221. *Oxidation of Polyhalogeno-compounds. Part IV.*[1] *Photochemical Oxidation and Auto-oxidation of Chlorotrifluoroethylene.*

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Vapour-phase photochemical oxidation of chlorotrifluoroethylene gives chlorodifluoroacetyl fluoride in good yield. The acyl fluoride, together with a liquid peroxide, $[C_2ClF_3O]_n$, is also formed by the reaction between the liquid olefin and oxygen under autogenous pressure. Chlorotrifluoroethylene oxide is a probable by-product. Free-radical reaction schemes are postulated and correlated with earlier work on oxidation of polyhalogeno-olefins. Chlorodifluoroacetyl fluoride and oxalyl chloride fluoride were synthesised as reference compounds.

Earlier papers [1] in this series have been concerned with the photochemical or thermal oxidation of fluorine-containing polyhalogenoalkanes, and showed that under suitable conditions, *e.g.*, by the use of chlorine as initiator, suitable compounds of this type could be converted, without carbon–carbon bond cleavage, into fluoroalkanecarboxylic acids. Fluorine-containing polyhalogeno-olefins are now commercially available or readily prepared, and the controlled photochemical oxidation of such olefins without carbon–carbon cleavage offers another approach to the general problem of synthesis of fluoro-compounds containing functional groups. This paper is concerned with the photochemical oxidation and auto-oxidation of chlorotrifluoroethylene, which gives chlorodifluoroacetyl fluoride in good yield.

The photochemical oxidation of halogeno-olefins has been studied in some detail. Oxidation of tetrachloroethylene to trichloroacetyl chloride and carbonyl (di)chloride [2] is strongly inhibited by oxygen [3] and sensitised by chlorine [4] or fluorine; [5] kinetic studies [6] reveal the similarity to the chlorine-sensitised photochemical oxidation of pentachloroethane.[7] Tetrachloroethylene oxide has recently been isolated from the reaction products.[8] Photochemical chlorination of trichloroethylene is inhibited by oxygen,[9] and chlorine-initiated photochemical oxidation affords dichloroacetyl chloride.[10] Swarts [11] noted that bromofluoroethylenes readily absorbed oxygen to give acyl halides, *e.g.*,

$$CFBr{:}CFBr \longrightarrow CFBr_2{\cdot}COF;\quad CHF{:}CBr_2 \longrightarrow CHFBr{\cdot}COBr$$

Similar reactions [12,13] are:

$$CF_2Cl{\cdot}CF{:}CCl_2 \xrightarrow{O_2,\ Cl_2} CF_2Cl{\cdot}CFCl{\cdot}COCl + CF_2Cl{\cdot}CCl_2{\cdot}COCl$$

$$CF_2Cl{\cdot}CCl{:}CCl_2 \xrightarrow{O_2,\ Cl_2} CF_2Cl{\cdot}CCl_2{\cdot}COCl$$

$$CF_2Cl{\cdot}CF{:}CCl_2 \xrightarrow{O_2,\ Br_2} CF_2Cl{\cdot}CFBr{\cdot}COCl + CF_2Cl{\cdot}CFCl{\cdot}COCl$$

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[1] Francis and Haszeldine, *J.*, 1955, 6072 (Part I); Haszeldine and Nyman, *J.*, 1959, 387 (Part II); *J.*, 1959, 420 (Part III).
[2] Besson, *Compt. rend.*, 1895, **121**, 125.
[3] Leermakers and Dickinson, *J. Amer. Chem. Soc.*, 1932, **54**, 4648.
[4] Dickinson and Leermakers, *ibid.*, p. 3852; Dickinson and Carrico, *ibid.*, 1934, **56**, 1473.
[5] Miller and Dittman, *ibid.*, 1956, **78**, 2793.
[6] Schott and Schumacher, *Z. phys. Chem.*, 1941, *B*, **49**, 107.
[7] Schumacher and Thürauf, *ibid.*, 1941, *A*, **189**, 183.
[8] Kirkbride, U.S.P. 2,321,823 (1943); *Chem. Abs.*, 1943, **37**, 6676; Frenkel, Johnson, and Pitt, *J. Org. Chem.*, 1957, **22**, 1119.
[9] Müller and Schumacher, *Z. phys. Chem.*, 1937, *B*, **35**, 455.
[10] *Idem, ibid.*, 1937, *B*, **37**, 365.
[11] Swarts, *Bull. Acad. roy. Belg.*, 1897, **33**, 439; 1897, **34**, 307; 1897, **35**, 849; 1898, **36**, 532; *Rec. Trav. chim.*, 1898, **17**, 321; McBee, Pierce, and Christman, *J. Amer. Chem. Soc.*, 1955, **77**, 1851.
[12] Chaney, U.S.P. 2,439,505/1948; *Chem. Abs.*, 1948, **42**, 7315; U.S.P. 2,456,768/1948; *Chem. Abs.*, 1949, **43**, 4683; U.S.P. 2,514,473/1950; *Chem. Abs.*, 1950, **44**, 9474.
[13] Henne and Fox, *J. Amer. Chem. Soc.*, 1954, **76**, 479.

