ergy-transfer quenching than the low-lying rubrene triplet.

A second marked difference in this system's behavior, as compared to that of rubrene in benzonitrile, is that none of the luminescence parameters shows a dependence on the ion generation sequence. The dependence seen in the previous case was thought to result from ineffectual quenching of the rubrene triplet by its ion radicals, and it was further supposed that control of τ's magnitude was partially defaulted to anodically generated foreign substances. In the present case, the anodic potential excursions were less extreme than in the rubrene work; hence the lack of an effect of generation order may merely reflect the inconsequential production of foreign substances. In an alternative view, it may be that τ is totally governed by well-controlled substances, such as the ion radicals.

Triplet quenching by the ions may also bear importantly on the third important contrast these results show with the rubrene work: the concentration dependence of β. The ω_i *vs.* $(t_r/t_f)^{1/2}$ plots were, in all cases, highly linear; hence the existence of a time-independent $f(t)/\tau^2$ ratio is implied. At the higher concentrations, β decreases slowly with increasing concentration, but since the parameter's definition includes an inverse concentration term, this behavior seems entirely reasonable. At the lower concentrations, however, β quickly assumes very large values. At present it is not possible to thoroughly rationalize this phenomenon, but it should be noted that at low-substrate concentrations it is likely that the "walls" radical ions, which bound the reaction zone, will be less formidable than at higher concentrations. If so, as the concentrations of the aromatics are decreased, the control of τ may well shift from highly reproducible effects such as those associated with radical ions, to more obscure and variable ones, such as quenching by the solvent or trace impurities.

In addition to the foregoing contrasts, the results given here offer some noteworthy parallels with previous reports. Specifically, an extrapolation of α to higher concentrations indicates apparent triplet yields in accord with those measured earlier by sensitized isomerization of stilbene. Freed and Faulkner recorded a value of $7 \pm 2 \times 10^{-3}$ for the yield at [10-MP] = 2×10^{-2} *M*, compared to the value of 4×10^{-3} obtained from the current data by extrapolation. Considering the imprecision attendant to the extraction of ϕ_t from α and to the extrapolation, one can regard this agreement as encouraging support for the interpretation presented here.

It is further interesting to note that the triplet yields of fluoranthene–10-MP systems are comparable to those reported for the rubrene anion–cation reaction.[13] Moreover, it remains mildly surprising that the fractional participation of triplets in annihilation is so high, even though it is comparatively lower in this case. Thus one can reiterate the earlier conclusion that the low values of ϕ_{ecl} result primarily from inefficiencies in the annihilation process itself, rather than from low excitation yields.

Acknowledgment. The support of this work by a departmental grant from the E. I. du Pont de Nemours Co., Inc., and by Grant GP-28375 from the National Science Foundation is gratefully acknowledged. We wish to thank the National Science Foundation further for its award of a Graduate Fellowship to R. B.

Mechanism of Ozonolysis. Microwave Spectrum, Structure, and Dipole Moment of Ethylene Ozonide

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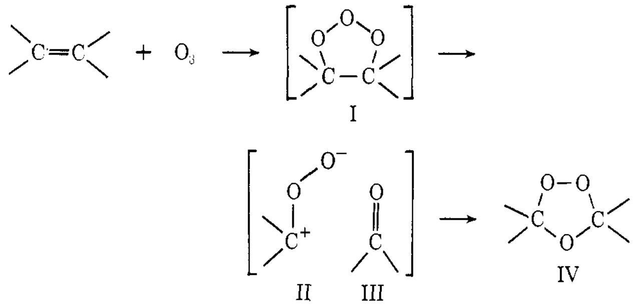
Abstract: The structure of ethylene ozonide, $\mathrm{H_2\overline{COOCH_2O}}$, has been determined from the microwave spectra of seven isotopic species. The half-chair conformation with C_2 symmetry has been established and there is no evidence for free or hindered pseudorotation. The parameters determined for the ring atoms are as follows: $r(\mathrm{C{-}O_e}) = 1.436 \pm 0.006$ Å, $r(\mathrm{C{-}O_p}) = 1.395 \pm 0.006$ Å, $r(\mathrm{O_p{-}O_p}) = 1.470 \pm 0.015$ Å, $\angle\mathrm{COC} = 102.83 \pm 0.44°$, $\angle\mathrm{COO} = 99.23 \pm 0.38°$, $\angle\mathrm{OCO} = 106.25 \pm 0.64°$, and the dihedral angles $\tau(\mathrm{C_1O_eC_2O_p}) = -16.60 \pm 0.40°$, $\tau(\mathrm{C_1O_pO_pC_2}) = -50.24 \pm 1.26°$, and $\tau(\mathrm{O_eCO_pO_p}) = 41.27 \pm 0.96°$. The dipole moment is $1.09 \pm .01$ D. Three excited vibrational states of the normal isotopic species arising from the asymmetric ring-bending vibration have been assigned. The ozonolysis of $\mathrm{HDC{=}CH_2}$ yielded six isotopic species of ethylene ozonide including two singly deuterated ozonides, three doubly deuterated ozonides, and the undeuterated ozonide. This result was analyzed in view of several proposals for the mechanism of ozonolysis.

