

Thermal Degradation Processes in Polysiloxanes and Thermal Stabilization by A Cerium Inhibitor

C. M. MURPHY AND H. RAVNER

*Surface Chemistry Branch
Chemistry Division*

and

R. E. KAGARISE

*Physical Chemistry Branch
Chemistry Division*

April 6, 1966



U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)		2 a. REPORT SECURITY CLASSIFICATION	
U.S. Naval Research Laboratory Washington, D.C. 20390		Unclassified	
3. REPORT TITLE		2 b. GROUP	
THERMAL DEGRADATION PROCESSES IN POLYSILOXANES AND THERMAL STABILIZATION BY A CERIUM INHIBITOR			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
An interim report on one phase of the problem.			
5. AUTHOR(S) (Last name, first name, initial)			
Murphy, C.M., Ravner, H., and Kagarise, R.E.			
6. REPORT DATE	7 a. TOTAL NO. OF PAGES	7 b. NO. OF REFS	
April 6, 1966	24	21	
8 a. CONTRACT OR GRANT NO.		9 a. ORIGINATOR'S REPORT NUMBER(S)	
NRL Problems C02-01, C02-02, and C07-01		NRL Report 6383	
b. PROJECT NO.		9 b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
RAP 41R-001/652-1/F012-03-05-41002		None	
c. RR 007-08-44-5500			
d. RR 001-01-43-4803			
10. AVAILABILITY/LIMITATION NOTICES			
Distribution of this document is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
None		Dept. of the Navy (Office of Naval Research and BuWeps)	
13. ABSTRACT			
<p>Studies have been made of the effect of cerium on the degradation of polyorganosiloxanes (silicones) at 400°C in the absence of oxygen. Thermally stressed polydimethyl siloxanes undergo —Si—O bond rupture, initiating anion-propagated degradation to cyclics and linear residues. One-hundred-percent polymethylphenylsiloxanes do not cyclize, but undergo rearrangements leading to crosslinking. In polydimethylsiloxanes, cerium is considered to form active sites which react reversibly with anion fragments, thus limiting further degradation. Cerium has little effect on polymethylphenylsiloxanes, but stabilizes copolymers in direct ratio to the dimethyl content. The excellent response of polydimethyl and lightly phenylated siloxanes to cerium, together with their desirable physical properties, make their use attractive as high-temperature lubricants and hydraulic fluids in selected applications.</p>			

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Siloxanes Thermal Stresses Rupture Pyrolysis Degradation-Inhibition High Temperature Stabilization Cerium Silicones						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	1
POLYDIMETHYLSILOXANES	3
Results of Pyrolysis in Sealed Tubes	3
Analysis of Major Degradation Products	6
Mechanism of DMS Thermal Degradation	9
Mechanism of DMS-Ce Thermal Stabilization	12
PHENYL-CONTAINING SILOXANES	14
Results of Pyrolysis in Sealed Tubes	14
Analysis of Major Degradation Products	15
Effect of Structure on Pyrolysis-Induced Property Changes	17
Mechanism of MPS (0.75) Degradation	17
CONCLUSIONS	19
ACKNOWLEDGMENT	20
REFERENCES	21

ABSTRACT

Studies have been made of the effect of cerium on the degradation of polyorganosiloxanes (silicones) at 400°C in the absence of oxygen. Thermally stressed polydimethylsiloxanes undergo —Si—O bond rupture, initiating anion-propagated degradation to cyclics and linear residues. One-hundred-percent polymethylphenylsiloxanes do not cyclize, but undergo rearrangements leading to crosslinking. In polydimethylsiloxanes, cerium is considered to form active sites which react reversibly with anion fragments, thus limiting further degradation. Cerium has little effect on polymethylphenylsiloxanes, but stabilizes copolymers in direct ratio to the dimethyl content. The excellent response of polydimethyl and lightly phenylated siloxanes to cerium, together with their desirable physical properties, make their use attractive as high-temperature lubricants and hydraulic fluids in selected applications.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

NRL Problems C02-01, C02-02, and C07-01
Project Nos. RAP 41R-001/652-1/F012-03-05-41002,
RR 007-08-44-5500, and RR 001-01-43-4802

Manuscript submitted January 5, 1966.

THERMAL DEGRADATION PROCESSES IN POLYSILOXANES AND THERMAL STABILIZATION BY A CERIUM INHIBITOR

INTRODUCTION

The polyorganosiloxanes (silicones) are one of the several classes of fluids receiving consideration as high-temperature ($> 250^{\circ}\text{C}$) hydraulic fluids and aircraft gas turbine lubricants. Of the many stringent operational requirements for such fluids, adequate resistance to pyrolysis is among the more important.

In the absence of air, pyrolysis of polydimethylsiloxanes becomes significant at 325° to 350°C (1-3). Thermal breakdown is manifested by molecular rearrangements to cyclic compounds of the general formula $[(\text{CH}_3)_2\text{SiO}]_n$ with n ranging from 3 to 11 (4), and probably higher. As dimethyl substituents are replaced by methylphenyl, resistance to pyrolysis is improved (5). Bulk lead, tellurium, and selenium adversely affect stability at temperatures as low as 250°C (6); trace quantities of metals present either as heterosiloxane components or as residual catalysts, or other stray impurities which form active sites (7-12), are also stated to exert a deleterious effect. Aluminum has been shown to be an active degradation catalyst for the oxidation of siloxanes at 300°C (13).

An improvement in the oxidation and thermal stabilities (below 200°C) of siloxanes containing active sites has been reported to result from the addition of such complexing materials as I_2 ; oxides of aluminum, beryllium, and iron; and amphoteric hydroxides. Studies at this Laboratory have demonstrated that other metals and metal compounds, particularly those of cerium, materially improve oxidative stability at 300° to 400°C (13,14). Since the upper limit of this temperature range is well above the accepted pyrolytic decomposition point of siloxanes, it appeared pertinent to reexamine the thermal behavior of the fluids at 400°C and to assess the effects of cerium. Preliminary results reported earlier (15) showed major differences in both the uninhibited thermal degradation processes and in the responses to cerium as the degree of phenylation was increased. Because of these differences, it will simplify the discussion of the present results to consider in separate sections the polydimethylsiloxanes (including lower homologs) and the copolymerized dimethyl-methylphenylsiloxanes and polymethylphenylsiloxanes.

EXPERIMENTAL PROCEDURE

Five representative, commercial, high-polymer fluids and two oligomers (the dimethyl hexamer and nonamer) were investigated. The high-polymer materials ranged in composition from a dimethyl silicone to one in which all of the dimethyl units were replaced by methylphenyl, the trimethyl end groups remaining unchanged. Complexed cerium was introduced into the commercial fluids by an improved version (14,16) of an earlier process (13); final cerium contents were in the range 0.02 to 0.03 wt-percent. Pertinent information about the high-polymer materials and their abbreviated designations for purposes of this report are listed in Table 1.

Pyrolytic stability tests were conducted at 400°C in a thermostatically controlled aluminum block furnace. Most of the data were obtained with two types of borosilicate glass cells: (a) straight tube cells, 16 x 150 mm, closed at the bottom, and sealed at the other end to a 3 x 60 mm capillary tube; and (b) side arm cells, similar to (a) except for the insertion, above the main body of the cell, of a side arm 6 x 200 mm to serve as an

air condenser closed at the end and inclined downward 60 degrees from the vertical. Modifications of these cells were made as required: (c) some straight tube cells were fabricated from quartz instead of borosilicate glass; and (d) side arm cells were modified by the introduction of a simple capillary viscometer axially supported from a ring seal in the upper section of the main tube. A bypass around the seal permitted repeated transfer of liquid for internal viscosity measurements. Because of the small length-to-diameter capillary ratios and short efflux times, the viscosity values have an accuracy of ± 10 percent at viscosities less than 20 cs.