The reaction between liquid chlorotrifluoroethylene and molecular oxygen has been investigated by Myers [14] whose results do not agree with those obtained in the present work; whilst this was in progress a patent was issued on the subject,[15] but the yields, etc., there claimed differ appreciably from our own.

Chlorotrifluoroethylene and oxygen react together only very slowly in the vapour phase in the absence of light; 85% of the olefin is recovered after six months, and chlorodifluoroacetyl fluoride is the only product. In the presence of water this vapour-phase reaction is even slower. The reaction is greatly accelerated by ultraviolet light, the major product being chlorodifluoroacetyl fluoride ($CF_2{:}CFCl \longrightarrow CF_2Cl{\cdot}COF$; 77% yield, 47% conversion of olefin after 5 days) together with smaller amounts of breakdown products such as carbonyl difluoride, carbon dioxide, and silicon tetrafluoride. Chlorodifluoroacetyl fluoride is itself slowly oxidised photochemically to carbon dioxide and carbonyl difluoride (together with silicon tetrafluoride). Photolysis of the acyl fluoride in absence of oxygen gives 1 : 2-dichlorotetrafluoroethane, dichlorodifluoromethane, carbonyl difluoride, and carbonyl chloride fluoride; chlorotrifluoromethane was not detected:

$$CF_2Cl{\cdot}COF \xrightarrow{h\nu} \dot{C}F_2Cl \xrightarrow{CF_2Cl{\cdot}COF} CF_2Cl_2$$
$$\dot{C}F_2Cl \longrightarrow (CF_2Cl)_2$$

Dichloro-tetrafluoroethane or -difluoromethane was not formed during photochemical oxidation of chlorotrifluoroethylene. The chlorodifluoroacetyl fluoride so obtained is spectroscopically identical with a sample prepared as follows:

$$CF_2Cl{\cdot}CO_2Na \xrightarrow{PCl_5} CF_2Cl{\cdot}COCl \xrightarrow{KF} CF_2Cl{\cdot}COF$$

The identified products of the photochemical oxidation of chlorotrifluoroethylene account for virtually all the olefin consumed; nevertheless, examination was made for two other products that could conceivably be formed without carbon–carbon fission, *i.e.*, oxalyl chloride fluoride and oxalyl difluoride. Oxalyl chloride fluoride has a characteristic absorption spectrum with double carbonyl absorption. Attempts to convert oxalyl dichloride or chloride fluoride into oxalyl difluoride failed, since only breakdown occurred under more forcing conditions. However, the absence of a double carbonyl peak from the infrared spectrum of the more volatile photolysis products of chlorotrifluoroethylene shows that oxalyl chloride fluoride or difluoride is absent, or present to only a very small extent.

The halogen-sensitised photochemical oxidation of chlorotrifluoroethylene was next investigated. Addition of even small quantities of chlorine, *e.g.*, a molar ratio of olefin to chlorine of *ca.* 200 : 1, caused spontaneous pyrolysis at low temperature when liquid olefin was still present. The introduction of bromine into vapour-phase mixtures of the olefin and oxygen resulted in an immediate explosion. The sensitivity of the reaction between chlorotrifluoroethylene and oxygen towards sources of free radicals is clearly demonstrated.