The mechanism of the ozonolysis of alkenes has recently been reviewed by Murray.[1] The most extensive mechanistic scheme previous to 1960 was proposed by Criegee.[2] According to his proposal (Scheme I), the initial ozone–alkene adduct I fragments to give a zwitterion II and a carbonyl compound III. The normal ozonide is formed by the recombination of II and III. Experimental data have accumulated which cannot be rationalized on the basis of the Criegee mechanism. In particular, the discovery that cis-

(1) R. W. Murray, *Accounts Chem. Res.*, **1**, 313 (1968).

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

Scheme I



trans ratios of cross ozonides prepared by the ozonolysis of cis and trans unsymmetrical alkenes depend on alkene geometry led Murray, *et al.*,[3] to suggest the possibility of a competing mechanism. The additional pathway suggested by them involves the attack of I, the molozonide, by a foreign or Criegee-produced aldehyde. Bailey, *et al.*,[4] suggested later that the accumulated data can be rationalized by refining the original Criegee mechanism. To account for the steric effects, it was proposed that the original Criegee zwitterion can exist as syn and anti isomers. Subsequent oxygen-18 labeling studies of some aliphatic alkenes[5-8] supported the Murray aldehyde interchange mechanism. The results of other oxygen-18 labeling investigations of phenylethylenes[9] were rationalized in terms of the original Criegee mechanism.

This microwave study of 1,2,4-trioxacyclopentane (ethylene ozonide) was undertaken in order to elucidate the mechanism of the ozonolysis of ethylene through isotopic labeling. Microwave spectroscopy is potentially a powerful tool in such investigations since the spectra of different isotopic species can be uniquely predicted once the structure is known. The resolution of a microwave spectrometer readily permits unambiguous detection of the different isotopic spectra even in a multicomponent mixture. The technique also does not require destruction of the ozonide in contrast to isotopic mass spectral studies or chemical degradation to simpler species with subsequent mass spectral analysis. Hence, assumptions about fragmentation patterns or degradation mechanisms are not necessary.

In order to pursue mechanistic studies, the detailed structure of ethylene ozonide had to be determined. The structure of this ozonide was interesting in its own right since little information is available in the literature on such compounds. In fact, previous to this work, the conformation had not been established unambiguously for any ozonide; moreover, the possibility of a nonrigid ring showing the effects of free or hindered pseudorotation had not been eliminated. An electron diffraction study of ethylene ozonide[10] found that molecular models with C_2 symmetry (half-chair conformation) and C_s symmetry (envelope conformation) both gave equally good fits to the experimental intensity and radial distribution curves. Models corresponding to free or restricted pseudorotation were also not excluded. Conformational energy calculations,[11] however, favored the model with C_2 symmetry by 0.81–1.29 kcal/mol. Recently, the structure of 3-carbomethoxy-5-anisyl-1,2,4-trioxacyclopentane was investigated by X-ray diffraction.[12] The conformation of the ozonide ring could not be established because of a structural disorder associated with the five-membered ring.

In this investigation, ethylene ozonide has been found to have the C_2 conformation in the ground vibrational state and a detailed structure is reported. The compound shows no evidence of free or hindered pseudorotation. Several low-frequency vibrational states arising from excitations of the ring-bending vibration were assigned and the dipole moment was determined. Information on the mechanism of ozonolysis was obtained by analyzing the products of the ozonolysis of $HDC{=}CH_2$. The presence of five partially deuterated species as well as the normal isotopic species of ethylene ozonide in the products of this ozonolysis is discussed in the final section.

Experimental Section

Ethylene ozonide was prepared by ozonizing 0.1 *M* solutions of ethylene (CP grade, Matheson Co.) in methyl chloride (high purity grade, Matheson Co.) at −78°. All ozonolyses were continued to 100% of the theoretically required amount of ozone. Ozonide yields ranged from 60–70%. Due to the unstable nature of ethylene ozonide, 1-mmol quantities were prepared. Flow rates of approximately 2 mg/min of ozone were used for the reaction. The sample outlet of a Welsbach Model T-408 ozonator was used to obtain the low ozone flow rates which were necessary to ozonize 1-mmol quantities of ethylene. The ozonide was separated from the solvent by low-temperature vacuum distillation. A series of traps cooled to −45.2, −95, and −196° were used; the ozonide was collected in the −95° trap, high boiling impurities were stopped by the −45.2° trap, and the solvent was trapped at −196°. An identical procedure was used for the ozonolysis of $HDC{=}CH_2$ (98% enriched from Merck and Co., Inc.).

