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Journal of Fluorine Chemistry 121 (2003) 147–152
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/jfluchem

Fluorinated olefins and oleum

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Received 11 November 2002; received in revised form 26 November 2002; accepted 6 December 2002

Abstract

Oleum has some advantages over pure sulfur trioxide and may be successfully used for preparation of beta-sultones from hexafluoropropene, 2H-pentafluoropropene, 6H-perfluoro-1-hexene and perfluoro(propylvinyl) ether (VE). Depending on the reaction conditions, the VE-sultone and tetrafluoroethane-beta-sultone (TFE-sultone) are different from other sultones. They are not stable in the presence of oleum and the oxidation of $–CF_2–SO_2$-group in the sultones leads to some new fluorooxalate derivatives.

Keywords: Fluorinated beta-sultones; Oleum; Fluoroolefins

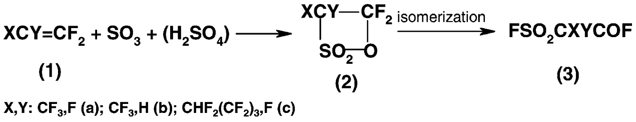
1. Introduction

Fluorinated beta-sultones are well documented compounds in fluorine chemistry [1,2]. Many sultones have been synthesized and used for the preparation of surfactants, battery electrolytes, alkylating agents and ion exchange resins. The interest in sultones increased after DuPont commercialized perfluorinated ionomer membranes (Nafion^{TM}), where the linear isomer of tetrafluoroethane-beta-sultone (TFE-sultone) was used as a source of pendant perfluoroalkylsulfonate groups in Nafion polymer [3]. Successful synthesis of fluorinated sultones depends on many conditions but there is reportedly one critical aspect in this synthesis: only pure, freshly distilled sulfur trioxide reacts with fluoroolefins to give sultones. Commercially available inhibited sulfur trioxide "Sulfan", or solid polymeric sulfur trioxide (trimer), or even freshly distilled but not dry sulfur trioxide are not useful for TFE-sultone synthesis because of low yields and the formation of many by-products. On the other hand, pure uninhibited sulfur trioxide is difficult to handle because it readily polymerizes, sometimes even during distillation if the condenser is too cold or is not thoroughly dried. Proper methods of sulfur trioxide handling may be found in a review [2] and in the work of England et al. [4]. Those methods include the use of sulfur trioxide complexes with organic solvents or dry box handling of SO_3 for distillation and charging the reactor. The use of organic solvents or a dry box is impractical for commercial processing. Pure monomeric and liquid sulfur trioxide is available from DuPont company but it should be shipped and stored at a temperature close to the boiling point of sulfur trioxide (45 °C) to prevent undesired polymerization.

In contrast to pure sulfur trioxide, the storage and handling of fuming sulfuric acid (or oleum), which may contain as much as 67 wt.% of monomeric SO_3, requires no temperature control or special containment. Oleum is not subject to polymer formation on freezing and it may be shipped and stored at any temperature and thus provides significant handling and safety advantages over pure sulfur trioxide.

2. Results and discussion

We investigated the reactions of oleum with hexafluoropropene, 2H-pentafluoropropene, 6H-perfluoro-1-hexene [5], perfluoro(propylvinyl) ether (VE) and tetrafluoroethylene and have found that in most cases oleum may be used in place of pure sulfur trioxide for the preparation of the corresponding sultones.



In the case of hexafluoropropene (**1a**), the reaction with oleum is fast and slightly exothermic, even at low temperatures (20 °C), indicating that sulfuric acid promotes the reaction. The analogous reaction of HFP with freshly distilled sulfur trioxide is much slower, requiring heating to 100 °C for many

