SYNTHESIS AND REACTIONS OF 1-PENTAFLUOROSULFUR-F-ETHYLSILVER

RONALD E. NOFTLE* and WILLIAM B. FOX

Chemistry Division, U. S. Naval Research Laboratory, Washington, D.C. 20375, U.S.A.

ABSTRACT

Trifluorovinylsulfurpentafluoride, $SF_5CF=CF_2$, reacted with silver(I) fluoride in acetonitrile solution to form 1-pentafluorosulfur-F-ethylsilver, $AgCF(SF_5)CF_3$, which was isolated as the acetonitrile solvate. $AgCF(SF_5)CF_3$ reacted with HCl, HBr, H_2O, and CH_3I to form good yields of $HCF(SF_5)CF_3$, with Br_2 to form $BrCF(SF_5)CF_3$ and $(CF_3CFSF_5)_2$, and with O_2 to produce SOF_4 and $CF_3C(O)F$. Thermolysis of $AgCF(SF_5)CF_3 \cdot CH_3CN$ resulted in the evolution of CH_3CN and formation of $(CF_3CFSF_5)_2$, $C_2F_5CF(SF_5)CF_3$, SF_4, S_2F_{10}, $CF_3CF=CFCF_3$, and Ag. $(CF_3CFSF_5)_2$ was found to be thermally unstable and decomposed at 100° to S_2F_{10} and $CF_3CF=CFCF_3$.

INTRODUCTION

As part of a program concerned with the synthesis and characterization of new pentafluorosulfur derivatives, we became interested in the development of a general route to compounds incorporating the (CF_3CFSF_5) group. The pioneering work of Miller and co-workers in the preparation and reactions

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*Visiting Scientist 1975-76. Permanent address: Department of Chemistry, Wake Forest University, Winston-Salem, N.C. 27109, U.S.A.

of F-alkylsilver compounds [1,2,3], as well as results reported
by others [4,5,6], suggested that the corresponding pentafluoro-
sulfur-F-alkylsilvers might be valuable reagents for this pur-
pose. Although pentafluorosulfur compounds of this type had not
been synthesized previously, it seemed likely that they might be
derived by addition of silver fluoride to F-vinylsulfurpenta-
fluorides.

In this paper we report the preparation of 1-pentafluoro-
sulfur-F-ethylsilver, $AgCF(SF_5)CF_3$, and its reactions with HCl,
HBr, H_2O, Br_2, O_2, and CH_3I. Thermolysis of $AgCF(SF_5)CF_3$ leads
to the formation of the novel $(CF_3CFSF_5)_2$ and probably
$C_2F_5CF(SF_5)CF_3$. Results are summarized in Fig. 1.

$HCF(SF_5)CF_3$ $BrCF(SF_5)CF_3* +$
                                           $(CF_3CFSF_5)_2*$

HX
(X=Cl,Br,OH,CH_2I) Br_2

$AgCF(SF_5)CF_3*$

>50° O_2

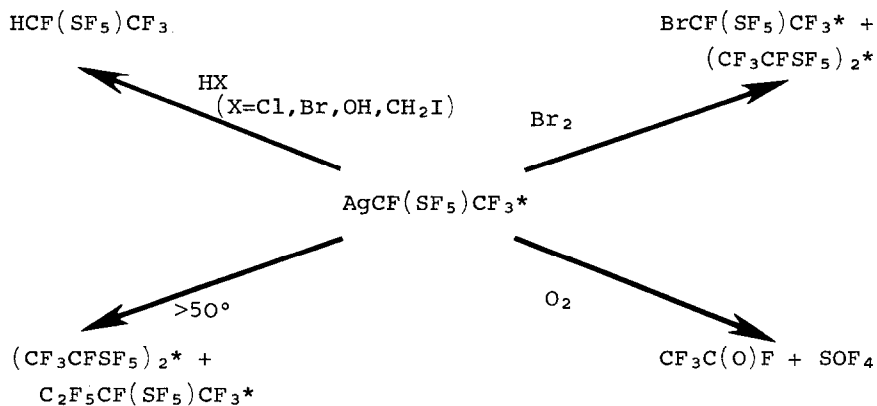$(CF_3CFSF_5)_2* +$ $CF_3C(O)F + SOF_4$
   $C_2F_5CF(SF_5)CF_3*$

Fig. 1. Reactions of 1-pentafluorosulfur-F-ethylsilver.
(*indicates new compound.)

