[Contribution from the Fluorine Laboratories of The Pennsylvania State College]

Fluorocarbon Chemistry. II. The Cleavage of Carbon–Carbon Bonds by Chlorine and Bromine[1]

By T. J. Brice, W. H. Pearlson[2] and J. H. Simons

The preparation of bromo- and chloro- fluorocarbons by the thermal, vapor-phase halogenation of the corresponding hydrogen compounds has been previously reported.[1]

It has been found that at higher temperatures the carbon chains in fluorocarbons can be broken in the presence of chlorine or bromine with the formation of shorter chain bromo- and chlorofluorocarbons. The temperatures at which these reactions occur vary with the length of the carbon chain, decreasing from about 900° for C_2F_6 to 800° for C_5F_{12}.

The products isolated were those to be expected from the cleavage of carbon–carbon bonds. Thus, from the reaction of C_2F_6 with bromine, CF_3Br was the only product isolated. Similarly, the reaction of C_2F_6 with chlorine produced essentially only CF_3Cl. The reaction of chlorine or bromine with C_2F_6 can result in the formation of polychlorides or polybromides, or of compounds having two carbon atoms per molecule and containing chlorine or bromine atoms, only when carbon–fluorine bonds are broken. Since such compounds were not found, it was concluded that in these instances carbon–fluorine bonds were not broken to any great extent. In reactions of chlorine or bromine with fluorocarbons having three or more carbon atoms per molecule, it is more difficult to decide definitely whether carbon–fluorine bonds are broken to any extent. This is because many polychlorides or polybromides could conceivably be formed either as a result of the cleavage of carbon–carbon bonds only, or as a result of a combination of carbon–carbon bond and carbon–fluorine bond cleavages. Thus, the CF_2Cl_2 formed in the reaction of C_5F_{12} with chlorine could result from either process. However, since these reactions were carried out under less drastic conditions than those used in reactions of C_2F_6, it seems reasonable to believe that carbon–fluorine bond cleavage did not occur to any great extent.

The method used consisted of passing a gaseous mixture of the fluorocarbon and halogen through an unpacked, electrically heated quartz tube and condensing the products in cold traps for subsequent investigation. The experiments were carried out at atmospheric pressure. In the reactions using bromine, the fluorocarbon–bromine mixture was obtained by passing the fluorocarbon vapors and dry nitrogen through a heated bubbler containing liquid bromine. In reactions using chlorine, the fluorocarbon and chlorine were metered and then mixed in a small chamber ahead of the reactor. The reactor tube was a 1″ i.d. quartz tube 24″ long heated along a 12″ section by an electric furnace. The flow rates used were between 0.1 and 0.5 mole of fluorocarbon per hour; assuming the tube was at reaction temperature over a 6″ section the contact times were six to thirty seconds. The products of the reaction were collected in a series of traps cooled in ice, Dry Ice–acetone and liquid air. They were then passed through bubblers containing basic bisulfite solution to remove acid gases, dried with concentrated sulfuric acid and then in most cases fractionated.

Except in the C_3F_8 experiment, fractionations were carried out in a small low-temperature column having a packed section of 11 mm. tubing 45 cm. long packed with single turn $^1/_{16}$″ stainless steel helices. The column was operated in conjunction with the vacuum system and a gas density balance.

In view of the high temperatures used some reaction of the fluorocarbons and the chlorine or bromine-containing products with the quartz reactor tube would be expected. Silicon halides were found, notably in reactions in which polybromides could be formed. The short contact times and the inertness of polyfluorides kept this decomposition from being a serious factor. The use of carbon reactor tubes would probably eliminate most of the losses due to such decomposition.

The Reaction of Chlorine with C_2F_6.—The cleavage of the carbon–carbon bond in C_2F_6 by chlorine should result in the formation of CF_3Cl; CF_3Cl boils very nearly at the same temperature as C_2F_6 making a separation by fractionation impractical. The C_2F_6 was therefore treated repeatedly with chlorine until molecular weight determinations indicated that essentially complete conversion to CF_3Cl had been accomplished. The molecular weight of the final product corresponded to 96 ± 3 mole per cent. CF_3Cl assuming only C_2F_6 and CF_3Cl were present; the uncertainty in the molecular weight —about 1%—introduces a 3% uncertainty in the composition of the mixture.

