70968-92-2; 8-HETE, 70968-93-3; 6-HETE, 70968-94-4; 5-HETE, 71030-39-2; 15-HETE methyl ester, 71030-40-5; 14-HETE methyl ester, 71000-87-8; 12-HETE methyl ester, 71030-41-6; 11-HETE methyl ester, 70968-95-5; 9-HETE methyl ester, 70968-96-6; 8-HETE methyl ester, 70968-97-7; 6-HETE methyl ester, 70968-98-8; 5-HETE methyl ester, 70968-99-9; methyl 15-(trimethylsiloxy)eicosanoate, 70969-00-5; methyl 14-(trimethylsiloxy)eicosanoate, 70969-01-6; methyl 12-(trimethylsiloxy)eicosanoate, 70969-02-7; methyl 11-(trimethylsiloxy)eicosanoate, 70969-03-8; methyl 9-(trimethylsiloxy)eicosanoate, 70969-04-9; methyl 8-(trimethylsiloxy)eicosanoate, 70969-05-0; methyl 6-(trimethylsiloxy)eicosanoate, 70969-06-1; methyl 5-(trimethylsiloxy)eicosanoate, 70969-07-2; arachidonic acid, 506-32-1.

Ozonolysis of Vinyl Fluoride: Identification of Ozonides and Doubly Fluorinated Products[1]

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A number of products have been identified upon ozonolysis of vinyl fluoride at low temperatures either neat or in CH_3Cl. The major volatile products are formyl fluoride and vinyl fluoride ozonide (3-fluoro-1,2,4-trioxolane). Small amounts of both cross ozonides have been observed and trace amounts of acetyl fluoride, fluoroacetyl fluoride, and *cis*-1,2-difluorooxirane. The formation of the three ozonides is consistent with a Criegee pathway involving both H_2COO and HFCOO intermediates. The other products can be accounted for by further reactions of intermediates derived from a Criegee pathway or by other unrelated processes. The decomposition of vinyl fluoride ozonide leads to additional volatile products including CO_2, HCOF, HCOOH, SiF_4 (in glass), and two minor compounds identified as bis(fluoromethyl) ether and fluoromethyl formate. The characterization of vinyl fluoride ozonide and fluoromethyl formate ($CH_2FOC(O)H$) by IR, NMR, mass, and microwave spectroscopy is reported.

The condensed phase ozonolysis of low molecular weight alkenes with halogen substitution at the double bond has recently received attention. Low-temperature IR studies[2] on chloroethylenes identified a stable primary ozonide (1,2,3-trioxolane) only for vinyl chloride. No secondary ozonide (1,2,4-trioxolane) formation was observed, unlike a similar study of unhalogenated alkenes.[3]

Griesbaum et al.[4] have examined the ozonolysis of 2,3-dichloro- and 2,3-dibromo-2-butene. Stable ozonides were not isolated. A variety of other products were identified which could be derived from subsequent reactions of the acetyl halide and halogenated carbonyl oxide (HXCOO) expected from a Criegee cleavage[5] of the alkene. However, as much as 30% of the alkene reacted by non-Criegee pathways to produce products such as epoxides or tetrahalobutanes. Ozonolysis of monochloroalkenes in a participating solvent capable of trapping a carbonyl oxide indicated that 80–95% of those alkenes cleaved to give an acyl chloride and carbonyl oxide.[6]

The ozonolysis of perfluoroethylene[7] or 1,2-difluoroethylene[8] has yielded some secondary ozonides. The ozonide yield was small in the case of C_2F_4 where perfluoroethylene oxide and CF_2O were the major volatile products with small amounts of perfluorocyclopropane also observed. The major volatile products from 1,2-$C_2H_2F_2$ are HCOF, the secondary ozonide, and *cis*-1,2-difluorooxirane. A trace amount of *cis*-1,2,3-trifluorocyclopropane was also obtained in methyl chloride solvent.

Such results raise a question as to what extent the normal ozonolysis mechanism[5,9–11] is applicable to halogenated alkenes. We report here our analysis of the ozonolysis of vinyl fluoride.