Table 1
Properties of Siloxane Fluids Studied

Designation	Structural Type	Approx. Molecular Ratio (ϕ /Me)*	Viscosity (cs)	
			77° F†	100° F‡
DMS DMS-Ce§	Dimethyl siloxane	—	50	39.5 41.0
MPS (0.05)¶ MPS-Ce (0.05)¶	Methylphenyl siloxane (slightly phenylated)	0.05	50	59.9 60.9
MPS (0.20)¶ MPS-Ce (0.20)¶	Methylphenyl siloxane (moderately phenylated)	0.20	75	98.1 98.2
MPS (0.30) MPS-Ce (0.30)	Methylphenyl siloxane (moderately to highly phenylated)	0.30	100	81.3 84.3
MPS (0.75) MPS-Ce (0.75)	Methylphenyl siloxane (highly phenylated)	0.75	300	249 258

*From Ref. 5.

†Manufacturers' nominal viscosities.

‡Determined values.

§Indicates cerium-treated material.

¶Stripped of volatile components in a molecular still at 200°C and 8 μ pressure.

Cells were charged with up to 15-g samples introduced by means of hypodermic syringes. The cells were evacuated to less than 0.05 mm mercury, during which time they were warmed to 100°C, vigorously agitated to remove dissolved air and water, and then sealed at the capillary stem. When the above procedure was prefaced by passing a stream of helium through the warmed samples for 1 hr, similar pyrolysis results were obtained.

The straight tube cells (a) were employed for the precise study of viscosity changes with time. Internal viscosity cells (d) permitted continuous semiquantitative viscosity measurements, and side arm cells (b) permitted the collection of volatile breakdown products.

The more volatile degradation products were identified and quantitatively determined in a Consolidated Electrodynamics Corp. Model 21-103c mass spectrometer. Those portions of the breakseal tubes containing the pyrolyzed fluid were immersed in a series of low-temperature baths (-196° to -23°C) before the volatile components were permitted to expand into the mass spectrometer for analysis.

Other studies of volatile degradation products employed a combination of gas chromatography, infrared spectroscopy, and mass spectrometry. The vapor phase chromatograph (VPC) used was a Beckman Model GS-2 fitted with either a 6-ft DC-550 silicone column operated at 190°C, or a 12-ft Ucon HB-2000 column operated at 100°C. Individual chromatographic fractions were collected for subsequent identification by infrared or mass spectroscopy using a fraction collector and techniques previously described (17,18). Trapped fractions were transferred (usually in the vapor phase) to an infrared absorption cell or introduced into the inlet system of a high-sensitivity Consolidated Engineering Corp. Model 21-610 mass spectrometer.

Infrared spectral studies were carried out with one or more of three commercial spectrometers. Routine spectra were obtained with a Perkin-Elmer Model 21 spectrometer equipped with sodium chloride optics. High-resolution studies, mainly in the C-H stretching region, were made with a Perkin-Elmer Model 112 instrument fitted with a 300-grooves/mm Bausch and Lomb plane grating blazed at 3 μ . Finally, a few spectra were obtained with a Beckman Model IR-12 spectrophotometer.

Samples were studied as pure liquids, in CS₂ solution, and in the vapor phase. Most liquids and solutions were studied in fixed absorption cells of known thickness. However, because of the exceptionally strong absorption encountered, thin films of unknown thicknesses were required in order to obtain satisfactory spectra in the 8-14 μ region. Depending upon the amount of sample available, vapor phase spectra were obtained on samples contained in either a conventional 10-cm gas cell, a Beckman microgas cell (20-ml volume, 60-cm path length), or a Beckman minimum volume gas cell (1.95-ml volume, 7.5-cm path length).

POLYDIMETHYLSILOXANES

Results of Pyrolysis in Sealed Tubes

Figure 1 shows that the viscosity of the polydimethylsiloxane (DMS) decreased drastically during the first hours, but leveled off asymptotically after about 48 hr (with a 70-percent viscosity loss). With cerium present, only a 20-percent viscosity loss occurred over a 7-day period. During pyrolysis in side arm tubes, Fig. 2, DMS generated approximately 50 percent by volume of low-boiling degradation products within 48 hr; in contrast, DMS-Ce produced only 20 percent in 7 days.

The possibility that the surface of the borosilicate glass cells was catalytically active was of some concern. To test this possibility, the pyrolysis of DMS and DMS-Ce was repeated in straight tube cells fabricated from quartz. Since these results were in excellent agreement with the earlier ones, it was concluded that borosilicate glass did not significantly catalyze pyrolysis.

The above data suggest that the overall pyrolysis of DMS may be conveniently characterized as follows:



Figure 1 indicates that, at equilibrium, the reaction has proceeded a substantial extent towards the right, in contrast to that of the inhibited fluid which has obviously generated far fewer low-molecular-weight entities. True equilibrium was not obtained in the side arm experiments because the more volatile degradation products were distilled from the reaction mixture as they formed.

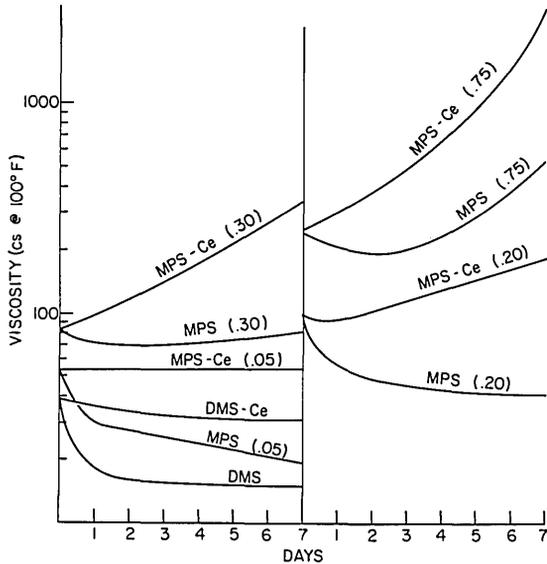


Fig. 1 - Viscosity changes of polysiloxanes with time during straight tube pyrolysis at 400°C (see Table 1 for identification of siloxanes)

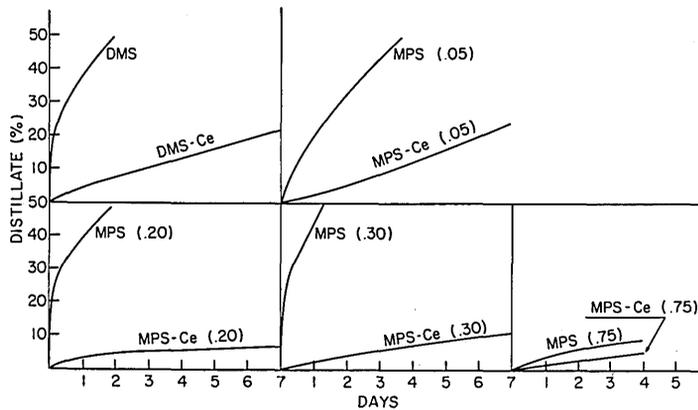


Fig. 2 - Generation of low-boiling products during side arm pyrolysis of polysiloxanes at 400°C (see Table 1 for identification of siloxanes)

Experiments with internal viscometer cells provide additional data on the effect of cerium on the generation of low-molecular-weight degradation products under equilibrium conditions. This was accomplished by pyrolyzing DMS and DMS-Ce in such cells and, during separate runs, collecting quantities of distillate judged to be either less than or greater than that present in a steady-state mixture. After freezing the distillate contained in the side arm, the viscosity of the residue in the reaction tube was determined *in situ*. The thawed distillate was then recombined with the residue, the side arm sealed off and detached from the cell, and the viscosity of the reconstituted fluid determined. Pyrolysis was then continued and viscosity changes were followed at appropriate intervals. The results are tabulated in Table 2.

