Kinetic Evidence for a Six-co-ordinate Silicon Intermediate in the Racemisation of Chlorosilanes

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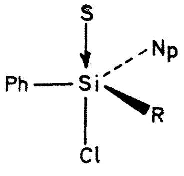
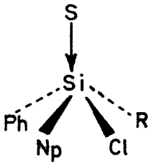
Summary A kinetic study of the racemisation of chlorosilanes shows that the racemisation is second-order with respect to reagent; thus the intermediate is probably octahedral, with each molecule of chlorosilane co-ordinated by two molecules of reagent.

THE racemisation of chlorosilanes is generally accepted[1] as not proceeding *via* a siliconium ion $R^1 R^2 R^3 Si^+$. We have shown[2] that the solvent-induced racemisation proceeds, rather, through an extension of the co-ordination of the silicon atom.

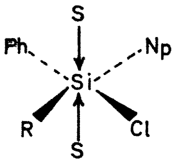
In this case, two kinds of intermediates may be involved: (i) the co-ordination of only one molecule of solvent provides a trigonal-bipyramidal intermediate (A) allowing racemisation *via* pseudorotation, as already postulated for the racemisation of fluorosilanes,[3] or *cis*–*trans*-isomerisation of difluorodisilacyclohexanes.[4] It does not matter whether the complex is a trigonal bipyramid (A) or a tetragonal pyramid (B). The interconversion of the two would be expected to be simple since (B) is the transition state between two pseudorotations.[5] However, an intermediate such as (A) should not undergo pseudorotation since this would require electronegative ligands S and Cl to occupy equatorial positions in the trigonal-bipyramidal complex.[6]



(A)



(B)



(C)

(ii) The racemisation may occur through a symmetrical octahedral intermediate (C) obtained by co-ordination of two solvent molecules, although this intermediate seems less likely than the one mentioned above.[7]

In order to distinguish between these two possibilities, we have studied the kinetics of the reaction, using highly effective reagents, diluted with inert solvents, and some optically active chlorosilanes prepared in our laboratory.[8]

We now report the results of a study of the racemisation of chloro-menthyloxy-α-naphthylphenylsilane,[8a] in HMPT–CCl_4. The reaction was found to be first-order in chlorosilane for concentrations $[R_3SiCl]$ varying from 0·025 to 0·2M and constant [HMPT]. We have also studied the effect of variations of [HMPT] in the range *ca.* 0·028 to 0·26M (0·5—4·5%). The results show that the k_1 values depend on the concentration of this reagent. A plot of k_1 against [HMPT] gives a parabolic curve, but a plot of k_1 against $[HMPT]^2$ (Figure) yields a straight line.

The same rate expression $V = k[R_3SiCl]\ [S]^2$ (S = racemisation reagent) is obtained with many other systems: chloro-ethyl-α-naphthylphenylsilane (DMF, HMPT, NMP, Me_2SO together in CCl_4, and Me_2SO in toluene), chloro-methyl-α-naphthylphenylsilane (DMF in CCl_4) and 2-chloro-2-α-naphthyl-1,2,3,4-tetrahydro-2-silanaphthalene (DMF in toluene). These results will be reported in detail later.

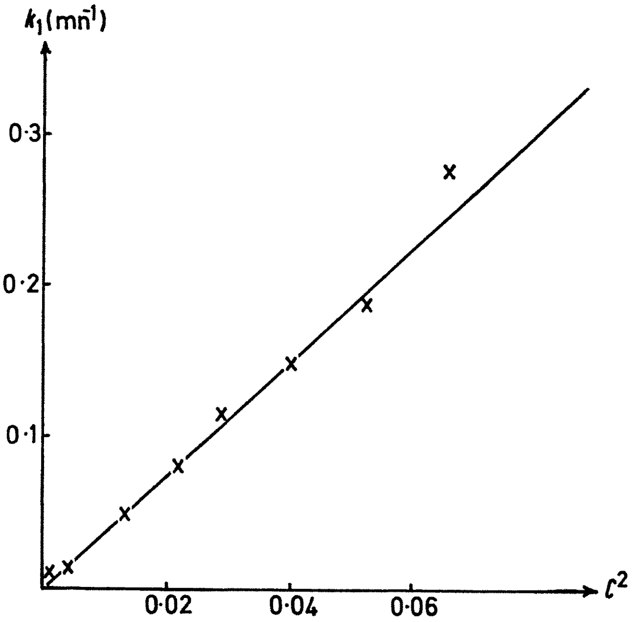


FIGURE. *Plot of* k_1 *against* $[HMPT]^2$ *with* [HMPT] *from* ca. 0·028 *to* 0·26 M.

Since the racemisation is second-order with respect to the reagent, the intermediate involved is certainly (C).

We suggest the following mechanism in which k_2 is the rate determining step:

$$R_3SiCl + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (A)$$

$$(A) + S \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} (C)$$

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