Internal Nucleophilic Displacements within Silanolate Ions. A New Mechanism of Substitution at Silicon

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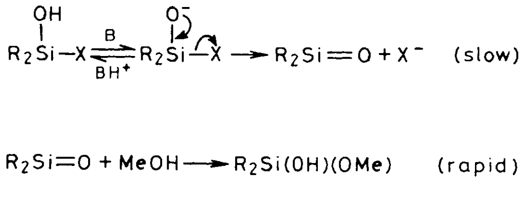
Unimolecular dissociation of $^-O{-}(X)Si{<}$ species to give X^- and $O{=}Si{<}$ (which immediately reacts with the solvent) is postulated to account for (a) features of the base-catalysed cleavage of R–Si bonds in solutions of $RSiMe_2OMe$ (R = *m*-$ClC_6H_4CH_2$ or $PhC{\equiv}C$) in 5% H_2O–MeOH and (b) the rapid conversion of $(Me_3Si)_3CSiPh(OH)I$ into $(Me_3Si)_3CSiPh(OH)(OMe)$ by methanolic MeONa.

We present evidence for a new mechanism of substitution at silicon. This mechanism has been detected in solvolysis under basic conditions of organosilicon species in which a hydroxy-group is present on the silicon bearing the leaving group X, and, as depicted in Scheme 1, involves an internal displacement within a silanolate ion to give a silanone, which reacts rapidly with the solvent (*e.g.* MeOH) to give the same product as would be expected for direct nucleophilic displacement of X.

We first suspected the existence of this mechanism when we



Scheme 1

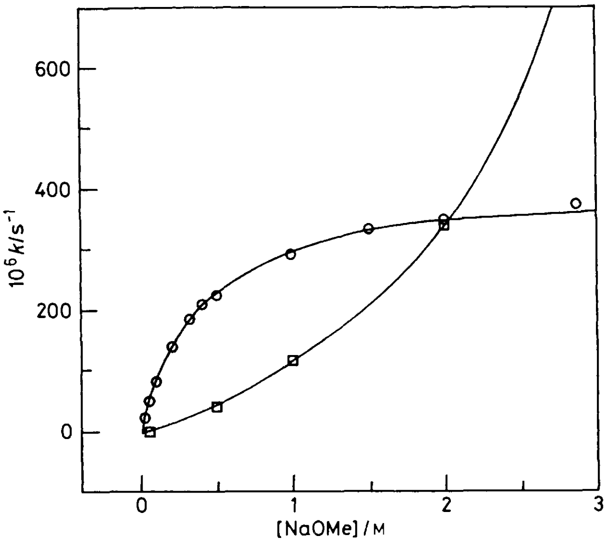


Figure 1. Plot of observed first-order rate constant, k, against the base concentration for cleavage of m-$ClC_6H_4CH_2SiMe_2OMe$ at 50.0 °C in (a) MeOH (squares) and (b) 5 vol-% H_2O–MeOH (circles). The curve in case (b) is that generated by equation (1).

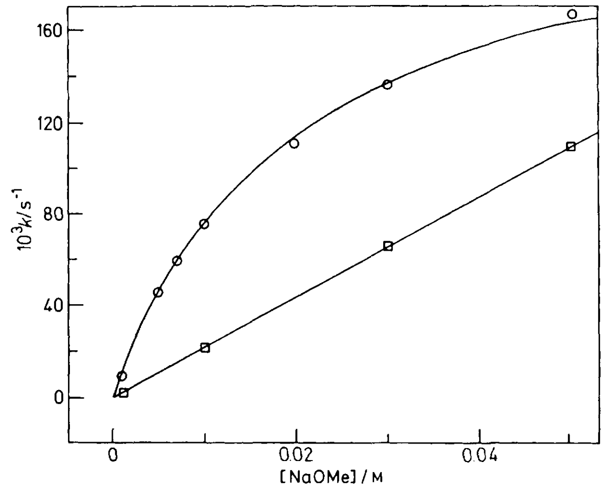


Figure 2. Plot of observed first order rate constant, k, against the base concentration for cleavage of $PhC{\equiv}CSiMe_2OMe$ at 30.0 °C in (a) MeOH (squares) and (b) 5 vol-% H_2O–MeOH (circles). The curve in case (b) is that generated by equation (2).

measured spectrophotometrically the rate of base-catalysed cleavage of the R–Si bonds of $RSiMe_2OMe$ species in MeOH and in 5 vol-% H_2O–MeOH. For R = m-$ClC_6H_4CH_2$ (initially 5×10^{-3} M) in MeOH the dependence of the observed first-order rate constant, k, at 50.0 °C on the base concentration was similar to that observed for cleavage of $RSiMe_3$ species,[1] but in the water-containing medium the dependence was very different, the value of k rising sharply with increasing base at low base concentrations and then levelling off (see Figure 1). We were aware that some of the $RSiMe_2OMe$ would be rapidly converted into the silanol $RSiMe_2OH$ and hence into $RSiMe_2O^-$ in 5% H_2O–MeOH containing base, but expected that the rate of cleavage of the silanol would be rather similar to that of $RSiMe_2OMe$ and that $RSiMe_2O^-$ would (because of repulsion of the OMe^-) be relatively inert, so that the observed rate constant would fall off progressively at higher base concentrations as silanolate ion was increasingly formed. Instead it appears that the R–Si bond of the anion $RSiMe_2O^-$ readily undergoes a rate-determining unimolecular dissociation to $Me_2Si{=}O$ and R^- [which rapidly react with MeOH to give $Me_2Si(OH)(OMe)$ and RH]. The observed rate constant, k, is thus made up of a contribution from this process, dependent upon the concentration of the anion, and another from $RSiMe_2OMe$, dependent upon the concentration of this species and that of the base. [For simplicity we treat $RSiMe_2OH$, as far as its direct contribution to the observed rate is concerned, as though it were $RSiMe_2OMe$, on the basis of the assumptions that relatively little of the silanol is present (say 20% of the amount of $RSiMe_2OMe$), and that in any case the rate of its direct cleavage will not be very different from that of the methoxide.]

