Ozonolysis of *cis*- and *trans*-1,2-Difluoroethylene. Mechanism of Fluorinated Epoxide, Ozonide, and Cyclopropane Formation

Charles W. Gillies[†]

Contribution from the Mallinckrodt Laboratories, Harvard University, Cambridge, Massachusetts 02138, and Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. *Received April 13, 1977.*

Abstract: The reaction of ozone with *cis*- and *trans*-1,2-difluoroethylene was investigated in isobutane, methyl chloride, and dichlorodifluoromethane solvents. Deuterium labeling experiments show that there is no carbon scrambling in epoxide formation. These results are consistent with a partial cleavage pathway. They do not eliminate a complete cleavage pathway in which the terminal oxygen of fluorocarbonyl oxide attacks the olefin. Additional deuterium results indicate that if the fluorinated cyclopropane is formed via a carbene mechanism the carbene does not come from epoxide decomposition. Orbital symmetry arguments are used to rationalize the cis/trans ozonide ratio of 10/90 which was determined to be approximately identical for both olefin isomers in the three solvents studied. Solvent effects on product yields are related to solvent polarity and discussed in view of the mechanism of ozonolysis.

The reaction of ozone with simple hydrocarbon olefins in solution has been investigated extensively.[1] In contrast, the ozonolyses of olefins with halogen substitutents at the double bond have received far less attention.[2-7] Simple hydrocarbons such as ethylene, propylene, and 2-butene yield predominantly ozonides.[8] A syn-anti carbonyl oxide mechanism was developed to rationalize ozonide formation.[9,10] Preliminary studies of vinyl fluoride[4] and 1,1-difluoroethylene[11] find that ozonides are among the major products under normal ozonolysis conditions.

Studies of the ozonolyses of perfluoroethylene[2] and 1,2-difluoroethylene[3] show that the chemistry differs markedly from simple hydrocarbon olefins and from ethylenes substituted with fluorines on one side of the double bond. Perfluoroethylene gives perfluoroethylene oxide and carbonyl fluoride as the major volatile products; smaller amounts of perfluorocyclopropane and perfluoroethylene ozonide are also produced in the reaction. Analogous products are formed from the reaction of 1,2-difluoroethylene with ozone in methyl chloride and isobutane solvent. *cis*-1,2-Difluoroethylene oxide, formyl fluoride, and *cis*- and *trans*-1,2-difluoroethylene ozonide are the predominant volatile products from both the cis and trans olefin isomer. A trace amount of *cis*-1,2,3-trifluorocyclopropane is also obtained from the cis olefin in methyl chloride solvent.

Little is known about the reaction mechanism for the ozonolysis of ethylenes substituted with fluorines on both sides of the double bond. Gozzo and Camaggi suggested that perfluoroethylene oxide is formed via a complete cleavage pathway in which a peroxidic intermediate, CF_2O_2, reacts with perfluoroethylene to give epoxide.[2] Perfluoroethylene ozonide is produced via a Criegee pathway and difluorocarbene addition to perfluoroethylene yields perfluorocyclopropane.[2] Recent results on the ozonolysis of *cis*-1,2-difluoroethylene in the presence of formaldehyde or ethylene argue strongly for the intermediacy of the fluorocarbonyl oxide, $HFCO_2$, and are consistent with the Criegee mechanism.[4] Stereochemical results concerning epoxide formation in the ozonolysis of *cis*- and *trans*-1,2-difluoroethylene[3] have not distinguished between Gozzo and Camaggi's mechanism and a partial cleavage pathway proposed to account for epoxide products in the ozonolysis of sterically hindered 1-olefins.[12]

This paper provides a full account of the reaction of ozone with *cis*- and *trans*-1,2-difluoroethylene which was reported in a preliminary communication.[3] In addition deuterium labeling experiments are described which rule out certain reaction pathways in epoxide and cyclopropane formation. Also, the effect of solvent on product yield is related to solvent polarity and discussed in terms of the syn-anti carbonyl oxide mechanism.[9,10]

Experimental Section

Instrumental. A conventional 100-kHz Stark-modulated spectrometer and a Hewlett-Packard 8460A spectrometer were used to investigate the microwave spectra of the products. Details of the microwave studies of *cis*-1,2,3-trifluorocyclopropane[13] and *cis*-1,2-difluoroethylene oxide[14] have been reported elsewhere. Isotopic compositions of the deuterated samples of *cis*-1,2-difluoroethylene oxide (obtained from the ozonolysis of CHF═CHF + CDF═CDF) were determined quantitatively by relative intensity measurements using the Hewlett-Packard spectrometer.[15] The following transitions were used for the intensity measurements: 1_{01}–2_{11} (d_0 and d_1), 1_{10}–2_{20} (d_0, d_1, and d_2), 1_{11}–2_{21} (d_0, d_1, and d_2), 3_{13}–4_{04} (d_0, d_1, and d_2), and 2_{02}–3_{13} (d_0 and d_2). The measurements were performed at 24 °C with a sample pressure of 12 mTorr and a constant detector crystal current of 50 μA. The determination of the intensities consisted of first measuring the baseline voltages at the transition frequencies three times. Then the sample was introduced into the cell and the signal voltages were measured three times, varying the sequence each time. Using a fresh sample each time, this entire procedure was repeated twice and the results were averaged for all the measurements. Systematic errors resulting from changes in sample composition and total pressure as well as changes in baseline voltages should be avoided with this procedure.

The same procedure described above was used to estimate the isotopic composition of *cis*-1,2-3-trifluorocyclopropane obtained from the reaction of ozone with *cis*-1,2-difluoroethylene-d_2 in the presence of *cis*-1,2-difluoroethylene oxide. Only the d_2 and d_3 species were observed. Microwave relative intensity measurements were performed using the following transitions: $J = 2$–3 for d_3 species and 2_{20}–3_{30} for the d_2 species.[13] Cell pressure was 17 mTorr at 24 °C and the crystal current was maintained at a constant value of 40 μA.

Mass spectra were recorded with an AEI MS-9 spectrometer by introducing the sample through the evaporative inlet directly into the source. The following ionizing voltages and source temperatures were used for the products: 70 V at 160 °C for *cis*-1,2-difluoroethylene oxide, 40 V at 180 °C for *cis*-1,2,3-trifluorocyclopropane, and 40 V at 70 °C for the cis and trans isomers of 1,2-difluoroethylene ozonide.

