Chem. Mater. **1993,** *5,* 1481-1486

Influence of Steric Effects on the Kinetics of Ethyltrimethoxysilane Hydrolysis in a Fast Sol–Gel System

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Received May 7, 1993. Revised Manuscript Received July 23, 1993[●]

The kinetics of acid-catalyzed hydrolysis of ethyltrimethoxysilane (ETMS) and tetramethoxysilane (TMOS) in dilute methanol have been followed at several temperatures by ^{29}Si NMR. The rates of appearance and disappearance of all monomeric silanol intermediates, which are resolved quantitatively in the NMR spectrum, are fit using integrated rate expressions for competitive-consecutive second-order reactions to obtain the rate constants for the individual steps of hydrolysis. At all temperatures, the rate constants increase with each successive hydrolysis. Specifically, the rate constant for the second step is roughly twice that for the initial hydrolysis. In addition, both ETMS and TMOS hydrolyses demonstrate relatively well-behaved Arrhenius behavior over the observed temperature range. The trend observed in this study is opposite that predicted from earlier reports of general siloxane reactivity. Previously proposed mechanisms have invoked variations in the inductive effects as the principal rate-controlling parameter. The results reported here indicate that instead steric effects control the relative rates of hydrolysis, which is the first step of the oligomerization producing the sol–gel. A comparison of these results with those from the hydrolysis of tetraalkoxysilanes suggests that steric control may be general in the acid-catalyzed hydrolysis of silanes and siloxanes.

Introduction

The preparation of sol–gels and derived ceramics has been the subject of several recent books and symposia[1–6] focusing on silicon oxides as thin films for a variety of applications.[7–14] This synthetic effort has been supported by ^{29}Si NMR mechanistic studies[15–26] which have characterized the sol–gel reactions of alkoxysilanes in alcoholic solution. Recently we reported a fast sol–gel synthesis for the rapid preparation of homogeneous crack-free thin films.[11] This fast sol–gel synthesis involves the acid-

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[●] Abstract published in *Advance ACS Abstracts,* September 1, 1993.

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0897-4756/93/2805-1481$04.00/0

catalyzed hydrolysis of trialkoxysilanes utilizing small amounts of water to initiate the reaction. The H_2O:Si ratio was found to be an important parameter for controlling the formation of clear films. Specifically, optically clear, fracture-free films could be prepared utilizing a H_2O:Si ratio of 1.5:1. Methyltrimethoxysilane (MTMS) was found to be most amenable for the preparation of homogeneous thin films by this route.

The formation of the sol–gel proceeds by a hydrolysis step (eq 1), followed by condensation and polymerization steps (eq 2 and 3).[5] The hydrolysis step (eq 1), in particular,

$$\mathrm{RSi(OR')_3 + H_2O \rightarrow RSi(OH)(OR')_2 + R'OH} \qquad (1)$$

$$\mathrm{2RSi(OH)(OR')_2 \rightarrow R(OR')_2SiOSiR(OR')_2 + H_2O} \qquad (2)$$

$$\mathrm{RSi(OH)(OR')_2 + RSi(OR')_3 \rightarrow R(OR')_2SiOSiR(OR')_2 + ROH} \qquad (3)$$

involves monomeric species with varying degrees of hydroxyl substitution. The amounts of water used in the fast sol–gel process correspond to 0.5 equiv of H_2O/alkoxide group. Although the macroscopic characteristics of the product gel are known to depend on the mix of hydrated monomers present during the initial stages of condensation,[11] no detailed kinetic analysis of the individual rate constants for the hydrolysis reactions that comprise equation 1 (eqs 1a–c) have been reported for the alkyltrialkoxysilanes.

$$\mathrm{RSi(OR')_3 + H_2O \rightarrow RSi(OH)(OR')_2 + R'OH} \qquad (1a)$$

$$\mathrm{RSi(OH)(OR')_2 + H_2O \rightarrow RSi(OH)_2(OR') + R'OH} \qquad (1b)$$

$$\mathrm{RSi(OH)_2(OR') + H_2O \rightarrow RSi(OH)_3 + R'OH} \qquad (1c)$$

In several reports on the hydrolysis of tetraalkoxysilanes, simulation of ^{29}Si NMR data was used to evaluate the individual rate constants.[16–18] Spectroscopic techniques have been used to evaluate the rate constants for the acid-catalyzed hydrolysis, condensation, and polymerization (eqs 1–3) of alkyltrialkoxysilanes in dilute buffered solutions near pH 7.[27] However, some disagreement exists regarding whether the rate constants increase[17] or decrease[5,18c] in subsequent hydrolysis reactions (eqs 1b and 1c) under acid-catalyzed conditions.

