

70. Oxidation of Polyhalogeno-compounds. Part II.¹ Photolysis and Photochemical Oxidation of Some Chlorofluoroethanes.*

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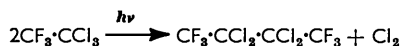
The vapour-phase photolysis and photochemical oxidation of the compounds $\text{CF}_3\cdot\text{CCl}_3$, $\text{CF}_3\cdot\text{CHCl}_2$, and $\text{CF}_3\cdot\text{CH}_2\text{Cl}$ have been studied. Oxidation of the compounds $\text{CF}_3\cdot\text{CHCl}_2$ and $\text{CF}_3\cdot\text{CH}_2\text{Cl}$ gives trifluoroacetyl chloride and trifluoroacetic acid. This is a new and convenient route for the preparation of this acid. Yields are greatly increased when chlorine is used as initiator. The compound $\text{CF}_3\cdot\text{CCl}_3$ is oxidised to carbonyl fluoride, but yields trifluoroacetic acid when water is present. Reaction mechanisms are proposed.

IN Part I¹ the photochemical vapour-phase oxidation of compounds of the type $\text{CF}_3\cdot[\text{CF}_2]_n\text{-CFXY}$ (X or Y = H, F, Cl, Br, or I) was described. It was shown that by carrying out the reaction in the presence of water, or by the use of bromine or chlorine as sensitiser, carbon-carbon bond cleavage could often be substantially prevented, so that the corresponding perfluoro-carboxylic acid or -acyl fluoride was obtained. A free-radical mechanism was proposed for these reactions. The present paper is concerned (a) with the photolysis and photochemical oxidation of the readily available 1 : 1 : 1-trichlorotrifluoroethane, 1 : 1-dichloro-2 : 2 : 2-trifluoroethane and 1-chloro-2 : 2 : 2-trifluoroethane, (b) with the establishment of conditions for their conversion in high yield into trifluoroacetyl chloride or trifluoroacetic acid, and (c) with the mechanism of these photolytic and photochemical oxidations.

Light of wavelength $>2200 \text{ \AA}$ was used, with silica reaction vessels. Molecular oxygen was added to effect photochemical oxidation. Despite the high resistance of these chlorofluoroethanes to attack by conventional acidic, basic, or oxidising agents, photochemical oxidation is often rapid and quantitative. The main problem is to control the photochemical oxidation so that carbon-carbon cleavage does not predominate, to give only carbonyl halides and their decomposition products. Such carbon-carbon cleavage can occur by degradation of a perhalogenoalkoxy-radical,¹ or by photolysis of an initial oxidation product such as trifluoroacetic acid or trifluoroacetyl chloride. In general, an initiator, usually chlorine, is advantageous, since it enables the irradiation time to be shortened, and water can be added to convert the readily photolysed trifluoroacetyl chloride into aqueous trifluoroacetic acid; the last technique is particularly necessary for 1 : 1 : 1-trichlorotrifluoroethane which is oxidised photochemically only slowly, and at a rate comparable with that of trifluoroacetyl chloride, its oxidation product.

Typical results are given in Table I and the main features are now summarised:

1 : 1 : 1-Trichlorotrifluoroethane.—This compound is resistant to concentrated acids and alkalis and to conventional nucleophilic reagents such as ethoxide ion; it gives trifluoroacetic acid in 10% yield only with oleum in presence of mercury salts.² The vapour-phase photolysis was slow (54% in 36 days) and yielded the dimer:



Vapour-phase photochemical oxidation was much faster (85% in 2 days) and gave none of the dimer, but a small amount (2%) of trifluoroacetyl chloride, carbon dioxide, and, by attack on the reaction vessel, silicon tetrafluoride. In presence of chlorine or bromine the yield of the acyl chloride was increased, and presence of water or aqueous alkali during

* Preliminary communication, *Proc. Chem. Soc.*, 1957, 146. Presented at Amer. Chem. Soc. Meeting, New York, 1957.

¹ Part I, Francis and Haszeldine, *J.*, 1955, 2151.

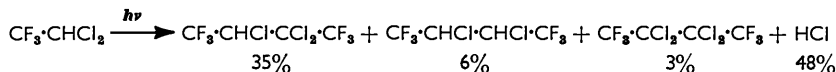
² Benning and Park, U.S.P. 2,396,076/1946; *Chem. Abs.*, 1946, 40, 3128.

the photolysis produced a marked increase in yield of trifluoroacetic acid (51%); highest yields (65%) were obtained when both water and chlorine or bromine were present.

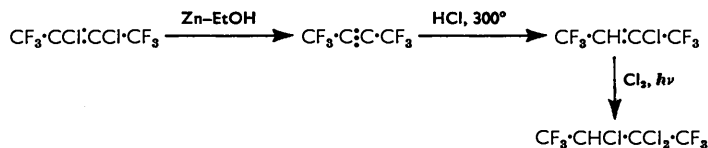
TABLE 1. Photochemical oxidation of some chlorofluoroethanes.

