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## The Polymerization of Monosilicic Acid

BY G. B. ALEXANDER

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The polymerization of monosilicic acid in 0.1 molar solution at 1.90° has been studied over the pH range of about 1 to 6. It is concluded that there must be different mechanisms for polymerization of silicic acid at 1.90° above and below about pH 3.2, since the slope of the polymerization rate curves is quite different in these two ranges. At low pH, the degree of polymerization increases linearly with the square root of time. Also in this range, the polymer appears to be relatively homogeneous with regard to molecular weight distribution while, above pH 3, a more heterogeneous distribution is obtained. At pH 6, monosilicic acid polymerizes almost instantaneously. Not only is polymerization influenced by pH, but the rate increases with increasing temperature, increasing concentration, and also by certain catalysts, particularly fluoride ions at low pH. The number average molecular weight of the polysilicic acid was determined by the freezing point method, while an indication of the molecular weight distribution was obtained by measuring the rate at which the polysilicic acid depolymerizes in the presence of molybdic acid to form silicomolybdic acid.

### Introduction

Although the chemistry of silica and silicates has been studied for over a century, the polymerization of silica is not well understood. This paper deals with the effect of pH and temperature on the polymerization of monosilicic acid and the reactions of silicic acid polymers.

### Experimental

Monosilicic acid was prepared by the reaction of sodium metasilicate hydrate crystals with a slurry of an ion exchange resin in dilute acid.<sup>1</sup> After adjusting the pH with sodium metasilicate or sulfuric acid, these silicic acid solutions were stored in a thermostated bath at 1.90 ± 0.01° and the degree of polymerization was followed by the freezing point method.<sup>1</sup>

**The Effect of pH on the Polymerization of Silicic Acid.**—From the slopes of polymerization curves shown in Fig. 1, it is concluded that there must be different mechanisms for polymerization of silicic acid at 1.90° above and below about pH 3.2. At low pH (1.70 and 2.10), a plot of the square of the degree of polymerization (D.P.) vs. time (Fig. 2) gives a linear relationship. Graphically, third-order reactions give this relationship when  $(1/c)^2$  (where  $c$  is the concentration of the reactive species) is plotted against time. Since D.P. is inversely proportional to the total concentration of all silicic acid polymers in solution, and if one assumes that the reaction rate of silicic acid polymers in these acid solutions is independent of the number of functional groups, *i.e.*, all polymer species, including monosilicic, disilicic, trisilicic acid, etc., are equally reactive, then the polymerization curve shown in Fig. 2 may be taken to indicate that polymerization follows the third-order reaction

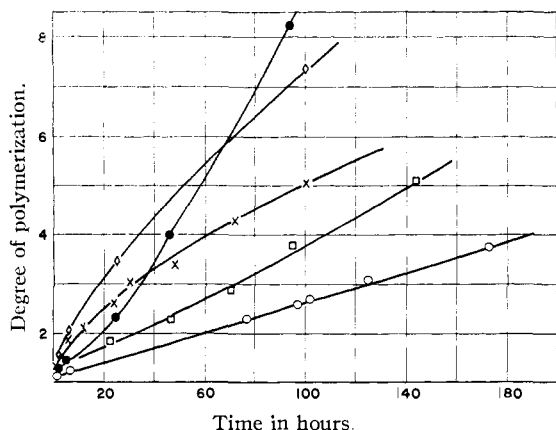


Fig. 1.—Polymerization of monosilicic acid at 1.90°:  $\diamond$ , pH 1.70;  $\times$ , pH 2.10;  $\circ$ , pH 3.20;  $\square$ , pH 3.82;  $\bullet$ , pH 4.36.

(1) G. B. Alexander, *THIS JOURNAL*, **75**, 2887 (1953).

rate law at low pH. At higher pH (pH 4.36, Fig. 1), the polymerization curve has an entirely different shape and might be explained by assuming a second-order reaction type and a rate which is dependent on the number of functional groups. (Note that monosilicic acid has 4 polymerizable silanol groups, disilicic has 6, trisilicic acid as a chain has 8, and as a ring has 6, etc.).

