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Journal of Non-Crystalline Solids 171 (1994) 68–79

JOURNAL OF NON-CRYSTALLINE SOLIDS

Sol–gel polymerization: analysis of molecular mechanisms and the effect of hydrogen

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Received 23 July 1993; revised manuscript received 6 December 1993

Abstract

The polymerization of silicic acid molecules (H_4SiO_4) was simulated using classical molecular dynamics with multibody potentials. The mechanisms involved in the condensation process were analyzed. Although a condensation mechanism was observed in the simulations which corresponds to the mechanism commonly assumed, additional mechanisms not previously presented were also observed. The advancement of polymerization was found to depend on the non-bridging oxygens' coordination with hydrogen, the number of bridging oxygens around five-coordinated silicons and atomic momentum. The results show consistency with the chemistry described for the acid catalyzed sol–gel process where hydrogen acts as the catalyst and chains form before rings.

1. Introduction

The sol–gel process begins with a solution of metal alkoxide molecules, water, a mutual solvent (alcohol) and a catalyst. The molecules are subsequently polymerized though catalysis to form a porous amorphous gel. Tetraethyl orthosilicates (TEOS) and tetramethyl silicates (TMOS) are two of the alkoxide precursors used in the formation of silica gels [1] which is the material discussed in this paper. In gelation, properties of the gel are dependent on the chemical conditions. Understanding the reaction mechanisms and transition states involved in polymerization is essential to optimizing and controling the gelling process.

Silicon alkoxides need to be catalyzed with an acid or base to promote polymerization at low temperatures. Hydrochloric acid and ammonium hydroxide are often used as the catalyst [2]. Acid-catalyzed systems show a more open, less cross-linked monolith structure while the basic catalyzed systems create highly cross-linked colloidal particles [3].

Gelation involves a two-step process. First, the TEOS molecules are hydrolyzed by the water and then catalyzed condensation occurs. Condensation can create either alcohol (Eq. (2)) or water (Eq. (3)), depending on the extent of hydrolysis [4]:

$$\text{hydrolysis} \quad \equiv\text{SiOR} + \text{H}_2\text{O} \Rightarrow \equiv\text{SiOH} + \text{ROH} \qquad (1)$$

$$\text{condensation} \quad \equiv\text{SiOR} + \equiv\text{SiOH} \Rightarrow \equiv\text{SiOSi}\equiv + \text{ROH} \qquad (2)$$

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SSDI 0022-3093(94)00119-8

$$\text{condensation} \quad \equiv\text{SiOH} + \equiv\text{SiOH} \Rightarrow \equiv\text{SiOSi}\equiv + H_2O. \qquad (3)$$

In the work reported here, only the condensation reaction in Eq. (3) was investigated by assuming that full hydrolysis to silicic acid occurred prior to condensation.

Several factors affect the kinetics of sol–gel condensation. Increasing the pressure [4] or temperature will increase the polymerization rate. Water decreases the condensation rate, while $[H^+]$ increases it [3]. There have been several models proposed for polymerization rate calculations based on the above and other variables [3,5–9].

There are a few mechanisms proposed for the condensation process. The basic considerations are applicable for all tetrahedrally coordinated oxide systems. The widely accepted condensation mechanism is believed to involve a five-coordinated silicon transition configuration in an SN_2-type reaction [10–12]. This condensation is believed to proceed through nucleophilic attachment of an $H_3O_3Si{-}O^-$ group (Fig. 1(a)) to another four-coordinated silicon creating a dimer with one five-coordinated silicon (Fig. 1(b)) and the subsequent release of an OH_x ($x = 1$–3) group (Fig. 1(c)) [13–16] to form a stable dimer with two four-coordinated silicons. At a lower pH (acid catalysis), this process is slower because NBOs are more likely to have one or more hydrogens attached, which helps to prevent the approach of an NBO to a silicon of another tetrahedron. However, it is thought that these extra hydrogens catalyze the reaction by creating better leaving OH_x ($x = 0$–3) groups which allow an NBO to more easily break free from the five-coordinated silicon which was able to form [17,12]. This process can be shown schematically by the following equations [18]:

$$(HO)_3{-}Si{-}OH + H^+ = (HO)_3{-}Si{-}OH_2^+;$$

$$(HO)_3{-}Si{-}O^- + H^+ + (HO)_3{-}Si{-}OH_2^+ = (HO)_3{-}Si{-}O{-}Si{-}(OH)_3 + H_3O^+.$$

If groups cannot depart easily from a five-coordinated silicon, the dimer will ‘depolymerize’, moving back to the left in the reaction shown in Fig. 1, leaving no net condensation. The ease of protonization of the OH group decreases with the connectivity of the adjacent silicon atom, thus slowing the rate of polymerization with respect to time. Acid catalysis is preferential towards the end of a polymer chain for this same reason [12]. A five-coordinated silicon at the end of a siloxane chain is more likely to have a good leaving group because the silicon has only one bridging oxygen as opposed to two or more if it were within the chain.

