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Hydrolysis and Esterification in Organically Modified Alkoxysilanes: A ^{29}Si NMR Investigation of Methyltrimethoxysilane[†]

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High-resolution ^{29}Si NMR was used to investigate the acid-catalyzed hydrolysis and esterification reactions of methyltrimethoxysilane (MTMS) in methanol. The INEPT experiment, adapted for spin systems with multiple heteronuclear coupling constants, was used to assign the closely spaced resonances of the MTMS hydrolysis products. Due to the rapid reaction rates, only the pseudoequilibrium concentration distribution for the resulting hydrolysis products could be determined. Models based on thermodynamically statistical distributions, irreversible hydrolysis reactions, and reversible hydrolysis reactions were nearly equally successful in accounting for the concentration distributions over a wide range of H_2O/Si ratios (R_w) and temperatures. However, preparation of hydrolyzed MTMS in a *nonpseudoequilibrium* state unequivocally demonstrated the reversibility of hydrolysis reactions on a short time scale. By measuring the extent of reaction of MTMS systems at high water concentrations, the ratio of the hydrolysis to esterification rate constant was determined to be approximately 100.

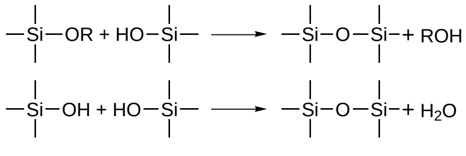
Introduction

The preparation of silica and organically modified silica by the sol−gel polymerization method continues to be an area of active research.[1,2] Chemical modification of the starting compounds allows control of both the physical and chemical properties of the resulting sol−gels, with a basic understanding of the chemistry and kinetics of the polymerization process aiding in the rational design of new and improved materials. Polymerization in acid-catalyzed sol−gel systems can be described as resulting from hydrolysis and esterification (the reverse of hydrolysis) reactions, followed by water-producing and alcohol-producing condensation reactions:

hydrolysis/esterification:

$$\mathrm{Si(OR)_4} + n\mathrm{H_2O} \rightleftharpoons \mathrm{Si(OR)}_{4-n}\mathrm{(OH)}_n + n\mathrm{ROH}$$

condensation:



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OR} + \mathrm{HO}-\overset{|}{\underset{|}{\mathrm{Si}}}- \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{ROH}$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{HO}-\overset{|}{\underset{|}{\mathrm{Si}}}- \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{H_2O}$$

During hydrolysis, the stepwise substitution of the alkoxide ligands by hydroxyl groups produces the essential reactive hydrolyzed monomers that are consumed in the subsequent condensation reactions.

The relative concentration of hydrolyzed monomers should play an important role in the structure of the final sol−gel material. To understand the results of the subsequent polymerization reactions, a basic understanding of the hydrolysis reaction is important. Acid-catalyzed hydrolysis is postulated to proceed via a bimolecular S_N2-Si nucleophilic displacement reaction involving pentacoordinate intermediates.[3,4] The hydrolysis rate is predicted to increase with substituents that reduce the steric crowding around silicon. If the equilibrium protonation of the silane governs the hydrolysis rate, electron providing substituents that stabilize the development of small positive charges in the transition state are expected to increase the rate of hydrolysis. Increasing the number of electron-withdrawing substituents by exchanging hydroxyl for methoxy ligands is therefore expected to *decrease* the rate of subsequent hydrolysis reactions. It has also been argued that substituents that affect the rate in which water can displace the protonated alkoxy ligand will also influence the hydrolysis rate.[4,5] For this description, increasing the number of electronegative hydroxyl groups makes the silicon group more susceptible to nucleophilic attack by water, resulting in an *increase* in subsequent hydrolysis rates.

The initial hydrolysis and esterification steps for a variety of sol−gel systems, including the tetraalkoxysilanes[5−13] and mixed alkoxide systems,[14,15] have been

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investigated using high resolution ^{29}Si NMR. The initial hydrolysis in organically modified sol–gels including ethyltriethoxysilane (ETES),[16] ethyltrimethoxysilane (ETMS),[17] trimethylethoxysilane (TMES),[18] methyltriethoxysilane (MTES),[16,19] octyltriethoxysilane (OTES),[16] methyltrimethoxysilane (MTMS),[20] and mixed MTMS:TEOS systems[15] have also been the subject of investigations.

Models of various complexity have been used to describe the hydrolysis kinetics in alkoxysilanes. The majority of investigators have modeled acid-hydrolysis reactions either as series of consecutive irreversible[6,8,9,17,18,21,22] or reversible reactions.[5,7,10–13,23,24] Including reversibility or reesterification improves the agreement between theoretical and experimental hydrolyzed monomer concentration profiles as a function of reaction time for TEOS and TMOS.[5,7,11,13,24] Recent investigations of mixed alkoxide systems have also revealed that esterification may play an important role in the sol–gel condensation reactions.[25] One simplifying assumption that has been made within the framework of either an irreversible or reversible reaction is the use of a statistical model. This variation assumes that the hydrolysis rates of the functional groups are independent of the identity of the silicon,[8–10,12,18,21] resulting in hydrolysis rates that decrease linearly with decreasing availability of alkoxy ligands. Increasing rates of hydrolysis with each consecutive reaction has been reported for some systems.[5,7,11,13,17,24]

The distribution of the hydrolyzed species can also be described without any direct reference to time. It is shown here, that in certain limiting cases both the reversible and irreversible reactions result in statistical binomial distributions that are a function of the extent of reaction. Binomial distributions have been previously been utilized to describe the concentration distributions of the condensed species of TEOS and the organically modified silanes, MTES, and vinyltriethoxysilane (VTES) as a function of the degree of condensation.[26] Binomial distributions were also found using a statistical reaction model for the condensed species of tetraalkoxysilane systems.[9] These equilibrium distributions were found to be very sensitive to the actual ratio of rate coefficients. In this paper the formalism is extended to describe the concentration distribution of the hydrolyzed monomer species in alkoxysilanes.

The effect of organic modification on hydrolysis in organotrialkoxysilane sol–gel systems has yet to be established, due to the lack of detailed kinetic studies for these systems. A preliminary study of hydrolysis and polycondensation of MTMS in acetone and acetonitrile, catalyzed by *p*-toluensulfonic acid has been reported,[20] but little information beyond hydrolysis being first order in MTMS concentration was given. Also reported was a preliminary study on the effect of the alkyl modification which found that the rate of hydrolysis is approximately MTES > ETES > OTES.[16]

In this paper, the hydrolysis reactions of MTMS in methanol were investigated using ^{29}Si NMR. MTMS is the simplest alkyltrialkoxysilane and provides a good system with which to test mechanisms and models describing hydrolysis and esterification reactions. Reported applications of alkyltrialkoxysilanes in materials include the preparation of poly(methylsilsesquioxanes) from methyltrialkoxysilanes for coatings in optical and electrical devices,[27] as well as the production of thin, crack-free films from MTMS.[28] The ^{29}Si NMR studies reported here were performed under time frames and conditions in which the hydrolysis reaction is nearly complete and the condensation reaction was minimal. Prior to the onset of significant condensation, hydrolysis is considered to be in a pseudoequilibrium or preequilibrium state.[5] The results for MTMS were analyzed using both irreversible and reversible models, allowing comparison to previous studies of organotrialkoxysilanes.

