Reaction Rates of Trimethylethoxysilane and Trimethylmethoxysilane in Alkaline Alcohol Solutions

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The kinetics of the reaction \((\text{CH}_3)_2\text{SiOC}H_5 + \text{OH}^- \rightleftharpoons (\text{CH}_3)_3\text{SiOCH}_3 + \text{C}_2\text{H}_5\text{O}^-\) have been investigated in both directions by means of FTIR spectroscopy. To obtain \(k_f\), trimethylethoxysilane was reacted with methoxide in a methanol solution, while \(k_r\) was determined from the reaction of trimethylmethoxysilane with ethoxide in an ethanol solution.

The rate constants at \(T = 295 \text{ K}\) for the forward and the reverse reaction have been established as \(k_f = 2.70 \pm 0.08 \text{ M}^{-1} \text{s}^{-1}\) and \(k_r = 3.0 \pm 0.2 \text{ M}^{-1} \text{s}^{-1}\), respectively, giving an equilibrium constant of \(0.90 \pm 0.05\).

The activation energies were found to be 14.8 ± 0.1 kJ mol\(^{-1}\) for the forward reaction and 11.7 ± 0.2 kJ mol\(^{-1}\) for the reverse reaction, corresponding to the temperature–rate expressions, \(k_f = 1.11 \times 10^6 \exp (-1781/T) \text{ M}^{-1} \text{s}^{-1}\) and \(k_r = 0.34 \times 10^6 \exp (-1404/T) \text{ M}^{-1} \text{s}^{-1}\).

The equilibrium constant for the net alcoholysis reaction \((\text{CH}_3)_2\text{SiOC}H_5 + \text{CH}_2\text{OH} = (\text{CH}_3)_3\text{SiOCH}_3 + \text{C}_2\text{H}_5\text{OH}\) has been determined as 1.19 ± 0.04 at \(T = 295 \text{ K}\).

Several techniques have been applied in order to study the reactivity of alkoxysilanes. One of the earliest methods is the titration with a Karl Fischer reagent of silanol groups formed during hydrolysis. Reaction mechanisms have also been proposed from these early experiments.

Later, techniques like \(^{29}\text{Si}-\text{NMR}\), gas chromatography and FTIR spectroscopy have been used. \(^{29}\text{Si}-\text{NMR}\) is a powerful tool in the interpretation of reaction products of alkoxysilanes. Studies of alkoxysilanes have also been performed by gas chromatography and FTIR spectroscopy, with its relatively fast scanning speed, has shown to be suitable for kinetic studies. UV spectroscopy has also proved to be useful, e.g. in the investigations of phenoxysilanes.

For many reasons tetrathoxysilane has become one of the most studied alkoxysilanes. Its capability to polymerize and form a more or less complete network of Si–O–Si bridges makes it very useful in many applications, e.g. stone preservation and conservation, as binders in refractory technology and in sol–gel processing. Large efforts have therefore been made to investigate the influence of various parameters such as the silane/water ratio, temperature, catalytic activities and solvent effects on the reaction rates.

The polymerization of tetrathoxysilane is a very complicated process. To understand the fundamental reactions of alkoxysilanes in detail, it is of importance to have a basic knowledge of more simplified systems.

Thus, alkoxysilanes with only one alkoxy group are suitable for study, since only monomers and/or dimers may be present among the products after different times of reaction.

Experimental

Trimethylethoxysilane, trimethylmethoxysilane, anhydrous (< 0.01 % water) methanol, sodium hydroxide standard solution (all of proanalysis grade), ethanol and Milli-Q water were used in the experiments. The alkoxide solutions were prepared from the reaction of alcohol and freshly cut sodium. The alkoxide and hydroxide solutions were titrated against potassium hydrogen phthalate.

The purity of the silanes was tested by FTIR spectroscopy. No signs of impurities were detected and no further distillation was considered necessary.

