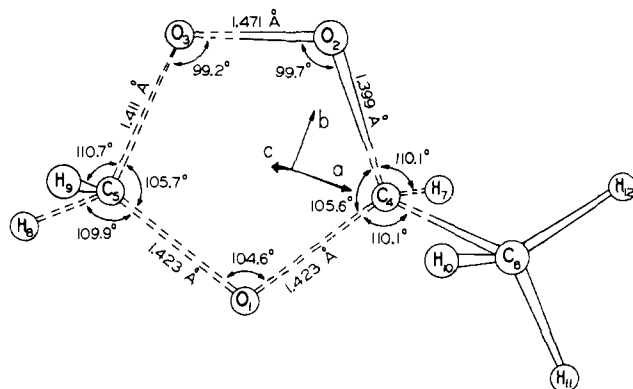


Figure 2. Structure of equatorial propylene ozonide, projection from top of ring.

atoms are arranged symmetrically about the axis of the C_4-C_6 bond, the coordinates b_4 and b_6 could be solved for exactly.²⁶ It is important to note that this calculation does not require one to assume a methyl C-H bond length or a methyl H-C-H bond angle. Any deviation of the methyl group from threefold symmetry, however, will affect the accuracy of the b_4 - b_6 determinations. No direct determination of the small a_1 and a_2 coordinates was possible without making additional assumptions. The coordinate a_1 was solved for by assuming the two C-O_e bond lengths (O_1-C_4 and O_1-C_3) to be equal. The resulting C-O_e bond length (1.423 \AA) should approximate an average of the two C-O_e lengths, which are of course nonequivalent in the molecule. This procedure for calculating a_1 seems justified since the resulting C-O_e bond length is essentially identical with the same parameter in ethylene ozonide ($r_s = 1.425 \text{ \AA}$).²⁷ The coordinate a_2 was solved for by assuming an O_2-O_3 bond length of 1.471 \AA , the r_s value of this parameter in ethylene ozonide.²⁷ This assumption seems justified since the two ozonides are known to be very similar in structure, and in view of the fact that reported O-O bond lengths fall in the relatively narrow range of 1.470 - 1.482 \AA .^{12, 27, 28} Also, the C_1-O_2 bond length which results from this calculation (1.399 \AA) is close to that in ethylene ozonide ($r_s = 1.396 \text{ \AA}$).²⁷

The uncertainties listed in Table IX have been estimated with vibration-rotation effects in mind. Although zero-point vibrational effects are known to be at least partially canceled using the Kraitchman method,^{25b} there nevertheless remains some unknown uncertainty in each coordinate due to these effects. Consequently, an empirical uncertainty was attached to each substitution coordinate using the following formula: $\delta = 0.0015/\chi$, where χ is the substitution coordinate and δ is its uncertainty. An uncertainty of this type attempts to account for zero-point vibrational effects, and the arbitrary constant used here (0.0015) is probably conservatively large, especially for the heavier atoms. Uncertainties in substitution coordinates might also be obtained by propagating the experimental errors in rota-

(26) The equations used to calculate these coordinates were $\sum m_i b_i = \sum m_i c_i = 0$ and the distance formulas for $d(C_4-C_6)$ and $d(C_6-\text{Me})$. The latter distance was defined as the distance between the methyl carbon (C_6) and the center of mass of a symmetrical H_3 group along the C_4-C_6 bond axis.

(27) C. W. Gillies and R. L. Kuczkowski, unpublished results.

(28) (a) R. L. Redington, W. B. Olson, and P. C. Cross, *J. Chem. Phys.*, **36**, 1311 (1962); (b) P. Groth, *Acta Chem. Scand.*, **21**, 2608, 2631, 2695, 2711 (1967); (c) *ibid.*, **23**, 2277 (1969).

Table IX. Atomic Coordinates for Equatorial Propylene Ozonide

Atom ^a	<i>a</i> , Å ^b	<i>b</i> , Å	<i>c</i> , Å
O ₁	-0.017 ± 0.022	-1.1422 ± 0.0013	-0.1062 ± 0.0141
O ₂	-0.002 ± 0.013	1.0880 ± 0.0014	0.1747 ± 0.0086
O ₃	-1.3719 ± 0.0011	0.6645 ± 0.0022	-0.1538 ± 0.0098
C ₄	0.7160 ± 0.0021	0.039 ± 0.016	-0.4091 ± 0.0037
C ₅	-1.3037 ± 0.0012	-0.6757 ± 0.0022	0.2817 ± 0.0053
C ₆	2.1022 ± 0.0007	-0.018 ± 0.053	0.2463 ± 0.0061
H ₇	0.7445 ± 0.0020	0.1617 ± 0.0093	-1.5010 ± 0.0010
H ₈	-2.0885 ± 0.0007	-1.2183 ± 0.0012	-0.2827 ± 0.0053
H ₉	-1.4093 ± 0.0011	-0.7349 ± 0.0020	1.3664 ± 0.0011

^a See Figure 1 for numbering scheme. Coordinates for H₁₀, H₁₁, and H₁₂ were not determined. ¹²C atomic mass scale was used. ^b See "Structure" section for discussion of uncertainties.

tional constants through the Kraitchman equations. These calculations were performed; they showed that the experimental uncertainties derived from the rotational constants are less in every case than the values reported in Table IX.

