Oxidation of Polyhalogeno-compounds.   Part I.   Photochemical Oxidation of Certain Fluoroalkanes.*

By W. C. FRANCIS and R. N. HASZELDINE.

[Reprint Order No. 6072.]

Photochemical vapour-phase oxidation of compounds of the type $CF_3 \cdot [CF_2]_n \cdot CFYX$ (X or Y = H, F, Cl, Br, or I) is surprisingly easy.   The compounds CHF_3, CF_3Cl, CF_3Br, CF_2ClBr, CF_2Br_2, and CF_3I are degraded to carbonyl fluoride, carbon dioxide, and, by attack on the reaction vessel, silicon tetrafluoride.   Carbon–carbon cleavage occurs readily in the propane series, and C_3HF_7, C_3F_7Cl, C_3F_7Br, and C_3F_7I yield carbonyl fluoride; the rate of oxidation increases in the order shown.   Carbon–carbon cleavage can be substantially prevented in certain cases (a) by carrying out the reaction in presence of water, (b) by introduction of chlorine or bromine as sensitisers, particularly for compounds containing a CHF_2 group, (c) by control of reaction pressure and oxygen concentration, and (d) by use where possible of a compound which contains a CFXY group, where X and Y = halogen other than fluorine.   Reaction mechanisms are proposed and correlated with the factors which affect the reactions.

THIS paper marks the beginning of a series of investigations designed to enable polyhalogeno-compounds, and in particular polyfluoro-compounds, to be converted by controlled oxidation into compounds which contain a functional group such as COF, CO_2H, CHO, or >CO. Convenient and economical methods are now available for the synthesis of fluorocarbons, and of compounds of the type RH, RCl, RBr, etc. (where R is a polyfluoro-group), but in general such compounds are chemically extremely inert and cannot be used for further synthetic work.   The present paper is concerned mainly with the photochemical oxidation of compounds of the type $CF_3 \cdot [CF_2]_n \cdot CFXY$ (X or Y = H, F, Cl, Br, or I), the conversion of certain of these into fluoro-acids, and the mechanism of the oxidation.

Earlier studies on the oxidation of halogeno-alkanes have usually involved methane or ethane derivatives, since only a few poly-bromo-, -chloro-, or -iodo-compounds containing more than two carbon atoms are known.   Harteck and Kopsch (Z. *physikal. Chem.*, 1931, **12**, *B*, 327) showed that carbon tetrachloride reacted only slowly with oxygen atoms produced by a silent electrical discharge at low pressure, but that chloroform and methylene chloride rapidly gave carbonyl chloride.   Brenschede and Schumacher (*ibid.*, 1936, **177**, *A*, 245) found that the quantum yield for the chlorine-sensitised photochemical oxidation of methane, methyl chloride, and methylene chloride increased from 80 to 800 in the order shown, and that carbon monoxide and hydrogen chloride, with small amounts of carbonyl chloride and water, were the main products; an unidentified explosive oil which gave a positive test for a peroxide was also isolated.   Chapman (*J. Amer. Chem. Soc.*, 1935, **57**, 419) postulated that the photochemical oxidation of chloroform to give carbonyl

* Presented at the Amer. Chem. Soc. Meeting, New York, 1954.

chloride, chlorine, carbon dioxide, and hydrogen chloride involved a peroxide such as

$CCl_3 \cdot O \cdot OH$ or $\overline{CCl_2 \cdot O \cdot O}$ as intermediate. Lyons and Dickinson (*ibid.*, 1935, **57**, 443) considered that the CCl_3O_2 radical was the intermediate in the photochemical oxidation of carbon tetrachloride and that it decomposed to give carbonyl chloride, oxygen, and chlorine. More recently, Schumacher and Thürauf (*Z. physikal. Chem.*, 1941, **189**, *A*, 183) showed that pentachloroethane was photochemically oxidised to trichloroacetyl chloride and carbonyl chloride. Pentachloroethane is the only polychloro-compound containing more than one carbon atom to be studied. Polybromo-compounds similarly yielded the carbonyl halide (*e.g.*, $CBr_4 \longrightarrow COBr_2 + Br_2$; Koblitz, Meissner, and Schumacher, *Ber.*, 1937, **70**, 1080). The velocity of the photochemical decomposition of alkyl iodides has long been known to be increased markedly by traces of oxygen, and peroxide intermediates have usually been postulated; these, on decomposition, are believed to give the aldehydes, alcohols, acids, etc., which are the products of such photochemical oxidations (see, *e.g.*, Olaert and Jungers, *Discuss. Faraday Soc.*, 1947, **2**, 222). Polyiodo-compounds have also been studied : methylene iodide, which yields carbon monoxide, hydrogen, iodine, iodine pentoxide, formaldehyde, formic acid, and glycol (Gregory and Style, *Trans. Faraday Soc.*, 1936, **32**, 724; Emschwiller, *Compt. rend.*, 1938, **206**, 746); and iodoform, carbon tetraiodide, and 1 : 1-di-iodoethane, which yield mainly carbon monoxide and are assumed to form initially the substances CHI_3O_2, CI_4O_2, and $CH_3 \cdot CHI_2O_2$, respectively.

The fluorine compounds studied during the present work have been surprisingly readily oxidised, even those which are usually almost completely resistant to attack by basic or acidic reagents or conventional oxidising media. Light of wavelength >2200 Å was used, with silica reaction vessels; details of the techniques are given in the Experimental section. The results for the vapour-phase photochemical oxidation of a series of halogeno-methanes and -propanes are summarised in Tables 1 and 2, and are now considered under the various types of compound studied.

$CF_3 \cdot [CF_2]_n \cdot H$, *e.g.*, CF_3H, C_3F_7H. These compounds are oxidised with difficulty, and then give only carbon dioxide and silicon tetrafluoride; the hydrogen is converted into water. An increase in the initial pressure of oxygen used decreases the rate of oxidation of fluoroform.

$CF_3 \cdot [CF_2]_n \cdot Cl$, *e.g.*, CF_3Cl, C_3F_7Cl. Chlorotrifluoromethane is oxidised slowly, but more rapidly than fluoroform under comparable conditions, and yields carbon dioxide and silicon tetrafluoride. Chloroheptafluoropropane is similarly converted into carbon dioxide and silicon tetrafluoride more rapidly than is heptafluoropropane. The reaction involves complete carbon–carbon fission, and possible intermediate products such as chloropentafluoroethane or chlorotrifluoromethane are not produced. Table 2 reveals the retardation of oxidation of chloroheptafluoropropane by use of too high an initial pressure.

$CF_3 \cdot [CF_2]_n \cdot Br$, *e.g.*, CF_3Br, C_3F_7Br. There is a marked difference between chloro- and bromo-trifluoromethane in ease of oxidation; the time required for the former compound is measured in days, for the latter in hours. Bromoheptafluoropropane is oxidised, with complete breakdown of the chain, at approximately the same rate as bromotrifluoro-methane, so, once started, the breakdown of the fluorocarbon chain must occur rapidly. Possible intermediate products such as bromotrifluoromethane or bromopentafluoroethane cannot be detected.

$CF_3 \cdot [CF_2]_n \cdot I$, *e.g.*, CF_3I, C_3F_7I. The perfluoroiodoalkanes undergo extensive decomposition in 1—2 hours. Not even traces of possible intermediates from heptafluoroiodopropane such as pentafluoroiodoethane, trifluoroiodomethane, trifluoroacetyl fluoride, or penta-fluoropropionyl fluoride could be detected; carbon–carbon fission is complete and the oxidation of both fluoroiodides yields only carbonyl fluoride, etc.

In an attempt to isolate possible reaction intermediates or products which might be oxidised at a rate comparable with that of heptafluoroiodopropane itself, an excess of heptafluoroiodopropane over oxygen was used in one experiment; possible products such as $(C_3F_7)_2O_2$, $C_2F_5 \cdot COF$, $C_3F_7 \cdot OF$, C_6F_{14}, or C_2F_5I were not detected, and only carbonyl fluoride and the excess of heptafluoroiodopropane remained. That acyl fluorides are not unstable intermediates in the oxidation follows because pentafluoropropionyl fluoride is

decomposed only slowly under the conditions used; further, acyl fluorides are in fact isolated in substantial yield from the photochemical oxidation of other compounds (see Table 3).