EXPERIMENTAL

Trifluorovinylsulfurpentafluoride, $SF_5CF=CF_2$ [7], was pre-
pared by the method of Steward et al. [8]. The preparative
sequence involved the synthesis of SF_5Br [9,10] and its reac-
tion with vinyl fluoride (PCR, Inc.) to yield SF_5CHFCF_2Br [8].
Dehydrohalogenation of the latter with KOH in mineral oil
yielded $SF_5CF=CF_2$ of very high purity after fractionation at

-80° [8]. AgF (Ventron Corp.) was handled under inert atmos-
phere conditions. Br_2 was dried over P_4O_{10} prior to use. CH_3I
(Fisher Scientific Co.) was analyzed by gas chromatography and
infrared spectroscopy [11] to determine whether or not HI was
present. None was found. CH_3CN (Fisher Scientific Co.) was
dried and stored over CaH_2.

Infrared spectra were recorded on a P-E Model 457 infrared
spectrophotometer using a 10 cm gas cell with KBr windows. [19]F
nmr measurements were obtained using a JEOL Co. Model MH-100
high resolution nmr spectrometer operating at 91.4 MHz; chemical
shifts are reported with respect to an external reference of
CCl_3F. Mass spectra were recorded on a CVC Model MA-2 time-of-
flight mass spectrometer at an ionizing potential of 70 V. Gas
chromatographic separations were carried out using a Gow-Mac
Model 69-500 gas chromatograph equipped with a nickel filament
detector and a 4'x1/4" column packed with 20% DCQF-1 on 30/60
mesh Chromosorb P. Vapor pressure measurements were made by the
isoteniscope method using a calibrated copper-constantan thermo-
couple; the data were refined by the method of least-squares*.
Chemical analyses were performed by Beller Mikroanalytisches
Laboratorium, Gottingen, F.D.R.

Preparation of $AgCF(SF_5)CF_3$

AgF (0.5258 g, 4.1 mmol) was placed in a 30 cm^3 evacuated
bulb and CH_3CN (2.7116 g) was added. $SF_5CF=CF_2$ (2.5657 g, 12.3
mmol) was condensed onto the frozen slurry, and the mixture was
allowed to warm slowly to 25° after which it was stirred for
one hour in subdued light. During this time most of the AgF
dissolved to give a dark muddy-looking suspension. The mixture
was filtered under vacuum through a 30/60 micron glass frit; a
very small amount of dark material remained on the frit, and

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*Dr. John C. Cooper, "Linear Least-Squares," Program for use
 with HP-65 calculator.

the filtrate was a clear, pale yellow solution. The volatile
materials were pumped away, leaving a white residue which on
further pumping turned gray. Pumping was continued until the
residue did not appear moist and the pressure above the solid
fell to about 1 mm. Theor. wt. for composition $AgCF(SF_5)CF_3 \cdot$
CH_3CN: 1.5583 g. Found: 1.5783 g. Infrared analysis of the
volatile materials indicated the presence of $SF_5CF=CF_2$ [7],
CH_3CN [12], and a trace of $HCF(SF_5)CF_3$ [13].