In the present work, we have employed ^{29}Si NMR to monitor the formation of the hydrolyzed monomeric derivatives of ethyltrimethoxysilane (ETMS) under acid catalysis using a H_2O:silane molar ratio (MR) of 1.5:1 at several temperatures. Moderate dilution of the systems by alcohol was necessary for reproducible kinetic resolution. The rate constants reported here were determined by a direct fit of the NMR data and are supported by a statistical analysis of the results. Although MTMS was found to be optimal for rapid thin-film formation in the original fast sol–gel process, results here and elsewhere[28] indicate that its hydrolyzed monomeric derivatives are not resolved by ^{29}Si NMR spectroscopy: the three hydrolyzed silanol species appear as a single peak. Hence, a comparative study of another alkyltrialkoxysilane (ETMS) was necessary to resolve the hydrolysis kinetics and to determine mechanism. Hydrolytic reactivity of a tetraalkoxysilane, tetramethoxysilane (TMOS), is also reported.

Each of the hydrolyzed monomers derived from ETMS and TMOS is easily resolved by ^{29}Si NMR. Accordingly, the progress of the hydrolysis of ETMS and TMOS can be monitored and its implication for the hydrolysis mechanism(s) determined. For convenience, the silanes and partially hydrolyzed monomers are denoted in this article by a slight modification of the typical notation, using T_m and Q_m where T and Q refer to the trialkoxy- and tetraalkoxysilanes, respectively, and m refers to the number of hydroxyl substituents.

Experimental Methods

Materials. Reagent grade ethyltrimethoxysilane (Hüls Chemicals) and tetramethoxysilane (Aldrich) were used without further purification. *Caution: Siloxanes in general and TMOS specifically are severe irritants and may cause blindness.* The NMR locking (C_6D_6, Cambridge Isotope), reference (tetramethylsilane, Aldrich), and spin relaxation materials (chromium(III) acetylacetonate, [Cr(acac)$_3$], Aldrich) were used as received. Methanol obtained from Fisher was freshly distilled from sodium under nitrogen immediately before use.

Hydrolysis Reactions. The molar ratios of ETMS:MeOH:H_2O and TMOS:MeOH:H_2O were 1:4:1.5 and 1:4:2.0, respectively, in all cases (the water content corresponds to 0.5 equiv H_2O/initial alkoxide group). The amount of added spin relaxation agent Cr(acac)$_3$ [Si:Cr(acac)$_3$] was 1500:1 and 700:1 for ETMS and TMOS, respectively. All reactions were carried out in 10-mm-o.d. NMR tubes and were monitored by ^{29}Si NMR. In a typical reaction, a homogeneous mixture of ETMS (22 mmol), MeOH, and Cr(acac)$_3$ containing TMS (1.7 mmol) and C_6D_6 (1.8 mmol) was placed in a dried NMR tube before being cooled to the appropriate temperature. The magnetic field was shimmed for each sample immediately before initiation of hydrolysis.

Hydrolysis was initiated by the addition of chilled (1 ± 2 °C) hydrochloride acid (0.01 M) to the NMR tube which was immersed in a bath at the specified reaction temperature (−15, −8, 0 °C). The sample tube was removed from the bath, shaken several times, and then immediately placed in the NMR probe. This mixing protocol was sufficient to ensure uniformity throughout the sample and the time delay between the cold bath and the NMR probe was kept to a minimum (<15 s). After a short shimming routine, successive measurements were made. Typically, 60–80 s elapsed from hydrolysis initiation to collection of the first measurements.

NMR Measurements. Proton-decoupled ^{29}Si NMR spectra were recorded on a Nicolet NT-360 spectrometer using a broadband probe tuned to 71.7 MHz. The probe was equilibrated at the specified temperature (±2 °C) prior to sample analysis. In all cases, TMS was used as the internal reference and shifts to higher frequencies are recorded as negative chemical shifts. Typically, 600 scans were taken with 30° pulses and a delay time of 0.5 ms. A total window of 10 kHz was used, with 2K data points providing a chemical shift accuracy of ±0.14 ppm. The acquisition time for the 600 scans was about 1.0 min. Exponential manipulation of the data was performed before the Fourier transform routine. In all experiments, increased hydroxyl substitution resulted in shifts of the silicon resonance to lower frequencies relative to the unhydrolyzed species. These results are in accord with the observations of other groups.[5,16–19,22–24] Triplicate experiments were conducted under identical conditions.

