

흡착 상태의 알킬실록산의 방사 : 2. 액상 메틸 실록산의 올리고마의 방사화학

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The Irradiation of Alkyl Siloxanes in the Adsorbed State: Part 2. The Irradiation Chemistry of Liquid Oligomeric Methyl Siloxanes

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요약 : 옥타메틸트리실록산, 데카메틸테트라실록산, 도데카메틸펜타실록산, 헥사메틸시클로트리실록산과 옥타메틸시클로테트라실록산의 감마선방사화학을 연구하였다. 기체와 액체 생성물의 수율을 각각 보고하였으며, 생성물 형성의 기구를 질량분광학적 분열 패턴에 의해 규명하였다.

Abstract : The gamma-ray irradiation chemistry of octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane, hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane has been studied. Gas and liquid product yields are reported. The mechanism of product formation is rationalized in terms of mass spectrographic fragmentation patterns.

INTRODUCTION

The phenomena associated with the irradiation

of organic molecules in the adsorbed state is of interest for a variety of reasons. Among these is the need for this knowledge in

order that we may define the structures of elastomers and other composites which have been polymerized or crosslinked by ionizing radiation. However, the basic question of energy transfer at the interfaces between polymers and solids is a broader and more fundamental problem and is increasingly the subject of investigation.

In the present paper, part 2 of a series, we discuss the irradiation of chemistry of a number of "higher" siloxanes. Specifically these were octamethyltrisiloxane (MDM), decamethyltetrasiloxane (MD₂M), dodecamethylpentasiloxane (MD₃M), hexamethylcyclotrisiloxane(D₃) and octamethylcyclotetrasiloxane (D₄).

A number of these materials have been studied in the past but, in view of the fact that the radiation yields from the present work will be used as the basis for defining energy transfer, it was deemed necessary to undertake this new study in order that we might have a constant base to which we could compare the radiation chemistry in the liquid and adsorbed states.

Experimental

The samples were all supplied through the courtesy of the General Electric Company, Silicone Products Department, Waterford, New York. Their purification and analyses were performed in an identical way to that described for hexamethyldisiloxane, in part 1 of this series.

The specifics as to the irradiation source, methodology and data treatment are also described in the above mentioned paper.

Results and Discussion

The volatile products (at -82°C) from the irradiation of MD₂M, D₃, and D₄ were similar to those found for MM, specifically hydrogen,

methane, and ethane. The gaseous product yields from the MD₂M, are compared to the MM yields in Table I while those for D₃ and D₄ are given in Table II.

The major liquid products for the linear siloxanes MDM, MD₂M, MD₃M and the cyclic siloxane, D₄, were analyzed by vapour phase chromatography. The resultant chromatograms with product assignments based on coincidental retention times are shown in Figs. 1 through 4. G values for each compound, based in part on the calibrations of Carmichael et al.¹⁾ are also listed in these figures. While exact assignments must await further experiments involving product isolation followed by mass spectrometric analysis a high level of confidence is warranted in the product peak assignments below MD₃M.

From Tables I and II the consistency in the separate and total gas yields from MM, MD₂M, D₃ and D₄ indicate a near independence of gas yield on the molecular weight of the parent compound.

The only significant difference lies in the methane yields and which are to be expected in view of the higher CH₃ content of MM and

Table I. G Values for Gas Yields from MD₂M

Gas	MM	MD ₂ M
H ₂	0.65	0.57
CH ₄	2.22	2.08
C ₂ H ₆	0.35	0.36
Total	3.22	3.01

Table II. G Values for Gas Yields from Cyclic Siloxanes D₃ and D₄

Gas	Siloxane D ₃	D ₄
H ₂	0.49	0.55 (0.89)*
CH ₄	1.91	1.91 (2.08)
C ₂ H ₆	0.35	0.29 (0.29)
Total	2.75	2.75 (3.26)

*Wolf and Stewart²⁾.

