low temperatures, the anisotropic coupling components are not averaged and the total splitting due to the α-fluorine atom is about 20 mT [4]. We also note that the liquid-phase radiolysis of the perfluoroalkane analog of PMP, perfluoro-2-methylpentane, does not lead to the formation of stable radicals. Highly shielded radicals such as perfluoroisobutyl radicals are also not stable in the liquid state [3, 7]. On the other hand, perfluorocumyl radicals, in which a significant part of the spin density is delocalized in the pentafluorophenyl substituent, are stable [7]. Thus, the observed inability of radical (I) to recombine is of fundamental interest. This effect may involve both the steric isolation of the free valence by the perfluoroisopropyl groups and the presence of an α-fluorine atom. Further study of perfluorohydrocarbon radicals will permit elucidation of the reasons for the hindrance to recombination.

The authors express their gratitude to Yu. L. Bakhmutov for assistance in this work.

CONCLUSIONS

The radiolysis of perfluoro-4-methyl-2-pentene gives a stable radical whose ESR spectrum corresponds to $(CF_3)_2CF\dot{C}FCF(CF_3)_2$.

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REACTION OF CHLORINE FLUOROSULFATE WITH 1-TRIFLUOROMETHOXY-1,2-DICHLOROTRIFLUOROETHANE AND 1,2-DICHLOROHEXAFLUOROPROPANE

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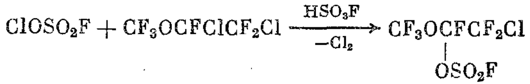
Chlorine fluorosulfate $ClOSO_2F$ does not react with 1,2-dichlorohexafluoropropane $CF_3CFClCF_2Cl$ even in the presence of HSO_3F upon heating at 90-100°C in a sealed ampule for 15-20 h [1]. On the other hand, 1-trifluoromethoxy-1,2-dichlorotrifluoroethane $CF_3OCFClCF_2Cl$ readily undergoes substitution of the internal chlorine atom by a fluorosulfate group upon the action of $ClOSO_2F$ in the presence of HSO_3F.



$$ClOSO_2F + CF_3OCFClCF_2Cl \xrightarrow[-Cl_2]{HSO_3F} CF_3OC\underset{OSO_2F}{F}CF_2Cl$$

(I)

The substitution of both chlorine atoms in $CF_3OCFClCF_2Cl$ or the chlorine atom in (I) by a fluorosulfate group using $ClOSO_2F$ in the presence of HSO_3F could not be achieved even upon prolonged heating at 90-100°C.

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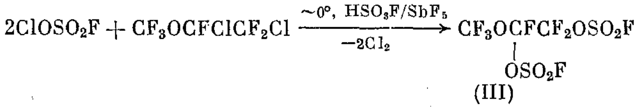
In the superacid mixture of HSO_3F and SbF_5, $ClOSO_2F$ reacts exothermally with $CF_3CFClCF_2Cl$ to form 2-chlorohexafluoropropyl fluorosulfate (II).

$$ClOSO_2F + CF_3CFClCF_2Cl \xrightarrow[-Cl_2]{HSO_3F/SbF_5} \underset{(II)}{CF_3CFClCF_2OSO_2F}$$

However, the internal chlorine atom in $CF_3CFClCF_2Cl$ or in (II) could not be substituted in this superacid even at 90-100°C.

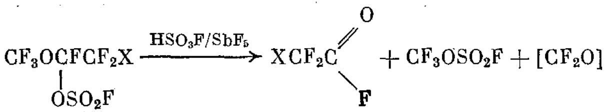
$ClOSO_2F$ reacts even more vigorously with $CF_3OCFClCF_2Cl$ in the presence of HSO_3F/SbF_5. For a 2:1 mole ratio of the starting reagents, about two moles of Cl_2 are released, which indicates the substitution of both the chlorine atoms in $CF_3OCFClCF_2Cl$.



$$2ClOSO_2F + CF_3OCFClCF_2Cl \xrightarrow[-2Cl_2]{\sim 0^\circ,\ HSO_3F/SbF_5} CF_3O\underset{\displaystyle OSO_2F}{\underset{|}{C}}FCF_2OSO_2F$$

(III)

Bis(fluorosulfate) (III) could be obtained only by carrying out the reaction at about 0°C. Above 0°C, the decomposition products of (I) and (III) are the final products of the action of HSO_3F/SbF_5. Among these products, trifluoromethyl fluorosulfate was unexpectedly detected along with the acid fluorides of fluorosulfonyloxydifluoroacetic and chlorodifluoroacetic acids.