Other experiments were in accord with these observations.
The best results were obtained when a ratio of $SF_5CF=CF_2$ to AgF
of 2:1 or greater was used. If equimolar amounts of reactants
were used, the reaction was slow and incomplete. It was ob-
served that filtered solutions of $AgCF(SF_5)CF_3$ in CH_3CN decom-
posed on standing at room temperature to give a black precipi-
tate (Ag) and $HCF(SF_5)CF_3$ as two of the products. Solid
$AgCF(SF_5)CF_3$, isolated as the acetonitrile solvate, appeared
to be considerably more stable (see thermolysis below), but
gradual darkening of the substance was observed to occur even
in subdued light.

Reactions of AgCF(SF$_5$)CF$_3$

With HX

A sample of $AgCF(SF_5)CF_3 \cdot CH_3CN$ (8 mmol) was prepared in a
30 cm^3 reaction vessel, and HCl (4.2 mmol) was added. An immed-
iate reaction occurred, and the originally gray solid whitened
considerably. After 1 hr., the volatile materials were removed
and separated by repeated fractionation at -35°, -80°, and
-196°. The -196° fraction consisted of $HCF(SF_5)CF_3$ (2.6 mmol)
and a trace of SiF_4. The -80° fraction was mainly CH_3CN but a
trace of $HCF(SF_5)CF_3$ was present. The -35° fraction consisted
of CH_3CN contaminated with a small amount of $(CF_3CFSF_5)_2$. No
unreacted HCl was detected in any of the fractions. An excess
of HBr (6.2 mmol) was then added to the $AgCF(SF_5)CF_3 \cdot CH_3CN/AgCl$
residue, and a further reaction took place in which a pale
yellow solid (AgBr) was produced. Fractionation of the vola-
tile materials yielded HBr (-196°), $HCF(SF_5)CF_3$ (1.9 mmol,
-118°), and CH_3CN contaminated with some $(CF_3CFSF_5)_2$ (-80°).

In a separate experiment, moisture was admitted to a small sample of $AgCF(SF_5)CF_3 \cdot CH_3CN$. The solid immediately darkened and bubbled vigorously. Infrared analysis of the volatile materials revealed the presence of $HCF(SF_5)CF_3$ and CH_3CN.

With Br_2

A sample of $AgCF(SF_5)CF_3 \cdot CH_3CN$ (3.24 mmol) was allowed to react with an excess of dry Br_2 (3.83 mmol). A reaction took place as the reaction vessel warmed from $-196°$ to room temperature with the formation of a liquid and a pale yellow solid. After 12 hr., the volatile materials (1.2334 g) were removed, leaving a pale yellow residue of AgBr (0.5952 g, 3.17 mmol). The excess Br_2 in the volatile materials was removed by shaking with Hg. The resulting clear, colorless, two-phase liquid was further separated by fractional condensation at $-196°$, $-120°$, and $-80°$. $BrCF(SF_5)CF_3$ (0.4482 g, 1.46 mmol, 45%) was recovered from the $-196°$ fraction by gas chromatographic separation from the impurities $CF_3CF=CFCF_3$ [14], $HCF(SF_5)CF_3$, $SF_5CF=CF_2$, S_2F_{10} [15a,b] and CH_3CN initially present.

The two-phase liquid trapped at $-80°$ was separated into two fractions by carefully evaporating the top layer without disturbing the bottom layer. Gas chromatographic and infrared analysis indicated that the top layer contained mainly CH_3CN with $CF_3CF=CFCF_3$, S_2F_{10} and $(CF_3CFSF_5)_2$ present as impurities. The bottom layer consisted mainly of $(CF_3CFSF_5)_2$ contaminated with $CF_3CF=CFCF_3$, S_2F_{10}, and CH_3CN. Attempts to isolate pure $(CF_3CFSF_5)_2$ from this reaction failed owing to lack of sufficient quantity of the substance and decomposition during chromatographic separations.

