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THE THERMODYNAMICS AND KINETICS OF THE POLYMERIZATION OF SILICIC ACID IN DILUTE AQUEOUS SOLUTION

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ABSTRACT

The polymerization of silicic acid has been investigated at a pH of 8.5 and initial monomer concentration of 300 p.p.m. The rate of polymerization was determined at 25, 30, 35, 40 and 45°C so that the activation energies could be calculated. The activation energies were found to be -16 ± 4 kcal/mole in the 25–35°C region and 14 ± 4 kcal/mole in the 35–40°C region. The negative activation energy is explained by assuming a pre-equilibrium step involving a hydrogen bonded species. The thermodynamic parameters were also determined for the polymerization process. A mechanism has been proposed for the polymerization reaction.

INTRODUCTION

The polymerization of silicic acid and its relationship to natural systems has been of interest to chemists for almost a hundred years. Although a large amount of work has been done on aqueous systems of relatively high concentrations of silicic acid, little has been done on silica solutions of low concentrations. The reactivity at high temperature and pressure is well-known through the works of Morey and Hesselgesser[1] and Kennedy[2], but studies of the low temperature reactivity have been hindered by the sluggishness of the reaction and the great pseudostability of the hydrated silica sols.

A considerable amount of study has been devoted to the polymerization of silicic acid, but little work has been done on the mechanism involved in the process. It has been suggested by Treadwell and Wieland[3] and Iler[4] that in order to explain the polymerization of silicic acid, it must be considered that the tetravalent silicon atom is unsaturated coordinatively. The coordination number of the silicon(IV) ion is six if the anion is singly charged, small, or of low polarizability, *e.g.*, the fluoride ion. The hydroxyl group has a great similarity to the fluoride ion and the two species are equivalent in many structures. Thus the instability of the tetrahedral monosilicic acid molecule is reportedly due to the incomplete coordination of silicon with respect to the hydroxyl ion. The polymerization of $Si(OH)_4$ is visualized as involving the sharing of an hydroxyl ion by two silicon atoms, leading to the formation of polymeric units in which each silicon atom is surrounded by six hydroxyls. The subsequent formation of chain-like polymers leads to a second process which involves the elimination of water from the polymer with the formation of siloxane bonds.

Finally, investigations on the rate of polymerization of silicic acid have resulted in a complete gamut of kinetic orders. Here again, the majority of the work has been done in relatively concentrated solutions. Greenberg[5] studied the rate of the polymerization of silicic acid in basic medium by following changes in the refractive index of the polymerizing solution. Since the pH of the medium was held constant throughout the polymerization process, the reaction was found to follow first order kinetics.

Ikamoto, Okura and Goto[6] have studied extensively the solution and precipitation of silica in concentrations approaching those found in natural systems. In an examination of an aqueous solution of silicic acid in the pH range 7–10, the rate of disappearance of monomeric silicic acid was found to follow third order kinetics. The third order kinetic behavior of silicic acid polymerization has also been noted by Hurd[7] and by Moulik and Mullick[8] in acid solutions, but as the pH of the system is increased there is a noticeable change in the mechanism.

The area of greatest agreement of reaction rates is that the polymerization of silicic acid in basic medium follows second order kinetics. For example, the polymerization reaction of triethylsilane in the presence of base was found to follow second order kinetics[9]. Iler[4] and Alexander[10] have both reported that the polymerization process follows second order kinetics in basic solution, but both investigators studied silica systems in the concentration range of 1.8–3.0% by weight, and as was the case with triethylsilane, the reaction was first order with respect to SiO_2 and first order with respect to hydroxide.

Thus, the mechanism of polymerization of silica systems of low concentrations is not completely understood. This investigation was undertaken to better understand the mechanism involved in the polymerization processes in silica systems of relatively low concentrations.

EXPERIMENTAL

Reagents

The silica solution used for the standardization of the analytical procedures was obtained from the Bio-Rad Laboratories, Richmond, Virginia. The samples consisted of plastic ampoules containing 1.0 g ±0.2% sodium silicate, which, upon dissolving in a liter of solution, yielded a 1000 mg/liter standard solution of SiO_2. The silica used for the rate investigation was reagent grade sodium metasilicate which was obtained from the J. T. Baker Chemical Company. All other chemicals used in the course of this investigation were of reagent quality.

