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IODINE FLUOROSULFATE REACTIONS WITH FLUOROCARBONS

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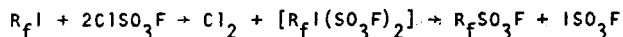
SUMMARY

Iodine monofluorosulfate has been found to react with fluorolefins in the absence of a solvent to give the corresponding iodo alkyl fluorosulfates by addition of $-I$ and $-OSO_2F$ across the double bond. The observed products were $ICF_2CF_2SO_3F$, $CF_3CFICF_2SO_3F$, and the isomer mixture $ICF_2CFICSO_3F$ and $ICFICF_2SO_3F$. Perfluorocyclobutene was unreactive. The iodine fluorosulfate used for this study was synthesized from the reactions of either I_2 or R_fI with $ClSO_3F$, with both reactions being new routes to this compound. These iodo fluorocarbon fluorosulfates are novel compounds and were characterized by spectroscopy and by formation of the derivatives $CF_3CFICFO$ and ICF_2CFO .

INTRODUCTION

The halogen fluorosulfates are very reactive materials in general, being capable of oxidation or substitution processes in either organic or inorganic systems [1]. One of the earliest reactions described was the addition of XSO_3F to carbon-carbon double bonds [2] where $X=F, Cl,$ or Br . However, despite the fact that iodine monofluorosulfate became known at about the same time [3], no reports on similar reactions of $IOSO_2F$ have appeared. Indeed, the chemistry of $IOSO_2F$ (commonly written, ISO_3F) and $I(SO_3F)_3$ is practically non-existent [1,4] and no organic derivatives have been reported.

In a previous study [5] of fluorocarbon halide-chlorine fluorosulfate displacement reactions the following products were noted.



Based on the observed material balance, the by-product iodine fluorosulfate was formed in nearly quantitative yield, but was identified only by its physical appearance, i.e. a black solid at ambient temperature [3]. Thus having samples of ISO_3F readily available, it was interesting to determine whether this compound would be useful for the preparation of simple organic derivatives. We now report the results of experiments utilizing olefins.

EXPERIMENTAL

Volatile materials were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps, 316 stainless steel bellows seal valves and a Heise Bourdon tube-type pressure gauge. Transfers outside the vacuum line were carried out in a drybox. Infrared spectra were obtained using 5 cm path stainless steel cells with AgCl windows and a PE Model 283 spectrophotometer. Mass spectra were measured with an EAI Quad 300 quadrupole spectrometer and ^{19}F nmr spectra were determined with a Varian EM390 spectrometer operating at 84.6 MHz, using $CFCl_3$ as an internal standard. Chlorine fluorosulfate was prepared from ClF and SO_3 [6]. The fluorocarbon starting materials were purchased from PCR Research Chemicals, Inc., and used as received.

ISO_3F Preparations

A 30 ml stainless steel cylinder was loaded with I_2 (4.02 mmol) and $ClSO_3F$ (8.09 mmol) and maintained at -78° overnight followed by a day at -45° . While warming to ambient temperature the volatile products were pumped from the cylinder and trapped at -196° . These consisted of Cl_2 and a trace of $ClSO_3F$ (4.02 mmol total) indicating an essentially quantitative reaction of the $ClSO_3F$. The weight increase of the cylinder corresponded to that expected for the formation of ISO_3F . When this reaction was carried out in a Teflon ampoule, it was noted that the solid product was orange at low temperatures and only changed to the black color typical of ISO_3F on standing at 0° or higher for some time.