A second reaction of $AgCF(SF_5)CF_3 \cdot CH_3CN$ with Br_2 was carried out in which the Br_2 was added in two increments in order to maximize the yield of $(CF_3CFSF_5)_2$. $AgCF(SF_5)CF_3 \cdot CH_3CN$ (2.1949 g, 5.84 mmol) was allowed to react with Br_2 (3.01 mmol) for 1 hr., after which time the red-brown color of Br_2 had been discharged. The volatile materials (1.3519 g) were removed and worked-up as before. $BrCF(SF_5)CF_3$ (0.3817 g, 1.24 mmol, 21%) and $(CF_3CFSF_5)_2$ (0.6024 g, 1.33 mmol, 46%) were isolated from the other components (0.3678g) $CF_3CF=CFCF_3$, S_2F_{10}, CH_3CN, and a trace of $HCF(SF_5)CF_3$.

A second portion of Br_2 (3.86 mmol) was added to the solid residue. After 12 hrs., the red-brown color had not been discharged, and the volatile materials were removed. The excess Br_2 was removed as described previously. Work-up of the remainder yielded $BrCF(SF_5)CF_3$ (0.0834 g., 0.27 mmol, 5%) and $CF_3CF=CFCF_3$, S_2F_{10}, $(CF_3CFSF_5)_2$ and CH_3CN (0.0150 g). The residue was a pale yellow and gray solid. Theor. wt. for AgBr: 1.0966 g. Found: 1.1671 g.

With O_2

A solution of $AgCF(SF_5)CF_3$ (2.70 mmol) in CH_3CN (1.4675 g) was allowed to react with a twofold excess of dry O_2 for a period of 12 hrs. The volatile materials were separated from O_2 at -196°, -118°, and -80°. The -196° fraction consisted of CF_3COF [14] and SOF_4 [16] (0.3892 g, Calcd M. for equimolar mixture SOF_4 and CF_3COF: 120 g/gmv. Found: 122 g/gmv). The -118° fraction (0.0522 g) was identified as $HCF(SF_5)CF_3$ contaminated with a small amount of CF_3COF. The -80° fraction (1.3456 g) was mainly CH_3CN with a small amount of $HCF(SF_5)CF_3$ and $(CF_3CFSF_5)_2$ present. The solid residue (0.7468 g) hydrolyzed vigorously and SO_2F_2 [14] was observed as the only volatile product. In another trial, similar results were observed when the reaction mixture was allowed to warm very slowly from -78° to 25°.

With CH_3I

A sample of $AgCF(SF_5)CF_3 \cdot CH_3CN$ (2.9 mmol) was allowed to react with CH_3I (2.0 mmol) for 2 hrs. After this time, the solid had turned to a sticky yellow slurry. Gas chromatographic and infrared analysis indicated the presence of $HCF(SF_5)CF_3$ as well as two unidentified trace components. A second portion of CH_3I (1.4 mmol) was added to the residue, and the mixture was allowed to stand for 12 hours with stirring. Analysis of the volatile materials revealed the presence of SOF_2, SiF_4, $HCF(SF_5)CF_3$, CH_3CN, and two unidentified trace components, one of which appeared early in the chromatogram and contained C-H bonds. The residue in the reaction vessel was a dark yellow-green solid.