Experimental Methods

Sample Preparation. Methyltrimethoxysilane (MTMS) and MeOH were obtained from Petrarch Systems and Aldrich, respectively, and were used as received. A 2.24 M stock solution of MTMS in MeOH was prepared and analyzed for hydrolysis or condensation contaminants using ^{29}Si NMR prior to use. Different H_2O/Si molar ratios (R_w) ranging from 0.5 to 8 were obtained by adding the appropriate amounts of chilled, doubly distilled H_2O (+1 °C) to the 2.24 M stock solution at the desired temperature. The H_2O solutions were acidified with 1 N HCl such that the acid concentration in the final MTMS solutions was 1.58 mM, a nominal pH of 2.8. To help reduce the ^{29}Si NMR spin–lattice relaxation times, chromium acetylacetonate, Cr(acac)$_3$, was added for a final concentration of 15.7 mM. For hydrolysis and condensation investigations at different temperatures, samples were equilibrated in the NMR probe at the desired temperature prior to the addition of water. Hydrolysis was initiated by the addition of chilled, acidified water to the NMR tube, mixing the sample, and immediately returning to the NMR probe. Typically 60–90 s elapsed between the initiation of hydrolysis and the first ^{29}Si NMR acquisition. All pseudoequilibrium hydrolysis concentration ratios were determined from reaction mixtures 120 s after initiation of hydrolysis.

NMR Measurements. All ^{29}Si NMR spectra were obtained at 79.49 MHz on a Bruker AMX400 spectrometer, using a standard 10 mm broad-band probe. Spectra were obtained using inverse gate experiments to reduce NOE effects, with standard Waltz ^{1}H decoupling. Spectra were obtained using 2–8 scan averages, depending on the signal to noise required,

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an 18 s relaxation delay, and a 20 μs $\pi/2$ ^{29}Si pulse. The temperature was controlled to ±0.2 K using a previously calibrated thermocouple. All chemical shifts are referenced to internal TMS, added at completion of the study.

Mathematical Analysis. Minimization of errors for estimations of the rate constants was obtained using a multidimensional downhill simplex routine,[29] while the first-order differential equation described in the theory section were numerically integrated using a variable step size, fourth-order Runge–Kutta algorithm.[29] All analysis programs were written in FORTRAN and were executed on a 66 MHz PC.

Theory of Kinetics and Distribution

Silicon NMR provides a powerful tool to investigate the distribution of functional groups around a specific silicon environment. If only functionalities immediately adjacent to the silicon of interest are considered, there are 10 distinguishable local silicon environments possible during the hydrolysis and condensation of MTMS. Contrast this with the 15 distinct silicon environments available in the tetraalkoxysilanes systems. This difference results from the invariance of the methyl coordination environment during hydrolysis and condensation. In MTMS the silicon environments are designated by T_i^k, where i is the number of hydroxyls groups attached to the silicon and k represents the number of siloxane bonds attached to the silicon.

Thermodynamic Distributions. If the observed number of SiOH bonds surrounding a silicon is governed entirely by statistics (not influenced by the chemical identity), then the concentration of the various hydrolysis products can be defined by a binomial distribution. For hydroxyl groups distributed randomly over n Si–O bonds the population or probability of silicons having ν hydroxyl groups, $P(\nu,n)$ is given by[30]

$$P(\nu,n) = \binom{n}{\nu} p^{\nu} q^{n-\nu} \qquad (1)$$

where p gives the probability of hydrolysis for a single bond, $q = 1 - p$ defines the probability for an alkoxy SiOR bond, and $\binom{n}{\nu}$ is the binomial coefficient. The probability p is equivalent to the extent of reaction (ϵ) and defines the probability of a siloxane bond being a hydroxyl. For the monomeric hydrolysis products in MTMS the extent of reaction is given by

$$\epsilon = \frac{[\mathrm{SiOH}]}{[\mathrm{SiO}]} = \frac{[\mathrm{SiOH}]}{[\mathrm{SiOCH_3}]_0} = \frac{[\mathrm{T}_1^0] + 2[\mathrm{T}_2^0] + 3[\mathrm{T}_3^0]}{3[\mathrm{T}_0^0]_0} \qquad (2)$$

where $[\mathrm{T}_1^0]$, $[\mathrm{T}_2^0]$, and $[\mathrm{T}_3^0]$ are the observed concentrations of the various hydrolysis species and $[\mathrm{T}_0^0]_0$ is the initial concentration of the unhydrolyzed monomer. For MTMS there are three possible sites for hydrolysis ($n = 3$) allowing the distribution for each of the hydrolyzed monomer species to be easily evaluated. The species $[\mathrm{T}_0^0]$, $[\mathrm{T}_1^0]$, $[\mathrm{T}_2^0]$, and $[\mathrm{T}_3^0]$ are defined by the different number of hydroxyl groups bound to the silicon ($\nu = 0$, 1, 2, 3, respectively), such that the concentration distributions are given by

$$[\mathrm{T}_0^0]/[\mathrm{T}_0^0]_0 = (1 - \epsilon)^3 \qquad (3)$$

$$[\mathrm{T}_1^0]/[\mathrm{T}_0^0]_0 = 3\epsilon(1 - \epsilon)^2 \qquad (4)$$

$$[\mathrm{T}_2^0]/[\mathrm{T}_0^0]_0 = 3\epsilon^2(1 - \epsilon) \qquad (5)$$

$$[\mathrm{T}_3^0]/[\mathrm{T}_0^0]_0 = \epsilon^3 \qquad (6)$$

For the present investigation of MTMS it is these concentration distributions of the hydrolyzed monomers that will be experimentally evaluated.

Irreversible Hydrolysis Reactions. The hydrolysis reaction of alkoxysilanes can be described by consecutive, second-order reactions:

$$\mathrm{H_2O} + \mathrm{T}_0^0 \xrightarrow{k_1} \mathrm{T}_1^0 + \mathrm{ROH} \qquad (7)$$

$$\mathrm{H_2O} + \mathrm{T}_1^0 \xrightarrow{k_2} \mathrm{T}_2^0 + \mathrm{ROH} \qquad (8)$$

$$\mathrm{H_2O} + \mathrm{T}_2^0 \xrightarrow{k_3} \mathrm{T}_3^0 + \mathrm{ROH} \qquad (9)$$

where k_i is the rate constant for the ith hydrolysis step. The pertinent rate equations in terms of molecular concentrations are then defined by

$$\mathrm{d}[\mathrm{T}_0^0]/\mathrm{d}t = -k_1[\mathrm{T}_0^0][\mathrm{H_2O}] \qquad (10)$$

$$\mathrm{d}[\mathrm{T}_1^0]/\mathrm{d}t = k_1[\mathrm{T}_0^0][\mathrm{H_2O}] - k_2[\mathrm{T}_1^0][\mathrm{H_2O}] \qquad (11)$$

$$\mathrm{d}[\mathrm{T}_2^0]/\mathrm{d}t = k_2[\mathrm{T}_1^0][\mathrm{H_2O}] - k_3[\mathrm{T}_2^0][\mathrm{H_2O}] \qquad (12)$$

$$\mathrm{d}[\mathrm{T}_3^0]/\mathrm{d}t = k_3[\mathrm{T}_2^0][\mathrm{H_2O}] \qquad (13)$$

