

# A Kinetic Study of Tetraethoxysilane in an Alkaline Medium in Methanol Solution

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The kinetics of tetraethoxysilane,  $\text{Si}(\text{OEt})_4$ , in alkaline methanol solution have been studied by FTIR spectroscopy. Initially the reaction proceeds as:  
 $\text{MeOH} + \text{OH}^- \rightleftharpoons \text{MeO}^- + \text{H}_2\text{O}$ ,  $\text{Si}(\text{OEt})_4 + \text{MeO}^- \rightarrow \text{Si}(\text{OEt})_3\text{OMe} + \text{EtO}^-$ ,  
 $\text{MeOH} + \text{EtO}^- \rightleftharpoons \text{MeO}^- + \text{EtOH}$ ,  $\text{EtO}^- + \text{H}_2\text{O} \rightleftharpoons \text{EtOH} + \text{OH}^-$ .

The rate constant for the initial reaction, being first order with respect to tetraethoxysilane and proportional to the concentration of base, has been established as  $0.33 \pm 0.01 [\text{base}] \text{ M}^{-1} \text{ s}^{-1}$ . When the reaction proceeds, condensation reactions complicate the picture, but on varying the concentration of tetraethoxysilane and the concentration of the NaOH, an empirical relation between the initial concentrations and the rate of the formation of ethanol could be established.

The relative rates of hydrolysis and condensation of tetraethoxysilane,  $\text{Si}(\text{OEt})_4$ , are strongly influenced by temperature, time and various parameters such as  $\text{H}_2\text{O}/\text{Si}(\text{OEt})_4$  ratio, catalytic action, molecular separation (concentration of reactants) and solvent. For the complete hydrolysis of  $\text{Si}(\text{OEt})_4$  in a dilute solution, a maximum of four water molecules are needed for each silicon atom, giving silicic acid,  $\text{Si}(\text{OH})_4$ , as a reaction product. The hydrolysis followed by a condensation to a linear polymer,  $(-\text{Si}(\text{OEt})_2(\text{OH})_2)_n$ , or a completely reacted  $\text{SiO}_2$  network, would consume two water molecules.<sup>1</sup> In real solutions, no well defined reactions like these are likely to dominate completely. To achieve silicic acid an infinite separation of  $\text{Si}(\text{OEt})_4$  molecules is required in order to avoid condensation. An infinite branched polymer requires an infinite polymerization without any terminal bonds. In reality, the condensation end-product can then be characterized as a finite branched polymer with terminal OR and OH groups. During the progress of the hydrolysis, the reacting species are likely to be very inhomogeneous, consisting of monomers, oligomers and of even more condensed products.

Experiments based on <sup>29</sup>Si-NMR and size-exclusion liquid chromatography, SEC,<sup>1</sup> have indicated a bimodal distribution of molecular weights after hydrolysis and condensation. One of the peaks corresponds to the reaction between low-polymer products with a slow increase of relative weight. The other peak originates from the combination reaction with a relatively large weight increase.

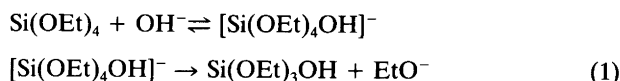
The hydrolysis of  $\text{Si}(\text{OEt})_4$  without any catalyst is a very slow process.<sup>2,3</sup> However, several compounds have catalytic activity. The most common are acids, bases and organometallic compounds. Among the organometallic cata-

lysts the tin carboxylates<sup>4</sup> are of special interest, because they are selective toward side reactions. The rate of the hydrolysis and condensation may be increased through refluxing<sup>5</sup>  $\text{H}_2\text{O}$  and  $\text{Si}(\text{OEt})_4$  at 40°C. If the temperature is increased, the diffusion also increases. This fact leads to a polymer (gel) with higher oxide content.<sup>6</sup> If the reaction time is extended and if there is an excess of  $\text{H}_2\text{O}$ , the OEt/OH ratio will diminish and the polymer may be regarded as an inorganic network of Si–O–Si bridges.

The concentrations of the reactants play an important role during the hydrolysis and condensation. With an increased molecular separation (decreased concentration of the reactants) diffusion-controlled polymerization will decrease. The hydrolysis reaction is therefore most favourable in very diluted solutions. This has also been observed.<sup>6</sup> In alcohols, the formation of alkoxide ions must be taken into account. Thus, in alkaline alcohol solutions, alkoxide ions will dominate over hydroxide ions at low water concentrations.

