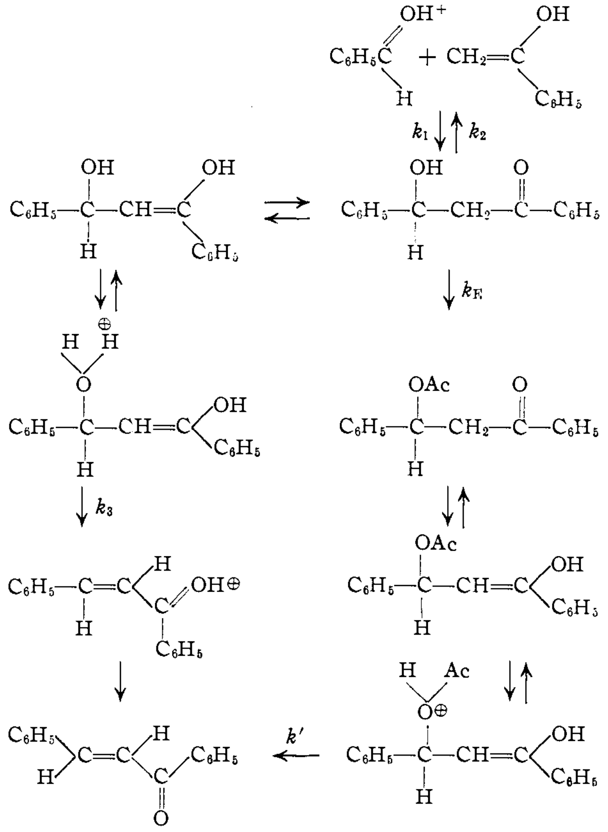
compared with an extrapolated value from the data reported earlier[3] of -4.97.

More extensive data determined in anhydrous acetic acid are presented in Table V. At higher concentrations of acetophenone the value of the pseudo unimolecular rate constant $k_{\lim}$ does not increase as rapidly as would be predicted, as shown in Fig. 2. At the higher concentrations of acetophenone, the rate of the condensation approaches the rate of the elimination, k_3'.

Conclusions Regarding the Mechanism of the Forward Condensation Reaction.—Because of the complexity of the steps succeeding the actual bond-forming reaction, where even the observed rate of appearance of chalcone from the ketol in acid is a function of several competing reactions, it is not feasible to determine all of the rate constants from the present data.

However it may be concluded that the rate of the dehydration of the ketol is faster than the rate of the loss of acetic acid from the ketol acetate. This result is probably due to the greater basicity of the alcohol as compared to the ester.

One may present a fairly detailed picture of the pathway(s) by which chalcone arises under the conditions investigated. Such a reaction scheme is outlined below. Under the differing experimental conditions investigated, the value of the bimolecular rate constant determined is not exactly the same in both the anhydrous and the wet acetic acid media, at the same H_0. This difference is presumably due to the difference in the branching ratio of the different possible reactions of the intermediate ketol. It is also attractive to suggest that the elimination step takes place through the intermediate enol. The rate of enolization is of the appropriate order of magnitude for this to be feasible.



BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Kinetics of the Polymerization of a Cyclic Dimethylsiloxane[1]

BY W. T. GRUBB AND ROBERT C. OSTHOFF

RECEIVED OCTOBER 13, 1954

Cyclic dimethylsiloxanes are converted into high polymers by the action of potassium hydroxide at elevated temperatures. The kinetics of this process has been studied using the monomer, octamethylcyclotetrasiloxane (I). Precipitation and distillation analysis of this system at small conversions reveals that I and high polymer make up at least 90% of the material present. Because of this, the well known theories of polymer–solvent systems have been applied. In particular, the vapor pressure above the polymerizing system is a convenient measure of the extent of reaction. The kinetics have been measured by continuously monitoring the vapor pressure above the polymerizing solution. The reaction proceeds at a rate which is first order in the volume fraction of I in the solution attaining an equilibrium at about 94% polymer. A reversion reaction of the polymer takes place at a rate proportional to the volume fraction of polymer present. The rate law based on these concepts is in excellent agreement with the experimental kinetics. The apparent activation energy of the over-all polymerization is found to be 19.6 kcal. The rate of the polymerization is proportional to the square root of the potassium hydroxide concentration.

Many cyclic siloxanes undergo reaction in the presence of acidic or basic catalysts to form high molecular weight siloxane polymers. For example, dimethylsiloxane polymers may be formed from low molecular weight octamethylcyclotetrasiloxane (I) by the action of potassium hydroxide or other alkali metal hydroxides at elevated temperatures.[2] Some qualitative features of this reaction have been investigated previously,[3] and a mechanism involving the formation of intermediate alkali metal silanolates was proposed, but no exact kinetic data were obtained. It was therefore the purpose of the present investigation to develop a suitable experimental method for measuring the kinetics of polymerization of I under carefully controlled conditions and to investigate the effects of temperature and other conditions upon the reaction

---

[1] Presented at the 126th meeting of the American Chemical Society, New York, N. Y., September, 1954.

[2] J. F. Hyde, U. S. Patent 2,490,357 (December 6, 1949).

[3] D. T. Hurd, R. C. Osthoff and M. L. Corrin, THIS JOURNAL, **76**, 249 (1954).

rate in order to obtain a better understanding of the mechanism and thermodynamics of the reaction.

