Microwave and Mass Spectral Studies of the Ozonolyses of Ethylene, Propylene, and *cis*- and *trans*-2-Butene with Added Oxygen-18 Formaldehyde and Acetaldehyde

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Abstract: The ozonolyses of ethylene, propylene, and *cis*- and *trans*-2-butene in the presence of ^{18}O-enriched-formaldehyde and acetaldehyde were investigated at −95 and −126°. The site and quantity of ^{18}O enrichment were determined by microwave spectroscopy and/or mass spectrometry. Assignments of the microwave spectra of ^{18}O-enriched ethylene and propylene ozonide prepared by an independent synthesis provided a way to observe directly the ^{18}O enrichment at either the peroxy site or the epoxy site in the ozonide ring. These two techniques demonstrated that in all cases aldehydic oxygen appears exclusively at the epoxy site in the ozonide. These results are consistent with the Criegee mechanism and any of its revisions; however, they show that the aldehyde interchange mechanism is unimportant for the ozonolyses of ethylene, propylene, and *cis*- and *trans*-2-butene.

In the past several years, there have been a number of investigations directed at elucidating the formation of ozonides (1,2,4-trioxacyclopentane derivatives) upon the ozonization of an alkene in solution. Three mechanistic proposals have received prominent attention: the Criegee zwitterion mechanism;[1] the syn–anti zwitterion mechanisms,[2-4] and the aldehyde interchange mechanism.[5]

In principle, oxygen-18 tracer studies can distinguish between a zwitterion mechanism and the aldehyde interchange proposal. This can be accomplished by addition of ^{18}O-enriched aldehyde to the ozonolysis reaction, followed by determination of the site of ^{18}O enrichment in the ozonide. As shown in Scheme I

Scheme I
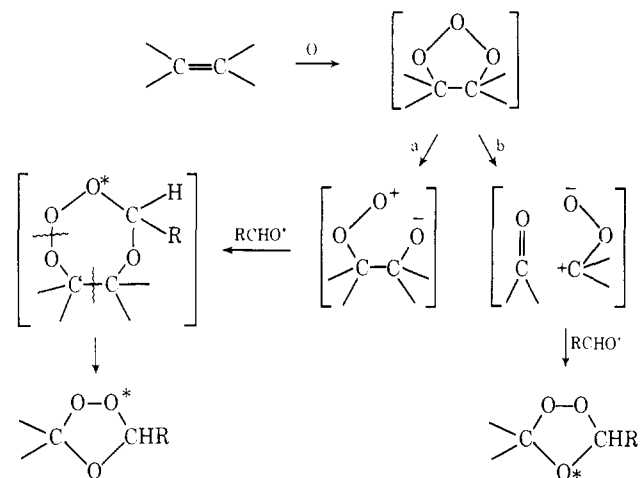
pathway b, the zwitterion proposals[1-4] predict that the labeled oxygen will appear only at the epoxy oxygen in the ozonide ring. For the aldehyde interchange mechanism,[5] following pathway a, the labeled oxygen will

appear exclusively at one of the peroxy sites. In the original discussions of the aldehyde interchange mechanism, it was proposed that mechanisms a and b may occur as competing pathways to ozonide formation.

Several investigations have been conducted to determine the site of ^{18}O enrichment in the ozonide products. In a study of the ozonolysis of several phenylethylenes in the presence of benzaldehyde-^{18}O, it was concluded that the ^{18}O label incorporated exclusively at the epoxy bridge.[6] Mass spectrometry was used to determine the site of ^{18}O enrichment in the ozonide ring.[7] Similar studies of aliphatic alkenes, *viz.*, *cis*- and *trans*-diisopropylethylene with labeled acetaldehyde or isobutyraldehyde[8,9] and ethylidenecyclohexane with labeled propionaldehyde,[10] have indicated that significant amounts of the label are incorporated at both the peroxy and epoxy sites. The site of enrichment in the ozonides was determined by mass spectrometry of the ozonides or of the alcohols obtained by reduction of the ozonides.[8-10] These results suggested that the route to ozonide formation for aliphatic alkenes may be different from that for aromatic alkenes. However, a recent communication concerned with the ozonolysis of ethylene in the presence of ^{18}O-labeled formaldehyde reported ^{18}O enrichment only at the epoxy site.[11] In this study, the position of ^{18}O labeling was determined by microwave spectroscopy and it was concluded that at least 90% of the aldehydic oxygen which incorporated into the ozonide ring went to the epoxy site.

In this paper, we report further investigations of the reaction of ethylene with enriched formaldehyde and also with enriched acetaldehyde. In addition, the ozonolyses of propylene and *cis*- and *trans*-2-butene in the presence of enriched formaldehyde and acetaldehyde were investigated. The site of ^{18}O enrichment in the products of these reactions (ethylene ozonide, propylene ozonide, *cis*-2-butene ozonide, and/or *trans*-2-butene

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(2) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *J. Amer. Chem. Soc.*, **90**, 1822 (1968).
(3) R. P. Lattimer, C. W. Gillies, and R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **95**, 348 (1973).
(4) R. P. Lattimer, R. L. Kuczkowski, and C. W. Gillies, *J. Amer. Chem. Soc.*, **96**, 348 (1974).
(5) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *J. Amer. Chem. Soc.*, **88**, 3144 (1966); R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **89**, 2429 (1967).