Mathematical Analysis. The individual rate constants for the hydrolysis steps of eqs 1a–c were evaluated according to the method of Svirbely *et al.*[29] Rate constants for TMOS hydrolysis

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were evaluated in a completely parallel manner.[30] The general mechanism for the competitive-consecutive second-order hydrolysis of alkyltrialkoxysilanes can be written as

$$H_2O + T_0 \xrightarrow{k_1} T_1 + MeOH \quad (4)$$

$$H_2O + T_1 \xrightarrow{k_2} T_2 + MeOH \quad (5)$$

$$H_2O + T_2 \xrightarrow{k_3} T_3 + MeOH \quad (6)$$

Defining a variable λ as

$$\lambda = \int [H_2O]_t \, dt \quad (7)$$

the rate equations in terms of λ can be written

$$-dT_0/d\lambda = k_1T_0 \quad (8)$$

$$-dT_1/d\lambda = -k_1T_0 + k_2T_1 \quad (9)$$

$$-dT_2/d\lambda = -k_2T_1 + k_3T_2 \quad (10)$$

$$-dT_3/d\lambda = -k_3T_2 \quad (11)$$

Using the boundary conditions $[T_1] = [T_2] = [T_3] = \lambda = 0$, $[H_2O] = [H_2O]_0$, and $[T_0] = [T_0]_0$ at $t = 0$, eqs 8–11 can be integrated in terms of λ to yield

$$T_0 = [T_0]_0 e^{-k_1\lambda} \quad (12)$$

$$T_1 = \{[T_0]_0 k_1/(k_2 - k_1)\}(e^{-k_1\lambda} - e^{-k_2\lambda}) \quad (13)$$

$$T_2 = [T_0]_0 k_1 k_2 \{[e^{-k_1\lambda}/(k_2 - k_1)(k_3 - k_1)] - [e^{-k_2\lambda}/(k_2 - k_1)(k_3 - k_2)] + [e^{-k_2\lambda}/(k_3 - k_1)(k_3 - k_2)]\} \quad (14)$$

$$T_3 = [T_0]_0\{[k_2k_3/(k_2 - k_1)(k_3 - k_1)](1 - e^{-k_1\lambda}) - [k_1k_3/(k_2 - k_1)(k_3 - k_2)](1 - e^{-k_2\lambda}) + [k_1k_2/(k_3 - k_1)(k_3 - k_2)](1 - e^{-k_3\lambda})\} \quad (15)$$

From the initial quantity of silane, we can write an expression, eq 16, describing the silane balance. An analogous expression for the water balance can be rewritten as eq 17. Equation 17 and

$$[T_0]_0 = [T_0] + [T_1] + [T_2] + [T_3] \quad (16)$$

$$[H_2O] = [H_2O]_0 + 3\{[T_0] - [T_0]_0\} + 2[T_1] + [T_2] \quad (17)$$

the integrated rate equations (eqs 12–15) can be used to derive eq 18, which is simplified by introducing two new variables, β and G_i, as defined

$$\beta = \sum G_i e^{-k_i\lambda} \quad (18)$$

where

$$\beta = \{[H_2O] - [H_2O]_0\}/\{[T_0]_0\} + 3 \quad (19)$$

$$G_1 = 3 + 2k_1/(k_2 - k_1) + k_1k_2/(k_2 - k_1)(k_3 - k_1) \quad (20)$$

$$G_2 = 2k_1/(k_2 - k_1) + k_1k_2/(k_2 - k_1)(k_3 - k_2) \quad (21)$$

$$G_3 = k_1k_2/(k_2 - k_1)(k_3 - k_1) \quad (22)$$

Integration of the ETMS ^{29}Si NMR spectrum was used to quantify the various monomeric silicon-containing species. The concentration of water was then back-calculated at various reaction times using eq 23 for ETMS, where $[H_2O]_i$ = initial concentration of water, $[T_m]_t$ = concentration of the m hydrolyzed species.

$$[H_2O]_t = [H_2O]_i - [T_1]_t - 2[T_2]_t - 3[T_3]_t \quad (23)$$

A computer program for the solution of the competitive-consecutive second-order rate equations was written in ASYST vs 4.0. In this routine λ was estimated by numerical integration of water loss with time. Estimations of the various rate constants, along with the initial concentrations of H_2O and unhydrolyzed monomer, were then used to calculate the time-dependent concentrations of the intermediates T_m and water using eq 18. The quality of the estimated rate constants were then evaluated based on the sum of the squared errors between the experimental and calculated curves and by visual inspection of the residuals. Subsequent variations in the rate constant estimates allowed for minimization of these errors. Reported rate constants are the average of three independent data sets collected under identical conditions.

