sodium acetate by the same method gave a molar ratio of deuterated to non-deuterated acetate ion of $1/27$, corresponding well with the $1/28$ naturally occurring.

The total acetate ion present in the same reaction product as that used for hydrolysis with deuterium oxide was determined as follows:

A weighed sample (approx. 10 g.) of the reaction product was hydrolyzed and dissolved in 500 ml. of water. A 10-ml. aliquot was taken and added slowly to phosphoric acid heated to 140°, and the acetic acid formed was collected by steam distillation. Titration with sodium hydroxide gave the acetate ion content of the original sample.

The sodium α-sodioacetate content of the fusion product of sodium amide and sodium acetate was calculated from the total acetate ion content and the ratio of sodium α-sodioacetate to unreacted sodium acetate.

Thermal Stability.—The thermal stability of the α-sodio compound was determined by placing a small sample of the material in a 20-ml. test-tube through which a slow current of nitrogen was passed. The tube was placed in an oil-bath and the temperature gradually raised. Gas flow rates to and from the tube were observed, as well as the appearance of the material in the tube.

The material appeared stable until a temperature of 280° was reached. Decomposition became quite rapid at 295°.

Acknowledgment.—The authors are indebted to Dr. H. C. Brown of Purdue University for the suggestion of deuterium oxide as an analytical reagent for sodium α-sodioacetate.

BATON ROUGE 1, LA.

High Temperature, Vapor Phase Reactions of Some Fluorocarbon Derivatives with Oxidizing Agents

BY W. A. SEVERSON AND T. J. BRICE

Vapor phase, high temperature (450–650°) reactions of perfluoroalkanesulfonyl fluorides or fluorocarbon derivatives having the structures R_fCF_2X (X = H, Cl, Br, I) with oxidizing agents, principally NO_2, were carried out. NO_2 gave, in several cases, good yields of perfluoroalkanecarboxylic acid fluorides; the products usually were isolated as the acids because of hydrolysis and separation problems. R_fCF_2H compounds require a sensitizing agent in addition to NO_2 before the reaction to form the acid fluoride proceeds; chlorine and bromine were successfully used as sensitizing agents.

High temperature, vapor phase oxidation reactions of three classes of fluorocarbon derivatives were studied; these classes are (1) perfluoroalkanesulfonyl fluorides, (2) fluorocarbon derivatives containing $-CF_2H$ groups and (3) fluorocarbon halides. The principal reaction studied was that with NO_2, although other oxidizing agents were used with sulfonyl fluorides. The reaction of the $-CF_2H$ derivatives required chlorine or bromine as a sensitizing agent before reaction with NO_2 would proceed.

The perfluoroalkanesulfonyl fluorides used were prepared in good yield by electrochemical fluorination of hydrocarbon sulfonyl halides in liquid hydrogen fluoride as described by Brice and Trott.[1]

Perfluoroalkyl or chloroperfluoroalkyl compounds containing, as a potentially reactive group, a terminal $-CF_2H$ group, are well known to be rather inert chemically and have not been extensively studied. They can be converted to the corresponding $-CF_3$, $-CF_2Cl$ or $-CF_2Br$ derivatives by high temperature thermal halogenation or by ultraviolet light catalyzed halogenation. Thus C_3F_7H can be converted to C_3F_7Br or C_3F_7Cl.[2] No other well-controlled chemical reactions have been reported.

These $-CF_2H$-containing compounds can be obtained by several methods, as, for example, by electrochemical fluorination of organic compounds in anhydrous hydrogen fluoride[3] or by the pyrolysis of CF_2HCl.[4] The electrochemical process yields compounds such as $F(CF_2)_nCF_2H$, while the CF_2HCl pyrolysis yields $Cl(CF_2)_nCF_2H$. An alternate convenient method for preparing the compounds $F(CF_2)_nCF_2H$ is the pyrolysis in ethylene glycol of the salt $F(CF_2)_nCF_2CO_2Na$.[5] This method was used in the present work.

