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Ozonolysis of 1,1-Difluoroethylene, Trifluoroethylene, and Perfluoroethylene: Mechanism of Ozonide, Epoxide, and Cyclopropane Formation[1]

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Abstract: The ozonolyses of 1,1-difluoroethylene and trifluoroethylene have been studied in $CF_2ClCFCl_2$, CF_2Cl_2, and CF_3Cl. Ozonolysis of 1,1-difluoroethylene produces normal secondary ozonide and carbonyl fluoride as major products. Ethylene ozonide was detected in lower yield in the reactions carried out in CF_2Cl_2 and CF_3Cl. Results from aldehyde insertion experiments are in agreement with a preferred direction of cleavage of the primary ozonide to H_2CO_2 and F_2CO over F_2CO_2 and H_2CO. Trifluoroethylene ozonolyses yield trifluoroethylene ozonide, trifluoroethylene oxide, carbonyl fluoride, and formyl fluoride as major products. *cis*- and *trans*-1,2-difluoroethylene ozonide and *cis*- and *trans*-1,1,2,3-tetrafluorocyclopropane are produced in lower yield. The cis and trans ozonides are formed in a ~10/90 cis/trans ratio. Ozonolysis of perfluoroethylene in $CF_2ClCFCl_2$ yields epoxide and carbonyl fluoride as major products. Aldehyde insertion experiments with HFCO give evidence for the intermediacy of difluorocarbonyl oxide (F_2CO_2) in the perfluoroethylene ozonolysis.

Investigations of the solution reaction of ozone with vinyl fluoride,[2] 1,1-difluoroethylene,[3-5] *cis*- and *trans*-1,2-difluoroethylene,[6-8] and trifluoroethylene[4] show that secondary ozonides and fluorinated aldehydes are major products. Experimental data[4,5,9,10] provide good evidence that the formation of these products proceeds via the Criegee mechanism.[11] In this respect, the fluorinated ethylenes are similar to the small hydrocarbon alkenes.[12]

However, fluorinated epoxides are major products in the ozonolysis of *cis*- and *trans*-1,2-difluoroethylene,[6-8] trifluoroethylene,[4] and perfluoroethylene.[4,13] In addition, small amounts of fluorinated cyclopropanes are found in th ozonolysis of the 1,2-difluoroethylenes[6-8] and perfluoroethylene.[13] The reaction pathways leading to these products are not as well defined as those for secondary ozonides.

Perfluoroethylene epoxidation is thought to proceed via a complete cleavage process in which the Criegee intermediate, F_2CO_2, reacts with $CF_2=CF_2$ to produce perfluoroethylene oxide.[13] Experimental results for *cis*- and *trans*-1,2-difluoroethylene[6-8] and trifluoroethylene[4] do not distinguish between this complete cleavage mechanism and a partial cleavage pathway (epoxidation by the terminal oxygen of ozone).[14]

Gozzo and Camaggi suggested that perfluorocyclopropane is formed by the addition of difluorocarbene to perfluoroethylene.[13] The carbene arises from deoxygenation of F_2CO_2. Stereochemical results for *cis*- and *trans*-1,2-difluoroethylene show that the 1,2,3-trifluorocyclopropane isomers are produced via a concerted process.[8,15]

In this paper, the preliminary studies with the ozonolyses of trifluoroethylene and 1,1-difluoroethylene are extended to low-temperature reaction conditions (-78 and -95 °C), and a complete product analysis is reported for both olefins. The isolation and identification of two previously unknown cyclopropane isomers, *cis*- and *trans*-1,1,2,3-tetrafluorocyclopropane, is discussed. The characterization of an unknown component in the trifluoroethylene ozonolyses as *cis*-1,2-difluoroethylene ozonide permits a determination of the *cis*-/*trans*-1,2-difluoroethylene ozonide ratio in these reactions. Results from aldehyde insertion experiments in the ozonolysis of $CH_2=CF_2$ and $CF_2=CF_2$ are related to the ozonide and epoxide mechanisms.

Experimental Section

Materials. 1,1-Difluoroethylene, trifluoroethylene, and perfluoroethylene were obtained from PCR, Inc. The purity was checked by gas-phase IR, and in all cases there was excellent agreement with the literature.[16] The olefins were stored at liquid N_2 temperature (-196 °C) and used without further purification.

Reaction solvents $CF_2ClCFCl_2$ (Freon 113, 98% Eastman Kodak), CF_2Cl_2 (Freon 12, Matheson, Co., CP grade), and CF_3Cl (Freon 13, Matheson, Co., CP grade) were used without any additional purification.

Formyl fluoride (HFCO) was synthesized by the procedure of Morgan et al., and its purity was established by gas-phase IR.[17]

Ozone was prepared with a Welsbach T-23 ozonator. Oxygen dried by passing it through a -78 °C slush bath was used to produce a few percent ozone in an oxygen stream. The ozone was adsorbed on silica gel at -78 °C and purged with helium to remove any traces of oxygen.[18] The ozone concentration in He was determined iodiometrically and controlled by raising the gel temperature to -30 °C.

Instrumental Analysis. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E mass spectrometer by expanding the sample directly into the source to minimize decomposition by contact with the gas handling system. An ionization voltage of 70 eV was used to record mass spectra with the source heaters turned off.

Gas-phase infrared spectra were recorded by using a Hitachi Perkin-Elmer 298 spectrometer. A 10-cm home-built gas cell with sodium chloride windows secured with Viton 0-rings was used to contain samples

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(1) Taken in part from the Ph.D. Thesis of John W. Agopovich, Rensselaer Polytechnic Institute, 1982.

(2) Mazur, U.; Lattimer, R. P.; Lopata, A.; Kuczkowski, R. L. *J. Org. Chem.* **1979**, *44*, 3181-3185.

(3) Gillies, C. W.; Sponseller, S. P.; Kuczkowski, R. L. *J. Phys. Chem.* **179**, *83*, 1545-1549.

(4) Agopovich, J. W.; Gillies, C. W. *J. Am. Chem. Soc.* **1980**, *102*, 7572-7574.

(5) Hillig, K. W.; Kuczkowski, R. L. *J. Phys. Chem.* **1982**, *86*, 1415-1420.

(6) Gillies, C. W. *J. Am. Chem. Soc.* **1975**, *97*, 1276-1278.

(7) Gillies, C. w. *J. Am. Chem. Soc.* **1977**, *99*, 7239-7245.

(8) Agopovich, J. W.; Gillies, C. W. *J. Am. Chem. Soc.* **1982**, *104*, 813-817.

(9) Hillig, K. W.; Lattimer, R. P.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 988-993.

(10) Mazur, U.; Kuczkowski, R. L. *J. Org. Chem.* **1979**, *44*, 3185-3188.

(11) Criegee, R. *Rec. Chem. Prog.* **1957**, *18*, 111-120; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745-751.

(12) Gillies, C. W.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 6337-6343; Gillies, C. W.; Lattimer, R. P.; Kuczkowski, R. L. *Ibid.* **1974**, *96*, 1536-1552.

(13) Gozzo, F.; Camaggi, G. *Chim. Ind.* (*Milan*) **1968**, *50*, 197-199.

(14) Bailey, P. S.; Lane, A. G. *J. Am. Chem. Soc.* **1967**, *89*, 4473-4478.

(15) Agopovich, J. W.; Gillies, C. W. Paper RB 7, presented at the Thiryseventh Symposium on Molecular Spectroscopy, Columbus, OH, June 1982.

(16) Simons, J. H. "Fluorine Chemistry"; Academic Press: New York, 1954; Vol. II.

(17) Morgan, H. W.; Staats, P. A.; Goldstein, J. H. *J. Chem. Phys.* **1956**, *25*, 337-342.

(18) The Silica gel was typically heated under vacuum 24 h. before the ozone was adsorbed on it. See: Bailey, P. S.; Reader, A. M. *Chem. Ind.* (*London*) **1961**, 1063-1064.