Since no compounds containing trifluoromethyl or pentafluoroethyl groups are formed during the oxidation of heptafluoroiodopropane, it follows that the product from the initial reaction of a heptafluoropropyl radical with oxygen must decompose by carbon–carbon cleavage and complete disruption of the fluorocarbon chain at a much faster rate than the initiation reaction, which is thus rate-determining. As noted for other compounds, the

TABLE 1. *Photochemical oxidation of some halogenomethanes.*

Compound	Ratio O_2 : Compound	Press. (atm.)	Time of irradiation	Oxidation (%)	Products *
CF_3H	6·4	1·9	24 days	18	H_2O; no C_2F_6; no COF_2
CF_3Cl	4·8	1·9	25 days	32	No COF_2 or C_2F_6
CF_3Br	6·4	5·6	6·0 hr.	21	COF_2, Br_2; no C_2F_6
CF_2ClBr	6·8	5·8	6·5 hr.	58	COF_2, Br_2
CF_2Br_2	6·6	5·6	6·5 hr.	98	COF_2, Br_2
	6·6	5·6	4·0 hr.	88	COF_2, Br_2
CF_3I	6·4	1·9	1·3 hr.	40	COF_2, I_2; no C_2F_6
	6·5	5·8	4·0 hr.	95	COF_2, I_2

* CO_2 and SiF_4 produced in every case.

TABLE 2. *Photochemical oxidation of some halogenopropanes.*

Compound	Ratio O_2 : Compound	Press. (atm.)	Time of irradiation	Oxidation (%)	Products *
C_3F_7H	5	2·5	40 days	17	H_2O; no C_6F_{14}
C_3F_7Cl	9	5·4	25 days	26	No C_6F_{14}; no CF_3Cl, C_2F_5Cl
	9·6	1·2	45 days	100	No C_6F_{14}; no CF_3Cl, C_2F_5Cl
C_3F_7Br	6·4	5·6	18 hr.	67	Br_2; no C_6F_{14}; no CF_3Br, C_2F_5Br
C_3F_7I	5	2·5	1·5 hr.	48	COF_2, I_2; no C_6F_{14}
$C_2F_5 \cdot CFCl_2$	4	1·5	6 hr.	2	COF_2
	4	2	28 hr.	38	$C_2F_5 \cdot COF$, $CF_2 \cdot COF$. Cl_2, COF_2
$C_2F_5 \cdot CFClBr$	4	4·7	0·5 hr.	3	COF_2
$C_2F_5 \cdot CFClBr$	4	4·7	10 hr.	40	$C_2F_5 \cdot COF$, $CF_2 \cdot COF$, COF_2, Br_2
$C_2F_5 \cdot CFClI$	4	1·8	0·5 hr.	75	I_2, ICl, $C_2F_5 \cdot COF$, $CF_2 \cdot COF$, COF_2
$C_2F_5 \cdot CFClI$	10	4·6	0·5 hr.	35	I_2, ICl, $C_2F_5 \cdot COF$, $CF_2 \cdot COF$, COF_2

* CO_2 and SiF_4 produced in every case.

rate of oxidation of trifluoroiodomethane or heptafluoroiodopropane is faster for a low than for a high initial pressure,

$CF_3 \cdot [CF_2]_n \cdot CFCl_2$, *e.g.*, $C_2F_5 \cdot CFCl_2$. This compound was photochemically oxidised much faster than chloroheptafluoropropane, *i.e.*, introduction of a second chlorine atom on the terminal carbon atom facilitates reaction. Unlike chloroheptafluoropropane and the compounds discussed above, products were obtained which resulted from other than complete carbon–carbon fission, namely, pentafluoropropionyl fluoride and a small amount of trifluoroacetyl fluoride (Table 3).

$CF_3 \cdot [CF_2]_n \cdot CFClBr$, *e.g.*, CF_2ClBr, $C_2F_5 \cdot CFClBr$. Bromochlorodifluoromethane liberates bromine on exposure to light in presence of oxygen, and is rapidly and completely oxidised to carbonyl fluoride, carbon dioxide, and silicon tetrafluoride.

1-Bromo-1-chlorohexafluoropropane was prepared by the reaction of 1-chloro-1-iodohexafluoropropane with bromine in the dark : $C_2F_5 \cdot CFClI \xrightarrow{Br_2} C_2F_5 \cdot CFClBr + IBr$. It is oxidised more readily than 1 : 1-dichlorohexafluoropropane, and gives a greater yield of pentafluoropropionyl and trifluoroacetyl fluorides (Table 3).

$F \cdot [CF_2]_n \cdot CFBr_2$, *e.g.*, CF_2Br_2. Apart from compounds which contain iodine, dibromodifluoromethane oxidises the most readily of the compounds studied; oxidation is complete in 6 hours (Table 1). The products are carbonyl fluoride, carbon dioxide, silicon tetrafluoride, and bromine, and by-products were not detected.

$CF_3 \cdot [CF_2]_n \cdot CFClI$, *e.g.*, $C_2F_5 \cdot CFClI$. The extensive photochemical oxidation of 1-chloro-1-iodohexafluoropropane occurring in only a few minutes strongly suggests that radical-chain reaction is involved (cf. the oxidation of C_3F_7Cl which is incomplete after 25 days). Comparatively little carbon–carbon cleavage occurs, and the main product is

pentafluoropropionyl fluoride (65% yield) together with smaller amounts of trifluoroacetyl fluoride (Table 3). The rate of oxidation is decreased by use of a relatively high initial pressure (Table 2).

The oxidation of this iodo-compound is probably the most convenient method available for the preparation of small amounts of pentafluoropropionic acid (cf. Haszeldine and Leedham, *J.*, 1953, 1548). The isolation of pentafluoropropionyl fluoride proves that 1-chloro-1-iodohexafluoropropane contains a C_2F_5 group, and thus further substantiates Haszeldine and Steele's claim (*J.*, 1953, 1592) that the reaction of trifluoroiodomethane with chlorotrifluorothylene yields exclusively (I) and not (II).

$$\text{(I)} \quad CF_3 \cdot CF_2 \cdot CFClI \qquad\qquad CF_3 \cdot CFCl \cdot CF_2I \quad \text{(II)}$$

Long-chain perfluoro-acids can thus be obtained by ascent of the homologous series :

$$CF_3 \cdot [CF_2]_n \cdot I \xrightarrow{\ CF_2:CFCl\ } CF_3 \cdot [CF_2]_n \cdot CF_2 \cdot CFClI \xrightarrow{\ O_2,\ h\nu\ } CF_3 \cdot [CF_2]_n \cdot CF_2 \cdot CO_2H$$

The small amount (3%) of trifluoroacetyl fluoride which is produced by the photochemical oxidation of 1-chloro-1-iodohexafluoropropane is believed to arise by breakdown of the C_2F_5 group (see p. 2155), rather than by oxidation of small amounts of (II) present in (I), and this view is supported by the fact that a compound containing a trifluoromethyl group can be isolated from the oxidation of heptafluoroiodopropane, *i.e.*, by breakdown of a C_3F_7 group under suitable conditions (Table 3).

1-Chloro-1-iodohexafluoropropane is only very slightly attacked by oxygen in absence of light to give a small amount of a solid which is possibly a peroxide such as $(C_2F_5 \cdot CFCl)_2O_2$; attempts to purify the material failed.

Prevention of Carbon–Carbon Cleavage.—The reactions summarised above and in Tables 1 and 2 show that photochemical oxidation is a powerful tool for the breakdown of a fluorocarbon chain. Of particular interest, however, are those reactions where carbon–carbon fission can be prevented, and a study has been made of some of the factors which might lead to an increased yield of acyl fluoride; *i.e.*, oxygen ratio, initial pressure, addition of water or aqueous base, addition of chlorine or bromine as sensitisers, and the effect of bromine or chlorine in presence of water.

Studies with bromochlorodifluoromethane support the conclusions reached earlier for fluoroform, chloroheptafluoropropane, trifluoroiodomethane, heptafluoroiodopropane, and 1-chloro-1-iodohexafluoropropane, namely, that the oxygen ratio and the initial pressure substantially affect the reaction rate. An increase in the ratio of oxygen to bromochlorodifluoromethane, the total initial pressure being kept constant, increases the percentage decomposition in any given time. An increase in the initial pressure, the oxygen to bromochlorodifluoromethane ratio being kept constant, decreases the rate of oxidation (see Table 4). The initial pressure and the ratio of oxygen to the compound under study do not change the reaction products, only their rate of formation, but, since the products can themselves be photolysed, control of these factors to give rapid oxidation with only slight destruction of products is clearly desirable. The intensity and wavelength of the light used similarly affect the rate of formation but not the nature of the products.

