[CONTRIBUTION FROM BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Mechanism of Fluorination. I. Fluorine Sensitized Oxidation of Trichloro- and Tetrachloroethylene

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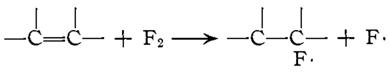
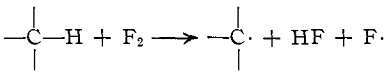
Fluorine is shown to promote the reaction of oxygen with trichloroethylene and tetrachloroethylene at low temperatures to produce acid halides. The products obtained correspond to those produced by photochemical chlorine sensitized oxidation but with initiation by fluorine rather than by chlorine atoms. These results furnish convincing evidence that the free radical chain initiation step consists of reaction between fluorine and the olefinic linkage to yield a free radical containing fluorine and a fluorine atom. This type of reaction with fluorine, in which the carbon–carbon double bond functions as a one electron reducing agent, provides a new method for the production of free radicals by reaction between stable molecules.

It has been recognized for some time that organic fluorination reactions with elemental fluorine exhibit the general characteristics of free radical processes.[1] The frequently explosive nature of reactions and the type and complexity of reaction products obtained under non-polar conditions all support this view. Detailed free radical mechanisms have been postulated by Bigelow and his co-workers in an important series of papers on the vapor phase fluorination of organic compounds to explain the formation of the observed products.[2] Initiation was assumed to occur by thermal or catalytic dissociation of fluorine into atoms. On the other hand, for reactions at low to moderate temperatures, we have accumulated evidence pointing to free radical initiation by reactions between fluorine molecules and organic systems as shown below.[3,4] As general processes, these reactions appear to be unique with fluorine.


$$-\overset{|}{C}=\overset{|}{C}- + F_2 \longrightarrow -\overset{|}{C}-\underset{F\cdot}{\overset{|}{C}}- + F\cdot \qquad (1)$$


$$-\underset{|}{\overset{|}{C}}-H + F_2 \longrightarrow -\underset{|}{\overset{|}{C}}\cdot + HF + F\cdot \qquad (2)$$

The possible occurrence of the above reactions in the case of fluorine but not for the other halogens is consistent with the relatively low fluorine–fluorine bond energy and the high carbon–fluorine and hydrogen–fluorine bond energies. The recently determined "low" dissociation energy for fluorine of 37.7 ± 0.4 kcal.[5] as compared with the older value of 63.5 kcal.[6] not only makes reactions (1) and (2) appear more probable but also suggest that thermal dissociation can become important at a lower temperature than was previously considered possible.[7] Table I summarizes algebraic sums for reactions (1) and (2) for the different halogens utilizing average heats of formation for the bonds involved given by Sidgwick[9] except for the fluorine–fluorine value which was determined by Doescher.[5]

TABLE I

Halogen	Reaction (1), kcal.	Reaction (2), kcal.
F	−1.2	4.1
Cl	22.5	53.9
Br	23.3	67.6
I	21.9	63.6

A large and favorable energy difference between the reactions of fluorine and chlorine is indicated for these free radical type reactions in which the fluorine molecule is split symmetrically. The ease with which fluorine attacks olefins even at Dry Ice temperature is consistent with an extremely low activation energy for 1.

The present paper presents the results of an experimental test of the free radical nature of the reactions of elemental fluorine with olefins and of the occurrence of reaction 1. This consisted of determining the effect of added oxygen upon the fluorination of tetrachloroethylene and trichloroethylene at 0°. The reactions of these compounds with elementary fluorine at 0° had previously been investigated and shown to yield principally addition and dimer products.[1] They had also been found to undergo oxidation with chlorine–oxygen mixtures which was initiated by chlorine atoms produced photochemically.[10-12] On the basis of this previous work it was expected that if free radicals were produced by reaction of molecular fluorine with the above olefins, in the presence of oxygen, fluorination would be inhibited and oxidation would be initiated with the formation of acid halides as major products by free radical mechanisms analogous to those of the chlorine sensitized reactions.

Dickinson and Leermakers[10] working in carbon tetrachloride solution at from 3 to 36° found that

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[1] W. T. Miller, Jr., THIS JOURNAL, **62**, 341 (1940).

[2] E. H. Hadley and L. A. Bigelow, *ibid.*, **62**, 3302 (1940), and subsequent papers; summarized by L. A. Bigelow, *Chem. Revs.*, **40**, 51 (1947).

[3] W. T. Miller, Jr., "Nat. Nuclear Energy Ser.," I, VII, Ed. by C. Slesser and S. R. Schram, McGraw-Hill Book Co., New York, N. Y., 1951, Chap. 32, p. 582. Orig. A.E.C. Report MDDC-1177, Aug. 1946.

