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Bifunctional catalysis in the condensation of silanols and alkoxysilanes *

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Abstract

The condensation reaction of a model silanol, nonamethyltetrasiloxane-1-ol, with methyltrimethoxysilane to form 1,1-dimethoxydecamethylpentasiloxane was studied. Various catalysts were used to study the rate of the condensation. A reactivity order of $CCl_3COOH > Et_2NOH > CH_3COOH >$ MeEtC=NOH $\gg Et_3N$ was observed for the catalysis. Formation of a transition state from slow protonation of the alkoxysilane by catalyst followed by its condensation with the silanol is deemed insufficient to explain the catalysis. Reaction of catalyst with the alkoxysilane to form an intermediate followed by silanol condensation with this intermediate is also considered and cannot be ruled out. Rate considerations, however, favors a cyclic transition state where bifunctional catalysis is invoked. With the slow triethylamine catalysis, still another mechanism is needed. A transition state where the amine is acting as a base in assisting the dissociation of the proton on the silanol is suggested.

Introduction

The condensation reaction of silanol terminated siloxanes with alkoxysilanes is a very important industrial process in the manufacture of room temperature vulcanizing sealants [1–3]. The reaction has also been of interest to polymer chemists in providing a model elastomeric network [4–8] for their theoretical studies.

Although the reaction has been used extensively in both industry and academia, surprisingly little is known about the mechanism of the reaction. The difficulty in analyzing the endgroups of the polydimethylsiloxanes (PDMS) has certainly contributed to the lack of understanding of this reaction. In his study of the silanol condensation reaction in methyl alcohol, Grubb [9] proposed that the reaction, in the acidic media, proceeded via the protonation of the alkoxysilane to form a protonated alkoxysilane transition state. Condensation of silanol with the protonated alkoxysilane can then take place to complete the reaction. In base catalysis, nucleophilic displacement of the alkoxy group by silanolate ion was considered to

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be the mechanism for the reaction. However, only very strong acid (HCl) and bases (KOH, NaOH) were used in his study, and trimethylsilanol was exclusively used for the condensation reaction. Neither conditions bear much resemblance to the endcapping reactions of silanol terminated polydimethylsiloxanes with alkoxysilanes where acetic acid, triethylamine, tin and titanate esters and a number of other catalysts are more often used.

Our interests in understanding the endcapping of silanol terminated polydimethylsiloxanes with alkoxysilane crosslinkers during the manufacture of sealant and in understanding its subsequent hydrolysis and curing led us to the present investigations. We chose to use a model silanol oligomer, nonamethyltetrasiloxane-1-ol (**I**) to simulate the silanol terminated polydimethylsiloxanes. The silanol group of the model oligomer is situated in an environment virtually identical to that of the silanol terminated polydimethylsiloxanes. The model oligomer and its reaction product can be conveniently analyzed by GC, thus allowing easy monitoring of the reaction. To fully simulate the environment of PDMS, octamethyltrisiloxane was further used as the solvent during the reaction.

Results and discussion

Effect of alkoxysilanes

We initially compared the reactivities of alkoxysilanes $Me_nSi(OMe)_{4-n}$ ($n = 0$–3) with the model silanol as shown below:

$$\underset{\textbf{(I)}}{Me_3Si(OMe_2Si)_3OH} + \underset{\textbf{(II)}}{Me_nSi(OMe)_{4-n}} \xrightarrow{\text{catalyst}}$$

$$\underset{\textbf{(III)}}{Me_3Si(OMe_2Si)_3OSiMe_n(OMe)_{3-n}} + MeOH \qquad (1)$$

In a typical reaction, with 0.1 *M* silanol **I**, 0.15 *M* $Me_nSi(OMe)_{4-n}$ and with 0.3% (weight) acetic acid used as catalyst, tetramethoxysilane (**II**, $n = 0$) gave complete reaction in less than 2 h at room temperature. Reaction with methyltrimethoxysilane (**II**, $n = 1$) was considerably slower. The reaction was complete only after standing overnight and with considerable side reactions taking place. Notable side reactions include further reaction between **I** and **III** as well as possible redistribution reactions of **I** or **III**. With dimethyldimethoxysilane (**II**, $n = 2$) the endcapping reaction was very slow. With trimethylmethoxysilane (**II**, $n = 3$) no desired reaction was observed within a reasonable time frame (a few days).