0002-7863/83/1505-5047$01.50/0

Table I. Product Yields[a,b] (%) from the Ozonolysis of Trifluoroethylene

	epoxide	1,1,2 ozonide	1,2[e] ozonide	cis/trans[f] ratio	HFCO	F_2CO	*trans*-$CHFCHFCF_2$	*cis*-$CHFCHFCF_2$	$-(O-O)_x-$[g]	unknown material
0 °C, $CF_2ClCFCl_2$	10	13	1.0	~10/90	*c*	*c*	*d*	*d*	<1	<1
−78 °C, CF_2Cl_2	7	7	1.0	12/88	25	30	0.7	1.0	10	~2
−95 °C, CF_3Cl	6	5	0.5	20/80	20	25	0.8	1.0	13	~3

[a] Based on 100% olefin consumed, average of several reactions. [b] Small amounts of SiF_4 and HCOOH were also formed in some reactions. [c] Identified by IR, but yields were not determined. [d] Not detected by GC. [e] Yield of both isomers. [f] Determined by GC using total peak areas over several injections. [g] Detected by reaction with 0.1 M KI.

at various pressures. The cell windows were polished frequently with Fe_2O_3 in methanol to remove impurity bands that appear with continued use of the IR cell.

^1H and ^{19}F NMR spectra were obtained by using 60-MHz Hitachi Perkin-Elmer R-600 and Varian XL-200 spectrometers at R.P.I. and a Bruker CXP 200-MHz spectrometer at the NSF NMR facility at Yale University. Tetramethylsilane and trichlorofluoromethane were used as internal references for the ^1H and ^{19}F spectra, respectively. All NMR samples were prepared with the aid of a vacuum line to manipulate and measure specific amounts of sample, reference, and solvent.

An 8400C Hewlett-Packard microwave spectrometer was used to examine the microwave spectrum of perfluoroethylene oxide at a microwave cell temperature of approximately −60 °C.

Preparative gas chromatography was accomplished using Varian Aerograph Autoprep 700 and Perkin-Elmer Sigma 3B gas chromatographs equipped with thermal conductivity detectors. All eluted components were collected in multilooped glass U traps cooled to −196 °C. Unless otherwise stated, flow rates of helium were 40 mL/min and the injector, detector, and oven were kept at ambient temperatures. This procedure was followed to avoid decomposition of some of the elutants. It required routine elevation of the injector, detector, and oven (column) temperatures to drive off nonvolatile material. All purified samples were than stored under vacuum at liquid nitrogen temperature to avoid possible decomposition.

Ozonolysis Procedure. (1) Ozonolysis of Trifluoroethylene in $CF_2ClCFCl_2$. Ozone and olefin were flowed separately into ~30 mL of $CF_2ClCFCl_2$ at 0 °C. Typically 3 mmol of olefin and flow rates of 0.10–0.15 mmol of O_3/min were used to ozonize to ~100% completion. Both material remaining in the solvent and bubbled out of the solvent into post reactor bulbs were analyzed. The solvent contained trifluoroethylene ozonide and *cis*- and *trans*-1,2-difluoroethylene ozonide. Distillation through a −78 °C trap removed some of the solvent from the more volatile ozonide products. This fraction was further purified by preparative GC using liquid injections on a 10 ft × 0.25 in. stainless-steel column packed with 10% Halocarbon K-352 on 60/80 Supelcoport. Temperature programming was used to drive off the $CF_2ClCFCl_2$ more efficiently. The ozonides were finally resolved on a 17 ft × 0.25 in. Teflon column packed with 10% Halocarbon oil on 40–60 mesh chromosorb T at 22 °C. The relative retention times were 1.0 (340 s) for trifluoroethylene ozonide, 1.8 for *trans*-1,2-difluoroethylene ozonide, 2.3 for *cis*-1,2-difluoroethylene ozonide (apparent as a shoulder on the trans isomer peak), and 3.1 for $CF_2ClCFCl_2$.

The bulb material was purified by distillation through traps maintained at −116,−131, and −196 °C. The −116 °C trap consisted of small amounts of trifluoroethylene ozonide and solvent. The −131 °C fraction was found to contain trifluoroethylene oxide, formyl fluoride, and small amounts of trifluoroethylene ozonide. The −196 °C trap contained mostly carbonyl fluoride with smaller amounts of the epoxide and formyl fluoride. The −131 °C trap was purified by preparative GC with the Teflon Halocarbon oil column. The relative retention times were 1.0 (180 s) for HFCO, 1.4 for trifluoroethylene oxide, and 2.1 for trifluoroethylene ozonide. A second pass through the GC was needed to purify the epoxide. Yields were determined manometrically and are given in Table I.

(2) Ozonolysis of Trifluoroethylene in CF_2Cl_2 at −78 °C. Olefin, 4 mmol, was dissolved in 4–5 mL of CF_2Cl_2 at −78 °C. The olefin was ozonized to ~100% completion with ozone flow rates of 0.08–0.12 mmol/min. With the reactor maintained at −78 °C, noncondensibles were pumped away and the condensible volatile material was allowed to distill through traps cooled to −140 and −196 °C. As with 1,2-difluoroethylene ozonolyses,[7,8] a liquid peroxidic material remained in the bottom of the reaction flask. This material reacted quickly with aqueous KI at −78 °C under vacuum.

The contents of the −140 °C fraction were further purified by a trap-to-trap distillation through traps maintained at −95, −116, and −196 °C. Each of these fractions were separately passed through the preparatory GC. A 20 ft × 0.125 in. stainless-steel column packed with 23% didecyl phthalate 45/60 Firebrick was used for initial purification. In some cases, it was necessary to use the Teflon Halocarbon oil column for separation of unresolved components obtained from the didecyl phthalate column.

The −95 °C trap contained mostly *trans*-1,2-difluoroethylene ozonide, *cis*-1,2-difluoroethylene ozonide, *cis*-1,1,2,3-tetrafluorocyclopropane, and smaller amounts of trifluoroethylene ozonide, formic acid, and unknown materials. The relative retention times on the didecyl phthalate column for the major components were 1.0 (600 s) for unknown 1, 1.5 for unknown 2, 1.7 for trifluoroethylene ozonide, 2.1 for unknown 3, 2.4 for *cis*-1,1,2,3-tetrafluorocyclopropane plus small amounts of an unknown material, 8.0 for *trans*-1,2-difluoroethylene ozonide, and 12.5 for *cis*-1,2-difluoroethylene ozonide. The *cis*-tetrafluorocyclopropane was purified further by duplicate passes through the Teflon Halocarbon oil column. The retention time of the cis tetrafluorocyclopropane on this column is 420 s.

The −116 °C trap consisted mainly of solvent, CF_2Cl_2. The major products included *trans*-1,1,2,3-tetrafluorocyclopropane, unknown 1, trifluoroethylene ozonide, and smaller amounts of *cis*-1,1,2,3-tetrafluorocyclopropane, formyl fluoride, trifluoroethylene oxide, and unknown components. The relative retention times on the didecyl phthalate column were 1.0 (250 s) for CF_2Cl_2, 1.2 for formyl fluoride, 1.4 for trifluoroethylene oxide, 1.8 for the *trans*-tetrafluorocyclopropane, 2.4 for unknown 1, 4.0 for trifluoroethylene ozonide, and 7.6 for the *cis*-tetrafluorocyclopropane. As with the *cis*-tetrafluorocyclopropane, the *trans*-tetrafluorocyclopropane was passed through the Teflon Halocarbon oil colum to achieve maximum purity. The retention time is 310 s on this column.

Formyl fluoride, carbonyl fluoride, CF_2Cl_2, trifluoroethylene oxide, and smaller amounts of the *trans*-tetrafluorocyclopropane and trifluoroethylene ozonide were identified in the −196 °C trap. The relative retention times on the didecyl phthalate column were 1.0 (160 s) for F_2CO, 1.6 for CF_2Cl_2, 1.8 for HFCO, 2.2 for the epoxide, 2.8 for the *trans*-tetrafluorocyclopropane, and 6.3 for trifluoroethylene ozonide. Further purification was accomplished by repetitive passes through the same column. Yields were determined manometrically and are listed in Table I. The material present in the −196 °C trap from the initial distillation contained CF_2Cl_2 and small amounts of F_2CO and SiF_4.