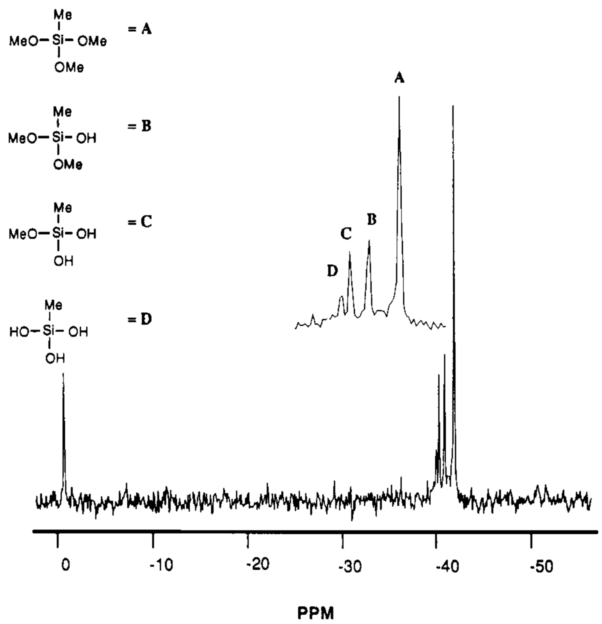

Figure 1. ^{29}Si NMR of ETMS hydrolysis at 0 °C. Conditions: 10 mmol of H_2O, 6.667 mmol of ETMS, 26.67 mmol of MeOH. NMR parameters: spectrometer frequency = 71.7 MHz, 340 scans, spectral width = 10 kHz. Spectrum represents measurement taken from 4.0 to 5.0 min.

The reesterification of a hydrolyzed specie, i.e., the reverse of eq 1

$$RSi(OR')_2(OH) + R'OH \rightarrow RSi(OR')_3 + H_2O \quad (24)$$

has been shown to be insignificant when compared with the much faster forward hydrolysis rates.[17] ^{1}H NMR results on the alcoholysis of tetramethoxysilane by isopropyl alcohol also indicate that the rate of hydrolysis is much faster than the rate of the back reesterification.[31] Because the present kinetic treatment deals only with early reaction times, the contribution of the back reactions to the overall reaction profile can be assumed to be negligible.

Molecular Orbital Calculations. Semiempirical AM1[32] calculations were carried out with the AMPAC program (version 2.1), where the typical parameters were employed.[33] The initial geometries of the silanes and silanols were optimized using PCMODEL (Version 89.0).

Results and Discussion

^{29}Si NMR has been used extensively for identifying the various silicon-containing species in sol–gel reaction mixtures and describing the temporal evolution of hydrolysis and condensation products.[15–26] A representative ^{29}Si NMR spectrum from the acid-catalyzed hydrolysis of ethyltrimethoxysilane (ETMS) is displayed in Figure 1.

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(30) TMOS rate constants were calculated using: $[H_2O] = [H_2O]_0 + 4\{[Q_0] - [Q_0]_0\} + 3[Q_1] + 2[Q_2] + [Q_3]$ for the material balance equation. Water concentration at various times was calculated with an equation analogous to eq 23.

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Even in dilute alcohol at low temperature, hydrolysis of ETMS is rapid. For this reason, a "fast" NMR acquisition sequence was employed to monitor the silicon resonances. Relaxation of the Si nuclei, even in the presence of the spin relaxation agent $Cr(acac)_3$, was incomplete. Control reactions established that the integration of the various silanol species were the same under the fast NMR conditions and when the Si nuclei were allowed to completely relax (>95%, "slow" sequence).[28] Because more transients could be collected by the fast sequence than with the slow sequence, the former resulted in better signal:noise and was therefore used routinely in the kinetic evaluation. As has been previously observed, successive hydrolysis reactions lead to products with ^{29}Si NMR resonances shifted sequentially to lower frequencies.[5,16-19,22-24] The identities of the partially and completely hydrolyzed species denoted in Figure 1 were assigned by comparison with literature examples.[5] In a similar fashion, the identities of the TMOS hydrolysis products were assigned and quantified.[5,16-19,22-24]