From a general point of view an increase of the  $\text{H}_2\text{O}/\text{Si}(\text{OEt})_4$  ratio, catalyst concentration, temperature and time lead to the formation of a high-polymer or a gel product.<sup>7–11</sup>

A nucleophilic substitution reaction mechanism has been proposed<sup>12,13</sup> for the alkaline hydrolysis of  $\text{Si}(\text{OEt})_4$ , according to reaction (1). This mechanism differs from the



acid catalytic reaction, which is proposed to have an electrophilic mechanism. A five-coordinated intermediate is formed during the reaction. The hydroxide ion attacks the  $\text{Si}(\text{OEt})_4$  molecule and the molecule inverts. The same mechanism should also be valid for other bases, e.g. alkox-

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ide ions. This is analogous to similar organic nucleophilic reactions. The rate of the reaction decreases with increasing size and decreasing basicity of the substituted groups. Hence the Si(OEt)<sub>4</sub> molecule hydrolyzes more slowly than the silanols, and this favours condensation to a high-polymer product. In the first stage of the reaction the formation of ethanol originates mainly from the hydrolysis of tetrathoxysilane and its hydrolysis products. In alkaline alcohol solutions with low water content the formation of ethanol originates from the reactions between alkoxide ions and tetraethoxysilane and its reaction products. A nucleophile mechanism has been proposed<sup>14</sup> for the condensation reaction (2). It has also been proposed<sup>15,16</sup> that the condensation reaction may produce ethanol by reaction (3).



**Experimental**

Using a methanol solution of Si(OEt)<sub>4</sub>, H<sub>2</sub>O and NaOH, the reaction rate can be followed through the formation of ethanol. The reaction was started by a rapid mixing of methanolic Si(OEt)<sub>4</sub> solution with methanolic water and NaOH solution. The mixture was immediately injected into an infrared liquid cell.

Si(OEt)<sub>4</sub> of FO Optipur quality from Merck, NaOH of pro analysi grade and Milli-Q water were used. The purity of Si(OEt)<sub>4</sub> was also tested with FTIR spectroscopy; it showed no signs of impurities and no further distillation was necessary. The concentrations of NaOH and Si(OEt)<sub>4</sub> were varied in the ranges 0.0235–0.0450 and 0.112–0.336 M, respectively. Methanol of *pro analysi* quality from Merck was used as a solvent in all experiments. The ethanol concentration was followed with a Perkin-Elmer 1800 Fourier-transform infrared spectrometer at 880 cm<sup>-1</sup> and integrated between 896 and 871 cm<sup>-1</sup>. In all experiments a variable-pathlength infrared cell was used with a pathlength fixed at 0.029 mm. The window material was BaF<sub>2</sub> with a useful infrared range of 5000–750 cm<sup>-1</sup>. The mixing

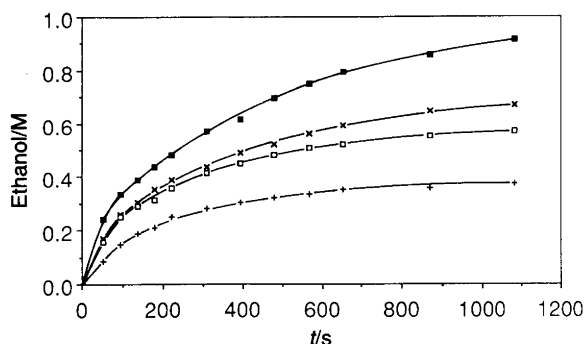


Fig. 1. Formation of ethanol as a function of time and [Si(OEt)<sub>4</sub>], with constant initial concentration of NaOH (0.0450 M). [Si(OEt)<sub>4</sub>] = ■, 0.3360; ×, 0.2240; □, 0.1792 and +, 0.1120 M.

