

## Effect of Oxygen Pressure on the Thermal Degradation of a Methylphenylsilicone

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### I. Introduction

Aging of a silicone at relatively high temperatures involves the rupture of both the Si—C and of the Si—O bonds. When a Si—C bond is broken various volatile organic materials are evolved. In place of an organic group, a siloxane bond is formed, and more branching of the polymer occurs, followed by chain linking. The newly formed siloxane bonds impede the easy admittance of oxygen into the polymer molecule, slowing down the destruction process.<sup>1-3</sup> The rupture of Si—O bonds brings about the formation of silicone fragments of lower molecular weights.

Schemes involving the formation of labile hydroperoxides and free radicals have been proposed<sup>1,4-11</sup> to explain the formation of carbon monoxide, carbon dioxide, hydrogen, formaldehyde, and water obtained from the thermal and oxidative attack on methyl chain substituents. Methane, benzene, phenol, methanol, propane, and higher molecular weight materials may be considered as oxidation or recombination products of the activated phenyl and methyl radicals.

This paper describes the degradation of a methylphenyl-substituted silicone at 400°C. in air at less than atmospheric pressures. The experiments were carried out at initial pressures of air of 700, 600, 500, 300, 100, and 50 mm. Hg. In order to differentiate between oxidative-thermal and simple thermal effects, runs were carried out in argon at 300 mm. Hg pressure.

### II. MATERIALS

The silicone used was a methylphenylsilicone polymer having an R/Si ratio of 1.3 and a Me/Ph ratio of 0.9. This particular polymer was chosen because of its relatively high stability toward

oxygen attack at 400°C. The material was conditioned by heating in air for 3 hr. at 250°C., ground to 20-40 mesh (average particle size 15 mils), and heated for 26 hr. at 65°C. and 10 mm. Hg to eliminate any residual solvent. In its final stage, the ground polymer was pale yellow and hard. Mass spectrometric analysis of the products evolved by heating this silicone for 6 hr. *in vacuo* at 400°C. showed the presence of methane, ethane, carbon dioxide, hydrogen, propylene and ethylene at low individual levels averaging  $5 \times 10^{-6}$  mole/g. of sample. Approximately  $100 \times 10^{-6}$  mole of benzene/g. of sample was evolved, together with a clear silicone oil. No water, oxygen, or toluene was found.

### III. APPARATUS AND PROCEDURES

The investigation was carried out in a 1500-cc. closed gas-circulating system incorporating a magnetic balance<sup>12</sup> and connected to a mass spectrometer. This arrangement permits continuous monitoring of the amount of each gaseous constituent in the circulating system during oxidation and of changes in sample weight.

The sample (about 2.8 g.) is accurately weighed and placed in a platinum mesh basket which hangs from one end of the balance beam. The apparatus is evacuated and then filled with dry air or argon to a measured pressure. The pump is started to circulate the internal gas at a predetermined rate and the initial atmosphere is analyzed by mass spectrometer. The traps are then cooled with Dry Ice and the furnace, preheated to 400°C., is raised to surround the sample. The duration of the run is usually 6.5-7 hr. Weight readings are taken every 3 min. for the first 2 hr., then less frequently. Mass spectrometric analysis of the

internal atmosphere is made approximately every 20 min.

During the course of previous investigations<sup>8</sup> it was established that nitrogen did not react with silicone materials at temperatures up to 400°C. Having determined the number of moles of argon and nitrogen within the entire system at room temperature, it is then possible to use either of these gases as an internal standard to measure accurately the number of moles of gas evolved or consumed, in spite of the appreciable thermal gradient in the system.

#### IV. RESULTS

##### A. Weight Loss and Condensed Products

The behavior of the weight loss on varying the initial pressure is shown by Figure 1. The reduction in weight and the rates of weight loss in air remain practically constant from 700 to 300 mm. and then decrease with further decreasing pressures, until at 50 mm. they approach the values observed in argon. Comparison of the final weight losses in air with that obtained in argon indicates that a simple thermal effect is responsible for about 70% of the weight loss in the 700–300-mm. range, and about 92% of the loss at 50 mm. The balance of the weight loss is a result of oxidation. The weight loss rates in air and argon are very rapid within the first hour: approximately one half of the weight loss occurs within this period.

