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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Electrochemical Fluorination of Unsaturated Sulfides and Sulfones

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Abstract—Electrochemical fluorination of some unsaturated sulfides and sulfones and their reactions with anhydrous HF were studied.

Electrochemical fluorination (ECF) of organosulfur compounds in anhydrous HF was studied with saturated or aromatic sulfides, disulfides [1–3], thiols [4–6], sulfoxides [1], and sulfones [7]. On the whole, ECF of S(II) derivativres involves cleavage of one or both S–C bonds. The C–S(O)–C moiety in sulfoxides is not preserved in ECF [1], whereas ECF of sulfones yielded, along with perfluoroalkylsulfonyl fluorides R_fSO_2F, also the corresponding sulfones $R_fSO_2R_f$ [7]. Virtually no data are available, except a single paper [9], on ECF of unsaturated aliphatic or alkenylaromatic sulfides and sulfones.

In this work, we studied ECF of ethyl vinyl sulfide $C_2H_5SCH{=}CH_2$ (**I**), di(1-propenyl) sulfide $(CH_3{-}CH{=}CH)_2S$ (**II**), phenyl vinyl sulfide $C_6H_5SCH{=}CH_2$ (**III**), and phenyl vinyl sulfone $C_6H_5SO_2CH{=}CH_2$ (**IV**), and also reactions of anhydrous HF with **III**, **IV**, and divinyl sulfide $(CH_2{=}CH)_2S$ (**V**). We failed to perform ECF of dichlorovinyl aryl sulfones $ArSO_2{-}CH{=}CCl_2$ (Ar = Ph, *m*-ClC_6H_4, *m*-$NO_2C_6H_4$) because of their insolubility in HF. The compositions and structures of liquid ECF products were determined by GLC, GC–MS, elemental analysis, IR spectroscopy, and ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy. Gaseous ECF products were analyzed by IR spectroscopy and gas chromatography (GC).

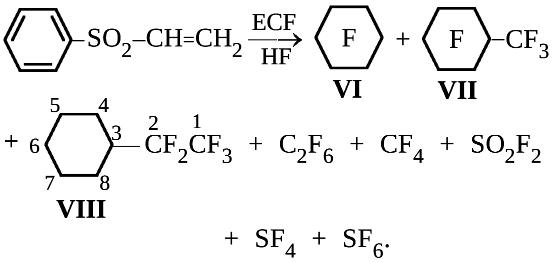
Electrochemical fluorination of sulfide **I** yields gaseous products among which we identified by GC and IR spectroscopy CF_4, C_2F_6, C_3F_8, C_4F_{10}, SF_4, SF_6, SO_2F_2, F_2O, and also liquid low-boiling products (bp 30–35°C) exhibiting no IR absorption in the range above 1350 cm^{-1}, which indicates that these products contain no C=C and C–H bonds. The ^{13}C NMR spectra of liquid ECF products of **I** contain a quartet of triplets at 116 ppm corresponding to the C_2F_5 group. As judged from the boiling points, the major products of ECF of **I** are dodecafluoropentane C_5F_{12} (bp 29.3°C [10]) and pentafluoro(1,1,2,2,2-pentafluoroethyl)-λ^6-sulfane $C_2F_5SF_5$ (the boiling point of the closest homolog, $C_3F_7SF_5$, is 43°C [6]). Formation of dodecafluoropentane was confirmed by the fact that the intensity of ^{19}F NMR signal at –84.2 ppm (CF_3) was equal to the sum of the intensities of the signals at –125.3 (C^3F_2) and –128.9 ppm ($C^{2,4}F_2$), by its refractive index, which was close to the reference value [10], and by the IR spectrum of the distilled product, which coincided with the reference spectrum [11]. The presence of pentafluoro(1,1,2,2,2-pentafluoroethyl)-λ^6-sulfane is confirmed by the substantial (>6%) sulfur content in the liquid products and by the presence in the ^{19}F NMR spectrum of downfield signals at δ_F 46.53 and 64.15 ppm with the intensity ratio of 4 : 1 and J_{FF} 143 Hz. According to [12], the downfield signal belongs to the axial fluorine, and the upfield signal, to equatorial fluorine atoms of the SF_5 group. On the whole, ECF can be described by the equation

