TABLE II. PRODUCTS OBTAINED FROM FLUORINATED 4-CHLORO-1,3-BIS(TRIFLUOROMETHYL)BENZENE

Formula	Description	B.P., ° C.	Constant Refractive Index (° C.)	Mol. Wt. Calcd.	Mol. Wt. Found
C_6F_{12}	Perfluorocyclohexane	48–50	...	300	301
$C_6F_{11}(CF_3)$	Perfluoromethylcyclohexane	77.5	...	350	352
1,3-$C_6F_{10}(CF_3)_2$	Perfluoro-1,3-dimethylcyclohexane	99–100	...	400	395
$C_6H_3F_7(CF_3)_2$	Heptafluoride azeotrope	113–114	1.3190(31)	...	334
$C_6H_3F_4Cl(CF_3)_2$	Pure tetrafluoride	143	1.3607(32)	325	323
$C_6H_3F_2Cl(CF_3)_2$	Difluoride azeotrope	147	1.3922(32)	...	278
1,3,4-$C_6H_3Cl(CF_3)_2$	Original compound	148–50	...	...	...

matic nucleus, with constant physical properties, has been completely characterized by precise, accurate analyses and molecular weights:

Formula	$C_6H_3F_4(CF_3)_2$	
Constant boiling point, ° C.	143	
Constant refractive index at 32°	1.3607	
	Calcd.	Found
Analysis		
Fluorine	58.5	58.4, 58.6
Chlorine	10.9	11.1, 11.2
Molecular weight	325	322, 324

Figure 6 shows the reactions which took place in this fluorination. All the compounds given here were shown to have been formed except IV, and even this may well have been present in the complex product. Compounds II and III, the di- and tetrafluorides, are represented empirically, since no definite evidence was available to distinguish between the possible structural isomers which could result from 1,2 and 1,4 addition. No account has been taken of stereoisomers in any case. All of these changes, including the appearance of high boiling residues, may readily be explained on the basis of atomic reactions involving addition, substitution, fragmentation, and ultimately polymerization; all are in complete accord with modern theoretical concepts.

LITERATURE CITED

(1) Bockemueller, *Ann.*, **506**, 20 (1933).
(2) Bower and Cooke, IND. ENG. CHEM., ANAL. ED., **15**, 290 (1943).
(3) Fukuhara and Bigelow, *J. Am. Chem. Soc.*, **63**, 788 (1941) and other papers of this series.
(4) *Ibid.*, **63**, 2792 (1941).
(5) Linden, van der, *Rec. trav. chim.*, **53**, 45 (1934); **55**, 569 (1936); **57**, 217 (1938).
(6) Simons and Herman, *J. Am. Chem. Soc.*, **65**, 2064 (1943).
(7) Tompson, Tarrant, and Bigelow, *Ibid.*, **68**, 2187 (1946).

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Oxidation of organic compounds in
LIQUID HYDROGEN FLUORIDE[1]

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THE oxidation of aromatic, alicylic, and aliphatic compounds in the liquid phase with oxygen under pressure was accomplished in a medium of hydrogen fluoride. The variation of the conditions of the reactions were studied. Various oxygen carriers were used in different amounts. Temperature, pressure, and time as well as dilution were also varied over wide limits. Benzene was oxidized to phenol in very high yield. Carbon was formed under other conditions, and benzoic acid and biphenyl were also found. Toluene yielded *o*-cresol, carbon, and water with only a small amount of benzoic acid. *m*-Xylene yielded 1,3-xylen-4-ol, some *m*-toluic acid, and carbon. β-Naphthol and a trinaphthyl were identified from the oxidation of naphthalene. Benzotrifluoride was oxidized to benzoyl fluoride and hydrolyzed to benzoic acid. Benzoic acid, cyclohexane, methylcyclohexane, *tert*-butylbenzene, and *n*-heptane gave carbon and water. The oxides of carbon, dicarboxylic acids, and tars were not detected in the products in most experiments.