The infrared spectra were recorded with a Perkin-Elmer 457 infrared spectrometer using a 10-cm path length gas cell. The sodium chloride windows were secured to the cell with Viton O-rings. This arrangement permitted frequent refinishing of the windows which was

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[†] Address correspondence to Department of Chemistry, Rensselaer Polytechnic Institute, Troy, N.Y. 12181.

necessary owing to the appearance of impurity bands in the blank spectra.

Varian XL-100, HA-100, and T-60 spectrometers were used to obtain the ^{1}H and ^{19}F NMR spectra.

Materials. *cis-* and *trans-*1,2-difluoroethylene (PCR, Inc.) were purified by preparative gas chromatography. A 10 ft × $^3/_8$ in. stainless steel column packed with 15% diisodecyl phthalate on 60/80 mesh Chromosorb P was used at a column temperature of 25 °C and flow rate of 45 mL He/min. The isomeric purity of the olefins was estimated to be better than 99.5% by gas chromatography. Purified samples of *cis-* and *trans-*1,2-difluoroethylene were stored in Pyrex gas bulbs in the dark for periods of 3 months without any detectable change in isomeric content. CP grade isobutane, methyl chloride, and Freon 12 were obtained from Matheson Co. and used without further purification.

Deuterated samples of *cis-* and *trans-*1,2-difluoroethylene were prepared after the method described by Craig and Overend.[16] Highly deuterated samples were made by rotating a sealed 150-mL Pyrex cylinder containing 10 mL of ~2.0 M NaOD and 6 mmol of olefin in an oil bath maintained at 90 °C for 48 h. The 2.0 M NaOD was obtained by dissolving ~0.5 g of Na in 10 mL of deuterium oxide (99.9% enriched in deuterium from Bio-Rad, Inc.). Olefin recovery consisted of trap-to-trap distillation at −95 °C. Gas chromatographic analysis of the deuterated olefin indicated no change in isomeric purity. Partially deuterated olefin was prepared in a similar fashion; however, the 2.0 M NaOD was obtained by dissolving ~0.5 g of Na in 4 mL of H_2O and 6 mL of D_2O.

The enrichments of the highly deuterated olefin sample were determined by mass spectrometry. Spectra were recorded at 20 V to avoid fragmentation of the molecular ion. These samples were used in the isotopic labeling experiments described below.

The sample outlet of a Welsback Model T-408 ozonator was used to obtain a few percent ozone in an oxygen stream. The oxygen gas was dried prior to entry into the ozonator by flowing it through a trap cooled to dry ice temperature.

Ozonolysis of *cis-* and *trans-*1,2-Difluoroethylene. Olefin (3 mmol) was ozonized in 3 mL of solvent at dry ice temperature to 60% completion using flow rates of 0.26 ± 0.01 mmol of O_3/min. Ozone flow rates were determined by iodimetric titration immediately before and after the ozonolyses. During the course of each reaction the exit gases from the ozonolysis vessel were sampled by diverting the flow into 1-L Pyrex bulbs. Immediately after each ozonolysis, the contents of the reaction vessel were trap-to-trap distilled at −95 °C employing fast warm-up procedures.[17] After the distillation, the −95 °C fraction and the −196 °C fraction were stored at liquid nitrogen temperature. The identical distillation procedure was followed for the exit gas samples. A viscous residue remained in the reaction flask from the ozonolyses of both olefin isomers. Although no attempt was made to characterize this material, it does slowly react with aqueous potassium iodide indicating that it is probably peroxidic in nature.

The −95 °C fractions from the reaction vessel were further purified by gas chromatography using a 12 ft by $^1/_4$ in. Teflon column packed with 10% halocarbon oil on 40–60 mesh Chromosorb T at 23 °C. All samples were introduced into the gas chromatograph by gas injection[18] and the eluted components were collected in traps cooled to −196 °C. Relative elution times for the 12-ft Teflon column under conditions described above at flow rates of 45 mL helium/min were 1.0 for formyl fluoride, 2.2 for *cis-*1,2-difluoroethylene oxide, 3.7 and 4.6 for the *trans-* and *cis-*1,2-difluoroethylene ozonide isomers, respectively, and 7.2 for *cis-*1,2,3-trifluorocyclopropane. Final purification of the products included a second pass through the gas chromatograph. The yields of *cis-*1,2-difluoroethylene oxide and the ozonide isomers were determined manometrically. The yield of *cis-*1,2,3-trifluorocyclopropane, a trace product in several of the ozonolyses, was obtained by using an MKS Baratron pressure meter Type 77 to measure the pressure in a known volume. Nothing collected in the −95 °C trap from the exit gas samples.

Gas-phase infrared spectra of the −196 °C fractions from the reaction vessel and the exit gases demonstrated that both of these fractions contain solvent, olefin, and formyl fluoride. Since formyl fluoride is the only product which passes the −95 °C trap and none of the other products found in the −95 °C trap are swept out of the reaction vessel by the oxygen–ozone gas stream, the product yields determined for the −95 °C trap are total product yields. These yields are listed in Table I for the cis and trans olefin in Freon 12, methyl chloride, and isobutane.

Table I. Product Yields from Ozonolysis of *cis-* and *trans-*1,2-Difluoroethylene

	% yield[a]		
	Freon 12	Methyl chloride	Isobutane
Cis olefin			
*cis-*CHFCHFO	15	14	8
HFCOOCHFO[b]	30	5	26
(Cis/trans ratio)[c]	(10/90)	(8/92)	(9/91)
*cis-*CHFCHFCHF	0.4	0.5	*d*
Trans olefin			
*cis-*CHFCHFO	4	5	3
HFCOOCHFO	14	3	14
(Cis/trans ratio)[c]	(9/91)	(11/89)	(6/94)
*cis-*CHFCHFCHF	*d*	*d*	*d*

[a] Percent yields are average values from several reactions and are based upon total ozone consumed. [b] Percent yield of both isomers. [c] Isomer ratios are average values obtained from several reactions using cut and weigh technique for the gas chromatographic peaks. [d] Not detected by gas chromatography.