$$C_2H_5SCH{=}CH_2 \xrightarrow[HF]{ECF} C_nF_{2n+2}\ (n = 1\text{–}5) + C_2F_5SF_5$$

$$+ SF_4 + SF_6 + SO_2F_2 + F_2O. \qquad (1)$$

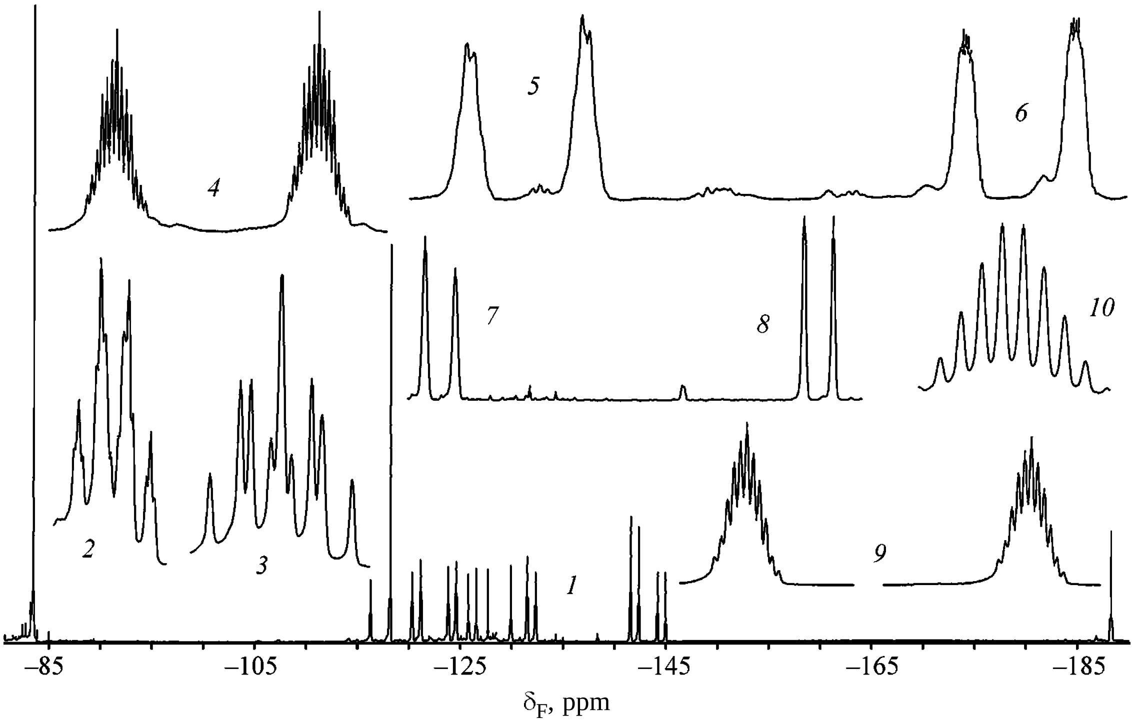
The gaseous products of ECF of sulfide **II** include HF, CF_4, C_2F_6, CO, CO_2, F_2O, and SO_2F_2. CO, CO_2, and SO_2F_2 are formed by electrochemical fluorination of oxygen-containing organic impurities present in the initial compound. Oxygen difluoride OF_2 is the product of electrochemical fluorination of water present in small amounts in liquid HF and in the substrate. The content of sulfur in liquid ECF products is about 2%, and that of hydrogen, about 0.5% (at the level of the determination error); the absence of absorption bands above 1350 cm^{-1} indicates that C=C and C–H bonds are absent. This means that ECF involves substitution of all hydrogen atoms, addition of fluorine to all double bonds, and noticeable removal of sulfur. A GC–MS analysis revealed formation of four products, For all of them, the base peak is that of the CF_3^+ ion, and the other peaks (5–20%) are those of C_bF_m ions (n = 1–6, m = 3–13, odd m). Since perfluorocarbons typically give in the mass spectra the $[M - F]^-$ ion and ions corresponding to successive loss of CF_2 up to formation of CF_3^+, our mass spectra confirm formation of perfluorohexanes. Liquid products were fractionated at 50–86°C. The ^{19}F NMR spectra of all the fractions show signals at –75 to –85 (CF_3), –110 to –130 (CF_2), and –185 to –190 ppm (CF). The presence of several CF_3 signals suggests formation of both linear (CF_3CF_2, δ_{CF_3} –80 to –85 ppm) and branched [$(CF_3)_2CF$, δ_{CF_3} –70 to –75 ppm] perfluoroalkanes; the presence of branched perfluoroalkanes is also confirmed by the CF signal at –185 to –190 ppm. As judged from the boiling points, the major ECF products of **II** are linear and branched perfluoroalkanes C_6–C_7. The downfield region of the ^{19}F NMR spectrum of the fraction with bp 80–85°C contains signals at δ_F 46.62 and 61.20 ppm (intensity ratio 4 : 1, J_{FF} 138.8 Hz) belonging, apparently, to pentafluoro(1,1,2,2,3,3,3-heptafluoropropyl)-λ^6-sulfane $C_3F_7SF_5$. The ^{19}F NMR spectrum of the fraction with bp 100°C contains signals at δ_F 42.82 and 61 ppm (J_{FF} 137.7 Hz), belonging, apparently, to equatorial and axial fluorine atoms of the SF_5 group in $C_5F_{11}SF_5$. The signal at δ_F = 28.09 ppm, characteristic of the SF_4 group [12], belongs, apparently, to tetrafluoro[bis(1,1,2,2,3,3,3-heptafluoropropyl)]-λ^6-sulfane $(CF_3CF_2CF_2)_2SF_4$. These data indicate that ECF involved desulfuration with formation of linear and branched C_6–C_8 perfluorocarbons, and also oxidation of sulfur.