Under the reaction conditions used for fast sol-gel formation (low H_2O:Si ratio), typical pseudo-first-order kinetic evaluations are not appropriate for determination of the individual rate constants. In the past, graphical fitting methods have been used to determine rate constants for two competitive-consecutive second-order reactions.[34,35] However, the presence of a third step in this system complicates the overall kinetic description of the reaction and eliminates this method as a viable data analysis technique. For this reason, computer modeling and fitting of the evolution and subsequent hydrolysis of the various silanol species were used to assign values to the rate constants for the individual second-order reactions. Simulations of tetraethoxysilane[17] and TMOS[18] hydrolysis as followed by ^{29}Si NMR have been previously reported. The rate constants reported here were determined by a direct fit of the NMR data and are supported by a statistical analysis of the results. Furthermore, the previous TMOS hydrolysis analysis[18] involved simulating the experimental data with a purely functional group statistical model, which took into account condensation reactions as well. In this work, only short reaction times have been evaluated. This treatment only involves the monomeric species and is free from any complicating influence of the condensation reactions upon the hydrolysis kinetics. Several silanes are also examined here and compared. The range of rate constant values was determined by the standard deviation of the computer fit to the experimental data. A 90% confidence level in the rate constants was achieved in this manner.

With this method, the individual rate constants for the hydrolysis of ethyltrimethoxysilane (ETMS) and tetramethoxysilane (TMOS) could be evaluated at various temperatures between −15 and 0 °C. Using the initial concentrations of silane and water as well as the calculated $[H_2O]$ at various times t (eq 23), formation of all of the silane hydrolysis products could be fit. Rate constants for both ETMS and TMOS hydrolysis above 0 °C could not be fit as the reactions proceed too rapidly for the collection of sufficient data points. A representative plot of the experimentally observed concentrations for the various ETMS silanol species and water, together with the calculated fits, is presented in Figure 2. Figure 2 also contains the numerically integrated fit for water loss, λ.

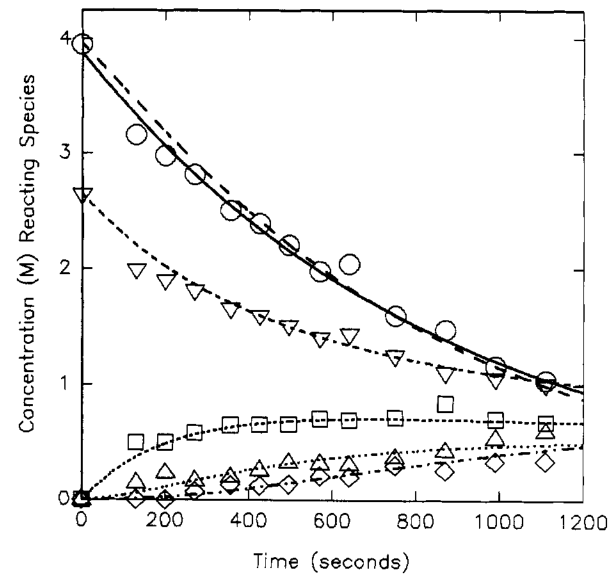

Figure 2. Reaction profile of ETMS hydrolysis at −15 °C, experimental and fitted values for $[H_2O]_t$ and $[T^0{}_m]_t$. Experimental points: $[H_2O]$, □; $[T^0{}_0]$, ▽; $[T^0{}_1]$, ○; $[T^0{}_2]$, △; $[T^0{}_3]$, ◇. Fitted curves: λ, —; $[H_2O]$, – –; $[T^0{}_0]$, - -; $[T^0{}_1]$, - - -, $[T^0{}_2]$, ···, $[T^0{}_3]$, - · -.

Table I. Second-Order Rate Constants ($x = 10^{-4}$, $M^{-1}\ s^{-1}$) for Acid-Catalyzed Methoxysilane Hydrolysis with Low H_2O:Si at Several Temperatures[a]

Si	T (±2) (°C)	k_1	k_2	k_3	k_4[b]
ETMS	−15	4.29 ± 0.35	8.68 ± 1.4	8.76 ± 0.62	
ETMS	−8	5.92 ± 0.16	11.8 ± 1.4	11.9 ± 0.4	
ETMS	0	8.60 ± 0.3	17.8 ± 0.3	17.9 ± 0.8	
TMOS	−15	3.23 ± 0.1	7.89 ± 0.3	12.7 ± 0.5	18.3 ± 0.8
TMOS	−8	3.78 ± 0.3	9.45 ± 0.3	13.5 ± 0.6	16.2 ± 1.5
TMOS	0	4.1 ± 0.5	10.3 ± 0.4	14.3 ± 1.0	16.2 ± 1.5

