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Reactivity of pyridinium poly(hydrogen fluoride) towards silicon tetrachloride, trichlorosilane and tris(amino)silanes

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Abstract

The reaction of silicon tetrachloride ($SiCl_4$), trichlorosilane ($HSiCl_3$) and tris(amino)silanes [$(R_2N)_3SiH$] with pyridinium poly(hydrogen fluoride) (PPHF) gives rise to hexafluorosilicate salts in good yields. They have been characterized as pyridinium hexafluorosilicate $(C_5H_5NH)_2SiF_6$ (in the case of $SiCl_4$ and $HSiCl_3$) and the corresponding dialkyl ammonium hexafluorosilicate $(R_2NH_2)_2SiF_6$ salts [for tris(amino)silanes] (where R_2N = pyrrolidino, piperidino, hexamethyleneimino, morpholino, *N*-methylpiperazino and diethylamino). The interesting features of these reactions are the cleavage of Si–Cl, Si–H and Si–N bonds at room temperature by PPHF and fluorination of the silicon moiety to a hexa-coordinated doubly charged anionic species. These compounds have been characterized by NMR (^1H, ^{29}Si, ^{19}F) and IR spectroscopy, and by chemical analysis.

Introduction

During the course of our investigations exploring the use of pyridinium poly(hydrogen fluoride) (PPHF) (which is a rich source of hydrogen fluoride at room temperature) as an efficient and convenient fluorinating reagent for inorganic compounds [1–3], it was observed that both silica (SiO_2) and silicic acid (H_2SiO_3) react with PPHF to form pyridinium hexafluorosilicate $(C_5H_5NH)_2SiF_6$ [4] indicating cleavage of the Si–O bond. For this reason, it was of interest to examine the effect of PPHF on Si–Cl, Si–H and Si–N bonds, and hence the model compounds $SiCl_4$, $HSiCl_3$ and $(R_2N)_3SiH$ were chosen for study. Preliminary experiments indicated that reactions with these compounds result in the formation of pyridinium hexafluorosilicate $(C_5H_5NH)_2SiF_6$ and the corresponding dialkylammonium salts $(R_2NH_2)_2SiF_6$. Other products of the reactions were hydrogen chloride and pyridine. Details of these interesting cleavage reactions are given below.

Experimental

Materials and methods

All reagents employed in the present study were of LR/AR grade. Tris(amino)silanes and pyridinium poly(hydrogen fluoride) were prepared by

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methods described earlier [1, 5]. Trichlorosilane and silicon tetrachloride (Chemplast, India) were used as such without further purification.

The spectra of the compounds were recorded on the following spectrometers: IR, Hitachi model 270-50; ^{1}H NMR Bruker ACF 200 (TMS external standard); ^{29}Si NMR, Bruker AMX-400 (TMS external standard); ^{19}F NMR, Varian T60FT (CF_3COOH external standard).

Procedure

The apparatus consisted of a 500 ml polyethylene flask fitted with a polyethylene dropping funnel and an outlet attached to a polyethylene tower containing sodium fluoride. Approximately 2 ml of trichlorosilane/silicon tetrachloride or tris(amino)silane were introduced into a flask containing cooled dry ether (50 ml) and the contents stirred. A cooled (0 °C) solution of PPHF was added dropwise to the flask and its contents stirred over a period of 15 min when an instantaneous exothermic reaction occurred with the liberation of hydrogen chloride in the case of $SiCl_4$ and $HSiCl_3$, and the corresponding cleaved amine in the case of the tris(amino)silanes. The mixture was stirred for a further 30 min, following which the ether was evaporated on a water bath. The remaining PPHF solution containing the products was then treated with 25 ml chloroform in a polyethylene separating funnel. The HF layer was treated with dry acetone (100 ml) when the hexafluorosilicate salt formed separated out as a white solid which was filtered, washed with acetone and recrystallized from methanol. The yield of hexafluorosilicates was found to be 89–92% in all cases. Spectral data for the compounds are listed in Table 1. The IR spectra were similar in all cases and exhibited absorption bands due to ν(Si−F) and δ(Si−F) together with vibrations due to the amine moieties.

The hexafluorosilicates were analyzed using methods described earlier [4].

Results and discussion

The SiF_6^{2-} anion formed is present as its pyridinium salt, $(C_5H_5NH)_2SiF_6$, in all cases. However, with aminosilanes, bis(alkylammonium) hexafluorosilicate salts are formed by displacement of the pyridine by the extruded amine. Such facile displacements of pyridinium salts by amines have been noted earlier [6–8].

