On the Reaction of Phenylsilicon Fluorides with Primary Amines

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Phenyltrifluorosilane and diphenyldifluorosilane reacted readily with primary amines but triphenylfluorosilane failed to react.

Phenyltrifluorosilane co-ordinated two fluoride ions to give the pentafluoro(phenyl)silicate ion, analogous to the hexafluorosilicate ion. Probably also diphenyldifluorosilane co-ordinates fluoride ions but triphenylfluorosilane revealed no tendency to six-coordination.

That alkyltrifluorosilanes react exothermically in a mole ratio of about 1:2 with primary amines while dialkyl- and trialkylfluorosilanes fail to react with these donor molecules was described in a previous paper. This study of the behaviour of organosilicon fluorides has now been extended to the phenylsilicon fluorides. It should be noted that among arylsilicon fluorides, 1-naphthyltrifluorosilane and di-1-naphthyldifluorosilane have previously been reported to give the corresponding aminosilanes according to the general formula

$$R_{4-n}SiF_n + 2nRNH_2 \rightarrow R_{4-n}Si(NHR)_n + nR\cdot NH_2F$$  \hspace{1cm} (1)

but tri-1-naphthylfluorosilane and triphenylfluorosilane reacted only with the alkali-metal amides.

As distinguished from the case of alkyltrifluorosilanes, precipitation immediately occurred whenever phenyltrifluorosilane and a primary aliphatic amine were mixed in ether or benzene, and the composition and properties of the solids were those expected for the pentfluoro(phenyl)silicate of the amine. Obviously some of the fluoride in phenyltrifluorosilane is easily replaced by amino groups and the fluoride ions released then immediately combine with unreacted phenyltrifluorosilane forming the complex pentfluoro(phenyl)silicate ion which precipitates as the amine salt i.e. the reaction proceeds according to the scheme

$$Si-F + RNH_2 \rightarrow Si-NHR + F^-$$  \hspace{1cm} (2)

$$R NH_2 \downarrow \quad \downarrow 1/2 \quad C_6H_4SiF_3$$

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The reaction is reversible. Thus on heating the reaction mixture obtained from phenyltrifluorosilane and a volatile amine, all of it distilled at the distillation temperature of the phenyltrifluorosilane (104°) and deposited as a white solid in the cold part of the system, while the alkylammonium pentafluoro-(phenyl)silicates do not sublime below 200°. The question then arises to what extent fluorine in phenyltrifluorosilane is replaced by amino groups when the reaction mixture is kept at room temperature in a solvent which does not dissolve the alkylammonium pentafluoro(phenyl)silicate. From the experiments so far performed no definite answer can be given, but some observations described in the experimental part indicate that only one of the fluorine atoms is replaced, i.e. the reaction would take place according to the equation

\[ 3 \text{PhSiF}_3 + 4 \text{RNH}_2 \rightarrow 2 \text{PhSi(NHR)}_3 \text{F} + (\text{RNH}_3)_2 \left[ \text{SiF}_6(\text{C}_6\text{H}_5) \right] \]  

(3)

and go completely to the right in ether at room temperature.

The alkylammonium pentafluoro(phenyl)silicates obtained in the way described were white solids which did not melt below 250°, and sublimed in the range 225—275°. Like the corresponding pentafluoro(alkyl)silicates, they dissolved in water to give acidic solutions. It was earlier described\(^1\) that pentafluoro(alkyl)silicates have an intense absorption in the infra-red near 750 cm\(^{-1}\) which was associated with the Si-F bonds in the octahedral position, but just in this region phenylsilicon fluorides with silicon in the tetravalent state have intense bands probably due to the bending vibration of the C-H bonds in the substituted aromatic nuclei\(^4\) (Fig. 1).

Diphenyldifluorosilane too reacted exothermically with primary aliphatic amines, and solids formed far above the melting points of the components, but no precipitation occurred at room temperature in ether or benzene. At moderately decreased temperatures two liquid layers were obtained in petroleum ether when excess of amine was omitted but no reaction product could be isolated by extraction with the solvent in the way described for alkyltrifluorosilanes. In acetonitrile, an appreciable increase in conductivity was observed indicating that ion formation is also involved in the reaction of this fluorosilane with protic amines.