Uncertainties in the four small coordinates not determined by substitution (*a*₁, *a*₂, *b*₄, and *b*₆) were estimated using a different procedure. Values for these small coordinates were calculated using various combinations of the three first moment, the three diagonal second moment, and the three off-diagonal second moment equations for the normal isotopic species.²⁹ Calculations were also made in which the methyl C-H bond length and HCH bond angle were varied over reasonable limits to test the sensitivity of the small coordinates to these parameters.²⁹ These calculations give a range of values for the small coordinates, and the uncertainties reported in Table IX represent the standard deviations of the values thus obtained. Thus, the uncertainties listed give some indication of the extent of zero-point vibrational effects in these coordinates.

No attempt was made to derive coordinates or structural parameters for the three methyl hydrogen atoms, since these were not isotopically substituted. The spectral results are consistent with normal methyl group parameters, however, and it was not deemed worthwhile to speculate further on the methyl bond lengths and angles.

The structural parameters for equatorial propylene ozonide are listed in Table X, and two projections of the structure are illustrated in Figures 1 and 2. The uncertainties listed in Table X were derived directly from the uncertainties in the atomic coordinates of Table IX. The ring parameters agree quite well with the structure of ethylene ozonide,^{12, 27} indicating that the addition of a methyl group to the ring influences the ring geometry only to a very small extent. The large CO_pO_pC dihedral angle of 49.2° is close to that in ethylene ozonide, where it was 50.2°.¹² This suggests that the largest ring torsional forces in these ozonides involve the peroxy linkage. The C-O_p bonds are seen to be slightly shorter than normally found for single bonds; this effect was also observed in ethylene ozonide. The C-C bond length is rather normal at 1.534 Å.

Conformation of *trans*-2-Butene Ozonide. Only the normal isotopic species of *trans*-2-butene ozonide has been studied. This permits the conformation of the molecule to be determined but not any detailed parameters. The conformational assignment for this mole-

Table X. Structural Parameters for Equatorial Propylene Ozonide^a

Bond lengths, Å		Bond angles, deg	
O ₁ -C ₄	1.423 ± 0.018 ^b	C ₄ O ₁ C ₅	104.6 ± 0.6
O ₁ -C ₅	1.423 ± 0.020	O ₁ C ₄ O ₂	105.6 ± 0.8
O ₂ -C ₄	1.399 ± 0.014	O ₁ C ₅ O ₃	105.7 ± 0.4
O ₃ -C ₅	1.411 ± 0.005	C ₄ O ₂ O ₃	99.7 ± 0.5
O ₂ -O ₃	1.471 (assumed)	C ₅ O ₃ O ₂	99.2 ± 0.3
C ₄ -H ₇	1.099 ± 0.004	O ₁ C ₄ H ₇	108.5 ± 1.1
C ₅ -H ₉	1.091 ± 0.005	O ₁ C ₅ H ₉	109.9 ± 0.7
C ₆ -H ₈	1.108 ± 0.004	O ₂ C ₄ H ₇	110.1 ± 1.1
C ₆ -H _{10, 11, 12}	1.09 (assumed)	O ₂ C ₅ H ₉	110.7 ± 0.5
C ₄ -C ₆	1.534 ± 0.004	O ₁ C ₅ H ₈	109.9 ± 0.6
Dihedral angles, deg			
O ₁ C ₄ O ₂ O ₃	-41.0	O ₂ C ₅ H ₈	105.9 ± 0.4
C ₄ O ₂ O ₃ C ₅	49.2	O ₁ C ₄ C ₆	110.1 ± 2.1
O ₂ O ₃ C ₅ O ₁	-39.8	O ₂ C ₄ C ₆	108.3 ± 1.7
O ₃ C ₅ O ₁ C ₄	15.5	C ₆ C ₄ H ₇	113.9 ± 0.4
C ₅ O ₁ C ₄ O ₂	16.9	H ₈ C ₅ H ₉	114.3 ± 0.3
		C ₄ C ₆ H _{10, 11, 12}	109.5 (assumed)

^a See Figures 1 and 2 for numbering scheme. ^b See Structure section for discussion of uncertainties.

cule is based on comparison of observed rotational constants to constants predicted from models possessing the ethylene ozonide ring structure and differing only in the arrangement of the two methyl groups, either axial (a) or equatorial (e). The observed rotational constants (Table VI) may be compared to the following predicted constants (*A*, *B*, *C*): *trans* (e, e), 6063, 2110, 1709; *trans* (a, a), 6284, 3970, 3208; and *cis* (a, e), 4759, 2417, 2102. The closeness of the observed constants to the constants predicted for biequatorial (e, e) methyl groups shows unambiguously that *trans*-2-butene ozonide has the same O-O half-chair conformation as ethylene and propylene ozonides. In addition, the expected C₂ symmetry axis (unique to the *trans* isomer) is confirmed by the dipole moment measurements which show only a single nonzero dipole component for the molecule.

