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Reaction of Organyltrifluorosilanes with Dimethylsulfoxide and Domethylformamide and Its Spectroscopic Investigation

M. G. Voronkov, E. V. Boyarkina, G. A. Gavrilova, and S. V. Basenko

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia

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Abstract—Reaction of organyltrifluorosilanes $RSiF_3$ (R = C_6H_5, 3-$O_2NC_6H_4$, and $C_6H_5CH_2$) with DMSO and DMF (B) results in formation of the complexes $2B \cdot SiF_4$ and R_2SiF_2. Besides, biphenyl, benzene, methyl(fluoromethyl)sulfoxide, and *S,S'*-dimethyldisulfide-*S,S'*-dioxide $CH_3S(O)S(O)CH_3$ were either isolated or identified by chromatomass-spectrometry. Speculative mechanism of the reaction proceeding is discussed. IR spectra of the reaction mixtures and those of $2B \cdot SiF_4$ adduct were studied in details; they indicate octahedron structure of the complex with cis arrangement of B ligands.

We found that reaction of $PhSiF_3$ with DMSO (1 : 1 mole ratio) at 20°C for 48–72 h unexpectedly results in formation of stable crystalline adduct $2Me_2SO \cdot SiF_4$ (**I**) [1]. Other reaction products were diphenyldichlorosilane, biphenyl, benzene, methyl(fluoromethyl)sulfoxide and *S,S'*-dimethyldisulfide-*S,S'*-dioxide $CH_3S(O)S(O)CH_3$. Their formation was proven by chromatomassspectrometry; obviously it can be illustrated by the steps 1–7.

$$2\mathrm{PhSiF_3} \xrightarrow{\mathrm{Me_2SO}} 2[(\mathrm{Me_2SO})\cdot\mathrm{PhSiF_3}] \longrightarrow 2\mathrm{PH}^{\cdot} + \mathrm{Si_2F_6}, \qquad (1)$$

$$\mathrm{Si_2F_6} \longrightarrow \mathrm{SiF_4} + \mathrm{F_2Si{:}}, \qquad (2)$$

$$2\mathrm{Me_2SO} + \mathrm{SiF_4} \longrightarrow 2(\mathrm{Me_2SO})\cdot\mathrm{SiF_4}, \qquad (3)$$

$$2\mathrm{Ph}^{\cdot} \begin{cases} \longrightarrow \mathrm{Ph_2SiF_2}, & (4) \\ \longrightarrow \mathrm{PhPh}. & (5) \end{cases}$$

Benzene is obviously formed due to splitting off a hydrogen atom from DMSO by phenyl radical.

$$\mathrm{Ph}^{\cdot} + \mathrm{CH_3S(O)CH_3} \longrightarrow \mathrm{PhH} + {}^{\cdot}\mathrm{CH_2S(O)CH_3}. \qquad (6)$$

The fate of the last formed radical from DMSO is not established yet.

It cannot also be excluded that SiF4 is formed in the disproportion reaction induced by the initially formed $Me_2SO \cdot PhSiF_3$ adduct.

$$2\mathrm{PhSiF_3} \xrightarrow{\mathrm{Me_2SO}} \mathrm{Ph_2SiF_2} + \mathrm{SiF_4}. \qquad (7)$$

However, reaction (7) does not allow to explain the formation of biphenyl. In the absence of DMSO or DMF such a rearrangement does not occur.

The adduct 2Me2SO.SiF4 is also formed in the reaction of dimethylsulfoxide with other organylfluorosilanes $RSiF_3$ (R = $PhCH_2$ and 3-$NO_2C_6H_4$). In the last case, nitrobenzene was isolated, similarly. Similarly to DMSO, DMF reacts with phenyltrifluorosilane under the same conditions forming the complex $2Me_2NCHO \cdot SiF_4$ and diphenyldifluorosilane.

It is noteworthy that tertiary amines (Et3N and pyridine) and acetonitrile does not enter to the reaction (7). Reaction (7) of $PhSiF_3$ with DMSO in CS_2 proceeds poorly with no formation of complex **I**.

