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Effect of Solvents on the Hydrolysis Reaction of Tetramethyl Orthosilicate

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High-pressure Raman spectroscopy is used to monitor the hydrolysis reaction of tetramethyl orthosilicate, TMOS, in solutions with methanol, acetonitrile, acetone, dioxane and formamide. The rate constants are experimentally determined for different temperatures and pressures. The volume of activation, dielectric constant, and vibrational frequency shifts are experimentally determined and discussed in terms of solvent properties. The acceleration of hydrolysis in formamide is explained in terms of interactions between formamide and TMOS.

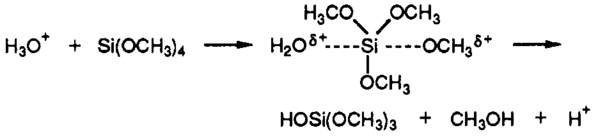
Introduction

In the sol–gel process glasses are prepared from liquid precursors rather than from powders or clays. This process can be separated into four steps, hydrolysis, condensation, drying, and firing, none of which is fully understood. Many factors may affect various stages of the sol–gel process: pH, temperature, molar ratio of alkoxide to water, pressure, and solvents. Solvents that include methanol, acetone, acetonitrile, dioxane, formamide, glycerol, and dimethylformamide may change the rate of hydrolysis and condensation, pore size distribution, surface tension, and other characteristics.[1-9] Several research groups have studied the role of these chemicals during sol–gel processing with most studies concentrating on effects due to formamide. It was found that at neutral conditions, formamide shortens the hydrolysis reaction,[4,11] causes SiO_2 to polymerize into large particles,[6,10] and reduces capillary forces allowing gels to be dried without cracks.[10] Artaki et al.[4] tentatively explained the shortening of hydrolysis reaction as an effect related to the viscosity and hydrogen-bonding properties of this solvent. Grimmer et al.[9] suggested that the observed changes in the hydrolysis reaction are due to the decomposition of formamide into formic acid and ammonia. Boonstra and co-workers[11] postulated that hydrolysis and condensation are affected by the reduction in the H^+ concentration due to the following reaction:

$$HCONH_2 + H^+ \rightarrow HCONH_3^+ \qquad (1)$$

These different explanations of the effect of formamide on the hydrolysis reaction prompted us to study the mechanism of the hydrolysis reaction in different solvents. Since the mechanism is similar to that of the condensation reaction, an understanding of one of these processes will help to predict the properties of the other reaction.

The mechanism of the hydrolysis reaction of silicon alkoxides has been studied by Aelion et al.,[12] Pohl and Osterholz,[13] Assink and Kay,[14] Brinker,[15] Zerda and Hoang,[16] and others. It is now well established[15-20] that this is an S_N2 reaction involving a pentacoordinate intermediate. All the experiments reported here were performed at pH = 6, where the reaction is acid catalyzed. Under acidic conditions, a hydronium attack on a silicon atom results in a five-coordinate transition state. Equation 1 illustrates the formation of the transition state for tetramethyl orthosilicate (TMOS). The transition state decays with inversion of the silicon tetrahedron. Pohl and Osterholz[13] suggested that the intermediate decays through a second transition state in which any of the surrounding ligands can acquire a partial negative charge, but because of lack of sufficient experimental data, this hypothesis has not been tested.



$$H_3O^+ + Si(OCH_3)_4 \longrightarrow H_2O^{\delta+}\text{----}\overset{H_3CO\ \ OCH_3}{\underset{OCH_3}{Si}}\text{----}OCH_3^{\delta+} \longrightarrow HOSi(OCH_3)_3 + CH_3OH + H^+ \qquad (2)$$

Solvents may alter the electrostatic and hydrogen bond interactions and a proper selection of solvents may allow a study of the role of these interactions on the mechanism of reaction 2. The choice of solvents used in this investigation is limited because they must dissolve both TMOS and water. We have chosen solvents that have permanent dipole moments and can form hydrogen bonds by accepting or donating protons: (polar protic, e.g., formamide, methanol), polar aprotic (acetone, acetonitrile), and nonpolar aprotic (dioxane) molecules.

