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흡착 상태의 알킬 실록산의 방사 : 1. 액상 헥사메틸디실록산의 방사화학

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The Irradiation of Alkyl Siloxanes in the Adsorbed State: Part 1. The Irradiation Chemistry of Liquid Hexamethyldisiloxane

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요약 : 헥사메틸디실옥산의 방사화학을 에너지전달의 연구에 이용하고져 세밀히 연구하였다. 내부 표준을 이용한 생성물의 수율은 이미 보고된 값과 상당한 차이가 있음을 알았으며 메탄의 수율G는 2.22이었고, 이 값은 이미 보고된 값의 3.5배이다. 또한 이량체수율에 있어서도 상당한 차이가 있음을 알았다.

Abstract The irradiation chemistry of hexamethyldisiloxane has been reinvestigated preparatory to it's use in energy transfer studies. Using internal standards significantly different values in product yields from those previously reported have been found. The methane yield, G=2.22, is three halves that previously reported. Significant differences were also found in the dimer yields.

Introduction:

The ability of ionizing radiation to produce chemical changes in polyatomic molecules has been the subject of scientific investigation for a number of decades. Many types of radiation have been studied but in the main experimenters have utilized high energy electrons or gamma-rays.

Considering the energies associated with ionizing radiation, 1.17 and 1.33 m.e.v. in the case of the Co^{60} gamma-ray, relative to the ionization potential of an organic molecule, 10 -15 e.v.[1~3], it would be considered surprising if there was any degree of specificity to the pattern of products derived from a molecule-gamma-ray interaction. Indeed, at first glance it would seem that a complete dissociation of the molecule would occur followed by "random" recombination. Such is not the case. Despite the high energies involved, polyatomic molecules exhibit a high specificity in the manner in which they dissociate and recombine in an irradiation field. Often dissociation patterns are so well defined that radiation products of high molecular weight homologues can be predicted from the behaviour of small molecules.[4,5]

The acceptance of this basic premise, plus an interest in the more recent innovation in radiation chemistry of studying radiation induced reactions of adsorbed species served as the objective of the present work, that is, to determine the radiation chemistry of small siloxane molecules adsorbed on silica and to compare this chemistry both quantitatively and qualitatively to the radiation chemistry of the-same molecules in the liquid state.

In such a study, however, four factors are of predominant interest. First, a knowledge of the radiation chemistry pattern of siloxanes both small and large in the pure state; second, the changes in the radiation chemistry pattern of the adsorbed molecules relative to their behaviour in the pure state; third, the nature of the radiation-induced chemical reactions which occur between the adsorbent and adsorbate and fourth, the extent of energy transfer from one species, usually the adsorbent to the other.

In the present paper the radiation chemistry of hexamethyldisiloxane in the pure state is presented. In later papers the irradiation of this molecule in the adsorbed state will be discussed.

Experimental

Monomer Preparation

The hexamethyldisiloxane (MM), b.p. 100°C, was supplied through the courtesy of the General Electric Company. It was identified by elemental analysis, purified through repeated distillation, and shown by vapour phase chromatography to be of high purity (more than 99.9 %).

Irradiation Source

The cobalt-60 Gammacell 220 radiation source used is located at McGill University and operates at a dose rate of 0.37 MR/hr. The intensity of the source was measured by means of the Fricke Dosimeter. A $G_{Fe}3+=15.6$ was used in computing the dose rate.

Preparation of Samples for Irradiation

Samples were degassed on a vacuum line using the freeze-thaw procedure. To ensure the removal of any dissolved gases, the samples were subjected to seven such cycles. The MM was then condensed into glass ampoules, provided with break seals to allow the collection of the gas products, at liquid nitrogen temperatures. Samples were normally 2 ml (1.528g).

The dose to which a sample was subjected was measured by first irradiating the dosimeter solution in the irradiation cell used and then correcting for the nature of the sample being irradiated, using the electron density method. In this way the geometry of the cell was taken into account.