In order to determine whether olefin isomerization occurred during the reaction, the −196 °C fractions were further analyzed by gas chromatography. The olefin isomers and formyl fluoride were separated from the solvent using a 17 ft by $^1/_4$ in. Teflon column packed with 10% halocarbon oil on 40–60 mesh Chromosorb T at ~23 °C with a flow rate of 25 mL He/min. Relative elution times under these conditions are 1.0 for formyl fluoride, 1.13 for *cis-*CHFCHF, 1.21 for *trans-*CHFCHF, and ~1.5 for the various solvents. The formyl fluoride and olefin fraction was trapped at −196 °C and passed through the 10-ft diisodecyl phthalate column used for the olefin purification described earlier.[19] At a flow rate of 25 mL He/min, formyl fluoride and the olefin isomers are resolved and it was estimated that the isomeric purity of the olefin remained the same at >99.5%.

Ozonolysis of *cis-*1,2-Difluoroethylene in the Absence of Oxygen. In order to determine the effects of oxygen in the ozone–oxygen gas stream upon the reaction products, *cis-*1,2-difluoroethylene was ozonized with a nitrogen carrier gas via a method described previously.[10] Oxygen gas (0.76 mmol) was converted to ozone in a static generator at liquid nitrogen temperature. A nitrogen gas stream at a flow rate of ~100 mL/min carried the ozone into approximately 3 mL of dichlorodifluoromethane containing 2.7 mmol olefin. Oxygen impurities in the nitrogen carrier gas and from the oxygen to ozone conversion amount to an upper limit of 0.03 mmol. The reaction products obtained by this method were identical with those reported in Table I. Product yields also were similar to the values reported in Table I. Therefore, epoxide and ozonide formation must result in part if not completely by reaction of the olefin with ozone.

Ozonolysis of d_0–d_2 Mixtures of 1,2-Difluoroethylene. Equal volumes of unenriched and highly deuterated olefin (isomerically pure by gas chromatography) were dissolved in a solvent and ozonized using the same conditions and procedures described above for the normal olefin ozonolyses. Identical procedures were also used for product purification. The *cis-*1,2-difluoroethylene oxide samples obtained from these ozonolyses were examined by microwave spectroscopy and mass spectrometry to determine the deuterium distributions. The sites of deuterium enrichment in the *cis-*1,2,3-trifluorocyclopropane samples were identified by microwave spectroscopy. The deuterium enrichments of the olefin samples are listed in Table II. The reported uncertainties in the deuterium enrichments are the errors propagated from the mass spectral analysis of the highly deuterated olefin and from the gas manometer measurements of the d_0 and d_2 olefin pressures.

Ozonolysis of *cis-*1,2-Difluoroethylene-d_2 Plus *cis-*1,2-Difluoroethylene-d_0 Oxide. *cis-*1,2-Difluoroethylene-d_2 (2.6 mmol) was ozonized in the presence of 1.3 mmol of *cis-*1,2-difluoroethylene-d_0 oxide in CF_2Cl_2 solvent at dry ice temperature to 60% completion using an ozone flow rate of 0.29 mmol O_3/min. Purification of the

Table II. Ozonolyses of Highly Deuterated + Unenriched 1,2-Difluoroethylene

Olefin isomer	Solvent	Olefin enrichment			Epoxide enrichment—mass spectrum			Epoxide enrichment—microwave		
		% d_0	% d_1	% d_2	% d_0	% d_1	% d_2	% d_0	% d_1	% d_2
Cis	CF_2Cl_2	50.5 ± 1.1	1.45 ± 0.51	48.1 ± 1.2	49.5 ± 0.5	1.65 ± 0.45	48.8 ± 0.5	47.9 ± 5.1	1.04 ± 0.67	51.1 ± 5.1
Cis	CH_3Cl	49.3 ± 1.1	1.47 ± 0.51	49.2 ± 1.2	50.0 ± 0.4	2.28 ± 0.20	47.8 ± 0.3	46.8 ± 6.1	0.79 ± 0.65	52.4 ± 6.1
Cis	Isobutane	50.1 ± 1.1	1.45 ± 0.50	48.4 ± 1.2	47.3 ± 0.7	2.59 ± 0.34	50.2 ± 0.7	46.4 ± 4.8	1.92 ± 0.84	51.6 ± 4.8
Trans	CF_2Cl_2	50.3 ± 1.2	1.46 ± 0.52	48.2 ± 1.2	49.6 ± 0.6	1.92 ± 0.41	48.4 ± 0.4	48.1 ± 5.3	1.51 ± 0.72	50.3 ± 5.2
Trans	CH_3Cl	51.1 ± 1.0	1.32 ± 0.48	47.5 ± 1.1	50.2 ± 0.4	0.92 ± 0.25	48.8 ± 0.3	47.4 ± 4.5	1.21 ± 0.79	51.4 ± 4.5
Trans	Isobutane	48.5 ± 1.1	1.50 ± 0.53	50.0 ± 1.2	49.2 ± 0.7	1.11 ± 0.51	49.7 ± 0.7	46.2 ± 6.0	1.81 ± 0.84	52.0 ± 6.0

products from this reaction was accomplished in the same way described above for the normal ozonolyses. The isotopic enrichment of the olefin was 96.5 ± 1.5% d_2, 2.9 ± 1.0% d_1, and $\leq 0.6 \pm 1.0\%$ d_0 as determined by mass spectrometry. Microwave spectroscopy was used to locate the site and measure the enrichment of the deuterium label in *cis*-1,2,3-trifluorocyclopropane.