In Run A with DMS, the low-molecular-weight distillate collected represented 27 percent of the original charge, and in Run B, 87 percent. Continued pyrolysis of the recombined distillates and residues showed that, for Run A, viscosities decreased to

Table 2
 Pyrolysis Studies of Dimethylsiloxanes at 400°C in Internal Viscometer Cells

	DMS				DMS-Ce			
	Run A		Run B		Run C		Run D	
Orig. visc. (cs at 100°F)	39.5		39.5		40.7		40.7	
Percent distilled vs time	%	Hr	%	Hr	%	Hr	%	Hr
	27	4	14	1	19	28	64	750
			20	2				
			51	48				
		87	96					
Residue visc. (cs at 100°F)	36		—		47		84	
Visc. change at 100°F (%)	-10		—		+17		+106	
Visc. (cs at 100°F) of combined residue and distillate vs time	Visc.	Hr	Visc.	Hr	Visc.	Hr	Visc.	Hr
	23	0	9.5	0	34	0	22	0
	19	3	12	17	34	3	23	2
	17	6	11	24	33	6	25	72
	13	9	11	114	32	9		
	12	26			33	26		

approximately the steady-state value shown in Fig. 1, and for Run B, they increased to this value.

Similar experiments were conducted with DMS-Ce, Runs C and D. In Run C, 19 per cent of the original charge was collected in 28 hr. The viscosity (34 cs) of the combined residue and distillate was virtually unchanged after additional pyrolysis.—an indication that, by coincidence, the quantity of distillate collected approximated that which would have been present at pseudo equilibrium in the reaction mixture after this period of heating if the reaction products had not been distilled away. This conclusion was confirmed by the viscosity data of Fig. 1. Considerably more distillate was collected in Run D, 64 percent over a 750-hr period. During the final 100 hr of this run, distillation virtually ceased. A slow viscosity increase occurred when the combined residue and distillate were heated for 72 hr. Had the pyrolysis of the recombined fractions been continued, it appears possible that the viscosity would have risen to about the value observed in the final treatment of Run C. The fact that the steady-state viscosity arrived at in the DMS-Ce sample is nearly three times that for equilibrium in the uninhibited DMS suggests that the pyrolysis reaction follows a different, as well as a slower, course when cerium is present.

Analysis of Major Degradation Products

To acquire additional information about the uninhibited process, the degradation products of two oligomers of the polydimethylsiloxanes were examined, in addition to those of the longer chain DMS. A simple nomenclature was used to designate the various dimethylsiloxanes detected in the decomposition products. Linear dimethylsiloxanes are represented by the symbol Si_x , where the subscript x refers to the number of silicon atoms in the molecule. Thus, Si_2 describes hexamethyldisiloxane; Si_3 , octamethyltrisiloxane; etc. Cyclic compounds are designated in a similar manner as $c\text{-Si}_x$.

Hexamer — Chromatographic analyses of the linear hexamer Si_6 showed it to be a very pure compound, there being no observable peaks other than the main one. A 15-g sample was sealed in a straight tube, which had been modified to include a breakseal, and heated at 400°C for 96 hr. This tube could be sealed to the vacuum system and the volatiles sampled without exposing them to air. Because of the volatility of the starting material, no separation of volatiles and nonvolatiles was attempted. A VPC of the thermally degraded material was obtained using the DC-550 silicone column. The results are summarized in Table 3. Perhaps the most surprising aspect of these data was the relatively small amount of degradation; 85 percent of the hexamer remained unchanged after subjection to conditions which would have seriously degraded a high-molecular-weight polydimethylsiloxane. To obtain a more useful description for the relative abundances of the various degradation products, the number of moles present in 100-g samples of degraded hexamer were calculated and are listed in the fourth column of Table 3. In making these calculations it has been assumed that each component has a density of 1.0 g/cc. The molar concentrations of the major products were nearly equal and very close to 0.01 moles/100 g.

Table 3
VPC Analysis of Thermal Degradation Products from
Linear Siloxane Hexamer (Si_6)* After 96 Hr at 400°C

Compound	Percent Concentration† (by Volume)	Molecular Weight	Moles/100 g‡	Equivalent Moles of Si	Equivalent Moles of CH_3
$\text{Si}(\text{CH}_3)_4$	trace	88	—	—	—
Si_2	1.4	146	0.010	0.020	0.060
$c\text{-Si}_3$	1.9	174	0.011	0.033	0.066
Si_3	2.1	204	0.010	0.030	0.080
$c\text{-Si}_4$	2.0	232	0.009	0.036	0.072
Si_4	3.0	262	0.011	0.044	0.110
$c\text{-Si}_5$	0.2	290	0.001	0.005	0.005
Si_5	2.8	320	0.009	0.045	0.108
Si_6	85.0	378	0.225	1.350	3.150
Si_7	1.7	436	0.004	0.028	0.064
			Total:	1.591	3.715

*Gas chromatography indicates this material to be better than 99 percent pure.

†Approximate values, based on area of chromatographic peaks only.

‡Assuming all compounds to have a density of 1.0 g/cc.

Listed in the last two columns of Table 3 are the equivalent moles of Si atoms and CH_3 groups contained in the various compounds. By individually summing these two columns and taking their ratio, the average value for the CH_3/Si ratio, 2.335, was calculated. This ratio agreed very well with the CH_3/Si ratio of 2.333 for the pure hexamer, suggesting a reasonably high degree of internal consistency for the analytical method.

Nonamer — The sample of nonamer Si_9 , of unknown purity, was pyrolyzed for approximately 48 hr at 400°C . Infrared and VPC analysis of the volatile fraction showed it to consist mainly of cyclic trimer, together with a moderate amount of linear dimer and a trace of cyclic tetramer. The liquid portion of the sample was analyzed by VPC using the DC-550 silicone column. Unfortunately, the maximum column temperature achieved (190°C) was not sufficient to elute any components boiling higher than the linear heptamer Si_7 , or the cyclic octamer $c\text{-Si}_8$, and a complete analysis of the sample was not possible. The observed components and their relative concentrations, again based on peak areas, are summarized in Table 4. As in the case of the hexamer, the average value for the CH_3/Si ratio in the degradation products could be calculated. The value thus obtained, 2.268, fell between the CH_3/Si ratios for Si_7 and Si_8 , which are 2.285 and 2.250, respectively. The corresponding ratio for the nonamer is 2.222. The discrepancy between the theoretical and observed CH_3/Si ratios may be due to several factors, e.g., (a) loss of some of the volatile portion of the sample, which consisted mainly of $c\text{-Si}_3$ and $c\text{-Si}_4$, during the sampling procedures, and (b) inability to elute siloxanes, having boiling points above that of Si_7 , from the chromatograph as distinct peaks, so that the analysis given in Table 4 does not include the concentration of Si_8 , Si_9 , or higher homologs.

Table 4
VPC Analysis of Thermal Degradation Products from
Linear Siloxane Nonamer (Si_9)* After 48 Hr at 400°C

Compound	Percent Concentration [†] (by Volume)	Molecular Weight	Moles/100 g [‡]	Equivalent Moles of Si	Equivalent Moles of CH_3
Si_2	0.1	146	0.001	0.002	0.006
$c\text{-Si}_3 + \text{Si}_3$	11.4	174	0.066	0.198	0.396
$c\text{-Si}_4$	9.1	232	0.039	0.156	0.312
Si_4	11.9	262	0.045	0.180	0.450
$c\text{-Si}_5$	4.0	290	0.014	0.070	0.140
Si_5	21.0	320	0.066	0.330	0.792
$c\text{-Si}_6$	0.6	348	0.002	0.012	0.024
Si_6	25.8	378	0.068	0.408	0.952
Si_7	16.2	436	0.037	0.259	0.592
			Total:	1.615	3.664

*Purity of nonamer unknown.