No reaction at all was observed in the case of triphenylfluorosilane. Precipitation did not occur even at low temperatures in ether or benzene and only a slight increase in conductivity was observed in acetonitrile.

Nor did triphenylfluorosilane reveal any tendency to co-ordinate fluoride ions. When anhydrous hydrogen fluoride was added to an ether solution of the silane and a primary amine, the only solid product was that of alkylammonium fluoride and no combination was observed even on standing for a week.

Diphenyldifluorosilane, however, reacted readily with alkylammonium fluorides but in a somewhat surprising way. Instead of the expected alkylammonium tetrafluorodiphenylsilicate, the pentafluoro(phenyl)silicate of the amine was obtained, and benzene appeared in the reaction mixture, i.e. one of the Si-Aryl bonds had been cleaved; the over-all reaction being according to the equation

\[ (\text{C}_6\text{H}_5)_2\text{SiF}_3 + 3 \text{RNH}_2\text{F} \rightarrow (\text{RNH}_3)_2 \left[ \text{SiF}_6(\text{C}_6\text{H}_5) \right] + \text{RNH}_2 + \text{C}_6\text{H}_6 \]  

(4)

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Fig. 1. IR-spectra of a) phenyltrifluorosilane (60 mg/ml CS₂) b) diphenyl difluorosilane (73 mg/ml CS₂) c) triphenylfluorosilane (70 mg/ml CS₂) d) propylammonium pentafluoro(phenyl)silicate (in pressed KBr) in the region 4000–600 cm⁻¹.

It is probable that this reaction is initiated by complex formation rather than acid cleavage of one of the Si-Aryl bonds in diphenyl difluorosilane, i.e. the route of reaction would be

\[
\text{Ph}_2\text{SiF}_2 \xrightarrow{2F^-} [\text{SiF}_4(\text{Ph})_2]^+ \xrightarrow{\text{RNH}_2F} [\text{SiF}_4\text{Ph}]^+ + \text{PhH} + \text{RNH}_3
\]  

rather than

\[
\begin{align*}
\text{Ph}_2\text{SiF}_2 & \xrightarrow{\text{RNH}_2F} \text{PhSiF}_3 \\
& \xrightarrow{\text{PhH}} -\text{RNH}_3
\end{align*}
\]

\[
\text{Ph}_2\text{SiF}_2 \xrightarrow{2F^-} [\text{SiF}_4(\text{C}_6\text{H}_4)]^+
\]

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For if Si-Aryl cleavage was the first step, triphenylfluorosilane would be expected to be still more susceptible to the action of alkylammonium fluoride than diphenyldifluorosilane owing to the less electron-withdrawing nature of the groups attached to the silicon in the triphenylfluorosilane. And this is demonstrated by the fact that the first phenyl group in triphenylfluorosilane is more readily removed than the second one by anhydrous hydrogen fluoride. Initial complex formation, however, according to (a), should facilitate acid cleavage owing to the greater electron density around the central silicon atom in the complex compared with that in diphenyldifluorosilane.

The fact that the Si-Aryl bonds in triphenylfluorosilane survive the action of alkylammonium fluoride would then be explained as the result of its inability to co-ordinate fluoride ions, which in turn — according to the hypothesis of Craig et al. — would be the result of insufficient electron-withdrawal by the groups around the silicon atom in this molecule.

**EXPERIMENTAL**

The preparation of phenyltrifluorosilane has been described in a previous paper.  

_Diphenyldifluorosilane_ was obtained as described by Marans et al. from diphenyl-dichlorosilane and 48 % hydrofluoric acid. Yields 40—50 %. B.p. 118°/10 mm, nD₂₀ 1.5252,  d²₀ 1.1582 (lit. values: b.p. 93.5—94°/3 mm, nD₂₀ 1.5221, d²₀ 1.1554). (Found: Equiv. wt. 109.5. Calc. 110.1).