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Table I. Hydrolysis Reaction Rate of TMOS in Different Solvents as a Function of Pressure[a]

pressure, bar	rate constants for different additives, × 10^{-6} s^{-1}				
	methanol	methanol + acetone	methanol + acetonitrile	methanol + dioxane	methanol + formamide
1	48.9	34.4	27.2	32.5	149.4
100	56.4	41.1	32.5	36.4	174.2
150	61.4	43.5	39.4	41.4	188.3
250	71.7	52.5	40.8	46.4	208.6
500	99.4	69.2	59.1	71.7	327.8
1000	151.4	110.6	85.6	82.5	575.3
1500	255.2	156.9	127.2	113.6	769.4
2000	369.7	218.1	153.1	123.9	1117.2

[a] Temperature 25 °C. The data are accurate within 5%.

Raman spectroscopy was used by Artaki et al.[7] and Zerda and Hoang[16] to monitor hydrolysis of TMOS simply by recording the time dependence of the Raman intensity of the band assigned to the $Si-O-CH_3$ vibration. A decay of the band intensity results from the hydrolysis reaction producing hydrolyzed species, $Si(OCH_3)_{4-n}(OH)_n$, vibrating at frequencies different from those of TMOS. Raman intensity is related to the number of molecules in a solution. Assuming the pseudo-first-order kinetics because of an excess of water used in the reaction, the time dependence of the intensity of the Si-O-C band gives the following rate of hydrolysis reaction, k:

$$k = d(\ln I(t))/dt \qquad (3)$$

where I is the normalized intensity and t is the time.

The classical theory[16,21-24] of the transition state leads to an expression for the pressure dependence of the rate constant that provides information on the volume of activation, $\Delta V^\ddagger$:

$$\Delta V^\ddagger = -RT\, d(\ln k)/dp \qquad (4)$$

The volume of activation is the difference between the molar volume of the transition state and the total volume of the reactants before the reaction. Usually the plot of ln k versus p is curved toward the pressure axis, so that the numerical value of $\Delta V^\ddagger$ decreases with increasing pressure. This effect is independent of the sign of $\Delta V^\ddagger$ and may be attributed to compressibility of the liquid.[22,24] To find the volume of activation from eq 4, the experimental data on the reaction rate are usually approximated by an empirical analytical function, such as the one developed by Asano[25] and recommended by le Noble:[22]

$$\ln (k_p/k_l) = ap + b \ln (l + cp) \qquad (5)$$

a, b, and c are constants and k_p and k_l are the values of rate constant at pressures p and l, respectively. Parameters a, b, and c can be found by a fitting procedure. The main advantage of this approach is that eq 4 can be solved analytically.

Experimental Section

The silica sol-gels were prepared by adding a mixture of water and solvent to TMOS premixed with the respective additive. The final composition of the sol-gels was 1.0 M of silicon, 10 M of water, and 5.5 M of solvents. Additives were premixed with methanol, and the molar ratio of an additive to methanol was 1:2. Water of pH = 6.0 was used in all experiments. The solvents have been distilled before the reaction; we found that it was especially important in the case of formamide. We used the vacuum distillation technique described by Perrin and Notely.[26] Formamide may decompose in time, and it is absolutely necessary to prepare a fresh batch of this solvent before each series of measurements. The pH of the mixtures was measured as a function of time by using Hach free-flowing reference junction electrode, and no changes in pH values were recorded. However, when nondistilled solvents were used, we observed that the pH of the sol-gels varied in time.