All samples of the ozonide were stored at liquid nitrogen temperature because samples were found to decompose overnight at room temperature. The sample cell of the microwave spectrometer was maintained at Dry Ice temperature for all spectroscopic work. Even at this temperature, frequent fresh doses of the sample were necessary due to ozonide decomposition.

All rotational transitions were measured with a conventional 80-kHz Stark-modulated spectrometer to an accuracy of ±0.1 MHz.[13] A precision dc power supply (Fluke, Model 412B) was employed for Stark shift measurements[14] and the dipole moment of OCS[15] was used to determine the average spacing of the Stark septum in the cell.

Spectra

The rotational spectrum of ethylene ozonide, a near-oblate rotor with $\kappa \sim 0.92$, consisted of a number of strong b-type R-branch transitions. Each transition was accompanied by several regularly spaced vibrational satellites on the low-frequency side. The rotational transitions assigned to the ground state and three vibrational satellites are given in Tables I and II. The frequencies of all transitions from each state fit well to a rigid-rotor model, indicative of a ring with

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(3) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **89**, 2429 (1967).

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(14) W. H. Kirchhoff, *ibid.*, **89**, 1312 (1967).

(15) J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).

Table I. Observed Frequencies (MHz) for the Normal Isotopic Species of Ethylene Ozonide. Ground and First-Excited Vibrational States

	$V = 0$		$V = 1$	
Transition	ν_{obsd}	$\Delta\nu$[a]	ν_{obsd}	$\Delta\nu$
$1_{11}-2_{02}$	21843.34	0.02	21827.67	0.00
$1_{11}-2_{20}$	36189.11	0.07	36173.05	0.00
$1_{10}-2_{21}$	29316.24	−0.02	29288.14	0.02
$1_{01}-2_{12}$	21998.15	0.08	21975.97	0.09
$2_{12}-3_{03}$	31089.60	0.06	31061.11	0.03
$2_{11}-3_{22}$	38485.68	−0.06	38447.96	0.04
$2_{02}-3_{13}$	31094.33	−0.02	31065.43	−0.06
$2_{21}-3_{12}$	38012.05	−0.07		
$4_{14}-4_{23}$	25080.10	−0.05		
$4_{04}-4_{13}$	25079.45	−0.06		

[a] $\Delta\nu = \nu_{obsd} - \nu_{calcd}$.

Table II. Observed Frequencies (MHz) for Ethylene Ozonide. Excited Vibrational States

	$V = 2$		$V = 3$	
Transition	ν_{obsd}	$\Delta\nu$	ν_{obsd}	$\Delta\nu$
$1_{11}-2_{02}$	21811.36	0.07		
$1_{11}-2_{20}$	36156.65	0.00		
$1_{10}-2_{21}$	29261.85	−0.15	29233.90	0.00
$1_{01}-2_{12}$	21954.46	0.11	21931.68	0.00
$2_{12}-3_{03}$	(31032.10)[a]	−0.44	31003.72	−0.02
$2_{11}-3_{22}$	38412.41	0.15		
$2_{02}-3_{13}$	31036.49	−0.17	31007.38	0.02

[a] Frequencies in parentheses were not included in the least-squares fit. They fell near neighboring transitions and were less accurately measured.

Table III. Rotational Constants (MHz), Principal Moments of Inertia (μÅ^2), and Second Moments (μÅ^2) for the Normal Isotopic Species of Ethylene Ozonide

	$V = 0$	$V = 1$	$V = 2$	$V = 3$
A	8243.84 ± 0.04[a]	8236.06 ± 0.04	8228.96 ± 0.08	8221.25 ± 0.02
B	8093.80 ± 0.04	8092.18 ± 0.04	8089.94 ± 0.12	8089.35 ± 0.24
C	4584.74 ± 0.02	4579.94 ± 0.02	4575.13 ± 0.06	4570.14 ± 0.02
I_a	61.3035	61.3614	61.4143	61.4719
I_b	62.4399	62.4524	62.4697	62.4742
I_c	110.2300	110.3456	110.4616	110.5822
P_{aa}	55.6832	55.7183	55.7585	55.7923
P_{bb}	54.5468	54.6273	54.7031	54.7900
P_{cc}	6.7567	6.7341	6.7112	6.6820

[a] The uncertainty is twice the standard deviation obtained from the least-squares fit of the transitions.

