Oligomerization of Hydrosiloxanes in the Presence of Tris(pentafluorophenyl)borane

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ABSTRACT: Oligomerization reactions of 1,3-dihydro-1,1,3,3-tetramethyldisiloxane ($^HMM^H$) and of 1-hydro-1,1,3,3,3-pentamethyldisiloxane (^HMM) catalyzed by tris(pentafluorophenyl)borane were studied. In the presence of this catalyst, $^HMM^H$ is converted to a series of linear α,*ω*-dihydrooligodimethylsiloxanes of general formula $HSiMe_2(OSiMe_2)_nOSiHMe_2$ ($^HMD_nM^H$) and dihydrodimethylsilane (Me_2SiH_2). In addition to these linear products, cyclic oligodimethylsiloxanes—hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4)—are also formed. The conversion of $^HMM^H$ follows second-order kinetics to almost full substrate consumption. Trimer 1,5-dihydro-1,1,3,3,5,5-hexamethyltrisiloxane ($^HMDM^H$) and dihydrodimethylsilane are formed as primary products. Consecutive reactions of $^HMM^H$ and the reactions between oligomeric products, i.e., higher oligomers, occur much more slowly. An exception is formation of D_3 that is generated from linear tetramer 1,7-dihydrooctamethyltetrasiloxane ($^HMD_2M^H$) in a fast consecutive reaction. The dismutation of ^HMM occurs much more slowly than that of $^HMM^H$ and takes a more complex course. Permethyloligosiloxanes $Me_3Si(OSiMe_2)_nOSiMe_3$ (MD_nM) are the dominant products. Oligomers of the homologous series, α-hydro-*ω*-methylsilyloligodimethylsiloxanes (^HMD_nM), are also formed, but they appear at lower concentrations than corresponding oligomers MD_nM. The metathetic mechanism of this oligomerization, which includes transient formation of trisilyloxonium ion is discussed.

Introduction

Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, is a versatile synthetic tool in organic, metalloorganic, and polymer chemistry.[1−4] It is a very effective Lewis acid catalyst similar in strength to $AlCl_3$. It has been used as a co-initiator for the polymerization of olefin, diene, and vinyl monomers providing significant enhancements of activity, selectivity, and duration of metallorganic initiation systems used in these processes.[4−7] It promotes many reactions in organic chemistry,[1−3] such as aldol-type condensations,[8−10] Diels−Alder reactions,[3] allylation of alcohols,[11] allylstannylation, and some rearrangement processes.[12,13] The borane is an useful catalyst for the reduction of organic compounds by hydrosilanes. Silyl hydride reagents in combination with $B(C_6F_5)_3$ readily reduce carbonyl compounds, such as aldehydes, esters, acyl chlorides, and carboxylic acids.[14−18] The same combination promotes the hydrosilylation of imines[19] and olefins[20] and the silylation of alcohols and phenols.[21] Alcohols and ethers can be completely reduced to hydrocarbons using the Si−H/borane system.[22,23] These reductions can be thought of as redox processes in which the organohydrosilane reagents are oxidized to siloxanes as the final silicon products. Recently, $B(C_6F_5)_3$ has been recognized as useful catalyst in the organosilicon chemistry. It promotes polycondensation of dihydrosilanes with dialkoxysilanes[24,25] and also affects the stereoselective polycondensation of dihydrosilanes with silanediols.[26]

In general, $B(C_6F_5)_3$ does not catalyze the cleavage of siloxane bonds. For example, it does not initiate cyclosiloxane polymerization. It also is not very effective as a catalyst for reactions of silyl hydrides with hexamethyldisiloxane or octamethylcyclotetrasiloxane. However, for some hydro-substituted oligosiloxanes the cleavage of the SiOSi bond induced by $B(C_6F_5)_3$ occurs very readily. In this paper we present such a case, which is a dismutation process for hydrosiloxanes. One such substrate is 1,3-dihydro-1,1,3,3,-tetramethyldisiloxane ($^HMM^H$), which is easily available by hydrolysis of dimethylchlorosilane, Me_2HSiCl. Its dismutation, readily catalyzed by $B(C_6F_5)_3$, leads to α,*ω*-dihydrooligodimethylsiloxanes. These oligomers are useful as reactive oligodimethylsiloxane blocks in synthesis of various block and graft copolymers.[27] A coproduct of this dismutation, dihydrodimethylsilane, is a very good precursor in CVD processes[28] and a potentially useful monomer for polysilane synthesis.[29] This paper describes in detail the $B(C_6F_5)_3$-catalyzed dismutation of 1,3-dihydro-1,1,3,3,-tetramethyldisiloxane and also of the unsymmetrical 1-hydro-1,1,3,3,3-pentamethyldisiloxane.

A similar process of the dismutation of $^HMM^H$ reported by Lewis et al.[30] occurs under heterogeneous catalysis by a protic acid-treated clay at elevated temperature and requires a large amount of catalyst. The major products are cyclic oligodimethylsiloxanes, mostly D_4, with lesser amounts of open chain hydrosilyl-terminated products. No kinetic and mechanistic studies were performed, but since on further heating cyclics content decreases and open chains are elongated in that case, most probably, the dismutation occurs together with the protic acid-catalyzed redistribution of oligosiloxanes.

Experimental Section

Chemicals. 1,3-Dihydro-1,1,3,3-tetramethyldisiloxane and 1-hydro-1,1,3,3,3-pentamethyldisiloxane were reagent grade products obtained from ABCR. They were purified by long storage over fresh calcium hydride followed by distillation. 1,7-Dihydro-1,1,3,3,5,5,7,7-octamethyltetradisiloxane was kindly offered by Dr. J. Chrusciel from Łódź Technical University. It was dried over CaH_2 prior to use.