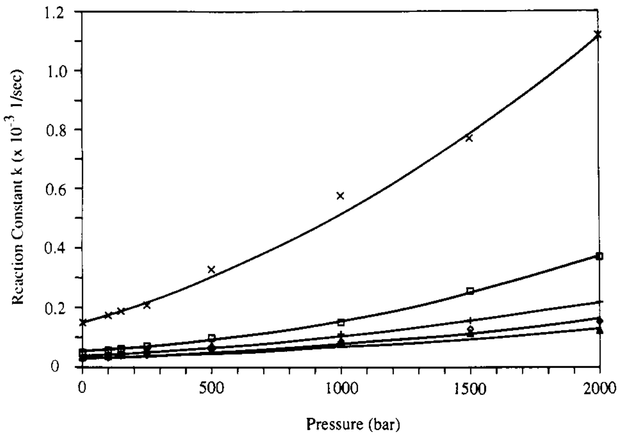

Figure 1. Hydrolysis rate constant as a function of pressure. The molar ratio of TMOS:water:solvent was set to 1:10:5.5. The molar ratio of methanol to additive was 2:1. △, experimental data for solution with dioxane; ◇, acetonitrile; □, methanol; +, acetone; ×, formamide. Solid lines show Asano functions fitted to the experimental points.

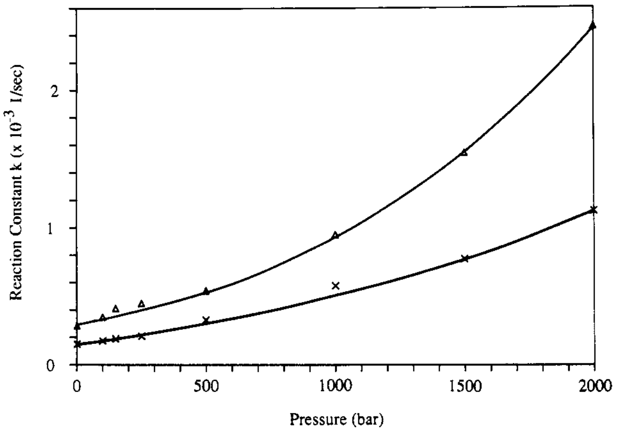

Figure 2. Hydrolysis reaction rates for solution containing formamide. △, data obtained for solutions containing 50%; ×, 25% of formamide.

Samples were placed in sealed glass containers, and the Raman spectra of the Si-O-C bands were recorded by using an argon laser

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Table II. Reaction Rate, *k*, for Various Concentrations of Methanol in the TMOS–Water–Dioxane–Methanol System[a]

molar fraction of methanol, %	0.0	33.3	50.0	66.7	100.0
rate constant k, 10^{-6} s^{-1}	3.9	13.1	19.7	25.3	27.2

[a] Total molar concentration of methanol and dioxane was kept constant and equals 5.5 mol.

Table III. Volume of Activation, ΔV^* (cm^3/mol) for Various Additives

	methanol	methanol + acetone	methanol + acetonitrile	methanol + dioxane	methanol + formamide
ΔV^*	-42.1 ± 5	-39.8 ± 2	-45.4 ± 2	-40.8 ± 2	-43.5 ± 2

and a Spex double monochromator. The details of high-pressure measurements are given in ref 16. The high-pressure measurements were taken at a temperature of 298 K. All the measurements were repeated at least four times.

The dielectric constant was measured by using a stainless steel precision capacitor and a Hewlett-Packard 4268 universal bridge. Accuracy of dielectric constant measurements was better than 5%.

Results

Because of the excess of water in solutions, the reaction described by eq 2 can be approximated by first-order kinetics, and the rate constant can be obtained from eq 3. The rate constants were found from the initial slope of the logarithm of the Raman intensity data plotted versus time elapsed from the beginning of the reaction. The least-squares procedure was used. The absolute values of the rate constants are listed in Table I, and their pressure dependences are shown in Figures 1 and 2. It is seen that the fastest reaction occurs in formamide and the slowest rate is observed in dioxane. Our finding that *formamide accelerates the hydrolysis reaction* is consistent with that previously reported by Artaki et al.[3,4] and Orcel et al.,[27] who presented their results in the reduced time scale, t/t_{gel}, where t_{gel} is the gelation time. In general, the reaction rate also depends upon the concentration of additives, but we limited our concentration dependence study only to dioxane and formamide. Formamide does not mix with TMOS and water; therefore, it is necessary to add methanol to the solution. In the formamide–methanol solution, the reaction rate doubles when the molar concentration of formamide increases by a factor of 2; compare Figure 2. Dioxane is miscible with TMOS and water at any concentration, and it is possible to study the reaction rate in the solution containing only TMOS, water, and dioxane. For this mixture we observed the lowest reaction rate of 3.89×10^{-6} s^{-1}. As dioxane is replaced by methanol, the rate of the reaction increases to 27.2×10^{-6} s^{-1}; compare Table II.