An alternative preparation of ISO_3F used in this study was the reaction of R_fI with ClSO_3F . Thus, $n\text{-C}_3\text{F}_7\text{I}$ (2.90 mmol) and ClSO_3F (6.16 mmol) were combined in a stainless steel cylinder and maintained at -45° for several days. While warming to ambient temperature the volatile products were separated by fractional condensation in traps cooled to -45 , -78 and -196° . The latter contained Cl_2 (2.91 mmol) and a little $\text{C}_3\text{F}_7\text{SO}_3\text{F}$ and $\text{C}_3\text{F}_7\text{I}$. The warmer traps contained only $\text{C}_3\text{F}_7\text{SO}_3\text{F}$ (2.77 mmol) in 95% yield. Iodine fluorosulfate remained in the cylinder, however, the observed weight (0.682g) was somewhat higher than the theoretical weight (0.656g) possibly due to the formation of some $\text{I}(\text{SO}_3\text{F})_3$ as an impurity.

$\text{CF}_3\text{CFICF}_2\text{SO}_3\text{F}$

To the ISO_3F (~2.90 mmol) formed from $\text{C}_3\text{F}_7\text{I}$ and ClSO_3F was added $\text{CF}_3\text{CF}=\text{CF}_2$ (2.40 mmol) at -196° . The mixture was allowed to react by warming the cylinder to room temperature for several days. The only volatile product was $\text{CF}_3\text{CFICF}_2\text{SO}_3\text{F}$ (2.35 mmol, 98% yield), a colorless liquid with a vapor pressure of 13 mm at 25° . This liquid was identified by its; ^{19}F NMR, infrared, and mass spectra. IR, cm^{-1} (intens.): 1494 (vs), 1262 (vs), 1232 (vs), 1190 (vw), 1115 (s), 979 (s), 962 (sh), 924 (w), 905 (m), 846 (s), 764 (m), 727 (w), 611 (vw), 574 (m), and 537 (vw). Intense ions found in the mass spectra were m/e (assign.): 376 ($\text{C}_3\text{F}_6\text{ISO}_3\text{F}$), 277 ($\text{C}_3\text{F}_6\text{I}$), 249 ($\text{C}_3\text{F}_6\text{SO}_3\text{F}$), 150 (C_3F_6), 149 ($\text{CF}_2\text{SO}_3\text{F}$), 131 (C_3F_5), 127 (I), 100 (C_2F_4), 83 (SO_2F), 69 (CF_3 , base), 67 (SOF), 64 (SO_2), 50 (CF_2), 48 (SO), and 47 (CFO).

$\text{ICF}_2\text{CF}_2\text{SO}_3\text{F}$

A cylinder containing ISO_3F (6.56 mmol), prepared from I_2 and ClSO_3F , was cooled to -196° and C_2F_4 (7.05 mmol) was added. The cylinder was placed in a liquid nitrogen/ CO_2 slush and allowed to warm slowly to ambient temperature. After a few days the volatile products were pumped through traps cooled at -30 , -78 , and -196° . The latter contained a mixture (0.25 mmol) of $\text{ClCF}_2\text{CF}_2\text{SO}_3\text{F}$ [2], Cl_2 , and an unidentified acyl fluoride. The -30° fraction contained small amounts of $\text{FO}_3\text{SCF}_2\text{CF}_2\text{SO}_3\text{F}$ [7] and $\text{ICF}_2\text{CF}_2\text{SO}_3\text{F}$ while the -78° fraction was good quality $\text{ICF}_2\text{CF}_2\text{SO}_3\text{F}$ (3.98 mmol, 61% yield) colorless liquid with a vapor pressure of 24 mm at 22° . The remaining unaccounted for reactants were found in the cylinder in the form of a white solid polymer and dark oil, presumably $\text{I}(\text{C}_2\text{F}_4)_n\text{SO}_3\text{F}$, $\text{I}(\text{C}_2\text{F}_4)_n\text{I}$, or $\text{FO}_3\text{S}(\text{C}_2\text{F}_4)_n\text{SO}_3\text{F}$ type materials which were not examined further. The $\text{ISO}_3\text{F} - \text{C}_2\text{F}_4$

