J. Am. Chem. Soc. **2000,** *122,* 10063−10072

Neutral Alkoxysilanes from Silica

Hengqin Cheng,[†] Ryo Tamaki,[†,‡] Richard M. Laine,*[,†] Florence Babonneau,[§] Yoshiki Chujo,[‡] and David R. Treadwell[†]

Contribution from the Departments of Chemistry and Materials Science and Engineering, Macromolecular Science and Engineering Center, The University of Michigan, Ann Arbor, Michigan 48109-2136, Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan, and Laboratoire Chimie de la Matiere Condensée, Université de Pierre et Marie Curie, Tour 54 E5, 4 Place Jussieu, 75252 Paris Cedex 05, France

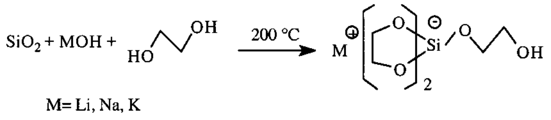
Received May 30, 2000

Abstract: Silica (SiO_2) is found to react readily with ethylene glycol (EGH_2) to form neutral glycoxysilanes in the presence of catalytic amounts of high-boiling organic amines, such as triethylenetetramine (TETA), trishydroxymethyleneaminomethane [$H_2NC(CH_2OH)_3$, $THAMH_3$], and triethanolamine [$N(CH_2CH_2OH)_3$, $TEAH_3$]. Kinetic studies show that these amines offer similar catalytic efficiencies although their pK_b values differ by 3 orders of magnitude. In addition, silica dissolution is found to be pseudo-zero order in silica. These kinetic data can be explained by a rate-limiting step involving release of free base from an intermediate pentacoordinated silicate coincident with the formation of a tetraalkoxysilane. The products from these reactions were characterized by ^1H, ^{13}C, and ^{29}Si solution and solid-state NMR, thermal gravimetric analysis, and mass spectroscopy. Depending on the type and amount of base used, different products form: either neutral tetraalkoxysilanes, such as $Si(OCH_2CH_2OH)_4$ and its soluble oligomers, or neutral pentacoordinate silanes, such as $N(CH_2CH_2O)_3SiOCH_2CH_2OH$ and $H_3N^+C(CH_2O)_3Si^-(OCH_2CH_2O)$. Comparative studies demonstrate that Group I metal hydroxides also catalyze silica dissolution in ethylene glycol with better catalytic efficiencies than the amine bases. The products of silica dissolution using Group I metal hydroxide catalysts were also identified by ^{29}Si solution NMR and mass spectroscopy and found to consist primarily of $Si(OCH_2CH_2OH)_4$ and its oligomeric derivatives.

Introduction

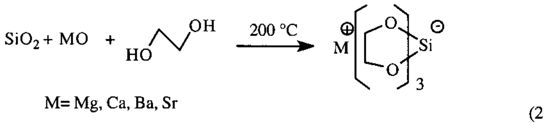
A primary challenge in silicon chemistry is to use silica (SiO_2) as a direct source of chemicals and polymers. To this end, several groups have explored dissolution of silica in basic, aqueous, or nonaqueous environments to produce anionic alkoxy and aryloxy silicates.[1−7] Most recently Kinrade and co-workers demonstrated that aliphatic polyols will react with aqueous silicates to form high concentrations of stable polyolate complexes containing penta- and hexacoordinated alkoxysilanes.[8]

In earlier studies, we explored silica dissolution in excess ethylene glycol (EGH_2) and reported the syntheses of penta- and hexacoordinate anionic glycolato silicate complexes from reactions of silica gel, fused silica, or sand with equivalent amounts of Group I metal hydroxides (reaction 1) or Group II metal oxides (reaction 2).[9,10] Compounds **1** and **2** provide access to novel materials that offer ion conducting,[11] liquid crystalline,[12] charge transfer,[13] or ceramic precursor properties.[14] Compound **1** has also been recently reported to play a key role in the nonaqueous synthesis of silica sodalite.[15]



(1)

1



(2)

2

Kinetic studies on the mechanism of silica dissolution in ethylene glycol promoted by equivalent amounts of alkali hydroxides indicate that silica dissolution is linearly dependent on both [MOH] and silica surface area. We proposed a reaction

---

[†] The University of Michigan.

[‡] Kyoto University.

[§] Université de Pierre et Marie Curie.

(1) (a) Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *Angew. Chem.* **1986**, *98*, 473. (b) Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *Angew. Chem., Int. Ed.* **1986**, *25*, 473.

(2) Corriu, R. J. P.; Perz, R.; Reye, C. *Organometallics* **1988**, *7*, 1165.

(3) Frye, C. L. *J. Am. Chem. Soc.* **1964**, *86*, 3170.

(4) Rosenheim, A.; Raibmann, B.; Schendel, G. *Z. Anorg. Allg. Chem.* **1931**, *196*, 160.

(5) (a) Barnum, D. W. *Inorg. Chem.* **1970**, *9*, 1942. (b) Barnum, D. W. *Inorg. Chem.* **1972**, *11*, 1424.

(6) Weiss, A.; Reiff, G.; Weiss, A. *Z. Anorg. Allg. Chem.* **1961**, *311*, 142, 151.

(7) (a) Boer, F. P.; Flynn, J. J.; Turley, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 6973. (b) Glynn, J. J.; Boer, F. P. *J. Am. Chem. Soc.* **1969**, *91*, 5756.

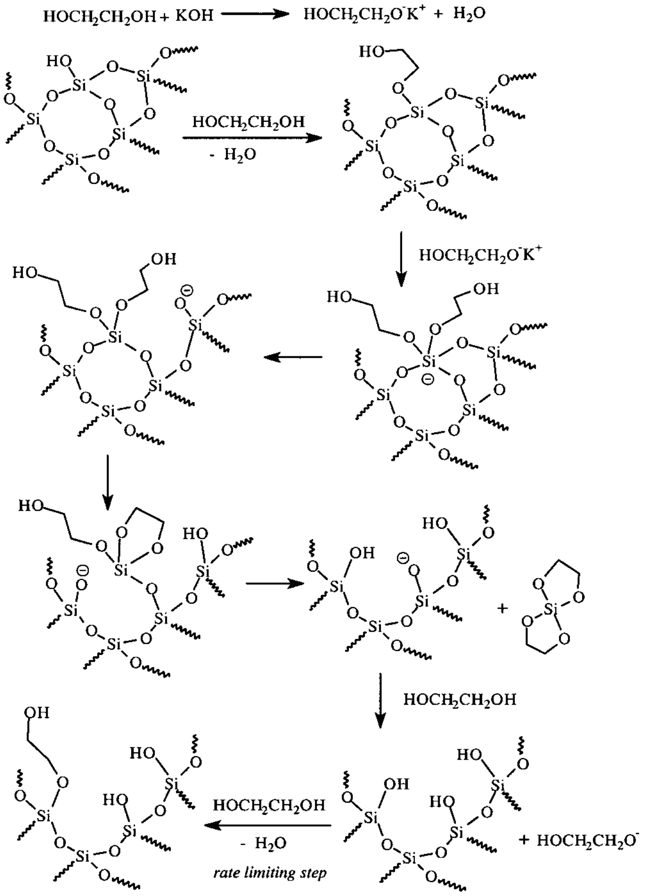
(8) Kinrade, S. D.; Del Nin, J. W.; Schach, A. S.; Sloan, T. A.; Wilson, K. L.; Knight, C. T. G. *Science* **1999**, *285*, 1542.

(9) (a) Laine, R. M.; Blohowiak, K. Y.; Robinson, T. R.; Hoppe, M. L.; Nardi, P.; Kampf, J.; Uhm, J. *Nature* **1991**, *353*, 642. (b) Laine, R. M.; Mueller, B. L.; Hinklin, T. U.S. Patent No. 5,418,298, May 23, **1995**. (c) Laine, R. M. U.S. Patent No. 5,440,011, Aug 8, **1995**. (d) Laine, R. M.; Waldner, K.; Bickmore, C.; Treadwell, D. R. U.S. Patent 5,614,596, March, **1997**.

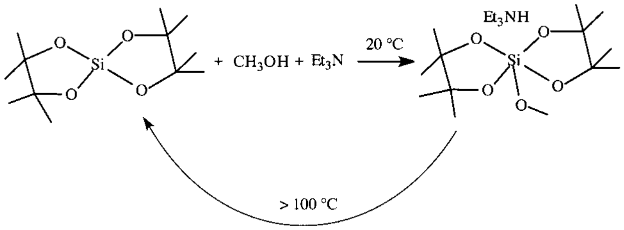
(10) (a) Blohowiak, K. Y.; Treadwell, D. R.; Mueller, B. L.; Hoppe, M. L.; Jouppi, S.; Kansal, P.; Chew, K. W.; Scotto, C. L.; Babonneau, F.; Kampf, J.; Laine, R. M. *Chem. Mater.* **1994**, *6*, 2177. (b) Hoppe, M. L.; Laine, R. M.; Kampf, J.; Gordon, M. S.; Burggraf, L. W. *Angew. Chem.* **1993**, *105*, 283; *Angew. Chem., Int. Ed.* **1993**, *32*, 287.

