Summary

1. The kinetics of the alkaline hydrolysis of potassium ethyl malonate has been studied over a temperature range 5 to 35° in two isocomposition media, water and 27.57 wt. % dioxane in water; in three isodielectric dioxane–water mixtures corresponding to dielectric constants of 50, 55 and 60; and at 25° in three isodielectric *t*-butyl alcohol–water mixtures at the above dielectric values.

2. A positive primary salt effect has been found, which is in accord with the mechanism postulated for the reaction.

3. The distance of closest approach of the reacting ions is shown to be 4.8 Å. in water and in the dioxane–water mixtures. It is shown to be 4.3 Å. in the *t*-butyl alcohol–water mixtures.

4. A comparison is made between the use of volume concentration and mole fraction units for the expression of rate constants.

5. The energy of activation at zero ionic strength is greater in isodielectric media than in isocomposition media which is in accord with theory for a reaction between ions of like sign. Comparisons are made with theoretical calculations.

6. The effect of ionic strength upon the energy of activation is in excellent agreement with theory.

7. The influence of dielectric constant upon the rate constants is in good agreement with the Scatchard–Christiansen theory in dioxane–water mixtures.

8. Various thermodynamic activation values have been calculated. It is shown that the free energy of activation, energy of activation, and the entropy of activation, if calculated for $D = \infty$, are independent of solution composition.

9. It is shown that the simple collision theory and the thermodynamic treatment of La Mer are not in agreement for this reaction.

COLLEGE PARK, MARYLAND RECEIVED MAY 22, 1950

[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Hydrolysis of Ethyl Silicate*

BY R. AELION, A. LOEBEL AND F. EIRICH

The hydrolysis of ethyl silicate is used in industrial applications as a convenient process for obtaining an adhesive type of silica. Hydrolysis will occur readily in the presence of acidic or basic catalysts, but due to the immiscibility of water and ethyl silicate, a mutual solvent is often used to obtain homogeneous reaction. A great deal of attention has been focussed on the development of the most convenient methods of obtaining the right degree of conversion of ethyl silicate to silica. For example, diagrams of solubilities of ternary mixtures of water, ethyl silicate and mutual solvent have been determined,[1] and special commercial processes for hydrolysis have been developed.[2] Quantitative information on the rate of hydrolysis of ethyl silicate in acidic and basic media and on the stability of hydrolysis products to gel formation is, however, still very scant.[3] The purpose of the work described in this paper was the collection of quantitative information regarding the rate of ethyl silicate hydrolysis, and the formulation of a possible reaction mechanism.

The over-all hydrolysis of ethyl silicate and the subsequent dehydration of the product formed may be formulated as

$$n\mathrm{Si(OC_2H_5)_4} + 4n\mathrm{H_2O} \longrightarrow n\mathrm{Si(OH)_4} + 4n\mathrm{C_2H_5OH} \quad \text{(1a)}$$

$$n\mathrm{Si(OH)_4} \longrightarrow (\mathrm{SiO_2})n + 2n\mathrm{H_2O} \quad \text{(1b)}$$

Depending on conditions, one or both of these consecutive reactions may only go to partial completion, leaving ethoxy or hydroxyl groups unreacted. The changes with time in the following quantities were experimentally determined: (1) The total loss of water, L_T, equal to the difference between the water taken up by the hydrolysis and the water regenerated by dehydration. (2) The production of alcohol, L_H, equivalent to the amount of water used in the hydrolysis reaction. (3) The degree of conversion of monomer.

Expressing L_T and L_H in moles per mole of ethyl silicate, a simple equation relates these two quantities at any stage of the reaction

$$L_T = L_H - aL_H/2 \quad (2)$$

where a is the degree of completion of the dehydration reaction.

By determination of L_H and L_T the rate and extent of both reactions and therefore the number of unreacted ethoxy and hydroxyl groups can be calculated. The average composition of the polyethoxysiloxanes formed is then obtained by evaluating the degree of conversion of the monomer.

Experimental

Titration with Karl Fischer reagent[4] allows the instantaneous determinations of water content. This method

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* Taken in part from a thesis in preparation by M. Arnold Loebel for presentation to the Graduate School of the Polytechnic Institute of Brooklyn for the degree of Doctor of Philosophy in Chemistry.

(1) H. D. Cogan and C. A. Setterstrom, *Chem. Eng. News*, **24**, 2499 (1946); *Ind. Eng. Chem.*, **39**, 1364 (1947).

(2) C. Shaw and J. E. Hackford, *Ind. Chem.*, **21**, 130 (1945); **22**, 61 (1946); **22**, 1230 (1946).

(3) G. King, *J. Oil and Colour Chem. Assoc.*, **13**, 116 (1930).

(4) J. Mitchell and D. M. Smith, "Chemical Analysis," Vol. 5, Aquametry, Interscience Publishers, New York, N. Y., 1948, Chap. 4.

requires the use of a mutual solvent to obtain a homogeneous reaction medium. If M_{t_0} and M_t are the number of moles of water per liter at time t_0 and time t, respectively, then L_T is given by

$$L_T = (M_{t_0} - M_t)/S_{t_0} \tag{3}$$

where S_{t_0} is the initial concentration of silicate in moles per liter. Although the absolute accuracy of this method is similar to the accuracy of the usual volumetric titrations (1%), the relative accuracy is much better and allows assessment of very small variations of the water content (0.2%).

