# Fluoride Ion Catalyzed Formation of Perfluoro Esters

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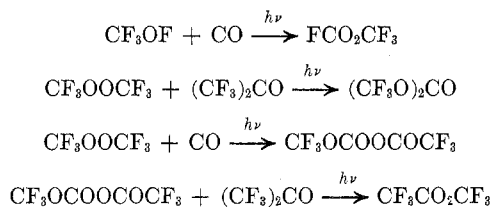*Department of Chemistry, University of Idaho, Moscow, Idaho 83843*

Trifluoroacetyl fluoride dimerizes at $-108°$ in the presence of CsF to form $CF_3CO_2C_2F_5$. With $(CF_3)_2CFO^- Cs^+$, COF_2, $CF_3C(O)F$, $C_2F_5C(O)F$, and $C_3F_7C(O)F$ react to form the heptafluoroisopropyl esters, $FCO_2CF(CF_3)_2$, $CF_3CO_2CF(CF_3)_2$, $C_2F_5CO_2CF(CF_3)_2$, and $C_3F_7CO_2CF(CF_3)_2$. Although these compounds are formed only at low temperature, when pure they are stable at $25°$ and above.

Although Haszeldine[2] reported the low yield preparation of perfluoro esters in the synthesis of perfluoroalkyl iodides, these were not characterized. In
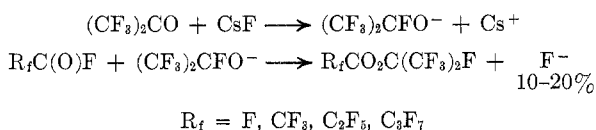
$$R_fCO_2Ag + I_2 \longrightarrow R_fI + CO_2 + R_fCO_2R_f$$
$$R_f = CF_3, C_3F_7$$
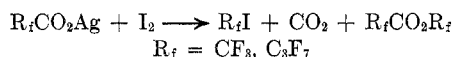
the interim, with the exception of the dimerization and trimerization[3] of COF_2 to yield FCO_2CF_3 and $(CF_3O)_2CO$ and photolysis reactions by Varetti and Aymonino[4-7] little synthetic information on perfluoro esters has appeared in the literature.

$$CF_3OF + CO \xrightarrow{h\nu} FCO_2CF_3$$

$$CF_3OOCF_3 + (CF_3)_2CO \xrightarrow{h\nu} (CF_3O)_2CO$$

$$CF_3OOCF_3 + CO \xrightarrow{h\nu} CF_3OCOOCOCF_3$$

$$CF_3OCOOCOCF_3 + (CF_3)_2CO \xrightarrow{h\nu} CF_3CO_2CF_3$$

During a study of the reactions of the HNF_2–KF adduct with perfluoroacyl fluorides at $-78°$ we isolated the ester $CF_3CO_2C(NF_2)_2CF_3$ in the case of $CF_3C(O)F$, in addition to the totally fluorinated amides,[8] $R_fC(O)NF_2$. When the reaction temperature was lowered to $-105°$, bis(difluoramino)trifluoroethyl trifluoroacetate was not formed but instead $CF_3CO_2C_2F_5$, the dimer of $CF_3C(O)F$, was obtained. Since the literature contains relatively few totally fluorinated esters and fewer methods of preparing them, the reactions of perfluoroacyl fluorides with alkali metal fluorides and perfluoroalkoxides was investigated.[9]

Results and Discussion

The reaction of cesium heptafluoroisopropoxide with acyl fluorides provides a convenient route to esters of the hypothetical *i*-C$_3$F$_7$OH. Esters of the type R$_f$C(O)-

$$(CF_3)_2CO + CsF \longrightarrow (CF_3)_2CFO^- + Cs^+$$

$$R_fC(O)F + (CF_3)_2CFO^- \longrightarrow R_fCO_2C(CF_3)_2F + \underset{10-20\%}{F^-}$$

$$R_f = F, CF_3, C_2F_5, C_3F_7$$

$OC(CF_3)_2F$ have been postulated[10] as intermediates in the fluorination of $R_fC(O)Cl$ by *i*-C$_3$F$_7$OCs, but these esters appeared to be unstable. The bulky CF_3

groups were thought to prevent free rotation and the enhanced electrophilic nature of the ester carbonyl would facilitate fluoride ion transfer. Contrary to