Product Characterization

Formyl fluoride was identified by its known gas-phase infrared[20] and microwave spectrum.[21]

cis-1,2-Difluoroethylene oxide was characterized by IR, NMR, microwave, and mass spectral means as well as by an independent synthesis. The prominent features of the gas-phase infrared spectrum were bands at 3582, 3090, 1460 (doublet with strong shoulder to high frequency), 1337 (triplet), 1278 (doublet), complex patterns at ~1050–1170 and ~840, 637 (triplet), 562, and 430 cm^{-1}. Impurities in the spectrum included small quantities of formyl fluoride and unidentified bands which remained after the cell was pumped out and increased in intensity with continued cell use. The band at 1460 cm^{-1} is consistent with the ring-breathing mode that is characteristic of fluorinated cyclopropanes and perfluoroethylene oxide.[22-24] Most of the other bands compare well with the infrared spectrum of *cis*-1,2-difluorocyclopropane.[23]

The ^{19}F and ^{1}H NMR spectra of *cis*-1,2-difluoroethylene oxide were identical and consisted of six transitions located centrosymmetrically at 29.0, 41.1, and 69.3 Hz from the center. The chemical shifts in acetone-d_6 for ^{19}F and ^{1}H are 165 ($CFCl_3$ external reference) and 5.81 ppm (Me_4Si internal reference), respectively. Analysis of the spectrum as an AA′XX′ spin system yielded $J_{HF(gem)} = 85.9$, $J_{HF(trans)} = -3.8$, $J_{FF} = 40.3$, and $J_{HH} \approx 0$ Hz. This assignment reproduced the observed spectrum and yielded calculated transition intensities in satisfactory agreement with the observed values. Since $J_{HF(gem)}$ cannot be distinguished from $J_{HF(trans)}$ nor J_{HH} from J_{FF} and the relative signs of J_{HH} and J_{FF} cannot be determined,[26] the coupling constant assignment was made by comparison with those found in related molecules.

Gas chromatography indicated that only one epoxide isomer was present in the sample from the ozonolysis reactions. The ^{19}F and ^{1}H NMR spectra confirmed the isomeric purity by demonstrating the presence of only one AA′XX′ species. An investigation of the microwave spectrum of this single isomer yielded an unambiguous configurational assignment. The microwave results prove that the epoxide is the cis isomer.[14]

The mass spectral fragmentation of the epoxide is similar to perfluoroethylene oxide.[27] The main peaks observed for *cis*-1,2-difluoroethylene oxide are [*m/e* (rel intensity, assigned ion)] 80 (25.3, $C_2H_2F_2O^+$), 60 (7.3, C_2HFO^+), 52 (11.1), 51 (17.7, CHF_2^+), 49 (22.8), 48 (6.2, $CHFO^+$), 47 (15.2, CFO^+), 44 (11.1, C_2HF^+), 33 (100, CH_2F^+), 32 (87.5, CHF^+), 31 (31.4, CF^+), 29 (100, HCO^+), and 28 (76.7, CO^+). This ion assignment is consistent with the mass spectrum of a sample containing approximately equal amounts of d_0 and d_2 isotopic species.[28] The observed spectrum is [*m/e* (rel intensity)] 82 (14.8), 80 (15.6), 61 (10.2), 60 (9.4), 52 (40.6), 51 (43.8), 49 (25.0), 48 (10.0), 47 (30.50, 45 (9.4) 44 (10.2), 35 (99.2), 34 (12.5), 33 (100), 32 (64.1), 31 (93.8), 30 (99.6), 29 (99.4), and 28 (22.4).

The photooxidation of *trans*-1,2-difluoroethylene using the method described by Craig[24] for the synthesis of perfluoroethylene oxide from perfluoroethylene provided an independent route to the cis epoxide. *cis*-1,2-Difluoroethylene oxide was formed in low yield and identified by its microwave spectrum.

In a preliminary communication, *cis*-1,2,3-trifluorocyclopropane was identified by its symmetric top microwave spectrum and electric dipole moment.[3] Recently, a more complete microwave study of this compound was reported which provides additional data in support of its identity.[13] The mass spectrum confirms the microwave work and correlates well with the mass spectrum of 1,1,2,2-tetrafluorocyclopropane.[22] Principal peaks of *cis*-1,2,3-trifluorocyclopropane are [*m/e* (rel intensity, assigned ion)] 96 (12.9, $C_3H_3F_3^+$), 95 (100, $C_3H_2F_3^+$), 77 (9.4, $C_3H_3F_2^+$), 76 (4.1, $C_3H_2F_2^+$), 75 (15.2, $C_3HF_2^+$), 69 (21.1, CF_3^+), 64 (10.5, $C_2H_2F_2^+$), 58 (10.5, $C_3H_3F^+$), 57 (8.2, $C_3H_2F^+$), 56 (3.5, C_3HF^+), 51 (97.1, CHF_2^+), 46 (27.5, $C_2H_3F^+$), 45 (14.6, $C_2H_2F^+$), 44 (33.9, C_2HF^+), 43 (30.5, C_2F^+), 41 (4.1), 33 (14.6, CH_2F^+), 32 (9.9, CHF^+), 31 (19.3, CF^+). This ion assignment is supported by the mass spectrum of a deuterated sample [*m/e* rel intensity)]:[29] 99 (5.0), 98 (7.6), 97 (108), 96 (106), 95 (100), 80 (5.7), 79 (5.6), 78 (6.6), 77 (7.0), 76 (14.2), 75 (11.6), 69 (39.8), 66 (8.7), 65 (7.7), 64 (9.3), 59 (4.9), 58 (5.0), 57 (5.9), 52 (107), 51 (113), 49 (14.4), 48 (14.9), 47 (22.2), 46 (21.8), 45 (13.9), 44 (10.1), 35 (9.4), 34 (9.4), 33 (22.5), 32 (7.4), 31 (35.0).

The cis and trans isomers of 1,2-difluoroethylene ozonide were characterized by infrared and nuclear magnetic resonance spectroscopy and mass spectrometry. Infrared spectra of the trans ozonide were recorded at pressures of 4–90 Torr and the following bands were observed: 3023 (w), 2118 (vw), 1976 (vw), 1270 (w), 1219 (w), 1351 (m), 1113 (s), 1089 (vs), and 1048 cm^{-1} (m). The cis isomer is formed in much lower yield and a maximum of 5 Torr vapor pressure was available to record its spectrum. Bands were observed at 3018 (w), 1782 (vw), 1356 (m), 1263 (w), 1119 (vs), 1090 (s), 1037 (s), and 816 cm^{-1} (vw). Both isomers slowly decompose to formyl fluoride in the cell; however, spectra run immediately after introduction into the cell lacked any carbonyl stretching absorption. The observed spectra of both isomers agree qualitatively with gas-phase infrared spectra of other simple ozonides.[4,30]