Fluorocarbon halides having the structure $F(CF_2)_nCF_2X$, where X = Br or I, were prepared by the reactions of silver salts of carboxylic acids with the proper halogen.

General Procedure.—The general procedure was to pass the fluorocarbon derivative and the oxidizing agent in the vapor phase through an unpacked tube. The tubes were made of resistant metals such as nickel, nickel alloys, stainless steel or platinum; nickel tubes usually were used. The products were collected in a series of cold traps, then separated and identified.

Reactions of Perfluoroalkanesulfonyl Fluorides with NO or NO_2.[6]—The reactions with NO_2 and NO were not first oxidation experiments performed, but proved to be the most interesting and are described more fully. The reaction threshold lies at about 450° with about a constant product distribution obtainable up to about 650°. After a series of preliminary experiments had established that a major product from $C_8F_{17}SO_2F$ and NO_2 was C_7-$F_{15}COF$ plus a little $C_6F_{13}COF$, the effects of certain variables on the yields of acid fluorides were studied in more detail. The variables studied were NO_2: $C_8F_{16}SO_2F$ mole ratio, temperature, contact time and reactor material.

At the optimum tube temperature of 550° and a contact time of 15 to 20 seconds, it was found that

(1) T. J. Brice and P. W. Trott, U. S. Patent 2,732,398, January 24, 1956; Abstracts of 126th A.C.S. Meeting, Sept., 1954, p. 42M; see also T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 173 (1956).

(2) T. J. Brice, W. H. Pearlson and J. H. Simons, THIS JOURNAL, **68**, 968 (1946).

(3) J. H. Simons, *et al.*, *Trans. Electrochem. Soc.*, **95**, 47 (1949).

(4) J. D. Park, A. F. Benning, F. B. Downing, J. F. Laucius and R. C. McHarness, *Ind. Eng. Chem.*, **39**, 359 (1947).
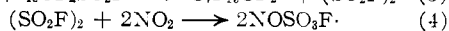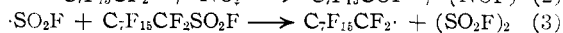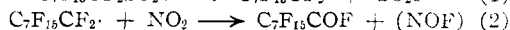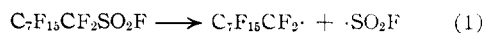
(5) I. Auerbach, F. H. Verhoek and A. L. Henne, THIS JOURNAL, **72**, 299 (1950).

(6) See W. A. Severson and T. J. Brice, U. S. Patent 2,765,326, October 2, 1956.

the yield of acid fluoride increased as the NO_2:$C_8F_{17}SO_2F$ mole ratio was increased from 1:1 to about 3.5:1 to 4:1 and then leveled off (at about 70% R_fCOF) with only a gradual decrease as the ratio is increased to about 7:1. When NO was used, a $NO:C_8F_{17}SO_2F$ mole ratio somewhat in excess of 1:1 gave better yields than lower mole ratios, although the NO reaction was not studied as thoroughly as the NO_2 reaction. NO_2 is the preferred reactant since it is inexpensive and readily available as compared to NO, and, in addition, gave generally better yields of R_fCOF. The material of construction of the tube did not appear to be important in these experiments as long as it was a resistant metal tube. The need to maintain NO_2:$R_fCF_2SO_2F$ ratios above 1:1 is at least partly due to the reaction of one mole of NO_2 with $\cdot SO_2F$ to form nitrosyl fluorosulfonate, $NOSO_3F$.

At the temperatures involved in these experiments, appreciable dissociation of the NO_2 to NO and O_2 must have occurred. However, the reaction with the nitrogen oxide (either NO_2 or NO) is evidently so much more rapid than the reaction with oxygen that little decomposition of the fluorocarbon occurs. Reaction with oxygen leads to complete destruction of the fluorocarbon chain; this reaction is discussed later.