[†]Approximate values, based on area of chromatographic peaks only.

[‡]Assuming all compounds to have a density of 1.0 g/cc.

A comparison of the volatile pyrolysis reaction products from the nonamer and the hexamer reveals that the former contained larger proportions of both the linear and cyclic polymers of lower molecular weight. Calculations for the nonamer assumed that the 11.4-percent fraction containing the combined c-Si₃ and Si₃ was divided approximately equally between the two components.

Long-Chain Polydimethylsiloxane (DMS) — A sample of DMS was heated in a side arm cell for 3 hr at 400°C, after which the degradation products in the side arm amounted to 10-15 percent by volume of the original sample. The side arm was cooled in liquid nitrogen and the main tube was heated to 100°C so as to transfer the remaining volatiles to the side arm tube, which was then sealed off. After being warmed to room temperature, the side arm was opened and the contents analyzed by VPC using the 6-ft DC 550 column.

Table 5
VPC Analysis of Thermal Degradation Products from Polydimethylsiloxane (DMS) After 3 Hr at 400°C in Side Arm Cell

Compound	Percent Concentration (by Volume)*
Si ₂	0.2
c-Si ₃	56.5
c-Si ₄	32.9
c-Si ₅	5.2
Si ₅	1.5
c-Si ₆	3.7
Si ₇	trace
c-Si ₇	none

*These figures represent the percent concentrations of that side arm material which volatilized into the chromatograph at 190°C. (This material represents about 15 percent of the total collected in the side arm.)

The total area under the chromatographic curve was about 85 percent less than one would expect from the total injected sample, indicating that the material collected in the side arm contained an appreciable fraction that was relatively nonvolatile at 190°C, the operating temperature of the chromatographic column. The results from the remaining 15-percent, analyzable, low-boiling fraction differed markedly from those obtained for the hexamer and nonamer in that mainly cyclic siloxanes, together with a trace of what were probably linear dimer and heptamer, were observed. The percent concentrations of these products are summarized in Table 5. The major products for which chromatographic peaks were obtained were the cyclic trimer and tetramer, which constituted almost 90 percent of the total. Of the remainder, 9 percent were accounted for by c-Si₅ and c-Si₆.

Another portion of the side arm fraction was attached to a vacuum system and stripped of volatiles. A chromatograph of the residue showed no peaks, indicating that all of the volatile linear and cyclic polymers had been removed leaving only siloxanes having chain lengths greater than Si₇. An infrared spectrum of this residue showed a higher trimethyl end-group concentration than did the original DMS, indicating a shorter average chain length. This result is consistent with the strong predominance of cyclic products in the more volatile decomposition products.

Cerium-Inhibited Polydimethylsiloxane (DMS-Ce) — A sample of DMS-Ce was sealed in a side arm cell and heated for 70 hr at 400°C. The proportion of volatile material collected in the side arm was approximately one-fourth that produced by a 3-hr heating of uninhibited DMS. As with DMS, almost all of the condensate from the stabilized material contained cyclics, and the less volatile portion consisted of linear polymers larger than Si₇. (The results are shown in Table 6.)

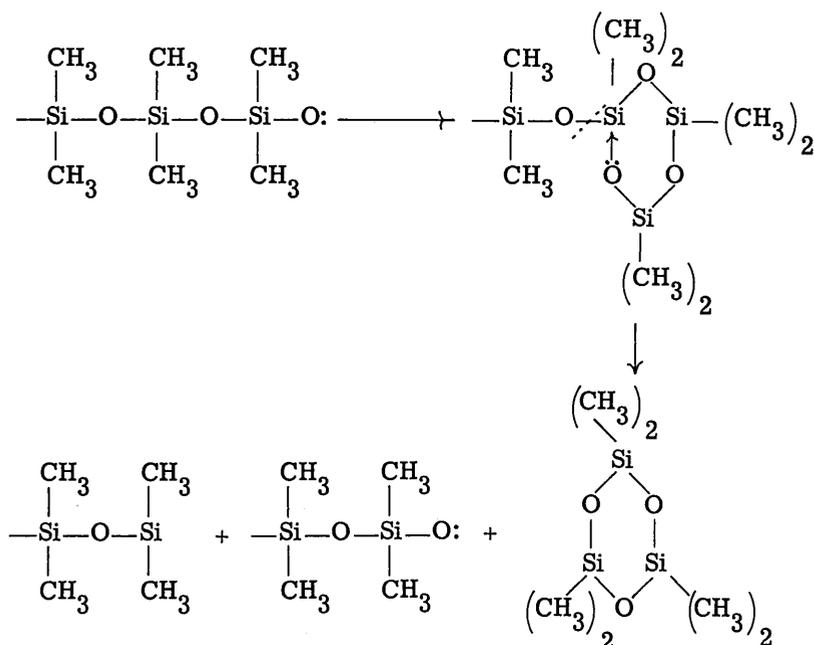
The above experiments with DMS and DMS-Ce were repeated, except that heating times of 6 and 72 hr, respectively, were employed to obtain equal proportions of distillate (20 percent). The composition of the degradation products was the same as that of the earlier experiments.

Table 6
 VPS Analysis of Thermal Degradation Products from Cerium-Treated Polydimethylsiloxane (DMS-Ce) After 70 Hr at 400°C in Side Arm Cell

Compound	Percent Concentration (by Volume)
Si ₂	trace
c-Si ₃	40.2
c-Si ₄	50.1
c-Si ₅	6.2
Si ₅	trace
c-Si ₆	3.6

Mechanism of DMS Thermal Degradation

The disparity between the rates of evolution of volatiles from cerium-treated and untreated polydimethylsiloxanes is remarkable when it is considered that the quantity of cerium present is very small, approximately one atom for every 200 to 250 molecules of polymer. Since the major pyrolytic degradation products of polydimethylsiloxanes are cyclic and short-chain linear polymers, rupture of $-\text{Si}-\text{O}-$ linkages must occur considerably more readily than that of $-\text{Si}-\text{C}$. As the bond energy of the former is approximately twice that of the latter, the basis for the preferential rupture of the $-\text{Si}-\text{O}-$ bond is not obvious. A commonly postulated explanation, which does not necessarily assume the influence of a metal impurity, is that rearrangement takes place through a low-energy path (19), e.g.,



Although this reaction sequence is possibly oversimplified, it provides a valid rationale of the observed facts.

The commercial DMS fluid used in the present investigation contained a normal complement of trace metal impurities, as shown by spark spectrographic analysis. The extraneous metal contents of the two lower polymers, the hexamer and nonamer, are not known but are probably not significantly different from that of the DMS. Reference has already been made to the catalytic thermal degradative effect of certain metals in siloxanes. It is, however, not necessary for the purpose of this study to make a choice between a pyrolysis mechanism based on uncatalyzed $-\text{Si}-\text{O}-$ bond rupture and one requiring the presence of extraneous metals.