10.1021/ja001885h CCC: $19.00

Scheme 1. Proposed Reaction Mechanism for Silica Dissolution with 1 Equiv of KOH



Scheme 2. Formation of Spiro-Tetralkoxysilicate Ammonium Salts



mechanism (Scheme 1) driven by constant removal of water, in which ethylene glycol reacts with alkali base to form alkoxide that attacks the silica surface to form pendant alkoxysilanes. Then, through a series of "unzipping" steps, a neutral spirosiloxane is released generating SiO^- groups on the silica surface, which are subsequently protonated to give Si−OH groups. For the reaction to continue, the surface Si−OH groups most likely condense with ethylene glycol producing H_2O as byproduct, which we proposed to be the rate-limiting step. Compound **1** forms when the neutral spirosiloxane reacts with free alkoxide.

At this point, following a thorough review of the literature, it occurred to us that it might be possible to catalyze silica dissolution to produce neutral alkoxysilanes. In contrast to the numerous reports on the syntheses of organic anionic silicate species from silica,[1−10] much less work has been done on the syntheses of neutral alkoxysilanes directly from mineral sources. Goodwin and Kinney have described acidification of mineral silicates to form silicic acid which is then esterified with ethanol or propanol to give good yields of alkoxysilanes.[16] A patent by Bailey describes heating silica in mixed solvents of alcohols (ethanol or propanol) and aromatic hydrocarbons (benzene or xylene) with 0.1 equiv of KOH (CsOH) for 16 h (120 h) at 200 °C (120 °C) to give 50−80% conversion to the corresponding alkoxysilanes.[17] Suzuki et al. find that gaseous dimethyl and diethyl carbonate will react with alkali treated silica at 225 to 325 °C to form the respective alkoxysilanes quantitatively.[18]

We describe here a new, simple, and low-cost synthetic route to neutral alkoxy and polyalkoxysilanes directly from silica. This work was prompted by Frye's observation that spirosilicates will react with methanol and amines (e.g. Et_3N) to form pentacoordinate, anionic silicates that revert to tetracoordinate spirosilicates on heating.[19] These results suggested that catalytic quantities of amine bases might promote silica dissolution to generate neutral alkoxysilanes.

We have now explored this approach and find that silica will dissolve in ethylene glycol in the presence of catalytic amounts of amine bases. Dissolution can also be catalyzed effectively by Group I metal hydroxides under conditions much simpler than used by Bailey et al.[17] In the following, we present detailed studies on this dissolution, including kinetic data which illuminate specific aspects of the dissolution mechanism, and identify the reaction products.

Experimental Section

General Procedures. All chemicals were reagent grade, purchased from standard vendors, and used as received except ethylene glycol (EGH_2). EGH_2 used in these experiments was (1) purchased from standard vendors and used as received, (2) recycled from reaction distillate by double distillation under N_2, or (3) recovered from used antifreeze by double distillation under N_2. All reactions were carried out under N_2 to minimize the chances of exposing the solution to air or moisture.

Analytical Methods. (a) ^{29}Si Nuclear magnetic resonance (NMR) studies were carried out on a Bruker 360 MHz spectrometer using 11° pulse widths and a scanning width of 20000 Hz. The FID signals were treated with a LB value of 5. Samples (200−500 mg estimated by TGA data) in 10−15 mL of EGH_2 were placed in 10-mm NMR tubes with an inner 5-mm NMR tube containing acetone-d_6 as lock solvent and tetramethylsilane (TMS) as an external given reference. Samples were scanned 1000−4000 times.

(b) Solid-state ^{29}Si MAS NMR spectra were recorded (Laboratoire de la Matière Condensée) on a Bruker MSL 400 at 79.5 MHz, using pulse widths of 2 μs (30°), delays between pulses of 30 s, and a spinning rate of 5 kHz.

(c) Solid-state ^{13}C and ^{1}H MAS NMR spectra were recorded on a Bruker MSL 300 (75.5 and 300.1 MHz). ^{13}C NMR spectra were recorded with cross polarization (CP) techniques with contact times of

---

(11) Chew, K. W.; Dunn, B.; Faltens, T. A.; Hoppe, M. L.; Laine, R. M.; Nazar, L.; Wu, H. K. *J. Am. Chem. Soc. Polym. Prprts.* **1993**, *34*, 254.

(12) Ray, D. J.; Laine, R. M.; Robinson, T. R.; Viney, C. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1992**, *225*, 153.

(13) Youngdahl, K. A.; Nardi, P.; Robinson, T. R.; Laine, R. M. *NATO Asi Ser. E: Appl. Sci.* **1991**, *206*, 99.

(14) (a) Kansal, P.; Laine, R. M. *J. Am. Ceram. Soc.* **1994**, *77*, 875. (b) Kansal, P.; Laine, R. M. *J. Am. Chem. Soc.* **1995**, *78*, 529.

(15) (a) Bibby, D. M.; Dale, M. P. *Nature*, **1985**, *317*, 157. (b) van Erp, W. A.; Kouwenhoven, H. W.; Nanne, J. M. *Zeolites* **1987**, *7*, 268. (c) Herron, B.; Carr, S. W.; Klinowski, J. *Science* **1994**, *263*, 1585.

(16) (a) Kenny, M. E.; Goodwin, G. B. U. S. Patent, No. 4,717,773, Jan, **1988**. (b) Kenny, M. E.; Goodwin, G. B. In *Inorganic and Organometallic Polymers*; ACS. Symp. Ser. Vol. 360; American Chemical Society: Washington, DC, 1988; p 238. (c) Goodwin, G. B.; Kenney, M. E. *Adv. Chem. Ser.* **1990**, *224*, 251.

(17) Bailey, D. L.; Snyder, A.; O'Connor, F. M. U.S. Patent No. 2,881,198, April 7, **1959**.

(18) Suzuki, E.; Akiyama, M.; Ono, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 136.

(19) Fry, C. L. *J. Am. Chem. Soc.* **1979**, *92*, 1205. Frye, C. L. *J. Am. Chem. Soc.* **1971**, *93*, 6805.

2 ms, 10 s delays between pulses, and a spinning rate of 5 kHz. Sample sizes for all solid-state spectra were 300−500 mg.

(d) Thermal gravimetric analysis (TGA) was conducted using a TA Instruments 2950 Thermal Analysis Instrument. Samples (30−60 mg) were loaded in platinum pans and heated under N_2 balance (40 cm^3/min) with an air purge (60 cm^3/min), using a high-resolution (Hi-Res 4) program with a maximum ramp rate of 50 °C/min to temperatures of 950 °C.

(e) Mass spectroscopic (MS) analyses were carried out using a VG 70-70-E mass spectrometer (Micromass Corporation) by fast atom bombardment ionization in the positive ion mode (FAB+). The instrument was calibrated using CsI salt clusters. The FAB atom gun was run with xenon gas, at settings of 1 mA and 8 KV voltage. The mass range was scanned from *m*/*z* 2800 to 75 at 8 s/decade and run at 5 kV accelerating voltage. The samples in ethylene glycol were placed directly on the sample target, and three to five scans were signal averaged while being collected in a continuum or MCA mode.

Selected samples were also analyzed by chemical ionization (CI) with ammonia on a VG 70-250-S mass spectrometer (Micromass Corporation). The instrument was calibrated with perfluorokerosene and scanned from *m*/*z* 1000 to 35 at 10 s/decade and 6 kV accelerating voltage.

Standard Conditions for Kinetic Studies. To a 250-mL round-bottom flask containing 100.0 mL of ethylene glycol (EGH_2) were added a certain amount of silica and various amounts of amine or alkali bases. The flask, equipped with magnetic stirring and standard distillation setup, was immersed in an oil bath preheated to 200 ± 2 °C for a pre-set reaction time. The flask was then cooled quickly in an ice water bath. The undissolved silica was separated from the solution by centrifuging for 15 min. This undissolved silica was then washed with about 100 mL of distilled ethanol, followed by separation again using centrifugation. The recovered silica was then heated in a box furnace at 1 °C /min to 60 °C and held for 2 h, then heated at 1 °C/min to 80 °C and held for 2 h, and then finally heated at 5 °C /min to 500 °C and held for 6 h. The heat treatment was used to oxidize any organic residues. The weight of unreacted silica could be weighed then and the amount of silica dissolved determined. All experiments were repeated a minimum of twice. Blanks were also run for each set of kinetic studies.

Comparison of Catalytic Efficiencies of the Organic Amine Bases. Silica (1.50 g, 25.0 mmol) and 10 mol % of each above amine base were added into 100.0 mL of EGH_2 and standard reaction conditions described above were applied. The reaction time was set to 3 h. A blank test, in which only silica and EGH_2 were mixed and no amine base was added, was also heated for 3 h. Dissolution yields were then determined by the method described above. The results are shown in Figure 1.

Effect of Reaction Times for Amine-Catalyzed Silica Dissolution. Silica (1.50 g, 25.0 mmol) and $THAMH_3$ (0.300 g, 2.48 mmol) were added to 100.0 mL of EGH_2 and standard reaction conditions were applied. A series of reaction times were used: 1.5, 3, 6, 9, and 12 h. A blank in which silica and $THAMH_3$ were mixed in EGH_2 with no heating was also examined. The results are shown in Figure 2. A similar reaction was run using 2.48 mmol THAMSiegH. The results are also plotted in Figure 2.