Table IV. Observed Frequencies for Ethylene Ozonide. Isotopic Species

	$H_2{}^{13}\overline{COOCH_2O}$		$HD_A\overline{COOCH_2O}$		$HD_B\overline{COOCH_2O}$	
Transition	ν_{obsd}	$\Delta\nu$	ν_{obsd}	$\Delta\nu$	ν_{obsd}	$\Delta\nu$
$1_{11}-2_{02}$	21499.25	0.09	20748.66	0.01	21138.20	−0.04
$1_{11}-2_{20}$	35740.72	−0.03	34803.22	0.01	34637.06	0.05
$1_{10}-2_{21}$	29230.06	0.04	29029.51	−0.01	28651.67	−0.07
$1_{01}-2_{12}$	21823.81	−0.02	21459.82	0.01	21552.87	0.05
$2_{12}-3_{03}$	30718.96	−0.03	29927.14	0.03	30342.24	0.03
$2_{11}-3_{22}$					(37653.03)	−0.39
$2_{02}-3_{13}$	30739.38	−0.03	30018.63	−0.03	30376.47	0.01
$2_{21}-3_{12}$			35574.44	−0.01	36346.16	−0.03
$3_{03}-4_{14}$			(38812.07)	−0.16		

a high barrier to pseudorotation.[16,17] The assignments of the vibrational satellites are discussed more completely in a subsequent section. The rotational constants were determined by a least-squares fit of the transitions and they are listed in Table III with the moments of inertia and the second moments.

The spectrum of the carbon-13 isotopic species, $H_2{}^{13}\overline{COOCH_2O}$, was assigned in natural abundance. The assignment of the species is given in Table IV and the corresponding rotational constants, moments of inertia, and second moments are listed in Table V.

Transitions arising from the normal isotopic species and five partially deuterated species were observed in the sample obtained from the ozonolysis of HDC=CH$_2$. The two hydrogen atoms (designated H$_A$ and H$_B$ in Figure 1) which are bonded to the carbon atom must not be equivalent if the ring is nonplanar. If the ring has C_2 symmetry (as shown in the structure section) two distinct monodeuterated species

$$HD_A\overline{COOCH_2O} \qquad D_BH\overline{COOCH_2O}$$

are expected as well as the three dideuterated species

$$cis\text{-}HD_A\overline{COOCD_BHO} \qquad trans\text{-}HD_A\overline{COOCHD_AO}$$

$$trans\text{-}HD_B\overline{COOCHD_BO}$$

The mechanistic importance of the presence of these six isotopic species in the ozonolysis product of HDC=CH$_2$ is discussed in the last section. The transitions assigned for the deuterated species are listed in Tables IV and VI and the corresponding rotational constants, moments of inertia, and second moments are listed in Table V.

The assignments of all isotopic species and vibrational satellites were confirmed by (1) the agreement with the spectra calculated for a rigid rotor, (2) the observation of correct Stark splittings for all transitions, (3) the intensities of the transitions and the pres-

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(17) E. C. Thomas and V. W. Laurie, *ibid.*, **51**, 4327 (1969).

Table V. Rotational Constants (MHz), Principal Moments of Inertia (μÅ^2), and Second Moments (μÅ^2) for Various Isotopic Species of Ethylene Ozonide

	$H_2{}^{13}COOCH_2O$	HD_ACOOCH_2O	HD_BCOOCH_2O	*cis*- HDCOOCHDO	*trans*- $HD_ACOOCHD_AO$	*trans*- $HD_BCOOCHD_BO$
A	8233.28 ± 0.04	8203.59 ± 0.02	8050.30 ± 0.04	7971.70 ± 0.02	8084.21 ± 0.04	7861.84 ± 0.04
B	7928.25 ± 0.04	7576.80 ± 0.01	7668.24 ± 0.02	7225.88 ± 0.02	7175.87 ± 0.08	7288.19 ± 0.30
C	4530.18 ± 0.02	4418.74 ± 0.01	4500.84 ± 0.02	4340.32 ± 0.01	4260.34 ± 0.02	4413.44 ± 0.04
I_a	61.3821	61.6042	62.7773	63.3963	62.5140	64.2822
I_b	63.7437	66.7005	65.9051	69.9397	70.4272	69.3418
I_c	111.5576	114.3711	112.2848	116.4376	118.6234	114.5083
P_{aa}	56.9596	59.7337	57.7063	61.4905	63.2683	59.7840
P_{bb}	54.5980	54.6374	55.4785	54.9471	55.3551	54.7244
P_{cc}	6.7841	6.9668	8.1988	8.4492	7.1589	9.5579

