Journal of Fluorine Chemistry, *65* (1993) 67–71

Interaction of perfluorocarbons with carbon*

F.J. Weigert

Central Research and Development Department, E.I. Du Pont de Nemours & Co., Wilmington, DE 19880-0328 (USA)

(Received August 18, 1992; accepted January 12, 1993)

Abstract

Activated carbon is an effective stoichiometric fluorine acceptor which defluorinates perfluoroalkanes with the partial structure $(R_f)_2CFCF(R_f)_2$ to alkenes and perfluoroalkenes to dienes. Carbon catalyzes double-bond shifts, as well as *cis/trans* and ring-chain perfluoro-olefin isomerizations. Carbon effectively catalyzes TFE and HFP dimerizations. Less effectively, carbon catalyzes further oligomerization of TFE to give low yields of linear, internal olefins.

Free radicals may be the key surface intermediates.

Introduction

Much is known about the catalytic chemistry of saturated hydrocarbons, primarily through the efforts of the petroleum industry [1]. The chemistry of the perfluorocarbon alkanes is less well-developed. For example, there is a voluminous literature on the dehydrogenation of alkanes to alkenes. However, there are only a few references to the defluorination of perfluoroalkanes to perfluoroalkenes [2]. In contrast to catalysts which produce hydrocarbon olefins and H_2, perfluoroalkane defluorination requires a stoichiometric amount of fluorine acceptor. The thermodynamics of F_2 elimination is unfavorable because of fluorine's low bond strength. Metals with strong M–F bonds are good acceptors [3]. Harsh conditions have limited the studies to simple perfluorocarbons mostly to make perfluoroaromatics. There is one report of carbon as a defluorinating reagent. Passing perfluoro-1,2-dimethylcyclohexane over *unactivated granular carbon* at 600 °C produced a complex mixture of aromatic fluorocarbons [4].

The chemistry of fluoro-olefins is slightly better developed. Fluoride anion plays a similar role in oligomerizing fluoro-olefins by anionic processes [5] as does that of a proton in oligomerizing hydrocarbon olefins by cationic processes [6]. Heating tetrafluoroethene (TFE) or hexafluoropropene (HFP) in the liquid phase with no catalyst gives 2+2 cyclodimers. Carbon catalytically dimerizes HFP to perfluoro-2-methyl-2-pentene in the vapor phase [7]. This same dimer can be produced in the liquid phase by fluoride-ion catalysis [8]. Harmon reported carbon-catalyzed, vapor-phase, TFE dimerization and oligomerization nearly 40 years ago [9]. By analogy with the thermal reaction, he *assumed* the dimer product was perfluorocyclobutane and the higher oligomers were larger rings.

By analogy with previous work, using carbon acts as a dealkylation catalyst [10] allows other chemistry [11] and accelerates free-radical mechanisms.

Results

Defluorination

High-surface-area carbon can act as a fluorine acceptor in the defluorination of perfluoroalkanes [12] or perfluoroalkenes [13]. The defluorinations occur in either the liquid or vapor phase. The temperatures required are below those required by traditional defluorinating agents such as nickel, iron or platinum. The necessary structural features of the defluorination reaction were found by the pattern of successes and failures with specific substrates.

Perfluoro-2, 3-dimethylbutane

Perfluoro-2,3-dimethylbutane (**1**) is thermally stable at 400 °C in the presence of SiC. In the vapor phase, in the presence of carbon, two volatile products form in a sequential reaction scheme. Carbon is not a catalyst, because the ratio of products to starting material decreases as measured by on-line GC methods over timescales of a few minutes. Table 1 shows the normalized product analyses of a sequence of samples under identical conditions.

---

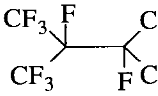
*Contribution No. 6303.

0022-1139/93/$6.00

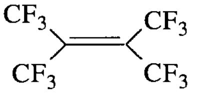
TABLE 1. Production distribution in 2,3-dimethylbutane defluorination[a]

Product (mol%)		
1	**2**	**3**
55	20	20
62	21	9
71	16	2
79	13	1

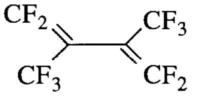
[a]Conditions: Carbon 2.5 g; liquid flow, 2 ml h^{-1}; N_2 flow, 5 ml min^{-1}.