Addition of water as a reactant does not markedly affect the reaction involving 1-chloro-1-iodohexafluoropropane (see Table 3); the total yield of perfluorocarboxylic acids is the same as in absence of water, but there is an increase in the trifluoroacetic acid content. Sulphuric acid has no effect on the photochemical oxidation of heptafluoroiodopropane, but the addition of aqueous sodium hydroxide causes a distinct improvement, since low yields of fluoro-acids (10%, see Table 3) can be isolated.

The addition of bromine or chlorine as sensitiser can markedly change the speed and course of the reaction. The rate of decomposition of trifluoroiodomethane or fluoroform is markedly increased, but the products are the same as for the non-sensitised reaction; in particular, chlorotrifluoromethane is not produced. The rate of oxidation is similarly increased for the bromine- or chlorine-sensitised oxidation of heptafluoroiodopropane, and of particular interest is the isolation of pentafluoropropionyl and trifluoroacetyl fluoride in satisfactory yields (51%), thus showing that carbon–carbon fission can be prevented or stopped at an intermediate stage; bromine is more effective than chlorine in preventing
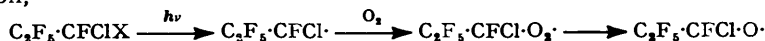
carbon–carbon fission. Bromine-sensitisation similarly enables acyl fluorides to be prepared from heptafluoropropane (Table 3). By contrast, addition of bromine has little or no effect on the rate of oxidation of chloroheptafluoropropane, and fails to prevent complete breakdown. Bromine increases the rate of oxidation of 1-chloro-1-iodohexafluoropropane, but does not increase the yield of pentafluoropropionyl fluoride, although the yield of trifluoroacetyl fluoride is markedly increased. In none of the halogen-sensitised reactions has the formation of compounds such as chloro- or bromo-trifluoromethane formed by the combination of perfluoroalkyl radicals with the sensitising halogen been observed.

Chlorine- or bromine-sensitisation in the presence of water gives still higher yields of fluorine compounds containing functional groups. This is illustrated by heptafluoroiodopropane and 1-bromo-1-chlorohexafluoropropane (Table 3). Studies on heptafluoropropane show that increase in the $Cl_2 : O_2$ ratio from 1 : 8 to 1 : 4 decreases markedly the extent of breakdown, yet increases the rate of oxidation considerably; bromine acts in similar manner (Table 3). Presence of both chlorine and water in the reaction mixture for the oxidation of 1-chloro-1-iodohexafluoropropane leads to a further improvement in the yield of the perfluoro-acids, with a combined yield of 91%.

The optimum conditions for the preparation of perfluoroacyl fluorides and thence perfluoro-acids from polyfluoroalkanes thus involve (*a*) a low initial pressure, (*b*) a high ratio of oxygen to polyfluoroalkane, (*c*) sensitisation by bromine or chlorine, (*d*) presence of water, (*e*) where possible presence of a CFZY group (Z or Y = H, Cl, Br, or I) at the point where oxidation is required.

Discussion.—Any mechanism for the vapour-phase oxidation of a fluoro-iodide $CF_3 \cdot [CF_2]_n \cdot I$ must explain the following facts: (*a*) The reaction is fast and presumably involves a branching chain. (*b*) Fluorocarbons such as CF_4 or C_2F_6, and hypofluorites such as $CF_3 \cdot OF$ are not reaction products. (*c*) A fluorocarbon chain is completely disrupted under relatively mild conditions. (*d*) Carbonyl fluoride is the main initial reaction product. (*e*) Compounds which absorb ultraviolet light readily are those most easily oxidised. (*f*) Addition of water and/or of chlorine or bromine prevents complete carbon–carbon fission. (*g*) Chlorine attached to the carbon atom of a terminal CFCl, CFBr, or CFI group prevents carbon–carbon fission almost completely. A chain reaction of the following type is therefore proposed, heptafluoroiodopropane being taken as example :

$$C_3F_7I \xrightarrow{h\nu} C_3F_7 \cdot + I \cdot \quad \dots \dots \dots \dots \quad (1)$$

$$C_3F_7 \cdot + O_2 \longrightarrow C_3F_7 \cdot O_2 \cdot \quad \dots \dots \dots \dots \quad (2)$$

$$C_3F_7 \cdot O_2 \cdot + C_3F_7I \longrightarrow C_3F_7 \cdot O \cdot OI + C_3F_7 \cdot \quad \dots \dots \quad (3)$$

$$\downarrow O_2$$

$$C_3F_7 \cdot O_2 \cdot \longrightarrow \text{etc.}$$

$$C_3F_7 \cdot O \cdot OI \xrightarrow{h\nu} C_3F_7 \cdot O \cdot + \cdot OI \quad \dots \dots \dots \quad (4)$$

$$C_3F_7 \cdot O \cdot \longrightarrow C_2F_5 \cdot + COF_2 \quad \dots \dots \dots \quad (5)$$

and/or
$$C_3F_7 \cdot O \cdot + C_3F_7I \longrightarrow C_3F_7 \cdot OI + C_3F_7 \cdot \quad \dots \dots \quad (5a)$$

$$\downarrow O_2$$

$$C_3F_7 \cdot O_2 \cdot \longrightarrow \text{etc.}$$

$$C_3F_7 \cdot OI \longrightarrow C_2F_5 \cdot + COF_2 + I \cdot \quad \dots \dots \quad (5b)$$

$$C_2F_5 \cdot + O_2 \longrightarrow C_2F_5 \cdot O_2 \cdot \xrightarrow{C_3F_7I} C_2F_5 \cdot O \cdot + C_3F_7 \cdot + \cdot OI \quad \dots \quad (6)$$

$$\downarrow \qquad \qquad \downarrow O_2$$

$$CF_3 \cdot + COF_2 \quad \text{etc.}$$

$$CF_3 \cdot \longrightarrow CF_3 \cdot O_2 \cdot \longrightarrow CF_3 \cdot O \cdot \xrightarrow{SiO_2} COF_2 + SiF_4$$

The following facts support this scheme. First, the rate of oxidation of a fluorine compound RX increases with its ability to absorb ultraviolet light, and when R = perfluoroalkyl this ability is in the decreasing sequence $X = CFClI > CF_2I \sim CFBr_2 > CFClBr$

$> CF_2Br > CFCl_2 > CF_2Cl > CF_2H > CF_3$ (see *J.*, 1953, 1764, for ultraviolet spectra). This strongly suggests that the first step in the oxidation is the formation of a free radical (*e.g.*, $CF_2Br_2 \longrightarrow CF_2Br \cdot + Br \cdot$; $C_3F_7Cl \longrightarrow C_3F_7 \cdot + Cl \cdot$). Thus, the larger the halogen atoms Z and Y in a compound RCFZY (R = fluorine or perfluoroalkyl; Z smaller than or equal to Y), *i.e.*, the smaller the C–Y bond dissociation energy (*J.*, 1953, 1764), the greater the rate of oxidation. Hydrogen abstraction by oxygen can initiate reaction for hepta-fluoropropane (*e.g.*, $C_3HF_7 \xrightarrow{O_2 \cdot} C_3F_7 \cdot + HO_2 \cdot \longrightarrow$ etc.).

Secondly, that the combination of a perfluoroalkyl radical with oxygen (equation 2) proceeds extremely readily may be deduced from the fact that the rapid photochemical chlorination of trifluoroiodomethane ($Cl \cdot + CF_3I \longrightarrow ICl + CF_3 \cdot \xrightarrow{Cl_2} CF_3Cl + Cl \cdot$) is completely prevented by addition of oxygen, even with a chlorine : oxygen ratio as high as 3 : 1; the CF_3 radical combines exclusively with oxygen to give ultimately carbonyl fluoride. This also explains why products such as C_2F_5X or CF_3X are not formed during photochemical oxidation of C_3F_7X (X = Cl or Br).