Experimental

General Considerations.—The polymerization of I may be represented as

$$x/4[(CH_3)_2SiO]_4 \xrightarrow[\text{heat}]{\text{KOH}} [(CH_3)_2SiO]_x$$

The cyclic structure I rearranges to form a long chain molecule which is terminated by small traces of various end-groups. These include silanols formed from the reaction of water with the siloxane, silanolates formed from the reaction of potassium hydroxide with the siloxane, and the monofunctional siloxane end group $(CH_3)_3SiO_{1/2}$ which may be accidentally present. The rearrangement reaction of I containing large amounts of monofunctional siloxanes in the presence of basic catalysts has been studied previously by viscosity measurements.[4] In order to study the formation of high molecular weight polymers by the above reaction, it was necessary to maintain conditions of high purity at all times during the reaction. A suitable method for measuring the polymerization rates would consist of some physical measurement not involving sampling or exposure of the system to atmospheric contamination (moisture, etc.).

The most successful method was found to be the continuous monitoring of the vapor pressure above the polymerizing system. In order to interpret such measurements, the composition of the system after short polymerization times was analyzed by three methods to be described. The results of these analyses permitted an unambiguous interpretation of the vapor pressure measurements in terms of the amount of I reacted to form non-volatile products.

Preparation of Materials. A. Tetramer (Octamethylcyclotetrasiloxane).—Crude I was obtained by distilling the products of hydrolysis of dimethyldichlorosilane.[5] This material was then dried over calcium hydride and redistilled to obtain tetramer of 99.8 mole % purity, b.p. 175°, $n^{20}D$ 1.3968.[6] The mean water content of this material was found by Karl Fischer titration[7] to be 30 ± 10 parts per million.

B. **Potassium Hydroxide Catalyst.**—Potassium hydroxide is not sufficiently soluble in I at room temperature to permit the use of homogeneous solutions to catalyze the polymerization reaction. It has been necessary, therefore, to prepare suspensions of finely divided potassium hydroxide in I in the concentration range of 0.01% by weight of base. Preliminary investigations showed that suspensions in the desired 0.01% concentration range are not stable for periods of a few days, are difficult to analyze accurately, and are somewhat sensitive to prior treatment of the glassware in which they are prepared. In order to avoid these difficulties, a concentrated suspension (*ca.* 0.2% by weight) was first prepared and standardized in the following manner.

Pellets of potassium hydroxide (reagent grade containing about 85% potassium hydroxide and 15% water) were ground as fine as possible in a nitrogen dry-box (dew point of the nitrogen was less than −50°). Approximately two grams of this powder was then agitated with 250 ml. of I in a Waring Blendor for five minutes under a blanket of dry nitrogen. The suspension obtained in this fashion was then poured into a storage flask and allowed to stand overnight. It was then transferred into a second storage flask, leaving behind any large particles of potassium hydroxide and/or materials adhering to the flask walls.

The analysis of the suspension was then carried out by pipetting a sample of suitable size, shaking it thoroughly with twice its volume of distilled water, and then titrating the two-phase system against standard 0.1 *N* aqueous hydrogen chloride solution using two indicators (phenolphthalein and methyl orange). The correction for the presence of potassium carbonate was made in the usual manner and usually amounted to about 5% of the potassium hydroxide. Satisfactory homogeneity of the suspension during sampling has been achieved by means of continuous magnetic stirring during sampling. Reproducible extraction of the potassium hydroxide into the water layer was achieved only by several minutes of vigorous shaking. When prepared in this manner, the concentrated suspension gave reproducible analyses (within 1%) over periods of one month or more. These suspensions contained 2–4 mg. ml.$^{-1}$ of potassium hydroxide in I.

In order to prepare a suspension for a polymerization rate experiment, the calculated amount of the concentrated suspension was diluted to form 250 ml. of suspension of the desired concentration, *i.e.*, 0.01% by weight of potassium hydroxide. The volumetric flasks used in these operations had been steamed previously for two hours and oven dried to remove any acidic surface contaminants present.[8]

For the rate studies, about 35 ml. of the dilute suspension was added by means of a hypodermic syringe to an isoteniscope, or a suitable bulb, the construction and operation of both of which are described below. The authors estimate that the procedure just described results in the formation of a suspension of potassium hydroxide of concentration 0.01% which is known with a relative error of ±2%.

An analysis by Karl Fischer titration[9] was carried out upon two 250-ml. batches of I plus 0.01% potassium hydroxide with the results indicated in Table I. It will be noted that water, potassium hydroxide,[9] and silanol[7,10] are all equivalent mole-for-mole toward reaction with the Karl Fischer reagent.

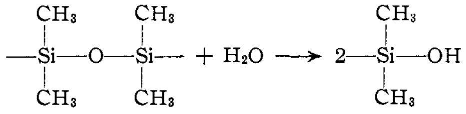
Table I

Water Analyses in Tetramer–Potassium Hydroxide Suspensions

Batch no.	H_2O, moles/l. Total[a]	Initial[b]	KOH,[c] moles l.$^{-1}$
1	0.0063	0.0020	0.0014
2	.0060	.0020	.0014

[a] Total apparent water, includes the KOH, H_2O and $\geqslant SiOH$. [b] Determined by titration of I blank. [c] Calculated based on assumption that the Reagent Grade KOH contained 85% KOH and 15% H_2O.