Effects of Initial Amine Concentration on Silica Dissolution. SiO_2 (1.50 g, 25.0 mmol) and 5−150 mol % $THAMH_3$ were added to 100.0 mL of EGH_2 and standard reaction conditions were applied. Reaction time was set to 3 h. A blank was run in which the mixture of silica with ethylene glycol without any amine was heated for 3 h. The results are shown in Figure 3.

^{29}Si NMR Study of Equilibria between Tetra- and Pentacoordinate Silanes. Tetraethoxysilane (TEOS; 2.07 g, 10.0 mmol) was mixed with 36.0 mL of EGH_2 and heated at 155 °C in a 100-mL round-bottom flask equipped with magnetic stirring and a standard Pyrex distillation setup under N_2 to distill off ethanol. To the resulting solution was added 1.00 equiv of base (amine or alkali hydroxide). The mixture was placed in an oil bath preheated to 200 °C for pre-set times (10 min, 1, 3, or 12 h). At the end of each reaction time, the reaction flask was immediately cooled in an ice bath and a ^{29}Si NMR spectrum was recorded. Two peaks were observed for each spectrum: one at −106 ppm and one at −82 ppm. The height of each peak was measured and the ratio of heights (−106 to −82 ppm) was calculated and plotted in Figure 4.

Effects of Reaction Temperature on Silica Dissolution. SiO_2 (1.50 g, 25.0 mmol) and $THAMH_3$ (0.75 g, 6.25 mmol) were added to 100.0 mL of EGH_2 in a 250-mL round-bottom flask equipped with magnetic stirring and standard distillation setup. The mixture was immersed into an oil bath preheated to the desired temperature (170, 180, 190, and 200 °C) using an Omega CN76000 temperature controller. The mixture was heated at that temperature for 3 h before it was immediately cooled by an ice bath. The silica dissolution yield was then determined by the method described in the section of Standard Reaction Conditions. The results are shown in Figure 5.

Effects of Initial Concentration of Alkali Base on Silica Dissolution. Silica was mixed with various amounts of KOH (1−10 mol %) in 100.0 mL of ethylene glycol. Standard conditions were applied to this mixture and the reaction time was set to 1 h. A blank in which silica was mixed with EGH_2 without any base was also performed. The results are shown in Figures 6 and 7.

Effects of Reaction Temperature on Silica Dissolution with Alkali Base Catalysis. Silica mixed with 1 mol % of KOH in EGH_2 was heated for 1 h using standard reaction conditions with the reaction temperature set at 170, 180, 190, and 200 °C. The dissolution yields were determined as described above. The results are shown in Figure 8.

Mass Spectral Studies for Silica Dissolution Catalyzed by Alkali Base. Silica (30.0 g, 0.500 mol) and different amounts of NaOH (from 0.05 to 0.1 equiv) were mixed with 600 mL of EGH_2 in a 1-L round-bottom flask equipped with a magnetic stirrer and distillation head. This mixture was heated to >200 °C to distill off EGH_2 and byproduct water. As distillation continues, additional doubly distilled EGH_2 was added to retain the total reaction volume. Distillation was continued for 30 h to allow a full study of the reactions. A series of samples were taken at different reaction times. These samples were analyzed by mass and ^{29}Si NMR spectroscopy. The results are listed in Table 3.

Synthesis of Si(eg)$_x$. Mixtures of silica (10.0 g, 166 mmol), 5−10 mol % of amine or alkali base, and EGH_2 (500 mL) were heated under N_2 with magnetic stirring in a standard Pyrex distillation setup such that EGH_2 and byproduct H_2O distill off slowly. After all the silica dissolved, the solution volume was reduced to ∼50 mL and a clear liquid was obtained. Further removal of the remaining EGH_2 (10^{-2} Torr/220 °C) gave a cross-linked polymer. This material was characterized by TGA and solid-state MAS ^{29}Si NMR. Characterization data are listed in Table 1.

Synthesis of TEASiegH. Fumed silica (240.0 g, 4.00 mol) and triethanolamine ($TEAH_3$) (565.0 mL, 1.05 equiv) were mixed with ≈3 L of EGH_2 in a 5-L round-bottom flask equipped with a mechanical stirrer and still head. All silica dissolved in 10 h. The solution was kept heating at >200 °C under normal pressure to distill off EGH_2 until the solution was very viscous. Then the solution was heated at 150 °C under vacuum to obtain additional drying. The remaining residue was washed with freshly distilled ethanol, and after filtration, 850 g of white solid was collected (90% yield). Characterization data are listed in Table 2.

Synthesis of THAMSieg. Fumed silica (30.0 g, 0.500 mol) was mixed with 500 mL of EGH_2 in a 1-L round-bottom flask equipped with magnetic stirring and standard still head. Trishydroxymethyleneaminomethane (60.5 g, 0.550 mol) was then added. This mixture was heated to >200 °C to distill off EGH_2 and water produced during the reaction. After all the silica dissolved, the solution volume was reduced initially by simple distillation, followed by distillation under reduced pressure. The resulting solid was washed with dry THF. The resulting pure white solid is isolated in quantitative yield. Characterization data are listed in Table 3.

Results and Discussion

As mentioned above, prompted by Frye's observations,[19] we decided to explore the possibility of using organic amines to catalyze silica dissolution in ethylene glycol. For silica dissolution to proceed, the reaction must be run under conditions where

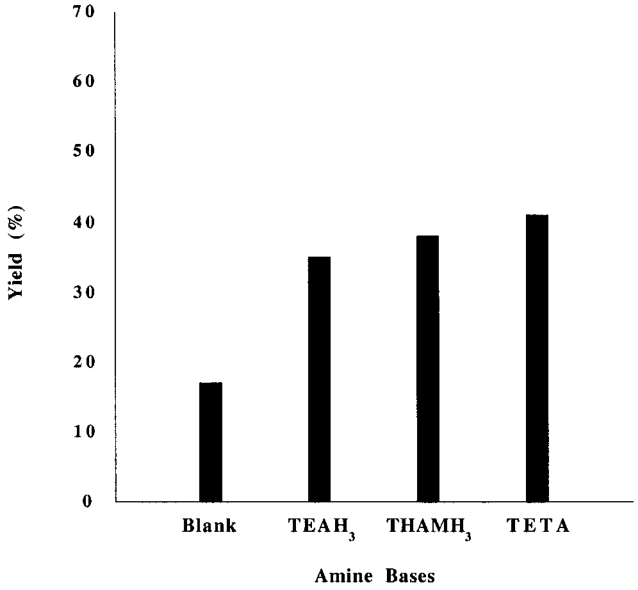
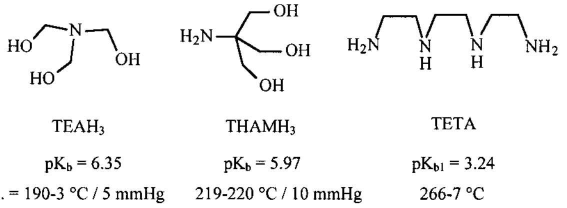


Figure 1. Silica dissolution yields vs type of amine base.

byproduct water is removed continuously. This also obviates the potential for forming zeolites.[15,20,21] Thus, organic amines used in the reaction must have high boiling points to minimized co-distillation. With this in mind, three high-boiling amines were chosen: triethanolamine ($TEAH_3$), trishydroxymethyleneaminomethane ($THAMH_3$), and triethylenetetramine (TETA).



Initial dissolution studies showed that silica would dissolve in ethylene glycol when any one of the above amines was present in catalytic amounts. This result was encouraging and thorough kinetic studies were then carried out.

Standard Conditions for Kinetic Studies. The first step was to establish standard conditions modeled on our earlier studies.[10] A flask containing a mixture of silica and ethylene glycol with various millimolar amounts of amines or alkali base was attached to a distillation setup above an oil bath preheated to 200 ± 2 °C. The bath was raised to immerse the flask and the reaction was run for a pre-set reaction time. The flask was then cooled quickly in an ice water bath. The silica dissolution yields were then determined as described in the Experimental Section. Initial dissolution rates were then calculated. Blanks were also run for each set of kinetic studies.

Catalytic Efficiencies of Organic Bases. The first set of kinetic studies established the catalytic efficiencies of the organic amines chosen. Using the standard experimental procedure, 10 mol % of $TEAH_3$, $THAMH_3$ and 2.4 mol % of TETA (10 mol % nitrogen content) were tested with a reaction time of 3 h. The dissolution yields are plotted in Figure 1. A blank, run without amine, gave 20 mol % silica dissolution.

As Figure 1 shows, all three amines are modest catalysts for silica dissolution with similar catalytic efficiencies as dissolution yields all fall in the 16−20 mol % range (corrected for blank as are all data presented). Although the yields are not high for 3 h reaction times, they clearly show that amines will catalyze dissolution as more than stoichiometric amounts of silica dissolve.