[a] The values for the second-order rate constants under acid-catalyzed conditions were determined by a calculated fit to experimental ^{29}Si NMR data; each reaction mixture contained 4 equiv of methanol/silane molecule; hydrolysis was initiated by addition of chilled (1 ± 2 °C) 0.01 M HCl; water content was adjusted to correspond to 0.5 equiv of H_2O/initial alkoxide group; amount of $Cr(acac)_3$ [Si: $Cr(acac)_3$] was 1500:1 and 700:1 for ETMS and TMOS, respectively. [b] ETMS hydrolysis involves only three reaction steps.

As seen in Figure 2, a rapid decrease of T_0 is accompanied by an initially sharp increase of the first hydrolysis product, T_1. The concentration of T_1 reaches a plateau and then begins to decrease slightly as T_2 and T_3 are formed. With the addition of a fourth possible silanol product, a nearly identical pattern of hydrolysis is observed for the TMOS hydrolysis. Kinetic fits of the experimental data for ETMS and TMOS were made only in the initial stages of the hydrolysis, i.e., before condensation products were observed by NMR. For both ETMS and TMOS, the time evolution of the various silanol species is similar to that observed for the hydrolysis of tetraethoxysilane.[17]

The second-order rate constants determined by computer fitting of ETMS and TMOS hydrolysis at several temperatures are listed in Table I. From these data, we see, first, that the second-order rate constants increase with the number of hydroxyl substituents attached to silicon for both reactions at all temperatures. Second, in both cases $k_1 \sim {}^1/_2k_2$, whereas k_3 is about equal to k_2 for ETMS, but somewhat larger for TMOS, a trend that continues for k_4 in TMOS. Third, with the exception of

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Table II. Activation Parameters for Acid-Catalyzed Siloxane Hydrolysis[a]

k	A (mol^{-1} s^{-1})	E_a (kcal/mol)	ΔH^* (kcal/mol)	ΔS^* (cal/K mol)
$k_{1_{ETMS}}$	4.8 × 10^4	6.5	5.4	-41
$k_{2_{ETMS}}$	6.4 × 10^4	6.3	5.2	-40
$k_{3_{ETMS}}$	5.5 × 10^4	6.2	5.1	-41
$k_{1_{TMOS}}$	9	2.2	1.1	-58
$k_{2_{TMOS}}$	37	2.5	1.4	-55
$k_{3_{TMOS}}$	4	1.1	0.2	-58

[a] Values calculated from plots of ln k vs $1/T$. Rate constants for TMOS k_4 were not linear over the narrow temperature range examined here.

TMOS k_4, all rate constants demonstrate expected Arrhenius temperature dependence over the narrow range examined here. Fourth, although the first hydrolysis step for ETMS is higher than that for TMOS, the other rate constants for ETMS and the analogous TMOS hydrolyses at all temperatures are very similar.

Clearly, the individual rates of hydrolysis are dependent upon the degree of hydroxyl substitution at silicon. A kinetic analysis of tetraethoxysilane hydrolysis showed the same increase in rate constants with increased hydroxyl substitution.[17] The trend here was observed regardless of the initial estimates used in the fitting routine.

Although the temperature range examined here is small, the activation parameters for hydrolysis of the two monomers can be determined. The activation parameters derived from the ETMS and TMOS hydrolysis rate constants are collected in Table II. A plot of ln k_4 *vs* $1/T$ for TMOS was not linear over the temperature range -15 to 0 °C. For all of the other rate constants, only minimal change in the activation parameters is observed for a family of monomers through each of the hydrolysis steps. This indicates that the same basic mechanism is involved at each step of the hydrolysis. Each of the hydrolysis steps possesses a fairly negative entropy of activation, suggestive of a highly ordered transition state. The ΔH^* and ΔS^* values for both ETMS and TMOS are similar to those previously estimated for other alkyltrialkoxysilanes.[27] Similar parameters have also been determined in some studies of R_3SiOR systems.[36,37] It is also observed from Table II that the A, E_a, and ΔH^* values for the TMOS hydrolysis reactions are smaller than those determined for the corresponding ETMS steps. This reflects a greater temperature dependence of the ETMS hydrolysis.