1



2



3

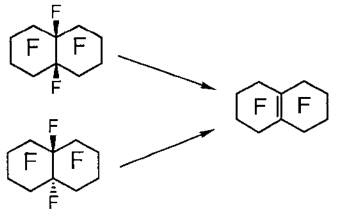
^{19}F NMR spectroscopy [14] and GC–MS methods identified the two products. Tetrakis(trifluoromethyl)ethene (**2**) is the primary product and perfluoro-2,3-dimethylbutadiene (**3**) the secondary. Only traces were found of the ring-closed isomer of **3**, perfluoro-1,2-dimethylcyclobutene (**4**). A kinetic analysis of the three-component composition showed that the defluorination of **2** is 1.8-times faster than the defluorination of **1** [15].

Elemental analysis of the recovered carbon showed approximately 15% fluorine. The fluorine lost by **1** and **2** appears bonded to the carbon. Carbon is thus a REAGENT!

Perfluorodecalin

Perfluorodecalin (**5**) was a nearly equal mixture of the *cis* and *trans* isomers. Passing **5** through a bed of SiC at 400 °C with a contact time of a few seconds produces no products. Under the same conditions, carbon defluorinates *cis*-(**5**) to perfluoro-9,10-octalin (**6**) while *trans*-(**5**) survives intact.

At higher temperatures, further defluorination occurs. NMR peaks consistent with perfluorotetralin are visible, and GC–MS analysis suggested a hexalin isomer as a minor product. Heating perfluorodecalin with carbon in a closed system at 450 °C/2 h produced only **6** with complete conversion of both isomers of **5**. In neither case was perfluoronaphthalene a product.



5 **6**

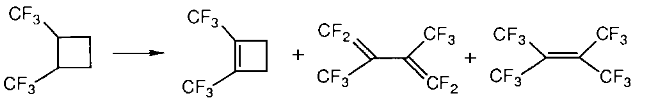
Perfluoro-1-methyldecalin

Perfluoro-1-methyldecalin was passed over carbon at 400 °C. The product still contained three isomers of the starting material $C_{11}F_{20}$. MS showed that of the three new GC peaks, one was an octalin, $C_{11}F_{18}$, and two were tetralins $C_{11}F_{14}$. The ^{19}F NMR peak at δ −57.8 ppm (t, 23; 7%) is consistent with the CF_3 resonances of perfluoro-2-methyltetralin. The peak at −55.2 ppm (t, 26; d, 29; 1%) is consistent with that of perfluoro-1-methyltetralin. ^{19}F NMR spectroscopy suggested that the double bond of the octalin was in the 9–10 position, because there were no resonances in the region expected for $C{=}C(CF_3)$ [14]. There were no perfluoromethylnaphthalenes. A batch experiment gave the same products in different ratios.

HFP cyclic dimer

No products were formed from passing HFP cyclic dimer **7** over SiC at 450 °C. The ^{19}F NMR spectrum of the effluent from passing **7** over carbon at 400 °C showed four components, starting material and three products **2**, **3** and **4**. Table 2 shows the selectivity as a function of the conversion of compound **7**.

Olefin **2** is formally an *isomer* of the starting material, while the other two result from defluorination. All three products form by parallel paths from **7**. Diene **3** is also a secondary product formed by ring-opening of cyclobutene **4**.