The difference, [0.0060 − (0.0020 + 0.0014)] = 0.0026 moles l.$^{-1}$ of material titratable as water, may be accounted for either by moisture picked up during handling or by the reaction of a siloxane with water



$$-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}- + H_2O \longrightarrow 2-\overset{CH_3}{\underset{CH_3}{Si}}-OH$$

The authors suggest the latter explanation as causing the increase in apparent water, since methods of handling the I have been tested previously and found to introduce little or no atmospheric moisture.[7]

C. **Potassium Silanolate Catalyst.**—A modification of the method of Hyde[11] was employed for the preparation of the potassium silanolate catalyst. Anhydrous toluene containing about 33% by weight of hexamethylcyclotrisiloxane and about 0.5% by weight of finely powdered reagent grade potassium hydroxide was refluxed under dry nitrogen and the water formed by the reaction of the potassium hydroxide with the siloxane (to form SiOK and SiOH followed by condensation of the silanols) was removed and measured by a Dean–Stark trap. After the theoretical amount of water had been recovered, the solution was refluxed for 10 more hours and no further water was formed. The total reflux time was 24 hours. The toluene solution then consisted of a solution of $KO[(CH_3)_2SiO]_xK$. This material was analyzed by conventional acid–base titration in a manner similar to that employed for the suspensions of potassium hydroxide in I. In order to prepare a solution for a polymerization experiment, a suitable amount of the toluene solution of the silanolate was introduced into the polymerization bulb and pumped for 24 hours in high vacuum to remove all the toluene leaving behind the oily silanolate. More I was then added and the polymerization experiment carried out in the

---

(4) S. W. Kantor, W. T. Grubb and R. C. Osthoff, This Journal, **76**, 5190 (1954).

(5) W. I. Patnode and D. F. Wilcock, *ibid.*, **68**, 358 (1946).

(6) R. C. Osthoff and W. T. Grubb, *ibid.*, **76**, 399 (1954).

(7) W. T. Grubb, *ibid.*, **76**, 3408 (1954).

(8) M. L. Corrin, private communication, 1953.

(9) J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, New York, N. Y., 1948, p. 259.

(10) H. Gilman and L. S. Miller, This Journal, **73**, 2367 (1951).

(11) J. F. Hyde, U. S. Patent 2,567,110 (Sept. 4, 1951).

same manner described for the experiments using potassium hydroxide.

D. Preparation of Solvents for Use.—Baker and Adamson C.P. toluene was dried over calcium hydride and distilled. Baker and Adamson C.P. methanol was used without further treatment.

Determination of the Rate of Disappearance of I by Distillation.—I was polymerized for various times and the unchanged I was recovered by distillation. In these experiments, about 150 ml. of the I-potassium hydroxide suspension of 0.01% base concentration was prepared in the usual fashion (*vide supra*) and placed in a 180-ml. seal-off bulb. The suspension was then thoroughly out-gassed[12] and the bulb was sealed under high vacuum. These bulbs were then placed in a silicone oil-bath at 140.0 ± 0.1° for various times. The bulbs were removed from the bath at the appropriate times and quenched in an ice-bath and then a liquid nitrogen bath to stop the polymerization reaction. The bulbs were then opened and 0.5 g. of powdered iodine was added to neutralize the potassium hydroxide catalyst.[13] A known weight of the partially polymerized I was then added to a given amount of decamethyltetrasiloxane MD_2M, ($M = [(CH_3)_3SiO_{1/2}]-$ and $D = -[(CH_3)_2SiO]-$. The purification of MD_2M has been described previously[3]) and the mixture was set aside until a homogeneous solution was obtained. At this time about 1 g. of powdered silver was added to the solution to react with the excess iodine present. This heterogeneous reaction of iodine and silver required about two weeks at room temperature. After the solutions had become colorless, I was determined by quantitative distillation techniques. The amount of I which had reacted was then evaluated by calculation.

In general, about 140 g. of the partially polymerized I was added to the MD_2M. However, the amount of MD_2M was increased as the polymerization time was lengthened from 7.5 to 90 minutes in order to maintain a sufficiently low viscosity for the distillation sample. For example, the amount of MD_2M employed was increased from 100 to 700 g. as the polymerization time was increased from 7.5 to 90 minutes. The MD_2M functioned not solely as a solvent, but also as a "chaser" for the distillation of I.[14]

In order to determine an estimate of the accuracy with which a quantitative distillation of this type could be carried out a solution consisting of 50.0% by weight of I and 50.0% by weight of neutral polydimethylsiloxane was prepared. About 140 g. of the 50-50 solution was added to an approximately equal weight of MD_2M. The solution was treated with iodine and silver powder as described previously. Upon distillation, the I concentration in the original solution was determined to be 50.2% by weight (made up to 50.0%). Thus, the accuracy of this type of determination was considered to be sufficient for the authors' purposes.

This procedure was applied to a series of runs with I containing 0.01% of potassium hydroxide. The bulbs used in these experiments were subjected to mechanical agitation during the entire period of time that they were in the bath, in order to aid in the attainment of thermal equilibrium. The amounts of I which were consumed after various polymerization times, as determined by distillation, are recorded in Table II.

TABLE II

RATE OF DISAPPEARANCE OF OCTAMETHYLCYCLOTETRASILOXANE AT 140° WITH 0.01% POTASSIUM HYDROXIDE

Polymerization time (min.)	% Tetramer consumed (wt.)	Polymerization time (min.)	% Tetramer consumed (wt.)
7.5	0	45	56.2
15	11.4	75	84.4
22.5	19.0	90	84.8
30	33.1	1080	94.9
35	41.0		

The equilibrium amount of I is about 5% by weight under the conditions of the experiment.

An examination of the data of Table II indicates that tetramer consumption does not begin until *ca.* 10 minutes after immersion in the 140° bath. This was at least in part due to the time delay in reaching temperature. To determine the time–temperature relationship, a single junction copper–constantan thermocouple was placed in the center of a polymerization bulb containing 150 ml. of I at 25°. The thermocouple leads were attached to a Leeds and Northrup recording potentiometer, and the bulb was immersed in the bath. The center of the bulb reached 132° after 10 minutes, and the final temperature of 140° was obtained after a total time of 20–25 minutes in the bath. Thus, some of the reaction occurred at the lower temperatures present during the early stages.