Table VI. Observed Frequencies (MHz) for Ethylene Ozonide. Isotopic Species

	cis-HDCOOCHDO		*trans*-$HD_ACOOCHD_AO$		*trans*-$HD_BCOOCHD_BO$	
Transition	ν_{obsd}	$\Delta\nu$	ν_{obsd}	$\Delta\nu$	ν_{obsd}	$\Delta\nu$
1_{11}–2_{02}			19775.69	0.01		
1_{11}–2_{20}	33407.54	0.01				
1_{01}–2_{12}			(20865.20)	−0.03		
2_{12}–3_{03}	29213.18	0.02	28804.69	−0.03	29589.99	0.00
2_{11}–3_{22}	36936.04	−0.01	37033.66	0.01	36825.85	0.00
2_{02}–3_{13}	(29354.14)	0.47	29009.11	0.04	29674.18	−0.03
2_{21}–3_{12}	34087.13	−0.01				
3_{13}–4_{04}					38453.65	0.02
3_{03}–4_{14}					(38460.84)	0.11

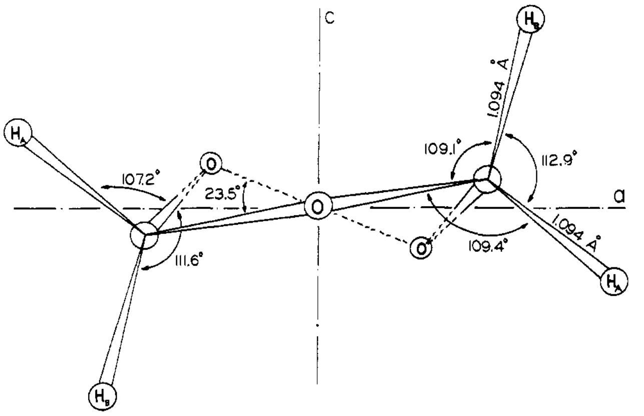

Figure 1. Structure of ethylene ozonide, projection in the *ac* plane.

ence or absence of effects from nuclear spin statistics, and (4) the expected isotope shifts. For example, the transitions of the three dideuterated species were observed within several megahertz of those predicted for the structure which was calculated by using the data from the normal isotopic species, the carbon-13 species, and the two monodeuterated species.

Nuclear Spin Effects. The correct conformation of ethylene ozonide was first indicated by observation of an alternation in the intensity of transitions from rotational levels of opposite symmetry in the normal isotopic species. This alternation in intensity arises in ethylene ozonide only if a C_2 rotational symmetry axis is present; therefore the molecule cannot have C_s symmetry. Although our spectrometer is not designed for accurate intensity measurements, an accuracy of 10–20% can be attained using the method of Esbitt and Wilson.[18] The observed ratio of the intensity of transitions arising from symmetric rotational states to antisymmetric rotational states was 1.70 ± 0.15 after all other intensity factors were considered. This result is consistent with the 5/3 ratio which is expected for a molecule with two pairs of equivalent hydrogen nuclei with nuclear spins of $^1/_2$.

The assignments of the carbon-13 species and the deuterated species were confirmed by a consideration of nuclear spin statistics. No alternation of intensity was observed for the carbon-13 species which is consistent with the absence of a C_2 symmetry axis. The absence of an intensity alternation for these transitions also precludes the possibility that they arise from an excited vibrational state of the normal isotopic species. The monodeuterated species and the cis dideuterated species also do not have a C_2 symmetry axis and no alternation of intensity was observed for them. The two trans dideuterated species have a C_2 symmetry axis with equivalent pairs of deuterium atoms and hydrogen atoms. These species are fermions since deuterium has a nuclear spin of 1; therefore, Fermi-Dirac statistics apply. The observed ratios of intensities of antisymmetric states to symmetric states were consistent with the theoretically expected value of 7/5.

Dipole Moment. The second-order Stark coefficients which were measured for the ground state of ethylene ozonide are listed in Table VII. All the transitions exhibited Stark shifts which were quadratic in the

Table VII. Stark Coefficients (MHz/V^2 cm^2) and Dipole Moment of Ethylene Ozonide

Transition	Obsd[a]	Calcd
1_{10}–2_{21} $\lvert M\rvert = 1$	-0.1812×10^{-4}	-0.1815×10^{-4}
1_{11}–2_{20} $\lvert M\rvert = 1$	0.8323×10^{-5}	0.8339×10^{-5}
1_{01}–2_{12} $\lvert M\rvert = 1$	0.2197×10^{-4}	0.2201×10^{-4}
$\lvert\mu_{total}\rvert = \lvert\mu_b\rvert = 1.09 \pm 0.01$ D		

[a] The estimated experimental uncertainty is 1%.

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

applied electric field. From the Stark effect, the *b* component of the dipole moment was calculated to be 1.09 ± 0.01 D. Since the C_2 axis lies along the *b* principal axis, $\mu_b = \mu_{total}$.