Mass spectra of both ozonide isomers were recorded at source temperatures of 70–130 °C. Over this temperature interval the ions and their intensities exhibited no significant changes. Since the observed spectra of these fluorinated ozonides are similar to other simple ozonide mass spectra where it has been shown that the spectra do not arise from thermal decomposition,[10] it is likely that the mass spectra observed here result from the ozonides. The mass spectrum of the trans isomer consisted of the following ions [*m/e* (rel intensity, assigned ion)]: 112 (23.6, $C_2H_2F_2O_3^+$), 85 (1.2, $^{13}CH_2F_2O_2^+$), 84 (72.9, $CH_2F_2O_2^+$),[31] 80 (3.5, $C_2H_2F_2O^+$), 69 (30.6, CF_3^+), 65 (5.6?,[13] $CHFO_2^+$ plus unknown ion), 64 (100, $CHFO_2^+$), 51 (21.5?), 49 (16.0?), 48 (90.3, $CHFO^+$), 47 (58.3, CFO^+), 46 (3.5, $CH_2O_2^+$), 45 (22.2, CHO_2^+), 44 (85.4, CO_2^+), 29 (73.6, CHO^+), and 28 (30.6, CO^+). The mass spectrum of the cis isomer shows no major differences from the trans isomer.

The ^{19}F and ^{1}H NMR spectra of the isomer assigned by GLC to *trans*-1,2-difluoroethylene ozonide were identical and consisted of ten transitions located centrosymmetrically at 33.7, 34.7, 40.7, 48.3, and 49.7 Hz from the center. The chemical shifts in $CDCl_3$ for ^{19}F and ^{1}H are 83.7 ($CFCl_3$ internal reference) and 6.59 ppm (Me_4Si internal reference), respectively. Treated as an AA′XX′ spin system, analysis of either the AA′ or XX′ ten-line spectrum yields $J_{HF(gem)} = 82.0$, $J_{HF(cis)} = -0.5$, $J_{FF} = 15.3$, and $J_{HH} = 1.1$ Hz. This assignment reproduces the observed spectra and yields calculated line intensities in agreement with the observed values. As discussed for *cis*-1,2-difluoroethylene oxide, the coupling constant assignment must be made by comparison with related molecules.

Preliminary NMR work on the cis ozonide indicated that the spectrum is more complex and lacks the symmetry of an AA′XX′ spectrum. Without a complete spectral analysis it is not possible to obtain the chemical shift of this isomer for correlation with the trans ozonide chemical shift.

Microwave Spectra of Deuterated Epoxide Samples. The microwave spectra of *cis*-1,2-difluoroethylene oxide samples obtained from the ozonolyses of highly deuterated and unenriched olefin were examined in order to determine the site and extent of deuterium enrichment. Rotational transitions arising from the normal isotopic species, $\overline{\mathrm{CHFCHFO}}$, the monodeuterated species, $\overline{\mathrm{CHFCDFO}}$, and the dideuterated species, $\overline{\mathrm{CDFCHFO}}$, were observed for all the cases reported in Table I. The enrichment of the epoxide samples was determined quantitatively by microwave intensity measurements. Table II lists the isotopic composition of the epoxide samples determined by microwave techniques in columns 6–8. The percentage of each isotope was obtained from the observed peak signal voltages.[32] As discussed in the Experimental Section, average values of the signal voltages were obtained for each transition used in the analysis. Intensity ratios, I_S (d_1/d_2, d_1/d_0, and d_2/d_0) and their standard deviations σ_S were calculated from these signal voltages for each transition. Then the average values, I_A, of the I_S values of all transitions and the corresponding standard deviation σ_A were determined. The percent composition of the samples was calculated from I_A intensity ratios. In all cases, σ_A exceeded σ_S; consequently σ_A was used to determine the error in the percent composition given in Table II.

A number of approximations in the conversion of the peak signal voltages to percent composition were made which contribute to the error. It was assumed that the lines were free of saturation effects. Scharpen, Rauskolb, and Tolman found power saturation to be small in the case of deuterated propenes.[15] Differences in the vibrational partition function between the isotopic species were also neglected. Although no complete vibrational analysis of this molecule has been published, by analogy to related molecules,[22,23] the lowest vibration is around 200 cm^{-1} and probably arises from a C–F bending mode. Hence, there should not be a large difference in the energy of this mode for the various isotopic species. Possible differences in the magnitude of the total dipole moment between the isotopic species were not considered. Muenter and Laurie have found differences of 0.01 D or less between the hydrogen and deuterium species for a number of simple molecules.[33] It is likely that this difference is small for the various epoxide isotopic species. Other factors which were included in this analysis are rotational constants, line frequencies, dipole moment matrix elements,[34] and absorption line half-widths.

Mass Spectra of Deuterated Epoxide Samples. The deuterium enrichment of the *cis*-1,2-difluoroethylene oxide samples was determined by mass spectrometry to serve as an independent check on the microwave intensity measurements. The percent enrichments are given by

$$\{I(i)/[I(d_0) + I(d_1) + I(d_2)]\}100$$

where $I(i)$ refer to intensities of the normal, monodeuterated, and dideuterated epoxide molecular ions. $I(d_1)$ and $I(d_2)$ are the ion intensities corrected for the naturally occurring heavy isotopes. At an ionizing voltage of 70 V, it is estimated that the intensity of the M − 1 ion in the mass spectrum of the normal isotopic species is about 0.25% of the intensity of the molecular ion. The effects of the M − 1 peaks arising from the deuterated molecular ions should be small also and were not included in the analysis.

Table II gives the enrichments of the epoxide samples. Each enrichment is the mean obtained from at least ten or more spectra of the same sample. The reported uncertainty is the standard deviation of the enrichment determined from all the spectra of each sample. As shown in Table II, there is satisfactory agreement in the epoxide enrichments obtained from the microwave intensity measurements and the mass spectral data. Furthermore, there is little significant difference between the olefin enrichment and epoxide enrichment for all the ozonolyses studied.