For this model it is assumed that the reaction is not reversible and that condensation reactions are negligible. If the variable λ is introduced

$$\lambda = \int_0^t [\mathrm{H_2O}]_t \,\mathrm{d}t \qquad (14)$$

with

$$\mathrm{d}\lambda = [\mathrm{H_2O}]\,\mathrm{d}t \qquad (15)$$

integrated rate equations for unequal hydrolysis rates are obtained assuming only the T_0^0 species is present initially (correcting eq 14 of ref 17):[31]

$$\mathrm{T}_0^0 = [\mathrm{T}_0^0]_0 \mathrm{e}^{-k_1\lambda} \qquad (16)$$

$$\mathrm{T}_1^0 = \{[\mathrm{T}_0^0]_0 k_1/(k_2 - k_1)\}[\mathrm{e}^{-k_1\lambda} - \mathrm{e}^{-k_2\lambda}) \qquad (17)$$

$$\mathrm{T}_2^0 = ([\mathrm{T}_0^0]_0 k_1 k_2)\{[\mathrm{e}^{-k_1\lambda}/(k_2 - k_1)(k_3 - k_1)] - [\mathrm{e}^{-k_2\lambda}/(k_2 - k_1)(k_3 - k_2)] + [\mathrm{e}^{-k_3\lambda}/(k_3 - k_1)(k_3 - k_2)]\} \qquad (18)$$

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(31) Rate equations for irreversible hydrolysis in organically modified silanes have previously been published by Chambers et al.,[17] but several typographical errors need to be corrected. For example, the last exponential term in eq 14 of ref 17 should involve the rate constant k_3 not k_2. The first term in eq 21 of ref 17 should be multiplied by −1, and the denominator in eq 22 should read $(k_3 - k_2)(k_3 - k_1)$. The validity of these proposed corrections can be seen be considering the limit of zero reaction time ($t \to 0$). For this limiting case (i.e., no reaction) both β and the summation should equal 3. The corrected equations are given below.

$$T_3^0 = [T_0^0]_0\{[k_2k_3/(k_2 - k_1)(k_3 - k_1)](1 - e^{-k_1\lambda}) - [k_1k_3/(k_2 - k_1)(k_3 - k_2)](1 - e^{-k_2\lambda})] + [k_1k_2/(k_3 - k_1)(k_3 - k_2)](1 - e^{-k_3\lambda})]\} \quad (19)$$

where $[T_0^0]_0$ is the initial unhydrolyzed monomer concentration. Prior to any condensation the silane balance is given by

$$[T_0^0]_0 = [T_0^0] + [T_1^0] + [T_2^0] + [T_3^0] \quad (20)$$

while the water concentration is

$$[H_2O] = [H_2O]_0 + 3([T_0^0] - [T_0^0]_0) + 2[T_1^0] + [T_2^0] \quad (21)$$

Utilizing eqs 16−19 the integrated rate equations can be expressed as a summation:[32]

$$\beta = \sum_{i=1}^{3} G_i e^{-k_i\lambda} \quad (22)$$

where

$$\beta = ([H_2O] - [H_2O]_0)/[T_0^0]_0 + 3 \quad (23)$$

and the expansion coefficients are given by (correcting eqs 21 and 22 of ref 17):[31]

$$G_1 = 3 + 2k_1/(k_2 - k_1) + k_1k_2/(k_2 - k_1)(k_3 - k_1) \quad (24)$$

$$G_2 = -2k_1/(k_2 - k_1) - k_1k_2/(k_2 - k_1)(k_3 - k_2) \quad (25)$$

$$G_3 = k_1k_2/(k_3 - k_1)(k_3 - k_2) \quad (26)$$

Using the extent of reaction ϵ in eq 2, β can be recast as

$$\beta = 3(1 - \epsilon) \quad (27)$$

In this manner the extent of reaction can be directly related to the rate constants. Again, the concentration distributions of the hydrolyzed MTMS species as defined by eqs 16−19 will be the relevant values experimentally determined.

Reversible Hydrolysis Reactions. Hydrolysis in the alkyltrialkoxysilane systems can also be described as consecutive, reversible reactions:

$$T_0^0 + H_2O \underset{k_{E_1}}{\overset{k_{H_1}}{\rightleftharpoons}} T_1^0 + ROH \quad (28)$$

$$T_1^0 + H_2O \underset{k_{E_2}}{\overset{k_{H_2}}{\rightleftharpoons}} T_2^0 + ROH \quad (29)$$

$$T_2^0 + H_2O \underset{k_{E_3}}{\overset{k_{H_3}}{\rightleftharpoons}} T_3^0 + ROH \quad (30)$$

where k_{H_i} and k_{E_i} refer to the ith hydrolysis or esterfication reaction, respectively. It should be noted that k_i and k_{H_i} both represent hydrolysis reaction, but the subscript H is retained only for the reversible reaction to help distinguish between the irreversible and reversible hydrolysis models. The important rate equations in terms of molecular concentration for this reversible model are given by

$$d[T_0^0]/dt = -k_{H_1}[H_2O][T_0^0] + k_{E_1}[T_1^0][ROH] \quad (31)$$

$$d[T_1^0]/dt = -k_{H_2}[T_1^0][H_2O] + k_{E_2}[T_2^0][ROH] + k_{H_1}[T_0^0][H_2O] - k_{E_1}[T_1^0][ROH] \quad (32)$$

$$d[T_2^0]/dt = -k_{H_3}[T_2^0][H_2O] + k_{E_3}[T_3^0][ROH] + k_{H_2}[T_1^0][H_2O] - k_{E_2}[T_2^0][ROH] \quad (33)$$

$$d[T_3^0]/dt = k_{H_3}[T_2^0][H_2O] - k_{E_3}[T_3^0][ROH] \quad (34)$$

$$d[H_2O]/dt = -k_{H_1}[T_0^0][H_2O] - k_{H_2}[T_1^0][H_2O] - k_{H_3}[T_2^0][H_2O] + k_{E_1}[T_1^0][ROH] + k_{E_2}[T_2^0][ROH] + k_{E_3}[T_3^0][ROH] \quad (35)$$

$$d[H_2O]/dt = -d[ROH]/dt \quad (36)$$

Generalized solutions for the rate equations for eqs 31−36 are not available, but these differentials can be solved by numerical integration to provide the temporal evolution of the various species and can be compared to the concentration distributions experimentally observed.

Results and Discussion

Figure 1 shows the ^{29}Si NMR spectra of a MTMS (2.24 M) solution in methanol, 233 K, pH = 2.8, following the addition of 1.5 mol equiv of H_2O (R_W = 1.5), as a function of reaction time. Under these conditions hydrolyzed monomers and some condensed species were afforded, but no gels were obtained, making the system amenable to high resolution ^{29}Si NMR. Three distinct regions were observed for these sol−gel reactions in all experiments up to 7 h. Uncondensed T^0 silicons gave those resonances between $\delta = -37$ and -39, the singly condensed T^1 silicons between $\delta = -46$ and -47.5, and the T^2 condensed silicons between $\delta = -56$ and -57. No T^3 species were observed during the time frame investigated. The different hydrolysis products for these monomer and condensed species were observed and show a very narrow chemical shift dispersion.