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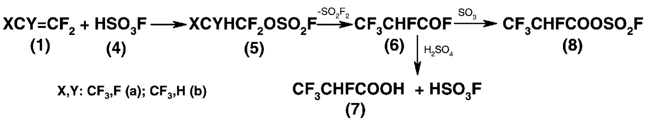
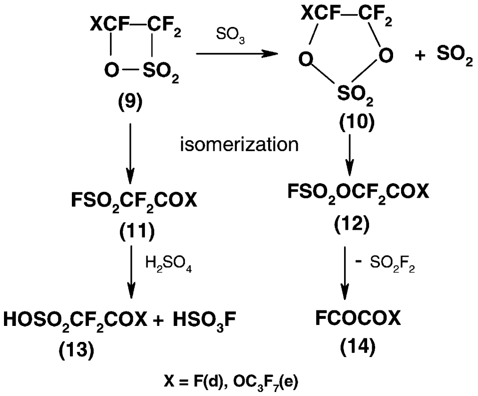
doi:10.1016/S0022-1139(03)00005-8

hours [4] to achieve high conversions. Along with the product sultones (**2**) and their linear isomers (**3**), the reactions with oleum always produce fluorosulfuric acid (**4**) and many other by-products (**5**–**8**). The source of fluorosulfuric acid may be any reaction that produces hydrogen fluoride, which is readily scavenged by SO_3 to give FSO_3H. For instance, the reaction of concentrated sulfuric acid with compounds containing difluoromethylene groups adjacent to oxygen atom ($-OCF_2-$) as in alkylperfluoroalkyl ethers, perfluoroalkylsulfonates etc, is well known to produce hydrogen fluoride (fluorosulfuric acid in case of oleum). Fluorosulfuric acid may react with the fluorinated propenes **1a** and **1b** to give fluoroalkylfluorosulfates (**5a** and **5b**) and the products of further transformations of the sulfates like 2H-terafluoropropionyl fluoride (**6**), 2H-terafluoropropionic acid (**7**) and the 2H-terafluoropropionylfluorosulfate (**8**).

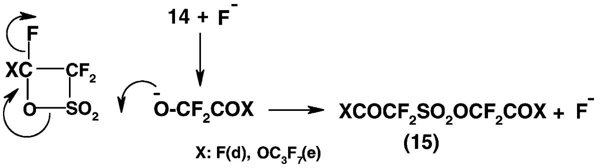


We believe that many other fluoroolefins will react with oleum this same way, with the exception of fluorinated ethylenes and vinyl ethers, which are investigated in this work, and probably perfluorovinyl amines [6].

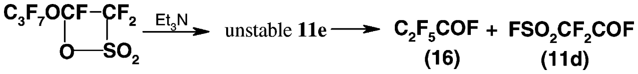
Both TFE-sultone (**9d**) and VE-sultone (**9e**) [4,7,8] are distinct from other fluorinated sultones because of the presence of a difluoromethylene—sulfurdioxide bond in the molecule. This structural feature appears to influence the final products obtained from the reaction of fluorinated ethylenes and vinyl ethers with oleum. Reaction of perfluoro(propylvinyl) ether with oleum gives VE-sultone **9e** in high yield and takes only 2–3 h to complete at 0 °C. A high yield of the sultone may also be obtained in reactions run at room temperature. In this case, the reaction exotherm and reaction time must be controlled in order to prevent further transformations of the sultone product. The reaction is generally complete in 10 min at room temperature to give the VE-sultone in 68% yield after quenching. Therefore, sulfuric acid promotes the sultone formation exactly the same as in the case of HFP-sultone. If the reaction of perfluoro(propylvinyl)ether with oleum is not quenched in 10 min and allowed to run until the exotherm has subsided, there will be no VE-sultone remaining and four new products are formed: heptafluoropropyloxycarbonyldifluoromethanesulfonic acid (**13e**), heptafluoropropylfluorosulfatodifluoroacetate (**12e**), heptafluoropropylfluorooxalate (**14e**) and the condensation product of the oxalate with the sultone—perfluorodiester with sulfonato group in the middle of the molecule (**15e**). The main step in this process is probably the oxidation of carbon–sulfur bond in the sultone **9e** followed by isomerization of both **9e** and the cyclic sulfate **10e** into their linear isomers **11e** and **12e**. Though the cyclic sulfate **10** has not been found in the reaction mixture, its existence as an intermediate compound is surmised from identification of compounds like **12** and **15** containing the $\mathbf{CF_2{-}O{-}SO_2}$ fragments.