Microwave Spectrum of *cis*-1,2,3-Trifluorocyclopropane. The sample of *cis*-1,2,3-trifluorocyclopropane produced from the reaction of ozone with *cis*-1,2-difluoroethylene-d_2 plus *cis*-1,2-difluoroethylene-d_0 oxide was examined for deuterium enrichment by microwave spectroscopy. The microwave spectra of all deuterium isotopic species are known;[13] however, only the d_3 and d_2 species were observed in this sample. The ratio of the concentration of these two species was estimated to be 0.038 ± 0.023 by microwave relative intensity measurements. The intensity ratio and standard deviation reported here correspond to the average value of the signal voltages, I_S, and its standard deviation, σ_S, since only one transition for each isotopic species was used. Besides this difference the identical procedure and approximations described for the epoxide microwave intensity work were used here.

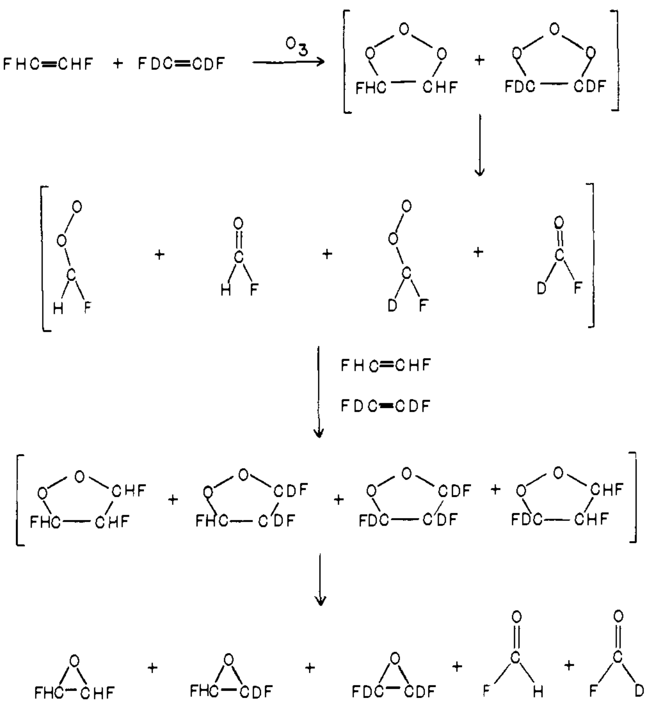
Discussion and Conclusions

Epoxide Formation. It was found that the formation of only the cis epoxide from the ozonolysis of *cis*- and *trans*-1,2-difluoroethylene in methyl chloride and isobutane solvent was consistent with partial cleavage and complete cleavage pathways.[3] As shown in Table I, the present work extends these observations to dichlorodifluoromethane solvent where again only the cis epoxide is obtained from both olefin isomers. It is unlikely that the experimental procedures used in the reaction and separation are affecting these results. Gas chromatographic analysis of the olefins recovered from the ozonolyses show that there is no olefin isomerization. In the trans olefin ozonolyses, the cis epoxide yield is a factor of 5–10 larger than the amount estimated from the upper limit of 0.5% cis olefin impurity.

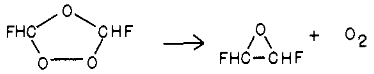
It also does not seem likely that the trans olefin produces trans epoxide which then isomerizes to cis epoxide either in the reaction vessel or during the separation. The reaction temperatures are low and the trans epoxide as well as epoxide cleavage products such as 2,2-difluoroacetaldehyde and fluoroacetyl fluoride could not be identified. Furthermore, microwave spectra of the −95 °C fractions from the trans olefin ozonolyses demonstrated the presence of the cis epoxide prior to gas chromatographic separation.

The deuterium isotope results (Table II) show that there is no scrambling of the carbon–carbon bond in epoxide formation. They are consistent with the partial cleavage pathway because the carbon–carbon bond remains intact in going to epoxide via a π or a σ complex.[12] As shown below, they are inconsistent with a complete cleavage pathway involving olefin epoxidation by fluorocarbonyl oxide via a 3,4,5-trifluoro-

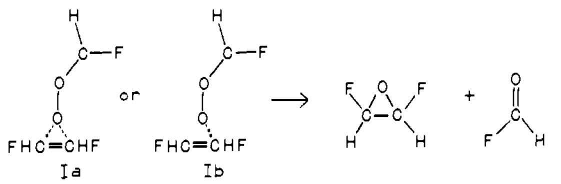
1,2-dioxacylopentane intermediate.[35] This mechanism predicts that the ozonolysis of CHF=CHF plus CDF=CDF will lead to the scrambled d_0, d_1, and d_2 epoxide isotopes, contrary to the results.



Another complete cleavage pathway is not likely in view of the deuterium isotope experiments. If 1,2-difluoroethylene ozonide yields epoxide plus molecular oxygen, then an enhancement of the 1,2-difluoroethylene-d_1 ozonide enrichment relative to the 1,2-difluoroethylene-d_1 enrichment will occur via the Criegee mechanism. Recent data support the Criegee mechanism for the ozonolysis of *cis*-1,2-difluoroethylene.[4] This will lead to an enhanced deuterium enrichment of the d_1 epoxide which is inconsistent with our results.



The isotope results do not eliminate the possibility of attack of the terminal oxygen of the fluorocarbonyl oxide upon the olefin. Either form of intermediate I (a or b) will lead to the cis epoxide from the cis olefin. Only Ib will give the cis epoxide directly from the trans olefin. The carbon-carbon bond remains intact through this epoxidation pathway in agreement with the deuterium results.



Ozonide Formation. In a preliminary report,[3] the stereochemical assignment was based on the assumption that the trans ozonide has the shortest GLC retention time.[36] The NMR data reported here are not inconsistent with this assignment. If it is assumed the 1,2-difluoroethylene ozonide isomers have predominantly the twisted ring conformation found for other ozonides,[4,8,9] then the two hydrogen and two fluorine nuclei are chemically but not magnetically equivalent for the trans isomer. Hence, the observed spectra will be that of an AA′XX′ spin system. For the cis ozonide, neither the fluorine nor the hydrogen nuclei are chemically equivalent, which means that it should exhibit a more complex spectrum that is characteristic of an ABXY spin system. The observed AA′XX′ spectrum of the trans ozonide and the more complex spectrum of the cis ozonide are consistent with this reasoning and support the GLC assignment.