The measurements were made with a Perkin–Elmer 1800 Fourier-transform infrared spectrometer, purged with dry air and equipped with a TGS detector. An infrared liquid cell with BaF\(_2\) windows (range 5000–750 cm\(^{-1}\)) and variable pathlength was connected to an electrical temperature jacket. The temperature was measured with a Pt-100 probe, calibrated in the interval \(T = 293–323 \text{ K}\) within an accuracy of 0.1 %. The pathlength was adjusted to 0.015 mm ± 0.2 %. This pathlength made it possible to use alcohols as solvents.

The concentration of trimethylethoxysilane was followed at 938 cm\(^{-1}\) and integrated between 951 and 931 cm\(^{-1}\), and the concentration of trimethylmethoxysilane was followed at 1189 cm\(^{-1}\) and integrated between 1200 and 1179 cm\(^{-1}\). These two peaks are characteristic and originate from the alkoxy group substituted on the silicon atom.
The scan speed was set to 4 s with a nominal resolution of 4 cm\(^{-1}\). The mixing time before the first FTIR measurement started was 70–90 s. In the kinetic studies the spectra were saved on disc at an interval of \(\Delta t = 20\) s.

**Results and discussion**

The reaction of alkoxy silanes in alkaline solutions is proposed to have a nucleophilic substitution mechanism.\(^{18}\)

The reaction of trimethylethoxysilane and methoxide in methanol solution is then assumed to be given by reactions (1) and (2).

\[
(\text{CH}_3\text{SiOC}_2\text{H}_5 + \text{CH}_3\text{O}^- \rightleftharpoons (\text{CH}_3)\text{SiOCH}_3 + \text{C}_2\text{H}_5\text{O}^-) \quad (1)
\]

\[
\text{C}_2\text{H}_5\text{O}^- + \text{CH}_3\text{OH} \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{O}^- \quad (2)
\]

The rate expression for reaction (1) can be written as eqn. (3).

\[
\frac{-d[(\text{CH}_3)\text{SiOC}_2\text{H}_5]}{dt} = k_1 [(\text{CH}_3)\text{SiOC}_2\text{H}_5][\text{CH}_3\text{O}^-] - k_{-1} [(\text{CH}_3)\text{SiOCH}_3][\text{C}_2\text{H}_5\text{O}^-] \quad (3)
\]

Starting with trimethylethoxysilane and methoxide ions (low concentration) in methanol solution, the chemical equilibrium in reaction (2) lies far to the right, since there is a large excess of methanol. Assuming that reaction (2) is reaching equilibrium fast, the concentration of methoxide ions must be nearly constant. The reverse of reactions (1) and (2) can then be neglected. Thus, the rate expression (3) can be reduced to eqn. (4). The forward reaction (1) can then be evaluated as a first-order reaction with respect to the disappearance of trimethylethoxysilane and proportional to the concentration of methoxide ions according to the integrated rate expression (5).

\[
\ln \left( \frac{[(\text{CH}_3)\text{SiOC}_2\text{H}_5]}{[(\text{CH}_3)\text{SiOC}_2\text{H}_5]_0} \right) = \text{CH}_3\text{O}^- \cdot k_1 t \quad (5)
\]

In Fig. 1 the reaction of trimethylethoxysilane is plotted as a first-order reaction with respect to trimethylethoxysilane and with different initial concentrations of methoxide ions. The individual slope of each curve is defined as \(k'_1 = k_1[\text{CH}_3\text{O}^-]\). The rate constant for the forward reaction (1) is evaluated in Table 1 for different concentrations, giving an average value of \(k_1 = 2.70 \pm 0.08\) M\(^{-1}\) s\(^{-1}\) at \(T = 295\) K.