Results

The ozonolyses of C_2H_3F were conducted at low temperature either in methyl chloride or in isobutane or neat, using standard techniques[9] as described in the Experimental Section. A workup procedure involving distillation of the crude reaction mixture through traps held at −63, −95, and −196 °C and subsequent VPC and spectroscopic analysis of each trap was devised. The coldest trap was found to contain HCOF, C_2H_3F, and (where applicable) solvent. The −95 °C trap after VPC separation was found to contain vinyl fluoride ozonide [3-fluoro-1,2,4-trioxolane (**1**)], both cross ozonides [ethylene ozonide (**2**) and 3,5-difluoro-1,2,4-trioxolane (**3**)], and minor amounts of *cis*-1,2-difluorooxirane (**4**), acetyl fluoride (**5**), and fluoroacetyl fluoride (**6**). Variable amounts of H_2CO and HCOOH were found but they could be reduced to trace amounts in favorable runs. The −63 °C trap contained a clear, unstable liquid which usually generated heat and effervesced upon warming to room temperature. This liquid was predominantly vinyl fluoride ozonide. Its decomposition products were CO_2, HCOF, SiF_4, a brown viscous liquid which needs further characterization, and two minor compounds identified as bis(fluoromethyl) ether [$(CH_2F)_2O$ (**7**)] and fluoromethyl formate [$CH_2FOC(O)H$

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(1) (a) A partial report of this work was presented at the Symposium on Ozonolysis, CIC-ACS Meeting, Montreal, June, 1977. (b) Preliminary communication: R. P. Lattimer, U. Mazur, and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **98**, 4012 (1976).

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Table I. Products and Typical Yields from the Ozonolysis of Vinyl Fluoride

	neat	CH_3Cl (24.9 mmol)
reaction temp, °C	−126	−95
C_2H_3F (mmol, initial)	25.4	2.52
C_2H_3F (mmol, consumed)	3.60	2.13
O_3 (mmol, consumed)	2.54	1.79
Products, mol %[a]		
HCOF	36	40
$H_2COOCHFO$ (1)	45	33
H_2COOCH_2O (2)	3	1
trans-HFCOOCHFO (3a)	1	<0.05
cis-HFCOOCHFO (3b)	0.05	not obsd
cis-HFCOCHF (4)	0.4	not obsd
CH_3COF (5)	0.2	0.2
CH_2FCOF (6)	traces	not obsd
H_2CO	<1	<1
HCOOH	<1	4
$(\text{-O-O-})_x$ in solid residue	6	5
Mass Balance, %		
carbon	69	56
oxygen	94	64
fluorine	84	74

[a] Based on olefin consumed as 100%.

Table II. Products from the Decomposition of Vinyl Fluoride Ozonide

product	mol %[a]	product	mol %
CO_2	40	HCOOH	0.4
SiF_4	1	CH_2FOCH_2F (7)	1.2
H_2CO	<1	$CH_2FOC(O)H$ (8)	0.4
HFCO	<1	viscous residue	not det.[b]

[a] Based on ozonide decomposed as 100%. [b] This most abundant product (see Experimental Section) was an incompletely characterized complex mixture.

(8)]. A sizable amount of solid white residue always remained in the reaction vessel, but it was not thoroughly characterized. This residue oxidized aqueous KI and easily exploded upon handling. One mass spectrum of this solid material was obtained. Although the results were not conclusive they could be explained in part by an oligimeric material containing CH_2O and CH_2OO fragments.

Average quantitative yields from several reactions of C_2H_3F neat or in CH_3Cl are listed in Table I. The analysis of the decomposition products of vinyl fluoride ozonide are listed in Table II. Quantitative yields were not obtained from the ozonolyses in isobutane solvent which was employed in some of the early work, except to ascertain that HCOF and 1 were the major products and that cross ozonide 2 was also produced. This suggests that there is no substantive change in the predominant reaction processes in that solvent.

Reaction workup was not highly reproducible. Difficulties arose from the necessity of dealing with small quantities of reactive and volatile products. Nevertheless, the major volatile reaction products have been identified and most of the minor products have been isolated and confirmed. A few trace constituents detected sporadically by VPC remain unidentified.

The mass balance reflected in Table I is not very satisfactory. Based on the consumption of starting materials, the products in Table I account for 60–70% of the carbon, 75–85% of the fluorine, and 65–95% of the oxygen. The O_3/C_2H_3F ratios were 1.4 ± 0.3 (neat) and 1.2 ± 0.2 in solvents. Presumably, much of the carbon and perhaps some of the fluorine deficiency can be accounted for in the sizable amounts of solid residues. However, the seemingly low oxygen content of the solid residues as indicated by its peroxy content and the good overall oxygen balance for the neat reaction does not readily suggest appealing polymer structures.[12] This unsatisfactory situation is difficult and tedious to pursue experimentally and remains unresolved.