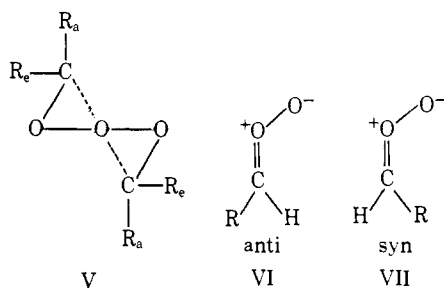
Mechanistic Aspects. The results of this study are quite interesting with regard to the mechanism of ozonolysis. The Bauld-Bailey syn-anti zwitterion mechanism³ will principally be discussed here. Of proposed mechanisms,^{1-3, 30} it alone explicitly discusses the conformation of the final ozonide. It is, of course, an extension of the original Criegee mechanism¹ which contained no provisions for stereochemical effects in ozonolysis. These effects are clearly important even for the ozonolysis of small alkenes such as propylene and 2-butene. Two other recent mechanistic proposals

(29) We are indebted to Professor R. H. Schwendeman for the computer program used in these calculations.

(30) (a) P. R. Story, J. A. Alford, W. C. Ray, and J. R. Burgess, *J. Amer. Chem. Soc.*, **93**, 3044 (1971); (b) P. R. Story, E. A. Whited, and J. A. Alford, *ibid.*, **94**, 2143 (1972).

will not be discussed here.^{2,30} The aldehyde interchange scheme² will be addressed in a forthcoming paper; preliminary results indicate that this scheme is not important in the ozonolysis of ethylene, propylene, and 2-butene,^{8,20} although it is possibly important in some other cases.¹⁰ Finally, the experimental basis for the recent proposal of Story, *et al.*,³⁰ has not been verified in recent studies.³¹

The stereochemical course of ozonide formation as predicted by the Bauld–Bailey mechanism begins with the assumption that a primary ozonide will have a 1,2,3-trioxolane structure with a C–C half-chair conformation.³² In this conformation the primary ozonide possesses clearly defined axial and equatorial sites (V).



This species then cleaves in a concerted fashion (Scheme I) to give a carbonyl compound and a zwitterion intermediate with either a syn or anti configuration (VI, VII). In order to rationalize observed cis–trans ratios in final ozonides, the following three rules were postulated. (1) Equatorial substituents in the primary ozonide are preferentially converted into anti (VI) and axial substituents into syn zwitterions (VII). (2) An equatorial substituent is incorporated into a zwitterion moiety in preference to an axial substituent. (3) Aldehydes preferentially interact 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. The stereochemical implications of these rules for the configuration and conformation of the final ozonides are summarized in Table XI.

Table XI. Stereochemical Course of Ozonide Formation (Bauld–Bailey Proposal³)

Olefin con-fig	Primary ozonide		Zwitterion con-fig ^d	Final ozonide	
	Con-fig	Con-form ^a		Con-fig	Con-form ^e
Cis	Cis	a,e	Anti	Cis	e,e
Trans	Trans	a,a ^b	Syn	Trans	a,e
Trans	Trans	e,e ^c	Anti	Cis	e,e

^a C–C half-chair. ^b Preferred with large substituents. ^c Preferred with small substituents. ^d Predominant. ^e C–O half-chair.

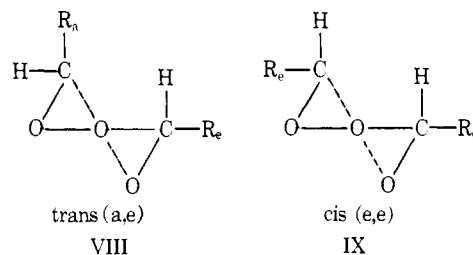
The Bauld–Bailey mechanism is capable of rationalizing a large amount of experimental data involving the cis–trans ratios of both normal and cross ozonides, particularly those with bulky substituents. Bauld, *et*

(31) (a) K. R. Kopecky, P. A. Lockwood, J. E. Filby, and R. W. Reid, *Can. J. Chem.*, **51**, 468 (1973); (b) P. S. Bailey, T. P. Carter, C. M. Fischer, and J. A. Thompson, *ibid.*, **51**, 1278 (1973).

(32) Although this conformation was chosen, the authors indicate (ref 3) that other nonplanar models for the ring could lead to similar predictions.

al., predict that trans olefins will give more trans final ozonide and that cis olefins will give more cis ozonide. While this is generally true for bulky olefins (R = isopropyl and *tert*-butyl), it is with small olefins (R = methyl, ethyl, and propyl) that the original scheme seems to break down. Both cis and trans small olefins in general tend to produce more trans than cis final ozonide.³³ The cis–trans ratio of 2-butene ozonide, for example, is always less than or close to unity (generally ~38:62), whether obtained as a normal or cross ozonide from either cis or trans olefin. The cis–trans ratio of 3-hexene ozonide is also generally less than 1 (averaging ~45:55), regardless of how the ozonide is obtained. The cis–trans ratios of 2-pentene and 2-hexene ozonides are similarly less than unity (~40:60). One weakness of the Bauld–Bailey proposal, then, lies in its inability to correctly predict the stereochemical course of ozonolysis for small olefins.

A second weakness lies in the third rule, which is based on a consideration of the preferred conformation for the final ozonide. Bauld, *et al.*, postulate a C–O half-chair as the most stable conformer (VIII–IX).