HYDROGEN fluoride has been found to furnish a medium for the liquid-phase oxidation of organic compounds at temperatures under 200° C., with molecular oxygen as the agent. The products formed are not those usually found in either the liquid- or vapor-phase oxidation of the same substances. For example, phenol is obtained by the oxidation of benzene and cresol by oxidation of toluene, without the formation of ring-rupture products and their oxidized fragments. Complete combustion of certain compounds results in the formation of carbon and water without detectable amounts of carbon dioxide or carbon monoxide. The product is an activated carbon with decolorizing properties. This reaction was studied under several conditions of temperature, pressure, and concentration, with different inorganic substances as oxygen carriers for a variety of organic compounds. Conditions were found where the yield of phenol from benzene was essentially 100% although the percentage conversion was considerably less.

The formation of *o*-cresol from toluene in much greater amounts than benzoic acid and the formation of β-naphthol from naphthalene indicated that a reaction has been found for ring oxidation in preference to side-chain oxidation, and that it can be accomplished without ring splitting. Under drastic conditions an activated form of carbon was formed rather than the oxides of carbon from both aliphatic and aromatic compounds. Tars were not found as products.

OXIDATION PROCEDURE

Regular stock chemicals were used. They included aromatic, alicyclic, and aliphatic compounds such as benzene, toluene, *m*-xylene, *tert*-butylbenzene, naphthalene, benzotrifluoride, benzoic acid, cyclohexane, methylcyclohexane, and *n*-heptane.

A heavy-walled copper bomb of 750 cc. capacity was used in all experiments. To this a water-cooled condenser was connected, and a valve and pressure gage were provided at the top of the condenser. This unit was constructed to withstand 3000 pounds per square inch at 300° C. The bomb fit into an electric furnace which was mounted on the cradle of a shaking machine. The frame of this machine was built of angle iron, and the swinging cradle hung into it. Motion was provided by a motor, speed reducer, and crank. A coil of copper tubing within the furnace enabled water cooling to be used when desired. All current and

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[1] This is paper XIX of the series, Hydrogen Fluoride as a Condensing Agent, which has been published in *Journal of the American Chemical Society*; the preceding paper appeared in Vol. 65, p. 1390 (1943).

