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Nucleophile-assisted racemizations of halosilanes: thermodynamic studies ☆

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Abstract

Thermodynamic studies have been carried out for the nucleophile-induced racemisation of $PhCHMeSiMe_2X$ (**2**) (X = Br or Cl). The values of $\Delta H^{\ddagger}$ (≈ 45 kJ mol^{-1}) and $\Delta S^{\ddagger}$(≈ -15 – -50 J K^{-1} mol^{-1}) for the racemization of **2** (X = Br or Cl) in the presence of *N*-methylimidazole and **2** (X = Br) in the presence of hexamethylphosphoramide are compatible with a mechanism for racemization in which the nucleophile displaces halide ion from the silane in the first step and the rate-determining step is attack of halide ion on halosilane. For **2** (X = Cl) in the presence of hexamethylphosphoramide a curved Eyring plot shows that different racemization mechanisms are competing. At low temperatures the halide–halosilane mechanism dominates where at high temperatures a double-displacement mechanism dominates, in which the rate-determining step is the attack of nucleophile on $PhCHMeSiMe_2HMPA^+$. The approximate thermodynamic parameters for this latter process are $\Delta H^{\ddagger}$, ≈ 0 kJ mol^{-1} and $\Delta S^{\ddagger} \approx -180$ J K^{-1} mol^{-1}. Analysis of the thermodynamics of these reactions does not allow a definitive distinction to be made between nucleophilic activation involving attack at extracoordinated silicon and that at teracoordinated silicon.

Keywords: Silicon; Kinetics; Mechanism; Nuclear magnetic resonance

1. Introduction

Nucleophilic substitution at silicon is one of the fundamental reactions of organosilicon chemistry and is a crucial step in the synthesis of silicones. Understanding the mechanisms of nucleophilic substitution at silicon is particularly challenging [1–3] given the superficial simplicity of the replacement of one group attached to silicon by another. The ability of silicon to adopt coordination numbers greater than four widens considerably the variety of available mechanisms. Nucleophilic substitution mechanisms have been reported [1–3] that proceed stereoselectively with either retention or inversion of configuration at silicon via pentacoordinated or hexacoordinated silicon species. The published mechanisms [2,3] accounting for these stereochemical observations are now generally accepted.

Recently, the phenomenon of nucleophilic activation of nucleophilic substitution has aroused significant attention [2–17] and there are still questions to be answered about the mechanistic pathways. The observation by Corriu and Henner Leard [5] that hydrolysis of halosilanes can be accelerated in the presence of nucleophiles and that the predominant stereochemistry is retention of configuration initiated the current interest. The kinetic rate law was reported to be

$$\text{rate of hydrolysis} = k[\text{halosilane}][H_2O][\text{Nu}] \quad (1)$$

Similarly, chiral halosilanes are racemized in the presence of nucleophiles according to the expression [5,6]

$$\text{rate of racemization} = k[\text{halosilane}][\text{Nu}]^2 \quad (2)$$

The interpretation of such apparently simple kinetic laws in mechanistic terms is not simple. The mechanistic possibilities are shown in Scheme 1.

Corriu and coworkers [3,5–9,17] prefer a mechanism involving extracoordinated silicon intermediates (an anticlockwise route from **1** to **1'**) for the racemisation of their α-napthylphenylmethylhalosilanes. In addition to the kinetic data, Corriu and Henner Leard [5,18] have

☆ Dedicated to Professor Hideki Sakurai in recognition of his major contribution to silicon chemistry and on the occasion of his retirement from Tohoku University.