Experimental procedure

Following the rate of polymerization of silicic acid at a concentration level as low as that found in natural waters is prohibitive from the standpoint of both time and degree of experimental accuracy. Thus, the initial concentration of silicic acid in these experiments is somewhat above the equilibrium concentration (with respect to amorphous silica), but not sufficiently high to involve serious colloidal problems.

It was on this basis that 300 mg/liter was chosen as the basic concentration level for the rate studies.

The solutions were prepared by dissolving 4.733 g of reagent grade sodium metasilicate in doubly-distilled water to yield 100 ml of 1000 mg/liter stock solution of SiO_2 at a pH of approximately 11. A 150 ml aliquot of this solution was titrated to a pH of 8.5 with 0.25 *N* $HClO_4$ and diluted to 500 ml to yield a solution containing initially 300 mg/liter of silica. The solution (pH 11) was freshly prepared before each rate study in order to minimize pre-reaction polymerization.

Analytical procedures

In all cases the rate data were obtained from 500 ml of reaction solution. The polyethylene reaction vessel was fitted with a rubber septum to allow withdrawal of a sample for analysis. Samples were taken every hour for the first 13 h of reaction and then at 2 h intervals for the next 50–60 h and at 3 h intervals for the remainder of the 200 h reaction time. A 4 ml sample was taken at each time interval and a 0.5 ml portion used for the determination of monomeric silica. The remaining sample was utilized for a pH determination using a Fisher combination electrode and a Beckmann Zeromatic II pH meter and then returned to the reaction solution to minimize the loss in sample size over the 200 h sample time.

The 200 h limit on the reaction time was chosen because it was found that most of the systems had reached a state of equilibrium by 160–180 h of elapsed time.

The temperature of the reaction systems was controlled in a 26 gallon insulated water bath using a Precision Micro-Set thermoregulator and a 1000 watt heating unit. The temperature was controlled within ±0.2°C.

The method used for determining the concentration of monomeric silica in the rate studies is essentially that developed by Mullin and Riley[11] which involves the reaction of the monomeric silica with acid molybdate and subsequent reduction of the complex to molybdenum blue. It was found that the most satisfactory reducing agent for the process was *p*-methylaminophenol sulfate.

A standard working curve for silica determination was made using the standard silica solution obtained from Bio-Rad Laboratories. The asorbances of the solutions were determined in a 1-cm cell at 812 mμ with a Hitachi Perkin–Elmer Model 139 Spectrophotometer.

RESULTS AND DISCUSSION

The rate of polymerization of silicic acid was studied at five different temperatures. The initial concentration of monomeric silica was 300 mg/liter. The rate constants for the different temperatures are shown in Table I. In Fig. 1 is shown a plot of concentration of monomeric silic *vs.* time. The concentration of monomeric silica decreased rapidly in the initial portion of the plot and after approximately 120–160 h tends to approach a state of equilibrium. This trend is more pronounced in the lower temperature ranges that were investigated.

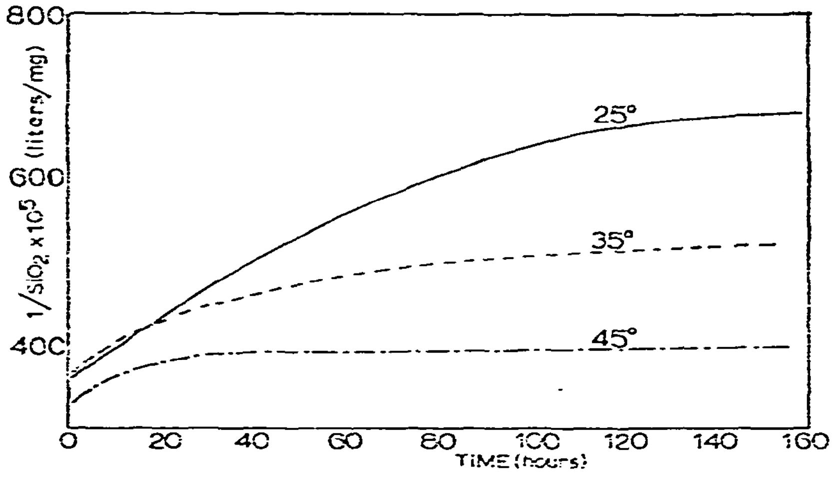


Fig. 1. A plot of the change in concentration of monomeric silicic acid as a function of time for three temperature regions.