7 **4** **3** **2**

Perfluoroperhydrophenanthrene

Perfluoroperhydrophenanthrene (**8**) (1 ml) reacted completely with 2 g of carbon in a sealed vessel at 400 °C for 4 h. Defluorination of **8** might lead to several defluorinated products. We easily identified the NMR

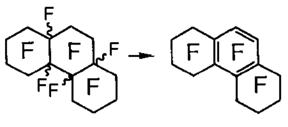
TABLE 2. Product distribution in HFP cyclic dimer defluorination[a]

Conversion of 7 (%)	Product (mol%)		
	2	**4**	**3**
18	17	24	59
11	28	23	49
12	39	19	42
12	45	18	36[b]
9	44	17	39[c]

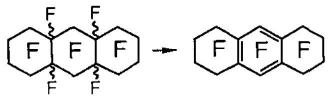
[a]Conditions: Carbon, 10 g; N_2 flow, 20 ml min^{-1}; liquid flow, 2 ml h^{-1}; temp., 400 °C.
[b]Liquid flow, 1 ml h^{-1}; N_2 flow, 10 ml min^{-1}.
[c]Liquid flow, 1 ml h^{-1}.

peaks arising from octadecafluorophenanthrene (**9**) [14, 16]. However, no amount of juggling could fit the remaining peaks in the NMR spectrum to other fluorination states of perfluorinated phenanthrenes.

Our fluorine chemical shift database [14] contained the spectrum of octadecafluoroanthracene (**10**) [16]. These resonances matched exactly with the extra peaks in the defluorination mixture. The product contained both anthracene and phenanthrene derivatives, in the ratio of 1:2. Compounds **9** and **10** did not further defluorinate over carbon in the vapor phase at temperatures up to 600 °C.



9



10

Perfluoromethylcyclohexanes

Perfluoromethylcyclohexanes defluorinate over carbon at 400 °C to give perfluorocyclohexenes. However, defluorinations to cyclohexenes are only marginally competitive with further reactions to form aromatic products.

Perfluoro-1,3-dimethylcyclohexane (**11**) produced all three perfluoroxylenes, along with perfluorotoluene and three isomers of perfluorotrimethylbenzene. We do not know at what oxidation level disproportionation and methyl scrambling occurred. Heating **11** with carbon in a sealed system gave low yields of aromatic products along with extensive fragmentation.

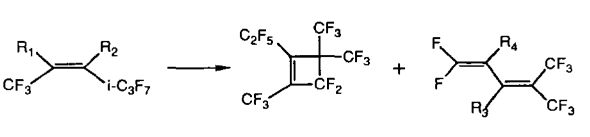
Heating perfluoromethylcyclohexane with carbon at 450 °C for 2 h in a sealed system gave a mixture containing 36% starting material, 7% perfluoro-1-methylcyclohexene and 45% perfluorotoluene as established by ^{19}F NMR spectroscopy.

HFP trimers

HFP trimers **12** and **13** survived (84%) passage, through SiC at 400 °C in a flow system with a contact time of a few seconds. The products were HFP and its linear dimer, the result of cracking. Carbon produced products even at 250 °C and only traces of the trimers survived at 350 °C. GC–MS and NMR methods identified four products in two pairs.

The first set, HFP and its dimer **21**, are the same as those seen with SiC. The other products were perfluoro-2,3-dimethylbutane (**1**) and the perfluorocyclobutene **14**. These result from a formal disproportionation, as **1** has the two fluorines lost by **14**.

The same HFP trimers were heated with carbon in a closed system at 400 °C for 2 h. The resulting product contained three isomers of C_9F_{16}. Detailed analysis of the GC–MS patterns suggested the structures **14**, **15** and **16** for the products. Compound **14** results from the cyclization of **16**. Compounds **15** and **16** are 1,3-fluorine shift isomers. Compound **1** was not present in the liquid-phase reaction. These products have been observed previously in HFP oligomerization with KF/carbon [17], but the complexity of the reaction was not appreciated. The products, including those of fluorine disproportionation, were referred to simply as HFP oligomers.



	R_1	R_2		R_3	R_4
12	F	i-C_3F_7	**15**	F	i-C_3F_7
13	CF_3	C_2F_5	**16**	C_2F_5	CF_3

14

Miscellaneous

Neither octafluorocyclobutane nor decafluorobutane formed any products when passed over carbon at 400 °C.

Isomerization

Carbon catalyzes double-bond shifts, as well as *cis*/*trans* and ring-chain perfluoro-olefin isomerizations.

