361. *The Acid-catalysed Polymerisation of Cyclosiloxanes. Part I. The Kinetics of the Polymerisation of Octamethylcyclotetrasiloxane Catalysed by Anhydrous Ferric Chloride–Hydrogen Chloride*

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The polymerisation of octamethylcyclotetrasiloxane catalysed by anhydrous ferric chloride–hydrogen chloride has been studied dilatometrically. The active iron species is hydrogen tetrachloroferrate(III), and no polymerisation occurs in the absence of either the hydrogen chloride or the ferric chloride. The rate of polymerisation is first-order in octamethylcyclotetrasiloxane, but exhibits a changing order in both ferric chloride and hydrogen chloride. At low hydrogen chloride concentrations the predominant termination reaction is a degradative transfer to siloxane, and it is proposed that this reaction takes place by silicon–methyl cleavage. The propagation step is thought to involve the rearrangement of a tertiary oxonium ion to a transient siliconium ion, the tertiary oxonium ion being formed by a three-stage initiation process, the rate of which is independent of octamethylcyclotetrasiloxane concentration.

OCTAMETHYLCYCLOTETRASILOXANE can be polymerised with acidic or basic catalysts to form high-molecular-weight polysiloxanes. The base-catalysed polymerisation proceeds by growth from a silanolate anion,[1] but the nature of the active centre in the acid-catalysed polymerisation is more obscure. Acids such as concentrated sulphuric acid,[2] acid-activated clay,[3] anhydrous hydrogen chloride,[2a,4] and certain Lewis acids, *e.g.*, antimony pentachloride,[2a] stannic chloride,[5] and ferric chloride,[6] are reported to be catalysts for the polymerisation of octamethylcyclotetrasiloxane. Kinetic investigations have been confined to the polymerisation of octamethylcyclotetrasiloxane catalysed by concentrated sulphuric acid,[7] and ferric chloride,[8] and for the former catalyst, it has been established that polymerisation proceeds by addition of octamethylcyclotetrasiloxane units to an active chain-end, but the nature of the chain-end is uncertain.

In this Paper the kinetics of the polymerisation of octamethylcyclotetrasiloxane catalysed by anhydrous ferric chloride–hydrogen chloride are reported.

EXPERIMENTAL

The polymerisation of octamethylcyclotetrasiloxane is accompanied by an appreciable volume contraction, and has a measurable rate at room temperature. Hence, the reaction is conveniently followed dilatometrically. Because the polymerisation mixture is sensitive to trace impurities, particularly water, a high-vacuum technique, combined with rigorous purification of solvents, etc., was employed. Under these conditions a mixed nitrobenzene–toluene solvent was used in order to dissolve the ferric chloride. It was observed that anhydrous ferric chloride in nitrobenzene–toluene–dimethylsiloxane is light-sensitive (cf. Elliot and Boldebuck [9]). Storage vessels, dilatometer bulbs, etc., were therefore painted black, and manipulations were carried out in semi-darkness.

Materials.—AnalaR toluene was washed twice with 10% of its volume of concentrated

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[1] W. T. Grubb and R. C. Osthoff, *J. Amer. Chem. Soc.*, 1955, **77**, 1405.

[2] (*a*) D. W. Scott, *J. Amer. Chem. Soc.*, 1946, **68**, 2294; (*b*) W. Patnode and D. F. Wilcock, *ibid.*, p. 358; (*c*) D. T. Hurd, *ibid.*, 1955, **77**, 2998.

[3] S. Ishizuka and T. Aihara, *J. Chem. Soc. Japan*, 1956, **59**, 1198.

[4] H. Bentkowska, *Roczniki Chem.*, 1963, **37**, 717.

[5] K. A. Andrianov and S. E. Yakushkina, *Vysokomol. Soedineniya*, 1960, **2**, 1508.

[6] B.P. 594,481; B.P. 658,640.

[7] (*a*) K. Kojima, N. Tarumi, and S. Wakatuki, *Nippon Kagaku Zasshi*, 1955, **76**, 1205 (*Chem. Abs.*, 1957, **51**, 17369); (*b*) D. P. Shine, Ph.D. Thesis, University of Akron, Akron, Ohio, 1961; (*c*) T. P. Hankerd, Masters' Thesis, University of Akron, Akron, Ohio, 1957.

[8] F. M. Johnson, Masters' Thesis, University of Akron, Akron, Ohio, 1957.

[9] J. E. Elliot and E. M. Boldebuck, *J. Amer. Chem. Soc.*, 1952, **74**, 1853.

sulphuric acid, then with aqueous sodium carbonate, and finally with water. The toluene was dried over anhydrous calcium chloride, and distilled from sodium through a 2 ft. Vigreaux column. The middle fraction, which was collected over sodium, was further distilled under high vacuum into a receiver containing sodium–potassium alloy.

