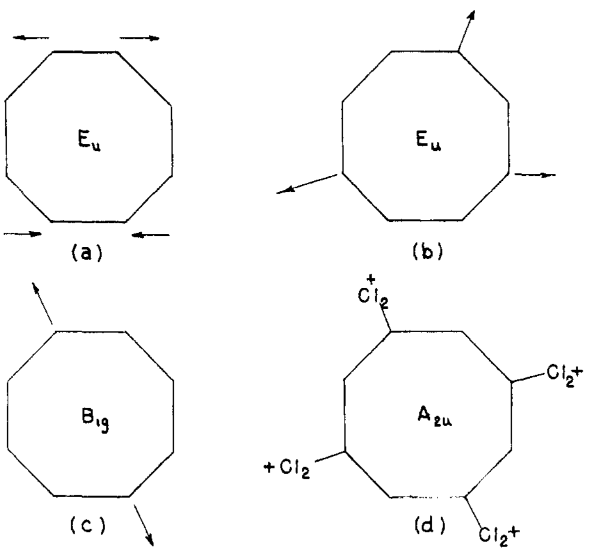


Fig. 4.—Approximate motion of $(PNCl_2)_4$ in certain of its fundamental modes.

ing motion. This is a class B_1 vibration for D_4 symmetry and has been assigned in cycloöctatetraene to a frequency of 1601 cm.$^{-1}$. The form of the vibration must be something like (c) in Fig. 4 which is actually more comparable to what has been called a ring elongation vibration and which in III has been assigned to the infrared band at 885 cm.$^{-1}$. Therefore in IV, where this vibration is now in the Raman active class B_{1g}, it has been assigned to the 895 cm.$^{-1}$ Raman line.

One further assignment might be made and that is the infrared active–Raman inactive band at 790 cm.$^{-1}$. In III there was believed to be an overlapping of A_1' and A_2'' modes at about this frequency. The A_2'' mode was assigned to a PCl_2 wagging, in phase vibration. This same type of motion in IV does come in class A_{2u} which matches the selection rules of the observed band at 790 cm.$^{-1}$.

Other than to say that the three vibrations of class E_g probably occur among the six observed Raman lines below 260 cm.$^{-1}$, nothing further in the way of assignment has been made. There are still $3B_{1g} + 4B_{2g} + 1A_{2u} + 3E_u$ whose range cannot be given, much less proposals for assignment to observed frequencies.

Conclusions

The selection rules for D_{3h} symmetry in the molecule $(PNCl_2)_3$ are shown to account for the observed infrared and Raman data. Selection rules for neither D_{4h} or D_{2d} fully account for the observed data on $(PNCl_2)_3$ and yet the molecule is believed to have one of these two symmetries. The data at present favor the D_{4h} structure. Vibrational assignments, as yet incomplete, are given for both molecules.

Acknowledgment.—The author is happy to acknowledge the assistance of R. B. Fox and E. J. Kohn of our High Polymer Branch in making available samples of the trimer and tetramer.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC CO.]

A Rate Study of the Silanol Condensation Reaction at 25° in Alcoholic Solvents[1]

BY W. T. GRUBB

RECEIVED JANUARY 16, 1954

A method is described for measuring the rates of silanol condensation reactions. The method consists of a titration of samples of the reacting solution with Karl Fischer reagent. This titration measures the total content of SiOH groups plus H_2O in the solution. Complete condensation of a silanol solution results in a reduction of the apparent water concentration to one-half of its initial value. Using this method of analysis, a detailed study has been made of the condensation of trimethylsilanol in the solvent methanol with the following results. The condensation of trimethylsilanol is found to be incomplete in this system. Incomplete condensation is caused by the rapid reaction $(CH_3)_3SiOH + CH_3OH \rightleftarrows (CH_3)_3SiOCH_3 + H_2O$, which removes silanol from the system, while the following condensation equilibrium is established slowly. $(CH_3)_3SiOH + (CH_3)_3SiOCH_3 \rightleftarrows (CH_3)_3SiOSi(CH_3)_3 + CH_3OH$. The formula for the condensation equilibrium constant is $K = [(CH_3)_3SiOCH_3]^2[H_2O]/[(CH_3)_3SiOSi(CH_3)_3]$. This form for the equilibrium constant reveals that essentially no free trimethylsilanol is present at equilibrium. The equilibrium constant has the same value when different concentrations of both acidic and basic catalysts are employed, and the same equilibrium is attained by starting from a mixture of hexamethyldisiloxane and water, thus demonstrating that this is a true thermodynamic equilibrium. It is found by studying the rate of attainment of the condensation equilibrium that the rate determining reaction in condensation is $(CH_3)_3SiOCH_3 + (CH_3)_3SiOH \rightarrow (CH_3)_3SiOSi(CH_3)_3 + CH_3OH$. A rate law deduced from this reaction agrees with the experimental results. The rate law is found to be the same for both acidic and basic catalysts although HCl is about 500 times as active as KOH in promoting condensation. Silanols containing bulkier substituents react much more slowly. Triethylsilanol and triphenylsilanol react, respectively, 1/600 and $<2 \times 10^{-6}$ as fast as trimethylsilanol under the same conditions. The proposed mechanisms for the silanol condensation reaction in methanol are: in acidic catalysis, $-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}\underset{|\,\mathrm{H}}{:} \rightarrow \overset{|}{\underset{|}{\mathrm{Si}}}\overset{|\,\mathrm{H}}{\mathrm{O}}\mathrm{CH_3}^+ \rightleftarrows -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}\overset{|}{\underset{|}{\mathrm{Si}}}- + CH_3OH + H^+$; and in basic catalysis, $-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}^-: \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OCH_3} \rightleftarrows -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}\overset{|}{\underset{|}{\mathrm{Si}}}- + CH_3O^-$. These mechanisms account for the observed rate law, the linear relation between rate of condensation and catalyst concentration, and the large effect of steric factors upon the rate of condensation. No evidence for the formation of R_3Si^+ has been found.