In the experiment on ECF of **III**, we analyzed only the gaseous products by IR spectroscopy. Similar to ECF of **I** and **II**, HF, CF_4, SF_4, SF_6, SOF_2, and SO_2F_2 are formed, i.e., the reaction involves oxidation of sulfur and cleavage of the C–S bonds. Electrochemical fluorination of **IV** occurs with complete saturation and desulfuration and is accompanied by fragmentation, yielding perfluorocarbons of the cyclohexane series:



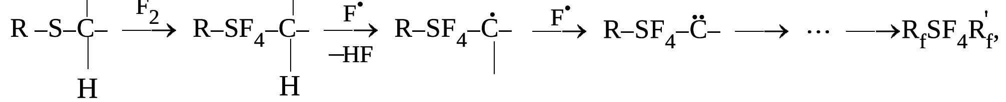
(2)

Along with the compounds indicated in the scheme, we identified in the gas phase HF, CO, CO_2, and F_2O. The sulfur content in the liquid products is less than 3%, and the hydrogen content, less than 1%. A GC–MS analysis revealed three major products with the fragmentation pattenrs similar to that given for **II**. The ^{19}F NMR spectrum of the products before distillation contained downfield signals at δ_F 65.8 and 61.4 ppm, suggesting formation of R_fSF_5 derivatives, as in ECF of **I** and **II**. The low-boiling (48°C) fraction from distillation of liquid ECF products of **IV** solidifies; its ^{19}F NMR spectrum contains a very broad signal at δ_F –134 ppm. These data confirm formation of perfluorocyclohexane **VI** (mp 51°C, bp 52°C [13]; δ_F –133.25 ppm [14]). The large width of the signal is due to mutual transformations of conformers of **VI** [15]; the signal width varies by two orders of magnitude with temperature [13]. Perfluorocyclohexane **VI** is formed by ECF of various aromatic compounds, including thiophenol [16]. Formation of perfluoroalkylperfluorocyclohexanes **VII** and **VIII** is confirmed by the presence of CF in the ^{13}C NMR spectrum (doublets of multiplets at 96 ppm for **VII** and at 88 ppm for **VIII**) and, in the case of **VIII**, of a quartet of triplets at 116.6 ppm belonging to the CF_3 gorup. The presence of perfluoroethylperfluorocyclohexane **VIII** was confirmed by GLC and by comparison of the ^{13}C and ^{19}F NMR spectra with those of an authentic sample. The content of **VIII** in the product mixture is 19.3%. The ^{19}F NMR spectrum is a complex set of multiplets (see figure). Consideration of the chemical shifts, multiplicities, and integral intensities of signals and comparison with the ^{19}F NMR spectrum of **VII** [17] lead to the following assignments, δ_F, ppm: CF_3 –83.51 d.t.t, 3F, ^2J 2.3, ^3J 14.0, ^3J 12.8 