Octamethylcyclotetrasiloxane, b. p. 175°, obtained by fractionation of mixed cyclic dimethylsiloxanes using a 2 ft. column packed with glass helices, was dried over sodium and distilled under high vacuum into a storage vessel containing sodium–potassium alloy.

AnalaR nitrobenzene was refluxed over phosphorus pentoxide for 18 hr. and fractionated under reduced pressure through a 2 ft. column packed with glass helices, the fraction b. p. 96°/11 mm. being collected over phosphorus pentoxide. The nitrobenzene was further distilled in an all-glass apparatus under high vacuum, and the middle fraction collected.

Hydrogen chloride was generated by the action of AnalaR concentrated sulphuric acid on AnalaR sodium chloride and collected in a liquid-nitrogen trap attached to the high-vacuum line. The non-condensable gases were pumped off and the hydrogen chloride distilled from a trap at −80° into a liquid-nitrogen trap. The cycle was repeated several times. Glass bulbs of known volume, and provided with fragile sealed capillaries, were filled with known pressures of dry hydrogen chloride.

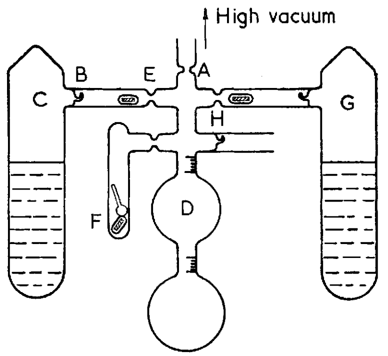

FIGURE 1. Apparatus for preparation of monomer solutions

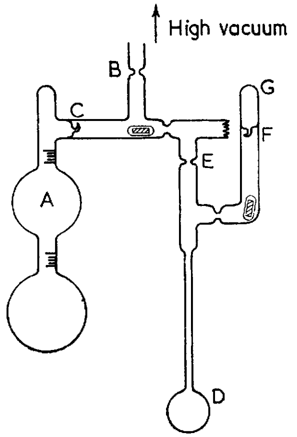

FIGURE 2. Apparatus for dilatometry

Anhydrous ferric chloride was sublimed five times under dry chlorine (dried by bulb-to-bulb distillation from a trap at −60° to one at −195°) at 600 mm. into small glass bulbs provided with fragile sealed capillaries. The chlorine was pumped off, and the bulbs sealed under high vacuum.

Procedure.—A master solution of ferric chloride in nitrobenzene was prepared under high vacuum, and the ferric chloride concentration determined by extracting a known volume of the solution with several portions of aqueous dilute hydrochloric acid, and estimating the iron in the aqueous phase.

Dilatomers were filled by means of the apparatus illustrated in Figures 1 and 2. A solution containing known concentrations of ferric chloride and monomer in toluene was prepared by the following method, using the apparatus illustrated in Figure 1. The apparatus was baked out under high vacuum and sealed at A. The interconnecting capillary seal B was broken and the octamethylcyclotetrasiloxane distilled from C into D to a point on the lower set of graduations. C was removed by sealing at E. Similarly, toluene was distilled from G into D to a point on the upper set of graduations, and G then removed at H. D was painted black and the ferric chloride bulb F broken. The toluene–octamethylcyclotetrasiloxane–ferric chloride solution was mixed, and a final reading of the solution volume taken. Dilatometers were filled by means of the apparatus illustrated in Figure 2. Six dilatometer assemblies (one is shown), were attached to the mixing vessel A, and the apparatus baked out under high vacuum and sealed at B. Capillary seal C was broken, and the solution from A poured into D until the liquid level was approximately half way up the graduated stem. The dilatometer assembly was then removed by sealing at E. Capillary seal F was broken, and hydrogen chloride from bulb G condensed into D using liquid nitrogen. The dilatometer was removed by sealing at the top of the graduated stem and, after painting the bulb D black, the dilatometer was immersed in a thermostat-bath at 30·6° ± 0·01°.

Volume changes in the dilatometer were recorded as a function of time. Plots of $\log_{10}(C_\infty - C_t)$ against t (where C_∞ represents the final contraction and C_t the contraction at time t) are linear signifying that the rate of polymerisation is first-order with respect to octamethylcyclotetrasiloxane. The first-order rate constants were obtained from the slopes of these lines.

Where initial rates are quoted these were obtained from the initial slopes of the contraction (ml. $l.^{-1}$) against time plots. To compute initial rates in mole $l.^{-1}$ $sec.^{-1}$ a value for the contraction (ml. $l.^{-1}$) per mole of octamethylcyclotetrasiloxane was obtained from the values of the equilibrium conversion of octamethylcyclotetrasiloxane into polymer, and the equilibrium contraction, for ten runs.

