Radiation Stability of Organosilicon Compounds

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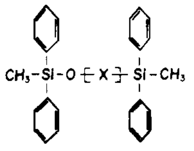
ORGANOSILICON COMPOUNDS exhibit a wide range of stability to high energy radiation. Quantitative data obtained on materials which received gamma radiation from a cobalt-60 source show that organosilicon compounds vary from rather sensitive to highly resistant. Remarks in the literature which classify silicones as poor in radiation resistance have been based on observations with a limited number of the less stable materials.

PROCEDURE

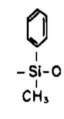
A quantitative measure of radiation damage was sought. Practically, this was achieved by determination of G values (number of molecules of gas produced per 100 e.v. of energy absorbed). The gas measured was formed initially on irradiation at room temperature in evacuated sealed vials, by γ-rays produced by cobalt-60 at rates between 100,000 and 550,000 rads per hour. Actual doses are indicated for each series of compounds. The doses were determined according to ASTM specifications (*1*).

Vials containing a breakoff tip were filled with the compounds, pumped on a vacuum line to less than 1-micron pressure, then sealed off and irradiated. Following irradiation, the arm containing the breakoff tip was sealed to a vacuum line containing a Toepler pump and calibrated gas buret. When the vial was opened, the contents were pumped through a liquid nitrogen trap into the gas buret. From the volume and pressure on this gas sample the G value for noncondensable gases ($G_{\text{noncondensable}}$) was obtained. On warming the trap, the condensed fraction was admitted to the buret. This gave the total volume of gas evolved and yielded a G gas value. After thorough mixing by the pump the total gas volume was sampled by admitting it to a small bulb. This was sealed off and analyzed by mass spectrometer.

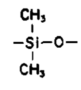
Table I. Phenyl-Containing Silicones



Compound Number	Central Group	G Gas	$G_{\text{cond.}}$	$G_{\text{noncond.}}$	ϵ_{methyl}
I	—	0.0144	0.011	0.00341	0.0826
II	A	0.031	0.0108	0.0202	0.093
III	B	0.0475	0.0120	0.0355	0.140
IV	C	0.0813	0.0111	0.0702	0.195
V	D	0.157	0.0096	0.147	0.245

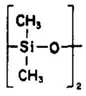


A



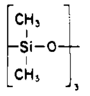
$$-\underset{CH_3}{\overset{CH_3}{Si}}-O-$$

B



$$\left[-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right]_2$$

C



$$\left[-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right]_3$$

D

RESULTS

The first series of compounds studied comprises siloxanes having methyldiphenylsiloxane end-blocking groups (Table I). The actual doses received by compounds in this series were between 76 and 159 megarads. These compounds were carefully purified by distillation. The first compound is a solid with a melting point of 50° C., and all the others are liquids. As the relative number of phenyl groups in the molecules increases, the G values for total gas evolution decrease.

The yield of noncondensable gases varies directly with the concentration of methyl groups. These G values for the noncondensable gases have been related to the composition of the samples by an adaptation of the method used by Burton (*2*), which defines an electron fraction parameter ϵ_{methyl} as:

$$\epsilon_{\text{methyl}} = \frac{\Sigma \text{ all electrons associated with methyl groups}}{\Sigma \text{ all electrons in molecule}}$$

This counts all electrons, not just valence state electrons.

The correlation between the electron fraction methyl, ϵ_{methyl}, and the $G_{\text{noncondensable}}$ is good (Figure 1). Here the logarithm of the $G_{\text{noncondensable}}$ is plotted against the electron fraction methyl. The equation of the straight line which fits the data is

$$\text{Log } G_{\text{noncondensable}} = 5.65\, \epsilon_{\text{methyl}} + \log 0.006$$