Ethylene glycol with a pK_a of ~15 is quite similar to water.[22−24] Thus, as Frye noted, simple amines are strong enough to deprotonate simple alcohols to form alkoxides.[19] Thus, ethylene glycol should be easily deprotonated by the chosen amine bases to form ammonium alkoxides (TETA pK_{b1} = 3.24,[25] $THAMH_3$ pK_b = 5.97,[26] and $TEAH_3$ pK_b = 6.35[27]), which in turn can be expected to attack the silica surface, initiating a series of steps leading to silica dissolution.

In principle, the differences in catalytic efficiencies among these three amines should be related to their basicities. The literature pK_b values indicate 3 orders of magnitude difference in basicities for these amines. These differences should affect their abilities to deprotonate EGH_2 to form the alkoxide, which is the reactive intermediate for silica dissolution.[10] However, the dissolution yields do not reflect these differences. All three amines have similar "apparent" basicities toward silica dissolution in EGH_2.

A plausible explanation (see below) for this behavior was sought through further kinetic studies, which were conducted also with the goal of improving dissolution rates. Below we first present the results from kinetic studies examining the effects of reaction time, temperature, and amine concentrations on the dissolution rates, followed by a discussion of possible dissolution mechanisms.

Reaction Time. A second set of kinetic studies was carried out to examine the effects of reaction time on silica dissolution. $THAMH_3$ was used for this set of studies. Data are plotted in Figure 2. A blank test consisted of stirring a mixture of silica, EGH_2, and $THAMH_3$ without heating for 3 h which results in 13 mol % silica dissolution. Figure 2 clearly shows the catalytic effects of $THAMH_3$ in silica dissolution as over 80 mol % of the silica dissolves in 12 h with the aid of 5 mol % base.

An important additional observation seen in Figure 2 is that dissolution is linear over the 12 h reaction period, implying a constant dissolution rate. This suggests that the rate determining step does not involve silica since the total silica surface area should change significantly with reaction times. Furthermore, reaction rates should diminish as observed in our previous dissolution studies with equivalent amounts of alkali bases.[10]

The data from Figure 2 were quite confusing initially. As discussed above, the first step in silica dissolution is most likely deprotonation of EGH_2 by amine to form an alkoxide as an active intermediate. One might interpret the data from Figure 2 to suggest that the slow step is formation of alkoxide. However, if this were true, we would have observed a much higher silica dissolution rate for TETA with a pK_b of 3 vs the other two amines with pK_b values of ~6, which contradicts the Figure 1 data showing that all three amines give similar dissolution yields despite the differences in their basicities.

---

[20] Szostak, R.; *Molecular Sieves. Principles of Synthesis and Identificaion*; Van Nostrand Reinhold: New York, 1989; Catalysis Series.

[21] (a) Qisheng, H.; Shouhua, F.; Ruren, X. *J. Chem. Soc., Chem. Commun.* **1988**, 1486. (b) Qisheng, H.; Ruren, X. *J. Chem. Soc., Chem. Commun.* **1992**, 168.

[22] Arnet, E. M.; Small, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 808.

[23] Ballinger, P.; Long, F. A. *J. Am. Chem. Soc.* **1959**, *81*, 1050.

[24] Takahashi, S.; Cohen, L. A.; Miller, H. K.; Peake, E. G. *J. Org. Chem.* **1971**, *36*, 1205.

[25] (a) Jonassen, H. B.; LeBlanc, R. B.; Meibohm, A. W.; Rogan, R. M. *J. Am. Chem. Soc.* **1950**, *72*, 2430. (b) von Schwarzenbach, G. *Helv. Chim. Acta* **1950**, *33*, 975.

[26] Glasstone, S.; Schram, A. F. *J. Am. Chem. Soc.* **1947**, *69*, 1214.

[27] (a) Alner, D. J.; Smeeth, A. G. *J. Chem. Soc.* **1958**, 4207. (b) Bates, R. G.; Schwarzenbach, G. *Helv. Chim. Acta* **1954**, *37*, 1437.

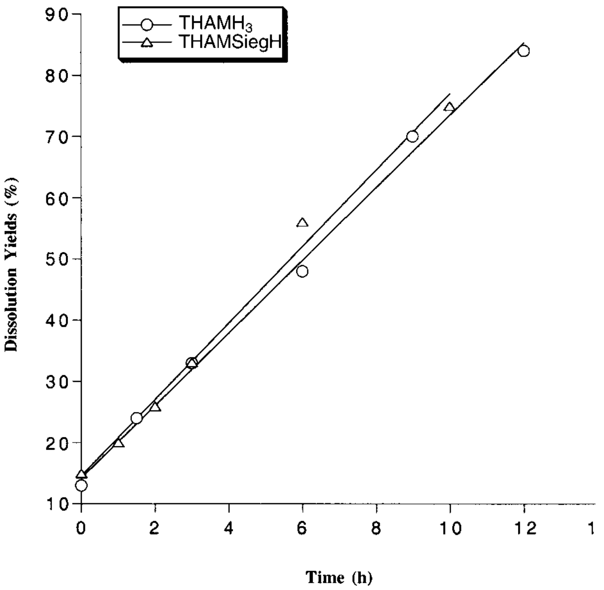
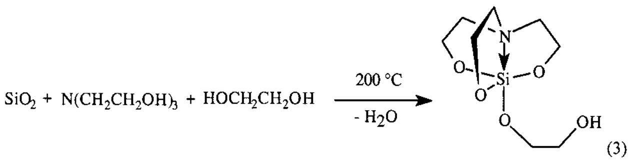


Figure 2. Silica dissolution as a function of reaction time with 5 mol % THAMH$_3$ or THAMSiegH.

Amine Concentration Studies. A third set of kinetic studies was run to explore the effects of initial base concentrations on dissolution rates by using different initial THAMH$_3$ concentrations under standard reaction conditions. Theoretically, if THAMH$_3$ functions only as catalyst, the reaction rate should be linearly dependent on initial THAMH$_3$ concentration. The Figure 3 results do not show such a trend.

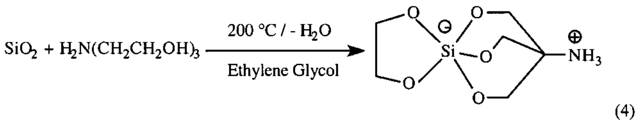
Although reaction rates increase with increases in initial THAMH$_3$ concentrations, the increase is not linear and reaction rate increases fall behind increases in initial THAMH$_3$ concentrations. This change in dissolution rates can be explained if THAMH$_3$ also acts as a reactant in addition to serving as a catalyst.

This was not unexpected because from previous studies, we know that TEAH$_3$ reacts with silica to form silatrane glycol when equivalent amounts are used, (3). Thus, we examined silica dissolution in EGH$_2$ with an equivalent amount of THAMH$_3$ and found reaction 4 (see product identification section). This suggests that even when THAMH$_3$ is used in catalytic amounts, reaction 4 occurs. However, if compound **4** can also react with EGH$_2$ to generate tetraalkoxysilanes and release "free" amine, then this may be the source of base needed to catalyze silica dissolution. Because EGH$_2$ is used in large excess, it is likely that the tetraalkoxysilane formed would be Si(OCH$_2$CH$_2$OH)$_4$ [Si(egH)$_4$]. Thus, if we can observe an equilibrium between compound **4** and Si(egH)$_4$, it likely provides some evidence for this assumption.



(3)

3



(4)

4

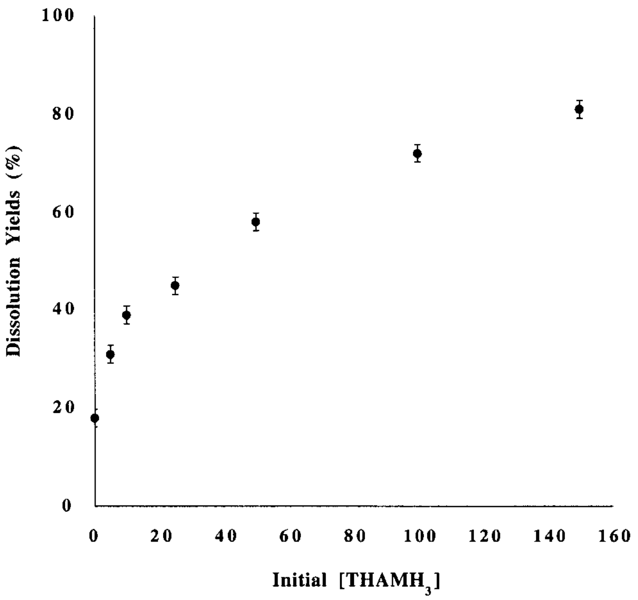
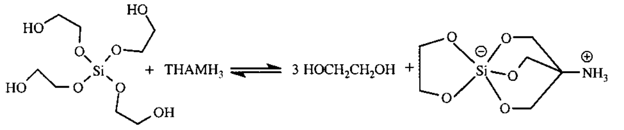


Figure 3. Silica dissolution as a function of initial [THAMH$_3$].