Introduction

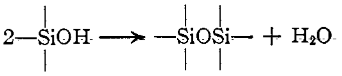
Rate studies in organosilicon chemistry have been confined chiefly to hydrolysis or cleavage reactions of atoms or groups attached to silicon, *e.g.*, Si–H,[2a]

---

[1] Paper presented at a Symposium on Inorganic Polymers at the 124th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1953.

[2] (a) F. P. Price, THIS JOURNAL, **69**, 2600 (1947); (b) C. G. Swain, R. M. Esteve and R. H. Jones, *ibid.*, **71**, 965 (1949).

Si–F,[2b] Si–CH_3,[3] Si–OR.[4] The interesting and important silanol condensation reaction


$$2\underset{|}{\overset{|}{\text{—Si}}}\text{OH} \longrightarrow \underset{|}{\overset{|}{\text{—Si}}}\text{O}\underset{|}{\overset{|}{\text{Si—}}} + H_2O$$

has not been investigated because of the lack of suitable experimental methods. Practical interest in this reaction results from its role in forming both simple siloxanes and polymeric silicones from the action of water upon organochlorosilanes.[5] The mechanism of the reaction is of considerable interest, first because of the absence of any exact analog in carbon chemistry, and secondly because it might take place either by way of R_3Si^+ intermediates or by a bimolecular displacement mechanism.

It is the purpose of the present paper to describe a general experimental technique for measuring rates of silanol condensations and to illustrate the use of this technique in a study of the condensation of monofunctional silanols in alcoholic solvents. The condensation of monofunctional silanols is a simple one-step reaction

$$2R_3SiOH \longrightarrow R_3SiOSiR_3 + H_2O$$

and it is known to be catalyzed by both acidic and basic catalysts.

Experimental Method

The method which has been employed in the measurement of silanol condensations involves Karl Fischer titration analyses. It has been reported by Gilman and Miller[6] that several silanols reacted quantitatively with Karl Fischer reagent. By analysis of some ethyl-, phenyl- and substituted phenylsilanols these authors illustrated a 1:1 molar equivalence of R_3SiOH and H_2O within a 1% relative error. From the reaction of some silanediols, *i.e.*, $R_2Si(OH)_2$, they observed that each OH attached to silicon was equivalent to one water molecule. In order to account for these results they proposed a reaction between silanol and methanol

$$R_3SiOH + CH_3OH \longrightarrow R_3SiOCH_3 + H_2O$$

Since the Karl Fischer reagent contains methanol (approx. $^2/_3$ by volume) and strong acids such as CH_3HSO_4 (comparable to H_2SO_4 in strength) it is not surprising to find that the above reaction occurs and that it is essentially complete under conditions in which the H_2O is continuously taken up by its usual reaction with the Karl Fischer reagent. In order to be useful for measuring silanol condensation rates, however, it is required that the silanol react quantitatively with Karl Fischer reagent without undergoing any appreciable intermolecular condensation. The ability to analyze sensitive or easily condensable silanols would constitute a suitable proof that intermolecular condensation does not interfere with Karl Fischer titration of silanols. Thus several sensitive silanols including $(CH_3)_3SiOH$, $(CH_3)_2\underset{\underset{OH}{|}}{Si}O\underset{\underset{OH}{|}}{Si}(CH_3)_2$, and $(CH_3)_2Si(OH)_2$ have been analyzed. The results of these analyses are presented in Table I. The sensitivity of these silanols toward intermolecular condensation has been previously reported.[7–9] In fact $(CH_3)_2Si(OH)_2$, the most reactive silanol which has been isolated, condenses at room temperature in contact with a trace of alkali from ordinary laboratory glassware.[8] Referring to Table I it will be observed that any intermolecular condensation of silanols would lead to a ratio $^1/_2 \leqslant B/A \leqslant 1$ for R_3SiOH or $1 \leqslant B/A \leqslant 2$ for $R_2Si(OH)_2$. It is apparent that even $(CH_3)_2Si(OH)_2$ undergoes preferentially a reaction with methanol and each molecule is equivalent to two water molecules in a Karl Fischer analysis.

TABLE I

THE ANALYSIS OF SILANOLS BY KARL FISCHER TITRATION

	Silanol present, mmoles *A*	Water found by titration, mmoles *B*	(*B*/*A*)	(*B*/*A*)[a]
$(CH_3)_3SiOH$	6.13	6.11	0.997	...
$(CH_3)_2Si(OH)_2$	2.30	4.60	2.00	...
$HOSi(CH_3)_2OSi(CH_3)_2OH$	3.24	6.53	2.02	...
$(C_6H_5)_3SiOH$	3.58	3.56	0.995	0.99
$(C_6H_5)_2Si(OH)_2$	2.08	4.09	1.97	1.98
0.258 Molar $(CH_3)_3SiOH$ in methanol	2.58	2.58	1.00	...
10 ml. of 0.295 *M* H_2O + 0.258 *M* $(CH_3)_3SiOSi(CH_3)_3$ in methanol	...	2.96	...	...

[a] Values reported by H. Gilman and L. S. Miller, THIS JOURNAL, **73**, 2367 (1951).

The results of Table I suggest that silanol-condensation rates may be measured by periodic sampling and titration of solutions of condensing silanol, but in order to be practically useful the hydrolysis (or alcoholysis) of siloxane linkages must not interfere with the titration. Such reaction would lead to spurious high analyses for H_2O in mixtures of siloxane with water. Direct analysis of solutions containing both water and hexamethyldisiloxane in methanol confirm that no detectable hydrolysis or alcoholysis takes place during the titration. This point is illustrated by the last entry of Table I.