For *cis*- and *trans*-1,2-difluoroethylene, it was found that 1,2-difluoroethylene ozonide is produced in a 10/90 cis to trans ratio in isobutane and methyl chloride solvent.[3] This work extends those results to dichlorodifluoromethane where the same cis to trans ozonide ratio of 10/90 is observed. According to orbital symmetry arguments,[9] trans alkenes yield more trans ozonide via an oxygen envelope primary ozonide in which substituents are pseudodiaxial. This species gives syn carbonyl oxide preferentially which reacts with aldehyde to produce more trans ozonide. Experimentally, there is a general tendency for bulky and nonbulky trans olefins to give more trans ozonide. As the olefin substituents become bulkier the cis/trans ratio decreases somewhat. *trans*-1,2-Difluoroethylene does not fit into this trend since it has one of the lowest cis/trans ozonide ratios reported. This suggests that the pseudodiaxial transition state of the trans primary ozonide is much preferred in spite of the absence of bulky substituents. With fluorines it seems that gauche fluorine oxygen lone electron-pair interactions are most important in determining axial-equatorial preference in the oxygen envelope primary ozonide. If the nonbonding electrons of the oxygen are somewhat localized in sp^3 lobes, then there are two gauche fluorine lone pair interactions for the equatorial site and only one for the axial site.[37] A contributing factor or alternate explanation for the preference of the diaxial transition state is the minimization of dipole-dipole interactions for the CF bonds in this conformer.

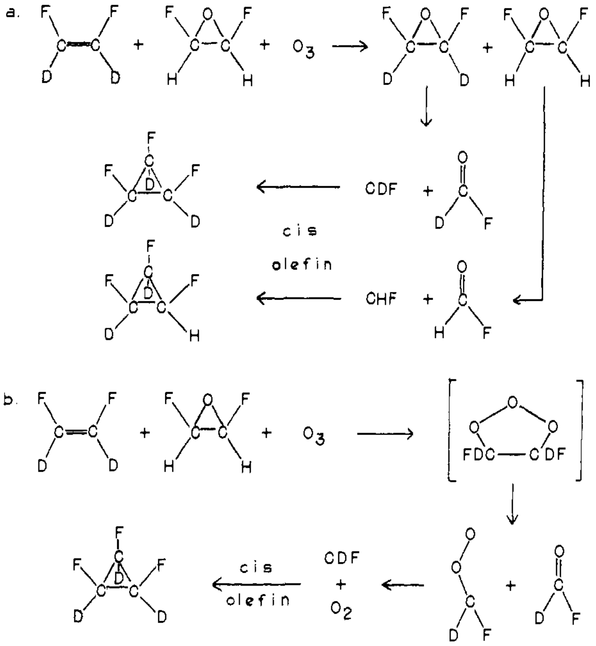
If the diaxial transition state has a lower activation energy than the diequatorial, it will cleave faster leading to more syn carbonyl oxide. On the cycloaddition of the syn carbonyl oxide to the aldehyde two orientations for the transition state are possible.[9] Although there are no bulky substituents in this case, dipole-dipole interactions are still minimized for the CF bonds when they are trans to each other (orientation A in ref 9). Hence the orbital symmetry approach predicts more trans ozonide. It is interesting to note that *anti*-fluorocarbonyl oxide is expected to add to formyl fluoride in a trans orientation (denoted D in ref 9) if the dipole-dipole interactions of the CF bonds largely determine the preferred transition state. Contrary to the predictions for bulky substituents, this pathway leads to more trans ozonide also.[9]

In the case of symmetrical cis olefins the two substituents will be positioned axially and equatorially in the oxygen envelope transition state. For bulky substituents, the orbital symmetry analysis concluded that the transition state leading to anti carbonyl oxide possesses one more trans and one less gauche bonded pair interaction than the one leading to the syn configuration. This corresponds to the equatorial substituent going to anti carbonyl oxide which reacts with aldehyde to give more cis ozonide in agreement with experimental data. Fluorines are sterically similar to hydrogens so that the gauche fluorine bonded pair oxygen lone pair interactions are likely to be more important than the gauche trans fluorine ring bond and fluorine-fluorine bonded pair interactions. Since there are two gauche fluorine bonded pair oxygen lone pair interactions for the equatorial site and one for the axial site, the axial fluorine leading to syn carbonyl oxide is preferred which reacts with formyl fluoride to produce more trans ozonide.

Cyclopropane Formation. Gozzo and Camaggi suggested that perfluorocyclopropane is produced in the ozonolysis of perfluoroethylene through the addition of difluorocarbene to the olefin.[2] The carbene is generated through loss of oxygen from difluorocarbonyl oxide. The stereochemical results which are summarized in Table I for the ozonolysis of *cis*- and *trans*-1,2-difluoroethylene cannot distinguish between concerted and nonconcerted pathways for fluorocarbene addition.

However, the deuterium experiments indicate that epoxide decomposition to carbene under ozonolysis conditions is unlikely. They are consistent with fluorocarbonyl oxide acting as either a free fluorocarbene source or carbenoid in the addition to olefin.

These two pathways may be distinguished experimentally by ozonizing a solution of *cis*-1,2-difluoroethylene-d_2 containing *cis*-1,2-difluoroethylene-d_0 oxide. If the epoxide is the carbene source via a decomposition[38] both the deuterated and normal isotopic species of monofluorocarbene will react with the olefin. As illustrated below (path a) *cis*-1,2,3-trifluorocyclopropane will show significant enrichment of the dideuterated species. If the monofluorocarbonyl oxide is the carbene source (path b), the cyclopropane enrichment is determined wholly by the olefin enrichment. Assuming that by path a all the carbene comes from epoxide decomposition then the ratio of the concentration of the d_2/d_3 isotopic species of *cis*-1,2,3-trifluorocyclopropane is 5.72.[39] This same ratio is calculated to be 0.0505 ± 0.0155 via path b. The ratio for path b is within the uncertainty of the experimental value of 0.0379 ± 0.0228 determined by microwave relative intensity measurements.