The volume of activation was found analytically from eq 4 with $k(p)$ approximated by the Asano function (eq 5). Solid lines in Figures 1 and 2 illustrates Asano functions (eq 5) found by using a fitting procedure. Because the results of the fitting routine and ultimately the data on the volume of activation are affected by experimental errors, we repeated all high-pressure experiments at least four times. In most cases the rate constants listed in Table I are results of more than five independent measurements. This procedure enabled us to determine the volume of activation, listed in Table III, with a precision better than 5%. The data on the volume of activation are independent of a fitting function used since similar results were obtained when the Asano function (eq 5) was replaced by a parabolic or a Tait-like functions.[16]

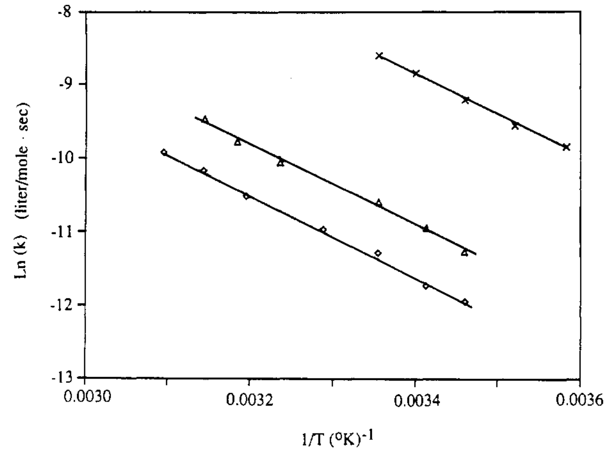

Figure 3. Arrhenius plot for the hydrolysis reaction of TMOS in different solvents. ×, formamide; △, dioxane; ◇, acetonitrile. The energy of activation is similar for all the solvents and is given by $E = 10.6 \pm 0.6$ kcal/mol.

Discussion

Typically for S_N2 reactions involving charge dispersion the energy of activation depends strongly on the reaction medium, and it is attributed to differential solvation of reactants and of the activated complex.[28] Before the hydronium ion and TMOS molecule can come into contact, the solvation shells around the two reactants must be at least partially disrupted. It was expected that the resistance to breaking the solvation shell varies with solvent and should be reflected by different energies of activation. However, our experimental results indicate that the energy of activation for the hydrolysis reaction is independent of additives and equals 10.6 ± 0.6 kcal/mol, meaning that other processes are also important and may determine the rate of the reaction. The energies of activation have been found from the slope of ln k plotted against $1/T$; compare Figure 3.

Several physical properties are affected at the same time when a solvent is changed. Electrostatic interactions, steric effects, mobility of molecules, and collisional frequencies depend on the solvents used and all may change the reaction rate.

For liquids of low viscosity, the viscosity is proportional to the collisional frequency.[29,30] Because the viscosity of sol–gels is low and only slightly affected by additives[4] and because viscosity increases only by 30% when pressure is increased from 1 bar to 2 kbar,[16] we concluded that collisional frequencies are similar in all the solutions studied. This conclusion is in agreement with the results of ref 16 that viscosity is not the rate-determining factor.