The amount of alcohol formed cannot be titrated by direct chemical methods which rely on a hydroxyl group determination (*e. g.*, Zeisel's method), since the products of the reaction have the same functional groups. The alcohol has, therefore, to be separated from the reacting medium, *e. g.*, by distillation. A complete separation can be obtained by using a mutual solvent of higher boiling point than that of the ethyl alcohol. A rapid partial distillation under vacuum of an aliquot sample removed during reaction yields a distillate containing all the alcohol and the unreacted water. The concentration of alcohol in the mixture is determined by density, refractive index measurements, etc., which have been previously standardized. If C_t is the concentration of ethyl alcohol found, expressed in weight per cent., L_H is obtained by

$$L_H = \frac{W_A - (M_t V_B \times 18.02)/1000}{V_B} C_t \times \frac{1000}{S_{t_0} \times 46.07} \tag{4}$$

where V_B is the volume of the sample before distillation, and W_A the weight of the distillate. The accuracy of the method varies from 1 to 4% depending mainly on the completeness and the speed of separation of the alcohol and on the determination of C_t.

The distillation carried out for the determination of alcohol (L_H) is continued until all the unreacted monomer is removed; the monomer which distils over can be transformed into pure silica by reacting with an excess of very concentrated hydrochloric acid solution and its amount be determined by drying and weighing the silica. If m is the weight of silica, the number of moles of unreacted ethyl silicate per mole of ethyl silicate initially used is equivalent to: $1000m/60.06\ V_B S_{t_0}$.

All of the experiments reported as acid-catalyzed hydrolyses were carried out with hydrochloric acid but tests showed that with other strong acids similar results were obtained. Of weak acids much larger quantities are needed to obtain comparable speeds of hydrolysis. The results will be published in a later paper.

The reaction between ethyl silicate and concentrated hydrochloric acid (12 N) was noted to be very exothermic. The acid solution introduced drop by drop dissolves readily in pure ethyl silicate and gel formation occurs immediately. In the range of moderate and low acidity the reaction is slower, samples can be removed during the reaction and instantaneous values, L_H, of the alcohol produced can be obtained.

For the hydrolysis in basic media, sodium hydroxide, ammonium hydroxide and pyridine have been used at a number of concentrations. Dioxane, methyl and ethyl alcohol served in all cases as mutual solvents.

As pointed out above, though the hydrolysis and dehydration reactions occur side by side, the kinetics of the hydrolysis can be studied separately by determining L_H and the variation of the total water content, so that the contribution due to dehydration during the reaction can be deducted. The order of the reaction can then be determined by comparing the ratios τ_i'/τ_i of the respective times τ required to complete different experiments to the same degree "i." These experiments are carried out at constant HCl concentrations and with different over-all concentrations of equivalent amounts of water and ethyl silicate.

Experimental Results

The rate and extent of the hydrolysis reaction were found to be greatly influenced by the presence and concentration of strong acids or bases. Temperature and the type of solvent produce secondary effects. To obtain results which lend themselves to easy interpretation, either the catalyst concentration or the concentrations of water and ethyl silicate were kept practically constant. The data listed in Table I were obtained from runs made at decreasing concentrations of hydrochloric acid, employing dioxane as solvent.

Table I

Hydrolysis of Ethyl Silicate with Strong Hydrochloric Acid Solutions

Expt.	HCl, m./l.	S_{t_0} ethyl silicate, m./l.	M_t water, m./l.	L_T m./mole Si-$(OC_2H_5)_4$	L_H, m./mole Si-$(OC_2H_5)_4$	a, %	Unreacted monomer, m./Si-$(OC_2H_5)_4$	Time, min.
I	0.063	0.1924	1.432	0	0		1	0
			1.044	2.017				4
			0.975	2.37				12
			0.983	2.34	4.08	86	0.0	120
II	.0281	.2043	1.592	0	0		1	0
			1.556	0.176				2
			1.203	1.904				7
			1.184	2.00				25
			1.156	2.13	3.89	91	0.0	80
			1.156	2.13				120
III	.0053	.2132	1.47	0	0		1	0
			1.09	1.78				170
			1.05	2.05	4.0	97	0	400

The rates of these three reactions (Fig. 1) were too fast to enable determinations of instantaneous values of L_H, and consequently only the final values are tabulated. The reactions at lower acidity were carried out with dilute hydrochloric acid or distilled water. The results are summarized in Table II and Fig. 1.

Table II

Hydrolysis of Ethyl Silicate with Dilute Hydrochloric Acid Solutions

Expt.	HCl, m./l.	S_{t_0}, ethyl silicate, m./l.	M_t water, m./l.	L_T	L_H	a, %	Time, hours
IV	0.0016	0.2095	1.207	0	0	0	0
			1.197	0.047			0:13
					1.61	103	1:00
			0.980	1.07			1:45
			0.935	1.29	2.65	102	2:40
			0.852	1.69	3.50	102	5:20
			0.851	1.69	3.53		170:00
V	.000022	.2132	1.249	0			0
			1.225	0.18			24:00
			1.220	.20	0.4		170:00
VI	Distil. H_2O	.220	1.355	0			0
			1.34	.068			18:00
			1.32	.159			44:00
			1.28	.310			196:00

The results of both tables indicate that in acid catalyzed reactions the hydrolysis step is rate determining, except at very high HCl concentrations where dehydration lags somewhat behind.