Thirdly, the reaction scheme enables the rapid destruction of a fluorocarbon chain to be readily visualised. Direct analogies with mechanisms proposed for oxidation of hydro-carbon radicals are unsuitable, since there is probably a fundamental difference in mech-anism caused by the fact that the C–F bond dissociation energy is higher than that for C–H, so that radical abstraction and disproportionation reactions to give products such as $C_2F_5 \cdot OF$, C_3F_8, C_3F_6, or $C_2F_5 \cdot COF$ do not occur. The fate of a C_3F_7O radical produced by the chain reaction (equations 3 and 4) will depend upon its environment. In the gas phase it will decompose according to equation 5 by loss of carbonyl fluoride and formation of a fluorocarbon radical containing one less CF_2 group; this new radical can then undergo a similar cycle of reactions to yield carbonyl fluoride and a CF_3 radical. In presence of liquid fluoroiodoalkane the alternative mode of decomposition of a $C_3F_7 \cdot O$ radical [equations (5*a*) and (5*b*)] will be of particular importance.

Fourthly, decomposition of intermediates in the chain reaction in presence of water (*e.g.*, $C_3F_7 \cdot OI \xrightarrow{NaOH} C_3F_7 \cdot OH + NaOI \xrightarrow{-2F-} C_2F_5 \cdot CO_2H$) explains why small amounts of trifluoroacetic and pentafluoropropionic acids are formed during photochemical oxid-ation of heptafluoroiodopropane in presence of aqueous sodium hydroxide although the acyl fluorides are not produced under anhydrous conditions.
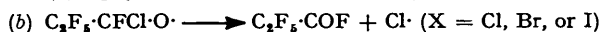
The photochemical oxidation of 1 : 1-dichloro-, 1-bromo-1-chloro-, and 1-chloro-1-iodo-hexafluoropropane gives high yields of acyl fluorides (Table 3) in sharp contrast to the oxidation of 1-bromo-, -chloro-, or -iodo-heptafluoropropane. Introduction of chlorine on to the terminal carbon atom must thus cause the change, and it is suggested that the initial reaction,

$$C_2F_5 \cdot CFClX \xrightarrow{h\nu} C_2F_5 \cdot CFCl \cdot \xrightarrow{O_2} C_2F_5 \cdot CFCl \cdot O_2 \cdot \longrightarrow C_2F_5 \cdot CFCl \cdot O \cdot$$

is followed by the competing reactions,

$$(a) \quad C_2F_5 \cdot CFCl \cdot O \cdot \longrightarrow COFCl + C_2F_5 \cdot \xrightarrow{O_2} \text{etc.}$$

and

$$(b) \quad C_2F_5 \cdot CFCl \cdot O \cdot \longrightarrow C_2F_5 \cdot COF + Cl \cdot \quad (X = Cl, Br, \text{ or } I)$$
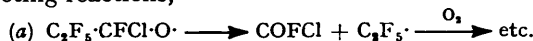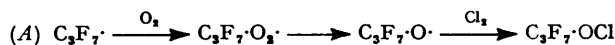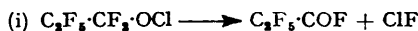
with the chlorine-atom expulsion reaction (*b*) predominating over the chain-degradation reaction (*a*) under suitable conditions.
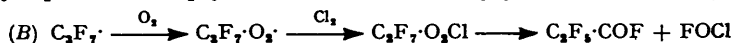
The most interesting results of the present work are those summarised in Table 3, since they show that it is possible to prevent complete breakdown of a perfluoroalkyl radical by introducing chlorine or bromine as sensitisers. The formation of acyl fluorides in this way probably means that a radical intermediate containing bromine or chlorine is involved, *e.g.*,
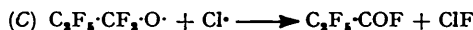
$$(A) \quad C_3F_7 \cdot \xrightarrow{O_2} C_3F_7 \cdot O_2 \cdot \longrightarrow C_3F_7 \cdot O \cdot \xrightarrow{Cl_2} C_3F_7 \cdot OCl$$

followed by either

$$(i) \quad C_2F_5 \cdot CF_2 \cdot OCl \longrightarrow C_2F_5 \cdot COF + ClF$$

or

$$(ii) \quad C_2F_5 \cdot CF_2 \cdot OCl \longrightarrow C_2F_5 \cdot CFCl \cdot OF \xrightarrow{C_3F_7I} IF + C_2F_5 \cdot CFCl \cdot O \cdot \longrightarrow C_2F_5 \cdot COF + Cl \cdot$$

$$(B) \quad C_3F_7 \cdot \xrightarrow{O_2} C_3F_7 \cdot O_2 \cdot \xrightarrow{Cl_2} C_3F_7 \cdot O_2Cl \longrightarrow C_2F_5 \cdot COF + FOCl$$

An alternative would be

$$(C) \quad C_2F_5 \cdot CF_2 \cdot O\cdot + Cl\cdot \longrightarrow C_2F_5 \cdot COF + ClF$$

The following points have to be considered in this connection. First, for A(i) or B to be valid, the reactions must be made energetically more favourable by presence of chlorine in the molecule of the intermediate than are the analogous reactions with $C_3F_7 \cdot OI$ or $C_3F_7 \cdot O_2I$. Secondly, rearrangement of the $C_2F_5 \cdot CF_2 \cdot OCl$ is postulated in A(ii), since once an intermediate such as $C_2F_5 \cdot CFCl \cdot O$ has been formed, with chlorine attached to the terminal carbon atom, the subsequent reactions will follow the same course as for 1-chloro-1-iodohexafluoropropane discussed earlier to give a high yield of the acyl fluoride. This mechanism also explains why bromine is more efficient than chlorine as sensitiser, since the C–Br bond in $C_2F_5 \cdot CFBr \cdot O\cdot$ will cleave homolytically more readily than C–Cl in $C_2F_5 \cdot CFCl \cdot O\cdot$. Thirdly, scheme C would imply that the carbon–fluorine bond attached to a carbon atom carrying the oxygen with its lone electron is so appreciably weakened

(*e.g.*, by resonance of the type $C_2F_5 - \overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}} - O\cdot \longleftrightarrow C_2F_5 - \overset{\overset{\displaystyle F}{|}}{C} = O$) that abstraction of fluorine $\overset{}{\underset{\displaystyle F\cdot}{}}$

by a chlorine atom becomes possible. Fourthly, the formation of trifluoroacetyl fluoride during the chlorine-sensitised photochemical oxidation of 1-chloro- or 1-bromo-1-iodohexafluoropropane or of heptafluoroiodopropane shows that chlorine is preventing complete destruction of the C_2F_5 radicals, produced by loss of carbonyl halide from the $C_2F_5 \cdot CFCl \cdot O\cdot$ or $C_2F_5 \cdot CF_2 \cdot O\cdot$ radical, by some mechanism of type A, B, or C. The fact that the amount of trifluoroacetyl fluoride formed from 1-chloro-1-iodohexafluoropropane is increased further by use of bromine supports schemes A or B, since although bromine cannot influence the rate of formation of the C_2F_5 radical from $C_2F_5 \cdot CFCl \cdot O$, or the yield of pentafluoropropionyl