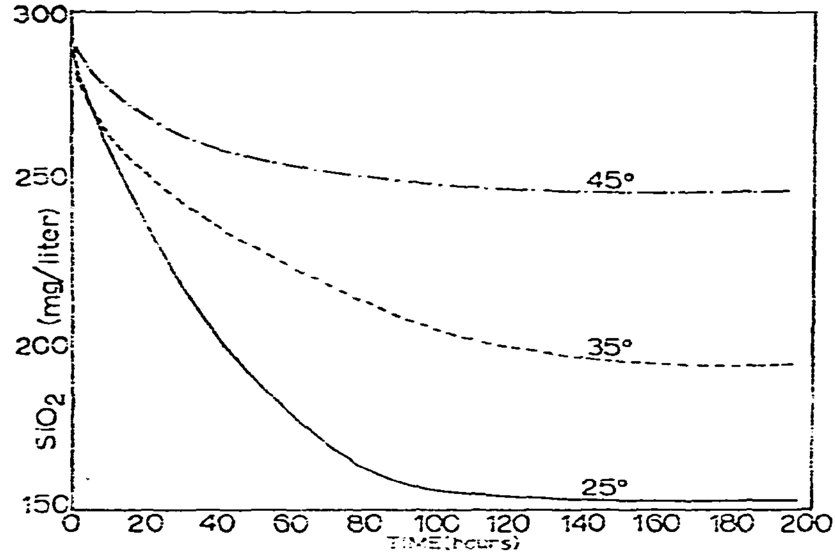


Fig. 2. Second order rate plots for the polymerization process at 25, 35 and 45°C.

TABLE I

INITIAL RATE CONSTANTS FOR THE POLYMERIZATION OF SILICIC ACID IN THE TEMPERATURE REGION OF 25°–45°C

Temperature (°C)	$Kk_f \times 10^6$ *(liters/mole/sec)*
25	57±6
30	38±4
35	23±3
40	38±6
45	52±7