The conformational results presented in this work for propylene and *trans*-2-butene ozonides and the earlier result for ethylene ozonide¹² demonstrate that these ozonides have the O–O half-chair conformation (Figure 1). With this conformation, diaxial or diequatorial substituents are trans and axial, equatorial substituents are cis, contrary to rule 3 in the original proposal.³ The obvious implication is that rule 3, at least for methyl groups, must be revised in order to agree with the observed conformations.

In a preliminary communication of these results¹³ two possible revisions of the Bauld–Bailey proposal were discussed. The first revision was the simpler; the configurational assignment in the third rule was changed so that it agreed with the observed conformations. Thus, the revised third rule stated that aldehydes preferentially interact with anti zwitterions so as to orient substituents diequatorially (trans) and with syn zwitterions to orient substituents in an equatorial, axial (cis) conformation. On the basis of extensive studies by Fliszár and coworkers,³⁴ a second revision was proposed which involved changes in rules 2 and 3. It was suggested that rule 2 does not always hold. In some cases, an axial substituent might be incorporated into the zwitterion in preference to an equatorial substituent. *cis*-2-Butene primary ozonide was cited as one example of an exception to rule 2.^{34b} In addition, rule 3 was changed to state that anti zwitterions react with aldehydes to produce a cis configuration while syn zwitterions will produce a trans configuration. In this

(33) See (a) Tables II and III of ref 3; (b) Tables I–IV of ref 2b; (c) Table I of ref 11.

(34) (a) J. Renard and S. Fliszár, *J. Amer. Chem. Soc.*, **92**, 2628 (1970); (b) S. Fliszár, J. Renard, and D. Z. Simon, *ibid.*, **93**, 6953 (1971); (c) S. Fliszár, *ibid.*, **94**, 7386 (1972).

revision, rule 3 was not dependent on the final ozonide conformation.³⁵

The ability of these revisions to predict correctly the stereochemical course of ozonide formation was discussed in the preliminary communication.¹³ The first revision successfully accounts for the stereochemical effects observed for cis and trans alkenes with small substituents, but it cannot be directly extended to alkenes with bulky groups. It also cannot rationalize the high cis-trans ratio (81:19) of 2-butene ozonide obtained from propylene. The second revision is able to explain the low cis-trans ratios obtained in the ozonolysis of small cis and trans alkenes but in addition the high cis-trans ratio of 2-butene ozonide obtained from propylene. This revision can also be more readily extended to alkenes with bulky groups.

While both of these revisions can rationalize a good deal of data (the second revision more consistently than the first), a number of reservations can be stated regarding them as well as the original Bauld-Bailey scheme from which they were derived. These reservations, which are summarized below, deal more with the underlying rationale for the three rules rather than with their ability to predict stereochemical results. (1) These schemes argue that the primary ozonide exists in a stable C-C half-chair conformation and cleaves in a concerted fashion from that conformation.³² While the C-C half-chair was supported by earlier EHT-MO calculations,^{34a} more recent CNDO calculations³⁶ indicate that an O-O half-chair conformer may be the most stable conformation with a number of others not too much higher in energy. In any event, it is not clear that the most stable conformation of the primary ozonide will be the one of mechanistic importance. Of more significance is the conformation of the transition state which leads to cleavage; this conformation may or may not resemble the most stable conformer of the primary ozonide. (2) The physical basis for rule 1 is not very clear. While it seems reasonable that equatorial substituents will produce anti zwitterion, it is not obvious through examination of models that axial substituents will necessarily produce syn zwitterions. (3) Similarly in rule 2, it is not clear for a cis alkene why the equatorial substituent will be preferentially incorporated into zwitterions. It would appear that in the proposed concerted disrotatory outward cleavage that an axial substituent could also produce an anti zwitterion. A more basic point that can be raised is whether or not a *rotatory* cleavage is even necessary. (4) An assumption underlying rule 3 (in the original scheme and revision 1) is that the transition state for zwitterion and aldehyde recombination is similar to the final ozonide conformation. Since this reaction is irreversible and presumably exothermic,³⁷ application of

(35) In this case, rule 3 is revised to retain the sequence in the original Bauld-Bailey proposal that syn (anti) zwitterion produces trans (cis) final ozonide, but it alters the final conformations to agree with experiment. While this change may at first glance appear trivial, it is important to note that this postulate is counter to the basic rationale of the original Bauld-Bailey proposal (and revision 1), in which equatorial (axial) groups in the primary ozonide appear at equatorial (axial) sites in the final ozonide. In the preliminary communication (ref 13), no rationalization for this change was presented; it was introduced solely on a phenomenological basis.

(36) R. A. Rouse, *J. Amer. Chem. Soc.*, **95**, 3460 (1973).

(37) The heat of decomposition for *trans*-di-*tert*-butylethylene primary ozonide was determined as ~ 38 kcal/mol: R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960).