The reaction is considered to be a free radical reaction with the initial step a dissociation of the fluorocarbon sulfonyl fluoride into $R_fCF_2\cdot$ and $\cdot SO_2F$ radicals. The $R_fCF_2\cdot$ radical then interacts with NO_2 (or perhaps NO) with the formation of R_fCOF. In the process, an oxygen atom is transferred to the fluorocarbon group. The formation of a cyclic intermediate which can rearrange to the final product is considered possible. The $\cdot SO_2F$ group is converted to nitrosyl fluorosulfonate, $NOSO_3F$, which was isolated in high yield. Possible reaction steps are summarized as follows, using $C_8F_{17}SO_2F$ as an example

$$C_7F_{15}CF_2SO_2F \longrightarrow C_7F_{15}CF_2\cdot + \cdot SO_2F \quad (1)$$
$$C_7F_{15}CF_2\cdot + NO_2 \longrightarrow C_7F_{15}COF + (NOF) \quad (2)$$
$$\cdot SO_2F + C_7F_{15}CF_2SO_2F \longrightarrow C_7F_{15}CF_2\cdot + (SO_2F)_2 \quad (3)$$
$$(SO_2F)_2 + 2NO_2 \longrightarrow 2NOSO_3F \cdot \quad (4)$$

The choice of reaction 1 as the initial step is based partly on the observation that the NO_2 reaction becomes detectable at essentially the same temperature as the thermal decomposition of $C_8F_{17}SO_2F$ and it may reasonably be expected to be initiated in the same manner. In the thermal decomposition, an initial C–S bond cleavage is very probable. An alternate to step 3 would be the reaction 3a
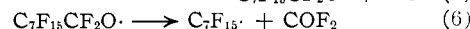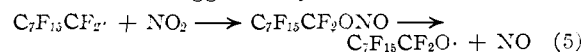
$$NOF + C_8F_{17}SO_2F \longrightarrow C_8F_{17}\cdot + NO + SO_2F_2\cdot \quad (3a)$$

However, SO_2F_2 which is stable and relatively inert, was not detected so this possibility was not considered further. Attempts to isolate and identify NOF were unsuccessful, so its presence was not established. However, NOF, although stable, is very reactive and easily could have been destroyed. The fate of the F atom removed from the CF_2 groups is thus not known with certainty. Steps 3 and 4 provide a route to the $NOSO_3F$ which is one of the actual products of the reaction found in high yield.

The mechanism by which reaction 2 occurs, and specifically how the oxygen atom becomes attached to carbon, is of interest. One possibility is that an NO_2 molecule attacks the fluorocarbon radical to form a C–O bond rather than a C–N bond and that rearrangement occurs through a cyclic intermediate to form the final products
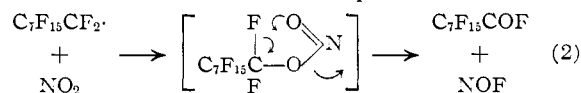
In reactions of NO_2 with $C_8F_{17}SO_2F$, it was observed that the $C_7F_{15}COF:C_6F_{13}COF$ ratio was usually about 3:1, although still higher ratios were also obtained. Loss of one carbon atom to form the next lower free radical can be accounted for by a mechanism suggested by Barr and Haszeldine.[7]

$$C_7F_{15}CF_2\cdot + NO_2 \longrightarrow C_7F_{15}CF_2ONO \longrightarrow$$
$$C_7F_{15}CF_2O\cdot + NO \quad (5)$$
$$C_7F_{15}CF_2O\cdot \longrightarrow C_7F_{15}\cdot + COF_2 \quad (6)$$

The $C_6F_{13}CF_2\cdot$ radical then reacts with NO_2 via step 2 to form $C_6F_{13}COF$.

Reaction of R_fSO_2F with Oxygen.—The fluorocarbon sulfonyl fluorides appear not to react with oxygen (or air) below a threshold temperature of about 450°. Above this temperature, reaction proceeds with great rapidity and violence, resulting in destruction of the fluorocarbon chain. The product is chiefly COF_2 with CO_2 and SOF_2 also identified. Intermediate oxidation products were not found.