Apparatus.—The Karl Fischer titration apparatus employed in this study consisted of a moisture-protected buret system of conventional design.[10] The titration flask itself was provided with a side arm and ground joint for the addition of samples to be titrated. Dry nitrogen gas (dew point < −60°) was supplied to a by-pass arrangement on the side arm to prevent the advent of atmospheric moisture. Similar precaution against moisture was provided on the reaction flask during the sampling of reacting solutions. Using these precautions no detectable atmospheric moisture was picked up during transfer of 10-ml. samples from the reaction vessel to the titration flask even though the titration was capable of detecting 0.2 mg. of H_2O.

The Karl Fischer reagent was standardized frequently against standard water in methanol, and occasionally against water weighed in small sealed off bulbs which were crushed directly in the titrating flask. The Karl Fischer end-point was determined by an adaptation of the "Dead Stop" method.[11] This method as applied here consisted of measuring the change of conductance between two platinum electrodes inserted into the titration flask.

This change in conductance is thought to be produced by a polarizing action of ions which is nullified at the end-point by the depolarizing action of the free iodine present[11] when excess Karl Fischer reagent has been added. The simple circuit employed consisted of a 1.5-volt dry cell in series with the platinum electrodes, a 0–20 microampere panel meter, and current limiting resistors. When the current was adjusted to read full scale (20 μamp.) in the presence of an *excess* of Karl Fischer reagent, it fell to 15 μamp. in the presence of excess water (*cf.* ref. 11). This value was insensitive to geometry of the electrodes. Under these conditions, a rapid direct titration of water or silanol samples was accomplished. There was no doubt that the end-point circuit used under conditions just described gave a sharper end-point in direct titrations than in back titrations. This is contrary to usual experience with the Karl Fischer end-point[10] using various electrical detection methods.

---

(3) L. H. Sommer, W. P. Barrie and J. R. Gould, THIS JOURNAL, **75**, 3765 (1953).

(4) R. Aelion, A. Loebel and F. Eirich, "Proceedings of the International Colloquium on Macromolecules," Amsterdam, 1949, p. 118; R. Aelion, A. Loebel and F. Eirich, *ibid.*, **72**, 5705 (1950).

(5) E. G. Rochow and W. F. Gilliam, *ibid.*, **63**, 798 (1941).

(6) H. Gilman and L. S. Miller, THIS JOURNAL, **73**, 2367 (1951).

(7) R. O. Sauer, *ibid.*, **66**, 1707 (1944).

(8) S. W. Kantor, *ibid.*, **75**, 2712 (1953).

(9) G. R. Lucas and R. W. Martin, *ibid.*, **74**, 5225 (1952).

(10) J. Mitchell and D. M. Smith "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 80.

(11) Reference 10, p. 93.

In the present investigation all experiments have been carried out at 25.00 ± 0.02° by maintaining the reacting solutions in a rapidly stirred water thermostat.

Materials.—Commercial[12] Karl Fischer reagent prepared according to the directions supplied by the manufacturers was used throughout this investigation.

Trimethylsilanol was prepared by the hydrolysis of trimethylfluorosilane according to the method of Sommer, Pietrusza and Whitmore.[13] This material boiled at 98.9° at one atmosphere and the refractive index of the sample was 1.3889 at 20° (lit. values b.p. 99° (734 mm.), $n^{20}\text{D}$ 1.3888,[13] $n^{20}\text{D}$ 1.3880[7]).

Triethylsilanol was prepared by the hydrolysis of triethylfluorosilane, b.p. 63° (12 mm.), $n^{20}\text{D}$ 1.4329,[13] previous value $n^{20}\text{D}$ 1.4329.[13]

Commercial[14] triphenylsilanol was twice recrystallized from benzene. The resultant material melted at 154–155°, previous value 155°.[15]

Commercial[14] diphenylsilanediol was recrystallized from chloroform–methyl ethyl ketone, m.p. 148° dec., previous value 148° dec.,[16a] 132°.[16b]

Tetramethyldisiloxanediol-1,3 was recrystallized from *n*-hexane, m.p. 6.5–66.5°, previous value,[17] 67–68°. (The author is indebted to Drs. Martin and Lucas for supplying samples of this material.)

Dimethylsilanediol was prepared by Dr. S. W. Kantor of this Laboratory by a method previously described.[8] (The author is indebted to Dr. S. W. Kantor for furnishing a sample of this compound from his original preparation.)

Trimethylmethoxysilane was prepared by the reaction of trimethylchlorosilane with methanol.[7] The product boiled at 55° (previous value 57.2°). (The author is indebted to Dr. S. W. Kantor for supplying a sample of this compound.)

Methanol was refluxed for 12 hours with magnesium turnings[18] and distilled. The methanol prepared in this way had a water content below 0.05% by weight, b.p. 64.2°.

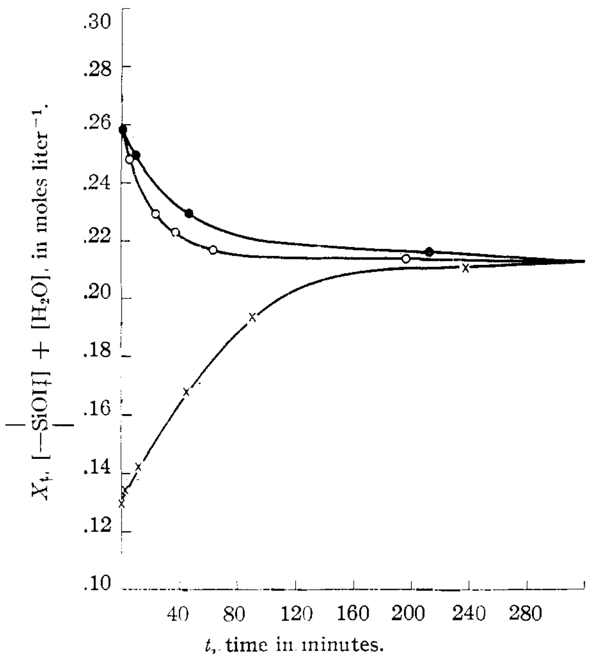


Fig. 1.—The attainment of the silanol siloxane equilibrium in methanol at 25°: ●, 0.258 *M* $(CH_3)_3SiOH$ + 2.0 × 10^{-4} *M* HCl; O, 0.258 *M* $(CH_3)_3SiOH$ + 4.0 × 10^{-4} *N* HCl; ×, 0.130 *M* $(CH_3)_3SiOSi(CH_3)_3$ + 0.130 *M* H_2O + 2.0 × 10^{-4} *N* HCl.