[4] W. T. Miller, Jr., A. L. Dittman and S. D. Koch, Abstracts of 116th A.C.S. Meeting, p. 15K, Sept. 1949.

[5] Determined within the temperature range 486 to 842°. R. N. Doescher, *J. Chem. Phys.*, **20**, 330 (1952). Other recent values fall within the range of 36 ± 3 kcal. P. W. Gilles and J. L. Margrave, *ibid.*, **21**, 381 (1953).

[6] L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell Univ. Press, Ithaca, N. Y., 1944.

[7] In terms of usual reaction conditions relatively high temperatures are required to produce appreciable concentrations of fluorine atoms. At 25° the calculated equilibrium constant for the dissociation of fluorine, $F_2 \leftrightharpoons 2F\cdot$, is 2.9×10^{-21}; at 127°, 1.3×10^{-14}.[8]

[8] L. G. Cole, M. Farber and G. W. Elverum, Jr., *J. Chem. Phys.*, **20**, 586 (1952).

[9] N. V. Sidgwick, "Chemical Elements and Their Compounds," Oxford Univ. Press, London, 1950, p. xxxi.

[10] R. G. Dickinson and J. A. Leermakers, THIS JOURNAL, **54**, 3852 (1932).

[11] J. A. Leermakers and R. G. Dickinson, *ibid.*, **54**, 4648 (1932).

[12] K. L. Müller and H. J. Schumacher, *Z. physik. Chem.*, B**37**, 367 (1937).

in the presence of oxygen photochemical chlorination of tetrachloroethylene was inhibited and instead a chlorine sensitized oxidation occurred without appreciable net consumption of chlorine, leading to trichloroacetyl chloride and carbonyl chloride. Between one and two molecules of tetrachloroethylene were oxidized per einstein absorbed, a very low quantum yield by comparison with chlorination under similar conditions.[11] No dark reaction was observed. The same products were also obtained in the gas phase but with much longer reaction chains giving a quantum yield of about 300.[13] Müller and Schumacher[12] obtained similar results with trichloroethylene and chlorine–oxygen mixtures in the vapor phase at 95°. Approximately 80% dichloroacetyl chloride was formed along with carbonyl chloride, carbon dioxide and hydrogen chloride with a quantum yield of about 40.

Based on the work of the above authors and similar chlorine sensitized oxidations observed with chloroform[14] and with pentachloroethane[15] the mechanism of oxidation for the chloro olefins appears to be most satisfactorily represented by the following free radical chain mechanism.[16]

$$\mathrm{Cl_2} + h\nu \longrightarrow \mathrm{2Cl\cdot} \qquad (3)$$

$$\mathrm{Cl\cdot + Cl_2{=}Cl_2} \longrightarrow \mathrm{CCl_3CCl_2\cdot} \qquad (4)$$

$$\mathrm{CCl_3CCl_2\cdot + O_2} \longrightarrow \mathrm{CCl_3CCl_2COO\cdot} \qquad (5)$$

$$\mathrm{CCl_3CCl_2OO\cdot} - \begin{cases} \xrightarrow{a} \mathrm{CCl_3COCl + ClO\cdot} \\ \xrightarrow{b} \mathrm{2\,COCl_2 + Cl\cdot} \end{cases} \qquad (6)$$

$$\mathrm{CCl_2{=}CCl_2 + ClO\cdot} \longrightarrow \mathrm{CCl_3COCl + Cl\cdot} \qquad (7)$$

With trichloroethylene attack by chlorine atoms occurs at the CHCl= carbon and reaction 6b produces phosgene, hydrogen chloride and carbon monoxide (which is further oxidized to carbon dioxide) as well as a chlorine atom.

In the present work, when elementary fluorine was added to excess oxygen and the mixture passed into tetrachloroethylene at 0° in the dark the formation of the previously observed direct fluorination products was almost completely inhibited. Oxidation products were obtained corresponding to those expected on the basis of the above type mechanism, involving chain propagation reactions 7 and 6, but with initiation occurring according to reactions 8 and 9 shown below. Reaction 8 corresponds to reaction 1.

