Journal of Fluorine Chemistry, *47* (1990) 261–272
Received: June 16, 1989; accepted: July 31, 1989

FREE-RADICAL INITIATED ADDITION OF CARBON TETRACHLORIDE TO FLUORO OLEFINS*

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SUMMARY

The reaction between carbon tetrachloride and unsymmetrical fluoro olefins, e.g. $RCF{=}CF_2$, where $R{=}n\text{-}C_5F_{11}$ and C_6F_5, has led to the addition product, $RCFClCF_2CCl_3$. Addition was apparently unidirectional under the conditions used since the isomeric adduct $RCF(CCl_3)CF_2Cl$ could not be detected. The effects of experimental conditions such as free radical initiators, temperature, and time are discussed for the different reactions studied. A probable mechanism is suggested for these additions.

INTRODUCTION

The free-radical addition reactions of halogenated paraffins to olefins have been reported to proceed according to the general reaction shown in Eqn.1.

$$>C{=}C< \; + \; CX_3Y \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\substack{|\\CX_3}}{C}}-Y \qquad (1)$$

The generalized process can be described as proceeding in various steps as shown by Eqns. 2 through 5.

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*Presented at the American Chemical Society 12th International Symposium on Fluorine Chemistry, August 7-12, 1988, Santa Cruz, CA, paper number P224.

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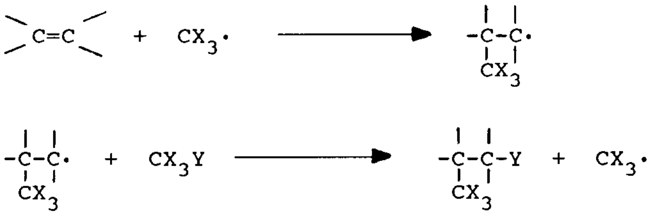
$$CX_3Y \xrightarrow{A\cdot} CX_3\cdot + AY \qquad (2)$$



$$>C=C< + CX_3\cdot \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\underset{CX_3}{|}}{C}}\cdot \qquad (3)$$

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\underset{CX_3}{|}}{C}}\cdot + CX_3Y \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\underset{CX_3}{|}}{C}}-Y + CX_3\cdot \qquad (4)$$

$$CX_3\cdot + CX_3\cdot \longrightarrow C_2X_6 \qquad (5)$$

The free-radical A· is generally produced from the thermolysis of compounds such as dibenzoyl peroxide, di-tert-butyl peroxide, azobisisobutyronitrile, etc. In high concentrations of CX_3Y, possessing a weak bond between CX_3 and Y the major product produced is from the addition of the halogenated paraffins to olefins [1,2]. As for example, the reaction between carbon tetrachloride, n-octene-1 and a $RuCl_2(Ph_3P)_3$ catalyst at 80°C produced the 1,1,1,3-tetrachlorononane in high yield (97%, 75% conversion) [3]. One might expect that the addition reaction between carbon tetrachloride and perfluoro olefins should be quite different from hydrocarbon olefins due to the electronic and/or steric effects of the fluorine atoms and perfluoroalkyl group. For example, Paciorek and coworkers [4] reported the attempted reactions between carbon tetrachloride and perfluoroheptene-1. No reaction products were detected at 295°C for 4 h, while the addition product $n\text{-}C_5F_{11}CFClCF_2CCl_3$ and two unknown products were detected after irradiation with ultraviolet light for 16 h. From these results it can be seen that the addition of carbon tetrachloride to perfluoro olefin is more difficult than the hydrocarbon olefin. The addition of carbon tetrachloride to fluorinated olefins promoted by Lewis' acids such as $AlCl_3$ is less desirable from the preparative point-of-view, since the desired product yields are usually lower and a complex mixture of inseparable products is formed [5,6].

Our present studies on the addition reactions of carbon tetrachloride to perfluoro olefins with various initiators under free-radical conditions are reported in this paper.