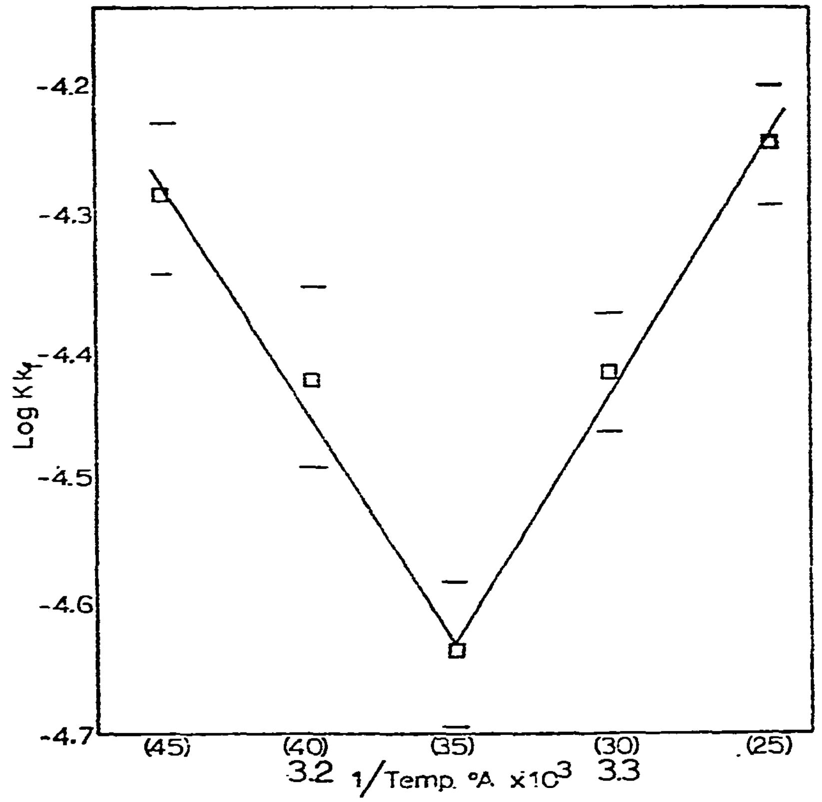


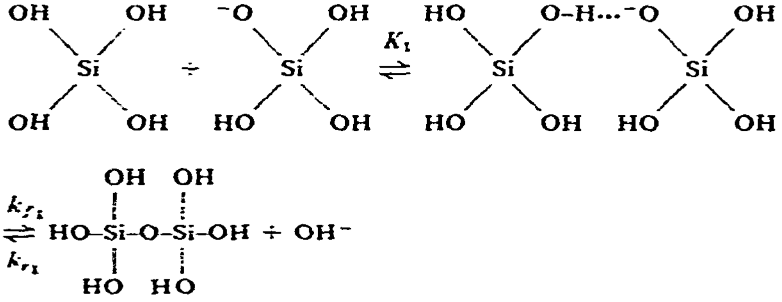
Fig. 3. Arrhenius plot for the polymerization system.

If the polymerization truly follows second order kinetics as proposed by several authors[1,4,9], a plot of the reciprocal of concentration of monomer *vs.* time should yield a straight line, at least in the initial phase of the reaction. The second order rate plots for several systems are shown in Fig. 2, and all systems yield a good straight line plot in the first few hours of the reaction but tail off exponentially at longer times. This tailing off would be expected as concentration of polymeric species build up to the point that other polymerization reactions and depolymerization reactions become appreciable.

The Arrhenius plots for the system studied are shown in Fig. 3. Since the system does not give a singular slope over the entire temperature range, each definite area of the plot is considered separately and the activation energy for that area calculated. The values are -16 ± 4 kcal/mole and 14 ± 4 kcal/mole for the 25–35°C region and 35–45°C region, respectively.

The fact that the activation energy is negative in the 25–35° region of the Arrhenius plot implies that there must be a pre-equilibrium step in the polymerization process. The slope becomes negative in the higher temperature region of the plot suggesting that the pre-equilibrium step probably involves a hydrogen bonding process.

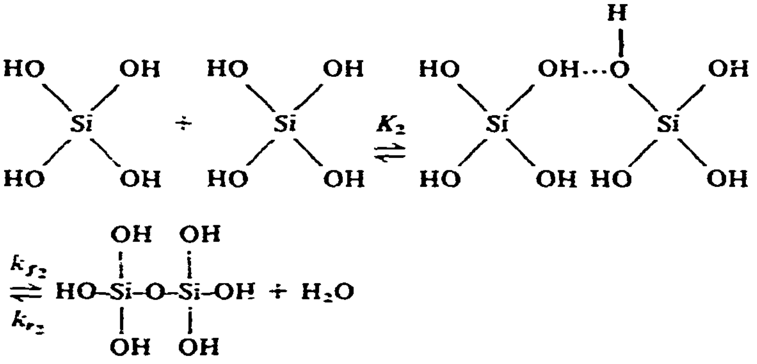
It appears that the two species necessary for the polymerization reaction to take place in a reasonable length of time are a silicic acid anion and a neutral silicic acid molecule[4,7,10,12,13]. As the two reactants approach each other in the solution, it is possible the first reaction involves the formation of a hydrogen-bonded intermediate. The hydrogen bond thus formed would allow the reactants to be held in close proximity, so that the splitting out of a hydroxyl, with subsequent formation of a silicon–oxygen bond, could occur.