The Determination of the Rate of Polymer Formation by Precipitation Experiments.—Another approach to the kinetic study of the polymerization of I was the precipitation of the polymer after various polymerization times and the determination of the amount of high molecular weight material. In carrying out such a study, the same general procedure was used as in the case of the distillation experiments described above. However, when the partially polymerized I from the 140° bath had been quenched and treated with iodine, the material was dissolved in anhydrous toluene rather than in MD_2M. The amount of toluene was increased with increasing polymerization times in order that the final solution would contain between 10 and 20% by weight of polymeric material. Once a homogeneous solution was obtained, about one gram of powdered silver was added to destroy the excess iodine. The solution was then suction filtered with *ca.* 5% of Johns–Manville Co. Celite 270. The polymer was obtained by precipitation with a large excess of C.P. methanol. After the polymer had settled, it was washed five times with methanol and placed in a vacuum desiccator. The polymer was then pumped until the pressure over the gum was reduced to less than 50 μ Hg and to constant weight. At this point, the amount of gum was determined.

A check determination was carried out upon a solution consisting of a synthetic mixture of 50.0% by weight of washed gum and 50.0% by weight of I. When the procedure outlined above was followed, precipitation led to a value of 50.2% of polymer in excellent agreement with the original composition.

A large series of runs of various times of polymerization were carried out and the amount of polymer determined. These data are summarized in Table III in which the polymerization time and the percentage of polymer are presented.

TABLE III

RATE OF FORMATION OF POLYMER AS A FUNCTION OF POLYMERIZATION TIME WITH 0.01% POTASSIUM HYDROXIDE AT 140°

Polymerization time (min.)	% Polymer	Polymerization time (min.)	% Polymer
7.5	0	45	42.2
15	*ca.* 1	60	63.2
22.5	10.3	60	62.2
22.5	13.3	90	74.5
30	23.0	90	79.4
30	24.0	90	76.8
45	43.2	1380	84.6
45	45.5		

It will be seen that the same general type of curve was obtained as in the case of the distillation experiments, including the time delay. However, the precipitated polymer is generally somewhat less than the amount of I which has been consumed. This is indicative of incomplete precipitation which may be due to the presence of intermediate molecular weight fractions. Other independent experiments have shown that all molecular weights down to *ca.* 10,000 are precipitated under the conditions of these experiments (this molecular weight corresponds to about 14 $[(CH_3)_2SiO]$ units).

Determination of the Rate of Polymer Formation by Vacuum Devolatilization.—An alternate method for the determination of the amount of polymer formed was investigated. This consisted of treating a portion of the partially polymerized I with powdered iodine to destroy the potassium hydroxide. At this point, a small (about 1 g.)

---

(12) W. T. Grubb and R. C. Osthoff, THIS JOURNAL, **75**, 2230 (1953).

(13) R. C. Osthoff, A. M. Bueche and W. T. Grubb, *ibid.*, **76**, 4659 (1954).

(14) E. M. Hadsell, private communication, 1954.

sample of the gum was placed in a high vacuum system and pumped to constant weight (±5 mg.). The results of several experiments of this type are summarized in Table IV.

TABEL IV

AMOUNT OF POLYMER FORMED AT VARIOUS POLYMERIZATION TIMES WITH 0.01 % POTASSIUM HYDROXIDE CATALYST AT 140° (PUMPING RUNS)

Polymerization time (min.)	% Polymer	Polymerization time (min.)	% Polymer
22.5	17.5	70	67.8
30	27.4	80	70.2
45	41.7	90	81.3
45	46.6	1080	87.8
60	61.3		

It is apparent that pumping and precipitation methods give comparable results. However, the distillation experiments indicate that an intermediate molecular weight fraction is formed during the course of the polymerization reaction, as mentioned previously. This fraction must have a much lower vapor pressure than I itself and may well consist of growing polymer chains. The probability of forming cycles in this molecular weight range is low.[15]

Molecular Weight Determinations.—It was of interest to determine the molecular weights of the polymers obtained from the 140° polymerization of tetramer with 0.01% of potassium hydroxide at various extents of polymerization. For this purpose, the decatalyzed samples from the precipitation experiments were employed.

The molecular weights were determined from the intrinsic viscosity in toluene solutions using Barry's equation[16]

$$[\eta] = 2 \times 10^{-4} M_n^{0.66} \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity and M_n is the number average molecular weight. In Table V the number average molecular weights of various samples are tabulated against polymerization time and percentage conversion to polymer.

TABLE V

NUMBER AVERAGE MOLECULAR WEIGHT *vs.* PER CENT. CONVERSION TO POLYMER AND POLYMERIZATION TIME

$Mn \times 10^{-5}$	Polymerization time (min.)	% Conversion[a]	$Mn \times 10^{-5}$	Polymerization time (min.)	% Conversion[a]
1.86	22.5	11.8	8.75	60	62.7
1.75	22.5	11.8	9.20	60	62.7
3.07	30	23.5	10.06	60	62.7
4.33	30	23.5	8.90	70	65[b]
7.59	45	43.6	8.84	90	76.9
5.78	45	43.6			

[a] Mean data of Table IV. [b] Estimated from Table IV.

An examination of Table V indicates that the molecular weight extrapolates to approximately zero at zero per cent. conversion. Also, the molecular weight is roughly proportional to the per cent. conversion to polymer up to about 60%. It is important to the interpretation of the vapor pressure experiments that the polymer molecular weight is high (>10^5) after only 10% conversion.