Because it has been established (4,20,21) that, at equilibrium, both linear and cyclic molecules are present in a pyrolyzed polydimethylsiloxane, the reaction in Eq. (1) may now be characterized more precisely as



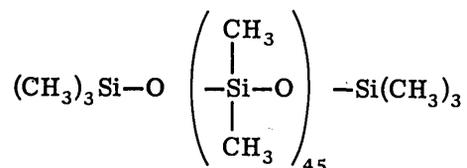
where $n \geq 2$ and $x \geq 3$. Using the hexamer Si_6 as an example, according to the reaction in Eq. (3) and the restrictions on n and x , two initial reactions can be written:



As a result of these reactions, the species formed may further react with the parent hexamer to generate larger linear molecules, and these in turn may either degrade into smaller linears and cyclics or increase in size. The final equilibrium concentration will depend on a large number of factors, especially the temperature and the equilibrium constants for the individual reactions, and a quantitative interpretation of the data would be difficult, if not impossible. It seems clear, however, that the qualitative aspects of the observed data are readily explainable in terms of the relatively simple equilibrium reactions listed above in Reactions 3 and 4.

The differences between the composition of the volatile pyrolysis degradation products of the hexamer and nonamer suggest that the shorter the chain length, the more stable the siloxane molecule. When the molecular chain is of sufficient dimension, possibly in the region Si_{10} , the effect of chain length on stability becomes of less significance because, for practical purposes, all $-\text{Si}-\text{O}-$ bonds are essentially equivalent, except for those subject to end-group effects.

With large polymers in the DMS category (mol wt about 3500) the average molecular structure is

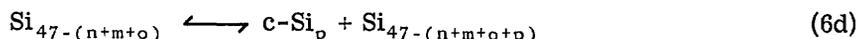
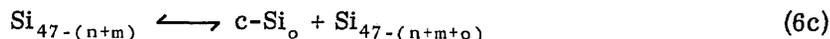
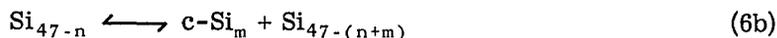


Thus an application of the reaction given by Eq. (3) yields the general degradation reaction



Although the formation of higher cyclics has been verified by other investigators, the data reported herein for DMS gives no evidence for the formation of significant amounts of cyclics in the $c\text{-Si}_{7-9}$ range, although they would have been detected if present. Thus n can assume values ranging from 3 to 6.

Further equilibration leads to the formation of increasing amounts of lower-molecular-weight linear siloxanes according to the reactions



where the subscripts n , m , o , and p can assume all possible combinations of integers ranging from 3 to 6. It is fairly obvious that such a process will lead to the formation of linear molecules having a wide distribution of molecular weights. Consider, for example, the molecular weight range possible after the completion of only four reaction steps, as given by Eq. (6d). The quantity $n+m+o+p$ can assume values ranging from 12 ($n=m=o=p=3$) to 24 ($n=m=o=p=6$), resulting in a linear siloxane distribution of Si_{23} to Si_{35} . Moreover, Si_{47} is only the average structure and, in reality, the original DMS has a size distribution of perhaps Si_{35} to Si_{60} . Application of the degradation process to such an initial distribution results in a size distribution of Si_{11} to Si_{60} . Such a process is consistent with the experimental observations described above.

Evidence for the degradation process postulated above is further fortified by the following experiment. A sample of DMS was heated in a side arm cell for 3 hr at 400°C , after which the side arm and its contents were removed, attached to a vacuum line, and the more volatile components (predominately cyclics) were separated by fractional distillation. The residue, which presumably contained mostly linear siloxanes of reduced molecular weight (about Si_8 to Si_{15}), was resealed under vacuum and again heated for 2 hr at 400°C . Results of the chromatographic examination of the pyrolyzed material are given in Table 7.

Table 7
VPC Analysis of Thermal Degradation
Products* from Additional Pyrolysis of
DMS Side Arm Tube Contents After 2 Hr
at 400°C

Compound	Percent Concentration (by Volume)
Si_2	0.6
c- Si_3	17.7
c- Si_4	48.4
c- Si_5	10.6
Si_5	3.7
c- Si_6	9.4
Si_6	5.1
c- Si_7	2.6
Si_7	1.7

*Side arm contents from DMS pyrolysis stripped of volatile components before additional pyrolysis of residue.

Comparison of the products from the twice-pyrolyzed material with those from the original DMS (Table 5) shows that, in the products of the second pyrolysis, the concentration of $c\text{-Si}_3$ was much smaller and that of the higher cyclics $c\text{-Si}_{5-7}$ was somewhat greater than at first. More significantly, the area under the chromatographic curve from the twice-pyrolyzed material indicated a higher proportion of lower-molecular-weight materials. These results were confirmed by infrared spectra.

It is also useful to compare the results in Table 7 with those for the straight tube pyrolysis of the hexamer Si_6 (Table 3) and the nonamer Si_9 (Table 4). The stability of the (about Si_8 to Si_{15}) material was not greatly different from that of the nonamer, and both were substantially less stable than the hexamer. This is additional confirmation of the earlier observation regarding the greater thermal stability of the lower oligomers.

The general reactions summarized above (Eqs. (3) through (6)) may now be examined from a slightly different point of view. They are consistent with a mechanism in which the initial thermal rupture of the polymer backbone, leading to the formation of a cyclic, initiates an anion-propagated chain reaction, which may be characterized as an "unzipping" process. Such a reaction would in all likelihood continue until (a) the residual linear residue was too short to cyclize readily, or (b) the anionic chain propagation was deactivated by recombination or proton acquisition, or (c) an appropriate site was available to absorb the activation energy involved in the degradation process.

Although the reactions described account for the greater part of the thermal degradation products of DMS, other reactions do occur. As shown in Table 8, mass spectrographic studies revealed that methane and hydrogen were also generated. No significant differences in concentration were noted between the DMS and DMS-Ce products; the quantities involved were sufficiently small to be considered second-order effects.

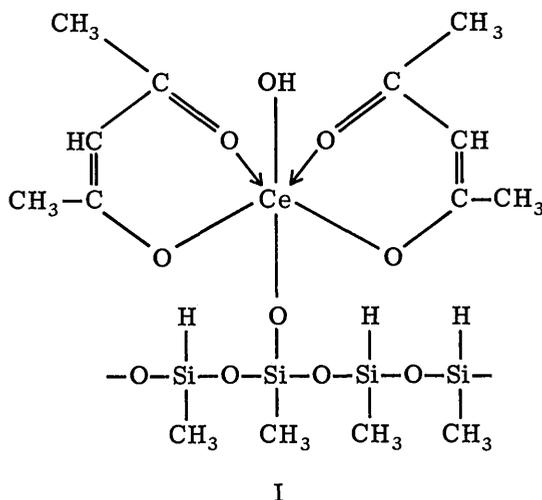
Table 8
Mass Spectrographic Analysis of Siloxanes After Pyrolysis in
Straight Tube Cells at 400°C for 72 Hr

Designation	Moles/100 g Siloxane		
	Hydrogen	Methane	Benzene
DMS	0.4×10^{-4}	0.4×10^{-3}	none
DMS-Ce	0.1×10^{-5}	0.3×10^{-3}	none
MPS (0.20)	0.3×10^{-3}	0.01×10^{-3}	3×10^{-6}
MPS-Ce (0.20)	0.3×10^{-3}	0.03×10^{-3}	3×10^{-6}
MPS (0.75)	0.4×10^{-3}	0.01×10^{-3}	1×10^{-6}
MPS-Ce (0.75)	0.3×10^{-3}	0.03×10^{-3}	2×10^{-6}

Mechanism of DMS-Ce Thermal Stabilization

The experiments described have revealed rather important changes that occur in the pyrolytic decomposition of polydimethylsiloxanes as a result of the addition of cerium. Before a mechanism is suggested to explain these changes, it is appropriate to summarize what is known about the form in which cerium is present in stabilized siloxanes (16).