For example, the expansion of the T^0 region, presented in Figure 2, shows that the hydrolysis products

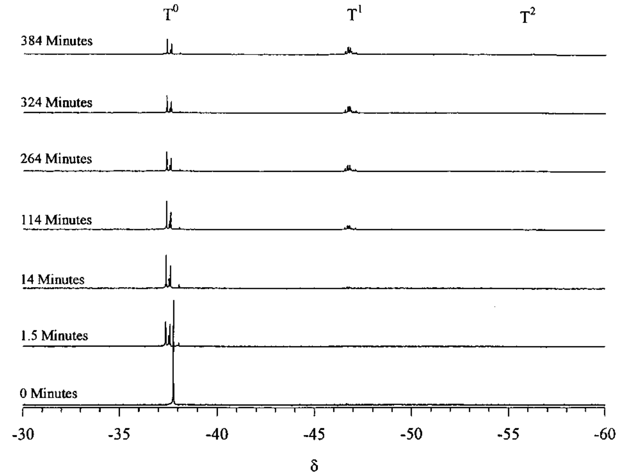

Figure 1. ^{29}Si NMR spectra of 2.24 M MTMS solution in MeOH, pH = 2.8, with a molar water ratio of R_w = 1.5 (theoretical extent of reaction, ϵ = 0.5) at 233 K as a function of hydrolysis time.

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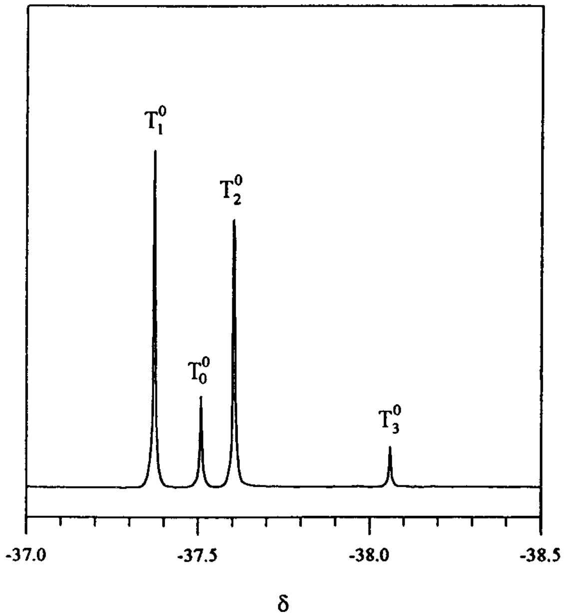

Figure 2. Expansion of the T^0 region in the ^{29}Si NMR for a MTMS solution (2.24 M) at 233 K, pH = 2.8, R_w = 1.5. The assignments for the different hydrolyzed monomer species is shown.

of the MTMS monomer all resonate within a 0.5 ppm range. This small dispersion contrasts with the large downfield chemical shifts with increasing hydroxyl number previously observed in studies of tetraalkoxysilanes.[33] The small chemical shift dispersion has prompted previous investigators to suggest that the hydrolysis products of MTMS were not resolvable.[17,20] In addition, the small dispersion of the T^0 resonances prohibits chemical shift assignments based on downfield shifts with increasing hydroxyl number as in tetraalkoxysilane systems. The four resonances in Figure 2 have been unambiguously assigned using the editing power of the INEPT experiment optimized for multiple heteronuclear J coupling constants as detailed elsewhere.[34] Unique signal intensity responses for the different hydrolyzed monomer species are observed due to the difference in methoxy and methyl couplings, J(Si,H) = 3.9 Hz and J(Si,H) = 8.3 Hz, respectively. Inspection of Figure 2 clearly shows there are no simple downfield or upfield trends in chemical shift with increasing hydroxyl number for these hydrolyzed monomer species. In fact, assignments made using previous chemical shift arguments would have been entirely incorrect and suggest care must be utilized in assignments of the hydrolyzed species in organic modified alkoxysilanes.

The first NMR spectrum were obtained within 60 s from the addition of H_2O and acid, with additional spectra being accumulated every 60 s up to 15 min. As seen in Figure 1, at 233 K the relative ratio of the hydrolysis species remain essentially *unchanged* for the first 10−15 min, at which point condensation reactions begin to significantly reduce the overall amount of hydrolyzed monomer present. Prior to condensation the concentrations of the hydrolyzed monomers can be considered to exist in a *pseudoequilibrium* or *preequilibrium* state.[5] In contrast to TEOS, these experiments show that the hydrolysis reaction in MTMS is extremely rapid compared to the preparation time for a NMR experiment. Even at the reduced temperature of 203 K (not shown), the hydrolysis reaction is completed or at equilibrium prior to the acquisition of the first NMR measurement (~60 s), while in TEOS this equilibrium may not be reached for over 1 h. Investigations of TMOS at the same pH conditions (pH = 2.8) also reveal a rapid hydrolysis rate. The existence of hydrolyzed MTMS monomers in a *pseudoequilibrated* state within 60 s, places the hydrolysis rates faster than approximately 0.01 M^{-1} s^{-1}. This hydrolysis rate is significantly faster than the hydrolysis rate of $\sim 7.0 \times 10^{-4}$ M^{-1} s^{-1} observed in ethyltrimethoxysilane (ETMS).[17]

In MTMS, hydrolysis is so rapid that only concentration ratios of the hydrolyzed species can be evaluated by ^{29}Si NMR. It is possible to determine the pseudoequilibrium concentration profiles for MTMS by investigating the initial stages of the sol−gel polymerization prior to the onset of condensation. The remainder of the results presented here will discuss this pseudoequilibrated state for hydrolysis in MTMS. The condensation reaction will be described in detail elsewhere.

In Figure 3A the relative pseudoequilibrium concentration ratios for the hydrolyzed monomer species in solution of MTMS (2.24 M, pH = 2.8) at 233 K, 120 s after the initiation of hydrolysis, for different water concentrations (R_w) is presented as a function of the extent of reaction ϵ (as defined in eq 2). In Figure 3B pseudoequilibrium concentration ratios for MTMS solutions (2.24 M, pH = 2.8) at 203 and 273 K are also presented. Note that the observed extent of reaction is lower than the predicted theoretical extent of reaction for all water concentrations investigated. This discrepancy can be attributed to esterification or reversible hydrolysis as discussed in detail below. Inspection of Figure 3A,B also show that the observed pseudoequilibrium concentration ratios of the hydrolyzed monomers are not greatly affected by temperature. The inability to follow the temporal evolution of the hydrolyzed species excludes the determination of *absolute* rates of hydrolysis. Fortunately, information about the hydrolysis reactions can still be obtained from analysis of the reaction product ratios in these pseudoequilibrated states. Use of the hydrolyzed monomer concentration ratios in MTMS allows the *relative* ratios of the different hydrolysis rates to be evaluated for a variety of models as discussed below.