(6) S. Fliszár and J. Carles, *J. Amer. Chem. Soc.*, **91**, 2637 (1969).
(7) J. Castonguay, M. Bertrand, J. Carles, S. Fliszár, and Y. Rousseau, *Can. J. Chem.*, **47**, 919 (1969).
(8) P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *J. Amer. Chem. Soc.*, **90**, 1907 (1968).
(9) R. W. Murray and R. Hagen, *J. Org. Chem.*, **36**, 1103 (1971).
(10) P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, *J. Amer. Chem. Soc.*, **93**, 3042 (1971).
(11) C. W. Gillies and R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **94**, 7609 (1972).

ozonide) was determined by microwave spectroscopy and/or mass spectrometry. Microwave spectroscopy is an excellent nondestructive technique for determining the site of enrichment because the spectrum of each different isotopic species in a mixture is distinct and unique. This technique was used to determine the site of enrichment for the ethylene and propylene ozonides, since their microwave spectra have been thoroughly investigated previously.[4,12] In order to establish unambiguously the precise frequencies for the rotational transitions of the various isotopic species of ethylene and propylene ozonide, an independent synthesis of these ozonides was carried out using ^{18}O-enriched ozone. The details of the synthesis are reported here as well as the spectra of ^{18}O-labeled ethylene ozonide. The spectra of ^{18}O-enriched propylene ozonide are reported elsewhere.[4] Although microwave spectroscopy proved to be an excellent technique for qualitative analysis of the site of enrichment in ethylene and propylene ozonide, the type of spectrometer available in our laboratory is not suitable for obtaining very precise quantitative data on the amount of enrichment. Also, the microwave spectra of the 2-butene ozonides have not been analyzed in sufficient detail to be useful for tracer studies. Mass spectrometry was therefore used to support the site of enrichment found by microwave spectroscopy and to determine quantitatively the amount of enrichment. Combination of the results of these two techniques showed unambiguously where the ^{18}O label occurs in the ozonide products and the extent of enrichment. These data are discussed in the last section in terms of the results expected for the zwitterion mechanisms vs. the aldehyde interchange mechanism.

Experimental Section

Synthesis of Randomly Labeled ^{18}O Ozonides. ^{18}O-Labeled ethylene and propylene ozonides were prepared by ozonizing excess propylene (C. P. Grade, Matheson Co.) in difluorodichloromethane (Freon-12, C. P. Grade, Matheson Co.) at $-126°$ with ^{18}O-labeled ozone. The labeled ozone was synthesized from ^{18}O-labeled oxygen gas (54% enriched, Bio-Rad Laboratories) by electrical discharge in a static ozone generator. The ozonides were separated from the solvent by low temperature vacuum distillation.[12] Ethylene and 2-butene ozonides (obtained as cross-ozonides from propylene) were separated from propylene ozonide by gas chromatography as described previously.[3,4]

The apparatus used for the synthesis of ^{18}O-labeled ozonides is illustrated in Figure 1 and was connected to a vacuum line via two manifolds. Vessel A contained the ^{18}O-enriched oxygen gas. The ozone generator B had the approximate dimensions of the static generator described by Griggs and Kaye.[13] The ozonolysis vessel C consisted of an outer tube (1.2 cm i.d.) approximately 22 cm long and an inner tube (0.6 cm i.d.) which extended to within 0.5 cm of the bottom of the outer tube. The sequence followed during a run entailed first charging the ozonolysis vessel with about 2 ml of solvent and 4 mmol of propylene. Next, 1 mmol of oxygen gas was expanded into the ozone generator and a 12-kV potential was applied across the inner and outer walls. The discharge was continued at $-196°$ until all of the oxygen was converted to ozone. Then the ozone was warmed up (behind Plexiglas shielding) and carried into the ozonolysis vessel with a stream of dry nitrogen gas. After the ozonolysis, the ozonides were separated from the solvent by warming up the reaction vessel and passing the mixture through a distillation train as described previously.[12]

Synthesis of ^{18}O-Labeled Aldehydes. ^{18}O-Enriched formaldehyde and acetaldehyde were prepared by exchanging the unenriched aldehydes with ^{18}O-enriched water (unnormalized, Miles Laboratories, Inc.). Monomeric formaldehyde was prepared by heating
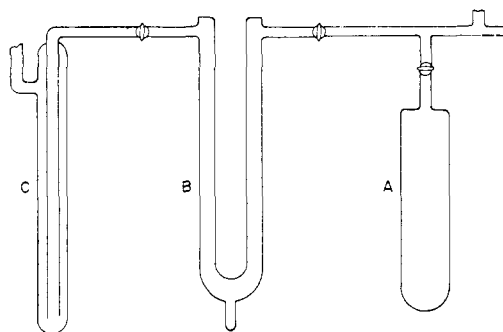

Figure 1. Static ozone generator and ozonolysis cell.