Thermolysis

A sample of $AgCF(SF_5)CF_3 \cdot CH_3CN$ (1.5783 g, 4.20 mmol) was heated to 50° under dynamic vacuum for 1 hr. The materials that evolved (0.0845 g) were collected at -196° and shown to be CH_3CN and traces of $SF_5CF=CF_2$, $HCF(SF_5)CF_3$, SOF_4 and CF_3COF. The residue was then maintained at 80-90° for several hours, and the volatile materials collected at -196° (1.1068 g) were separated by fractional condensation at -196° and -80°. The -196° fraction (0.1191 g) consisted of SF_4 [17], $CF_3CF=CFCF_3$, and a trace of SOF_2. The -80° fraction consisted of two immiscible liquids. The top layer (0.1028 g) was distilled away without disturbing the bottom layer and subjected to gas chromatographic analysis which indicated that it consisted mostly of CH_3CN along with a small amount of $C_2F_5CF(SF_5)CF_3$ and traces of low boiling compounds (SF_6 [14], SF_4, SOF_2, $CF_3CF=CFCF_3$). The more volatile portion of the bottom layer (0.1419 g) was treated similarly, and $C_2F_5CF(SF_5)CF_3$ (0.0566 g, 0.16 mmol, 8%) was isolated from the other components (SF_4, $CF_3CF=CFCF_3$, S_2F_{10}, CH_3CN). The remainder (0.6585 g) was mainly $(CF_3CFSF_5)_2$ contaminated with $C_2F_5CF(SF_5)CF_3$, S_2F_{10}, CH_3CN, and a trace of $CF_3CF=CFCF_3$. Pure $(CF_3CFSF_5)_2$ (0.3953 g, 0.87 mmol, 41%) was eventually isolated from the mixture. The reaction bulb was completely coated with a silver mirror. Theor. wt. for Ag: 0.4530 g. Found: 0.4715 g.

Characterization of $BrCF(SF_5)CF_3$, $C_3F_5CF(SF_5)CF_3$, and $(CF_3CFSF_5)_2$

$BrCF(SF_5)CF_3$: Analysis. Calcd: Br, 26.03; C, 7.82; F, 55.69; S, 10.45. Found: Br, 26.00; C, 7.92; F, 56.0; S, 10.47. Infrared spectrum (cm^{-1}): 1273(s), 1248(vs), 1223(s), 1141(ms), 950(m), 909(vvs), 824(vs), 735(m), 699(w), 612(m), 583(vw), 553(vw), 483(vvw). ^{19}F nmr SF, -63.8 ppm (9 lines split into doublets, J_{SF-CF} = 4.8 Hz); SF_4, -50.2 (complex doublet, J_{SF-SF_4} = 146.6 Hz); CF_3, 80.0 (sextet); CF, 100.3 (complex) area ratio: 1.12/4.00/3.27/1.16. Mass

spectrum: Table I. Vapor pressure equation (range 21° to
57°): $\log p_{mm} = -\frac{1603}{T} + 7.732$, T_b (calcd) = 57.2°, ΔH_v^o = 7.36
kcal/mol, ΔS_v^o = 22.2 eu.

$C_2F_5CF(SF_5)CF_3$: Analysis. Calcd: C, 14.67; F, 76.8; S,
9.21. Found: C, 13.87; F, 76.5; S, 8.65. Infrared spectrum
(cm^{-1}): 1317(w), 1270(vs), 1255(s), 1245(sh), 1218(m), 1203(sh),
1190(vs), 1153(w), 1084(w), 970(w), 912(vvs), 893(m), 846(w),
823(m), 743(w), 701(vs), 612(w), 535(vvs). Mass spectrum:
Table 1.

$(CF_3CFSF_5)_2$: Analysis. Calcd: C, 10.58; F, 75.30; S,
14.12. Found: C, 10.67; F, 75.4; S, 13.98. Infrared spectrum
(cm^{-1}): 1380(vvw), 1288(vw), 1264(sh), 1255(sh), 1247(vs),
1228(s), 1195(s), 1150(vw), 1128(w), 959(vw), 940(sh), 930(sh),
918(vvw), 898(s), 855(m), 814(m), 792(w), 748(vw), 722(vw),
702(w), 625(vw), 600(w), 580(vvw), 543(vw). ^{19}F nmr = -71.2
ppm (multiplet 10 lines), -66.2 ppm (doublet), -63.8 ppm
(singlet), 64.7 ppm (complex multiplet), 66.5 ppm (complex
multiplet), 126.8 ppm (broadened multiplet). Mass spectrum:
Table 1. Vapor pressure at 25° = 7 mm. Thermal stability:
A sample of $(CF_3CFSF_5)_2$ was placed in a Pyrex reactor and held
at 100° for 48 hr. The products were approximately equimolar
amounts of $CF_3CF=CFCF_3$ and S_2F_{10} as indicated by gas chroma-
tographic and infrared analysis. Several runs gave similar
results. $(CF_3CFSF_5)_2$ was also observed to undergo decomposi-
tion to these products on a heated chromatographic column.