Myers [14] stated that in the absence of liquid olefin the reaction between chlorotrifluoroethylene and oxygen is immeasurably slow, and in general this agrees with our results. From the reaction of the liquid olefin and oxygen he obtained a product of b. p. *ca.* 15° higher than that of the olefin (b. p. −26·8°) and postulated that this was the peroxide $\overline{CF_2{\cdot}CFCl{\cdot}O{\cdot}O}$. Products of higher b. p. were not obtained. Myers discounted the possibility of chlorodifluoroacetyl fluoride, since hydrolysis gave oxalate, fluoride, and chloride ions in the ratio 1 : 3 : 1, and chlorodifluoroacetic acid is known to be stable in aqueous solution; it should be noted, however, that the acid will break down if heated with concentrated aqueous alkali. Our own investigation of the reaction between liquid chlorotrifluoroethylene and oxygen shows that one mole of olefin reacts with only ½ mole

[14] Myers, *Ind. Eng. Chem.*, 1953, **45**, 1783.
[15] Hurka, U.S.P. 2,676,983/1954; *Chem. Abs.*, 1955, **49**, 5510.

of oxygen in accord with the stoicheiometry, $CF_2{:}CFCl + \frac{1}{2}O_2 \longrightarrow CF_2Cl{\cdot}COF$; Myers found the oxygen uptake to be equimolar. The products are chlorodifluoroacetyl fluoride and the volatile breakdown materials mentioned earlier, but in addition a relatively involatile liquid, not hitherto reported, was isolated. This detonated when warmed and had other peroxidic properties. Its yield decreases with reaction time in favour of increased formation of chlorodifluoroacetyl fluoride. The analytical data give the formula $(C_2ClF_3O)_n$ and show that the oxygen is peroxidic with one O–O link per two C_2ClF_3O units. Hydrolysis affords chlorodifluoroacetic and oxalic acid together with carbon dioxide, chloride, and fluoride.

An attempt was made to detect the formation of the epoxide $\overline{CF_2{\cdot}CFCl{\cdot}O}$ during the oxidation of chlorotrifluoroethylene. When oxygen was bubbled into refluxing liquid chlorotrifluoroethylene at atmospheric pressure, chlorodifluoroacetyl fluoride and an unstable compound characterised by a strong band at 6·4 μ in its infrared spectrum were formed. Complete separation of this new compound from chlorodifluoroacetyl fluoride could not be effected even when the excess of olefin was removed by rapid treatment with chlorine, but analysis of the mixture indicated that it is an isomer of chlorodifluoroacetyl fluoride, but not trifluoroacetyl chloride, and is thus probably chlorotrifluoroethylene oxide. This is presumably the unknown compound noted by Myers; its hydrolysis to oxalic acid is as expected:

$$CF_2\!-\!CFCl + H_2O \longrightarrow CF_2(OH){\cdot}CFCl{\cdot}OH \xrightarrow{H_2O} (CO_2H)_2 + 3F^- + Cl^-$$

Discussion.—It is suggested that chlorotrifluoroethylene and oxygen react slowly, even in the dark, to give a cyclic peroxide as an unstable intermediate:

$$CF_2{:}CFCl + O_2 \longrightarrow \dot{C}FCl{\cdot}CF_2{\cdot}O{\cdot}O{\cdot} \xrightarrow{CF_2{:}CFCl} \begin{matrix} CFCl{\cdot}CF_2{\cdot}O \\ | \qquad\quad | \\ CFCl{\cdot}CF_2{\cdot}O \end{matrix}$$

Attack of oxygen on the CF_2 group of chlorotrifluoroethylene is followed, in the liquid phase, by attack on a second molecule of the olefin to give the relatively involatile peroxide $[C_2ClF_3O]_2$. This satisfies the analytical data for the explosive liquid $[C_2ClF_3O]_n$, with one peroxy-group per two molecules of olefin, isolated from the reaction of liquid chlorotrifluoroethylene with oxygen. A linear structure for $[C_2F_3ClO]_n$ must be discounted, since it would be a chlorofluoroalkyl ether, not a peroxide, and chemically and thermally would be much more stable. The peroxide could then function as a source of free radicals on exposure to light, or as a source of chlorotrifluoroethylene oxide.

The photochemical oxidation of chlorotrifluoroethylene was carried out in Pyrex vessels so that the wavelength of the initiating radiation is >3000 Å. A peroxide would absorb light of wavelength > 3000 Å and its photolysis would give rise to a free radical capable of initiating the photochemical oxidation chain reaction. The decrease in the rate of the dark reaction in presence of water can be attributed to removal of the peroxide by hydrolysis. The ability of chlorotrifluoroethylene, after " activation " by being kept with small amounts of oxygen, to oxidise fresh olefin can also be accounted for by peroxide formation.