Experimental.—The C_2F_6 used in the reactions with chlorine and bromine was obtained by fractionation and purification of the products from the operation of the electrochemical process for producing fluorocarbons using propionic acid.[3] It had a molecular weight of 136;

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(1) For Paper I of this series see T. J. Brice, W. H. Pearlson and J. H. Simons, This Journal, **68**, 968 (1946).

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(3) J. H. Simons, *et al.*, presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, 114th Meeting, Portland, Oregon, September, 1948; *J. Electrochem. Soc.*, **95**, 47 (1949).

calcd. for C_2F_6, 138; b. p. *ca.* −80°. The material probably contained a small amount of C_2F_5H, a contaminant known to have been present in the original mixture.

The C_2F_6, 46 g., was treated four times with chlorine at 900° using chlorine: C_2F_6 mole ratios of about 2:1 and C_2F_6 flow rates of 0.4 to 0.5 mole per hour. The molecular weight of the base-washed material corresponded to that of a mixture containing 75 mole per cent. CF_3Cl and 25 mole per cent. C_2F_6. Treatment of this material with chlorine at 868–880° gave no change in molecular weight, and it was concluded that 900° was about the lowest useful temperature. In the final step the temperature was raised to 937–944° and the chlorine:C_2F_6 mole ratio to 9:1. The final base-washed, air-free product weighed 41.6 g. Molecular weight determinations made during a simple distillation of the product gave uniformly 106. Analysis: Cl, 30.5. Calcd. for a 96:4 mixture of CF_3Cl:C_2F_6: Cl, 32.4; mol. wt., 106. The analysis indicates that there may be present a small amount of material other than CF_3Cl and C_2F_6.

The Reaction of Bromine with C_2F_6.—The reaction of bromine with C_2F_6 at about 900° produced CF_3Br. Under the conditions used there was little decomposition.

Experimental.—A mixture of 30.5 g. of C_2F_6, bromine and dry nitrogen having the mole ratios $C_2F_6:Br_2:N_2$ = 2:2:1 was passed through the reactor at 896–912° with a fluorocarbon flow rate of 0.22 mole per hour. The material (chiefly C_2F_6) collected in the liquid air trap (not weighed) was repassed under the same conditions at 910–924°. The base-washed, air-free product weighed 38 g. Fractionation yielded 14.5 g. of CF_3Br, b. p., −60°, mol. wt., 149. Calcd. for CF_3Br: mol. wt., 149; lit. b. p., −60.5 to −59°.[1] The remainder was unreacted C_2F_6 and a C_2F_6–CF_3Br intercut.

The Reaction of Bromine with C_3F_8.—This reaction was the first reaction of halogen with fluorocarbon carried out, and from it an approximation of the temperatures most useful in such experiments was obtained. CF_3Br was definitely identified, and there were indications of the formation of higher boiling compounds.

Experimental.—The C_3F_8 used was obtained by fractionation of the products of the operation of the electrochemical process with butyric acid; b. p., −38 to −35°; mol. wt., 186.[3] Preliminary trials at 795° and 810–820° gave little indication of reaction so a higher temperature was used: 46.4 g. of C_3F_8 was mixed with bromine and passed through the reactor at 840–857° with a fluorocarbon flow rate of 0.2 mole per hour. The $C_3F_8:Br_2$ ratio was about 1:1. The dry, base-washed product weighed 50.5 g. It was fractionated in a small portable column of the type described by Ramler and Simons.[4]

Low boiling product escaped through the Dry Ice-cooled head; it was tentatively identified as crude C_2F_6: wt., *ca.* 3 g.; mol. wt., 136–144. Fractionation of the remainder gave 21 g. of CF_3Br: b. p., −63 to −58°; mol. wt., 150. The higher boiling material did not yield any definite fractions in the column used.

The Reaction of Chlorine with C_5F_{12}.—The reaction of longer chain fluorocarbons with chlorine can be accomplished at somewhat lower temperatures than are required for C_2F_6 and C_3F_8; this lowered reaction temperature plus the greater stability of polychlorides as compared to polybromides partly account for the presence of considerable amounts of polychlorides in the products of the reaction of chlorine with C_5F_{12}. Degradation of intermediate products would lead to the formation of relatively large amounts of the one-carbon compounds CF_2Cl_2 and CF_3Cl and these products predominated under the conditions used.