Hz; CF_2 –118.13 t.t, 2F, ^3J 15.8, ^4J 21.5 Hz; CF –187.97 m, 1F, ^3J 15.0 Hz; C^4F_{eq}, C^8F_{eq} –120.67 d.m, 2F, ^2J 303.0 Hz; C^5F_{eq}, C^7F_{eq} –124.11 d.m, 2F, ^2J 288.5 Hz; C^6F_{eq} –126.05 d.m, 1F, ^2J 289.4, ^3J 7.0 Hz; C^4F_{ax}, C^8F_{ax} –131.78 d.m, 2F, ^2J 303.0 Hz; C^5F_{ax}, C^7F_{ax} –141.7 d.m, 2F, ^2J 288.5 Hz; C^6F_{ax} –144.37 d.m, 1F, ^2J 289.4, ^3J 7.0 Hz.

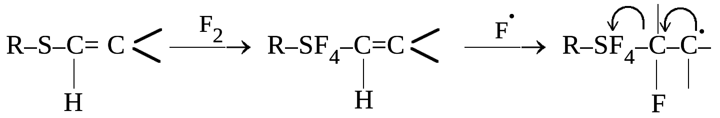


^{19}F NMR spectrum of perfluoroethylperfluorocyclohexane: (*1*) total, (*2*) CF_3, (*3*) CF_2, (*4*) C^6F_{eq}, (*5*) $C^{4(8)}F_{eq}$, (*6*) $C^{5(7)}F_{eq}$, (*7*) $C^{4(8)}F_{ax}$, (*8*) $C^{5(7)}F_{ax}$, (*9*) C^6F_{ax}, and (*10*) CF.

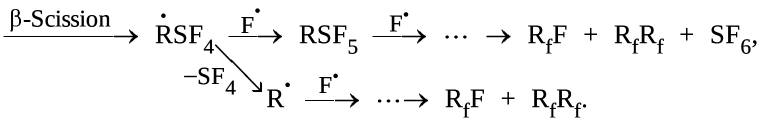
The compounds studied in this work differ from the previously studied alkanethiols, dialkyl sulfides, and dialkyl sulfones in that, in ECF of unsaturated sulfides and sulfones, the yield of sulfur-containing organic compounds is extremely low. For example, in ECF of vinyl sulfides, perfluoroalkyl derivatives of sulfur hexafluoride R_fSF_5 and $R_fSF_4R_f$, which are typical products of ECF of saturated S(II) derivatives [1–6], are formed in minor amounts. As for S(VI) derivatives, it is noted in the literature that the S=O bonds show very high stability in the process, which opens up possibilities for commercial synthesis of trifluoromethanesulfofluoride and, starting from this compound, of the whole class of triflates. However, this is true only for the lower representatives of this series. The yield of perfluoroalkanesulfonyl fluorides R_fSO_2F in ECF oof sulfonyl chlorides RSO_2Cl decreases in the order R = C_1–C_8 from 87 to 25% [18]. In unsaturated sulfones, as shown by the example of **IV**, the ECF products contain virtually no organic sulfonyl detivatives. An increased tendency of unsaturated sulfides and sulfones to undergo desulfuration in ECF is probably due to the fact that the C=C bond is fluorinated more readily than the C–H bond. In the first stage of ECF of S(II) derivatives, S(II) is oxidized to S(VI) [5]. Then, in the case of saturated sulfides, an α-centered radical is formed, and, in the case of unsaturated sulfides, the fluorine atom can add to the α-C atom with subsequent β-scission, which increases the probability of formation of desulfuration products. The general scheme of the process can be represented as follows:



$$\mathrm{R{-}S{-}\underset{H}{\overset{|}{C}}{-}} \xrightarrow{F_2} \mathrm{R{-}SF_4{-}\underset{H}{\overset{|}{C}}{-}} \xrightarrow[-HF]{F^\bullet} \mathrm{R{-}SF_4{-}\underset{|}{\dot{C}}{-}} \xrightarrow{F^\bullet} \mathrm{R{-}SF_4{-}\ddot{C}{-}} \longrightarrow \cdots \longrightarrow \mathrm{R_fSF_4R'_f},$$

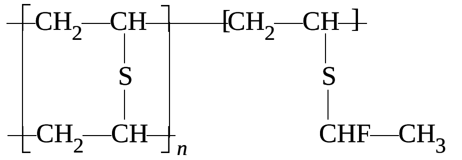


$$\mathrm{R{-}S{-}\underset{H}{C}{=}C{<}} \xrightarrow{F_2} \mathrm{R{-}SF_4{-}\underset{H}{C}{=}C{<}} \xrightarrow{F^\bullet} \mathrm{R{-}SF_4{-}\underset{F}{C}{-}\underset{|}{\dot{C}}{-}}$$

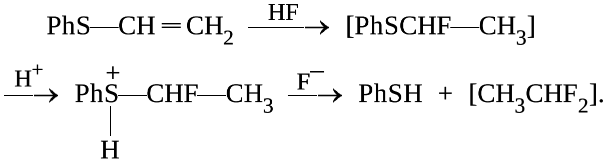


$$\xrightarrow{\beta\text{-Scission}} \dot{R}SF_4 \xrightarrow{F^\bullet} RSF_5 \xrightarrow{F^\bullet} \cdots \rightarrow R_fF + R_fR_f + SF_6,$$
$$\dot{R}SF_4 \xrightarrow{-SF_4} R^\bullet \xrightarrow{F^\bullet} \cdots \rightarrow R_fF + R_fR_f. \quad (3)$$

To examine the possibility of fluorination of vinyl sulfides and vinyl sulfones on dissolution in HF prior to ECF, compounds **III**–**V** were treated with anhydrous HF. We found that sulfone **IV** in which the vinyl group shows a decreased reactivity toward electrophilic agents due to the electron-withdrawing effect of the sulfonyl group does not react with HF even at 90°C (4 h). At the same time, sulfides **III** and **V**, when brought in contact with anhydrous HF, undergo transformations, probably due to the catalytic effect of HF as acid. For example, divinyl sulfide, when kept in HF at room temperature for several hours, polymerizes to give a light creamy powdered polymer containing 36% sulfur and 5% fluorine; prolonged heating does not change the chemical composition of the polymer, which indicates that the polymer contains chemically bound fluorine rather than adsorbed HF. The polymer is insoluble in organic solvents (benzene, methanol, dichloroethane, CCl_4, DMSO, DMF) and decomposes on heating above 290°C, which suggests its cross-linked structure. We propose the following structure of the polymers (n = 3 on the average):