Chlorine atoms are the chain carriers in the free-radical chain reaction which sets in after initiation by a free radical R [*e.g.*, $(CFCl{\cdot}CF_2{\cdot}O{\cdot})_2$] acting in the same manner as a chlorine atom in the following sequence:

Chain reaction:

$$Cl{\cdot} + CF_2{:}CFCl \longrightarrow CF_2Cl{\cdot}CFCl{\cdot} \xrightarrow{O_2} CF_2Cl{\cdot}CFCl{\cdot}O_2{\cdot}$$

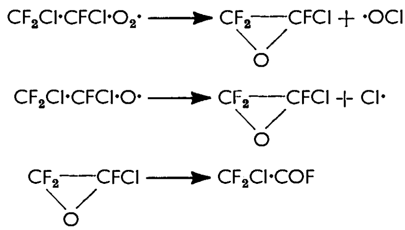
$$CF_2Cl{\cdot}CFCl{\cdot}O_2{\cdot} \xrightarrow{Cl_2} CF_2Cl{\cdot}CFCl{\cdot}O_2Cl \xrightarrow{h\nu} CF_2Cl{\cdot}CFCl{\cdot}O{\cdot} + {\cdot}OCl$$

$$2{\cdot}OCl \longrightarrow O_2 + Cl_2$$

$$CF_2Cl{\cdot}CFCl{\cdot}O{\cdot} \longrightarrow CF_2Cl{\cdot}COF + Cl{\cdot} \longrightarrow \text{etc.}$$

The sensitivity of mixtures of chlorotrifluoroethylene and oxygen to small quantities of chlorine or bromine indicates long reaction chains. That atom or radical attack is exclusively on the CF_2 group of chlorotrifluoroethylene has already been established.[16] The formation of the $CF_2Cl{\cdot}CFCl{\cdot}O_2{\cdot}$ radical, its conversion into the perhalogenoalkoxy-radical $CF_2Cl{\cdot}CFCl{\cdot}O{\cdot}$ with chlorine on the α-carbon atom, and loss of this chlorine as an atom, are steps analogous to those proposed for the photochemical oxidation of chlorofluoroethanes to trifluoroacetyl chloride.[1]

Chlorodifluoroacetyl fluoride could also be formed *via* rearrangement of chlorotrifluoroethylene oxide:



Support for the postulate that the chlorine atom is the chain carrier in the above reactions comes from consideration of the products from other unsymmetrical polyhalogeno-olefins. Thus, a similar reaction scheme can be formulated for the bromofluoroethylenes with bromine atom as carrier, and for trichloroethylene:

$$Br{\cdot} + CFX{:}CBr_2 \longrightarrow CFXBr{\cdot}CBr_2{\cdot} \xrightarrow{O_2} CFXBr{\cdot}COBr \quad (X = H \text{ or } Br)$$

$$Cl{\cdot} + CHCl{:}CCl_2 \longrightarrow CHCl_2{\cdot}CCl_2{\cdot} \xrightarrow{O_2} CHCl_2{\cdot}COCl$$

The direction of free-radical or atom attack on these olefins is either established [17] or can be predicted with certainty from recent work on the direction of addition of a free radical to unsymmetrical olefins.[18] Similarly, Chaney's [12] and Henne and Fox's [13] results can be reinterpreted as:

$$X{\cdot} + CF_2Cl{\cdot}CF{:}CCl_2 \longrightarrow CF_2Cl{\cdot}CFX{\cdot}CCl_2{\cdot}$$

$$CF_2Cl{\cdot}CFX{\cdot}CCl_2{\cdot} \xrightarrow{O_2} CF_2Cl{\cdot}CFX{\cdot}CCl_2{\cdot}O{\cdot} \longrightarrow Cl{\cdot} + CF_2Cl{\cdot}CFX{\cdot}COCl$$

(where X = Cl or Br)

The direction of radical or atom addition to an olefin of the type $CZ_3{\cdot}CF{:}CCl_2$ (where Z = halogen) can be predicted with certainty to be to the CF group.[17] There is thus no need to postulate halogen-atom attack on the epoxide $CF_2Cl{\cdot}\overline{CF{\cdot}CCl_2{\cdot}O}$, and it is noteworthy that Henne and Fox cited no evidence for the formation of an epoxide.