Sulfur Trioxide.—Sulfur trioxide caused burning of the fluorocarbon chain of $C_8F_{17}SO_2F$ to COF_2 at 550°. At this temperature, SO_3 is appreciably dissociated to SO_2 and oxygen; it may be that the oxygen so formed is responsible for the reaction observed.
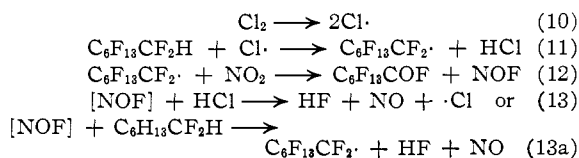
Sulfur Dioxide.—The products of the pyrolysis of $C_8F_{17}SO_2F$ in the presence of SO_2 were essentially the same as those obtained when SO_2 was absent.

Oxidation of Fluorocarbon Derivatives Containing-CF_2H Groups.—In the course of the study of the chemistry of these fluorocarbon derivatives, it was found that reaction of R_fCF_2H simultaneously with chlorine or bromine and NO_2 gave good yields of carboxylic acid fluorides having the structure R_fCOF. The product usually was isolated as the acid, although in one case the acid fluoride was recovered as such. In this reaction, it is necessary to have both NO_2 and the halogen present; in the absence of halogen, NO_2 does not react with R_fCF_2H at the temperatures used, and the halogen (X_2) alone simply yields the R_fCF_2X derivative. Compounds such as NO_2Cl and NO_2Br should also be useful since they decompose at the temperatures used to give Cl_2 or Br_2 and NO_2. The process consists simply of passing a gaseous mixture of the fluorinated starting compound, NO_2 and Cl_2 (or Br_2) through an empty tube (usually nickel) which is maintained at a temperature of the order of 500 to 650°. Contact times of the order of 10 to 15 seconds were used. The minimum amount of reactant theoretically needed is one mole of NO_2 per mole of fluorinated starting compound. However, it is best to use an excess of NO_2 and of chlo-

(7) D. A. Barr and R. N. Haszeldine, J. Chem. Soc., 3416 (1955).

rine (these are the preferred reactants). Mole ratios of about 1:3:2 for fluorinated starting compound, nitrogen dioxide and chlorine, respectively, gave good results.

The reaction is believed to proceed by a free radical chain mechanism; one possibility is illustrated for $C_7F_{15}H$.

$$Cl_2 \longrightarrow 2Cl\cdot \qquad (10)$$
$$C_6F_{13}CF_2H + Cl\cdot \longrightarrow C_6F_{13}CF_2\cdot + HCl \quad (11)$$
$$C_6F_{13}CF_2\cdot + NO_2 \longrightarrow C_6F_{13}COF + NOF \quad (12)$$
$$[NOF] + HCl \longrightarrow HF + NO + \cdot Cl \quad \text{or} \quad (13)$$
$$[NOF] + C_6H_{13}CF_2H \longrightarrow$$
$$\qquad\qquad C_6F_{13}CF_2\cdot + HF + NO \quad (13a)$$

The critical point in the reaction process occurs at step 12; in the absence of NO_2, an alternate step (12a) would occur to produce the fluorocarbon chloride

$$C_6F_{13}CF_2\cdot + Cl_2 \longrightarrow C_6F_{13}CF_2Cl + \cdot Cl \quad (12a)$$
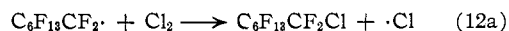
Evidently NO_2 has no favorable reaction path by which it can attack the fluorocarbon hydride, but once the fluorocarbon radical is formed by hydrogen abstraction, reaction with NO_2 is by far the fastest reaction that can occur. Experimentally, no fluorocarbon chlorides (or bromides) were found, an illustration of the dominance of the NO_2 reaction. Other experiments showed that R_fCF_2Cl does not react with NO_2 under the conditions of these reactions and is therefore not an intermediate. Fluorocarbon bromides do react with NO_2 to form acid fluorides; however, the NO_2 reaction is overwhelmingly faster than the chlorination reaction, and it seems likely that similar relative rates of reaction would exist in the bromine system so that fluorocarbon bromides probably are not intermediates. The mechanism of the reaction of the fluorocarbon radical with NO_2 was discussed earlier.