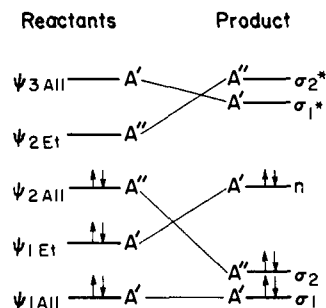


Figure 3. Orbital correlation diagram for the 1,3-dipolar cycloaddition of the allyl anion (All) and ethylene (Et).

the Hammond postulate would suggest that the final conformation could be of little importance in interpreting the transition state. (5) Rule 3 emphasizes the role of bulk for the group attached to the zwitterion and makes it difficult to rationalize results which indicate that the bulk on the reacting aldehyde is also important.³⁸ (6) As mentioned in ref 35, no physical model based on interpretation of the transition state has been proposed to justify rule 3 in the second revision.

Because of these reservations the ozonolysis reaction was examined with regard to the conservation of orbital symmetry in the hope of obtaining a more physically appealing model. The initial reaction of ozone with an alkene is often cited as an example of a 1,3-cycloaddition.³⁹ Likewise, Bauld, *et al.*, in the original proposal³ assumed concerted O-O and C-C bond cleavage in the primary ozonide to produce zwitterion and carbonyl; this can be considered a 1,3-cycloreversion. Finally, Bauld, *et al.*, considered the recombination of the zwitterion and carbonyl another example of a 1,3-cycloaddition. Accepting this pathway, the steps can be analyzed by the symmetry arguments for cycloadditions and cycloreversions developed by Woodward and Hoffmann.⁴⁰

Ozone and the zwitterion are isoelectronic and have a π system containing four electrons. Likewise, an alkene and a carbonyl contain a π system with two electrons. Consequently, the three concerted reactions discussed above fall into the classification of [$\pi 4_s + \pi 2_s$] reactions which are symmetry allowed.⁴⁰ This is based on an analysis of the analogous isoelectronic reaction of the allyl anion with ethylene. This has been analyzed by Huisgen *et al.*, who have presented the orbital correlation diagram and electronic state diagram.⁴¹ The orbital diagram is reproduced in Figure 3 for convenience. The diagram shows that the four-electron π system of the "three atom" moiety will react by a symmetry-allowed process with the two-electron π system of the "two atom" moiety to produce two σ bonds and one nonbonding pair (or lone pair) in the five-atom ring. An even more interesting result of this interpretation is the stereo constraints on the transition state. The reaction will be *supra, supra*; that is, for the cycloaddition the process must proceed as il-

(38) R. W. Murray and G. J. Williams, *J. Org. Chem.*, **34**, 1891 (1969).

(39) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963).

(40) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH, Weinheim, 1971.

(41) A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillich, D. Grashay, and E. Spindler, *Chem. Ber.*, **100**, 2192 (1967).

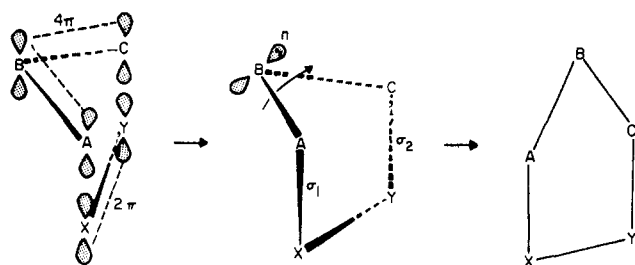


Figure 4. Orbital diagram of the *supra, supra* addition of a 4π and 2π system to produce a five-membered ring.

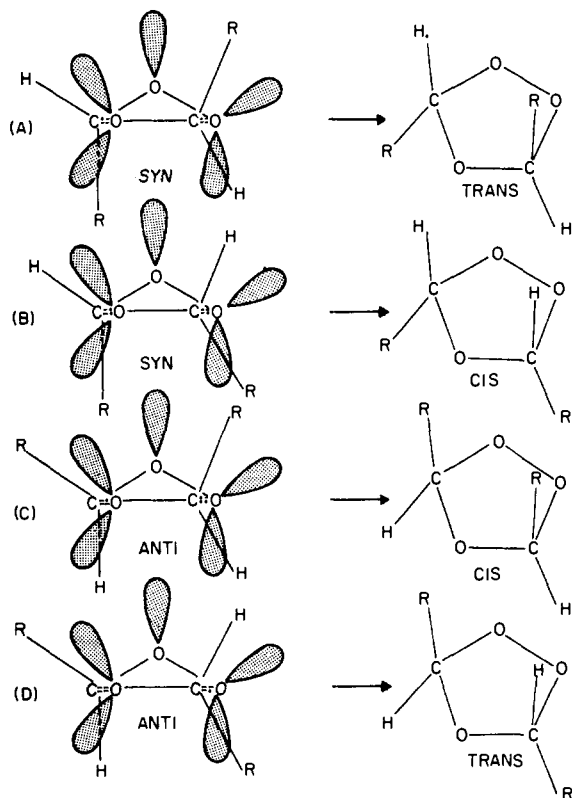


Figure 5. Reaction of syn and anti zwitterions to produce cis or trans final ozonide. Pathways A and C are preferred. The plane of the carbonyl is approaching the plane of the zwitterion.

illustrated in Figure 4, with the plane of the 2π system approaching parallel to the plane of the 4π system. In a cycloreversion of a five-membered ring which is symmetry allowed, the transition state leading toward decomposition would therefore also be an exaggerated envelope conformation leading toward cleavage or the reverse process in Figure 4.