$$R_fC(O)Cl + i\text{-}C_3F_7OCs \longrightarrow CsCl + [R_fCOOC(CF_3)_2F]$$
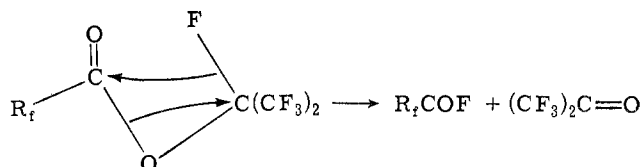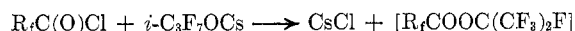
this, we have found that these esters are stable and do not disproportionate once isolated. The esters are decomposed rapidly in the presence of alkali metal fluorides at $-78°$ or above, which undoubtedly accounts for the previously reported results. The utilization of low reaction temperatures retards decomposition sufficiently to allow ester isolation but also may hamper the yield as seen in Figure 1.

Although the dimer of $CF_3C(O)F$ does form in low yield with CsF at low temperature, the dimerization occurs more efficiently when KF–HNF$_2$ is used. The formation of pentafluoroethyl trifluoroacetate by the latter method could at first glance be readily explained *via* the formation of the pentafluoroethoxide anion and subsequent reaction with $CF_3C(O)F$. However,

$$CF_3C(O)F + KF \longrightarrow C_2F_5O^- + K^+$$

$$CF_3C(O)F + C_2F_5O^- \longrightarrow CF_3CO_2C_2F_5 + F^-$$
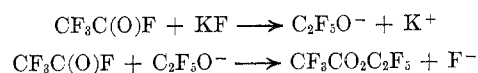
when the reaction was run under identical conditions but without HNF$_2$, in order to confirm this pathway, none of the ester was isolated. Addition of HNF$_2$ to the vessel with KF and $CF_3C(O)F$ again resulted in the formation of the ester.

At $-105°$ the extrapolated dissociation pressure of HNF$_2$ from the HNF$_2$–KF adduct is negligible[11] and therefore the HNF$_2$ cannot be assumed only to be forming "activated" KF *via* complexation and dissociation. To confirm this, KF was "activated" by the formation and decomposition of the hexafluoroacetone adduct but no ester was isolated with $CF_3C(O)F$. In an attempt to understand the role of the HNF$_2$, other reagents, such as $(CF_3)_2NOH$, which undergo complexation and substitution in an analogous manner, were used, but no ester could be isolated. Also, vacuum dried KF–HF, which would be present after HNF$_2$ reacted with $CF_3C(O)F$, was used without success.

Although the exact effect of the HNF$_2$ could not be ascertained, the above-described pathway would indicate that the low temperature reactions of perfluoroacyl fluorides with perfluoroalkoxide salts would lead to a general synthesis of totally fluorinated esters.

(1) Alfred P. Sloan Foundation Fellow, 1970-1972.
(2) R. N. Haszeldine, *Nature (London)*, **168**, 1028 (1951).
(3) B. C. Anderson, G. Crest, and G. R. Morlock, U. S. Patent 3,226,418; *Chem. Abstr.*, **64**, 9598 (1966).
(4) P. J. Aymonino, *Chem. Commun.*, 241 (1965).
(5) E. L. Varetti and P. J. Aymonino, *ibid.*, 680 (1967).
(6) E. L. Varetti and P. J. Aymonino, *An. Asoc. Quim. Argent.*, **55**, 153 (1967).
(7) E. L. Varetti and P. J. Aymonino, *ibid.*, **58**, 17 (1970).
(8) R. A. De Marco and J. M. Shreeve, *Inorg. Chem.*, **10**, 911 (1971).
(9) D. A. Couch, R. A. De Marco, and J. M. Shreeve, *Chem. Commun.*, 91 (1971).
(10) A. G. Pittman and D. J. Sharp, *J. Org. Chem.*, **31**, 2316 (1966).
(11) E. A. Lawton, D. Pilipovich, and R. D. Wilson, *Inorg. Chem.*, **4**, 118 (1965).