Steps 13 and 13a represent possible means by which a chain reaction could proceed; then steps 11, 12 and 13 or 12 and 13a constitute the chain steps.

As mentioned above, compounds of the class $Cl(CF_2)_nCF_2H$ can be converted to $Cl(CF_2)_nCOF$ and these in turn to the free acids and other derivatives.

The product as found is a mixture of acid and acid fluoride, suggesting that water is formed at some stage and hydrolyzes the initial acid fluoride. This possibility would alter some steps of the mechanism but not the essentials.

Two ω-chloroperfluoroalkane carboxylic acids prepared are $Cl(CF_2)_5CO_2H$ and $Cl(CF_2)_7CO_2H$, obtained from $Cl(CF_2)_5CF_2H$ and $Cl(CF_2)_7CF_2H$, respectively. These acids are believed to be new compounds; some physical properties are given in the Experimental section.

Chlorine-sensitized oxidation reactions, including the oxidation of highly halogenated compounds, are well known. For example, the chlorine-sensitized photo-oxidation (with oxygen) of CCl_3CCl_2H to produce largely CCl_3COCl has been studied by Schumacher and Thurauf[8]; they postulate that a $CCl_3CCl_2\cdot$ radical is formed by hydrogen abstraction by a chlorine atom and that this radical then
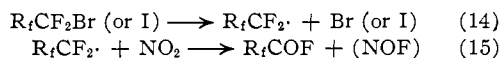
reacts with an oxygen molecule to form, eventually, CCl_3COCl.

Haszeldine and Nyman[9] produced CF_3CO_2H by the chlorine-sensitized photochemical oxidation of CF_3CH_2Cl or CF_3CHCl_2. A similar reaction mechanism was postulated.

In the present case, an oxidizing agent, NO_2, which has been shown to have controlled reactivity under conditions similar to those where oxygen does not (see oxidation of R_fSO_2F), has been used in place of oxygen and has given good results.

Oxidation of Fluorocarbon Derivatives Containing CF_2X Groups.

Experiments on the reactions of compounds of the type R_fCF_2X (R_f = perfluorocarbon group, X = Cl, Br, I) with NO_2 were carried out. It was found that R_fCF_2Cl did not react up to 590°, R_fCF_2Br does react partially at 600°, and that R_fCF_2I reacts smoothly and completely at 550°.

The reactions of R_fCF_2Br and R_fCF_2I with NO_2 yield R_fCOF in both instances. One possible mechanism for the reaction is

$$R_fCF_2Br \text{ (or I)} \longrightarrow R_fCF_2\cdot + Br \text{ (or I)} \quad (14)$$
$$R_fCF_2\cdot + NO_2 \longrightarrow R_fCOF + (NOF) \quad (15)$$

A possible mechanism for step 15 was discussed earlier.

The reaction of R_fCF_2I with NO in the presence of mercury and ultraviolet light has been found to yield the nitroso compounds, R_fCF_2NO.[10]

Experimental

General Procedure.—The reactor for most experiments was an inclined empty nickel pipe 1″ × 21″ heated by a 13″ electric furnace. Temperatures were measured by chromel-alumel thermocouples embedded in the pipe halfway along the heated zone. Gases were metered through calibrated flowmeters. The perfluoroalkanesulfonyl fluorides (or other fluorocarbon derivatives) in liquid form were added to the gas stream from a calibrated constant-flow dropping buret and vaporized to provide the gaseous charging stock which was fed in at the upper end of the reactor. The system was purged with nitrogen before and after each experiment.

Products were collected in two traps; the first was cooled by ice, the second by liquid air. All experiments were conducted at atmospheric pressure. Contact times were calculated on the assumption that the reaction zone was that portion of the tube where the wall temperature was above 475°. The products from $R_fCF_2SO_2F$ and NO_2 consisted of (1) the crude acid fluorides mixed with small amounts of inert fluorocarbon product, (2) solid $NOSO_3F$, sometimes mixed with a little tube corrosion product and (3) low boiling gases.