Table III. Stereochemical Comparisons of Relative Ozonide Yields and Configurations

alkene (solvent)	ethylene	R-ozonide	*cis*-R_2 ozonide	*trans*-R_2-ozonide	ref
vinyl fluoride (neat)	6	92	0.1[a]	2[a]	
vinyl fluoride (CH_3Cl)	3	97	not obsd	0.1	
propylene (isobutane)	11	85	3.2	0.8	10
t-$C_2H_2F_2$ (CH_3Cl)			11	89	8
c-$C_2H_2F_2$(CH_3Cl)			8	92	8
trans-2-butene (pentane)			38	61	30
cis-2-butene (pentane)			39	62	30

[a] For comparison with the results from $C_2H_2F_2$ in this table, this cis/trans ratio normalizes to 5:95.

The problems with the reaction stoichiometry notwithstanding, it is nevertheless reasonable to conclude that a major reaction pathway of the alkene is a Criegee cleavage to aldehyde and carbonyl oxide.[5,9-11] This can account for the normal ozonide formation (1) and the small amounts of cross ozonides (**2**, **3**). Some of the HCOF and the peroxide solid residues which appear to be low in fluorine content would also partly derive from this cleavage pathway with the solids resulting from reactions involving H_2COO fragments.[13]

Positive evidence for other non-Criegee cleavage reaction pathways involving the starting alkene include the identification of products 4–6 and the O_3/C_2H_3F stoichiometry. The former data indicates quite minor reaction processes and they will be discussed subsequently. The reaction stoichiometry along with the apparently low peroxy content of the solid might suggest a more sizable non-Criegee reaction pathway. In summary, depending upon the assumptions made regarding the origin of the HCOF, a Criegee cleavage of the alkene accounts for 40–85% of the alkene consumption.

For this unsymmetrical alkene undergoing a Criegee cleavage, it is interesting to know the relative proportions of the two possible pathways, (a) $H_2COO + HFCO$ and (b) $H_2CO + HFCOO$. It is not possible to infer this from the present data except to note that the observation of both cross ozonides (**2**, **3**) provides support for occurrence of both pathways. Preliminary results of trapping experiments also support this and will be discussed in the following paper.

There has been recent interest in the stereochemistry transmitted from an alkene to a secondary ozonide.[9,10] The cis/trans ratio of the difluoro cross ozonide from C_2H_3F can be examined in Table III, along with results for 2-

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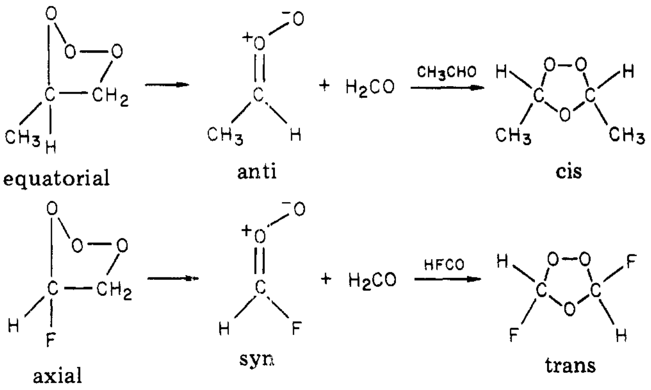
(12) One possibility is that CH_2OO fragments polymerize with C_2H_3F producing $(\text{-}CH_2OO\text{-})_x(CH_2CHF)_y$ oligomers. Another possibility is that some polymerization of C_2H_3F itself occurs perhaps triggered by catalytic amounts of radicals.

(13) In this regard, it is interesting to observe that the solid residues are largely absent upon ozonolysis of C_2H_4 or 1,2-$C_2H_2F_2$, presumably because of a higher reactivity between their respective zwitterions and aldehydes than for oligimer formation involving zwitterions.

Scheme I



butene ozonide obtained from propylene. The contrast is striking.