Table I. Oxidation of Organic Compounds with the Aid of Hydrogen Fluoride

Expt. No.	Hydrocarbon, Moles[a]	Mole Ratio, Hydrocarbon to HF	O_2 Pressure, Lb./Sq. In.	Oxygen Carrier, Grams	Diluent, Grams	Temp., ° C.	Time, Hours	Yield[b] of Products					
								Carbon	CO_2	Phenolic	Carboxylic	Hydrocarbon	Hydrocarbon polymer
1	B, 1	1-6	50	....	....	150	7	72%	...	28% p	....	...	...
2	B, 3	1-2.3	550	Ag_2O, 30	....	160	4	87%	...	13% p	....	...	...
3	B, 3	1-2.6	700	Ag_2O, 30	....	25	2	...	...	Trace p	....	...	...
4	B, 3	1-1.17	850	Ag_2O, 30	....	100	3	61%	...	39% p	....	...	...
5	B, 3	1-2	900	Ag_2O, 30	....	65	2	...	...	100% p	....	...	...
6	B, 3	3-1	1000	Ag_2O, 30	....	85	5	...	Yes	....	....	...	Trace
7	B, 3	1-1.25	1000	As_2O_3, 30	....	80	3.5	...	...	100% p	....	...	...
8	B, 3	1-2.92	950	As_2O_3, 30	....	120	3	94%	...	6% p	....	...	...
9	B, 3	1-1.7	500	As_2O_3, 30	....	80	2	2.5g.	...	1.8g. p	....	...	...
10	B, 1.75	1-2	1000	SeO_2, S	....	100	3	23%	...	77% p	....	...	...
11	B, 3	1-2.3	1000	Fe_2O_3, 23	....	140	2	78%	...	22% p	....	...	...
12	B, 3	1-2.27	850	As_2O_5, 35	....	100	4	89%	...	11% p	....	...	...
13	B, 3	1-2.42	850	MoO_3, 30	....	150	4	98%	...	....	....	2% b	...
14	B, 3	1-2	1000	MoO_3, 32	....	100	3.5	85%	...	....	5% a	10% b	...
15	B, 3	1-2	1050	MoO_3, 30	....	120	8	93%	...	1% p	3% a	3% b	1.3g.
16	B, 3	1-2.08	1000	As_2O_3, 30	H_2O, 18	100	4	54%	...	21% p	....	25% b	0.3g.
17	B, 3	1-2	1000	As_2O_3, 30	H_2O, 18	150	6	92%	...	5% p	3% a	...	...
18	B, 3	1-2.08	1400	As_2O_3, 30	H_2O, 36	200	8	73%	...	6% p	17% a	4% b	0.3g.
19	B, 3	1-2.3	1000	As_2O_3, 30	CH_3OH, 32	100	6	83%	...	2% p	11% a	4% b	Trace
20	B, 3	1-2.27	1000	As_2O_3, 30	CH_3OH, 64	120	7	33%	...	51% p	....	16% b	0.4g.
21	B, 3	1-2	1000	As_2O_5, 32	H_2SO_4, 10	120	5	96%	...	1% p	3% a	Trace	Trace
22	B, 3	1-2	850	....	....	130	1.5	88%	Yes	10% p	2% a	...	0.9g.
23	B, 2	1-2	...	H_3AsO_4, 45	....	130	17			No reaction			
24	B, 1	1-7	...	....	p, 45	150	7			No reaction			
25	B, 2	1-7.5	15	....	....	25	5	...	...	Trace p	....	...	...
26	B, 3	1-1.7	500	As_2O_3, 30	p, 10	80	2	12.6g.	...	1.6g. p	....	...	...
27	T, 3	1-1.7	300	As_2O_3, 25	....	100	2	10%	...	84% c	6% a	...	...
28	T, 3	1-2	1000	Ag_2O, 25	....	100	1	92%	...	8% c	0.2% a	0.8g. d	...
29	T, 3	1-2	1000	As_2O_3, 25	....	100	3	86%	...	14% c	0.4% a	0.8g. d	...
30	M, 3	1-2	1050	As_2O_3, 32	....	120	6	12%	...	70% x	12% m	...	14.9g.
31	N, 1	1-6.5	1000	FeO_3, 34	....	140	3	98%	...	2% n	....	...	1.2g.
32	N, 1	1-6	1000	Ag_2O, 30	....	120	3.5	99%	...	1% n	....	2.4g. t	12.8g.
33	A, 1	1-5.5	850	....	....	100	0.3	...		Explosive reaction			
34	A, 0.1	1-60	500	As_2O_3, 30	....	130	6	83%	Yes	....	....	...	...
35	F, 0.5	1-10	500	As_2O_3, 30	H_2O	100	5	...	...	....	76% a	...	[c]
36	F, 0.5	1-12	550	....	....	130	6	...	...	....	6% a	...	[d]
37	F, 0.5	1-24	...	....	H_2O, 18	100	12	...	...	....	100% a	...	...
38	a, 0.1	1-132	...	....	....	150	6	...	...	....	100% a	...	[e]
39	a, 0.1	1-50	500	As_2O_3, 30	....	130	7	0.5g.	...	....	a	...	...
40	C, 0.25	1-8	500	As_2O_3, 30	....	100	5	...	...	....	....	...	...
41	C, 0.20	1-15	600	As_2O_3, 30	....	120	5	0.2g.	...	....	....	...	...
42	H, 0.5	1-5	550	As_2O_3, 30	....	100	6	0.2g.	...	....	....	...	...
43	H, 0.5	1-6.5	550	As_2O_3, 30	....	120	6	2.6g.	...	....	....	...	...
44	D, 0.20	1-20	550	As_2O_3, 30	....	100	5	...	...	....	....	...	...
45	D, 0.17	1-18	550	As_2O_3, 30	....	130	5	0.2g.	...	....	....	...	...