To allow direct comparison to previous investigations of hydrolysis in organically modified alkoxysilanes, it is important to evaluate MTMS using the same irreversible hydrolysis reaction models; even though it will be unequivocally demonstrated that the hydrolysis in MTMS is reversible (*vide infra*). In the previous study of the organically modified alkoxysilane ETMS,[17] the acid-catalyzed hydrolysis of the monomer was analyzed in terms of three, irreversible, sequential reactions given by eqs 7−9. The differential rate equations that describe the change in the concentration of the hydrolyzed monomer species as a function of time are given by eqs 10−13. The pseudoequilibrium concentration profiles for the hydrolyzed monomers of MTMS were analyzed within the framework of this irreversible model allowing direct comparison of rates between MTMS and ETMS.[17] It was assumed that

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[33] Assink, R. A.; Kay, B. D. *Annu. Rev. Mater. Sci.* **1991**, *21*, 491−513.

[34] Alam, T. M.; Assink, R. A.; Prabakar, S.; Loy, D. A. *Magn. Reson. Chem.*, in press.

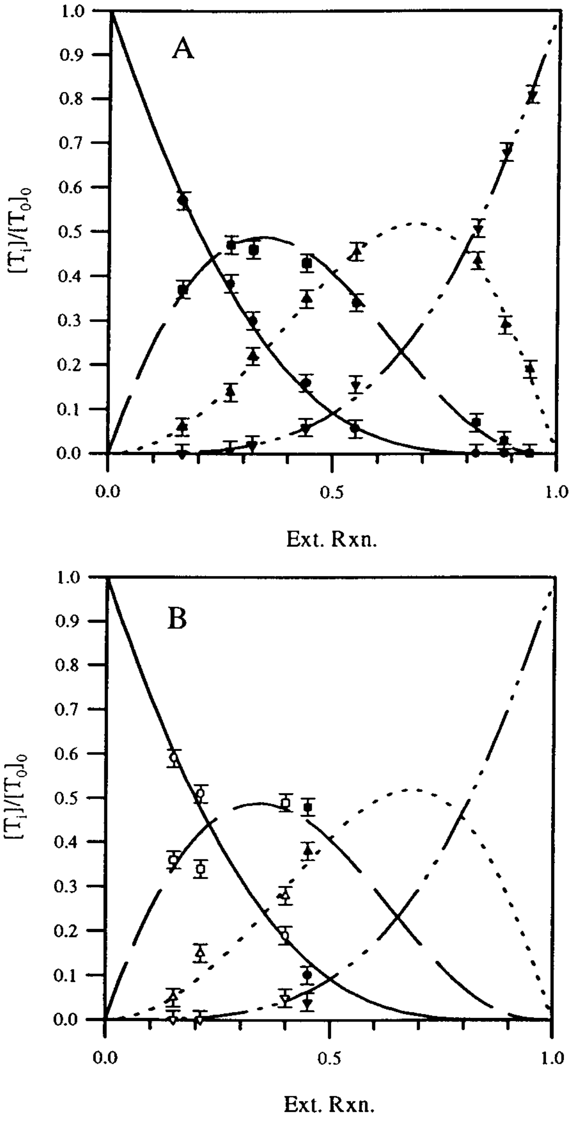

Figure 3. Experimental and theoretical concentration ratios for a MTMS solution (2.24 M), pH = 2.8, 120 s after initiation of hydrolysis for different extents of reactions ϵ. Theoretical lines are predictions using an irreversible hydrolysis model using $k_2/k_1 = 0.53$ and $k_3/k_1 = 0.20$ for $[T_i^0]/[T_0^0]_0$, (—) $i = 0$, (– – –) $i = 1$, (· · ·) $i = 2$, (– · · · –) $i = 3$. The experimental concentration ratios $[T_i^0]/[T_0^0]_0$ are given by the symbols (●) $i = 0$, (■) $i = 1$, (▲) $i = 2$, (▼) $i = 3$ at (A) 233 K for $R_w = 8.0$, 6.0, 4.0, 2.0, 1.5, 1.0, 0.8, and 0.5 and (B) 203 K for $R_w = 1.5$, 1.0, and 0.5 (solid symbols) and 273 K for $R_w = 1.5$ (open symbols). Note that the observed extent of reaction (ϵ) is less than the predicted theoretically maximum for the range of water concentrations investigated, due to reversibility as discussed in the text.

hydrolyzed monomer species of MTMS were in a preequilibrated state[5] and that the condensation reactions produced negligible variations in the hydrolyzed monomer species. For the concentrations, temperature and short reaction times chosen these assumptions are fulfilled. The differential equations describing the evolution of the hydrolyzed species can be solved analytically[17,35] providing expressions for the concentrations as a function of the new time variable λ (see eqs 16–19). The concentration ratio of these hydrolyzed species at any time in the reaction can be related to the variable β (eqs 22–23), or more usefully to the extent of reaction (ϵ). This means that the extent of reaction (as defined by eq 2) can be directly related to the hydrolysis rate constants k_1, k_2, and k_3.

The relative ratios of hydrolysis rates were evaluated for an irreversible model, by using the concentration ratios in Figure 3A,B and minimizing the error function defined by the sum of differences squared:

$$(E) = \sum_i \left[\frac{[T_i^0]^{\mathrm{exp}} - [T_i^0]^{\mathrm{calc}}}{[T_0^0]_0}\right]^2 \qquad (37)$$

Here $[T_i^0]^{\mathrm{exp}}$ are the experimentally observed concentrations and $[T_i^0]^{\mathrm{calc}}$ are calculated concentrations using eqs 16–19. The ratios of hydrolysis rates that produced the minimum error were $k_2/k_1 = 0.46$ and $k_3/k_1 = 0.10$ at 203 K (four concentration ratios), $k_2/k_1 = 0.59$ and $k_3/k_1 = 0.22$ at 233 K (32 concentration ratios), and $k_2/k_1 = 0.60$ and $k_3/k_1 = 0.29$ at 273 K (12 concentration ratios). At 203 K only one water concentration was evaluated, providing a low number of constraints, such that the error inherent in these two rate ratios is significantly larger than the other temperatures investigated. The combined concentration ratios for all the temperatures and water concentrations (ignoring any variations that may be inherent between temperatures) were also used to evaluate the rate constant ratios, thus providing 48 different experimental constraints, giving $k_2/k_1 = 0.53$ and $k_3/k_1 = 0.20$. The theoretical concentration ratios of the hydrolyzed monomer as a function of the extent of reaction ϵ predicted using these rate constants ratios and a second-order irreversible model are given by the lines in Figure 3A,B. The agreement with experimental values is good for a wide range of both ϵ and temperatures.