We found that there is no correlation between the dipole moment and the reaction rate. For dioxane, a molecule with no dipole moment, the reaction is very slow and for formamide, a solvent with large dipole moment of 3.73 D, the reaction is relatively fast. It seems reasonable to expect that for acetonitrile, a molecule of a large dipole moment ($\mu = 3.92$ D) comparable to that of formamide, the reaction also should be fast, but in contrast, the experimental results show that the reaction is slow and is even slower than that observed in actone of smaller dipole moment, $\mu = 2.88$

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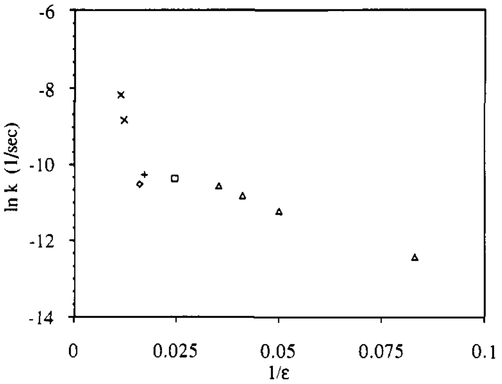

Figure 4. Hydrolysis rate versus dielectric constant. △, experimental data obtained for sol–gel prepared with dioxane; ◇, acetonitrile; □, methanol; +, acetone; ×, formamide.

D; moreover, it is also slower than in methanol of dipole moment $\mu = 1.70$ D. Although the role of the dipole moment cannot be ignored, it does not seem likely that these interactions play an important role in the hydrolysis reaction.

Rate of reactions between neutral molecules and ions may be estimated from a simple electrostatic theory:[31]

$$\ln k = \ln k_0 + A/\epsilon \qquad (6)$$

where A is a constant that depends on electrostatic charges and radii of ions and activated complexes, and ϵ is the dielectric constant of the medium. For the hydrolysis of TMOS, the radius of the intermediate is greater than the radius of the ion (OH^- or H_3O^+) and the constant A is positive,[32] which means that the rate should be greater in a medium of lower dielectric constant. In Figure 4 we plot the observed reaction rates as a function of the dielectric constant of the solvents. There is a correlation between those two quantities, but it is exactly opposite to that predicted by the electrostatic model. This finding suggests that specific solvent effects and the spatial charge distribution within the TMOS molecule are important, and both may produce larger effects than those of dielectric constant.

Because water was the major component of mixtures used to dissolve TMOS, it may be expected that the dielectric constant of such mixtures should be similar to that of pure water. Instead, we found that ϵ varied over a wide range between 12 and 95. Despite the small dipole moment of water, its dielectric constant is large, and this is explained as a result of local molecular order due to hydrogen bonding. When dioxane, a nonpolar molecule, is dissolved in water, ϵ of the mixture decreases to a value smaller than that predicted assuming additivity of dielectric constants. Dioxane breaks hydrogen bonding and thus effectively reduces sizes of water agglomerates, resulting in smaller values of the dielectric constant.[33] When methanol replaces dioxane, the hydrogen-bonding network is reinforced because methanol is amphoteric and may replace water in the hydrogen-bond network. As a result dielectric constant increases. Formamide also is an amphoteric molecule and may both donate and accept protons; therefore, one may expect effects similar to those observed in methanol. However, when formamide is introduced into the system, the dielectric constant is much larger than that predicted by assuming additivity of dielectric constants of components. Kessler and co-workers[34] explained the increase in ϵ of water–formamide mixtures as a result of formation of stable water–formamide complexes. This short discussion may be summarized with the conclusion that there is a correlation between the dielectric constant and the hydrogen bonding and it reflects the ability of solvents to reinforce or weaken the hydrogen-bond network. In aprotic solvents fewer water molecules are connected together (H-bond network may be approximated by a sponge structure) and the mobility of H^+ or OH^- ions is reduced, although it is usually assumed that this is not a significant reduction. The mechanism of proton transfer in sol–gel mixtures was discussed in ref 16. Protic solvents can effectively substitute water molecules in the network and do not limit the charge transfer.