$$\mathrm{CCl_2{=}CCl_2 + F_2} \longrightarrow \mathrm{CCl_2FCCl_2\cdot + F\cdot} \qquad (8)$$

$$\mathrm{CCl_2{=}CCl_2 + F\cdot} \longrightarrow \mathrm{CCl_2FCCl_2\cdot} \qquad (9)$$

$$\mathrm{CCl_2FCCl_2\cdot + O_2} \longrightarrow \mathrm{CCl_2FCCl_2O_2\cdot} \qquad (10)$$

$$\mathrm{CCl_2FCCl_2O_2\cdot} \longrightarrow \mathrm{CCl_2FCOCl + ClO\cdot} \qquad (11)$$

For separate experiments, utilizing oxygen–fluorine ratios of 2.8 and 4.7 and tetrachloroethylene, the products were dichlorofluoroacetyl chloride, trichloroacetyl chloride and phosgene in the proportions 1.0:4.5:1.5 and 1.0:3.0:0.40, and in amounts accounting for 73 and 71% of the unrecovered tetrachloroethylene without correction for handling losses. Chlorine and fluorine were present in the exit gases throughout and with increased oxygen flow less fluorine was absorbed. Hexachloroethane was isolated in appreciable amounts, 3 and 6%, and the presence of the normal fluorination products, *sym*-difluorotetrachloroethane and pentachlorofluoroethane in very small amounts was shown. Since in the case of the photochemical chlorine sensitized oxidations the concentration of chlorine remained essentially constant, it was expected that with fluorine initiation chlorine would be produced, presumably by the termination reaction involving combination of chlorine atoms. It should be pointed out, however, that the observed hexachloroethane may have been partly or largely formed from dissolved chlorine after removal of oxygen in working up the products. The low values observed for the ratios of trichloroacetyl chloride to dichlorofluoroacetyl chloride, corresponding to the initiation step, were consistent with the low quantum yields, corresponding to very short reaction chains, found by Dickinson and Leermakers for the photochemical chlorine sensitized oxidation of tetrachloroethylene in carbon tetrachloride solution. The observed short reaction chains are significant with regard to the question of initiation by thermally produced fluorine atoms. Since the dissociation of fluorine requires a minimum activation energy of 37 kcal., corresponding to the bond energy, too few fluorine atoms can be produced at 0 or −15° to account for appreciable rates of reaction by short chains.

The reaction of chlorotrifluoroethylene with a dilute fluorine–oxygen mixture in the vapor phase was shown to yield carbonyl fluoride, carbonyl chlorofluoride, trifluoroacetyl fluoride, and, in largest amount, chlorodifluoroacetyl fluoride. These products would be expected on the basis of the fluorine sensitized oxidation mechanism presented above for tetrachloroethylene with preferential fission of carbon–chlorine bonds to produce chlorine atoms as chain carriers.[17]

Trichloroethylene was also found to undergo sensitized oxidation at 0° with inhibition of fluorination to yield preponderantly dichloroacetyl chloride and carbonyl chloride as in the case of photochemical chlorine sensitized oxidation. With oxygen fluorine ratios of 3.8 and 12.5, yields of 12 and 9% carbonyl chloride and 56 and 52% dichloroacetyl chloride were found. Chlorofluoroacetyl chloride corresponding to the initiation step was shown to be formed but the amount could not be determined because of the presence of other closely boiling acyl halides. However, longer oxidation chains were indicated in comparison with the tetrachloroethylene reactions by higher conversions to oxidized products. Chlorine was also liberated and pentachloroethane was isolated. Oxalyl chloride was identified as the anilide and traces of acid fluorides were formed, presumably by reaction of hydrogen fluoride with acid chlorides. From the reaction of excess trichloroethylene with oxygen and fluorine,

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(13) R. G. Dickinson and J. L. Carrico, THIS JOURNAL, **56**, 1473 (1934).

(14) A. T. Chapman, *ibid.*, **57**, 416 (1935).

(15) H. J. Schumacher and J. W. Thürauf, *Z. physik. Chem.*, **A189**, 183 (1941).

(16) For additional references and discussion of mechanism see E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1954.

(17) Experimental work by S. K. Reed and G. Gavlin. We are also indebted to H. F. Furber, Jr., for performing a preliminary experiment on the fluorine sensitized oxidation of tetrachloroethylene

in addition to the above products, a dimer of trichloroethylene, hexachlorobutene, corresponding to 4.8% of the unrecovered trichloroethylene, was isolated as well as some higher molecular weight fluorine-free neutral material. The same dimer had previously been obtained from the reaction of fluorine alone with undiluted trichloroethylene at 0° and in both instances was indicated by freezing point to be largely a single isomer. Its physical properties and resistance to chlorination appear to differentiate it from 1,1,2,3,4,4-hexachloro-2-butene[18] and from the dimer of trichloroethylene previously prepared with benzoyl peroxide and irradiation and characterized by Henne and Ruh[19] as a mixture of isomers with the two hydrogens in the 1,3-relation.