Commercial absolute ethanol was dried by treatment with sodium and ethyl phthalate[18] followed by distillation. The water content of this material was below 0.05% as determined by Karl Fischer titration.

Commercial *n*-propanol was dried over calcium hydride and distilled.

Anhydrous HCl in methanol solution was prepared by dissolving Matheson "anhydrous" HCl directly in anhydrous methanol prepared in the above manner. This solution was then standardized against aqueous NaOH using phenolphthalein indicator. (The methanol–HCl reaction has been reported to be very slow at room temperature in dilute solutions.[19]) In a similar manner KOH in methanol was prepared by dissolving reagent grade KOH in anhydrous methanol and standardizing against aqueous HCl solution.

These relatively concentrated (*e.g.*, 0.01–0.10 *N*) solutions were added in small amount to the silanol solutions to begin the condensation reaction. The final catalyst concentrations were known with a relative error of ±1%.

Timing Procedure.—Timing of the reaction was begun upon addition of catalyst to the silanol solution which had previously been brought to 25.00 ± 0.02°. The solutions were made homogeneous by shaking at the time of the catalyst addition. Aliquots of the solution were analyzed at intervals by Karl Fischer titration. The time of addition to a water Karl Fischer end-point mixture was recorded as the time of sampling. Smooth curves of "H_2O equivalent" *vs.* time extrapolating to the known initial concentration with an error of less than 1% were obtained. This fact appears to justify the validity of the timing procedures just described.

Definition of Symbols and Units.—In the present study, concentrations have been expressed throughout in moles per liter of solution at 25.0° and time has been expressed in minutes. The following notation has been used: X_t = water equivalent in moles/liter of solution at time t (concentration of SiOH + H_2O in moles liter^{-1}); X_0 = water equivalent in moles liter^{-1} at zero time (concentration of SiOH). From these quantities the concentrations of various species at any time t are: $X_0 - X_t$ = concentration of siloxane; $2(X_0 - X_t)$ = concentration of silanol condensed; $2X_t - X_0$ = concentration of uncondensed silanol. In some cases a very small concentration of free water was present in the solution at time zero. X_0 and X_t as defined above have been corrected where necessary for free water initially present. It is apparent that the value of X_t remains unchanged when the reaction $-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OH} + \mathrm{CH_3OH} \rightleftarrows -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OCH_3} + \mathrm{H_2O}$ occurs. The extent of this reaction has been determined indirectly by the study of the condensation equilibrium.

The Equilibrium State of Silanols in Alcohols.—

Trimethylsilanol condenses in the solvent methyl alcohol at a conveniently measurable rate in the presence of *ca.* 10^{-4} *N* HCl. The condensation is not complete in this solvent but reaches an equilibrium state as shown in Fig. 1. This state is a true equilibrium since its position is constant when approached from both directions and when different concentrations of HCl are employed. Alkaline catalysts such as KOH promote the reaction at a much slower rate for equal catalyst concentration and attain the same equilibrium position within a relative error of ±1%.

The incomplete condensation observed here might have resulted either from an inherent instability of siloxanes in solution toward small concentrations of water or by the removal of silanol from

---

[12] Fischer Scientific Co.

[13] L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, This Journal, **68**, 2282 (1946).

[14] Dow Corning Corp., Midland, Michigan.

[15] W. Dilthey and F. Edouardoff, *Ber.*, **37**, 1139 (1904).

[16] (a) C. A. Burkhard, This Journal, **67**, 2173 (1945); (b) F. S. Kipping, *J. Chem. Soc.*, **101**, 2108 (1912).

[17] G. R. Lucas and R. W. Martin, This Journal, **74**, 5225 (1952).

[18] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., New York, N. Y., 1941, p. 359.

[19] R. L. Loening, A. B. Garrett and M. S. Newman, This Journal, **74**, 3929 (1952).

TABLE II

A COMPARISON OF TWO FORMULAS FOR THE EQUILIBRIUM CONSTANT OF THE TRIMETHYLSILANOL–HEXAMETHYLDISILOXANE EQUILIBRIUM IN METHANOL

$$K_3 = [(CH_3)_3SiOH]^2/[(CH_3)_3SiOSi(CH_3)_3][H_2O] = (2X_e - X_0)^2/(X_0 - X_e)^2$$

$$K_4 = [(CH_3)_3SiOCH_3]^2[H_2O]/[(CH_3)_3SiOSi(CH_3)_3] = (Y + 2X_e - X_0)^2(X_e)/(X_0 - X_e) = K_1K_2{}^b$$

The constant, $[CH_3OH]$, has been omitted from the above expressions.

