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# The Hydrolysis of Ethyl Orthosilicate and Preparation of Silicic Acid Gels from It

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This thesis is presented to the Department of Chemistry  
of Union College in partial fulfillment of the requirements for the  
Degree of Bachelor of Science in Chemistry.

By M. W. Wilson

Approved Charles B. Sturd

June 1938



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THE HYDROLYSIS OF ETHYL ORTHOSILICATE AND PREPARATION OF  
SILICIC ACID GELS FROM IT

Introduction

Ethyl orthosilicate,  $(C_2H_5O)_4Si$ , the ester of orthosilicic acid and ethyl alcohol, is a colorless liquid boiling at  $165^{\circ}C$ . It can be hydrolyzed to produce what is known as a hydrated silica sol or a sol of condensed silicic acid and ethyl alcohol; and under suitable conditions the hydrated silica sol or condensed silicic acid sol can be made to form a gel. It was decided to study the rates of the hydrolysis and gel formation.

We have thus two reactions to be studied:

1. Ethyl orthosilicate + water  $\rightarrow$  silicic acid or  
condensed silicic acid + ethyl alcohol
2. Silicic acid  $\rightarrow$  condensed silicic acid  $\rightarrow$  gel

The hydrolysis of ethyl silicate and subsequent gel formation has been studied in the most general way by King<sup>1</sup>. The formation of a silicic acid gel from the kinetics of reaction standpoint has been studied by Hurd. (see Hurd and Letteron<sup>2</sup>)

The ethyl orthosilicate used in this study was obtained from the Union Carbide Company. It had a very pure appearance; a sample taken distilled at  $165-169^{\circ}C$ . for the most part. No attempt was made to purify it further before use in these experiments. It was used as furnished by the Union Carbide Company. In any studies on ethyl silicate an impurity



which should be especially watched for is acid, since it is a catalyst for the hydrolysis of ethyl silicate and a very small amount of strong acid produces quite an effect on the hydrolysis. As will be explained later, the U. C. C. ethyl silicate seemed to be quite acid free.

Ethyl silicate, as might be expected from its structure, is highly insoluble in water. No attempt was made to determine the solubility, but one may readily determine that its solubility is less than .5% and no doubt is really much less than this. It was observed that at least .3 c.c. of ethyl silicate formed an immiscible mixture with 60 c.c. water.

Since ethyl silicate is so insoluble in water, its hydrolysis must be conducted by some special method. Brintzinger and Brintzinger<sup>3</sup> have prepared silicic acid sols by passing ethyl silicate vapor in a stream of dry air into .002 N HCl and .001 N HCl solutions. The hydrolysis may also be conducted heterogeneously by shaking ethyl silicate with water (very slowly, however) or with water containing some HCl to catalyze the reaction. The hydrolysis may be conducted in a homogeneous system by mixing ethyl silicate into a mixture of ethyl alcohol and water with or without HCl. The ethyl alcohol serves as a mutual solvent for the ethyl silicate and water. By increasing the HCl concentration, one can use less alcohol and get homogeneous systems by a little shaking.

The formation of a gel from hydrolyzed ethyl silicate is undoubtedly similar to the formation of silicic acid gels from sodium silicate. It was decided to study the rate of formation of the gel from the point of view which Hurd and his co-workers have in their studies on silicic acid gels. The factors affecting the formation of silicic acid gels have been investigated by Hurd and his co-workers. Hurd and Letteron have found that the log of time of set of the gels is a linear function of the reciprocal absolute temperature, and Hurd, Raymond and Miller<sup>4</sup> have shown that between



a pH of 4 and 6 the log of the time of set decreases with increasing pH, and is practically a straight line function. The effect of acid concentration over a wide range is shown by Hurd and Letteron. Of great interest in the study of the gel formation is the work of Buntzinger and Buntzinger, who have studied the condensation of the silicic acids formed by the hydrolysis of ethyl silicate.

The time for instantly homogeneous mixtures of ethyl silicate, ethyl alcohol and water to set to gels was studied at a constant temperature as a function of pH. The solutions were made more acidic with acetic acid and less acidic with sodium acetate. One does not hereby obtain the time taken by the gel reaction alone, but obtains the time required by a combination of two reactions, a hydrolysis of ethyl silicate, and a gel formation from the silicic acids produced by the hydrolysis. If one wished to study the gel formation reaction independent of the hydrolysis reaction, it would be necessary that one complete the hydrolysis reaction with the gel formation reaction controlled so that it could only proceed a very short distance, then adjust conditions for conducting the gel formation reaction.

The gels formed from mixtures of  $(\text{EtO})_4\text{Si}$ ,  $\text{EtOH}$  and  $\text{H}_2\text{O}$  which are instantly homogeneous are really alcohol gels for the most part. The gel mixtures which were made up (the instantly homogeneous mixtures) were 45 c.c.  $\text{EtOH}$  to 10 c.c.  $(\text{EtO})_4\text{Si}$  and 15 c.c.  $\text{H}_2\text{O}$ . The 10 c.c. ethyl silicate will approximately yield 10 c.c. more ethyl alcohol upon hydrolysis. Therefore the dispersion medium for the most part is ethyl alcohol. It is possible by making a mixture with the right water content to obtain a gel in which the dispersion medium will be practically totally ethyl alcohol.