The above results point to the electrophilic nature of the alkoxysilanes during condensation reactions. It can be rationalized that if the transition state involves an incoming nucleophile with its charge stabilized by the alkoxy ligands of the silane, more alkoxy groups on silicon tend to stabilize the transition state better and thus result in higher rates. A similar trend has also been observed in the base cleavage of the alkoxysilanes [10].

Effect of catalysts

After the initial studies, we then concentrated on reactions between the model silanol **I** and methyltrimethoxysilane **II** ($n = 1$) using various catalysts. Reaction

Table 1

Approximate relative rates of various catalysts in the condensation of $Me_3Si(OSiMe_2)_3OH + MeSi(OMe)_3 \longrightarrow Me_3Si(OSiMe_2)_3OSiMe(OMe)_2 + MeOH$

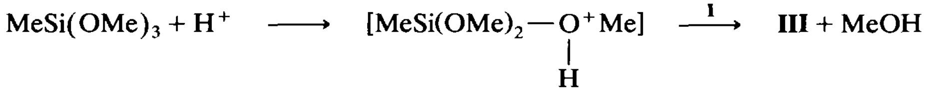
Catalyst	Relative rate [a]
Trichloroacetic acid	500
Dichloroacetic acid	40
Diethylhydroxylamine	20
Acetic acid-triethylamine	10
Chloroacetic acid	5
Acetic acid	1
t-Butylacetic acid	1
Bis(ethoxyacetylacetonate)di-isopropyl titanate	0.5
Methylethylketoxime	0.3
3-Hydroxypyridine [b]	0.2
2-Hydroxypyridine [b]	0.1
Triethylamine	0.03
Diethylethanolamine	0.03
Trichloroacetic acid-triethylamine	0.02
Pyridine	0
2,4-Pentadione	0
N-Methyl-2-pyridone	0
2-Methoxypyridine	0

[a] Reactions were performed in octamethyltrisiloxane solution with 0.1 *M* (**I**), 0.15 *M* (**II**) and 0.3% (by weight) of catalyst. The reactions were performed at 25–70°C depending on the catalysts chosen. The time required for 50% consumption of **I** using a certain catalyst was compared with that of using acetic acid. The relative rates represent the best estimate of the activities of the various catalysts. [b] Catalysts were insoluble in octamethyltrisiloxane. Reactions were performed in toluene instead.

rates were determined by monitoring both the disappearance of the silanol **I** and the formation of the product **III** ($n = 1$) on a gas chromatograph. During the initial stage, up to approximately 50% of the reaction, the disappearance of **I** led to the direct formation of **III** ($n = 1$) with no observable side products. Relative reaction rates were obtained by comparing the rate of the reaction using a certain catalyst versus the rate using acetic acid catalyst. Since the relative rates varied greatly, the studies were carried out at various temperatures. Our best estimate of the relative rates of all the catalysts used are shown in Table 1.

A series of carboxylic acid catalysts were used initially to compare the rates. A typical reaction was run at 25°C in octamethyltrisiloxane with 0.1 *M* silanol **I** and 0.15 *M* methyltrimethoxysilane, and with 0.3% catalyst added by weight. Although a rigorous rate law was not established, the reaction appeared to be trimolecular in nature. The reaction was accelerated not only by increased concentrations of either silanol I or methyltrimethoxysilane but also by the increased concentrations of the catalyst.