Iler’s [3] schematic of the condensation reaction showed that the energetically unfavorable five-coordinated silicon relaxes by the release of an oxygen of OH^- group which then forms water by acquiring a nearby hydrogen. The oxygens around this pentacoordinated silicon form a distorted trigonal bipyramid with the peak of one pyramid being the incoming bridging oxygen from the other molecule (Fig. 1(b)). The positions around a five-coordinated silicon are described in this paper as either *opposite* or *adjacent* to the incoming bridge as shown in Fig. 1(b). Iler’s proposed mechanism shows the binding of the fifth oxygen to the silicon which causes the elongation

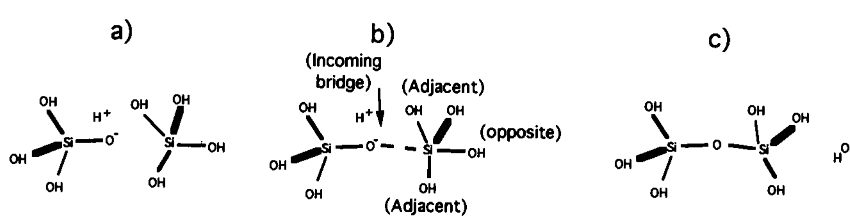

Fig. 1. Schematic of (a) two tetrahedra approaching, (b) the formation of a trigonal bipyramid five-coordinated silicon structure with incoming bridge and opposite and adjacent OH groups, and (c) the departure of an opposite OH group.

and breakage of the *opposite* bond. Feuston and Garofalini observed this mechanism in computer simulation [19].

There have been a large number of experimental studies of sol–gel polymerization. ^1H and ^{29}Si NMR [1,4,18,5–9,20–22], IR and Raman spectroscopy [23,24], X-ray scattering [25], X-ray absorption [11] and light scattering [1,7,22–24] have been used to evaluate the condensation process. Such techniques do not have sufficient time and space resolution to provide details of polymerization mechanisms.

Computational techniques, however, offer an approach by which such molecular mechanics can be studied. For simplification, silicic acid (H_4SiO_4) can be used as the starting molecules in the polymerization, assuming complete hydrolysis before the condensation process begins. This assumption allows the condensation process alone to be studied. The interaction between a silicic acid molecule and a water molecule has been used in ab initio molecular orbital (MO) calculations as a model for water interacting with hydrated silica surfaces [26–30]. However, ab initio computations are currently limited to small numbers of atoms, thus making the study of polymerization with large numbers of atoms difficult. MD simulations can be used to study large systems of 10^2–10^5 atoms and have already been used in studies of polymerization of silicic acid molecules [19,31].

In this study, we examine the condensation reaction in greater detail. We propose polymerization mechanisms which explain why a particular oxygen breaks free from a penta-coordinated silicon while the others do not. Also, the time dependence, 'mechanics' and 'chemistry' of this process are discussed in relation to the stability of the polymer formed.

2. Computational procedure

The multibody interatomic potential designed for simulations of silica has been previously presented and discussed. Bond angles, lengths and distributions, and static structure factors for silica glasses simulated with these potentials are in good agreement with experiment and theory [32]. The potentials used for interactions with hydrogen in the MD simulations were designed from quantum mechanical calculations and, therefore,

Table 1
Parameters for the two- and three-body potentials

Two-body	*A* ($\times 10^{-9}$ erg)	*ρ* (Å)	*β* (Å)	*a* (10^{-12} erg)	*b* ($Å^{-1}$)	*c* (Å)
Si–Si	1.8770	0.29	2.29			
Si–O	2.9620	0.29	2.34			
O–O	0.7250	0.29	2.34			
Si–H	0.0690	0.29	2.31	−4.6542	6.0	2.20
H–H	0.0340	0.35	2.10	−5.2793	6.0	1.51
				+0.3473	2.0	2.42
O–H	0.3984	0.29	2.26	−2.0840	15.0	1.05
				+7.6412	3.2	1.50
				−0.8336	5.0	2.00

Three-body	*λ* (10^{-11} erg)	*γ* (Å)			r^0 (Å)			*θ*° (deg)
		Si–O	O–Si	O–H	Si–O	O–Si	O–H	
O–Si–O	19.0	2.8	–	–	3.0	–	–	109.5
Si–O–Si	0.3	–	2.0	–	–	2.6	–	109.5
Si–O–H	5.0	–	2.0	1.2	–	2.6	1.5	109.5
H–O–H	35.0	–	–	1.3	–	–	1.6	104.5

yield proper molecular configurations and binding energies [19]. Further, simulations of both dry and hydrated glass surfaces with these potentials give results which are both qualitatively and quantitatively consistent with experimental data [33,34].