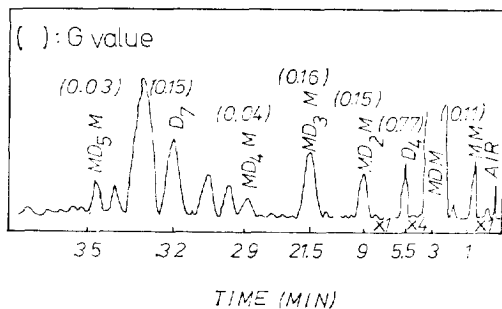


Fig. 1. Vapour-phase chromatogram of liquid products obtained from the radiolysis of octamethyltrisiloxane(MDM). (Column conditions: 90°C for 29 minutes, then programmed at 4°C/min.). (dose=111.65 Mrads).

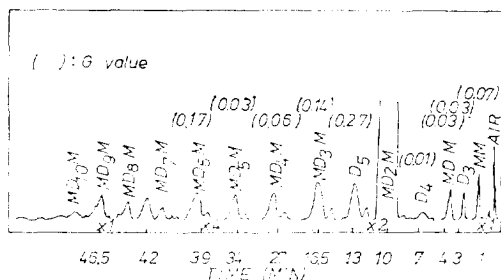


Fig. 2. Vapour-phase chromatogram of liquid products obtained from the radiolysis of decamethyltetrasiloxane(MD₂M). (Column conditions: initial temperature 70°C, temperature programmed at 4°C/min. from 170°—300°C). (dose=103.84Mrads).

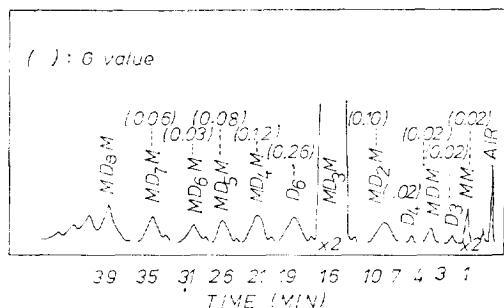


Fig.3. Vapour-phase chromatogram of liquid products obtained from radiolysis of dodecamethylpentasiloxane (MD₃M). (Column conditions: initial temperature 70°C, programmed at 4°C/min. to 300°C). (dose=103.84Mrads).

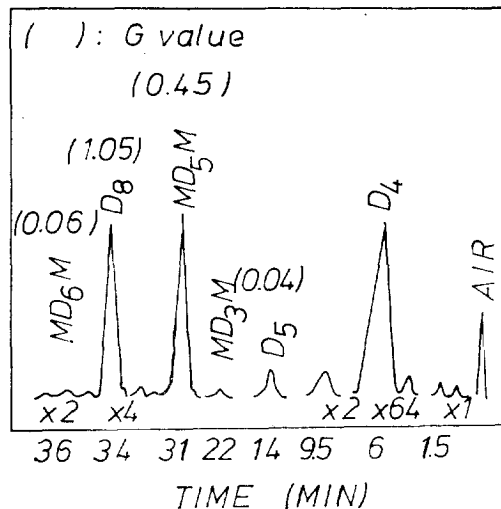


Fig. 4. Vapour-phase chromatogram of liquid products obtained from radiolysis of octamethylcyclotetrasiloxane (D₄). (Column conditions: initial temperature 90°C for 10 minutes; temperature programmed at 4°C/min). (dose=108.16 Mrads).

MD₂M. Comparison of these yields with the values reported by Wolf and Stewart²⁾ shows their hydrogen yields to be considerably higher than those found in the present work. This may well be due to their higher dose rate. Miller³⁾ has shown that all three gas yields can be markedly changed by increasing the dose rate.