Solution Viscosity Measurements.—Solution viscosity measurements were carried out on the fully equilibrated polymer. The catalyst was destroyed with anhydrous sodium carbonate, and the excess of carbonate removed by centrifuging. The solvent, and low-molecular-weight cyclics, were removed from the polymer solution by heating the solution to 120° for 48 hr. Solution viscosities were measured in a Ubbelohde viscometer at 25° for four concentrations of the polymer in toluene, such that the relative viscosity at each concentration was less than 2. The intrinsic viscosity $[\eta]$ of the polymer was obtained from the intercept of η_{sp}/C, and $(\log_e \eta_r)/C$, against C plots, where C is the polymer concentration in g./100 ml., and η_{sp} and η_r are the specific and relative viscosities of the solution, respectively. Values of α in the Huggins [10] equation

$$\eta_{sp}/C = [\eta] + \alpha[\eta]^2C$$

and β in the equation of Mead and Fuoss [11]

$$(\log_e \eta_r)/C = [\eta] + \beta[\eta]^2C$$

were obtained from the gradients of these plots. Both intercepts and gradients were determined by least-squares analysis.

RESULTS

Many potential solvents for ferric chloride and high-molecular-weight polysiloxanes inhibit the polymerisation, *e.g.*, when octamethylcyclotetrasiloxane (1·17 mole $l.^{-1}$), ferric chloride ($2·5 \times 10^{-4}$ mole $l.^{-1}$), and hydrogen chloride ($4·9 \times 10^{-3}$ mole $l.^{-1}$), were mixed in anhydrous toluene containing 2% by volume anhydrous diethyl ether, no polymerisation was observed. However, nitrobenzene, in amounts varying from 0·5 to 5% by volume, did not affect the rate of polymerisation in toluene.

When octamethylcyclotetrasiloxane (1·17 mole $l.^{-1}$), and hydrogen chloride ($4·4 \times 10^{-3}$, and $1·06 \times 10^{-1}$ mole $l.^{-1}$) were mixed in toluene containing 5% nitrobenzene under anhydrous conditions, no polymerisation was observed over 8 months. Similarly, mixtures of octamethylcyclotetrasiloxane (1·17 mole $l.^{-1}$) and anhydrous ferric chloride ($1·1 \times 10^{-4}$ mole $l.^{-1}$) in toluene–nitrobenzene did not polymerise over identical periods. However, when the two systems were combined, polymerisation was 50% complete in five days and two days, respectively. Thus, to polymerise octamethylcyclotetrasiloxane at 30°, both ferric chloride and hydrogen chloride are necessary.

For all hydrogen chloride concentrations used in this study the rate of polymerisation is first-order in octamethylcyclotetrasiloxane for 90% of the reaction, *i.e.*,

$$\text{Rate of polymerisation} = k([D_4] - [D_4]_e)$$

where $[D_4]$ represents the octamethylcyclotetrasiloxane concentration and $[D_4]_e$ the total

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[10] M. L. Huggins, *J. Amer. Chem. Soc.*, 1942, **64**, 2716.
[11] D. J. Mead and R. M. Fuoss, *J. Amer. Chem. Soc.*, 1942, **64**, 277.

TABLE 1

Variation of initial rate of polymerisation with initial octamethylcyclotetrasiloxane concentration

[Initial monomer] (mole l.$^{-1}$)	10^4[$FeCl_3$] (mole l.$^{-1}$)	10^3[HCl] (mole l.$^{-1}$)	10^5 Initial rate (mole l.$^{-1}$ sec.$^{-1}$)	10^5 Initial rate/ $D_0 - D_e$ (sec.$^{-1}$)
1·17	1·15	7·5	1·49	2·2
1·99	1·12	7·7	3·12	2·1
1·17	1·15	1·3	0·13	0·20
1·99	1·12	1·28	0·33	0·22
3·18	1·09	1·29	0·55	0·21
1·44	7·1	7·83	39·8	42
2·09	6·7	7·36	66·7	42
3·03	6·3	7·53	106	43
1·24	6·5	19·3	39·7	53
1·44	6·7	20·1	53·0	56
2·16	6·6	18·5	91·0	54

equilibrium cyclosiloxane concentration expressed as a concentration of octamethylcyclotetrasiloxane. The order in octamethylcyclotetrasiloxane obtained from the variation of the initial rate of polymerisation with initial octamethylcyclotetrasiloxane concentration $[D_4]_0$ is also one over a considerable range of hydrogen chloride concentrations (Table 1). However, at low hydrogen chloride concentrations, the first-order rate constant is inversely proportional to the total dimethylsiloxane concentration (Table 2), whilst at high hydrogen chloride concentrations, the rate of polymerisation decreases rapidly with increasing initial octamethylcyclotetrasiloxane concentration (Table 3).