Table 1 shows the relative rates for the following acids: CCl_3COOH 500, CCl_2HCOOH 40, $CClH_2COOH$ 5, CH_3COOH 1, ${}^tBuCOOH$ 1. Based on these data, we were tempted to accept Grubb's mechanism as shown below:



$$MeSi(OMe)_3 + H^+ \longrightarrow [MeSi(OMe)_2{-}\underset{\displaystyle H}{\underset{|}{O^+}}Me] \xrightarrow{\mathbf{I}} \mathbf{III} + MeOH \qquad (2)$$

In this mechanism, a transition state is initially formed by the protonation of the alkoxysilane. The silanol can then react with the protonated alkoxysilane in a rate determining step to complete the reaction. A stronger acid would protonate the alkoxysilane better, which in turn would result in a higher rate of reaction. However, acetic acid-amine complex has been reported to be a good endcapping catalyst [11]. Two such complexes, $CH_3COOH–Et_3N$ and $CCl_3COOH–Et_3N$ were therefore evaluated. To our surprise, although trichloroacetic acid-triethylamine complex was found to be a poor catalyst (relative rate = 0.02), acetic acid-triethylamine complex was an excellent condensation catalyst (relative rate = 10), much superior to acetic acid itself. Clearly, the mechanism cannot be rationalized by the acidities of catalysts alone. Thus, although Grubb's mechanism may be valid for simple acid catalysis, it is not sufficient to explain the total reaction.

Recent patent literature has also indicated that both diethylhydroxylamine [12] and methylethylketoxime [13] are efficient endcapping catalysts. Our present studies indicated that their activities were 20 and 0.3, respectively. Since both are relatively weak acids, the results again illustrate the non-correlation of the acidities with reaction rates.

An alternative mechanism is therefore considered. Replacement of an alkoxy group of the alkoxysilane by the catalyst may initially form an intermediate silane in a rate determining step. The intermediate silane can then rapidly react with the silanol to complete the condensation reaction as shown below:

$$\underset{\textbf{(II)}}{MeSi(OMe)_3} + \text{Cat-H} \rightleftharpoons \underset{\textbf{(IV)}}{MeSi(OMe)_2(Cat)} + MeOH \qquad (3)$$

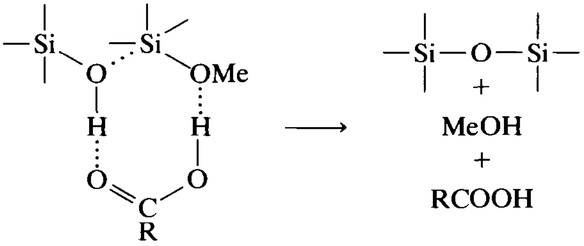
$$\underset{\textbf{(IV)}}{MeSi(OMe)_2(Cat)} + \underset{\textbf{(I)}}{Me_3Si(OSiMe_2)_3O{-}H} \longrightarrow$$

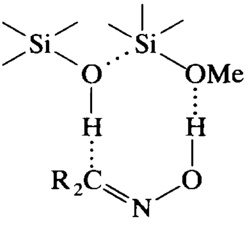
$$\underset{\textbf{(III)}}{Me_3Si(OSiMe_2)OSiMe(OMe)_2} + \text{Cat—H} \qquad (4)$$