The propylene system has been previously discussed in terms of the Criegee mechanism considering stereochemistry.[9,10] The essential, common features of these proposals for a 1-alkene are the following. (1) The methyl or alkyl group prefers an equatorial ring site on the 1,2,3-trioxolane which subsequently cleaves to carbonyl oxide (zwitterion) and aldehyde. (2) Equatorial substituents on the 1,2,3-trioxolane favor formation of anti carbonyl oxides while axial substituents favor syn. (3) An anti carbonyl oxide upon reaction with an aldehyde leads to cis ozonides and a syn carbonyl oxide leads to trans ozonides. Hence, ozonolysis of propylene leads to preference for the cis configuration for the 2-butene cross ozonide.

One possibility to rationalize the preference for trans configuration for the difluoro cross ozonide from C_2H_3F is to postulate that fluorine prefers instead an axial site in the 1,2,3-trioxolane of C_2H_3F. This would lead to a preference for the syn configuration for HFCOO and the predominance of the *trans*-difluoro cross ozonide. This could correlate with the observation that fluorine prefers the axial site (cf. Experimental Section) in the gas-phase conformation of the final ozonide while methyl prefers the equatorial site.[9] This axial preference for F can be interpreted as an anomeric effect[14] and might be expected to also apply to the primary ozonide. This cross ozonide stereo rationale is outlined in Scheme I starting with the envelope form[9] of the 1,2,3-trioxolanes from C_3H_6 and C_2H_3F. Other conformations for the 1,2,3-trioxolanes are possible and should proceed similarly.[10]

By emphasizing an axial preference for F in the initial trioxolane, it is possible to rationalize[8] the relative constancy of the cis/trans ratio of **3** whether derived from C_2H_3F, *cis*-$C_2H_2F_2$, or *trans*-$C_2H_2F_2$. Nevertheless an alternative interpretation is possible; this constancy might also suggest that a trans orientation is preferred in the recombination step of HFCOO and HCOF regardless of the zwitterion configuration. This would seem plausible if strong dipole–dipole interactions of the C–F bonds are important in the recombination step.

Evidence obtained for reaction processes not readily incorporated into a Criegee reaction scheme include the small amounts of **4**–**6** that were isolated. The partially oxidized product, CH_3COF, presumably occurs via a direct oxidation of the starting material. It is an isomer of the monofluoro epoxide and it might result from an epoxidation–rearrangement. However, no trace of this novel epoxide was observed. This result is in contrast to the more sizable epoxide formation observed in 1,2-$C_2H_2F_2$ and C_2F_4 ozonolyses.

The production of trace amounts of **4** and **6** as well as the decomposition reaction of **1** to produce **7** and **8** are discussed in the following paper involving isotopic labeling experiments. The decomposition reaction of **1** has not been extensively explored except for some labeling data, since it is difficult to obtain stoichiometry results for it. This decomposition, once initiated, occurs rapidly with total loss of **1**. Whether the reaction results from the inherent instability of **1** or is catalyzed by trace amounts of H_2O or acid is unclear.

In summary, the ozonolysis of vinyl fluoride appears more similar to the ozonolysis of ethylene and alkylated alkenes than has been observed for most other halogenated alkenes since sizable quantities of the normal ozonide can be obtained. Also, the cross ozonide formation suggests that both Criegee cleavage pathways can occur. There is much less direct evidence for reactions retaining the C–C bonding of the alkene than in other halogenated systems although it does occur to a minor extent. The increasing amount of solid residues seems to suggest a low reactivity for the zwitterion and carbonyl recombination step which bears a similarity to most other halogenated alkene systems.

Experimental Section

IR spectra were obtained with Beckman 4240 and PE 457 spectrometers using either a 10-cm gas cell or a liquid nitrogen chilled CsI-window cold cell of conventional design. Proton nuclear magnetic resonance spectra were obtained with a Varian T-60A spectrometer or a JEOL FT-100 NMR spectrometer. Mass spectra were obtained with an Associated Electrical Industries MS-902 spectrometer with a cooled source to prevent ozonide decompositions. Microwave spectra were recorded with a Hewlett-Packard 8460A spectrometer. Gas chromatography was obtained with a Varian Model 920 chromatograph using an 18 ft, 15% Dow SE 710 column (on Chromosorb W, 80–100 mesh) which was modified to accept gaseous samples directly from a vacuum line. Typical conditions were: column, 35 °C; detector, 50 °C; flow rate 45 mL/min. Retention times (minutes): HCOF, 3.8; C_2H_3F, 3.9; CH_3Cl, 5.5; **7**, 10; **4**, 12; **8**, 13; HCOOH, 14; **3a**, 20; **3b**, 26; **2**, 31; 1, 35. A Welsbach Model T-408 ozonator was employed.