The fluorooxalate **14e** is the product of sulfuryl fluoride elimination from the VE-sulfate linear isomer **12e**. The sulfonic acid **13e** is probably the product of exchange between fluorine in **11** and the OH group in sulfuric acid. The second product of this exchange is fluorosulfuric acid, HSO_3F. The perfluorodiester **15e** appears to be a product of condensation of heptafluoropropylfluorooxalate **14e** with the sultone **9e**. Although the mechanistic details are unclear, this reaction could be viewed as proceeding by the reaction of the fluorooxalate **14** with fluoride ion to give the corresponding alkoxide anion followed by nucleophilic ring opening of the sultone. However, it would be somewhat surprising that this mechanism could be operative in the presence of concentrated sulfuric acid.



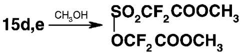
In contrast to other known fluorinated beta-sultones, the reaction of the VE-sultone with just a few drops of triethylamine does not give the sultone linear isomer **11e**, but only its decomposition products, pentafluoropionyl fluoride (**16**) and fluorosulfonyldifluoroacetyl fluoride (**11d**)—the linear isomer of the TFE-sultone.



The reaction allows preparation of commercially important fluorosulfonyldifluoroacetylfluoride from any trifluorovinyl ethers or their mixtures using inexpensive reagents via a simple procedure.

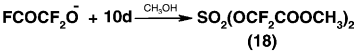
It is known that when TFE is bubbled through sulfur trioxide at atmospheric pressure in a moisture-protected flask, essentially no reaction is observed [4]. In 1969, Russian chemists described the reaction of TFE-sultone with sulfuric acid to give difluoroacetic and fluorosulfuric acids [9].

They used sulfur trioxide and sulfuric acid independently as reagents, not as a mixture (oleum) as we report here. In our hands, TFE reacted with 65% oleum exothermically, even while bubbling, but no sultone or difluoroacetic acid was found in the reaction mixture. TFE-sultone, like VE-sultone, contains the –CF_2–SO_2– fragment in the four-membered ring and this is probably why we observe the evidence of oxidation of the presumed sultone intermediate. The main reaction products are gases: sulfur dioxide and oxalyldifluoride (**14d**) as well as its low boiling precursor fluorosulfatodifluoroacetylfluoride (**12d**). Small amounts of liquid condensation products were also identified after methanol quenching, including the methyl diesters (**17**) and (**18**). The sulfate **18** is probably the product of cyclic sulfate **10d** ring opening by $\mathbf{XCOCF_2O^-}$ anion.



$$\mathbf{15d,e} \xrightarrow{CH_3OH} \begin{array}{l} SO_2CF_2COOCH_3 \\ | \\ OCF_2COOCH_3 \end{array}$$

(17)



$$FCOCF_2O^- + \mathbf{10d} \xrightarrow{CH_3OH} SO_2(OCF_2COOCH_3)_2$$

(18)

Chlorotrifluoroethylene (CTFE) reacts with oleum in the same way as tetrafluoroethylene. The main reaction products are oxalylchloridefluoride and sulfur dioxide. Because two different halogens are present in CTFE molecule, the reaction mixture is very complex. For instance, for halogenosulfatodihalogenoacetic acid halide, we observed three isomers in the mass spectrum with M212: probably $\mathbf{FSO_3CFClCOF}$, $\mathbf{FSO_3CF_2COCl}$ and $\mathbf{ClSO_3CF_2COF}$.

In summary, the perfluorosultones with CF_2–SO_2 fragments in the four-membered ring, like TFE/VE/CTFE-sultones, react with oleum via carbon–sulfur bond oxidation to give derivatives of alkylsulfonates and dialkylsulfates. Most other known fluorinated sultones, like HFP-sultone, are stable in the presence of concentrated sulfuric acid and oleum.