Mole ratio O ₂ : Compound	Initial press. (atm.)	Other reactants	Time of irradiation (hr.)	Oxidation (%)	Product (% yield)
<i>Oxidation of CF₃·CCl₃</i>					
5:3	1.9	—	48	85	CF ₃ ·COCl 2
4:6	2.6	Cl ₂ (Cl ₂ : O ₂ = 1 : 6)	48	64	CF ₃ ·COCl 7
4:4	2.6	Br ₂ (Br ₂ : O ₂ = 1 : 4)	51	62	CF ₃ ·COCl 7
2:8	3.3	H ₂ O	60	68	CF ₃ ·CO ₂ H 51
2:4	3.1	Cl ₂ (Cl ₂ : O ₂ = 1.7 : 1), H ₂ O	77	80	CF ₃ ·CO ₂ H 64
2:5	2.2	Br ₂ (Br ₂ : O ₂ = 1.7 : 1), H ₂ O	124	81	CF ₃ ·CO ₂ H 65
<i>Oxidation of CF₃·CHCl₂</i>					
11:0	1.5	—	5.0	99	{ CF ₃ ·CO ₂ H 16 CF ₃ ·COCl 60
4:5	1.8	—	6.0	100	{ CF ₃ ·CO ₂ H 13 CF ₃ ·COCl 60
4:2	2.5	Cl ₂ (Cl ₂ : O ₂ = 1 : 1.9)	0.08	100	{ CF ₃ ·CO ₂ H 11 CF ₃ ·COCl 80
4:9	2.8	Cl ₂ (Cl ₂ : O ₂ = 1 : 1.7)	0.5	100	CF ₃ ·COCl 90
5:2	2.7	Cl ₂ (Cl ₂ : O ₂ = 1 : 2.1)	1.2	100	{ CF ₃ ·CO ₂ H 7 CF ₃ ·COCl 82
5:8	2.4	Br ₂ (Br ₂ : O ₂ = 1 : 1.7)	113	79	CF ₃ ·CO ₂ H 2
2:5	1.7	H ₂ O	72	100	CF ₃ ·CO ₂ H 71
2:5	1.8	Cl ₂ (Cl ₂ : O ₂ = 1 : 1.2), H ₂ O	72	100	CF ₃ ·CO ₂ H 73
<i>Oxidation of CF₃·CH₂Cl</i>					
2:2	1.8	—	31	40	CF ₃ ·CO ₂ H 53
2:3	2.2	Cl ₂ (Cl ₂ : O ₂ = 1 : 2.0)	0.4	49	{ CF ₃ ·CO ₂ H 16 CF ₃ ·COCl 61
2:5	2.0	Br ₂ (Br ₂ : O ₂ = 1 : 3.8)	116	18	—
2:0	1.8	H ₂ O	174	76	CF ₃ ·CO ₂ H 47
1:9	1.9	Cl ₂ (Cl ₂ : O ₂ = 1 : 1.6), H ₂ O	72	100	CF ₃ ·CO ₂ H 75

1 : 1-Dichloro-2 : 2 : 2-trifluoroethane.—The vapour-phase photolysis of this compound was more rapid than for 1 : 1 : 1-trichlorotrifluoroethane:



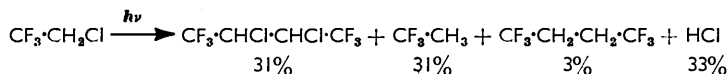
2 : 2 : 3-Trichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane was identified by comparison with a sample prepared by the following route:



The vapour-phase photochemical oxidation of 1 : 1-dichloro-2 : 2 : 2-trifluoroethane was also much more rapid than that of 1 : 1 : 1-trichlorotrifluoroethane and gave a mixture of trifluoroacetyl chloride (60%) and trifluoroacetic acid (13%). The addition of chlorine greatly increased the rate of oxidation (100% oxidation in 5 min.) and improved the yields of the required products (CF₃·COCl 80%; CF₃·CO₂H 11%). Unexpectedly, however, the presence of bromine reduced the rate of oxidation, and carbon dioxide and silicon tetrafluoride were then the main products. The ethane was also photochemically oxidised in the presence of water (yield of CF₃·CO₂H 71%), and water and chlorine (yield of CF₃·CO₂H 73%).

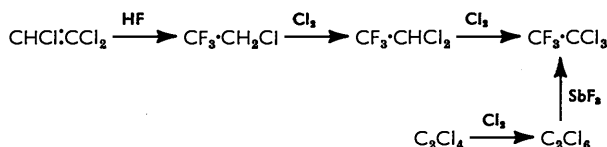
1-Chloro-2 : 2 : 2-trifluoroethane.—The vapour-phase photolysis of this ethane was

slower than that of 1 : 1-dichloro-2 : 2 : 2-trifluoroethane but faster than that of 1 : 1 : 1-trichlorotrifluoroethane:



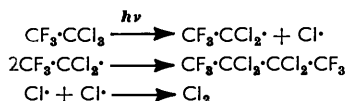
Photochemical oxidation of 1-chloro-2 : 2 : 2-trifluoroethane gave results in general similar to those obtained for 1 : 1-dichloro-2 : 2 : 2-trifluoroethane; presence of chlorine increased the rate of reaction and improved the yields of trifluoroacetyl chloride and trifluoroacetic acid, whereas bromine inhibited the reaction.

Discussion.—The three chlorofluoroethanes discussed above are readily made from tri- or tetra-chloroethylene:

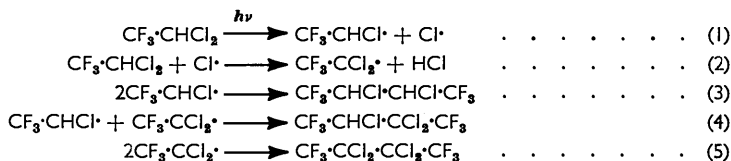


The present work establishes that their $-\text{CH}_2\text{Cl}$, $-\text{CHCl}_2$, or $-\text{CCl}_3$ group can be oxidised to $-\text{COCl}$ or $-\text{CO}_2\text{H}$ in good or excellent yield. This provides a new and convenient route for the synthesis of trifluoroacetic acid. In a laboratory the oxidations can be effected on a half-mole scale by use of the apparatus described earlier.³

(a) *Photolysis of the chlorofluoroethanes.* The photolysis of 1 : 1 : 1-trichlorotrifluoroethane to give 2 : 2 : 3 : 3-tetrachlorohexafluoroethane and chlorine is accounted for by the following scheme:

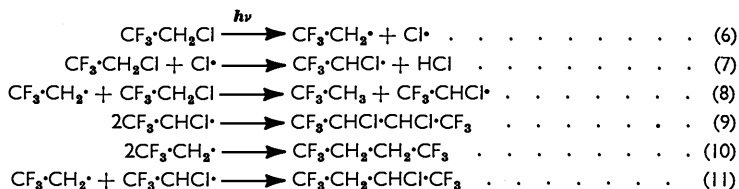


The products resulting from the photolysis of 1 : 1-dichloro-2 : 2 : 2-trifluoroethane suggest the following scheme:



Step 2 accounts both for the observed formation of hydrogen chloride and for the faster photolysis of the dichloro-compound than of 1 : 1 : 1-trichlorotrifluoroethane.

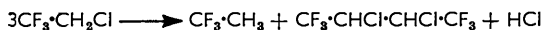
The photolysis products of 1-chloro-2 : 2 : 2-trifluoroethane are similarly accounted for by the sequence:



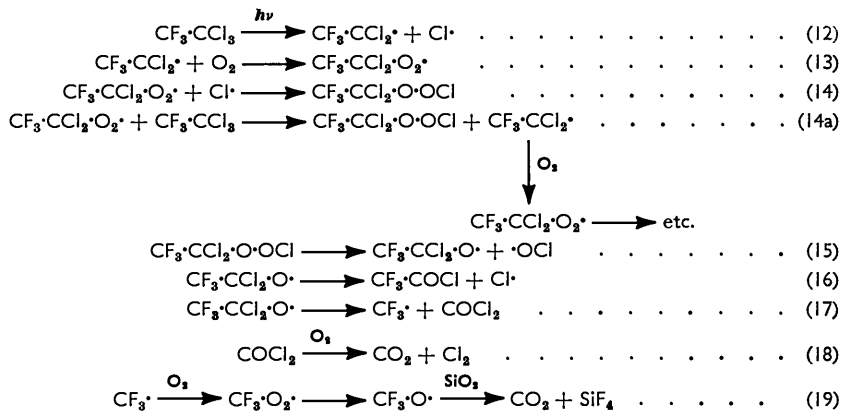
Steps 7 and 8 account for the formation of hydrogen chloride (33%) and 1 : 1 : 1-trifluoroethane (31%) respectively, and lead to a relatively high concentration of $\text{CF}_3\cdot\text{CHCl}\cdot$ radicals which dimerise to give the observed 2 : 3-dichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (31%). The $\text{CF}_3\cdot\text{CH}_2\cdot$ radical is rapidly consumed by step 8 rather than by steps 10 and 11 since the

³ Barr and Haszeldine, *J.*, 1955, 1881.

starting material is present in excess. Although a small quantity of 1:1:1:4:4:4-hexafluorobutane was isolated, none of the expected 2-chloro-1:1:1:4:4:4-hexafluorobutane (reaction 11) was found. The overall reaction is thus predominantly:



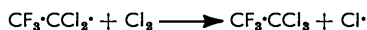
(b) *Photochemical oxidation of 1:1:1-trichlorotrifluoroethane.* The photochemical oxidation of 1:1:1-trichlorotrifluoroethane is explained by the following scheme:



which is similar to that suggested earlier for photochemical oxidation of perhalogeno-radicals.¹ The following facts support this.

First, the occurrence of step 12 is required by the results obtained when 1:1:1-trichlorotrifluoroethane was photolysed alone.

Secondly, the much greater rate of photochemical oxidation than of photolysis in absence of oxygen is to be attributed to the very rapid combination of $\text{CF}_3\cdot\text{CCl}_2\cdot$ radicals with oxygen (step 13), thus preventing reversal of the primary step:



Evidence for the rapidity of the combination of the $\text{CF}_3\cdot\text{CCl}_2\cdot$ radical with oxygen also arises from studies on 1:1-dichloro-2:2:2-trifluoroethane in presence of chlorine; it is noteworthy that the $\text{CF}_3\cdot\text{CCl}_2\cdot$ radical produced by hydrogen abstraction:



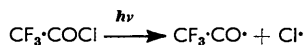
rapidly combines with chlorine to give 1:1:1-trichlorotrifluoroethane quantitatively when oxygen is absent, whereas when both chlorine and oxygen are present only the oxidation products of the $\text{CF}_3\cdot\text{CCl}_2\cdot$ radical result, and not even a trace of 1:1:1-trichlorotrifluoroethane can be found.

Thirdly, the formation of the $\text{CF}_3\cdot\text{CCl}_2\cdot\text{O}\cdot$ radical by steps 13—15 can be followed by elimination of a chlorine atom to give trifluoroacetyl chloride (step 16), or by carbon-carbon fission to give carbonyl chloride and a trifluoromethyl radical (step 17) which then breaks down as outlined earlier.¹

Fourthly, one can account for the increased yield of trifluoroacetyl chloride in the presence of added chlorine or bromine, and the formation of trifluoroacetic acid when water (yield of $\text{CF}_3\cdot\text{CO}_2\text{H}$ 51%), or water and halogen (yield of $\text{CF}_3\cdot\text{CO}_2\text{H}$ 65%), are present. A radical such as $\text{CF}_3\cdot\text{CCl}_2\cdot\text{O}\cdot$, which contains chlorine on the α -carbon atom, breaks down mainly by loss of a chlorine atom rather than by carbon-carbon bond fission; separate experiments show that the failure to isolate more than very small quantities (2%) of trifluoroacetyl chloride when 1:1:1-trichlorotrifluoroethane is oxidised in absence

of water is caused by the faster photochemical oxidation of trifluoroacetyl chloride under these conditions. Aqueous trifluoroacetic acid is photochemically oxidised only very slowly, and when water is present to remove trifluoroacetyl chloride as formed, the yield of trifluoroacetic acid is increased.