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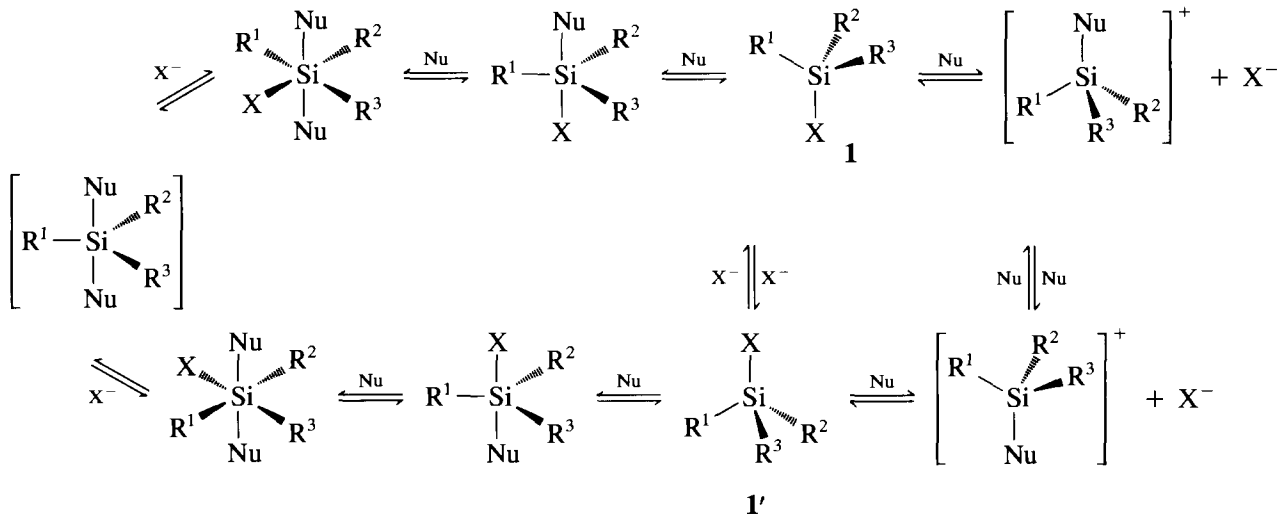
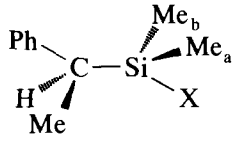


Scheme 1.

reported thermodynamic activation parameters for the nucleophile-induced racemizations (Table 1) which show very small energies of activation and very large entropies of activation. The small activation enthalpies and large entropies of activation showed that the racemization is entropy controlled [18].

We have suggested [19,20] that in the racemization of **2** there are two competing pathways: double-displacement [11] and a halide–halide inversion resulting from halide liberation following nucleophile coordination [19]. There was no evidence to support a mechanism involving nucleophilic attack at extracoordinated silicon for these particular compounds. The two routes are shown in Scheme 1 as the clockwise route and the vertical route respectively in the transformation of **1** to **1'**.



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Under conditions where inversion of configuration at the silicon centre is slow on the NMR time scale, the diastereotopic methyl groups Me_a and Me_b have separate distinct signals in the ^{13}C NMR spectrum. When inversion of configuration at silicon is fast, the resonances collapse to a frequency-averaged singlet. At intermediate rates of inversion of configuration the lifetime of the silicon species can be determined by simulation of the spectrum using a commercially available program such as DNMR4 [21]. The pseudo-first-order rate constant k_{obs} is given by

$$\frac{\text{rate of reaction}}{[R_3SiX]} = \frac{d[R_3SiX]}{dt}\frac{1}{[R_3SiX]} = k_{obs} \qquad (3)$$

The coalescence to a singlet of the separate ^{13}C resonances of the diastereotopic methyl in racemic **2** in the presence of different nucleophiles was used to measure the rate of inversion of configuration at silicon [19,20]. The kinetic data and detailed kinetic analyses were used to make mechanistic hypotheses [20]. The kinetic orders in nucleophile obtained for the racemiza-

Table 1
Thermodynamic activation parameters for nucleophile-induced racemizations