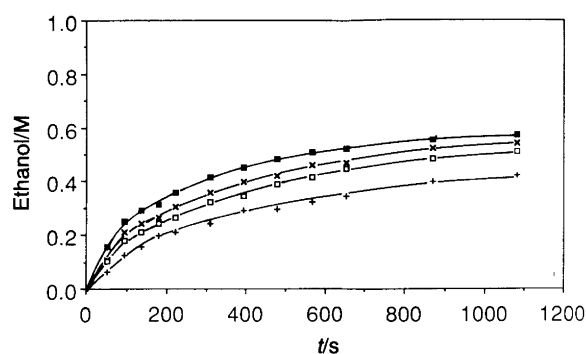


Fig. 2. Formation of ethanol as a function of time and [base], with constant initial concentration of Si(OEt)<sub>4</sub> (0.1792 M). [NaOH] = ■, 0.0450; ×, 0.0360; □, 0.0315 and +, 0.0235 M.

time before the first FTIR measurement was started was 29 s. The infrared spectra were saved on disc at an interval of Δt = 43 s. The spectra were taken with 2 cm<sup>-1</sup> resolution and at T = 293 K.

**Results and discussion**

Experimental difficulties existed in the form of bubble formation, and flocculation if the concentration of the reactants was too high. After a number of initial experiments the reactions were followed by eight successful spectra,

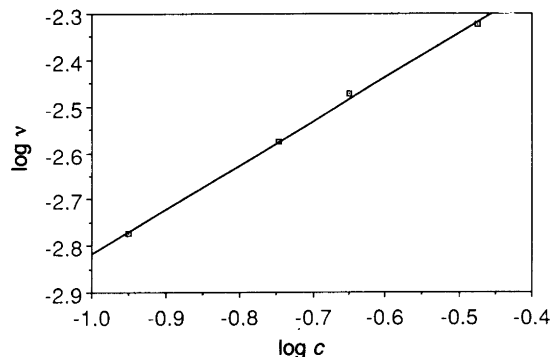


Fig. 3. Plot of the logarithm of the initial concentration of Si(OEt)<sub>4</sub> against the logarithm of the reaction rate. n = 0.95.

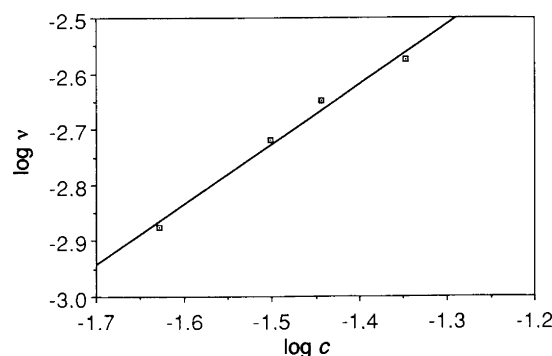
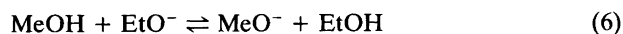
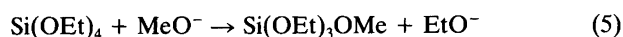
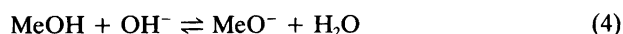


Fig. 4. Plot of the logarithm of the initial concentration of base against the logarithm of the reaction rate. n = 1.07.

each during 20 min. The formation of ethanol as a function of time and different concentrations of  $\text{Si}(\text{OEt})_4$  and  $\text{NaOH}$  is shown in Figs. 1 and 2, respectively. Since the reaction becomes very complicated after some time, the data have to be interpreted in two steps. First, we consider the  $\text{p}K_a$  values of methanol and ethanol (15.5 and 16.0, respectively) and the equilibrium constant for water,  $K_{\text{eq}} = 10^{-14}/55.5$ . From this, approximate values of the equilibrium constant for reactions (4), (6) and (7) can be calculated to be 1.8, 3.2 and 1.8, respectively. Initially, this means that  $\sim 98\%$  of the hydroxide ions have been converted into methoxide ions. Assuming fast equilibria, the rate-determining step will thus be reaction (5).



The initial rate of ethanol formation was estimated from the tangential slope at  $t = 0$  s, which in practice was approximated as the ethanol concentration obtained at the first FTIR measurement assuming a nearly linear increase of the formation of ethanol during the first 51 s.