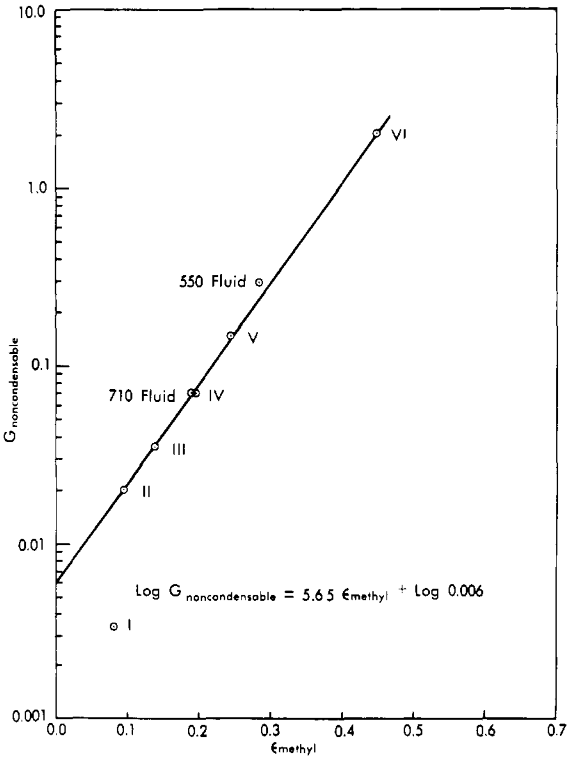


Figure 1. Relationship of electron fraction of methyl groups to $G_{\text{noncondensable}}$

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This equation seems valid for a range of fluids from a very high phenyl content to dimethylpolysiloxanes containing no phenyl groups. Point VI, for example, represents data for octamethylcyclotetrasiloxane and might be indicative of the behavior of linear dimethylpolysiloxane fluids of high molecular weight.

The one point which falls below the curve represents tetraphenyldimethyldisiloxane, a crystalline solid. This is the only compound in the list which was irradiated in the solid state. One might expect the mechanisms and extent of radiation damage to be different from those in a liquid. This is confirmed by dissolving the solid in the next higher liquid member of the series. The *G* value of the noncondensable gases produced by irradiation of this solution falls at the predicted point on the line.

Data published in a government report yield *G* values for two commercial fluids (Dow Corning 550 and 710 fluids) which also fit the curve very well (*3*). These fluids are silicone polymers containing both phenyl and methyl substituents, so the *G* gas values for total gas evolution had to be corrected for condensable gas evolution to yield points on the curve, $G_{\text{noncondensable}}$.

This correction was made possible by noting in Table I that the $G_{\text{condensable}}$ remains rather constant at an average value of 0.011. The condensable portion of the gas results from cleavage and fragmentation of the phenyl group, as can be shown by mass spectrometer analyses. The mass spectrometer analysis of the gases produced on irradiation of compound IV, in mole per cent, is:

Methane	47.1	Ethylene	1.2	Toluene	0.3
Hydrogen	46.7	Propane	1.2	C_2benzenes	0.07
Benzene	2.4	Ethane	0.5	Styrene	0.02
Propadiene	2.4	Acetylene	0.5		

This sample received 94 megarads.

Methane and hydrogen, the chief gaseous products, appear in the noncondensable fraction. The much smaller amounts of benzene and substituted benzenes appear in the condensable fraction and presumably arise from cleavage of phenyl groups.

The noncondensable methane and hydrogen seem most logically to stem from cleavage or decomposition of the methyl groups. The mass spectrometer analysis of the gases produced on irradiation of a low molecular weight dimethylcyclosiloxane, in mole per cent, is:

Methane	63.5	Ethane	5.7	Nitrogen	5.1
Hydrogen	24.5	Ethylene	0.2	Oxygen	0.98

This sample received 60 megarads.

Here the chief products are methane and hydrogen, methane being most abundant. The chief gaseous radiolytic decomposition product of most organic compounds is hydrogen. The possibility of dehydrogenation in an organic to produce an unsaturation no longer exists in an all methylsiloxane. Hence, methylsiloxanes produce chiefly methane by total group cleavage.

The second series of compounds was siloxanes containing only methyl substituents. The *G* gas values and electron fraction methyl data are:

		G Gas	ϵ_{methyl}
VI	$[(CH_3)_2SiO]_4$	2.01	0.45
VII	$[(CH_3)_3Si]_2O$	1.84	0.60
VIII	$[(CH_3)_3SiO]_4Si$	2.34	0.54

These samples received a dose of 60 megarads. There is no detectable condensable fraction other than the undecomposed volatile compounds themselves. Apparently there is no simple correlation in methylsiloxanes between *G* gas values and the electron fraction methyl. The differences observed may be the result of differences in structural features of the compounds.

Samples of one "all-methyl" siloxane, hexamethyldisiloxane, were irradiated separately in a nuclear pile and by γ-rays from cobalt-60. The comparison, in mole per cent, is:

	Methane	Hydrogen	Ethane
Cobalt-60	69.0	30.9	Not detected
Nuclear reactor	69.6	29.6	0.41

The dose from cobalt-60 was 60 megarads and the integrated dose from the reactor was 10^{17} μg. per sq. cm. and 10^{16} *nvt* (fast). Not only were the gas compositions nearly equivalent, but the total yields of gas were nearly equal, based on the absorption of approximately the same total amount of energy. There are some indications, not completely proved as yet, that the phenyl-containing siloxanes are more susceptible to neutron damage than to γ-rays. This phase of the work requires more study.