[a] B = benzene, T = toluene, M = *m*-xylene, N = naphthalene, A = *tert*-butylbenzene, F = benzotrifluoride, C = cyclohexane, H = methylcyclohexane, D = *n*-heptane, a = benzoic acid.

[b] Yields given in per cent are based on total amount of hydrocarbon consumed to form products: a = benzoic acid, p = phenol, b = biphenyl, c = *o*-cresol, d = ditolyl polymer, x = 1,3-xylen-4-ol, m = *m*-toluic acid, n = β-naphthol, t = trinaphthyl.

[c] 24% benzoyl fluoride. [d] 7% benzoyl fluoride. [e] Trace of benzoyl fluoride.

water connections were made at the center of motion of the cradle, and the valve and gage were also located in this region.

The general method was as follows: The solid reagents were placed in the high-pressure copper vessel, and the desired amount of hydrogen fluoride was distilled from the storage tank into the vessel. The liquid reagents were cooled in ice and added to the reaction mixture through a copper funnel. The condenser was attached, the bomb inserted in the furnace, and the condenser fastened to the frame of the cradle. The oxygen was added through the valve at the top of the condenser and from an intermediate pressure vessel. The source of oxygen was the regular commercial cylinder. When the desired pressure was reached, the oxygen source was disconnected, the furnace heated to the desired temperature, and the shaker started. After the reaction was judged to be complete, the furnace was cooled and the reaction mixture removed and subjected to an exhaustive analytical separation for all of the suspected products.

A large number of reactions were performed with a variety of substances, under a range of conditions, and with different oxygen carriers.

Table I summarizes the conditions and results of some of the experiments. As the object of this study was to explore the scope of this new oxidation procedure for organic compounds rather than to determine the optimum conditions for the preparation of any one product, the results reported represent individual experiments. Essential agreement in regard to the reaction products under a large number of different conditions amply confirms the fact that the procedure does function as indicated.

BENZENE OXIDATION

Among the oxygen carriers employed were silver compounds such as the oxide, three- and five-valent arsenic compounds, four-valent selenium compounds, three-valent iron compounds, six-valent molybdenum compounds, six-valent sulfur compounds, and copper compounds. Although the carriers were frequently added as the oxides, because of the action of hydrogen fluoride, fluorides or oxyfluorides were certainly present in most cases. Because of the oxidizing action of the molecular oxygen and the reducing action of the organic substances, the valence of the carrier certainly had the opportunity to change in the reaction mixture. Silver, for example, was probably present as the oxide, fluoride, and free metal. The copper was always present, as copper vessels were used. The oxides and fluorides of the metal were present, as shown by the fact that the reaction mixtures always contained some copper compounds when they were removed from the bomb. As the same vessels were used for the series of reactions, some of the carriers from preceding experiments probably remained in the vessel so that mixtures of carriers may have been present in some cases. Phenol and carbon were formed in all experiments in which oxygen carriers were used. Carbon monoxide and carbon dioxide were not found as reaction products except when no oxygen carrier was added. All the carriers seemed to act in a similar manner in that phenol and carbon were formed and products of ring rupture, if any, were small. There were some differences, however; for example, arsenic and selenium compounds caused the reaction to proceed at a lower temperature. When molybdenum compounds were used, the yield of phenol was small, that of carbon was high, and both biphenyl and benzoic acid were obtained. When experiments were run without the addition of an extra substance (other than the wall of the vessel), the reaction proceeded more slowly. In an experiment without extra substance at 130° C., a sudden rapid reaction occurred after a period of 1 to 2 hours. The usual products were found, but in addition carbon dioxide was obtained. In some of the experiments a small amount of higher-molecular-weight hydrocarbon was found. This could not be separated and identified, but appeared to be triphenyls and similar compounds of high molecular weight.