Under similar conditions, phenyl vinyl sulfide gives products containing no vinyl group. After treatment of the reaction mixture with chloroform, removal of excess HF with NaF, distillation of the solvent, and evacuation, we obtained a blue-green viscous oil, from which we isolated by distillation thiophenol, which is probably formed by addition of HF, followed by protonation of sulfur and scission of the C–S bond with the release of volatile fluorocarbons:



$$PhS—CH{=}CH_2 \xrightarrow{HF} [PhSCHF—CH_3]$$
$$\xrightarrow{H^+} Ph\overset{+}{\underset{\displaystyle H}{S}}—CHF—CH_3 \xrightarrow{F^-} PhSH + [CH_3CHF_2].$$

The residue is a complex mixture; its ^1H NMR spectrum contains no signals from vinyl proton of the initial compound but contains complex multiplets in the range of aromatic (7.1–7.8 ppm) and aliphatic (1.0–3.5 ppm) protons, intensity ratio 5 : 4. According to elemental analysis, the product contains no fluorine. These facts suggest oligomerization of the initially formed $[PhSCHCH_3]^+$ ion with the formation of oligomers of the composition close to $(PhSC_2H_4)_n$. We failed to isolate or identify any individual products.

EXPERIMENTAL

The IR spectra of the products in the liquid phase were taken on an IKS-29 spectrometer in a thin film. The ^1H, ^{13}C, and ^{19}F NMR spectra were measured on a Bruker DPX 400 spectrometer (400, 100, and 376 MHz, respectively) with neat samples, external reference DMSO-d_6; the chemical shifts are given relative to TMS (^1H, ^{13}C) and $CFCl_3$ (^{19}F). The GC–MS analysis was performed with an LKB 2091 device (EI, 70 eV), and GLC analysis, on a Tsvet-100 chromatograph [thermal conductivity detector, carrier gas helium, 3000 × 3-mm columns, stationary phase 20% α,α,α-tris(β-cyanoethyl)acetophenone on Silochrom-80 (France)].

The IR spectra of gaseous electrolysis products were recorded on a Specord-20M spectrometer in a 10-cm Monel metal cell with AgCl windows. The GC analysis was performed with an LKhM-80 chromatograph (thermal conductivity detector, carrier gas helium, 3000 × 3-mm columns, sorbent MgF_2-17, particle diameter 0.25–0.5 mm).

Electrochemical fluorination was performed in a 150 cm^3 cylindrical cell made from St.3 steel and equipped with a reflux condenser and with stopcocks for supplying HF and removing liquid fluorination products; surface area of the nickel anode 54 cm^2. The reflux condenser was kept at –35°C with HCFC 22 as coolant.

Electrochemical fluorination of **I**–**IV** was performed as follows.

Ethyl vinyl sulfide I. An electrochemical cell was filled with 125 ml of anhydrous HF, and 10 g of divinyl sulfide was added. Electrolysis was performed at 14–16°C for 38 h (38 A h) at the anodic current density of 2 A dm^{-2} and cell voltage of 4.4–4.8 V. Electrolysis gases from the reflux condenser were sampled into an IR cell. IR spectrum of the gas, ν, cm^{-1}: 3700–4000 (HF); 1502, 1269, 848, 885, 925 (O_2F_2); 1300, 1290, 1250, 1120, 715 (C_2F_6); 900, 830, 610 (SF_4, SF_6); 828, 930 (F_2O). Gaseous samples for GC analysis were passed through aqueous KI. The following products were identified by GC: CF_4, C_2F_6, C_3F_8, C_4F_{10}, SO_2F_2, and SF_6. High-boiling fluorination products (1.6 g) were removed through the stopcock on the electrolyzer bottom into a polyethylene vessel filled with water. Found, %: C 19.46, H 0.58, F 70.86, S 6.24. By distillaiton, we isolated a fraction with bp 30–35°C, consisting mainly of dodecafluoropentane, n_D^{20} 1.2805 (bp 29.3°C, n_D^{15} 1.2411 [9]). The IR spectrum is in agreement with published data [10]. ^{19}F NMR spectrum, δ_F, ppm: –84.2 (CF_3), –125.3 ($CF_2CF_2CF_2$), *–128.9* (CF_3CF_2). ^{13}C NMR spectrum, δ_C, ppm: 116.2 q.t (CF_3CF_2, $^1J_{CF}$ 286.5, $^2J_{CF}$ 34.0 Hz), 109.4 m ($CF_2CF_2CF_2$). The fraction contains a minor amount of pentafluoro(1,1,2,2,2-pentafluoroethyl)-λ^6-sulfane. ^{19}F NMR spectrum, δ_F, ppm: –83.54 [CF_3, $J(CF_3–SF_4)$ 9 Hz], –100.1 [CF_2, $J(CF_2–F_{eq})$ 13 Hz], 46.53 d (SF_4), 64.15 quintet [$J(F_{ax}–F_{eq})$ 143 Hz].