TABLE 3. *Preparation of fluoro-acids by photochemical oxidation.*

Compound.	Ratio O_2 : Compound	Initial press. (atm.)	Other reactants	Time of irradiation	Oxidation (%)	Products (yield)
C_3F_7I	5	2	None	1·5 hr.	48	No acyl fluorides
C_3F_7I	4	5	45% aq. NaOH	24 hr.	100	$C_2F_5 \cdot CO_2Na$ (5%), $CF_3 \cdot CO_2Na$ (5%)
C_3F_7I	4·2	2	$Cl_2(O_2 : Cl_2 = 8·4 : 1)$	1·5 hr.	92	$C_2F_5 \cdot COF$ (24%), $CF_3 \cdot COF$ (1%)
C_3F_7I	2	2	$Br_2(O_2 : Br_2 = 8·5 : 1)$	1·5 hr.	95	$C_2F_5 \cdot COF$ (38%), $CF_3 \cdot COF$ (19%)
C_3F_7I	2	2	$Br_2(O_2 : Br_2 = 8·5 : 1)$ H_2O	2 hr.	100	$C_2F_5 \cdot CO_2H$ (45%), $CF_3 \cdot CO_2H$ (23%)
C_3F_7H	5	3	$Br_2(O_2 : Br_2 = 8 : 1)$	30 days	58	$C_2F_5 \cdot COF$ (17%), $CF_3 \cdot COF$ (6%)
C_3F_7H	5	3	$Cl_2(O_2 : Cl_2 = 8·5 : 1)$ H_2O	45 days	69	$C_2F_5 \cdot CO_2H$ (12%), $CF_3 \cdot CO_2H$ (<1%)
C_3F_7H	5	3	$Cl_2(O_2 : Cl_2 = 4 : 1)$ H_2O	10 days	73	$C_2F_5 \cdot CO_2H$ (43%), $CF_3 \cdot CO_2H$ (10%)
C_3F_7H	5	3	$Br_2(O_2 : Br_2 = 4 : 1)$ H_2O	10 days	69	$C_2F_5 \cdot CO_2H$ (45%), $CF_3 \cdot CO_2H$ (16%)
C_3F_7Cl	5	6	$Cl_2(O_2 : Cl_2 = 4 : 1)$ H_2O	30 days	29	No $C_2F_5 \cdot CO_2H$; no $CF_3 \cdot CO_2H$
C_3F_7Cl	5	6	$Br_2(O_2 : Br_2 = 4 : 1)$	30 days	25	No acyl fluorides
$C_2F_5 \cdot CFCl_2$	4	2	None	28 hr.	38	$C_2F_5 \cdot COF$ (21%), $CF_3 \cdot COF$ (2%)
$C_2F_5 \cdot CFClBr$	5	5	None	10 hr.	40	$C_2F_5 \cdot COF$ (45%), $CF_3 \cdot COF$ (8%)
$C_2F_5 \cdot CFClBr$	5	5	$Br_2(O_2 : Br_2 = 4 : 1)$ H_2O	10 hr.	47	$C_2F_5 \cdot CO_2H$ (51%), $CF_3 \cdot CO_2H$ (16%)
$C_2F_5 \cdot CFClI$	4	2	None	0·5 hr.	75	$C_2F_5 \cdot COF$ (65%), $CF_3 \cdot COF$ (3%)
$C_2F_5 \cdot CFClI$	5	2	Water	4·5 hr.	100	$C_2F_5 \cdot CO_2H$ (55%), $CF_3 \cdot CO_2H$ (13%)
$C_2F_5 \cdot CFClI$	5	2	$Br_2(O_2 : Br_2 = 4 : 1)$	0·5 hr.	90	$C_2F_5 \cdot COF$ (69%), $CF_3 \cdot COF$ (21%)
$C_2F_5 \cdot CFClI$	5	3	$Cl_2(O_2 : Cl_2 = 1 : 1)$ H_2O	4·5 hr.	100	$C_2F_5 \cdot CO_2H$ (73%), $CF_3 \cdot CO_2H$ (18%)

fluoride, it is more efficient than chlorine in preventing breakdown of a perfluoroalkyl radical such as C_2F_5 (*e.g.*, cf. C_3F_7I, Table 3).

The effect of sensitisers is well illustrated by comparison of the photolytic oxidation of 1-chloro- and 1*H*-heptafluoropropane. In absence of sensitiser the chloro-compound is photolysed only slowly, but more rapidly than is heptafluoropropane, and the rate is scarcely affected by bromine or chlorine sensitisation, since these halogens cannot facilitate the initiation step ($C_3F_7Cl \longrightarrow C_3F_7\cdot + Cl\cdot$). By contrast the photolysis of heptafluoro-propane is appreciably accelerated, since hydrogen is abstracted by the sensitiser (*e.g.*, $Br\cdot + C_3F_7H \longrightarrow C_3F_7\cdot + HBr$; cf. $Cl\cdot + C_3F_7I \longrightarrow C_3F_7\cdot + ICl$), and the rate of reaction is now faster than that for chloroheptafluoropropane; furthermore, the subsequent break-down of the C_3F_7 and C_2F_5 radicals is prevented, and acyl fluorides are formed in good yield from a compound which until now could not be converted into a compound containing a functional group.

<div align="center">EXPERIMENTAL</div>

General Technique.—The oxidation reactions were carried out in sealed Pyrex or silica tubes of the capacity indicated. The tubes were carefully cleaned and, unless deliberately added, water, oxygen, air, mercury, iodine, etc., which might promote or inhibit free-radical reactions, were excluded. The reaction tubes were filled by condensation from a vacuum system, and were sealed whilst evacuated; the volatile reaction products were transferred to a vacuum-system for distillation and identification. Products with a b. p. too high for convenient manipulation in a vacuum-system were distilled through a short column in an apparatus designed to give minimum hold-up. Yields are based on material consumed.

All reactants were distilled before use and were spectroscopically pure; weights were obtained by measurement of the pressure change in containers of known volume or by direct weighing. Reaction products were identified by b. p., molecular weight, vapour pressure, etc., and identity was confirmed by infrared spectroscopic examination using a Perkin-Elmer Model 21 instrument. Mixtures of products which could not be separated conveniently by distillation were analysed by means of infrared spectra, sometimes after preliminary chemical separation.

Oxygen was condensed into the reaction tube from a reservoir attached to the vacuum-system by cooling the tube in liquid nitrogen. Initial pressures of oxygen up to 12 atm. were thus obtained after the tube had been sealed and allowed to reach room temperature; this pressure was considered to be the maximum for safety with the silica used (2—4-cm. diam., 1·5—2-mm. wall thickness). Usually no attempt was made to measure the amount of oxygen unchanged after reaction, and the products examined are those which are condensable by liquid oxygen. A Hanovia S-250 ultraviolet lamp was used, without the Wood's filter, at 5—15 cm. from the reaction tube. The reaction temperature was 30—40°, and the final pressure in the reaction vessel varied up to 12 atm. Pressures are calculated at 35°, and unless otherwise stated the oxidation reactions were carried out completely in the vapour phase. In experiments where the compound to be oxidised was partly in the liquid phase, the reaction vessel was shaken vigorously in a horizontal position so that both liquid and vapour were irradiated. The area of the 50-ml. silica tube which was exposed to ultraviolet light was *ca.* 50 sq. cm.; that of the 150-ml. tube was *ca.* 75 sq. cm.

Tables 1, 2, and 3 summarise the main results. Details of typical experiments follow.

Compounds of Type $CF_3\cdot[CF_2]_n\cdot H$.—(a) *Fluoroform.* The starting material, prepared from tristrifluoromethylphosphine by hydrolysis with aqueous sodium hydroxide, was spectroscopically pure (Found : *M*, 70. Calc. for CHF_3 : *M*, 70). Fluoroform (0·105 g., 0·00150 mole) and oxygen (0·307 g. 0·0096 mole) in a 150-ml. silica tube (initial pressure 1·9 atm.) were irradiated for 24 days to give (*a*) water containing hydrogen fluoride and fluorosilicic acid (total *ca.* 0·00003 mole), and (*b*) carbon dioxide, silicon tetrafluoride, and fluoroform (total 0·00166 mole). Spectro-scopic examination of (*b*) showed that it was mainly fluoroform and that hexafluoroethane was not a reaction product; the fraction was shaken with 20% aqueous sodium hydroxide, then redistilled to give fluoroform (0·086 g., 0·00123 mole, 82%); 18% of fluoroform had thus been oxidised.

In a second experiment, fluoroform (0·084 g., 0·0012 mole) and oxygen (0·253 g., 0·0079 mole) in a 50-ml. silica tube (initial pressure *ca.* 4·6 atm.) underwent only slight reaction (*ca.* 1%) after 31 days' irradiation. Even after allowance for the difference in the amount of radiation falling on the 50-ml. tube compared with that on the 150-ml. tube used in the first experiment

(*ca.* ⅔), it is evident that much less oxidation occurred in the second experiment. This is attributed to the effect of a higher initial pressure.

(b) 1H-*Heptafluoropropane.* Spectroscopically pure 1H-heptafluoropropane (0·425 g., 0·0025 mole) and oxygen (0·400 g., 0·0125 mole) in a 150-ml. silica reaction tube (initial pressure *ca.* 2·5 atm.) were irradiated for 40 days to give carbon dioxide, silicon tetrafluoride, water, and unchanged heptafluoropropane (83%).

Chlorine-sensitised Oxidation of Fluoroform.—Fluoroform (0·112 g., 0·00160 mole), oxygen (0·336 g., 0·0105 mole), and chlorine (0·0805 g., 0·001135 mole) were completely vaporised in a 150-ml. silica tube at 35° (initial pressure *ca.* 2·2 atm.). Irradiation for 13 days yielded water, hydrogen fluoride, silicon tetrafluoride, and unchanged fluoroform. Only fluoroform (0·00123 mole, 77%) remained unchanged after treatment of the gaseous products with 10% aqueous sodium hydroxide, and spectroscopic examination showed it to be uncontaminated by chloro-trifluoromethane; 23% of the fluoroform had thus been oxidised.