A third class of siloxanes is rather sensitive to radiation damage. When the *G*-gas value for hexamethyldisiloxane is compared with the of tetramethyldisiloxane:

	G Gas	H_2, Mole %	CH_4, Mole %	G_{H_2}	G_{CH_4}
Hexamethyldisiloxane	1.84	31.0	69.4	0.57	1.27
Tetramethyldisiloxane	4.18	72.0	26.0	3.01	1.09

it is evident that the compound containing the Si-H linkage is much more susceptible to radiation damage. Hexamethyldisiloxane in this experiment received 60 megarads, while tetramethyldisiloxane received 20 megarads. The mass spectrometer analysis is even more startling, for the ratio of methane to hydrogen is inverted in the case of tetramethyldisiloxane. From the composition data *G* values can be calculated for the two gases as shown above.

To obtain some idea of the relative stability of the Si-H linkage, it was convenient to define a specific *G* value for the cleavage of a particular bond.

$$G_{sp}(\text{Si-C}) = \frac{G(CH_4)}{\epsilon_C}$$

$$G_{sp}(\text{C-H}) = \frac{G_{H_2}}{\epsilon_H(\text{CH})}$$

$$G_{sp}(\text{Si-H}) = \frac{G_{H_2} - [G_{sp}(\text{CH}) \times \epsilon_H(\text{CH})]}{\epsilon_H(\text{SiH})}$$

where ϵ_C = electron fraction of the carbon atoms, $\epsilon_H(\text{CH})$ = electron fraction of hydrogen atoms on methyl, and $\epsilon_H(\text{SiH})$ = electron fraction of the hydrogen atoms on silicon.

Essentially a G_{sp} value is calculated for a linkage by dividing the *G* value for the gas produced by the cleavage of that bond by the electron fraction of the atom that is cleaved. To do this for the Si-H bond one must subtract from the total yield of hydrogen the gas derived from fragmentation of the methyl group.

	G_{sp}(Si-C)	G_{sp}(C-H)	G_{sp}(SiH)
Hexamethyldisiloxane	3.18	2.85	. . .
Tetramethyldisiloxane	3.34	2.85[a]	94.5 (calcd.)

[a] Assumed value.

G_{sp}(Si-C) is approximately the same in hexamethyldisiloxane and in tetramethyldisiloxane. G_{sp}(C-H) for hexamethyldisiloxane can be calculated directly. If this value is assumed to hold also in tetramethyldisiloxane, it is possible to calculate G_{sp}(Si-H). If these assumptions are correct, the Si-H bond appears to be about 30 times more sensitive to radiation rupture than C-H bonds or Si-C bonds.

The electron spin resonance (ESR) spectra of several irradiated siloxanes have been studied, in cooperation with E.B. Baker and B.R. Loy of The Dow Chemical Co. The spectrum of hexamethyldisiloxane irradiated with γ-rays from cobalt-60 while immersed in liquid nitrogen shows very definitely the presence of free radicals. Figure 2 shows the curve, which seems to be the result of superposition of two separate curves: a symmetrical triplet which would result from the presence of a $-CH_2\cdot$ radical in the material, and a central singlet peak, which might be produced from an $-O\cdot$, $-Si\cdot$, or electron spin not coupled to a magnetic nucleus.

The concentrations of these radicals can be estimated by comparison to diphenylpicrylhydrazyl standards. This sample received a total dose of 7.2 megarads of γ-rays over an 13.8-hour interval at −197° C. The concentration of the methylene free radical is estimated at 1.3×10^{-5} mole per gram. The concentration of the radical that produced the singlet is about 4×10^{-7} mole per gram. The G value for the formation of the methylene radical is 1.7 and that for the singlet 0.05. These G values are much lower than the G values for gas evolution from this compound.

The stability of these radicals at various temperatures was studied briefly. Figure 3 shows what happens if a sample of dimethylpolysiloxane irradiated in liquid nitrogen is allowed to warm slowly, while the radical concentrations are determined periodically. Both radicals appear reasonably stable to about −120° C. At this temperature the concentration of radicals begins to fall rapidly and the radical activity has disappeared completely at −60° C. The second-order transition temperature of dimethylpolysiloxanes is −123° C.