TABLE 2

Variation of the first-order rate constant with total dimethylsiloxane concentration at low hydrogen chloride concentrations

10^4[HCl] (mole l.$^{-1}$)	10^4[$FeCl_3$] (mole l.$^{-1}$)	[Total dimethylsiloxane] (mole l.$^{-1}$)	10^7k (sec.$^{-1}$)	k[Total dimethylsiloxane]/[HCl]^2 (l. mole^{-1} sec.$^{-1}$)
4·37	6·7	2·09	3·8	4·2
4·7	6·5	1·24	7·4	4·1
4·6	6·3	1·44	6·2	4·3
4·14	6·6	2·16	3·4	4·2
4·32	6·3	3·03	2·5	4·0

TABLE 3

Vatiation of the rate of polymerisation with initial octamethylcyclotetrasiloxane concentration at high hydrogen chloride concentrations

10^3[HCl] (mole l.$^{-1}$)	30·5	30·0	64	64	44·7	45·2	46·9
10^4[$FeCl_3$] (mole l.$^{-1}$)	8·2	8·4	6·3	6·6	1·1	1·11	1·1
[Initial monomer] (mole l.$^{-1}$)	3·18	2·03	3·03	2·16	1·16	1·99	3·18
10^6k (sec.$^{-1}$)	10	88	3·3	11·4	3·1	1·04	0·23

The order in ferric chloride has been determined at three hydrogen chloride concentrations, $1·6 \times 10^{-4}$, $4·0 \times 10^{-3}$, and $3·0 \times 10^{-2}$ mole l.$^{-1}$, and order plots are reproduced in Figure 3. The order in ferric chloride changes from 1·1 at [HCl] $1·6 \times 10^{-4}$ mole l.$^{-1}$ to 1·4 at $4·0 \times 10^{-3}$ mole l.$^{-1}$ and eventually to 2·0 at $3·0 \times 10^{-2}$ mole l.$^{-1}$.

The dependence of the first-order rate constant on the hydrogen chloride concentration is shown (Figure 4) for two ferric chloride concentrations. The order in hydrogen chloride, which is 2 at low hydrogen chloride concentrations, changes rapidly to zero at [HCl] $1·2 \times 10^{-2}$ mole l.$^{-1}$. From this point the rate decreases with increasing hydrogen chloride concentration. The position of the maximum in the order plot is independent of the ferric chloride concentration (Figure 4).

The rate of polymerisation has been measured at 30·6, 40·1, and 55·2° for constant initial monomer concentration and ferric chloride concentration, and at [HCl] $3·5 \times 10^{-3}$ and $3·2 \times 10^{-4}$ mole l.$^{-1}$. Plots of $\log_{10}$ (rate constant) against the reciprocal of the absolute temperature are reproduced in Figure 5, the overall activation energies are 5 ± 1 kcal. mole^{-1}, and 8 ± 3 kcal. mole^{-1}, respectively.

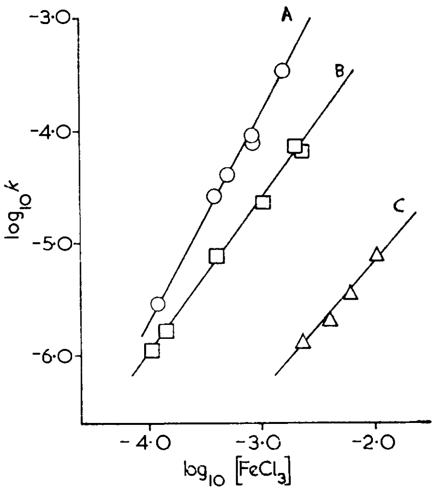

FIGURE 3. Variation of the first-order rate constant with ferric chloride concentration. Curves A and B at 30·1°, curve C at 40·1°. [HCl] A = 3·0 ± 0·1 × 10^{-2} mole $l.^{-1}$ B = 3·9 ± 0·3 × 10^{-3} mole $l.^{-1}$ C = 1·6 ± 0·1 × 10^{-4} mole $l.^{-1}$

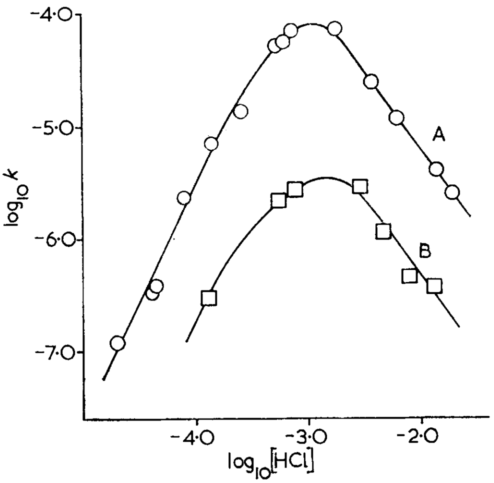

FIGURE 4. Variation of the first-order rate constant with hydrogen chloride concentration at 30·1°. [FeCl$_3$] A = 6·7 × 10^{-4} mole $l.^{-1}$ B = 1·1 × 10^{-4} mole $l.^{-1}$