The temperature dependence of the rate constant from the Arrhenius relation is shown in Fig. 2. The rate constant follows the temperature relation, \(k_1 = 1.11 \times 10^{10} \exp \left(\frac{-1781}{T}\right)\) M\(^{-1}\) s\(^{-1}\). The corresponding activation energy is 14.8 ± 0.1 kJ mol\(^{-1}\) and the enthalpy of activation has been estimated as \(\Delta H_{295} = 12.3 \pm 0.1\) kJ mol\(^{-1}\).

The reverse of reaction (1), starting with trimethylmeth-
oxysilane and ethoxide in ethanol solution, was studied in a similar manner as for the forward reaction, resulting in the rate expression (6).

\[
\frac{-d[\text{SiOCH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}]}{dt} = k_1[\text{SiOCH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}][\text{C}_2\text{H}_5\text{O}^-]
\]  

(6)

In Fig. 3 the reaction of trimethylmethoxysilane is plotted as a first-order reaction with respect to trimethylmethoxysilane and with different initial concentrations of ethoxide ions. The rate constant was established as \(k_1 = 3.0 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}\) at \(T = 295 \text{ K}\) (cf. Table 2). The temperature dependence of the rate constant is shown in Fig. 4. It follows the relation \(k_1 = 0.34 \times 10^9 \exp\left(-1404/T\right) \text{ M}^{-1} \text{ s}^{-1}\).

The activation energy was determined as \(11.7 \pm 0.2 \text{ kJ mol}^{-1}\) and the activation enthalpy was estimated as \(\Delta H_{295} = 9.2 \pm 0.2 \text{ kJ mol}^{-1}\).

From the rate constants of the forward and reverse reaction the equilibrium constant for reaction (1) could be estimated as \(0.90 \pm 0.05 \text{ at } T = 295 \text{ K}\).

The proposed nucleophilic attack will be sensitive to steric effects of the substituents and the electron density around the silicon atom. The more bulky and highly basic alkoxy group surrounding the silicon, the less subject it is to attack by, e.g., the alkoxy ion. Thus, the methoxide ion should react faster with trimethylethoxysilane than with tetraethoxysilane. This is also the case, and the initial rate constant for the reaction of tetraethoxysilane and methoxide has been determined as \(0.33 \pm 0.01 \text{ M}^{-1} \text{ s}^{-1}\) compared to \(2.70 \pm 0.08 \text{ M}^{-1} \text{ s}^{-1}\) for trimethylethoxysilane, determined in this study.

The equilibrium constant for the net alcoholysis reaction (7), given by eqn. (8), was also investigated (Table 3).

\[
\text{(CH}_3\text{)}_3\text{SiOC}_2\text{H}_5 + \text{CH}_3\text{OH} = (\text{CH}_3\text{)}_3\text{SiOCH}_3\text{CH}_2\text{OH}
\]

(7)

\[
K_1 = \frac{[\text{(CH}_3\text{)}_3\text{SiOC}_2\text{H}_5][\text{C}_2\text{H}_5\text{OH}]}{[\text{(CH}_3\text{)}_3\text{SiOCH}_3\text{CH}_2\text{OH}]}
\]

(8)

This equilibrium constant can be directly derived from the equilibrium constants of reactions (1) and (2), eqns. (9) and (10), with \(K_1 = K_2 K_3\). The equilibrium constant \(K_2\) was determined as \(0.90 \pm 0.05 \text{ in this study, and a rough estimation of } K_3\text{ can be made using the dissociation constants for reactions (11) and (12). If the equilibrium constant } K_1\text{ is evaluated from the dissociation constants of methanol and ethanol determined in the same medium, the solvation of methoxide and ethoxide ions can then be assumed to be of the same magnitude. Hence the value of } K_1\text{ should then only differ slightly in different media.}

Table 2. Rate constant and concentration data for the reaction of trimethylmethoxysilane and ethoxide ions.