We studied IR adsorption spectra in the range of 4000–400 cm^{-1} of the products in the reactions of $RSiF_3$ (R = C_6H_5, 3-$NO_2C_6H_4$ and $C_6H_5CH_2$) in 1 : 1 ratio with dimethylsulfoxide and dimethylformamide. The IR spectra of stable crystalline complexes isolated from the mixtures of the organyltrifluorosilanes with dimethylsulfoxide are identical and correspond to the spectrum of the complex $2Me_2SO \cdot SiF_4$ (**I**). Similar complex, $2Me_2NCHO \cdot Sif_4$ (**II**) is formed in the reaction of phenyltrifluorosilane with dimethylformamide.

In the spectrum of complex **I** (Fig. 1a) the strongest broad and structurized band with maximum at 735 cm^{-1} occurs in the region of ν(Si–F) stretching vibrations at hexacoorsinated silicon atom [2, 3]. Bending vibrations δ(Si–F) induce a band at ~480 cm^{-1}. Other bands in the IR spectra of all the samples of adduct **I** correspond to vibrations in the DMSO molecule coordinated with silicon atom [4]: stretching ν_{as}(C–H) and ν_s(C–H) at 2990 and 2920 cm^{-1}, and planar bending vibrations of methyl

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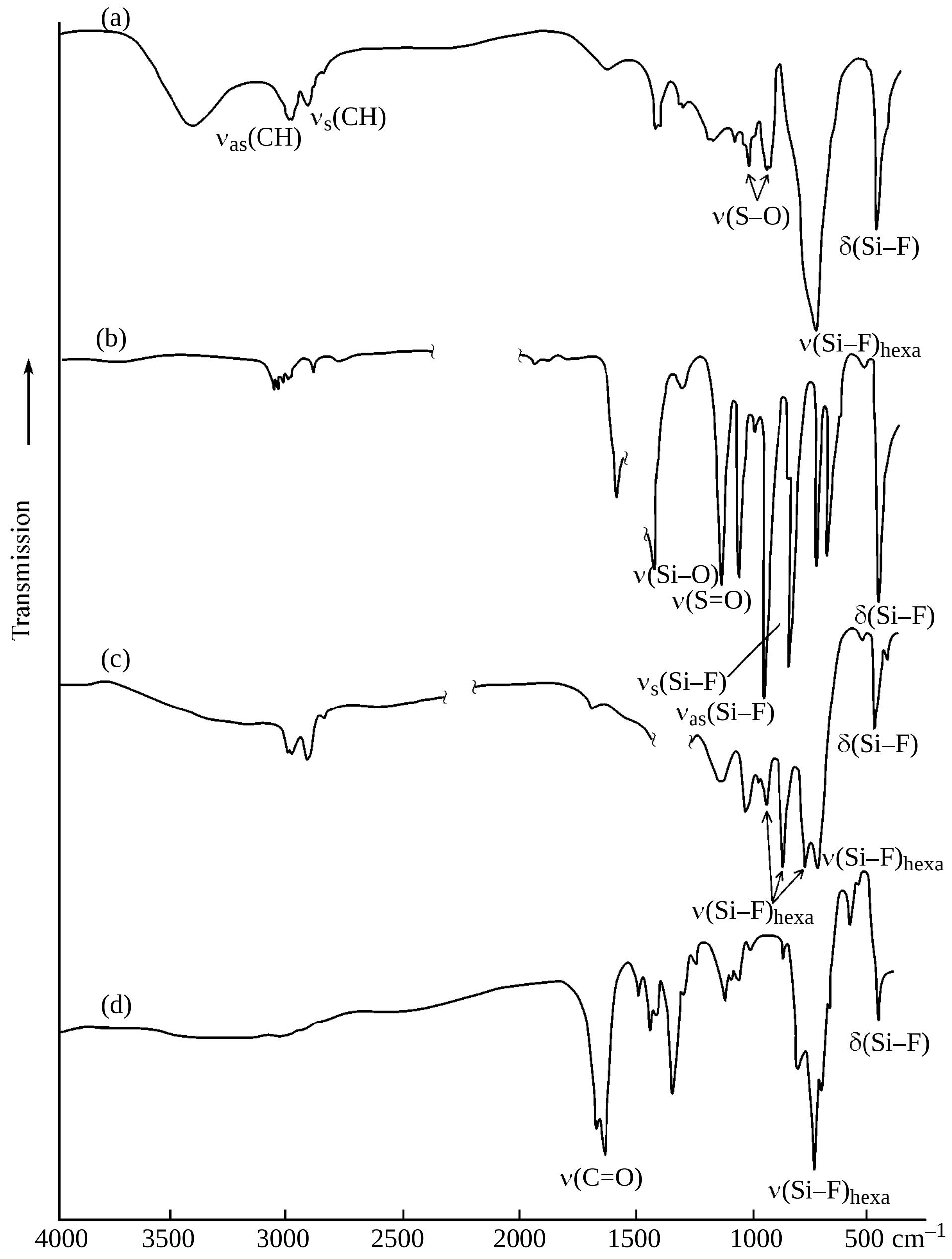