Collection and Analyses of the Gaseous Products

The gaseous products from the irradiated samples were collected and their total volumes measured using a Toepler pump. To prevent the loss of liquid products, the samples were held in dry ice during gas removal. A sample of the gaseous mixture was then removed for vapour phase chromatographic analysis. The chromatography was done on a 5 Å molecular sieve column, using helium as the carrier gas and having a thermal conductivity detector. Resolution of the hydrogen, methane, and ethane peaks was achieved by operating the column at room temperature for hydrogen and methane and then raising the column temperature to 150°C at 24°C/min for the measurement of the ethane. To make the measurements quantitative, calibration curves were made for the three gases. As a rule the response of peak height versus amount of gas injected was found to be linear. These calibration curves were then used to calculate the yields.

Analyses of the Liquid Products

Liquid products(i.e. non-volatiles at −82°C) were measured chromatographically on a 6′ X 1/4" SE-30 chrom W, silicone column using helium as the carrier gas. Because of the range in boiling points, the column was temperature programmed from 50 to 300°C.

The product assignments were based on a comparison of retention times with the retention times of known compounds. Further confirmation was made, in some cases, by comparing the chromatograms with those obtained by Dewhurst and St. Pierre[6] who used a dodecyl phthalate column. While the columns are not the same, it is assumed that the order of appearance of the products is. This assumption was borne out by the positions of the known compounds.

The effect of operating the column under isothermal conditions at various temperatures and different rates of heating was investigated to ascertain the optimum operating conditions.

To measure quantitatively the liquid products, a gas chromatographic method developed by Carmichael[7,8] and co-workers for determining the amounts of linear and cyclic methylsiloxanes in an equilibrated mixture, up to a molecular weight of 2530, was used. The method consists of analyzing standard mixtures containing accurately known quantities of toluene, linear and cyclic siloxanes. The weight response factors for each linear and cyclic species in the mixture are then calculated using the expression

$$R \text{ of } X = \frac{\text{wt. \% of X}}{\text{area of X}} \cdot \frac{\text{area of toluene}}{\text{wt. \% of toluene}}$$

where R is the weight response factor based on toluene. A component in an unknown mixture is then determined by adding a precise amount of toluene as an internal standard to a given weight of the mixture and measuring the toluene peak during the chromatographic analysis. The weight percent of the constituent is then obtained by multiplying the area percent, determined from the chromatograph by the corresponding weight response factor.

The composition of the standard mixture and the weight response factors are shown in Fig.1. The weight response factors for D_6 and other higher cyclic species and MD_4M through higher linear species were obtained by extrapolation, assuming the trend indicated by Carmichael et al.[7,8] This method of quantitatively determining the liquid products circumvents the assumption of Dewhurst and St. Pierre[6] that the sensitivity of the column for all products is equal and thus it is considered to yield more accurate results than they reported.

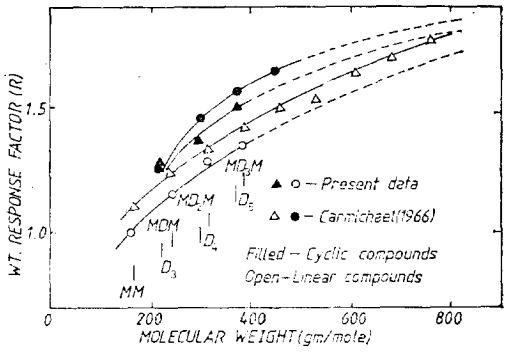

Fig. 1. Weight response factor (R) versus molecular weight of siloxanes.
MM : hexamethyldisiloxane
MDM : octamethyltrisiloxane
MD_2M : decamethyltetrasiloxane
MD_3M ; dodecamethylpentasiloxane
D_3; : hexamethylcyclotrisiloxane
D_4 : octamethylcyclotetrasiloxane
D_5 : decamethylcyclopentasiloxane

Table Ⅰ. G Values from Irradiated Hexamethyldisiloxne (MM)