Plots of the logarithm of the initial concentrations of  $\text{Si}(\text{OEt})_4$  and base versus the logarithm of the initial rates of the reaction give straight lines with slopes 0.95 and 1.07, respectively (Figs. 3 and 4). From this, the initial reaction was determined to be of first order with respect to  $\text{Si}(\text{OEt})_4$  and proportional to the concentration of base according to the rate expression (8).

$$\frac{-d[\text{Si}(\text{OEt})_4]}{dt} = \frac{d[\text{EtOH}]}{dt} = k_1[\text{Si}(\text{OEt})_4] \quad (8)$$

The initial rates for different concentrations of  $\text{Si}(\text{OEt})_4$  and  $\text{NaOH}$  are shown in Table 1, and the rate constant for the initial reaction has been established as  $0.33 \pm 0.01$  [base]  $\text{M}^{-1} \text{s}^{-1}$  from the eight different experiments.

Table 1. Initial hydrolysis of  $\text{Si}(\text{OEt})_4$  following the rate expression;  $v = k_1[\text{Si}(\text{OEt})_4]$ .

$\text{Si}(\text{OEt})_4/\text{M}$	$\text{NaOH}/\text{M}$	$\text{H}_2\text{O}/\text{M}$	Initial rate/ $10^{-3} \text{ M s}^{-1}$	$k_1/[\text{base}] \text{ M}^{-1} \text{ s}^{-1}$
0.1792	0.0450	1.11	2.656	0.329
0.1792	0.0360	1.11	2.242	0.347
0.1792	0.0315	1.11	1.910	0.338
0.1792	0.0235	1.11	1.329	0.316
0.3360	0.0450	1.11	4.754	0.330
0.2240	0.0450	1.11	3.367	0.334
0.1120	0.0450	1.11	1.684	0.334
0.1792	0.0450	2.22	2.657	0.330

In the second stage of the reaction the picture is much more complicated. Now, the hydroxide ions may react with the alkoxy silanes. The indication of flocculation during late stages of the experiments supports the assumption that hydroxide ions start the hydrolysis and condensation process. The number of OEt groups remaining on each silicon atom declines faster with increasing concentration of  $\text{NaOH}$  and for constant initial concentration of  $\text{Si}(\text{OEt})_4$ . The opposite has been observed to occur with increasing concentration of  $\text{Si}(\text{OEt})_4$  and with constant initial concentration of  $\text{NaOH}$ .

No real mechanistical interpretation of this stage of the reaction could be made owing to the complex nature of the system, but the reactions seemed to follow an empirical second-order expression [eqn. (9)] with respect to the conversion of OEt groups (substituted on the silicon atoms) into ethanol.

$$\frac{d[\text{EtOH}]}{dt} = \frac{-d[-\text{OEt}]}{dt} = \lambda[-\text{OEt}]^2 \quad (9)$$

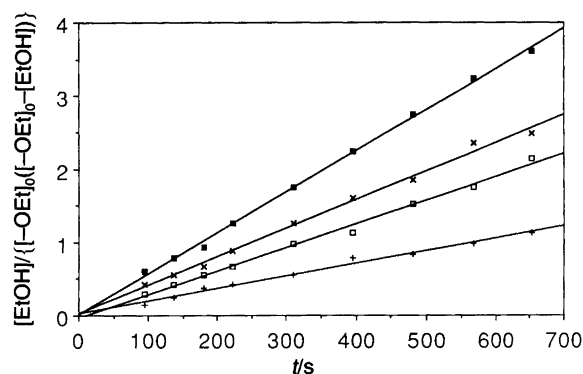


Fig. 5. The liberation of OEt groups substituted on the silicon plotted as a second-order reaction, starting with constant initial concentration of  $\text{Si}(\text{OEt})_4$  (0.1792 M). ■, 0.0450 M  $\text{NaOH}$ ,  $C = 0.0055$ ; ×, 0.0360 M  $\text{NaOH}$ ,  $C = 0.0037$ ; □, 0.0315 M  $\text{NaOH}$ ,  $C = 0.0027$ ; +, 0.0235 M  $\text{NaOH}$ ,  $C = 0.0016$ .