The Determination of Rates of Polymerization by Vapor Pressure Measurements.—The preceding results have shown that the polymerization of I takes place by the continuous utilization of monomer units and its conversion into relatively high molecular weight polydimethylsiloxane chains. It has been established that these chains have a number average molecular weight of *ca.* 100,000 (330 units of I) after approximately 10% conversion, and that I is the major volatile component in the polymerizing system. Thus, the polymerizing system should obey the thermodynamic equations for solvent–polymer solutions. For instance, Huggins[17,18] has shown that

$$\Delta \bar{F}_0 = RT \left\{ \ln \phi_0 + \left[1 - \frac{1}{m}\right] \phi_p + \mu \phi_p^2 \right\} \qquad (2)$$

where $\Delta \bar{F}_0$ is the partial molal free energy of the solvent, ϕ_0 is the volume fraction of the solvent, ϕ_p is the volume fraction of the polymer, R is the gas constant, T is the absolute temperature, m is the number of elementary units in the polymer, and μ is the polymer–solvent interaction parameter.

If $\Delta \bar{F}_0$ is replaced by $RT \ln P/P_0$ where P is the vapor pressure of the solvent in the solution and P_0 is the vapor pressure of pure solvent at the same temperature, it is evident that by measurements of vapor pressure above a solvent–polymer mixture, one might directly determine ϕ_0, provided the empirical constant μ has been obtained for the system in question. Application of such a method to the polymerization of I is simplified by neglecting the term $1/m$ which becomes negligible above 10% conversion, since m is very large. The constant μ for this system has been previously evaluated by measurements of vapor pressure[5] and has a mean value of 0.28 for the system I polydimethylsiloxane at 140°. However, in this type of system, considerable variation in the value of μ occurs over the range of ϕ_0 from zero to one.[19,20] The experimental ϕ_0 *vs.* P/P_0 points has been used to calculate a table of values of ϕ_0 and $(1 - \phi_0)$ as a function of the relative pressure, P/P_0, see Table VI. The individual values have been interpolated from previous results.[6] Although the values of Table VI have been obtained from experimental data at one temperature, 140.0°, they may be applied over a considerable range of temperatures in the vicinity of 140° because the heat of mixing of polymer and I has been shown to be zero.[6]

TABLE VI

RELATIVE PRESSURES (P/P_0) *vs.* VOLUME FRACTION (ϕ_0) OF I IN POLYMER SOLUTION

(P/P_0)	ϕ_0	$(1 - \phi_0)$	(P/P_0)	ϕ_0	$(1 - \phi_0)$
0.20	0.060	0.940	0.70	0.300	0.700
2	.068	.932	1	.306	.694
4	.075	.925	2	.313	.687
6	.082	.918	3	.320	.680
8	.090	.910	4	.327	.673
0.30	0.096	0.904	5	.335	.665
2	.103	.897	6	.342	.658
4	.111	.889	7	.349	.651
6	.118	.882	8	.356	.644
8	.130	.870	9	.365	.635
0.40	0.140	0.860	0.80	0.373	0.627
2	.150	.850	1	.382	.618
4	.160	.840	2	.391	.609
6	.170	.830	3	.401	.599
8	.180	.820	4	.411	.589
0.50	0.191	0.809	5	.421	.579
2	.200	.800	6	.432	.568
4	.212	.788	7	.445	.555
6	.224	.776	8	.458	.542
8	.234	.766	9	.473	.527
0.60	0.245	0.755	0.90	0.488	0.512
1	.250	.750	1	.507	.493
2	.255	.745	2	.527	.473
3	.260	.740	3	.546	.454
4	.265	.735	4	.572	.428
5	.270	.730	5	.600	.400
6	.275	.725	6	.633	.367
7	.281	.719	7	.675	.325
8	.287	.713	8	.730	.270
9	.293	.707	9	.805	.195
0.70	0.300	0.700	0.995	.850	.150
			0.997	.875	.125

The method of measuring the vapor pressures has been described previously.[6] The modified isoteniscope of Smith

---

(15) D. W. Scott, THIS JOURNAL, **68**, 2294 (1946).

(16) A. J. Barry, *J. App. Phys.*, **17**, 1020 (1946).

(17) M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941).

(18) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

(19) G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, **38**, 147 (1942).

(20) G. Gee and W. J. C. Orr, *ibid.*, **42**, 507 (1946).

and Menzies[21,22] was further modified by the use of a larger bulb to accommodate the vapor pressure sample (*ca.* 70 ml. total volume). An approximately 35-ml. sample of I plus 0.01% potassium hydroxide was introduced through a constricted side arm into the bulb using a hypodermic syringe. After the isoteniscope was sealed at the constriction, the sample was thoroughly out-gassed and the mercury was then tipped into the "U" section to form a differential manometer. The vapor pressures were then measured in the conventional fashion. The bulb and differential manometer sections of the isoteniscope were maintained at temperature by immersing them in a silicone oil thermostat (±0.1°).

A typical experiment will be described in detail. Figure 1 presents a plot of P (the measured vapor pressure) as a function of time above a solution of 0.01% potassium hydroxide in I at 152.6 ± 0.1° for experiment No. VT-20. An inverted S-shaped curve was obtained. The final pressure reading corresponds to an equilibrium state. In order to demonstrate this more directly, the polymerized I was cooled to room temperature and pumped out thoroughly on a high vacuum system in order to remove all the volatile materials. The system was then returned to the high temperature thermostat and the pressure gradually rose to values very near the final pressure in the original polymerization experiment. In general, the final pressure represented about 0.06 to 0.07 volume fraction of I at all temperatures (see below for the method calculating volume fraction of I from relative pressure reading).