In applying this to the ozonolysis mechanism, the reaction of zwitterion and carbonyl to give the final ozonide will be considered first, and the decomposition of the primary ozonide will be examined second.

Two orientations in the transition state are possible for the reaction of a syn (or anti) zwitterion with an aldehyde, as illustrated in Figure 5. For a syn zwitterion, attack by orientation A will lead to a trans configuration while for orientation B a cis configuration will result. For an anti zwitterion mode C will result in a cis configuration while mode D will result in a trans configuration. It appears that modes A and C will be the preferred orientations, since the bulky group on the aldehyde seems to interact less with the lone pairs

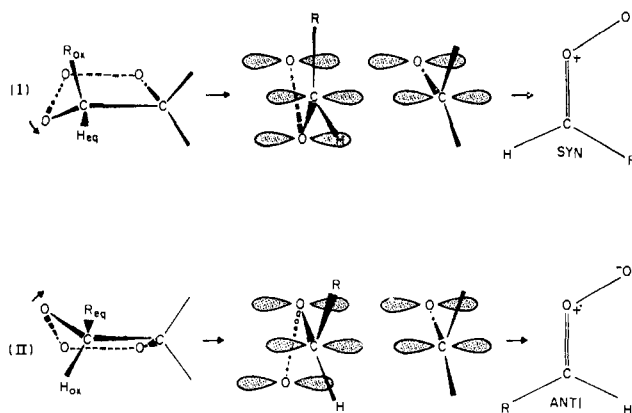


Figure 6. Cycloreversion cleavage of the primary ozonide to give syn or anti zwitterion and a carbonyl species.

on the terminal oxygen in the zwitterion moiety. One concludes that syn zwitterions will produce more trans final ozonide, while anti zwitterions will produce more cis final ozonide. Also note that this scheme emphasizes the role of bulk in the aldehyde as the primary directing influence of this step in the reaction.

Next consider the cycloreversion reaction that leads to zwitterion formation, *i.e.*, the cleavage of the 1,2,3-trioxolane primary ozonide. Following the reverse reaction in Figure 4, it is seen that the transition state leading to decomposition will be one in which the oxygen adjacent to the carbon going to zwitterion must begin to move markedly away from the "plane" of the ring. This will correspond to an oxygen envelope conformation in the transition state toward cleavage. If one considers the oxygen-envelope motion and examines the orientations of substituents on the carbon going to zwitterion, it is apparent that the two possible directions for formation of the oxygen envelope will lead naturally to either syn or anti zwitterion. This is illustrated in Figure 6. Thus *via* pathway I (Figure 6), the motion of the oxygen away from the R group on the adjacent carbon, associated with the concerted cleavage of the necessary bonds and formation of the π system in the zwitterion, leads smoothly to the syn zwitterion by a symmetry-allowed process. The opposite motion *via* pathway II (Figure 6) leads to an anti zwitterion.

In assessing which cleavage pathway should be favored for a given alkene, one must evaluate the relative energies of the two transition states. The more stable transition state will presumably lead to a lower activation energy and greater rate of cleavage. In assessing the relative transition state stabilities, three interactions seem of primary importance. These are (1) the placement of carbon substituents either axial or equatorial on the ring and their gauche-trans interactions with the ring, (2) across-ring interactions, and (3) gauche-trans interactions between substituents on adjacent carbon atoms. Three general classes of alkenes will be considered separately: 1-alkenes, trans alkenes, and cis alkenes.

1-Alkenes. This is the simplest case. In pathway I (Figure 6) the transition state places the R group in an axial position where it will be gauche to the ring bonds. Pathway II places the R group in an equatorial position where it is trans to the ring bonds (Figure 7). It would

appear that the latter would be the more stable conformer and hence anti zwitterion should predominate.^{42,43} Anti zwitterions will then react with aldehyde to give predominately cis final ozonide. This conclusion readily correlates with the observations of Murray and Williams³⁸ which show that cis final ozonide is favored in the reaction of a 1-alkene (*tert*-butylethylene) with foreign aldehyde and that this tendency increases with the bulk of the added aldehyde. It also correlates with the observation reported here that *cis*-2-butene ozonide is predominantly produced as the cross ozonide from the ozonolysis of propylene.

Trans Alkenes. For trans alkenes following pathway I (Figure 6), the R group will be gauche to the ring bonds but trans to the R group on the adjacent carbon. This is a pseudodiaxial conformer.⁴⁴ For pathway II, the R group will be trans to the ring bonds but gauche to the R group on the adjacent carbon (Figure 7), giving a pseudodiequatorial conformer. When the R groups are very bulky, the gauche interactions in pathway II should make this route less favored, leading to a preference for syn zwitterion.⁴⁵ It is more difficult to choose between pathway I and II when the groups are not too bulky; it would appear that pathway I is still preferred.⁴⁶ A predominance of syn zwitterions leads to more trans final ozonide. This conclusion correlates with the general tendency of symmetrical and unsymmetrical trans alkenes, bulky and nonbulky, to produce more trans final ozonide, including cross ozonides.^{47,48} This tendency increases somewhat with bulk in the R groups.