Experimental

General techniques were described in Parts I—III. Reactants and products were measured, purified, etc., in an apparatus for manipulation of volatile compounds, *in vacuo*. The reactants could thus be freed from traces of air or other impurities and, since reactions were carried out in sealed Pyrex or Dreadnought tubes filled directly from the vacuum-apparatus and sealed *in vacuo*, there was no danger that unwanted catalysts, moisture, etc., could become incorporated. Products were identified by b. p., vapour pressure, molecular weight, infrared spectroscopy, analysis, etc. Spectroscopically pure chlorotrifluoroethylene was redistilled, and a middle cut degassed by repeated freezing and thawing, then redistilled several times. Tests for peroxides were negative. A Hanovia S. 250 ultraviolet lamp was used without the Wood's filter at 5—15 cm. from the reaction vessel. Typical experiments are reported below.

[16] Haszeldine and Steele, *J.*, 1953, 1592; 1954, 3747.
[17] Kharasch, Norton, and Mayo, *J. Org. Chem.*, 1939, **3**, 48; Haszeldine and Liptrot, unpublished results.
[18] See, *e.g.*, Cadogan and Hey, *Quart. Rev.*, 1954, **8**, 308; Haszeldine, *J.*, 1952, 2504 *et seq.*

The Vapour-phase Dark Reaction.—Chlorotrifluoroethylene (0·381 g., 3·27 mmoles) and oxygen (0·111 g., 3·47 mmoles) were sealed in a 50-ml. Pyrex tube (initial pressure *ca.* 3·2 atm.) and kept in darkness for *ca.* 6 months. The volatile products were distilled *in vacuo* to give unchanged chlorotrifluoroethylene (0·324 g., 2·78 mmoles, 85%) and chlorodifluoroacetyl fluoride (0·065 g., 0·49 mmole, 100% based on olefin used), shown spectroscopically to be the only product and identified by comparison of its infrared spectrum with that of a known sample.

The Vapour-phase Dark Reaction in the Presence of Water.—Chlorotrifluoroethylene (0·348 g., 2·99 mmoles), water (3·0 ml.), and oxygen (0·098 g., 3·06 mmoles), sealed in a 50-ml. Pyrex tube (initial pressure *ca.* 2·9 atm.) and kept in darkness for *ca.* 6 months, gave only unchanged chlorotrifluoroethylene (0·335 g., 2·88 mmoles, 96%).

Photochemical Oxidation.—Chlorotrifluoroethylene (1·270 g., 10·9 mmoles) and oxygen (0·308 g., 9·63 mmoles) were sealed in a 75-ml. Pyrex tube (initial pressure *ca.* 7·0 atm.) and exposed to ultraviolet light for 126 hr. The volatile products were distilled to give: (*a*) an unidentified residue (*ca.* 0·1 g.); (*b*) a fraction shown spectroscopically to consist of chlorotrifluoroethylene (0·429 g., 5·00 mmoles, 53% recovery) and chlorodifluoroacetyl fluoride (0·520 g., 3·93 mmoles, 77% yield), and (*c*) a mixture (0·165 g., 2·43 mmoles) of carbon dioxide, silicon tetrafluoride, and carbonyl difluoride. Shorter irradiation times with lower conversions or longer irradiation times with higher conversions of olefin failed to give significantly higher yields of the acyl fluoride.

Fractions (*b*) from several such tubes were combined and refractionated several times *in vacuo* to give pure chlorodifluoroacetyl fluoride (Found: *M*, 133. Calc. for C_2ClF_3O: *M*, 132·5), spectroscopically identical with a known sample. Further proof of structure was obtained by treating a sample (0·402 g.) with water (1·0 ml.) in a sealed tube for 1 hr. The aqueous solution was treated with an excess of silver carbonate, filtered, and freeze-dried. The residue was extracted with ether, and the ethereal extract evaporated *in vacuo* to give silver chlorodifluoroacetate, spectroscopically identical with a sample prepared directly from chlorodifluoroacetic acid.

Initiation by Activated Olefin.—Chlorotrifluoroethylene (0·735 g., 6·30 mmoles), which had been kept with oxygen (*ca.* 10%) for two weeks, was sealed with oxygen (0·256 g., 8·00 mmoles) in a 100-ml. Pyrex tube (initial pressure *ca.* 3·7 atm.) and exposed to ultraviolet light for 70 min. The products were distilled *in vacuo* to give: (*a*) an unidentified residue (*ca.* 0·1 g.), (*b*) a fraction shown spectroscopically to consist of chlorotrifluoroethylene (0·079 g., 0·68 mmole, 11% recovery) and chlorodifluoroacetyl fluoride (0·445 g., 3·36 mmoles, 60% yield), and (*c*) a mixture (0·108 g., 1·44 mmoles) of carbon dioxide, silicon tetrafluoride, carbonyl difluoride, and carbonyl chloride fluoride.