Mechanism 1

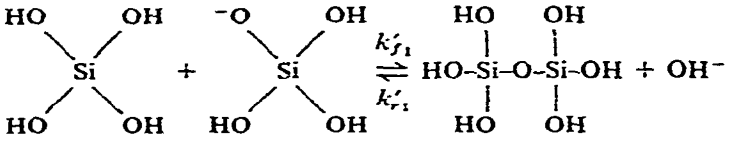
This mechanism, of course, is controlled by the ionization of silicic acid, which depends on the pH of the system. Also, in the above reaction sequence and other reactions shown in this paper, we have used the four coordinated silicic acid and its anion. It could be that the reacting species are octahedral with two waters of solvation in the inner coordination sphere. It is impossible to distinguish between these two possibilities so all we can say is that there is some type of hydrogen bonded species in the first step in the polymerization reactions. Two hydrogen bonds could also be involved in this step instead of one.

Calculations have been made by Greenberg and Sinclair[13] on the ratio of the singly ionized to unionized silicic acid $[H_3SiO_4^-]/[H_4SiO_4]$. At a pH of 8 the ratio is 1.6/100 and at a pH of 9 it is 1.6/10. Thus, in the region under investigation, there is a reasonable concentration of both ions and molecules of silicic acid in solution. In the region below a pH of 8 where the concentration of the ionized form is very small, polymerization still occurs, and since the concentration of the unionized molecule is predominant, an alternate mechanism must also be considered. This reaction may also proceed by a hydrogen bonding step similar to the one described for the anion–neutral silicic acid reaction.



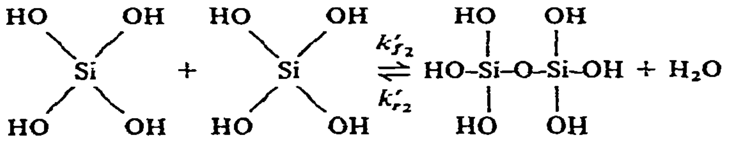
Mechanism 2

Finally consideration must be given to the fact that the reaction may occur without the hydrogen bonding mechanism, since in the 35–45°C temperature range the activation energy is positive. In each of the steps proposed, it is possible that the reactions may occur by simple collision with the subsequent formation of polymer and the splitting out of an hydroxyl or water, *e.g.*,



Mechanism 3

and



Mechanism 4

From a consideration of the proposed mechanism, rate expressions can be formulated for the contributing paths.

$$R_1 = K_1 k_{f_1} [\mathrm{Si(OH)_4}] [\mathrm{(OH)_3SiO^-}] - k_{r_1} [\mathrm{H_6Si_2O_7}] [\mathrm{OH^-}]$$

$$R'_1 = k'_{f_1} [\mathrm{Si(OH)_4}] [\mathrm{(OH)_3SiO^-}] - k'_{r_1} [\mathrm{H_6Si_2O_7}] [\mathrm{OH^-}]$$

$$R_2 = K_2 k_{f_2} [\mathrm{Si(OH)_4}]^2 - k_{r_2} [\mathrm{H_6Si_2O_7}]$$

$$R'_2 = k'_{f_2} [\mathrm{Si(OH)_4}]^2 - k'_{r_2} [\mathrm{H_6Si_2O_7}]$$

The evaluation of the proposed paths are complicated by the fact that all systems are reversible and do not follow a set of singular courses to completion. Only in the initial portion of the reaction can we look primarily at the forward portion of the reactions.

By taking only the forward portions of the reactions into consideration the following rate expressions are obtained.

$$R_1^f = K_1 k_{f_1} [\mathrm{Si(OH)_4}] [\mathrm{(OH)_3SiO^-}]$$

$$R_1^{f'} = k'_{f_1} [\mathrm{Si(OH)_4}] [\mathrm{(OH)_3SiO^-}]$$

The acid dissociation constant is given by

$$K_A = [\mathrm{(OH)_3SiO^-}] [\mathrm{H^+}]/[\mathrm{Si(OH)_4}]$$

where

$$[\mathrm{(OH)_3SiO^-}] = K_A [\mathrm{Si(OH)_4}]/[\mathrm{H^+}]$$

Substituting this into the rate expression gives:

$$R_1^f = K_1 K_A k_{f_1} [\mathrm{Si(OH)_4}]^2/[\mathrm{H}^+]$$

$$R_1^{f'} = K_A k'_{f_1} [\mathrm{Si(OH)_4}]^2/[\mathrm{H}^+]$$

$$R_2^f = K_2 k_{f_2} [\mathrm{Si(OH)_4}]^2$$

and

$$R_2^{f'} = k'_{f_2} [\mathrm{Si(OH)_4}]^2$$

Combining the above rate expressions we obtain the following expression for the total forward reaction rate:

$$R_t^f = [K_1 K_A k_{f_1}/(\mathrm{H}^+) + K_A k'_{f_1}/(\mathrm{H}^+) + K_2 k_{f_2} + k'_{f_2}]\,[\mathrm{Si(OH)_4}]^2$$