Di(propen-1-yl) sulfide II was treated similarly to **I**. Electrolysis was performed with a 30-g portion of **II** at 14–16°C for 122 h (122 A h) at the anodic current density of 2 A dm^{-2} and cell voltage of 5.3–6.8 V. IR spectrum of gaseous electrolysis products, ν, cm^{-1}: 3700–4000 (HF); 1502, 1269, 848, 885, 925 (SO_2F_2); 1300, 1290, 1250, 1120, 715 (C_2F_6); 828, 930 (F_2O); 900, 830, 610 (SF_4, SF_6). CF_4, C_2F_6, CO_2, and SO_2F_2 were identified by GC. Heavy fluorination products (7.35 g) were discharged into a polyethylene vessel filled with water. Found, %: C 21.2, H 0.76, F 62.65, S 2.10. The mixture of liquid products was fractionated. Fraction with bp 50–60°C. ^{19}F NMR spectrum, δ_F, ppm (the most intense signals are given): –74.96, –75.17 (*iso*-CF_3), –83.80, –84.17 (*n*-CF_3), –108.54, –127.64, –128.79 (CF_2), –185.66, –188.70 (CF). Fraction with bp 84–86°C. ^{19}F NMR spectrum, δ_F, ppm: 46.62, 61.20 (SF_5), –73.00, –74.86, –75.09 (*iso*-CF_3), –83.85, –84.07, –84.15 (*n*-CF_3), –114.06, –114.90, –122.75, –124.97, –126.58, –128.39 (CF_2), –184.87, –185.18, –187.46, –188.40 (CF). The ^{13}C NMR spectra of all the fractions contain doublets of multiplets in the range 90–92 ppm (CF), multiplets in the range 104–112 ppm (CF_2), and signals of two types of CF_3 groups: 118.11 q.d [CF_3CF, $^1J_{CF}$ 288.8, $^2J_{CF}$ 22.5 Hz] and 116.61 q.t [CF_3CF_2, $^1J_{CF}$ 286.5, $^2J_{CF}$ 34.4 Hz].

Phenyl vinyl sulfide III was treated similarly. Electrolysis was performed with a 18-g portion of **III** at 14–16°C for 45 h (45 A h) at the anodic current density of 2 A dm^{-2} and cell voltage of 5.7–7.6 V. IR spectrum of gaseous electrolysis products, ν, cm^{-1}: 3700–4000 (HF); 1502, 1269, 848, 885, 925 (SO_2F_2); 1300, 1290, 1250, 1120, 715 (C_2F_6); 828, 930 (F_2O); 900, 830, 610 (SF_4, SF_6).

Phenyl vinyl sulfone IV. A 20-g portion of phenyl vinyl sulfone was placed in an electrochemical cell, and 125 ml of anhydrous HF was added. Electrolysis was performed at 14–16°C for 64 h (64 A h) at the anodic current density of 2 A dm^{-2} and cell voltage of 5.5–6.6 V. IR spectrum of gaseous electrolysis products, ν, cm^{-1}: 3700–400 (HF); 2320, 2350 (CO, CO_2); 1502, 1269, 848, 885, 925 (SO_2F_2); 1300, 1290, 1250, 1120, 715 (C_2F_6); 828, 930 (F_2O). CF_4, C_2F_6, CO_2, and SO_2F_2 were identified by GC. The heavy fluorination products (8.74 g) were discharged into a polyethylene vessel filled with water. Found, %: C 17.2, H 0.80, F 66.41, S 2.92.