It will be observed that in certain ranges of pH which will be pointed out later, the  $H^+$  has the opposite effect upon the speed of the hydrolysis reaction that it has on the speed of the gel formation reaction, while in another range the  $H^+$  has the same effect on the speed of both reactions. That is, the  $H^+$  always tends to speed up the hydrolysis, while with some concentrations it tends to speed up the gel reaction, and at other concentrations to slow it down.

### Experimental

The system upon which most of the work was performed was that resulting from mixing ethyl silicate into a solution of water and ethyl alcohol containing a varying amount of  $H^+$  for catalyst. This system was essentially the one studied by King. The following ratio of  $(EtO)_4Si$ , EtOH (95%) and  $H_2O$  (with or without acid) was chosen - 1:4.5:1.5 by volume. Most of the mixtures were made using 10 c.c.  $(EtO)_4Si$ , 45 c.c. EtOH, and 15 c.c.  $H_2O$  (with or without acid). This mixture gives nearly the same  $SiO_2$  concentration (.641 molar) as is found in the gels from sodium silicate which are studied in this laboratory. It is a mixture which is immediately homogeneous, and it contains about as much water as is possible with the given amount of ethyl silicate, while remaining a homogeneous mixture. By increasing the  $H^+$  concentration one may cut down on the ethyl alcohol and increase the water and get systems which will become homogeneous in a short time by shaking. That is, one conducts a rapid hydrolysis. Although the ratio of  $H_2O$  to  $(EtO)_4Si$  is small by volume, the mol ratio is about 20:1.

There is no simple way to study the rate of the hydrolysis; that is (as far as the writer knows) there is no substance formed or diminished



whose concentration at a given instant can be determined by a quantitative analytical method. King states that some idea of the rapidity of hydrolysis of ethyl silicate in aqueous alcohol can be obtained from the temperature rise which occurs upon mixing. He gives a temperature rise vs. time curve for methyl silicate in aqueous alcohol. However, King's ethyl silicate - aqueous alcohol mixtures must have been quite acidic, although he simply states that he mixed ethyl silicate with aqueous alcohol. In mixing 10 c.c.  $(\text{EtO})_4\text{Si}$  with 45 c.c. EtOH and 15 c.c.  $\text{H}_2\text{O}$ , no temperature rise whatever was observed by the writer. In solutions catalyzed with HCl, the temperature rise was observed and note made of the amount of rise.

The ethyl alcohol and water used were not purified from carbon dioxide, and a solution of  $(\text{EtO})_4\text{Si}$ ,  $\text{H}_2\text{O}$  and EtOH of the given ratio showed a pH of approximately 4.4. Much of this acidity was due, no doubt, to the dissolved carbon dioxide. Incidentally, this pH shows that the ethyl silicate from U.C.C. must have been quite free of any acid.

Concerning the rate of hydrolysis, it was decided to find whether any conductivity change might take place in some reaction mixture which would have enough conductance to be conveniently measured. Such a mixture would be one of the homogeneous mixtures just described, with a little HCl added as catalyst. The HCl would provide the conductivity.

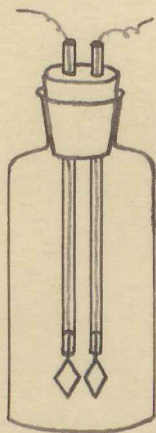
The resistance of one of these acid homogeneous reaction systems was measured in a conductivity cell and found to change a small amount. Since the ethyl silicate takes up 1/7 of the original reaction solution, its hydrolysis to ethyl alcohol and silicic acid will greatly change the character of the solution. Consequently one might assume that the conductivity of an electrolyte present, such as HCl, would be changed. Rice<sup>5</sup>



shows the effect upon an HCl solution by the addition of ethyl acetate - the conductivity is depressed. Likewise in the case of the ethyl silicate reaction mixture, the conductivity of the HCl is apparently depressed by the ester ethyl silicate, more so than by the hydrolyzed EtSi. That is, the conductivity increases upon hydrolysis.

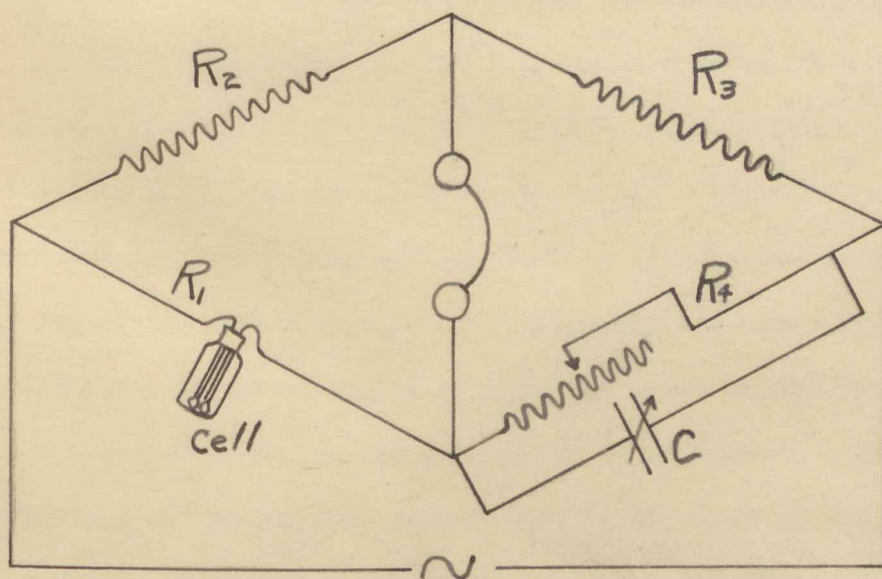
Some  $(\text{EtO})_4\text{Si}$ ,  $\text{H}_2\text{O}$ ,  $\text{EtOH}$  and HCl mixtures were therefore studied for conductivity change. Since HCl strongly catalyzes the reaction, and since a fast reaction causes a temperature rise, in order to attempt to conduct the reaction at a constant temperature only a small amount of HCl can be used. The HCl solutions which were used were approximately .1, .05, and .025 N. The latter two were made up by dilution of the first. These are the concentrations of the 15 c.c. of HCl solution which is added to the other components. The actual concentrations of HCl in the reaction mixtures were therefore approximately .02, .01 and .005 N.