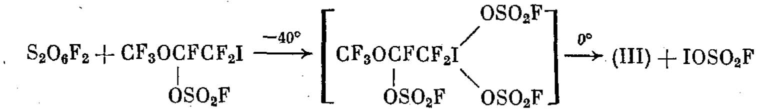
(I), (III)

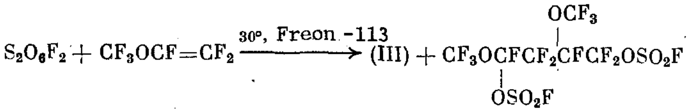
X = Cl (I), OSO_2F (III).

We should note that bis(fluorosulfate) (III) was also obtained under the above conditions by the substitution of the chlorine atom in fluorosulfate (I).

$$ClOSO_2F + (I) \xrightarrow[-Cl_2]{\sim 0^\circ,\ HSO_3F/SbF_5} (III)$$

as well as by the reaction of peroxydisulfuryl difluoride $S_2O_6F_2$ with 1-trifluoromethoxy-2-iodotrifluoroethyl fluorosulfate and perfluoromethyl vinyl ether (PMVE). In the latter case, the bis(fluorosulfate) of the dimer of PMVE (IV) is the major product.





$$S_2O_6F_2 + CF_3OCF{=}CF_2 \xrightarrow{30^\circ,\ \text{Freon-113}} (III) + CF_3O\underset{\displaystyle OSO_2F}{\underset{|}{C}}FCF_2\overset{\displaystyle OCF_3}{\overset{|}{C}}FCF_2OSO_2F$$

(IV)

The results and our previous data [1] indicate that substituents X may be placed in the following series relative to their effect hindering the replacement of a chlorine atom by a fluorosulfate group in chlorine-containing perfluorinated compounds with the general formula R_FCFClX: $CF_3 \gg F > OSO_2F > OCF_3$. This series corresponds to the order of the electron-withdrawing capacity of these substituents.

The increase in the reactivity of $ClOSO_2F$ upon the replacement of the chlorine atoms by the fluorosulfate group with increasing acidity of the medium is apparently a consequence of increased polarization of the O—Cl bond and, as a result, enhanced electrophilic properties of $ClOSO_2F$.

EXPERIMENTAL

The ^{19}F NMR spectra were taken on a Hitachi R-20 spectrometer at 56.45 MHz relative to CF_3CO_2H as the external standard in $CHCl_3$ solution. The gas—liquid chromatography was carried out on an LKhM-8MD chromatograph on a 3 m × 3 mm column packed with 5% SE-30 on Chromatone N-AW-DMCS (0.200-0.250 mm) and a 6 m × 3 mm column packed with 5% QF-1 on Chezasorb AW-NMDS with 18.5 ml/min helium gas carrier flow rate.

The spectra of (III) and (IV) were taken by M. V. Galakhov on a WP-200 CY spectrometer at 188 MHz.

1-Trifluoromethoxy-2-chlorotrifluoroethyl Fluorosulfate (I). A sample of 19 g (141.3 mmole) $ClOSO_2F$ was added dropwise with stirring to a mixture of 30 g (126 mmoles) 1-trifluoromethoxy-1,2-dichlorotrifluoroethane and 3 ml HSO_3F and stirred for 3 h at 40°C. Fractionation gave 36.7 g (96.8%) (I), bp 83-84°C, d_4^{20} 1.700, n_D^{20} 1.3050 [2]. The ^{19}F NMR spectrum was identical to that given in our previous work [2].

2-Chlorohexafluoropropyl Fluorosulfate (II). A sample of 13 g (58.8 mmoles) 1,2-dichlorohexafluoropropane was added dropwise with stirring to a mixture of 9 g (67 mmoles) $ClOSO_2F$, 1.5 g SbF_5 and 4 g HSO_3F and stirred for 3 h at 40°C. The volatile products were collected in a trap at −78°C (30 mm Hg). Fractionation of the trap contents gave 14.1 g (34.2%) (II), bp 76°C, d_4^{20} 1.701, n_D^{20} 1.3070 [3]. ^{19}F NMR spectrum of (II): $\delta_1 = 0.8$ d. t (CF_3), $\delta_2 = 62.2$ t. q (CF), $\delta_3 = 3.3$ d. d. q (CF_2), $\delta_4 = -127.3$ (SF), $J_{12} = 6.5$, $J_{13} = J_{34} = 9.0$, $J_{23} = 12.0$ Hz.