paraformaldehyde in vacuo and distilling the gas through a $-95°$ trap; monomeric formaldehyde was collected at $-196°$. The formaldehyde thus prepared was bubbled through ^{18}O-enriched water at room temperature using dry nitrogen as a carrier gas, and the resulting mixture was allowed to stand overnight. Water and formaldehyde were separated using gas chromatography. A 6 ft 60-80 mesh Carbosieve B, $^{1}/_{8}$ in. i.d. glass column (Supelco, Inc.) was employed under the following conditions: injector, 175°; column, 125°; detector, 175°; and He flow rate, 75 ml/min. To avoid polymerization of the eluted monomeric formaldehyde, copper tubing leading from the exit port to two U-shaped traps was heated to 120°. The formaldehyde was collected in one trap at $-196°$ and the water was collected in the other trap at $-196°$. Acetaldehyde and enriched water were mixed (using a vacuum line for transfer of samples) and kept overnight at room temperature. In some preparations the enriched acetaldehyde was separated from the water by vacuum distillation through a $-78°$ trap. Better recovery of aldehyde was obtained using gas chromatographic separation; the Carbosieve B column described above was employed at column temperatures of 175-180° and similar He flow rates. The enrichments of the ^{18}O-labeled aldehydes were determined by mass spectrometry.

Synthesis of ^{18}O-Labeled Ozonides with Added Aldehydes. The ^{18}O-labeled ozonides were prepared by ozonizing solutions of the alkene (ethylene, propylene, and cis- and trans-2-butene were C. P. Grade from Matheson Co.) in the presence of ^{18}O-enriched formaldehyde or acetaldehyde. The alkene and aldehyde concentrations, the ^{18}O aldehyde enrichments, solvent, reaction temperature, and relative ozonide yields for each ozonolysis are listed in Tables I and II. The ozonolysis procedure described in ref 4 was used in this study. Polymerization of monomeric formaldehyde on glass surfaces in the ozonolysis vessel was minimized by condensing the gas directly on top of the frozen solvent. A similar procedure was followed with acetaldehyde. The ozonides were separated from the solvent by low temperature vacuum distillation[12] employing fast warm-up procedures.[14] Gas chromatographic techniques were used to separate ethylene, propylene, and 2-butene ozonides.[4] All ozonide samples were stored at liquid nitrogen temperature to avoid decomposition.[12]

Microwave Spectra of Ozonides. A conventional 80-kHz Stark-modulated microwave spectrometer[15] was used to obtain spectra of the ozonides. All rotational transitions were measured to an accuracy of ±0.10 MHz. Weak transitions were traced out using a recorder. The sample cell was cooled to Dry Ice temperature to obtain spectra of ethylene ozonide, while temperatures intermediate between room temperature and Dry Ice temperature were used for propylene ozonide.

Mass Spectra of Ozonides. An AEI MS-902 mass spectrometer was used to obtain the mass spectra of all ozonide samples. The compounds were introduced through the gas inlet into the water-cooled source maintained between 50 and 80°. At source temperatures above 80°, the mass spectra of the ozonides exhibited different patterns, which could be attributed to ozonide decomposition products. These results indicate that the mass spectra observed at source temperatures between 50 and 80° arise from the ozonides and not their decomposition products. Ionizing voltages of 45 V for ethylene ozonide and 70 V for propylene and 2-butene ozonides were used.

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

(13) M. Griggs and S. Kaye, *Rev. Sci. Instrum.*, **36**, 1685 (1968).

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

(15) R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **90**, 1705 (1968).

Table I. Ozonolyses of Ethylene, Propylene, and 2-Butene with Added Formaldehyde-*18-O*

Alkene concn, M	Aldehyde concn, M	Aldehyde, % ^{18}O enrichment	Solvent	Reaction temp, °C	Ozonide	Rel %, Ozonide[a]	% total ozonide-*18-O* enrichment	% epoxy ozonide-*18-O* enrichment
Ethylene								
0.74	1.1	53.2 ± 1.5	Methyl chloride	−78	Ethylene	100	46.7 ± 1.2[b]	46.5 ± 1.3
1.1	0.69	72.6 ± 0.9	Isobutane	−95	Ethylene	100	4.1 ± 0.3	4.2 ± 0.4
1.1	1.5	62.7 ± 0.4	Isobutane	−126	Ethylene	100	9.0 ± 0.5	9.4 ± 0.6
Propylene								
0.82	2.5	72.4 ± 1.5	Isobutane	−95	Propylene	85	35.0 ± 0.5	34.5 ± 1.1
					Ethylene	14	49.7 ± 0.7	49.8 ± 2.0
					2-Butene	1	ND[c]	ND
1.5	2.1	62.7 ± 0.4	Isobutane	−126	Propylene	90	31.8 ± 0.5	32.0 ± 0.7
					Ethylene	9	ND	ND[e]
					2-Butene	1	ND	ND
trans-2-Butene								
1.2	0.58	83.2 ± 0.3	Isobutane	−95	2-Butene	87	0.1 ± 0.9	0.0 ± 1.0
					Propylene[d]	13	78.9 ± 1.0	78.1 ± 1.0
1.0	1.0	72.4 ± 1.5	Isobutane	−126	2-Butene	81	0.2 ± 0.4	0.0 ± 0.6
					Propylene[d]	19	65.9 ± 0.5	65.3 ± 0.7
cis-2-Butene								
1.2	1.9	83.2 ± 0.3	Isobutane	−126	2-Butene	73	0.2 ± 0.3	0.0 ± 0.7
					Propylene[d]	27	82.0 ± 0.4	82.6 ± 1.1

[a] The relative amounts of the ozonides were estimated from the ozonide peak areas of the gas chromatograms. [b] The high % total ozonide-^{18}O enrichment relative to the enrichment of the added formaldehyde is probably a result of the low solubility of ethylene in methyl chloride at −78°. On the basis of ozonide yields reported previously,[12] the effective ethylene concentration is estimated to be 0.20 *M*. [c] ND = not determined. [d] Discussed in Discussion and Conclusions section. [e] Epoxy-^{18}O enrichment (but no peroxy-^{18}O) was observed in the microwave spectrum.