Gas	Dewhurst and St. Pierre 11.6×10^{21}ev/g.	This work 5.9×10^{21}ev/g.
H_2	0.7	0.65
CH_4	1.4	2.22
C_2H_6	0.4	0.35
Total	2.5	3.22

Table Ⅱ. G Value of Silicone Compound Gases

Componnds	G value				
	H_2	CH_4	C_2H_6	Total	
MM	0.65 (0.7)	2.22 (1.4)	0.35 (0.4)	3.22 (2.5)*	
D_3	0.49	1.91	0.35	2.75	
D_4	0.55 (0.89)	1.91 (2.08)	0.29 (0.29)	2.75 (3.26)**	
MD_2M	0.57	2.08	0.36	3.01	
Polydimethylsiloxane	1.34	1.8	0.54	3.7	dose rate at 0.138 mr/min
by Miller(43)	1.25	1.07	0.76	3.1	13.8mr/min

*Dewhurst and St.-Pierre[6]
**Wolf et al.[9]

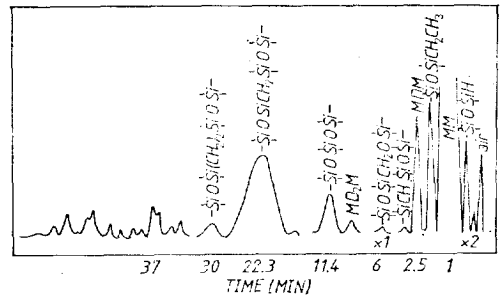

Fig. 2. vapour-phase chromatogram of the liquid products from the irradiation of hexamethyldisiloxane (MM). (Total dose 93.8 Mrads) (Column conditions: 90°C for first 33 minutes, temperature programmed at 24°C/min.).

Results and Discussion

The volatile products (at -82°C) from irradiated samples of hexamethyldisiloxane were found to be hydrogen, methane and ethane. The gas yields expressed as G values were calculated from yield versus dose curves and are compared to the data of Dewhurst and St.-Pierre[6] in Table Ⅰ. The gas yields were found to be linear with dose up to 95.6 MR.

It is evident from the data in Table Ⅰ that the results of Dewhurst and St. Pierre and those from the present study are in good agreement with exception of the case of methane. The difference may be due in part to their method of calibration between peak height and mole fractions or their values may be correct but a dose rate effect could be in evidence since their dose rate was considerably higher than that used in the present work. However, comparison of their yields with those obtanied by other workers on higher siloxanes would suggest their reported value for CH_4 is simply too low (Table Ⅱ). The observed difference from the present work is considerable, representing a 0.7 G or 50% increase, and an

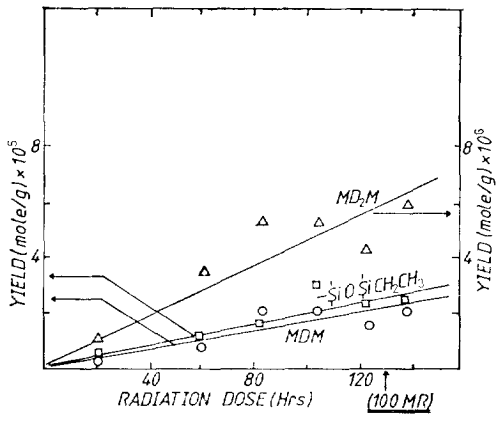

Fig. 3. Liquid product yields versus irradiation time for hexamethyldisiloxane (MM). (dose rate=0.77Mrad/hr.)

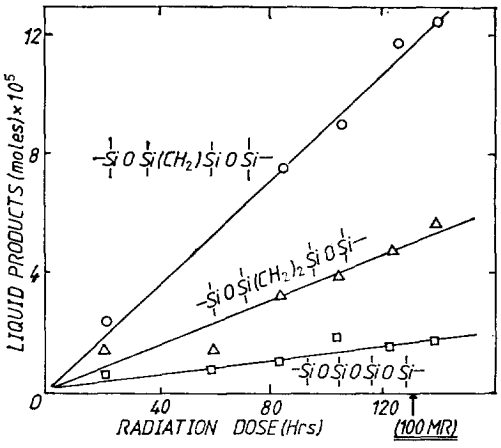

Fig. 4. Yields of dimeric liquid products versus irradiation time for hexamethyldisiloxane (MM). (dose rate=0.77 Mrad/hr.)

increase in the total G gas of more than 25%. This observation is of great importance to later discussions of the irradiation of adsorbed species where comparative yields are used as the criterion for energy transfer.