_Triphenylfluorosilane._ 33.5 g (0.15 mole) of diphenyldifluorosilane in 100 ml of anhydrous ether were added to 0.15 mole of phenylmagnesium bromide in 100 ml of ether. The reaction mixture was refluxed for 3 h with continual stirring. Only a very small amount of precipitate was formed. After standing overnight the ether was distilled off until the temperature in the viscous mixture had risen to 100—110°, which temperature was kept for 6 h. The ether was again added and the precipitate was dissolved by adding, with cooling, 150 ml of 2.5 N hydrochloric acid. The organic layer was separated and the aqueous solution extracted twice with ether. The combined extracts were washed several times with water and then dried over magnesium sulfate. Fractionation gave 22 g (53 %) of triphenylfluorosilane, boiling at 193—195° at 10 mm Hg as a viscous oil. After standing for some hours the substance solidified, m.p. 60—62°. Some of it was recrystallized from ether to give m.p. 62—63° (lit. values: b.p. 245—250°/30 mm, m.p. 64°). (Found: Equiv. wt. 278.0. Calc. 278.4).

_Phenyltrifluorosilane and amines._ A vigorous reaction occurred whenever an aliphatic primary amine was added to phenyltrifluorosilane, and a solid product formed which dissolved at room temperature in excess of amine. When the mixture was heated, amine distilled at its ordinary boiling point and then the residue distilled at the boiling point of phenyltrifluorosilane (104°) and deposited in the cold part of the system as a white solid which fumed vigorously in contact with the atmosphere.

When ether solutions of phenyltrifluorosilane and amine were mixed, a white precipitate of alkylammonium pentfluoro(phenyl)silicate immediately formed and could be removed by filtration. In a range of experiments (Table 1) with propylamine the amount of salt obtained was that expected for reaction (3), i.e. 0.33 molar equivalents of salt per mole of phenyltrifluorosilane. On cooling the filtrate, which fumed vigorously in contact with the atmosphere, only traces of more salt precipitated which indicated that practically no salt remained in the solution at room temperature. That the salt precipitated almost quantitatively is also supported by the following experiments. Propylamine was added in excess to phenyltrifluorosilane to give a liquid system. The pressure was reduced and excess of amine removed on heating until the content of the flask began to sublime (70—80°). The solid residue fumed vigorously in moist air, melted at 60—80°, and boiled from the melting point tube at about 100°. The amine content of the product was determined by back-titrating an acid fixed condensate from a boiling basic solution containing the substance (insoluble) using methyl red as the indicator. In three different experiments.
the equivalent weights of the products were 178, 173, and 180, corresponding to a mole ratio phenyltrifluorosilane:amine of 1:1.36, 1:1.42, and 1:1.34, i.e. in good agreement with the ratio expected for reaction (3). It can therefore be stated with some certainty that the amount of salt obtained corresponds to the amount of replacement of Si-F bonds, and as was described, this amount is that expected for the complete reaction (3). It should be noted that if reaction proceeded until all phenyltrifluorosilane was consumed with the stepwise replacement of the halogen,

\[
\text{PhSiF}_2 + \text{RNH}_2 \rightarrow \text{PhSi(NHR)}_2\text{F} + (\text{RNH}_2)_2[\text{SiF}_4(\text{C}_6\text{H}_5)]
\]

\[
\text{PhSi(NHR)}_3\text{F} + \text{RNH}_2 \rightarrow \text{PhSi(NHR)}_2\text{F} + (\text{RNH}_2)_2[\text{SiF}_4(\text{C}_6\text{H}_5)]
\]

\[
\text{PhSi}(\text{NHR})_n\text{F} + \text{RNH}_2 \rightarrow \text{PhSi}(\text{NHR})_{n-1}\text{F} + (\text{RNH}_2)_2[\text{SiF}_4(\text{C}_6\text{H}_5)]
\]

and if the halosilylamines, \(\text{PhSi(NHR)}_n\text{F}_{3-n} (n = 1, 2, 3)\) were formed at random distribution, 0.46 molar equivalents of salt would fall out from the mixture (see Appendix), i.e. considerably more than the 0.33 molar equivalents obtained. And it should be added that about 0.33 molar equivalents of salt was obtained also in the case of ammonia or methyamine which have a less steric requirement than propylamine.