**Table II.** Ozonolyses of Ethylene, Propylene, and 2-Butene with Added Acetaldehyde-*18-O*

Alkene concn, M	Aldehyde concn, M	Aldehyde, % ^{18}O enrichment	Solvent	Reaction temp, °C	Ozonide	Relative % ozonide[a]	% total ozonide-*18-O* enrichment	% epoxy ozonide-*18-O* enrichment
Ethylene								
1.4	0.70	70.1 ± 1.9	Isobutane	−95	Ethylene	91	ND[b]	ND[e]
					Propylene	9	ND	ND[f]
1.5	0.70	76.0 ± 0.4	Isobutane	−126	Ethylene	85	0.3 ± 0.4	0.0 ± 0.6
					Propylene[d]	15	70.3 ± 0.7	69.7 ± 0.6
Propylene								
0.71	2.1	79.0 ± 0.8	Isobutane	−95	Propylene	80	10.3 ± 0.4	10.4 ± 0.3
					2-Butene[c]	11	76.7 ± 2.1	76.0 ± 3.6
					Ethylene	9	ND	ND[e]
0.59	1.2	70.1 ± 1.9	Isobutane	−95	Propylene	84	3.8 ± 0.4	3.2 ± 0.3
					2-Butene	7	ND	ND
					Ethylene	9	ND	ND[e]
0.55	0.86	67.7 ± 0.5	Isobutane	−126	Propylene	ND	2.6 ± 0.1	2.6 ± 0.2
					2-Butene	ND	ND	ND
					Ethylene	ND	ND	ND[e]
trans-2-Butene								
0.61	1.6	79.0 ± 0.8	Isobutane	−95	*cis*-2-Butene	35	47.2 ± 0.8	45.6 ± 3.6
					trans-2-Butene	65	45.6 ± 0.5	45.9 ± 0.7
cis-2-Butene								
0.48	1.3	67.7 ± 0.5	Isobutane	−126	2-Butene[c]	100	22.0 ± 0.4	22.1 ± 0.9

[a] The relative amounts of the ozonides were estimated from the ozonide peak area of the gas chromatograms. [b] ND = not determined. [c] The cis and trans isomers were not separated. [d] Discussed in Discussion and Conclusions section. [e] No epoxy-^{18}O or peroxy-^{18}O enrichment was observed in the microwave spectrum. [f] Epoxy-^{18}O enrichment (but no peroxy-^{18}O) was observed in the microwave spectrum.

Results

Microwave Spectra of ^{18}O-Enriched Ozonides. The samples of ethylene and propylene ozonide obtained from the ozonolysis of propylene with ^{18}O-enriched ozone were used to assign the ^{18}O microwave spectra of these compounds. The assignments of ^{18}O-labeled propylene ozonide species have been reported previously.[4] These include all the singly substituted species required for this investigation.

$$\overbrace{CH_3CHOOCH_2{}^{18}O}$$

a

$$\overbrace{CH_3CHO^{18}OCH_2O}$$

b

$$\overbrace{CH_3CH^{18}OOCH_2O}$$

c
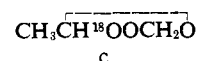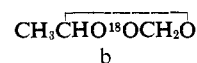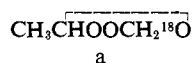
The spectra of the ^{18}O-labeled ethylene ozonide species were assigned with the aid of predictions based on the structural parameters previously reported for the molecule.[12] The assignments were complicated by large rotations in the principal axes upon isotopic substitution at the oxygen positions. In the normal isotopic species, the total dipole moment lies along the C_2

symmetry axis (b principal axis). Upon ^{18}O substitution at the epoxy position, the C_2 symmetry axis is preserved; however, it becomes the a principal axis. Therefore, a-type dipole transitions were observed. ^{18}O-Substitution at the peroxy position rotates the b principal axis by almost 45° so that both a- and b-type transitions were observed for the

$$H_2C\overline{^{18}OOCH_2O}$$
d
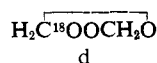
species. The frequencies of rotational transitions assigned to the peroxy ^{18}O species, d, and the epoxy ^{18}O species
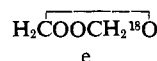
$$H_2\overline{COOCH_2{}^{18}O}$$
e

are listed in Table III.[16] The rotational constants,

Table III. Observed Frequencies (MHz) for the Epoxy and Peroxy ^{18}O Species of Ethylene Ozonide

Transition	$H_2\overline{COOCH_2{}^{18}O}$		$H_2C\overline{^{18}OOCH_2O}$	
	ν_{obsd}	$\Delta\nu^a$	ν_{obsd}	$\Delta\nu$
$1_{11}-2_{02}$			21253.59	0.06
$1_{11}-2_{12}$	21284.39	0.06	21274.36	0.03
$1_{01}-2_{12}$			21586.36	0.00
$1_{01}-2_{02}$	21491.43	0.01	21565.56	−0.01
$1_{01}-2_{21}$			28911.41	−0.03
$1_{10}-2_{11}$	28100.16	0.04	27975.33	−0.01
$1_{11}-2_{20}$			35321.23	0.03
$1_{01}-2_{20}$	35577.26	−0.10	35633.25	0.01
$2_{12}-3_{13}$	30324.99	0.01		
$2_{02}-3_{03}$	30334.71	−0.03		
$2_{21}-3_{22}$	37038.29	−0.06	36937.19	−0.06

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

determined by least-squares fitting of the frequencies, and the moments of inertia are given in Table IV.