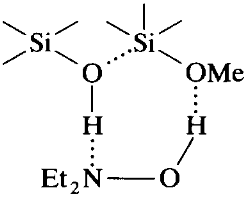
We were indeed able to prepare intermediate **IV** (Cat-H = methylethylketoxime) by reacting methyltrimethoxysilane with methylethylketoxime. However, removal of methanol by distillation was needed to shift the equilibrium to the right of eq. 3. No intermediate **IV** formation was observed without the removal of methanol. Since no intermediate **IV** formation was observed by GC in the condensation reactions (eq. 1, $n = 1$), it follows that for **IV** to be the intermediate of the reaction, its reaction with silanol will have to be much faster than its formation. Kinetically, the rate of the reaction should then be independent of the concentration of the silanol **I**. In our study, when both concentrations of **II** and catalyst (diethylhydroxylamine) were held constant and only varying the concentration of **I**, initially both the disappearance of **I** and the formation of **III** appeared to be first order with regard to **I**. Thus, doubling of the concentration of **I** led to the approximate doubling of the rates of both the disappearance of **I** and the formation of **III** during the initial stage of the reaction. It should be pointed out that although the initial rate of the reaction appeared to be trimolecular, the rate became quite complicated as the reaction proceeded further. Subsequent side reaction between **I** and **III** made the determinations of the kinetics by either the disappearance of **I** or the appearance of **III** very difficult. Nevertheless, the dependence of the rate on the concentration of **I** was clearly demonstrated. Therefore, we considered still another mechanism for kinetic reasons.

Bifunctional catalysis

We noticed that all the catalysts studied so far are bifunctional, i.e. catalysts containing both an active proton and a base. A transition state involving the bifunctional nature of the catalysts was therefore considered. In this mechanism, all three components come together to form a cyclic transition state. The catalyst acts both as a proton acceptor and as a proton donor. The mechanism explains the trimolecularity of the reaction and agrees with the nucleophilic substitution nature of alkoxysilanes. After the condensation, the catalyst is regenerated via either tautomerization (*e.g.* nitroso-oxime tautomerism for methylethylketoxime) or simple proton transfer (e.g. diethylammonium oxide rearrangement to diethylhydroxylamine). The cyclic transition state [14*] with acetic acid catalysis shown below is similar to that proposed by Dogoplosk [15] for the condensation of silanols in the presence of neutral salt as well as that proposed by Chojnowski [16] to account for his observation of the redistribution reactions of siloxanols. Similar transition states for oxime and hydroxylamine catalyses are also shown below:







To add further credibility to the proposed bifunctional catalysis, the following bifunctional catalysts were studied for the condensation. Their relative activities are shown in parentheses: Bis(ethoxyacetylacetonate)di-isopropyl titanate (0.5), 3-hydroxypyridine (0.2), 2-hydroxypyridine (0.1), 2,4-pentanedione (0). The titanium chelate is a commonly used condensation catalyst in the silicone industry. Its catalytic activity indicated that even a Lewis acid-base catalyst without an active proton can be an effective bifunctional catalyst. In contrast, 2,4-pentanedione, with its enol form in a very stable six-membered ring, is not an active bifunctional catalyst. Comparing the activities of 3-hydroxypyridine with 2-hydroxypyridine, the

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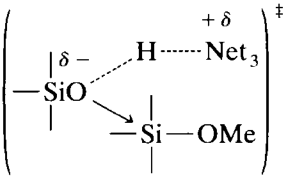
* Reference number with asterisk indicates a note in the list of references.

latter exists in an equilibrium with 2-pyridone, a possibly less active form of catalyst. The effective concentration of the active form is thus lower in 2-hydroxypyridine than in 3-hydroxypyridine.

The concept of bifunctional catalysis gains further support when it was observed that both *N*-methyl-2-pyridone and 2-methoxypyridine, the two methylated tautomers of 2-hydroxypyridine, were found to be catalytically inactive. Lack of active protons on either catalyst probably contributes to the inertness.

The observations that triethylamine, diethylethanolamine were both active catalysts, albeit very slow ones, and that pyridine was totally inactive clearly require some other explanations. None of the three catalysts are bifunctional, and therefore none are expected to be active. To account for the reactivities, a different mechanism is therefore needed. In their studies of condensation of silanols and chlorosilanes, Chojnowski *et al.* [17] were able to distinguish kinetically the nucleophilic character of the *N*-heterocyles and the basic character of triethylamine. In the case where the basic character of triethylamine alone was responsible for the reaction, a transition state where triethylamine functions as a proton acceptor was proposed. A similar transition state such as the one shown below can also explain our current observations. In this mechanism, triethylamine acts as the proton acceptor in promoting the condensation of silanol and alkoxysilane. Pyridine, a much weaker base, is incapable of accepting the proton and therefore is inactive.