(3) Ozonolysis of Trifluoroethylene in CF_3Cl at −95 °C. This reaction involved ozonizing 4 mmol of olefin in 4–5 mL of CF_3Cl at −95 °C. Ozone flow rates were typically 0.08–0.12 mmol/min and the olefin was ozonized to ~100% completion. Immediately after completion of the ozonolysis, the volatile materials were distilled through traps maintained at −140 and −196 °C. The reactor was maintained at −95 °C initially and then allowed to warm to −88 °C over a period of 2 h during the distillation. This procedure was followed to allow the volatile material to distill from the reactor.

The initial ozonolysis under these conditions involved an attempt to warm the reactor to room temperature during the distillation. This procedure resulted in a violent explosion of the reactor. Instead, aqueous KI was added to the reactor after the distillation of the volatile products. The liquid, nonvolatile material reacted quickly indicating it is peroxidic in nature and probably similar to what is formed in the −78 °C ozonolysis.

Warning. It is likely that this material is sensitive to sudden increases in temperature and should be handled with caution.

The components retained by the −140 °C trap were purified further following the same procedure described for the −78 °C reaction. The products produced were similar except in addition small amounts of perfluoroethylene were also detected. Because the solvent is not retained by a −140 °C trap, preparative GC purifications were significantly easier and less time consuming. It appears that carrying out the $CHF{=}CF_2$ ozonolyses under these conditions are superior to the two previous methods described. Product yields for the −95 °C reaction are given in Table I.

(4) Ozonolysis of 1,1-Difluoroethylene in $CF_2ClCFCl_2$ at 0 °C. Ozone with flow rates of 0.10–0.15 mmol/mm and olefin (3 mmol) were allowed

Table II. Product Yields[a] (%) from the Ozonolysis of $CH_2{=}CF_2$ and $CF_2{=}CF_2$

	$\overline{CF_2CF_2O}$	perfluoro-ozonide	1,1-ozonide	ethylene ozonide	F_2CO	SiF_4	HFCO/olefin	trifluoro-ozonide
$CH_2{=}CF_2$	*b*	*b*	22	*b*	*c*	3	5/1[f]	*b*
							3/1[f]	*b*
0 °C, $CF_2ClCFCl_2$							1/1[f]	*b*
$CH_2{=}CF_2$	*b*	*b*	10[d]	1[d]	*c*	*c*	1/1[f]	*b*
−78 °C, CF_2Cl_2								
$CH_2{=}CF_2$	*b*	*b*	8[d]	1[d]	*c*	*c*		
−95 °C, CF_3Cl								
$CF_2{=}CF_2$							5/1[e]	5
	8	*b*			16	*b*	3/1	3
0 °C, $CF_2ClCFCl_2$							1/1	<1

[a] Based on olefin consumed. [b] Not detected. [c] Identified by IR, but yields were not determined. [d] These numbers give the relative amounts of the two ozonides produced in the reaction; they are not product yields based on olefin consumed. [e] In each case, total of both materials was 3 mmol. [f] Due to the unstable nature of vinyl fluoride ozonide, no attempt was made to analyze for it's presence as a product.

to flow through separate inlets into 20–25 mL of $CF_2ClCFCl_2$ at 0 °C. Solvent and post reactor material were both recovered and analyzed. After the solvent material was removed from the reactor, a solid white material remained at the bottom of the reactor. This material reacted vigorously with aqueous KI.

Warning. Earlier studies with 1,1-difluoroethylene ozonolyses found this is a peroxidic species and is shock sensitive.[3]

The species remaining in the reaction solvent were analyzed by liquid injections on the Teflon Halocarbon oil column. The only product detected was 1,1-difluoroethylene ozonide. The retention time on this column was 525 s. Ethylene ozonide could not be detected because it has a similar retention time to $CF_2ClCFCl_2$ (1050, Halocarbon oil). 1,1-Difluoroethylene ozonide was further purified by gaseous injections to remove any residual $CF_2ClCFCl_2$.

The bulb material was initially purified by a trap-to-trap distillation through traps cooled to −95, −131, and −196 °C. The halocarbon oil column was used to analyze the −95 °C trap, which contained only $CF_2ClCFCl_2$ and 1,1-difluoroethylene ozonide. The −131 °C trap contained small amounts of ozonide and silicon tetrafluoride. The −196 °C trap consisted of materials that could not be separated with the halocarbon oil column. Infrared spectra of this fraction showed that SiF_4, $CH_2{=}CF_2$, and F_2CO are the major components. The relative retention times for these compounds were 1.0 (180 s) for SiF_4, $CH_2{=}CF_2$ and F_2CO, 2.9 for 1,1-difluoroethylene ozonide, and 5.8 for $CF_2ClCFCl_2$.

(5) Ozonolysis of 1,1-Difluoroethylene at −78 °C in CF_2Cl_2. Olefin, 4 mmol, was dissolved in 2–3 mol of CF_2Cl_2 at −78 °C. The ozone flow rates were 0.10–0.15 mmol/min. After completion of the ozonolysis, the reactor was allowed to warm to room temperature during the pumping of noncondensibles and the distillation of volatile condensibles through traps cooled to −95, −131, and −196 °C. The solid white peroxidic material left in the reactor was digested with aqueous KI under vacuum. The −95 °C fraction consisted mostly of 1,1-difluoroethylene ozonide, ethylene ozonide, and smaller amounts of formic acid. The −95 °C trap was purified by gaseous injections on the Halocarbon oil column. The relative retention times were 1.0 (550 s) for 1,1-difluoroethylene ozonide and 1.8 for ethylene ozonide. The −131 °C trap contained chiefly solvent and SiF_4; the −196 °C trap consisted of smaller amounts of solvent, unreacted olefin, and carbonyl fluoride. The species were identified by gas-phase IR of the mixtures.

(6) Ozonolysis of 1,1-Difluoroethylene at −95 °C in CF_3Cl. Olefin, 4 mmol, was dissolved into 3–4 mL of CF_3Cl at −95 °C. The ozone flow rate was 0.10–0.15 mmol/min. During the reaction the solvent had a blue color indicating the presence of unreacted ozone. The reaction was continued and then terminated after 45 min. The workup was identical with that of the reaction at −78 °C in CF_2Cl_2 and yielded the same products.

A complete yield analysis was not possible for 1,1-difluoroethylene ozonolyses. Significant amounts of unreacted olefin were associated with each reaction. It appears that 1,1-difluoroethylene is much less reactive to ozone as compared to trifluoroethylene. Partial yields are available for the 0 °C ozonolysis. In this case they are based on total olefin consumed (Table II).

(7) Ozonolysis of Perfluoroethylene in $CF_2ClCFCl_2$ at 0 °C. Ozone and 3 mmol of olefin were separately bubbled into 20–30 mL of $CF_2ClCFCl_2$ at 0 °C. The flow rates of both starting material were 0.10–0.15 mmol/min. Both solvent material and contents of the post reactor bulbs were recovered and analyzed.

The contents of the solvent were examined directly by GC with liquid injection on the Halocarbon oil column. The only compound detected was perfluorocyclobutane. This is commonly found when perfluoroethylene is removed from a cylinder in a lighted laboratory and is not an ozonolysis product. The relative retention times were 1.0 (340 s) for perfluorocyclobutane and 3.0 for $CF_2ClCFCl_2$.

The bulb material was allowed to pass through traps maintained at −95 and −196 °C. The −95 °C trap consisted of solvent and perfluorocyclobutane. Gas-phase infrared spectra showed that the −196 °C trap consisted of perfluoroethylene oxide, carbonyl fluoride, and small amounts of unreacted olefin. Perfluoroethylene oxide was purified by chemical techniques discussed previously.[4] Yields were determined manometrically and are given in Table II.

(8) Ozonolysis of Perfluoroethylene in the Presence of Formyl Fluoride. Various molar ratios of a mixture of formyl fluoride and perfluoroethylene were flowed together through one inlet port and ozone through another into 20–25 mL of $CF_2ClCFCl_2$. The reaction temperature was maintained at 0 °C and the ozone flow rate was 0.12 mmol/min. Solvent material was analyzed by liquid injections on the Halocarbon oil column. The relative retention times were 1.0 (290 s) for perfluorocyclobutane, 1.2 for trifluoroethylene ozonide, and 3.1 for $CF_2ClCFCl_2$. The bulb materials were analyzed similarly as in the perfluoroethylene reaction without the foreign aldehyde. HFCO was the only additional species. Yields were determined manometrically based on olefin consumed (Table II).