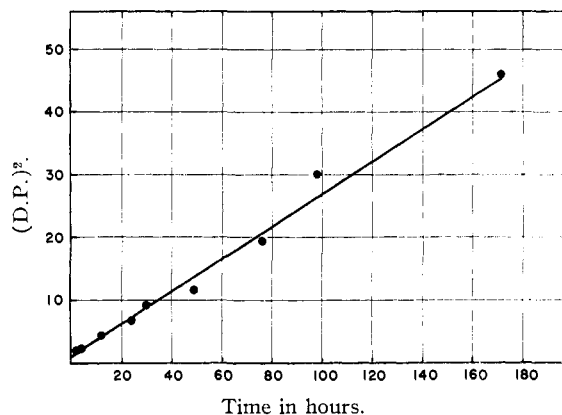


Fig. 2.—Polymerization of silicic acid at pH 2.10.

At present there is no clear-cut explanation of the difference in polymerization mechanism in these two pH ranges. However, it may be significant that polymerization is catalyzed by fluoride ions.<sup>2</sup> It is probable that this catalytic effect is due to a fluosilicic acid. Since the concentration of fluosilicic acid will be proportional to the silica concentration, a third-order reaction might be expected, *i.e.*, the activated reaction complex may consist of two silicic acid units and a fluosilicic acid unit. At higher pH, it is expected that the polymerization is catalyzed by hydroxyl ion and a second-order reaction is logical. These two catalysts, hydroxyl ion and fluoride ion, can be varied independently.

From Fig. 1, it is concluded that monosilicic acid is most stable in solution of 2° at a pH about 3.2. This is in agreement with Willstätter,<sup>3</sup> who observed that monosilicic acid is relatively stable in  $N/700$  HCl. However, his statement that disilicic acid is relatively stable in 0.5  $N$  HCl, while monomer cannot be detected therein, has not been substantiated.

At about pH 6, monosilicic acid in 0.1  $M$  solutions polymerizes almost instantaneously, even at 2°.

A clue as to the type of polymers formed is afforded by the reaction of the silicic acids with molybdic acid reagent,<sup>4</sup> *i.e.*, the rate at which the reaction proceeds gives an indication of the molecular distribution (Fig. 3). In the case of low pH (below 3.2), it is concluded that the polymers formed are relatively uniform with respect to molecular weight dis-

(2) R. K. Iler, *J. Phys. Chem.*, **56**, 680 (1952).

(3) Richard Willstätter, *et al.*, *Ber.*, **62**, 2027 (1929).

(4) G. B. Alexander, *THIS JOURNAL*, **75**, 5655 (1953).

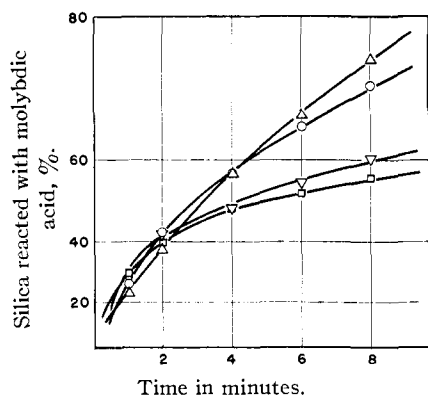


Fig. 3.—Rate of reaction of molybdic acid with silicic acid polymers at D.P. 3.5:  $\Delta$ , silicic acid polymer prepared at pH 1.70;  $\circ$ , silicic acid polymer prepared at pH 2.10;  $\nabla$ , silicic acid polymer prepared at pH 3.20;  $\square$ , silicic acid polymer prepared at pH 3.82.

