Short Communication

Equilibrium Constants for the Alkoxy Exchange Reactions of Ethoxy- and Methoxy-Substituted Alkoxymethylsilanes and Tetraalkoxysilanes in Mixed Alkaline Ethanol and Methanol Solutions

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Alkoxysilanes are widely used as precursor molecules in polymerization processes where inorganic Si–O–Si bridges are sought.[1,2] The siloxane bonds are formed upon the hydrolysis of the alkoxy substituents followed by polymerization of the produced silanols. In alcohol solution the silicon-bonded alkoxy groups may be readily exchanged, a reaction that can compete with the hydrolysis and polymerization reactions.[3–5] The alkoxy exchange reactions are particularly important in alkoxysilane-containing coating solutions where mixtures of different alcohols are used to achieve suitable rheological properties of the applied solution.[6] The transesterification under anhydrous conditions has a direct commercial value, since alkoxysilanes with mixed alkoxy substituents are extensively prepared this way.[7,8]
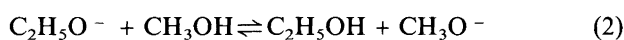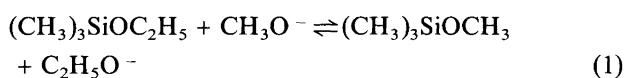
The objective of this study was to investigate the transesterification equilibria of mono-, di-, tri- and tetraalkoxysilanes in mixed alcohol solution. The equilibria were studied in alkaline ethanol–methanol solutions under anhydrous conditions to avoid hydrolysis and polymerization reactions, using ^{29}Si NMR spectroscopy, since this technique has previously proved to be powerful in the interpretation of mixtures of alkoxysilanes.[9]

A total of ten equilibrium constants were determined in this study. The equilibrium constants are given subscripts that give both the total number of consecutive reactions and the specific reaction step. For example, the reaction $CH_3Si(OC_2H_5)_3 + CH_3OH = CH_3Si(OC_2H_5)_2(OCH_3) + C_2H_5OH$, which is the first consecutive step out of three, is assigned K_{31}. The examined transesterification reactions are presented in Table 1. The equilibrium con-

stant K_{11} was established by allowing the reaction mixture to approach equilibrium from both the forward and the reverse directions. The established value for K_{11} in this study is in agreement with the previously reported value of 1.37 ± 0.31, determined with FTIR spectroscopy.[10] The equilibrium constants K_{21}–K_{44} were established after approaching equilibrium from the forward reactions starting with the corresponding ethoxysilanes.

A nucleophilic substitution mechanism, where the reaction intermediate is pentacoordinated, is generally accepted for the alkaline hydrolysis of alkoxysilanes.[11,12] The same mechanism is also assumed for the transesterification reactions between alkoxysilanes and alkoxide ions.[10] Strong evidence for the possibility of five coordination in the alkoxy exchange is provided by the formation of pentacoordinated anionic silicates from reactions of alkoxysilanes and alkoxide ions in presence of 18-crown-6.[13]

The proposed nucleophilic mechanism implies that the reaction corresponding to e.g. K_{11} is the sum of the reactions

$$(CH_3)_3SiOC_2H_5 + CH_3O^- \rightleftharpoons (CH_3)_3SiOCH_3 + C_2H_5O^- \quad (1)$$

$$C_2H_5O^- + CH_3OH \rightleftharpoons C_2H_5OH + CH_3O^- \quad (2)$$

The reactions that correspond to the equilibrium constants K_{21}–K_{44} may in the same way be considered as net reactions.

To determine the effect of the alkoxide ions on the distribution reactions, the equilibrium constant for reaction (2) must be known. The equilibrium constant can be es-

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Table 1. Consecutive equilibrium constants for mono-, di-, tri- and tetraalkoxysilanes in alkaline ethanol–methanol solution at 295 K.