Experiment No.	$(CH_3)_3SiOH$ (initial concn.) X_0, moles $l.^{-1}$	X_e,[a] moles $l.^{-1}$	$(CH_3)_3SiOCH_3$ (initial concn.) $= Y$, moles $l.^{-1}$	Catalyst, N HCl	K_3	K_4
F-1	0.128	0.1188	...	2×10^{-4}	122	0.15
F-2	.258	.213	...	2×10^{-4}	14	0.13
F-3	.258	.213	...	4×10^{-4}	14	0.13
F-10	.444	.332	...	1×10^{-4}	3.8	0.14
F-17	.258	.214	...	1.0×10^{-2}	14	0.13
F-8	.260		0.214	2×10^{-4}	...	0.15
F-9	.258		.074	2×10^{-4}	...	0.14
F-11	.259		.361	2×10^{-4}	...	0.13
F-12	.257		.503	2×10^{-4}	...	0.12

[a] $X_e = [H_2O] + [SiOH]$ at equilibrium (brackets are used to indicate concentrations in moles liter^{-1}). [b] See text.

the equilibrium by reaction with the solvent methanol to form trimethylmethoxysilane. The former seems more likely since it is known that alcohol–silanol reactions occur. For instance, the Karl Fischer analysis of silanols depends upon such reaction. It is possible to estimate the extent of the silanol–methanol reaction by a study of the form of the equilibrium constant for the condensation equilibrium. In the case of trimethylsilanol in methanol, this constant has been derived under two different sets of assumptions by considering the following reactions

$$(CH_3)_3SiOH + CH_3OH \underset{k_2}{\overset{k_1}{\rightleftarrows}} (CH_3)_3SiOCH_3 + H_2O$$

$$(CH_3)_3SiOH + (CH_3)_3SiOCH_3 \underset{k_4}{\overset{k_3}{\rightleftarrows}} (CH_3)_3SiOSi(CH_3)_3 + CH_3OH$$

$$2(CH_3)_3SiOH \underset{k_6}{\overset{k_6}{\rightleftarrows}} (CH_3)_3SiOSi(CH_3)_3 + H_2O$$

The *k*'s are rate constants for the reactions, and the equilibrium constants for each equilibrium are

$$K_1 = \frac{[(CH_3)_3SiOCH_3][H_2O]}{[(CH_3)_3SiOH]} = k_1/k_2$$

$$K_2 = \frac{[(CH_3)_3SiOH][(CH_3)_3SiOCH_3]}{[(CH_3)_3SiOSi(CH_3)_3]} = k_4/k_3$$

$$K_3 = \frac{[(CH_3)_3SiOH]^2}{[(CH_3)_3SiOSi(CH_3)_3][H_2O]} = k_6/k_6$$

(brackets are used to indicate concentrations in moles liters^{-1}). Then, combining reactions 1, 2, 3 and 4 and assuming that no free silanol is present at equilibrium the following constant is derived for the condensation equilibrium

$$K_4 = \frac{[(CH_3)_3SiOCH_3]^2[H_2O]}{[(CH_3)_3SiOSi(CH_3)_3]} = K_1K_2$$

Two possibilities are now presented. If the experimental results show that K_3 is constant over a range of concentrations, then the reaction between trimethylsilanol and methanol may be considered negligibly small. However, if K_4 is constant, then the reaction between trimethylsilanol and methanol must be substantially complete and practically no free trimethylsilanol is present at equilibrium. In Table II are presented the values of K_3 and K_4, derived from the various equilibration experiments; the expression K_4 is clearly the correct equilibrium constant. Strong confirmation of this picture results from the observation that K_4 is constant in experiments in which pure trimethylmethoxysilane (concentration Y in Table II) has been purposely added to the solutions of trimethylsilanol in methanol before equilibration. In Table II, experiments F8, F9, F11 and F12 illustrate that K_4 has the same value under these conditions. The variation of K_4 is considered to be within experimental error. Its value is, in fact, quite sensitive to slight changes in X_e.

By equilibrating trimethylsilanol in various alcohols the various values of K_4 shown in Table III have been obtained. It may be observed that the condensation becomes more complete in solvent alcohols of higher molecular weight in the range from methyl alcohol through *n*-propyl alcohol. It will also be noted that triethylsilanol condenses more completely than trimethylsilanol does in methanol.

TABLE III

THE VALUES OF K_4 FOR SILANOLS IN VARIOUS ALCOHOLS

$$K_4 = [R_3SiOR']^2[H_2O]/[R_3SiOSiR_3]$$

Silanol (R_3SiOH)	Alcohol R'OH	K_4
$(CH_3)_3SiOH$	Methanol	0.13
$(CH_3)_3SiOH$	Ethanol	.030
$(CH_3)_3SiOH$	*n*-Propanol	.0072
$(CH_3CH_2)_3SiOH$	Methanol	.055

In order to study the rates of silanol condensations it would be desirable to employ a solvent medium which did not react with silanols. Some of the water miscible ethers such as dioxane and 1,2-dimethoxyethane fulfill this requirement. Dioxane, however, sometimes presents difficulties in the Karl Fischer titration.[20] In a preliminary experiment the condensation of trimethylsilanol in 1,2-dimethoxyethane was measured in the presence of 1.0×10^{-3} N HCl. The condensation was at least 98% complete in this system, but a simple rate law (*e.g.*, 1st order or 2nd order in silanol) was not observed because the catalytic activity of HCl is

---

(20) Reference 10, p. 104.

