A new method for dissolution of silica gel in a pentafluoropropionyl fluoride—tertiary amine system

S. A. Lermontov and A. N. Malkova*

Institute of Physiologically Active Compounds, Russian Academy of Sciences, 1 Severnyi pr., 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 (496) 524 9508. E-mail: lermon@ipac.ac.ru

A new procedure for the preparation of amino complexes of silicon tetrafluoride was proposed. For this purpose, silica gel is dissolved in a fluoroanhydride—methanol system at room temperature followed by the precipitation of SiF_4 solvate that was formed with tertiary amine (pyridine, 1,10-phenanthroline, 2,2′-bipyridyl). The yields of the formed complexes are 69—83%.

Key words: silica gel, pentafluoropropionyl fluoride, silicon tetrafluoride, tertiary amines.

Silicon dioxide (SiO_2, silica) is one of the most abundant materials on the Earth and the most available source of silicon. The use of silica in chemical synthesis is restricted to a great extent because of its high chemical stability: SiO_2 is a polymer that can be destroyed only under specific conditions. Depolymerization of SiO_2 (followed by dissolution) in the reactions with alkalis and hydrogen fluoride is well known (Scheme 1, reactions (1) and (2)).

Scheme 1

$$SiO_2 + 2\,NaOH \longrightarrow Na_2SiO_3 + H_2O \quad (1)$$

$$SiO_2 + 4\,HF \longrightarrow SiF_4 + 2\,H_2O \quad (2)$$

$$SiO_2 + 2\,C \xrightarrow{1200\ ^\circ C} Si + 2\,CO \quad (3)$$

$$SiO_2 + 2\,C + 2\,Cl_2 \xrightarrow{1000—1100\ ^\circ C} SiCl_4 + 2\,CO \quad (4)$$

The main reactions of SiO_2 applied in industry are the high-temperature reduction ($T > 1200$ °C) of silica with carbon to form metallic silicon[1] or (after chlorination) silicon tetrachloride $SiCl_4$ (see Scheme 1, reactions (3) and (4)).[2]

A new procedure of SiO_2 depolymerization, namely, dissolution in alkoxides with distilling off water[3,4] (Scheme 2), has been developed in recent years.

This procedure is rather time-consuming and results, as a rule, in crystalline solvates containing water and glycol, which suppresses the use of these compounds in organometallic synthesis.

The purpose of the present work is a search for methods of silica (in the form of silica gel) dissolution satisfying the following requirements: (a) keep away from too high temperature; (b) afford silicon-containing products appropriate for organoelement synthesis or as a source of silicon for electronic industry.

Scheme 2

$$SiO_2 + 3\,HOCH_2CH_2OH + 2\,NaOH \overset{200\ ^\circ C}{\rightleftharpoons} \rightleftharpoons Na_2Si\left[\begin{array}{c}O\\ \diagup\ \diagdown\\ O\end{array}\right]_3 + 2\,H_2O$$

We found that silica gel is readily dissolved in an alcoholic medium when interacting with easily available fluoroanhydride of pentafluoropropionic acid and after treatment with aromatic amines it forms stable complexes in good yield (Scheme 3).

Scheme 3

$$SiO_2 + 4\,C_2F_5\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}F \xrightarrow[2\,L]{MeOH} SiF_4 \cdot L_2$$

1a—c

L_2 = 2,2′-bipyridyl (**a**), 1,10-phenanthroline (**b**), Py_2 (**c**)

Compounds **1a—c** are colorless stable crystalline substances soluble in DMSO and DMF; compound **1c** is also soluble in water and methanol. The structures of compounds **1a—c** were characterized spectrally and by elemental analysis data. Silica is rapidly dissolved at room temperature when fluoroanhydride is added to afford compounds **1a—c** as precipitates, which do not require further

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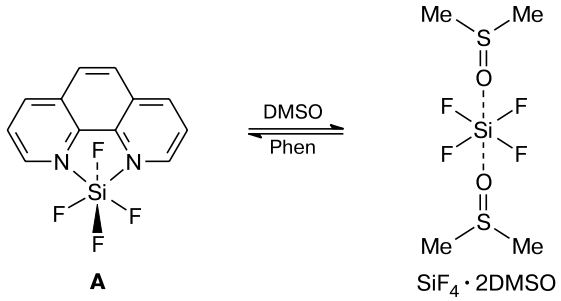
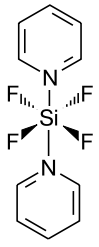
purification after filtration and drying. The ^{19}F NMR spectra of compounds **1a** and **1b** consist of two triplets in a ratio of 1 : 1 (A_2X_2 system). This indicates the formation of *cis*-complexes of the type **A**, which agrees with published data.[5,6] The spectra of analytically pure samples of the both complexes contain, in addition to two triplets, a broadened singlet, which is probably related to the presence of a SiF_4 complex with DMSO in a solution[7] (Scheme 4).