The hypothesis that reaction proceeds mainly according to the formula (3) could, however, not be directly supported by showing that phenyl-(propylamino)-difluorosilane is the only halosilane present in the reaction mixture of propylamine and phenyltrifluorosilane in ether. Even when fractionation of the filtrate was performed at 1.5 mm Hg the presence of all compounds \(\text{PhSi(NHR)}_n\text{F}_{3-n} (n = 0, 1, 2, 3)\) was indicated. A white solid deposited at the beginning of heating, indicating \(\text{PhSiF}_3\), then at 64—70°, a substance was obtained the composition of which roughly corresponded to \(\text{PhSi(NHR)}\text{F}_2\), and at 70—110° a product which gave basic reaction against methyl red — indicating \(\text{PhSi(NHR)}_2\text{F}\) — and a basic viscous residue was left. But it was found that when the fraction obtained at 64—70° was redistilled at reduced pressure some solid again distilled at low temperature and almost half of it was left as a viscous oil which gave basic reaction against methyl red. This indicates that disproportionation and intermolecular condensation of \(\text{PhSi(NHR)}\text{F}_2\) easily takes place and the presence of all species in the distillate on fractionation of the filtrate need not contradict the assumption that reaction of phenyltrifluorosilane with primary amines proceeds mainly according to formula (3).

In Table 2 are given the equivalent weights of five ammonium pentafuoro(phenyl)-silicates left on the filter from the reaction mixtures of phenyltrifluorosilane with ammonia and some primary amines in ether. The products were carefully washed with the solvent and dried before determination of the amine and fluoride content. Like the corresponding pentafuoro(alkyl)silicates they were all white non-hygrosopic powders insoluble in organic solvents. They did not melt below 250° and sublimed rapidly — probably with considerable decomposition — in the region 235—275°. They dissolved in water to give acidic solutions which on standing became turbid due to hydrolysis but phenyltrifluorosilane did not separate when the salts were dissolved in 48% hydrofluoric acid. It should be noted that alkylfluorosilicic acid was immediately liberated from pentafuoro(alkyl)silicate by the action of this acid.

The salts reacted with \(\text{N}\)-substituted phenyl- and alklytriaminosilanes. Thus, when the mixture of 0.342 g (1.22 \times 10^{-3} \text{ mole}) of phenyltri-(propylamino)-silane and 0.587 g (1.83 \times 10^{-3} \text{ mole}) of propylammonium pentafuoro(phenyl)silicate had been heated to 60° for 1 h a liquid mixture was obtained at room temperature. On addition of ether and filtration, 0.330 g of pentafuoro(phenyl)silicate was left on the filter and free amine was found in the filtrate which fumed vigorously in contact with the atmosphere. The amount of salt was that expected (0.326 g) for the reaction

\[
3 \text{PhSi(NHR-)}_n\text{F} + 2 (n-\text{PrNH}_2)[\text{SiF}_4\text{Ph}] \rightarrow 5 \text{PhSi(NHR-)}_n\text{F}_2 + 8 n-\text{PrNH}_2
\]

**Diphenyldifluorosilane and amines.** A strongly exothermic reaction occurred whenever a primary amine was added to diphenyldifluorosilane. On heating, the volatile amine could again be removed. When a mixture with methyamine had been kept at 6° for 2 h under a pressure of 10 mm Hg there still remained 0.62 mole of amine per mole of diphenyldifluorosilane in the residue, while all but traces of amine had been removed after 0.5 h when triamylfluorosilane and excess of methyamine was treated in the same way.

No precipitation was obtained in ether or benzene at room temperature but a solid phase formed on cooling far above the melting points of the components. In petroleum

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**Table 1.** C₅H₅SiF₃ and n-C₅H₅NH₃ in ether.

<table>
<thead>
<tr>
<th></th>
<th>PhSiF₃</th>
<th>n-PrNH₃</th>
<th>Ether ml</th>
<th>Yield</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>g</td>
<td>mole</td>
<td>g</td>
<td>mole n-PrNH₃ moles PhSiF₃</td>
</tr>
<tr>
<td>9.7</td>
<td>0.060</td>
<td>7.0</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>3.4</td>
<td>0.021</td>
<td>12</td>
<td>0.20</td>
<td>10</td>
</tr>
<tr>
<td>3.4</td>
<td>0.021</td>
<td>11</td>
<td>0.19</td>
<td>9</td>
</tr>
<tr>
<td>1.6</td>
<td>0.010</td>
<td>2.4</td>
<td>0.24</td>
<td>3</td>
</tr>
<tr>
<td>3.6</td>
<td>0.022</td>
<td>6.0</td>
<td>0.10</td>
<td>5</td>
</tr>
<tr>
<td>21.1</td>
<td>0.13</td>
<td>30</td>
<td>0.52</td>
<td>4</td>
</tr>
</tbody>
</table>