The potential energy calculations for v-SiO_2 contain both two- and three-body terms:

$$V(\{R_i\}) = \sum V_2(r_i, r_j) + \sum V_3(r_i, r_j, r_k),$$

where $\{R_i\} = (r_1, r_2, \ldots, r_n)$ for an n-atom system and r_i, r_j and r_k are atomic positions. The two-body term is of the Born–Mayer–Huggins (BMH) type:

$$V_2(r_i, r_j) = V^{\mathrm{BMH}}(r_{ij}) = A_{ij} \exp(-r_{ij}/\rho_{ij}) + Z_i Z_j \operatorname{erfc}(r_{ij}/\beta_{ij})/r_{ij},$$

with $r_{ij} = |r_i - r_j|$, Z_i is the formal ionic charge, and where A, ρ, and β are adjustable parameters. The three-body term contains the functional form

$$V_3(r_i, r_j, r_k) = v_3(r_{ij}, r_{ik}, \theta_{jik}) + v_3(r_{jk}, r_{ji}, \theta_{kji}) + v_3(r_{ki}, r_{kj}, \theta_{ijk}),$$

where

$$\begin{aligned} v_3(r_{ij}, r_{ik}, \theta_{jik}) &= \lambda_{jik} \exp\left[\gamma_{ij}/\left(r_{ij} - r_{ij}^0\right) + \gamma_{ik}/\left(r_{kk} - r_{ik}^0\right)\right] \\ &\quad \times \left[\cos(\theta_{jik}) - \cos\left(\theta_{jik}^0\right)\right]^2 \\ &\qquad \text{for } r_{ij} < r_{ij}^0 \text{ and } r_{ik} < r_{ik}^0, \\ &= 0 \quad \text{otherwise,} \end{aligned}$$

with θ_{jik} being the angle subtended by r_{ij} and r_{ik} with a vertex at i. The three-body term may be viewed as a penalty function which raises the energy of the system when the angle, θ, differs from the preferred angle, θ^0. The parameters for the equations are given in Table 1.

With hydrogen in the system, additional terms for hydrogen interactions were included via

$$V'(r_{ij}) = a_{ij}/\{1 + \exp[b_{ij}(r_{ij} - c_{ij})]\},$$

where a_{ij}, b_{ij} and c_{ij} are parameters. For more details on the potential calculations and parameters, see Refs. [19,32].

The starting configuration for the simulation included 64 silicic acid (H_4SiO_4) molecules in a $2.0 \times 2.0 \times 2.0$ nm^3 box. The configuration was allowed to relax at a low effective temperature (14 K) for 1 ps and then raised to an elevated effective temperature (700 K) for 6 ps. The effective temperature is obtained by dividing the simulation temperature by the simulation melting temperature of silica and then multiplying this by the experimental melting temperature of silica. The time step used was 0.1 fs giving 60000 moves total at the elevated temperature. This 576 atom system had periodic boundaries in the x, y and z directions.

The simulation was carried out at high effective temperature (700 K) and density of 1.3 g/cm^3 to promote oligomerization in the time of the simulation. Hua et al. [4] examined the relationship between pressure and polymerization with results similar to those seen in these simulations. The pressure and temperature conditions make the model analogous to an autoclave process to produce aerogels using sol–gel methods.

The system was analyzed for the coordination of non-bridging oxygens by hydrogen at different cut-off distances and at different positions on the five-coordinated silicon. The term non-bridging oxygen (NBO) used in this paper refers to oxygens that are bonded to only one silicon although they may be bonded to hydrogens as well. Data on the relationship of a Si–NBO and Si–bridging oxygen bond rupture from a transition state (Fig. 1(b)) with respect to the position of the newly formed bridging oxygen on the five-coordinated silicon were gathered. Further, the number of oxygen bridges involved in each five-coordinated silicon was determined. The non-bridging oxygens which broke free in a condensation reaction and then immediately reattached, and the number of hydrogens near a bridging oxygen bond rupture was measured.

Theories of mechanisms developed from the analysis of the simulations were tested by removing hydrogen atoms or changing the mass of the silicon in mid-reaction. By doing so, the result of

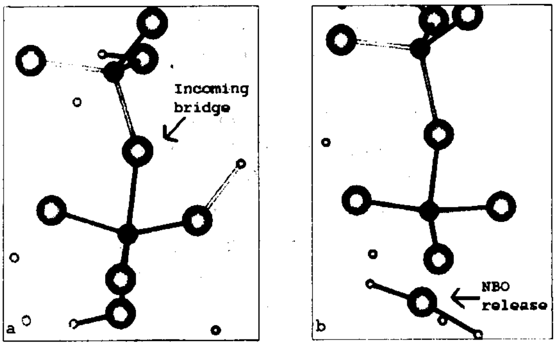

Fig. 2. Condensation reaction in which the bond opposite the incoming bridge is broken (large = oxygen, medium = silicon, small = hydrogen).

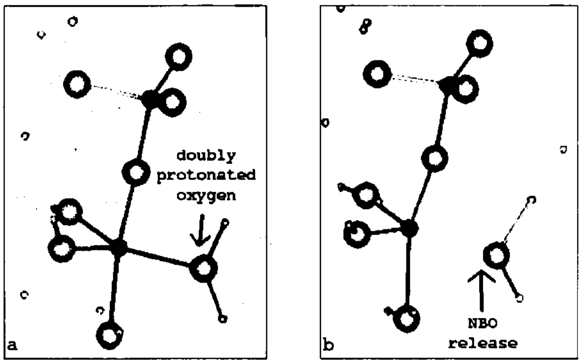

Fig. 3. Condensation reaction in which the bond adjacent to the incoming bridge is broken (large = oxygen, medium = silicon, small = hydrogen).

the reaction could be changed and, therefore, mechanisms tested.