Tris(pentafluorophenyl)borane, Aldrich reagent grade, was purified by resublimation. Toluene (Polskie Odczynniki Chemiczne,

10.1021/ma060080c CCC: $33.50

POCH), analytical grade, was additionally purified by shaking with concentrated H_2SO_4 followed by washing with $NaHCO_3$(aq) and water. It was dried over $MgSO_4$ and distilled from sodium.

n-Dodecane (standard for gas chromatographs) Aldrich, was stored over CaH_2 and distilled from it.

Oligomerization Procedures. Stock solutions of $B(C_6F_5)_3$, 9.71 $\times 10^{-2}$ and 3.97 $\times 10^{-3}$ mol/kg, were prepared by dissolving a known amount in a known volume of toluene.

Oligomerizations were carried out in a 10 mL glass Schlenk-type reactor equipped with magnetic stirrer and a three-way glass stopcock connected to a nitrogen gas circulating system fitted with an apparatus and a bubbler ensuring a positive pressure of nitrogen. The reactor was immersed in a thermostated silicone oil bath. The reactor was purged with nitrogen and known amounts of substrate, and the standard for the gas chromatography analysis was introduced by means of a gastight precision Hamilton syringe using the three-way stopcock through which nitrogen was flowing. The zero-time sample was withdrawn by a Hamilton syringe, and a known amount of the catalyst solution was introduced by a Hamilton precision syringe. Samples were withdrawn at timed intervals and introduced to Eppendorfer vessels containing 4-ethylpyridine used for the quenching of the reaction. Time of the introduction of the sample to the quencher solution, measured from zero time, was considered as the time of reaction. The samples were analyzed by gas chromatography.

Analysis. *Gas Chromatography.* The gas chromatographic analyses of the reaction mixture were performed using a Hewlett-Packard HP 6890 chromatograph equipped with a thermal conductivity detector TDC. An HP1 capillary column of 30 m length and 0.53 mm diameter was used for separations. The carrier gas was helium, flow rate 5 mL/min. The detector temperature was 250 °C and injector temperature 250 °C. The temperature was programmed, in most cases: 3 min 40 °C isothermal, 40−240 °C with rate 10 °C/min, 10−15 min 240 °C isothermal.

n-Dodecane was used as internal standard. The response factors were determined for some isolated compounds: hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and representatives of $HMe_2Si(OSiMe_2)_nOSiMe_2H$ series $n = 0$, 2, and 5. The response factors for the remaining compounds of the oligo-homologue series were found by interpolation and extrapolation procedure assuming that linear dependence in the double-logarithmic plot exists between the response factor and the number of silicon atoms in homologues.

Gas Chromatography−Mass Spectroscopy. Mass spectra of volatile products were recorded with JEOL SX-102 mass spectrometer (sector instrument, BE geometry) connected to a HP5890 series II gas chromatograph. Approximately 100 μL of the volatile product was injected onto an Agilent J&W DB5 ms column (30 m long, 0.32 mm i.d., 1.0 μm film thickness). The column temperature was maintained at −50 °C (cryo-gas valve, liquid nitrogen as cryogen) for 2.5 min and was subsequently programmed to 270 °C with rate10 °C/min. The mass spectrometer mass resolution was set to 1000 (10% valley definition) and repetitively scanned from 0 to 100 with frequency 1 spectrum/s during the chromatography. Normal electron ionization at 70 eV mass spectra were acquired.

Mass spectra of the reaction mixture were recorded with a GC-MS Finnigan MAT 95 instrument using chemical ionization technique. The reactive gas (H^+ carrier) was isobutane at a pressure of 10^{-4} Torr. The mass spectrometer worked in tandem with a gas chromatograph which was fitted with standard capillary column DB-1 of length 30 m. The program was tuned to obtain chromatograms fitted corresponding to those recorded on the HP-6890 machine.

Nuclear Magnetic Resonance. ^1H NMR spectra were acquired on a Bruker Avance 400 spectrometer. ^{29}Si NMR spectra were obtained on a Varian 500 MHz Inova instrument with ^{29}Si and ^1H frequency of 119.16 and 599.8 MHz, respectively. Eight scans were accumulated with a recycle delay of 60 s. For decoupled spectra, inverse gated decoupling was used to decouple ^1H from ^{29}Si during the acquisition of the free induction decay, but avoiding the nuclear Overhauser effect. A 9.75 μs ^{29}Si pulse was used corresponding to a 90° pulse.