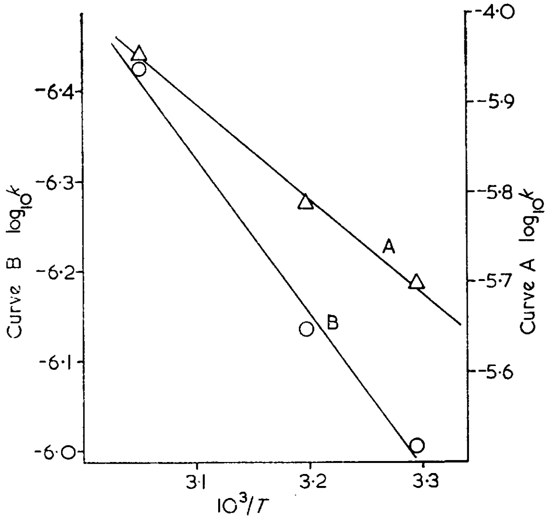

FIGURE 5. Variation of the first-order rate constant with temperature. [HCl] A = 3·5 ± 0·5 × 10^{-3} mole $l.^{-1}$ B = 3·2 ± 0·2 × 10^{-4} mole $l.^{-1}$

TABLE 4

Solution viscosity measurements on the fully equilibrated polymer

[Initial monomer] (mole $l.^{-1}$)	10^4[FeCl$_3$] (mole $l.^{-1}$)	10^4[HCl] (mole $l.^{-1}$)	[η] d. $l.g^{-1}$	α	$-\beta$
2·09	6·7	4·4	1·12	0·41	0·13
1·44	6·5	4·7	1·02	0·40	0·12
1·24	6·3	4·6	0·81	0·39	0·13
Polymer (A)			0·45	0·36	0·14
Polymer (B)			0·33	0·33	0·16
Polymer (C)			1·27	0·35	0·15

Polymer (A) is a commercial polysiloxane of 100,000 cS. bulk viscosity. Polymers (B) and (C) are polysiloxanes prepared by the potassium hydroxide-catalysed polymerization of octamethylcyclotetrasiloxane under controlled conditions.

Data for solution viscosity measurements carried out on the fully equilibrated polymers derived from three runs at low hydrogen chloride concentration are listed in Table 4. The equivalent information for a typical commercial dimethylpolysiloxane, and for polymers prepared by the potassium hydroxide-catalysed polymerisation of octamethylcyclotetrasiloxane, is included for comparison.

DISCUSSION

Any mechanism for the polymerisation must account for the following observations.

(*a*) At low hydrogen chloride concentrations the rate of polymerisation follows the equation

$$\text{Rate} = \frac{k[\text{HCl}]^2[\text{FeCl}_3]([\text{D}_4] - [\text{D}_4]_e)}{[\text{D}_4]_0}$$

(*b*) At intermediate hydrogen chloride concentrations the rate of polymerisation is given by the equation

$$\text{Rate} = k[\text{HCl}]^a[\text{FeCl}_3]^b([\text{D}_4] - [\text{D}_4]_e)$$

the values of a and b being determined by [HCl]. As this is increased up to $1{\cdot}2 \times 10^{-2}$ mole l.^{-1}, a tends to zero and b changes from one to two.

(*c*) At hydrogen chloride concentrations in excess of $1{\cdot}2 \times 10^{-2}$ mole l.^{-1} the rate of polymerisation decreases with increasing hydrogen chloride and octamethylcyclotetrasiloxane concentrations and is second-order with respect to ferric chloride.

The following mechanism for the polymerisation is proposed, where D_4 represents octamethylcyclotetrasiloxane, D_n polymer, and HA hydrogen tetrachloroferrate(III)

Initiation:

$$\text{Fe}_2\text{Cl}_6 + 2\text{HCl} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} 2\text{HA} \qquad (1)$$

$$2\text{HA} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} \text{H}^+(\text{A}{\cdot}\text{HA})^- \qquad (2)$$

$$\text{D}_4 + \text{H}^+(\text{A}{\cdot}\text{HA})^- \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} \text{D}_4\text{H}^+(\text{A}{\cdot}\text{HA})^- \qquad (3)$$

$$\text{D}_4\text{H}^+(\text{A}{\cdot}\text{HA})^- \underset{k_4'}{\overset{k_4}{\rightleftharpoons}} \text{HD}_4^+(\text{A}{\cdot}\text{HA})^- \qquad (4)$$

Propagation:

$$\text{HD}_n^+(\text{A}{\cdot}\text{HA})^- + \text{D}_4 \underset{k_5'}{\overset{k_5}{\rightleftharpoons}} \text{HD}_{(n+4)}^+(\text{A}{\cdot}\text{HA})^- \qquad (5)$$