tribution. On the other hand, at higher pH, the silicic acids appear to consist of monomer along with polysilicic acids of much higher molecular weight, or at least species which do not readily react with molybdic acid. This can be shown more clearly by resolving "silicomolybdic acid" curves into two fractions; for example, see Fig. 4, for the case of a polymer having a degree of polymerization of 3.5, prepared at pH 3.82 and 1.90°. If the straight line portion due to the higher molecular weight fraction in the original curve is extrapolated, it intersects the ordinate at 41%, indicating 41% of a lower molecular weight fraction. The color contribution of the higher molecular weight fraction at any given time can be predicted by drawing a line parallel to the extrapolated portion through the origin, line B. By subtracting the color due to this fraction from the total color, curve A can be drawn. From A it appears that the lower molecular weight fraction is a mixture of monomer and dimer. At pH 0.59, the color curve for a polymer of degree of polymerization of 3.5 was resolved into two parts; in this case, the lower molecular weight fraction was essentially monomer.

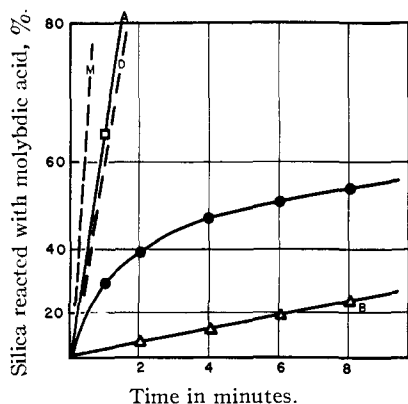


Fig. 4.—Resolution of molybdic acid curve; degree of polymerization, 3.5; polymerization pH, 3.82: O, original curve; M, reaction of monosilicic acid; D, reaction of disilicic acid; A, low molecular weight polymer fraction; B, high molecular weight polymer fraction.

The observations regarding polymer distributions may be explained by the following hypothesis: At low pH (below pH 3.2), the polymerization is only very slowly reversible. Upon these circumstances, the silicic acid polymerizes to linear or openly branched polysilicic acids, which are readily accessible to reaction with molybdic acid. On the other hand, at higher pH, siloxane bonds are more labile, permitting depolymerization-polymerization rearrangement of polymer structures. Thus, linear units which may form in-

itially tend to condense to cyclic or highly crosslinked polymers.

If the hypothesis regarding fluoride and hydroxide catalysis is correct, then it is assumed that fluoride favors polymerization, whereas hydroxide promotes both polymerization and depolymerization.

**The Effect of Temperature on Polymerization.**—As expected, the polymerization rate increases as the temperature is increased. However, at any given pH the polymer distribution appears to become more heterogeneous as temperature increases. Thus, at pH 1.7 and 35°, polymerization was very rapid; in 1.5 hours over 80% of the monomer originally present in a solution of 0.1 M SiO<sub>2</sub> had polymerized to a product which, upon reaction with molybdic acid, showed monomer-dimer and "inactive" polymer fractions.

The effect of temperature was exaggerated by heating a solution of monosilicic acid (pH 2.2) to 90° for 30 minutes. The degree of polymerization increased only to 2.4, as determined by the freezing point method, and the silicomolybdic acid color test indicated that the silicic acid present consisted of monomer (about 40% of the total SiO<sub>2</sub>), and high ("molybdic acid inactive") polymer. Apparently as temperature is increased cyclization or crosslinking is favored, with the result that "molybdate inactive" polymers are produced at higher temperatures.

Heating a low molecular weight silicic acid at pH 3.82 caused gel formation, leaving only about 15% of the silica in the "molybdic acid active" state.

At ordinary temperature (25–30°) the minimum rate of polymerization is reported to be pH 1.8,<sup>5</sup> and at 90° may be lower than pH 1.0. The pH at which there is maximum stability evidently represents a point where the hydrogen and/or fluoride ion catalyzed reaction and the hydroxyl ion catalyzed reaction are at a minimum. The shift in this pH of maximum stability with temperature indicates that there is a marked decrease between the energy of activation of the two types of polymerization. This agrees with the report by Hurd<sup>6</sup> that at low pH the energy of activation is 9,000–11,000 cal./mole, while at higher pH it is 24,000 cal./mole.