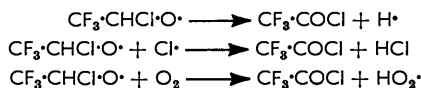
The presence of an excess of halogen stabilises the acyl chloride by reversal of its primary photolysis step:



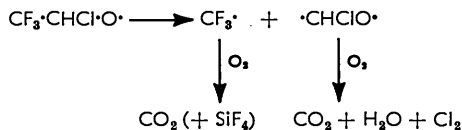
Direct reaction of an intermediate species such as $\text{CF}_3\cdot\text{CCl}_2\cdot\text{O}\cdot\text{Cl}$ with water could also serve as a source of trifluoroacetic acid, so that the yield of the acid is not necessarily a measure of the extent to which step 16 predominates over step 17.

(c) *Photochemical oxidation of 1:1-dichloro-2:2:2-trifluoroethane.* This provides further information about the relative occurrence of oxidation to trifluoroacetyl chloride and carbon-carbon fission, and the effect of added water. The great ease of oxidation is caused by the chlorine produced by the primary photolysis reaction (1), reacting as in reaction (2); addition of chlorine as initiator markedly increases the oxidation rate. The major product in absence of added water is trifluoroacetyl chloride (60%); the trifluoroacetic acid (13%) also formed arises by hydrolysis of trifluoroacetyl chloride by water also produced during the oxidation. The much greater yield of trifluoroacetyl chloride thus obtained compared with that in the oxidation of 1:1:1-trichlorotrifluoroethane (2%), even though both involve $\text{CF}_3\cdot\text{CCl}_2\cdot$ radicals, is attributed to the much shorter irradiation time required which greatly reduces the photochemical decomposition of trifluoroacetyl chloride.

The $\text{CF}_3\cdot\text{CCl}_2\cdot$ radical produced by reaction (2) gives rise to trifluoroacetyl chloride (reactions 13—16). The $\text{CF}_3\cdot\text{CHCl}\cdot$ radical of step (1) would similarly form the $\text{CF}_3\cdot\text{CHCl}\cdot\text{O}\cdot$ radical, and this could either give trifluoroacetyl chloride by the loss of its hydrogen atom in several ways:



or break down by carbon-carbon bond fission:



In the absence of added chlorine, $\text{CF}_3\cdot\text{CCl}_2\cdot\text{O}\cdot$ and $\text{CF}_3\cdot\text{CHCl}\cdot\text{O}\cdot$ radicals are produced in approximately equal amounts and since the yield of trifluoroacetyl chloride is well above 50% a substantial part of it must arise from the $\text{CF}_3\cdot\text{CHCl}\cdot\text{O}\cdot$ radicals in one or more of the ways indicated above.

The $\text{CF}_3\cdot\text{CHCl}\cdot\text{O}\cdot$ radical could also break down by loss of a chlorine atom to give trifluoroacetaldehyde. Control experiments with the aldehyde showed that it is readily photolysed in the absence of oxygen to give trifluoromethyl radicals and that it reacts rapidly with chlorine on exposure to ultraviolet light to give chlorotrifluoromethane (54%). The $\text{CF}_3\cdot\text{CHCl}\cdot\text{O}\cdot$ radical when formed by photochemical oxidation of 1-chloro-2:2:2-trifluoroethane (see below) gives trifluoroacetyl chloride in 77% yield. Since trifluoroacetyl chloride is produced in only very low yield by photochemical chlorination of trifluoroacetaldehyde, it follows that not more than *ca.* 23% of the $\text{CF}_3\cdot\text{CHCl}\cdot\text{O}\cdot$ radicals can have formed trifluoroacetaldehyde. Thus, if trifluoroacetaldehyde is formed at all in the photochemical oxidation of 1:1-dichloro-2:2:2-trifluoroethane, its maximum yield can only be about 12%.

When chlorine is present so that the molar ratio $\text{CF}_3\cdot\text{CHCl}_2 : \text{Cl}_2$ is about 1:1, the

photochemical oxidation is complete within a few minutes and trifluoroacetyl chloride is produced in 90% yield. The speed of the reaction and the formation of hydrogen chloride show that initiation must be virtually exclusively by hydrogen abstraction to give $\text{CF}_3\cdot\text{CCl}_2\cdot\text{O}$ radicals. The $\text{CF}_3\cdot\text{CCl}_2\cdot\text{O}$ radicals must also break down by loss of a chlorine atom and only to a small extent by carbon-carbon bond fission. This behaviour is in marked contrast to that of perfluoroalkoxy-radicals which undergo carbon-carbon bond fission exclusively, *e.g.*, in the photochemical oxidation of 1-iodoheptafluoropropane:¹



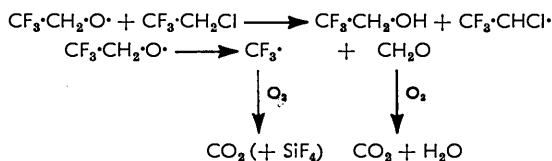
This may be attributed to the relative energies of the C-F and C-Cl bonds, since the alternative mode of breakdown



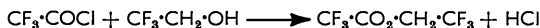
would require the breaking of the strong C-F bond.