Ring-Puckering Vibration. A five-membered ring with C_2 symmetry has two ring-puckering vibrational modes: a symmetric, twisting vibration and an asymmetric, bending vibration. Since no other low-frequency vibrations are expected to occur, the vibrational satellites observed for ethylene ozonide must arise from either one or both of the ring-puckering modes. The linear variation of rotational constants with vibrational state and the regular decrease in the intensity of successive excited vibrational states suggest that these excited states are successive excitations of a single mode. The presence of nuclear spin statistics provides an unambiguous way to determine the symmetry of this vibrational mode. If the vibrational states are symmetric to the C_2 operation, then the ratio of the intensity of lines arising from antisymmetric rotational states to symmetric rotational states is identical for all excited states of this mode. The symmetry of the vibrational wave function for an asymmetric mode must alternate in successive excited states; therefore, the nuclear spin factors also alternate so the ratio of the population of asymmetric rotational states to symmetric rotational states will be 3/5 for $V = 0$, 5/3 for $V = 1$, etc. This alternation in the ratio of intensities for the 2_{12} and 2_{02} levels was observed through $V = 3$ providing conclusive evidence that these vibrational satellites are successive excited states of the asymmetric ring-bending fundamental. No transitions were observed which could be assigned to the ring-twisting vibration.

Preliminary relative intensity measurements were done to obtain an estimate of the fundamental frequency of the ring-bending mode. Using the Boltzmann formula for $T = 195°K$, a value of $200 \pm 40\ cm^{-1}$ was obtained after accounting for the spin statistics and other intensity factors. Since three successive excitations of this mode were observed, a lower limit of the barrier to pseudorotation can be set at about 500–600 cm^{-1}. With the structural information provided from this work and with a more complete investigation of the energy spacings of the excited states, a more accurate barrier to pseudorotation may be calculated using the theory of Harris, *et al.*[19] Further work along this line is planned.

Structure

Spectral evidence from nuclear spin statistics as well as dipole moment data demonstrate that ethylene ozonide has a C_2 symmetry axis. The possibility of C_{2v} symmetry can be excluded on the basis of the carbon-13 data. The increase in P_{cc} upon substitution of a carbon-13 atom for a carbon-12 atom shows that the carbon atoms do not lie in a plane of symmetry (see Tables III and V). Therefore from the microwave data alone, ethylene ozonide must have C_2 symmetry. The assignments of two conformers of both the monodeuterated and trans dideuterated species further confirm the C_2 symmetry.

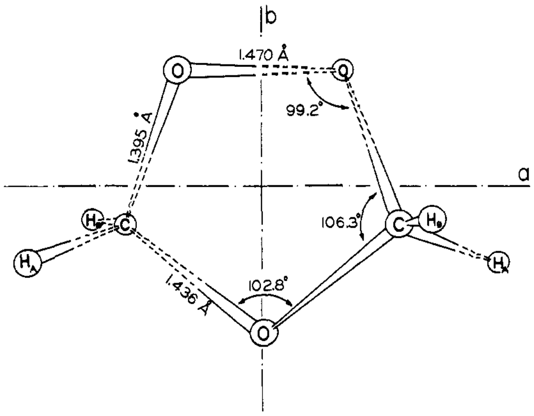

Figure 2. Structure of ethylene ozonide, projection in the *ab* plane.

With the C_2 symmetry requirement eleven independent structural parameters have to be determined. There are several different ways of calculating these parameters with the data from the seven isotopic species plus the first moment equation ($\Sigma m_i b_i = 0$) and the product equation ($\Sigma m_i a_i c_i = 0$). The coordinates of the carbon and the two nonequivalent hydrogens can be obtained by the substitution method.[20] The remaining four coordinates of the ether oxygen (O_e) and the peroxide oxygen (O_p) can be calculated from various combinations of the first moment, cross-product, and three second moment equations. This method would use as data the normal, carbon-13, and monodeuterated species. A complete r_0 structure can be obtained by a least-squares fit of the moments of inertia of all the isotopic species plus the first moment and product equations for the normal species. The latter method has the advantage of including the moments of inertia of all the isotopic species. The coordinates of the atoms determined by such a least-squares fit[21] and the structural parameters calculated from these coordinates are given in Tables VIII and IX, respectively. The structure is illustrated in Figures 1 and 2. The uncertainties in the structural parameters represent the maximum deviations obtained by calculating the structure using the alternative procedures outlined above. Thus, the uncertainties reported give an indication of the extent of zero-point vibrational effects. The large uncertainty in the O–O bond is the result of a mixed r_0-r_s calculation in which a first moment and cross-product equation as well as two

Table VIII. Principal Axis Coordinates (Å) of Ethylene Ozonide[a]

Atom	*a*	*b*	*c*
O_e	0.0	−1.2243	0.0
C	1.1095	−0.3286	0.1711
O_p	0.6784	0.9181	−0.2825
H_A	1.9339	−0.6423	−0.4767
H_B	1.3859	−0.2997	1.2287
C′	−1.1095	−0.3286	−0.1711
O_p'	−0.6784	0.9181	0.2825
H_A'	−1.9339	−0.6423	0.4767
H_B'	−1.3859	−0.2997	−1.2287

[a] Coordinates were calculated based on ^{12}C atomic mass scale.