^{29}Si NMR Evidence for Proposed Equilibrium. As mentioned above, an equilibrium between tetra- and pentacoordinated silane species may exist. For THAMH$_3$-catalyzed reactions, the likely equilibrium is given in eq 5. To test this possibility, tetraethoxysilane (TEOS) was mixed with excess EGH$_2$ and heated at 155 °C to form Si(egH)$_4$ by distillative removal of ethanol. The resulting Si(egH)$_4$ was cooled to room temperature before an equivalent amount of THAMH$_3$ was added. The mixture was then heated at 200 °C for a pre-set time (10 min and 1, 3, and 12 h) and then cooled immediately in ice water. ^{29}Si NMRs were then recorded. Two signals were observed for all samples: a major signal at −106 ppm and a weak signal at −82 ppm, corresponding to penta- and tetraalkoxy silanes, respectively. This observation clearly supports the existence of the above equilibrium.



(5)

A crude estimate of the equilibration process can be obtained by measuring the peak heights of the two signals for each spectrum and calculating the relative ratio of these two signals. The peak ratios as a function of reaction time are plotted in Figure 4, which indicates that the equilibrium favors formation of the pentacoordinate species. Furthermore, Figure 4 suggests that this equilibrium is established very quickly as the peak ratio at 10 min is quite close to the remaining data points. The ratios of the two peak heights are ~8:1, which roughly indicates the ratio of the two species in solution.

Similar experiments were run with TETA. That is, the Si(egH)$_4$ in EGH$_2$ was mixed with an equivalent amount of TETA following the same experimental procedure described above and in the Experimental Section, and ^{29}Si NMRs were taken. Again, we observed two signals, one at −106 and one at −82 ppm for reactions of 10 min, 1 h, and 3 h with the −106 ppm peak as the major peak. The ratio of the two peaks is ~11 (−106/−82

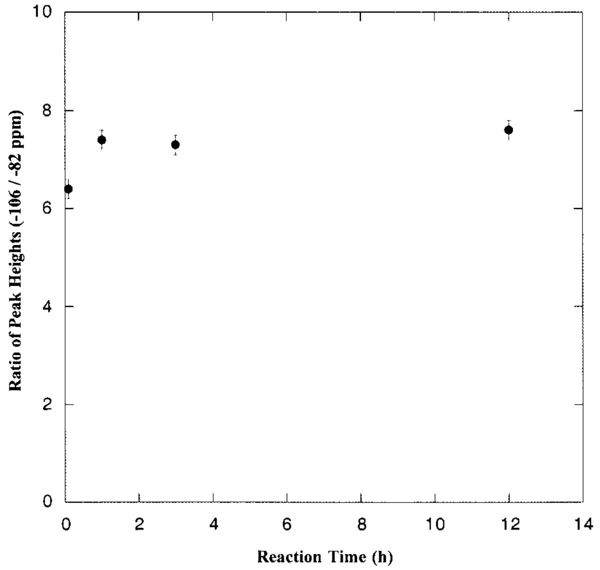
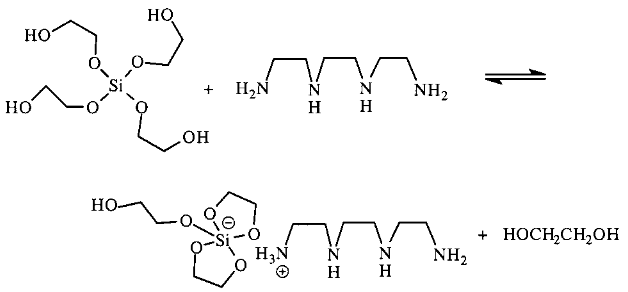


Figure 4. ^{29}Si NMR peak height ratios −106:−82 ppm for reaction of Si(egH)$_4$ with equivalent amounts of THAMH$_3$ as a function of reaction time.

ppm) for these reaction times. This supports the assumption that the equilibrium between the tetraalkoxysilanes and the pentaalkoxysilicates strongly favors the formation of pentaalkoxysilicates. Similar to the THAMH$_3$ reaction, equilibration is very quick as the 10-min sample has a peak ratio almost identical to those at longer reaction times.



(6)

Temperature Effects. A fourth set of kinetic studies was run to follow silica dissolution as a function of temperature at a constant [THAMH$_3$] of 25 mol %. The results, plotted in Figure 5a, indicate that the dissolution process over the 170 to 200 °C range has an activation energy of 58 kJ/mol or 14 kcal/mol (Figure 5b).

Silica Dissolution Mechanism with Catalytic Amounts of Amine Bases. Kinetic studies show that the three amines, TETA, TEAH$_3$, and THAMH$_3$, all catalyze silica dissolution in EGH$_2$. The catalytic efficiencies are quite similar despite 3 orders of magnitude differences in basicities. The dissolution rates appear to be pseudo-zero order with respect to silica surface area. ^{29}Si NMR studies reveal the existence of equilibria between the free amines and tetraalkoxysilanes and the ammonium pentaalkoxysilicates that favors the pentaalkoxysilicates. With the above facts in mind, we can propose a dissolution mechanism similar to that shown in Scheme 1.

Dissolution most likely begins with amine deprotonation of ethylene glycol to form an alkoxide and ends with the release of spirosiloxane from the silica surface (Scheme 3). In addition to the steps shown in Scheme 1, the equilibria shown in (5) and (6) are rapidly established such that most of the amine base in solution reacts with tetraalkoxysilane to form the pentaalkoxysilicates. The overall effect is that the concentration of "free" alkoxide/amine in solution, essential to the silica dissolution process, drops to such a low level that (1) the differences in basicity between these amines are no longer relevant and (2) the silica surface areas are large enough to be treated as a constant, resulting in pseudo-zero order reaction rates.

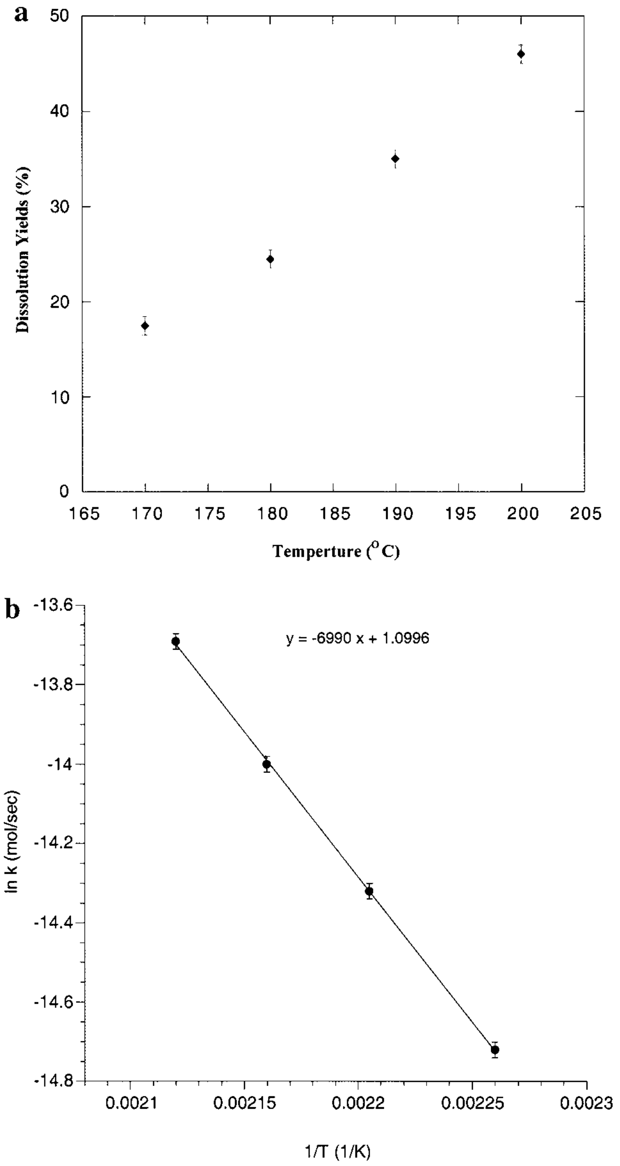
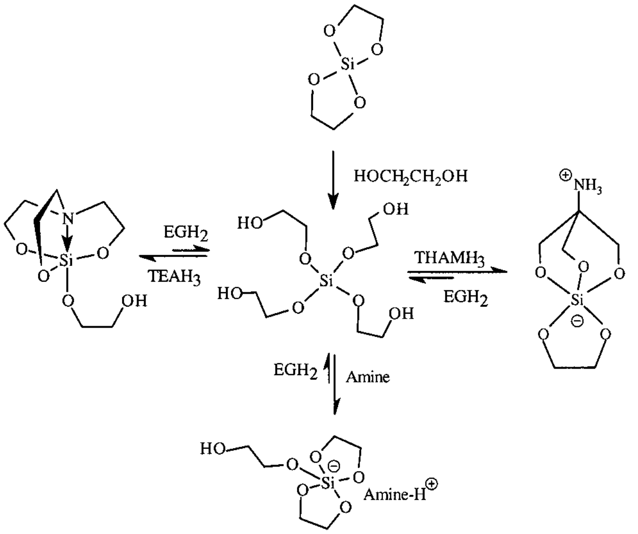


Figure 5. (a) Silica dissolution as a function of temperature with 25 mol % THAMH$_3$. (b) Arrenius plot for part a.