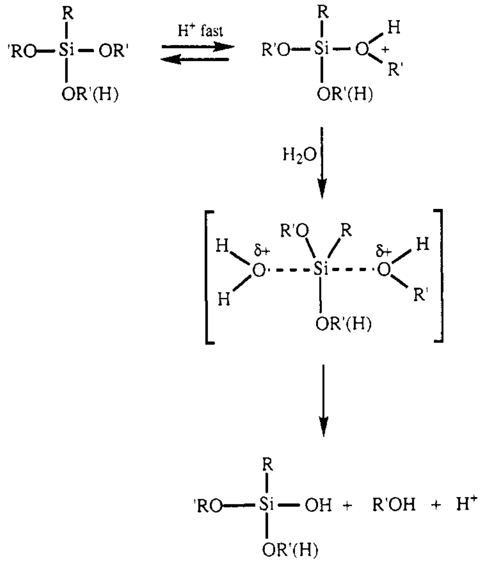
Semiempirical AM1[32] molecular orbital calculations were used to determine the ground state charge density matrix in methyltrimethoxysilane (MTMS), ETMS, and TMOS and the corresponding family of hydrolyzed monomers (see Table III). A slight increase in the ground-state charge is observed for each monomer with increased hydroxyl substitution. However, the results in Table III indicate the positive charge on Si is only altered minimally by hydroxyl substitution for an alkoxyl group. Variations in calculated charges correspond to changes of approximately 6% for MTMS and ETMS, while TMOS is altered ~9%.

The generally accepted mechanism for the acid-catalyzed hydrolysis of an alkoxysilane[5] is presented in Scheme I. Following a fast, reversible protonation step, S_N2 attack by water generates the hydrolyzed product and an alcohol

Table III. Partial Positive Charge Density at Silicon by Semiempirical (AM1) MO Calculations

Si	δ^+ Si
$CH_3Si(OCH_3)_3$	1.57
$CH_3Si(OCH_3)_2(OH)$	1.58
$CH_3Si(OCH_3)(OH)_2$	1.61
$CH_3CH_2Si(OCH_3)_3$	1.57
$CH_3CH_2Si(OCH_3)_2(OH)$	1.58
$CH_3CH_2Si(OCH_3)(OH)_2$	1.61
$Si(OCH_3)_4$	1.62
$Si(OCH_3)_3(OH)$	1.65
$Si(OCH_3)_2(OH)_2$	1.66
$Si(OCH_3)(OH)_3$	1.68

Scheme I. General Mechanism for Acid-Catalyzed Alkoxysilane Hydrolysis



molecule. The relatively large negative entropy of activation values observed here (Table II), suggestive of a highly ordered transition state, are in accord with Scheme I.

Kinetic analyses suggest that both steric[38] and inductive[6b] effects are important for controlling the rate of alkoxysilane hydrolysis.[5] Steric hindrance to nucleophilic attack at silicon has been found to be an important parameter affecting the overall rate of hydrolysis.[5] An increase in steric bulk of the alkoxyl ligands results in a decrease in the overall hydrolysis rate.[38] In addition, substitution with more sterically demanding alkyl groups in alkylalkoxysilane monomers also retards the relative hydrolysis rate.[5,38]

The mechanism in Scheme I involves the dispersal of positive charge in the transition state. If charge dispersal in the transition state is rate determining, then the relative electron-donating capabilities of the alkyl, alkoxyl, and hydroxyl ligands should be reflected in changes in the rate(s) of hydrolysis for successive steps of eqs 1a, 1b, and 1c. It has been previously observed that the overall hydrolysis rate for methyl-substituted methoxysilanes, $Me_xSi(OMe)_{4-x}$ is sensitive to differences in the electron-donating capabilities of methyl and methoxyl substituents, with the rate increasing with increased alkyl substitution.[5,6b] On the basis of this observation, it has been argued that the better electron π release and weaker σ withdrawal by

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(38) (a) Voronkov, M. G.; Mileshkevich, V. P.; Yuzhelevski, Y. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978. (b) Aelion, R.; Loebel, A.; Eirich, F. *J. Am. Chem. Soc.* **1950**, *72*, 5705.

methoxyl than hydroxyl groups stabilize the protonated reactant relative to the transition state, thus raising the activation barrier.[5] Accordingly, to the extent that inductive effects govern the reactivity, Scheme I requires the acid-catalyzed hydrolysis rates of alkoxysilanes to remain constant or to decrease somewhat as a slightly less electron-donating hydroxyl substituent replaces an alkoxyl group.