reaction was repeated using ISO_3F (3.41 mmol) which was the 2 year old by-product of a $\text{C}_7\text{F}_{15}\text{I} - \text{ClSO}_3\text{F}$ reaction [5]. Together with C_2F_4 (3.96 mmol) and a more controlled warm-up, this reaction produced a yield of purified $\text{ICF}_2\text{CF}_2\text{SO}_3\text{F}$ of 76% based on ISO_3F :vapor density obs'd. 330; calc'd. 326g/mol. Spectral characterization included infrared, cm^{-1} (intens.); 1497 (vs), 1301 (ms), 1262 (vs), 1226 (ms), 1167 (s), 1147 (s), 1105 (s), 1080 (s), 952 (ms), 931 (ms), 845 (s), 792 (m), 600 (w), and 555 (w); mass spectra, m/e (assign.): 326 ($\text{C}_2\text{F}_4\text{ISO}_3\text{F}$), 227 ($\text{C}_2\text{F}_4\text{I}$), 199 ($\text{C}_2\text{F}_4\text{SO}_3\text{F}$), 177 (CF_2I), 158 (CFI), 149 ($\text{CF}_2\text{SO}_3\text{F}$), 127 (I), 119 (C_2F_5), 100 (C_2F_4), 97 ($\text{C}_2\text{F}_3\text{O}$), 83 (SO_2F , base) 81 (C_2F_3), 69 (CF_3), 67 (SOF), 64 (SO_2), 50 (CF_2), 48 (SO) and 47 (CFO); and ^{19}F NMR spectra (Table 1).

$\text{ICF}_2\text{CFCISO}_3\text{F} - \text{ICFCICF}_2\text{SO}_3\text{F}$

A cylinder containing ISO_3F (4.02 mmol) prepared from I_2 and ClSO_3F was cooled to 0° and $\text{CF}_2=\text{CFCl}$ (8.12 mmol) was gradually added with intermittent shaking and keeping the pressure below 300 mm. After the first half of the olefin was added the uptake of $\text{CF}_2=\text{CFCl}$ became slow. Consequently, the final 2 mmol was condensed at -196° into the cylinder and the mixture kept at ambient temperature overnight. Fractional condensation though traps cooled at 0, -30 , -78 , and -196° served to separate unreacted $\text{CF}_2=\text{CFCl}$ (1.22 mmol) retained at -196° , and I_2 (a few crystals) retained at 0° . The other two traps contained a slightly purplish liquid which was recombined and treated with Hg to remove I_2 and refractionated through 0, -30 , and -78° . The -78° material (0.5 mmol) was mainly $\text{ClCF}_2\text{CFCISO}_3\text{F}$ based on its infrared and ^{19}F NMR spectra [8]. The 0 and -30° fractions (6.40 mmol total, 79.6% yield) were colorless liquids with quite similar infrared, mass, and NMR spectra. The latter showed clearly that three compounds were present in the mixture; $\text{ICF}_2\text{CFCISO}_3\text{F}$, $\text{ICFCICF}_2\text{SO}_3\text{F}$, and $\text{FO}_3\text{SCFCICF}_2\text{SO}_3\text{F}$. Based on the measured peak areas, the ratio of the first two isomeric materials was 1.5 and they comprised 95% of the sample. The infrared spectrum of the isomers was recorded, cm^{-1} (intens.): 1491 (vs), 1306 (vw), 1253 (vs), 1219 (m), 1167 (s), 1134 (s), 1080 (s), 1058 (s), 1010 (m), 987 (m), 945 (w), 927 (w), 860 (sh), 842 (vs), 780 (m), 700 (w), and 569 (m). Intense ion peaks noted in the mass spectrum were m/e (assign.) (^{35}Cl only given): 342 ($\text{C}_2\text{F}_3\text{ClISO}_3\text{F}$), 243 ($\text{C}_2\text{F}_3\text{ClI}$), 215 ($\text{C}_2\text{F}_3\text{ClSO}_3\text{F}$), 193 (CFCI), 177 (CF_2I), 165 (CFCISO_3F), 149 ($\text{CF}_2\text{SO}_3\text{F}$), 127 (I), 116 ($\text{C}_2\text{F}_3\text{Cl}$), 113 ($\text{C}_2\text{F}_3\text{ClO}$), 97 ($\text{C}_2\text{F}_3\text{O}$), 85 (CF_2Cl), 83 (SO_2F , base) 69 (CF_3), 67 (SOF), 66 (CFCI), 64 (SO_2), 63 (CClO), 50 (CF_2), 48 (SO), and 47 (CFO). The ^{19}F NMR spectra are listed in Table 1.