The infrared spectra of the new perfluoro esters are found in Table I. The carbonyl stretching frequency

TABLE I
INFRARED SPECTRA OF $R_fCO_2R_f'$

Compd	cm^{-1}
$CF_3CO_2C_2F_5$	1851 (s), 1336 (m), 1257 (s, sh), 1247 (vs), 1220 (s), 1206 (s), 1179 (s), 1110 (vs), 1092 (s), 858 (w, br), 760 (m), 740 (sh), 708 (vw), 679 (m), 529 (m)
$FCO_2C(CF_3)_2F$	1906 (s), 1881 (m), 1309 (m), 1269 (vs), 1219 (ms), 1179 (ms), 1147 (s), 1018 (ms), 948 (w), 753 (w), 726 (w), 659 (w)
$CF_3CO_2C(CF_3)_2F$	1851 (s), 1339 (s), 1305 (s), 1260 (vs), 1207 (s), 1175 (s), 1120 (vs), 1086 (s), 1010 (s), 839 (w), 758 (m), 724 (m), 677 (m), 544 (m), 525 (sh)
$C_2F_5CO_2C(CF_3)_2F$	1845 (vs), 1340 (m), 1310 (s), 1277 (vs), 1264 (vs), 1237 (vs), 1225 (s, sh), 1172 (s), 1135 (vs), 1109 (vs), 1006 (vs), 820 (w), 752 (sh), 738 (sh), 722 (m), 677 (mw), 535 (mw)
$C_3F_7CO_2C(CF_3)_2F$	1844 (s), 1360 (m), 1332 (sh), 1310 (s), 1260 (vs), 1229 (s), 1204 (s), 1176 (s), 1144 (s), 1120 (s), 1095 (sh), 1061 (m), 1010 (s), 960 (m), 921 (ms), 820 (m), 755 (m), 740 (vw), 723 (m), 680 (mw), 540 (m)

is characteristically found in the 1840–1850-cm^{-1} region for these esters and is reasonably independent of both the perfluoroacyl and perfluoroalkyl groups. In considering the trifluoroacetate esters $CF_3CO_2CF_3$, $CF_3CO_2C_2F_5$, and $CF_3CO_2C(CF_3)_2F$ the carbonyl stretching frequencies are 1852,[7] 1851, and 1851 cm^{-1}, respectively, and, for the heptafluoroisopropyl esters, $CF_3CO_2C(CF_3)_2F$, $C_2F_5CO_2C(CF_3)_2F$, and $C_3F_7CO_2C(CF_3)_2F$, the stretching frequencies are 1851, 1845, and 1844 cm^{-1}. These shifts follow the same trend as the perfluoroacyl fluorides which are found at $\sim$1880–1895 cm^{-1} and the perfluoroacyl chlorides located at $\sim$1800–1815 cm^{-1}. The tentative assignment of the C–O single bond stretching frequency may be accomplished by using the empirical relationship observed by Varetti and Aymonino.[12] The C–O stretching

$$\nu_{C-O} = 4112 - 1.625\nu_{C=O}$$

frequencies for $CF_3CO_2C_2F_5$, $FCO_2C(CF_3)_2F$, $CF_3CO_2C(CF_3)_2F$, $C_2F_5CO_2C(CF_3)_2F$, and $C_3F_7CO_2C(CF_3)_2F$ can then be assigned at 1110, 1018, 1120, 1109, and 1120 cm^{-1}, respectively. These values agree very well with those assigned to FCO_2CF_3 (1020 cm^{-1}) and $CF_3CO_2CF_3$ (1111 cm^{-1}) by Varetti and Aymonino.

The mass spectra are found in Table II. Although parent peaks are not observed, a small peak corresponding to M − F is seen for each derivative. For the general ester $R_fCO_2R_f'$ a consistant cracking pattern can be found with the exception of the carbonyl fluoride derivative. Fragments are observed in each ester corresponding to R_f, R_fCO, R_f', $R_f'O$, and $R_f'CO_2$ but none is found for R_fCO_2.

^{19}F nmr data for these esters are found in Table III. The CF$_3$ groups of the heptafluoroisopropyl esters are
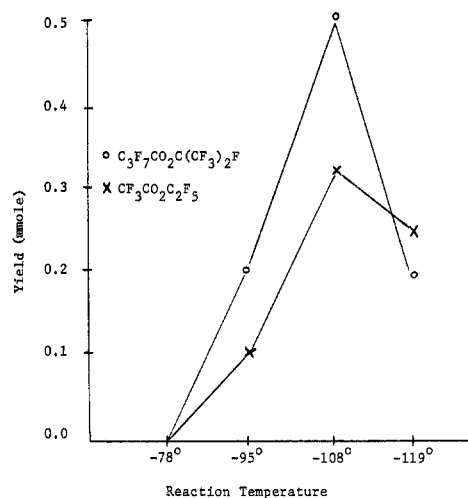
(12) E. L. Varetti and P. J. Aymonino, *Spectrochim. Acta, Part A*, **27**, 183 (1971).