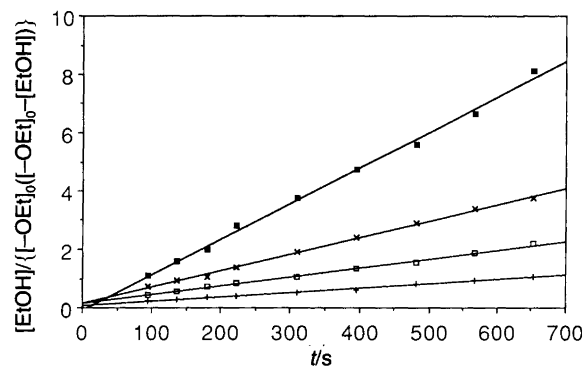


Fig. 6. The liberation of OEt groups substituted on the silicon plotted as a second-order reaction, starting with constant initial concentration of  $\text{NaOH}$  (0.0450 M). ■, 0.1120 M  $\text{Si}(\text{OEt})_4$ ,  $C = 0.0124$ ; ×, 0.1792 M  $\text{Si}(\text{OEt})_4$ ,  $C = 0.0055$ ; □, 0.2240 M  $\text{Si}(\text{OEt})_4$ ,  $C = 0.0031$ ; +, 0.3360 M  $\text{Si}(\text{OEt})_4$ ,  $C = 0.0015$ .

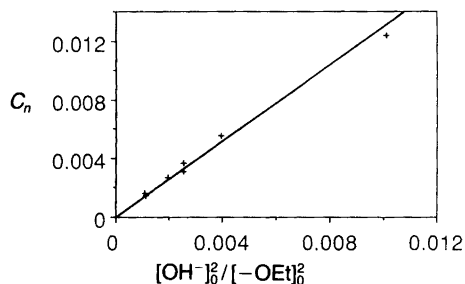


Fig. 7. Plot of  $[\text{OH}^-]_0^2 / [-\text{OEt}]_0^2$  against the slopes from Figs. 5 and 6, giving the  $\lambda$ -value of expression (9), i.e. 1.20.

The integrated form of expression (9) is shown in Figs. 5 and 6, together with the individual slope,  $C_n$ , of each curve. If  $C_n$  is set equal to  $([\text{OH}^-]_0^2 / [-\text{OEt}]_0^2)$ , it gives a constant value, which is evident from Fig. 7.

The concentration of  $\text{H}_2\text{O}$  has a minor effect, if any, under the investigated conditions (i.e. a system with relatively low  $\text{H}_2\text{O}$  content). In an experiment with initial concentrations of 0.0450 M NaOH, 0.1792 M  $\text{Si}(\text{OEt})_4$  and 2.22 M  $\text{H}_2\text{O}$  no change in reaction rate was observed compared to 1.11 M  $\text{H}_2\text{O}$  (Table 1), but a strong influence may be expected if there is an excess of  $\text{H}_2\text{O}$ , i.e. in a system with an excess of hydroxide ions or comparable concentrations of hydroxide and methoxide ions.

## References

1. Yoldas, B. E. *J. Non-Cryst. Solids* 82 (1986) 11.
2. Schmidt, H. and Kaiser, A. *Glastechn. Ber.* 54 (1981) 338.
3. Schmidt, H., Scholze, H. and Kaiser, A. *J. Non-Cryst. Solids* 48 (1982) 65.
4. van der Weij, F. W. *Makromol. Chem.* 181 (1980) 2541.
5. Emblem, H. G. and Walters, I. R. *J. Appl. Chem. Biotechnol.* 27 (1977) 618.
6. Yoldas, B. E. *J. Non-Cryst. Solids* 63 (1984) 145.
7. Schmidt, H., Scholze, H. and Kaiser, A. *J. Non-Cryst. Solids* 63 (1984) 1.
8. Brinker, C. J. and Scherer, G. W. *J. Non-Cryst. Solids* 70 (1985) 301.
9. Kelts, L. W., Effinger, N. J. and Melpolder, S. M. *J. Non-Cryst. Solids* 83 (1986) 353.
10. Biddle, K. D., Das, A. K., Jones, K. and Emblem, H. G. *J. Appl. Chem. Biotechnol.* 27 (1977) 565.
11. Emblem, H. G. *Trans. J. Brit. Ceram. Soc.* 74 (1975) 223.
12. Keefer, K. D. *Mater. Res. Soc. Symp. Proc.* 32 (1984) 15.
13. Aelion, R., Loebel, A. and Eirich, F. *J. Am. Chem. Soc.* 72 (1950) 5705.
14. Iler, R. K. *The Chemistry of Silica*, Wiley, New York 1979.
15. Brinker, C. J., Keefer, K. D., Schaefer, D. W., Assink, R. A., Kay, B. D. and Ashley, C. S. *J. Non-Cryst. Solids* 63 (1984) 45.
16. Yoldas, B. E. *J. Non-Cryst. Solids* 63 (1984) 145.

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