CF₃CFICFO

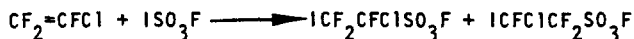
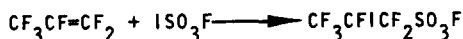
A 30 ml stainless steel cylinder containing CsF (1.24g) and CF₃CFICF₂SO₃F (1.12 mmol) was placed in an oven at 100° for 1 hour. The products volatile at 25° were removed from the cylinder by pumping and were found to be SO₂F₂ (1.2 mmol) with traces of R_f- material. Pyrolysis of the solid left in the cylinder (heat gun, 15 min.) while pumping through a -196° trap yielded CF₃CFICFO (1.03 mmol, 92% yield). This compound was identified by its vapor density; obs'd. 271g/mol, calc'd. 274g/mol and spectral parameters. Infrared bands were, cm⁻¹ (intens.): 1862 (vs), 1278 (vs), 1256 (vs), 1211 (vs), 1117 (s), 974 (w), 954 (m), 886 (m), 755 (w), and 683 (m). The intense mass fragments were, m/e (assign.): 274 (C₃F₅IO), 227 (C₂F₄I), 177 (CF₂I), 147 (C₃F₅O), 128 (C₃F₄O), 127 (I), 119 (C₂F₅), 100 (C₂F₄), 97 (C₂F₃O), 81 (C₂F₃), 69 (CF₃, base), 50 (CF₂), and 47 (CFO). The ¹⁹F NMR spectrum is listed in Table 1.

ICF₂CFO

A mixture of ICF₂CF₂SO₃F (0.42 mmol) and CsF was heated at 100° for 2 hours. Recooling to room temperature and fractionation of the volatile products through traps cooled at -126 and -196° permitted the separation of SO₂F₂ and traces of R_fCFO from ICF₂CFO (0.38 mmol, 91% yield) which was retained at -126°. The observed infrared bands were, cm⁻¹ (intens.): 1870 (vs), 1243 (vs), 1175 (s), 1083 (vs), 901 (s), 842 (w), and 645 (m). The ¹⁹F NMR spectrum is listed in Table 1.

RESULTS AND DISCUSSION

Iodine monofluorsulfate was found to add across olefinic double bonds according to:



The tetrafluoroethylene reaction was sometimes quite vigorous, resulting in oily or solid polymer formation. The chlorotrifluoroethylene reaction, however, required little moderation and proceeded at a rather slow rate after about half the available ISO₃F was consumed. The least reactive olefin was

perfluorocyclobutene which did not react with SO_3F under comparable conditions although it does add ClSO_3F readily to give $\text{C-C}_4\text{F}_6\text{Cl}(\text{SO}_3\text{F})$. [6]. The reactions of SO_3F with the above olefins occur in yields of 76-98% in agreement with the anticipated 1:1 stoichiometry. All of the products are mobile, colorless liquids of low volatility.

Measurement of the spectral properties of the products confirmed their identity. The formulation as $\text{I-R}_f\text{-SO}_3\text{F}$ adducts was confirmed by the mass spectra which in all cases exhibited a readily detectable m/e peak attributable to the expected parent ion. This is in agreement with general observations for iodofluorocarbons. The other mass fragments support the formulated structures. Noteworthy is the fact that m/e 83, attributable to the SO_2F^+ ion, constitutes the base peak in those fluorosulfates lacking a