RESULTS AND DISCUSSION

The free-radical addition reaction between carbon tetrachloride and n-perfluoroheptene-1 was examined in more detail. The reactions were carried out under various experimental conditions of free-radical initiators, temperature and time. From the experimental results (see Table 1), it can be seen that azobisisobutyronitrile was the best initiator at 180°C and one day reaction time. Table 2 indicates that the yield of product increased as a function of temperature and reaction time. After three days the rate of addition was very slow (see Table 2, exp. 3). In order to increase the yield, it was necessary to add fresh azobisisobutyronitrile (3 mole % based on olefin) periodically (see Table 2, exp. 4). Increasing the temperature, >190°C, increased the by-products, n-$C_5F_{11}CFHCF_2CCl_3$, C_2Cl_6, etc. The GC trace and MS data are listed in Figure 1 for the reaction

TABLE 1

Addition Reactions of CCl_4 with $n\text{-}C_5F_{11}CF{=}CF_2$ - Free Radical Effect

Free Radical Initiator[a]	Conditions		Product, GC Area %		
	°C	Day	Unreacted Olefin	$n\text{-}C_5F_{11}CFClCF_2CCl_3$	Others[d]
$Ni(Ph_3P)_4$	180	1	97	1	2
$Ni(Ph_3P)_2(CO)_2$	180	1	82	4	14
	200	5	74	12	14
Bz_2O_2[b]	200	1	88	5	7
		5	73	12	15
ABN[c]	180	1	85	10	5
		4	59	29	7

[a] No reaction using initiators CuCl, $Co_2(CO)_8$, $RuCl_2(Ph_3P)_3$ and $(CH_3)_3COOC(CH_3)_3$. 3 mole % of initiator with olefin was used.

[b] Bz_2O_2: dibenzoyl peroxide.

[c] ABN: azobisisobutyronitrile.

[d] $n\text{-}C_5F_{11}CFHCF_2CCl_3$ and unknown compounds.

TABLE 2

Addition Reactions of CCl_4 with n-$C_5F_{11}CF{=}CF_2$ - Temperature and Time Effect[a]

	Conditions		Product, GC Area %		
Experiment	°C	Day	Unreacted Olefin	n-$C_5F_{11}CFClCF_2CCl_3$	Others[b]
1	64	3	100	--	--
2	100	3	86	10	4
3	180	2 h	100	--	--
		1	85	10	5
		3	65	28	7
		7	60	30	10
4	185	3	64	28	8
		5[c]	51	40	9
		7[c]	38	52	10
		9[c]	29	60	11

[a] Initiator: azobisisobutyronitrile, 3 mole % based on olefin.

[b] n-$C_5F_{11}CFHCF_2CCl_3$ and trace unknown compounds.

[c] Fresh azobisisobutyronitrile (3 mole % based on olefin) was added periodically (once every two days) at 25°C under N_2 gas.