<table>
<thead>
<tr>
<th>[\text{(CH}_3\text{)}_3\text{SiOCH}_3\text{CH}_2\text{OH}]</th>
<th>[\text{CH}_3\text{H}_2\text{O}^-]/\text{mM}</th>
<th>k_1/\text{M}^{-1} \text{ s}^{-1}</th>
</tr>
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<tr>
<td>0.725</td>
<td>1.750</td>
<td>2.80</td>
</tr>
<tr>
<td>0.518</td>
<td>1.750</td>
<td>3.20</td>
</tr>
<tr>
<td>0.906</td>
<td>1.361</td>
<td>3.00</td>
</tr>
<tr>
<td>0.725</td>
<td>1.361</td>
<td>3.00</td>
</tr>
<tr>
<td>0.725</td>
<td>1.114</td>
<td>3.14</td>
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Table 3. Initial concentration data and the alcoholysis equilibrium constant of \((\text{CH}_3)_2\text{SiOCH}_3 + \text{CH}_3\text{OH} = (\text{CH}_3)_2\text{SiOCH}_3 + \text{C}_2\text{H}_5\text{OH}\).

<table>
<thead>
<tr>
<th>((\text{CH}_3)_2\text{SiOCH}_3)/M</th>
<th>([\text{CH}_3\text{OH}]/\text{M})</th>
<th>([\text{CH}_3\text{O}^-]/\text{mM})</th>
<th>((\text{CH}_3)_2\text{SiOCH}_3)/M</th>
<th>([\text{C}_2\text{H}_5\text{OH}]/\text{M})</th>
<th>([\text{C}_2\text{H}_5\text{O}^-]/\text{mM})</th>
<th>(K_i)</th>
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<tr>
<td>5.33</td>
<td>4.11</td>
<td>5.20</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.23</td>
</tr>
<tr>
<td>5.12</td>
<td>4.94</td>
<td>8.90</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.15</td>
</tr>
<tr>
<td>4.80</td>
<td>6.17</td>
<td>7.80</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.14</td>
</tr>
<tr>
<td>4.57</td>
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<td>5.44</td>
<td>4.28</td>
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<tr>
<td>–</td>
<td>–</td>
<td>–</td>
<td>5.18</td>
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<td>7.00</td>
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<td>–</td>
<td>–</td>
<td>4.83</td>
<td>5.71</td>
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</tr>
<tr>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4.35</td>
<td>6.85</td>
<td>9.80</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Table 4. Rate constant and concentration data for the reaction of trimethylthoxyxilane in low water content alkaline methanol solution.

<table>
<thead>
<tr>
<th>((\text{CH}_3)_2\text{SiOCH}_3)/M</th>
<th>([\text{H}_2\text{O}]/\text{M})</th>
<th>([\text{base}]/\text{mM})</th>
<th>([\text{CH}_3\text{OH}]/\text{M})</th>
<th>(k_f/\text{M}^{-1}\text{ s}^{-1})</th>
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<tr>
<td>0.873</td>
<td>2.523</td>
<td>1.590</td>
<td>20.249</td>
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<tr>
<td>0.800</td>
<td>2.523</td>
<td>1.590</td>
<td>20.530</td>
<td>2.55</td>
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<tr>
<td>0.640</td>
<td>2.523</td>
<td>1.590</td>
<td>21.149</td>
<td>2.55</td>
</tr>
<tr>
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<td>1.345</td>
<td>20.422</td>
<td>2.63</td>
</tr>
<tr>
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<td>2.135</td>
<td>1.345</td>
<td>20.703</td>
<td>2.52</td>
</tr>
<tr>
<td>0.640</td>
<td>2.135</td>
<td>1.345</td>
<td>21.322</td>
<td>2.63</td>
</tr>
<tr>
<td>0.873</td>
<td>1.633</td>
<td>1.029</td>
<td>20.646</td>
<td>2.61</td>
</tr>
<tr>
<td>0.800</td>
<td>1.633</td>
<td>1.029</td>
<td>20.927</td>
<td>2.59</td>
</tr>
<tr>
<td>0.640</td>
<td>1.633</td>
<td>1.029</td>
<td>21.546</td>
<td>2.65</td>
</tr>
</tbody>
</table>

\begin{align*}
\text{CH}_3\text{OH} & \rightleftharpoons \text{CH}_3\text{O}^- + \text{H}^+ \quad (11) \\
\text{C}_2\text{H}_5\text{OH} & \rightleftharpoons \text{C}_2\text{H}_5\text{O}^- + \text{H}^+ \quad (12)
\end{align*}