In experiments (VII) and (VIII), Table III, the concentration of hydrochloric acid was

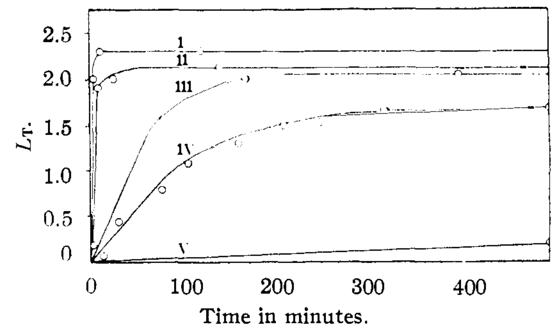

Fig. 1.—Acid-catalyzed hydrolysis of ethyl silicate in dioxane. L_T is the total loss of water in moles per mole of ethyl silicate for several acid (HCl) concentrations.

chosen within the range where complete dehydration occurs (0.0037 mole acid per liter). The ratio of the initial concentrations of the reactants in the two experiments was 2.02:1. The average value of τ_i'/τ_i was found to be 2.04, indicating that the reaction is second order.

TABLE III

HYDROLYSIS OF ETHYL SILICATE—ORDER OF THE REACTION

Expt.	HCl, m./l.	Ethyl silicate S_{t_0}, m./l.	Ethyl silicate $2S_{t_0}$, equiv. gr.	M_{t_0}, water, m./l.	Order of reaction (relative times)
VII	0.00368	1.248	2.496	2.34	τ_i
VIII	.0037	0.622	1.245	1.16	$\tau_i' = 2.04\,\tau_i$
IX	.0034	0.624	1.248	2.32	$\tau_{0.5}'' = 0.258\tau_{0.5}$ $= 0.126\,\tau_{0.5}$

Experiment (IX), carried out with an excess of water shows an increase of rate, appropriate to a second order reaction with respect to the water and ethyl silicate, and follows the usual expression

$$-\,dx/dt = K(M_{t_0} - x)(2S_{t_0} - x) \qquad (6)$$

which by integration gives

$$\log \frac{M_{t_0} - x}{2S_{t_0} - x} = \frac{K(M_{t_0} - 2S_{t_0})t}{2.303} + \log \frac{M_{t_0}}{2S_{t_0}} \qquad (7)$$

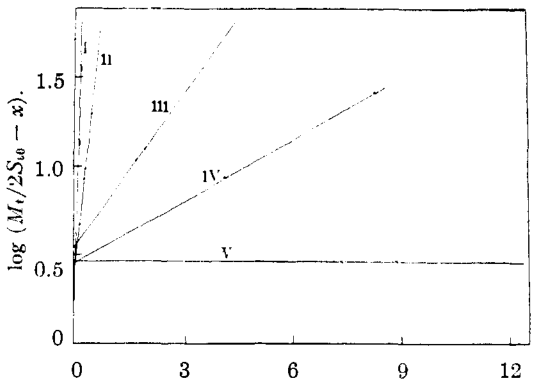

Fig. 2.—Rate of reaction of acid-catalyzed hydrolysis of ethyl silicate in dioxane for several acid concentrations.

If the extent a of dehydration is less than unity, the number of moles of water per liter consumed in hydrolysis, $2x$, is given by

$$2x = \frac{2}{2 - a}(M_{t_0} - M_t) \qquad (8)$$

Taking this into account in cases of incomplete dehydration, the plots of $\log \frac{M_{t_0} - x}{2S_{t_0} - x}$ *versus* time for all experiments performed give straight lines (Fig. 2). From the slopes of the lines the rate constants are calculated. As regards the variations of reaction rate with catalyst, Table IV shows the effect of acid concentration.

TABLE IV

VARIATION OF THE RATE OF THE REACTION WITH THE ACID CONCENTRATION

HCl concn., mole/l.	Rate K, l. mole^{-1} sec.$^{-1}$
0.063	5.72×10^{-3}
.0281	2.86×10^{-3}
.0053	1.80×10^{-4}
.0016	1.04×10^{-4}
.000022	5.16×10^{-6}
Distill. H_2O	4.12×10^{-6}

By plotting log K *versus* log [HCl] the following linear relationship is obtained (Fig. 3).

$$\log K = 1.0 \log [\mathrm{HCl}] + \log 0.051 \qquad (9)$$

The rate is thus directly proportional to the [acid] and the rate constant k expressed in liter mole^{-1} sec.$^{-1}$ [acid]$^{-1}$ is 0.051 at 20° in dioxane as a mutual solvent.