Table IV. Rotational Constants (MHz) and Principal Moments of Inertia (μA^2) for the Epoxy and Peroxy ^{18}O Species of Ethylene Ozonide

	$H_2\overline{COOCH_2{}^{18}O}$	$H_2C\overline{^{18}OOCH_2O}$
A	8094.14 ± 0.16^a	8143.49 ± 0.02
B	7877.01 ± 0.03	7831.46 ± 0.02
C	4469.11 ± 0.02	4480.96 ± 0.01
I_a	62.4373	62.0589
I_b	64.1584	64.5315
I_c	113.0820	112.7830

^{a} The uncertainty is twice the standard deviation obtained from the least-squares fit.

These assignments were confirmed by (1) the agreement with the spectra calculated for a rigid rotor, (2) the observation of correct second-order Stark splittings for all transitions, (3) the presence of an intensity alternation arising from the effect of nuclear spin statistics for the epoxy ^{18}O species which corroborates its C_2 symmetry axis, and (4) the lack of an intensity alternation arising from the effect of nuclear spin statistics for the peroxy ^{18}O species in agreement with the absence of a C_2 sym-

(16) The assignment of the epoxy ^{18}O species in this study confirms the assignment of the same species obtained by a different synthetic route that is reported in ref 11.

metry axis for this species. These assignments were further confirmed by assignments of the spectra arising from the doubly and triply substituted ^{18}O species of ethylene ozonide. This eliminates the remote possibility that the singly substituted species were misassigned to these species.[17]

$$H_2C\overline{^{18}OOCH_2{}^{18}O}$$
f

$$H_2C\overline{^{18}O^{18}OCH_2O}$$
g

$$H_2C\overline{^{18}O^{18}OCH_2{}^{18}O}$$
h
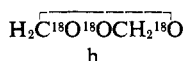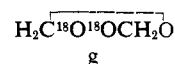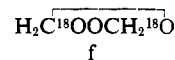
Microwave Spectra of ^{18}O-Labeled Ozonides Produced from Added Aldehydes-^{18}O. The microwave spectra of all samples of ethylene and propylene ozonide obtained from the added aldehyde-^{18}O reactions (see Tables I and II) were examined for ^{18}O enrichment at the epoxy and peroxy positions in the ozonide ring. Rotational transitions arising from the normal isotopic species were observed in all the samples of ethylene and propylene ozonide listed in Tables I and II. Microwave transitions from the epoxy ^{18}O propylene ozonide species, a, were observed in all the samples of propylene ozonide. Epoxy ^{18}O transitions of ethylene ozonide, e, were observed in all ethylene ozonide samples except those derived from the ozonolysis of ethylene with acetaldehyde-^{18}O and propylene with acetaldehyde-^{18}O. Rotational transitions of the peroxy ^{18}O species of ethylene and propylene ozonide were not seen in any of the samples listed in Tables I and II. Careful searches for known transitions of these species (see Table III and ref 4 for the observed transition frequencies) were made using recorder traces to maximize the sensitivity of the spectrometer. The results of these searches were negative. In most cases, it was estimated that 1–2% peroxy ^{18}O enrichment could have been detected in these searches.

Mass Spectra of ^{18}O-Enriched Ozonides. The mass spectra of ethylene, propylene, and 2-butene ozonides are shown in Figures 2–4. The general fragmentation scheme proposed by Castonguay, et al.,[7] to account for the mass spectra of a number of aromatic and aliphatic ozonides is consistent with the spectra obtained in this study. Fragmentation of the ozonide ring may occur by several different paths in this scheme. Cleavage of the two $C-O_p$ bonds (O_p designates the peroxy oxygen) gives rise to the $[R_1R_2COCR_3R_4]^+$ ion. The second path involves cleavage of the O_p-O_p bond and one $C-O_e$ bond (O_e designates the epoxy oxygen); if the ozonide is unsymmetrical, four ions may be produced: $[R_1R_2-CO_p]^+$ and $[R_3R_4C(-O)_2]^+$ as well as $[R_1R_2C(-O)_2]^+$ and $[R_3R_4CO_p]^+$. Cleavage of a $C-O_p$ bond and a $C-O_e$ bond leads to ions having the same m/e as the ions formed by the second path: $[R_1R_2CO_e]^+$ and $[R_3R_4-COO]^+$ as well as $[R_1R_2COO]^+$ and $[R_3R_4CO_e]^+$.