The photochemical oxidation of 1 : 1 : 1-trichlorotrifluoroethane in presence of water gives a lower yield of trifluoroacetic acid than expected if $\text{CF}_3\cdot\text{CCl}_2\cdot\text{O}$ radicals are intermediates; some of these radicals or other intermediate species must thus react with water by carbon-carbon bond fission. Similarly, the yield of trifluoroacetic acid from 1 : 1-dichloro-2 : 2 : 2-trifluoroethane when both chlorine and water were added (73%) was markedly lower than that of trifluoroacetyl chloride when only chlorine was added (90%).

(d) *Photochemical oxidation of 1-chloro-2 : 2 : 2-trifluoroethane.* The $\text{CF}_3\cdot\text{CH}_2\cdot$ and $\text{CF}_3\cdot\text{CHCl}\cdot$ radicals produced by steps (6) and (7) are similarly considered to give rise to $\text{CF}_3\cdot\text{CH}_2\cdot\text{O}$ and $\text{CF}_3\cdot\text{CHCl}\cdot\text{O}$ radicals. The fate of the $\text{CF}_3\cdot\text{CHCl}\cdot\text{O}$ radical has been discussed. The $\text{CF}_3\cdot\text{CH}_2\cdot\text{O}$ radical might be expected to behave like a primary hydrocarbon alkoxy-radical, $\text{R}\cdot\text{CH}_2\cdot\text{O}$, which⁴ reacts by hydrogen-abstraction or by carbon-carbon bond fission to give formaldehyde, *i.e.*,



Control experiments with 2 : 2 : 2-trifluoroethanol show that it is stable to ultraviolet light in absence of oxygen, and that photolysis in presence of chlorine rapidly converts it into 2 : 2 : 2-trifluoroethyl trifluoroacetate (60%), chlorotrifluoromethane (13%), and fluoroform (9%). The ester arises by the intermediate formation of trifluoroacetyl chloride:



Neither trifluoroethanol nor its trifluoroacetate could be detected amongst the photochemical oxidation products of 1-chloro-2 : 2 : 2-trifluoroethane.

The $\text{CF}_3\cdot\text{CH}_2\cdot\text{O}$ radical could also break down by loss of a hydrogen atom:

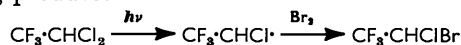


Some distinction can be made between the various possible reaction steps outlined above. Oxidation with oxygen alone gives trifluoroacetic acid (53%) which presumably arises from the hydrolysis of trifluoroacetyl chloride by water also produced during the photolysis. The $\text{CF}_3\cdot\text{CHCl}\cdot$ and $\text{CF}_3\cdot\text{CH}_2\cdot$ radicals and hence also the $\text{CF}_3\cdot\text{CHCl}\cdot\text{O}$ and $\text{CF}_3\cdot\text{CH}_2\cdot\text{O}$ radicals are produced in approximately equal amounts under these conditions, and some $\text{CF}_3\cdot\text{CH}_2\cdot\text{O}$ radicals must thus give rise to trifluoroacetyl chloride or trifluoroacetic acid. The primary process with chlorine present is almost exclusively hydrogen abstraction, so that only $\text{CF}_3\cdot\text{CHCl}\cdot\text{O}$ radicals need be considered; the high yield ($\text{CF}_3\cdot\text{COCl} +$

⁴ See, for example, Levy, *J. Amer. Chem. Soc.*, 1953, **75**, 1801; Levy and Adrian, *ibid.*, 1955, **77**, 2015; Tipper, *Quart. Rev.*, 1957, **4**, 334—337.

$\text{CF}_3\cdot\text{CO}_2\text{H}$ 77%) shows that this radical is efficiently converted into trifluoroacetyl chloride. The lower yield (53%) in the absence of chlorine shows that most of the $\text{CF}_3\cdot\text{CH}_2\cdot\text{O}$ radicals break down by carbon-carbon fission or *via* trifluoroacetaldehyde.

The failure of bromine to act as a sensitizer in the oxidation of 1-chloro- and 1:1-dichloro-2:2:2-trifluoroethane must be attributed to the inability of a bromine atom to abstract a hydrogen atom, since the photolysis of 1:1-dichloro-2:2:2-trifluoroethane in the presence of bromine gave 1-bromo-1-chloro-2:2:2-trifluoroethane (68%) as the only bromine-containing product:



and in particular 1-bromo-1:1-dichlorotrifluoroethane was not detected. The failure to obtain significant amounts of trifluoroacetyl chloride, trifluoroacetyl bromide, or trifluoroacetic acid from 1:1-dichloro-2:2:2-trifluoroethane in the experiments in which bromine was added is caused by the inhibiting effect of bromine; the irradiation time required to produce a significant degree of oxidation of the starting material was more than sufficient to ensure the complete oxidation of any of these possible products. The reason for the inhibiting effect is not known.

EXPERIMENTAL

The general techniques were described in Part I.¹ The reactants were either commercial samples or were prepared by standard methods; all were distilled before use and were analytically and spectroscopically pure and free from peroxide. Yields are based on material consumed. Only typical experiments are described. Products were identified by their b. p., molecular weight, and infrared spectra; mixtures were analysed by a combination of infrared spectroscopy and chemical analysis.

Photolysis of 1:1:1-Trichlorotrifluoroethane.—1:1:1-Trichlorotrifluoroethane (0.506 g., 2.98 mmole), sealed in a 320 ml. silica tube and exposed to ultraviolet light for 36 days, gave both liquid and solid products. The volatile products were shaken with mercury in a sealed tube to remove the chlorine produced, then fractionally distilled *in vacuo*, to give only unchanged 1:1:1-trichlorotrifluoroethane (0.261 g., 1.38 mmole, 46%) (Found: *M*, 187. Calc. for $\text{C}_2\text{Cl}_3\text{F}_3$: *M*, 187.5). The solid was purified by sublimation at atmospheric pressure, to give 2:2:3:3-tetrachlorohexafluorobutane (0.151 g., 0.496 mmole, 76%), spectroscopically identical with a known sample.