To measure conductances of solutions such as these reaction mixtures, a conductivity cell for high resistances is necessary. The cell used was made from a 4 oz. glass stoppered bottle with the glass stopper replaced with a hard wooden plug impregnated with paraffin and fitted closely to the opening. In this plug were cemented firmly two glass tubes which held the electrodes. The latter were platinized platinum, about 1 cm. square, and placed about 1 cm. apart. A diagram is shown.



The stopper has one particularly bad point. Paraffin is very slowly dissolved by ethyl silicate. However, the amount of ethyl silicate vapor condensed and absorbed in the stopper is not worth considering in this preliminary investigation whose purpose was after all mainly to find whether this conductivity method can be used to measure the rate of the reaction. The type of cell shown has the advantage that a gel, if formed, could be more conveniently removed than from one of the Washburn type. In order to see whether any fault in the cell might cause a change of conductivity, a solution of HCl and ethyl alcohol was placed in the cell and its resistance measured over a period of a few hours, and also about 20 hours later. The change during 5 hours amounted to about .2% at the most, and in a period of 20 hours about .4%. The data are given in Table I.

The set up used for measuring the cell resistance of the reaction solutions was the standard modified Wheatstone bridge for conductivity measurements. A diagram is given.



The bridge was balanced with  $R_2$  and  $R_3$  equal and of about the same magnitude as  $R_1$  (for most sensitive balance).  $R_4$  then gives the



resistance of  $R_1$ . The variable condenser C is very important in obtaining a good balance. The resistance of the reaction mixtures with this set up could be measured with less than .2% error as far as obtaining a balance was concerned.

In none of the reaction mixtures upon which this method was tried (using the acid concentration mentioned) did the reaction proceed slowly enough so that there was no temperature rise from heat of reaction. An initial rise of about 4-5 degrees took place with all of the reaction mixtures tried; the rise was more rapid with the solutions of higher  $H^+$  concentration. The reactants were therefore mixed from 4 to 10 degrees below the temperature of the thermostat (a water thermostat controlled within less than .1 degree), the idea being to keep the reaction mixture temperature from going above thermostat temperature. In this procedure the reaction temperature was not greatly different from thermostat temperature for long. It is realized, of course, that one cannot study a reaction rate quantitatively when such a procedure is necessary, but in this investigation the primary interest was in the magnitude of the conductivity change.

It was found, however, that the reaction gave off heat rapidly enough for some time after the initial burst of heat to raise the reaction mixture a little above the thermostat temperature. Therefore the resistance measurements in the early part of the reaction are for the most part lower than they should be, had the reaction temperature not been above the thermostat temperature. It is of course well known that a slight rise in temperature of a solution causes its resistance to be lowered considerably. An investigation of the general temperature coefficient of resistances measured in these experiments showed it to be about 2.5% lowering of resistance per degree rise in temperature, or about 12 ohms in 500 per degree.



Since the total change in resistance which takes place in the course of the reaction is estimated at about 10% or thereabout, it is seen that the temperature of the reaction mixture should not differ from that of the thermostat by as much as .1 degree in order that any quantitative data be obtained. As far as showing the possibility of this conductivity method in measuring the rate of the hydrolysis, this event of the reaction temperature being higher than thermostat temperature only prevents the showing of the full change in resistance which takes place.

The experiment was actually carried out as follows. The EtOH (45 c.c.) and HCl solution (15 c.c.) for the reaction solution were mixed in a small glass stoppered bottle. At a temperature of from 4 to 10 degrees below the reaction thermostat temperature, 10 c.c. of  $(\text{EtO})_4\text{Si}$  was pipetted into the EtOH - HCl solution at a recorded time, and the mixture vigorously shaken to insure homogeneity. A thermometer was then inserted in the bottle and the initial temperature rise observed. When the temperature had apparently ceased to rise, the reaction mixture was poured in the conductivity cell and the latter inserted in the thermostat. Resistance readings about 10 min. later were taken as either resistances of the reaction mixture at thermostat temperature or above thermostat temperature. After the conductivity cell with the reaction mixture had been inserted in the thermostat, the process was repeated with another identical reaction mixture, and this mixture was poured into a bottle of same size and shape as the conductivity cell, placed also in the thermostat, and a thermometer inserted in this solution.

If was found that the temperature of this reaction mixture came either to thermostat temperature or above thermostat temperature within about 10 minutes. The thermometer was not calibrated with the thermostat



thermometer. Readings two or three hours later are equivalent to thermostat temperature.