3. Results

After a condensation reaction reaches the transition state shown in Fig. 1(b) any of three paths may be followed:

(i) the reaction continues to the right via removal of an opposite oxygen (Fig. 1(c));

(ii) the reaction continues to the right via the removal of an adjacent oxygen;

(iii) the reaction moves back to the left via the breaking of the incoming bridging bond (Fig. 1(a)).

Three distinct types of condensation reaction were observed in the simulation and are shown in Figs. 2–4. The first two condensation reactions shown involve the typical trigonal bipyramid configuration described in the introduction. Fig. 2 shows a condensation reaction which was previously shown and discussed [19]. The *opposite* oxygen breaks free (Fig. 2(b)) from the five-coordinated silicon transition state similar to the schematic originally shown by Iler [3]. Figs. 3(a) and (b), however, show a case where the *adjacent* oxygen breaks free (fig. 3(b)) after additional protonization of that oxygen (Fig. 3(a)). Yet another configuration, shown in Fig. 4, involves a trigonal bipyramid forming orthogonal to that which is the expected configuration. In this case there is not a truly *opposite* oxygen and one of the *adjacent* NBOs at the tips of the bipyramid always breaks free (Fig. 4(b)).

Data taken on the coordination with hydrogen of all NBOs around a five-coordinated silicon showed that, in most of the cases, the oxygen with the most hydrogens nearby came off. Over the entire 60000-move run, the average coordination

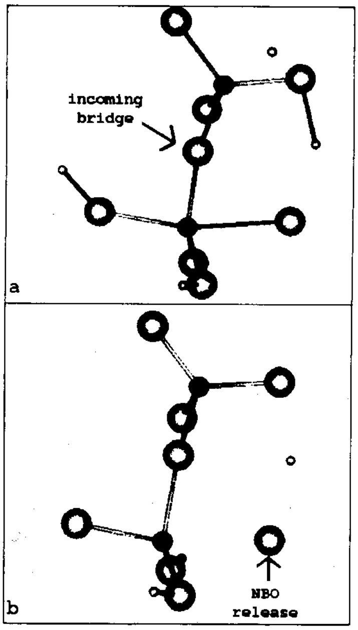

Fig. 4. Condensation mechanism forming a trigonal bipyrimid orthogonal to the expected orientation shown in Fig. 1 and 2 encouraging an adjacent oxygen break (large = oxygen, medium = silicon, small = hydrogen).

of an NBO with hydrogen right before the oxygen broke free from a five-coordinated silicon was 1.02 at a 1.5 Å cut-off for all NBO breaks. By contrast, the average coordination of all NBOs in the system with hydrogen was only 0.613 at the same cut-off, thus showing the importance of hydrogen in the bond rupture reaction. There was an increase in the number of NBOs that returned promptly to the silicon from which they broke as the polymerization (or simulation time) increased. More exactly, over the first 3 ps of a run, an average over four different starting configurations showed that 50 ± 3% of the oxygens that broke off, stayed off. In the second 3 ps, an average of only 34 ± 4% did the same. These results may be related to the increase in bridging oxygen concentration as polymerization increases, as is discussed below.

From simulation analysis it was found that 90% of the bridges that broke over the 60 000-move run did so without a hydrogen within a 1.8 Å radius of the oxygen. A possible connection is that the condensation reactions did not go to completion, but rather there was a breaking of the incoming bridge (process (iii) above). This can be seen in Fig. 5. An incomplete reaction may involve the break of the incoming bridge without the release of an NBO, or an NBO bond may rupture momentarily only to return (within a vibrational period) to once again create a five-coordination of silicon (Fig. 1(b)), after which process (iii) is followed. This happened in simulation when either an *adjacent* or *opposite* oxygen returned.

Fig. 6 shows a comparison of the frequency of leaving groups from different positions on the five-coordinated bipyramid structure with respect to time, giving insight into the time dependence of the different condensation reactions. In the first 30 000 moves, 88 of the 123 (71%) oxygen breaks in single-bridge reactions in five runs with

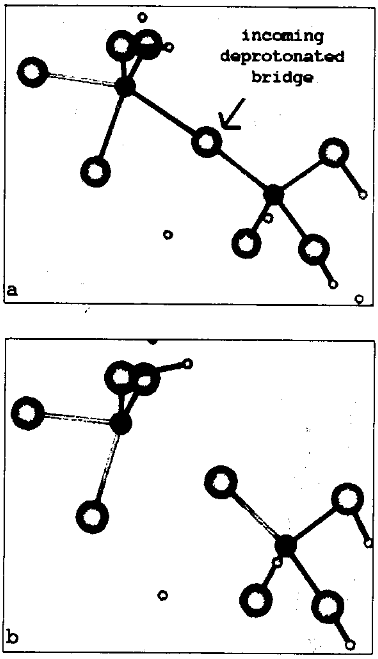

Fig. 5. Breaking of the incoming bridge in an incomplete condensation reaction (large = oxygen, medium = silicon, small = hydrogen).