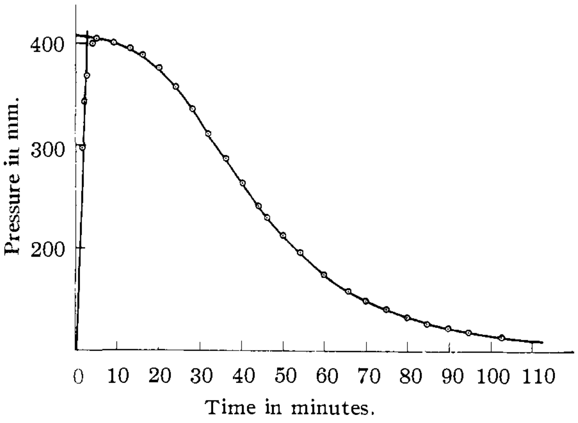


Fig. 1.—Vapor pressure (mm.) as a function of polymerization time, at 152.6°, 0.01% potassium hydroxide.

The vapor pressure of the system decreased from a maximum value close to the vapor pressure of I itself (vapor pressure of I at 152.6° = 407.0 mm.).[6] Since P_0 appears in all calculations, its exact evaluation assumed considerable importance. Fortunately, a good linear extrapolation was obtained by plotting pressure against the square of the time. This plot was linear over the initial 15-minute interval in experiment VT-20. Zero time has been arbitrarily set at the time of immersion of the isoteniscope into the thermostat. Approximate pressure readings on the initial rising part of the curve (Fig. 1) are roughly linear. The steep line when extended intersects the P *vs.* the square of the time line at about 2.7 minutes in experiment No. VT-20. The authors have arbitrarily taken one-half of this time interval as the zero time correction. Thus, P_0 was obtained from the value of the pressure at about 1.3 minutes on the linear pressure *vs.* the square of the time.

The value of P_0 calculated in this way is then used to obtain P/P_0 and $(1 - \phi_0)$ by the use of Table VI. A typical plot of $(1 - \phi_0)$ *vs.* time is presented in Fig. 2. It is very evident that the accuracy of determining $(1 - \phi_0)$ is quite poor at low conversions.

Fortunately, the dependence of ϕ_0 as determined by measurements of vapor pressure upon time follows a simple rate expression derived as follows.

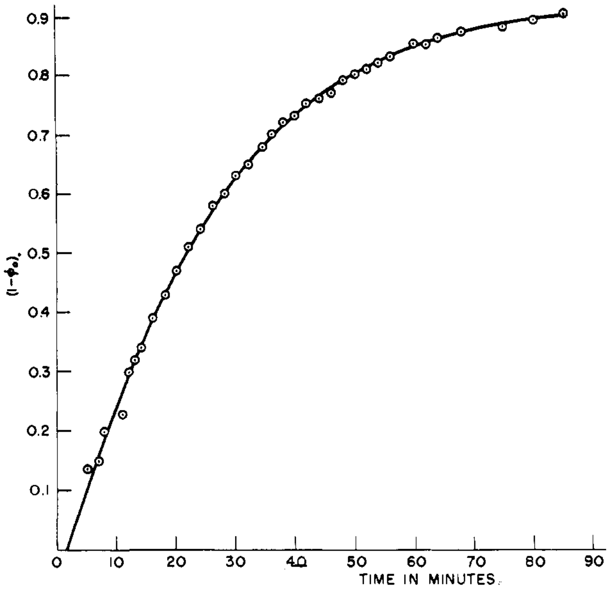


Fig. 2.—Volume fraction of polymer $(1 - \phi_0)$ as a function of time at 152.6°, 0.01% potassium hydroxide.

If I polymerizes at a rate proportional to its volume fraction

$$\frac{d\phi_0'}{dt} = -k\phi_0 \qquad (3)$$

where ϕ'_0 is the apparent volume fraction of I at time t determined by the polymerization reaction alone and also I is reformed at a rate proportional to the volume fraction of polymer.

$$\frac{d\phi_0''}{dt} = +k'(1 - \phi_0) \qquad (4)$$

where ϕ_0'' is the apparent volume fraction of I at time t determined by the depolymerization reaction alone. Combining equations 3 and 4, the net rate of reaction of I becomes

$$\frac{d\phi_0}{dt} = -k\phi_0 + k'(1 - \phi_0) \qquad (5)$$

where $\phi_0 = \phi'_0 + \phi''_0$. It is apparent that at equilibrium, when $\phi_0 = 0.06$, $d\phi_0/dt = 0$, and hence $k'/k = 0.06$. The rate equation in its integrated form then becomes

$$\ln[\phi_0 - 0.06(1 - \phi_0)] = -kt \qquad (6)$$

A plot of log $[\phi_0 - 0.06(1 - \phi_0)]$ *vs.* time for the data of experiment No. VT-20 is shown in Fig. 3. A linear relation is found to exist at least up to 80% conversion of I and this substantiates the postulated rate expression. The constant k is expected to vary as temperature, catalyst and catalyst concentration are varied, and this presents a convenient measure of the rate of polymerization of I under a variety of conditions. The rate constant of k has been evaluated by plotting equation 6, above, from the experimental results and determining the slope graphically. Equation 6 always gave good straight lines such that determination of k was a simple matter. (It was of course necessary to convert the slope determined with common logarithms to that value of k appropriate to equation 6 in terms of natural logarithms.)