**Table 2.** Analyses of (RNH₃)₂[SiF₅(C₅H₅)].

<table>
<thead>
<tr>
<th>Compound</th>
<th>E₁ᵃ</th>
<th>E₂ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>found</td>
<td>calc.</td>
</tr>
<tr>
<td>(H₄N)₂[SiF₅(C₅H₅)]</td>
<td>116</td>
<td>118.1</td>
</tr>
<tr>
<td>(CH₃NH₃)₂[SiF₅(C₅H₅)]</td>
<td>135</td>
<td>132.2</td>
</tr>
<tr>
<td>(C₅H₅NH₃)₂[SiF₅(C₅H₅)]</td>
<td>146</td>
<td>146.2</td>
</tr>
<tr>
<td>(n-C₅H₅NH₃)₂[SiF₅(C₅H₅)]</td>
<td>159</td>
<td>160.2</td>
</tr>
<tr>
<td>(n-C₅H₅NH₃)₂[SiF₅(C₅H₅)]</td>
<td>173</td>
<td>174.2</td>
</tr>
</tbody>
</table>

ᵃ Amine content
ᵇ Fluorine content

ether, two liquid layers were obtained at 0° when great excess of amine was omitted, but after repeated washing of the bottom layer with small portions of the solvent, the only residue was a very small amount of alkylammonium fluoride.

1.4 g (6.35 × 10⁻⁵ mole) of freshly distilled diphenylidifluorosilane was dissolved in 80 ml of acetonitrile to give a solution of specific conductivity 6.3 × 10⁻⁸ ohm⁻¹ cm⁻¹. When 1.4 g of propylamine were added by distillation over potassium hydroxide in an atmosphere of dry nitrogen the specific conductivity increased to 1.0 × 10⁻⁸ ohm⁻¹ cm⁻¹, i.e., an appreciable increase indicating that to some extent ion formation is involved in the reaction between diphenylidifluorosilane and protic amines.

In a series of experiments, anhydrous hydrogen fluoride was added to solutions of diphenylidifluorosilane (in excess) and propylamine in ether until no more solid precipitated. It was found that the composition of the solid, which always contained silicon, was rather ill-defined, but if filtration was performed after the reaction mixture had been standing overnight, it was in good agreement with that of propylammonium pentfluoro-(phenyl)silicate. (Found: Equiv. wt. E₁ 158; E₂ 63. Calc. for (n-C₅H₅NH₃)₂ [SiF₅Ph]: E₁ 160; E₂ 64). And its IR-spectrum was identical with that of authentic propylammonium pentfluoro(phenyl)silicate. The products which were obtained on the filter when filtration was performed soon after the addition of hydrogen fluoride had compositions which indicated that they were mixtures of propylammonium pentfluoro(phenyl)silicate and propylammonium fluoride.

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It could be directly shown that alkylammonium fluorides react with diphenyldifluorosilane. 0.238 g (0.003 mole) of propylammonium fluoride and 1.5 g (0.007 mole) of diphenyldifluorosilane were mixed. A small evolution of heat was noted and the heterogeneous mixture was soon converted into a colourless viscous oil. 10 ml of ether were added. On shaking, a white solid appeared and benzene was found in the solution by gas chromatography. After standing for 24 h the amount of benzene in the ether solution was estimated to be 0.063 g by gas chromatography (calc. for reaction (4): 0.078 g). On filtration of the reaction mixture, 0.238 g (calc. for reaction (4): 0.320 g) of propylammonium pentfluorosilicate was left on the filter. The filtrate was taken up in ether containing excess of hydrogen chloride and on filtration of the mixture 0.066 g of propylammonium chloride were left on the filter (calc. for reaction (4): 0.095 g).