Silane (concentration (M))	Nucleophile (solvent) (concentration (M))	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	Reference
EtPh-1-NpSiBr	HMPA (CCl_4)	10.4	−236	[18]
EtPh-1-NpSiCl	HMPA (CCl_4)	1.63	−238	[5]
^{i}PrPh-1-NpSiCl	HMPA (CCl_4)	13.1	−229	[5]
EtPh-1-NpSiCl	DMF(CCl_4)	0	−290	[5]
$PhCHMeSiMe_2Br$ (2.3)	HMPA (CD_2Cl_2) (0.01)	45	−51	This work
$PhCHMeSiMe_2Br$ (2.3)	NMI (CD_2Cl_2) (0.1)	45	−50	This work
$PhCHMeSiMe_2Cl$ (2.3)	NMI (CD_2Cl_2) (0.21)	44	−15	This work
$PhCHMeSiMe_2Cl$ (2.3)	HMPA (CD_2Cl_2) (0.1)	< 6 (high T) > 25 (low T)	−180 (high T) −100 (low T)	This work

tion of **2** were non-integral, between 1 and 2, when nucleophile aggregation effects were absent. It was apparent that it is difficult to distinguish between pathways involving attack at hypercoordinated intermediates in the rate limiting step and attack at tetracoordinated silicon simply from kinetic data. Our mechanistic proposals were also supported by NMR studies [19]. Solutions of **2** in the presence of nucleophiles were studied under conditions that used the diastereotopic methyl groups to determine relative rates of inversion of configuration of the tetracoordinate species in solution. There was no evidence for the presence of significant amounts of extracoordinated silicon species in those systems, and $PhCHMeSiMe_2Cl$ and $PhCHMeSiMe_2NMI^+$ in the same solution were shown to undergo racemization at different rates. It is now clear that the variety of mechanisms that can operate during nucleophilic substitutions at silicon are very diverse. Problems can arise if attempts are made to extrapolate mechanisms from one system to another, even to a closely related system. We are engaged in a systematic exploration [13,14,19,20,22–27] of the factors influencing coordination states and mechanisms of silicon substitutions using NMR spectroscopy and kinetic and thermodynamic measurements.

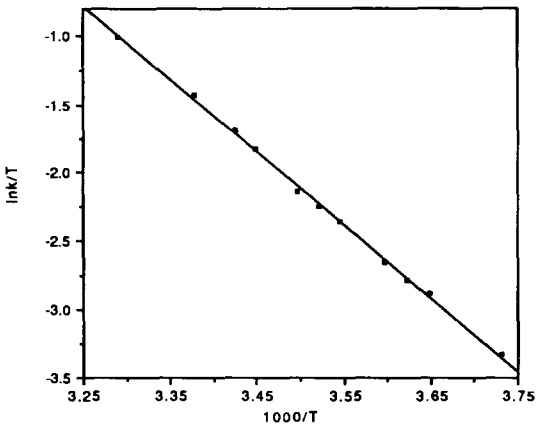
In this paper we report some thermodynamic data for the racemisation of **2** which we determined in order to evaluate the usefulness of such data in distinguishing between activated extracoordinated silicon mechanisms and double-displacement-related mechanisms.

2. Results and discussion

Activation parameters were obtained for the racemization of **2** (X = Cl or Br) induced by *N*-methylimidazole (NMI) and hexamethylphosphoramide (HMPA). The ^{13}C NMR spectra of a mixture of **2** and nucleophile were measured at a variety of temperatures and the rate constants calculated for each temperature by use of DNMR4 in the usual way [20,21]. The thermodynamic parameters were calculated by application of the integrated form of the Eyring equation [28]:

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + 23.76 \qquad (4)$$

For a simple reaction, a straight-line graph is obtained when $\ln(k/T)$ is plotted against $1/T$. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are obtained from the gradient and intercept respectively. The good straight-line plot ($r^2 = 0.998$) for the racemization of **2** (X = Br) in the presence of NMI is shown in Fig. 1 and the thermodynamic parameters derived from the plot are given in Table 1. Excellent straight lines were also obtained over the entire temperature range available for study (between 30 and 40 K)