TABLE 1

 ^{19}F Chemical Shifts^a and Coupling Constants^b

	CF_3	CFI	CF_2	CFCI	CF_2	SO_3F	$J_{\text{FF}}(\text{Hz})$
$\text{ICF}_2\text{CF}_2\text{SO}_3\text{F}$			64.8		85.3	-48.6	$J_{12}4.7, J_{23}8.0$
$\text{ICF}_2\text{CFCISO}_3\text{F}$			58.5	72.8		-49.6	$J_{12}9.4, J_{23}9.4$
$\text{CICF}_2\text{CFCISO}_3\text{F}$			69.0	75.8		-48.9	$J_{12}5.6, J_{23}9.6$
$\text{FO}_3\text{SCFCICF}_2\text{SO}_3\text{F}$				79.7	86.1	-50.6	$J_{12}8.0, J_{23}3.4$
						-49.4	$J_{34}8.2$
$\text{ICFCICF}_2\text{SO}_3\text{F}$				78.0	82.3	-48.4	$J_{12}11.8, J_{22}9.3$
							$J_{23}8.2$
$\text{CF}_3\text{CFICF}_2\text{SO}_3\text{F}$	74.8	148.6			77.5	-48.1	$J_{12}11.8, J_{13}9.4$
							$J_{22}11.8, J_{34}8.1$
ICF_2CFO			59.8				$J_{12}3.7$
						-7.8	
CF_3CFICFO	76.9	142.9					$J_{12}12.3, J_{13}8.8$
						-19.6	$J_{23}26.8$

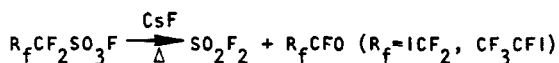
^a Ppm upfield from internal CFCI_3 . The observed area ratios, multiplicities and coupling constants verified the above assignments.

^b The subscripts of the coupling constants refer to the sequence of the carbon or sulfur atoms in the molecular structures given in the first column of the table and increase from left to right.

a CF_3 -group. In the latter case, m/e 69 due to CF_3^+ is the peak. The infrared spectra of these compounds show the bands characteristic for a monodentate SO_3F group ($\sim 1500\text{ cm}^{-1}$, vs, vs SO_2 ; $\sim 850\text{ cm}^{-1}$ S-O, S-F stretch). In addition to the expected strong C-F stretching modes there are moderately strong bands in the $900\text{-}1000\text{ cm}^{-1}$ region due to both C-C and C-O stretching vibrations.

Definitive results regarding the structure of the compounds was furnished by their ^{19}F NMR spectra which are summarized in Table 1. These data, when compared to literature values [9] for similar compounds, are very characteristic. The $-\text{SO}_3\text{F}$ fluorine shift is always near -49 ppm, while other carbon-fluorine groups exhibit well established and distinct chemical shifts. It is noteworthy that the isomer $1\text{CFClCF}_2\text{SO}_3\text{F}$ shows hindered rotation about the C-C bond up to at least 80° as evidenced by the magnetic non-equivalence ($\Delta\nu=9.3\text{Hz}$) of the two fluorines of the CF_2 resonance. This is often found for similar ethane derivatives [10].

Two of the new fluorocarbon fluorosulfates were catalytically decomposed as shown in the equation.



These high yield reactions are very useful in furnishing a derivative for identification of the parent compound [5,11]. The acyl fluorides obtained were characterized in the same manner as the fluorosulfates.

Overall these reactions of ISO_3F and olefins resemble those of ClSO_3F [12]. Thus, $\text{CF}_3\text{CF}=\text{CF}_2$ gives only the one isomer expected for a directed polar addition, while $\text{CF}_2=\text{CFCl}$ gives two, even though both systems might be expected to proceed by the same reaction path [13]. Steric factors cannot be important in these cases since the double bonds are not sufficiently hindered to account for the difference. Thus, a single mechanism to explain this behavior is not readily apparent. Nevertheless, it has been shown that potentially useful organic derivatives of ISO_3F can be easily made. Additional studies of ISO_3F reactions are planned. Also it should be mentioned that INO_3 , generated in solution as a pyridinium salt, has recently been successfully added to unsaturated hydrocarbon substrates [14].

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