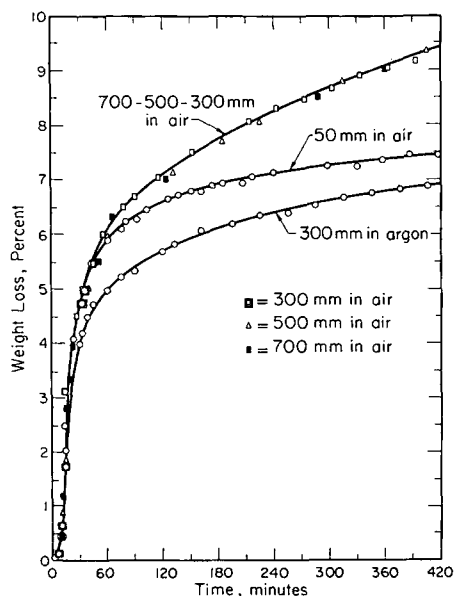


Fig. 1. Weight loss at 700, 500, 300, and 50 mm. initial air pressure and at 300 mm. in argon (400°C.).

The greatest fraction of the weight lost consists of a low molecular weight silicone which distills into the cold traps. Its basic structure is substantially that of the starting material. However, a well-defined peak at 6.9 microns is observed in the infrared spectra of the distillates from experiments carried out at 700, 600, 500, and 300 mm. This absorption peak, which falls in the region assigned to C=O, is not evident in the distillates from runs made at pressures below 300 mm. or in any of the residues. The absence of this peak in all the residues may indicate that, at least under these experimental conditions, the oxidized silicone fragments tend to volatilize rather than remain in the residue. Its absence from the distillates obtained from the low pressure runs may represent a change in the reaction mechanisms.

Water and benzene are the next most abundant oxidation products. The final amounts of benzene generated, at levels ranging from  $200 \times 10^{-6}$  to  $100 \times 10^{-6}$  mole/g. sample, decrease with decreasing initial air pressure. Carbon dioxide, carbon monoxide, methane, and hydrogen are evolved. Trace quantities of phenol, formaldehyde, methanol, propane, and higher molecular weight hydrocarbons are also formed.

All residues are darker than the original material, the degree of darkening increasing with rising initial pressures of air. At the conclusion of all the experiments the polymeric residue is harder than the starting polymer.

##### B. Consumption of Oxygen and Evolution of Gases

In all experiments, approximately one half of the oxygen consumption occurs within the initial 1-hr. period. The same is true for gas evolution.

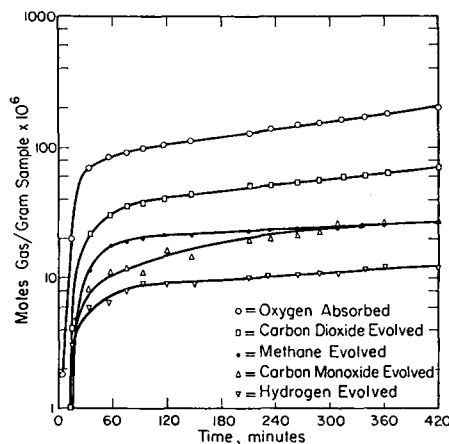


Fig. 2. Oxygen consumption and gas evolution at 100 mm. initial air pressure (400°C.).

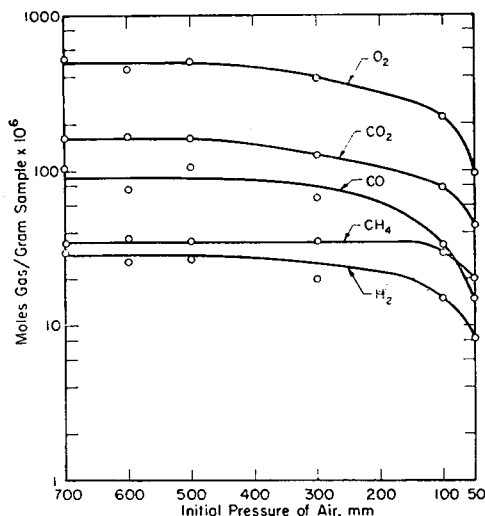


Fig. 3. Effect of pressure on oxygen consumption and gas evolution (400°C., 405 min.).

This is shown in Figure 2, where oxygen consumption and gas evolution at 100 mm. are plotted as functions of time.

Final absorption of oxygen and evolution of gases as functions of the initial pressure of air are shown in Figure 3. In general, only within a range of 500 to 50 mm. Hg does a decrease of pressure bring about a diminution of oxygen absorption and gas evolution.

The data in Table I, in which moles of gas/gram of sample/minute are given for various initial air pressures, establishes that the rates of consumption of oxygen (Fig. 4) and evolution of carbon dioxide decrease with decreasing pressures after the first hour of oxidation.

Considerable quantities of oxygen are consumed before any gas evolution begins (Fig. 2). This effect is true at all the pressures investigated. The induction period may be due to the time required for oxygen to reach an equilibrium concentration within the sample and for the formation of hydroperoxidic groups.