Ozonolysis Procedure. Reactions were conducted using flow rates of 0.15–0.30 mmol of O_3/min using standard techniques.[8,9] A dry ice trap preceded the ozonator and the reaction vessel. Three −126 °C traps were placed after the ozonolysis cell to collect volatile materials swept out of the reactor. Typically, only the first trap contained small amounts of C_2H_3F, HCOF, 1 and solvent. These materials were then distilled back into the reaction vessel prior to distillation of the reaction mixture through traps held at −63, −95, and −196 °C.

The preparation of the reaction solution, the post-reaction distillations, and VPC analyses were conducted on a calibrated vacuum line. The basic workup of the reaction was outlined in the Results section. **Caution**: The workup is hazardous and we have had explosions at three stages. (1) The solid residue left in the reactor is shock and friction sensitive. It must be neutralized for at least 24 h with aqueous KI. (2) The spontaneous decomposition of materials in a −63 °C trap, which is predominantly **1**, once led to a severe explosion. (3) Attempts to syringe the liquid at −63 °C for GC analysis led to an explosion in the syringe needle.

Quantitative Analysis. The −63 and −95 °C traps were analyzed by VPC, NMR and manometric analysis. Low-temperature NMR analyses of the crude −95 °C mixture were only reliable for estimating **1** and **2**; the results agreed well with the GC analysis. NMR analysis of the bulk −63 °C fraction indicated it was predominantly **1** with much smaller amounts of **2**. Known amounts of HCOF were added to these samples to obtain quantitative NMR data. The −196 °C trap contained C_2H_3F,

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[14] (a) R. U. Lemieux, *Pure Appl. Chem.*, **25**, 527 (1971); (b) E. L. Eliel, *Angew. Chem., Int. Ed. Engl.*, 11, 739 (1972); (c) C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, 4, (1969); (d) S. David, O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffmann, *J. Am. Chem. Soc.*, **95**, 3806 (1973).

HCOF, and any solvent. The similar retention times for C_2H_3F and HCOF precluded a reliable GC analysis on the available column and the large quantities of material created practical problems for an NMR analysis. Consequently, this material was analyzed initially by IR and later more precisely by comparison of the peak intensity of selected MW transitions against calibrated mixtures.[15] These measurements determine, in part, the C_2H_3F/O_3 ratios. The uncertainties cited for this ratio arise from the data scatter from analysis of six reactions. The peroxidic content of the solid residue was determined by thiosulfate titration of I_2 generated after a 24-h aqueous KI digestion.

Materials. CP grade vinyl fluoride, methyl chloride, and isobutane were obtained from Matheson Co. They were dried by passage through a trap cooled to −95 °C. No traces of 1,2-$C_2H_2F_2$ could be detected in the C_2H_3F by mass and MW spectrometry or other less sensitive methods.[16] For identification and calibration purposes, authentic samples were obtained or prepared using literature recipes for CO_2, HCOOH, H_2CO, HCOF, SiF_4, and **2**–**5**.

Vinyl Fluoride Ozonide (1). This compound was first identified by gas-phase IR, mass spectrometry, and MW spectroscopy as a constituent of the −95 °C trap prior to GC separation. Later, the NMR analysis of this mixture confirmed its presence. It was contained predominantly in the −63 °C trap, where it remained as a clear liquid at this temperature with a low vapor pressure. The characterization of this trap was obtained by low-temperature NMR analysis in perdeuterioacetone and by the IR spectrum of the solid at −196 °C. **1** is unstable and the liquid usually decomposes upon standing at room temperature. It will frequently decompose when making transfers on a vacuum line. It decomposes in a gaseous IR cell at room temperature after 5–10 min, generating HCOF, H_2CO, HCOOH, CO_2, and SiF_4.