On the basis of these observations, the overall mode of reaction can be formulated as:

$$SiCl_4 + 2C_5H_5NH(HF)_xF \longrightarrow (C_5H_5NH)_2SiF_6 + 4HCl \qquad (1)$$

$$HSiCl_3 + 2C_5H_5NH(HF)_xF \longrightarrow (C_5H_5NH)_2SiF_6 + 3HCl + H_2 \qquad (2)$$

$$(C_4H_8N)_3SiH + 2[C_5H_5NH(HF)_xF] \longrightarrow (C_4H_8NH_2)_2SiF_6 + 2C_5H_5N + H_2 + C_4H_8NH \qquad (3)$$

TABLE 1

Data relating to the hexafluorosilicates synthesized

Expt. No.	Starting material (mol)	Compound synthesized (mol)	Yield (%)	M.p. (°C)	NMR δ (ppm)		
					^1H	^{29}Si	^{19}F
1	$(C_4H_8N)_3SiH$ (0.00836)	$(C_4H_8NH_2)_2SiF_6$ (0.00745)	89.0	215	3.07 N–CH_2 1.77 C–CH_2	−188.37	49.36
2	$(C_5H_{10}N)_3SiH$ (0.00710)	$(C_5H_{10}NH_2)_2SiF_6$ (0.00640)	90.0	232	2.92 N–CH_2 1.48 C–CH_2	−188.37	50.20
3	$(C_6H_{12}N)_3SiH$ (0.00464)	$(C_6H_{12}NH_2)_2SiF_6$ (0.00419)	90.2	210	2.99 N–CH_2 1.62 C–CH_2	−188.38	49.44
4	$(OC_4H_8N)_3SiH$ (0.00871)	$(OC_4H_8NH_2)_2SiF_6$ (0.00779)	89.5	233	3.62 O–CH_2 3.12 N–CH_2	−188.32	49.63
5	$(CH_3NC_4H_8N)_3SiH$ (0.00920)	$(CH_3NC_4H_8NH_2)_2SiF_6$ (0.00830)	90.3	226	2.96 C–N–CH_2 2.45 N–CH_2 2.24 N–CH_3	−188.31	49.72
6	$[(C_2H_5)_2N]_3SiH$ (0.01100)	$[(C_2H_5)_2NH_2)]_2SiF_6$ (0.00998)	90.8	205	2.85 N–CH_2 1.04 C–CH_3	−188.41	50.13
7	Cl_3SiH (0.01577)	$(C_5H_5NH)_2SiF_6$ (0.01448)	91.8	155	8.42 C–H	−188.35	50.25
8	$SiCl_4$ (0.01981)	$(C_5H_5NH)_2SiF_6$ (0.01823)	92.0	155	8.42 C–H	−188.35	50.25

TABLE 2

Analytical data for hexafluorosilicates prepared

Compound	Amine estimation		SiF_6^{-2} estimation	
	Calc. (%)	Found (%)	Calc. (%)	Found (%)
$(C_4H_8NH_2)_2SiF_6$	50.35	50.29	49.65	48.96
$(C_5H_{10}NH_2)_2SiF_6$	54.77	54.70	45.22	44.82
$(C_6H_{12}NH_2)_2SiF_6$	58.48	58.39	41.52	41.10
$(OC_4H_8NH_2)_2SiF_6$	55.35	55.30	44.65	44.11
$(CH_3NC_4H_8NH_2)_2SiF_6$	58.72	58.64	41.27	40.99
$[(C_2H_5)_2NH_2)]_2SiF_6$	51.03	50.90	48.97	48.56
$(C_5H_5NH)_2SiF_6$	52.98	52.93	47.01	46.53

Table 2 lists the analytical data for these hexafluorosilicates.

The two strong absorptions observed in the IR spectra at 735 cm^{-1} and 480 cm^{-1} correspond to ν(Si−F) and δ(Si−F) as reported for the hexafluorosilicate ion [4], indicating cleavage of the Si−Cl, Si−H and Si−N bonds. The ^1H NMR spectra for these compounds (Table 1) indicate a chemical shift to lower fields compared to that of the parent compound [5], which may be attributed to draining of the electron density as a result of salt formation. For the SiF_6^{-2} moiety, the ^{19}F resonance at 50 ppm downfield with respect to CF_3COOH and the ^{29}Si resonance at *c.* −188 ppm with respect to TMS is as expected [9], the Si–F coupling constant of *c.* 108 Hz in all the compounds indicating that it is independent of the cationic component of the salt.

Hence PPHF is capable of cleaving Si−Cl, Si−H and Si−N bonds at room temperature to form hexa-coordinated silicon associated with an interesting range of cationic salts.

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