An effort was made to measure the signal intensity at various times of a sample held at −78° C. Figure 4 shows the resulting curve of lifetime. It is apparent that these radicals are short-lived at −78° C.

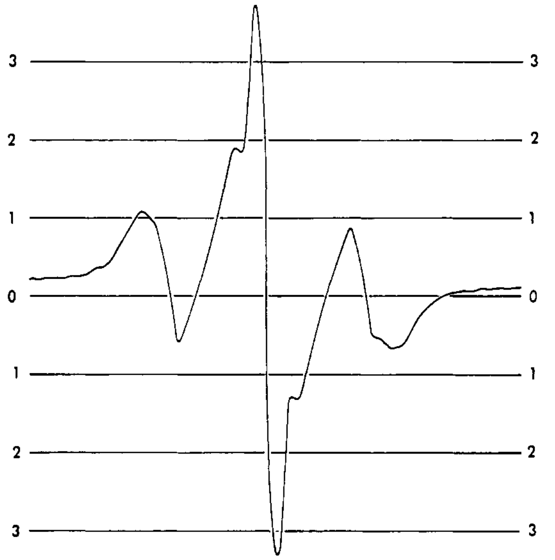

Figure 2. First derivative of ESR absorption spectra of hexamethyldisiloxane

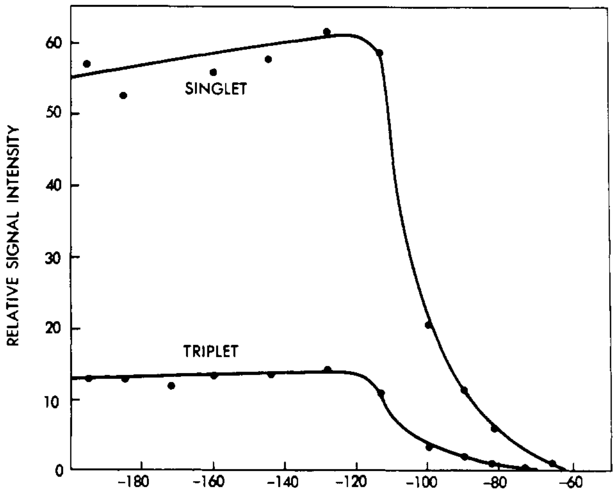

Figure 3. Warming curve of radicals in irradiated dimethylpolysiloxane

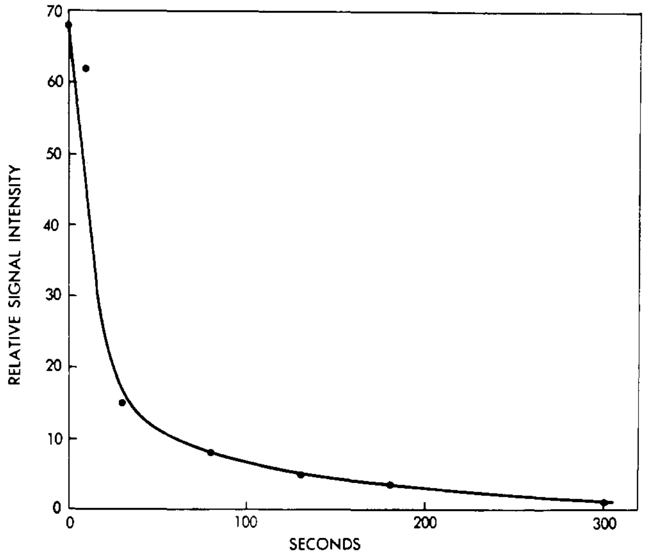

Figure 4. Decay of radicals in irradiated hexamethyldisiloxane

DISCUSSION

Within the general area of silicones compounds exist with a very wide range of sensitivity toward ionizing radiation. Siloxanes having a large amount of phenyl substitution exhibit a high degree of resistance to radiation damage. It is possible to estimate this degree of radiation resistance accurately as a function of composition. On the other hand, Si-H-containing compounds are particularly sensitive to radiation damage. Silicones should not be considered as a class, but be evaluated on the basis of specific siloxanes.

LITERATURE CITED

(1) Am. Soc. Testing Materials, Philadelphia, D 1617-59T.
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(3) California Research Corp., "Effects of Radiation of Aircraft Lubricants and Fuels," Quart. Rept. **6**, AF 33(616)-3184 (May 31, 1957).

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