A sample of $(CF_3CFSF_5)_2$ which gave the nmr spectrum
listed above was heated for 48 hr. at 50°. After this time,
the resonances due to the dimer had decreased and new reson-
ances at 67.5, 69.1 $(CF_3CF=CFCF_3)$ [21], and -58.7 ppm (S_2F_{10})
[22] had appeared. After holding the sample at 100° for 16 hr.,
all of the dimer resonances disappeared and the $CF_3CF=CFCF_3$
and S_2F_{10} resonances increased further. Some resonances ascrib-
able to small amounts of impurities appeared at very high field
and also near the Freon-11 standard.

TABLE 1

Mass spectral data

| m/e	BrCF(SF_5)CF$_3$ I/I$_o$ x 100	C$_2$F$_5$CF(SF$_5$)CF$_3$ I/I$_o$ x 100	CF$_3$CFSF$_5$)$_2$ I/I$_o$ x 100	Species
31	49	8	19	CF^+
32	5			S^+, O_2^+
50	6			CF_2^+
51	5			SF^+
69	65	100	100	CF_3^+
70	14	5	18	$SF_2^+ (^{13}CF^+)$
89	54	54	60	SF_3^+
91		3		$^{34}SF_3^+$
93			11	$C_3F_3^+$
100	10	9	18	$C_2F_4^+$
110	5			$^{79}BrCF^+$
112	5			$^{81}BrCF^+$
119	30	10		$C_2F_5^+$
127	12	24	26	SF_5^+
129	42			$^{79}BrCF_2^+$
131	40	17	61	$^{81}BrCF_2^+, CF_3CFCF^+$
150		3	5	$C_3F_6^+$
179	100			$^{79}BrCFCF_3^+$
181	100		25	$^{81}BrCFCF_3^+, CF_3CFCCF_3^+$
200			9	$CF_3CFCFCF_3^+$
219		3		$C_2F_5CFCF_3^+$

RESULTS AND DISCUSSION

The new compound, 1-pentafluorosulfur-F-ethylsilver, has been prepared by the reaction of trifluorovinylsulfurpentafluoride SF$_5$CF=CF$_2$, with AgF in acetonitrile. The reaction occurred readily in a few hours at room temperature or slightly above when a considerable excess of SF$_5$CF=CF$_2$ was present but pro-

ceeded much more slowly and incompletely when the stoichiometric quantities were present. When the molar ratio of reactants was 2:1, almost all of the AgF dissolved and only a small amount of a fine dark precipitate (Ag/Ag_2O) remained. Upon filtration under vacuum, a pale yellow solution of $AgCF(SF_5)CF_3$ resulted.

$$SF_5CF=CF_2 + AgF \quad \overset{CH_3CN}{=} \quad AgCF(SF_5)CF_3$$
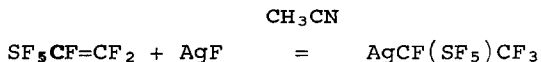
Solutions of $AgCF(SF_5)CF_3$ in CH_3CN appeared to be stable for a short time in the dark, but, eventually, a black material precipitated and $HCF(SF_5)CF_3$ formed. The decomposition was more rapid in the presence of light and probably involved formation of Ag and $\cdot CF(SF_5)CF_3$ radicals which abstracted hydrogen atoms from the solvent. Miller et al. [1,2,3] have interpreted their results from studies of F-alkylsilver systems on the basis of radical participation.