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(21) We are indebted to Dr. R. Schwendeman for the computer program which was used for the least-squares fit.

Table IX. Structural Parameters of Ethylene Ozonide

Bond lengths, Å		Bond angles, deg		Dihedral angles, deg[a]	
C–H_A	1.094 ± 0.005	COC	102.83 ± 0.44	$C_1O_eC_2O_p$	−16.60 ± 0.40
C–H_B	1.094 ± 0.005	COO	99.23 ± 0.38	$C_1O_pO_pC_2$	−50.24 ± 1.26
C–O_e	1.436 ± 0.006	OCO	106.25 ± 0.64	$O_eCO_pO_p$	41.27 ± 0.96
C–O_p	1.395 ± 0.006	HCH	112.93 ± 0.48	$C_1O_eC_2H_A$	−132.09 ± 0.50
O–O	1.470 ± 0.015	O_eCH_A	109.43 ± 0.34	$C_1O_eC_2H_B$	103.90 ± 0.98
		O_eCH_B	109.08 ± 0.64		

[a] Dihedral angles are defined as in "Molecular Vibrations," E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, Ed., McGraw-Hill, New York, N. Y., 1955, p 60.

second moment equations were used to calculate the oxygen coordinates. All other methods deviated from the reported value of the O–O bond length by no more than 0.008 Å.

The structural parameters of this study agree favorably with the parameters from electron diffraction which were obtained by assuming C_2 symmetry.[10] The electron diffraction value of 1.487 (+0.004 or −0.006) Å for the O–O bond distance is longer than that found in this study; however, this parameter is not well determined in either study. The C–O bond distance of 1.414 (0.0025) Å reported by the ED group for both types of CO bonds lies between the CO_p and CO_e distances found in this study. The bond angles and dihedral angles also agree closely.

The two different CO bond lengths in ethylene ozonide fall close to those expected for CO single bonds. Most CO single bonds are about 1.42 ± 0.02 Å although they range from 1.36 Å in furan[22] to 1.45 Å in trimethylene oxide.[23] The CO_e bond length of 1.436 Å in ethylene ozonide is identical with that reported in ethylene oxide.[24] The CO_p bond length of 1.395 Å is slightly shorter than most other CO bonds reported although it is not as short as that found for furan,[22] a conjugated five-membered ring system. The peroxide O–O bond length of 1.470 Å falls close to that in H_2O_2 (1.475 Å)[25] and to that found in cyclic peroxides and hydroperoxides (1.472–1.482 Å).[26]

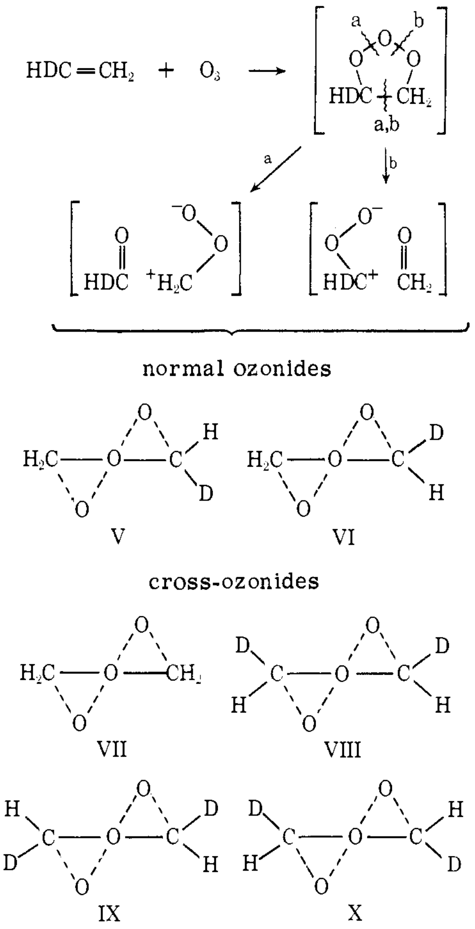
The O_p–O_p dihedral angle of ~50° defined as the angle between the $C_1O_pO_p$ and $C_2O_pO_p$ planes looking down the O–O bond indicates that the peroxide oxygens are twisted quite far out of the $C_1O_eC_2$ plane. In five-membered rings the conformation is determined by a balance of ring strain and torsional forces. Torsional forces tend to stagger the hydrogens of interacting methylene groups. Perhaps in ethylene ozonide where there are no adjacent methylene groups, the strongest torsional forces principally arise from the repulsion of lone electron pairs on adjacent oxygen atoms. This would give rise to the C_2 conformation with a large O_p–O_p dihedral angle and with a high barrier to inversion or pseudorotation.