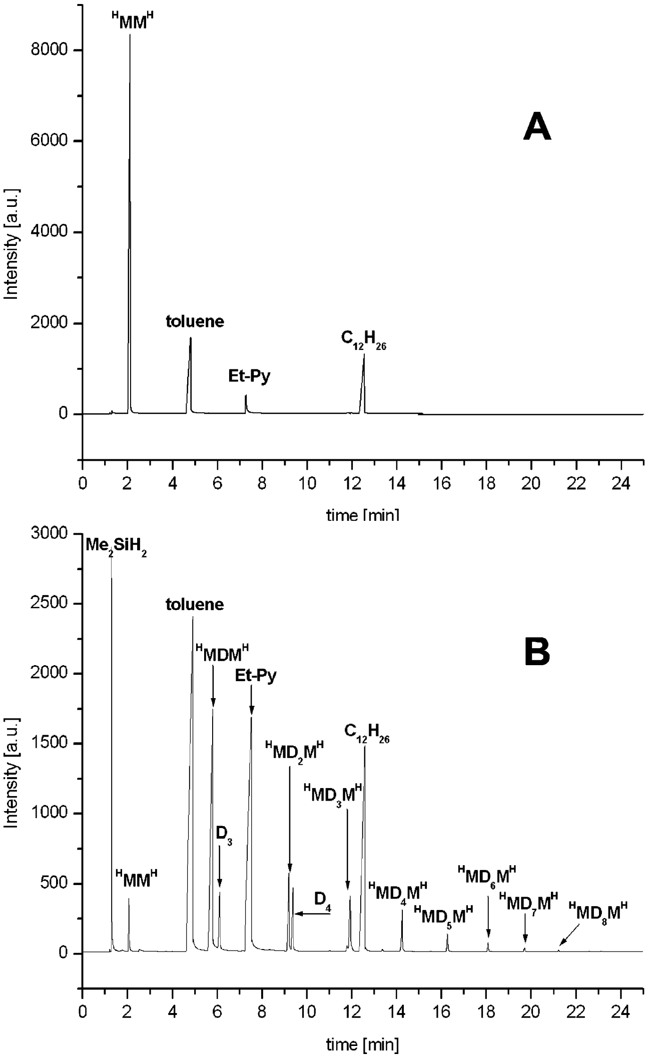


Figure 1. Gas chromatograms of the reaction system of the oligomerization of 1,3-dihydro-1,1,3,3-tetramethyldisiloxane ($^HMM^H$) in concentrated solution in toluene catalyzed by tris(pentafluorophenyl)borane, $[^HMM^H]_0 = 3.81$ mol/kg, $[B(C_6F_5)_3]_0 = 1.63 \times 10^{-2}$ mol/kg, temperature 25 °C. The chromatograms were taken (A) before the addition of catalyst and (B) after 19 min since the catalyst addition.

Results and Discussion

Oligomerization of 1,3-dihydro-1,1,3,3-tetramethyldisiloxane by $B(C_6F_5)_3$. Addition of tris(pentafluorophenyl)borane to 1,3-dihydro-1,1,3,3-tetramethyldisiloxane ($^HMM^H$) results in a rapid exothermic reaction accompanied by the evolution of a volatile product. The course of the reaction was monitored by the gas chromatographic analysis of samples withdrawn from the reaction mixture. The pattern of peaks on the chromatogram (Figure 1B) suggests the formation of a homologous series of oligomers. The assignment of peaks was accomplished by the GC-MS analysis in the chemical ionization mode. All species giving separate peaks on the chromatogram were analyzed. The results indicated that α,ω-dihydrooligodimethylsiloxane homologues were produced in this reaction. All oligomers of this series exhibit a characteristic $M - 1$ peak in the MS−chemical ionization spectrum due to loss of H_2 from the protonated molecule. Only the starting disiloxane, $^HMM^H$, displays an $M + 1$ peak ($M = 135$) for the protonated complex though its intensity was less than half of that of $M - 1$ peak ($M = 133$). The volatile product of the oligomerization process was trapped in a cooled receiver and identified by GC-MS and ^{29}Si NMR. GC-MS analysis shows a characteristic fragmentation pattern

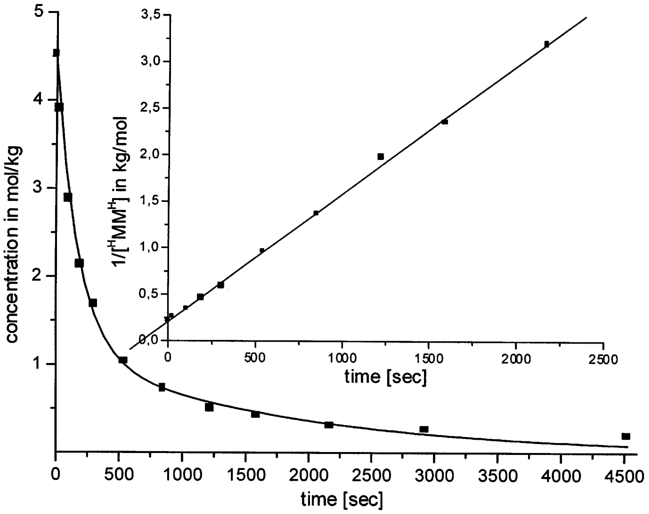


Figure 2. Conversion time dependence for the oligomerization of $^{H}MM^{H}$ in the presence of $B(C_6F_5)_3$, $[^{H}MM^{H}]_0 = 4.53$ mol/kg, $[B(C_6F_5)_3]_0 = 8.37 \times 10^{-4}$ mol/kg, temperature 21.7 °C. The transposition of this dependence into the second-order plot is shown in the upper right-hand corner. The specific rate $k = 1.38 \times 10^{-3}$ kg/(mol s), correlation factor $r = 0.999$.

for Me_2SiH_2.[31] A completely decoupled ^{29}Si NMR spectrum shows a singlet at −37.9 ppm. The coupled spectrum shows a triplet of heptads with $^{29}Si-H$ coupling constant, $J = 187.2$ Hz, and $^{29}Si-C-H$ coupling constant, $J = 7.5$ Hz, which confirms the identity of Me_2SiH_2. Thus, the dismutation of $^{H}MM^{H}$ in this process may be represented in general by eq 1.

$$\left(\frac{m+1}{2}\right)\mathrm{HMe_2SiOSiMe_2H} \xrightarrow{\mathrm{B(C_6F_5)_3}} \mathrm{HSiMe_2(OSiMe_2)_{\mathit{m}}H}, \qquad m = 0, 1, 2, ... \quad (1)$$

Besides linear oligomers and Me_2SiH_2 (eq 1, $m = 0$), small amounts of cyclic oligomers—hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4)—are also produced.

The kinetics for conversion of the substrate and the formation of products were evaluated by gas chromatography. Results indicate that the disappearance of $^{H}MM^{H}$ proceeds almost to completion and follows the second-order kinetics (Figure 2) to very high conversion.