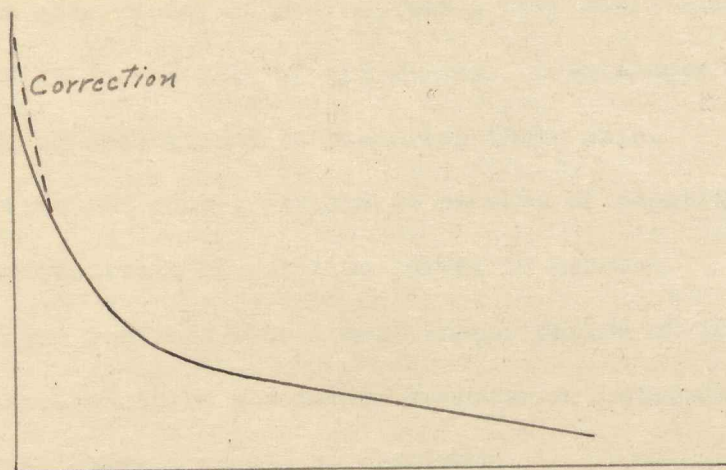
The resistance change was only followed at most for about 1200 minutes, due to a desire to try as many reaction solutions as possible, and because of doubt about the reliability of the cell over a longer period than that.

The runs made using .1 and .025 HCl solutions are plotted, resistance vs. time. All runs were made at 32° C. except one at 25° C. Although the reaction mixture may not have been at constant temperature, the points lie on a smooth curve because the temperature having rapidly reached some point above the temperature of the thermostat, comes down gradually to thermostat temperature. No attempt was made to transpose resistances into specific conductances (although the latter, of course, are more fundamental), since one could depend on the electrodes being fixed in a definite position only in the course of a single run, and one could not therefore have a dependable cell constant.

Extrapolation back to zero time has been made on the curves, but it is not considered to have much value outside of showing the possibility of the resistance change which might be measured if the reaction were slowed down by running it at 0° C. or by using a weaker acid which would catalyze the reaction less rapidly. A weaker acid would, of course, give a higher resistance and the corresponding cell would have to be designed. Dilution of HCl to lower concentrations than .025 N should, of course, be made and tried.

It has already been stated that since the reaction mixture is a little above the thermostat temperature at the beginning, the resistances measured in this period are lower than they would be at thermostat temperature. The curves should therefore be corrected something like this:





The question now must be answered, can this method have any quantitative value in studying the hydrolysis of ethyl silicate, or is it only of qualitative significance if it is that? The change in resistance which occurs is, of course, very small as compared with the changes which are measured in studying other reactions; for example, the change in conductivity in the saponification of ethyl acetate and the change in the rotation of the plane of polarized light by a hydrolyzing sugar solution. However, although the change in resistance of the reaction mixture is small, it can be measured very accurately for a given temperature, provided that temperature is controlled very closely. This can be done if the reaction is made to run slowly enough. Having an accurate resistance vs. time curve, will this show quantitatively the rate at which ethyl silicate is hydrolyzing? It will if the lowering of the resistance is proportional to the amount of  $\text{C}_2\text{H}_5\text{-O-}$  groups which have been hydrolyzed. Such an assumption would not appear to be a very bad one.

Interpretation of the curves which are given on the above assumption show that the reaction is very rapid even when catalyzed with an HCl concentration as low as .005 N (approx.).



It has been known, of course, that a very small amount of HCl will have a great effect on the rate of hydrolysis. Brintzinger and Brintzinger use very low HCl concentrations in preparing their sols.

Otherwise the curves assumed to be rate of reaction curves show the typical characteristic of reaction curves in general.

By taking readings over a much longer period of time with a cell which could be assumed to be absolutely dependable, interesting data of at least qualitative interest should be obtained.

There are two factors entering into this experiment, the importance of which the writer cannot venture to guess, but whose importance should be determined. One is the possibility of a volume change in the solution during the reaction. This determination would require a dilatometer experiment with very accurate temperature control. Such an experiment should be made. It should prove interesting. It has already been suggested to the writer as a possibility for measuring the reaction rate. The other thing is the conductance effect of the charged polymerized silicic acid particles which have been shown to have considerable conducting power.

No picture of the mechanism of the reaction can be given from the data. King gives a good discussion of what he believes to be taking place. He pictures the condensation of OH groups on the silicon even before all the  $\text{C}_2\text{H}_5\text{-O-}$  groups have been hydrolyzed, and points out that the  $\text{H}_2\text{O}$  concentration will determine the extent of this kind of reaction - that is, the lower the water concentration, the more condensation before complete hydrolysis. Brintzinger and Brintzinger, already referred to, have investigated the polymerization of the silicic acids obtained by the hydrolysis of ethyl silicate.

A few trials were made to get some idea of how rapidly ethyl silicate would hydrolyze in a heterogeneous system, a mixture in which ethyl



silicate formed an insoluble phase. In considering heterogeneous hydrolysis, one must bear in mind that ethyl alcohol is formed in the hydrolysis, and that this will tend to bring ethyl silicate into solution; that is, one does not have the same heterogeneous condition throughout the hydrolysis.

A mixture of 10 c.c.  $(\text{EtO})_4\text{Si}$  and 60 c.c.  $\text{H}_2\text{O}$  was shaken vigorously for about an hour in an eccentric shaker. A semi-stable emulsion was formed, which shaken a little from day to day gave after a few days a homogeneous system. It is still under observation.

A mixture of 10 c.c.  $(\text{EtO})_4\text{Si}$  and 60 c.c. .5 N HCl was shaken. Within about 30 min. this gave a homogeneous system except for a slight milkiness - whether a silicic acid colloid or unhydrolyzed EtSi was not determined.