The liquid products from MDM, MD₂M, and MD₃M, shown in Figs. 1 through 4, are in the main linear siloxanes with minor amounts of cyclic siloxanes. At a dose of 104.0 MR one gets, on the average, 10% decomposition. A perusal of the chromatograms shows that in all cases there are peaks which have not been identified. These are expected to be the products resulting from the formation of such crosslinks as -Si-CH₂-Si-, -Si-CH₂-CH₂-Si-, -SiCH₂CH₃, and Si-Si. The consistency in the pattern, i.e. linear products followed by smaller amounts of cyclics, suggests that the mechanism which is operative in the case of MM is not extended to the high-

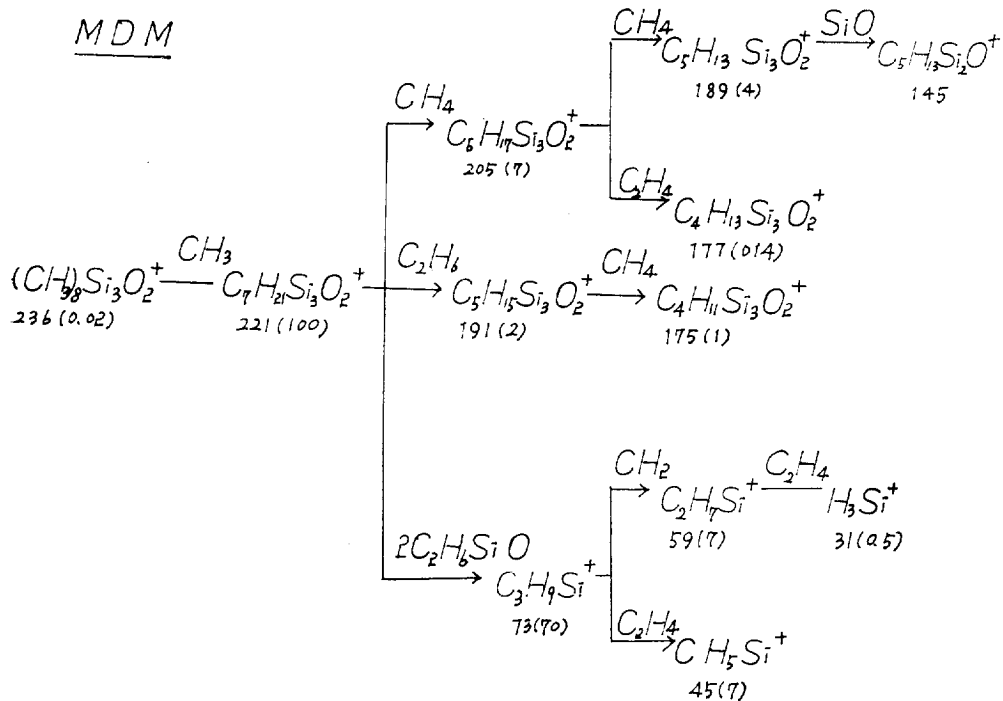


Fig. 5. Mass Spectrometric Fragmentation Pattern for Octamethytrisiloxane (Reference 4)

er siloxanes. The variation and amount of the products tentatively identified display the number of decay paths available to the particular molecule. This is exemplified by the mass spectrometric studies conducted by Orlov⁴⁾ on MDM, MD₂M and MD₃M. Orlov's pattern for MDM is reproduced here, Fig.5, to illustrate this point. Fragmentation patterns for MD₂M and MD₃M, would serve the rationale equally well.

The observations of the present work agree with the Orlov pattern in that CH₃ is a major irradiation fragment. Such a high yield of CH₃ would suggest a high yield of the remaining (or complementary) fragments which, on coupling, would result in a large amount of dimer products. Examination of the chromatograms shows this to be the case.

The liquid products from the gamma-radiolysis of D₄, octamethycyclotetrasiloxane, Fig.4,

illustrates a different trend to that shown by the linear siloxanes in that the major portions of the liquid products are apparently cyclic dimer and the linear siloxane MD₆M. These observations agree with the results of Wolf and Stewart²⁾ from their studies on the gamma-radiolysis of D₄. Two general types of higher molecular weight products were identified, cyclic dimers and linear polydimethylsiloxanes, with the latter being formed in the greater amount. Kantor³⁵⁾ whose product isolations were evidently carried out by classical distillation techniques observed only the formation of cyclic dimers in his studies on the radiolysis of D₄.