Figure 1.—Effect of temperature on perfluorinated ester yields.

TABLE II
MASS SPECTRA OF $R_fCO_2R_f'$

Compd	m/e (assignments, rel %)
$CF_3CO_2C_2F_5$	213 (M − F, 0.5); 180 (?, 0.3); 163 (M − CF$_3$, 2); 135 (C_2F_5O, 1); 119 (C_2F_5, 38); 116 (C_2F_4O, 2); 100 (C_2F_4, 1); 97 (C_2F_3O, 26); 78 (C_2F_2O, 1); 69 (CF$_3$, 100); 50 (CF$_2$, 33); 47 (CFO, 27); 43 (C_2F, 2); 31 (CF, 14)
$FCO_2C(CF_3)_2F$	213 (M − F, 0.5); 185 (C_3F_7O, 0.1); 169 (C_3F_7, 3.5); 166 (C_3F_6O, 1); 163 (M − CF$_3$, 7); 147 (C_3F_5O, 4); 119 (C_2F_5, 3); 100 (C_2F_4, 2); 97 (C_2F_3O, 24); 78 (C_2F_2O, 1); 69 (CF$_3$, 100); 66 (CF$_2O$, 26); 50 (CF$_2$, 8); 47 (CFO, 60); 31 (CF, 10)
$CF_3CO_2C(CF_3)_2F$	263 (M − F, 1); 213 (M − CF$_3$, 3); 169 (C_3F_7, 8); 147 (C_3F_5O, 2); 119 (C_2F_5, 3); 100 (C_2F_4, 1); 97 (C_2F_3O, 30); 78 (C_2F_2O, 1); 69 (CF$_3$, 100); 50 (CF$_2$, 10); 47 (CFO, 5); 31 (CF, 6)
$C_2F_5CO_2C(CF_3)_2F$	313 (M − F, 2); 213 (M − C_2F_5, 8); 169 (C_3F_7, 25); 147 (C_2F_5O, 25); 119 (C_2F_5, 26); 100 (C_2F_4, 8); 97 (C_2F_3O, 6); 81 (C_2F_3, 1); 78 (C_2F_2O, 2); 69 CF$_3$, 100); 50 (CF$_2$, 8); 47 (CFO, 3); 31 (CF, 13)
$C_3F_7CO_2C(CF_3)_2F$	363 (M − F, 2); 213 (M − C_3F_7, 4); 197 (C_4F_7O, 3); 169 (C_3F_7, 59); 147 (C_3F_5O 2); 119 (C_2F_5, 7); 100 (C_2F_4, 6); 97 (C_2F_3O, 5); 85 (CF$_3O$, 2); 78 (C_2F_2O, 2); 69 (CF$_3$, 100); 50 (CF$_2$, 4); 47 (CFO, 2); 31 (CF, 7)

magnetically equivalent, even with the large C_3F_7 acyl side chain, which argues further against hindered rotation.[10] The spectra are first order and directly interpretable. Although no spin–spin coupling of the acyl CF$_3$ group with the isopropyl CF$_3$ in $CF_3CO_2C(CF_3)_2F$ occurs, because of through space coupling the CF$_3$ of the acyl group in $C_2F_5CO_2C(CF_3)_2F$ and $C_3F_7CO_2C-(CF_3)_2F$ is split by the isopropyl CF$_3$.

Experimental Section

TABLE III
^{19}F NMR SPECTRA[a]

76.1 92.1 87.1 83.5 121.8 142.4 79.3

C F₃ C O₂ C F₂ C F₃ C F₃ C F₂ C O₂ C F (C F₃)₂

t   q, q   t   b, q, d   sept,   d, q
└─0.4─┘ └─2.4─┘ unres   unres
                 └─1.7─┘ └─0.2─┘└─2.1─┘
                        └────0.4────┘

11.4 144.0 79.1 81.4 127.0 119.0 142.6 79.3

F C O₂ C F (C F₃)₂ C F₃ C F₂ C F₂ C O₂ C F (C F₃)₂

d, sept d, sept d, d   t,   b,   q   sept,   d, q
└─2.45─┘ └─1.77─┘ unres unres   unres
└────0.82────┘   └─9.0─┘   └─2.0─┘
                          └────0.5────┘