Operating at low resolution, several of the important ions in the mass spectra of ethylene and propylene ozonides are not completely resolved. These ions in-

(17) The rotational constants (MHz) determined by a least-squares fit of the frequencies are as follows: 8026.57 ± 0.02, 7588.67 ± 0.01, and 4366.09 ± 0.01 for f; 7825.73 ± 0.32, 7793.92 ± 0.08, and 4383.34 ± 0.05 for g; and 7825.94 ± 0.09, 7440.34 ± 0.05, and 4269.37 ± 0.03 for h.
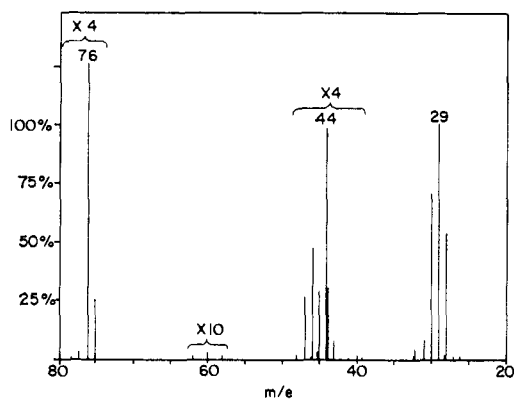
Figure 2. Mass spectrum of ethylene ozonide. (×4 indicates mass peaks are increased by that factor on illustration.)
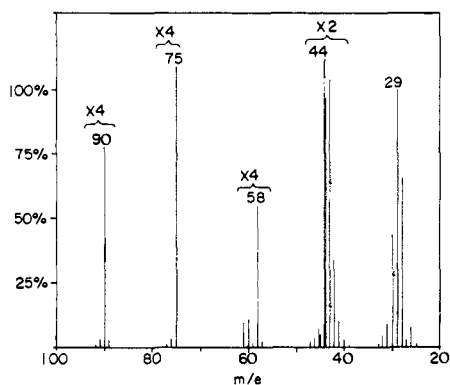

Figure 4. Mass spectrum of 2-butene ozonide (~60% trans, 40% cis).

Figure 3. Mass spectrum of propylene ozonide.

Table V. Relative Intensities of Mass Peaks Pertinent to ^{18}O Analysis for Several Unenriched Ozonides

	$H_2C\overset{O-O}{\underset{O}{\diagup}}CH_2$		$H_2C\overset{O-O}{\underset{O}{\diagup}}CHCH_3$		$CH_3CH\overset{O-O}{\underset{O}{\diagup}}CHCH_3{}^a$
m/e	Rel intensity	m/e	Rel intensity	m/e	Rel intensity
78	0.7	92	0.5	106	0.7
77	2.5	91	2.5	105	4.1
76	100	90	72.5	104	79.0
75	18.4	89	2.6	103	3.1
74	0.0	88	0.0	102	0.0
46.031	0.2	77	0.6	91	0.8
46.005	36.0	76	2.5	90	4.3
45	22.3	75	100	89	100
44.026	75.5	74	0.0	88	0.0
43.990	25.8	73	0.0	87	0.0
43	7.0	61	8.5	74	0.1
42	0.0	60.046	0.2	73	1.1
		60.021	9.8	72	25.4
		59	1.7	71	0.8
		58	50.1	70	0.0
		57	2.2		
		56	0.0		

^{a} ~60% trans, 40% cis.

clude: (1) for ethylene ozonide, $[H_2CO_2]^+$ at 46.005 and $[H_2C^{18}OCH_2]^+$ at 46.031 as well as $[CO_2]^+$ at 43.990 and $[H_2C^{16}OCH_2]^+$ at 44.026; and (2) for propylene ozonide, $[CH_3CHO_2]^+$ at 60.021 and $[CH_3CH^{18}OCH_2]^+$ at 60.046. All of these ions were resolved when the AEI MS-902 mass spectrometer was operated at higher resolution.

The total ^{18}O enrichment was obtained from the molecular ion for all three ozonides; the M − 15 ions of propylene and 2-butene ozonides (corresponding to loss of a methyl group) were used also to determine total ^{18}O enrichment. For all three ozonides, the $[R_1HCOCHR_2]^+$ ions were observed and used to determine the epoxy ^{18}O enrichment. The per cent ^{18}O enrichment is given by

$$\left[\frac{\dfrac{I(M+2)}{I(M)} - \dfrac{I_0(M+2)}{I_0(M)}}{1 + \dfrac{I(M+2)}{I(M)} - \dfrac{I_0(M+2)}{I_0(M)}} \right] \times 100$$

$I(M+2)$ and $I(M)$ are the peak intensities of the labeled and unlabeled ions, respectively, in the ^{18}O-enriched sample. The ratio, $I_0(M+2)/I_0(M)$, subtracts out the intensity contributions of naturally occurring heavy isotopes. The experimentally determined ratios obtained from the spectra of the unenriched samples are in agreement with the calculated values. The intensities of the mass peaks for the unenriched ozonides in the regions used for the ^{18}O analysis are listed in Table V.