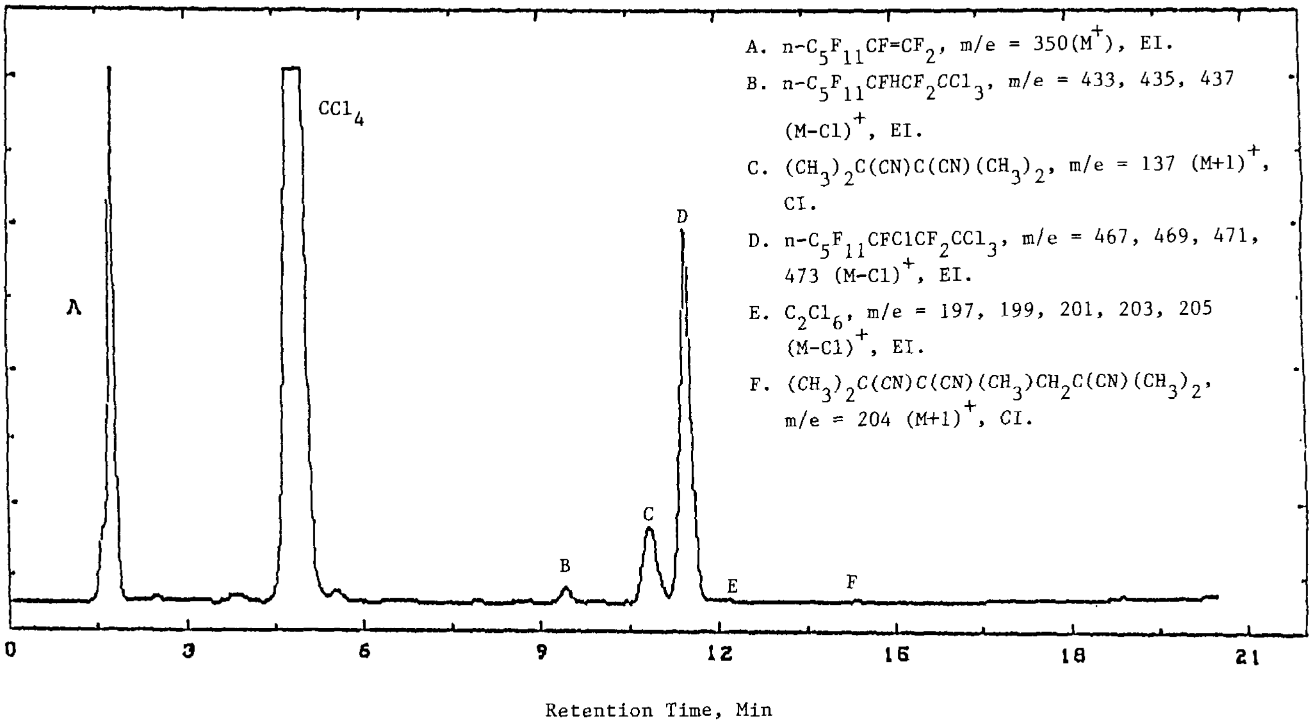


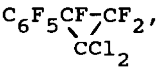
Fig.1. GC Trace and MS Data for Addition of CCl_4 to $n-C_5F_{11}CF=CF_2$.

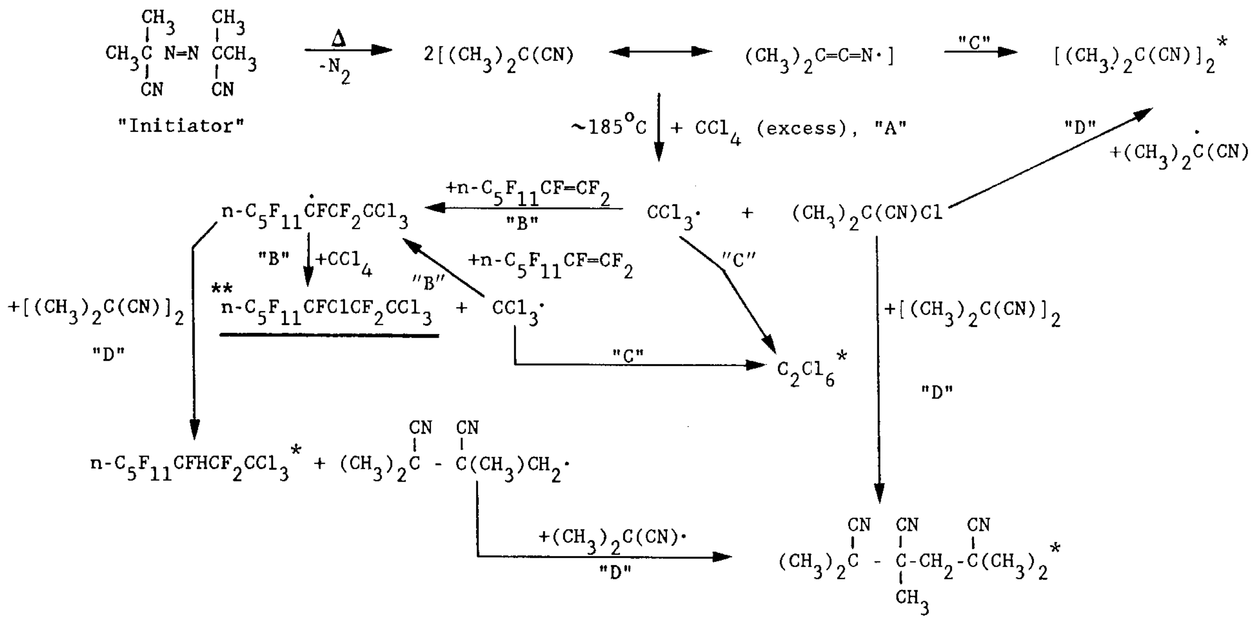
GC: 10% SP-2100 on 100/120 Supelcoport, 4' x 1/4" SS packed column, column temp.: 60-275°C, 10°/min, inj. and det. temp.: 280°C, flow rate: 30 ml/min., Det.: FID.