3. Experimental details

Analytical data was provided by Specialty Materials Manufacturing Division analytical group at 3 M. The ^1H and ^{19}F NMR spectra were acquired using Varian UNITY plus 400 FT-NMR spectrometer and include 400 MHz ^1H and 376 MHz ^{19}F spectra. The samples were placed in an NMR tube, spiked with small amount $CFCl_3$ and TMS for both ^{19}F and ^1H chemical shifts zero references given in ppm, and spiked with small amount of *p*-hexafluoroxylene (*p*-HFX) for use as a cross integration standard. Use of *p*-HFX facilitates the cross-correlation of various fluorine and proton signal intensities for quantitative purposes [10]. $CDCl_3$ was the solvent for ^{19}F as well as ^1H NMR spectroscopy, unless otherwise noted. GC/MS analysis was performed using an HP 5890 Series 2 gas chromatograph with a 105 m × 0.32 mm Rtx-5 capillary column to introduce the sample to a Finnigan SSQ-700 mass spectrometer. The samples were ionized using chemical ionization with methane as the reagent gas. A gas chromatograph HP 5890 Series 2 with a J&W Scientific fused silica capillary column DB 210 (30 m × 0.325 mm) with an FID detector was used for GC analysis. IR spectra were recorded on a Digilab FTS-40 spectrometer.

3.1. Reaction HFP with oleum

A 100 ml Parr™ reactor was charged with 63.8 g of 65% oleum (0.52 mol SO_3), cooled to −45 °C, slightly evacuated and charged with 62 g (0.44 mol) liquid HFP **1a** from a cold trap. The reaction mixture was allowed to warm to room temperature and at 20 °C, a slight exotherm was observed with a maximum temperature of 56 °C and pressure 8.96 bar over a 9-min period. The reactor was heated at 42 °C for 6 h while the mixture was agitated to give 103.8 g of a two-phase reaction product. The upper organic layer (90.6 g) was separated, washed with concentrated sulfuric acid to remove residual SO_3 and distilled to give 63.3 g (66%) of HFP-sultone **2a** with bp 47 °C (Lit. [4] bp 46.5 °C). The sultone ^{19}F and ^1H NMR ($CFCl_3$): −73.69 (CF_3 ddd), −51.8 (CF 5-fold), −82.3 m and −88.2 q (CF_2 ABq). NMR analysis of higher boiling point fraction (25 g, bp 50–167 °C) revealed a mixture of $CF_3CHFCOOH$ ^{19}F NMR ($CFCl_3$): −75.47 (CF_3 dd), −204.1 (CF dq); $CF_3CHFCOOSO_2F$ ^{19}F NMR: −75.13 (CF_3 dd), −203.8 (CHF dq) 47.29 (SO_2F s) and HSO_3F ^{19}F NMR: 41.74 (SO_3F s), 10.28 (H s).

3.2. Reaction 2H-pentafluoropropene (PFP) with oleum

PFP **1b** (22 g) was bubbled from a cold trap through 20.2 g of 67 wt.% oleum (0.17 mol SO_3) in a flask, fitted with magnetic bar stirrer and two condensers in series at −8 °C and −78 °C. A slight exotherm was observed during the addition. The reaction mixture was held at room temperature for 4 h and then purged with nitrogen to sweep unreacted PFP into the end trap. A total of 18.6 g (0.14 mol) of PFP was consumed. The reaction mixture (39.8 g) was distilled on an ACE Glass Inc. concentric tube column to give 10.3 g (34%) of a mixture of PFP-sultone **2b** and its linear isomer **3b** with bp 85–87 °C (Lit. [11] sultone bp 92 °C). The sultone ^{19}F and ^1H NMR ($CFCl_3$): −65.31 (CF_3 ddd), −70.80 and −83.65 (CF_2 ABq), 5.57 (CH m); MS: 213 [$(m+1)^+$ 100]; the linear isomer $CF_3CH(SO_2F)COF$ ^{19}F and ^1H NMR: −67.70 (CF_3 m), 63.73 (SO_2F dqd), 49.74 (COF 5-fold), 5.17 (CH ddq). Also isolated by distillation was 3.94 g (12%) of the fluorosulphonate **5b** with bp 92–108 °C $CF_3CH_2CF_2OSO_2F$ ^{19}F and ^1H NMR ($CFCl_3$): −63.19 (CF_3 5-fold), −66.27 (CF_2 7-fold), 48.10 (SO_2F t), 3.08 (CH_2 tq); MS: 233 [$(m+1)^+$ 16], 213 (20), 133 (100), 113 (76) and 9.7 g HSO_3F with bp 165–168 °C.