TABLE I

Rates of Oxygen Consumption and Carbon Dioxide Evolution After Initial Hour

Initial air pressure, mm. Hg	O <sub>2</sub> consumed, moles/g. sample/min. × 10 <sup>6</sup>	CO <sub>2</sub> evolved, moles/g. sample/min. × 10 <sup>6</sup>
700	0.91	0.28
500	0.80	0.22
300	0.65	0.18
100	0.35	0.049
50	0.054	0.020

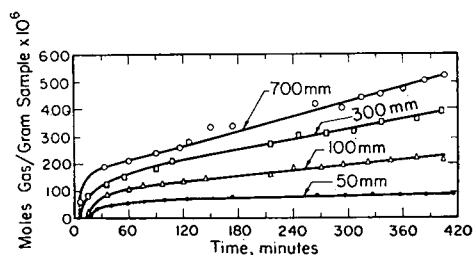


Fig. 4. Oxygen consumption at 700, 300, 100, and 50 mm. initial air pressure (400°C.).

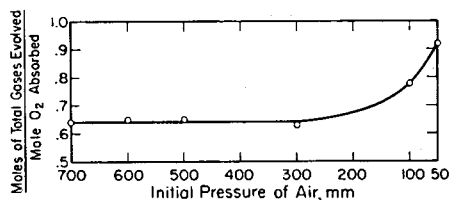


Fig. 5. Effect of pressure on ratio of total noncondensed gases generated to O<sub>2</sub> consumed (400°C., 405 min.).

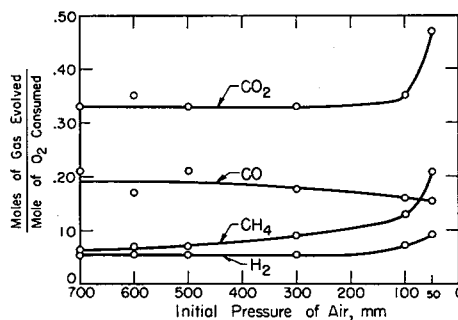


Fig. 6. Effect of pressure on ratio of individual noncondensed gases generated to O<sub>2</sub> consumed (400°C., 405 min.).

Within the initial 1-hr. period, approximately one half of the total weight loss is observed, both in air and in argon (Fig. 1). This is interpreted as representing the distillation of lower molecular weight silicone, either that originally present in the sample or that formed by the rupture of the Si—O bond. Consequently, the gas evolution within the first hour may be primarily associated with the oxidation of lower molecular weight silicones. The slowing down of the rates of oxygen consumption and of gas evolution indicates that the resulting residue is more resistant to oxidation.

Figure 5 indicates that the molar ratio of total noncondensed gases generated to the total oxygen consumed remains nearly constant from 700 to 300 mm. and increases with further decrease in pressure. This effect may be due to a change in reaction mechanism. This supposition is supported by the fact that while the carbon dioxide/

oxygen ratio increases with decreasing pressure, the carbon monoxide/oxygen ratio decreases (Fig. 6); also no carbonyl groups are observed in the silicone distillates obtained at the lower pressures.

The total pressure in the system remains approximately constant during the course of a run, since the oxygen consumption roughly equals the gas evolution. The maximum oxygen consumption and gas evolution represent only about 2% of the total gas in the system initially.

The change in oxygen partial pressure between the start and the completion of a run in the closed circulating system is only about 10% at 700 mm. of initial air pressure, increasing to about 30% at 50 mm. The conclusions reached are consistent with this experimental condition, and the results obtained extrapolate smoothly to those obtained from experiments conducted in an atmosphere of inert gas.

### V. Summary

The processes of the oxidative degradation of a methylphenylsilicone polymer at 400°C. in air are not altered appreciably by changing the pressure from 700 to about 300 mm. Further decrease in pressure to 50 mm. brings about a decrease in weight loss and in the absolute quantities of reaction products. The type and rate of reactions involving the fate of the oxygen consumed appear to become dependent on the pressure and oxygen concentration at the lower pressures (300 to 50 mm.).

A major percentage of the weight loss is due to thermal effect. This, coupled with the relatively small quantity of oxygen consumed, indicates that this type of silicone polymer is relatively stable to the oxidative thermal attack under the accelerated conditions of the experiments.