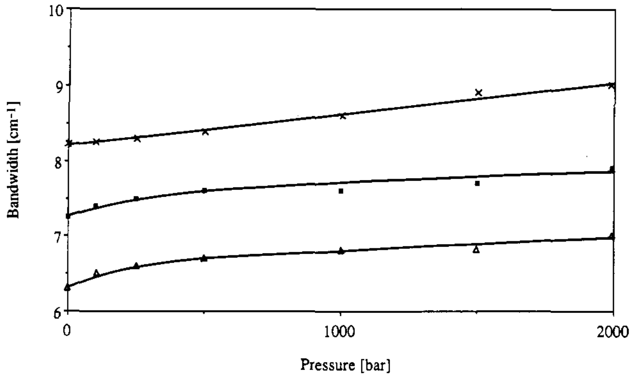

Figure 5. Band broadening of the Si–O–C vibration as a function of pressure for solutions with formamide (crosses), methanol (squares), and dioxane (triangles).

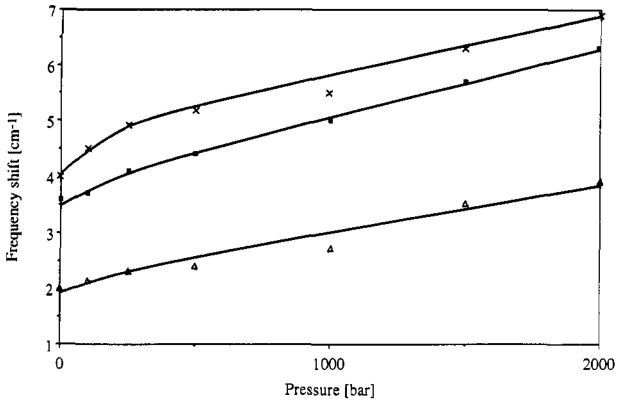

Figure 6. Frequency shift of the Si–O–C band as a function of pressure. Symbols are the same as in Figure 5.

Hydrogen bonding may affect not only solvation but also TMOS. Steric hindrance effects are limited, and oxygen atoms of TMOS are easily accessibly to water or other proton-donating molecules and may form hydrogen bonds. The Si–O–C mode at 645 cm^{-1} is a bending vibration, and it is known that the frequency of bending vibrations increases when a hydrogen bond is formed.[35] The band width of bending modes can be used to measure the strength of H bond; a rule of thumb is that stronger bonds result in wider bands. In Figure 5 we plot the band width as a function of pressure for mixtures with formamide, methanol, and dioxane. In Figure 6 we plot the frequency shifts of the band maximum as a function of pressure. The frequency shift is defined as the difference between the

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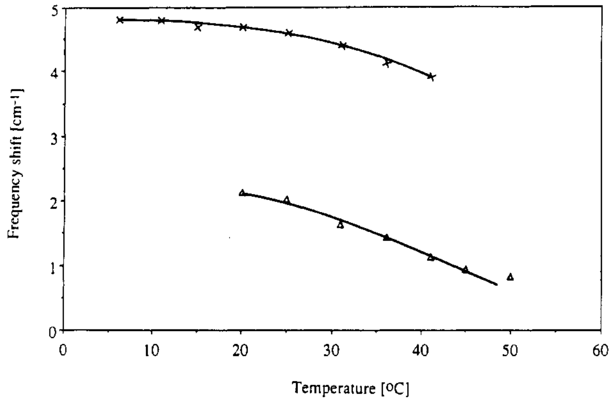

Figure 7. Temperature dependence of the frequency shift of the Si–O–C mode. Crosses depict data for formamide and triangles for dioxane.

band position at pressure p and the band position at ambient pressure. Because TMOS does not mix with water, we were not able to record the position of the Si–O–C band in pure water. In the mixture of TMOS, water, and dioxane, we found only a small, positive frequency shift (blue shift), which we explain as due to hydrogen bonding between TMOS and water. Significantly larger blue shifts and broader bands were measured in water–methanol and even larger in formamide–water mixtures (Figures 5 and 6). The pressure and temperature dependence of band frequency and band width are also typical for systems with H bonding. With increased pressure, intermolecular distances decrease, H bond interactions become stronger, and the changes in the band shapes are more pronounced. When temperature increases, the frequency shifts gradully decrease to zero (Figure 7), a process that can be explained by bond breaking due to the increase in the thermal energy.