In the absence of structure evidence, it may be postulated that the formation of the butene isolated was due to attack of $CHCl_2CCl_2\cdot$ radicals on trichloroethylene followed by chlorine transfer[20,21] as an alternate path to oxidation. However, a mechanism involving the intermediate formation of trichlorovinyl radicals by reaction of trichloroethylene with fluorine, or more probably fluorine atoms, is supported by a number of experimental observations.

$$CHCl{=}CCl_2 + F\cdot \longrightarrow CCl_2{=}CCl\cdot + HF \quad (12)$$

$$CCl_2{=}CCl\cdot + CHCl{=}CCl_2 \longrightarrow CCl_2{=}CClCHClCCl_2\cdot \quad (13)$$

$$CCl_2{=}CClCHClCCl_2\cdot + CHCl{=}CCl_2 \longrightarrow CCl_2{=}CClCHClCHCl_2 + CCl_2{=}CCl\cdot \quad (14)$$

It is considered that the formation of oxalyl chloride can be best explained by the intermediate formation of trichlorovinyl radicals. A mechanism involving formation of oxalyl chloride from a two carbon unit

$$CCl_2{=}CCl\cdot + O_2 \longrightarrow CCl_2{=}CClO_2\cdot \quad (15)$$

$$CCl_2{=}CClO_2\cdot \longrightarrow COClCOCl + Cl\cdot \quad (16)$$

appears preferable to a bimolecular process such as the combination of two $COCl\cdot$ radicals, necessarily arising from two trichloroethylene molecules, under the reaction conditions utilized. The isolation of trichlorofluoroethylene from the fluorination of trichloroethylene[1] also furnishes evidence for the intermediate formation of trichlorovinyl radicals. The formation of a dimer of trichloroethylene by any free radical mechanism in the presence of excess oxygen is rather surprising but may be explained by local depletion of oxygen in the liquid phase.

It is considered that the above results confirm the free radical nature of the reactions of fluorine with olefins at low temperatures, and furnish satisfactory evidence that the initiation step is reaction 1. The occurrence of reaction 1 may be attributed to the high order of electrophilic reactivity shown by fluorine and a favorable energy relationship for the one-electron type process. The "simultaneous" addition of a fluorine molecule to the double bond appears to be prevented by the highly exothermic nature of such a process. As far as the authors are aware, no other examples of reactions between stable neutral molecules at low temperatures to yield highly reactive free radicals have been shown to occur.

In the light of free radical initiation mechanisms, the deleterious effect of oxygen upon the reactions of fluorine with organic compounds,[1] even at low temperatures, is readily understood.

Experimental Results

General Procedure.—Reactions were carried out in metal apparatus, of a type previously described.[22] Fluorine was prepared by electrolysis of carefully dried KF·HF in a small nickel cell[22] and metered by measurement of electrolysis current utilizing current efficiency data. Commercial oxygen was added, with a calibrated orifice type flow meter for measurement, and mixed with the fluorine at a T-connection in 1/4" copper tubing before passing into the reaction vessel. Freshly redistilled samples of trichloroethylene and tetrachloroethylene were utilized.

In operation, the reaction vessel was charged with the liquid chloroethylene reactant, tightly closed, placed in the cooling bath, and the outlet connected to a flow meter and two Dry Ice traps in series. The stirrer was started and oxygen passed into the system, at the rate to be utilized during the run, until the air had been displaced and the apparatus reached bath temperature. The flow of fluorine was then started and maintained constant until the desired amount had been added. During the reactions the outlet gases turned moist starch–iodide paper blue and aqueous extracts gave qualitative tests for chloride and fluoride ions. Reaction of the chloroethylenes with oxygen alone was shown to be negligible under the conditions utilized.

The reaction product boiling above room temperature was separated into fractions, in the case of major products, usually indicated by boiling point as containing only one acid halide, utilizing a total reflux partial take-off distillation column with a 50 × 1.5 cm. section packed with 1/4" glass helices. Derivatives, ordinarily anilides, were prepared from the resulting fractions and examined for purity and identity. The anilides derived from the di- and trihaloacetyl halides were especially useful because advantage could be taken of their alkali solubility[23] for isolation and purification with little loss. The total amounts of acid halide major products were then estimated by titration of aliquots of appropriate fractions.