MS: duPont Model 21-490 mass spectrometer used in electron impact (EI) and chemical ionization (CI) modes.

between n-$C_5F_{11}CF{=}CF_2$ and CCl_4. The maximum yield of product obtained was 60 GC area % (50% isolated). The chemical structure of n-$C_5F_{11}CFClCF_2CCl_3$ was determined by mass spectral data, ^{19}F NMR, and infrared analyses.

The starting material, n-$C_5F_{11}CF{=}CF_2$, can be recovered and reused for subsequent addition reaction with carbon tetrachloride. The impurity from the decomposition of the initiator, e.g. $(CH_3)_2C(CN)C(CN)(CH_3)_2$ and $(CH_3)_2C(CN)C(CH_3)(CN)CH_2C(CN)(CH_3)_2$, was easily removed by silica gel column chromatography. The chemical structure of the by-products were characterized by GC/MS only. A possible mechanism for the formation of these by-products is suggested in Scheme 1.

Under similar reaction conditions, the addition reactions between carbon tetrachloride and other perfluoro olefins were investigated. No reaction was observed for either the internal olefin $C_3F_7CF{=}CFC_2F_5$ or the perfluorocyclohexene. The reaction between $C_6F_5CF{=}CF_2$ and CCl_4 produced the major product, $C_6F_5CFClCF_2CCl_3$ (65 GC area %; 51% isolated). The numerous by-products (total ~5 GC area %) from this reaction included $C_6F_5C(O)F$, $C_6F_5CFClCF_2Cl$,  $C_6F_5\underset{CCl_2}{CF{-}CF_2}$, $C_6F_5CF{=}CFCCl_3$, $C_6F_5CFHCF_2CCl_3$, $C_6F_5CF_2CF{=}CFCF_2C_6F_5$, and $C_6F_5CF(CF_2CCl_3)-CF{=}CFC_6F_5$. The chemical structures of these by-products were determined by GC/MS and are tentative assignments. Some unreacted olefin was recovered in 23% isolated yield. The reaction between the perfluorostyrene and CCl_4 appears to be more complicated than the perfluoro aliphatic olefins and CCl_4.



*By-products - detected by GC/MS; **Desired product.
"A" - Initiation; "B" - Propagation; "C" - Termination; "D" - Side Reaction

SCHEME 1. Suggested Mechanism.

From these experimental results, two conclusions for the free-radical addition of carbon tetrachloride to fluoro olefins have been reached: (a) reaction occurs only for terminal olefins; and (b) addition was unidirectional under the conditions used since the isomeric adduct $R_fCF(CCl_3)CF_2Cl$ could not be detected. Steric considerations may be the cause for the unidirectional addition.

EXPERIMENTAL

The $n-C_5F_{11}CF=CF_2$ (97% pure) was synthesized from thermal decomposition of dry sodium perfluorooctanate [7] in vacuum (10^{-2} mm Hg) at 280-320°C. Other perfluoro olefins were commercial products which were shown by GC to be ~97% pure. The carbon tetrachloride was a HPLC grade >99.9% pure and purchased from Aldrich Chemical Company, Inc. The high pressure reactor was a 4562 mini reactor with a 4842 controller (Parr Instrument Company, Moline, IL). The major compounds were characterized by IR, MS, ^{19}F NMR and combustion analysis. Infrared spectra were obtained on a Perkin-Elmer Model 600 infrared spectrophotometer. Gas chromatographic analyses (GC) were performed on a Perkin-Elmer Sigma 1 chromatograph using a six-foot stainless steel column (1/4" d) packed with 10 percent SP-2100 on chromasorb-W. Mass spectra were carried out on a duPont Model 21-490 mass spectrometer using an electron impact and chemical ionization modes. ^{19}F NMR spectra were recorded on a NT-300 spectrometer (at 282.3 MHz) using $CFCl_3$ for references and $CDCl_3$ for solvent.