The bringing of ethyl silicate into solution by saponification was tried. In saponifying ethyl silicate one must bear in mind that alcohol and sodium silicate are formed, and that sodium silicate being highly insoluble in alcohol, may give a non-homogeneous system upon the saponification of the ethyl silicate.

A mixture of 10 c.c.  $(\text{EtO})_4\text{Si}$  and 60 c.c. 3 N NaOH was shaken vigorously. Within about 20 minutes the system became homogeneous except for a little precipitate which settled out - probably a sodium silicate. In conducting these heterogeneous hydrolyses and saponifications, one must bear in mind that the vigor with which the system is shaken is a very important factor; for example, stirring a system with an electric stirrer does not give anywhere nearly the speed of reaction that violent shaking with an eccentric shaker does.

A discussion of the preparation of gels will now be given, and involved in this will again be the hydrolysis reaction. In preparing the



tel from  $\text{EtSi}$ , one should work with the point of view which one has in preparing gels from sodium silicate - that is, one should appreciate the extremely great importance of the  $\text{H}^+$  concentration and the temperature. Silicic acid gels from sodium silicate are formed most rapidly at the neutral point and at high  $\text{H}^+$  concentrations. In order to form gels from ethyl silicate, one must of course first hydrolyze the ethyl silicate in order to get silicic acid, the starting material for the gel. One may hydrolyze ethyl silicate very rapidly catalytically with  $\text{H}^+$  as has been discussed. One can tell the relative rapidity of hydrolysis by the amount of temperature rise. Using a very strong  $\text{HCl}$  reaction solution which would have that acidity which would enable the rapid formation of a gel (see Hurd and Letteron), one would obtain both a rapid hydrolysis, thus a rapid production of silicic acid and following this a rapid gel formation. However, if for rapid hydrolysis an  $\text{HCl}$  reaction solution of a concentration which places the reaction mixture in the region in which the time of set of a silicic acid gel is increased with increasing  $\text{H}^+$  (see again Hurd and Letteron), one may have a gel mixture whose setting time may run into months. From this type of solution (assuming enough  $\text{H}^+$  has been used to hydrolyze enough ethyl silicate) a gel may be very rapidly produced by neutralizing the  $\text{HCl}$  with  $\text{NH}_3$  or by repressing the  $\text{H}^+$  with sodium acetate solution.

Examples of the first method of preparing the gel from ethyl silicate:

A mixture of 5 c.c.  $(\text{EtO})_4\text{Si}$  and 50 c.c. concentrated  $\text{HCl}$  (12 N) was shaken. Immediately small gel like clusters were observed in the mixture. These were apparently droplets of ethyl silicate which had hydrolyzed and condensed on the outside before they had a chance to be totally hydrolyzed. Within a short time a gel formed, non-homogeneous, due to the unhydrolyzed ethyl silicate.



A mixture of 10 c.c.  $(\text{EtO})_4\text{Si}$ , 30 c.c.  $\text{H}_2\text{O}$  and 30 c.c. concentrated  $\text{HCl}$  was made. The mixture was stirred with an electric mixer to hydrolyze the ethyl silicate and bring it into solution. In about 15 minutes, the mixture was milky and viscous, the milkiess undoubtedly a sol of condensed silicic acid. A gel formed from this mixture in about 10 more minutes.

Examples of the second method above mentioned:

A mixture of 10 c.c.  $(\text{EtO})_4\text{Si}$ , 10 c.c. .25 N  $\text{HCl}$  and 20 c.c.  $\text{EtOH}$  was made. An  $8^\circ$  temperature rise was observed upon mixing. The mixture was allowed to stand for about 10 minutes and 25 c.c. more  $\text{EtOH}$  was then added (in order that final solution would be about .64 molar in  $\text{SiO}_2$ ). 5 c.c.  $\text{NaAC}$  (2.5 N) was now added. The pH rose to 6.4 and a gel formed in 12 minutes at room temperature.

Repeating this procedure, but using 5 c.c. less  $\text{EtOH}$  and 10 c.c. 2.5 N  $\text{NaAC}$ , a gel was formed in 9 minutes, pH 6.5.

A mixture of 10 c.c.  $(\text{EtO})_4\text{Si}$ , 10 c.c. .05  $\text{HCl}$  and 20 c.c.  $\text{EtOH}$  was made. Temperature rise,  $8^\circ$ . 20 c.c. more  $\text{EtOH}$  was added. 10 c.c.  $\text{NaAC}$  (2.5 N) was added. pH, 6.9. Time of set was 15 minutes at room temperature.

A mixture of 10 c.c.  $(\text{EtO})_4\text{Si}$ , 10 c.c. .025 N  $\text{HCl}$  and 20 c.c.  $\text{EtOH}$  was made. Temperature rise,  $7^\circ$  (a slower rise in this case). The mixture was immiscible for a few seconds. 20 c.c. more  $\text{EtOH}$  was added; 10 c.c. 2.5 N  $\text{NaAC}$  was then added, bringing the pH to 7.0. The gel set in 6 minutes.

A gel was formed similarly by adding  $\text{NH}_4\text{OH}$  in place of  $\text{NaAC}$ , causing the gel to form very rapidly.