It should be noted that no assumptions were made concerning the relative ratios of the hydrolysis rate constants during the minimization of error. Even though there are small variations in the ratio of rates for MTMS over the temperature range investigated, it is clear that the ratio of hydrolysis rates *decrease* with increasing number of hydroxyls attached to the silicon. This is opposite to the trend of *increasing* ratio of hydrolysis rates observed in ETMS.[17] For example at 273 K ratios in ETMS of $k_2/k_1 = 2.07$ and $k_3/k_1 = 2.08$ were reported. Increasing hydrolysis ratios have also been reported in the tetraalkoxide, TEOS,[5,7,11,13] and TMOS systems.[5] Attempts to obtain the observed hydrolysis species ratios in MTMS using increasing rate constants were unsuccessful. For example, if the hydrolysis rates were assumed to have the ratio $k_2/k_1 = 2$ and $k_3/k_1 = 2$, the predicted concentration ratios ($[T_i^0]/[T_0^0]_0$) for $R_w = 1.5$ ($\epsilon = 0.5$) would be 0.29, 0.22, 0.20, and 0.30 for $i = 0, 1, 2, 3$. Inspection of Figure 3A,B clearly shows that this is a significant departure from what was observed experimentally. In MTMS at 233 K and $R_w = 1.5$ (experimentally observed ϵ is 0.43, see reversible discussion below) the observed concentration ratios are 0.16, 0.43, 0.35, and 0.06. Note in particular the concentration of the unhydrolyzed and fully hydrolyzed species is smaller than the intermediate hydrolysis species, opposite to those concentrations predicted by increasing hydrolysis rates. In TEOS sol–gel systems, hydrolysis rates that *increase* with decreasing number of alkoxy ligands bound to the silicon have been reported. These increasing ratios of hydrolysis rates are expected to produce concentration ratios in

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(35) Rodiguin, N. M.; Rodiguina, E. N. *Consecutive Chemical Reactions Mathematical Analysis and Development*; D. Van Nostrand Company, Inc.: Princeton, N. J., 1964.

which the fully hydrolyzed and unhydrolyzed species dominate (for example, see Figure 2 of ref 13). For MTMS, the subsequent hydrolysis rates do *not* increase using an irreversible model but instead the hydrolysis rates *decrease* with decreasing number of alkoxy ligands. These results are consistent with a S_N2-Si mechanism with a pentacoordinate transition state, in which the equilibrium protonation of the silane ester governs the hydrolysis rates.

A simplifying assumption that has been used to successfully describe the hydrolysis in tetraalkoxy systems is the use of a statistical model with functional group kinetics.[8,9] In this statistical model, the ratio of hydrolysis rate constants are based on the concentration of the alkoxide group (methoxy functional groups for MTMS), without any specification to the local silicon chemical environment. For example, the k_1 hydrolysis rate constant (i.e., the hydrolysis of the T_0^0 species) is predicted to be 3 times faster than the k_3 rate constant (hydrolysis of the T_2^0 species). Assuming this statistical model the rate constant ratios would be $k_2/k_1 = 0.67$ and $k_3/k_1 = 0.33$. With these ratios, the hydrolysis species concentrations predicted for an irreversible reaction (eqs 16−19) reduce to the binomial distribution given by eqs 3−6. This simply means that the binomial distribution is obtained if hydrolysis kinetics are governed by the number of OH substituents attached to a specific silicon and are not related to the chemical identity of the silicon. The equivalence of the binomial distribution and the irreversible kinetic model assuming a statistical ratio of hydrolysis rate constants allows the hydrolysis species concentrations to be described by a single parameter, the extent of reaction ϵ as defined in eq 2. Theoretical concentration ratios obtained assuming this simple binomial distribution are presented as lines in Figure 4A,B. It is evident that the binomial predictions using the single extent of reaction parameter (ϵ) are within experimental error of the experimentally observed values and are nearly identical with the ratios predicted using irreversible kinetics (two rate ratios). Note that the theoretical curves in Figure 3 are asymmetric in comparison to the curves in Figure 4, a result of the nonstatistical ratio of rate constants employed in Figure 3.

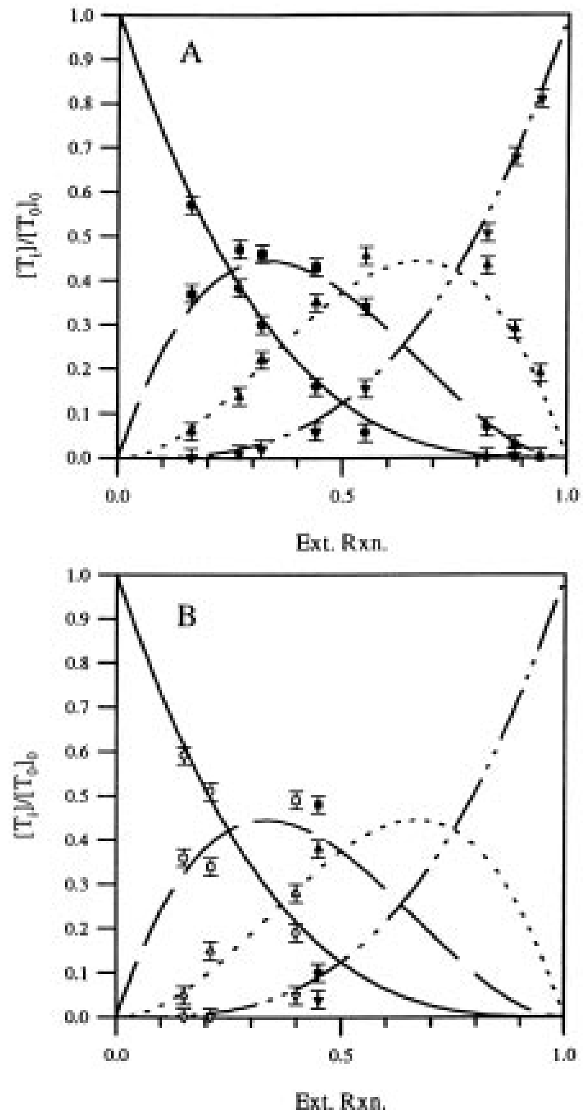

Figure 4. Experimental and theoretical concentration ratios for a solution of MTMS (2.24 M), pH = 2.8, 120 s after initiation of hydrolysis for different extents of reaction ϵ. Theoretical lines are predictions assuming a binomial distribution as a function of ϵ for $[T_i^0]/[T_0^0]_0$, (—) $i = 0$, (− − −) $i = 1$, (· · ·) $i = 2$, (− · · −) $i = 3$. The experimental concentration ratios $[T_i^0]/[T_0^0]_0$ are given by the symbols (●) $i = 0$, (■) $i = 1$, (▲) $i = 2$, (▼) $i = 3$ at (A) 233 K for $R_w = 8.0, 6.0, 4.0, 2.0, 1.5, 1.0, 0.8$, and 0.5 and (B) 203 K for $R_w = 1.5, 1.0$, and 0.5 (solid symbols) and 273 K for $R_w = 1.5$ (open symbols).

To address the error introduced by utilizing a simple binomial distribution over an irreversible hydrolysis model, the error (E) defined by eq 38 is presented in Figure 5, as a function of different ratios of k_2/k_1 and k_3/k_1. This error surface was calculated using all 48 experimental concentration ratios for the hydrolyzed MTMS monomer, as given in Figure 3A,B. It is clear that the magnitude of error is rather small in the general vicinity of the global minimum. These suggest that a range of hydrolysis rate constant ratios can adequately describe the observed concentration ratios. The hydrolysis rate ratios predicted by simple binomial distributions are also shown in Figure 5 and are very near the global minimum of $k_2/k_1 = 0.53$ and $k_3/k_1 = 0.20$. If the rate constants actually increased with decreasing alkoxy number, it is clear from Figure 5 that these would result in larger error. The error function (E) plotted in Figure 5 can be related to the standard deviation by $\sigma = \sqrt{E/(N-1)}$, *where N* is the number of experimental points. The standard deviations for the ratios predicted by the binomial or the irreversible minimum were on the order of $\sigma < 0.05$. If the hydrolysis rates were assumed to have the ratio $k_2/k_1 = 2$ and $k_3/k_1 = 2$ as seen in the ETMS study, then a larger standard deviation of $\sigma > 0.15$ is observed. It is clear that within experimental error the observed MTMS concentration distribution is adequately described by a statistical ratio of rates and that substituent effects on the hydrolysis rates are nonexistent or negligibly small.