If the individual steps in the mechanism are considered as separate entities contributing to the total forward reaction rate, the separate Arrhenius equations can be written for each step and the total forward reaction as a sum of the individual equations. Thus:

$$K_1^f = \frac{A_1 A_A A_{f_1}}{[\mathrm{H}^+]} \exp(-[E_1 + E_A + E^*_{f_1}]/RT) + A_{f'_2} \exp(-[E^*_{f'_2}]/RT)$$

and

$$K_t^f = \frac{A_1 A_A A_{f_1}}{[\mathrm{H}^+]} \exp(-[E_1 + E^*_{f_1}]/RT) + \frac{A_A A_{f'_1}}{[\mathrm{H}^+]} \exp(-[E_A + E^*_{f'_1}]/RT)$$

$$+ A_2 A_{f_2} \exp(-[E_2 + E^*_{f_2}]/RT) + A_{f'_2} \exp(-[E^*_{f'_2}]/RT)$$

In all cases the energy measured is not truly an activation energy, but the sum of thermodynamic and activation energy terms.

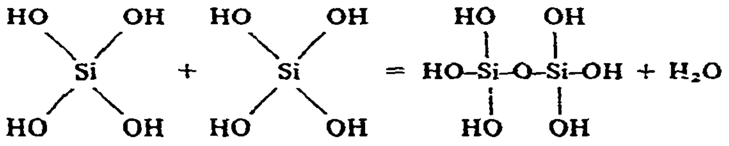
To better understand the mechanism, each region of the Arrhenius plot should be considered separately. First, consider the system in the 25–35°C region. In this region the predominant paths of reaction are those described as Mechanisms 1 and 2. The total activation energy calculated for this region is −16±4 kcal/mole. If we neglect such contributions as solvent effects, there are only two energy involving processes in the mechanism, *e.g.*, the pre-equilibrium hydrogen bonding step, and the splitting out of a water or hydroxyl with subsequent lengthening of the polymeric chain. The splitting out of the water or hydroxyl group should be the rate controlling step in that it would require energy, and this step alone would yield a positive activation energy.

In the region above 35°C, the Arrhenius plot yields a positive value. The calculated overall activation energy for this region is 14 ±4 kcal/mole, which compares with 9.6 kcal/mole obtained by Brady, Brown and Huff[14] for the same pH range. Thus, it appears that in the temperature region above 35°C, the degree of hydrogen bonding occurring in the reaction decreases rapidly, and the reaction must occur primarily via collission reaction.

In the region below 35°C where hydrogen bonding processes are quite important, the energy terms E_1 and E_2 will be the controlling factors in the energy of the reaction. Primarily, the energy comes from E_1, since the ion-molecule interaction will be expected to be much stronger than the molecule-molecule reaction proposed for E_2. Thus, in the region below 35°C, the first term in the equation will be the predominant one. As the temperature is increased above 35°C, the amount of hydrogen bonding is decreased; therefore E_1 becomes very small, causing the collision controlled portion of the equation to become the predominant one.

All of the reaction systems appear to approach a stable equilibrium after approximately 160 h. From this we can calculate the total equilibrium constant for the system.

There are several possible approaches to the total mechanism of the polymerization of silicic acid. One generally accepted fact is that the reaction is one of simple condensation which proceeds in the following manner:



If we also consider the pre-equilibrium step proposed in the reaction mechanism, a general format of the polymerization process can be visualized:

$$M+M \overset{K_1''}{\rightleftharpoons} M_2^* \underset{k_{r_1}''}{\overset{k_{f_1}''}{\rightleftharpoons}} M_2$$

and

$$M_2+M \overset{K_2''}{\rightleftharpoons} M_3^* \underset{k_{r_2}''}{\overset{k_{f_2}''}{\rightleftharpoons}} M_3$$

to

$$M_{n-1}+M \overset{K_{n-1}''}{\rightleftharpoons} M_n^* \underset{k_{r_{n-1}}''}{\overset{k_{f_{n-1}}''}{\rightleftharpoons}} M_n$$

where M_2^*, M_3^*, ... are hydrogen bonded species.