These equilibria strongly control the rate-limiting step for amine-catalyzed silica dissolution. In our previous studies with equivalent amounts of alkali base, water removal from the silica surface was proposed to be the rate-limiting step.[10] However, for silica dissolution with catalytic amounts of amines, the kinetic studies suggest that the above-mentioned equilibria limit the "free" amine concentrations so much that the rate-limiting step changes to the step of generating "free" alkoxide. Further support for this comes from kinetic studies wherein isolated THAMSiegH (see below and the Experimental Section) is used in place of added free THAMH$_3$ in the dissolution vs time studies (Figure 2). The dissolution rate is essentially identical and linear to that obtained with free THAMH$_3$.

Scheme 3. Proposed Mechanism for Silica Dissolution with Catalytic Amounts of Organic Amines



Alkali Base Catalysis. Our previous studies demonstrated that stoichiometric amounts of alkali bases dissolve silica in ethylene glycol to produce pentacoordinate anionic glycolatosilicate complexes.[10] However, their utility as catalysts was not tested. Given that organic amines catalyze silica dissolution in ethylene glycol, we decided to run a comparative experiment wherein 10 mol % of KOH was used under the standard reaction conditions. In 3 h, 70 mol % of silica dissolution was obtained, much higher than found with the amine bases, which are all ~20 mol % under the same conditions. Following this initial result, other alkali bases were also tested under identical conditions using 1 h instead of 3 h reaction times to obtain initial dissolution rates. All these alkali bases give similar dissolution yields of ~40 mol %.

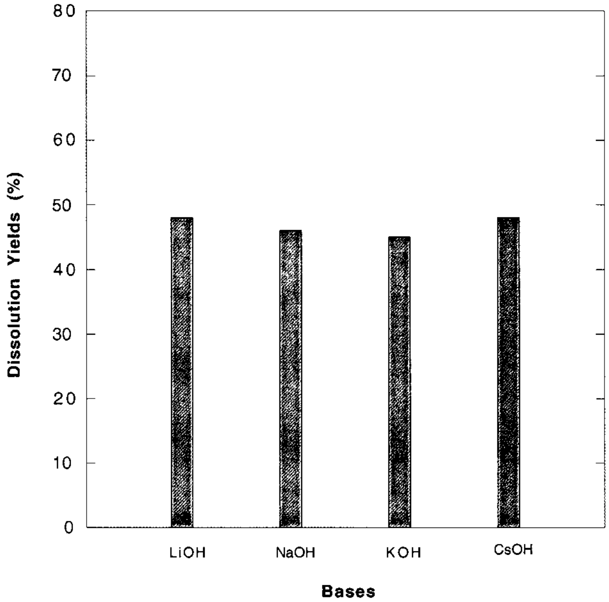


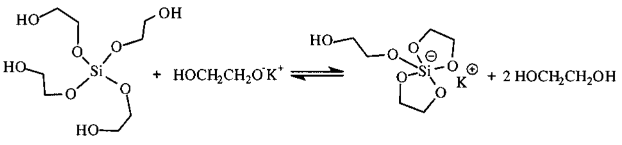
Figure 6. Silica dissolution with alkali hydroxides (1 h, 1 mol % MOH).

These much faster dissolution rates for the alkali base-catalyzed reaction reflect the differences in base strengths between the alkali and amine bases. To further understand the catalytic effects of alkali bases, kinetic studies similar to those done with the amines were conducted. Since all the alkali bases provide similar catalytic efficiencies, KOH was chosen for these studies.

Base Concentration Studies. First, silica dissolution as a function of initial [KOH] was examined. Standard reaction conditions were applied with KOH at 1−10 mol % of silica used. Given the fact that the above comparative tests showed 70% dissolution in 3 h which does not allow comparison of initial rates, 1 h reaction times were used. A blank without KOH, heating for 1 h, gave 13 mol % dissolution.

Results from this set of experiments, plotted in Figure 7, show that silica dissolution increases linearly as [KOH] increases up to 3 mol % (Figure 7b). This linear relationship is expected for a purely catalytic reaction, unlike that found for THAM, Figure 3. At 3 mol % [KOH], dissolution is essentially quantitative, thus the data beyond [KOH] of 3 mol % lose their meaning.

^{29}Si NMR Study of Possible Equilibria. Similar to the studies of amine reactions, $Si(egH)_4$ was mixed with an equivalent amount of $KOCH_2CH_2OH$ and heated at 200 °C for a set of time before it cooled and NMR spectra were taken. A single peak at −105 ppm is observed for all spectra taken from this series, even for sample heated just 15 min. However, the S/N ratio is ~15:1 (Bruker 360 MHz) after 3000 scans, which sets the signal detection limit. Thus, if the equilibrium between penta- and tetraalkoxysilanes is >15:1, it cannot be detected.



(7)

The primary difference between (7) and equilibria 5 and 6 is that in (7), alkoxide is directly regenerated on equilibration, unlike in (5) or (6) where the amine is first produced and alkoxide must then be regenerated by deprotonation of EGH_2.

Temperature Effects. The effect of temperature on the initial reaction rates for KOH-catalyzed silica dissolution is plotted in Figure 8a. The activation energy calculated from Figure 8b gives 20.6 kJ/mol, or ~5 kcal/mol. This activation energy is lower than the 14 kcal/mol value found in our previous study with equivalent amounts of KOH,[10] which implies a different rate-limiting step.

Dissolution Mechanism with Alkali Base Catalysis. Silica dissolution catalyzed by alkali base most likely goes through the same cycle as the amine-catalyzed one. However, the important difference is the rate-controlling step. In the amine-catalyzed reaction, generation of free amine or alkoxide thereafter appears to be rate limiting. In the alkali base catalyzed reaction, the alkoxide is directly regenerated during equilibration per (7); however, the ^{29}Si NMR attempts to detect the presence of the tetraalkoxysilane in a 1:1 mixture of alkoxide and tetraglycoxysilane after just a few minutes of reaction were unsuccessful. This suggests that this equilibrium also strongly favors the pentacoordinated species. Hence, direct generation of the alkoxide may still be rate limiting in alkali base catalysis but it is not complicated by a deprotonation step. However, one crucial set of experiments proves the process quite different.

A study of dissolution rate vs time (analogous to the Figure 2 studies) reveals that the rate slows (data not shown) in a typical first-order fashion. This indicates that the rate-determining step occurs after glycoxide attack at the silica surface. The found E_a of 5 kcal/mol is different from the 14 kcal/mol found for the stoichiometric reaction, thus the rate-controlling step must be different. It may be that the slow step involves one of the surface

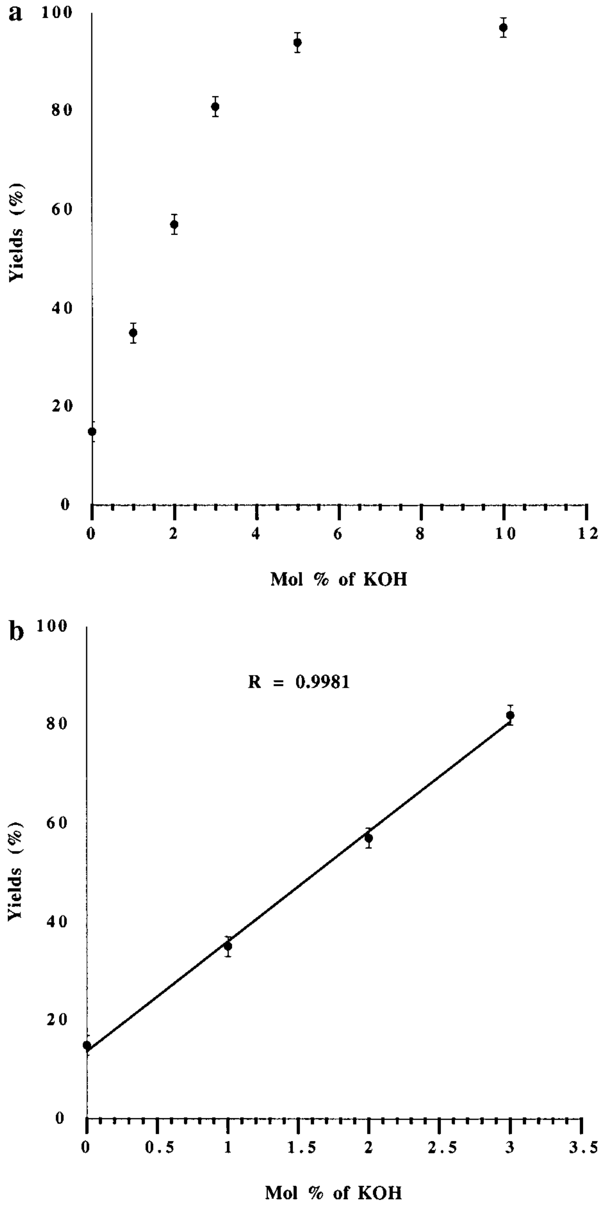


Figure 7. (a) Silica dissolution as a function of KOH concentration. (b) Expansion of the plot for [KOH] up to 3 mol %.