Reaction of $C_8F_{17}SO_2F$ with NO_2.—The general procedure was used with a center wall temperature of 550°. The reactants, 11 g. of NO_2 and 30 g. of $C_8F_{17}SO_2F$ (a mole ratio of 4:1), were fed to the reactor over a 24-minute period, contact time, 16 seconds; 23.8 g. of product was collected in an ice-cooled trap, stabilized to 40° and then hydrolyzed with 150 ml. of cold water. Sufficient concentrated H_2SO_4 was added to form a 20 wt. % aqueous solution. Then 100 ml. of c-$C_6F_{12}O$, an inert volatile cyclic fluorocarbon ether, was added to extract the fluorocarbon acids out of the aqueous phase. The c-$C_6F_{12}O$ phase was separated, a second extraction with fresh c-$C_6F_{12}O$ made and the combined extracts distilled. After removal of c-$C_6F_{12}O$, there was obtained 17.5 g. (71%) of mixed fluorocarbon acids. Distillation yielded 13.4 g. (54%) of $C_7F_{15}CO_2H$, b.p. 185–189°, and 3.1 g. of crude $C_6F_{13}CO_2H$ (13%).

Anal. Calcd. for $C_7F_{15}CO_2H$: neut. equiv., 414. Found: neut. equiv., 414.

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

(9) R. N. Haszeldine and F. Nyman, *Proc. Chem. Soc.*, 46 (1957).

(10) J. Banus, *J. Chem. Soc.*, 3755 (1953); R. N. Haszeldine, *ibid.*, 2075 (1953).

The $C_7F_{15}CO_2H$ was converted to the methyl ester, b.p. 159–160°, $n^{25}D$ 1.3026.

Anal. Calcd. for $C_9F_{15}H_3O_2$: C, 25.2; F, 66.5. Found: C, 25.4; F, 66.5.

A number of variations on the procedure were made in experiments designed to provide information about specific points. (1) Identification of the primary product as the acid fluoride: The products in the ice-cooled trap were distilled, and the acid fluorides separated as such. Experiments also showed that about 15% of the $C_8F_{17}SO_2F$ was converted to high boiling inert fluorocarbons including at least some C_8F_{18}. This might result from the reaction $C_8F_{17}\cdot + NOF \rightarrow C_8F_{18} + NO$.

(2) Identification of $NOSO_3F$: $NOSO_3F$ is a white solid and was found largely in the cooler portions of the exit end of the reactor. In one experiment $NOSO_3F$ corresponding to 61% of the sulfur in the $C_8F_{17}SO_2F$ was collected in pure form; additional $NOSO_3F$ contaminated with nickel salts also was found. The relatively pure $NOSO_2F$ was analyzed.

Anal. Calcd. for $NOSO_3F$: S, 24.8; F, 14.7. Found: S, 24.7; F, 14.0.

(3) Composition of the low boiling products: These constituted only a small part of the total product, and were mixed with excess NO_2 so that separation was difficult. Examination showed that the major portion of the low boilers was hydrolyzed by NaOH; the resulting sodium salts were shown by infrared analysis to contain perfluorocarboxylic acid salts, probably CF_3CO_2Na. The portion inert to base was a mixture of CF_4, C_2F_6, C_3F_8 and C_4F_{10}. A separate analysis showed that only 1.7% of the total sulfur was present in the low boilers in a readily hydrolyzable form.

Reactions of $C_5F_{11}SO_2F$, $C_{10}F_{21}SO_2F$ and CF_3SO_2F with NO_2.—$C_5F_{11}SO_2F$ and $C_{10}F_{21}SO_2F$ were found to react normally with NO_2 to yield C_4F_9COF and $C_9F_{19}COF$, respectively. CF_3SO_2F is thermally more stable than longer chain alkanesulfonyl fluorides and a temperature of 600° instead of the usual 550° was needed to effect complete conversion. The CF_3– group was converted to the expected COF_2 plus a little CO_2.