IR spectra of the complexes of tetrafluorosilane in the region of 4000–400 cm^{-1}. (a) $2Me_2SO\cdot SiF_4$, a pellet with KBr; (b) $Me_2SO + PhSiF_3$ in CS_2; (c) $2Me_2S\cdot OSiF_4$ in CH_3CN; (d) $2Me_2NCHO\cdot SiF4$, a pellet with KBr. The discontinuities in the spectra (b) and (c) correspond to the areas of solvents absorption.

groups δ_{as}(Me) at 1430, 1416 and δ_s(Me) at 1317, 1330 cm^{-1}. Stretching vibration of sulfoxide group coordinated with silicon appears as two bands at 960 and 1030 cm^{-1}. The multiple structure with the maximum at 960 cm^{-1} is probably induced by mixing of stretching vibration $\nu(S{=}O)_{coord}$ with energetically close out-of-plane bending vibration ρ(Me) (in the spectrum of DMSO there is a related band at 920 cm^{-1}). Position of the maxima of the above bands and a lowfrequency shift of ν(S=O) in particular, as compared with free free sulfoxide group (1040 cm^{-1}) reliably confirm coordination of DMSO molecules with tetrafluorosilane through oxygen atom. This fact does not contradict to the discussion about donor type of the DMSO reaction center (O or S) at its coordination with a Lewis acid [5, 6]. The complexes of SiF_4 with dimethylsulfoxide (1 : 2) similarly to the complexes with other oxygencontaining ligands are well studied with various physico-chemical methods, in part by vibration spectroscopy [7, 8].

Hexacoordinated tetrafluorosilane complexes $2B \cdot SiF_4$ have octahedron structure [8]. The ligands B in such complexes can be *cis* or *trans* arranged, and such complexes have C_s or C_{4v} symmetry, respectively. In the case of *trans*-octahedral structure of complex **I** only asymmetric stretching vibrations of two sulfoxide groups, ν_{as}(S=O), are active and should induce one band only. As we noted above, in the spectra of the complexes occur two absorption bands corresponding to the stretching vibrations of the sulfoxide groups coordinated with the silicon atom, with the maxima at 960 and 1030 cm^{-1}. This points to *cis*-octahedral structure of complex I with no symmetry elements. The band at higher frequency 1030 cm^{-1} is obviously belongs to sulfoxide group in the equatorial plane (in *cis* position) of the octahedron, and therefore it is less shifted to the low-frequency region relatively to the ν(S=O) 1040 cm^{-1} of free sulfoxide group, in the comparison with the band at 960 cm^{-1} corresponding to the sulfoxide group with its oxygen atom interacting with both silicon atom and the electronegative fluorine atom in the axial fragment of the octahedron. In this fragment the bond orders Si–F$_{ax}$ and S=O are considerably reduced due to electron density redistribution at the three-center four-electron bonding, as compared with the equatorial plane of the octahedron.