Mechanistic Aspects

The Criegee mechanism[2] contains no provision for stereochemical effects in the ozonolysis reaction. The ozonolysis of $HDC{=}CH_2$ provides an excellent opportunity to investigate an unsymmetrical 1-alkene where stereochemical effects from bulky groups can be clearly ignored. It therefore provides a way of testing the applicability of the Criegee mechanism for the simplest alkene. The aldehyde interchange mechanism[3] and the modified Criegee mechanism[4] can also be examined for consistency with the results obtained for $HDC{=}CH_2$.

The products predicted by the Criegee mechanism for the ozonolysis of $HDC{=}CH_2$ are depicted in Scheme II. The reaction should produce one normal ozonide, $\overline{HDCOOCH_2O}$, and two cross ozonides, $\overline{H_2COOCH_2O}$ and $\overline{HDCOOCHDO}$. Because of the C_2 symmetry requirement for the ring conformation, the monodeuterated species will consist of two isomers while the dideuterated cross ozonide will consist of three isomers. Assuming that the heterolysis of the molozonide (I) and recombination of the zwitterions and carbonyl

Scheme II



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species are statistical, the six isotopic species should be formed in the ratio $1:1:1:{}^1/_2:{}^1/_4:{}^1/_4$ (V–X).

The microwave spectra of the mixture obtained from the ozonolysis of $HDC{=}CH_2$ has clearly demonstrated that the expected six isotopic species are obtained (Table IV–VI). An extensive attempt was not made to obtain quantitative relative intensity data which are necessary to accurately ascertain the relative quantity of each species. However, the apparent intensities of the observed transitions from rough measurements indicate that there is no gross discrepancy between the actual relative abundances of the various species and the statistical ratios given above. Therefore, the Criegee mechanism is consistent with our present data on the ozonolysis of $HDC{=}CH_2$. Further experiments to test this conclusion are planned. More accurate estimates of the relative amounts of the various isotopic species should be obtained and the effects of ethylene concentration and solvent should also be investigated.

The aldehyde interchange mechanism[3] and the modified Criegee mechanism[4] attempt to take into account the effect of alkene stereochemistry and alkene steric factors in the ozonolysis reaction. These effects are most pronounced for cis and trans alkenes which are substituted with bulky alkyl groups; however, any mechanism of ozonolysis should also be consistent with alkenes where steric effects are negligible. The mechanism proposed by Murray, Youssefyeh, and Story[3] suggests that a pathway exists competing with the Criegee mechanism which involves the reaction between Criegee generated aldehyde and the molozonide (I). The intermediate formed by the reaction of the aldehyde with the molozonide has a preferred conformation which is determined by the stereochemistry of the alkene. The subsequent loss of an aldehyde from the intermediate leads to the final ozonide. In the case of $HDC{=}CH_2$ the reaction products expected by this mechanism are identical with those predicted *via* the Criegee mechanism because alkene steric factors can be ignored. Consequently, the aldehyde interchange mechanism is not inconsistent with our results.

The modified Criegee mechanism,[4] however, does not smoothly correlate with our results. Intrinsic to this proposal is a preferred conformation of the final ozonide. This mechanism assumes a half-chair conformation of the ozonide ring with a twist of the C_1–O_e bond out of the $C_2O_pO_p$ plane. For a rigid ring, the two carbon atoms cannot be equivalent and there can be no steric preference for axial or equatorial sites in the deuterated species of ethylene ozonide. Hence, four monodeuterated species and four dideuterated species are expected. The two deuterium atoms are located axial–equatorial for the two trans isomers and either both axial or both equatorial for the two cis isomers. Our results show that the preferred half-chair conformation for ethylene ozonide has a twist of the O_p–O_p bond out of the $C_1O_eC_2$ plane (Figure 1). The carbon atoms are equivalent resulting in two monodeuterated species and three dideuterated species. Contrary to the Bailey proposal, our results demonstrate that the two deuterium atoms are located axial–equatorial for the cis isomer and either both axial or both equatorial for the two trans isomers.

Although the modified Criegee mechanism by Bailey, *et al.*, does not apply to the case of ethylene ozonide, it would be ill-advised at this time to conclude the mechanism is invalid for other alkenes. It is recognized that the conformation of the ozonide was postulated by Bailey, *et al.*, to account for experimental results obtained for ozonides with bulky substituents. Ethylene ozonide may have a unique conformation. This would be possible if the interactions discussed by Bailey, *et al.*, between carbon substituents and oxygen lone pairs determine the conformation of other ozonide rings. However, a conformation which is different from ethylene ozonide is unlikely if the repulsions between the lone pairs on the adjacent oxygens in the peroxide bond are the principal interactions which determine the most stable conformation. The resolution of this question must await further conformational studies of alkyl-substituted ozonides.

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