Reaction of $C_8F_{17}SO_2F$ with NO.—The charging stock consisted of 10.8 g. of $C_7F_{15}CF_2SO_2F$ and 4.4 g. of NO, fed into the reactor during a period of approximately 15 minutes. The temperature was approximately 550°. From the liquid collected in the ice-cooled trap, there was recovered by fractional distillation 3.1 g. of crude $C_7F_{15}COF$ (yield of 37%).

Reaction of $C_8F_{17}SO_2F$ with O_2.—Reaction of oxygen with $C_8F_{17}SO_2F$ (mole ratio O_2:$C_8F_{17}SO_2F$ = 2:1) at 540° gave complete fragmentation with COF_2 the chief product and smaller amounts of CO_2 and SOF_2. Reaction proceeds at 480° but not at 440°. Thermal decomposition in the absence of O_2 starts at about 450°.

Reaction of $C_8F_{17}SO_2F$ with SO_2 and with SO_3.—$C_8F_{17}SO_2F$ and SO_2 (1:3.3 mole ratio) were passed through the reaction tube at 550°; the products were essentially the same as those obtained by thermal decomposition of $C_8F_{17}SO_2F$. $C_8F_{17}SO_2F$ and SO_3 (1:4.5 mole ratio) at 555° gave COF_2 and CO_2 but no R_fCOF.

The Reaction of $C_7F_{15}H$ with NO_2 and Cl_2.—The reactor was a 1″ × 21″ empty nickel pipe mounted in an inclined position in a 13″ electric tube furnace. The temperature was measured with a thermocouple embedded in the pipe midway along the heated zone. The NO_2 and Cl_2 were metered at controlled rates through flowmeters, and the $C_7F_{15}H$ in liquid form was continuously mixed into the gas stream from a calibrated buret and vaporized to form the gaseous mixture charging stock, which was fed in through a tube connected to the upper end of the reactor. The exit end of the reactor pipe was connected to a trap cooled in ice, and the volatile products passing from the latter were condensed in a liquid air-cooled trap. The experiment was conducted at atmospheric pressure.

The $C_7F_{15}H$ was prepared by the reaction of $C_7F_{15}CO_2Na$ with ethylene glycol; the $C_7F_{15}H$ had b.p. 93–94°, $n^{25}D$ 1.2697.[11]

With the reactor at a wall temperature of 600°, a mixture of 24.7 g. of $C_7F_{15}H$, 6.6 g. of NO_2 and 5.2 g. of Cl_2 (mole ratio $C_7F_{15}H$:NO_2:Cl_2 = 1:2:1) was passed through the reactor in 15 minutes; contact time, 11 seconds. The product in the ice trap, 17.8 g., was hydrolyzed in 100 g. of cold water, and 25 ml. of concentrated H_2SO_4 added which caused the separation of a lower phase containing the fluorocarbon acid. The aqueous phase was extracted with 125 ml. of c-$C_6F_{12}O$, a volatile inert fluorocarbon cyclic ether in which fluorocarbon acids are soluble. The layers were separated and the $C_6F_{13}CO_2H$ recovered from the $C_6F_{12}O$ phase by distillation. The $C_6F_{13}CO_2H$, 11.1 g. (45.6%) was isolated as a fraction boiling at 170–175° (740 mm.). The sample contained 0.06 mg. F^-/g., <0.1% H_2O.

Anal. Calcd. for $C_6H_{13}CO_2H$: neut. equiv., 364. Found: neut. equiv., 361.

The Reaction of $C_7F_{15}H$ with NO_2 and Br_2.—Using the same equipment as before with a reactor temperature of 600° and a contact time of 12 seconds, 10.1 g. of $C_7F_{15}H$, 3.7 g. of NO_2 and 7.0 g. of Br_2 (mole ratio of $C_7F_{15}H$:NO_2:$Br_2 \cong$ 1:3:2) were allowed to react. The products boiling above room temperature (8.3 g.) were shown by infrared analysis to consist of mostly $C_6F_{13}COOH$ with a small amount of $C_7F_{15}H$ and unknown material.