Perfluoro-2-butene

Passing a mixture of commercial ‘perfluoro-2-butene’ (which contains all three linear isomers) over carbon changed the isomer ratio. At 300 °C, the equilibrium consisted of 66% perfluoro-*trans*-2-butene, 29% perfluoro-*cis*-2-butene and 3% perfluoro-1-butene. Up to 500 °C, no reaction other than this isomerization occurred. Data from carbon were combined with information from other catalysts. The slope of an Arrhenius plot gave an enthalpy difference of 8.1 kcal mol^{-1} for *F*-1-butene versus *F*-*trans*-2-butene.

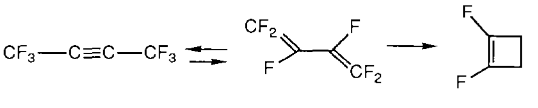
Perfluoro-1-heptene

Carbon isomerizes perfluoro-1-heptene at 400 °C in a vapor-phase reaction. ^{19}F NMR spectroscopy confirmed the presence of *cis* and *trans* isomers of both 2- and 3-heptene. The equilibrium is 5.6% *cis*-2, 17% *trans*-2, 15% *cis*-3 and 62% *trans*-3. Only traces of the starting material remained. Correlations from our database [14] aided product identification, because earlier work [18] had misassigned the configurational isomers. The most characteristic NMR resonances are those of the CF_3 group closest to the double bond. Their positions are *t*-2 (−69.4 ppm), *c*-2 (−65.9 ppm), *t*-3 (−85.2 ppm) and *t*-2 (−84.3 ppm).

$$F_2C{=}CFC_5F_{11} \longrightarrow c+t\text{-}CF_3CF{=}CFC_4F_9 \rightleftharpoons c+t\text{-}C_2F_5CF{=}CFC_3F_7$$

Perfluorobutadiene

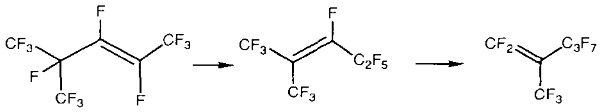
Miller and Resnick studied the fluoride ion-catalyzed isomerization of perfluorobutadiene **17** to perfluoro-2-butyne (**18**). They identified perfluoro-1,2-butadiene as an intermediate [19]. When passed over carbon in the vapor phase above 125 °C, **17** isomerizes first to **18**, but in a sequential process also cyclizes to perfluorocyclobutene **19**. Compound **18** isomerizes to **19** above 200 °C, but does not form any **17**. Compound **19** does not produce either of the other isomers. Adventitious proton sources also produce the HF addition product $CF_3CF{=}CHCF_3$.



18 **17** **19**

Linear HFP dimers

Carbon catalyzes the isomerization of HFP dimer **20** to **21** in the vapor phase. This process is not overwhelmingly faster than the formation of **20** directly from HFP [7]. Either **20** never forms in the carbon-catalyzed HFP dimerization reaction or surface **20** rearranges to surface **21** faster than it desorbs. Passing HFP dimer **21** over carbon produced a third isomer which NMR and GC–MS methods identified as perfluoro-2-methyl-1-pentene (**22**). Mixtures were produced containing up to 8% **22**. HFP dimer **22** is not stable at room temperature in an NMR tube. It is a homolog of the notoriously toxic, but reactive perfluoroisobutene.



20 **21** **22**

Oligomerization

Tetrafluoroethene

In hydrocarbon chemistry, different ethylene dimerization catalysts can produce different kinetically controlled mixtures of the three butene isomers [20, 21]. Treating TFE with F^- gives highly branched oligomers by anionic processes [8].

Passing TFE over carbon at 300 °C gives an equilibrium mixture of perfluorobutenes in high yield. Perfluorobutene isomerization is rapid compared to TFE dimerization. At higher temperature, further oligomerization occurs to mixtures of straight-chain, essentially linear, internal olefins.