This means that $^{H}MM^{H}$ reacts much faster in the dismutation process than the higher oligomers of the series, and it is primarily consumed in a reaction involving two molecules of substrate, as shown in eq 2. This is confirmed by the comparison of the conversion time dependence for $^{H}MM^{H}$ with formation time dependences for oligomers $HMe_2SiO(SiMe_2O)_nSiMe_2H$ ($^{H}MD_nM^{H}$) presented in Figures 3 and 4.

$$\mathrm{2HMe_2SiOSiMe_2H} \xrightarrow{\mathrm{B(C_6F_5)_3}} \mathrm{HMe_2SiOSiMe_2OSiMe_2H + Me_2SiH_2} \quad (2)$$

In this reaction, $^{H}MDM^{H}$ is initially formed in the largest concentration. Its concentration passes through a maximum and then decreases as the reaction proceeds. The $^{H}MDM^{H}$ is converted to higher oligomers, which are generated with a delay since reactions of the higher oligomers proceed more slowly than those of the lower members of the series.

The interesting feature of the process is that the concentration of cyclic D_3 achieves a relatively high value early in the reaction and then remains almost constant, decreasing only slightly as the reaction proceeds. In contrast, D_4 is produced much more slowly, and its concentration constantly increases (Figure 5).

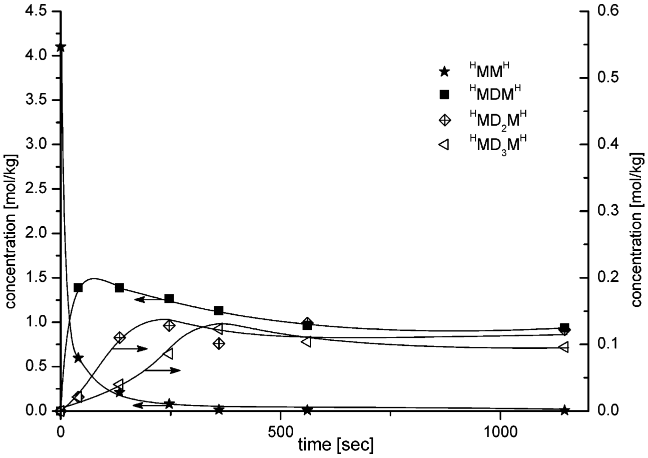


Figure 3. Conversion time and lower linear oligomer formation time dependences for the oligomerization of $^{H}MM^{H}$ in the presence of $B(C_6F_5)_3$, $[^{H}MM^{H}]_0 = 4.11$ mol/kg, $[B(C_6F_5)_3]_0 = 1.35 \times 10^{-2}$ mol/kg, temperature 25 °C.

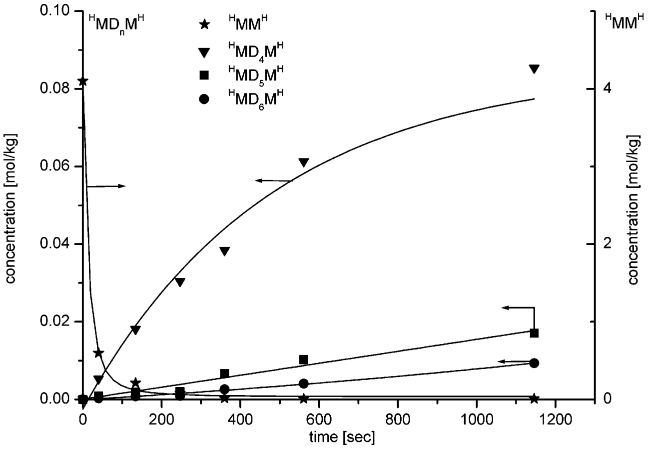


Figure 4. Conversion time of substrate and formation time of some higher oligomers of $^{H}MD_nM^{H}$ series dependences for the oligomerization of $^{H}MM^{H}$ in the presence of $B(C_6F_5)_3$, $[^{H}MM^{H}]_0 = 4.11$ mol/kg, $[B(C_6F_5)_3]_0 = 1.35 \times 10^{-2}$ mol/kg, temperature 25 °C.

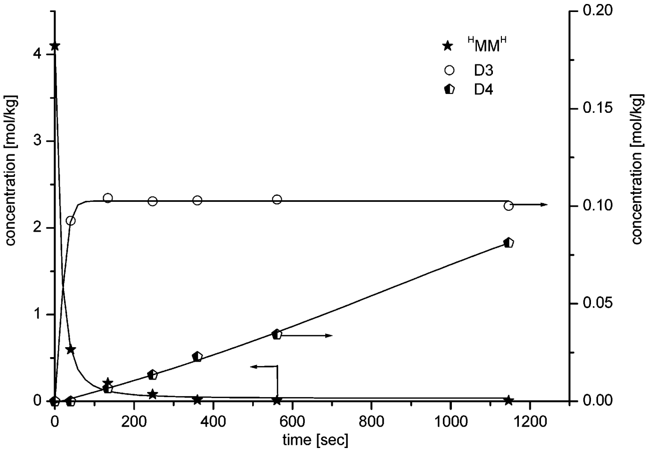


Figure 5. Substrate conversion time and cyclic-oligomer D_3 and D_4 formation time dependences for the oligomerization of $^{H}MM^{H}$ in the presence of $B(C_6F_5)_3$, $[^{H}MM^{H}]_0 = 4.11$ mol/kg, $[B(C_6F_5)_3]_0 = 1.35 \times 10^{-2}$ mol/kg, temperature 25 °C.

The D_3 concentration time dependence is similar to that of $^{H}MD_2M^{H}$, which suggests that D_3 is formed from $^{H}MD_2M^{H}$ in a relatively fast and reversible reaction. To verify this hypothesis and also to get more information about the mechanism of the dismutation process, the reaction of isolated $^{H}MD_2M^{H}$ catalyzed by $B(C_6F_5)_3$ was studied.