Triphenylfluorosilane and amines. No reaction at all was observed between this fluoro silane and primary amines. When 1.0 g of the fluoro silane was dissolved in 80 ml of acetonitrile a solution with a specific conductivity of $6.3 \times 10^{-4}$ ohm$^{-1}$cm$^{-1}$ was obtained. On addition of 1.4 g of propylamine the specific conductivity changed to $12.5 \times 10^{-4}$ ohm$^{-1}$cm$^{-1}$, i.e. no appreciable increase.

When anhydrous hydrogen fluoride was added to a mixture of triphenylfluorosilane (in excess) and propylamine in ether the only solid product was propylammonium fluoride. No silicon was found in the solid even if the mixture was kept for a week before filtration.

Phenylsilicon fluorides and hydrogen fluoride. In one series of experiments phenylsilsilicon fluorides and excess of anhydrous hydrogen fluoride were kept (heterogeneous mixtures) at room temperature in stoppered polythene flasks, and after standing for 20 h most of the excess of hydrogen fluoride was removed by evaporation for 4 h. The residual hydrogen fluoride was removed by passing the mixture through a column of sodium fluoride. The gas chromatograms of the filtrates showed that in the case of phenyltrifluorosilane only a very small amount of benzene had been formed (< 1 % reaction) while in the case of diphenyltrifluorosilane and triphenylfluorosilane large peaks indicating benzene and phenyltrifluorosilane were obtained. For comparison, the same experiment was performed with triamylfluorosilane. No trace of pentane was found in the mixture after 24 h indicating that the Si-Alkyl bond is much more stable than the Si-Aryl bond to the action of hydrogen fluoride.

7.9 g of diphenyldifluorosilane and excess of hydrogen fluoride were mixed. After 25 h at room temperature the excess of hydrogen fluoride was removed at 10 mm Hg — together with the phenyltrifluorosilane and benzene which had been formed — by warming the mixture to 50—60° for 20 min. Thereafter 4.4 g of diphenyldifluorosilane remained, i.e. 3.5 g (44 %) had reacted to give phenyltrifluorosilane and benzene.

The mixture of 7.8 g of triphenylfluorosilane and excess of hydrogen fluoride was treated in the same way. 3.5 g of diphenyldifluorosilane were left when the other reaction products had been removed, i.e. all of the triphenylfluorosilane had been converted to diphenyldifluorosilane and 43 % of this compound had reacted further to phenyltrifluorosilane.

It should be added that Pearson et al.8 did not detect silicon tetrafluoride nor hydrocarbons in the reaction products of alkyl- and arylsilyl chlorides with anhydrous hydrogen fluoride, which was interpreted as an indication of complete stability of the carbon-silicon bond to hydrogen fluoride at room temperature. The experiments described above, however, demonstrate that there is a great difference between Si-Alkyl and Si-Aryl bonds in this respect.

Gas chromatography. A Perkin-Elmer Vapour Fractometer, Model 116, was used. The mixtures were run through a 1 m silicon-oil filled column, and a flow of helium was employed as the mobile phase.

The infrared spectra were recorded with a Perkin-Elmer, Model 221, prism-grating instrument at the Infrared Laboratory of this Institute. Cell-thickness in CS$_2$ solution 0.1 mm.

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APPENDIX

Suppose that fluorine in phenyltrifluorosilane is replaced by amino groups in three consecutive competitive reactions and suppose that these reactions are irreversible owing to the removal of released hydrogen fluoride as pentafluoro(phenyl)silicate

\[
\begin{align*}
\text{PhSiF}_3 + \text{RNH}_2 & \rightarrow \text{PhSi(NHR)}_2\text{F} + \text{HF} \\
& \downarrow \\
& (\text{RNH}_3)_2[\text{SiF}_5\text{Ph}] \\
\text{PhSi(NHR)}_2\text{F} + \text{RNH}_2 & \rightarrow \text{PhSi(NHR)}_3\text{F} + \text{HF} \\
& \downarrow \\
& (\text{RNH}_3)_2[\text{SiF}_5\text{Ph}] \\
\text{PhSi(NHR)}_3\text{F} + \text{RNH}_2 & \rightarrow \text{PhSi(NHR)}_4 + \text{HF} \\
& \downarrow \\
& (\text{RNH}_3)_2[\text{SiF}_5\text{Ph}]
\end{align*}
\]

Let us also suppose that the probabilities of the three competitive reactions are only statistically determined, \textit{i.e.} being in the ratio \(1:2:3\).