Net reaction	Equilibrium constant	Reduced equilibrium constant[a]
$(CH_3)_3SiOC_2H_5 + CH_3OH = (CH_3)_3SiOCH_3 + C_2H_5OH$	$K_{11} = 1.38 \pm 0.04,^b$ 1.42 ± 0.11^c	$K_{11}/1 = 1.38 \pm 0.04^b$
$(CH_3)_2Si(OC_2H_5)_2 + 2\ CH_3OH = (CH_3)_2Si(OCH_3)_2 + 2\ C_2H_5OH$	$K_{21} = 2.47 \pm 0.02,$ 2.66 ± 0.29 $K_{22} = 0.60 \pm 0.01,$ 0.59 ± 0.03	$K_{21}/2 = 1.24 \pm 0.01$ $K_{22}/1/2 = 1.20 \pm 0.02$
$CH_3Si(OC_2H_5)_3 + 3\ CH_3OH = CH_3Si(OCH_3)_3 + 3\ C_2H_5OH$	$K_{31} = 3.49 \pm 0.18,$ 3.67 ± 0.53 $K_{32} = 1.14 \pm 0.03,$ 1.12 ± 0.02 $K_{33} = 0.36 \pm 0.01,$ 0.36 ± 0.02	$K_{31}/3 = 1.16 \pm 0.06$ $K_{32}/1 = 1.14 \pm 0.03$ $K_{33}/1/3 = 1.08 \pm 0.03$
$Si(OC_2H_5)_4 + 4\ CH_3OH = Si(OCH_3)_4 + 4\ C_2H_5OH$	$K_{41} = 3.56 \pm 0.28,$ 3.90 ± 1.15 $K_{42} = 1.48 \pm 0.09,$ 1.53 ± 0.13 $K_{43} = 0.64 \pm 0.04,$ 0.56 ± 0.09 $K_{44} = 0.23 \pm 0.02,$ 0.21 ± 0.05	$K_{41}/4 = 0.89 \pm 0.07$ $K_{42}/3/2 = 0.99 \pm 0.06$ $K_{43}/2/3 = 0.96 \pm 0.06$ $K_{44}/1/4 = 0.92 + 0.08$

[a] Reduced equilibrium constants are defined as equilibrium constant / statistical ratio, see text. [b] Constants in this column are evaluated from the intensities. [c] Constants in this column are evaluated from the integrals.

timated from the relation $K_2 = K_{11}k_{-1}/k_1$. The rate constants k_1 and k_{-1} for reaction (1) have been determined to be $2.70 \pm 0.07\ M^{-1}\ s^{-1}$ and $3.0 \pm 0.2\ M^{-1}\ s^{-1}$, respectively,[14] and the equilibrium constant K_2 can thus be estimated to be 1.53 ± 0.12. Although K_2 can be established from e.g. the pK_a values of ethanol and methanol ($K_2 = 2.9$ and 6.9, calculated from Refs. 15 and 16, respectively), it is thought that the estimation of K_2 from the rate constants made above is the most appropriate to use in the further discussion of the transesterification reactions, since it is derived from a system consisting of the components alkoxysilane/alcohol/alkoxide ions.

The nucleophilic attack of a methoxide ion on $(CH_3)_2Si(OC_2H_5)_2$, leading to an alkoxy exchange, is favoured over the attack of an ethoxide ion on $(CH_3)_2Si(OC_2H_5)(OCH_3)$ by a factor of two. Such statistical considerations apply to all equilibria. The analysis of consecutive equilibrium constants therefore requires that they be corrected according to the reaction statistics displayed in the last column of Table 1. For example, the equilibrium constants K_{41}–K_{44} should be divided by 4: 3/2: 2/3: 1/4.

If there is a purely statistical distribution of alkoxysilanes, the equilibrium constants divided by the statistical ratios should equal K_2, here estimated to be 1.53 (cf. above). However, all the reduced equilibrium constants are smaller than K_2 as shown in Table 1. This means, from a statistical point of view, that the reverse reactions of the equilibria occur more easily than the forward reactions.

As can be seen in Table 1, all the reduced equilibrium constants are close to unity and the free energy differences are therefore small, which makes interpretations uncertain. However, the observed trends are compatible with an inductive effect in which a decrease in the number of electron-donating methyl groups tends to favour ethoxy substitution over methoxy substitution. Moreover, it can also be an effect of lower stability (higher reactivity) of the ethoxide ion as compared with the methoxide ion.