The \(pK_a\) values of methanol and ethanol, in alkaline water/alcohol solutions of low alcohol content, were previously\(^{20}\) determined to be 15.09 and 15.93, respectively, giving a value of \(K_1 = 6.9\). Using \(K_1\) and the estimate of \(K_i\), an approximate value of 6 is obtained for \(K_i\). The \(pK_a\) values of methanol and ethanol have also been determined\(^{21}\) to be 15.54 and 16, respectively. In this case a value of ca. 3 is obtained for \(K_i\).

It is obvious that the estimated values only give a crude indication of the equilibrium constant \(K_i\). The equilibrium for reaction (7) has therefore been experimentally investigated. The equilibrium constant at \(T = 295\) K was determined as \(K_1 = 1.19 \pm 0.04\) from both the forward and reverse direction (Table 3).

The alcoholysis equilibrium constant for the equilibrium of triethylethoxysilane and triethylmethoxysilane catalysed by iodine has previously\(^{22}\) been determined as \(1.08 \pm 0.02\). This equilibrium constant may be compared to the alcoholysis equilibrium constant for reaction (7), determined in this study. Though the alkyl groups are different, the equilibrium constants are of similar magnitude, i.e. near unity. It has also been observed\(^{22}\) that the equilibrium constants seem to be near unity when the alcohols have similar reactivity and the binding ability of the alkoxy groups is of the same order.

The results presented so far have only been concerned with the reactions of trimethylalkoxysilanes and alkoxide ions in pure alcohol solutions. If water is present in the system, the equilibrium between alkoxide and hydroxide ions must be considered.

The reaction of trimethylthoxyxilane in an alkaline solution of methanol and water (low concentration) was also investigated (Table 4). Sodium hydroxide was used as base, and under the experimental conditions applied in this study, approximately 95% of the hydroxide ions was initially converted to methoxide ions, according to reaction (13).

\[
\text{OH}^- + \text{CH}_3\text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{CH}_3\text{O}^-
\]

\[
K_i = K_f/1.8 \times 10^{-16}
\]

Assuming a fast equilibrium for reaction (13), the rate-determining step will thus be the forward reaction (1). In Table 4 the concentration of base is referred to as the total concentration of hydroxide and methoxide ions.

Using the same evaluation as before, the reaction is assumed to be a first-order reaction with respect to trimethylthoxyxilane and proportional to the concentration of base.

In Fig. 5 the reaction of trimethylthoxyxilane is plotted as a first-order reaction with respect to trimethylthoxyxilane and with different concentrations of base, and \(k_f = k_{f_1}/[\text{base}]\) has been determined from the individual slopes of each curve.
The rate constant for reaction (1) determined in this way was obtained as 2.60 \pm 0.06 \text{ M}^{-1} \text{s}^{-1} at T = 295 \text{ K}, which is in good agreement with the results from the anhydrous experiment ($k_1 = 2.70 \pm 0.08 \text{ M}^{-1} \text{s}^{-1}$, cf. above). This means that the assumption that 95% of the hydroxide ions have been converted into methoxide seems to be correct.

In this work, rate and equilibrium constants have been determined for trimethylalkoxysilanes in alkaline alcohol solutions. A general conclusion that can be drawn is that the ester exchange will be of major importance in, e.g., sol-gel processing if the concentration of water is low, owing to the equilibrium between hydroxide and alkoxide ions.

References


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