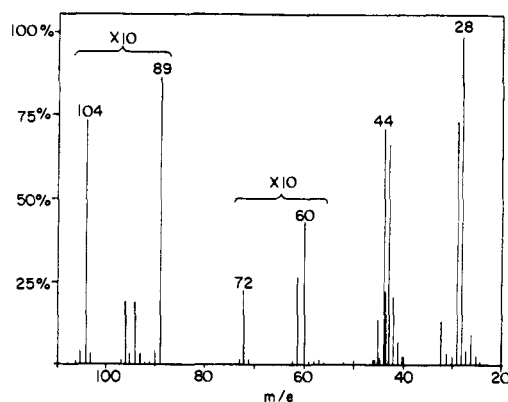The equation above was used to calculate the total

and the epoxy ^{18}O enrichments for the ozonide samples obtained from the added aldehyde ozonolyses. These enrichments are reported in Tables I and II; each enrichment is the mean obtained from five or more spectra of the identical sample. The standard errors were calculated at the 90% confidence level and represent the standard deviation of the enrichments determined from the five or more spectra of each sample. As shown in Tables I and II, the total ^{18}O enrichment is equal to the epoxy ^{18}O enrichment within the standard error of each value. This is true for all the ozonolyses of ethylene, propylene, and 2-butene listed in these tables.

Discussion and Conclusions

The results of this work are important to two aspects of the ozonolysis reaction. These include the techniques used for determining the site of ^{18}O enrichment in an ozonide and the mechanism of ozonide formation.

With regard to the first issue, all previous investigations[6-10] have used mass spectrometry of either the ozonides or derivatives of the ozonides to determine the site of enrichment. It was not possible in any of these

investigations to study directly ^{18}O enrichment at the peroxy site because unique mass peaks containing only the peroxy oxygens could not be found. In the present work, the microwave spectra of epoxy and peroxy ^{18}O-enriched species of ethylene and propylene ozonides were assigned with samples prepared by an independent synthesis. These microwave assignments provided a sensitive way to determine unambiguously the presence or absence of the ^{18}O-enriched species in the ozonide products of the added aldehyde ozonolyses. The fact that only epoxy ^{18}O enrichment was observed in the ozonide products from these reactions shows that the aldehydic oxygen incorporates exclusively at the epoxy position in the ozonide ring.

These microwave results also complement the mass spectral data on ethylene, propylene, and the 2-butene ozonides, as well as previous mass spectral studies of ozonides. As shown in Tables I and II, the total ^{18}O enrichment is equal to the ^{18}O enrichment in the epoxy fragment $[HR_1COCR_2H]^+$, within the standard error in all cases. This demonstrates that none of the aldehydic oxygen is incorporated at the peroxy site if it is assumed that the epoxy ion is formed by cleavage of the two C-O$_p$ bonds without any mixing of peroxy and epoxy oxygen atoms. This assumption is obviously corroborated by the microwave analysis, since no microwave transitions arising from peroxy ^{18}O species were observed. Support for this assumption can also be extended to the earlier mass spectral study of the phenyl-substituted ozonides, where an identical procedure was used to determine the site of enrichment and similar fragmentation patterns were observed.[6,7] Presumably the same holds true for the report involving cis- and trans-diisopropylethylene ozonide, although the complete fragmentation patterns were not reported in this case.[9]

The ^{18}O enrichment results obtained in this study are pertinent to recent discussions of the mechanism of ozonolysis. As discussed in the introduction, the ^{18}O-labeled aldehyde incorporations at the epoxy site for ethylene, propylene, cis-2-butene, and trans-2-butene ozonides are consistent with the Criegee mechanism[1] or any of its revisions[2-4] (see Scheme I, pathway b). The aldehyde interchange mechanism[5] (see Scheme I, pathway a) or any other mechanism which predicts peroxy aldehydic incorporation in the ozonide products[18] is clearly inconsistent with the results of this investigation. Therefore, these simple aliphatic alkenes incorporate aldehydic oxygen exclusively at the epoxy site in the ozonide just as Fliszár and Carles have found for several phenylethylenes[6] but in contrast to cis- and trans-diisopropylethylene[8,9] and ethylidenecyclohexane,[10] where aldehydic oxygen was found at both the peroxy and the epoxy sites.

Before arriving at the conclusion that the aldehyde interchange proposal is unimportant for ethylene, propylene, and cis- and trans-2-butene, reaction conditions and procedures were examined in order to provide a careful test of the mechanism. Solvents, concentrations, and temperatures were chosen similar to those in studies where appreciable peroxy incorporation was reported.[8-10] In those studies n-pentane was the solvent, while in this study isobutane was used in all reactions except one. Alkene and aldehyde concentrations

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

as well as ^{18}O enrichments are similar or higher than in previous ^{18}O studies. Although it might be argued that formaldehyde and acetaldehyde are associated in solution, thereby lowering their effective concentrations, sizable amounts of aldehyde insertion are observed (see relative per cent ozonide in Tables I and II), indicating that this effect is not important. It was also apparently unimportant in the study of ^{18}O-labeled acetaldehyde with trans-diisopropylethylene,[8] where quite high epoxy ^{18}O incorporation was observed.

Temperature may be a critical factor in testing the aldehyde interchange mechanism; it has been proposed that this pathway will be more important at lower temperatures where a primary ozonide intermediate will have sufficient lifetime to allow reaction with aldehyde.[5,8] For this reason, the added aldehyde ozonolyses were carried out at −95 and −126°. It seems likely that ethylene and trans-2-butene primary ozonides are stable species at −126°; previous investigations[19-21] have shown that these primary ozonides decompose at temperatures higher than −100°. Although propylene and cis-2-butene primary ozonides do not appear to be as stable, both species decompose in the −130 to −100° range,[20,21] which indicates that an intermediate derived from either one of these primary ozonides should have sufficient lifetime to react with aldehyde.