The chemical shifts were measured relative to tetra-

methylsilane (TMS) for the alkoxysilanes in the series $(CH_3)_xSi(OC_2H_5)_y(OCH_3)_z$. The chemical shifts reported in Table 2 for the pure ethoxy and methoxy substituted alkoxysilanes are consistent with the previously reported values.[18–21] The chemical shifts for the mixed alkoxysilanes seemed to be symmetrically distributed with a shift of 2.5, 1.8, 1.2 and 0.8 ppm between adjacent peaks for the mono-, di-, tri- and tetraalkoxysilanes, respectively. The distribution of the trialkoxymethylsilanes is shown in Fig. 1 as an example of the quality of the ^{29}Si NMR spectra.

Experimental

Ethoxytrimethylsilane, methoxytrimethylsilane, diethoxydimethylsilane, triethoxymethylsilane and tetraethoxysilane of pro analysi grade were used as starting material. The qualities of the alkoxysilanes were tested with ^{29}Si NMR. It was necessary to vacuum distill the triethoxymethylsilane reagent carefully before use. The other

Table 2. Chemical shifts in ppm relative to tetramethylsilane (10% TMS in chloroform-d) for the series $(CH_3)_xSi(OC_2H_5)_y$-$(OCH_3)_z$ in alkaline ethanol–methanol solutions.

| Alkoxysilane	Shift exp. (ppm)	Shift ref. (ppm)
$(CH_3)_3SiOCH_3$	20.16	$(17.75^{17}$ $17.2^{18})$
$(CH_3)_3SiOC_2H_5$	17.61	$(14.53^{18}$ $13.5^{17})$
$(CH_3)_2Si(OCH_3)_2$	0.14	$(-1.62^{17}$ $-2.5^{19})$
$(CH_3)_2Si((OC_2H_5)(OCH_3)$	-1.70	–
$(CH_3)_2Si(OC_2H_5)_2$	-3.54	(-6.1^{20})
$CH_3Si(OCH_3)_3$	-38.91	$(-39.8^{17}$ $-41.5^{19})$
$CH_3Si(OC_2H_5)(OCH_3)_2$	-40.11	–
$CH_3Si(OC_2H_5)_2(OCH_3)$	-41.32	–
$CH_3Si(OC_2H_5)_3$	-42.54	$(-44.2^{21}$ $-44.5^{17})$
$Si(OCH_3)_4$	-78.24	(-79.15^{17})
$Si(OC_2H_5)(OCH_3)_3$	-79.08	–
$Si(OC_2H_5)_2(OCH_3)_2$	-79.91	–
$Si(OC_2H_5)_3(OCH_3)$	-80.79	–
$Si(OC_2H_5)_4$	-81.63	(-83.5^{17})
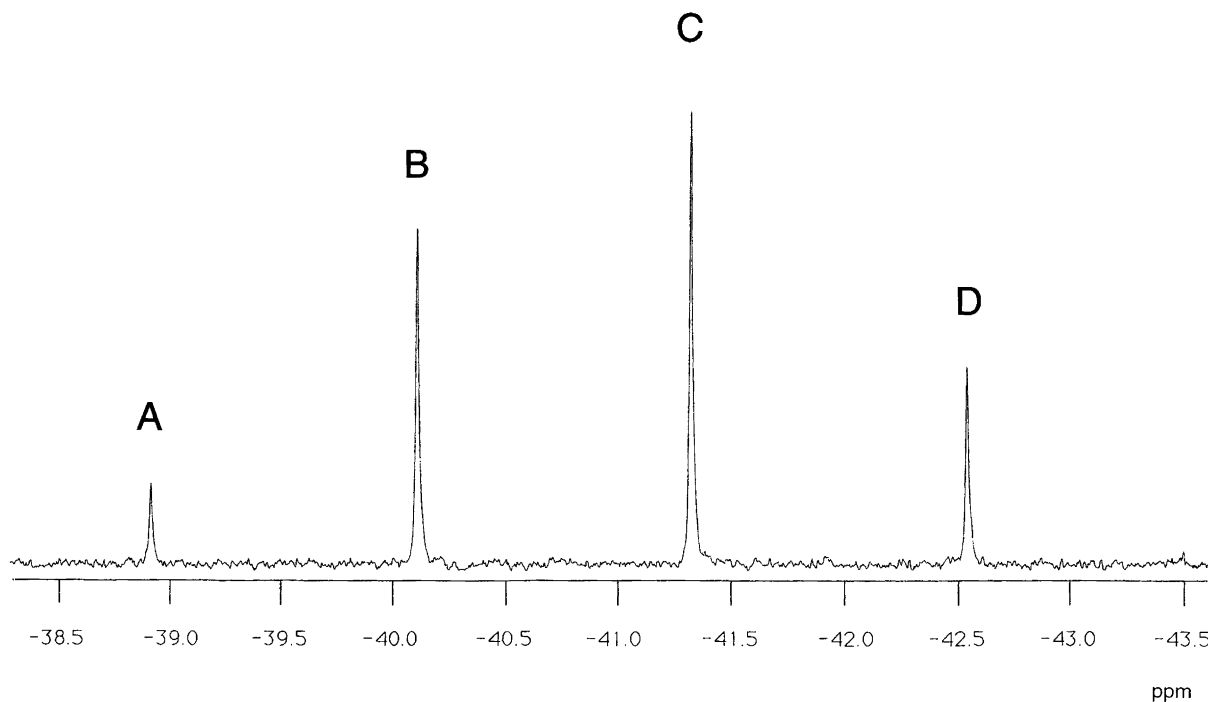
Fig. 1. ^{29}Si-NMR spectrum showing the distribution of the various trialkoxymethylsilanes in alkaline ethanol–methanol solution with the chemical shifts in ppm relative to TMS. The starting concentrations were 0.314 M $CH_3Si(OC_2H_5)_3$, 7.42 mM CH_3O^-, 10.65 M C_2H_5OH and 7.72 M CH_3OH. (A) $CH_3Si(OCH_3)_3$, (B) $CH_3Si(OC_2H_5)(OCH_3)_2$, (C) $CH_3Si(OC_2H_5)_2(OCH_3)$ and (D) $CH_3Si(OC_2H_5)_3$.