For titration, weight aliquots of about 1 g. were stirred with water in glass stoppered flasks and titrated with standard alkali. Utilizing known mixtures of trichloroacetyl chloride and carbon tetrachloride it was found that at least 99.7% of the trichloroacetyl chloride could be accounted for by titration. This procedure permitted the determination of the acid halide content of intermediate fractions and mixtures which could not be satisfactorily separated by distillation such as those containing trichloroacetyl chloride and tetrachloroethylene.

Phosgene and oxalyl chloride were determined by distillation of appropriate fractions into a solution of aniline in benzene and isolation of the resulting sparingly soluble anilides.

Tetrachloroethylene I.—The olefin, 3.67 moles, 610 g., was treated with oxygen, 1.40 moles, and fluorine 0.494 mole, during 5 hours and 45 minutes with ice-bath cooling to yield: (1) 4 g. of Dry Ice trap condensate, and (2) 639 g. of liquid product poured from the reaction vessel. Reaction occurred quite smoothly although it appeared that insufficient oxygen was added to maintain an excess since suction was intermittently observed at the outlet.

Distillation of product (2) yielded the following fractions: (3) b.p. to 35°, collected in a stirred solution of excess aniline in benzene; (4) 42.7 g., b.p. 67–74°; (5) 33.2 g., b.p. 74–111°; (6) 239.0 g., b.p. 111–119.2°; (7) 171.9 g., b.p. 119.2–120.7°; (8) 24 g., b.p. 120.7–160°. Simple distillation of the residue yielded: (9) 21 g. solid, subl. at 35 mm. with heating bath at 140°; (10) 7.8 g., b.p. 131–147° at 15 mm., partly crys. at room temp.; (11) 7.8 g. residue. Re-

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(18) E. Muller and F. Huther, *Ber.*, **64**, 589 (1931).

(19) A. L. Henne and R. P. Ruh, THIS JOURNAL, **69**, 279 (1947).

(20) K. E. Wilzbach, F. R. Mayo and R. VanMeter, *ibid.*, **70**, 4070 (1948).

(21) C. E. Frank and A. U. Blackham, *ibid.*, **72**, 3283 (1950).

(22) Ref. 3, p. 574.

(23) G. M. Weimann, "The Use of Trichloroacetyl Chloride as a Reagent for the Separation and Characterization of Amines," M.S. Thesis, Cornell University, 1943.

distillation of fractions (4) and (5) yielded: (12) 6.3 g., b.p. 68–70.5°; (13) 29.9 g., b.p. 70.5–71.5°; (14) 14.9 g., b.p. 71.5–78°; (15) 7.6 g., b.p. 78–89°; (16) 5.3 g., b.p. 89–92°; (17) 2.9 g., b.p. 92–110°; (18) 7.1 g. residue.

Carbonyl Chloride.—By reaction of fractions (1) and (3) with aniline in benzene *sym*-diphenylurea was precipitated, 90.2 g., m.p. 235.5–237.5°, after washing with dilute hydrochloric acid and drying, corresponding to 0.213 mole of tetrachloroethylene; previously reported for *sym*-diphenylurea, m.p. 238–239°.[24]

Dichlorofluoroacetyl Fluoride and Chloride.—Extraction of the benzene solution from the diphenylurea preparation utilizing fractions (1) and (3) with 5% sodium hydroxide yielded 6.1 g. of dichlorofluoroacetanilide, m.p. 72.0–73.5°; previously reported for dichlorofluoroacetyl fluoride: b.p. 31°.[25]

Portions of fractions (12), (13), (14) and (15) were reacted with aniline in chloroform solution in order to confirm the identity of the acid halide present. After extraction with alkali and crystallization from 50% aqueous alcohol the resulting anilides melted at: (12) 74.5–75.0°; (13) 74.2–75.0°; (14) 74.5–75.2°; (15) 70.5–71.8°. A corresponding fraction from another similar experiment was treated with ammonia to form dichlorofluoroacetamide, m.p. 128.5–129.0°. Previously reported for dichlorofluoroacetyl chloride, b.p. 75°; for dichlorofluoroacetamide, m.p. 126.5°.[25] Titration of weight aliquots of the same samples yielded results corresponding to the presence of the following amounts of dichlorofluoroacetyl chloride: (12) 4.0 g.; (13) 28.0 g.; (14) 11.3 g.; (15) 3.2 g.; a total of 46.5 g., 0.281 mole.