Some speculation would be justified relative to the reaction. The yield of phenol, based on the amount of total carbon compounds other than benzene found in the reaction products, approached 100% in some cases. However, the ratio of phenol to benzene did not exceed a relatively small value. This seemed to be true irrespective of the oxygen carrier used. In one experiment a quantity of phenol was added which was greatly (six times) in excess of this ratio. The excess phenol was consumed in the oxidation process, and the usual ratio was found. This indicates that, although benzene is oxidized to phenol, the latter is also oxidized if its concentration is high. Part of the carbon formed may be from the oxidation of phenol, and the first step in the oxidation process may be the formation of phenol. The lack of appreciable amounts of products which could be formed only by ring rupture during oxidation indicates that the phenol (or benzene) is oxidized to carbon and water under these conditions without ring rupture. The very low activity of water in a hydrogen fluoride medium may account for the reaction going in this direction rather than to the oxides of carbon, etc. The formation of biphenyl could be accounted for by the simultaneous oxidation of two adjacent benzene molecules. At the temperatures employed, it could hardly be accredited to pyrolysis. It is also not to be explained by the condensation of phenol with benzene, for previous work (*2*) had shown that this condensation does not take place in the presence of hydrogen fluoride without oxidizing conditions. The unexpected formation of benzoic acid by the oxidation of benzene might be thought to be due to the oxidation and breaking of one of the rings of the biphenyl molecule. Benzoic acid itself was found in another experiment to be oxidized to carbon and water.

Oxygen pressure and temperature were varied independently. Increasing the oxygen pressure from 300 to 1000 pounds per square inch apparently had the effect only of increasing the amount of carbon formed. Increasing the temperature from 65° to 200° C. also seemed only to increase carbon formation. Of course, with different oxygen carriers different temperatures were needed to obtain a rapid reaction. In one experiment oxygen was bubbled through a benzene and hydrogen fluoride mixture kept at room temperature and under a reflux condenser at atmospheric pressure. A trace of phenol was obtained. At higher temperatures the carbon formed was denser and harder than that formed at lower temperatures.

The concentration effects and the proportion of reactants were studied in a number of experiments. Varying the mole ratio of hydrocarbon to hydrogen fluoride between 1 to 6 and 3 to 1 seemed to have little influence on the amount of phenol produced. A slightly larger amount appeared to be formed when the ratio was 1 to 2. When the ratio approached 3 to 1, carbon dioxide began to be found in the reaction products. When the ratio approached 1 to 6, carbon formation increased even at the lower temperatures. In an attempt to reduce the activity of the hydrogen fluoride, both water and methanol were added. Mole ratios of water to hydrogen fluoride of 1 to 6 and 2 to 6 were tried. The only effect was to raise the temperature of the reaction. Methanol in the same ratios had the same effect as water, but the temperature increase needed was smaller.

OXIDATION OF OTHER AROMATIC COMPOUNDS

Toluene gave as the main products carbon and *o*-cresol, boiling at 190–200° C. This was identified by forming an aryl oxyacetic derivative, melting at 151–152° C. There were found a very small amount of benzoic acid and some hydrocarbon material of the nature of bi- or polytolyl mixtures. In general the effect of varying the temperature and oxygen pressure was similar to that found in the benzene experiments.

m-Xylene also oxidized in the ring to form a phenolic compound in greater amounts than in the side chain to form a carboxylic acid. The compound found was 1,2-xylen-4-ol, boiling at 209–212° C. It formed a solid derivative upon bromination, melting at 179–180° C. A small amount of *m*-toluic acid (melting at 107–108° C.) was also found. It formed an amide, melting at 94–95° C. Neither phthalic acid nor its anhydride was isolated. A relatively large amount of hydrocarbon polymer was obtained, which is probably a mixture of di- and polyxylyls.

In an experiment using *tert*-butylbenzene, the reaction products found were carbon, carbon dioxide, and water. No other substances were isolated and no *tert*-butylbenzene was recovered. In another experiment at 100° C. in which no extra oxygen carrier was added, an explosive reaction was obtained.