Experimental.—The C_5F_{12} used was obtained by the fractionation of the products of the operation of the electrochemical process using adipic and sebacic acids[3]; b. p., 28°; mol. wt., 278; calcd. mol. wt. for C_5F_{12}, 288. Chlorine and 43 g. of C_5F_{12} were mixed in a mole ratio of 4:1 and passed once through the reactor at 795–830° and at the rate of 0.10 mole of fluorocarbon per hour. The dry, base-washed products, 55.4 g., were then fractionated. Upon fractionation there were isolated several compounds and mixtures. The lowest boiling material was 3.6 g. of CF_3Cl, b. p., −80°; mol. wt., 103–104.5. Calcd. for CF_3Cl: mol. wt., 104.5; lit. b. p., −81°.[5] 7.9 g. of a 75–25 mole per cent. mixture of C_2F_5Cl and CF_2Cl_2, b. p., −38 to −37°, mol. wt., 148–146, was obtained. Calcd. for C_2F_5Cl: mol. wt., 154.5; lit. b. p., −38°.[6] There was 6 g. of CF_2Cl_2; b. p., −31°; mol. wt., 123–122. Calcd. for CF_2Cl_2: mol. wt., 121; lit. b. p., −29.8°.[7] There was also obtained 15 g. of a mixture boiling at +29°, mol. wt., 266; Cl, 3.62. This probably contains C_4F_9Cl which would be expected to boil at about 30° and hence would be difficult to separate from C_5F_{12}.

The Reaction of Bromine with C_3F_7Cl.—Under the conditions used in this experiment, the reaction products identified were CF_3Br and CF_3Cl. CF_3Br is an expected product of carbon–carbon bond cleavage. The formation of CF_3Cl cannot result from simply carbon–carbon bond cleavage. If a mechanism were suggested for its formation, the greater strength of the carbon–fluorine bond as compared to the carbon–chlorine bond indicates that it would result from reactions in which a carbon–chlorine bond was broken and a new carbon–chlorine bond formed, rather than from reactions in which carbon–fluorine bonds were broken. Considerable decomposition of the fluorocarbon derivatives to silicon halides was observed.

Experimental.—The C_3F_7Cl used was prepared by the thermal chlorination (at *ca.* 550°) of mixed isomers of C_3F_7H obtained by fractionation of the products of the operation of the electrochemical process using butyric acid.[3] Properties of the C_3F_7Cl used: b. p., −2.5 to −1°; mol. wt., 208. The C_3F_7Cl, 44 g., was mixed with bromine and nitrogen in an approximately 1:1:1 mole ratio and passed through the reactor at 852–870° and at a flow rate of 0.13 mole of C_3F_7Cl per hour. Considerable decomposition occurred as evidenced by the deposition of carbon on the inside of the reactor and of the formation of unusually large amounts of silicon halides. The base-washed products amounted to 39 g. Fractionation gave, in addition to intercuts: 4.5 g. of CF_3Cl, b. p., −82 to −81°, mol. wt., 103–104; 10.7 g. of CF_3Br, b. p., −59°, mol. wt., 149–151; 1.8 g., b. p., −11 to −9°, mol. wt., 161–172, which was probably crude CF_2ClBr. The column residue, 8.2 g., had a molecular wt. range of 210–214 and was considered chiefly unreacted C_3F_7Cl.

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Summary

Fluorocarbons have been shown to react with

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(4) E. O. Ramler and J. H. Simons, *Ind. Eng. Chem., Anal. Ed.*, **14**, 430 (1942).

(5) Ruff and Keim, *Z. anorg. allgem. Chem.*, **201**, 245 (1931).

(6) Locke, Brode and Henne, This Journal, **56**, 1726 (1934).

(7) Midgley and Henne, *Ind. Eng. Chem.*, **22**, 542 (1930).

chlorine and bromine at elevated temperatures to give shorter-chain bromo- and chloro- fluorocarbons. The products are those to be expected from the cleavage of carbon–carbon bonds in the fluorocarbon.