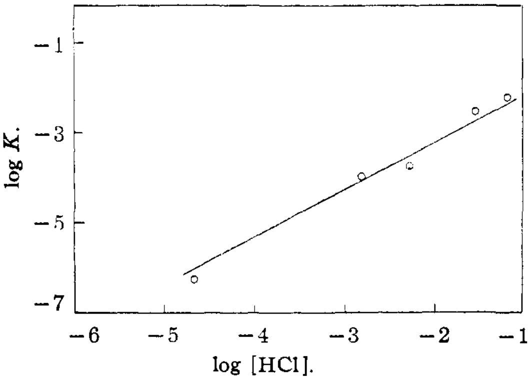

Fig. 3.—Determination of absolute rate constant (k) of acid-catalyzed hydrolysis of ethyl silicate.

Concerning the activation energy, a value of 6.8 kcal./mole has been obtained by comparing the rates of reactions carried out in dioxane at 20, 45.3 and 54° (Fig. 4). It was found that the increase of temperature from 20 to 45.5° increases the rate of hydrolysis ten-fold while the extent rises from 89 to 93%; however, at higher temperatures ($T \geq 50°$) the dehydration reaction is no longer complete.

No marked influence of the amount of silicate on the nature of the hydrolysis reaction was observed in several experiments in which ethyl and

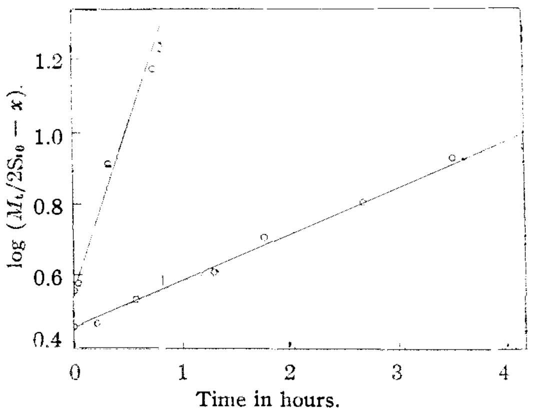

Fig. 4.—Activation energy of acid-catalyzed hydrolysis: curve 1, $T = 20.0°$; curve 2, $T = 45.3°$.

methyl alcohol were used. In ethyl alcohol the extent of hydrolysis (1a) decreases at acid concentrations smaller than 0.003 mole/liter. Table V shows that in experiment XI the extent has fallen off to 90% ($= L_T/2$).

Table V

Hydrolysis of Ethyl Silicate in Ethyl Alcohol

Expt.	HCl, m./l.	Ethyl silicate, m./l.	Water, m./l.	L_T	Time, hr.
X	0.0029	0.168	1.594	0	0
			1.28	1.77	12
			1.23	2.05	44
			1.23	2.05	160
XI	.0022	.758	2.45	0	0
			1.08	1.81	8
			1.08	1.81	500

Reactions carried out in methyl alcohol (Table VI) give an average value of the rate constant of the hydrolysis almost identical with the value found for runs in dioxane, and agree well with runs in ethyl alcohol. This would indicate that re-esterification does not play an important part. For the silicates of higher alcohols the mass action of the alcohol used as solvent is a little more marked, but still of minor importance. The value there of the constant depends mainly on the nature of the alkoxy groups attached to the silicon atom.[5]

Table VI

Hydrolysis of Ethyl Silicate in Methyl Alcohol

Expt.	Hydrochloric acid, m./l.	S_{t_0}, ethyl silicate, m./l.	M_{t_0}, water, m./l.	Rate K, liter mole^{-1} sec.$^{-1}$	k, rate constant liter, mole^{-1} sec.$^{-1}$ HCl^{-1}
XII	0.0034	0.624	2.32	0.20×10^{-3}	0.059
XIII	.0016	.210	1.207	$.104 \times 10^{-3}$	.065
XIV	.0037	.624	1.16	$.12 \times 10^{-3}$	.042

As in acid media, the hydrolysis of ethyl silicate in basic solution is a function of the concentration of the catalyst, in this case of the base. At the same time a stronger dependence on the nature of the solvent is observed in Table VII.

Table VII

Hydrolysis of Ethyl Silicate in Basic Media

Solvent	Concn. of NaOH, m./l.	S_{t_0}, ethyl silicate, m./l.	M_t, water, m./l.	L_T	L_H	Time, min.
Methyl alcohol	0.0347	0.235	1.06	0	0	0
			0.976	0.11		3
			.768	0.99		9
			.597	1.72		25
			.557	1.89	4.0	53
			.520	2.04	4.0	600
	.0185	1.25	2.44	0	0	0
			2.29	0.12		4
			2.12	.256		21
			1.81	.505		135
			1.70	.59		220
			1.13	.97		1085
						Hrs.
Ethyl alcohol	.0163	0.2305	0.985	0		0
			.89	0.41		2:25
			.835	.65		23:25
			.77	.93		47:00
			.72	1.14	2.2	119:00
Dioxane	.035	.236	2.0	0	0	0
				0.75	1.2	3:00
	.0145	.2144	1.62	0	0	0
				0.35	0.52	240:00
	.0083	.236	1.92	0	0	0
				0.3	0.5	300:00
	.00391	.236	1.67	0	0	0
				.2	0.5	300:00
	.000205	.236	1.424	0	0	0
				0	0	300:00
	1.56	.220	0.846	0		0
	(NH_4OH)		.855	.04		0:10
			.698	.75		24:00
	.144	.227	1.028	0		0
	(NH_4OH)		1.002	.114		22:30
			0.945	.365		147:00