ln k/T vs 1000/T for racemisation of 2 (X = Br) induced by HMPA

Fig. 1. ln k/T vs. 1000/T for racemization of **2** (X = Br) induced by HMPA

for the racemization of **2** (X = Br) in the presence of HMPA and for the racemization of **2** (X = Cl) in the presence of NMI. The activation parameters obtained for these reactions are very similar with low activation enthalpies and negative but not exceptionally large entropies of activation. The major route for each of the racemization reactions described above is according to our previous NMR and kinetic evidence, most probably a reaction of liberated halide ion with halosilane. This reaction takes place with inversion of configuration in a manner analogous to an S_N2 substitution at carbon, but the pentacoordinated species may well be a short-lived intermediate rather than a transition state. Racemization therefore proceeds through a series of inversions at silicon:

$$X^- + R\text{-}R_3SiX = S\text{-}R_3SiX + X^- \qquad (5)$$

Under the conditions of the reaction the equilibrium constant for complex formation is high for **2** (X = Cl or Br) with NMI and for **2** (X = Br) with HMPA [19]:

$$Nu + R_3SiX = R_3SiNu^+ + X^- \qquad (6)$$

As the nucleophile is initially in relatively low concentration, the reaction mixture consists mainly of R_3SiX with smaller concentrations of X and R_3SiNu^+. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the racemization of **2** (X = Br) induced by the two different nucleophiles are remarkably similar ($\Delta H^{\ddagger} = 45$ kJ mol^{-1} and $\Delta S^{\ddagger} = -50$ J K^{-1} mol^{-1}) as would be expected from reactions proceeding through the same mechanism via halide exchange. The concentration of nucleophile required to induce racemization at a given rate differs for the two nucleophiles. We have explained similar phenomena, including a deviation from first order in nucleophile kinetics [20,25], in terms of ion pairing of $R_3SiNu^+X^-$, which affects the availability of X^- for reaction. For these reactions, and the racemization of **2** (X = Cl) with

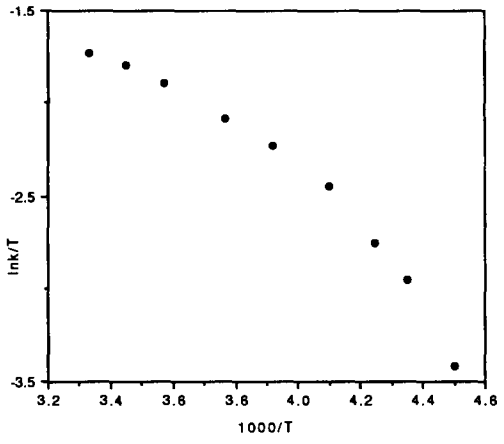


Fig. 2. ln k/T vs. 1000/T for racemization of **2** (X = Cl) induced by HMPA

NMI (Table 1) the numerical values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are entirely consistent with halide–halide exchange. The low activation enthalpy reflects the ease of forming pentacoordinated intermediates, particularly with identical groups in the two axial positions. This phenomenon was first recognised by Corriu [29] who described a "like-atom effect" and more recently by Holmes [30], Dieters and Holmes [31] and Gordon and co-workers [32,33] who have provided a theoretical framework for a more generalized description of ligand effects in pentacoordinated silicon intermediates. The small values of the activation entropy are consistent with a "loose" pentacoordinated intermediate.

A very different result was obtained for the racemization of **2** (X = Cl) with HMPA and the Eyring plot for the reaction is shown in Fig. 2. That plot is distinctly curved over the entire 80 K temperature range that could be studied, which strongly suggests the operation of two competing mechanisms for which the relative importance changes with temperature. We have previously reported [19] that there is very little salt formation observed by NMR spectroscopy when **2** (X = Cl) is mixed with HMPA. The equilibrium constant for the following reaction is therefore low:

$$PhCHMeSiMe_2Cl + HMPA = PhCHMeSiMe_2HMPA^+ + Cl^- \quad (7)$$

The reaction of Me_3SiCl with NMI shows little salt formation at ambient temperature but, at low temperatures, salt formation is essentially complete [25], as is the case for **2** (X = Cl) with HMPA [19]. The thermodynamic parameters for salt formation have been measured for reaction of Me_3SiCl with NMI and $\Delta H = -42$ kJ mol^{-1} and $\Delta S = -171$ J K^{-1} mol^{-1}. The reaction is exothermic and has a very large and negative standard entropy change. The parameters for reaction (7) have not been measured but are expected to be of a similar order. The nature of the mixture of **2** (X = Cl) with HMPA varies quite markedly over the range of temperatures of the thermodynamic measurements. At ambient and higher temperatures the mixture largely consists of HMPA and $PhCHMeSiMe_2Cl$ with a small amount of $PhCHMeSiMe_2HMPA^+Cl^-$. At the lowest temperature of 220 K, there is very little free HMPA as the formation of $PhCHMeSiMe_2HMPA^+Cl^-$ is substantially complete. It is therefore expected that different racemization mechanisms will dominate at different temperatures. At low temperatures the halide–halide exchange, as for the racemizations reported above, is the most likely mechanism, whereas at high temperatures the double displacement mechanism, in which HMPA attacks $PhCHMeSiMe_2HMPA^+$ with inversion of configuration, should dominate.

If the slopes of the Eyring plot for racemization of **2** (X = Cl) with HMPA at the low and high temperature limits are taken as limiting values for the two processes the data shown in Table 1 are obtained for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. At the low temperature extreme the minimum value for $\Delta H^{\ddagger}$ is 25 kJ mol^{-1} and $\Delta S^{\ddagger}$ is numerically less than -100 J K^{-1} mol^{-1} (i.e. closer to zero). These values are approaching those for the reaction of **2** with NMI. At the high temperature limit, $\Delta H^{\ddagger}$ is approaching zero and $\Delta S^{\ddagger}$ has a larger numerical value than -180 J K^{-1} mol^{-1}. The high temperature limiting values are quite consistent with the double-displacement mechanism. The values are typical for a pre-equilibrium reaction, in which the first step is exothermic (here salt formation). Such reactions typically have low or even negative activation enthalpies as the concentration of the active species is lower at higher temperatures. We note the similarity between our values and those reported by Corriu and Henner Leard [5,18] for racemization of RPh-1-NpSiX which are explained in terms of the nucleophilic activation model in which the rate-limiting step is the attack of nucleophile on a pentacoordinated intermediate. It is possible that both the system of Corriu and Henner Leard and our system are following the same mechanism, but it is also quite possible that they take place by different mechanisms. The nucleophilic activation model is also a pre-equilibrium system in which low or negative activation enthalpies and high negative entropies of activation are expected. In fact we suggest that the two mechanisms, nucleophilic activation and double displacement, are on the same reaction surface continuum. The first step in each is reversible coordination of a nucleophile to a tetracoordinated silicon. Whether the pentacoordinated species is a relatively long-lived intermediate or a transient species will depend critically on the nature of the silicon compound, the reaction conditions and the nucleophile.

3. Experimental details

The synthesis of $PhCHMeSiMe_2X$ (**2**), (X = Br or Cl) has been reported previously [19]. NMR experiments were carried out on a JEOL FX90Q NMR spectrometer fitted with a variable-temperature facility. Samples were made up immediately prior to use in NMR tubes fitted with screw caps and Teflon–silicone rubber septa. Freshly distilled **2** was used. HMPA was distilled from phosphorus pentoxide and stored over activated 4A molecular sieves. NMI was stood over 4A molecular sieves for 2 days, distilled from the sieves and stored over activated 4A molecular sieves. The temperature of the NMR samples was calibrated by using a Comark microprocessor thermometer thermocouple. Temperatures were accurate and consistent within 1 K.

References

[1] L.H. Sommer, *Stereochemistry, Mechanism and Silicon*, McGraw-Hill, New York, 1965.

[2] A.R. Bassindale and P.G. Taylor in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds*, Wiley, Chichester, 1989, Chapter 13, p. 839.