A chromatogram of the liquid or non-volatile products (−82°C) is shown in Fig. 2 along with the product identifications. The product yields as a function of dose are shown in Figs. 3 and 4 and the G values for the various products are listed in Table Ⅲ along with values previously reported. In assessing the apparent low precision of the MD_2M yields, Fig.3, it is necessary to keep in mind that this compound is present in concentrations about 0.1 of those of the other intermediate compounds.

As Figs. 3 and 4 and Table Ⅲ indicate, the liquid yields from irradiated hexamethyldisiloxane show a linear dependence on dose to about 80 MR. The products have been classified into the categories of low molecular weight intermediate molecular weight, dimer products, and higher molecular weight products.

The present work exhibits consiederable differences from the previously reported values for the liquid product yields. The sum of the G value of the low molecular weight products is found to be only 0.15 aganst 0.5 reported earlier[6] and the intermediates only 0.62 versus 1.8. In the important dimer region the total values(1.88) are in very close agreement with previously reported values (1.80), but the individual yields are different. Such marked differences must of course be rationalized and, once again, we believe that the main problem lies with the dose rate effect and with the lack of calibration in the previous work. A third factor would be the increased sensitivity of modern instruments as compared to the older ones. The latter point is exemplified by the fact that a considerable number of postdimer products were visible in the current study but could not be resolved in the earlier work.

The calibration factor is perhaps best exemplified by reference to Fig. 1. It is seen that the internal weight response factor calibration for the $-SiOSiCH_2CH_2SiOSi-$ is 1.27. Thus the assumption of equal response used in the work of Dewhurst and St. Pierre results in an underestimate of 27%. Errors of this magnitude go a long way toward explaining the observed

Table Ⅲ. G Values of Liquid Products from Radiolysis of Hexamethyldisiloxane (Vacuum irradiated at R.T.)

Mins, (Retention time)	Peak assignment	Molecules/100e.v. This work.	Molecules/100e.v. Previous data[6]
	(Low molecular weight products)		
	$Si(Me)_4$	0.03	0.2
	$MeSiOSiH(Me)_2$	0.12	0.3
	(Intermediate molecular weight products)		
	$MeSiOSiCH_2Me(Me)_2$	0.34	1.1
2.5	$MeSiOSiOSiMe(Me)_3$ (MDM)	0.21	0.5
	$MeSiOSiCH_2SiMe(Me)_3$	0.03	trace
6.0	$MeSiOSiCH_2OSiMe(Me)_3$	0.04	0.2
	(Dimer products)		
9.3	$MeSiOSiOSiOSiMe(Me)_4$ (MD_2M)	0.06	0.0
	(Dimer products)		
11.4	$MeSiOSSiOSiMe(Me)_4$	0.17	0.5
22.3	$MeSiOSiCH_2SiOSiMe(MeMe)(Me)_2$	1.16	1.0
30.0	$MeSiOSi(CH_2)_2SiOSiMe(MeMe)(Me)_2$	0.49	0.3

differences in yields. A knowledge of the different values has, however, caused us to undertake extraordinary precautions in terms of repetitions, with the result that a high degree of confidence exists in the stated precision of the values in the current work.

