Evidence for Generation of the Unsaturated Sila-acetate Species Me(O⁻)Si=O by Dissociation of the Silanediolate Dianion *m*-ClC$_6$H$_4$CH$_2$SiMe(O⁻)$_2$

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Kinetic studies indicate that in the cleavage of *m*-ClC$_6$H$_4$CH$_2$SiMe(OH)$_2$ by NaOH in Me$_2$SO–H$_2$O there is a major contribution by unimolecular dissociation of the dianion *m*-ClC$_6$H$_4$CH$_2$SiMe(O$^-$)$_2$ to give the acetate ion analogue Me(O$^-$)Si=O.

We previously suggested that when the compounds RSiMe$_2$OMe (R = *m*-ClC$_6$H$_4$CH$_2$ or PhC≡C) are dissolved in 5% v/v H$_2$O–MeOH containing NaOH, the cleavages of the R–Si bonds involve concurrent reactions of the neutral species RSiMe$_2$OMe and RSiMe$_2$OH with base anion and the unimolecular dissociation of the anionic species RSiMe$_2$O$^-$ to give a silanone intermediate Me$_2$Si=O.[1,2] For those cleavages, the plots of the observed first-order rate constants (k_{obs}) against base concentration, [OH$^-$], initially rise steeply with increase in [OH$^-$] and then tail off to almost constant values of k_{obs}, and can be nicely accounted for in terms of a substantial contribution by the unimolecular decomposition. However, the plots of k_{obs} against [OH$^-$] could have the same form even if only cleavages of the neutral species were significant, and so (even though there is independent evidence for ejection of an anion from the silanolate ion to give a silanone[1,3]) we decided to seek unambiguous evidence for the unimolecular dissociation of a negatively charged species by examining the cleavage of the diol *m*-ClC$_6$H$_4$CH$_2$SiMe(OH)$_2$ [subsequently denoted by A(OH)$_2$] in Me$_2$SO—H$_2$O mixtures containing NaOH.

In basic solutions of the diol A(OH)$_2$ equilibria (i) and (ii) will be rapidly established. That the second ionization, to give A(O$^-$)$_2$, would be likely to be significant was suggested by the fact that the second dissociation constant for orthosilicic acid, Si(OH)$_4$, is only about 100 times smaller than the first, and that in more concentrated aqueous alkali there is virtually complete conversion into Si(OH)$_2$(O$^-$)$_2$.[4] A similar difference can be assumed between the first and second dissociation constants of A(OH)$_2$, and so conversion into the dianions A(O$^-$)$_2$ would be essentially complete in the very strongly basic solutions used in the present studies.

Bimolecular cleavage of the doubly charged species A(O$^-$)$_2$ by attack of OH$^-$ at silicon must be negligibly slow, but there is the possibility of unimolecular cleavage, analogous to that recognised for RSiMe$_2$O$^-$ species, as depicted in equation (iii).

$$A(\text{OH})_2 + \text{OH}^- \rightleftharpoons A(\text{OH})(\text{O}^-) + \text{H}_2\text{O} \qquad \text{(i)}$$

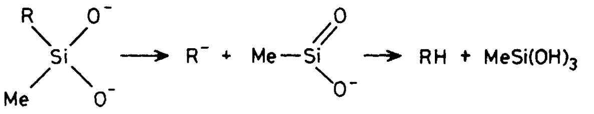
$$A(\text{OH})(\text{O}^-) + \text{OH}^- \rightleftharpoons A(\text{O}^-)_2 + \text{H}_2\text{O} \qquad \text{(ii)}$$

$$k_{\text{obs}} = k_{A(\text{OH})_2}[A(\text{OH})_2][\text{OH}^-] + k_{A(\text{OH})(\text{O}-)}[A(\text{OH})(\text{O}^-)] + k_{A(\text{O}-)_2}[A(\text{O}-)_2] \qquad (1)$$

$$k_{\text{obs}} = \left[\frac{B}{[\text{OH}]^-} + k_{A(\text{O}-)_2}\right] \frac{K_1 K_2 [\text{OH}^-]^2}{1 + K_1[\text{OH}] + K_1 K_2 [\text{OH}^-]^2} \qquad (2)$$

where $K_1 = [A(\text{OH})(\text{O}^-)]/[\text{OH}^-][A(\text{OH})_2]$, $K_2 = [A(\text{O}^-)_2]/[\text{OH}^-][\text{A}(\text{OH})(\text{O}^-)]$,
and $B = (k_{A(\text{OH})_2}/K_1K_2) + (k_{A(\text{OH})(\text{O}^-)}/K_2)$.