3.3. Reaction 6H-perfluoro-1-hexene with oleum

The hexene **1c** (2.27 g, 8 mmol) and 1.57 g of 65% oleum (13 mmol SO_3) were heated in a sealed glass tube for 13 h at

100 °C to give a two-phase reaction product. The upper sultone layer (2.69 g) was separated, washed with conc. sulfuric acid and distilled to yield 2.25 g (77%) sultone **2c** with bp 40 °C/13 mm, $HCF_2{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF^eCF_2{}^fOSO_2$ (cyclic CF^e–OSO_2) ^{19}F and ^1H NMR ($CFCl_3$): −137.3 (a, CF_2 d), −129.2 m and −129.7 (b, CF_2 ABq), −121.1 m and −121.6 m (c, CF_2 ABq), −116.8 m and −118.1 m (d, CF_2 ABq), −151.5 (e, CF m), −82.55 m and −85.88 m (f, CF_2 ABq), 5.94 (CH tt); MS: 363 [$(m+1)^+$ 100], 299 (24), 279 (20), 263 (8).

3.4. Reaction perfluoro(propylvinyl) ether (VE) with oleum

At 0 °C, a mixture of 20.0 g (7.5 mmol) VE with purity 99.9% and 13.77 g of 65% oleum (11 mmol SO_3) was stirred for 2 h, left to heat to room temperature and then heated to 40 °C to melt the bottom crystalline solid sulfuric acid phase to allow the two layers to be separated. The mixture was cooled again causing the bottom acid layer to freeze forming a separate upper liquid organic layer (26.8 g), which was decanted. Distillation of the decanted phase afforded 19.2 g (63% yield) of the sultone **9e** and 4.94 g of a high boiling fraction with bp 50–80 °C/2 mm. To remove fuming SO_3 impurity, the sultone was washed with 3 g of concentrated sulfuric acid and re-distilled to give a mixture of the sultone **9e** (85.7%) and its linear isomer **11e** (6%) with bp 103–105 °C (Lit. [7] sultone bp 66 °C/180 mm). The sultone $CF_3{}^aCF_2{}^bCF_2{}^cOCF^dCF_2{}^eSO_2O$ (cyclic CF^d–OSO_2) ^{19}F and ^1H NMR (neat): −81.4 (a, CF_3 t), −129.41 (b, CF_2 s), −84.44 m and −81.95 5-fold (c, CF_2 ABq $J = 161.1$ Hz), −88.15 (d, CF 7-fold), −97.52 d and 98.92 t (e, CF_2 ABq $J = 150.5$ Hz); MS: 347 [$(m+1)^+$ 18], 283 (8), 233 (62), 169 (100); the linear isomer **11e** $CF_3{}^aCF_2{}^bCF_2{}^cOCOCF_2{}^dSO_2F^e$ ^{19}F NMR: −81.40 (a, CF_3 t), −129.62 (b, CF_2 s), −86.84 (c, CF_2 q), −104.29 (d, CF_2 d), 43.12 (e, SO_2F t); MS: 347 [$(m+1)^+$ 100], 283 (30), 261 (28), 233 (18), 169 (52). The high boiling material (4.94 g) is a mixture with the main components: sulfonic acid **13e** (see MS and NMR in the experiment in Section 3.6) and HSO_3F.