Termination:

$$\text{HD}_n^+(\text{A}{\cdot}\text{HA})^- + \text{HCl} \xrightarrow{k_6} \text{HD}_n\text{Cl} + \text{H}^+(\text{A}{\cdot}\text{HA})^- \qquad (6)$$

$$\text{HD}_n^+(\text{A}{\cdot}\text{HA}) + \text{H}_2\text{O} \xrightarrow{k_7} \text{HD}_n\text{OH} + \text{H}^+(\text{A}{\cdot}\text{HA})^- \qquad (7)$$

$$\text{HD}_n^+(\text{A}{\cdot}\text{HA})^- \xrightarrow{k_8} \text{HD}_n\text{Cl} + \text{FeCl}_3 + \text{HA} \qquad (8)$$

Transfer:

$$\text{HD}_n^+(\text{A}{\cdot}\text{HA})^- + \text{D}_m \xrightarrow{k_9} \text{HD}_n + \text{D}_m^+(\text{A}{\cdot}\text{HA})^- \qquad (9)$$

From (5), the rate of disappearance of octamethylcyclotetrasiloxane is given by

$$-\text{d}[\text{D}_4]/\text{d}t = k_5[\text{D}_n^+][\text{D}_4] - k_5'[\text{D}_n^+]$$

where $[\text{D}_n^+]$ is the total active centre concentration, and k and k' refer to the forward and reverse reactions, respectively. For large values of n, k_5'/k_5 is equal to the [total equilibrium monomer], *i.e.*, $[D_4]_e$.

Hence
$$-dD_4/dt = k_5[D_n^+]([D_4] - [D_4]_e)$$

Making the assumption that the steady-state concentration of active centres is controlled by reactions k_4, k_6, k_7, k_8, and k_9, and that equilibrium (3) lies well over to the right, then

$$[D_n^+] = k_4K_1K_2[Fe_2Cl_6][HCl]^2/k_8 + k_9[D_4]_0 + k_7[H_2O] + k_6[HCl]$$

where K_1 and K_2 are the equilibrium constants for reactions (1) and (2). The rate of polymerisation now becomes,

$$\frac{-d[D_4]}{dt} = \frac{k_5k_4K_1K_2[FeCl_3][HCl]^2([D_4] - [D_4]_e)}{2(k_8 + k_9[D_4]_0 + k_7[H_2O] + k_6[HCl])}$$

$[D_4]_0$ appears in the denominator of this expression since the transfer reaction (9) involves silicon–carbon cleavage and thus is a function of the total dimethylsiloxane concentration, and not the octamethylcyclotetrasiloxane concentration.

At intermediate hydrogen chloride concentrations the predominant termination reactions are (6) and (9), with (6) becoming more important as [HCl] increases. Thus, the rate of polymerisation becomes

$$\frac{-d[D_4]}{dt} = \frac{k_5k_4K_1K_2[FeCl_3][HCl]^2([D_4] - [D_4]_e)}{2(k_9[D_4]_0 + k_6[HCl])}$$

Departures from simple integral orders for hydrogen chloride and ferric chloride in the observed rate expression may be explained by assuming that equilibrium (1) moves well over to the right as the hydrogen chloride concentration is increased. At [HCl] in excess of $1{\cdot}2 \times 10^{-2}$ mole $l.^{-1}$, the order in ferric chloride is two, signifying that the hydrogen tetrachloroferrate(III) concentration is now equal to the initial ferric chloride concentration. This would require a value for the dissociation constant of hydrogen tetrachloroferrate(III) of from 10^{-3} to 10^{-4} mole $l.^{-1}$. McCusker and Kennard[12] studied the interaction of anhydrous ferric chloride and hydrogen chloride in a series of anhydrous ethers. Their values for the dissociation constant of the complex acid range from 0·14 in dioxan to 1×10^{-4} in di-isopropyl ether, and the authors conclude that differences in the dissociation constant result primarily from differences in solvent–ferric chloride, and solvent–hydrogen chloride, interactions. The value of the dissociation constant in nitrobenzene would be expected to lie somewhere between these values, since the decreased solvent–ferric chloride and solvent–hydrogen chloride interactions would be offset by decreased solvation of the proton from the hydrogen tetrachloroferrate(III).