^1H NMR at −80 °C in $(CD_3)_2CO$ δ 5.02 (d, $J_{HF(trans)} = 8.5$ Hz, 1 H), 6.05 (s, 1 H), 7.05 (d, $J_{HF(gem)} = 86.4$ Hz); ^{13}C NMR (proton decoupled) δ 94.98 (s), 113.6 (d, $J_{CF} = 10$ Hz); IR (prominent Q branch listed, ±5 cm^{-1}, 5 torr) 3010 (vw), 2910 (w), 1390 (w), 1350 (w), 1300 (vw), 1112 (vs), 1078 (s), 1050 (s), 1005 (m); mass spectrum (70 eV) 94 (0.35, $C_2H_3FO_3^+$), 66 (0.25, $CH_3FO_2^+$), 65 (0.02, $CH_2FO_2^+$), 64 (0.07, $CHFO_2^+$), 62 (0.08, $CH_2O_3^+$, $C_2H_3FO^+$), 49 (0.05, CH_2FO^+), 48 (0.20, $CHFO^+$), 47 (0.10, CFO^+), 46 (0.90, $CH_2O_2^+$), 45 (0.15, CHO_2^+), 44 (1.00, CO_2^+). MW transitions (24) of the normal isotopic species have been assigned giving rotational constants in megahertz of $A = 6774.0$, $B = 3916.3$, $C = 3122.7$. MW spectra for six other isotopic species have also been assigned.[17]

The MW assignments are readily correlated with the O_p–O_p twisted half-chair conformation reported for other ozonides[9] but only if the fluorine occupies the axial site. The analysis has not been thorough enough to completely eliminate other conformations for the ring and fluorine but these possibilities appear slight. The axial fluorine conformer is in contrast to the preference for the equatorial site by methyl groups in other ozonides. This contrast seems attributable to the anomeric effect and has analogies to other haloheterocyclic systems.[14] The condensed phase ^1H NMR of **1** did not readily suggest its conformation and variation of temperature between −40 and −85 °C produced no change in the spectrum. The assignment of long-range coupling of fluorine to the trans H ($^4J_{HF}$(trans) = 8.5 Hz) is based on analogy to similar systems containing an ether moiety where trans couplings of similar magnitude were assigned.[18]

Ethylene ozonide (2) was identified by its characteristic IR,[19] MW,[20] and mass spectra.[21] The NMR at −80 °C in acetone-d_6 is a singlet at δ 5.2.

3,5-Difluoro-1,2,4-trioxolane (3a, 3b). These ozonides were tentatively identified by comparison of the VPC retention times with authentic samples[8] and confirmed by IR and mass spectra of VPC isolated samples. The stereo assignment of **3a** and **3b** as trans and cis, respectively, is based on Gillies analysis.[8]

***cis*-1,2-Difluorooxirane (4)** was identified in the −95 °C trap both before and after VPC separation. Its characteristic IR, NMR, MW, and mass spectra matched those of authentic samples.[8] It was detected by NMR in the reaction mixture isolated in the −95 °C trap in amounts close to those obtained after GC separation.

Acetyl fluoride (5) was identified in the −95 °C trap both before and after VPC separation by the IR spectrum.[22] Further confirmation was made by MW spectroscopy.[23]

Fluoroacetyl Fluoride (6). Only trace amounts were observed in the neat ozonolysis after VPC separation. It was suggested by its IR spectrum[24] and confirmed by its characteristic MW spectrum.[25] The possibility that it does not arise during ozonolysis cannot be excluded. However, it seems unlikely that it arises from decomposition of **3** or **4** since it was not apparently observed in their previous characterizations.[8]

Bis(fluoromethyl) Ether (7). This was isolated by VPC as a decomposition product of liquid **1**. Its mass spectrum, IR, and NMR concurred with the literature.[26]

Fluoromethyl Formate (8). This was isolated by VPC as a decomposition product of liquid **1**. It is unlikely that **7** and **8** have been co-condensed with **1** prior to its decomposition, since they are volatile enough to pass through a −63 °C trap. There is no previous literature on $HC(O)OCH_2F$. Characterization is based on the following data: IR, gas (prominent Q branch, ±5 cm^{-1}) 3010 (vw), 2960 (w), 1770 (s), 1185 (m), 1150 (vs), 1070 (vs), 980 (w); mass spectrum (70 eV) 78 (2.1, $C_2O_2H_3F^+$), 77 (0.7, $C_2O_2H_2F^+$), 58 (1.6, $C_2O_2H_2^+$, COH_3F^+), 50 (10, COH_3F^+), 30 (53, CH_2O^+), 29 (91, CHO^+), 28 (44, CO^+); ^1H NMR (−80 °C in $(CD_3)_2CO$) δ 5.93 (d, $J_{HF} = 51$ Hz, 2 H), 8.49 (s, 1 H). The microwave spectrum has also been assigned: $A = 11\,195$, $B = 3859$, $C = 3261$ MHz. These constants are consistent with (but not unique to) a conformer similar to methyl formate[27] except for the fluorine rotated about 85–90° out of the HC(O)OC plane.[28]