3.5. Interrupted reaction perfluoro(propylvinyl) ether (VE) with oleum

At room temperature, 13.3 g (50 mmol) VE was carefully added to 6.24 g 65% oleum (51 mmol SO_3) trying not to mix layers. While stirring, an exothermic reaction ensued causing the vinyl ether to boil and reflux. Boiling subsided in 10 min though the exothermic reaction continued and the reaction mixture formed two layers. The mixture was cooled to 0 °C, the bottom sulfuric acid phase (2.34 g) was separated, the upper sultone layer was washed two times with two 2-ml portions of concentrated sulfuric acid to obtain 16 g of crude VE-sultone **9e**. Distillation of the product with a few not removed drops of H_2SO_4 gave 11.9 g (69%) of the VE-sultone with bp 98–105 °C.

3.6. Reaction of VE with excess oleum and complete homogenization

To 42.7 g 65% oleum (0.35 mol SO_3) in a flask with magnetic bar stirrer, reflux condenser at −9 °C and end trap (−78 °C) was added 50.9 g (0.19 mol) VE at 0 °C. After addition was complete, the agitated mixture was allowed to warm to room temperature. An exothermic reaction was noted after about 10 min, which caused the VE to reflux. Refluxing continued until the reaction mixture became homogeneous (in 30 min). Then, the mixture was heated for 3 h at 50–55 °C to complete collection of 8.6 g sulfur dioxide in the end trap. The residue was washed two times by 7 ml portions of conc. H_2SO_4 to give 55.5 g of a mixture consisting of four main components (by GC) with 20–26% of each. Distillation on the ACE Glass Inc. concentric tube column gave: (1) bp 69.5 °C fluorooxalate **14e** with purity 96.9%, $F^aCOCOOCF_2{}^bCF_2{}^cCF_3{}^d$ ^{19}F NMR ($CFCl_3$): 20.68 (a, FCO s), −89.06 (b, CF_2 q), −130.03 (c, CF_2 s), −81.77 (d, CF_3 t); MS: 261 [$(m+1)^+$ 100], 233 (30), 169 (36), 75 (50); IR (neat, KBr, cm^{-1}): 1824 (CO), 1868 (COF); (2) bp 103 °C difluoroacetate **12e** with purity 94.9% F^aSO_2-$OCF_2{}^bCOOCF_2{}^cCF_2{}^dCF_3{}^e$ ^{19}F NMR (neat): 49.48 (a, FSO_2 t), −78.18 (b, CF_2 d), −87.90 (c, CF_2 q), −130.08 (d, CF_2 s), −81.84 (e, CF_3 t); MS: 363 [$(m+1)^+$ 100], 343 (2), 315 (2), 269 (30), 169 (8), 149 (80); IR (neat, KBr, cm^{-1}): 1487 (SO), 1848 (CO); (3) bp 54 °C/3 mm diester **15e** with purity 94.5% $CF_3{}^aCF_2{}^bCF_2{}^cOCOCF_2{}^dSO_2OCF_2{}^e$-$COOCF_2{}^fCF_2{}^gCF_3{}^h$ ^{19}F NMR ($CFCl_3$): −81.92 (a, CF_3 t), −130.18 (b, CF_2 s), −88.01 (c, CF_2 q), −104.72 (d, CF_2 t), –74.65 (e, CF_2 t), −87.60 (f, CF_2 q), −130.11 (g, CF_2 s), −81.88 (h, CF_3 t); MS: 607 [$(m+1)^+$ 10), 543 (8), 393 (2), 329 (32), 261 (22); IR (neat, KBr, cm^{-1}): 1451 (SO), 1844 (CO); (4) bp 88–89 °C/3 mm sulfonic acid **13e** with purity (NMR) 97% $CF_3{}^aCF_2{}^bCF_2{}^cOCOCF_2{}^dSO_3H$ ^{19}F and ^1H NMR: −81.30 (a, CF_3 t), −129.38 (b, CF_2 s), −86.89 (c, CF_2 q), −106.98 (d, CF_2 s), 7.70 (OH); MS: 345 [$(m+1)^+$ 8], 343 [$(m-1)^+$ 100], 261 (2), 249 (8); IR (neat, KBr, cm^{-1}): 1399 (SO), 1835 (CO), 2100–3400 (OH).