At low hydrogen chloride concentrations the principal termination reaction (actually a degradative transfer reaction) is k_9, and the corresponding rate expression.

$$\frac{-d[D_4]}{dt} = \frac{k_5k_4K_1K_2}{2k_9[D_4]_0}[FeCl_3][HCl]^2([D_4] - [D_4]_e)$$

Reaction (9) involves silicon–methyl cleavage, a reaction which is known to occur with strong acids,[13] and is thought to proceed by electrophilic attack at carbon. In this system methyl cleavage should give polysiloxanes containing trimethylsilyl chain-ends, together with trifunctional units, and hence chain-branching in the polymer. It has been observed [14,15] that the value of α in the Huggins equation

$$\eta_{sp}/C = [\eta] + \alpha[\eta]^2C$$

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[12] P. A. McCusker and S. M. S. Kennard, *J. Amer. Chem. Soc.*, 1959, **81**, 2976.

[13] C. Eaborn, " Organosilicon Chemistry," Butterworth, London, 1960.

[14] M. Takeda and A. Yamada, *Chem. High Polymers (Japan)*, 1960, **17**, 337.

[15] R. W. Kilb, *J. Phys. Chem.*, 1959, **63**, 1838.

increases as the degree of branching in the polysiloxane increases. Values of α for three runs at low initial hydrogen chloride concentrations are significantly higher than the equivalent values for polymers obtained from other sources, particularly for polymers obtained by the potassium hydroxide-catalysed polymerisation where silicon–methyl cleavage is unlikely to occur.[13] This can be taken as evidence for chain-branching in the polymer, and consequently justifies the assumption of a transfer reaction involving silicon–methyl cleavage.

The end-groups formed in the polymerisation, *viz.*, silanol and silicon–chlorine, are capable of further reaction, *e.g.*,

$$2D_nSiOH \xrightarrow{k_{10}} D_nSi{\cdot}O{\cdot}SiD_n + H_2O \qquad (10)$$

$$D_nSiOH + D_nSiCl \xrightarrow{k_{11}} D_nSi{\cdot}O{\cdot}SiD_n + HCl \qquad (11)$$

$$D_nSiOH + HCl \underset{k_{12}'}{\overset{k_{12}}{\rightleftharpoons}} D_nSiCl + H_2O \qquad (12)$$

where D_n represents a polymeric siloxane residue. Reaction (12) is the fundamental chlorosilane hydrolysis equilibrium and the relative proportions of the end-groups will be determined by the position of this equilibrium. It is obvious that the water concentration will increase with increasing hydrogen chloride concentration, and accordingly, at high hydrogen chloride concentrations, termination reactions such as k_7 will become important. In addition, the presence of water could adversely affect equilibrium (1) because of strong hydrogen chloride–water and ferric chloride–water interactions [the dissociation constant of hydrogen tetrachloroferrate(III) in water[16] is 97]. The variation of $[H_2O]$ with total siloxane concentration is complex, and may explain the unusual inverse variation of rate of polymerisation with initial octamethylcyclotetrasiloxane concentration which has been observed at high values of [HCl].

In order to explain the observed dependence of the rate of polymerisation on [HCl], and $[FeCl_3]$, the hydrogen tetrachloroferrate(III), has been represented as an ion-pair, with the tetrachloroferrate(III) anion solvated by a second molecule of the acid. Similar behaviour, *i.e.*, solvation of the anion by an additional molecule or molecules of the acid, had been observed for sulphuric acid in the aprotic solvents nitromethane[17] and sulpholane.[18] The poorly solvated proton of this ion-pair is extremely active, which in turn suggests that the initiation step involves protonation of the siloxane oxygen. This is supported by the work of Kantor, Grubb, and Osthoff,[19] who found that the order of reactivity of siloxanes to sulphuric acid is $D_3 > MM > MDM > MD_2M > D_4$, where D refers to the difunctional unit Me_2SiO, and M the monofunctional unit Me_3SiO. This is the same order as that found by West and his co-workers[20] for the basicity of oxygen in various siloxanes. Further evidence in support of a protonation step in the initiation is the failure to obtain polymer when anhydrous diethyl ether was used as co-solvent. Diethyl ether is a much stronger Lewis base than octamethylcyclotetrasiloxane,[20] and would compete favourably with the siloxane for the proton of the hydrogen tetrachloroferrate(III). Shine[7b] observed a similar effect in the sulphuric acid-catalysed polymerisation of octamethylcyclotetrasiloxane. He considers that the failure to obtain polymer in dioxan and in tetrahydrofuran is due to the formation of an oxonium salt between the acid and the ether.

This evidence, coupled with the low nucleophilicity of the tetrachloroferrate anion, suggests that the propagation step is also ionic, and involves a tetrachloroferrate anion solvated by a second molecule of the complex acid as in the initiation step. The nature of

[16] G. A. Gamlen and D. O. Jordan, *J.*, 1953, 1435.

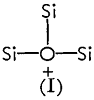
[17] L. P. Hammett and H. Van Looy, *J. Amer. Chem. Soc.*, 1959, **81**, 3872.

[18] E. M. Arnett and C. F. Douty, *J. Amer. Chem. Soc.*, 1964, **86**, 409.