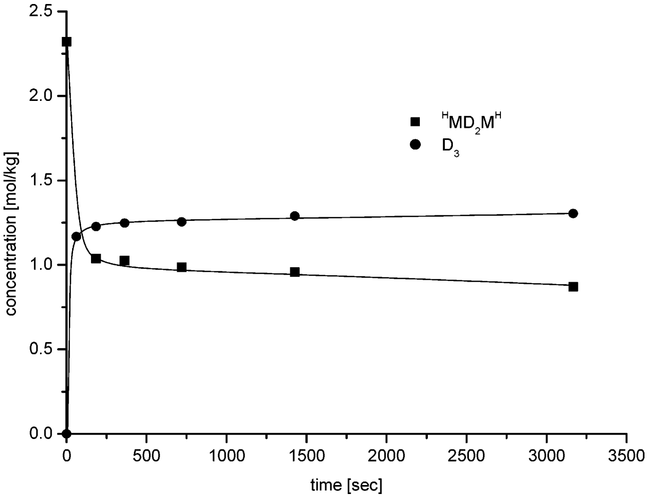
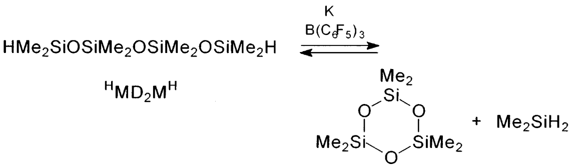


Figure 6. Substrate conversion time and D_3 formation time dependences in the oligomer transformation reaction of $^{H}MD_2M^{H}$ catalyzed by $B(C_6F_5)_3$, $[^{H}MD_2M^{H}]_0 = 2.32$ mol/kg, $[B(C_6F_5)_3]_0 = 8.04 \times 10^{-4}$ mol/kg, temperature 25 °C.

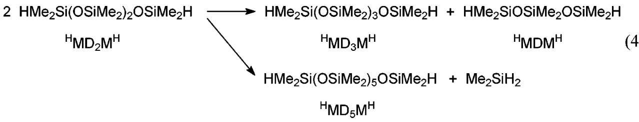
Initially, the $^{H}MD_2M^{H}$ redistribution is a relatively fast process. Its concentration drops to about 43% of its initial value and then remains almost constant, decreasing only slightly as the reaction proceeds. The exclusive product of this reaction in the initial period is D_3, which rapidly increases in concentration to a value corresponding to the amount of $^{H}MD_2M^{H}$ consumed, where it remains until much later in the process (Figure 6). This behavior indicates that $^{H}MD_2M^{H}$ and D_3 are rapidly interconverted according to eq 3.



(3)

The approximate equilibrium constant for this process $K = [Me_2SiH_2]_e[D_3]_e/[^{H}MD_2M^{H}]_e$, where $[\ ]_e$ are equilibrium concentrations, is 1.7 mol dm^{-3} (25 °C). This experiment proves that the $B(C_6F_5)_3$ in combination with a silyl hydride is able to cleave the siloxane bond in cyclotrisiloxanes.

In the later stages of the $^{H}MD_2M^{H}$ redistribution process, higher linear oligomers are formed, evidenced by gas chromatography, while concentrations of $^{H}MD_2M^{H}$ and D_3 decrease. The higher oligomers are formed in a very specific way; $^{H}MD_5M^{H}$ and $^{H}MD_9M^{H}$ were found in excess, while no $^{H}MD_4M^{H}$ and only a small amount of $^{H}MD_3M^{H}$ are seen in the chromatogram. Worthy of attention is also the absence of $^{H}MM^{H}$. These observations indicate that the reaction proceeds predominantly by cleavage of the terminal siloxane bonds (see discussion of mechanism). Thus, $^{H}MD_2M^{H}$ is transformed into open chain products according to eq 4:



(4)

Oligomerization of 1-Hydro-1,1,3,3,3-pentamethyldisiloxane. The oligomerization of 1-hydro-1,1,3,3,3-pentamethyldisiloxane (^{H}MM) initiated by $B(C_6F_5)_3$ proceeds more slowly and takes a more complex course than that of $^{H}MM^{H}$. It also requires a higher concentration of catalyst. Two homologous series of oligomers are produced, namely, linear oligodimethylsiloxanes ended by a hydrodimethylsilyl group at one terminus and by a trimethylsilyl group at the other, $H(CH_3)_2Si(OSiMe_2)_n$-$OSiMe_3$ ($^{H}MD_nM$) and linear oligodimethylsiloxane ended by the Me_3Si group at both chain termini, $Me_3Si(OSiMe_2)_nOSiMe_3$ (MD_nM). The dominant products are those of the MD_nM series. Small amounts of symmetrical oligomers $^{H}MD_nM^{H}$ are formed as well. A representative gas chromatogram of the reaction mixture is presented in Figure 7.

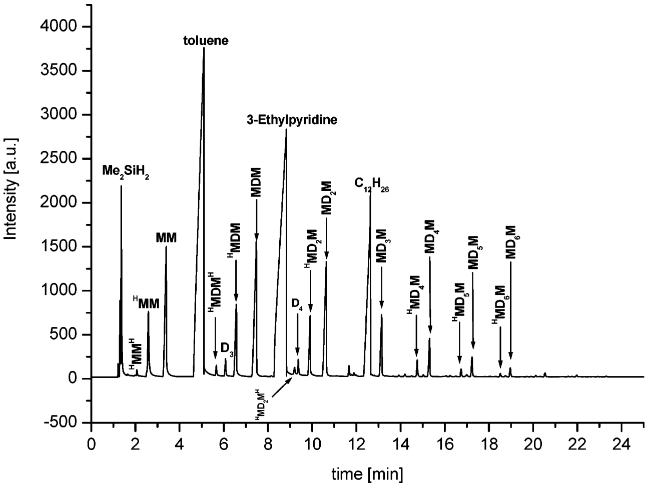
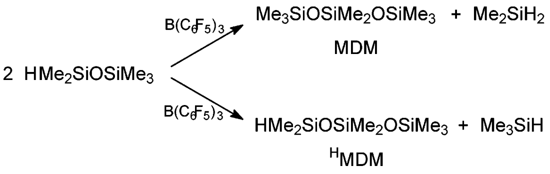