TABLE IV

INITIAL COMPOSITIONS OF SOLUTIONS AND INITIAL RATES OF CONDENSATION

Experiment number	Concn. of trimethylsilanol, M	Catalyst and concn.	Concn. of trimethylmethoxysilane added, M	Initial rate of siloxane formation $-(\mathrm{d}X_t/\mathrm{d}t)_0$, moles l.$^{-1}$ min.$^{-1}$
F-1	0.128	2.00×10^{-4} N HCl		1.05×10^{-4}
F-2	.258	2.00×10^{-4} N HCl		9.7×10^{-4}
F-3	.258	4.00×10^{-4} N HCl		20.4×10^{-4}
F-5[a]	.259	2.00×10^{-4} N HCl		3.3×10^{-4}
F-6	.251[b]	2.00×10^{-4} N HCl		$<1 \times 10^{-7}$
F-8	.260	2.00×10^{-4} N HCl	0.214	28.0×10^{-4}
F-9	.257	2.00×10^{-4} N HCl	.072	16.6×10^{-4}
F-10	.444	1.00×10^{-4} N HCl		22.0×10^{-4}
F-11	.259	2.00×10^{-4} N HCl	.361	46×10^{-4}
F-12	.257	2.00×10^{-4} N HCl	.503	72×10^{-4}
F-14	.257	4.00×10^{-4} N HCl		19.6×10^{-4}
F-16	.258	4.00×10^{-4} N KOH		4.9×10^{-6}
F-17	.258	1.00×10^{-2} N KOH		1.1×10^{-4}
F-19	.257	2.20×10^{-3} N NaOH		2.2×10^{-5}
F-20	.257	1.10×10^{-3} N LiOH		1.1×10^{-5}
F-21	.257[c]	2.00×10^{-4} N HCl		1.8×10^{-5}

[a] Solvent was ethanol instead of methanol. [b] Triphenylsilanol instead of trimethylsilanol. [c] Triethylsilanol instead of trimethylsilanol.

sensitive to small changes of water concentration in this solvent. It was observed by way of an analogy that the conductance of HCl in 1,2-dimethoxyethane is a strong function of the water content of the system.

The solvents methanol and ethanol are expected to be much less sensitive in this respect,[21] again drawing the rough analogy between electrical conductivity of HCl in solution and its catalytic activity in the condensation reaction. Thus, alcohols, in particular methanol, were chosen as solvents for the rate investigation. They have the additional property (see below) of reacting with siloxanes by the reaction

$$\mathrm{CH_3OH + R_3SiOSiR_3 \longrightarrow R_3SiOH + R_3SiOCH_3}$$

Thus the rate of this reverse reaction may be investigated by the same techniques described here in order to compare siloxane reactivities. The results of such a study will be reported in a subsequent paper.

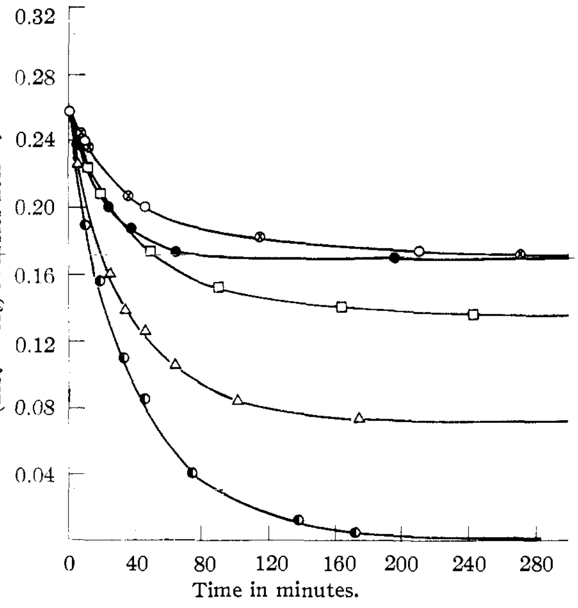


Fig. 2.—The condensation of trimethylsilanol in methanol at 25°, plot of uncondensed silanol $(2X_t - X_0)$ as a function of time: ○, experiment F-2; ⊗, experiment F-17; ●, experiment F-3; □, experiment F-9; △, experiment F-8 ◐, experiment F-11. In the case of experiment F-17, the time scale should be multiplied by 10.

The Rate of Condensation of Silanols in Alcohols.—The equilibrium studies have shown that silanol–alcohol reaction plays an important role in the alcoholic silanol condensation. The measurement of equilibrium states does not reveal the mechanism of reaction or the relative rates of various steps involved in attaining equilibrium. In order to elucidate these factors, silanol condensation rates have been measured over a range of conditions at 25.00 ± 0.02°. For this purpose solutions containing various silanols, catalysts and additives have been studied. The initial compositions of these solutions are listed in Table IV together with the initial rates of siloxane formation $-(\mathrm{d}X_t/\mathrm{d}t)$ which have been estimated from the slope at time zero of the experimental plot of (X_t) *vs.* time. Typical condensation curves plotted as uncondensed silanol, $(2X_t - X_0)$, *vs.* time in minutes are presented in Fig. 2. It is to be observed (Table IV) that the initial condensation rates are approximately proportional to catalyst concentration for all catalysts employed and that the alkali metal hydroxides are less active than HCl. Nevertheless, there is strong evidence that the acid- and base-catalyzed reactions obey the same rate law. In Fig. 2 the curve of $(2X_t - X_0)$ *vs.* time for experiment (F-17), a typical KOH, catalyzed reaction, coincides with that of an HCl-catalyzed reaction (F-2) when the time scale is adjusted to account for the difference in catalyst activity. The same is true of the other alkali metal hydroxides which have been used.

In deducing a rate law for silanol condensations in methanol the following reactions must again be considered.

---

[21] H. Goldschmidt and P. Dahll, *Z. physik. Chem.*, **108**, 121 (1924).