Liquid Residue. Several drops of a brown viscous liquid remained after decomposition of **1**. It was a complex mixture whose analysis remains at a preliminary stage. Its MS, NMR, and IR spectra were examined. The mass spectrum had mass peaks at 186, 167, 104, and 85 which are indications of SiF_4 and $O(SiF_3)_2$, which is presumably a hydrolysis product of SiF_4.[29] The SiF_4 must result from fluorination of the glass vessel. A number of additional mass peaks were also observed but no other species were positively identified except to note a medium intensity fragment at m/e 33, which suggests that CH_2F fragments may be abundant in the residue's components. The IR spectrum of the liquid (neat) resembled HCOOH with strong broad absorptions at 1750 cm^{-1} and in the region 1150-900 cm^{-1}. However, the NMR spectrum in $CDCl_3$ did not reveal sizable amounts of HCOOH but had multiplets at δ 5.25, 5.52, 5.79, and 8.05.

Solid Residue. Large quantities of peroxidic white solids were produced upon ozonolysis and remained after volatile species were distilled from the reaction vessel. These products occasionally would plug the ozone gas inlet. These solids were hazardous and readily exploded upon handling. Only one mass spectral characterization of a small sample was attempted. The observed peaks were: 184 (0.2), 149 (0.3), 138 (1.3), 121 (0.5), 110 (0.6), 105 (0.9), 93 (0.7), 92 (1.0), 77 (2.1), 75 (2.8), 73 (0.9), 64 (1.7), 61 (3.0), 60

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(15) This method is discussed by C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy", McGraw-Hill New York, 1955, p 495.

(16) Small amounts of 1,2-$C_2H_2F_2$ could lead to **3** and **4**. Hence, the argument cited above that observation of **3** (and **2**) suggests both cleavage pathways would need reexamination. This possibility seems unlikely from the chemical analysis, but also seems inconsistent with the absence of **4** in CH_3Cl (Table I) since in this solvent 1,2-$C_2H_2F_2$ produces more **4** than **3**.[8] This question is addressed more fully in the following paper.

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(1.2), 57 (0.8), 47 (15.2), 46 (44.4), 45 (40.7), 44 (100), 33 (0.3), 32 (3.7), 31 (40.7), 30 (37.0), 29 (85.2), 28 (40.7). It seems reasonable to propose that the peaks at 184, 138, 92, and 46 arise from $(H_2COO^+)_n$ fragments and that the fragment at 110 might arise from the $(HFCOO)(H_2COO)^+$ ion. However, vinyl fluoride has the same mass as H_2COO suggesting other possibilities.

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Registry No. **1**, 60553-18-6; **2**, 289-14-5; **3a**, 54892-65-8; **3b**, 54892-64-7; **4**, 54943-69-0; **5**, 557-99-3; **6**, 1514-42-7; **7**, 462-51-1; **8**, 70879-14-0; C_2H_3F, 75-02-5; HCOF, 1493-02-3; H_2CO, 50-00-0; HCOOH, 64-18-6; CO_2, 124-38-9; SiF_4, 7783-61-1.

Ozonolysis of Ethylene, Vinyl Fluoride, and 1,2-Difluoroethylene: Isotopic Labeling Experiments