Results

The Effect of Temperature upon the Rate of Polymerization.—The system I plus 0.01% KOH reacted at various temperatures and the k of equation 6 was evaluated using the methods described above. The temperature dependence of k was then used to evaluate the over-all activation energy for the polymerization reaction. The val-

---

[21] A. Smith and A. W. C. Menzies, THIS JOURNAL, **32**, 1412 (1910).

[22] H. S. Booth and H. S. Halbedel, *ibid.*, **68**, 2652 (1946).

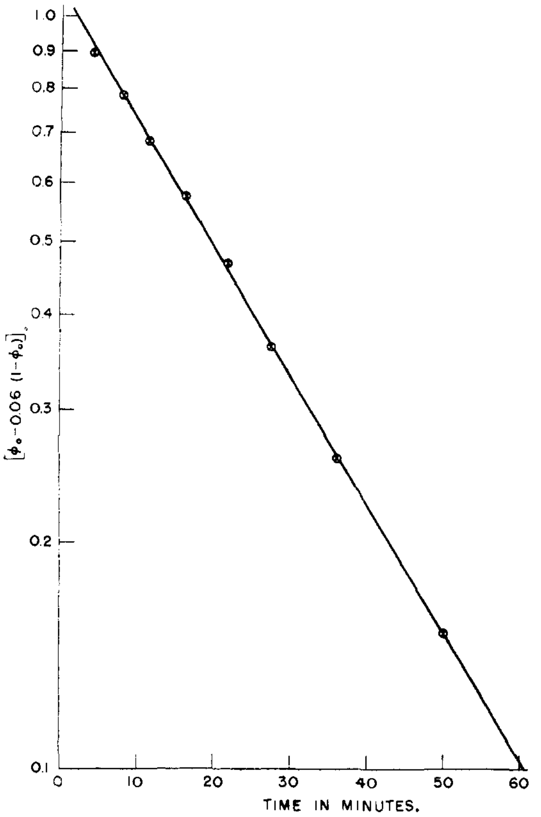


Fig. 3.—Log [ϕ_0 − 0.06 (1 − ϕ_0)] as a function of time of polymerization at 152.6°, 0.01% potassium hydroxide.

ues of k at various temperatures are presented in Table VII.

Table VII

The Rate Constant, k, at Various Temperatures

Temp., °C.	k (min.$^{-1}$)	Temp., °C.	k (min.$^{-1}$)
163	0.065	140.0	0.017
162	.059	140.0	.021
152.6	.041	123.6	.0076
152.6	.039	123.6	.0072
140.0	.019		

The relation between k and temperature is found by the method of least squares to be

$$\log k = 8.3042 - \frac{4291.1}{T} \qquad (7)$$

where T is the absolute temperature. From this equation, the over-all activation energy of the polymerization reaction is found to be 19.6 ± 1.0 kcal. mole^{-1}. The experimental values of k and a plot of equation 7 are presented in Fig. 4.

The Variation of the Polymerization Rate with Catalyst Concentration.—The temperature dependence of the rate of the polymerization reaction was determined at a single potassium hydroxide concentration, 0.01% by weight (1.78 × 10^{-3} molal). It was of considerable interest to determine the effect of catalyst concentration upon the rate at a single temperature. The temperature 152.6° was convenient for these measurements.

The rate constant, k was determined by means of equation 6. This quantity increased in a regular manner with increasing concentration of catalyst, but was not directly proportional to the catalyst concentration. The values of k at various potassium hydroxide concentrations are presented in Table VIII. It is observed that k is proportional to the square root of the catalyst concentration (Fig. 5). Furthermore, the best straight line through the experimental values of k passes through the origin, indicating that no polymerization takes place at 152.6° in the absence of a catalyst. In order to confirm this prediction, a separate experiment was carried out in which I was heated to 152.6 for 24 hours. During this time, no change in the vapor pressure of the system was observed.

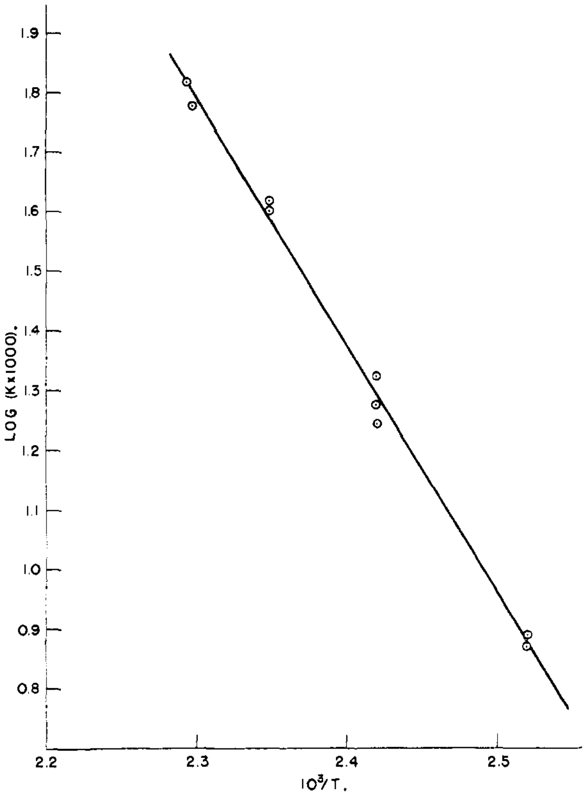


Fig. 4.—Activation energy plot for the polymerization of octamethylcyclotetrasiloxane (I) with 0.01% potassium hydroxide.