Here it may be stated that if one wishes to study the formation of a gel from hydrolyzed ethyl silicate, isolated from any hydrolysis reaction, this method of rapid hydrolysis and repression of the  $\text{H}^+$  concentration would apparently be the one to use. It would be necessary for one to determine when practically total hydrolysis had taken place. The time for this would



be a very small percent of the total time for a gel to form from a rapidly hydrolyzed solution when the  $H^+$  is such as to put the solution in that region of acidity where the time of set increases with increasing  $H^+$ . Repression of  $H^+$  now by mixing with a sodium acetate solution will bring about a gel reaction which may be completed in a convenient time. Energies of activation might be determined for these gels as have been determined for sodium silicate gels by Hurd and Letteron.

Under the preparation of gels it was also decided to study the rate of gel formation in the  $(EtO)_4Si:H_2O:EtOH - 1:1.5:4.5$  system as a function of  $H^+$  concentration or pH, and by leaving the system unmodified after it had once been made up. It was decided to run the gel formation at  $32^\circ C$ . As has been pointed out, if one conducts a rapid hydrolysis using low concentrations of strong acid, one will have a system which will require a long time for gel formation. The time for gel formation from systems which have been acidified with weak HCl should be studied. This will probably require observing the gel mixtures for a period of a few months. To study gel mixtures, which would set in a more reasonable time as a function of pH, the acidity of the mixture was varied with a weak acid - acetic acid - and dilute sodium acetate. Concerning acidifying with acetic acid, one must bear in mind that acetic acid and alcohol react to form ethyl acetate, and that these gel systems contain a large amount of ethyl alcohol. The amount of ethyl acetate, if any, which may have been formed in any of these gel mixtures is not known. The  $H_2O$  present, of course, would tend to cause any esterification to be very slow. Also, in using sodium acetate to make the solution more basic, one can use only very small amounts, since higher concentrations will cause saponification of ethyl silicate to a sodium silicate which will be insoluble in these gel mixtures which contain the large amount of ethyl alcohol that they do.



In studying the rate of gel formation from these homogeneous systems which are unmodified once they are made up, and whose acidity is weak, one is obtaining the result of two reactions, both of which are slow - the hydrolysis and gel formation.

It is seen that there are many complicating factors in this particular gel formation reaction study; nevertheless, the study of this kind of system is important and gives more or less interesting results.

The gels were set in an air bath at  $32^{\circ} \pm .1$  which must be able to run for two weeks at a stretch.

Solutions of acetic acid were made up of concentrations varying from 1 N to about 1/4000 N, and sodium acetate solutions from 1/2 N down to .00025 N. These solutions were made by progressively diluting the most concentrated one of the series. The first solutions of the series were made up approximately and were not standardized, it having been decided that the pH would be the variable of most significance in the gel formation.

The experiments were carried out as follows. 45 c.c. of 95% EtOH and 15 c.c. of HAc or NaAc were buretted and mixed in a small glass stoppered bottle. This solution was thermostated in the air bath (more or less unnecessary since the time for gel formation is about 60 hours with the fastest of these gels at this temperature). At a recorded time, 10 c.c. of EtSi was then pipetted into the EtOH - H<sub>2</sub>O solution and the mixture vigorously shaken to insure complete homogeneity. A portion was now poured into a 6" test tube, corked with a paraffin impregnated cork, labelled and placed in the thermostat. Another portion was placed in a 50 c.c. beaker and its pH determined at room temperature with quinhydrone using a shiny platinum electrode. Since the solution is highly alcoholic and since quinhydrone is quite soluble in alcohol, a considerable amount of quinhydrone



must be dissolved in the solution to saturate it. The question as to whether pH can be measured correctly in this system of ethyl silicate, ethyl alcohol and water has not been investigated by the writer. It is known, however, that pH can be measured in alcoholic solution with quinhydrone, and with this knowledge it was assumed that the pH as measured was probably all right. The potential of the quinhydrone cell (vs. saturated KCl calomel cell) was measured over a period of about two hours for most of the gel mixtures.

In general the potentiometer readings changed considerably in the first 5 to 30 minutes or so, and a slight amount thereafter. It could never be decided whether there was any pH drift in the solutions, either in those with acetic acid or with sodium acetate; or whether, at times, a considerable time was required for equilibrium to be established in the quinhydrone cell. There is a possibility of another drift occurring much later when the gel formation comes more into prominence. Such drifts have been observed by Hurd and his co-workers (see Hurd, Frederick and Haynes<sup>6</sup>).

It was decided to plot time of set against an initial pH. The potentiometer reading which was chosen to give the initial pH was that reading obtained after the first rapid changes had ceased and the further change of potentiometer reading, if any, had become a very gradual one.

For example, in a gel mixture which was made up using  $1/8$  N HAc, the potentiometer reading varied as follows:

<u>Time</u>	<u>E.M.F.</u>
10:05	-226 m.v.
10:15	-236
10:20	-236
10:21	-234
10:45	-234

-234 was taken to give initial pH.

Another example using  $1/256$  N HAc:

<u>Time</u>	<u>E.M.F.</u>
12:20	-206
12:25	-206
12:30	-210
1:00	-211

-210 taken to give initial pH.



The pH figures which were obtained from the potentiometer readings were obtained from the tables calculated for measurement made at 25° C. A correction for the temperature of actual measurement 20-22° C. would be in general about a 2% correction. Since the E.M.F. measurement for initial pH might readily be 2% error as may be seen from the above data, and since the time of set had an error undoubtedly as large or larger than 2%, temperature correction for potentiometer readings was not made.

