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Mechanism of the Formation of Complexes of Trimethylchlorosilane with Some Nitrogen Donors in Nitrobenzene

Short Communication

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Reactions of trimethylchlorosilane (Me_3SiCl) with some nitrogen donors viz. pyridine, 2-, 3- and 4-picolines, quinoline and isoquinoline in nitrobenzene have been studied conductometrically. The conductivities of the solutions during these reactions have been interpreted in terms of the formation of $(Me_3Si.D)^+$, $(Me_3SiCl_2)^-$ and $Me_3SiCl.D$ (D = N-donor molecule) species.

(Keywords: Conductance; Mechanism; Organosilicon halide complexes; Trimethylchlorosilane complexes)

Mechanismus der Komplexbildung von Trimethylchlorsilan mit einigen N-Donoren in Nitrobenzol

Die Reaktion von Trimethylchlorsilan (Me_3SiCl) mit Pyridin, 2-, 3- und 4-Picolinen, Chinolin und Isochinolin wurde in Nitrobenzol mittels Konduktometrie untersucht. Die Messungen wurden unter Annahme der Bildung von $(Me_3Si.D)^+$, $(Me_3SiCl_2)^-$ und $Me_3SiCl.D$ (D = N-Donor) erklärt.

Introduction

Interest in the chemistry of Me_3SiCl is quite evident from the reports which appear on its reactions with various organic[1–4] as well as inorganic reagents[5–7]. Keeping this in view it was thought worthwhile to investigate into the mechanism of its complex formation with some *Lewis* bases. The present investigations include its reactions with some nitrogen donors in nitrobenzene which appeared somewhat unusual when studied conductometrically.

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Experimental

Nitrobenzene was purified by the method already reported[8]. The bases were purified by distilling them over potassium hydroxide pellets. Me_3SiCl (Fluka), which was made HCl free by distilling it under vacuum, was used. Its complex with pyridine was prepared by mixing their solutions in petroleum ether (boiling range 40–60 °C) keeping pyridine in slight excess. The product formed was filtered, washed with the solvent several times and dried under vacuum. The stoichiometry of this white hygroscopic solid was determined by analysing it for chlorine and nitrogen contents (Found Cl 18.72%, N 7.28%. Required for Me_3SiCl. Pyridine Cl 18.93%, N 7.47%).

Conductance measurements were made on a Toshniwal Conductivity Bridge Type CLOI/02A using dip-type cells adopting the following procedure. A millimolar solution of Me_3SiCl in nitrobenzene was taken in the cell and thermostated at 30 ± 0.1 °C. To this a decimolar solution of the base prepared in nitrobenzene was added in small instalments. After each addition the solution was shaken and was allowed to come to constant temperature. The constant value of its conductance was recorded. Corrections for the increase in volume during each addition were applied to them and relative conductance values were calculated. Plots were made between relative conductance values and base to Me_3SiCl molar ratios (Fig. 1).

Results and Discussion

The low molar conductance value of Me_3SiCl in nitrobenzene suggests that it behaves as a weak electrolyte even in a medium of high dielectric constant. However, this small conductance of the solution may be interpreted in terms of the following equilibrium taking place in the solution[9]

$$Me_3\mathrm{SiCl} \overset{\mathrm{solv.}}{\rightleftharpoons} (Me_3\mathrm{Si.solv.})^+ + \mathrm{Cl}^- \qquad (1)$$

On the addition of base the conductance of the solution changes in a complex manner (see Fig. 1). The initial rapid increase in the conductance, the rate of which falls off slowly with the increasing amount of the base already present in the solution till it attains its maximum value at the molar concentration of the base approximately half of that of Me_3SiCl, may be explained by assuming reactions (2)-(4) taking place in solution (D is pyridine, 2-, 3- or 4-picoline, quinoline or isoquinoline).

$$Me_3\mathrm{SiCl} + D \rightleftharpoons Me_3\mathrm{SiCl}.D \qquad (2)$$

$$Me_3\mathrm{SiCl}.D \rightleftharpoons (Me_3\mathrm{Si}.D)^+ + \mathrm{Cl}^- \qquad (3)$$

$$Me_3\mathrm{SiCl} + \mathrm{Cl}^- \rightleftharpoons (Me_3\mathrm{SiCl}_2)^- \qquad (4)$$

Compounds containing penta-coordinated silicon are well known[10–12] and the formation of $(Me_3\mathrm{SiCl}_2)^-$ anion is not unusual[13].

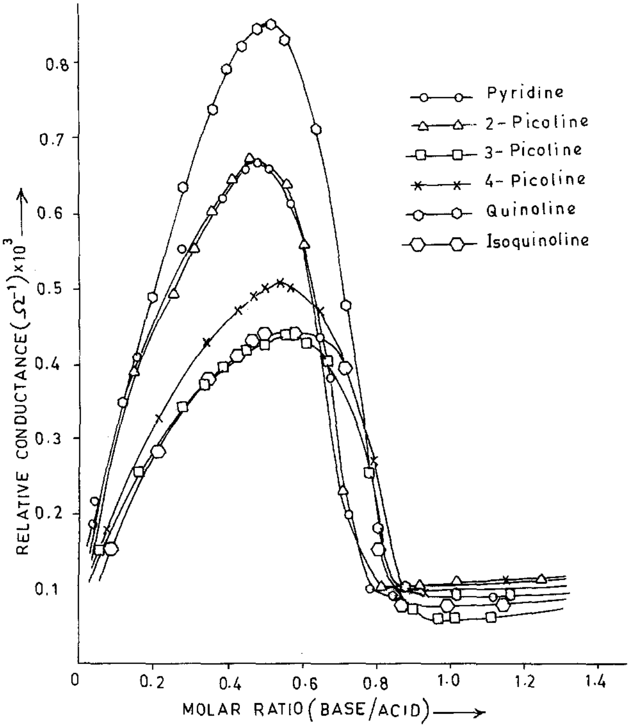

Fig. 1. Relative conductance curves for the addition of bases to the solution of Me_3SiCl in nitrobenzene at 30 ± 0.1 °C

The above interpretation is analogous to that given in the case of similar reactions of diorganotin dichlorides with some nitrogen donors in nitrobenzene[14–16]. Formation of 1 : 1 complexes of Me_3SiCl with some nitrogen donors has also been reported earlier[17].

Further addition of the base to the solution till its molar concentration becomes almost equal to that of Me_3SiCl causes a decrease in the relative conductance of the solution. This suggests the consumption of ions during the reaction (5).

$$(Me_3Si.D)^+ + (Me_3SiCl_2)^- \rightleftharpoons 2\,Me_3SiCl.D \qquad (5)$$

Higher ionisation of $Me_3SiCl.D$ in the presence of unreacted Me_3SiCl may be due to the consumption of the chloride ion liberated during its ionisation which shifts the equilibrium in the reaction (3) towards right[14].

No appreciable change in the relative conductance takes place after molar concentrations of the base and the acid become almost equal. This suggests that the reaction between the base and the products formed in the solution almost stops. This is supported by the fact that only a **1:1** complex of Me_3SiCl with pyridine could be isolated in petroleum ether (boiling range 40–60 °C) even when the base was present in excess in parallel with the observations made by *Tsuji* and *Tsukada*[17]. The molar conductance of the complex in nitrobenzene corresponded to that obtained from the Me_3SiCl-pyridine conductance curve at equal molar concentrations of Me_3SiCl and pyridine.

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