Halogen-sensitised Oxidation of 1H-*Heptafluoropropane.*—Heptafluoropropane (0·425 g., 0·0025 mole), oxygen (0·400 g., 0·0125 mole), water (3 ml.), and chlorine (0·1 g.) were sealed in a 150-ml. silica tube (initial pressure *ca.* 3 atm.) which was shaken vigorously in a horizontal position and exposed to ultraviolet light (45 days). The volatile products were washed with aqueous sodium hydroxide to remove the excess of chlorine and distilled *in vacuo* to give only heptafluoropropane (31%). The aqueous solution was treated with silver carbonate until neutral, and the filtered solution was evaporated to dryness to give a white solid. This was dried (P_2O_5) *in vacuo*, then extracted with ether. Evaporation of the ethereal solution to dryness gave silver pentafluoropropionate (12%) mixed with silver trifluoroacetate (<1%).

The same reaction tube, experimental techniques, and weights of heptafluoropropane and oxygen were used to investigate chlorine sensitisation with a higher chlorine concentration, and bromine sensitisation with and without the addition of water (3 ml.). The molar ratios of oxygen to halogen and the results of the experiments are summarised in Table 3.

Compounds of Type $CF_3 \cdot [CF_2]_n \cdot Cl$.—(a) *Chlorotrifluoromethane.* Spectroscopically pure chlorotrifluoromethane (0·209 g., 0·002 mole) and oxygen (0·307 g., 0·0096 mole) in a 150-ml. silica tube (initial pressure *ca.* 1·9 atm.), irradiated for 25 days, gave volatile products (0·0020 mole) (Found : *M*, 95), shown by spectroscopic examination to contain chlorotrifluoromethane, silicon tetrafluoride, carbon dioxide, and a small amount (*ca.* 0·00006 mole) of an unidentified, less volatile material. After being shaken with 20% aqueous sodium hydroxide, the products were redistilled to give unchanged chlorotrifluoromethane (0·142 g., 0·00136 mole, 68%) (Found : *M*, 105. Calc. for CClF₃ : *M*, 104·5).

(b) 1-*Chloroheptafluoropropane.* Spectroscopically pure chloro-compound (0·1329 g., 0·00065 mole) and oxygen (0·2000 g., 0·00625 mole) in a 150-ml. silica tube (initial pressure *ca.* 1·2 atm.), exposed to ultraviolet light for 45 days, yielded no unchanged compound, and the products were completely absorbed by aqueous base.

In a second experiment chloroheptafluoropropane (0·2188 g., 0·00107 mole) and oxygen (0·3072 g., 0·0096 mole) were completely in the vapour phase when sealed in a 50-ml. silica tube (initial pressure *ca.* 5·4 atm.), and irradiation for 25 days gave unchanged chloro-compound (0·1615 g., 0·00079 mole, 74%), a small unidentified fraction (0·00004 mole), and a fraction (0·00098 mole) comprising silicon tetrafluoride and carbon dioxide which was completely destroyed by aqueous sodium hydroxide. Increase in the oxygen pressure has thus considerably reduced the rate of oxidation.

Experiments carried out with chloroheptafluoropropane (0·736 g., 0·0036 mole) and oxygen (0·960 g., 0·030 mole) in a 150-ml. silica tube in presence of bromine or of chlorine and water are summarised in Table 3. Infrared spectroscopy was used to examine the products.

Compounds of Type $CF_3 \cdot [CF_2]_n \cdot Br$.—(a) *Bromotrifluoromethane.* The sample used was spectroscopically pure. Bromotrifluoromethane (0·2235 g., 0·00150 mole) and oxygen (0·3072 g., 0·0096 mole), sealed in a 50-ml. silica tube (initial pressure *ca.* 5·6 atm.) and completely in the vapour phase, were exposed to ultraviolet light. An immediate reaction was apparent and bromine was liberated. After 6 hr. the condensable products (0·00170 mole) were examined spectroscopically and found to contain bromotrifluoromethane, carbonyl fluoride, silicon tetrafluoride, and carbon dioxide. Hexafluoroethane was not a product. A small unidentified, less volatile fraction (0·00004 mole) was also separated. After being shaken with 20% aqueous sodium hydroxide the products yielded only bromotrifluoromethane (0·1758 g., 0·00118 mole, 79%) (Found : *M*, 150. Calc. for CBrF₃ : *M*, 149). Bromotrifluoromethane is not decomposed by treatment with 20% aqueous sodium hydroxide.

(b) 1-*Bromoheptafluoropropane.* Bromoheptafluoropropane was prepared in 73% yield

by irradiation of heptafluoroiodopropane (1·55 g.) and bromine (2 g.) in a sealed 150-ml. silica tube for 4·5 days. Spectroscopically pure bromoheptafluoropropane (0·374 g., 0·0015 mole) and oxygen (0·3072 g., 0·0096 mole) when sealed in a 50-ml. silica tube were completely in the vapour phase at 35° (initial pressure *ca.* 5·6 atm.). After irradiation for 18 hr. the mixture contained free bromine, unchanged bromoheptafluoropropane (0·125 g., 0·00050 mole, 33%) (Found : M, 253. Calc. for C_3BrF_7 : M, 249), and a more volatile fraction (0·0056 mole) shown by spectroscopic investigation to consist mainly of carbon dioxide and silicon tetrafluoride. The last fraction was almost completely decomposed when shaken with 20% aqueous sodium hydroxide, and bromotrifluoromethane or bromopentafluoroethane is thus not a product. Bromoheptafluoropropane is stable to aqueous sodium hydroxide.

Compounds of Type $CF_3·[CF_2]_n·I$.—(a) *Trifluoroiodomethane*. This was prepared from silver trifluoroacetate and iodine (*J.*, 1951, 584). The iodo-compound (0·2939 g., 0·0015 mole) and oxygen (0·3072 g., 0·0096 mole), sealed in a 150-ml. silica tube (initial pressure *ca.* 1·9 atm.) and irradiated, gave a marked liberation of iodine after 15 min.; after 80 min., distillation gave unchanged trifluoroiodomethane (0·1764 g., 0·0009 mole, 60%), carbonyl fluoride, silicon tetrafluoride, and a small amount of carbon dioxide. The weight of unchanged trifluoroiodomethane was obtained after spectroscopic examination and reaction with aqueous sodium hydroxide.

In a second experiment, trifluoroiodomethane (0·894 g., 0·00456 mole) and oxygen (0·96 g., 0·030 mole), sealed in a 150-ml. silica tube (initial pressure 5·8 atm.) and irradiated for 4 hr., yielded trifluoroiodomethane (5%) isolated after treatment of its mixture with carbonyl fluoride, carbon dioxide, and silicon tetrafluoride with aqueous base.

(b) *Heptafluoro*-1-*iodopropane*. The reaction of silver heptafluorobutyrate and iodine yielded spectroscopically pure heptafluoroiodopropane (*J.*, 1951, 584; 1952, 4259).

(i) The iodo-compound (0·5802 g., 0·00196 mole) and oxygen (0·3072 g., 0·0096 mole) in a 150-ml. silica tube (initial pressure *ca.* 2 atm.) liberated iodine after 15 minutes' irradiation with shaking (liquid phase present initially), and, after 90 min., distillation *in vacuo* gave unchanged heptafluoroiodopropane (0·3048 g., 0·00103 mole, 52%) and a mixture (0·0049 mole) of carbonyl fluoride, silicon tetrafluoride, and carbon dioxide. The products were identified spectroscopically.

(ii) In this experiment a deficiency of oxygen was used. Heptafluoroiodopropane (2·00 g., 0·0068 mole) and oxygen (0·045 g., 0·0014 mole) in a 150-ml. silica tube (initial pressure *ca.* 1·2 atm.) yielded solid iodine after 1 hour's irradiation (reaction tube shaken) and 30% of the oxygen was recovered. Fractionation and spectroscopic examination of the reaction products revealed (*a*) unchanged heptafluoroiodopropane, (*b*) a small amount of material which could not be identified by spectroscopic examination but did not contain an acyl fluoride, and (*c*) carbonyl fluoride (0·0019 mole). The carbonyl fluoride is equivalent to 67% of the oxygen taken in the initial reaction mixture, and this is in good agreement with the measured oxygen recovery (30%).