Upon oxidation naphthalene yielded three products that were identified. A small amount of β-naphthol was found. An abundance of carbon was obtained. A trinaphthyl was separated and obtained relatively pure. It was a yellow solid, melting at 119–120° C., boiling at 360–362°, soluble in cold benzene, hot methanol, and hot ethanol, and insoluble in water and in cold concentrated sulfuric acid. It was soluble in hot concentrated sulfuric acid, turning a violet color that became red-brown on further heating. Alcoholic solutions were fluorescent. A blue-black color formed on freshly sublimed aluminum chloride similar to that formed by a chloroform solution of naphthalene. The picrate of the trinaphthyl was in the form of orange-red needles, melting at 182–183° C. Fuming nitric acid in concentrated sulfuric acid formed a brown solid, melting at 220–224° C. A molecular weight estimation by the Rast camphor method gave 363 and 364. A small amount of other hydrocarbon polymer was also found.

Benzotrifluoride was treated with oxygen in a manner similar to that used for the other compounds. In an experiment in which a metallic oxide and some water were present, benzoic acid and benzoyl fluoride were found, and none of the benzotrifluoride was recovered. In another experiment in which care was taken to exclude water and no oxide was added, a small amount of benzoic acid and benxoyl fluoride were found. The rest of the starting material was recovered, and no carbon was obtained. Check experiments showed that benzotrifluoride is completely hydrolyzed to benzoic acid by a mixture of hydrogen fluoride and water at 100° C.; it was also found that benzoic acid, when mixed with hydrogen fluoride in a mole ratio of 1 to 24 and heated to 150°, yielded no more than a trace of benzoyl fluoride. These experiments indicate that two of the fluorine atoms can be removed by oxidation of benzotrifluoride but also show the more striking fact that the compound is very resistant to oxidation in the ring. Under similar conditions other compounds are oxidized either to phenolic compounds or to carbon and water. The benzotrifluoride used was prepared in a method similar to that reported previously (*1*) from benzotrichloride and hydrogen fluoride except that the mixture was placed in the bomb in the shaking machine. A 66% yield was obtained at 92° C. in 3.5 hours without working the residues. A pressure of 120 pounds per square inch was maintained.

OXIDATION OF ALIPHATIC COMPOUNDS

Experiments were performed using cyclohexane, methylcyclohexane, and *n*-heptane. In each case the only products found were carbon and water. A higher temperature was necessary than in experiments with aromatic compounds, which indicates a greater resistance to this type of oxidation. This agrees with the oxidation of toluene to form cresol in preference to benzoic acid.

CARBON FORMATION

The carbon formed in these experiments was, surprisingly, an activated char. It had decolorizing properties. Its density was a function of the temperature of the reaction, higher temperature producing a more dense form. It was not contaminated with tarry substances. Tars were not found as products from the oxidation of either aromatic or aliphatic substances. All of the organic compound may be converted to carbon without gaseous products, depending only upon the use of sufficient oxygen. In most of the experiments reported in Table I, only a relatively small amount of oxygen was present in the vessel and the reaction proceeded only as far as this was used.

LITERATURE CITED

(1) Simons, J. H., and Lewis, C. J., *J. Am. Chem. Soc.*, 60, 492 (1938)
(2) Simons, J. H., and Passino, H. J., *Ibid.*, 62, 1624 (1940).

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PROPERTIES OF FLUOROCARBONS

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THE main chemical characteristic of fluorocarbons is due to the great stability of the C—F bond. Thus, particularly in contrast to chlorocarbons, they show remarkable thermal stability and molecules with long carbon chains, similar to those of hydrocarbons and their derivatives, are possible. They are furthermore characterized by their great chemical inertness and resistance to oxidation. The physical properties of fluorocarbons are compared with those of hydrocarbons of the same carbon structure, and a number of regularities observed. Their boiling points and volatilities are close together, but the fluorocarbons have about double the density of hydrocarbons and remarkably low indices of refraction. On the basis of present information, it is not premature to conclude that we are confronted here with a vast new field of inorganic "organic chemistry", a field potentially as immense in size and as varied, both in compounds and reactions, as that of ordinary organic chemistry.