Up to this point, the hydrolysis reaction in MTMS has been discussed in terms of an irreversible reaction, primarily to allow direct comparison to previous results reported in organically modified alkoxysilanes. The role of esterification or reversibility in the hydrolysis of alkoxysilanes has been discussed by different authors.[5,7,10−13,36] To address the importance of the esterification reactions in MTMS−methanol solutions,

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(36) Sivade, A.; Bourret, D.; Sempéré, R.; Bouaziz, J. *J. Non-Cryst. Solids* **1992**, *147−148*, 167−169.

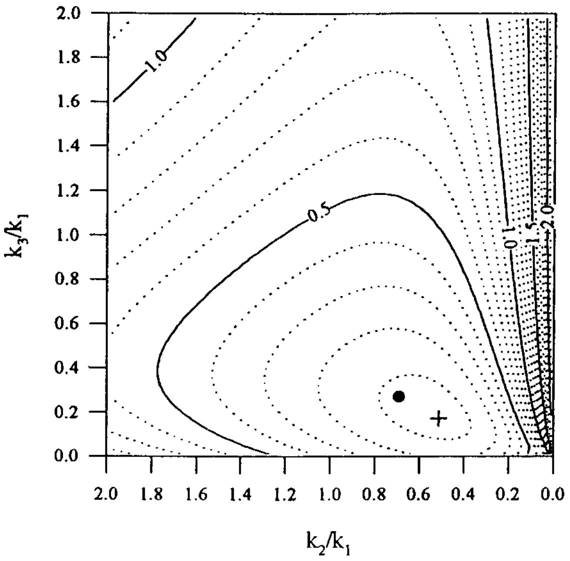

Figure 5. Contour surface representing of the error (as defined by eq 37) for the concentration ratios of the hydrolyzed monomer observed experimentally in Figure 3A,B, as a function of different ratios of the hydrolysis rates k_2/k_1 and k_3/k_1 assuming an irreversible model. The ratios of hydrolysis rates that produce the minimum error are designated by (+), while the ratio of rates that yield a simple binomial distribution of concentration is given by (●).

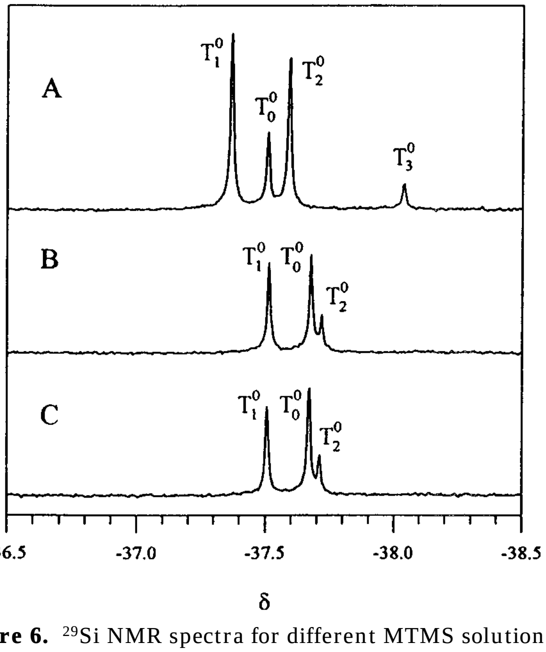

Figure 6. ^{29}Si NMR spectra for different MTMS solutions at 233 K, pH = 2.8. (A) Spectrum for $R_w = 1.5$, clearly showing all hydrolyzed species. (B) Spectrum of the $R_w = 1.5$ solution after the addition of 1.0 equivalent MTMS in MeOH, reducing the apparent water concentration to $R_w = 0.75$. Note the disappearance of fully hydrolyzed species. (C) Spectrum of MTMS solution for a water ratio of $R_w = 0.75$.

a series of ^{29}Si NMR experiments were performed. Figure 6A shows the 233 K spectra of hydrolyzed MTMS monomer species at 1.5 mol equiv of H_2O ($R_w = 1.5$). Note in particular the existence of the fully hydrolyzed species T_3^0, and that the observed concentration ratios are described well by the binomial distribution and the extent of reaction. The relative intensities of the different species in the MTMS solutions at 233 K were unchanged up to 15 min, at which point condensation begins to reduce the overall intensity. One equivalent of MTMS in MeOH (at 233 K) was injected into this $R_w = 1.5$ solution, reducing the overall water concentration to $R_w = 0.75$. The time elapsed between Figures 6A and 6B was approximately 90 s. There is an overall upfield shift with decreasing molar water content, an effect which has been described previously.[34] More importantly, there is a change in the relative species concentration, including the disappearance of the fully hydrolyzed species T_3^0 and the reduction in the relative concentration of T_2^0 species. The spectra for a $R_w = 0.75$ MTMS solution prepared by the conventional procedure is shown in Figure 6C. The occurrence of esterification is clearly demonstrated, with the hydrolysis species of MTMS reequilibrating based on the overall water content.

Demonstration of significant esterification in the organically modified alkoxysilane MTMS system reveals that hydrolysis is more accurately described by the reversible reactions as represented by eqs 29−31. The hydrolyzed monomer species concentrations are described by the differential equations in eqs 32−37 and contain terms proportional to the concentration of water, but also by terms proportional to the concentration of the free alcohol. For a reversible reaction there are six different rate constants that can be varied to describe the system (three for hydrolysis and three for esterification) and are designated k_{H_1}, k_{H_2}, k_{H_3}, k_{E_1}, k_{E_2}, and k_{E_3}. For investigations of TMOS and TEOS where the temporal evolution of the different hydrolyzed monomer concentrations could be obtained, analysis using all six or some portion of these rate constants was possible.[5,13] For the present investigation of MTMS, the amount of meaningful information that can be obtained by modeling the experimentally observed equilibrium concentration ratios using six variable rate constants is marginal. To simplify the complexity of the model, a statistical kinetic assumption concerning the relative ratio of rates was made, where the hydrolysis and esterification rates are governed by the number of methoxy and hydroxyl constituents attached to the silicon. The ratios of rates for the statistical model are given by $k_{H_2}/k_{H_1} = 0.67$ and $k_{H_3}/k_{H_1} = 0.33$ for hydrolysis, and $k_{E_2}/k_{E_1} = 2.0$ and $k_{E_3}/k_{E_1} = 3.0$ for esterification. The ratio between hydrolysis and esterification or equilibrium constant (k_H/k_E) remains the only variable. Once again the concentration of the hydrolyzed MTMS monomers is described by a binomial distribution (eqs 3−6) if a statistical kinetic model is employed.