Chlorine-sensitised Oxidation.—Chlorotrifluoroethylene (0·761 g., 6·52 mmoles), chlorine (0·002 g., 0·028 mmole), and oxygen (0·301 g., 9·40 mmoles) were sealed in a 70-ml. Pyrex tube. When the mixture reached *ca.* −30° in subdued daylight a luminous flame-front traversed the tube; a second appeared 15 sec. later, and carbon was deposited on each occasion. Fractionation *in vacuo* of the products from several such reactions gave chlorotrifluoroethylene, chlorodifluoroacetyl fluoride, 1 : 1 : 2-trichlorotrifluoroethane, and the breakdown products reported above.

Bromine-sensitised Oxidation.—Chlorotrifluoroethylene (0·757 g., 6·50 mmoles) and oxygen (0·308 g., 9·60 mmoles) were sealed in a 50-ml. Pyrex tube together with a fragile ampoule containing bromine (0·067 g., 0·42 mmole). When the temperature had reached that of the room the ampoule was broken to release the bromine; the tube immediately exploded.

Liquid-phase Auto-oxidation.—The results of a series of dark experiments carried out in thick-walled Dreadnought tubes of 18 ml. capacity are summarised in the annexed Table.

CF_2:CFCl (mmole)	O_2 (mmole)	H_2O	Initial press. (atm.)	(Time (hr.)	Products CF_2:CFCl (% recovery)	$CO_2 + SiF_4 + COF_2 + COFCl$ (mmole)	$CF_2Cl\cdot COF$ (mmole)	Yield (%)	Peroxide (g.)
12·4	14·2	0	25	1·0	97	0·50	0	0	0
8·66	12·2	3·68	24	1·0	92	0·45 [a]	0	0	0
4·36	9·20	0	18	12·5	16	0·33	1·19	33	0·240
4·87	9·50	0	19	24	18	0·66	2·13	53	0·150
3·69	3·70 [b]	0	12	48	0	0·31 [c]	2·29	62	0·160

[a] CO_2 only. [b] 40% of oxygen unchanged at end of expt. [c] COF_2 only.

In an experiment at atmospheric pressure, chlorotrifluoroethylene (10 g.) was placed in the still-pot of a small low-temperature distillation column, the condenser of which was cooled with an alcohol–solid carbon dioxide slurry. Oxygen was bubbled into the refluxing liquid for 24 hr. The products, other than a small liquid residue (0·4 g.), were volatile. These were distilled *in vacuo* to give a number of arbitrary fractions. Infrared spectroscopic examination of the last of these (0·62 g.) showed the presence of an unknown compound characterised by a strong absorption band at 6·4 μ, as well as unchanged olefin and chlorodifluoroacetyl fluoride. This fraction was treated rapidly with chlorine (0·1 g.) in order to remove the olefin as 1 : 1 : 2-trichlorotrifluoroethane by distillation *in vacuo*. Infrared spectroscopic examination of the remaining material showed that it contained chlorodifluoroacetyl fluoride and the unknown compound (Found for the mixture: C, 17·3%; *M*, 130. Calc. for C_2OClF_3: C, 18·1%; *M*, 132·5).

Chlorotrifluoroethylene Peroxide.—This was a product of the reaction of liquid chlorotrifluoroethylene with oxygen as described above. The *peroxide* is a clear, colourless liquid of vapour pressure *ca.* 3 mm. at 20°, which decomposes in moist air and detonates violently on heating [Found: C, 17·3; Cl, 26·5; F, 41·2%; iodine equiv., 0·54. $(C_2ClF_3O)_n$ requires C, 18·1; Cl, 26·8; F, 43·0%; iodine equiv., 0·50]. The peroxide was analysed for chlorine and fluorine by fusion of a sample with sodium at 600° for 2 hr. in a Parr bomb. Chloride was then determined gravimetrically as silver chloride, and fluoride as fluorosilicic acid by titration with thorium nitrate solution.