Scheme 4



Phen is 1,10-phenanthroline

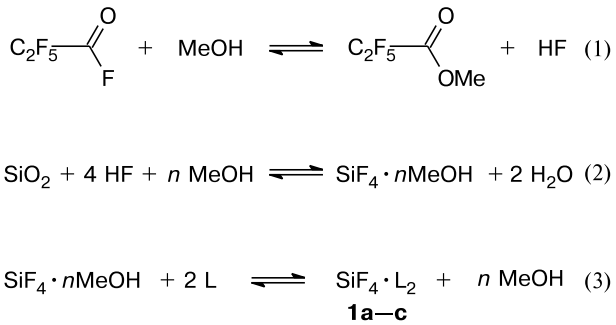
When non-chelating monoamine, *viz.*, pyridine, is used instead of bipyridyl and phenanthroline, diamino complex **1c** is formed with a structure of *trans*-arrangement of the ligands, which is confirmed by the ^{19}F NMR spectrum (singlet, unlike two triplets in the case of *cis*-arrangement of the ligands).



1c

The reaction of silica gel dissolution consists, most likely, of several steps (Scheme 5).

Scheme 5



The formation of comparatively stable SiF_4 complexes with alcohols (see Scheme 5, reaction (2)) was described.[8,9] Just these complexes favor gaseous SiF_4 to remain in solution: SiF_4 is not hydrolyzed with the evolved water to hexafluorosilicate[10] (Scheme 6).

Scheme 6

Phenanthroline complex **1b** was also synthesized by the reaction of tetraethyl orthosilicate with C_2F_5COF in acetonitrile (Scheme 7).

Scheme 7

Studies of the chemical properties of compounds **1a—c** and their use in organoelement synthesis are in progress.

Thus, in the present work we proposed the fast and convenient method for the depolymerization and dissolution of silica gel at room temperature affording stable forms of silicon tetrafluoride. These tetrafluorides can be used in both organoelement synthesis and as silicon products for electronic industry.

Experimental

^1H and ^{19}F NMR spectra were recorded on a Bruker DPX-200 spectrometer with working frequencies of 200 and 188 MHz, respectively, relative to Me_4Si and CF_3COOH in DMSO-d_6. Pentafluoropropionyl fluoride was synthesized by the isomerization of perfluoropropylene oxide according to an earlier described procedure.[11] Before the reaction, silica gel (Chemapol, L 100/250) was dried for 2 h at 150 °C. 2,2′-Bipyridyl (Lancaster), 1,10′-phenanthroline (Chemapol), and tetraethyl orthosilicate (Merck) were used without additional purification. Methanol, pyridine, and acetonitrile were purified by standard methods.

Dissolution of SiO_2 (general procedure). Water-free MeOH (10 mL) and silica gel (0.6 g, 0.01 mol) dried at 150 °C were placed in a Teflon flask equipped with a Teflon gas-injection tube, and pentafluoropropionyl fluoride (6.64 g, 0.04 mol, determined from the weight increase) was added under magnetic stirring. The reaction is slightly exothermic. After the end of pentafluoropropionyl fluoride addition, the reaction mixture was stirred for 1 h (whole amount of silica gel was dissolved). Then a solution of 2,2′-bipyridyl (0.01 mol) or 1,10′-phenanthroline (or 0.02 mole of pyridine) in absolute MeOH (5 mL) was added. A precipitate was formed immediately, stored for 1 h, separated by filtration, washed with MeOH, and dried *in vacuo*.

Compound 1a was isolated from a DMSO—MeOH mixture, 83.4% yield, m.p. > 230 °C. Found (%): C, 46.04; H, 3.04; F, 29.38. $C_{10}H_8F_4N_2Si$. Calculated (%): C, 46.14; H, 3.09; F, 29.20. The ^1H NMR spectrum contains two sets of signals corresponding to the bipyridyl ligand in a ratio of 2.5 : 1. ^{19}F NMR, δ: –42.12 (t, 2 F, $^2J_{F-F}$ = 15.9 Hz); –65.46 (t, 2 F, $^2J_{F-F}$ = 13.0 Hz).