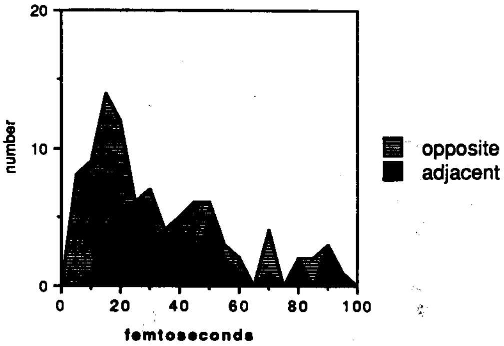

Fig. 6. Number of NBOs that detached from an opposite or adjacent position relative to the incoming bridge at a given elapsed time between the most recent bridge attachment to the silicon and the release of an NBO from that five-coordinated silicon.

Table 2
Coordination of oxygen with hydrogen with respect to the oxygen's position relative to the bridge on the five-coordinated silicon

Cut-off distance (Å)	Configuration 1		Configuration 2		Configuration 3		Configuration 4		Configuration 5	
	opposite	adjacent	opposite	adjacent	opposite	adjacent	opposite	adjacent	opposite	adjacent
1.2	0.411	0.414	0.338	0.36	0.4	0.33	0.328	0.325	0.383	0.343
2.1	1.601	1.612	1.46	1.615	1.5	1.33	1.53	1.45	1.39	1.35

different starting configurations were *opposite* to the incoming bridge. If those NBOs that reattached are eliminated from these data, the relationship is approximately 50%. This is supported by Table 2 which shows similar coordination of *opposite* versus *adjacent* oxygen with hydrogen on the five-coordinated silicons for five different starting configurations.

The effect of removing hydrogen from an NBO during condensation is shown in Fig. 7. The figure shows a time succession of a condensation reaction in the system. Time elapses from the top to the bottom of the figure. Originally an *adjacent* oxygen broke free from the five-coordinated silicon transition configuration (Fig. 7(c)). This oxygen had two hydrogens within 1.2 Å of it prior to the break (Fig. 7(a)). When these two hydrogens were removed from the system 10 fs before the break had originally occurred (Fig. 7(f)) the *adjacent* oxygen did not break free. Rather, the reaction proceeded by breaking free the *opposite* oxygen (Fig. 7(j)). This oxygen then reattached

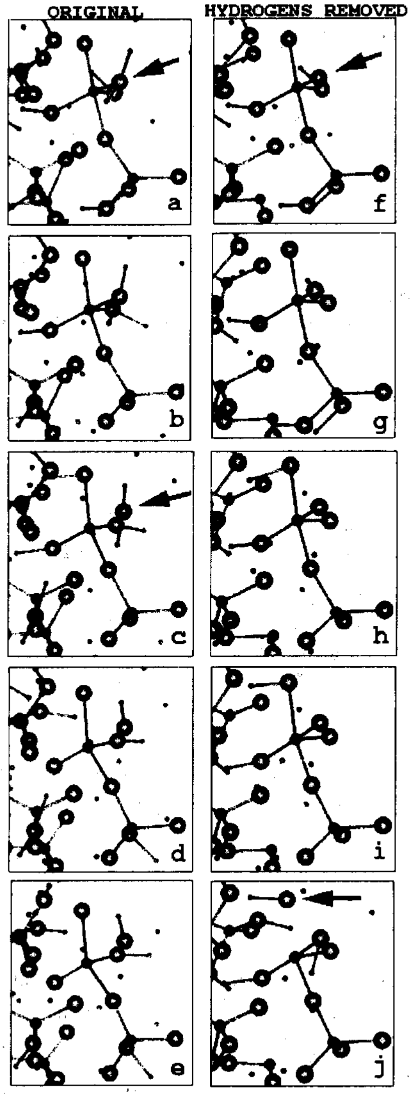

Fig. 7. Effect of removing hydrogens from an NBO in mid-reaction (large = oxygen, medium = silicon, small = hydrogen).