Iodine was liberated when the peroxide was treated with aqueous potassium iodide, but the predominant reaction was that of hydrolysis, and hence the usual methods for determining the oxidising power of peroxides could not be used. The method ultimately employed was based on a procedure described by Nosaki.[19] A weighed sample (*ca.* 0·2 g.) was added to 30 ml. of a solution of sodium iodide in acetic anhydride, whereupon iodine was liberated immediately. After 15 min., 50 ml. of distilled water were added and the iodine was determined by titration with standard sodium thiosulphate.

The peroxide was rapidly and exothermically hydrolysed by water, and attack on the glass vessel produced sodium fluorosilicate. Hydrolysis with water in a sealed tube gave Cl^-, 15·7%, and C as CO_2, 8·6%. The aqueous solution was also treated with an excess of silver carbonate, filtered, and freeze-dried. The residue was extracted with ether, and the ether evaporated *in vacuo* to give a mixture of sodium and silver chlorodifluoroacetates and sodium oxalate, all identified spectroscopically. The sodium arose from attack on the glass vessel by the hydrofluoric acid formed in the hydrolysis. The peroxide thus hydrolyses with approx. 50% breakdown to chloride, fluoride, and carbonate [Calc. for $(C_2ClF_3O)_{2n} \xrightarrow{H_2O} 2nCO_2 + nCl^-$: Cl^-, 13·4%; C as CO_2, 9·0%], and approx. 50% conversion, probably *via* chlorotrifluoroethylene oxide and chlorodifluoroacetyl fluoride, into chlorodifluoroacetic acid, oxalic acid, chloride, and fluoride.

Synthesis of Chlorodifluoroacetyl Fluoride.—Sodium chlorodifluoroacetate (5·2 g.) and phosphorus pentachloride (10·0 g.) were thoroughly mixed and heated to 100° under reflux. The volatile products were condensed in a liquid oxygen-cooled trap connected to the top of the condenser, then distilled *in vacuo* to give chlorodifluoroacetyl chloride (2·4 g., 47%) (Found: *M*, 150. Calc. for $C_2Cl_2F_2O$: *M*, 149), b. p. 24° (isoteniscope). Chlorodifluoroacetyl chloride (0·899 g.) and dry potassium fluoride (10 g.) were sealed in a 200-ml. Pyrex tube and kept at 100° for 36 hr. The volatile products were distilled *in vacuo* to give *chlorodifluoroacetyl fluoride* (0·52 g., 65%) (Found: C, 17·8%; *M*, 132·5. C_2ClF_3O requires C, 18·1%; *M*, 132·5), b. p. −17·5° (isoteniscope), and trifluoroacetyl fluoride (0·19 g.), identified spectroscopically.

The structure of the chlorodifluoroacetyl fluoride (easily distinguished from its isomer trifluoroacetyl chloride by infrared spectroscopy) was confirmed as follows. The acyl halide (0·334 g.) and water (1·0 ml.) were shaken together in a sealed tube for 1 hr., and the aqueous solution was then treated with an excess of silver carbonate, filtered, and freeze-dried. The residue was extracted with ether, and the ethereal extract evaporated *in vacuo* to give silver chlorodifluoroacetate (0·542 g., 91%), spectroscopically identical with a sample prepared directly from chlorodifluoroacetic acid.

Swarts [20] reported b. p. 34° for chlorodifluoroacetyl chloride prepared by chlorination of

[19] Nosaki, *Analyt. Chem.*, 1946, **18**, 583.
[20] Swarts, *Bull. Acad. roy. Belg.*, 1907, 339

2 : 2-difluoroethanol; the acyl chloride obtained recently [21] by pyrolysis of *sym*-dichlorotetrafluoroacetone at 500—750° had b. p. 24·8°.

Carbonyl absorption is shown as follows: $CF_2Cl{\cdot}COCl$, 5·47 μ; $CF_3{\cdot}COCl$, 5·40 μ; $CF_2Cl{\cdot}COF$, 5·30 μ; $CF_3{\cdot}COF$, 5·23 μ; $CF_2Cl{\cdot}CO_2Ag$, 6·01 μ.