If such a process occurs, then in appropriate regions of base concentration three cleavage processes should contribute to the observed rate constant k_{obs}, the value of which, provided that the concentration of base is much greater than that of A(OH)$_2$, will be given by equation (1). By use of the definitions shown of the equilibrium constants K_1 and K_2 for the first and second ionizations of A(OH)$_2$, equation (1) can be transformed into equation (2). It follows that when much of the substrate, say 90%, is present as the dianion, doubling of the base concentration will reduce the concentration of A(OH)$_2$ by a factor approaching four and that of A(OH)(O$^-$) by a factor approaching two. At the same time the rate of cleavage of the remaining A(OH)$_2$ should be doubled, but the contribution from this cleavage will still be halved, as will that from the unimolecular cleavage of A(OH)(O$^-$). Consequently, at the higher base concentrations the contributions from the cleavages of A(OH)$_2$ and A(OH)(O$^-$) will fall off rapidly, and in the limit the observed rate constant will be that for the unimolecular cleavage of A(O$^-$)$_2$. Thus a plot of k_{obs} against [OH$^-$] should show a steep initial steep rise in k_{obs} as the rate of bimolecular cleavage of the A(OH)$_2$ species rises in line with [OH$^-$], but then should begin to tail off (as in the cleavage of RSiMe$_2$OH) as the monoanion A(OH)(O$^-$) is formed. As [OH$^-$] is increased further and significant amounts of the dianion A(O$^-$)$_2$ are formed, then if the dianion



(iii)

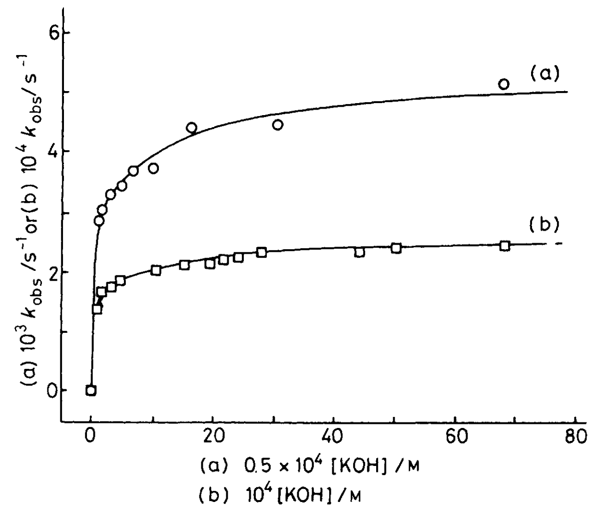


Figure 1. Plot of k_{obs} against concentration of KOH for cleavage of A(OH)$_2$ in 1 : 1 v/v Me$_2$SO–H$_2$O (a) at 50 °C and (b) at 25 °C. The lines shown are those generated from equation (2) by use of the values of K_1, K_2, B, and $k_{A(\text{O}-)_2}$ specified in the text.

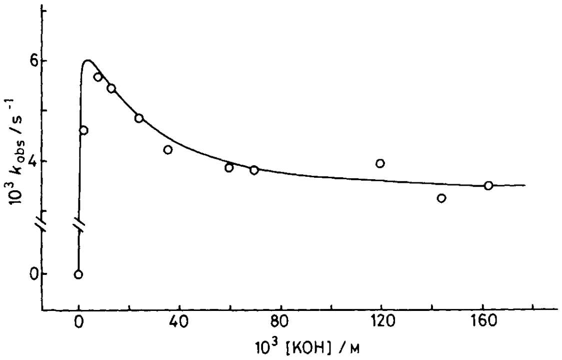


Figure 2. Plot of k_{obs} against concentration of KOH for cleavage of $A(OH)_2$ in 3:1 v/v Me_2SO–H_2O at 25 °C. The line shown is that generated from equation (2) by use of the values of K_1, K_2, B, and $k_{A(O^-)_2}$ specified in the text.

were unreactive, k_{obs} would begin to fall off sharply, ultimately falling effectively to zero, which is not observed. If, however, the dianion undergoes cleavage at a significant rate, then the value of k_{obs} should level off to a plateau, or pass through a maximum and subsequently level off at a constant value corresponding to the rate constant for the unimolecular cleavage of the dianion alone.

The plots of k_{obs} against $[OH^-]$ for cleavage of $A(OH)_2$ in 1:1 and 3:1 v/v Me_2SO–H_2O are shown in Figures 1 and 2, and in our view their shapes must mean that the dianionic species undergoes spontaneous cleavage at a substantial rate. This conclusion remains valid irrespective of the limitations of the rough quantitative analysis which follows.

Rough values of K_1 (based largely on measurements of the dissociation constant for $PhCH_2SiMe_2OH$ in the two media) of 400 and 6000 dm^3 mol$-^1$ can be estimated for $A(OH)_2$ in 1:1 and 3:1 Me_2SO–H_2O respectively. The values of K_2 are then assumed to be smaller by a factor of 10^2, the ratio between the first and second ionization constants of $Si(OH)_4$.[4] A computer analysis then gives values of $k_{A(O^-)_2}$ and B which produce the best fit to the plots of k_{obs} against $[OH^-]$, and in Figures 1 and 2 the lines shown are those based on equation (2) with values of $10^4 k_{A(O^-)_2}$ of 2.7 and 30 s^{-1} in 1:1 and 3:1 Me_2SO–H_2O and corresponding values of $10^5 B$ of 4.5 and 14 mol dm^{-3} s^{-1}.

We suggest that the results provide convincing evidence for the operation of the process depicted as reaction (iii). The postulated unsaturated intermediate $Me(O^-)Si{=}O$ [a derivative of the hypothetical metasilicous acid $H(OH)Si{=}O$] is an analogue of acetate ion, and should be stabilized in the same way as the latter (though to a smaller extent) by delocalization of the negative charge over both oxygen atoms.

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