**Depolymerization Rearrangement on Dilution of Silicic Acid Polymer Solutions.**—A very interesting phenomenon occurred when a solution of polysilicic acid having a degree of polymerization of above 3 was diluted to 0.004% SiO<sub>2</sub> at pH 1 and aged at room temperature. A rearrangement began and in about 10 minutes the monomer content, as shown by the molybdic acid reaction, had increased about 20%. After 1.5 hours, the monomer content had about doubled and a "molybdic acid less active" polymer had appeared. On standing for about 24 hours, the silica had completely depolymerized to monosilicic acid (see Fig. 5).

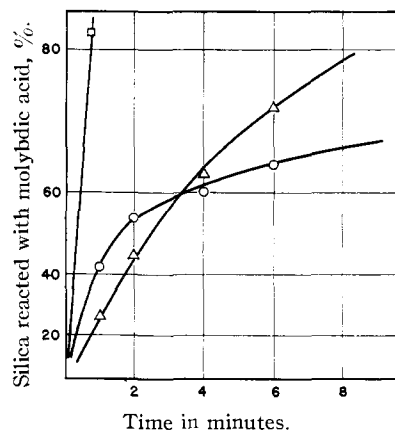


Fig. 5.—Depolymerization on dilution:  $\Delta$ , original silicic acid;  $\circ$ , diluted and aged 1.5 hours;  $\square$ , diluted and aged 8 hours.

From the above observations, one might conclude that (a) polymerization is a reversible reaction at room temperature in solutions of pH 1.0, and (b) the rate of depolymerization

(5) R. K. Iler, *J. Phys. Chem.*, **57**, 804 (1953).

(6) C. B. Hurd, *et al.*, *THIS JOURNAL*, **66**, 388 (1944).

is slow compared to the rate of polymerization. Thus, although the thermodynamically stable state under the conditions indicated appears to be 0.004% SiO<sub>2</sub> as monomer, the rate of polymerization is so fast as compared with the rate of depolymerization that polymerization to higher intermediate polymers takes place before the stable state is reached.

**The Effect of Catalysts on Polymerization of Monosilicic Acid.**—Experiments studying the effect of catalysts confirm results reported by Iler<sup>2</sup> regarding fluoride. Thus, the most active catalyst found was the fluoride ion, which, when added to the extent of one or two parts per million, doubles the rate of polymerization of silicic acid at pH 2.9 and 1.90°. This effect of fluoride ion is counteracted by the addition of 10 parts per million of aluminum ions, presumably due to the formation of the complex fluoaluminate ion.

The action of a wide variety of inorganic and organic compounds was investigated, but none of the materials investigated had a very profound effect, in the pH range of 2–3. Specifically, molybdic acid at 0.001 *M* or mannite at 10% increased the rate of polymerization slightly, but nickel sulfate, ferrous sulfate, silver nitrate, copper sulfate,

at 0.00006 *M*, aluminum sulfate or phosphoric acid at 0.001 *M*, or sodium thiocyanate, potassium bromide, beryllium sulfate, boric acid, stannic chloride, titanium sulfate, at 0.02 *M*, had no effect. The addition of 10% methyl alcohol caused a slight decrease in the polymerization rate.

**Strength of Silicic Acids.**—It was found that monosilicic and polysilicic acids are very weak acids, since they apparently do not contribute any appreciable hydrogen ion concentration to their solutions. Thus, when a solution of 0.1 *M* silicic acid was prepared in a solution of dilute H<sub>2</sub>SO<sub>4</sub> of pH 2.10, the pH of the resulting silicic acid solution (after complete removal of Na<sup>+</sup> by ion exchange) was 2.10. Moreover, when a monomer solution was prepared at pH 2 and then adjusted to pH 3.89 by the addition of a trace of sodium metasilicate, it was found that, in spite of the fact that the degree of polymerization increased from 1.34 to over 5, the pH remained constant. These observations agree with the values of dissociation constants of orthosilicic acid reported to be 10<sup>-9.8</sup> and 10<sup>-12.167</sup>.