It was shown by u.v. spectroscopy that the related $RSiMe_2OMe$ with R = $PhCH_2$, which is much less readily cleaved, is *ca.* half converted into $RSiMe_2O^-$ in 5% H_2O–MeOH containing 0.40 M NaOMe. (For simplicity we neglect the fact that hydroxide ion must also be present in solutions of NaOMe in H_2O–MeOH.) We assumed that for R = m-$ClC_6H_4CH_2$ there would be half conversion at a slightly lower base concentration, *viz.* 0.38 M (since the chloro-substituent will slightly increase the acidity of the silanol), and calculated the fraction, r, of the substrate present as silanolate ion at each base concentration. We estimated the value of the specific rate constant, k_S, for cleavage of the $RSiMe_2OMe$ in 5% H_2O–MeOH (at low base concentrations) as *ca.* 10×10^{-5} l mol^{-1} s^{-1} by applying to the value in MeOH the factor of 1.3 observed for this same solvent change with $RSiMe_3$. Thus we could estimate the contribution, k_{AMe}, to k from $RSiMe_2OMe$, given by $k_S(1-r) \times$ [NaOMe], and so derive the contribution, k_{A^-}, due to the silanolate ion.† The first-order rate constant for the decomposition of this ion is then given by k_{A^-}/r, which should be constant if our interpretations are correct, and this was approximately the case, all the values lying in the range 361—404 × 10^{-6} s^{-1} with a mean of 379 ± 14 (standard deviation) × 10^{-6} s^{-1}. The curve shown in Figure 1 for the 5% H_2O–MeOH medium is actually that generated by use of equation (1), and

$$10^6k = 100(1-r)[\text{NaOMe}] + 379r \tag{1}$$

the fit is very satisfactory in view of the simplifying assumptions made. (At high base concentrations the contribution of the methoxide should level off at *ca.* 34 × 10^{-6} s^{-1} and that of the anion at *ca.* 379 × 10^{-6} s^{-1}.)

Similar behaviour was observed for the much more readily cleaved $RSiMe_2OMe$ with R = $PhC{\equiv}C$ (Figure 2) at 30.0 °C, but much lower base concentrations are involved, and to interpret the results it has to be assumed that the $RSiMe_2OMe$ is half converted into $RSiMe_2O^-$ in 5% H_2O–MeOH containing 0.02 M base. The value of k_S for $RSiMe_2OMe$ in this medium is estimated to be 3.3 l mol^{-1} s^{-1} by applying to the value in NaOMe–MeOH the factor of 1.5 which applies in the case of $RSiMe_2OMe$ for this change of medium. The mean value of k_{A^-}/r then turns out to be 165 ± 7 (standard deviation) s^{-1}, and the upper curve in Figure 2 is then that generated by equation (2). (The analysis implies that $PhC{\equiv}CSiMe_2OH$ is

$$k = 3.3(1-r)[\text{NaOMe}] + 165r \times 10^3 \tag{2}$$

ca. 20 times as acidic as $PhCH_2SiMe_2OH$.) The contributions from the $RSiMe_2OMe$ and $RSiMe_2O^-$ are more comparable in this case, levelling off at *ca.* 60 × 10^{-3} and 165 × 10^{-3} s^{-1}, respectively, at higher bases concentrations.

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† The contribution from $RSiMe_2OMe$ can be assumed to be given by $k_S(1-r)$[NaOMe] even at high base concentrations at which k_S in fact varies; this is because acidity function effects on k_S and $(1-r)$ should approximately cancel out.

While the above experiments were in progress, we observed the operation of the new mechanism in a very different system, involving methanolysis of $(Me_3Si)_3CSiPhRX$ species in which steric hindrance inhibits attack of nucleophiles on silicon.[2] It is known that the methanolyses of $(Me_3Si)_3CSiPhHI$ and the more hindered $(Me_3Si)_3CSiMe_2I$ are not catalysed by NaOMe,[3,4] and that the latter undergoes solvolysis only very slowly in refluxing NaOMe–MeOH,[4] and so we were not surprised to find that $(Me_3Si)_3CSiPh(OMe)I$ did not undergo detectable reaction with 0.5 M NaOMe–MeOH in 2 h under reflux. Unexpectedly, however, $(Me_3Si)_3CSiPh(OH)I$ (which did not react with MeOH alone in 24 h under reflux) in 0.17 M solution in 0.25 M NaOMe in MeOH was found to be completely converted into $(Me_3Si)_3CSiPh(OH)(OMe)$ within 5 min at room temperature, as judged by the change in position of the peak for the $(Me_3Si)_3C$ protons in the ^1H n.m.r. spectrum, and subsequent isolation of the product. This abnormal reactivity of the silanol can reasonably be attributed to the mechanism shown in Scheme 1.

Although this mechanism [an $S_N1(cb)$ process] has not previously been observed or even postulated for silicon, there are close analogues in carbonyl chemistry (where the internal displacement is normally in a rapid step after the rate determining process) and in phosphorus chemistry (see *e.g.*, ref. 5).

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