The intermediate state is a pentacoordinate state that forms a strong quadrupole moment. The geometry of the transition state can be approximated by a deformed trigonal bipyramid in which the donor site occupies an axial site.[18,19] Three methoxy groups are in equatorial sites, and the fourth group is at the site opposite to the hydroxyl. Usually the axial bonds are significantly longer than the equatorial bonds,[19] and consequently they are weaker, and it is expected that the methoxy group opposite the attacking hydroxyl group will leave the system. When a molecule capable of forming a strong hydrogen bond, such as formamide, is coupled to an Si–OR group, this interaction may weaken the Si–O bond by shifting the electron cloud toward formamide, thus enabling more pronounced changes in bond lengths and angles that are necessary to accommodate the additional bond in the transition state. Also, by protonating the OCH_3 group the hydrogen-bond interaction improves the quality of the leaving group and thus the reaction may proceeds faster.[39] Acetone, dioxane, and acetonitrile are all aprotic and lack protons capable of hydrogen bonding to TMOS. But sol–gels prepared with those solvents contained also water and/or methanol, and because those two liquids may interact specifically with TMOS, it is not surprising that the reaction rates in those systems are similar with the reaction rate being the fastest for sol containing pure methanol.

This discussion would not be completed without mentioning the study of Rosenberger and co-workers[9,36] and Bradley et al.[40] NMR studies reported in refs 9 and 36 showed that addition of an acid into the solution resulted in hydrolysis of formamide. This effect was accompanied by an increase of pH from 1 to 3 within less than 2 h. The decomposition of formamide takes place only at low pH values[36] and has not been observed at neutral conditions.[40] We have not observed any change in the pH value during the reaction, and we conclude that at the neutral conditions, the observed acceleration of the reaction is related to hydrogen-bond interactions.

We expected that specific interactions between TMOS and solvent molecules should be reflected by the volume of activation. The observed differences in rate constants for the sols (Table I) may be attributed to solvational effects, such as different shielding of the reacting molecules by intermolecular hydrogen bonding, least effective in the solution containing dioxane and most effective for formamide. Consequently, we expected to find the solvational part of the volume of activation to be dependent upon the additives used in the reaction, but as seen from Table III, the experimental volume of activation for all of the solvents used is about -42 cm^3/mol.

The volume of activation stems from changes in the volume of the activated complex and from changes in solvation. Reaction 2 does not involve the formation of new charges, and the solvational part of the volume of activation may originate from the redistribution of charge in the activated complex. Whalley[37] studied the effect of pressure on solvation of an intermediate state with dipole and quadrupole moments in a cavity in a continuous dielectric. He found that in aqueous solutions the electrostrictions originated from the dipole and quadrupole moments of the activated complex are equally important but those contributions are usually less than 10 cm^3/mol, too small to explain the observed values of ΔV^*. Besides, if the electrostriction were important, then when more polar solvents were added into solutions the volume of activation should become less negative and the reaction should proceed at a slower rate. A similar conclusion was reached by Dack,[38] who analyzed solvent effects on cohesive forces and internal pressure during the reaction and offered the following explanation. In the absence of specific interactions, concentration of polar molecules about ions is greater than in the proximity of the intermediate state. Consequently, the volume of the reactants is smaller than that of the transition state and the volume of activation becomes more positive and reaction is slower. Our result do not follow those trends, indicating that electrostatic interactions alone cannot explain the mechanism of the hydrolysis reaction. This conclusion is in agreement with the discussion on the electrostatic effects and leads to the conclusion that the electrostriction of solvents is not the dominating factor in the volume of activation. We suggest after Whalley[37] that the contraction of the reactants may be important and may also contribute to ΔV^* values. However, due to the lack of data on the solvational component it is impossible at the present time to evaluate the magnitude of this contribution.

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