(9) Ozonolysis of 1,1-Difluoroethylene in the Presence of Formyl Fluoride in $CF_2ClCFCl_2$. The procedure used for this reaction was identical with that of the perfluoroethylene–HFCO experiments. The same 1,1-difluoroethylene ozonolyses products were found here as was found with the $CF_2ClCFCl_2$ solvent, 0 °C ozonolysis reaction without added formyl fluoride. No trifluoroethylene ozonide was detected by GC with the ozonolyses of any olefin/HFCO ratio (Table II).

(10) Ozonolysis of 1,1-Difluoroethylene in the Presence of Formyl Fluoride in CF_2Cl_2. Olefin, 3 mmol, and formyl fluoride were dissolved in 4–5 mL of CF_2Cl_2 at −78 °C. The solution was ozonized with flow rates of 0.10–0.15 mmol O_3/min. The workup was identical with the description of the reaction at −78 °C without HFCO. Analysis of the fractions by gas chromatography demonstrated the lack of any trifluoroethylene ozonide.

Product Characterization. Carbonyl fluoride,[19] silicon tetrafluoride,[20] and formyl fluoride[17] were identified by their known gas-phase infrared spectra. Formic acid was identified by comparison to the gas-phase IR of 98% reagent grade HCOOH from Aldrich.

Perfluoroethylene oxide was identified by its known gas-phase IR and microwave spectrum.[21-22]

cis- and *trans*-1,2-difluoroethylene ozonide were identified by their known gas-phase IR and ^1H and ^{19}F NMR spectra.[7,8]

Ethylene ozonide[23] and 1,1-difluoroethylene ozonide[3] were identified by their known gas-phase infrared spectra. In addition 1,1-difluoroethylene ozonide was characterized by ^1H and ^{19}F NMR. The ^1H and ^{19}F spectra consisted of identical triplets with a peak separation of 1.7 Hz. The chemical shifts were 5.50 and 71.3 ppm, respectively. Proton decoupling of the fluorine resonance yielded a singlet, indicating that the

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(19) Nielsen, A. A.; Burke, T. G.; Woltz, P. J. H.; Jones, E. A. *J. Chem. Phys.* **1956**, *20*, 569–604.

(20) Jones, E. A.; Kirby-Smith, J. S.; Woltz, P. J. H.; Nielson, A. H. *J. Chem. Phys.* **1951**, *19*, 242–245.

(21) Craig, N. C. *Spectrochim. Acta., Part A* **1972**, *28A*, 1195–1201.

(22) Agopovich, J. W.; Alexander, J.; Gillies, C. W. Paper RC48 presented at the Thirtyfifth Symposium on Molecular Spectroscopy, Columbus, OH, June 1980.

(23) Garvin, D.; Schubert, C. *J. Phys. Chem.* **1956**, *60*, 807–808.

origin of the triplet is HF coupling.

Trifluoroethylene ozonide was characterized by ^1H and ^{19}F NMR, gas-phase IR, and mass spectrometry as well as by an independent synthesis (reaction 8, Experimental Section). The ^1H chemical shift in $(CD_3)_2CO$ is 7.63 ppm (dd) with $J_{HF}(\text{gem}) = 75.8$, $J_{HF}(\text{trans}) = 2.4$, and $J_{HF}(\text{cis}) \cong 0$ Hz. The ^{19}F NMR spectrum consisted of three ^{19}F resonances located at 61.4 ppm (dd), 79.5 ppm (ddd), and 85.5 ppm (ddd). Analysis of the fluorine resonances provided the following chemical shift assignments: axial F (CF_2) 61.4, axial F (CHF) 79.5, and equatorial F (CF_2) 85.5. The analysis also confirmed the proton cooupling constant assignments and gave the following FF coupling constants: $J_{FF}(\text{cis}) = 1.4$ Hz, $J_{FF}(\text{trans}) = 10.1$ Hz, and $J_{FF}(\text{gem}) = 71.0$ Hz. These assignments are based upon previous chemical shift and coupling constant data known for other fluorinated ozonides.[2,7,8]

A gas-phase IR using pressures of 5–40 torr gave the following absorptions (cm^{-1}) with the prominent Q-branch listed: 3030 (w, singlet, C–H), 1980 (vw, singlet), 1348 (m, singlet), 1279 (s, singlet), 1210 (s, singlet), 1147 (m, singlet), 1125 (s, doublet), 1001 (w, singlet), 900 (w, singlet), and 850 (w, triplet) cm^{-1}. The strong absorptions in the 1350–1050-cm⁻1 region are likely associated with C–O and C–F stretching. They compare well with other similar ozonides.[2,3,7,13] The ozonide appears to be stable in the IR cell for the length of time required to record the spectrum (40 min). This was based on the lack of evidence of decomposition products, HFCO or F_2CO, in the spectrum. The mass spectrum is similar to that of other fluorinated ozonides.[2,3,7] The mass spectral fragmentation pattern was as follows: *m/e* 28 (12.8, CO^+), 29 (30.7, HCO^+), 31 (5.1, CF^+), 32 (5.8, HCF^+), 44 (64.1, CO_2^+), 45 (12.8, HCO_2^+), 47 (100, CFO^+), 48 (66.7, $HCFO^+$), 50 (15.4, CF_2^+), 64 (97.4, $HFCO_2^+$), 66 (46.2, CF_2O^+), 69 (21.8, CF_3^+), 82 (73.1, $CF_2O_2^+$), and 130 (6.4, $C_2HF_3O_3^+$).

Trifluoroethylene oxide was characterized by ^1H and ^{19}F NMR, gas-phase IR, and mass spectrometry. The ^1H NMR chemical shift in $CDCl_3$ was 5.81 ppm (ddd). Analysis of the proton spectrum yielded the following coupling constants: $J_{HF}(\text{gem}) = 78.6$, $J_{HF}(\text{cis}) = 5.1$, and $J_{HF}(\text{trans}) = 2.7$ Hz. Analysis of the ^{19}F NMR in $CDCl_3$ confirmed the proton assignments and provided the following chemical shift assigment and additional coupling constants: fluorine cis to proton (CF_2) 108.5 (ddd), flourine trans to proton (CF_2) 120 (ddd), and fluorine on CHF group 157.4 (ddd) ppm; $J_{FF}(\text{gem}) = 49.9$, $J_{FF}(\text{cis}) = 19.3$, and $J_{FF}(\text{trans}) = 9.3$ Hz. Chemical shift and coupling constant assignments were based upon information presented for other fluorinated epoxides[7,8,24] as well as the fact that $J_{FF}(\text{cis}) > J_{FF}(\text{trans})$ and $J_{HF}(\text{cis}) > J_{HF}(\text{trans})$ for most fluorinated cyclopropanes.[8,25–26]

The major bands (cm^{-1}) of the gas-phase IR using pressures of 5–50 torr are as follows with the prominent Q-branch listed: 3080 (vw, singlet, C–H), 1641 (w, triplet), 1536 (s, singlet), 1319 (s, doublet), 1248 (vs, doublet), 1181 (vs, triplet), 1130 (s, triplet), 1055 (s, triplet), 908 (s, triplet), 738 (m, triplet), and 645 (m, triplet) cm^{-1}. The strong band at 1536 cm^{-1} is assigned to the ring breathing mode. This frequency falls between frequencies observed for this mode in the case of perfluoroethylene oxide (1610 cm^{-1})[21] and 1,2-difluoroethylene oxide (1460 cm^{-1}, cis isomer, and 1477 cm^{-1}, trans isomer).[7,8] The mass spectrum is reasonable although no molecular ion was seen. It should be noted that the mass spectral data for $\overline{CF_2CF_2O}$,[24] $\overline{CFClCF_2O}$,[27] and $\overline{CCl_2CF_2O}$[27] did not show a molecular ion either. The fragmentation pattern was as follows: *m/e* 28 (100.0, CO^+), 29 (42.9, HCO^+), 31 (22.9, CF^+), 32 (51.4, HCF^+), 43 (80.0, C_2F^+), 47 (47.1, CFO^+), 50 (40.0, CF_2^+), 51 (54.2, HCF_2^+), 69 (71.4, CF_3^+), and 97 (17.1, $C_2F_3O^+$).