Cis Alkenes. For cis alkenes, *via* both pathways I and II (Figure 6), the R groups on adjacent carbons will always be gauche. Furthermore, the transition state conformers will both be pseudoaxial, equatorial, and across-ring interactions should be similar for the two transition states. Unsymmetrically disubstituted cis alkenes will be considered first. For these olefins one needs to consider which substituent is axial and which is equatorial in the transition state. One would expect the large substituent to be equatorial in every case, since this puts the bulkier group trans to the ring

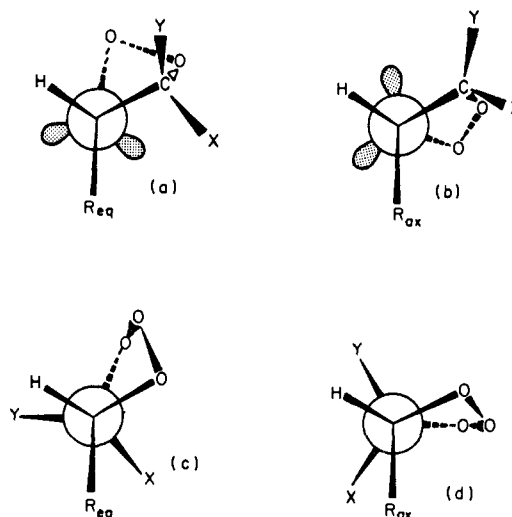


Figure 7. Oxygen envelope primary ozonide projections involving the carbon going to zwitterion: (a and b) C-O projection; (c and d), C-C projection; 1-alkene, X = Y = H; trans alkene, X = H and Y = R; cis alkene, X = R and Y = H.

bonds. Therefore, in the transition state leading to the larger zwitterion, the bulkier substituent will be equatorial and the predominant zwitterion will be anti (pathway II). One would thus expect more cis final high-cross ozonide. In the transition state leading to the smaller zwitterion, the smaller substituent will be axial and the predominant zwitterion will be syn (pathway I). One therefore expects more trans final low-cross ozonide. The normal ozonide *cis*-*trans* ratio should lie between the two cross ozonide ratios. These expectations correlate well with experimental *cis*-*trans* ratios.^{49,50}

It is interesting to speculate further regarding the normal ozonide *cis*-*trans* ratios expected for an unsymmetrical cis alkene. This requires information about the direction of primary ozonide cleavage to give the two possible zwitterions and the zwitterion reaction rates with carbonyls. This has been estimated in five cases by zwitterion trapping experiments.⁵¹ Based on these estimates, more trans normal ozonide is expected for *cis*-pentene-2, *cis*-hexene-2, and *cis*-4-methylpentene-2 and more cis normal ozonide for *cis*-4,4-dimethylpentene-2 and *cis*-2,2-dimethylhexene-3. The experimental results concur with this^{49,51} except in the case of *cis*-4,4-dimethylpentene-2 where the reported *cis*-*trans* ratio for the normal ozonide is less than unity in ref 11 but greater than unity in ref 2b. This agreement is pleasing since it rationalizes why the *cis*-*trans* normal ozonide ratio for unsymmetrical cis alkenes changes from less than unity to greater than unity as the size of the substituents increases.

For symmetrical cis alkenes, pathway II seems preferable, at least for bulky substituents. In this case the R group going to the zwitterion is equatorial and the transition state possesses one more trans and one less gauche interaction than in pathway I. Pathway II produces anti zwitterion, which correlates well with the

(42) It might be objected that in pathway II (Figure 6), the equatorial R group staggers both the lone pairs on the adjacent oxygen. This interaction, however, does not appear to be very strong. For example, the lowest energy conformation of methyl ethyl ether is the *trans* conformation (ref 43). Also in propylene and *trans*-2-butene final ozonides, the equatorial site is of lower energy, even though that site staggers both lone pairs on the adjacent epoxy as well as peroxy oxygen.

(43) L. Pierce and M. Hayashi, *Spectrochim. Acta*, **18**, 1370A (1962).

(44) This nomenclature will be used in discussing *cis* and *trans* alkenes, although the R group on the carbon going to the carbonyl does not change its orientation in the initial stages of the transition state. For a *trans* alkene *via* pathway I, the R group on the carbon going to carbonyl can be considered pseudoaxial since it interacts more with the envelope. *Via* pathway II, the R group can be considered pseudoequatorial to the envelope.

(45) It might be noted that across-ring interactions should be more severe for the diaxial conformer than for the diequatorial form (especially for bulky groups), but these interactions are apparently less important than the R group gauche interactions.

(46) It is interesting to note that in *trans*-1,2-dihalocyclopentanes an *a,a* conformer is more stable, although dipole interactions may be important there: C. Altona, H. R. Buys, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **85**, 973, 983, 998 (1966). *trans*-1,2-Dimethylcyclopentane also exists in a conformation with one axial methyl group: M. Christl, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 3463 (1971).

(47) See (a) Tables II and III of ref 3; (b) Tables II and III of ref 2b; (c) Table I of ref 11.

(48) One puzzling exception to this is the high cross ozonide from *trans*-2,2-dimethylhexene-3, for which a *cis*-*trans* ratio considerably greater than unity is reported (ref 11).

(49) See (a) Table III of ref 3; (b) Tables I and IV of ref 2b; (c) Table I of ref 11.