2:2:3:3-Tetrachlorohexafluorobutane.—2:3-Dichlorohexafluorobut-2-ene (1.033 g., 4.45 mmole) and chlorine (0.670 g., 9.44 mmole), sealed in a 50 ml. Pyrex tube, failed to react in the dark during 24 hr. Irradiation with ultraviolet light for 24 hr., followed by removal of the excess of chlorine, gave 2:2:3:3-tetrachlorohexafluorobutane (1.10 g., 3.62 mmole, 82%) (Found: C, 15.7. Calc. for $\text{C}_4\text{Cl}_4\text{F}_6$: C, 15.8%), m. p. 84°, purified by sublimation. Henne *et al.*⁵ record m. p. 83–84°.

Photochemical Oxidation of 1:1:1-Trichlorotrifluoroethane.—(i) *With oxygen alone.* 1:1:1-Trichlorotrifluoroethane (0.538 g., 2.87 mmole) and oxygen (0.486 g., 15.2 mmole) were exposed in a sealed 260 ml. silica tube (initial pressure *ca.* 1.9 atm.) to ultraviolet light for 48 hr. The volatile products were shaken with mercury in a sealed tube to remove chlorine, transferred to a vacuum-system, and fractionally distilled, to give unchanged 1:1:1-trichlorotrifluoroethane (0.080 g., 0.426 mmole, 15%), trifluoroacetyl chloride (0.005 g., 0.038 mmole, 2%), and a mixture (0.350 g., 5.83 mmole) of carbon dioxide and silicon tetrafluoride.

(ii) *In the presence of chlorine.* In a typical experiment, 1:1:1-trichlorotrifluoroethane (0.641 g., 3.41 mmole), chlorine (0.346 g., 4.87 mmole), and oxygen (0.512 g., 16.0 mmole) were irradiated in a sealed 260 ml. silica tube (initial pressure *ca.* 2.6 atm.) for 42 hr. The volatile products were treated as in (i), to give 1:1:1-trichlorotrifluoroethane (0.320 g., 1.71 mmole, 50%), trifluoroacetyl chloride (0.022 g., 0.168 mmole, 10%), and a mixture (0.148 g., 2.46 mmole) of carbon dioxide and silicon tetrafluoride.

(iii) *In the presence of bromine.* 1:1:1-Trichlorotrifluoroethane (0.716 g., 3.82 mmole), bromine (0.700 g., 4.38 mmole), and oxygen (0.537 g., 16.8 mmole), sealed in a 260 ml. silica tube (initial pressure *ca.* 2.6 atm.), were exposed to ultraviolet light for 51 hr. The volatile products were treated as in (i), to give 1:1:1-trichlorotrifluoroethane (0.272 g., 1.45 mmole,

⁵ Henne, Hinkamp, and Zimmerscheid, *J. Amer. Chem. Soc.*, 1945, **67**, 1906.

38%), trifluoroacetyl chloride (0.022 g., 0.168 mmole, 7%), and a mixture (0.300 g., 5.00 mmole) of carbon dioxide and silicon tetrafluoride.

(iv) *In the presence of water.* 1 : 1 : 1-Trichlorotrifluoroethane (1.091 g., 5.82 mmole), water (2.5 ml.), and oxygen (0.513 g., 16.0 mmole), sealed in a 150 ml. silica tube (initial pressure *ca.* 3.3 atm.) and exposed to ultraviolet light for 60 hr., gave unchanged 1 : 1 : 1-trichlorotrifluoroethane (0.345 g., 1.84 mmole, 32%) and carbon dioxide (0.020 g., 0.454 mmole). 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 was evaporated *in vacuo*, to give analytically and spectroscopically pure silver trifluoroacetate (0.450 g., 2.04 mmole, 51%). In presence of 5*N*-sodium hydroxide and under similar conditions, the yield of silver trifluoroacetate was 51%.

(v) *In the presence of water and chlorine.* 1 : 1 : 1-Trichlorotrifluoroethane (1.246 g., 6.65 mmole), water (3.0 ml.), chlorine (0.668 g., 9.41 mmole), and oxygen (0.504 g., 15.8 mmole) in a 260 ml. silica tube (initial pressure *ca.* 3.1 atm.), irradiated for 76 hr., gave chlorine (removed by reaction with mercury), unchanged 1 : 1 : 1-trichlorotrifluoroethane (0.250 g., 1.33 mmole, 20%), and carbon dioxide (0.040 g., 0.91 mmole). The aqueous solution was treated as in (iv), to give spectroscopically pure silver trifluoroacetate (0.753 g., 3.38 mmole, 64%).

(vi) *In the presence of water and bromine.* 1 : 1 : 1-Trichlorotrifluoroethane (1.171 g., 6.24 mmole), bromine (1.450 g., 9.07 mmole), water (3.0 ml.), and oxygen (0.497 g., 15.5 mmole), sealed in a 320 ml. silica tube, were exposed to ultraviolet light for 124 hr. The products, treated as in (iv), were shown to be 1 : 1 : 1-trichlorotrifluoroethane (0.228 g., 1.22 mmole, 19% recovery), carbon dioxide (0.085 g., 1.93 mmole), and trifluoroacetic acid identified as silver trifluoroacetate (0.733 g., 3.32 mmole, 65%).