cis- and *trans*-1,1,2,3-tetrafluorocyclopropane were characterized by gas-phase IR, ^1H and ^{19}F NMR, and mass spectrometry. Under pressures of 5–10 torr, the following bands (cm^{-1}) for the cis isomer with the prominent Q-branch listed are: 3058 (w, singlet, C–H), 1502 (m, doublet), 1318 (s, singlet), 1244 (s, triplet), 1181 (vs, triplet), 1020 (m, singlet), 965 (m, singlet), 855 (w, singlet), 719 (m, singlet), and 650 (m, doublet). Similarly the trans isomer bands are: 3055 (w, singlet, C–H), 1515 (m, singlet, with shoulder to low frequency), 1325 (m, singlet), 1260 (vs, doublet), 1172 (s, doublet), 955 (s, triplet), 750 (m, singlet), and 690 (m, triplet). The bands at 1502 and 1515 cm^{-1} are assigned to the ring breathing modes for the cis and trans isomers, respectively.[28,29] The mass spectra of both isomers are similar, with $M^+ - 1$ (113), CF_2^+ (69), and HCF_2^+ (51) being major ions. These are common fragments in other fluorinated cyclopropanes also.[7,8,28] The mass spectrum of the cis isomer consisted of the following ions, *m/e* 31 (14.8, CF^+), 32 (14.2, HCF^+), 33 (3.9, H_2CF^+), 44 (6.5, HC_2F^+), 45 (11.3, $H_2C_2F^+$), 50 (3.0, CF_2^+), 51 (51.6, HCF_2^+), 63 (5.2, $H_2C_2F^+$), 64 (81.9, $H_2C_2F_2^+$), 69 (71.6, CF_3^+), 75 (11.6, $HC_3F_2^+$), 82 (9.7, $HC_2F_3^+$), 93 (3.2, $C_3F_3^+$), 94 (2.6, $HC_3F_3^+$), 95 (20.6, $H_2C_3F_3^+$), 113 (100.0, $HC_3F_4^+$), and 114 (3.9, $H_2C_3F_4^+$, $H^{13}CC_2F_4^+$). Similarly the trans isomer consisted of the following fragments: *m/e* 31 (15.9, CF^+), 32 (6.8, HCF^+), 33 (2.3, H_2CF^+), 44 (6.8, HC_2F^+), 45 (10.2, $H_2C_2F^+$), 50 (5.7, CF_2^+), 51 (100, HCF_2^+), 63 (4.5, $HC_2F_2^+$), 64 (78.5, $H_2C_2F_2^+$) 69 (73.8, CF_3^+), 75 12.3, $HC_3F_2^+$) 93 (2.3, $C_3F_3^+$), 94 (2.3, $HC_3F_3^+$), 95 (17.0, $H_2C_3F_3^+$), 113 (80.6, $HC_3F_4^+$), and 114 (3.4, $H_2C_3F_4^+$, $H\ ^{13}CC_2F_4^+$).

^1H and ^{19}F NMR were used to unambiguously assign the correct stereochemistry for the 1,1,2,3-tetrafluorocyclopropanes. The ^1H chemical shift of the cis isomer was 4.68 ppm in $CDCl_3$. It consisted of a symmetrical 40-line pattern. The chemically equivalent but magnetically nonequivalent cis protons and cis fluorines constitute an AA′XX′ spin system with the possibility of giving a maximum of 10 lines.[30] Each of these lines may be split into a doublet of doublets through coupling of the chemically nonequivalent CF_2 fluorines. The reasoning predicts the 40 lines seen in the actual spectrum. Fitting the ^1H spectrum, using LAOCN3,[31] yielded the following coupling constants: $J_{HF}(\text{gem}) = 56.7$ $J_{HF}(\text{trans}) = 1.0$, $J_{FF}(\text{cis}) = 17.1$, and $J_{HH}(\text{cis}) = 6.0$ Hz. Coupling from the CF_2 group was $J_{HF}(\text{cis}) = 11.2$ and $J_{HF}(\text{trans}) = 1.2$ Hz.

As expected, the ^{19}F NMR spectrum consisted of three fluorine resonances. The chemical shifts and assignments were as follows: 244.8 (CHF), 162.0 (CF_2 trans to H), and 139.9 (CF_2 cis to H) ppm. Analysis of the ^{19}F resonances confirmed the coupling constants obtained from the ^1H spectra and provided the following additional coupling constants: $J_{FF}(\text{gem}) = 205.4$, $J_{FF}(\text{cis}) = 2.7$, and $J_{FF}(\text{trans}) = 4.6$ Hz. The CF_2 fluorine resonances were both doublets of overlapping triplets of triplets. Proton decoupling while observing the two CF_2 fluorine resonances aided in determination of the FF coupling constants. The CHF fluorine resonance pattern consisted of an AA′XX′ spin system identical with the ^1H spectra split by the CF_2 group to give a total of 40 lines. LAOCN3 was used to fit the ^{19}F spectrum. The agreement between the simulated and experimental ^{19}F spectra was excellent. The coupling constants and chemical shifts of the cis isomer are reasonable if compared to similar molecules.[8,25,26]

The proton spectrum of *trans*-1,1,2,3-tetrafluorocyclopropane consisted of a complicated, overlapping, symmetrical pattern centered at 5.01 ppm in $CDCl_3$. Unlike the cis isomer, the trans species exhibited only two fluorine resonances at 229.5 and 148.4 ppm ($CDCl_3$). The pattern at 229.5 ppm was similar in appearance to the ^1H spectrum and is assigned to the CHF fluorine resonance. The ^{19}F pattern assigned to the CF_2 resonance at 148.4 ppm bore no resemblance to the CHF fluorine resonance and consisted of a multiplet 25 Hz in width.

Decoupling of the CF_2 fluorine resonance while observing the ^1H spectrum produced a 10-line spectrum that is characteristic of an AA′XX′ spin system. Analysis of the spectrum gave the following coupling constant: $J_{HF}(\text{gem}) = 56.0$, $J_{HF}(\text{cis}) = 18.5$, $J_{FF}(\text{trans}) = 4.0$, and $J_{HH}(\text{trans}) = 1.3$ Hz. The coupling constant assignments were made by comparison to related fluorinated cyclopropanes.[8,25,26]

Additional work is required to obtain coupling constants related to the CF_2 group. However, the ^{19}F NMR unambiguously differentiates the two 1,1,2,3-tetrafluorocyclopropane isomers. The cis isomer has three chemically and magnetically nonequivalent fluorine resonances. The trans isomer has two magnetically nonequivalent ^{19}F resonances.

Results and Discussion

(1) $CH_2{=}CF_2$. Ozonolysis of 1,1-difluoroethylene, using three reaction conditions, produced 1,1-difluoroethylene ozonide and carbonyl fluoride as major products (Table II). In addition, ethylene ozonide was formed in lower yield in the −78 and −95 °C reactions. Due to separation problems, it was not possible to determine the presence of ethylene ozonide in the 0 °C reaction. Extensive product analysis of all 1,1-difluoroethylene ozonolyses did not reveal the presence of perfluoroethylene ozonide (high cross

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(24) Prager, J. H. *J. Org. Chem.* **1966**, *31*, 392–394.

(25) Mitsch, R. A. *J. Heterocycl. Chem.* **1964**, *1*, 271–274.

(26) Sargeant, P. B. *J. Org. Chem.* **1970**, *35*, 678–682.

(27) Chow, D.; Jones, M. H.; Thorne, M. P.; Wong, E. C. *Can. J. Chem.* **1967**, *47*, 2491–2494.