[3] R.J.P. Corriu, C. Guerin and J.J.E. Moreau, in S. Patai and Z. Rappoport, (eds.), *The Chemistry of Organic Silicon Compounds*, Wiley, Chichester, 1989, Chapter 4, p. 305.

[4] A.D. Allen, J.C. Charlton, C. Eaborn and G. Modena, *J. Chem. Soc.*, (1957) 3668.

[5] R.J.P. Corriu and M. Henner Leard, *J. Organomet. Chem., 64* (1974) 351.

[6] R.J.P. Corriu, F. Larcher and G. Royo, *J. Organomet. Chem., 104* (1976) 293.

[7] R.J.P. Corriu, and C. Guerin, *Adv. Organomet. Chem., 2* (1982) 265.

[8] R.J.P. Corriu, C. Guerin, and J.J.E. Moreau, *Top. Stereochem., 15* (1984) 43.

[9] R.J.P. Corriu, G. Dabosi and M. Martineau, *J. Organomet. Chem., 154* (1978) 33.

[10] F.K. Cartledge, B.G. McKinnie and J.M. Wolcott, *J. Organomet. Chem., 118* (1976) 7.

[11] J. Chojnowski, M. Cypryk and M. Michalska, *J. Organomet. Chem., 161* (1978) C31.

[12] H.K. Chu, M.O. Johnson and C.L. Frye, *J. Organomet. Chem., 271* (1984) 327.

[13] A.R. Bassindale and T. Stout, *J. Organomet. Chem., 238* (1982) C41.

[14] A.R. Bassindale and M. Borbaruah, *J. Chem. Soc., Chem. Commun.*, (1993) 352.

[15] H. Fujimoto, N. Arita amd K. Tamao, *Organometallics, 11* (1992) 3035.

[16] S.K. Chaudhary and O. Hernandez, *Tetrahedron Lett.*, (1979) 99.

[17] R.J.P. Corriu, *Chem. Rev.*, (1993) 1371.

[18] R.J.P. Corriu and M. Henner Leard, *J. Organomet. Chem., 65* (1974) C39.

[19] A.R. Bassindale, J.C-Y. Lau and P.G. Taylor, *J. Organomet. Chem., 341* (1988) 213.

[20] A.R. Bassindale, J.C-Y. Lau and P.G. Taylor, *J. Organomet. Chem., 490* (1995) 75.

[21] *DNMR4 Quantum Chemistry Program Exchange (QCPE) Program number 466*, Indiana University.

[22] A.R. Bassindale and J. Jiang *J. Organomet. Chem., 446* (1993) C3.

[23] AR Bassindale and T Stout, *Tetrahedron Lett., 26* (1985) 3403.

[24] A.R. Bassindale and T Stout, *J. Chem. Soc., Chem. Commun.*, (1984) 1387.

[25] A.R. Bassindale and T. Stout, *J. Chem. Soc., Perkin Trans. II*, (1986) 221.

[26] A.R. Bassindale, J.C-Y. Lau, T. Stout and P.G. Taylor, *J. Chem. Soc., Perkin Trans. II*, (1986) 227.

[27] A.R. Bassindale and M. Borbaruah, *J. Chem. Soc., Chem. Commun.*, (1991) 1501.

[28] W.F.K. Wynne-Jones and H. Eyring, *J. Chem. Phys., 3* (1935) 492.

[29] R.J.P. Corriu, *Phosphorus Sulfur, 27* (1986) 1.

[30] R.R. Holmes, *Chem. Rev., 90* (1990) 17.

[31] J.A. Dieters, R.R. Holmes and J.M. Holmes, *J. Am. Chem. Soc., 110* (1988) 7672.

[32] M.S. Gordon, L.P. Davis and L.W. Burggraf, *Chem. Phys. Lett., 163* (1989) 371

[33] M.S. Gordon, M.T. Carroll, J.H. Jensen, L.P. Davis, L.W. Burggraf and R.M. Guidry, *Organometallics, 10* (1991) 2657.