Conclusions

It is shown that the condensation reaction of silanols with alkoxysilanes appears to be of general acid catalysis in nature. A Bronsted relationship exists between the rates of condensation and the different carboxylic acids used. The rate of condensation, however, is not entirely dependent on the strengths of acids alone. Thus, the observation that an acetic acid-triethylamine mixture is an active catalyst clearly demands a different mechanism. Two mechanisms are then considered. In the first mechanism, the catalyst first reacts with alkoxysilane to form an intermediate. Silanol can then react with this intermediate to give the final product. Although we cannot rule out this mechanism, rate considerations led us to favor a bifunctional catalysis mechanism. In this second mechanism, a cyclic transition state is formed by silanol, alkoxysilane and the catalyst. The mechanism appears to adequately explain all the observations, *i.e.* the apparent trimolecularity of the reaction, the nucleophilic nature of the attacking species on alkoxysilane, and the catalytic activities of the bifunctional catalysts. However, the bifunctional mechanism is not demanded. Thus, in the very slow condensation reactions catalyzed by amines, a still different mechanism may be operating. Here, the basicity of the amine appears to determine the outcome of the reaction. Chojnowski's mechanism for amine catalyzed condensation of chlorosilanes and silanols, with slight modification, can account for the observations.

Thus, a simple condensation reaction appears to proceed via quite a few different mechanisms depending on the catalyst chosen. When a simple acid is used, the reaction may proceed according to the mechanism envisioned by Grubb. When a base is used, dissociation of the proton from silanol may play an important role. Yet, when a bifunctional catalyst is used, the reaction may proceed according to a cyclic transition state, although substitution of the alkoxysilane with the catalyst remains a distinct possibility.

Experimental

All the catalysts used, except bis(ethoxyacetylacetonate)-diisopropyl titanate, were purchased from Aldrich Chemical Company, Milwaukee, Wisconsin. The titanate was obtained from E.I. DuPont DeNemours & Co., Wilmington, Delaware. All the organosilicon containing chemicals were purchased from Huls America, Piscataway, New Jersey. All the chemical were used either as received or distilled and stored over molecular sieves where conditions warrant.

GC analysis was performed on a Perkin–Elmer 8310 gas chromatograph with a flame ionization detector and a 1/8 in × 6 ft stainless steel column with 10% OV-101 on Chromosorb W-HP. The column was treated with small amounts of trimethylchlorosilane to pacify the silanol groups in the stationary phase and on the solid support. The treatment eliminated the possibility of silanol–silanol condensation which may occur between silanol and the solid support of the column. GC–MS was performed on a Hewlett Packard 5985 GC–MS system and a Hewlett Packard GC–MSD system with HP 5890 GC and HP 5971A MSD.

Preparation of nonamethyltetrasiloxane-1-ol (I)

Nonamethyltetrasiloxane-1-ol (**I**) was prepared by first reacting hexamethylcyclotrisiloxane with trimethylchlorosilane to obtain the 1-chloro-nonamethyltetrasiloxane [18]. The chlorosiloxane was then rapidly hydrolyzed in an ice-water mixture. The ice-water solution was extracted by ether. The ether extract was then repeatedly washed by de-ionized water until the washings became neutral. Approximately 6–10 washings were needed. Failure to wash it clean until neutral will render the resulting silanol unstable. Ether was then evaporated and the resulting mixture vacuum distilled using a spinning band distillation apparatus. The fraction boiling at 60°C/0.5 mmHg was collected. The total isolated yield was typically 20–30% based on the starting hexamethylcyclotrisiloxane. The material thus obtained usually contained a small amount of dodecamethylpentasiloxane which can be used as an internal standard during GC analysis in the subsequent condensation studies.