We will calculate the amount of salt which on these assumptions would precipitate from a given amount of phenyltrifluorosilane (\(a\) moles) and excess of amine.

Let \(n_i\) be the number of moles of the species \(\text{PhSi(NHR)}_i\) which has been formed in the reaction. Then \((n_1 + n_2 + n_3)/2 = x\) is the number of molar equivalents of salt.

\(a - \frac{3}{2}n_1 - \frac{1}{2}n_2 - \frac{1}{2}n_3 = N_0\) is the number of moles of \(\text{PhSiF}_3\) in the reaction mixture

\[
\begin{align*}
n_1 - n_2 &= N_1 \\
n_2 - n_3 &= N_2 \\
n_1 - n_3 &= N_3
\end{align*}
\]

When \(dm\) moles of amine react, we obtain the following system of differential equations

\[
\begin{align*}
\frac{dn_1}{dm} &= \alpha \left(a - \frac{3}{2}n_1 - \frac{1}{2}n_2 - \frac{1}{2}n_3\right) \\
\frac{dn_2}{dm} &= \frac{3}{2} \alpha \left(n_1 - n_2\right) \\
\frac{dn_3}{dm} &= \frac{1}{2} \alpha \left(n_2 - n_3\right)
\end{align*}
\]

where

\[
\alpha^{-1} = N_0 + \frac{3}{2}N_1 + \frac{1}{2}N_2
\]

The equations (1)–(3) give

\[
\begin{align*}
\frac{dn_2}{dn_1} &= \frac{2}{3} \frac{n_1 - n_2}{a - \frac{3}{2}n_1 - \frac{1}{2}n_2 - \frac{1}{2}n_3} \\
\frac{dn_3}{dn_1} &= \frac{1}{3} \frac{n_2 - n_3}{a - \frac{3}{2}n_1 - \frac{1}{2}n_2 - \frac{1}{2}n_3}
\end{align*}
\]

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Introducing the variable \( u = n_2 + n_3 \) we obtain the differential equation
\[
\frac{du}{dn_1} = \frac{2(2n_1-u)}{3(2a-3n_1-u)} \tag{7}^*
\]
With \( \xi = n_1 - \frac{2}{3}a; \eta = u - \frac{2}{3}a \) the eqn. (7) takes the form
\[
\frac{d\eta}{d\xi} = \frac{2(2\xi-\eta)}{3(-3\xi-\eta)} \tag{8}
\]
and then by introducing \( \eta = \xi s \) we obtain
\[
\frac{d\xi}{ds} = -3 \xi \frac{3 + s}{3s^2 + 7s + 4} \tag{9}
\]
The solution of eqn. (9) is
\[
\xi = A \left( \frac{3s+4}{s+1} \right)^6 \tag{10}
\]
where \( A \) is an arbitrary constant.

With the original variables eqn. (10) takes the form
\[
(n_1 + n_2 + n_3 - \frac{2}{3}a)^6 = A \left( 4n_1 + 3n_2 + 3n_3 - 4a \right)^6 \tag{11}
\]
or
\[
(2x - \frac{2}{3}a)^6 = A \left( 6x + n_1 - 4a \right)^6 \tag{12}
\]
The initial condition \( x = 0 \) and \( n_1 = 0 \) gives
\[
A = - \frac{3^6a}{5^62^4} \]
We are interested in the value of \( x \) when all PhSiF$_3$ has been consumed, i.e. when \( a - n_1 - x = 0 \). Introducing \( n_1 = a - x \) in eqn. (12) we obtain the equation
\[
(2x - \frac{2}{3}a)^6 = - \frac{3^6a}{5^62^4} (5x - 3a)^6 \tag{13}
\]
and its solution
\[
x_1 = \frac{2343}{5120} a \sim 0.46 \ a
\]
\[
x_2 = 0.6 \ a
\]
where \( x_2 \Rightarrow 0.6 \ a \) represents the equation
\[
5 \text{ PhSiF}_3 + 12 \text{ RNH}_2 \rightarrow 2 \text{ PhSi(NHR)}_3 + 3 \text{ (RNH}_3)_2[\text{SiF}_5\text{Ph}] \]
and can be rejected.

REFERENCES

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