Polymerisation of the Silicate Anion in Acidic Solutions: Silicon-29 N.M.R. Studies

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Summary Silicon-29 n.m.r. spectra show that the rate of polymerisation of silicic acid produced from the hydrolysis of tetramethoxysilane is remarkably slow in the pH range 3·5—4·0 at −10 °C.

With the advent of high-resolution pulsed ^{29}Si n.m.r. spectroscopy renewed interest has been shown[1,2] in the study of aqueous silicate solutions. Using this technique we have successfully followed the condensation (polymerization) consequent upon hydrolysis of Si(OMe)$_4$. Previous workers have shown,[3] using the molybdate method, depression of freezing point, and turbidity measurements,[4–7] that the rate of condensation of monosilicic acid is markedly dependent upon the pH,[6] temperature,[3,7] and concentration[5] of the solution. Indeed, it is generally agreed[3,5] that the condensation of silicic acid is slowest in the pH range 1—3 (although considerable confusion exists in the literature).[4,8] Methanol is, however, also known to affect the rate of polymerization.[3,6,7,9] This fact, which is of potential importance in detergent chemistry[10] and in biochemistry,[11] needs to be quantified, a task for which silicon-29 n.m.r. spectroscopy seems well suited. Consequently, we have studied a series of 1·5 M Si(OMe)$_4$ solutions, at *ca.* −10 °C, using HCl or KOH to adjust the pH. The solutions, after complete hydrolysis, are consequently 6 M in MeOH. The tetramethyoxysilane was hydrolysed in this way for solutions with calculated pH values (ignoring the silicic acid) of 1—9. Under these conditions the solutions appear to be buffered. In aqueous solutions silicic acid has[10] a pK of 9·46 and hence a 1·5 M system would have a pH of 4·6. In fact, the pH (as measured with a combined glass and saturated KCl/calomel electrode) is similar to the 'calculated' value up to pH *ca.* 4, but then it remains roughly constant. For 'calculated' pH values higher than 9, hydrolysis appears to be no longer possible. In the discussion below, the term pH is used to mean the calculated quantity. The ^{29}Si n.m.r. measurements have enabled the following observations to be made. (a) The rate of condensation decreases on increasing the pH. The stability of solutions of pH 3·5—4·0 is such that monosilicic acid may be detected after several weeks. Work by Engelhardt *et al.*[1] used only pH values of 2·0 and below. (b) The hydrolysis of Si(OMe)$_4$ is fast (order of minutes) compared with the condensation reactions (order of days), so that only the latter process can be followed by ^{29}Si n.m.r. spectroscopy.

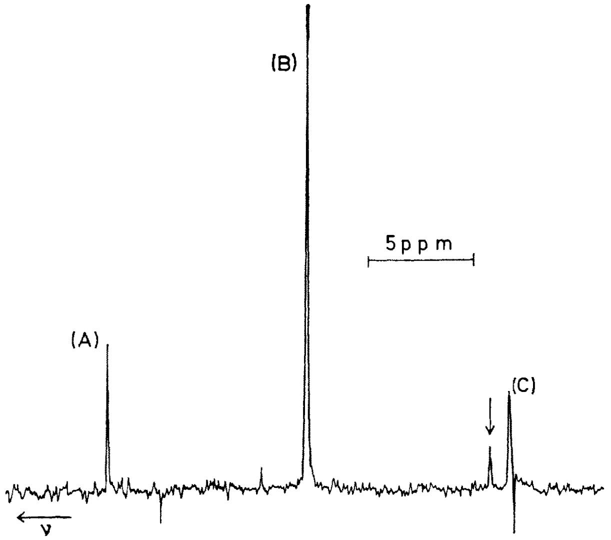

Figure. 19·87 MHz ^{29}Si n.m.r. spectrum of a methanolic aqueous silicate solution (see the text) at pH 3·5 and −10 °C, 52·5 h after hydrolysis. A Varian XL-100 spectrometer was used with spectral width 1 kHz, acquisition time 2 s, pulse angle *ca.* 55° and accumulation of 1889 transients. Peaks (B) and (C) lie at −9·3 and −18·7 p.p.m., respectively, with respect to peak (A).

The Figure shows a typical ^{29}Si n.m.r. spectrum of a solution at pH = 3·5, 52·5 h after hydrolysis. Peak (A) may be unambiguously assigned to monosilicic acid. In agreement with Engelhardt *et al.*,[1,12] we attribute peak (B) to both the disilicic acid and to the end groups of the linear trisilicic acid. Peak (C) arises from the centre unit of the latter species. The peak marked with an arrow is believed, from trimethylsilylation studies,[13] to be due to cyclotetrasilicic acid. For this solution, the rate constant, *k*, for the dimerisation was found, from the initial decay of the monomer concentration, to be *ca.* 1×10^{-5} mol^{-1} dm^{3} s^{-1}.

The remarkable persistence of low molecular weight oligomers in methanolic solutions of pH 3·5—4·0 contrasts with the traditional view[8] that silicate polymerisation in aqueous solutions is slowest in the pH range 1—3. New gelation and trimethylsilylation studies[14] have also thrown light on the behaviour of the methanolic solutions.

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