1-Trifluoromethoxy-1,2-bis(fluorosulfonyloxy)trifluoroethane (III). a) A mixture of 25 g (185.9 mmoles) $ClOSO_2F$, 3 g SbF_5 and 8 g HSO_3F was added dropwise with stirring to 20 g (84.3 mmoles) 1-trifluoromethoxy-1,2-dichlorotrifluoroethane at 0°C, stirred for 4 h at 0°C, and poured into 150 g ground ice. The organic layer was separated and washed with three 25-ml portions of ice water and dried over $MgSO_4$. Fractionation yielded 8.5 g (33.5%) (I), bp 82-84°C and 11.2 g (36.8%) (III), bp 118-120°C, d_4^{20} 1.784, n_D^{20} 1.3100. Found: C, 9.78; F, 41.71; S, 17.65%. Calculated for $C_3F_8O_7S_2$: C, 9.89; F, 41.76; S, 17.50%. ^{19}F NMR spectrum: $\delta_1 = -18.6$ d. d. t (CF_3), $\delta_2 = 24.3$ d. q (CF), $\delta_3 = -23.3$ d, q ($\underline{F}SO_2OCF$), $\delta_4 = 13.8$ m (CF_2), $\delta_5 = -123.5$ t ($CF_2OSO_2\underline{F}$), $J_{12} = 12.0$, $J_{13} = 2.2$, $J_{23} = 8.6$, $J_{24} < 1$, $J_{45} = 8.8$, $J_{14} = 2.2$ Hz.

b) A mixture of 13 g (96.7 mmoles) $ClOSO_2F$, 3 g SbF_5 and 8 g SHO_3F was added dropwise with stirring to 25.3 g (84.4 mmoles) (I) at 0°C, stirred for 6 h at 0°C and poured onto 150 g ice. The organic layer was separated, washed with water, and dried over $MgSO_4$. Fractionation gave 16.8 g (54.8%) (III), bp 118-120°C.

Decomposition of 1-Trifluoromethoxy-1,2-bis(fluorosulfonyloxy)trifluoroethane (III) by the Action of HSO_3F/SbF_5. A solution of 1 g SbF_5 in 4 g HSO_3F was placed in a reactor equipped with a condenser at 0°C and exit trap at −78°C. Then, 9 g (24.7 mmoles) (III) was added dropwise at 20-30°C and heated for 15 min at 40°C. A yield of 2.6 g (62.6%) trifluoromethyl fluorosulfate, bp from −4°C to −2°C [4], was collected in the trap. ^{19}F NMR spectrum: $\delta_1 = -20.3$ d (CF_3), $\delta_2 = -123.8$ q (SF), $J_{12} = 7.3$ Hz. Fractionation of the residue gave 3.2 g (66.6%) fluorosulfonyloxydifluoroacetyl fluoride, bp 41-43°C, d_4^{20} 1.670, $n_D^{20} > 1.30$. Found : C, 12.39; F, 38.53; S, 16.20%. Calculated for $C_2F_4O_4S$: C, 12.24; F, 38.77; S, 16.33%. ^{19}F NMR spectrum: $\delta_1 = -127.4$ t (SF), $\delta_2 = -92.5$ t (COF), $\delta_3 = -0.4$ d. d (CF_2), $J_{13} = 7.5$, $J_{23} = 3.9$ Hz.

Decomposition of 1-Trifluoromethoxy-2-chlorotrifluoroethyl Fluorosulfate (I) by the Action of HSO_3F/SbF_5. A sample of 10 g (33.3 mmoles) (I) was added dropwise to a solution of 0.5 g SbF_5 in 2 g HSO_3F and the gaseous products were collected in a trap at −78°C. The yield of the gaseous mixture was 7.8 g with bp from −20° to −2°C. Gas–liquid chromatographic analysis and ^{19}F NMR spectroscopy indicated that this mixture consisted of ∿40% trifluoromethyl fluorosulfate and ∿60% chlorodifluoroacetyl fluoride. ^{19}F NMR spectrum of chlorodifluoroacetyl fluoride: $\delta_1 = -86.9$ t (COF), $\delta_2 = -11.8$ d ($ClCF_2$), $J_{12} \sim 1$ Hz. The ^{19}F NMR spectrum of trifluoromethyl fluorosulfate was identical to that described above.