TABLE V

THE INITIAL RATE OF SILANOL CONDENSATION (dX_t/dt) AS A FUNCTION OF CONCENTRATION VARIABLES

Experiment no.	$[(CH_3)_3SiOCH_3]^2 \times [H_2O][HCl]$ (A)	$[(CH_3)_3SiOCH_3] \times [H_2O][HCl]$ (A')	$-(dX_t/dt)$ (B)	B/A	B/A'
F-1	4.18×10^{-7}	3.4×10^{-7}	1.05×10^{-4}	2.5×10^2	3.1×10^2
F-2	3.44×10^{-6}	1.34×10^{-6}	9.7×10^{-4}	2.8×10^2	7.2×10^2
F-3	3.44×10^{-6}	2.68×10^{-6}	20.4×10^{-4}	3.0×10^2	7.6×10^2
F-8	11.6×10^{-6}	2.46×10^{-6}	28.0×10^{-4}	2.2×10^2	11.4×10^2
F-9	5.56×10^{-6}	1.70×10^{-6}	17.0×10^{-4}	3.0×10^2	9.8×10^2
F-10	8.75×10^{-6}	1.97×10^{-6}	22.0×10^{-4}	2.5×10^2	11.1×10^2
F-11	19.8×10^{-6}	3.22×10^{-6}	46×10^{-4}	2.3×10^2	14.3×10^2
F-12	29.7×10^{-6}	3.90×10^{-6}	72×10^{-4}	2.5×10^2	18.5×10^2
F-14	3.40×10^{-6}	2.64×10^{-6}	19.6×10^{-4}	2.9×10^2	7.4×10^2

$$(CH_3)_3SiOH + CH_3OH \underset{k_2}{\overset{k_1}{\rightleftarrows}} (CH_3)_3SiOCH_3 + H_2O \qquad K_1 = k_1/k_2$$

$$(CH_3)_3SiOH + (CH_3)_3SiOCH_3 \underset{k_4}{\overset{k_3}{\rightleftarrows}} (CH_3)_3SiOSi(CH_3)_3 + CH_3OH \qquad K_2 = k_4/k_3$$

$$2(CH_3)_3SiOH \underset{k_6}{\overset{k_5}{\rightleftarrows}} (CH_3)_3SiOSi(CH_3)_3 + H_2O \qquad K_3 = k_6/k_5$$

A simplifying condition is provided by the observation that hexamethyldisiloxane "hydrolyzes" in anhydrous methanol. The rate in this case is somewhat faster than it is in the system containing a concentration of water equal to the concentration of the hexamethyldisiloxane. This removes reactions 5 and 6 from consideration, since 6 requires that the rate of hydrolysis be proportional to the water concentration. Among the remaining forward reactions either 2 or 3 may be rate determining. If reaction 2 is rate determining then the forward rate at time = 0 will be proportional to $[(CH_3)_3SiOCH_3]\ [H_2O]$ [catalyst], but if reaction 3 is rate determining then the forward rate at time = 0 will be proportional to $[(CH_3)_3SiOCH_3]^2\ [H_2O]$ [catalyst]. The data of Table V indicate that the second assumption is correct. The rate equation for trimethylsilanol condensation in methanol is given by the equation 1

$$dX_t/dt = -k_3/K_1\{[(CH_3)_3SiOCH_3]^2[H_2O]/ -K_4\ [(CH_3)_3SiOSi(CH_3)_3]\} \quad (1)$$

where $K_4 = 0.13$ (average from Table II). Hereafter the expression in braces will be designated as (C–D).

A substitution into eq. 1 of the concentrations in time of X_0 and X_t leads to an equation containing only one constant (k_3/K_1) and measurable quantities. The integration of this, however, requires a series expansion and is not convenient. A simpler test of equation 1 consists of plotting the values (dX_t/dt) determined graphically with the quantity in braces. The values (dX_t/dt) were measured from the curves of Fig. 2 and others of similar nature using a prism type tangentimeter reported to be capable of about ±2% precision.[22] These values (dX_t/dt) are plotted in Fig. 3 against ($C - D$). The straight lines of Fig. 3 were calculated by the method of least squares and have the equations

Expt. no.	Equation $-(dX_t/dt) = m(C - D) + b$
F_3	$-dX/dt = 0.123(C - D) - 0.00004$
F_2, F_9	$-dX/dt = .063(C - D) - 0.00008$
F_{10}	$-dX/dt = .031(C - D) - 0.00003$

The value of b is negligible in each case and $m = k_3/K_1$.

It is a confirmation of equation 1 that the data of Fig. 3 are best fitted by straight lines passing through the origin.

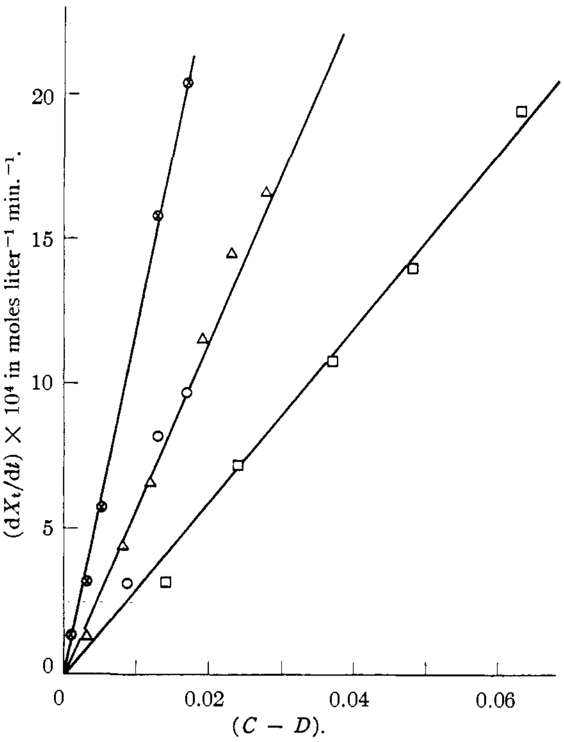


Fig. 3.—Test of the rate law $dX_t/dt = -(k_3/K_1)(C - D)$; $(C - D) = \{[(CH_3)_3SiOCH_3]^2[H_2O] - 0.13\ [(CH_3)_3SiOSi(CH_3)_3]\}$: ⊗, experiment F-3; △, experiment F-9; ○, experiment F-2; □, experiment F-10.

It is to be observed that (k_3/K_1) is proportional to the concentration of HCl catalyst. Analysis of other data in the same manner shows that the value of k_3/K_1 decreases somewhat at higher $(CH_3)_3SiOCH_3$ concentrations. This is attributed to an effect of high solute concentrations upon the catalyst activity since the equilibrium constant in Table II does not change very much under these conditions.