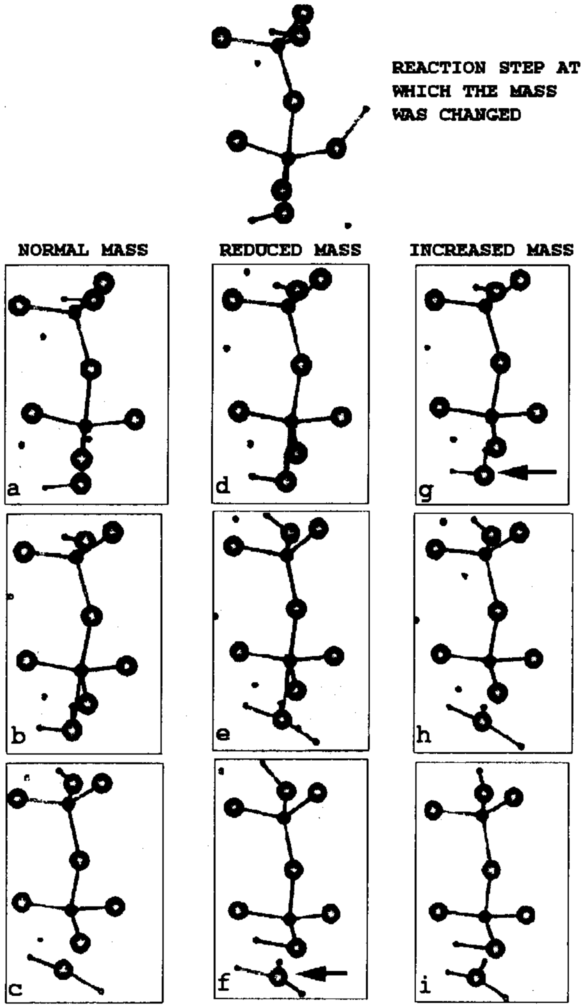

Fig. 8. Effect of changing silicon mass on outcome of a condensation reaction with a good leaving group (large = oxygen, medium = silicon, small = hydrogen).

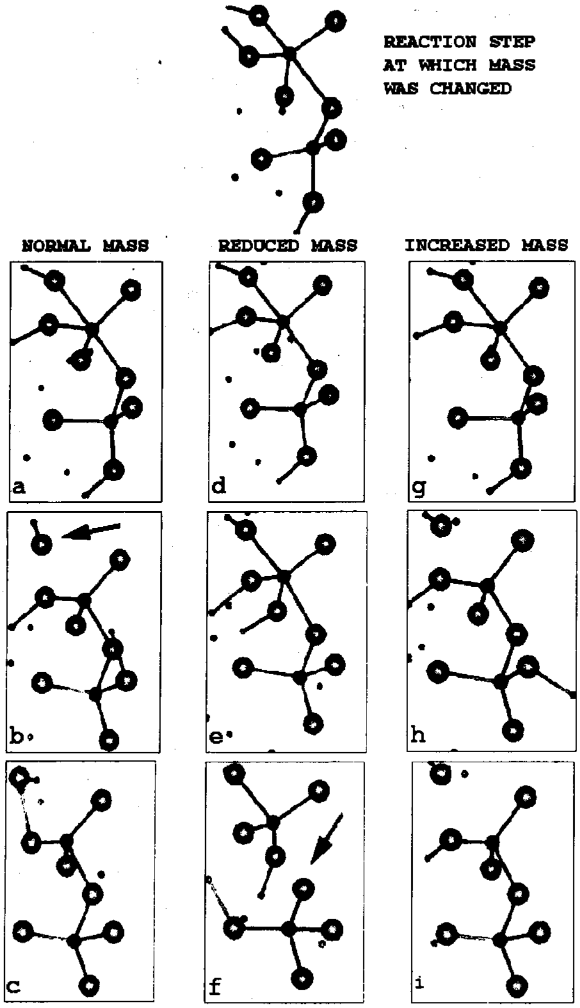

Fig. 9. Effect of changing silicon mass on a condensation reaction that does acquire a good leaving group (large = oxygen, medium = silicon, small = hydrogen).

because there were no hydrogens near it, and soon after the oxygen bridge broke (not shown). This indicates the important effect of hydrogen on the reaction and shows that the course of the reaction can be changed by removing hydrogens in mid-reaction.

Figs. 8 and 9 show that, by changing the mass of silicon in mid-reaction and keeping the same interaction potentials, the outcome of the reaction can be changed due purely to a momentum change. The first example is a reaction that originally had an oxygen that broke *opposite* a single incoming bridge and did not reattach due to multiple hydrogen coordination (Figs. 8(a)–(c)). A reduction of the silicon atomic mass to 5 amu 10 fs before the original break took place (Figs. 8(d)–(f)) showed no change in the reaction from what was seen originally. Increasing the atomic mass of the silicon to 50 amu (Figs. 8(g)–(i)) resulted in the oxygen breaking loose sooner (Fig. 8(g)). The second example is one where an oxygen broke off *opposite* a single oxygen bridge and then reattached (Figs. 9(a)–(i)). In this case, reducing the atomic mass of the silicon caused the bridge to break (Fig. 9(f)) instead of the original oxygen. With the heavier silicon, the oxygen is expected to break free earlier, as in the first example (Fig. 8), but the time between each stored graphics configuration did not allow this to be seen.

4. Discussion

4.1. *'Chemistry' and 'mechanics'*

Obviously, bonding and chemistry govern reactions, either by interatomic potentials, as used here or, more accurately, electronic structure. However, in this paper, we distinguish the chemical aspects of the reactions from the mechanical aspects for the purposes of the discussion. Here, we use the term 'chemistry' as related to the local atomic structure and bond coordination of the oxygen to the hydrogen atoms in the reaction, which we arbitrarily distinguish from 'mechanics' of the reaction. For this paper, 'mechanics' is defined as the physical movement and momentum of the ions created by the reaction which may cause bond elongation or rupture due to a physical or mechanical process rather than by specific bonding considerations. Each aspect is considered in the descriptions below.