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### Synopsis

The manner in which changes in air pressure affect the thermal and oxidative degradation of a methylphenylsilicone was investigated as a function of time. A closed, gas-circulating system of 1500-cc. volume, incorporating a magnetic balance for following loss of weight in the sample, was employed. Finely ground samples were heated at 400°C. for 7 hours with initial pressures of air ranging from 700 to 50 mm. Hg. Mass spectrometric and infrared analyses identified the gaseous and the volatile products. At all pressures, low molecular weight silicones represented a major portion of the weight loss. Final weight losses in air approximated 10%, and approached, at the lowest pressure (50 mm.), the 7% observed in argon. Water and benzene were evolved, the latter at a rate that decreased with decrease in pressure. Traces of phenol, formaldehyde, propane, and higher molecular weight hydrocarbons were also given off. The evolution of carbon dioxide, carbon monoxide, methane, and hydrogen and the consumption of oxygen were followed in detail. Changes in air pressure from 700 to 300 mm. did not alter appreciably the rates of product evolution, oxygen consumption, and of weight loss. At lower pressures (300 to 50 mm.), however, the molar ratio of the total noncondensed gases generated to total oxygen consumed increased, indicating a possible change in reaction mechanism.

### Résumé

On recherche de quelle manière des changements dans la pression de l'air affectent la dégradation thermique et oxydante de la méthylphénylsilicone en fonction du temps. On emploie un système fermé, à circulation de gaz, d'un volume de 1500 ml. en y incorporant une balance magnétique pour suivre la perte de poids de l'échantillon. Des échantillons finement pulvérisés sont chauffés à 400° durant 7 heures, la pression initiale d'air variant de 700 à 50 mm. de mercure. La spectrographie de masse et l'analyse infrarouge identifient les produits gazeux, et volatils. A toutes les pressions les silicones de bas poids moléculaires constituent la majeure partie de la perte de poids. Les pertes finales en poids s'élèvent environ à 10% et se rapprochent à la plus basse pression (50 mm.), des 7% observés dans l'argon. Il se dégage de l'eau et du benzène, ce dernier à une vitesse qui décroît avec la pression. On trouve également des traces de phénol, de formol, de propane et d'hydrocarbure de poids moléculaire plus élevé. On suit en détails le dégagement d'anhydride carbonique, d'oxyde de carbone, de méthane et d'hydrogène ainsi que la consommation d'oxygène. Des changements dans la pression d'air de 700 à 300 mm. n'altèrent pas sensiblement la vitesse d'évolution des produits, la

consommation d'oxygène ni la perte de poids. A plus basses pressions (300 à 50 mm.) cependant, le rapport molaire de tous les gaz non-condensables dégagés par la réaction à la quantité d'oxygène consommée augmente, ce qui indique une possibilité de changement de mécanisme de réaction.

### Zusammenfassung

Die Art und Weise, in welcher Luftdruckänderungen den thermischen und oxydativen Abbau eines Methylphenylsilikons beeinflussen, wurde als Funktion der Zeit untersucht. Es wurde ein geschlossenes Gasumwälzsystem von 1500 cc Volumen verwendet, das mit einer magnetischen Waage zur Verfolgung des Gewichtsverlustes der Probe ausgestattet war. Fein gemahlene Proben wurden während 7 Stunden bei Ausgangsluftdrücken im Bereich von 700 bis 50 mm Hg auf 400°C erhitzt. Die gasförmigen und die flüchtigen Reaktionsprodukte wurden durch massenspektrometrische und Infrarot-Analysen identifiziert. Bei allen Drücken bildeten niedermolekulare Silikone einen Hauptanteil des Gewichtsverlustes. In Luft betrug der Gewichtsverlust am

Ende des Versuches etwa 10% und näherte sich beim niedrigsten Druck (50 mm) den 7%, die in Argon beobachtet wurden. Wasser und Benzol wurden gebildet, das letztere mit einer Geschwindigkeit, die mit fallendem Druck abnahm. Ausserdem wurden Spuren von Phenol, Formaldehyd, Propan und höhermolekularen Kohlenwasserstoffen abgegeben. Die Entwicklung von Kohlendioxyd, Kohlenmonoxyd, Methan und Wasserstoff, sowie der Verbrauch von Sauerstoff wurden genauer verfolgt. Änderungen des Luftdruckes zwischen 700 und 300 mm ergaben keine merkliche Änderung der Geschwindigkeiten der Bildung der Reaktionsprodukte, des Verbrauches des Sauerstoffs und des Gewichtsverlustes. Bei niedrigeren Drücken (300 bis 50 mm) nahm jedoch das Molverhältnis der gesamten entstandenen, nichtkondensierbaren Gase zum insgesamt verbrauchten Sauerstoff zu, was möglicherweise auf eine Änderung des Reaktionsmechanismus schliessen lässt.

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