***sym*-Tetrachlorodifluoroethane.**—Fractions (15), (16) and (17), after removal of samples for titration were combined, washed to remove acid halide, dried over phosphorus pentoxide, and distilled to yield: 4 g., b.p. 90.8–92.2°, m.p. 17.0–18.5°, and 1.4 g. residue m.p. 5–12°; previously reported for *sym*-tetrachlorodifluoroethane: b.p. 92.8°; m.p. 24.65°.[26]

Tetrachloroethylene.—Calculated by difference from the trichloroacetyl chloride content given above, fractions (18), (6), (7), and (8) contained 214.6 g., 1.29 moles, of unreacted tetrachloroethylene. As an additional check on the titration analysis 38.6 g. of fraction (6) was washed with alkali to remove the acid halide, dried and distilled to yield 14.6 g. of tetrachloroethylene, b.p. 118.5–120.5°. This amount corresponded to 38% of fraction (6) as compared with 43% determined by titration.

No pentachlorofluoroethane could be isolated from fraction (8). However, its presence in small amounts was considered probable.

Trichloroacetyl Chloride.—A portion of fraction (6) was treated with aniline in chloroform solution as described above to yield an anilide m.p. 93.4–94.2°. Fraction (18) similarly yielded an anilide of m.p. 93.5–94.0°. Previously reported: trichloroacetyl chloride, b.p. 117–118°[27]; trichloroacetanilide, m.p. 94–95°.[28] Titration results for fractions (18), (6), (7), and (8) corresponded to the following amounts of trichloroacetyl chloride: (18) 4.3 g.; (6) 136.3 g., (7) 79.6 g.; (8) 7.2 g.; a total of 227.4 g., 1.25 moles.

Hexachloroethane.—Recrystallization of fraction (9) from methyl alcohol yielded 18 g., 0.076 mole, m.p. in a sealed tube 185–187°; previously reported: triple point 186.6°.[26]

Tetrachloroethylene II.—With the reaction vessel immersed in a water–alcohol bath maintained at −15 ± 3° by adding Dry Ice, tetrachloroethylene, 2.96 moles, 491 g., was treated with oxygen, 2.3 moles, and fluorine 0.486 mole during 5 hours and 45 minutes. The oxygen flow was sufficient to provide an excess. The trap condensate, about 1.5 ml., and the liquid product poured from the reaction vessel, 501.5 g., were combined for distillation. A yellow color apparently due to free chlorine disappeared on warming to reflux. Separation of the reaction product as described above gave the following results.

Carbonyl Chloride.—*sym*-Diphenylurea, 33.4 g., corresponding to 0.079 mole of tetrachloroethylene was obtained.

Dichlorofluoroacetyl Chloride.—A total of 28.6 g., 0.173 mole, was indicated by titration.

***sym*-Tetrachlorodifluoroethane.**—A 4.4-g. sample was isolated, b.p. 89.0–93.5°, m.p. 18.5–20.0°.

Trichloroacetyl Chloride.—A total of 95.1 g., 0.523 mole, was found by titration.

Tetrachloroethylene.—A total of 291.6 g., 1.76 moles, was determined by difference utilizing titration values for trichloroacetyl chloride.

Pentachlorofluoroethane.—Approximately 0.02 g., m.p. 100–102° in a sealed tube, was isolated; previously reported m.p. 101.3°.[29]

Hexachloroethane.—Recrystallization of 18.9 g. of sublimed crystalline product from alcohol gave material, m.p. 185.5–186.0° in a sealed tube.

Trichloroethylene I.—Four and four-tenths moles of trichloroethylene, 578 g., was treated with 3.5 moles of oxygen and 0.930 mole fluorine during five hours with ice-bath cooling. The reaction appeared to be quite vigorous as shown by fluctuation in gas flow and consumption of ice in the cooling bath.

The Dry Ice trap condensate, (1) 31.3 g., and liquid product poured from the reaction vessel, (2) 586.8 g., possessed sharp acid odors and fumed in moist air. The portion of the Dry Ice trap condensate volatile at room temperature, (3) 12.0 g., was distilled into a solution of aniline in benzene. The residue, (4) 19.3 g., was combined with (2) and distilled to yield: (5) 45.3 g. of Dry Ice trap condensate, b.p. below room temperature; (6) 18.4 g., b.p. 62–74°; (7) 10.5 g., b.p. 74–78°; (8) 43.9 g., b.p. 78–89°; (9) 73.9 g., b.p. 89–104°; (10) 185.4 g., b.p. 104–106°; (11) 116.4 g., b.p. 106°; (12) 42.3 g., b.p. 106–106.2°; (13) 5.2 g., b.p. 106–107°; (14) 7.2 g., b.p. to 45° at 15 mm.; (15) 14.5 g., b.p. 45–51° at 15 mm.; (16) 9.4 g., b.p. 55–80° at 5 mm.; (17) 7.8 g. residue. Redistillation of fractions (6), (7), (8) and (9) with progressive addition yielded: (18) 6.0 g., b.p. 61–66°; (19) 7.5 g., b.p. 66–68°; (20) 5.1 g., b.p. 68–74°; (21) 5.4 g., b.p. 74–84°; (22) 31.7 g., b.p. 84–87°; (23) 20.7 g., b.p. 82–88°; (24) 6.0 g., b.p. 88–90°; (25) 17.9 g., b.p. 90–103°; (26) 28.7 g., b.p. 103–106°; (27) 6 g. residue.