Reaction of $S_2O_6F_2$ with 1-Trifluoromethoxy-2-iodotrifluoroethyl Fluorosulfate. A solution of 8 g (40.4 mmoles) $S_2O_6F_2$ in 5 ml Freon-113 was added dropwise to a solution of 15 g (38.3 mmoles) 1-trifluoromethoxy-2-iodotrifluoroethyl fluorosulfate in 20 ml Freon-113 at −40°C and the reaction mass was gradually warmed to 20°C (decomposition of the yellow solid formed at −40°C occurs at about 0°C with the liberation of dark green $IOSO_2F$). The liquid phase was separated and fractionated to yield 11.3 g (81.3%) (III), bp 118-120°C. The physical indices and ^{19}F NMR spectrum of (III) were identical to those given above. $IOSO_2F$ was identified by addition to hexafluoropropylene according to our previous work [4].

Reaction of $S_2O_6F_2$ with Perfluoro(methyl vinyl ether). A sample of 20 g (96.4 mmoles) PMVE in a 1:3 gaseous mixture with N_2 was bubbled through a solution of 18 g (90.9 mmoles) $S_2O_6F_2$ in 60 ml Freon-113 at 30°C for 48 h. Fractionation gave 5 g (15.1%) (III) and 30.1 g

(62.5%) 1,3-bis(trifluoromethoxy)-1,4-bis(fluorosulfonyloxy)hexafluorobutane (IV), bp 85-90°C (44 mm), d_4^{25} 1.848, n_D^{25} 1.3100. Found: C, 13.99; F, 50.35; S, 12.02%. Calculated for $C_6F_{14}O_8S_2$: C, 13.58; F, 50.19; S, 12.07%. ^{19}F NMR spectrum (mixture of diastereomers) (IV): −123.0 m, −123.1 m ($CFOSO_2\underline{F}$), −123.4 t, −123.4 t, −123.5 t (CF_2OSO_2F), −13.2 m, −13.0 m, −12.9 m, −11.7 m ($2CF_3O$), 13.7 m, 14.0 m, 14.6 m, 15.1 m (CF_2O), 25.9 m, 26.5 m (CFOS), 54.6 m, 55.1 m, 56.2 m (CF_2), 73.7 m, 74.6 m (CFOC).

CONCLUSIONS

The reactivity of chlorine fluorosulfate increases with increasing acidity of the medium. In HSO_3F/SbF_5, chlorine fluorosulfate under mild conditions replaces the terminal chlorine atom in 1,2-dichlorohexafluoropropane and both chlorine atoms in 1-trifluoromethoxy-1,2-dichlorotrifluoroethane by fluorosulfate groups.

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INTERMOLECULAR HYDROGEN BONDING IN β-HYDROXYCARBONYL FERROCENE COMPOUNDS

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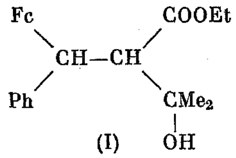
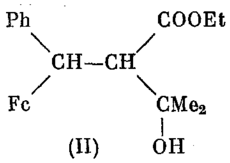
There is continuing discussion of the problem of Fe···HO hydrogen bonding in ferrocene hydroxy derivatives since there is no unequivocal proof of the presence or absence of such bonds. The search for convenient models and a critical evaluation of the spectral data would permit, in our opinion, a more definite conclusion concerning the existence of intramolecular hydrogen bonds at the iron atom.

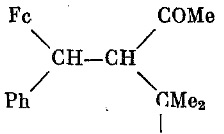
We recently prepared β-hydroxycarbonyl ferrocene derivatives (I)-(III) [1]



(I)



(II)



(III)

which have several sites, which, in principle, may give rise to intra- and intermolecular hydrogen bonds. Derivatives (I)-(III) are readily prepared by the action of MeMgI on β-dicarbonyl compounds Fc(Ph)CH—CH(COR)COR', where R, R' = Me, OEt. The study of the IR spectra of these compounds and of those of model compounds (IV)-(VII) in the region of the stretching vibrations νCO and νOH showed that various types of intramolecular CO···HO and π-arom···HO hydrogen bonds exist in solution in the molecular systems studied (I)-(III).

The bands were assigned to the CO···HO and π-arom···HO types unequivocally on the basis of 1) study of the concentration and temperature dependence of the IR spectra of (I)-(VII)

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*Deceased.

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