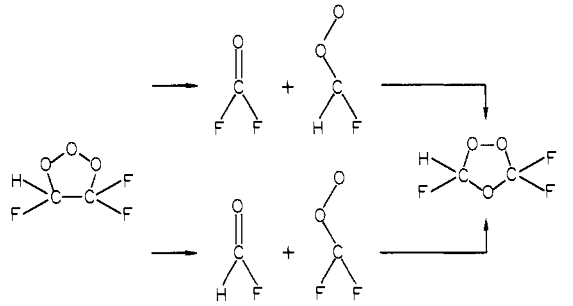
(28) See: Craig, N. C.; Chao, T.-N. Hu; Cuellar, E.; Hendrickson, D. E.; Koepke, J. W. *J. Phys. Chem.* **1975**, *79*, 2270–2282; Craig, N. C.; Anderson, G. J.; Cuellar-Ferreira, E.; Koepke, J. W.; Martyn, P. H. *Spectrochim. Acta., Part A* **1972**, *28A*, 1175–1193, for discussion of ring breathing in fluorinated cyclopropanes.

(29) Prof N. C. Craig of Oberlin College has independently synthesized *cis*- and *trans*-1,1,2,3-tetrafluorocyclopropane. There is good agreement between the IR spectra obtained in our laboratory and Prof Craig's laboratory.

(30) See: McConnell, H. M.; McLean, A. D.; Reilly, C. A. *J. Chem. Phys.* **1955**, *23*, 1152–1159. Garbisch, E. W., Jr. *J. Chem. Educ.* **1968**, *45*, 480–493, for examples and methods of analyses of AA′XX′ spin systems.

(31) LAOCN3 was developed by A. A. Bothner-By and S. Castellano at Carnegie-Mellon University. See: Bothner-By, A. A.; Castellano, S. *J. Chem. Phys.* **1964**, *41*, 3863–3869.

Scheme I



ozonide) as well as epoxides or cyclopropanes.

These results are in agreement with the previous investigations of the ozonolysis of 1,1-difluoroethylene.[3-5] The product analyses show that the ozonolysis of 1,1-difluoroethylene is similar to the solution ozonolysis of vinyl fluoride.[2] In both cases, the normal secondary ozonide and fluorinated aldehyde are major products with smaller amounts of ethylene ozonide detected as the lower cross ozonide. There is substantial evidence that indicates these ozonides are produced via a Criegee process.[3-5,10]

Experimental[2,10] and theoretical[32] studies suggest that the cleavage of the primary ozonide of vinyl fluoride proceeds preferentially to H_2CO_2 and HFCO over $HFCO_2$ and H_2CO. Hillig and Kuczkowski[5] have argued that aldehyde insertion experiments for 1,1-difluoroethylene are best rationalized by a preferential cleavage of the primary ozonide to H_2CO_2 and F_2CO over F_2CO_2 and H_2CO. Aldehyde insertion studies in the present work offer support for such a preferential cleavage. Ozonolysis of 1,1-difluoroethylene in the presence of formyl fluoride did not produce detectable amounts of trifluoroethylene ozonide at aldehyde/olefin molar ratios up to 5/1. It seems likely that this result cannot be exclusively due to low reactivity of F_2CO_2 with HFCO since the ozonolysis of perfluoroethylene in the presence of formyl fluoride produces trifluoroethylene ozonide over a range of aldehyde/olefin ratios (see Table II).

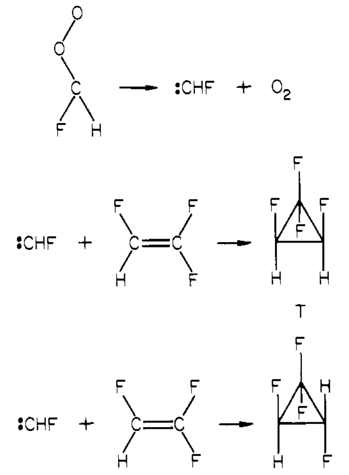
There are significant differences in the relative amounts of normal ozonide and ethylene ozonide produced in the vinyl fluoride and 1,1-difluoroethylene ozonolyses. In CH_3Cl solvent at −95 °C the ratio of $CH_2OOCHFO/CH_2OOCH_2O$ is 33/1 for the vinyl fluoride ozonolyses.[2] It compares with a ratio of 10/1 or 8/1 (CH_2OOCF_2O/CH_2OOCH_2O) for the ozonolyses of 1,1-difluoroethylene in CF_2Cl_2 at −78 °C and in CF_3Cl at −95 °C, respectively. The reason for this three to fourfold difference in the relative quantities of ethylene ozonide to normal ozonide in the two olefin ozonolyses is not certain.

It is possible to conclude that this effect implies cleavage to H_2CO and the fluorinated carbonyl oxide occurs to a greater extent in 1,1-difluoroethylene than in vinyl fluoride. However, the presence of significant amounts of F_2CO_2 should lead to trifluoroethylene ozonide when the olefin is ozonized in the presence of HFCO. This is contrary to the results in Table II.

It seems more likely that 1,1-difluoroethylene follows vinyl fluoride ozonolyses and cleavage of the primary ozonide produces mainly H_2CO_2 and F_2CO. The low normal to cross ozonide ratios in the 1,1-$CH_2{=}CF_2$ ozonolyses may result from a decreased reactivity of H_2CO_2 with F_2CO compared to H_2CO_2 with HFCO as in the vinyl fluoride reactions.[2,10] This reasoning is consistent with isotopic trapping experiments that indicate that H_2CO is more reactive than HFCO toward H_2CO_2.[10]

(2) $CHF{=}CF_2$. The results of secondary ozonide formation in the ozonolysis of trifluoroethylene are similar to those of 1,1-difluoroethylene. The normal secondary ozonide, trifluoroethylene ozonide, is produced in significant yield for all reaction conditions (Table I). Formed in much lower yield are the low cross ozonides, *cis*- and *trans*-1,2-difluoroethylene ozonide. No perfluoroethylene ozonide could be found even with extensive purification of various low-boiling product fractions. The observation of normal and cross ozonide formation is strong evidence that the ozonolysis of $CHF{=}CF_2$ is proceeding via a Criegee pathway in part. Cleavage of the primary ozonide can occur via two pathways, as shown in Scheme I. The presence of cross ozonide as a product suggests that both cleavage pathways must take place. If the ozonolysis of trifluoroethylene follows the trend noted for vinyl flouride[2,10] and 1,1-difluoroethylene,[5] path 1a is more favorable than 1b. Trapping experiments are needed to investigate whether 1a or 1b is the preferred pathway.

Scheme II



It was predicted that the *cis*-/*trans*-1,2-difluoroethylene ozonide ratio from trifluoroethylene ozonolyses would be ~10/90.[7] The reasoning in that work also suggested that the cis/trans ratio of the 1,2-difluoroethylene ozonides formed as a cross ozonide would have little dependence on the reaction solvent. Table I lists the cis/trans ratio of *cis*- and *trans*-1,2-difluoroethylene ozonide for three reaction temperatures and solvents. The experimental ratios range from 10/90 to 20/80. The results are in agreement with the predicted 10/90 cis/trans ratio.[7]

The results also show that the cis/trans ratio is independent of reaction temperatures. Changes in temperature should not affect the argument that dipole–dipole interactions in the transition state leading to secondary ozonide favor trans ozonide formation for both *syn*- and *anti*-carbonyl oxide ($HFCO_2$). Hence, changes in temperature will not affect the final cis/trans secondary ozonide ratio. Recent theoretical studies considered both II orbital overlap and dipole–dipole interactions in the transition state leading to secondary ozonide.[32] The conclusion was that more trans ozonide is produced from the addition of both *syn*- and *anti*-monofluorocarbonyl oxide to HFCO.

Trifluoroethylene oxide is found to be a major product in the ozonolysis of $CHF{=}CF_2$ under all ozonolysis reaction conditions. The production of $CHFCF_2O$ can be rationalized by either the partial cleavage[14] or complete cleavage mechanisms.[13] In this case the complete cleavage pathway involves epoxidation of trifluoroethylene by $HFCO_2$ and/or F_2CO_2 to give epoxide and fluorinated aldehyde.