The ability of the statistical model to adequately describe the kinetics of MTMS using an irreversible model has been demonstrated above, suggesting a similar approach for the irreversible model. With the ratios of hydrolysis and esterification rates defined by the statistical model, the observed concentration of the hydrolyzed monomer species again analytically reduces to the binomial distribution expressions given in eqs 3−6. The unique aspect of the reversible reaction is that the extent of reaction (ϵ) in comparison to the theoretically extent ϵ, is controlled by the ratio of the hydrolysis and esterification rates. If esterification plays a minor role, the observed ϵ will be close to that expected theoretically for the number of molar equivalents of H_2O added. As the ratio of the hydrolysis over esterification rate becomes smaller (i.e., the esterification rate becomes larger), the observed ϵ begins to deviate from the theoretical maximum. In Figure 7, the observed ϵ for a MTMS solution (2.24 M, 233 K, pH = 2.8) in methanol

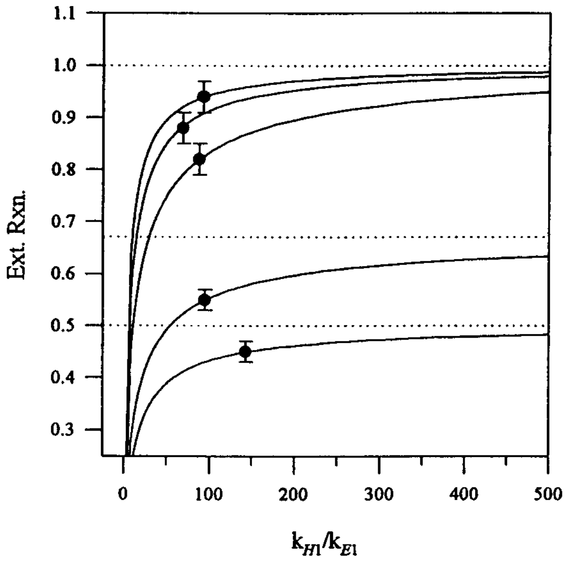

Figure 7. Extent of reaction ϵ (as defined by eq 2) for different hydrolysis/esterification ratios k_{H_1}/k_{E_1} at different concentrations of water assuming a reversible hydrolysis model. The horizontal straight lines represent the theoretical maximum for extent of reaction (ϵ_{max}), assuming no reversibility. Theoretical curves and experimental ϵ (●) for $R_w = 1.5$ ($\epsilon_{max} = 0.5$), $R_w = 2.0$ ($\epsilon_{max} = 0.67$), and $R_w = 4.0$, 6.0, and 8.0 ($\epsilon_{max} = 1.0$).

as a function of different water contents in presented. Theoretical predictions of ϵ as a function of the hydrolysis to esterification ratio k_{H_1}/k_{E_1} are also presented in Figure 7 as solid curves. The dashed lines represent the theoretical maximum ϵ for a given amount of H_2O added. As the water content increases the deviation from theoretical ϵ becomes more pronounced. Evaluating the observed ϵ for the different H_2O concentrations; $R_w = 1.5$ (theoretical $\epsilon = 0.5$), $R_w = 8$, 6, and 4 (all having a theoretical $\epsilon = 1.0$), the k_{H_1}/k_{E_1} ratio was estimated to be approximately 100. Care should be exercised in evaluation of the k_{H_1}/k_{E_1} ratio using low water concentrations due to the error inherent in determining the experimental ϵ. For example, the lower water concentration of $R_w = 1.5$ shown in Figure 7 (corresponding to a theoretical extent of reaction $\epsilon = 0.5$) has error bars that satisfy k_{H_1}/k_{E_1} ratios from ~100 to ~300. By investigating these deviations at higher water content allowed an improved estimation of the k_{H_1}/k_{E_1} ratio. This MTMS k_{H_1}/k_{E_1} ratio of ~100 is larger than the 5:15 or the 1.6:24 hydrolysis/esterification ratios found for TEOS,[7,11] as well as the MTMS ratio of 16.3 found for TMOS systems.[12] The analysis by Sanchez and McCormick found the hydrolysis−esterification ratios for the first and second reaction in TMOS and TEOS to be greater than 50, while the third and fourth hydrolysis reactions had ratios ranging from 3 to 12.[5] In the TMOS and TEOS systems this decrease in the hydrolysis−esterification ratio for subsequent steps in the hydrolysis reaction, offsets the effect of increasing hydrolysis rates with decreasing number of alkoxy groups.

It may be argued that the reversible statistical model used above to describe the hydrolysis in MTMS may not represent a unique solution. For example, a reversible model in which all six rate constants are allowed to vary may provide an improved fit of the experimental data. Strongly nonstatistical hydrolysis rates could possibly produce concentration profiles that are approximately binomial, however, the corresponding equilibrium constants (k_H/k_E) would need to compensate. In Figure 7 a single equilibration ratio is observed for a wide range of water concentrations. This range of concentrations effectively probe different equilibrium constants for the hydrolysis reaction. At high water concentrations ($R_w > 5$) the T_2^0 to T_3^0 equilibration dominates, while at lower water concentrations the T_0^0 to T_1^0 and T_1^0 to T_2^0 reactions become important. The observation of a single equilibrium ratio is therefore inconsistent with a strongly nonstatistical variation of hydrolysis rates. Only by increasing both the number of experimental constraints (for example, monitoring temporal evolution of individual hydrolysis species prior to reaching an equilibrated state) and the quality of the data could an analysis of individual hydrolysis and esterification rate constants be justified. Given the reduced number of constraints obtained by measuring the pseudoequilibrated hydrolysis concentrations of MTMS, only a reversible statistical model with the single variable (the k_{H_1}/k_{E_1} ratio) was pursued in this investigation.

Conclusions

In the present work the hydrolysis and esterification reactions in MTMS have been characterized by high-resolution ^{29}Si NMR. By use of the refocused INEPT experiment optimized for multiple heteronuclear *J* couplings, the hydrolyzed MTMS monomer species were unambiguously assigned. These assignments allowed the relative concentration ratios for a wide range of water content and temperatures to be evaluated. The concentration profiles of the hydrolyzed MTMS were evaluated using both irreversible and reversible kinetic models. The ratio of hydrolysis rates were found to decrease with increasing hydroxyl substituents for the irreversible mode, supporting a bimolecular nucleophilic S_N2-Si type mechanism for acid-catalyzed hydrolysis in MTMS. It was also shown that if a statistical kinetic model is employed the concentration of the hydrolyzed species are described by binomial distributions for both the irreversible and reversible reactions. These binomial distributions are shown to adequately describe the concentration profiles for hydrolyzed MTMS species over a wide range of water concentrations, suggesting that any substituent effects are small. Clear experimental evidence for the occurrence of the esterification reaction in MTMS was obtained using ^{29}Si NMR, with the ratio of hydrolysis to esterification rates being determined from the deviation of the extent of reaction from theoretical. Measurement of the hydrolysis to esterification ratio in other alkylalkoxysilane systems will help address the role of the alkyl group in chemically controlling these reactions. The role of the rapid and reversible hydrolysis on the subsequent condensation reactions in MTMS is being investigated and will be presented elsewhere.

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