The observed products, both gaseous and liquid, can be reasonably accounted for on the basis of the free radical scheme proposed by Dewhurst and St. Pierre[6], assuming one radiation event per molecule.

$$(CH_3)SiOSi(CH_3)_2\cdot + CH_3\cdot \cdots 1$$

$$(CH_3)_3SiOSi(CH_3)_3 \rightarrow (CH_3)_3SiOSi(CH_3)_2CH_2\cdot + H\cdot \cdots 2$$

$$(CH_3)_3SiO\cdot + \cdot Si(CH_3)_3 \cdots\cdots 3$$

$$(CH_3)_3SiOSi(CH_3)_2^+ + CH_3\cdot + e \cdots 4^{11}$$

Although subsequent recombination reactions of the various fragments shown above can qualitatively account for the observed low molecular weight products, it is evident from the results that a consideration of only random recombination of these radical fragments cannot explain all the observations. This is particularly true for the higher molecular weight products, beyond SiOSi $(CH_2)_2SiOSi$, which were some fourteen in number and were undetected by Dewhurst and St.-Pierre[6]. However, because of their small yields, they made no attempt to identify these or to measure them quantitatively.

Assuming the radical scheme to be correct, hydrogen, methane, and ethane would be formed by such reactions as

$$H\cdot + H\cdot \longrightarrow H_2 \cdots\cdots 5$$

$$H\cdot + RH \longrightarrow H_2 + R\cdot \cdots\cdots 6$$

$$CH_3\cdot + H\cdot \longrightarrow CH_4 \cdots\cdots 7$$

$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot \cdots\cdots 8$$

$$CH_3\cdot + CH_3\cdot \longrightarrow C_2H_6 \cdots\cdots 9$$

This scheme invokes a mechanism which is based entirely on free radicals for the production of the gaseous products. It is, however, too simple a rationale, since both Wolf and Stewart[9] and Dewhurst and St.-Pierre[6] found

that the presence of the radical scavenger, iodine, had the effect of decreasing the methane and hydrogen yields without changing the ethane yield. Dewhurst and St. Pierre observed that 10^{-2} M iodine decreased the G values of hydrogen from 0.7 to 0.4 and methane from 1.4 to 0.7, while the ethane, in the manner of a "molecular reaction", remained unchanged at a G value of 0.4. If iodine so greatly affects the reactions by which H_2 and CH_4 are formed, why not the biradical reation, 7, in which ethane is formed? One can argue that reaction 7 occurs in the manner depicted but that it takes place within a radiation spur through a collision between an excited molecule with its neighbours. Iodine would thus be less able to intrude and interrupt the reaction. Charlesby et al.[10] have proposed such a mechanism for the unscavenged H_2 production, specifically:

$$\text{-Si-O-Si*} + \text{-Si-O-Si-} \longrightarrow \text{-Si-O-Si-CH}_2\text{-CH}_2\text{-Si-O-Si-} + H_2 \cdots\cdots 10$$

It is generally found in the irradiation of methyl silicones that the methane yield is two to three times the hydrogen and several times greater than the ethane yield[6,9]. This is also the pattern of the present data, as can be seen in Table Ⅱ where the gas yields obtained for a number of linear and cyclic silicones are shown. Any mechanism which satisfactorily accounts for the product ratios observed must explain both the high methane yield as well as the inability of I_2 to affect the ethane yield.

Some insight into such a mechanism may be gained from the work of Orlov[11] and Dibeler et al.[12] In gas phase mass spectrometric studies of MM, the following breakdown pattern was found.[11]

It is seen that methane is produced molecularly in steps b and i, both of which are low-yield events. Ethane is produced in a similar manner and again in low yield in step f. A possible precursor to both methane, through H abstraction, and ethane, through radical combination, is CH_3 which is produced in very high yield in step a. The susceptibility of the CH_4 yield to trapping by I_2 suggests that at least one-third of all methane is generated from the CH_3 radical. If this is so, it is difficult to rationalize the inability of I_2 to affect the C_2H_6 yield if CH_3 is a precursor to this compound.