The configuration of the cerium acetylacetonate-methylhydrogensiloxane (MHS) adduct is believed to approximate the following (16):



When DMS is stabilized by admixture with the MHS adduct and aerating at 270°C, the following reactions are likely to occur:

1. The ligands are oxidatively destroyed.
2. Residual hydrogen in the MHS is oxidized to silanols which:
 - a. react intermolecularly with basic ceryl acetylacetonate,
 - b. condense with themselves intramolecularly to form silsesquioxanes, or
 - c. condense intermolecularly with silanol groups produced in the DMS molecule by oxidation.

The precise configuration of the resultant cerium-containing structure has not yet been established. Useful discussion can be based on the postulate that cerium becomes essentially an integral component of the siloxane system, being bonded to silicon through oxygen. Its valence state can be 3 or 4, and it may have a coordination number of 6 or 8. In this state, cerium could reasonably constitute an active site, capable of participating in further reactions. One entity available for reaction at these sites is an anion generated as a result of thermally induced rupture of the $-\text{Si}-\text{O}-$ bond. Statistical considerations indicate that a cerium atom would nearly always be available in the vicinity of the rupture (14).

It could be assumed that the probability of this anion being within reacting distance of its own chain is greater than that of getting within reacting distance of the cerium. Since, however, the experimental evidence shows that the presence of cerium reduces the rate of cyclic formation, there is a strong implication that the activation energy required for reaction of the cerium complex with the anion must be substantially smaller than that for rupture of the $-\text{Si}-\text{O}-$ bond involved in the formation of a cyclic. The structure resulting from the interaction of the anion with the cerium site would have a net negative charge. Electrostatically attracted siloxane cations would be likely to react with one of the anions of the complex, thus regenerating the $-\text{Si}-\text{O}-$ bond originally destroyed by rupture and leaving the complex again neutral.

The above sequence, although oversimplified, does provide a useful point of departure to elucidate the role of cerium. In the normal course of events, rupture of an —Si—O— bond initiates the "unzipping" process; if, however, the Si—O anion is even momentarily stabilized, as by interaction with cerium, the subsequent reaction then need not follow its usual course leading to the formation of cyclics.

The suggested mechanism usefully explains a number of phenomena observed during the pyrolysis of DMS and DMS-Ce:

1. Primarily cyclics are evolved very slowly from DMS-Ce. If the proposed stabilization mechanism were completely efficient, there would of course be no evolution of low-molecular-weight entities. It is probable, however, that the process is not completely efficient; therefore, some cyclics would be formed, but it would be statistically improbable that the "unzipping" process of the type occurring in DMS would continue to any great extent before the termination reaction with the active cerium site would occur. A collateral result of this reduction in "unzipping" is that only a very few linear fragments are formed that are of sufficiently low molecular weight to be volatilized under the experimental conditions.

2. The viscosity of the nonvolatile residue from DMS is essentially unchanged from that of the original material, whereas that from DMS-Ce increases with time. Two factors probably account for the properties of the DMS residue: (a) the "unzipping" process, once commenced in a particular molecule, probably goes rapidly to completion; meanwhile, the majority of the remaining siloxane molecules are essentially unchanged, although they may be diluted to some extent with partially degraded, but relatively non-volatile, entities; and (b) secondary reactions do not occur to any significant extent because of the speed of the main reaction. With DMS-Ce, however, the "unzipping" reaction proceeds more slowly. Thus secondary processes resulting in fragmentation and recombination become increasingly important.

3. The evolution of volatile degradation products from DMS-Ce ceased after about 650 hr of pyrolysis. This increasing stability of the residue may be a result of the increasing concentration of cerium. No experiments were performed to establish the optimum cerium concentration for thermal stability at 400°C .

PHENYL-CONTAINING SILOXANES

Results of Pyrolysis in Sealed Tubes

The behavior of these phenyl-substituted siloxanes under thermal stress differs in important respects from that of the dimethylsiloxanes. In the straight tube cell experiments, as the phenyl content of the untreated methylphenylsiloxanes (MPS) increased, the viscosity-time patterns increasingly diverged from that of DMS. Although viscosity decreases similar to those shown by DMS were encountered with MPS (0.05) and MPS (0.20), they were smaller than that of the fully methylated fluid. With MPS (0.30) an initial minor viscosity decrease was followed by a slow increase, so that by the end of 7 days its viscosity had returned to its original value. The behavior of MPS (0.75) resembled that of MPS (0.30), except that its viscosity increase was more pronounced. Commencing on the 2nd or 3rd day, the viscosity of the former increased rapidly; at the conclusion of the run it was about twice that of the original oil.

Like DMS-Ce, cerium-inhibited MPS fluids displayed viscosity changes markedly different from those of their uninhibited precursors. MPS-Ce (0.05) underwent virtually no change, whereas MPS-Ce (0.20) showed an initial viscosity decrease of minor proportions, followed by an increase. The two more highly phenylated fluids showed no initial viscosity decrease, but rather an immediate and relatively steep rise — MPS-Ce (0.75)

exhibiting the larger rate of increase. When runs with the latter fluid were extended for an additional 2 or 3 days, gelation resulted.

In the side arm tube experiments, Fig. 2, with the exception of the highly phenylated MPS (0.75), all uninhibited phenyl-containing fluids produced at least 50 volume percent of low-boiling degradation products within 48 hr. In this respect they resembled the behavior of DMS. The condensate from MPS (0.75) was only about 10 percent of the original volume after 4 days of pyrolysis, and the run was terminated at this point because the residue became excessively viscous. Except in the case of MPS (0.75), the cerium additive significantly reduced the rate of evolution of degradation products from all of the MPS fluids. The addition of cerium to MPS (0.75) reduced the rate of evolution of volatiles only slightly.

Analysis of Major Degradation Products

Samples of MPS (0.75) and MPS-Ce (0.75) were pyrolyzed for several days at 400°C in side arm cells, and approximately equal volumes of condensate were collected. Condensates were chromatographed in the 12-in Ucon HB-2000 column; the results are shown in Table 9. The largest individual component was benzene, about 95 percent in the case of MPS (0.75) and 99 percent for MPS-Ce (0.75). The remaining volatile material in each case consisted of the disiloxane Si_2 and a mixture of compounds containing Si-H groups.

Table 9
Thermal Degradation Products from MPS (0.75) and
MPS-Ce (0.75) Collected as Side Arm Distillate During
Pyrolysis at 400°C (VPC Analysis)

Compound	Relative Concentration (by Volume)	
	MPS (0.75)	MPS-Ce (0.75)
Benzene	94.6	99.2
$(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$	1.9	0.4
$\begin{array}{c} \text{H} \\ \\ (\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3 \\ \\ \text{CH}_3 \end{array}$	1.7	0.2
$(\text{CH}_3)_3\text{SiH}$	1.1	0.1
$\begin{array}{c} \text{H} \\ \\ (\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_2 \end{array}$	0.5	< 0.1
Other	*	*

*Traces of seven other unidentified constituents.

The residues in the main cell bodies appeared to be identical. Infrared absorption analysis revealed bands attributable to residual benzene and Si-H. In comparison with the original material, intensities of bands due to Si- ϕ and Si-(CH₃)₃, decreased, whereas those due to Si-O increased.

Additional studies were made in straight tube cells of the generation of hydrides from MPS (0.20) and MPS (0.75) fluids and from their cerium-containing counterparts; for comparison DMS and DMS-Ce were also examined (Table 10). Neither DMS nor DMS-Ce developed hydrides during exposure to 400°C; in fact the minor quantity of hydride present in the original DMS-Ce, probably a result of unreacted MHS in the adduct, disappeared during pyrolysis. On the other hand, the nearly hydride-free highly phenylated MPS (0.75) fluids, both with and without cerium, contained 0.65 and 0.86 percent hydride groups, respectively, after 7 days at 400°C. When the heating period for MPS (0.75) was extended for an additional 3 days, the hydride content increased to 0.77 percent. Pyrolysis of MPS (0.20) and MPS-Ce (0.20) produced hydride contents which were approximately half those of the highly phenylated fluids. It is apparent, therefore, that the pyrolysis-induced hydride content of the siloxanes is a direct function both of their phenyl contents and of exposure time to heat; it is not significantly affected by the presence of cerium.