The Reactions of $Cl(CF_2)_6H$ and $Cl(CF_2)_8H$ with NO_2 and Cl_2.—The same equipment and procedure as before was used. From 25.2 g. of $Cl(CF_2)_6H$ there was obtained a 72% yield (100% conversion) of a mixture of $Cl(CF_2)_5COF$ and $Cl(CF_2)_5CO_2H$. The acid fluoride was recovered as such by distillation, b.p. 81° (740 mm.). The acid was freed of fluoride ion and distilled. $Cl(CF_2)_5CO_2H$ has b.p. 180–183° (740 mm.), $n^{25}D$ 1.3280. The sample contained 0.29 mg. F^-/g., <0.1% H_2O.

Anal. Calcd. for $Cl(CF_2)_5CO_2H$: neut. equiv., 330; Cl, 10.8. Found: neut. equiv., 326; Cl, 11.2.

$Cl(CF_2)_7CO_2H$ was prepared in a similar manner from $Cl(CF_2)_8H$, NO_2 and Cl_2. From 5.6 g. of $Cl(CF_2)_8H$ there was obtained a 40% yield (100% conversion) of $Cl(CF_2)_7$-COOH. The acid is a solid at room temperature but no reliable melting point could be obtained.

Anal. Calcd. for $C_8F_{14}ClHO_2$: neut. equiv., 430.5; Cl, 8.1. Found: neut. equiv., 428; Cl, 8.4.

Reaction of $C_7F_{15}I$ with NO_2.—The $C_7F_{15}I$ used was prepared by the reaction of $C_7F_{15}CO_2Ag$ with I_2; b.p. 130–133°, $n^{25}D$ 1.3280.[12] The experiment was carried out by passing 25.1 g. of $C_7F_{15}I$ and NO_2 in a 1:3.2 mole ratio through the inclined 1″ × 21″ nickel tube heated by a 13″ electric furnace. The wall temperature was 550°; contact time, 16 seconds. There was obtained, after hydrolysis of the initial acid fluoride product, 10.9 g. (59%) of C_6F_{13}-CO_2H, b.p. 170–175°.

Reaction of $C_7F_{15}Br$ with NO_2.—The $C_7F_{15}Br$ used had a boiling point of 120–125° and a refractive index ($n^{25}D$) of 1.2998. The experiment was carried out by passing 4.9 g. of $C_7F_{15}Br$ and NO_2 in a 1:5.4 mole ratio through the nickel tube reactor heated to a wall temperature of 600°. The products boiling above 40° (3.5 g.) were shown by infrared analysis to contain largely unreacted $C_7F_{15}Br$ and a medium amount of $C_6F_{13}COF$.

Reaction of $C_8F_{17}Cl$ with NO_2.—The $C_8F_{17}Cl$ used had a boiling point of 128–131° and a refractive index ($n^{25}D$) of 1.2902. A total of 9.3 g. of $C_8F_{17}Cl$ and NO_2 in a 1:3.9 mole ratio was passed through a nickel tube heated to a wall temperature of 590°. The product boiling above 40° (8.3 g.) was shown by infrared analysis to be unreacted $C_8F_{17}Cl$. The recovery of starting material was 89%; no R_fCOF or R_fCO_2H was detected.

(11) (a) For the general method, see I. Auerbach, F. H. Verhoek, and A. L. Henne, This Journal, **72**, 299 (1950); (b) A. F. Benning and J. D. Park, U. S. Patent 2,490,764, report b.p. 96–97, d^{25}_{25} 1.725.

(12) For general process, see J. H. Simons and T. J. Brice, U. S. Patent 2,554,219, May 22, 1951, or A. L. Henne and W. G. Finnegan, This Journal, **72**, 3806 (1950)