$$F_2C{=}CF_2 \longrightarrow CF_3CF{=}CFCF_3 \longrightarrow R_fCF{=}CFR_f$$

The ^{19}F NMR spectrum of these oligomers is quite different from that reported for the fluoride ion-catalyzed product [22]. Harmon's [9] assignment of structures as cyclo-oligomers is incorrect based on the ^{19}F NMR spectrum. Each perfluorocycloalkane has a single, sharp NMR resonance at distinct chemical shifts. The major NMR resonances of the TFE oligomer between −110 and −130 ppm are consistent with CF_2 groups in an aliphatic chain [14]. Minor resonances between −154 and −158 ppm are characteristic of $=CF$ in *trans*, internal olefins. There are no tertiary fluorines with resonances upfield of −170 ppm. The major CF_3 resonance at −81 ppm is consistent with the end of an unbranched aliphatic chain. The minor resonance at −85 ppm is consistent with $\mathit{CF_3}CF_2CF{=}$. The ratio of CF_3 groups below −80 ppm to those above is 1:3.

GC–MS analysis established both compounds of formula C_nF_{2n}, true TFE oligomers and defluorination products with the formulas C_nF_{2n-2}. The product distribution arises from a true catalytic oligomerization coupled with stoichiometric defluorination. GC–MS found oligomers up to C-12. The major by-product was perfluoroethane, the result of fluorine transfer to TFE. Since linear olefins isomerize, but do not defluorinate, under the reaction conditions, the dienes may form from an intermediate via a radical termination step. Stoichiometric defluorinations limit catalyst life.

Discussion

Carbon is an effective stoichiometric reagent for defluorinating perfluoroalkanes to olefins when the olefin product has four carbon substituents on the double bond. The defluorination works with acyclic, monocyclic and polycyclic compounds.

Defluorination of the commercial product called perfluoroperhydrophenanthrene produces products with anthracene rings. When is the anthracene ring formed? It could be during the fluorination or the defluorination. Fluorination is a more likely point for ring-catenation isomers to form because carbenium ions are produced [23, 24]. The ^{19}F NMR spectrum of the starting material is too complex to even count the number of isomers present. We believe it is a mixture of all possible *cis*/*trans* isomers of the two tricyclic ring structures.

Thermodynamically, this defluorination is a reasonable reaction. For every olefin created by the loss of fluorine from the low molecular weight materials, presumably one carbon double bond is fluorinated.

Olefin isomerization was the predominant reaction in any olefin with less than four carbon substituents on the double bond. Olefins with four substituents defluorinated to dienes and, if possible, further to aromatic products. Olefin isomerization can re-establish structures conducive to further defluorination.

The isomerization of the HFP cyclic dimer **7** to olefin **2** was unexpected. Carbon, partially fluorinated during the initial stages of the reaction, might itself be a mild fluorinating agent. A formal 1,4-addition of F_2 to diene **3** would give **2**. Diene **3**, formed by ring-opening of the initial defluorinated product **4**, might not desorb rapidly in competition with fluorination to **2**. Thus, there seems to be a direct path from **7** to **2**. Similarly, fluorinated carbon may transfer fluorine to TFE to form perfluoroethane. This reaction mode is restricted to the more energy-rich perfluoro-olefins.

Experimental

General remarks

^{19}F NMR spectra in $CDCl_3$ with $CFCl_3$ as internal standard were recorded on a Nicolet NT-220 spectrometer at 188.2 MHz. The carbon used in this work was a coconut charcoal sold by Calgon as 'PCB'. Product analyses were first conducted by on-line capillary GC methods. If new peaks were present, the product was collected and submitted for NMR and GC–MS analyses. A 30 m FS-1265 capillary column, a CF_3CH_2O–silicone derivative, separated most of the mixtures by empirical formula. The column only rarely separated individual isomers. A 25 m Carbowax capillary operating isothermally at 65 °C separated all four isomers of the internal perfluoroheptenes with retention times of less than 1 min. A 6 ft.×1.8 in. Carbopack C column separated the three linear perfluorobutene isomers. The He flow rate used was 20 ml min^{-1} and the column was operated isothermally at 70 °C. The retention times were *F-trans*-2-butene, 1.6 min; *F-cis*-2-butene, 1.9 min; and *F*-1-butene, 2.4 min.