(iii) Heptafluoroiodopropane (1·64 g., 0·0055 mole), oxygen (0·5280 g., 0·0165 mole), and 50% aqueous sulphuric acid (10 ml.) in a 110-ml. silica tube (initial pressure *ca.* 4 atm.) were shaken and exposed to ultraviolet light for 36 hr. The contents of four such tubes were combined, and the aqueous solution was filtered to remove solid iodine, saturated with sodium chloride, and extracted with ether (10 × 20 ml.). After drying (Na_2SO_4), distillation gave ether and a residue (0·32 g.) which did not possess the characteristic odour of perfluorocarboxylic acids; distillation of the residue failed to give a clear-cut fraction. Heptafluoroiodopropane was completely oxidised under the conditions used, and spectroscopic examination of the volatile reaction products revealed the presence of only carbon dioxide and silicon tetrafluoride.

(iv) Heptafluoroiodopropane (4·00 g., 0·0135 mole) and oxygen (1·728 g., 0·054 mole) were sealed with an excess of sodium hydroxide (9·0 g., 0·23 mole) and water (20 ml.) in a 170-ml. silica tube (initial pressure *ca.* 9 atm.), which was shaken (liquid phase present) and irradiated for 24 hr. The contents of the tube were combined with those of a second tube (295 ml.) in which had been sealed heptafluoroiodopropane (4·00 g., 0·0135 mole), oxygen (1·728 g., 0·054 mole), sodium hydroxide (9·0 g., 0·23 mole), and water (20 ml.) (initial pressure *ca.* 5 atm.) before exposure to ultraviolet light for 48 hr. No unchanged heptafluoroiodopropane was detected. The aqueous solution was strongly acidified with 50% sulphuric acid, filtered to remove iodine, and extracted with ether (10 × 20 ml.). The dried (Na_2SO_4) ethereal solution was shaken with mercury to remove iodine, evaporated to small bulk, and neutralised with 10% aqueous sodium carbonate. Evaporation to dryness gave a solid which was extracted with anhydrous ethanol to give a mixture of sodium salts of perfluoro-carboxylic acids (0·44 g.).

The thoroughly dried mixture, analysed by means of infrared spectroscopy, authentic samples of sodium trifluoroacetate and sodium pentafluoropropionate being used to give the reference data, contained sodium pentafluoropropionate (60%) and sodium trifluoroacetate (40%). The yields of sodium pentafluoropropionate (0·00142 mole) and sodium trifluoroacetate (0·00130 mole) based on heptafluoroiodopropane are 5·3 and 4·8%.

Chlorine-sensitised Oxidation of Trifluoroiodomethane.—Trifluoroiodomethane (0·298 g., 0·00152 mole), chlorine (0·531 g., 0·00748 mole), and oxygen (0·081 g., 0·00252 mole), sealed in a 50-ml. silica tube (initial pressure 5·8 atm.), irradiated for 4 hr., yielded only carbonyl fluoride, silicon tetrafluoride, and carbon dioxide. Spectroscopic examination of the very small amount (<2%) of gas remaining after treatment with aqueous sodium hydroxide showed that it was not chlorotrifluoromethane, hexafluoroethane, or trifluoroiodomethane.

Halogen-sensitised Oxidation of Heptafluoroiodopropane.—Heptafluoroiodopropane (0·550 g., 0·00185 mole), oxygen (0·256 g., 0·008 mole), and chlorine (0·069 g., 0·00097 mole), sealed in a 150-ml. silica tube (liquid phase present; initial pressure *ca.* 2 atm.) and irradiated for 90 min., deposited iodine and iodine monochloride on the walls of the tube. The condensable products were shaken with an excess of mercury in a sealed tube to remove free halogens and then distilled *in vacuo* to give (*a*) unchanged heptafluoroiodopropane (0·044 g., 0·00015 mole, 8%); (*b*) a fraction (0·00029 mole) comprising 80% pentafluoropropionyl fluoride, heptafluoroiodopropane, and a small amount of an unidentified material (trifluoroacetyl fluoride, chloropentafluoroethane, and chloroheptafluoropropane were absent); (*c*) a fraction (0·00023 mole) comprising pentafluoropropionyl fluoride (90%) and trifluoroacetyl fluoride (10%), with no carbonyl chlorofluoride; and (*d*) a fraction (0·00394 mole) comprising carbonyl fluoride, carbon dioxide, and silicon tetrafluoride; chlorotrifluoromethane was absent, since the fraction was completely absorbed by aqueous sodium hydroxide. These fractions were analysed spectroscopically. The yield of pentafluoropropionyl fluoride (0·00044 mole) is thus 24% and of trifluoroacetyl fluoride (0·000023 mole) is 1%.

Experiments carried out with heptafluoroiodopropane (0·550 g., 0·00185 mole) and oxygen (0·256 g., 0·008 mole) in the reaction vessel used in the last experiment and with comparable conditions and techniques but with bromine as sensitiser are shown in Table 3. The carboxylic acid was converted into its silver salt for identification.

Compounds of Type $CF_3 \cdot [CF_2]_n \cdot CFCl_2$.—1 : 1 - *Dichlorohexafluoropropane.* Reaction of 1-chloro-1-iodohexafluoropropane with an excess of chlorine at 60° in the dark (48 hr.) (cf. *J.*, 1953, 1592) gave a quantitative yield of dichlorohexafluoropropane, purified *in vacuo* (Found : *M*, 221. Calc. for $C_3Cl_2F_6$: *M*, 221).

Irradiation for 6 hr. of 1 : 1-dichlorohexafluoropropane (0·440 g., 0·00199 mole) and oxygen (0·008 mole) in a 180-ml. silica tube caused only 2% decomposition.

In a second experiment, dichlorohexafluoropropane (0·435 g., 0·00197 mole) and oxygen (0·008 mole) in a 150-ml. silica tube, irradiated for 28 hr., gave unchanged dichloro-compound (62%), pentafluoropropionyl fluoride (21%), trifluoroacetyl fluoride (2%), and the usual mixture of breakdown products.

Compounds of Type $CF_3 \cdot [CF_2]_n \cdot CFClBr$.—(a) 1-*Bromo*-1-*chlorohexafluoropropane.* 1-Chloro-1-iodohexafluoropropane (1·77 g., 0·0057 mole; prepared as described in *J.*, 1953, 1592) and bromine (2·00 g., 0·0125 mole) were sealed in a 50-ml. silica tube which was shaken, exposed to ultraviolet light for 6 hr., then kept in the dark (5 days). The excess of bromine was removed from the volatile products by reaction with mercury in a sealed tube, and fractionation *in vacuo* gave unchanged 1-chloro-1-iodohexafluoropropane (0·28 g., 16%) and 1-*bromo*-1-*chlorohexafluoropropane* (0·9556 g., 0·00366 mole, 64%), b. p. (isoteniscope) 54° (Found : C, 13·3% ; *M*, 265. C_3BrClF_6 requires C, 13·5% ; *M*, 265).

1-Bromo-1-chlorohexafluoropropane (0·5865 g., 0·0022 mole) and oxygen (0·2816 g., 0·0088 mole) were sealed in a 50-ml. silica tube (liquid phase present; initial pressure *ca.* 4·7 atm.) which was shaken and irradiated for 30 min.; 3% of the bromo-compound was oxidised to carbonyl fluoride, carbon dioxide, and silicon tetrafluoride. The experiment repeated with an irradiation time of 10 hr. gave 60% of unchanged bromo-compound; pentafluoropropionyl fluoride (45%) and trifluoroacetyl fluoride (8%) were formed and identified spectroscopically before hydrolysis and conversion into salts for analysis. A further experiment using weights of reactants as above but with the addition of bromine and water (2 ml.) is summarised in Table 3.

For comparison of reaction rates, 1-chloro-1-iodohexafluoropropane (0·6886 g., 0·0022 mole) and oxygen (0·2816 g., 0·0088 mole) were sealed in a 50-ml. silica tube identical with that used in the last experiment (liquid phase present; initial pressure *ca.* 4·6 atm.) and shaken by the

side of the tube containing the 1-bromo-1-chlorohexafluoropropane. After 30 minutes' irradiation under the same conditions as used for the bromo-compound, 1-chloro-1-iodohexafluoropropane had undergone oxidation to an extent of 35% to give carbonyl fluoride, carbon dioxide, silicon tetrafluoride, and pentafluoropropionyl fluoride (0·088 g., 0·00053 mole). The oxidation under the conditions specified above gives a 69% yield (24% conversion) of the acyl fluoride; the slower rate of oxidation of the iodo-compound compared with that under the conditions given below (see also Table 2) is caused by the difference in pressure.