Photolysis of 1 : 1-Dichloro-2 : 2 : 2-trifluoroethane.—(i) *Alone.* 1 : 1-Dichloro-2 : 2 : 2-trifluoroethane (1.402 g., 9.16 mmole) was exposed in a sealed 320 ml. silica tube to ultraviolet light for 28 days. Hydrogen chloride (0.160 g., 4.39 mmole, 48%) (Found: *M*, 36.7. Calc. for HCl: *M*, 36.5) was the only volatile product. The higher-boiling products were distilled at atmospheric pressure through a semi-micro Vigreux column to give: (a) a mixture shown spectroscopically and by molecular-weight determination to consist of 2 : 3-dichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (0.12 g., 0.51 mmole) and 2 : 2 : 3-trichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (0.25 g., 0.94 mmole); (b) 2 : 2 : 3-trichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (0.50 g., 1.88 mmole), b. p. 104° (Found: C, 18.1; H, 0.8. Calc. for C₄HCl₃F₆: C, 17.8; H, 0.4%), spectroscopically identical with a known sample; and (c) a mixture shown spectroscopically to consist of 2 : 2 : 3-trichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (0.1 g., 0.4 mmole) and 2 : 2 : 3-tetrachlorohexafluorobutane (0.08 g., 0.26 mmole). The products of photolysis are thus: HCl 48%, CF₃·CHCl·CHCl·CF₃ 6%, CF₃·CHCl·CCl₂·CF₃ 35%, and CF₃·CCl₂·CCl₂·CF₃ 3%.

(ii) *In the presence of bromine.* 1 : 1-Dichloro-2 : 2 : 2-trifluoroethane (0.541 g., 3.54 mmole) and bromine (0.473 g., 2.95 mmole), irradiated in a 150 ml. silica tube for 12 days, gave, after removal of bromine by shaking with mercury, (a) 1 : 1-dichloro-2 : 2 : 2-trifluoroethane (0.105 g., 0.696 mmole, 19%), (b) hydrogen chloride (0.058 g., 1.56 mmole, 69%), and (c) a mixture of 1 : 1 : 1-trifluorobromochloroethane (*ca.* 0.30 g.), 2 : 3-dichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (*ca.* 0.08 g.), and 2 : 2 : 3-trichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (*ca.* 0.06 g.). The photolysis products are thus: HCl 69%, CF₃·CHClBr 68%, CF₃·CHCl·CHCl·CF₃ 15%, and CF₃·CHCl·CCl₂·CF₃ 9%.

*Synthesis of 2 : 2 : 3-Trichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane.*⁶—Hexafluorobut-2-yne (1.843 g., 11.9 mmole), prepared in 54% yield by dechlorination of 2 : 3-dichlorohexafluorobut-2-ene, and hydrogen chloride (0.495 g., 13.5 mmole) did not react in a 200 ml. Pyrex tube at 200° in 24 hr. Reaction at 300° (24 hr.) gave (a) hexafluorobut-2-yne (0.050 g., 0.31 mmole, 30%), (b) hydrogen chloride (0.116 g., 3.18 mmole, 24%), (c) a mixture (0.477 g.) of 2 : 3-dichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane and unidentified olefins, and (d) 2-chloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene (1.395 g., 7.04 mmole, 62%) (Found: C, 24.3; H, 0.7%; *M*, 198. Calc. for C₄HClF₆: C, 24.2; H, 0.5%; *M*, 198.5). No reaction took place at temperatures up to 100° in presence of anhydrous ferric or aluminium chloride (cf. Haszeldine⁶). The butene (1.914 g., 9.65 mmole) and chlorine (0.770 g., 10.8 mmole), sealed in a 50 ml. Pyrex tube and exposed to ultraviolet light for 24 hr., gave 2 : 2 : 3-trichloro-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutane (2.47 g., 9.16 mmole, 95%), b. p. 104° (Found: C, 17.9; H, 0.6. Calc. for C₄HCl₃F₆: C, 17.8; H, 0.4%).

⁶ Henne and Finnegan, *J. Amer. Chem. Soc.*, 1949, 71, 298; Haszeldine, *J.*, 1952, 2504

Photochemical Oxidation of 1:1-Dichloro-2:2:2-trifluoroethane and 1-Chloro-2:2:2-trifluoroethane.—The experimental procedure was similar to that described for 1:1:1-trichlorotrifluoroethane and details for typical experiments are summarised in Table 2.

Photolysis of 1-Chloro-2:2:2-trifluoroethane.—1-Chloro-2:2:2-trifluoroethane (14.8 g., 0.124 mmole) was exposed in a sealed 360 ml. silica tube to ultraviolet light for 52 days. A small amount of non-condensable gas was pumped off, and a small amount of free chlorine was removed by mercury. Distillation *in vacuo* gave (a) 2:2-dichloro-1:1:1:4:4:4-hexafluorobutane (1.26 g., 5.37 mmole) (Found: *M*, 235. Calc. for $C_4H_2Cl_2F_6$: *M*, 235), (b) a mixture of 2:3-dichloro-1:1:1:4:4:4-hexafluorobutane (0.12 g., 0.5 mmole), (c) 1-chloro-2:2:2-trifluoroethane (12.47 g., 0.105 mole, 85%), (d) 1:1:1-trifluoroethane (0.450 g., 5.36 mmole) (Found: *M*, 85. Calc. for $C_2H_3F_3$: *M*, 84) identified spectroscopically, and (e) a mixture of 1:1:1-trifluoroethane (0.039 g., 0.47 mmole) and hydrogen chloride (0.232 g., 6.35 mmole). The products were thus $CF_3\cdot CHCl\cdot CHCl\cdot CF_3$ 31%, $CF_3\cdot CH_3$ 31%, $CF_3\cdot CH_2\cdot CH_2\cdot CF_3$ 3%, and HCl 33%.

Photochemical Oxidation of Trifluoroacetyl Chloride.—In a typical experiment, trifluoroacetyl chloride (0.170 g., 1.28 mmole) and oxygen (0.312 g., 9.75 mmole) were exposed in a

TABLE 2.