It is likely that a 1,3-dipolar cycloaddition[33] of the carbonyl oxide to the olefin to form a 1,2-dioxacyclopentane intermediate can be ruled out. This mechanism involves carbon–carbon scrambling during the epoxidation process.[7] Application of this scheme to trifluoroethylene should produce $CHFCF_2CF_2OO$ and $CHFCHFCF_2OO$ through addition of F_2CO_2 and $HFCO_2$ to $CHF{=}CF_2$. Cleavage of these intermediates followed by ring closure will give CF_2CF_2O and $CHFCHFO$ in addition to $CHFCF_2O$. CF_2CF_2O and $CHFCHFO$ were not detected in the product analysis of the ozonolysis of $CHF{=}CF_2$.

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(32) Cremer, D. *J. Am. Chem. Soc.* **1981**, *103*, 3633–3638.

(33) Kwart, H.; Hoffmann, D. M. *J. Org. Chem.* **1966**, *31*, 419–424.

The two low-temperature ozonolyses (−78 and −95 °C) of trifluoroethylene produced both *cis*- and *trans*-1,1,2,3-tetrafluorocyclopropane isomers in low yield. This is analogous to the ozonolysis of *cis*- and *trans*-1,2-difluoroethylene and perfluoroethylene where fluorinated cyclopropanes are also found as products present in low yield.[7,8,13] Application of the mechanism proposed for those olefins to trifluoroethylene would require the addition of either the free carbene :CHF or the carbenoid $HFCO_2$ to $CHF{=}CF_2$ in order to produce *cis*- and *trans*-1,1,2,3-tetrafluorocyclopropane. Scheme II shows the formation of :CHF from $HFCO_2$ and subsequent addition to $CHF{=}CF_2$.

Pentafluorocyclopropane is also a possible product from the ozonolysis of $CHF{=}CF_2$. In this case difluorocarbonyl oxide or $:CF_2$ derived from the carbonyl oxide adds to the olefin to produce cyclopropane. This is a known compound,[25,26] but extensive searches in various product fractions were not successful in identifying it. There are two possible explanations why this compound is not produced in detectable yield. Initially, the cleavage of the primary ozonide of trifluoroethylene may produce more $HFCO_2$ than F_2CO_2 as suggested earlier. Therefore, less $:CF_2$ or F_2CO_2 will be available to add to the olefin. Also, carbenes are electrophilic in nature, which means $:CF_2$ is less reactive than :CHF in addition to olefins.[34]

The yields of the tetrafluorocyclopropane isomers in Table I show a minor preference for the formation of the cis isomer. These isomers are formed in such low yield that the uncertainty in the measurement likely exceeds the difference in the yield of the two isomers. Hence, it is not possible to determine a preference for syn or anti addition of the carbene or carbenoid to the olefin.

(3) $CF_2{=}CF_2$. The reaction of ozone with perfluoroethylene in the presence of formyl fluoride was investigated using very similar conditions to those described by Gozzo and Camaggi.[13] Carbonyl fluoride and perflouroethylene oxide are produced in reactions either with or without formyl fluoride (Table II). No significant change in the yields of these two products was seen as the HFCO to $CF_2{=}CF_2$ ratio increased. However, the absolute yields of the products decreased with increasing HFCO/olefin ratios, which introduced a large uncertainty in the manometric measurements of these products.

The epoxidation mechanism proposed by Gozzo and Camaggi for perfluoroethylene is summarized by the following equations:[13]

$$CF_2{=}CF_2 + O_3 \rightarrow [C_2F_4O_3] \rightarrow F_2CO + F_2CO_2 \qquad (1)$$

$$F_2CO_2 + CF_2{=}CF_2 \rightarrow \overline{CF_2CF_2O} + F_2CO \qquad (2)$$

The formation of trifluoroethylene ozonide in the ozonolyses of perfluoroethylene with added formyl fluoride is consistent with a complete cleavage process as shown in reaction 1 and provides evidence for the intermediacy of F_2CO_2. Hence, the results indicate that F_2CO_2 is present and might react with perfluoroethylene to form perfluoroethylene oxide via reaction 2. More direct experimental results are required to confirm this reaction pathway.

The very low yield of perfluoroethylene ozonide in the earlier study[13] combined with the present F_2CO_2 trapping results suggest that the 1,3-dipolar cycloaddition of F_2CO_2 to F_2CO is not competitive with other reactions. In particular they indicate that HFCO is a better 1,3-dipolarophile than F_2CO toward the cycloaddition with F_2CO_2. This may be part of the explanation as to why perfluoroethylene ozonide is not produced as a cross ozonide in $CH_2{=}CF_2$ and $CHF{=}CF_2$ ozonolyses.

Conclusions

The present work in conjunction with previous studies[2-10] shows that four fluorinated products are produced in solution ozonolysis of fluorinated ethylenes. These include normal and cross secondary ozonides, aldehyde, epoxides, and cyclopropanes. The production of fluorinated epoxides and cyclopropanes takes place only when fluorine atoms are bonded to both carbons.[6-8,13] Secondary ozonides are major products in all fluorinated ethylene ozonolyses except for perfluoroethylene where small amounts of perfluoroethylene ozonide are observed only with ozone/olefin molar concentrations close to unity. Either carbonyl and/or formyl fluoride are major products of all fluorinated ethylene ozonolyses. Nonvolatile peroxidic residues of unknown composition are left in the reaction vessels of all these ozonolyses.[2-10] In the case of perfluoroethylene, molecular oxygen is a major product only at ozone olefin ratios approaching unity.[13] Oxygen analyses have not been carried out for other fluorinated ethylene ozonolyses.

Experimental data obtained in this work and previous work[2-10] are consistent with a Criegee pathway leading to the formation of secondary ozonides for all fluorinated ethylenes. Hence the evidence indirectly supports the intermediacy of carbonyl oxides in solution. A variety of data derived from aldehyde insertion reactions and cross ozonide formation suggests that the 1,3-dipolarophilic reactivity of aldehydes is reduced by substitution of hydrogen by fluorine. The increasing carbonyl stretching frequency (1744[35] vs. 1837[17] vs. 1934 cm^{-1} [19]) and shorter bond distance (1.206[36] vs. 1.183[37] vs. 1.174 Å[38]) of the series H_2CO, HFCO, and F_2CO are indicative of a stronger bond and lower reactivity of the aldehyde with increasing fluorination.[10] The estimated C=O bond moment of ~2.80 for H_2CO compared to ~2.60 for F_2CO also is consistent with a higher 1,3-dipolarophilic reactivity for H_2CO as compared to F_2CO.[39]

Epoxides are formed in the ozonolyses of *cis*- and *trans*-$CHF{=}CHF$,[6-8] $CHF{=}CF_2$,[4] and $CF_2{=}CF_2$.[4,13] The results of earlier work argue strongly against the partial cleavage mechanism proposed by Bailey and Lane[14] in the case of $CF_2 = CF_2$. Gozzo and Camaggi found that equimolar production of oxygen did not accompany epoxide formation over a wide range of ozone/olefin concentrations.[40] This observation is contrary to the partial-cleavage mechanism.

The carbonyl oxide epoxidation mechanism is in agreement with the product yield data and the HFCO addition reactions for $CF_2{=}CF_2$ ozonolyses. Also, there is precedence in the literature for carbonyl oxide epoxidations.[41,42] The experimental data related to epoxide formation in $CHF{=}CF_2$ and *cis*- and *trans*-$CHF{=}CHF$ ozonolyses do not distinguish between the partial cleavage mechanism and the carbonyl oxide epoxidation. However, the partial cleavage mechanism was proposed to explain epoxide formation from the ozonolyses of sterically hindered 1-olefins. Steric problems are not important for fluorinated ethylenes, and it seems likely that a complete cleavage pathway also is involved in epoxide formation for $CHF{=}CF_2$ and $CHF{=}CHF$.

There is not sufficient evidence to rule out the possibility that other peroxidic intermediates epoxidize $CHF{=}CHF$, $CHF{=}CF_2$, and $CF_2{=}CF_2$. These might include the primary ozonide or a fluorinated dioxirane. More direct, spectroscopic experiments are required to elucidate the possible role of these species in the epoxide mechanism.