4.2. *Importance of hydrogen*

The presence of hydrogen can affect the reaction by enabling it to move to the right via process (i) or (ii) above with the release of a stable hydroxide leaving group. As stated above, those NBOs which break from the five-coordinated silicon have a much higher average coordination to hydrogen than those that do not break off. In most of the cases, the oxygen with the most hydrogens nearby comes off. Fig. 3 shows a breaking away of a non-bridging oxygen that is over-coordinated with hydrogen. This type of reaction is predicted under acidic conditions [12,18].

Further proof of hydrogen's importance in the reaction is provided by examining how the reactions proceed as polymerization increases. An increase in the number of NBOs that returned promptly to the silicon from which they broke as the polymerization (or simulation time) increased suggests that it is more difficult to form a stable leaving group as time elapses. This can be attributed to the fact that often there are fewer hydrogens in the reaction area resulting from the five-coordinated silicons having more than one bridging oxygen as time elapses (i.e., polymerization increases). This may result in the inability to form a stable leaving group. Hence, these silicons had a tendency to break a bridging oxygen bond rather than release an NBO permanently to become a water molecule. Livage and Sanchez [12] stated that the ease of protonization of an OH group decreases with the connectivity of the adjacent silicon atoms and, hence, acid catalysis is preferential toward the end of chains. This can also be used to explain why the number of oxygens that broke free and reattached increased with time. Lack of protonization as connectivity (time) increases results in fewer leaving groups for multi-bridged five coordinated silicons. Therefore, acid catalyzed polymerization shows a preference for chain growth.

4.3. Incomplete reactions

Reactions that do not go to completion (do not follow path (iii)) were responsible for most of the bridge breaks in the simulated sol–gel system. This statement can be supported by analyzing the conditions under which bridges break. 90% of bridge breaks in the system take place with no hydrogens within 1.8 Å of the bridging oxygen. The fact that hydrogen was not present near a majority of the bridge breaks indicates that a nearby hydrogen was not the cause for the rupture of the bridging bond. For a condensation reaction to initiate, the oxygen that forms the bridge is deprotonated [12,18,19]. Therefore, if this reaction does not go to completion (process (iii)), the bridging oxygen that breaks from the five-coordinated silicon usually should not have a hydrogen nearby (Fig. 5(b)). Therefore, since there were no hydrogens near 90% of the bridging oxygen when they broke off, it is deduced that the majority of bridge breaks in the system were caused by the incomplete condensation reaction.

The fact that an NBO which breaks from a five-coordinated silicon returns is due either to a lack of hydrogens present upon oxygen separation or to the deprotonization of the oxygen after the silicon–NBO bond broke. If an NBO does not break free, there must not be a good hydroxide leaving group available.

4.4. 'Mechanics' of reaction

The reason why some oxygens break off only to return may be explained by the 'mechanics' of the reaction. As a silicon forms a fifth bond to the incoming oxygen, the adjacent oxygens usually form a plane in the distorted trigonal bipyramid structure of the five-coordinated silicon (Fig. 1(b)). This silicon can move through this plane of oxygens towards the incoming bridging oxygen, thus stretching, and possibly breaking the bond to the opposite oxygen. This oxygen will return to the silicon if there are no hydrogens available to form an hydroxide leaving group. In other reactions which were observed, the incoming bridging oxygen became one of the three oxygens that formed the base of the bipyramid configuration and two adjacent oxygens were the peaks of the bipyramid (Fig. 4(a)). In this case, the momentum created by the attaching molecule may cause the temporary adjacent bond rupture, but this is not clear. What is clear is that the NBOs that broke free in this configuration returned, indicating that the break was probably mechanical, not chemically activated. Oxygens that separate purely due to the 'mechanics' of the process are more apt to reattach because of a lack of hydrogens to provide a good leaving group.

By looking at the time between the initiation of the five-coordination and detachment of an NBO, an idea of how the 'mechanics' of the reaction affect the outcome can be established, therefore pointing out the oxygens that may not break off permanently. Based on the above descriptions ('mechanics' versus 'chemistry'), it would be expected that an NBO bond rupture due to the physical 'mechanics' of the reaction would occur soon after the bridging bond formation since it is momentum-induced, while bond rupture due to 'chemistry' would be more evenly distributed over time since that would require that the proper atomic bonding configuration be attained. Fig. 6 shows this relationship for oxygens that broke opposite and adjacent to a bridging oxygen for a compilation of three simulations with different starting configurations (each individual result was similar to the average shown here). The majority of opposite breaks occurred less than 40 fs after nucleophilic attack. The adjacent breaks were more evenly distributed over the 100 fs time span. This suggests that there is more of a mechanical aspect to the breaking of opposite oxygens.