The hydrolysis as well as the dehydration of low concentrations of ethyl silicate in methyl alcohol with large amounts of hydroxyl ion catalyst is fast and complete. But as soon as the concentration of the monomer is increased, the polymer does not stay in solution any longer but precipitates, giving a white turbid appearance to the reaction mixture. This same phenomenon occurs in ethyl alcohol, where the reaction is slower, with smaller concentrations of ethyl silicate. Reactions carried out in dioxane, which exhibit the slowest observed speed, at very high concentrations of sodium hydroxide result in the formation of two liquid phases. The lower layer consists mainly of an aqueous solution of sodium hydroxide and of partially hydrolyzed polymer, the upper one contains the dioxane and the remaining monomer. Thus the growing polymer, having a silicate structure, collects most of the water of hydration and coalesces into a liquid precipitate. At lower concentrations of base than about 10^{-3} *m.* no reaction occurs. Ammonium hydroxide and pyridine produce a measurable speed of the reaction only if they are present in large concentrations. In the case of ammonium hydroxide-catalyzed reactions, flocculation of the polymer formed occurs almost immediately.

The rate constant in dilute solutions of ethyl silicate can be represented by the first order relation

$$2.303 \log (2S_{t_0} - x) = -Kt + C \qquad (10)$$

K being the rate of the reaction. For very dilute solutions, the values of K vary proportionally with the concentration of the base (Fig. 5). In the particular example given in Table VIII, the data are from hydrolysis in methyl alcohol at a temperature of 20.0° yielding values for k which are very close to those found for acid-catalyzed reactions.

TABLE VIII

NaOH, m./l.	S_{t_0}, Ethyl silicate, m./l.	Rate $K \times 10^{+3}$ liter mole^{-1} sec.$^{-1}$	Rate constant, k, liter mole^{-1} sec.$^{-1}$ [OH]$^{-1}$
0.0347	0.235	1.67	0.047
.0180	.161	0.70	.039

The order of the reaction was again determined by comparing the times required to complete definite degrees, "i" of the hydrolysis of very dilute solutions of ethyl silicate in methyl alcohol. The data are found in Table IX. A large increase of the concentration of water does not affect the rate of the reaction. The experiments, therefore, show the reaction to be first order with respect to the silicate concentration.

TABLE IX

HYDROLYSIS OF ETHYL SILICATE IN BASIC MEDIA. KINETICS OF THE REACTION

Expt.	NaOH, m./l.	S_{t_0}, ethyl silicate, m./l.	M_{t_0}, water, m./l.	Order of reaction
XV	0.0180	0.161	0.386	τ_i
XVI	.0185	.312	0.644	$\tau_i' = 1.06\ \tau_i$
XVII	.01805	.312	1.26	$\tau_i'' = 0.98\ \tau_i$

In the case of more concentrated solutions of ethyl silicate, the rate of the reaction decreases very rapidly (Table X), and the ratios τ_i'/τ_i are not constant but vary with "i," the degree of completion. This indicates that the reactions do not any longer follow a simple order but become complicated by secondary reactions. In experiment XIX, *e. g.*, the reaction follows a first order rate up to 3/10 of its completion, at which time the reaction medium becomes turbid and the ratio τ_i'/τ_i does not remain constant but becomes proportional to "i." In experiment XX the reaction medium clouds immediately and the reaction is very slow. The lack of constancy of τ_i'/τ_i may be taken as a sign that the reaction does not proceed any longer in true solution but changes into a heterogeneous reaction. Similarly, the part played by the base becomes more complex for higher ethyl silicate concentrations (Table XI). By changing only the catalyst concentration, the times, τ_i, required to complete definite degrees of reaction, "i," are found to form a well defined ratio, independent of "i." This ratio is not proportional to the catalyst concentration but follows the empirical relation (15) deduced from the data of Table XI.

TABLE X

HYDROLYSIS OF ETHYL SILICATE IN BASIC MEDIA

Expt.	NaOH, m./l.	S_{t_0}, ethyl silicate, m./l.	M_{t_0}, water, m./l.	Time, τ_i
XVIII	0.0185	0.312	0.644	τ_i
XIX	.0189	0.936	1.85	$i < 0.3,\ \tau_i' = \tau_i$ $i > 0.3,\ \tau_i' = 6.8\ \tau_i$
XX	.0185	1.25	2.45	$\tau_i'' = 12.6\ \tau_i$

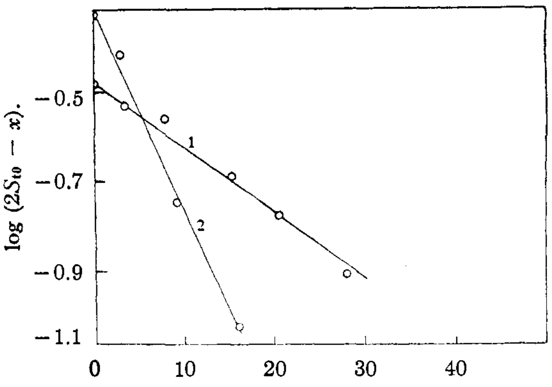

Fig. 5.—Rate of reaction of alkaline-catalyzed hydrolysis of ethyl silicate in methyl alcohol: curve 1, ethyl silicate 0.161 m/liter; NaOH 0.018 m/liter; curve 2, ethyl silicate 0.235 m/liter; NaOH 0.0347 m/liter.