$AgCF(SF_5)CF_3$, isolated as the acetonitrile solvate, reacted rapidly with substances containing acidic hydrogen, such as HCl, HBr, and H_2O, to produce mainly $HCF(SF_5)CF_3$ which was prepared earlier by De Marco and Fox [13] using a different route. A small amount of $(CF_3CFSF_5)_2$, the dimer of the radical $\cdot CF(SF_5)CF_3$, was also produced in these reactions, suggesting again that $AgCF(SF_5)CF_3$ was a good radical source.

$$AgCF(SF_5)CF_3 \longrightarrow Ag^\circ + \cdot CF(SF_5)CF_3$$
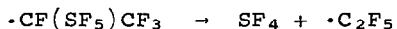
$$2 \cdot CF(SF_5)CF_3 \longrightarrow (CF_3CFSF_5)_2$$
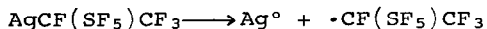
To further investigate this possibility, thermal decomposition experiments were carried out. The results indicated that $AgCF(SF_5)CF_3 \cdot CH_3CN$ was fairly stable up to about 50°, evolving only CH_3CN and traces of other substances. Above 50°, the dimer, $(CF_3CFSF_5)_2$, was the predominant product and was isolated in 41% yield. $CF_3CF=CFCF_3$ and S_2F_{10} were also found in the product mixture, which suggested that the dimer was not stable at elevated temperature; this was confirmed in separate experiments and may explain why synthesis of SF_5 derivatives by addition of S_2F_{10} to olefins has been relatively unsuccessful [23]. The presence of a significant amount of SF_4 in the product mixture indicated that another mode of decomposition of the silver product was operative, and

a small amount of $C_2F_5CF(SF_5)CF_3$ was isolated and partially characterized. $C_2F_5CF(SF_5)CF_3$ may have arisen by elimination of SF_4 from the silver fluoride-olefin complex and subsequent reaction of the unstable F-ethylsilver with $\cdot CF(SF_5)CF_3$

$$AgCF(SF_5)CF_3 \rightarrow [AgC_2F_5] + SF_4$$

$$[AgC_2F_5] + \cdot CF(SF_5)CF_3 \rightarrow C_2F_5CF(SF_5)CF_3 + Ag$$
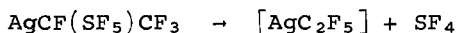
or, possibly, from SF_4 elimination by the radical $\cdot CF(SF_5)CF_3$ and subsequent radical combination

$$\cdot CF(SF_5)CF_3 \rightarrow SF_4 + \cdot C_2F_5$$

$$\cdot CF(SF_5)CF_3 + \cdot C_2F_5 \rightarrow C_2F_5CF(SF_5)CF_3.$$
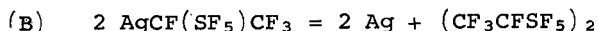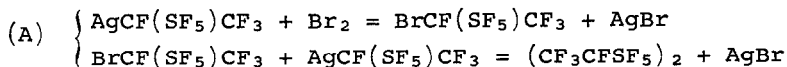
Apparently $C_2F_5CF(SF_5)CF_3$ does not arise by decomposition of $(CF_3CFSF_5)_2$, since the thermolysis of the dimer yielded only $CF_3CF = CFCF_3$ and S_2F_{10}. These possibilities are speculative, and further work will be necessary to establish the reaction pathways involved in the thermal decomposition of $AgCF(SF_5)CF_3$.

$AgCF(SF_5)CF_3$ reacted rapidly with Br_2 to give $BrCF(SF_5)CF_3$ in good yield:

$$AgCF(SF_5)CF_3 + Br_2 = BrCF(SF_5)CF_3 + AgBr.$$
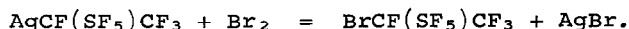
$(CF_3CFSF_5)_2$, which also formed in these reactions, may have been produced by direct reaction of 1-bromo-1-pentafluorosulfur-F-ethane with the silver fluoride-olefin complex (scheme A) or by thermolysis of the silver fluoride-olefin complex during the exothermic reaction with Br_2 (scheme B).