Carbonyl Chloride.—Fraction 3 yielded 25.7 g. of diphenylurea corresponding to 12.9 g. of carbonyl chloride. Fraction (5) was distilled at room temperature into a standard solution of carbonate-free sodium hydroxide cooled in an ice-bath. A 3.8-g. residue remained, about two-thirds of which dissolved in ice-water with gas evolution. The insoluble residue, *ca.* 1 g., decolorized acetone permanganate and resembled trichloroethylene in odor. Aliquots of the standard sodium hydroxide solution utilized to absorb (5) were analyzed for strong acid produced and for carbonate by differential titration to phenolphthalein and methyl orange end-points after addition of barium chloride, and for chloride ion gravimetrically as silver chloride. The carbonyl chloride content of the volatile portion of (5) was found to be: 98.3% on the basis of the acid produced calculated as HCl; 95.6% by chloride analysis; and 88% by carbonate content. Little if any hydrogen fluoride was indicated. Calculated on the basis of the chloride analysis the carbonyl chloride accounted for was 39.6 g., with fraction (3) a total of 52.5 g., 0.530 mole.

Oxalyl Chloride, Dichloroacetyl Fluoride and Chlorofluoroacetyl Chloride.—Fractions (18), (19) and (20) were redistilled to yield a number of small fractions of gradually increasing boiling point from 62 to 71.5°. Anilides and *o*-toluides were then prepared and qualitative tests made for the halogen eliminated in each case. Although impure products were obtained initially the presence of oxalyl chloride and dichloroacetyl fluoride was demonstrated and chlorofluoroacetyl chloride strongly indicated.

Oxalyl Chloride.—Found: anilide, m.p. 247–249°, *o*-toluidide, m.p. 210–212°. Previously reported for oxalyl chloride, b.p. 62.1–62.3°[30]; for oxanilide, m.p. 254°[31]; ox-*o*-toluidide, m.p. 210–212°.[32]

Dichloroacetyl Fluoride.—Found: anilide, m.p. 117–117.8°; *o*-toluidide, m.p. 132.6–133.8°. Previously re-

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[25] F. Swartz, *Bull. soc. chim. France*, [3] **13**, 992 (1895).

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ported for dichloroacetyl fluoride, b.p. 71–72°[33]; for dichloroacetanilide, m.p. 118°[34]; dichloroacet-*o*-toluidide, m.p. 134°.[35] Hydrolysis yielded HF.

The more soluble derivatives of chlorofluoroacetyl chloride were not obtained pure. However, mixed melting points with authentic derivatives gave results consistent with the presence of this material.

Dichloroacetyl Chloride.—Anilides were prepared from the following fractions with the melting points given after recrystallization: (11) 117.5–118.1°; (13) 117.0–118.0°; (14) 116.5–118.0°; (16) 116.5–117.5°. In all cases the yields and purity of products obtained indicated the absence of appreciable amounts of other acid halides. Titration values were obtained corresponding to the following amounts of dichloroacetyl chloride: (9) 35.7 g.; (10) 167.0 g.; (11) 113.2 g.; (12) 40.8 g.; (13) 5.4 g.; (14) 3.9 g.; for a total of 366.0 g., 2.48 moles.

Pentachloroethane.—The inert portions of fractions (14) and (15), a total of 17.1 g., was indicated as largely pentachloroethane by boiling point. The portion of fraction (15) remaining after titration was washed with water, dried and distilled to yield: 1.4 g., b.p. 158.5–160.0°; 1.6 g., b.p. 160.0–160.5°; 5.0 g., b.p. 160.5° at 735 mm., cor. b.p. 161.5°; 2.9 g. residue; previously reported for pentachloroethane: b.p. 162°.[28]

Trichloroethylene II.—A second reaction was carried out with 8.79 moles, 1155 g., of trichloroethylene, 600 moles of oxygen and 0.48 moles of fluorine during ten hours with ice-bath cooling. Most of the oxygen was consumed and the reaction proceeded very smoothly.