TABLE XI

NaOH, m./l.	S_{t_0}, ethyl silicate, m./l.	M_{t_0}, water, m./l.	Time, τ_i
0.00927	0.612	1.19	τ_i
.0189	.612	1.24	$\tau_i' = 3.95\ \tau_i$
.0370	.612	1.224	$\tau_i'' = 11.0\ \tau_i$

$$\frac{K}{K'} = \frac{3.1[\text{Base}]}{[\text{Base}]'} - 2.1$$

Concerning the reaction products, those from acid or alkaline solution are widely different and in each case again the concentration of catalyst or of silicate creates conditions for rather different condensation products.[5]

In strongly acid solutions, where the hydrolysis reaction (1a) is fast and complete, and the extent of dehydration increases from 86 to 100% as the acid concentration decreases, no unreacted monomer remains, while the polymer in solution shows no tendency to gel formation. The polymer molecules do not contain unreacted ethoxy groups but some hydroxy groups remain. The average formula of the polymer under the conditions of experiment (I) shows four remaining OH

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(5) R. Aelion, A. Loebel and F. Eirich, *Rec. Trav. Chim.*, **T69**, 61 (1950), also appears in "Proc. Internat. Coll. Macromolecules," Amsterdam, 1949.

groups per seven Si atoms. Under the conditions of experiment (II) only two undehydrated hydroxy groups remain for seven Si atoms. The lack of reaction of these remaining groups may be due to an enveloping action by the rapid growth of the polymer chains and to the small probability of a reactive collision between OH groups situated in the interior of large three dimensional molecules. In reaction (III) the hydrolysis has become sufficiently slow to permit a practically complete dehydration.

At all lower acid concentrations dehydration remains complete but hydrolysis becomes increasingly slow and incomplete, dropping to an extent of 15% for neutral solutions. These extents are obviously influenced by equilibria which vary with the concentration of the acid. At the same time the hydroxy groups formed are competitively dehydrated without dependence upon the HCl concentration. The dry polymer, even for incomplete reactions, is always an infusible and insoluble white powder similar to silica. At very low acid concentrations the amount of unreacted monomer is greatly increased and the reaction mixture resembles in molecular weight distribution that of a vinyl polymerization at a small degree of conversion. The polymer is again similar to silica, but now rather unstable in solution and gels rapidly.

In general, the rate of gelation depends on *p*H, concentration of unreacted monomer and concentration of polymer. The higher the concentration of polymer, the faster gelation occurs. X-Ray analysis[5a] of samples removed during hydrolysis after various times show the same kind of amorphous patterns, characterized by two broad rings at 11.6 and 4.1 Å. The polymer ceases to be soluble and gel formation occurs rapidly whenever the hydrogen ion concentration in the reaction medium drops below a value of 0.002 mole/liter. At higher concentration of HCl, gelation was not observed. The degree of conversion of the monomer varies widely with the conditions of the reaction and its value plays a very important part in the stability of the solutions, since gelation can be prevented by adding unreacted ethyl silicate. This solubilizing action of the monomer can be explained by the similarity of structure (as seen from X-ray diffraction) of frozen ethyl silicate and of the structure of oriented films obtained by evaporation of a polymerized solution on a mercury surface (Table XII).

In contrast to the acid reaction, high monomer concentrations in alkaline solution do not solubilize the polymer but aid precipitation, either by non-solvent action, or by increasing the polymer concentration. This shows that the polymer from alkaline hydrolysis must have a rather different structure, at least as far as its surface goes. Simultaneously with the formation of the precipitate the reaction velocity falls off but does not go to zero. This proves that the surface retains the ability to grow for some time provided it stays in contact with the solution. Together with the fact mentioned earlier of the phase separation in dioxane, the complications found during alkaline hydrolysis may be attributed to the formation of a polysilicate which becomes rapidly insoluble with increasing molecular weight. Thus, the formation of silicate may be considered as competing with the dehydration, and as interfering further by using up catalyst.

Table XII

X-Ray Data from a Film of Polyethoxysiloxane Spread on a Mercury Surface

Distances in Å.	Line breadth	Line intensity
Equatorial measurements		
10.5	Broad	Strong
7.72	Broad	Medium
4.89	Sharp	Faint
3.69	Broad	Faint
3.15	Sharp	Weak
2.72	Sharp	Faint
2.06	Sharp	Very faint
1.96	Sharp	Very faint
Meridional measurements		
10.6	Broad	Strong
6.84	Broad	Medium
4.14	Sharp	Medium
3.66	Broad	Weak
3.18	Sharp	Medium
3.11	Sharp	Strong
2.03	Sharp	Very faint
1.94	Sharp	Very faint