(A) $\begin{cases} AgCF(SF_5)CF_3 + Br_2 = BrCF(SF_5)CF_3 + AgBr \\ BrCF(SF_5)CF_3 + AgCF(SF_5)CF_3 = (CF_3CFSF_5)_2 + AgBr \end{cases}$

(B) $\quad 2\ AgCF(SF_5)CF_3 = 2\ Ag + (CF_3CFSF_5)_2$

We favor the first scheme because the weight of AgBr produced in the first reaction was close to the theoretical amount expected on the basis of complete reaction. Furthermore, when an amount of Br_2 which was stoichiometrically insufficient to effect a complete conversion to $BrCF(SF_5)CF_3$ was used, the yield of the bromo compound was about 21% and that of the dimer about 46%. When an excess of Br_2 was used, the yield of $BrCF(SF_5)CF_3$ increased to 45%.

The mass spectra of the new compounds $BrCF(SF_5)CF_3$, $C_2F_5CF(SF_5)CF_3$, and $(CF_3CFSF_5)_2$ are in agreement with their proposed structures, although it is probable that some decomposition of $(CF_3CFSF_5)_2$ occurred in the mass spectrometer. The ^{19}F nmr spectrum of $BrCF(SF_5)CF_3$ resembles those observed in similar systems [18] and also supports the proposed structure. The ^{19}F nmr spectrum of $(CF_3CFSF_5)_2$ is very complex and contains more resonances than would be expected for a system in which there are equivalent SF_5, CF_3 and CF groups. Chemical analysis of the sample indicated that no significant amounts of impurities were present. In addition, all of the resonances associated with the dimer decreased and eventually disappeared upon heating and were replaced mainly with the characteristic resonances of $CF_3CF=CFCF_3$ and S_2F_{10}. It seems likely that the extra resonances observed for the dimer are due to the presence of stereoisomers, since $(CF_3CFSF_5)_2$ possesses two asymmetric centers and can exist in a racemic mixture (R-R, S-S) and a meso form (R-S, S-R). The infrared spectra of these compounds show strong absorptions in the region of 900 and 830 cm^{-1} which are characteristic of the SF_5 group [19]. Bands in the region 1380-1100 are associated with CF stretching modes [19]. The band at 735 cm^{-1} in the spectrum of $BrCF(SF_5)CF_3$ may be the C-Br stretching mode [20].

In general, the chemistry of $AgCF(SF_5)CF_3$ is very similar to that of the F-alkylsilver compounds studied by Miller and co-workers [1,2,3]. The presence of the SF_5 group, however, is apparently responsible for some striking differences. For example, AgC_6F_5 and $AgC(CF_3)=C(CF_3)F$ were alkylated by CH_3I with formation of AgI [2,3], but $AgCF(SF_5)CF_3$ reacted with CH_3I to form mainly $HCF(SF_5)CF_3$ probably by abstraction of H atoms from the methyl group. Dyatkin et al [6] found that $AgCF(CF_3)_2$ was oxidized to $(CF_3)_2CO$ by molecular O_2, and Miller et al.[2,3] observed that AgC_6F_5 and $AgC(CF_3)=C(CF_3)F$ reacted with O_2 in CH_3CN to form mainly the hydro derivatives C_6F_5H and $CF_3C(H)=C(CF_3)F$. $AgCF(SF_5)CF_3$, however, reacted with O_2 to form mainly CF_3COF and SOF_4 in addition to a small amount of $HCF(SF_5)CF_3$. Hydrolysis of the residue produced SO_2F_2 suggesting the presence of $[AgOSF_5]$ as a reaction product.

ACKNOWLEDGEMENTS

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