75.8 142.5 79.2

C F₃ C O₂ C F (C F₃)₂

d   sept, q   d
└─0.4─┘ └─1.9─┘

[a] Upfield shifts relative to CCl₃F as internal reference.

windows. The ^{19}F nmr were obtained on a Varian Model HA-100 spectrometer operating at 94.1 MHz. The mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E mass spectrometer at 70 eV. Elemental analyses were obtained from Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

General Procedure.—In general, the new perfluorinated esters were prepared by preforming the $(CF_3)_2CFO^-Cs^+$ salt by condensing an excess of hexafluoroacetone on CsF[13] and allowing the mixture to warm. The unreacted hexafluoroacetone was pumped off and a measured amount of the particular perfluoroacyl fluoride was consensed onto the salt at $-183°$. The reaction mixture was warmed to and allowed to remain at $-108°$ for 4 to 6 hr. After this time, any volatile materials were pumped away and the vessel was warmed slowly under dynamic vacuum to minimize the contact time between the ester and CsF. For minimum loss due to fluoride ion catalyzed decomposition, the ester should be removed from the reaction vessel below $-78°$. However, for the higher molecular weight esters the rate of decomposition at $-78°$ was slow and successful isolation was possible. When pure, these esters are stable at 25° and above for long periods.

The yields of esters obtained *via* this procedure were highly variable so that two "identical" reactions may give 20 or 0% of the ester. While temperature effects are important, we feel that the state of division of the CsF is the largest single factor governing reproducibility. The experimental data are summarized in Table IV. These numbers represent average yields. These

TABLE IV

$R_fC(O)F$ (mmol)	$(CF_3)_2CFO^-Cs^+$, mmol	Time, ester, mmol	Trap temp,[a] °C	Mol wt[b]	C, %	F, %
CF₃C(O)F (12)	CsF only	5 hr, CF₃CO₂C₂F₅, 0.3	−116			
COF₂ (6)	6	4 hr, FCO₂C(CF₃)₂F, 1.0	−96	235 (232)[c]		
CF₃C(O)F (20)	3	4 hr, CF₃CO₂C(CF₃)₂F, 1.7	−78	284 (282)	21.7 (21.3)	68.3 (67.4)
C₂F₅C(O)F (6)	6	5 hr, C₂F₅CO₂C(CF₃)₂F, 1.1	−96	335 (332)	21.5 (21.7)	71.0 (68.7)
C₃F₇C(O)F (5)	6	4 hr, C₃F₇CO₂C(CF₃)₂F, 0.5	−63	382 (382)	21.9 (22.0)	68.8 (69.6)

[a] Temperature at which ester condensed under dynamic vacuum of 10^{-2}–10^{-3} Torr. [b] Vapor density determined assuming ideal gas behavior by Regnault's method. [c] Calculated value.

Chemical Corp.). Hexafluoroacetone was obtained from Allied Chemical Co. and also used without purification.

Apparatus.—Volatile liquids and gaseous materials were handled in a standard vacuum line equipped with a Heise-Bourdon tube gauge. The reactions were carried out in Pyrex glass vessels equipped with Fisher–Porter Teflon valves or in metal vessels. In general, the esters were readily separated from the slightly more volatile acid fluorides by fractional condensation (low temperature separation based on differences in volatility of components). Low temperature baths are made by cooling appropriate organic liquids to their freezing point with liquid nitrogen to give slushes.

Analysis.—Infrared spectra were taken on a Perkin–Elmer 457 spectrometer using a 10-cm Pyrex glass cell equipped with KBr

compounds exhibit moderate hydrolytic stability, *e.g.*, CF₃CO₂C-(CF₃)₂F, is 50% recovered after 2 hr at 25° in excess water.

Registry No.—CF₃CO₂C₂F₅, 30952-31-9; FCO₂C-(CF₃)₂F, 30952-33-1; CF₃CO₂C(CF₃)₂F, 30952-32-0; C₂F₅CO₂C(CF₃)₂F, 30952-34-2; C₃F₇CO₂C(CF₃)₂F, 30952-35-3.

(13) C. T. Ratcliffe and J. M. Shreeve, *Chem. Commun.*, 674 (1966).