It is curious that the fluorinated ethylenes that give fluorinated epoxides also yield fluorinated cyclopropanes. The present study has shown that $CHF{=}CF_2$ ozonolyses produce *cis*- and *trans*-1,1,2,3-tetrafluorocyclopropane isomers but not pentafluoro-

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[34] Kirnse, W. "Carbene Chemistry"; Academic Press: New York, 1969.

[35] Herzberg, G. "Infrared and Raman Spectra"; D. Von Nostrand Co., Inc., Princeton, NJ, 1945.

[36] Oka, T. *J. Phys. Soc. Jpn.* **1960**, *15*, 2274–2279.

[37] LeBlanc, O. H.; Laurie, V. W.; Gwinn, W. D. *J. Chem. Phys.* **1960**, *33*, 598–600.

[38] Laurie, V. W.; Pence, D. T.; Jackson, R. H. *J. Chem. Phys.* **1962**, *37*, 2995–2999.

[39] The C=O bond moments for H_2CO and F_2CO were calculated from the structural and dipole moment information given in ref 36 and 38. Approximate values of 0.4 and 1.41 were used for the C—H and C—F bond moments, respectively; see: Symth, C. P. "Dielectric Behavior and Structure"; McGraw-Hill: New York, 1955.

[40] Gozzo and Camaggi varied the ozone/olefin reaction ratios and found significant amounts of molecular oxygen as a product when the ratio was in the area of 0.5–0.8. Lower ratios produced very little oxygen. Bailey and Lane did not vary the ozone/olefin ratio in their experiments. The typical ratio they used was ~1/1 ozone/olefin.

[41] Hinrichs, T. A.; Ramachandran, V.; Murray, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 1282–1284.

[42] Greisbaum, K.; Bruggemann, J. *Adv. Chem. Ser.* **1972**, *No. 112*, 50–64.

cyclopropane. This is consistent with a direct attack of $HFCO_2$ or :CHF (obtained from decomposition of $HFCO_2$) upon the olefin.

$CHF{=}CH_2$ and $CH_2{=}CF_2$ ozonolyses do not yield epoxides and cyclopropanes.[2–5,9,10] In these cases there is evidence that indicates that the primary ozonides cleave preferentially to give H_2CO_2 and HFCO or F_2CO.[5,10] The primary ozonides of *cis*- and *trans*-$CHF{=}CHF$ and $CF_2{=}CF_2$ cleave to produce $HFCO_2$ + HFCO and F_2CO_2 + F_2CO, respectively. $CHF{=}CF_2$ primary ozonide may cleave to give either $HFCO_2$ and F_2CO or F_2CO_2 and HFCO. It is possible that H_2CO_2 addition to an aldehyde is favored over epoxidation or addition to the olefin to produce cyclopropane. Hence, $CHF{=}CH_2$ and $CF_2{=}CH_2$ ozonolyses are more similar to those of small alkyl-substituted olefins in terms of the types of major products. The other fluorinated ethylenes must give $HFCO_2$ or F_2CO_2 and these species may not add to HFCO and F_2CO as readily. Therefore, other processes such as epoxidation or cyclopropane formation may become competitive and even dominate in the case of $CF_2{=}CF_2$. Further work is required to identify the intermediates involved in the formation of epoxides and cyclopropanes.

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Registry No. 1,1-Difluoroethylene, 75-38-7; trifluoroethylene, 359-11-5; tetrafluoroethylene, 116-14-3; 1,1-difluoroethylene ozonide, 69932-17-8; trifluoroethylene ozonide, 86013-87-8; trifluoroethylene oxide, 2925-24-8; *cis*-1,2-difluoroethylene ozonide, 54892-64-7; *trans*-1,2-difluoroethylene ozonide, 54892-65-8; *cis*-1,1,2,3-tetrafluorocyclopropane, 49852-49-5; *trans*-1,1,2,3-tetrafluorocyclopropane, 49852-50-8; perfluoroethylene epoxide, 694-17-7.

Solid-State Chemistry, Kinetics, and Spectroscopy of 1,2-Diphenylpropylidene

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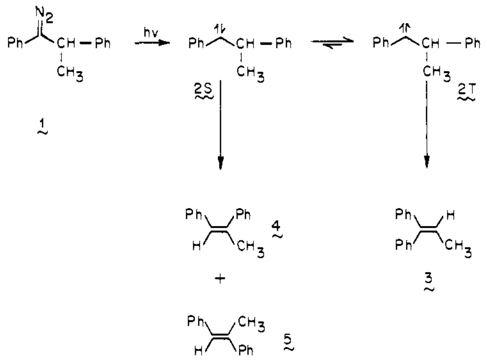
Abstract: Photolysis of diazo compound **1** at low temperatures produces the triplet ESR spectrum of carbene **2T**. The only kinetically important process of **2T** in glasses at low temperature is hydrogen atom abstraction from the matrix. Carbene **2T** is long lived in polycrystals. The products observed in polycrystals may be due in part to annealing a sample containing unreacted carbene. Studies of **2T** in perfluorinated matrices between −154 and −170 °C revealed that 1,2 hydrogen atom shifts do occur from the triplet (albeit slowly) by an unknown mechanism (Scheme I). Singlet carbene **2S** undergoes 1,2 hydrogen atom shifts without an appreciable product isotope effect. The chemistry and kinetics of both **2S** and **2T** in the solid state are strongly influenced by the matrix.

In the past few years several research groups have studied the chemistry of carbenes in polycrystalline solids and glasses at low temperature.[2] In the case of carbenes with triplet ground states there are profound differences between the chemistry observed in fluid solution at elevated temperatures (273–300 °C) and that obtaining in solids at −196 °C. Part of the change in chemistry can be attributed to the temperature difference. The product distribution obtained from carbenes responds to temperature variation because the activation parameters of singlet and triplet carbene processes are likely to be different. Furthermore, the equilibrium concentrations of the singlet and triplet carbenes (if equilibrium is achieved) will vary with temperature. In general, when one has a triplet ground state one observes a large increase in triplet chemistry (hydrogen atom abstraction–recombination and non-stereospecific cyclopropanation of alkenes) over singlet chemistry (intramolecular 1,2 hydrogen atom shift, stereospecific cyclopropanation, insertion into hydroxyl bonds) at the temperature of liquid nitrogen. Whether the rate of singlet–triplet equilibrium in a carbene is fast or slow relative to chemical reaction is a crucial mechanistic question. This question has been answered for a few systems.[3] However, it is quite possible that dramatic changes in temperature may alter the relative rates of non-radiative relaxation relative to chemical processes.

Scheme I



Temperature cannot be the sole determining factor, however. The solid-state environment exerts considerable control over matrix reactions. Tomioka, Griffin, and Nishiyama generated phenyl carbene from several precursors.[2e] The same chemistry from all

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(1) Alfred P. Sloan Research Fellow.

(2) (a) Moss, R. A.; Joyce, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 4475–4480. (b) Moss, R. A.; Huselton, J. K. *Ibid.* **1978**, *100*, 1314–1315. (c) Moss, R. A.; Joyce, M. A. *Ibid.* **1977**, *99*, 1262–1264. (d) Moss, R. A.; Dolling, U. H. *Ibid.* **1971**, *93*, 954–960. (e) Tomioka, H.; Griffin, G. W.; Nishiyama, K. *Ibid.* **1979**, *101*, 6009–6012. (f) Tomioka, H.; Inagaki, T.; Nakamura, S.; Izawa, Y. *J. Chem. Soc., Perkin Trans. 1* **1979**, 130–134. (g) Tomioka, H.; Izawa, Y. *J. Am. Chem. Soc.* **1977**, *99*, 6128–6129. (h) Tomioka, H. *Ibid.* **1979**, *101*, 256–257. (i) Tomioka, H.; Suzuki, H.; Izawa, Y. *Chem. Lett.* **1980**, *293*. (j) Moss, R. A.; Wetter, W. P. *Tetrahedron Lett.* **1981**, *22*, 997. (k) Tomioka, H.; Ueda, H.; Kondo, S.; Izawa, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7817.

0002-7863/83/1505-5053$01.50/0