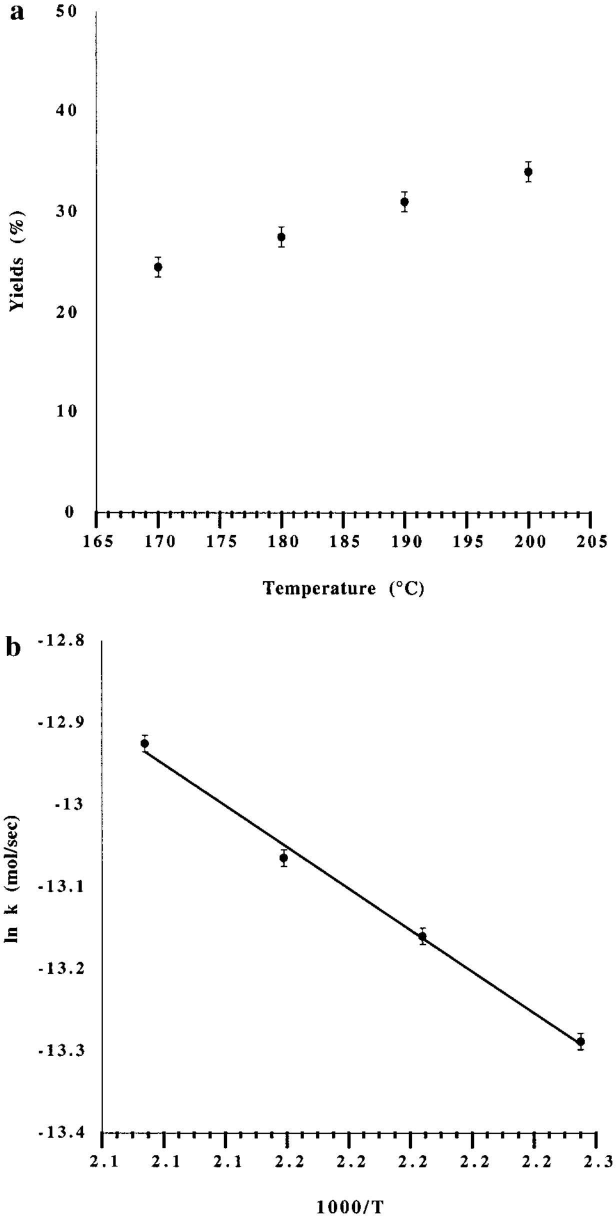
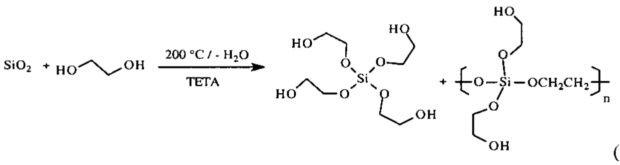


Figure 8. (a) Silica dissolution as a function of temperature with 1 mol % KOH. (b) Arrenius plot.

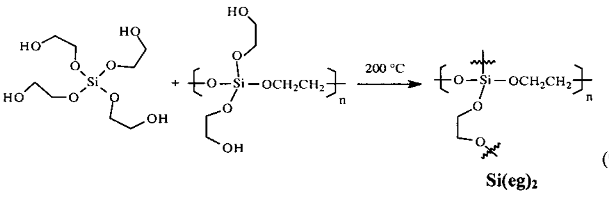
reorganization processes proposed in Scheme 1; however, further studies are necessary to delineate the exact course of events.

Characterization of the Products from Silica Dissolution. To better understand silica dissolution in EGH_2 catalyzed by either high-boiling amines or alkali bases, we attempted to isolate and identify the dissolution products.

TETA-Catalyzed Dissolution. Silica dissolution in ethylene glycol using catalytic amounts of TETA under continuous distillation conditions gives a clear solution with a ^{29}Si NMR exhibiting a single peak at − 82 ppm, which is in the same position as seen for neat $Si(OEt)_4$. This suggests the formation of neutral alkoxysilanes in solution. The simplest structure would be a spirosiloxane, $Si(OCH_2CH_2O)_2$, *which would be expected if the mechanism shown in Scheme 1 is correct*. However, Frye's efforts to prepare this compound were unsuccessful.[28] It is likely that in the presence of excess ethylene glycol and some base, this spirosiloxane reacts with ethylene glycol to form $Si(OCH_2CH_2OH)_4$ [$Si(egH_4)$] and/or oligomers thereof. No compounds containing Si−O−Si bonds are present in solution since only one singlet at −82 ppm is observed, whereas species with Si−O−Si bonds appear at ca. −97 ppm (see below).



(8)



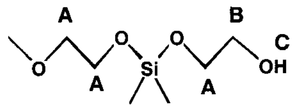
(9)

Continuous removal of solvent from the TETA-catalyzed dissolution in vacuo (220 °C) gives a brittle, transparent cross-linked polymer [$Si(eg)_2$] (reactions 8 and 9). This solid

---

(28) Frye, C. L. *J. Am. Chem. Soc.* **1969**, *34*, 2496.

Table 1. $Si(eg)_2$Characterization Data

	$Si(eg)_x$ 
^{1}H NMR	5.26,5.22 (br,2H)^a **C** 3.90 (br, 1H)^a **B** 3.74, 3.62 (8H)^a **A**
Solid State ^{1}H MAS NMR	5.24 **C** 3.90 **B** 3.65 **A**
^{13}C NMR	65.8^a 65.2 63.5
Solid State ^{13}C MAS NMR	63.7 (major) **A** 62.5 **B**
^{29}Si NMR	-82.1 (major) -89.0 (trace)^{b,c} -96.3 (trace)^{b,c}
Solid State ^{29}Si MAS NMR	-81.5 (major) -88.3 (trace)^c -95.3 (trace)^c -104.2 (trace)^d
Ceramic Yield for x=2 (Calc.)	39.8 % (40.5 %)
%C (Calc.)	31.31 (32.40)
%H (Calc.)	6.06 (5.44)
%N (Calc.)	0.69 (0.0)

[a] Sample dissolved in EG-d_6. Chemical shift of residual ^{1}H (in CD_3OD) δ 5.21 (br), 3.34 (multiplet); ^{13}C δ 62.31 (pentet, $J_{CD} = 21.3$ Hz). [b] Peak present in some samples only. [c] Species containing Si−O−Si linkages. [d] Pentacoordinate silicon.

completely redissolves in hot EGH_2. The solution ^{29}Si NMR of this redissolved $Si(eg)_2$ in EG exhibits a major peak at −82.1 ppm along with minor peaks at −88.3, −96.3, and −104.2 ppm. The solid-state ^{29}Si NMR was also taken and exhibits the same peaks. The NMR data are listed in Table 1.

As mentioned above, the peak at −82.1 ppm arises from tetraalkoxysilane. The −104.2 ppm peak arises from the ammonium analogue of compound **1** formed from the residual TETA retained in the solid (see below). The two peaks at −88.3 and −96.3 ppm most likely result from formation of Si−O−Si containing species during the solvent removal process. For example, the polymeric species $Si(eg)_2$ on prolonged heating may undergo β-elimination reactions leading to formation of $Si{-}OCH{=}CH_2$ and Si−OH in the presence of amine bases. The latter goes on to form Si−O−Si bonds. Indirect support comes from the observation that the −88.3 and −96.3 ppm peaks in ^{29}Si solution and solid-state NMR spectra are more significant for products obtained following prolonged heating at 220 °C. Nevertheless, these peaks are small, which suggests that the Si−O−Si content is low.

TGA analysis of the dry solid gives a ceramic yield of 39.8%. If we assume that the solid is polymeric "$Si(eg)_2$" (FW = 148.19 Da), and that $Si(eg)_2$ decomposes only to SiO_2, then the calculated ceramic yield would be 40.5%, which is very close but a little higher than the observed value. Chemical analysis of the dry solid gives C = 31.3, H = 6.1, and N = 0.69. If the N content defines the residual TETA, one can recalculate the expected ceramic yield of this solid to be 39.8%, which is exactly that found by TGA, supporting the formulation of a fully crosslinked polymer, $Si(eg)_2$.

The TGA analysis also shows this $Si(eg)_2$ polymer has good thermal stability in dry, synthetic air to ~390 °C, which suggests potential utility as a fire retardant material. $Si(eg)_2$ can also be easily transformed to other useful silicon-containing compounds (Scheme 4).