alkoxysilanes were used as supplied. Anhydrous methanol ($<0.01\%$ water) of pro analysi grade and dried and distilled ethanol ($<0.01\%$ water) were used as solvents. The water content in the alcohols was checked with FTIR spectroscopy. The alkaline alcohol solutions were prepared from the alcohols and freshly cut sodium. The concentrations of alkoxide ions were established by titration against potassium hydrogen phthalate, using phenolphthalein as indicator.

The equilibrium solutions were carefully prepared by mixing the alkoxysilanes with the alkaline solutions of ethanol and methanol. The solutions were then allowed to stand for at least 12 h before use to ensure that equilibrium had been reached.

The equilibrium reactions were studied in the concentration range 0.12–0.50 M with respect to the alkoxysilanes and with molar ratios for ethanol and methanol between 0.32–2.1. The alkoxide ion concentrations were low (1.8–7.4 mM) compared with the concentrations of the alcohols and alkoxysilanes. Hence the small changes in concentrations of the alcohols caused by alkoxide ions could be neglected in the evaluation of the equilibrium constants.

The ^{29}Si NMR spectra were acquired on a Varian XL 400 spectrometer upgraded to VXR capability, using a 10 mm broad-band probe. The resonance frequency for ^{29}Si was 79.45 MHz. A capillary tube containing D_2O inserted into the 10 mm sample tube provided the field-frequency lock. The 90° pulse was 50 μs and relaxation delays of 300 and 600 s (>10 T_1) were used. 100 transients were recorded at 295 K with a sweep width of 3 kHz with gated decoupling to avoid nuclear Overhauser effects, and the reported intensities are the average of three measured. The chemical shifts were measured relative to tetramethylsilane (10% in chloroform-d), and an exponential line broadening of 0.8 Hz was applied before Fourier transformation to optimize the signal-to-noise ratio.

The measurements of integrals in spectra with low signal-to-noise ratios give large uncertainties due to the difficulty in determining the baseline. In principle, resonance heights give the same information provided that the linewidths are the same, i.e. that the transverse relaxation rate is the same, or that the inhomogenity contribution dominates. In the present investigation, the integrals of the minor species in equilibria K_{3n} and K_{4n} exist in low concentrations and the integrals were estimated to have a 20% uncertainty, whereas the intensities can be measured much more accurately. In small molecules under extreme narrowing conditions, T_1 equals T_2. Here T_1 (and thus T_2) is 30 s or more, giving a contribution to the linewidth of only 10 mHz. It is thus to be expected that under the current experimental conditions observed linewidths will be the same for each species in the series, and that line intensities can be used.

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