To continue with the rate of gelation, the time of set was determined by the Fleming method - the test tube containing the gel is tilted; if the gel does not flow down the tube, it is considered set. As can be imagined, one must develop more or less skill in testing time of set by this method to obtain reproducible results. It is believed that most of the times of set obtained did not have an error of greater than 4%, in many cases perhaps less. It was not determined whether or not complete hydrolysis had taken place in these gel systems at the time of set, or whether all the available hydrolyzed EtSi took part in the forming of the gel.

The time of set is plotted against the pH. As has been stated, over the range of pH studied the time of set has depended upon the rate of two slow reactions. With the lower pH, the hydrolysis has been more rapid, but the greater acidity makes the gel formation slower. At the minimum of the curve pH = 4.75 approx., the speeds of hydrolysis and gel reaction have been adjusted to give the quickest results. Beyond pH = 4.75 apparently the hydrolysis has been slowed down considerably. The gel reaction here should, of course, be more rapid; it becomes more rapid as one approaches the neutral point in this vicinity. The slowing down of gel formation from pH 4.75 on is therefore due, no doubt, to the slowing down of the hydrolysis.



On the descending part of the curve, the pH of the mixture has been varied by HAc. On the ascending side of the curve the pH has been increased by NaAc. It is seen that the NaAc solutions are not basic, however, but have a pH less than 7. This is undoubtedly due to the fact that no attempt was made to free the ethyl alcohol or water used in the mixtures from carbon dioxide. The acidity at the minimum of the curve is due, no doubt, mainly to the carbon dioxide in the solution.

There is a limit to the sodium acetate concentrations which may be used for repressing the  $H^+$ . It was found that with sodium acetate concentrations which are a little higher than the ones which are recorded in the data, a precipitate and not a gel was obtained. This precipitate is undoubtedly one of some sodium silicate; the higher sodium acetate concentration has caused a saponification, and in such a system as the one which is studied, the large amount of alcohol will permit no more than a trace of sodium silicate to remain dissolved.

### Summary

The general problem of hydrolysis of ethyl orthosilicate and the formation of gels from it has been further investigated. Many refinements have been omitted in the study, the idea being that most of the experiments are preliminary in nature.

A conductivity method is suggested for studying the rate of hydrolysis of ethyl orthosilicate in a homogeneous system, and a few observations on the hydrolysis have been made.

The general methods of bringing ethyl silicate into solution have been reviewed and discussed with reference to the formation of gels.

Rapid formation of gels has been discussed from the viewpoint of a knowledge of  $H^+$  effect on the formation of silicic acid gels from sodium silicate.

Effect of  $H^+$  on gels from homogeneous mixtures, unmodified once mixed, has been investigated likewise from the viewpoint of a knowledge of  $H^+$  effect on the formation of silicic acid gels from sodium silicate.



Table I

A check on the conductivity cell.

Resistance vs. time for a solution of 15 c.c. .1 N HCl and 55 c.c. EtOH.

Thermostat temperature 32.0° C.

<u>Time</u>	<u>#1</u> <u>Resistance</u>	<u>Time</u>	<u>#2</u> <u>Resistance</u>
0 min.	113.0 ohms	0 min.	
8	106.0	3	114.0 ohms
16	105.6 - Thermostatted	20	101.9
20	105.5	30	101.7 - Thermostatted
27	105.5	37	101.7
34	105.5	50	101.7
41	105.4	65	101.5
55	105.4	79	101.7
79	105.3	100	101.9
97	105.3	101	101.7
163	105.3	120	101.7
181	105.3	130	101.7
231	105.3	137	101.7
232	105.3	157	101.7
		180	101.8
		200	101.7
		232	101.6
		260	101.7
		1497	101.4
		1501	101.4
		1505	101.3

.3% change in 200 minutes



Table II

Conductivity cell resistance vs. time for solution of 10 c.c.

EtSi; 15 c.c. HCl solution; 45 c.c. EtOH. Temperature variation of

identical solution (primed letter) in identical bottle in thermostat.

#9 (1); HCl used: .1 N

Initial temp. rise: 21°-25°

Thermostat temp.: 32.0° C.

#9 (1<sup>1</sup>)

<u>Time</u>	<u>Resistance</u>
0	mixed
8 min.	136.0 ohms
18	132.5
23	131.7 (begin plot)
26	131.6
32	131.2
36	131.0
37	130.8
39	130.9
40	130.8
45	130.6
50	130.5
60	129.9
75	129.9
85	129.6
90	129.4
222	128.6
223	128.5
228	128.4
332	127.8
365	127.7

<u>Time</u>	<u>Thermometer Reading</u>
0	mixed
10	31.9
14	31.9
21	31.9
35	31.9
60	31.9
225	31.9
	corresponds to thermostat tem- perature.



Table II (cont.)

#9 (n); HCl used: .1 N  
Initial temp. rise: 23.5°-27.9°  
Thermostat temp.: 32.0°

<u>Time</u>	<u>Resistance</u>
0	mixed
19 min.	129.7 ohms
22	129.1 (start plot)
23	128.8
26	128.4
29	128.2
30	128.0
33	127.8
35	127.8
44	127.3
47	127.2
60	126.8
66	126.7
72	126.5
81	126.6
100	126.1
142	125.7
172	125.4
200	125.2
260	124.8
395	124.1

#9 (n<sup>1</sup>)  
Initial temp. rise: 23.5°-27.7°

<u>Time</u>	<u>Thermometer Reading</u>
0	mixed
11 min	31.0
15	31.7
16	31.9
19	32.0
22	32.0
26	32.0
35	32.0
49	32.0
88	32.0
	corresponds to thermostat tem- perature.