(7) P. S. Roller and Guy Ervin, Jr., *THIS JOURNAL*, **62**, 461 (1940). WILMINGTON 98, DEL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

## An Electron Diffraction Investigation of the Molecular Structure of Hexafluoroethane<sup>1</sup>

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The interatomic distances in hexafluoroethane have been determined by electron diffraction using the visual correlation procedure. The following results were obtained: C–F = 1.330 ± 0.015 Å., C–C = 1.51 ± 0.06 Å., and ∠FCF = 108 ± 1.5°. The results are compared with two earlier electron diffraction investigations.

A previous electron diffraction investigation<sup>2</sup> of the structure of hexafluoroethane gave C–C = 1.45 ± 0.06 Å., C–F = 1.35 ± 0.02 Å., and ∠FCF = 107.5 ± 1.5°. Even with the rather large uncertainty on the C–C bond distance, these results indicated that this distance is considerably shorter than the value of 1.535 Å. found in ethane.<sup>3</sup> A second electron diffraction investigation<sup>2</sup> did not confirm this unusually short C–C bond but gave the following results: C–C = 1.52–1.60 Å., C–F = 1.37–1.34 Å., and ∠FCF = 107.5–109.5°.

The large discrepancy between these results suggested the present investigation of the structure of hexafluoroethane. It seemed that the earlier work might be improved upon in two ways: first, by obtaining diffraction patterns extending to larger scattering angles and, second, by a careful consideration of the vibrational and rotational effects within the molecule. These latter effects have often been neglected in electron diffraction studies.

### Experimental

The sample of hexafluoroethane (b.p. –76.2°) was supplied by the Central Research Department of the Minnesota Mining and Manufacturing Company; infrared spectroscopy indicated the sample to be better than 99% pure. Electron diffraction photographs were prepared in the customary manner<sup>4</sup> using an apparatus built by Dr. H. J. Yearian of the Purdue Physics Department. The camera

distance was about 10.7 cm. and the wave length of the electron beam, as determined from transmission pattern of ZnO, was about 0.055 Å. The recorded diffraction pattern for hexafluoroethane extended to a *q* value of about 105.

### Interpretation of the Pattern

The visual correlation method<sup>4,5</sup> and the radial distribution method<sup>6,7</sup> were used in the interpretation of the recorded pattern. The radial distribution function was calculated from the equation<sup>7</sup>

$$rD(r) = \sum_{q=1,2}^{q_{\max}} I(q) \exp(-bq^2) \sin\left(\frac{\pi qr}{10}\right) \quad (1)$$

by the use of punched cards.<sup>7</sup> *I*(*q*) is the visual intensity curve (curve vis., Fig. 2) which is drawn assuming no falling off of intensity with increasing *q*. The constant *b* was chosen so that exp(–*bq*<sup>2</sup>) = 0.10 at *q* = 105. The terms for the range *q* = 1 to *q* = 20 were obtained from one of the acceptable theoretical intensity curves which were calculated on I.B.M. machines, using the equation<sup>7</sup>

$$I(q) = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} \exp(-b_i q^2) \sin\left(\frac{\pi q}{10} r_{ij}\right) \quad (2)$$

All measurements and intensity estimates were made by three independent observers. The averages of the measurements of the three observers led to the *q*<sub>0</sub> values which are given in Table I.

Theoretical intensity curves were calculated over much of the parameter field indicated in Fig. 1 for rigid models of hexafluoroethane in which the symmetry of the point group *D*<sub>3d</sub> was assumed. Curve

(5) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(6) L. Pauling and L. O. Brockway, *THIS JOURNAL*, **57**, 2684 (1935).

(7) P. A. Shaffer, V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

(1) Contains material from the Ph.D. thesis of James L. Brandt, Purdue Research Foundation Fellow in Chemistry, 1951–1952.

(2) A survey of electron diffraction results through 1949 is found in the tabulation by P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

(3) This value is quite accurate and is based on a combination of electron diffraction and infrared spectroscopic data made by K. Hedberg and V. Schomaker, *THIS JOURNAL*, **73**, 1482 (1951).

(4) L. O. Brockway, *Revs. Modern Phys.*, **8**, 231 (1936).