Table 10
Effect of Siloxane Pyrolysis on Hydride Content at 400°C

Designation	Heating Period (Days)	Si-H Groups (Percent)
DMS	none	< 0.01
DMS	7	< 0.01
DMS-Ce	none	0.03
DMS-Ce	7	< 0.01
MPS (0.20)	none	< 0.01
MPS (0.20)	7	0.39
MPS-Ce (0.20)	none	0.05
MPS-Ce (0.20)	7	0.42
MPS (0.75)	none	< 0.01
MPS (0.75)	7	0.65
MPS (0.75)	10	0.77
MPS-Ce (0.75)	none	0.04
MPS-Ce (0.75)	7	0.86

When pyrolyzed methylphenyl-containing siloxanes were later exposed to air at ambient temperatures, they underwent significant viscosity increases. This behavior parallels that of methylhydrogensiloxane (MHS) and is a probable result of oxidation and/or hydrolysis of the hydride, followed by crosslinking through oxygen.

In other experiments, mass spectrographic analysis of volatile products from the pyrolysis of MPS (0.20) and MPS (0.75) fluids (Table 8) confirmed the presence of benzene, although only minute concentrations were observed because of its low vapor pressure at the analysis temperature. Both methane and hydrogen, on the other hand, have appreciable pressures under these conditions, and the low concentrations found were a reasonably accurate measure of the amounts actually generated. Cerium had little effect on the generation of these materials.

Effect of Structure on Pyrolysis-Induced Property Changes

The data presented are useful in explaining some of the gross changes observed during the pyrolysis of phenyl-substituted siloxanes. Figure 1 demonstrates that, as the phenyl content increases in going from DMS to MPS (0.75), the viscosity-time relationship undergoes drastic changes. In the case of DMS, the abrupt initial decrease in viscosity results from the formation of low-molecular-weight cyclics and linear entities; the limiting viscosity reflects the equilibrium mixture of dimethylsiloxanes. Since MPS (0.75) cannot form cyclic dimethylsiloxanes without undergoing rearrangement of a type which evidently does not occur, the "unzipping" process postulated for DMS cannot take place. What does in fact occur — a viscosity decrease followed by an increase — is evidently the result of at least two distinct processes. The first process reflects the diluting effect of the benzene generated. The second, crosslinking or some other polymerization process, takes place either concurrently with the first, or shortly thereafter. Since the second process is evidently the dominant reaction, the net result over a long time period is an increase in the viscosity of the fluid. Given a sufficient pyrolysis period, the fluid gels.

The effect of cerium on the pyrolysis of MPS (0.75) appears to be minor compared to its effect in the case of DMS. It will be recalled that the compositions of the degradation products from MPS (0.75) and MPS-Ce (0.75) were essentially identical, but the evolution rate from the latter fluid was slightly less than from the former (Fig. 2). With lesser amounts of low-molecular-weight degradation products thus available as diluents in MPS-Ce (0.75), the viscosity increase due to crosslinking would be more apparent (Fig. 1).

The thermal stability, in straight tube cells, of copolymers of dimethyl and methylphenylsiloxanes, i.e., MPS (0.05), MPS (0.20), and MPS (0.30), can be rationalized on the basis of their being hybrids of DMS and MPS (0.75). All are capable of forming cyclics and other low-molecular-weight siloxanes during pyrolysis, but as the methylphenyl content increases, the crosslinking effect, with its concomitant viscosity increase, assumes added significance. As a consequence, the viscosity-time behavior of pyrolyzed MPS (0.05) strongly resembles that of DMS, while the changes in MPS (0.30) more closely resemble those of MPS (0.75).

In view of the small quantity of degradation products resulting from the pyrolysis of MPS (0.75) in side arm tube cells, as compared to that from DMS (Fig. 2), it would be anticipated that MPS (0.30) would produce less volatiles than MPS (0.05). That no such relationship was observed over 24-hr test periods cannot be readily explained, unless it is assumed that MPS (0.30) contains some polydimethylsiloxane impurity.

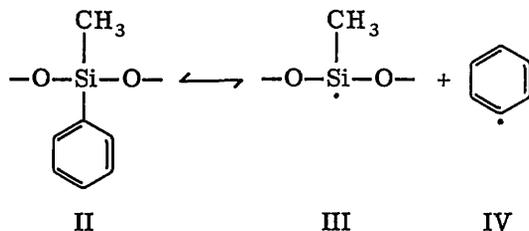
The effect of cerium on mixed dimethyl-methylphenylsiloxanes is consistent with the hypothesis that it effectively deactivates the ionic species formed by the rupture of —Si—O— bonds, thus diminishing degradation by "unzipping" when three or more such bonds occur consecutively. With the dimethylsiloxy bond thus deactivated, the fluid then approaches the stability of the remaining methylphenyl component. The data presented in Figs. 1 and 2 for these cerium-treated fluids support such an hypothesis.

Mechanism of MPS (0.75) Degradation

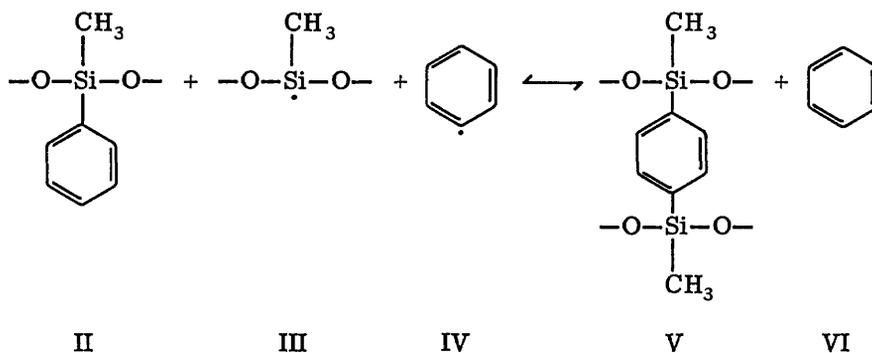
There remains to be discussed the mechanism of the more significant reactions involved in the pyrolysis of polymethylphenylsiloxanes. Although insufficient data are available to support a firm hypothesis regarding the decomposition mechanism of these fluids, enough have been obtained to justify limited speculation about the general processes involved. The most obvious chemical problem in the degradation of these siloxanes

is the source of hydrogen required for the formation of relatively large quantities of benzene and hydrides, and lesser amounts of hydrogen gas, methane, and other secondary decomposition products.