(b) *Bromochlorodifluoromethane.* This compound [0·2530 g., 0·00153 mole, prepared as described earlier (*J.*, 1952, 4259)] was condensed with oxygen (0·3200 g., 0·010 mole) into a previously evacuated 50-ml. silica tube. At reaction temperature there was no liquid phase and the initial pressure was *ca.* 5·8 atm. Reddish-yellow vapours were produced on irradiation, and after 6·5 hr., distillation of the reaction products gave crude bromochlorodifluoromethane, which was shaken with 20% aqueous sodium hydroxide to remove halogen then redistilled to give the unchanged bromochlorodifluoromethane (0·1058 g., 0·00064 mole, 42%). Bromochlorodifluoromethane is stable to aqueous sodium hydroxide. The more volatile products (carbonyl halides, silicon tetrafluoride, free halogens, etc., identified by infrared spectroscopic examination) were completely decomposed by 20% aqueous sodium hydroxide.

Experiments carried out under strictly comparable conditions are shown in Table 4, and reveal the effect of variation of reactant ratio under constant pressure and of variation of initial pressure with constant reactant ratio. A 150-ml. silica tube was used, and the reactants, which were completely in the vapour phase, were irradiated for 6·5 hr.

TABLE 4.

| CF$_2$ClBr : | | O$_2$ | | Ratio | Initial | Oxidation |
g.	mole	g.	mole	O$_2$: CF$_2$ClBr	pres. (atm.)	(%)
0·768	0·00464	0·994	0·0310	7	6	80
0·151	0·00091	0·199	0·00622	7	1	99
0·511	0·00309	0·129	0·00404	1·3	1	87

Compounds of Type CF$_3$·[CF$_2$]$_n$·CFClI. 1-*Chloro*-1-*iodohexafluoropropane.* This compound was prepared from chlorotrifluoroethylene by reaction with trifluoroiodomethane (Haszeldine and Steele, *J.*, 1953, 1592) or with trifluoroacetyl iodide (unpublished work). It was distilled *in vacuo* before use, and was spectroscopically pure and peroxide-free.

(i) *Photochemical oxidation.* 1-Chloro-1-iodohexafluoropropane (0·756 g., 0·00242 mole) and oxygen (0·3072 g., 0·0096 mole) in a 150-ml. silica tube (liquid phase present; initial pressure *ca.* 1·8 atm.) were irradiated and shaken until no liquid phase remained (25 min.). Iodine was deposited on the walls of the tube. The products were distilled to give (*a*) unchanged 1-chloro-1-iodohexafluoropropane (0·1843 g., 0·00059 mole; 24%), (*b*) carbonyl fluoride, carbon dioxide, and silicon tetrafluoride (0·00057 mole), (*c*) trifluoroacetyl fluoride (0·007 g., 0·00006 mole, 2% conversion), and (*d*) *pentafluoropropionyl fluoride* (0·1975 g., 0·00119 mole, 49% conversion), b. p. −26·5° (isoteniscope) (Found: C, 21·3%; equiv., 85; *M*, 165. C$_3$OF$_6$ requires C, 21·7%; equiv., 83; *M*, 166). The yields of pentafluoropropionyl fluoride and trifluoroacetyl fluoride were 65 and 3%, respectively. Trifluoroacetyl fluoride was identified by means of its infrared spectrum; the spectrum of pentafluoropropionyl fluoride revealed the acyl carbonyl band.

1-Chloro-1-iodohexafluoropropane (0·758 g., 0·00243 mole) and oxygen (0·801 g., 0·025 mole) in a 150-ml. silica tube (initial pressure *ca.* 4·6 atm.) were irradiated under conditions identical with those for the first reaction to give unchanged iodo-compound (65%), pentafluoropropionyl fluoride (59%), trifluoroacetyl fluoride (4%), and a mixture of carbon dioxide, silicon tetrafluoride, and carbonyl fluoride.

(ii) *Dark reaction.* 1-Chloro-1-iodohexafluoropropane (0·380 g., 0·0012 mole) and oxygen (0·1056 g., 0·0033 mole) in a sealed 50-ml. Pyrex tube (liquid phase present; initial pressure *ca.* 1·8 atm.) were shaken in complete darkness for 33 days. Less than 0·05% of oxidation (based on the absence of volatile products) had then occurred. The unchanged iodo-compound was removed by pumping, leaving a small amount of a white solid in the tube. This solid, which is believed to be a peroxide, decomposed when exposed to dry air and liberated iodine.

(iii) *Photochemical oxidation in presence of water.* A 150-ml. silica tube containing 1-chloro-1-iodohexafluoropropane (0·596 g., 0·00191 mole), oxygen (0·3072 g., 0·0096 mole, initial pressure *ca.* 1·8 atm.), and water (2·5 ml.) was shaken and irradiated for 4·5 hr. Iodine was deposited and the organic layer disappeared. The only volatile product was carbon dioxide (0·0135 g., 0·000307 mole, 16%). The aqueous solution was shaken with mercury to remove iodine and then treated with a slight excess of silver carbonate. The filtered solution was evaporated

to dryness, and the residual solid extracted several times with dry ether. The ethereal extracts were evaporated to give a mixture of silver salts (0·3381 g.). Analysis of the mixture by means of infrared spectroscopy showed it to contain only silver trifluoroacetate and pentafluoropropionate in the ratio 1 : 5. The yield of silver pentafluoropropionate (0·282 g.) is thus 55%, and of silver trifluoroacetate (0·056 g.) 13%.

(iv) *Halogen-sensitised oxidation.* The last experiment was repeated, with the addition of chlorine (0·71 g., 0·010 mole) to the reaction mixture. The products were treated as above, and yielded silver trifluoroacetate (18%) and silver pentafluoropropionate (73%).

A 150-ml. tube containing 1-chloro-1-iodohexafluoropropane (0·601 g., 0·00192 mole), oxygen (0·310 g., 0·0097 mole; initial pressure *ca.* 1·8 atm.), and bromine (0·402 g., 0·0025 mole) was irradiated for 0·5 hr. to give unchanged iodo-compound (10%), pentafluoropropionyl fluoride (69%), trifluoroacetyl fluoride (21%), and breakdown products.

Photochemical Oxidation of Pentafluoropropionyl Fluoride.—The acyl fluoride (0·1368 g., 0·000824 mole) and oxygen (0·1146 g., 0·00358 mole, pressure *ca.* 0·74 atm.) in a 150-ml. silica tube were irradiated for 65 min. Distillation of the condensable products *in vacuo* gave unchanged pentafluoropropionyl fluoride (0·1145 g., 0·00069 mole, 84%) and carbon dioxide, silicon tetrafluoride, and carbonyl fluoride. Infrared spectroscopic examination showed no trifluoroacetyl fluoride.

Irradiation for 21 days of a mixture of pentafluoropropionyl fluoride (0·1610 g., 0·00097 mole) and oxygen (0·1146 g., 0·00358 mole, pressure *ca.* 0·77 atm.) caused complete oxidation to carbon dioxide and silicon tetrafluoride. Spectroscopic examination showed that trifluoroacetyl fluoride and carbonyl fluoride were absent.

Compounds of Type $F \cdot [CF_2]_n \cdot CFBr_2$.—*Dibromodifluoromethane.* This compound (see *J.*, 1952, 4259) (0·3192 g., 0·00152 mole) and oxygen (0·3200 g., 0·010 mole) in a 50-ml. silica tube (pressure *ca.* 5·6 atm.) were exposed to ultraviolet light (6·5 hr.) to give products heavily contaminated with free bromine. After removal of bromine, carbonyl halides, etc., by treatment with 20% aqueous sodium hydroxide, only 2% of the dibromodifluoromethane was recovered unchanged. Dibromodifluoromethane is stable towards 20% aqueous sodium hydroxide under the conditions used.

The experiment was repeated with an irradiation time of 4 hr.; 88% of the dibromodifluoromethane had then decomposed.