Table II (cont.)

#9 (p); HCl used: .1 N  
Initial temp. rise: 23.5°-28.2°  
Thermostat temp.: 32.0°

<u>Time</u>	<u>Resistance</u>
0	mixed
8 min.	127.0 ohms
12	130.0
17	127.6
20	127.0 (start plot)
26	126.2
30	126.0
31	125.8
42	125.2
48	125.0
61	124.6
77	124.2
109	123.6
135	123.4
195	123.1
255	122.5
1335	120.3
1339	120.3
1351	120.2

#9 (p<sup>1</sup>)  
Initial temp. rise: 23.5°-28.3°

<u>Time</u>	<u>Thermometer Reading</u>
0	mixed
10 min.	31.8
20	32.2
28	32.2
34	32.2
40	32.1
46	32.1
67	32.0
101	32.0
125	32.0
	corresponds to thermostat tem- perature.



Table II (cont.)

#9 (s); HCl used: .025 N  
Temp. rise: 24.5°-27°  
Thermostat temp.: 32.0° C.

<u>Time</u>	<u>Resistance</u>
0	mixed
10 min.	495 ohms
13	486
16	479
20	476 (start plot)
22	475
25	474
27	473.5
29	473
31	472
32	472
36	471
37	470
39	470
40	470
44	469
48	468
60	468
129	462
131	461.5
149	461
162	460
172	460
183	459

#9 (sl)	
<u>Temp. rise: 24°-25°</u>	
<u>Time</u>	<u>Thermometer Reading</u>
0	mixed
7 min.	31.8
10	32.7
13	32.8
16	32.8
19	32.7
22	32.6
29	32.4
35	32.4
38	32.3
45	32.3
119	32.1
141	32.1
corresponds to thermostat tem- perature.	

Table II (cont.)

#9 (q); HCl used: .025 N  
Initial temp. rise: 21°-25° slow  
Thermostat temp.: 25.0°

#9 (q<sup>1</sup>)  
Temp. rise: 20.6°-25°  
Thermometer  
Reading

<u>Time</u>	<u>Resistance</u>
0	mixed
13 min.	572 ohms
15	571
16	570 (start plot)
19	568
21	567
26	565
31	564
34	563
38	562
44	560
54	559
59	558
69	558
71	557
85	556
90	556
94	555
103	555
111	554
116	553
125	553
139	552
154	551
160	550
180	549
196	548
224	547
1175	535

<u>Time</u>	<u>Thermometer Reading</u>
0	mixed
16 min.	25.6
20	25.7
28	25.5
34	25.4
37	25.3
43	25.3
50	25.3
72	25.2
85	25.2
110	25.2
122	25.2
159	25.2
170	25.2
190	25.2
	corresponds to thermostat tem- perature



Table III

Time of set vs. pH for gel mixtures. EtSi:H<sub>2</sub>O:EtOH ratio is  
1:1.5:4.5 by volume. pH varied by HAc and NaAc. Temperature 32° C.  
Preliminary determinations; marked + on graph.

<u>Concentration</u> <u>HAc used</u>	<u>Concentration</u> <u>NaAc used</u>	<u>Initial pH</u>	<u>Time of Set</u>
1 N (approx.)		3.49	212 hrs.
1/2 N		3.49	215
1/4 N		3.57	168
1/8 N		3.94	102
1/64 N		3.94	94
1/256 N		4.11	92
1/512 N		4.30	90
1/2 N		3.57	188
1/4 N		3.71	140
1/16 N		3.91	114
1/4056 N		4.25	70
	1/512 N (approx.)	6.00	289 (not on graph)
	1/2048 N	5.28	72

Table III (cont.)

More accurate determinations; marked ⊙ on graph.

<u>Concentration</u> <u>HAc used</u>	<u>Concentration</u> <u>NaAc used</u>	<u>Initial pH</u>	<u>Time of Set</u>
1 N (approx.)		3.42	261 hrs.
1/2 N		3.55	194
1/4 N		3.71	136
1/8 N		3.97	101
1/16 N		4.07	86
1/256 N		4.40	60
1/512 N		4.45	64
1/1024 N		4.20	76
1/2048 N		4.10	77
1/4096 N		4.15	80
1/4 N		3.66	151
1/8 N		3.73	121
1/16 N		3.88	99
1/256 N		4.15	68
1/512 N		4.21	73
1/1024 N		4.21	72
1/2048 N		4.28	75
1/4096 N		4.15	78
	1/1024 N	5.67	167
	1/4096 N	4.72	51
	.002 N	6.02	357 (not on graph)
	.001 N	5.59	189
	.0005 N	4.97	79
	.002 N	5.99	336 (not on graph)
	.0005 N	5.31	79



### References

1. King - Journal of the Oil and Colour Chemists Association, 13, 116 (Feb. 1930)
2. Hurd and Letteron - J. Phys. Chem., 36, 604 (1932)
3. Brintzinger and Brintzinger - Z. Anorg. Chemie, 196, 44 (1931)
4. Hurd, Raymond and Miller - J. Phys. Chem., 38, 663 (1934)
5. Rice - "Mechanism of Homogeneous Organic Reactions", Chem. Catalog Co., P. 113.
6. Hurd, Frederick and Haynes - J. Phys. Chem., 42, 85 (1938)