The mixture was separated by fractional distillation. The fraction with bp 38–48°C solidifies on cooling and mainly consists of perfluorocyclohexane **VI**. ^{19}F NMR spectrum, δ_F, ppm: –134 br.s. The fraction with bp 50–70°C contains perfluoromethylperfluorocyclohexane **VII**. ^{19}F NMR spectrum, δ_F, ppm: –188.7 m (CF), $^3J(CF_2–CF)$ 14.7 Hz. The fraction with bp 68–80°C mainly consists of perfluoroethylperfluorocyclohexane **VIII**. ^{13}C NMR spectrum (DMSO-d_6, δ_C, ppm: 116.26 q.t, CF_3, ^1J 287.12, ^2J 33.17 Hz; 103–112 m, CF_2; 87.42 d.sept, ^2J 218.93, ^3J 25.8 Hz.

Reactions of **III**–**V** with HF were performed as follows.

Phenyl vinyl sulfide III. Into a 100 cm^3 stainless steel autoclave, 3–5 ml of HF was condensed, and 3.0 g of **III** was added. The autoclave was kept at room temperature for 5 h. The mixture was diluted with 50 ml of chloroform and purged with air, after which NaF was added to pH 7.0. The solution was filtered and evaporated. From the resulting green viscous oil, 0.5 g of thiophenol was isolated by vacuum distillation (bp 50°C/23 mm Hg). ^1H NMR spectrum, δ, ppm: 3.54 s (SH, 1H), 7.21 m (*p*-CH, 1H), 7.29 m (*m*-CH, 2H), 7.33 m (*o*-CH, 2H). ^{13}C NMR spectrum, δ_C, ppm: 125.16 (C_p), 128.99 (C_o), 130.44 (C_1). The blue-green residue was analyzed by NMR. Found, %: C 73.10, H 6.74, S 20.66.

Phenyl vinyl sulfone IV. *a.* Similarly to the above procedure, 1.1 g of **IV** was added to HF. The autoclave was heated at 90°C for 4 h. Then 50 ml of chloroform was added, the mixture was purged with air, and NaF was added to pH 7.0. The solution was filtered and evaporated to dryness, and the residue was vacuum-dried (1 mm Hg). The initial sulfone **IV** (0.8 g) was recovered; its melting point and the ^{1}H and ^{13}C NMR spectra coincided with those of an authentic sample.

b. Gaseous HF was passed for 1.5 h through a solution of 0.84 g of **IV** in 30 ml of dry benzene, cooled with ice to 12–16°C. The mixture was purged with air under stirring, and NaF was added to pH 7.0. The solution was filtered and evaporated to dryness. The initial sulfone **IV** (0.5 g) was recovered; its melting point and the ^{1}H and ^{13}C NMR spectra coincided with those of an authentic sample.

Divinyl sulfide V. Into a stainless steel autoclave, 3–5 ml of HF was condensed, and 4.44 g of cooled sulfide **V** was added. The mixture was kept at room temperature for 24 h. A light creamy powdered polymer (4.48 g) was obtained. Found, %: C 51.35, H 6.72, F 5.90, S 36.02. Found after heating at 50°C for 24 h, %: C 50.33, H 6.52, F 5.10, S 36.34.

CONCLUSIONS

(1) Electrochemical fluorination of vinyl sulfides and sulfones occurs with complete substitution of all the hydrogen atoms by fluorine, addition of fluorine to the double bonds and benzene ring, and considerable desulfuration, yielding perfluorocarbons as major products, and also perfluoroalkyl derivatives of sulfur hexafluoride and fragmentation products.

(2) With no current applied, vinyl sulfones do not react with anhydrous HF even on prolonged heating, whereas vinyl sulfides take up HF (electrophilic addition to the double bond) with the subsequent scission of the C–S bond or polymerization.

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