Photolysis of Chlorodifluoroacetyl Fluoride.—Chlorodifluoroacetyl fluoride (0·394 g., 2·97 mmoles) was sealed in a 320-ml. silica tube and exposed to ultraviolet light for 24 hr. The volatile products were distilled *in vacuo* to give a mixture of chlorodifluoroacetyl fluoride (0·261 g., 1·97 mmoles, 66% recovery) and 1 : 2-dichlorotetrafluoroethane, and a fraction, separated by treatment with aqueous base, consisting of dichlorodifluoromethane (0·015 g., 0·12 mmole, 8%) and a mixture (0·042 g., 0·60 mmole) of carbonyl difluoride, carbonyl chloride fluoride, and a trace of silicon tetrafluoride.

Photochemical Oxidation of Chlorodifluoroacetyl Fluoride.—The acyl fluoride (0·402 g., 3·03 mmoles) and oxygen (0·308 g., 9·6 mmoles) were sealed in a 300-ml. silica tube (initial pressure *ca.* 1·0 atm.) and irradiated for 30 hr. The volatile products were shaken with mercury to remove chlorine and distilled *in vacuo* to give chlorodifluoroacetyl fluoride (0·050 g., 0·38 mmole, 12%) and a mixture (0·347 g., 5·56 mmoles) of carbon dioxide, silicon tetrafluoride, carbonyl difluoride, and a small amount of dichlorodifluoromethane.

Oxalyl Chloride Fluoride.—Oxalyl dichloride (2·15 g., 16·9 mmoles) and anhydrous potassium fluoride (10 g.) were sealed in a 200-ml. Pyrex tube and kept at 100° for 24 hr. The volatile products were (*a*) oxalyl dichloride (1·60 g., 12·6 mmoles, 75%), (*b*) *oxalyl chloride fluoride* (0·231 g., 2·09 mmoles, 49% yield based on oxalyl dichloride used) (Found: C, 21·4%; *M*, 110·5. C_2ClFO_2 requires C, 21·7 %; *M*, 110·5), b. p. −21°/140 mm., and (*c*) a mixture (0·080 g., 1·33 mmoles) of carbon dioxide and silicon tetrafluoride. Oxalyl chloride fluoride has characteristic double carbonyl absorption at 5·36, 5·58 μ; cf. $(COCl)_2$ 5·36, 5·8 μ.

Attempted Synthesis of Oxalyl Difluoride.—The dropwise addition of oxalyl dichloride to freshly sublimed antimony trifluoride (alone or with 10 moles % of antimony pentachloride added) at room temperature gave only a mixture of carbon dioxide and carbonyl chloride fluoride.

Reaction of oxalyl dichloride with anhydrous potassium fluoride in sealed tubes at temperatures between 100° and 150° for periods varying between 3 and 24 hr. gave only oxalyl dichloride, oxalyl chloride fluoride, and breakdown products.

Infrared Spectra.—These were determined on a Perkin–Elmer Model 21 Spectrophotometer with sodium chloride optics:

$CF_2Cl{\cdot}COCl$ (vapour): 2·87 (w), 5·30 (m), 5·47 (s), 5·80 (m), 7·38 (w), 8·47 (vs), 9·83 (vs), 11·63 (vs), 12·53 (s), 14·51, 14·60, 14·68 μ (m triplet). Here and below, s = strong, w = weak vs = very strong, m = medium strength.

$CF_2Cl{\cdot}COF$ (vapour): 2·68 (w), 5·30 (s), 7·88 (s), 8·40 (vs), 9·05 (vs), 10·25, 10·35 (vs doublet), 11·59 (w), 12·94, 13·03, 13·15 (s triplet), 14·30, 14·49, 14·60 μ (s triplet).

$CF_2Cl{\cdot}CO_2Ag$ (Nujol mull): 3·30 (w), 6·00, 6·15 (s doublet), 6·80 (w), 7·07 7·13 (s doublet), 7·65 (w), 7·95 (m), 8·67 (s), 10·42, 10·51 (s doublet) 12·20 (s), 13·70 (s).

$COF{\cdot}COCl$ (vapour): 2·71 2·82 (w doublet), 4·69 (w), 4·83, 4·87 (w doublet), 5·36 (vs), 5·58 (vs), 7·10 (w), 8·36 (vs), 9·67 (s), 10·65, 10·70 (vs doublet), 12·83 (vs), 14·00 (vs).

One of us (F. N.) is indebted to Courtaulds' Scientific and Educational Trust Fund for a Postgraduate Scholarship, 1955—1956.

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[21] Miller and Woolf, U.S.P. 2,741,634/1956.