Discussion

In trying to arrive from our results, and in particular from our kinetic data, at a possible reaction mechanism, a number of difficulties are encountered. For the acid catalysis the overall reaction is third order. This can be fitted into the kinetic schemes of two subsequent second order reactions, namely, either the formation of the conjugate acid from the addition of a proton to the ester oxygen and the subsequent hydrolysis with a molecule of water, or the formation of an oxonium ion followed by its reaction with the ester. The difficulty with both mechanisms lies in the fact that they are based on a hydrogen ion catalysis, which is by no means assured. General acid catalysis may be indicated since, despite the practical absence of conductivity, the same rates are observed in dioxane as in alcohols with their 10 times higher dielectric constants. The difficulty with general acid catalysis again rests with the observation that replacement of hydrochloric acid by equivalent amounts of weaker acids cuts the rate parallel with the strength of the acid; further (to be published later) hydrolysis in

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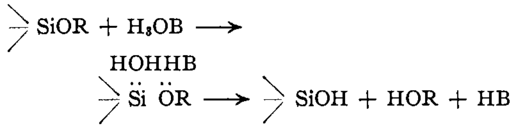
(5a) We wish to thank Mr. E. Miller for his assistance in the X-ray work.

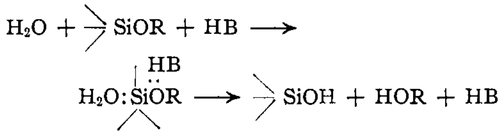
glacial acetic acid as solvent is not particularly fast. This leads one to the conclusion that an acid catalysis must be involved (I, II) of which the essential feature consists in the participation of the acid itself in the transition state, whereby a proton is donated toward the formation of the alcohol. The apparent contradiction between the required ease of acid dissociation and the practical absence of such dissociation in the solvent would thereby be removed.

As to the action of water, the acid has either to be present in the form of its oxonium salt, or attachment of a molecule of water would have to take place as a separate event rendering the reaction truly termolecular. There are some points in favor of the former scheme, such as the difference in the kinetics of acid and base catalysis and the rate dependence on the size of the alcohol, but they are not conclusive. We feel, however, that our findings are sufficiently akin to those of C. G. Swain, *et al.*,[6] in the case of the hydrolysis of triphenylsilyl fluoride, to apply their reaction scheme with minor modifications.

Swain postulates that rather than proceeding *via* the siliconium ion, a molecule of water is added to form the quinquevalent coördination compound with subsequent charge separation and ionization into the conjugated silol acid and fluorine ion. We see from the extremely slow and incomplete reaction of our silicates at pH 7 and from the influence of the molecular weight, that the uncatalyzed complex formation must be very minor; further, the resulting ethylate ion is much less stable than the halogen ion. Bearing the practical absence of ionization in mind, we propose the following modified schemes of Swain's dimolecular, or termolecular, reactions, respectively, (B = base)

(I)


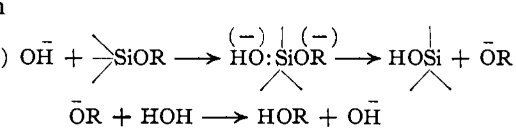
$$\rangle SiOR + H_3OB \longrightarrow \overset{HOHHB}{\rangle \ddot{Si}\ \ddot{O}R} \longrightarrow \rangle SiOH + HOR + HB$$

(II)


$$H_2O + \rangle SiOR + HB \longrightarrow H_2O{:}\overset{HB}{\ddot{Si}OR} \longrightarrow \rangle SiOH + HOR + HB$$

The acid is here written undissociated and in the most general way, including conjugate acids formed with the solvent. All charge separations are assumed to occur in the transition state, after the molecules of water and acid have been attached by means of the unshared pairs of electrons. The rate determining step may be the regrouping of bonds or the attachment to the hydrophobic silicate molecule. The effective rate in either case would depend on the product [acid] × [H_2O]. However, the existence of a preformed oxonium salt is likely in analogy, *e. g.*, to its formation in sulfur dioxide as shown by Bagster and Cooling.[7] If this salt does in fact exist and is regenerated by a fast reaction, we would expect reaction I to outstrip II in view of its bimolecular nature and of the spreading of the activation entropy over two reactions.

In alkaline solution too we must not expect ordinary hydrolysis of carboxyesters (which proceeds by attack of the hydroxyl ion on the carbonyl oxygen), nor can the pattern of carbon orthoesters be followed which shows no catalysis by bases.[8] The observations are rather compatible with nucleophilic displacement whereby the direct participation of water is excluded by the kinetics. In contrast to the acid catalysis we find further a large drop in reaction velocity with decreasing dielectric constant of the medium, *i. e.*, the participation of ions is indicated. We suggest therefore the simple displacement mechanism

(III)


$$\bar{O}H + \rangle SiOR \longrightarrow \overset{(-)\ |\ (-)}{HO{:}SiOR} \longrightarrow HOSi + \bar{O}R$$

$$\bar{O}R + HOH \longrightarrow HOR + \bar{O}H$$

We have here retained the expanded volume shell for the silicon, in accordance with Swain[6] and with Sidgwick,[9] to indicate the absence of siliconium ion in the transition state. In view of the ionic character of the displacement and of the lesser complexity of the transition state, we think the decomposition of the latter more likely to be the rate determining step than in the case of the acid catalysis.