Accordingly, on the basis of mass spectrometry patterns, one is led to the conclusion that path f, producing C_2H_6, and paths c,e and h of Orlov's scheme, all of which produce two carbon fragments, are the probable routes to ethane. The percent occurrence of reaction f is, as observed in the scheme, only 1.2% that of the primary breakdown, which is much less than we require to account for the ethane yield relative to that of methane shown in Table Ⅱ. However, in addition to ethane, the ethylene produced in the three subsequent reactions is sufficient to give a total amount of 10% relative to the methane. Assuming the ethylene can capture an H atom to form C_2H_5 then ethane could be formed by the hydrogen abstraction $C_2H_5\cdot + RH \rightarrow C_2H_6 + R\cdot$ reaction. This path would increase the ethane to 11.2%, thereby giving much better agreement between the measured and postulated ratio of methane to ethane, namely 6.3 and 9.5 respectively. This mechanistic path assumes that all of the $CH_3\cdot$ formed becomes CH_4. It is probable, however, that some of the ethane forms by a bimethyl radical combination, and this would bring the two values cited above still closer together.

On the basis of the products detected, the material balance for the radiolysis of MM would be that shown in Table Ⅳ.

The difference in the hydrogen balance and methyl balance is thought to be due to the

formation of higher unidentified products containing such crosslinks as -Si-Si-, -Si-CH_2-Si-, -Si-CH_2-CH_2-Si-, -SiCH_2-, -SiCH_2CH_2-. These products are not included in Table Ⅲ, but have been observed in radiolytic studies of hexamethyldisiloxane by Dewhurst and St. Pierre[6] and of polydimethylsiloxane by Miller[13]

Mechanistically there is little that need be added to the earlier discussion. However, since the present studies are being made for the purpose of comparison to the irradiation behaviour in the presence of a second species, SiO_2 consideration should be given to "non-visible" events. For instance, there are recombinations, by

Table Ⅳ. Materials Balance for Radiolysis of MM

H loss and gain Substance	Loss G value	Substance	Gain G value
$SiOSiCH_2CH_3$	0.34	$H_2(\times 2)$	1.30
$SiOSiCH_2Si$	0.03	CH_4	2.22
i $OSiCH_2OSi$	0.04	SiOSiH	0.12
$SiOSiCH_2SiOSi$	1.16		
$SiOSi(CH_2)_2$—SiOSi(×2)	0.98		
	2.55		3.64
	net gain 1.01		

CH_4 loss and gain Substance	Loss G value	Substance	Gain G value
SiOSiH	0.12	CH_4	2.22
SiOSiOSi	0.21	$C_2H_6(\times 2)$	0.70
SiOSiOSiOSi(×2)	0.12	$SiCH_3$	0.03
SiOSiSiOSi(×2)	0.34		
$SiOSiCH_2SiOSi$	1.16		
	1.95		2.95
	net gain 1.00		

either radical or ionic processes, which cannot be seen by the present method of analysis. Such a reaction would be (invoking homolytic bond cleavage) combinations of bd, ac

$\underset{a}{\text{-Si-O-}}\underset{b}{\text{Si}}\rightarrow \underset{b}{\text{-Si}}\cdot + \cdot\underset{a}{\text{O-Si-}}$ and cd. All form MM and all reactions are

$\underset{c}{\text{Si-O-}}\underset{d}{\text{Si-}}\rightarrow \underset{d}{\text{-Si-O}}\cdot + \cdot\underset{c}{\text{Si-}}$ "invisible".

Here there are not only a simple recombination phenomena ab or cd but an intermolecular reactions bd.

Summary and Conclusions

The irradiation chemistry of hexamethyldisiloxane has been studied in detail and product yields have been established for both gaseous and liquid products. Significant differences from previously reported values, most notably in the methane and in the methane and in the low and intermediae molecular weight liquid products, were found. It is difficult to account for the differences in the value found for methane, from that of a previous report, but it is shown that assumptions used in assigning yields in the previous work are unjustified and the new values reported herein are more dependable.

A materials balance is attempted and the products found are rationalized on the basis of fragmentation patterns found in mass spectrometric studies[11]

The new G values are sufficiently different from previous reports to have completely justified this investigation. More so in view of the fact that the present data are to be used as the standard for later investigations.

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