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The Exchange of Chlorine Dioxide with Chlorite Ion and with Chlorine in Other Oxidation States

BY HAROLD DODGEN[1] AND HENRY TAUBE

Chlorine dioxide and chlorite ion have, approximately at least, the same configurations, and differ principally only in their charge. It may be expected, therefore, that electron transfer will occur on the close approach of ClO_2 and ClO_2^-. This research was undertaken in the hope of finding evidence for such exchange in aqueous solution, and in the event that the exchange takes place, to study its rate and kinetics. One of these goals has been reached: it has been shown that a rapid exchange does take place in an aqueous solution containing ClO_2 and ClO_2^-, and a lower limit on the specific rate has been set. The research thus far encourages the hope that the rate can be measured quantitatively, and work toward this goal is being continued.

The work has been carried out using the technique, already frequently applied, of mixing a solution containing one of the reaction partners made radioactive with a solution of the other, and observing the rate at which radioactivity is lost from the first partner, or appears in the second. The separation of the partners after exchange was accomplished by extracting the chlorine dioxide from the reaction mixture with carbon tetrachloride. It seems likely that this procedure is unobjectionable, since the properties of ClO_2 are not altered drastically by changing from the solvent water to carbon tetrachloride. However, an actual proof that some exchange is not induced by the method of separation awaits the results of the work on the detailed kinetics.

In addition to offering a simple means for the separation of the exchange partners, the present system also has the important property that any exchange between ClO_2 and ClO_2^- brought about by the operation of the disproportionation equilibrium

$$2ClO_2 + H_2O = ClO_2^- + ClO_3^- + 2H^+$$

may be separately studied, and thus allowed for in considering the direct ClO_2–ClO_2^- exchange. Exchange through this equilibrium may be studied by observing the rate at which activity is transferred between ClO_2 and ClO_3^- in solutions containing these substances.

Experiments have also been carried out to study the exchange of ClO_2 with substances containing chlorine in all the other oxidation stages known to exist in water, namely, ClO_4^-, ClO^-, Cl_2 and Cl^-. It was observed that, with all the oxidation states except ClO_2^-, the rate of exchange is very slow. These results find application in further work using radiochlorine which is to be published later.

Experimental Procedure

The isotope used in this research was Cl^{38}, which decays with a half-life of 37 min., emitting β particles. It was produced by bombarding potassium chlorate with slow neutrons generated in the University of Chicago cyclotron by the impact of 8.5 mev. deuterons on beryllium. Chlorine dioxide was produced by heating a mixtue of 5 g. of bombarded potassium chlorate, 25 g. of oxalic acid and 3 g. of water at 60° in an apparatus similar to that used by Bray.[2] The chlorine dioxide was collected in water after being passed through a solution of 0.5 M in Na_2HPO_4, 1.0 M in NaCl and 0.5 M in $NaClO_3$ to remove any carriers for activity other than chlorine dioxide.

The exchange experiments were performed by mixing an aliquot of the radioactive chlorine dioxide solution with a solution containing the inert chlorine containing species and phosphate buffer or perchloric acid to give the required acidity. After the desired length of time for exchange had elapsed, carbon tetrachloride was added and the chlorine dioxide was extracted.[3] The specific activity was determined by counting the carbon tetrachloride solution in a thin-walled glass cell and measuring the concentration of chlorine dioxide by an iodimetric titration. Throughout this paper the quantity $I_0/100C$ represents the specific activity expressed in arbitrary units. I_0 is the counting rate in counts per minute corrected for decay, and C is the concentration in gram atoms per liter of chlorine in the substance being counted. The specific activity of the chlorine dioxide was determined both before and after contact with the inert chlorine containing species. A decrease in specific activity can take place only if there is exchange of radioactive chlorine dioxide with the other species present, or if non-radioactive chlorine dioxide is produced in the system. The latter process did not occur to a significant extent in any of the experiments performed.

In some of the experiments on the exchange of chlorine dioxide and chlorite the concentration of chlorine dioxide in the solutions counted was too low for analysis, hence the above procedure could not be used for determining the specific activity. These experiments were performed by first running a blank experiment in which a measured volume of inert chlorine dioxide solution of known concentration was added to a measured volume of a solution of the desired activity, then a measured volume of water was added, the mixture stirred and a measured volume of carbon tetrachloride added, the mixture shaken and some of the carbon tetrachloride layer withdrawn and counted.

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[1] Present address: The State College of Washington, Pullman, Washington.

[2] Bray, *Z. physik. Chem.*, **54**, 463 (1906).

[3] When chlorine was also present, the chlorine and chlorine exchangeable activity was removed from the carbon tetrachloride layer by extracting with solution containing Cl^- and $HPO_4^=$.