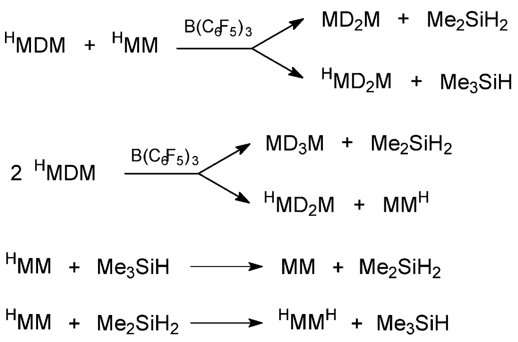
Figure 7. Gas chromatogram of the reaction mixture of the oligomerization of 1-hydro-1,1,3,3,3-pentamethyldisiloxane, ^{H}MM, in concentrated solution in toluene, catalyzed by $B(C_6F_5)_3$ taken 70 min after the introduction of catalyst (at 90% of the substrate conversion). $[^{H}MM]_0 = 3.31$ mol kg^{-1}, $[B(C_6F_5)_3]_0 = 6.75 \times 10^{-2}$ mol/kg^{-1}, temperature 25 °C.

The first step of this oligomerization proceeds according to eq 5.



(5)

Although the quantity of MDM was constantly increasing in the reaction system, the concentration of ^{H}MDM passed through a maximum (Figure 8), indicating that it was the transient product from which higher oligomers were formed as depicted in eqs 6. Me_2SiH_2 and Me_3SiH also enter into further reactions, such as those shown in eqs 6.



(6)

The conversion of ^{H}MM proceeds almost to completion (Figure 9). The conversion time dependence for this substrate does not conform to a first-order plot (Figure 9A) nor a second-order plot (Figure 9B), indicating that the apparent order lies

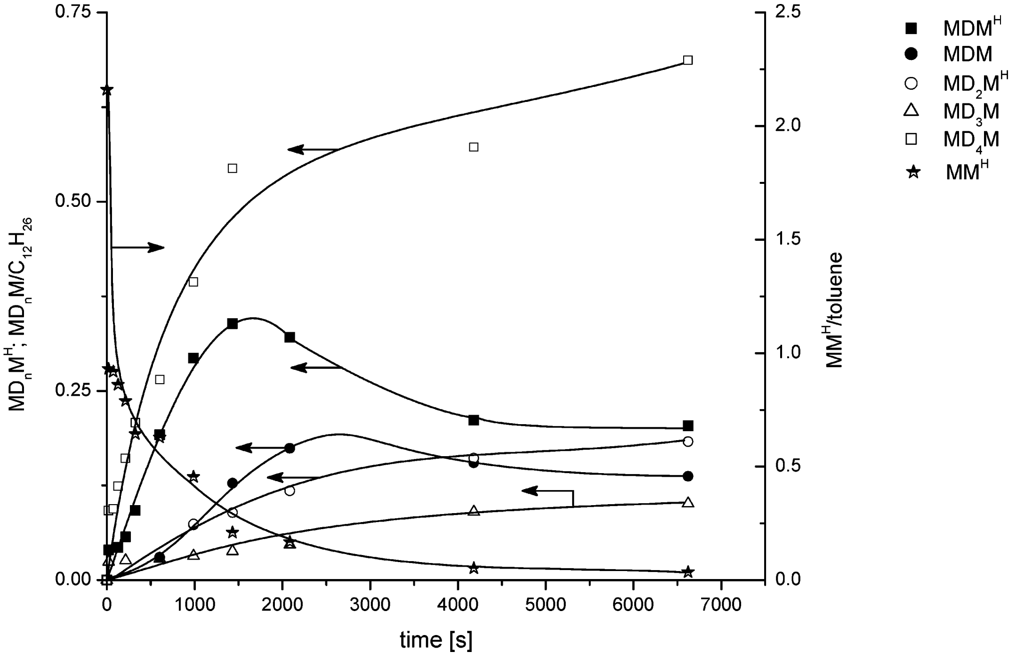
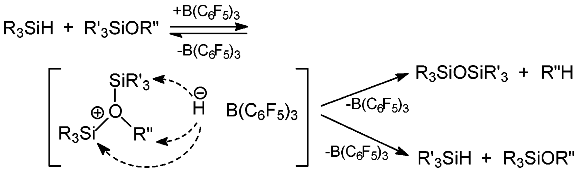


Figure 8. Relative intensities of gas chromatographic signals of the substrate and some products in oligomerization of ^HMM catalyzed by $B(C_6F_5)_3$, $[^HMM]_0 = 3.31$ mol kg^{-1}, $[B(C_6F_5)_3]_0 = 6.75 \times 10^{-2}$ mol/kg. The dependence for the MD_2M formation is omitted because it is affected by fortuitous water.

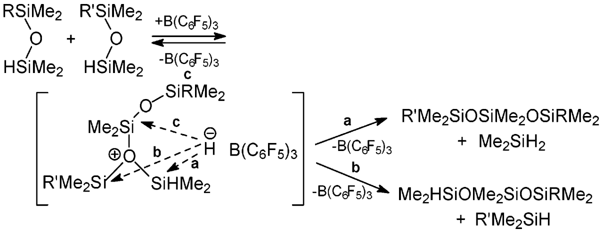
between first and second, which means that a considerable fraction of the substrate is consumed in consecutive reactions, mostly in those shown in scheme 6.