(50) The low cross ozonide from *cis*-2,2-dimethylhexene-3 is a possible exception; the *cis*-*trans* ratio is reported as 62:38 in ref 2b but as 42:58 in ref 33c.

(51) S. Fliszár and J. Renard, *Can. J. Chem.*, **48**, 3002 (1970).

increasing tendency for symmetrical cis alkenes to produce more cis final ozonides as the bulk of the alkene increases.³ Although this interpretation seems reasonable, one might question whether an alkene with two bulky cis substituents can actually exist in a stable primary ozonide conformation. Both experimental and theoretical results suggest that a different pathway to zwitterion formation may be necessary for these alkenes.^{2b, 4d, 34a, b} At any rate, the orbital symmetry arguments presented here seem consistent with normal zwitterion formation from a bulky *cis*-1,2,3-trioxolane primary ozonide.

Less bulky symmetrical cis alkenes are known to form at least reasonably stable primary ozonides.^{4c, d, 5} For these alkenes it would also appear that pathway II should be favored, and one would expect more cis final ozonide. This, however, does not correlate with the observation that the *cis*-*trans* ratio is about 40:60 for *cis*-2-butene and about unity for *cis*-3-hexene. One possibility around this difficulty is to introduce the suggestion of Fliszár, *et al.*,^{34b, c} that for *cis*-2-butene the axial substituent should promote zwitterion formation somewhat better than the equatorial substituent. This arises from a more favorable hyperconjugative effect from the axial site. Perhaps in symmetrical cis alkenes, when the groups are too bulky, the difference in energy between the two pathways due to steric nonbonded interactions is not very large, and pathway I becomes preferred due to this more subtle electronic effect. This possibility could explain the *cis*-*trans* final ozonide data, although it remains somewhat less pleasing since it must invoke an effect other than the nonbonded interactions which sufficed for all the other cases.

The stereochemical consequences of this reaction scheme are summarized in Table XII. It is interesting to compare this proposal with the three rules in the original Bauld-Bailey mechanism. It is seen that rule 1 remains unchanged; axial substituents in the primary ozonide transition state produce *syn* zwitterions and equatorial substituents produce *anti* zwitterions. Rule 2 is altered so that either axial or equatorial substituents (in the transition state) will be incorporated in the zwitterion, depending on the alkene. Rule 3 is changed to state that aldehydes preferentially interact with *anti* zwitterions to produce a *cis* configuration and with *syn* zwitterions to produce a *trans* configuration, with no emphasis on the final ozonide conformation.³⁵ These latter two rules (as well as the first) are seen to be identical with those in revision 2 discussed above. Of course the underlying rationale for the rules was arrived at differently. Also revision 2 and the orbital symmetry proposal appear to be similar in their ability to rationalize the stereochemical course of ozonolysis.

It appears to us that the orbital symmetry analysis

Table XII. Stereochemical Course of Normal and Cross Ozonide Formation as a Symmetry-Allowed 1,3-Dipolar Cycloreversion and Cycloaddition

Olefin config	Primary ozonide Con-fig	Con-form ^a	Zwitter-ion con-fig ^b	Final ozonide con-fig ^b
1-Alkene		e	Anti	Cis ^c
Trans	Trans	a ^d	Syn	Trans
Cis	Cis	e ^e	Anti	Cis
Cis	Cis	a ^f	Syn	Trans

^a Oxygen envelope transition state. a or e refers to axial or equatorial position of R group going to the zwitterion. ^b Predominant. ^c Obtained as a cross ozonide or by addition of a foreign aldehyde. ^d Preferred for symmetrical or unsymmetrical alkenes. ^e Preferred for symmetrical alkenes with bulky groups or when the larger substituent of an unsymmetrical alkene is incorporated into the zwitterion. ^f Preferred for symmetrical alkenes with small groups or when the smaller substituent of an unsymmetrical alkene is incorporated into the zwitterion.

has provided several of the hoped for advantages. It arrives at the same conclusions as revision 2¹³ but by a more physically intuitive and appealing model. It has responded to the six objections mentioned above by providing a model which can more naturally account for zwitterion formation during primary ozonide cleavage, as well as the formation of a *cis* or *trans* final ozonide during zwitterion and aldehyde recombination. The scheme, of course, is somewhat speculative with regard to the choices that were made involving the various interactions of attached groups. Also, the rationale involving small symmetrical cis alkenes is not very clear. The relationship of the recent CNDO calculations³⁶ to the orbital symmetry analysis is also unclear. The emphasis in the CNDO report was different, of course, since it was concerned with minimum energies for various primary ozonide conformers rather than the potential energy surface for decomposition to a zwitterion and carbonyl. The calculations do not seem to be inconsistent with the orbital symmetry analysis, since they indicate that the necessary conformers leading to the transition state are not inaccessibly high in energy.

In summary, although the Bauld-Bailey³ proposal and revisions 1 and 2¹³ cannot be eliminated from consideration at present, the orbital symmetry approach can rationalize as much or more data as any of those proposals and with a clearer physical model. It is hoped that this proposal will stimulate further experimental and theoretical tests of its utility.

Acknowledgment. The authors are grateful to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this work.