[19] S. W. Kantor, W. T. Grubb, and R. C. Osthoff, *J. Amer. Chem. Soc.*, 1954, **76**, 5190.

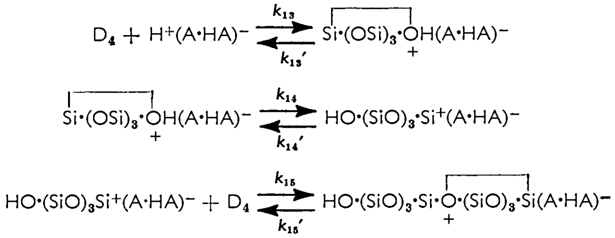
[20] R. West, L. S. Whatley, and K. J. Lake, *J. Amer. Chem. Soc.*, 1961, **83**, 761.

the cation is, however, not as clearly defined. The alternatives are a discrete siliconium ion, or a tertiary oxonium ion, *e.g.*, (I), of the type postulated by Kantor, Grubb, and Osthoff,[19] as the active intermediate in the sulphuric acid-catalysed polymerisation of octamethylcyclotetrasiloxane. It is well established that discrete siliconium ions are not formed under conditions where the analogous carbonium ions exist,[13] hence polymerisation *via* a discrete siliconium ion need not be considered. A mechanism based on a tertiary oxonium ion intermediate satisfies the observed kinetics if the following assumptions are made.



(I)

(*a*) The initiation stage is a three-step process:



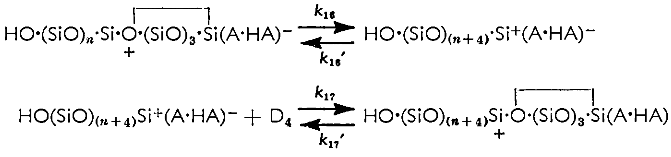
$$\mathrm{D_4 + H^+(A{\cdot}HA)^- \underset{k_{13}'}{\overset{k_{13}}{\rightleftharpoons}} \overline{Si{\cdot}(OSi)_3{\cdot}\underset{+}{O}}H(A{\cdot}HA)^-} \qquad (13)$$

$$\mathrm{\overline{Si{\cdot}(OSi)_3{\cdot}\underset{+}{O}}H(A{\cdot}HA)^- \underset{k_{14}'}{\overset{k_{14}}{\rightleftharpoons}} HO{\cdot}(SiO)_3{\cdot}Si^+(A{\cdot}HA)^-} \qquad (14)$$

$$\mathrm{HO{\cdot}(SiO)_3Si^+(A{\cdot}HA)^- + D_4 \underset{k_{15}'}{\overset{k_{15}}{\rightleftharpoons}} HO{\cdot}(SiO)_3{\cdot}Si{\cdot}\overline{\underset{+}{O}{\cdot}(SiO)_3{\cdot}Si}(A{\cdot}HA)^-} \qquad (15)$$

with the steady-state concentration of tertiary oxonium ions controlled by the balance between reaction k_{14}, and reactions k_6, k_7, k_8, and k_9.

(*b*) The propagation stage is:



$$\mathrm{HO{\cdot}(SiO)_n{\cdot}Si{\cdot}\overline{\underset{+}{O}{\cdot}(SiO)_3{\cdot}Si}(A{\cdot}HA)^- \underset{k_{16}'}{\overset{k_{16}}{\rightleftharpoons}} HO{\cdot}(SiO)_{(n+4)}{\cdot}Si^+(A{\cdot}HA)^-} \qquad (16)$$

$$\mathrm{HO(SiO)_{(n+4)}Si^+(A{\cdot}HA)^- + D_4 \underset{k_{17}'}{\overset{k_{17}}{\rightleftharpoons}} HO{\cdot}(SiO)_{(n+4)}Si{\cdot}\overline{\underset{+}{O}{\cdot}(SiO)_3{\cdot}Si}(A{\cdot}HA)^-} \qquad (17)$$

(The two methyl groups attached to each silicon atom have been omitted from the above scheme.)

There is no evidence to distinguish between the alternatives of growth from a transient siliconium ion as represented above, or a tertiary oxonium ion, since both satisfy the kinetics equally well. However, addition of octamethylcyclotetrasiloxane units to a siliconium ion gives a clearer interpretation of the transfer reaction (9), involving methyl cleavage.

A number of conclusions can be drawn from this work which appear to be general for the polymerisation of siloxanes catalysed by Brönsted acids. The rate-determining step in the initiation process is the rearrangement of a protonated siloxane, and in order to form this intermediate, the basicity of the solvent should not exceed that of the siloxane. Under these conditions a further molecule, or molecules, of the acid may be necessary to solvate the anion. In cases where other termination reactions are absent, silicon–carbon cleavage could be an important growth-limiting process in the polymerisation of cyclic siloxanes.

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