Mechanism of the Hydrooligosiloxane Dismutation. We have recently shown[32] that reactions of alkoxysilanes with silyl hydrides leading to the siloxane bond formation and generation of hydrocarbon are accompanied by metathesis of substrates, i.e., the exchange of hydride for alkoxy function between substrate molecules (eq 7). The mechanism of this reaction was studied and oxonium ion or limited oxonium ion[33] mediation was postulated (eq 7), where R and R′ are alkyl or aryl and R″ is alkyl.



(7)

The disproportionation reactions described in this study proceed by analogous routes and can be represented by general eq 8, where R and R′ are $(OSiMe_2)_nH$ or $(OSiMe_2)_nMe$, where n = 0, 1, 2, ...



(8)

In the process presented in scheme 7 the nucleophile may attack either the carbon or silicon centers. Consequently, the process leads either to formation of hydrocarbon and siloxane or to the exchange of hydride and alkoxy functions between silyl moieties. On the other hand, in the reaction studied here the H^- nucleophile may choose only between various electrophilic silicon centers in the oxonium ion intermediate. If the route a or b (eq 8) is chosen, the reaction leads to redistribution of the siloxane moieties which are the component reactions of the overall dismutation process. Route c re-forms substrates.

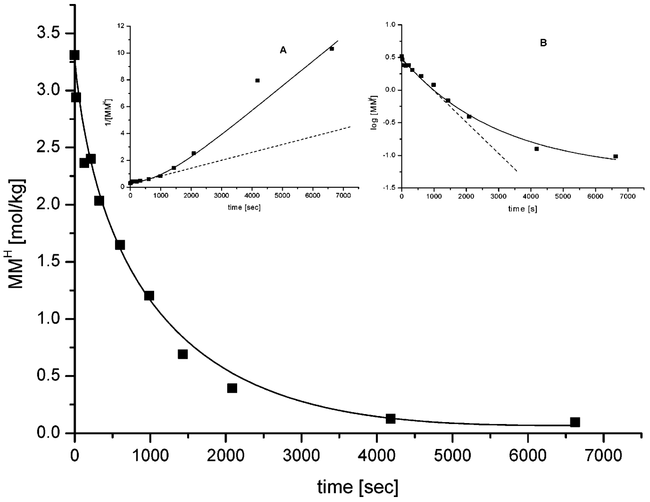
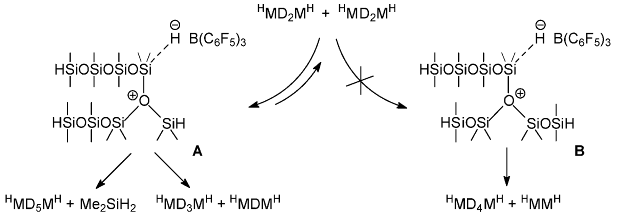


Figure 9. Substrate conversion time dependence for the oligomerization of ^HMM catalyzed by $B(C_6F_5)_3$, $[^HMM]_0 = 3.31$ mol kg^{-1}, $[B(C_6F_5)_3]_0 = 6.75 \times 10^{-2}$ mol kg^{-1}, temperature 25 °C. The transpositions of the dependence are (A) into the second-order plot and (B) into the first-order plot.

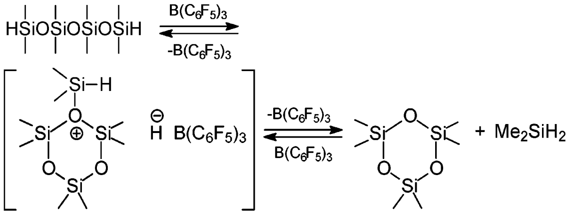
An important feature of these reactions is that only terminal siloxane groups are cleaved. This conclusion is drawn from the observations that $^HMD_5H^H$ is formed before $^HMD_4M^H$ in the dismutation process of $^HMD_2M^H$ and that there is complete absence of $^HMM^H$ in this system. As depicted in scheme 9, oxonium ion A is produced exclusively and oxonium ion B is not produced. The reaction is somewhat similar to the metathetic reaction of $Me_3SiOSiMe_3$ involving the methide transfer to trisilyloxonium ion and leading to poly(dimethylsiloxane) and tetramethylsilane described by Olah et al.,[34] although the route to the oxonium ion is quite different.

The pathway proceeding through intermediate A is also in agreement with the observation that permethyloligosiloxanes are



(9)

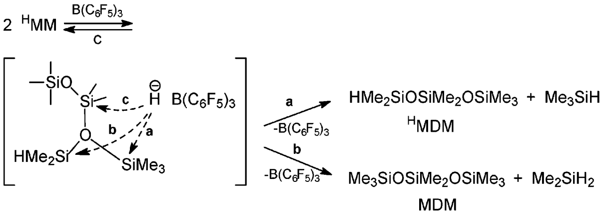
not cleaved by the $R_3SiH + B(C_6F_5)_3$ system. It is, however, interesting and to some extent puzzling that the conversion of $^{H}MD_2M^{H}$ is dominated by intramolecular reaction of $^{H}MD_2H^{H}$, producing D_3 and Me_2SiH_2. This reaction must occur via a ring strained cyclic intermediate (eq 10) that can form reversibly. The analogous oxonium ion generated from $^{H}MD_3M^{H}$ having eight-membered unstrained ring structure producing D_4 should be generated easier; however, D_4 is formed much more slowly than D_3 in the $^{H}MM^{H}$ dismutation system. This is likely to be an entropic effect similar to that observed by Le Roux et al. in a nonaqueous polysiloxane synthesis.[35]



(10)

It should be pointed out that the redistribution of polysiloxanes presented here differs considerably from that promoted by ordinary strong protic acid, such as CF_3SO_3H and CF_3CO_2H, where D_4 is the principal cyclic product.