According to the IR data, liquid mixtures of DMSO with $RSiF_3$ contain compounds R_2SiF_2, together with the adduct **I**. Their presence is indicated by the bands ν(C–H) >3000, ν(C=C) 1595, 1580, ν(Si–C) 1139 cm^{-1}, as well as ν(Si–F) bands characteristic of tetracoordinated silicon, ν_{as}(Si–F) 950, ν_s(Si–F) 854, and δ(Si–F) 467 cm^{-1}. The data of mass-spectrometry confirm this conclusion. IR spectra of liquid mixtures of DMSO and $RSiF_3$ contain also bands of free DMSO molecules, ν(C–H) 2920, 3000, δ_{as}(C–H) 1404, 1415, δ_s(C–H) 1308, 1327, and ν(S=O)$_{free}$ 1056 cm^{-1}.

The IR spectroscopy method allowed us also to establish unusual influence of nature of a solvent on the reaction of $C_6H_5SiF_3$ with DMSO. The IR spectrum of the ternary system $C_6H_5SiF_3$–DMSO–CS_2 (Fig. 1b) contains no ν(Si–F) or ν(Si–F) bands of complex **I** which would be corresponding to hexacoordinated silicon atom. The spectrum contains bands corresponding to vibration of free DMSO, $C_6H_5SiF_3$ and $(C_6H_5)_2SiF_2$ molecules. Spectrum of solution of complex **I** in acetonitrile (Fig. 1c) together with the bands of Si–F bond of hexacoordinated silicon [ν(Si–F)$_{hexa}$ 730, δ(Si–F)$_{hexa}$480 cm^{-1}] contains the bands ν(Si–F) of pebntacoordinated silicon. Therewith, occurs typical for trigonal-bipyramidal environment of silicon atom splitting of the bands of Si–F bonds into three components: the strongest low-frequency band at 790 cm^{-1} corresponding to the stretching vibration of axial Si–F bond and the bands of symmetric and asymmetric vibrations of the Si–F bonds in the equatorial plane of the trigonal bipyramid (880 and 955 cm^{-1}, respectively). Hence, in acetonitrile medium there is an equilibrium between the complexes with penta- and hexacoordinated silicon atom, that is, $Me_2SO \cdot SiF_4$ and $2Me_2SO \cdot SiF_4$.

The solvents CCl_4 and THF do not affect IR spectrum of the complex **I**.

In the reaction of $C_6H_5SiF_3$ with DMF (1 : 1 mole ratio) at 20°C for 48–72 h crystalline adduct $2Me_2NCHO \cdot SiF_4$ (**II**) is formed. The complex **II** was prepared earlier by reaction of gaseous SiF_4 with DMF. Its structure was proven by X-ray structural analysis [9]. The IR absorption spectrum of the complex **II** in the region of 4000–400 cm^{-1} studied by us (Fig. 1d) does not contradict to the earlier published spectrum in 1900–700 cm^{-1} region. The spectrum of the adduct **II** has the strongest band at ~730 cm^{-1}, corresponding to ν(Si–F) at hexacoordinated silicon atom. The doublet structure of ν(C=O) absorption band attests *cis*-octahedric configuration of the complex **II**. The band at ~475 cm^{-1} corresponds to δ(Si–F)$_{hexa}$ stretching vibrations.

The problem of effect of organic solvents with different macro characteristics on the thermodynamic composition of equilibrium mixtures of hypervalent silicon derivatives was studied by us in details for intracomplex compounds with pentacoordinated silicon, the aroyloxymethyltrifluorosilanes and their analogs [10]. For the intermolecular fluorosilane complexes with bases this problem was not discussed in literature comprehensively and gives rise to further separate investigations.

EXPERIMENTAL

IR spectra were recorded in the range 4000–400 cm^{-1} for liquid samples of DMSO, $PhSiF_3$ (in micro layer), crystalline adducts $2Me_2S \cdot OSiF_4$ (in KBr pellets) and solutions of $2Me_2SO \cdot SiF_4$ in CS_2 and CH_3CN (in KBr cells with layer thickness 0.1 mm, concentration ~0.1 M) on a Specord IR-75 instrument. ^{19}F NMR spectra were registered on a Jeol FX-90Q instrument (90 MHz) for the 15–20% solutions in $CDCl_3$ (CCl_3F).