GC analysis of nonamethyltetrasiloxane-1-ol (**I**) showed fragmentation patterns at 311 ($M-\mathrm{H}$), 297 ($M-\mathrm{Me}$), 281 (base peak), 265, 207 among other peaks.

Analysis of 1,1-dimethoxy-decamethylpentasiloxane (III)

The endcapping product, 1,1-dimethoxy-decamethylpentasiloxane (**III**) was not isolated. GC–MS analysis of this product showed fragmentation patterns at 401 ($M-\mathrm{Me}$), 385 ($M-\mathrm{OMe}$), 369, 355, 297 (base peak), 281 among other peaks.

Preparation of methyldimethoxymethylethylketoximinosilane (IV, Cat = MeEtC=NO–) and its reaction with nonamethyltetrasiloxane-1-ol

In a 100-ml round bottom flask was placed 50.00 g (0.37 mol) of methyltrimethoxysilane and 15.00 g (0.17 mol) of methylethylketoxime. The mixture turned yellowish on mixing. The round bottom flask then was fitted to a one piece distillation apparatus with a fractionating column. The mixture was heated under gentle reflux with nitrogen blanketing for 1 h. Care was taken to maintain the reflux temperature at around 70°C. The mixture gradually turned dark brownish during heating. The methanol formed was then slowly distilled under nitrogen. The distillate was periodically analyzed by GC. Initially, only methanol should be distilled. Heat should be reduced if the distillate contains a significant amount of methyltrimethoxysilane. After approximately 4 h, methanol formation ceased. The mixture was allowed to cool to room temperature. The round bottom flask containing the mixture then was fitted to a spinning band distillation apparatus. The mixture was first distilled at room temperature under vacuum to remove the excess methyltrimethoxysilane, trace amounts of unreacted methylethylketoxime and a small amount of 1,3-dimethyl-tetramethoxydisiloxane. The fraction that boiled at 57–58°C/1.5 mmHg was then collected. A total of 14.72 g of a colorless liquid **IV** (Cat = MeEtC=NO–; 45% yield) was isolated. GC analysis indicated it is a pure compound. Mass spectroscopy showed the following fragmentation patterns: 191 (M^+), 176 (M – Me), 162 (M – Et), 159, 146, 132, 121, 107 105, 91 (base peak) and peaks of lower masses.

Compound **IV** reacted with **I** slowly. Thus a solution of 0.50 g of **IV** (2.6 mmol), 0.50 g of **I** (1.6 mmol) in 5.00 g of octamethyltrisiloxane was found to react at room temperature to give **III**. However, even after 6 h, a small amount of **I** was found to be present in the reaction mixture. The reaction, nevertheless, was much faster than reacting **I** and **II** in the presence of methylethylketoxime. Thus a solution of 0.36 g of **II** (2.6 mmol), 0.50 g of **I** (1.6 mmol) and 0.23 g of methylethylketoxime (2.6 mmol) in 5.00 g of octamethyltrisiloxane under identical conditions only gave a trace amount of **III** in 6 h.

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14 One of the referees suggested that in a nucleophilic substitution reaction, both the incoming nucleophile and the leaving group should occupy axial positions in the transition state. Since the cyclic transition state we proposed cannot accommodate this co-lineality easily, the possibility of this cyclic transition state should only be briefly proposed. However, nucleophilic attack at silicon is quite different from that at carbon. When the leaving group is an alkoxy group, it has been established that the stereochemistry is the retention of configuration at silicon. Apparent equatorial attack or departure is then needed to explain the outcome. For a comprehensive review of this subject, please see: A.R. Bassindale and P.G. Taylor, in S. Patai and Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Part 1, Wiley, New York, 1989, Chap. 13, p. 839.
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