The formation of hexamethyldisiloxane and the various hydrides is probably a consequence of reactions and recombinations of trimethylsilyl and trimethylsiloxy end groups ruptured from the siloxane chain. Rupture of these groups from MPS (0.75) would result in mono- and difunctional fragments that could combine in a linear way to form higher-molecular-weight and more viscous siloxanes. The observed diminution in trimethylsilyl end-group concentration of the residual fluid with increasing pyrolysis time is consistent with such a mechanism. However, it seems unlikely that enough of such larger linear molecules result from this process to account for the rapid increase in viscosity and the final gelation observed in MPS (0.75) under thermal stress. It is probable, therefore, that much of the increased viscosity results from crosslinking reactions associated with the formation of benzene, Si-H groups, H₂ gas, etc. In the presence of air, bridging occurs through oxygen; in the absence of air, a phenylene bridge may be considered, particularly since it would account for many of the reaction products. Such a bridge may come about in many ways, the following reaction sequence being one possibility:

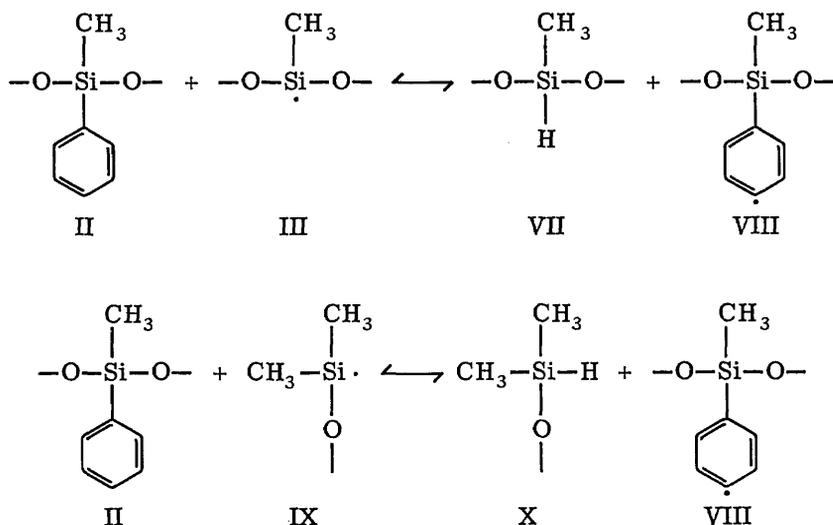


Abstraction of hydrogen from a phenyl substituent on another molecule would result in formation of the phenylene bridge and benzene:



Thus, for each such bridge formed, a mole of benzene would be generated. The quantity of benzene recovered from side arm cell experiments, after a pyrolysis period of sufficient duration to approach gelation of the residue, was of the order of 1.5 moles per mole of MPS (0.75). This is in reasonable agreement with the quantity which would result from the reaction sequence postulated above as crosslinking increased the viscosity towards the gelation point. Similar abstraction of hydrogen from a methyl, rather than a phenyl, substituent would result in methane and crosslinking through a methylene bridge. This reaction would appear to be of secondary importance in view of the relative quantities of benzene and methane found in degraded MPS (0.75).

Another degradation product which must be accounted for in any reasonable material balance is hydride. That hydride formation during pyrolysis is a function of phenyl content was shown in Table 10. Table 9 indicated that the hydride replaces either a phenyl or a terminal methyl group. Although the proportion of Si-H groups formed in pyrolyzed MPS (0.75) is significant, particularly when it is observed that no hydride is generated in DMS, its actual concentration is relatively small—approximately 1 mole per 10 moles of MPS (0.75). The hydride could be formed by a number of reactions, two possibilities being:



Other reactions involving, for example, formation of methyl rather than phenyl radicals would also account for these hydrides.

The reaction sequences depicted above show in a general way how the more important consequences of the thermal degradation of MPS (0.75) (and the cerium-containing derivative) could occur. Some of the postulated key reaction products, however, have not been identified, and it is probable that compounds or macromolecules were formed which have not been detected. These gaps in the data reflect the experimental and analytical difficulties inherent in reaction mechanism studies at high temperatures.

CONCLUSIONS

The effect of cerium in reducing the pyrolytic decomposition of polysiloxanes at 400°C has been studied. It is postulated that long-chain polydimethylsiloxanes decompose by an anion-propagated chain reaction leading primarily to the formation of cyclics. When complexed cerium is introduced into the polymer, this process is interrupted, presumably due to the interaction of the anion and cerium site. Recapture of an anion by the electrostatically induced approach of a cation results in a reconstituted siloxane chain, and a cerium site again is available for reaction.

Although cyclic compounds are not formed when polymethylphenylsiloxanes are pyrolyzed, rearrangements leading to crosslinking do occur. Cerium has little or no effect on this reaction; however, it stabilizes dimethyl-methylphenyl copolymers in proportion to the dimethyl content.

The practical utilization of siloxanes in high-temperature applications is dependent upon other factors of importance comparable to the resistance to pyrolysis, e.g., lubricity, oxidation stability, etc. Although work yet remains to improve the lubricating characteristics of these fluids, their useful attributes, particularly their stability and outstanding viscosity-temperature characteristics, make them attractive candidates in systems that can take advantage of the additional oxidation and thermal stability imparted by cerium. With regard to thermal stability, it would appear that in systems which can utilize siloxanes, the stabilized dimethyl or lightly phenylated materials would be of most interest because of their excellent inhibitor response and their resistance to major viscosity changes during long periods of exposure to heat.

ACKNOWLEDGMENT

The authors are indebted to Dr. Fred E. Saalfeld for the mass spectrographic analyses.

REFERENCES

1. Patnode, W., and Wilcock, D.F., *J. Am. Chem. Soc.*, 68:358 (1946)
2. Hunter, M.J., Hyde, J.F., Warrick, E.L., and Fletcher, H.J., *J. Am. Chem. Soc.* 68:667 (1946)
3. Andrianov, K.A., "Organic Silicon Compounds," State Scientific Technical Publishing House for Chemical Literature, Moscow, 1955; Translation F-TS-9191/V prepared by Technical Documents Liaison Office, Wright-Patterson Air Force Base, Columbus, Ohio, 1955
4. Carmichael, J.B., and Winger, R., *J. Polymer Sci., Part A*, 3:971 (1965)
5. Gunderson, R.C., and Hart, A.W., eds., "Synthetic Lubricants," New York:Reinhold, 1962, Chap. 7
6. Atkins, D.C., Murphy, C.M., and Saunders, C.E., *Ind. Eng. Chem.* 39:1396 (1947)
7. Lewis, C.W., *J. Polymer Sci.* 33:153 (1958)
8. Lewis, C.W., *J. Polymer Sci.* 37:425 (1959)
9. Kucera, M., Lanikova, J., and Jelinek, M., *J. Polymer Sci.* 53:301 (1961)
10. Kucera, M., and Lanikova, J., *J. Polymer Sci.* 54:375 (1961)
11. Kucera, M., Jelinek, M., Lanikova, J., and Vesely, K., *J. Polymer Sci.* 53:311 (1961)
12. Kucera, M., and Lanikova, J., *J. Polymer Sci.* 59:79 (1962)
13. Baker, H.R., and Singleterry, C.R., *J. Chem. Eng. Data* 6:146 (1961)
14. Baker, H.R., Kagarise, R.E., O'Rear, J.G., and Sniegowski, P.J., "The Stabilization of Silicone Lubricating Fluids at 300° to 400°C by Soluble Cerium Complexes," NRL Report 6156, Jan. 1965
15. Murphy, C.M., and Ravner, H., *J. Polymer Sci., Polymer Letters*, 2:715 (1964)
16. Baker, H.R., Kagarise, R.E., O'Rear, J.G., and Sniegowski, P.J., *J. Chem. Eng. Data* 7:560 (1962)
17. Saunders, R.A., "Analysis of the Spacecraft Atmosphere," NRL Report 5816, Oct. 1962
18. Saunders, R.A., "Contaminants in the SEALAB I Atmosphere," Report of NRL Progress, pp. 1-7, May 1965
19. Eilar, K.R., and Wagner, R.I., *Chem. and Eng. News* 40(No. 32):137 (1962)
20. Jacobson, H., and Stockmayer, W.H., *J. Chem. Phys.* 18:1600 (1950)
21. Gee, G., "Inorganic Polymers," pp. 67-77, London:The Chemical Society, 1961