IN THE fall of 1941 work was started at Columbia, and extended to various other universities, having as its objective the development of certain liquid and solid compounds with special properties required by the Atomic Energy Project. From the behavior of those fluorocarbons, C_xF_y, which were described by Simons (*26*), Grosse suggested in 1940 that compounds of this chemical type might be satisfactory for the intended purpose. A few cubic centimeters of a mixture of liquid fluorocarbons, practically all of the available supply, were secured from Simons, tested (*8*), and found to be satisfactory. Further intensive research was indicated.

As the result of a great cooperative effort by both university and industrial laboratories, a large number of new compounds containing only carbon and fluorine (fluorocarbons) were discovered. A large amount of data on their properties has accumulated, and the purpose of this paper is to compare the fluorocarbons with hydrocarbons of the same carbon skeleton.

On the basis of information now available, it is not premature to conclude that we are confronted here with a vast new field of inorganic "organic chemistry", which is potentially as immense and as varied as that of ordinary organic chemistry. If we consider, in addition, the mixing of fluorocarbon compounds or their radicals with classical organic compounds or their respective radicals these potentialities become staggering. (Approximately 10^6 organic compounds are now known; in view of the stability of fluorocarbons and their derivatives, a similar number is possible. The number of possible "mixed" compounds is thus 10^{12}.)

At the time that work on the fluorocarbons was started, only the first gaseous members of the fluorine paraffin series—namely, CF_4, C_2F_6, C_3F_8, and C_4F_{10}—and $CF_2{=}CF_2$, were known as pure compounds, and some information was available on one or two pure liquid fluorocarbons. By the summer of 1942 a large number of pure, liquid fluoroparaffins and -naphthenes, both mono- and bicyclic, were available.

The first practical and general way to produce them was the CoF_3 method of Fowler and associates (*6*) at Johns Hopkins. This was followed shortly after by Columbia's catalytic method and later by others.

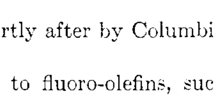
The first references to fluoro-olefins, such as $CF_2{=}CF_2$, are found in early papers by Otto Ruff and A. L. Henne. Since then our knowledge of fluoro-olefins has substantially increased. Fluorodiolefins, such as fluorobutadiene (C_4F_6), were first isolated by W. T. Miller, and cyclo-olefins, such as fluorocyclobutene (C_4F_6), by Henne. Representatives of fluoroaromatics, such as hexafluorobenzene (C_6F_6), have been synthesized by E. T. McBee and co-workers.

Table I lists all fluorocarbons known to date with their physical properties.

NOMENCLATURE OF FLUOROCARBONS

The classical nomenclature becomes cumbersome, particularly for compounds containing many atoms of fluorine and only a few of hydrogen. For example, $CF_3—CFH—CF_2—CF_2—CF_2—CF_2—CF_2—H$ would be called 1,1,1,2,3,3,4,4,5,5,6,6,7,7-tetradecafluoroheptane.

We have found it convenient to use the Greek letter phi as a symbol to indicate complete substitution of all hydrogen atoms attached to carbon by fluorine in the compound following the symbol. For example, Φ-heptane is C_7F_{16}, and the hydrofluorocarbon mentioned above is 1,6-dihydro-Φ-heptane. Similarly Φ-cyclohexane, pronounced phi-cyclohexane, is:



Bigelow's $C_6F_{11}H$ would be named monohydro-Φ-cyclohexane, whereas its regular Geneva organic name would be 1,2,2,3,3,4,4,5,5,6,6-undecafluorocyclohexane. Further examples are Φ-benzoic acid (C_6F_5COOH), Φ-ethyl alcohol (C_2F_5OH), and Φ-ethyl-Φ-benzoate ($C_6F_5—COOC_2F_5$). The letter Φ was chosen as the Greek equivalent for the Latin F, symbol of the element.

We believe that this departure from organic nomenclature is warranted, particularly since we do not consider this new field of chemistry a part of regular organic chemistry.

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