Scheme 4. Transformation of $Si(eg)_2$

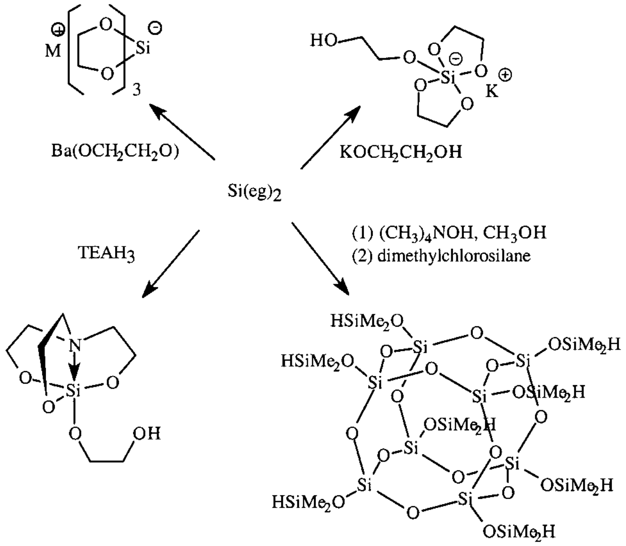
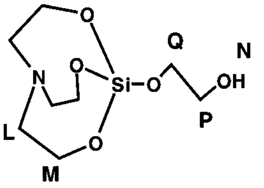


Table 2. Silatrane Glycol Characterization Data

Compound	TEASiegH 
^{1}H NMR	5.21^a **N** 3.80(t) **M** 3.60(t) **Q** 3.33(t) **P** 2.98(t) **L**
^{13}C NMR	63.5^a **Q** 62.6 **P** 57.8 **M** 50.9 **L**
^{29}Si NMR	-97.6^b
Ceramic Yield % (Calc.)	25.53 (24.93)
%C (Calc.)	40.06 (40.83)
%H (Calc.)	7.24 (7.28)
%N (Calc.)	6.46 (5.95)
High-res. mass spec.	235.0876 calc. 235.0882 found

[a] Sample dissolved in EGH_2-d_6. Chemical shift of residual ^{1}H (in CD_3OD) δ 5.21 (br), 3.34 (multiplet); ^{13}C δ 62.31 (pentet, $J_{CD} = 21.3$ Hz). [b] Sample dissolved in EGH_2.

Triethanolamine Reactions. Silatrane glycol (TEASiegH) can be produced directly from silica in quantitative yield (reaction 3). The compound has been characterized by high-resolution MS, solution NMRs, chemical analysis, and TGA as summarized in Table 2.[29]

Silatrane glycol can be used immediately in conjunction with alumatrane $[N(CH_2CH_2O)_3Al]$ and related compounds to formulate precursors to mullite $(3Al_2O_3{\cdot}2SiO_2)$, cordierite $(2MgO{\cdot}5SiO_2{\cdot}2Al_2O_3)$,[30] barium aluminosilicate (BAS, $BaO{\cdot}2SiO_2{\cdot}Al_2O_3$), strontium aluminosilicate (SAS, $SrO{\cdot}2SiO_2{\cdot}Al_2O_3$),[30] and porous silicon oxynitride particles.[31] Additional studies show that silatrane glycol is soluble and stable in cold, neutral water for days.[32] We have also successfully used silatrane glycol as a starting material to synthesize other silatrane compounds

---

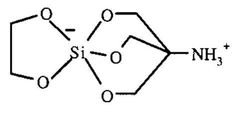
(29) Laine, R. M.; Treadwell, D. R.; Mueller, B. L.; Bickmore, C. R.; Waldner, K. F.; Hinklin, T. R. *J. Mater. Chem.* **1996**, *6*, 1441.

(30) Laine, R. M.; Sutorik, A. C.; Neo, S. S.; Treadwell, D. R. *J. Am. Ceram. Soc.* **1998**, *81*, 1477.

(31) Laine, R. M.; Bickmore, C. R. *J. Am. Ceram. Soc.* **1996**, *79*, 2865.

(32) Cheng, H.; Laine, R. M. *New J. Chem.* **1999**, *23*, 1181.

Table 3. THAMSieg Characterization

Compound	
^{1}H NMR	3.4 (s, 6H) 3.2 (s, 430H)
^{13}C NMR	63.5 62.8 56.7
^{29}Si NMR	-106
%C (Calc.)	34.5 (34.8)
%H (Calc.)	6.6 (6.3)
%N (Calc.)	7.1 (6.8)

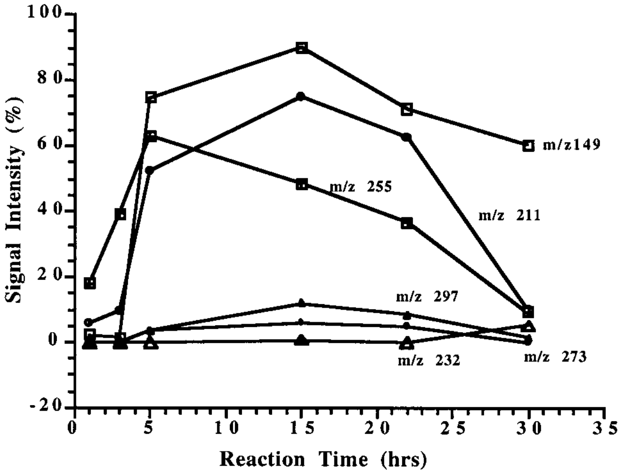


Figure 9. MS peak intensities vs reaction time for a 5 mol % NaOH catalyzed silica dissolution.

containing potentially polymerizable groups. These chemical transformations have been reported separately.[32]

Trishydroxymethyleneaminomethane Reactions. As mentioned above, THAMH$_3$ serves as a catalyst at low concentrations but functions as a reactant at high concentrations. White solid can be isolated from the reaction of silica with an equivalent amount of THAMH$_3$ in EGH$_2$ by removing the excess EGH$_2$ under vacuum. ^{29}Si, ^{1}H, and ^{13}C NMR spectra and chemical analysis all agree with the proposed structure (Table 3).

Products from Alkali Bases Catalyzed Silica Dissolution. The reaction solutions obtained using catalytic amounts of NaOH were examined by NMR. All give similar NMR signals (Table 3). Typically, three signals are observed: a major peak at −82.1 ppm and two minor peaks at −89.0 and −105.9 ppm. The −105.9 ppm peak corresponds to $Na^+[HOCH_2CH_2OSi(OCH_2CH_2O)_2]^-$. The major peak at −82.1 ppm, identical to the product from amine-catalyzed silica dissolution, suggests the tetraalkoxysilane, $Si(egH)_4$, and/or its oligomeric derivatives are the major products in solution. Similar to amine-catalyzed reactions, the peak at −89.0 ppm may arise from Si−O−Si bonds.

Mass spectra (MS) using fast atom bombardment in positive ion mode (FAB+) were also obtained. A typical plot of ion intensity as a function of reaction time is shown in Figure 9. The molecular peak corresponding to $Si(egH)_4$ should be at *m*/*z* 273 ($M + H^+$). But the relative intensity of this peak is very low in most cases. The peaks at *m*/*z* 149 and 255 have relatively high intensities. These are likely fragment peaks of the molecular ion: the *m*/*z* 255 results from the ($M + H^+$) molecule losing one molecule of H_2O and the *m*/*z* 149 is the ($M + H^+$) molecule losing two molecules of EGH_2, or the putative spirosiloxane (Figure 10).

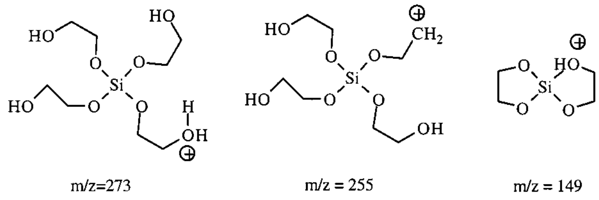


Figure 10. Proposed structures for species observed in MS spectra.

Thus, the NMR and MS data support the conclusion that the tetraalkoxysilanes, $Si(egH)_4$, and its oligomeric derivatives are the main components of silica dissolution in ethylene glycol. As ethylene glycol is removed, the degree of cross-linking increases and finally completely cross-linked $Si(eg)_2$ is formed.

Conclusions

New, low-cost syntheses of tetra- and pentacoordinated silicon alkoxides have been developed. Silica is found to readily dissolve in ethylene glycol in the presence of catalytic amounts of TETA, or TEAH$_3$, or THAMH$_3$. The products obtained are the neutral monomer $Si(OCH_2CH_2OH)_4$ and oligomeric forms, e.g. $Si(eg)_2$. This low-cost synthesis route may impact the use of chemical methods of processing oxide ceramic materials for applications ranging from ceramic fibers for structural applications to nanosized ceramic powders for diverse applications.

Kinetic studies show that all the amines provide similar catalytic efficiencies and the dissolution rate is pseudo-zero order to silica surface areas. These observations can be explained by equilibria between free amines and neutral tetraalkoxysilanes, and amine complexed pentacoordinated silicates, as supported by NMR studies. These equilibria greatly reduce the available "free" amine concentrations needed to promote dissolution thereby limiting dissolution rates.

Pentacoordinated silanes can also be obtained in high yield by reacting equivalent amounts of amine bases with silica in ethylene glycol. These compounds also provide unique properties and are useful for diverse applications.

The alkali hydroxides are found to be more active catalysts for silica dissolution in ethylene glycol than the organic amines. The dissolution rates are orders of magnitude greater than those found using organic amine bases. The products of silica dissolution with the alkali bases consist mostly of monomeric $Si(OCH_2CH_2OH)_4$ in solution and fully cross-linked $Si(eg)_2$ after solvent removal.

Acknowledgment. We would like to thank FAA for their generous support of this work through grant No. 95-G-026. We also thank Tal Materials, Inc. of Ann Arbor for partial support of this work through NSF SBIR sub-contract (grant No. DMI 9661236). Many of the compounds synthesized in this paper are now available from talmaterials.com.

JA001885H