The products of the reaction were Dry Ice trap condensate, (1) 43.0 g., and liquid product poured from the reaction vessel, (2) 1157 g. On warming (1) to room temperature, (3) 11.8 g., was distilled leaving a residue, (4), which was combined with (2) for distillation.

Distillation with a low temperature column yielded: (5) 50.9 g., b.p. 9–20°, largely 9°. A sample of 131 g. was removed and the residue distilled utilizing the standard column to yield: (6) 56.7 g., b.p. 64–79°; (7) 17.7 g., b.p. 79–82°; (8) 49.3 g., b.p. 82–85.5°; (9) 33.5 g., b.p. 85.5–86.5°; (10) 110.2 g., b.p. 86.5–88°; (11) 351.8 g., b.p. 88–105°; (12) 140.6 g., b.p. 105–106.5°; (13) 94.6 g., b.p. 106.5–107.0°; (14) 30.7 g., b.p. 45–55° at 15 mm.; (15) 80.6 g., b.p. 50–88° at 5 mm.; (16) 20.8 g. residue.

Carbonyl Chloride.—Fraction (5) which distilled principally at 9° was considered as carbonyl chloride, 0.515 mole. Fraction (3), presumed to be largely carbonyl chloride, was lost.

Oxalyl Chloride and Chlorofluoroacetyl Chloride.—The reactive halides in fractions (6), (7) and (8) were indicated as oxalyl chloride and chlorofluoroacetyl chloride together with small amounts of dichloroacetyl fluoride and dichloroacetyl chloride. A positive qualitative test for fluoride ion was obtained on a water extract of (6) and negative tests on (7) and (8). Chloride was present in all cases.

Treatment of fraction (6) with an ether solution of aniline yielded oxanilide, corresponding to 4 g. of oxalyl chloride, m.p. 248–250° after recrystallization, and an ether-soluble anilide fraction, m.p. 70–75° after washing and drying. A number of recrystallizations from petroleum ether, b.p. 60–70°, yielded chlorofluoroacetanilide, m.p. 84–85°. Calcd. for C_8H_7ClFNO: Cl, 18.9. Found: Cl, 18.4. Previously reported for chlorofluoroacetyl chloride, b.p. 69.5°.[36]

Reaction of a portion of (8) with aniline in petroleum ether yielded an anilide product, m.p. 70–80°, which, after extraction with petroleum ether and seven recrystallizations, yielded dichloroacetanilide, m.p. 117–118.5°. Evaporation of the petroleum ether extract yielded a crystalline anilide fraction, m.p. 70–75°, which contained fluorine.

Titration of aliquots of fractions (6), (7) and (8) required the following equivalents of sodium hydroxide per gram of sample: (6) 0.0072; (7) 0.0039; (8) 0.0024. Recovered inert products from the above fractions corresponded to 60, 80, and 75% respectively.

Trichloroethylene.—The inert portions of fractions (9) through (13) corresponded to 350.5 g., 2.67 moles, of trichloroethylene, or 3.02 moles corrected to original quantities of reactants.

Dichloroacetyl Chloride.—Titration values for fractions (9) through (15) corresponded to a total of 392.4 g., 2.66 moles, or 3.02 moles corrected to original quantities of reactants.

Pentachloroethane.—Fraction (14) contained 18.5 g. of an inert compound which was indicated by boiling point as largely pentachloroethane.

Hexachlorobutene.—Redistillation of a portion of fraction (15) yielded: (17) 10.4 g., b.p. 85–124.4° at 25 mm.; (18) 36.0 g., b.p. 124–125.6°, largely b.p. 125.4–125.6° at 25 mm. Fraction (18) contained chlorine but not fluorine. It reduced acetone permanganate, reacted with alcoholic silver nitrate, but did not add bromine in sunlight. Crystallization of a portion of (18) from petroleum ether, b.p. 30–60°, with Dry Ice cooling yielded material m.p. 11.0°, cooling curve, $n^{20}\text{D}$ 1.5463. Previously reported for hexachlorobutene formed during fluorination of trichloroethylene[2]: m.p. 9.5–11.0°; b.p. 125.5 at 25 mm.; $n^{20}\text{D}$ 1.5442.

Neutralization of fraction (15) required 0.06 equivalent of base.

High Boiling Residue.—The residue from the original distillation, fraction (16), was incompletely soluble in methyl alcohol. Treatment of the insoluble fraction with charcoal in ether and partial evaporation yielded crystalline material (19), m.p. 208–209.5° with decomposition. Fraction (19) contained chlorine but not fluorine and was saturated to cold acetone permanganate.

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