3.7. Fluorosulfonyldifluoroacetyl fluoride from VE-sultone

To chilled and solid VE-sultone (7.0 g with purity 86%, 17 mmol) in a flask with magnetic bar stirrer, condenser at –22 °C and the end trap at −78 °C was added three drops (0.028 g) triethylamine. Immediate melting and a gas evolution were observed. In approximately 1.5 h, after gas evolution ceased, three more drops of triethylamine was added and the reaction continued with reflux for three more hours. Perfluoropropionyl fluoride **16** (2.42 g, 84% yield) was collected in the end trap. Following this, distillation of the residue in the reactor gave 2.85 g (80% yield) fluoride **11d** with bp 24–31 °C and purity (GC) 88% (see NMR and MS in the experiment in Section 3.9).

3.8. Reaction TFE with oleum in open system

TFE from a cylinder was bubbled through 14.0 g 67% oleum (117 mmol SO_3) in a two-neck flask equipped with a magnetic stir bar, a condenser at −8 °C and an end trap (−78 °C). The slightly exothermic reaction with TFE ended in approximately 5 h and 7.8 g (78 mmol) of TFE was consumed to give a clear liquid in the reactor and 4.85 g of low boilers (mainly SO_2 according to FTIR) in the end trap. The clear liquid was distilled under vacuum up to 70 °C/25 mmHg to give a distillate that was in turn combined and treated with methanol at −20 °C, washed with water and dried to yield 2.16 g of mixed methyl esters. The main component of the mixture was dimethyloxalate $(COOCH_3)_2$ (GC 73%). The other compounds identified were known [4] methylfluorosulfonyldifluoroacetate (5.1%) $FSO_2CF_2COOCH_3$ ^{19}F and ^1H NMR: 40.82 (FSO_2 t), −103.75 (CF_2 d), 4.09 (CH_3 s) and [12] methylfluorosulfatodifluoroacetate (1.8%) $FSO_2OCF_2COOCH_3$ ^{19}F and ^1H NMR ($CFCl_3$): 48.55 (FSO_2 t), −77.72 (CF_2 d), 3.93 (CH_3 s) and also diester **17** (3.7%) $CH_3OCOCF_2{}^aSO_2$-$OCF_2{}^bCOOCH_3$ ^{19}F and ^1H NMR: −104.39 (a, CF_2 t), −74.27 (b, CF_2 t), 3.89 (CH_3 s); MS: 299 [$(m+1)^+$ 82], 235 (30), 215 (64), 173 (20), 109 (100) and bis(methoxycarbonyldifluoromethyl)sulfate **18** (5.1%) $SO_2(OCF_2$-$COOCH_3)_2$ ^{19}F and ^1H NMR: −77.63 (CF_2 s), 3.93 (CH_3 s); MS: 315 [$(m+1)^+$ 44], 189 (100).