General Procedure for the Reaction of Carbon Tetrachloride with Perfluoro Olefins

A mixture of n-$C_5F_{11}CF{=}CF_2$ (40.0 g, 0.114 mole), CCl_4 (176 g, 1.14 mole) and azobisisobutyronitrile (0.56 g, 3.42 mmole) were placed in a 300 ml stainless steel reactor under dry N_2 atmosphere. The reactor was heated at 185°C (±5°C) and ~160 psi. After every two days, the reactor was cooled to room temperature, and additional azobisisobutyronitrile (0.56 g, 3.42 mmole) was added periodically (see Table 2, exp. 4). After 10 days the whole reaction mixture was distilled to separate the low boiling compounds such as unreacted olefin and carbon tetrachloride. The pot residue was passed through a silica gel column (80 g) and eluted with petroleum ether (b.p. 35-60°C, 100 ml). The petroleum ether was removed by a rotary evaporator. Distillation of the crude product by a spinning band column distillation yielded n-$C_5F_{11}CFClCF_2CCl_3$ (28.7 g, 50% isolated and >99% pure).

n-$C_5F_{11}CFClCF_2CCl_3$ (n.c.)

Colorless liquid boiling at 80-81°C/10 mm Hg. IR spectrum (capillary film between NaCl plates) 1362 (m) 1310 (m), 1243-1124 (vs), 1013 (m), 965 (m), 955 (m), 887 (m), 850 (s) cm^{-1}. MS (EI) m/e 467, 469, 471, 473 (M^+-Cl), 351, 353, 355 $(C_6F_{11}Cl_2)^+$, 335, 337 $(C_6F_{12}Cl)^+$, 169 $(C_3F_7)^+$, 163, 165, 167 $(C_3F_3Cl_2)^+$, 147, 149 $(C_3F_4Cl)^+$, 131 $(C_3F_5)^+$, 117, 119, 121, 123 $(CCl_3)^+$, 101, 103, 105 $(CFCl_2)^+$, 85, 87 $(CF_2Cl)^+$, 69 $(CF_3)^+$. Anal. Calc'd. for $C_8F_{14}Cl_4$: C, 19.07; Cl, 28.14. Found: C, 19.05; Cl, 27.97%. ^{19}F NMR-chemical shifts (ppm), standard - $CFCl_3$: -81.5 (triplet of triplets, CF_3), -101.6 (AB pattern, CF_2 next CCl_3), -114.9 (AB pattern, CF_2), -118.7 (AB pattern, CF_2 next CFCl), -122.9 (AB pattern, CF_2), -126.4 (AB pattern, CF_2 next CF_3), -128.7 (multiplet, CFCl).

$\underline{C_6F_5CFClCF_2CCl_3}$ (n.c.)

Colorless liquid boiling at 62-63°C/0.25 mm Hg. IR spectrum (capillary film between NaCl plates) 1653 (m), 1528 (s), 1498 (vs), 1418 (m), 1321 (m), 1200 (m), 1165 (s), 1145 (s), 1094 (m), 1012 (m), 979 (m), 932 (m), 899 (m), 843 (s), 799 (m), 770 (m), 734 (m), 694 (m), 671 (m). MS (EI) m/e 400, 402, 404, 406, 408 (M^+), 295, 297 (M^+-3Cl), 233, 235 $(C_6F_5CFCl)^+$, 198 $(C_6F_5CF)^+$, 179 $(C_6F_5C)^+$, 160 $(C_6F_4)^+$, 148 $(C_6F_4)^+$, 117, 119, 121, 123 $(CCl_3)^+$. Anal. Calc'd. for $C_9F_8Cl_4$: C, 26.90; Cl, 35.28. Found: C, 26.97; Cl, 35.05%. ^{19}F NMR chemical shift (ppm), standard - $CFCl_3$: -102.6 (doublet, triplet, CF_2), -105.8 (doublet, quartet, CF_2), -114.3 (triplet, doublet, CFCl), -133.8 (broad, ortho F's), -148.1 (triplet, triplet, para F), -160.4 (triplet, doublet, meta F's).

ACKNOWLEDGEMENTS

This work was supported by the Wright Research and Development Center, Materials Laboratory, Wright-Patterson Air Force Base, Ohio. The author is pleased to acknowledge the contribution of Dr. Wallace S. Brey, Jr. of the University of Florida for the NMR data, and Dr. Chi Yu of the Technical Services Group of the Materials Laboratory for his mass spectral analysis.

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