From a consideration of the above paths, the following assumptions can be made concerning the mechanism:

(*1*) The rate determining step will be that of the splitting out of the hydroxyl or water group in the polymer formation.

(*2*) The K'' values for the hydrogen bonding steps are identical, *e.g.*, $K_1'' = K_2'' = K_3'' \ldots$

(*3*) All of the individual k_f and k_r values are identical, *e.g.*, $k''_{f_1} = k''_{f_2} = k''_{f_3}$ ... and $k''_{r_1} = k''_{r_2} = k''_{r_3}$ ...

(*4*) Bond breaking and bond formation occur only at terminal position.

All of the hydrogen-bonding steps involve the same type of bond formation, *e.g.*, a silicon–oxygen species bound to another silicon–oxygen species. Consequently, the bond formation step should be nearly identical in all cases.

There have been no reported instances in the literature of dilute silica solutions yielding branched chain polymers in solution. Whether the polymerization occurs through one oxygen bridge or two cannot be determined experimentally, but the system does appear to form only in linear chains[4].

At equilibrium each of the steps in the polymerization can be solved in terms of the rate constants and the monomer concentration, *e.g.*, $K_{eq} = [M_2]/K''_1\ [M]^2$. Each step in the polymerization scheme can thus be expressed in terms of the initial reactants, the hydrogen-bonding pre-equilibrium constant and the final product. At equilibrium the polymeric species may be expressed in terms of the total monomeric concentration, *e.g.*, $M_0 = M + 2M_2 + 3M_3 + 4M_4 + \ldots$ where M_0 = total silica concentration in the system, M = concentration of monomeric silica, and M_2, M_3, M_4, etc. = concentration of the individual polymeric species. From a consideration of the various polymeric steps at equilibrium, it is possible to express the system in terms of the rate constants and the monomer concentration.

$$M_0 = M + 2\left(K \frac{k_f}{k_r} [M]^2\right) + 3\left(\left(K \frac{k_f}{k_r}\right)^2 [M]^3\right) + \ldots$$

This equation can be simplified to

$$M_0 = M + 2a[M]^2 + 3a^2[M]^3 + 4a^3[M]^4 + \ldots$$

where $a = Kk_f/k_r$

If we now divide this equation through by M we obtain a simple binomial series which has the solution

$$M_0 - M - 2aMM_0 + a^2M^2M_0 = 0$$

At equilibrium, the value of M, the monomer concentration at equilibrium and M_0, and the total silica concentration, are known. Thus, the value of the equilibrium constant [*a*] can be determined from the solution of the above quadratic equation.

TABLE II

EQUILIBRIUM CONSTANTS FOR THE POLYMERIZATION PROCESS AT THE FIVE DIFFERENT TEMPERATURES

Temperature (°C)	*Total K_{eq} (liters/mole/sec)*
25	105.5
30	81.6
35	32.4
40	33.6
45	16.8

The calculated equilibrium constants for the systems studied are listed in Table II. A plot of the log of the equilibrium constant *vs.* reciprocal of temperature has a slope of 9.53 and the resultant ΔH is 15.7 kcal/mole.

The reactions appear to approach a state of equilibrium after 160 h, and if the average value of the monomeric silica concentration between 160 and 200 h can be taken as the equilibrium concentration, it is possible to calculate the total equilibrium constant for the systems [see Table II].

Unfortunately, the total reaction is too complicated to be considered with the data available. The reversibility of all steps, the large number of different reactions occuring simultaneously, and the inability of the analytical methods to distinguish between the many steps makes the evaluation of the total reaction on a molecular basis impractical.

Additional work has been carried out concerning the effect of the presence of chloride on the mechanism and will be presented in a subsequent paper.

ACKNOWLEDGEMENTS

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