Solvent Effects. The ozonolyses of *cis*- and *trans*-1,2-difluoroethylene were carried out in three solvents of varying polarity in order to determine the influence of solvent polarity on the nature and yield of reaction products. The results in Table I show a striking effect of solvent upon yield. The ozonide and epoxide yields are consistently higher for the cis olefin than the trans in all three solvents. Similar results were reported for the ozonolysis of *cis*- and trans-1-(1-naphthyl)phenyl-1-propene in diethyl ether.[40] For the cis olefin, the yields of epoxide are about equal in methyl chloride and dichlorodifluoromethane but drop by a factor of one-half in isobutane. A similar but less pronounced effect is observed for the trans olefin. In contrast, ozonide yields are comparable in dichlorodifluoromethane and isobutane but drop by a factor of 5–6 in methyl chloride for both olefin isomers. Finally, there is no dependence of cis/trans ozonide ratio upon solvent for either olefin isomer.

There are numerous earlier reports of ozonolyses where epoxides are not products in which cis olefins give more ozonide than the trans.[41,42] It was suggested that this is because the trans primary ozonide is more stable than the cis which increases the chance for side reactions to occur.[43] This is a possible explanation for the 1,2-difluoroethylenes; however, relative primary ozonide stabilities of the cis and trans isomers are not known. Bauld et al.[42] considered differences in syn-anti zwitterion reactivities as a contributing factor in explaining the larger ozonide yields obtained from cis olefins. In their scheme for the mechanism of ozonolysis, the trans olefin leads to more syn zwitterion which is more likely to undergo side reactions than the anti zwitterion obtained from the cis olefin. If the orbital symmetry arguments discussed above are correct, both *cis*- and *trans*-1,2-difluoroethylene produce more syn carbonyl oxide, yet the cis olefin yields more ozonide than the trans. Perhaps there are side reactions available for the trans olefin but not the cis which do not involve the carbonyl oxide intermediate.

For the ozonlysis of sterically hindered 1-olefins, Bailey and Lane found that the yields of partial cleavage products were slightly larger in methylene chloride–methanol mixture solvent than in either methylene chloride or pentane.[12] It appears that the solvent controls the competition between partial and complete cleavage products for these olefins to a small extent. The results for *cis*- and *trans*-1,2-difluoroethylene indicate that the effect is much greater here. The higher yields of epoxide in the polar solvents may be due to better solvation of the π and/or σ complex in the partial cleavage pathway. The more polar solvents may also favor the solvation of the carbonyl oxide and carbonyl intermediates which would allow them to react through other pathways such as via intermediate I rather than recombine to give ozonide.

The yields of 1,2-difluoroethylene ozonides as a function of solvent polarity are not entirely consistent with earlier reports.[42] Usually, ozonide yield from cis olefin is lower with polar than nonpolar solvents while the converse is true for trans olefins. For *cis*- and *trans*-1,2-difluoroethylene, ozonide yield is lower in methyl chloride, the most polar of the three solvents, than in isobutane, the most nonpolar solvent. In dichlorodifluoromethane, a solvent of intermediate polarity, the ozonide yields are similar to those with isobutane. The results indicate that the effect of solvent upon ozonide yield is more than just a difference in the dipole moment of the solvent.

Perhaps of most interest is the virtual absence of any solvent effect upon the observed cis/trans ozonide ratio for the 1,2-difluoroethylenes. The orbital symmetry analysis discussed in the ozonide formation section provides one possible explanation. Arguments were presented which indicate that the syn carbonyl oxide is formed from the primary ozonide in preference to the anti form. Addition of the syn carbonyl oxide to the aldehyde yields predominantly trans ozonide.

The syn-anti distribution should be affected by solvent polarity since the syn isomer of fluorocarbonyl oxide is expected to have a larger dipole moment. This point is supported by a vibrational spectroscopic study of rotational isomerization in 1,2-difluoroethane.[44] The gauche form has a dipole moment of 2.67 D[45] while the trans conformer has zero dipole moment by symmetry. It was found that the gauche/trans ratio increases in going from low to high dielectric solvents.

There are several ways that this might affect the cis/trans ozonide ratios obtained for the three solvents used here. The rate of carbonyl oxide aldehyde cycloaddition could be slow compared to the primary ozonide cycloreversion. A fast equilibration of the carbonyl oxide would lead to a thermodynamic syn/anti distribution which should depend on the solvent polarity. Even if the rate of the aldehyde carbonyl oxide cycloaddition is fast compared to the cycloreversion step, the solvent may affect the activation energy and hence the rate for the cycloreversion leading to the syn carbonyl oxide.

This reasoning predicts varying syn/anti carbonyl oxide distributions and consequently varying cis/trans ozonide ratios.[9] However, it was argued in the ozonide formation section that the monofluorinated anti carbonyl oxide and aldehyde, unlike bulky substituents,[9] should combine in a trans configuration yielding predominantly trans ozonide. This means that as long as the solvent does not change the argument that syn and anti fluorocarbonyl oxides combine with formyl fluoride to yield mostly trans ozonide, it will not affect the observed cis/trans ozonide ratios. Studies of 1,2-difluoroethylene ozonide formation obtained as cross ozonides from vinyl fluoride and 1,1,2-trifluoroethylene should test this argument. In these cases, the cis/trans ozonide ratios are predicted to be similar to the 10/90 cis/trans ozonide ratio found here. Furthermore, these ratios are not likely to be very solvent dependent.

Acknowledgments. The author thanks E. Bright Wilson and the microwave group at Harvard for advice and helpful discussions. He is grateful to Vince Marino for obtaining some of the NMR spectra and to N. Hepfinger and his group for discussions and assistance. He also acknowledges the support of the National Science Foundation.

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(19) It was necessary to use this combination of columns because of the poor resolution of the olefin isomers and formyl fluoride on the halocarbon oil column and because of *cis*-1,2-difluoroethylene and solvent overlap on the diisodecyl phthalate column.
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(29) The partially deuterated sample used for mass spectral work was obtained from the ozonolysis of *cis*-CHF═CHF plus *cis*-CDF═CDF in methyl chloride solvent. The microwave spectra of the following species were observed in this sample: $\overparen{\mathrm{CDFCDFC}}\mathrm{DF}$, $\overparen{\mathrm{CDFCDFC}}\mathrm{HF}$, $\overparen{\mathrm{CHFCHFC}}\mathrm{HF}$, and $\overparen{\mathrm{CHFCHFC}}\mathrm{HF}$.
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