Reaction of phenyltrifluorosilane with dimethylsulfoxide. To dimethylsulfoxide (7.8 g) was added dropwise phenyltrichlorosilane (16.2 g). On keeping the solution at room temperature after 2–3 days dropped colorless crystals of cubic form. The crystals were filtered off and dried in a vacuum (10 mm). We obtained 8.3 g (32%) of complex **I**, with sublimation temperature 110°C. IR spectrum, cm^{-1}: 734 [ν(Si–F)], 478 [δ(Si–F)$_{hexa}$], 940, 951 [ν(S=O)$_{coord}$], 1025, 1045 [ρ(Me)], 1317, 1330 [δ_s(C–H)], 1416, 1430 [δ_{as}(C–H)]. Found, %: C 18.73; H 4.87; F 29.23; S 24.47. $C_4H_{12}F_4O_2S_2Si$. Calculated, %: C 18.45; H 4.65; F 29.19; S 24.63.

The following compounds were registered in the liquid phase. (1) Diphenyldifluorosilane. IR spectrum, cm^{-1}: 467 [δ(Si–F)], 854 [ν_s(Si–F)], 950 [δ_{as}(Si–F)], 1139 [ν(Si–C)], 1581, 1595 [ν(C=C)], >3000 [ν(C–H)]. ^{19}F NMR spectrum (CCl_3F), δ_F, ppm: –142 (J_{SiF} 290.11, J_{CF} 110.23 Hz). Mass spectrum, *m/z* (*I*, %): 220 (100) ($M^{+\cdot}$), 154 (55), 143 (16) $(M - C_6H_5)^+$, 77 (34) ($C_6H_5^+$). (2) Biphenyl (from trace amount to 2–4%). Mass spectrum, *m/z* (*I*, %): 154 (100) ($M^{+\cdot}$), 77 (27) ($C_6H_5^+$). (3) (Benzene, 0.95 g (12%), bp 77°C (730 mm). (4) Methylfluoromethylsulfoxide. Mass spectrum, *m/z* (*I*, %): 96 (52) ($M^{+\cdot}$), 61 (100), 47 (57). (5) *S,S'*-Dimethyldisulfide-*S,S'*-dioxide $CH_3S(O)S(O) \cdot CH_3$. Mass spectrum, *m/z* (*I*, %): 111 (53) ($M^+ - CH_3$), 81 (100), 79 (93), 47 (37).

Reactions of dimethylsulfoxide with benzyltrifluorosilane and 3-nitrophenyltrifluorosilane were conducted similarly. In the last case, nitrobenzene (14%) was also isolated, bp 61–62°C (4 mm). Mass spectrum, *m/z* (*I*, %): 123 (43) ($M^{+\cdot}$), 77 (100) ($C_6H_5^+$).

Reaction of phenyltrifluorosilane with dimethylformamide. To Dimethylformamide (7.3 g) was added dropwise 16.2 g of phenyltrifluorosilane. On keeping the solution at room temperature, after 2–3 days dropped colorless crystals. The crystals were filtered off and dried in a vacuum (10 mm). We obtained 7.3 g (28%) of complex **II** with sublimation temperature 135°C (published sublimation point 135°C [9]). Found, %: C 28.73; H 5.77; F 30.29; N 11.27. $C_6H_{14}F_4N_2O_2Si$. Calculated, %: C 28.80; H 5.64; F 30.36; N 11.19.

Liquid pase contained the following compounds. (1) Diphenylfluorosilane. IR spectrum, cm^{-1}: 467 [δ(Si–F)], 854 [ν_s(Si–F)], 950 [δ_{as}(Si–F)], 1139 [ν(Si–C)], 1581, 1595 [ν(C=C)], >3000 [ν(C–H)]. Mass spectrum, *m/z* (*I*, %): 220 (100) ($M^{+\cdot}$), 154 (50), 143 (15) $(M - C_6H_5)^+$, 77 (35) ($C_6H_5^+$). (2) Biphenyl. Mass spectrum, *m/z* (*I*, %): 154 (100) ($M^{+\cdot}$), 77 (25) ($C_6H_5^+$). (3) Benzene.

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