3.9. Reaction TFE with oleum in pressure reactor

A 100 ml Parr reactor was charged with 32.9 g 67% oleum (0.27 mol SO_3), cooled to 10 °C and briefly evacuated. TFE was then charged at 10–15 °C from a steel cylinder to 2.8 bar. TFE was periodically added to maintain the pressure at 2.8 bar. In 4 h after 28.5 g TFE was charged to the Parr reactor, there was no evidence of reaction. The reactor was then heated at 60–70 °C for 3 h, slowly vented at 70 °C through two −78 °C traps in series (the second trap with methanol) and a gas bag at the end to give 38.2 g fuming liquid in reactor, 20.0 g in the first trap, 0.24 g CF_3COF in the second trap with methanol (identified by GC as methyltrifluoroacetate) and 0.95 g TFE were collected in the gas bag. A total of 27.1 g (0.27 mol) of TFE was consumed. The material collected in the first trap consisted mainly of SO_2 (34%) and 32% oxalylfluoride $(COF)_2$ FTIR (cm^{-1}): 1860.7 and 1896.8 (CO) and also 3% fluoride **11d** FSO_2CF_2COF ^{19}F NMR (CCl_4): 24.07 (FCO q), −104.98 (CF_2 t), 42.82 (FSO_2 q) and 7% fluoride **12d** [12] FSO_2OCF_2COF ^{19}F NMR (CCl_4): 15.14 (FCO t), −77.57 (CF_2 dd), 49.94 (FSO_2 t); MS: 197 [$(m+1)^+$ 60], 149 (100), 97 (14); plus 2% difluoride **15d** $F^aCOCF_2{}^bSO_2OCF_2{}^cCOF^d$ ^{19}F NMR (CCl_4): 25.07 (a, F t), −104.61 (b, CF_2 q), −73.80 (c, CF_2 t), 15.14 (d, F t); MS: 275 [$(m+1)^+$ 20], 161 (36), 133 (36), 97 (100). The clear fuming liquid in reactor was distilled (with decomposition) to give: 1.26 g fraction with bp 96–100 °C and 25.6 g fluoro-sulfonic acid with bp 155–172 °C. The fraction with a bp of 96–100 °C was treated with methanol to yield a mixture of two diesters (NMR, wt.%): 69.5% $SO_3(CF_2COOCH_3)_2$ and 12.8% $SO_2(OCF_2COOCH_3)_2$ (NMR and MS see in the experiment in Section 3.8). The main products of the reaction of TFE with oleum and yields are: oxalyldifluoride $(COF)_2$ 25%, fluorosulfonyldifluoroacetyl fluoride FSO_2CF_2COF 3%, fluorosulfatodifluoroacetyl fluoride FSO_2OCF_2COF 3% and also difluoride $FCOCF_2SO_2OCF_2COF$ and sulfate $(FCOCF_2)_2SO_4$ (identified as dimethyl esters **17** and **18**) 3%.

3.10. Reaction CTFE with oleum in an open system

CTFE (43.4 g) from steel cylinder was bubbled through 50.2 g 65% oleum (0.4 mol SO_3) stirred at 5–8 °C in a round bottom flask equipped with a condenser at 0 °C and an end trap (−78 °C). In 4 h, the CTFE addition was ended after 21.6 g (0.18 mol) CTFE was consumed. Excess CTFE, sulfur dioxide and low boiling products (15.6 g) collected in the trap were treated with methanol to give 5.1 g of a mixture of two esters (NMR wt.%): 60% methyldifluorofluorochloroacetate and 32% dimethyloxalate along with 6% difluorochloroacetic acid. The clear liquid left in the reactor was distilled under vacuum to give 37.7 g of distillate (collected in −78 °C trap) with a bp up to 81 °C/25 mm and 32.6 g of non-distilled residue. Re-distillation using an Ace Glass concentric tube column gave a low boiling fraction comprising SO_2 (in the trap) and 2.44 g of oxalylchloridefluoride [13] with a bp 23–27 °C and purity 88%, MS (CCl_4): 111 [$(m+1)^+$ 24), 75 (100). The following impurities were detected (GC/MS); 1.8% $(COF)_2$, 4.8% SO_2 and 4.8% fluorosulfatofluorochloroacetylfluoride $FSO_3CFClCOF$ or isomers. Continuation of the distillation gave a 7.0 g fraction with a bp of 74–89 °C and 18.7 g of a mixture of chloro- and fluoro-sulfonic acids with a bp of 145–165 °C. GC/MS analysis of the fraction with bp 74–89 °C showed that it consisted of: 21% of a compound with M132 (possibly CF_2ClCOF/isomer), 3.5% of compound with M196 (possibly $FSO_2CFClCOF$/isomers) and 27% of three isomeric compounds with M212 (possibly FSO_3-$CFClCOF$ and isomers).

Acknowledgements

The authors are grateful to the Specialty Materials Division Analytical group (T.A. Kestner, S.D. Kromer, G.J. Lillquist and J.F. Schulz) for MS and NMR spectra interpretation of complex mixtures of fluorine compounds.

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