Com- pound (mmole)	O ₂ (mmole)	Other reactants (mmole)	Vol. of tube (ml.)	Initial press. (atm.)	Irradiation time (hr.)	Oxid- ation (%)	Products * (mmole)
<i>Oxidation of CF₃·CHCl₂</i>							
1.26	13.9	None	260	1.5	5	99	{ CF ₃ ·CO ₂ H 0.193 CF ₃ ·COCl 0.730
3.31	15.0	,,	260	1.8	6.0	100	{ CF ₃ ·CO ₂ H 0.421 CF ₃ ·COCl 2.00
3.32	13.8	Cl ₂ 7.12	260	2.5	0.08	100	{ CF ₃ ·CO ₂ H 0.352 CF ₃ ·COCl 2.64
3.35	16.4	Cl ₂ 9.49	260	2.8	0.5	100	CF ₃ ·COCl 3.00
3.17	16.5	Cl ₂ 7.72	260	2.7	1.2	100	{ CF ₃ ·CO ₂ H 0.219 CF ₃ ·COCl 2.59
2.67	15.6	Br ₂ 9.41	300	2.4	113	79	CF ₃ ·CO ₂ H 0.044
6.74	16.8	H ₂ O 3.0 ml.	360	1.7	72	100	CF ₃ ·CO ₂ H 4.73
6.54	16.6	Cl ₂ 1.34, H ₂ O 3.0 ml.	360	1.8	72	100	CF ₃ ·CO ₂ H 4.78
<i>Oxidation of CF₃·CH₂Cl</i>							
6.77	15.1	None	320	1.8	31	40	CF ₃ ·CO ₂ H 1.44
6.88	16.0	Cl ₂ 8.23	360	2.2	0.4	49	{ CF ₃ ·CO ₂ H 0.53 CF ₃ ·COCl 2.05
6.99	17.4	Br ₂ 3.81	360	2.0	116	18	{ CF ₃ ·CO ₂ H 0 CF ₃ ·COCl 0
8.35	17.0	H ₂ O 5.0 ml.	360	1.8	174	76	CF ₃ ·CO ₂ H 2.95
8.76	16.4	Cl ₂ 10.1, H ₂ O 3.0 ml.	360	1.9	72	100	CF ₃ ·CO ₂ H 6.56

* CO₂, SiF₄, and HCl produced in every experiment.

sealed 260-ml. silica tube (initial pressure *ca.* 1.1 atm.) to ultraviolet light for 2.0 hr. The volatile products (after removal of chlorine with mercury) were fractionally distilled *in vacuo*, to give unchanged trifluoroacetyl chloride (0.138 g., 1.03 mmole, 81%) and a mixture (0.032 g., 0.53 mmole) of carbon dioxide and silicon tetrafluoride.

Photolysis of Trifluoroacetaldehyde.—(i) *Alone.* Trifluoroacetaldehyde (0.254 g., 2.59 mmole) was irradiated in a sealed 200 ml. silica tube with ultraviolet light for 4 hr. The non-condensable gas was pumped off, and the volatile products were distilled *in vacuo*, to give hexafluoroethane (0.097 g., 0.71 mmole, 55%), fluoroform (0.035 g., 0.50 mmole, 19%), and traces of silicon tetrafluoride and carbonyl fluoride. A solid (*ca.* 0.05 g.) remained in the reaction tube.

(ii) *In the presence of chlorine.* Trifluoroacetaldehyde (0.250 g., 2.55 mmole) and chlorine (0.122 g., 1.71 mmole) in a 260 ml. silica tube, exposed to ultraviolet light for 4 hrs., gave (a) a mixture of chlorotrifluoromethane (0.143 g., 1.37 mmole), fluoroform (0.051 g., 0.73 mmole), and hydrogen chloride (0.040 g., 1.1 mmole), and (b) a fraction (0.050 g.) containing trifluoroacetyl chloride and an unidentified compound containing a carbonyl group.

Photolysis of 2:2:2-Trifluoroethanol.—(i) *Alone.* 2:2:2-Trifluoroethanol (0.860 g.,

8.60 mmole) was recovered unchanged after exposure to ultraviolet light for 7 days in a 150 ml. silica tube.

(ii) *In the presence of chlorine.* 2 : 2 : 2-Trifluoroethanol (1.100 g., 1.0 mmole) and chlorine (0.829 g., 11.6 mmole) in a 320 ml. silica tube, irradiated for 6 hr., gave 2 : 2 : 2-trifluoroethyl trifluoroacetate (0.650 g., 3.31 mmole, 66%), hydrogen chloride (0.546 g., 15.0 mmole), fluoroform (0.070 g., 1.0 mmole), and chlorotrifluoromethane (0.146 g., 1.40 mmole). A residual high-boiling liquid (*ca.* 0.2 g.) was not investigated.

2 : 2 : 2-Trifluoroethyl Trifluoroacetate.—Trifluoroacetic acid (5.7 g., 5.0 mmole), 2 : 2 : 2-trifluoroethanol (5.0 g., 5.0 mmole), and concentrated sulphuric acid (0.2 ml.) were heated under reflux for 3 hr. Distillation gave 2 : 2 : 2-trifluoroethyl trifluoroacetate (7.2 g., 3.69 mmole, 74%), b. p. 56° (Found: C, 24.4; H, 1.1. Calc. for $C_4H_2O_2F_6$: C, 24.5; H, 0.5%). Husted and Ahlbrecht⁷ report b. p. 55–56°/741 mm.

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⁷ Husted and Ahlbrecht, *J. Amer. Chem. Soc.*, 1952, **74**, 5422.