The observed variation in the rate constants for consecutive hydrolyses under acid-catalyzed conditions is opposite to this predicted trend. Two alternatives can rationalize these results: (1) the mechanism of hydrolysis is different for the hydrolyzed products than for the nonhydrolyzed reactant; or (2) steric effects predominate over inductive effects in controlling the rate of hydrolysis, with the smaller hydroxyl group decreasing steric hindrance at the pentacoordinate Si atom in the S_N2 transition state, facilitating nucleophilic attack by water on the protonated reactant.

A different mechanism in the first and second hydrolysis steps is unlikely. Not only are ETMS and its hydrolysis products chemically similar, but an altered mechanism would most likely be accompanied by appreciable differences in the entropies and enthalpies of activation. The ΔH^* and ΔS^* values for the silane systems examined here remain relatively constant throughout the course of hydrolysis (Table II), indicating that the transition-state geometries and energies are similar in each hydrolysis step.

It is likely, therefore, that the lower steric bulk of a hydroxyl than a methoxyl substituent accounts for the increased reactivity of the hydrolyzed intermediates over the nonhydrolyzed silane. This is based on the reaction trend observed here; namely, larger rate constant values with successive hydroxyl substitutions. Both the ETMS and TMOS hydrolysis reactions were also found to be minimally affected by the extent of hydrolysis substitution. Steric hindrance would be expected to be greatest when the silane is completely coordinated with bulky alkoxyl ligands. Replacement of the first alkoxyl group by a hydroxyl would result in an enhanced rate of reaction if steric influences predominate. The second hydroxyl group would, however, have a lower impact on the steric crowding of the reaction center, so that only a small enhancement of the rate constant would be expected for subsequent hydrolysis steps. This is in accord with the observations reported here. This effect would also predict slower hydrolysis of ETMS than MTMS, as we and others[5,38] have observed.

The results here show that k_1 for ETMS is about twice as large as k_1 for TMOS at all temperatures. However, k_2 for ETMS at a specific temperature is very similar to the TMOS value. Likewise, the k_3 values for the two monomers are similar. Apparently, the increased hydrolytic reactivity of the trialkoxysilanes with respect to the corresponding tetraalkoxysilanes reflects significant differences in the first hydrolysis step. The lower steric bulk of an alkyl than an alkoxy group would have a rate accelerating effect on k_1. With the relief of steric strain in the first hydrolysis, the two monomers then become more equally reactive. In addition, the rate accelerations caused by alkyl for alkoxyl and hydroxyl for alkoxyl substitution follow the same general trend, in which the hydrolysis rate is enhanced. Namely, the first hydroxyl substitution increases the hydrolysis rate, but the relative rate constants are minimally affected by the further hydroxyl substitution.[5] Also, the several orders of magnitude change in Arrhenius factors for ETMS and TMOS are a result of these differences between $k_{1_{\mathrm{ETMS}}}$ and $k_{1_{\mathrm{TMOS}}}$ (Table II). This suggests that the various activation parameters primarily reflect the reactivity of an alkyl substituent relative to an alkoxy group for k_1.

Although the observations reported here deal only with the mechanism of hydrolysis, they may have important implications for the succeeding condensation and cluster growth steps. By reasonably assuming that condensation reactivity is controlled by the same parameters as hydrolysis, steric effects would be expected to predominate during cluster growth. A cluster–cluster growth model predicted for alkoxysilane condensation under acid-catalyzed conditions is consistent with these observations and assumptions.[5,39] Under this model, reactivity between clusters occurs at the "edges" of the oligomers. Steric crowding at some silicon sites would prohibit cluster–cluster condensation and growth.

Conclusions

Computer fitting of ^{29}Si NMR spectra recorded during ETMS and TMOS hydrolysis at low temperatures was used to derive the second-order rate constants for the individual reaction steps. We find that (1) hydroxyl substitution results in an increase in the rate constants for the subsequent hydrolysis reactions; (2) the rate constants of further hydrolysis of ETMS are minimally affected by the extent of hydroxyl substitution; (3) substitution of alkyl for alkoxyl results in different rate constants for the first hydrolysis step only; (4) molecular orbital calculations show that the ground state density at silicon changes minimally with hydroxyl for methoxyl substitution. These results strongly suggest that the rate of hydrolysis is principally controlled by steric rather than inductive effects. The similarity between these observations and those reported for tetraethoxysilane hydrolysis suggests that this effect may be general for the hydrolyses of many alkoxysilane monomers.

Acknowledgment. We gratefully acknowledge the Texas Advanced Technology Program for support of this work. We also thank Dr. Kevin W. Krosley for his assistance with the molecular orbital calculations.

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