Liquid-phase defluorination

A mixture consisting of 2 g carbon and 1 ml of 'perfluoroperhydrophenanthrene' (12089-9 from PCR division of SCM) was heated in a metal reactor at 400 °C for 4 h. The carbon recovered was extracted with chloroform and the product isolated by evaporation of the solvent.

Heating 3.5 ml perfluorodecalin and 2.8 g carbon in a 10 cm^3 reactor at 425 °C for 6 h gave about 90% selectivity to the octalin in three separate runs.

Vapor-phase defluorination

Liquids were fed using a Sage syringe pump to a bed of carbon in a 3/4 in×5 in. Vycor® reactor heated in a split tube furnace. A typical carbon charge was 3 g. Typical liquid flow rates were 0.5–2 ml h^{-1} liquid with 5–20 ml min^{-1} N_2 as carrier gas. The reaction effluent was passed through heated lines to a Valco® 10-port sample valve in a Varian-6000 GC instrument equipped with a flame ionization detector.

Acknowledgements

The author thanks Doug Anton for valuable discussions concerning the reversibility of the defluorination mechanism.

References

1 P.B. Venuto and E.T. Habib, Jr., *Fluid Catalytic Cracking with Zeolite Catalysts,* Marcel Dekker, New York, 1979.
2 B. Gething, C.R. Patrick, M. Stacey and J.C. Tatlow, *Nature (London), 183* (1959) 588.
3 D. Harrison, M. Stacey, R. Stephens and J.C. Tatlow, *Tetrahedron, 19* (1963) 1893.
4 C.R. Patrick, A.E. Pedler, A. Seabra, R. Stephens and J.C. Tatlow, *Chem. Ind. (London),* (1963) 1557.
5 R.E. Banks, *Fluorocarbons and Their Derivatives,* Oldbourne Press, London, 1964, p. 20.
6 J.P. Kennedy and E. Marechal, *Carbocationic Polymerization,* Wiley, New York, 1982.
7 L.G. Anello and R.F. Sweeney, *US Pat. 4 377 717* (1983); [*Chem. Abs., 98* (1983) 215 174].
8 R.D. Dresdner, F.N. Tlumac and J.A. Young, *J. Org. Chem., 30* (1965) 3524.
9 J. Harmon, *US Pat. 2 404 374* (1946); [*Chem. Abs., 40* (1946) 7234].
10 F.J. Weigert and J.M. Ragosta, *J. Mol. Catal.,* accepted for publication.
11 R.W. Coughlin, *Ind. Eng. Chem., Prod. Res. Dev., 8* (1969) 12.
12 F.J. Weigert, *US Pat. 4 820 883* (1989); [*Chem. Abs., 112* (1989) 7024].
13 F.J. Weigert, *US Pat. 4 820 884* (1989); [*Chem. Abs., 112* (1989) 8026].
14 F.J. Weigert and K.J. Karel, *J. Fluorine Chem., 37* (1987) 125.
15 F.J. Weigert, *Comput. Chem., 11* (1987) 273.
16 J. Burdon, J.R. Knights, I.W. Parsons and J.C. Tatlow, *Tetrahedron, 30* (1974) 3499.
17 Y. Ohsaka and T. Tohzuka (to Daikin Kogyo Co. Ltd.), *Ger. Offen 3 027 229* (1981); [*Chem. Abs., 94* (1981) 191 660].
18 A. Battais, W. Granier, B. Boutevin, Y. Pietrasanta and L. Cot, *J. Fluorine Chem., 13* (1976) 97.
19 W.T. Miller, W. Frass and P.R. Resnick, *J. Am. Chem. Soc., 83* (1966) 1767.
20 A.M. Al-Jarallah, J.A. Anabtawi, M.A.B. Siddiqui and A.M. Aitani, *Catalysis Today, 14* (1992) 1.
21 T. Alderson, E.J. Jenner and R.V. Lindsey, *J. Am. Chem. Soc., 87* (1965) 5638.
22 D.P. Graham, *J. Org. Chem., 31* (1966) 955.
23 J. Burdon, *J. Fluorine Chem., 35* (1987) 15.
24 J. Burdon, S.T. Ezmirly and T.N. Huckerby, *J. Fluorine Chem., 35* (1987) 15.