Although the hydrolysis rates could be found independently by our method, the rate of dehydration had to remain undetermined because of their large speed. We wish only to remark that, in view of the reluctance of silicon to form double bonds, the reaction has to occur intermolecularly, and that the speed, as pointed out by Swain[6] and by Sauer,[10] may also be considered a consequence of the power of silicon to add a fifth covalent bond. Further aspects of the condensation reaction will be found in our earlier paper,[5] where we also pointed out that all reaction constants, being functions of the degree of polymerization of the silicates as well as of the molecular weights of the alkoxy groups, must be considered as average values. Their remarkable constancy is due to the fact that the individual reaction times from monomer to polymer are insignificant compared with the shortest time intervals which can be measured during the course of the total reaction.

Acknowledgment.—We gratefully acknowledge the financial help and assistance with materials

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(7) L. S. Bagster and G. Cooling, *J. Chem. Soc.*, **117**, 693 (1920).

(8) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 219.

(9) N. V. Sidgwick, "Electron Theory of Valency," Oxford University Press, Oxford, 1927, p. 159.

(10) R. O. Sauer, THIS JOURNAL, **66**, 1707 (1944).

from the Union Carbide and Carbon Corp., and we wish to thank Dr. H. Mark for his encouragement of this work.

Summary

A kinetic study of acid- and alkaline-catalyzed hydrolysis of ethyl silicate reveals that the acid catalyzed hydrolysis is second order with respect to water and ethyl silicate, and that the rate is further directly proportional to the acid concentration used. The basic hydrolysis is first order with respect to ethyl silicate, proportional to the concentration of base and independent of the amount of water present. It is, moreover, complicated by silicate formation at higher concentrations.

The value of the activation energy of acid hydrolysis has been determined. The nature of the polymer formed and its stability in solution has been investigated. For the acid hydrolysis a mechanism intermediate between general acid and oxonium ion catalysis has to be postulated. A dimolecular as well as a termolecular reaction path appear possible. The base catalysis involves a nucleophilic displacement of the alkoxy group by the hydroxyl ion.

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[CONTRIBUTION FROM THE DIVISION OF PHARMACOLOGY AND TOXICOLOGY, UNIVERSITY OF ROCHESTER, SCHOOL OF MEDICINE AND DENTISTRY]

The Isolation and Characterization of Two Metabolic Products of Myanesin (3-(*o*-Toloxy)-1,2-propanediol)[1,2]

BY RICHARD F. RILEY[3]

Graves, Elliott and Bradley[4] have reported the isolation of β-(*o*-toloxy)-lactic acid, m. p. 146–147°, from the urine of man and rabbits which had received myanesin. Working independently, we isolated the same compound as well as a second metabolic acid, m. p. 168°, which is responsible for the positive Ehrlich diazo reaction[5] given by metabolic urines of man and experimental animals which have received the drug. The chromogenic substance, m. p. 168°, has now been identified as β-(2-methyl-4-hydroxyphenoxy)-lactic acid on the basis of its chemical and physical properties and by degradation to toluhydroquinone. A preliminary communication regarding this work has appeared.[6]

It is the purpose of the present paper to present (a) a method of isolation of these compounds, (b) pertinent data which have now led to a determination of the structure of the chromogen and (c) some information concerning the extent of metabolic conversion and excretion of the two substances.

Initially, we were successful in obtaining small quantities of the two compounds from human urine by a lengthy process involving adsorption on Darco G-60, elution with acetone and concentration of the carbon eluate followed by solvent and chromatographic fractionation. More recently, the counter-current distribution technique has been employed as a convenient means of isolation of both compounds, and has provided sufficient amounts of the chromogen to simplify degradation studies.

It was readily demonstrated, on the basis of carbon and hydrogen analyses, the neutral equivalent and ultraviolet absorption spectra, that the first metabolic product was β-(*o*-toloxy)-lactic acid.[6] That the chromogen was metabolically derived from β-(*o*-toloxy)-lactic acid was indicated since urine of rats which had received this compound showed the characteristic chromogenicity of urine of animals which had received myanesin. Combustion analyses on several different samples indicated that the empirical formula of the chromogen differed from that of the first metabolite by the addition of one oxygen atom. The second compound was, like the first, optically inactive. Electrometric titration showed the second compound to be a relatively strong acid, *pK* 3.5.

From these observations we concluded that the chromogen must be one of the four isomeric β-(hydroxy-2-methyl phenoxy)-lactic acids. Earlier observations that *o*-cresol, phenetol and diphenyl ether are metabolized to toluhydroquinone,[7] the glucuronide of *p*-ethoxyphenol[8] and *p*-hydroxydiphenyl ether,[9] respectively, led us to suspect that the chromogen was, in fact, β-(2-methyl-4-hydroxy phenoxy)-lactic acid, formed from β-(*o*-toloxy)-lactic acid by an analogous oxidation of the benzene ring para to the phenyl ether linkage. In further support

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(2) Aided by a grant from The National Foundation for Infantile Paralysis, Inc.

(3) University of California Atomic Energy Project, Post Office Box 31, Beverly Hills, California.

(4) Graves, Elliott and Bradley, *Nature*, **162**, 257 (1948).

(5) Hawk and Bergeim, "Practical Physiological Chemistry," 11th ed., P. Blakiston's Son and Co., Inc., Philadelphia, Pa., 1937, p. 669.

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