---

[22] O. W. Richards and P. M. Roope, *Science*, **71**, 290 (1930).

TABLE VI

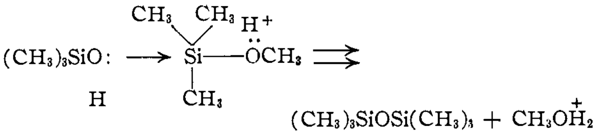
THE SPECIFIC RATE CONSTANTS FOR SILANOL CONDENSATION (k_f) AND SILOXANE ALCOHOLYSIS (k_r) AT 25°

Silanol	Solvent	Catalyst	k_f	k_r
$(CH_3)_3SiOH$	CH_3OH	HCl	3.1×10^2	4.0×10
$(CH_3)_3SiOH$	CH_3OH	KOH	6.4×10^{-1}	8.3×10^{-2}
$(CH_3)_3SiOH$	CH_3OH	NaOH	5.9×10^{-1}	7.7×10^{-2}
$(CH_3)_3SiOH$	CH_3OH	LiOH	5.9×10^{-1}	7.7×10^{-2}
$(CH_3)_3SiOH$	CH_3CH_2OH	HCl	8.0×10^1	2.4
$(CH_3CH_2)_3SiOH$	CH_3OH	HCl	0.5	2.8×10^{-2}
$(C_6H_5)_3SiOH$	CH_3OH	HCl	<.0002	....

The substitution of groups larger than methyl radicals in R_3SiOH decreases the condensation rate by orders of magnitude. The forward constant (k_3/K_1) has been determined in several systems by methods just described. The specific forward rate constant $k_f = (k_3/K_1)/[\text{catalyst}]$ is presented in Table VI for various silanols, catalysts and solvents. The constant $k_r = k_4/[\text{catalyst}]$, the specific rate constant for the siloxane methanolysis, has been evaluated from the value of k_f and the equilibrium constant for the system.

Mechanism of the Reaction.—The foregoing results have shown that the silanol condensation reaction is bimolecular and that its rate is sensitive to steric factors (Table VI). Reactions of this type occur in conventional carbon chemistry usually by a mechanism of rearward attack in which an electron donor molecule approaches the backside of the central atom undergoing displacement of one of its substituents. Such reactions follow a bimolecular rate law, and their rates are sensitive to steric factors.

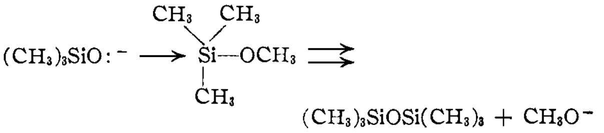
It is proposed therefore that silanol condensations occur in an analogous manner. For example the condensation of trimethylsilanol in methanol may occur in the following manner under acid catalysis.



$$\underset{\mathrm{H}}{(CH_3)_3SiO:} \longrightarrow \underset{CH_3}{\overset{CH_3\ CH_3}{\mathrm{Si}}}\text{—}\overset{H^+}{\ddot{O}}CH_3 \rightleftarrows (CH_3)_3SiOSi(CH_3)_3 + CH_3O\overset{+}{H}_2$$

All the protonated species are assumed to be in non-rate-determining equilibrium. The concentration of $(CH_3)_3Si\overset{H^+}{O}CH_3$ is proportional to the HCl concentration and thus the rate is first order in HCl.

Correspondingly, the following mechanism for the base-catalyzed condensation of trimethylsilanol in methanol is proposed

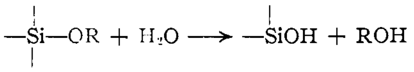


$$(CH_3)_3SiO:^- \longrightarrow \underset{CH_3}{\overset{CH_3\ CH_3}{\mathrm{Si}}}\text{—}OCH_3 \rightleftarrows (CH_3)_3SiOSi(CH_3)_3 + CH_3O^-$$

The silanolate ion (the concentration of which is proportional to that of the base catalyst) is considered to be the reactive species. This is proposed in order to account for the similar catalytic activity of the 3 alkali metal hydroxides, LiOH, NaOH and KOH. By contrast, Hurd, Osthoff and Corrin[23] have shown that in a relatively non-ionizing siloxane solvent medium the base strength of $\equiv$Si-OM (M = K, R_b, C_s) units is a rate-determining factor in siloxane rearrangement reactions, and that NaOH and LiOH are inactive as rearrangement catalysts.

Swain, *et al.*,[24] have proposed that silicon forms pentacovalent intermediates. The present results are also consistent with the "pentacovalent intermediate" theory. Further experimental evidence is required to elucidate this possibility. Lacking such evidence, the more conventional displacement mechanism has been suggested.

The hydrolysis of $Si(OR_4)$ by H_2O has been studied by Aelion, *et al.*[4] These authors have deduced that the reaction



$$-\overset{|}{\underset{|}{\mathrm{Si}}}\text{—}OR + H_2O \longrightarrow -\overset{|}{\mathrm{Si}}OH + ROH$$

is rate determining and is followed by a non rate-determining condensation of the evolved silanol. Their analysis which involves the Karl Fischer titration for the water formed by silanol condensation, apparently should be reinterpreted in light of the quantitative reaction of $-\overset{|}{\underset{|}{\mathrm{Si}}}OH$ with the Karl Fischer reagent, which is now known to occur.

Acknowledgment.—The author is indebted to Dr. J. R. Ladd for the synthesis of several silanols and to Dr. S. W. Kantor for many helpful discussions during the course of this investigation.

SCHENECTADY, NEW YORK

---

[23] D. T. Hurd, R. C. Osthoff and M. L. Corrin, THIS JOURNAL **76**, in press (1954).

[24] C. G. Swain, R. M. Esteve and R. H. Jones, *ibid.*, **71**, 965 (1949).