Overall there were more breaks opposite to the incoming bridge, but if those NBOs that reattached are eliminated from these data, the relationship between opposite and adjacent breaks is approximately one-to-one. This shows that, according to the earlier arguments, the opposite bond breaks are more mechanical in nature because more of these NBOs return. Unlike the schematic of the condensation reaction originally proposed by Iler [3] and commonly used in the literature, our results show that, in the initial stages of polymerization, there appears to be no preference for an opposite or adjacent permanent break (~ 50% for each). This is supported by the data in Table 2 which show the coordination of opposite versus adjacent oxygen with hydrogen on the five-coordinated silicons for simulations begun from five different starting configurations. Both oxygen positions showed similar coordination to hydrogen. No trend of one having a higher coordination than the other is present.

4.5. Test of 'mechanics' and 'chemistry'

Fig. 7 shows the effect of removing the hydrogens attached to an NBO on a five coordinated silicon. Originally, an adjacent NBO with attached hydrogen breaks from the five-coordinated Si. Removal of these hydrogens prior to the bond rupture reduces the chemical drive to remove this adjacent NBO. As a result, as seen in Fig. 7(j), an opposite NBO mechanically breaks free from the transition state (see arrows in the figure). This opposite NBO reattaches to the Si and the incoming bridge breaks off (not shown). This indicates that hydrogen plays an important part in the permanent rupture of an NBO bond and may dominate over 'mechanics' in that removing hydrogens from the reaction can change its course.

Further indications of the mechanical and chemical aspects of the reaction can be demonstrated by changing the mass of the five-coordinated silicon in the middle of the SN_2 condensation reaction. By decreasing the mass at constant temperature, the kinetic energy of the atom stays the same in the simulation but the momentum is reduced. This reduces the atom's ability to move against an opposing force such as an interatomic attraction opposite to its motion. The first example is a reaction that originally had an oxygen that broke opposite a single incoming bridge and did not reattach (Fig. 8). A reduction to an atomic mass showed no change in the reaction from what was seen originally and increasing the atomic mass of the silicon resulted in the oxygen breaking loose sooner. This demonstrates that the 'mechanics' can accelerate the chemical process because the additional momentum provided to the silicon causes it to break itself free from the oxygen more quickly. Yet, because the oxygen still broke free with the lighter silicon, the 'chemistry' must have been present to create a good leaving group as can be seen by the three-coordination with hydrogen of the NBO that broke (Fig. 8(f)). The second example is one where an oxygen broke off opposite a single oxygen bridge and then reattached perhaps because of improper 'chemistry' (Fig. 9). In this case, reducing the atomic mass of the silicon caused the bridge to break instead of the original oxygen, suggesting that the break was mechanical. With the heavier silicon, it is expected to break free earlier, similar to what was shown in Fig. 8.

While the trends observed in the simulation clearly show that the presence of hydrogen affects permanent Si–NBO bond rupture and 'mechanics' may cause temporary breaks, there are other processes that can take place. An oxygen without the proper 'chemistry' (bonding to H) may break free mechanically (from momentum effects) from a five-coordinated silicon and then pick up hydrogens and stay detached, or one may detach because of 'chemistry', lose its hydrogens and then return. At the elevated effective temperature used here, things are very dynamic so these possibilities are not eliminated.

In summary, three separate condensation mechanisms were observed, one of which corresponds to that which is most often referred to in the literature. The condensation process is seen to depend on non-bridging oxygens' coordination with hydrogen, the number of bridging oxygens in the transition state and the atomic momentum created as molecules approach each other. The process described as acid catalysis is observed as hydrogens join with NBOs to form OH_x leaving groups which separate from the transition state. Chains form before rings in the simulation, as is observed in experimental work.

5. Conclusions

The release of NBOs opposite and adjacent to an incoming bridge were observed in the molecular simulations of the condensation reactions. The mechanism commonly presented schematically in the literature only involves the removal of the opposite oxygen. Incomplete condensation reactions were also observed. There are 'chemical' and 'mechanical' aspects to the condensation reaction, as defined in the text. The 'chemical' aspect pertains to the role of hydrogen; the 'mechanical' aspect pertains to the physical movement of the ions.

Hydrogen plays an important role in the removal of a detaching NBO from the transition state and completion of the condensation reaction. The average coordination to hydrogen of NBOs that break free in a condensation reaction is higher than the average coordination to hydrogen of all NBOs in the system. Without hydrogen present to form a good leaving OH_x group, condensation reactions often do not go to completion, resulting in the break of a bridging oxygen bond, especially the newly formed Si–O bond with the incoming bridging oxygen.

The 'mechanical' aspect is more prominent in cases where an oxygen break occurs opposite the incoming oxygen bridge. An NBO that mechanically breaks away from the five-coordinated reaction transition state is more apt to reattach to the silicon from which it broke, thereby reversing the reaction.

When there is more than one bridging oxygen on a five-coordinated silicon, there is a tendency to break a bridge rather than release an NBO in the early stages of polymerization, thus resulting in chain formation prior to ring formation.

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