The formation of two homologous series $HMe_2SiO[SiMe_2O]_nSiMe_3$ and $Me_3SiO[SiMe_2O]_nSiMe_3$ in the oligomerization of ^{H}MM is also the result of choice by hydride ion of one of the two electrophilic centers in the oxonium ion intermediate (route a or b in eq 11).



(11)

Conclusions

Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, cleaves the $-Me_2SiOSiMe_2-$ grouping if at least one of its silicon is bonded to hydrogen. It is a very effective catalyst for the dismutation (disproportionation) of 1,3-dihydro-1,1,3,3-tetramethyldisiloxane. This reaction leads to oligodimethylsiloxanes terminated by the hydrodimethylsilyl groups and dihydrodimethylsilane. Small amounts of hexamethylcyclotrisiloxane, D_3, are formed from 1,7-dihydro-1,1,3,3,5,5,7,7-octamethyltetrasiloxane in a reversible unimolecular reaction. This reaction is fast on the dismutation process time scale, and a stationary D_3 concentration is established in the first period of the process. The eight-membered cyclosiloxane ring D_4 is generated much more slowly.

1-Hydro-1,1,3,3,3-pentamethyldisiloxane undergoes the dismutation less readily than 1,3-dihydro-1,1,3,3-tetramethyldisiloxane. Two series of linear oligosiloxane homologue series, $Me_3Si(OSiMe_2)_nOSiMe_3$, $n = 1, 2, 3, ...$, and $HMe_2Si(OSiMe_2)_nOSiMe_3$, $n = 1, 2, 3, ...$, as well as Me_2SiH_2 and Me_3SiH are the main products.

All these reactions involving the siloxane bond cleavage are proposed to proceed via a metathetic mechanism involving the intermediacy of a trisilyloxonium ion or limited trisilyloxonium ion.

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References and Notes

(1) Piers, W. E. *Adv. Organomet. Chem.* **2005**, *52*, 1−76.
(2) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345−354.
(3) Ishihara, K.; Yamamoto, H. *Eur. J. Org. Chem.* **1999**, *527*, 7−538.
(4) You-Xian Chen, E.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434.
(5) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236−2257.
(6) Jang, Y. G.; Choi, D. S.; Han, S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1164−1173.
(7) McKittrick, M. W.; Jones, C. W. *J. Catal.* **2004**, *227*, 186−201. Kawabe, M.; Murata, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3692−3706.
(8) Hassfeld, J.; Christmann, M.; Kalesse, M. *Org. Lett.* **2001**, *3*, 3561−3564.
(9) Erker, G. *J. Chem. Soc., Dalton Trans.* **2005**, 1883−1890.
(10) Ishihara, K.; Funahashi, M.; Hanaki, N.; Miyata, M.; Yamamoto, H. *Synlett.* **1994**, 963−964.
(11) Rubin, M.; Gevorgyan, V. *Org. Lett.* **2001**, *3*, 2705−2707.
(12) Marshall, J. A.; Gill, K. *J. Organomet. Chem.* **2001**, *624*, 294−299.
(13) Chandrasekhar, S.; Reddy, C. R.; Chandrasekhar, G. *Tetrahedron Lett.* **2004**, *45*, 6481−6484.
(14) Bajracharya, G. B.; Nogami, T.; Jin, T.; Matsudo, K.; Gevorgyan, V.; Yamamoto, Y. *Synthesis (Stuttgart)* **2004**, 308−311.
(15) Gevorgyan, V.; Rubin, M.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 1672−1675.
(16) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090−3098.
(17) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440.
(18) Blackwell, J. M.; Morrison, D. J.; Piers, W. E. *Tetrahedron* **2002**, *58*, 8247−8254.
(19) Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, *2*, 3921−3923.
(20) Rubin, M.; Schwier, T.; Gevorgyan, V. *J. Org. Chem.* **2002**, *67*, 1936−1940.
(21) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887−4892.
(22) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179−6186.
(23) Gevorgyan, V.; Liu, J.-X.; Rubin, M.; Benson, S.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 8919−8922.
(24) Rubinsztajn, S.; Cella, J. US Pat. Application 200/0127668 A1 to GE Co.
(25) Rubinsztajn, S.; Cella, J. *Macromolecules* **2005**, *38*, 1061−1063.
(26) Zhou, D. Q.; Kawakami, Y. *Macromolecules* **2005**, *38*, 6902−6908.
(27) Belorgey, G.; Sauvet, G. In *Silicon Containing Polymers*; Jones, R. G., Andu, W., Chojnowski, J., Eds.; Kluwer Academic Publishers: Dordrecht, 2000; Chapter 2, pp 43−78.
(28) Wróbel, A. M.; Walkiewicz-Pietrzykowska, A. *Adv. Mater. Chem. Vapor Depos.* **1998**, *4*, 133−141.
(29) Tilley, D. *Acc. Chem. Res.* **1993**, *26*, 22−29.
(30) Lewis, L. N.; Johnson, D. S.; Rich, J. D. *J. Organomet. Chem.* **1993**, *448*, 15−18.
(31) Wiley Reference Library of Mass Spectrometry, Registry 7th/NIST 2002 edition.
(32) Chojnowski, J.; Rubinsztajn, S.; Cella, J.; Fortuniak, W.; Cypryk, M.; Kurjata, J.; Kaźmierski, K. *Organometallics* **2005**, *24*, 6077−6084.
(33) The oxonium ion formed as intermediate in these reactions may be diffusionally unequilibrated species.
(34) Olah, G. A.; Li, X. Y.; Wang, Q.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 8962−8966.
(35) Le Roux, C.; Yang, H.; Wenzel, S.; Brook, M. A. *Organometallics* **1998**, *17*, 556−564.

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