Compound 1b was isolated from a DMSO—MeOH mixture, 68.94% yield, m.p. > 230 °C. Found (%): C, 50.61; H, 2.71; F, 26.52. $C_{12}H_8F_4N_2Si$. Calculated (%): C, 50.69; H, 2.84;

F, 26.73. The ^{1}H NMR spectrum contains two sets of signals corresponding to the phenanthroline ligand in a ratio of 1.5 : 1. ^{19}F NMR, δ: −37.20 (t, 2 F, $^2J_{F-F}$ = 20.9 Hz); −62.0 (t, 2 F, $^2J_{F-F}$ = 19.0 Hz).

Compound 1c was isolated from MeOH, 57.9% yield, m.p. 162—164 °C. The ^{1}H NMR spectrum contains signals corresponding to the pyridine ligand only. ^{19}F NMR, δ: −57.32 (s). The ^{1}H and ^{19}F NMR spectra and the melting point coincided completely with the data for sample **1c** synthesized by a described method.[12]

Reaction of tetraethyl orthosilicate with pentafluoropropionyl fluoride. Acetonitrile (18 mL), phenanthroline (0.5 g, 0.003 mol), and tetraethyl orthosilicate (0.58 g, 0.003 mol) were placed in a Teflon flask equipped with a Teflon gas-injection tube. Pentafluoropropionyl fluoride (6.64 g, 0.04 mol, determined by the weight increase) was added under magnetic stirring. The reaction is slightly exothermic. After the end of pentafluoropropionyl fluoride addition, the reaction mixture was stirred for 30 min. The precipitate was separated by filtration, washed with MeOH, and dried *in vacuo*. The yield was 64.7%. The ^{1}H and ^{19}F NMR spectra and melting point coincided completely with the data for compound **1b**.

References

1. K. Y. Blohowiak, D. R. Treadwell, B. L. Mueller, M. L. Hoppe, S. Jouppi, P. Kansal, K. W. Chew, C. L. S. Scotto, F. Babonneau, J. Kampf, and R. M. Laine, *Chem. Mater.*, 1994, **6**, 2177.
2. L. Sun and K. Gong, *Ind. Eng. Chem. Res.*, 2001, **40**, 5861.
3. R. M. Laine, K. Y. Blohowiak, T. R. Robinson, M. L. Hoppe, P. Nardy, J. Kampf, and J. Uhm, *J. Nature*, 1991, **353**, 642.
4. H. Cheng, R. Tamaki, R. M. Laine, F. Babonneau, Y. Chuj, and D. R. Treadwell, *J. Am. Chem. Soc.*, 2000, **122**, 10063.
5. A. D. Adley, P. H. Bird, A. R. Fraser, and M. Onyschuk, *Inorg. Chem.*, 1972, **11**, 1402.
6. A. N. Chekhlov, V. V. Tkachev, and S. A. Lermontov, *Zh. Strukt. Khim.*, 2003, **44**, 1165 [*Russ. J. Struct. Chem.*, 2003, **44**, No. 6 (Engl. Transl.)].
7. V. O. Gel´mbol´dt and S. P. Petrosyants, *Koord. Khim.*, 1989, **15**, 501 [*J. Coord. Chem. USSR*, 1989, **15**, No. 4 (Engl. Transl.)].
8. L. A. Gavrilova, V. O. Gel´mbol´dt, A. A. Ennan, P. N. Yurkevich, and L. V. Ostapchuk, *Koord. Khim.*, 1986, **12**, 489 [*J. Coord. Chem. USSR*, 1986, **12**, No. 4 (Engl. Transl.)].
9. J. P. Guertin and M. Onyszchuk, *Canad. J. Chem.*, 1963, **41**, 1477.
10. V. O. Gel´mbol´dt and A. A. Ennan, *Koord. Khim.*, 1983, **9**, 579 [*J. Coord. Chem. USSR*, 1983, **9**, No. 5 (Engl. Transl.)].
11. I. L. Knunyants, V. V. Shokina, and I. V. Galakhov, *Khim. Geterots. Soedin.*, 1966, **6**, 873 [*Chem. Heterocycl. Compd.*, 1966, **6** (Engl. Transl.)].
12. J. P. Guertin and M. Onyszchuk, *Canad. J. Chem.*, 1969, **47**, 1275.

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