The dimer products isolated by Kantor were the methylene and ethylene bridged compounds. These are to be expected on the basis of the high gas yields observed and are probably the

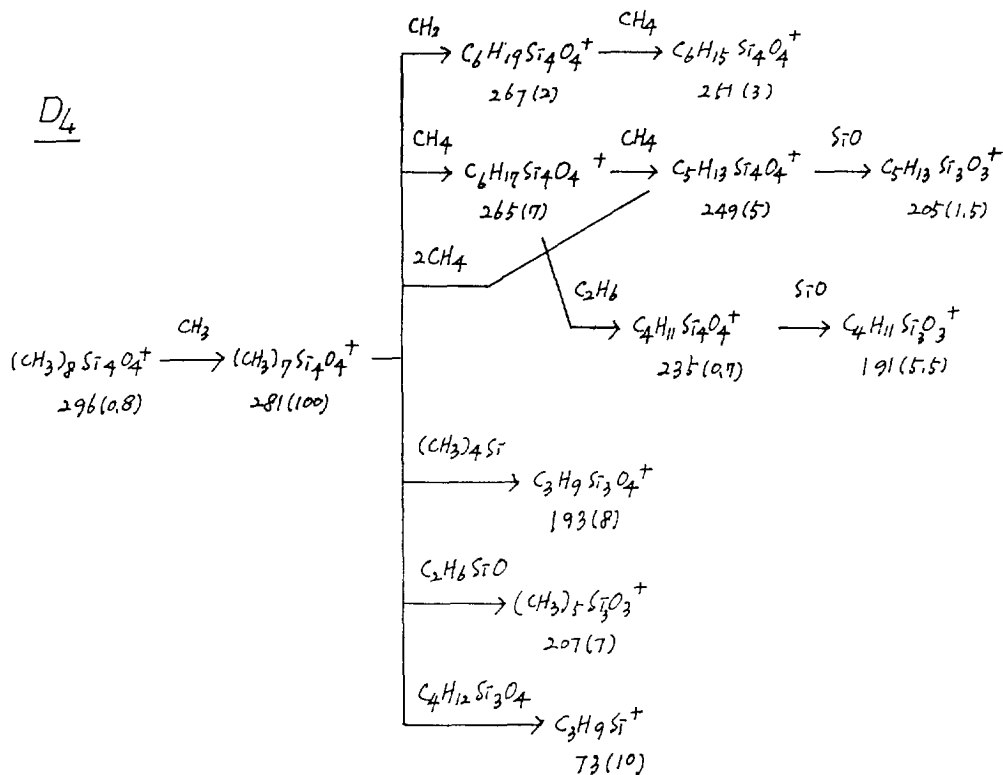


Fig. 6. Mass Spectrometric Fragmentation Pattern for Octamethylcyclotetrasiloxane (Reference 4)

result of free radicals combining. Further support for a predominant dimer yield is found in the mass spectrometric pattern reported by Orlov. In the case of D₄, the breakdown was as shown in Fig.6.

As can be seen, the primary ionization event involves a CH₃ ejection with the remaining(CH₃)₇Si₄O₄⁺ fragment being the only ion present in high yield. Neutralization followed by coupling could thus well explain the observed high dimer yields. Some caution in rationalizing mechanisms must be exercised however since to date no trapping or other such experiments which would shed further light on a radical path have been done.

Summary and Conclusions

The products found in the irradiation of the

higher siloxanes were similar in nature to those observed in the case of hexamethyldisiloxane and this indicates a common radiolytic pattern for the higher linear siloxanes. A number of compounds not found in previous investigations have been identified. The differences observed in the gaseous products yields, particularly methane, are discussed in terms of the different methyl contents of the various compounds.

While free radical chemistry has once again been assumed to be the primary path by which the majority of the radiation products have been formed, ionic mechanisms are also recognized as being important and the radiation chemistry of MDM, MD₂M, MD₃M and D₄. This latter mechanism has been discussed in terms of their fragmentation patterns in mass spect-

rographic studies.

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