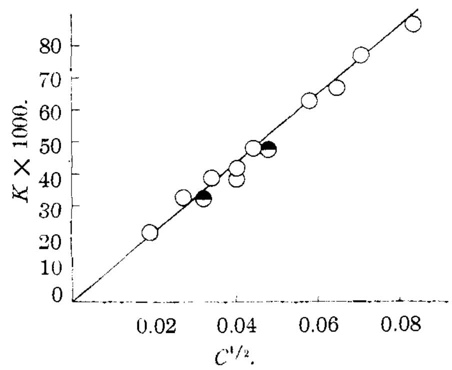


Fig. 5.—The polymerization rate constant k, *vs.* the square root of the molal catalyst concentration: ○, potassium hydroxide; ◓, potassium silanolate.

TABLE VIII

THE RATE CONSTANT, k, AS A FUNCTION OF THE CATALYST CONCENTRATION

Rate constant	Potassium hydroxide concn.		
k (min.$^{-1}$)	In weight, %	Molal, c	$c^{1/2}$
0.021	0.0022	0.39×10^{-3}	1.98×10^{-2}
.032	.0044	0.78×10^{-3}	2.8×10^{-2}
.038	.0071	1.26×10^{-3}	3.5×10^{-2}
.041	.010	1.78×10^{-3}	4.2×10^{-2}
.039	.010	1.78×10^{-3}	4.2×10^{-2}
.047	.013	2.3×10^{-3}	4.8×10^{-2}
.0625	.021	3.7×10^{-3}	6.1×10^{-2}
.066	.026	4.6×10^{-3}	6.8×10^{-2}
.076	.031	5.5×10^{-3}	7.4×10^{-2}
.086	.043	7.65×10^{-3}	8.7×10^{-2}

It was of interest to determine the rate of the polymerization using a potassium silanolate salt as the catalyst. The rate constant at two concentrations of potassium silanolate are shown in the plot of Fig. 5 as half shaded circles. It is apparent that the rate is approximately the same whether potassium hydroxide or the silanolate salt is the catalyst.

Discussion

The results just presented strongly indicate that potassium hydroxide reacts with siloxane bonds to form potassium silanolate groups as

$$\mathrm{KOH} + -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}\overset{|}{\underset{|}{\mathrm{Si}}}- \rightleftharpoons -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OK} + -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OH}$$

The near equivalence of potassium hydroxide and potassium silanolate as catalysts indicate that the above reaction is strongly shifted to the right. It will be observed that starting with the silanolate salt, the reverse of the above reaction cannot proceed if water is not present (to react either directly with the silanolate or to form silanols by reaction with siloxane bonds). Assuming that silanolate is formed essentially quantitatively when potassium hydroxide is added to a siloxane at high temperatures, the following mechanism explains the square root dependence of the rate constant upon the catalyst concentration. Assume that the potassium silanolate is partially ionized to form silanolate anions, which are the active polymerization species. This leads to the equilibrium

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OK} \rightleftharpoons -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}^- + \mathrm{K}^+$$

$$K_e = \frac{\left[-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}^-\right][\mathrm{K}^+]}{\left[-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OK}\right]} = \frac{\left[-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}^-\right]^2}{\left[-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OK}\right]}$$

where K_e is undoubtedly very small in the non-polar siloxane medium. We may therefore write

$$\left[-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}^-\right] = \sqrt{K_e\left[-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OK}\right]} = \sqrt{K_e[\mathrm{KOH}]_{\mathrm{added}}}$$

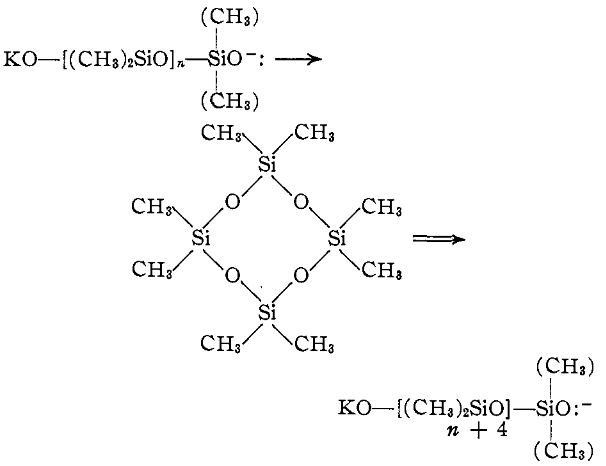
and the rate constant

$$k = A\sqrt{[\mathrm{KOH}]_{\mathrm{added}}} \qquad (8)$$

where A may be a function of the temperature and of other conditions. The value of 19.6 kcal./mole found for the over-all activation energy thus contains the temperature dependence of A in equation 7 and is not a true activation energy.

Previous work[2] has shown that the order of reactivity of alkali metal hydroxides as catalysts for the polymerization of I increases in the order potassium, rubidium, cesium hydroxide. The present results suggests that this represents the order of increasing ionization of the corresponding silanolate salts in a siloxane medium. In general, the addition of polar solvents to increase this ionization should result in more rapid polymerization rates.

Previous results have shown that the reaction of organosilicon molecules with electron donors probably takes place by means of a coördinate bond to the silicon atom in the transition state.[4,7] Thus the propagation step in the polymerization of I may be represented as



The growth of a chain might be halted by a deionization of the silanolate ion (reaction with a potassium ion) or reinitiated by the reionization of the potassium silanolate. In this manner the polymerization continues until an equilibrium concentration of about 6% by volume of I is present. This value for the equilibrium concentration of tetramer agrees well with that calculated from semi-theoretical considerations by Scott.[15]

Acknowledgment.—The authors are indebted to Dr. F. R. Mayo for several helpful discussions during the course of this investigation, and special thanks are due to E. M. Hadsell of this Laboratory for carrying out the many analytical distillations.

SCHENECTADY, N. Y.