In summary, we believe a careful test of the aldehyde interchange proposal was conducted for ethylene, propylene, and cis- and trans-2-butene and we conclude that it is an unimportant pathway for these aliphatic alkenes. It is difficult at this point to explain why these simple aliphatic alkenes behave differently than cis- and trans-diisopropylethylene and ethylidenecyclohexane, where aldehydic oxygen is observed at the peroxy and the epoxy sites. If the aldehyde interchange mechanism is important for these bulkier alkenes, it might imply a greater stability for their primary ozonides. However, this does not seem to be a very satisfactory rationale. In the case of cis-diisopropylethylene, it can be argued that its primary ozonide is less stable than the primary ozonide of cis-2-butene, since there is less steric interaction in the latter.[22] Hence, the aldehyde interchange proposal should be less likely to compete, contrary to observations. While these kinds of comparative arguments do not invalidate use of the aldehyde interchange proposal to rationalize ^{18}O incorporation at both peroxy and epoxy sites in cases where it is observed, they do suggest difficulty with the premise that primary ozonide stability is an important factor in the mechanism.[24] This matter will need further in-

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(22) Although cis-2-butene primary ozonide decomposes in the range −130 to −100 (see ref 19–21), there is no evidence for the existence of cis-di-tert-butylethylene primary ozonide at −110°.[23] This suggests that at −120° (the lowest temperature used for the ozonolysis of cis-diisopropylethylene with isobutyraldehyde-$^{18}O^9$), the primary ozonide from cis-diisopropylethylene is no more stable and probably less so than cis-2-butene primary ozonide.

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(24) A similar difficulty arises from the study of cis- and trans-diisopropylethylene with isobutyraldehyde-^{18}O.[9] Similar amounts of aldehydic oxygen incorporated at the peroxy site and the epoxy site in the ozonides from both alkene isomers, although the primary ozonide of the trans isomer is undoubtedly more stable than the cis isomer.

vestigation before being satisfactorily resolved.[25] Additional ^{18}O-labeling experiments would be desirable, especially with alkenes having medium and large substituents before speculating further on reasons for the differing behavior.

A final point can be noted with regard to the ozonides labeled *d* in Tables I and II. For these cases, a small loss of [18]O enrichment between added aldehyde and final ozonide is observed which may seem inconsistent with the Criegee[1] and other zwitterion mechanisms.[2-4] This effect appears to be real; it is not due to a propylene impurity in the alkene and it also is not a result of impurities in the aldehyde or solvent. Perhaps this can be accounted for by an isotope effect involving the aldehyde. Considering the low reaction temperatures and the low molecular weight of the aldehydes, the expected magnitude of an oxygen isotope effect is not in-

consistent with the small loss of enrichment observed. Other possible explanations are decompositions of ozonide or other reaction side products such as chain peroxides during the ozonolysis to produce an aldehyde. The latter reaction has already been proposed to account for aldehydes formed during ozonolysis of a number of alkenes.[26,27] Thus, any aldehyde produced from such decompositions will be mostly unenriched, and this will tend to decrease the overall enrichment of the aldehyde in solution.

(25) Another possibility is that exchange of [18]O between labeled aldehyde and "Criegee" zwitterion might occur by a mechanism which becomes more important for alkenes with bulkier electron-donating groups. Such a mechanism has been described by Fliszár and Carles (ref 18).

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Thermal Isomerization of 1,2-Dialkenylcyclopropanes[1]

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Abstract: The ctc, ctt, and ttt isomers of 1,2-di(prop-1'-enyl)cyclopropane isomerize at 165° at comparable rates to give, respectively, *cis,cis,cis*-di(prop-1'-enyl)cyclopropane, *trans*-6,7-dimethylcyclohepta-1,4-diene, and *cis*-6,7-dimethylcyclohepta-1,4-diene. These highly stereoselective and stereospecific reactions are interpreted in terms of a common mechanism involving a one-center epimerization as the rate-limiting step, followed by rapid Cope rearrangement of the *trans,cis,trans*- and *cis,cis,trans*-dipropenylcyclopropanes.

Among the archetypal thermal isomerizations, the *cis*-divinylcyclopropane (**1**) to 1,4-cycloheptadiene (**2**) reaction occupies a prominent interstice between
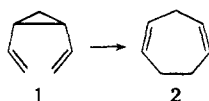
the electrocyclic conversion of 1,3,5-hexatriene to 1,3-cyclohexadiene and the degenerate [3,3] sigmatropic rearrangement of 1,5-hexadiene.

Since the initial demonstration of this process by Vogel in 1960,[2-5] and the first studies exploiting this reaction to demonstrate fluxional isomerism by Doering and Roth,[6,7] numerous examples have been investigated.

One major theme has been development of the fluxional isomerism field for the homotropylidene, semibullvalene, bullvalene, and related systems.[8] A second has been synthesis, detection, and characterization of *cis*-1,2-dialkenylcyclopropane systems unable to rearrange degenerately;[9-20] many cases are now documented, including *cis*-1,2-divinylcyclopropane itself.[16] Some *cis*-1,2-dialkenylcyclopropanes undergo Cope rearrange-

(1) This work was supported by grants from the National Science Foundation, Hoffmann-La Roche, Inc., and the Swedish Natural Science Research Council.

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