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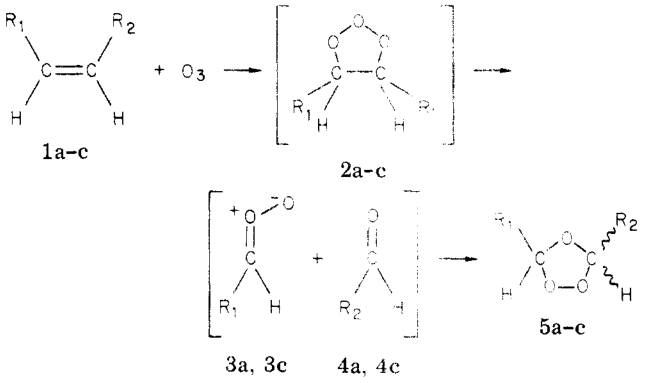
The condensed phase, low-temperature ozonolyses of ethylene, vinyl fluoride, and 1,2-difluoroethylene were investigated. Five trapping experiments are reported involving mixtures of these alkenes with an added aldehyde (formaldehyde or formyl fluoride). Four experiments are discussed where cross ozonide formation could be followed involving an isotopically enriched alkene or two different alkenes. These results indicate that the various synthetic routes to vinyl fluoride ozonide are consistent with a Criegee cleavage mechanism. It is likely that vinyl fluoride, upon ozonolysis, cleaves predominantly to H_2COO and HCOF, but that some production of HFCOO and H_2CO also occurs. Isotopic data suggest that the small amounts of *cis*-1,2-difluorooxirane produced upon ozonolysis of C_2H_3F (neat) may arise from trace amounts of $1,2\text{-}C_2H_2F_2$ present initially or produced during the ozonolysis.

Studies of the ozonolysis of C_2H_4,[1] C_2H_3F,[2] and $1,2\text{-}C_2H_2F_2$[3] at low temperatures in solution or solid phases have been previously reported. These reports analyzed the production of secondary ozonides in terms of the Criegee cleavage mechanism. The expected products from this mechanism for the three alkenes are outlined in Scheme I.[4-6]

Isotopic labeling experiments involving C_2H_4 and added aldehydes were shown to be consistent with the Criegee scheme.[1] Results for $1,2\text{-}C_2H_2F_2$ demonstrated that the secondary ozonide (**5c**) was formed along with HCOF, *cis*-1,2-difluorooxirane (**6**), and traces of *cis*-1,2,3-trifluorocyclopropane.[3] Mixtures of 1,2-difluoroethylene-d_0 and -d_2 were employed to show that **6** was formed without carbon–carbon bond cleavage. However, the isotopic content of the ozonide (**5c**) was not determined.

The ozonolysis of C_2H_3F has led to the three ozonides expected from Scheme I.[2] The total cross ozonide yields (relative to normal ozonide) were about 3% for ozonolysis in CH_3Cl solvent but rose to about 9% when no solvent was employed. HCOF and peroxidic solids were other major products along with trace amounts of CH_3COF. Trace amounts of **6** and $FC(O)CH_2F$ (**7**) were also observed when C_2H_3F was ozonized neat. **5b** was unstable and readily decomposed, giving a complex mixture which included small amounts of $(CH_2F)_2O$ (**8**) and $HC(O)OCH_2F$ (**9**).

Scheme I



a, $R_1 = R_2 = H$; b, $R_1 = H$, $R_2 = F$; c, $R_1 = R_2 = F$

Although the observation of both cross ozonides from C_2H_3F is consistent with Scheme I, the other two unexpected difluoro species raise the question whether another process could lead to **5c**. Consequently, a series of isotopic labeling experiments were conducted to study (1) the process of fluorinated ozonide formation, (2) the direction of cleavage of **2b** obtained from C_2H_3F, (3) the mechanism of formation of **6** from C_2H_3F, and (4) the decomposition of **5b** to produce **8** and **9**.

Results

Table I lists the results of five trapping experiments with added aldehydes and four experiments involving two chemically different and/or isotopically distinct alkenes where cross ozonide formation could be followed. The general procedure was to effect a crude separation of ozonolysis products by trap-to-trap distillation[2b] and then to further separate and isolate the components of the −95 °C trap by VPC. Mass and microwave spectra of these components afforded relative isotopic information of each component but not accurate relative or absolute yields of

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[5] For **1a**, the species expected are **2a** → **3a**, **4a** → **5a**. For **1b**, they are **2b** → **3a**, **3c**, **4a**, **4c** → **5a–c**. For **1c**, they are **2c** → **3c**, **4c** → **5c**. Note that **3a** is H_2COO and **3c** is HFCOO.

[6] (a) A diradical form for **3** has been identified as reflecting more accurately its ground electronic state.[6b] The chemistry does not provide a ready distinction between the diradical and zwitterionic representations and so in this paper we will retain the widely used Criegee zwitterionic form for the carbonyl oxide **3**. (b) W. R. Wadt and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 3004 (1975); L. B. Harding and W. A. Goddard III, *J. Am. Chem. Soc.*, **100**, 7180 (1978).