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Photolytic Oxidative Degradation of Octamethylcyclotetrasiloxane and Related Compounds

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Photolytic Oxidative Degradation of Octamethylcyclotetrasiloxane and Related Compounds

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ABSTRACT

A study on the gas-phase photolytic oxidative degradation of volatile methyl silicon species has been conducted with ozone O_3 as a convenient source of photolytic oxygen. Such a study would provide the relative reactivity data which may permit an immediate comparison of environmental persistence of volatile methyl silicon compounds such as octamethylcyclotetrasiloxane (D_4), hexamethyldisiloxane, and tetramethylsilane with n-octane. A reaction vessel was devised to allow convenient generation of ozone, measurement of its concentration, syringe introduction of the compounds, and periodic sampling of gas sample for GC analysis of their disappearance rates on irradiation with a UV source from which light shorter than 290 nm was filtered off. The results on the photolysis of O_3 and D_4 revealed that their decomposition is appreciably accelerated in the presence of water. The rate of decomposition of D_4 increased with increasing initial ozone concentrations. It was found that the plot of log HL_{D_4} vs log $[O_3]_0$ was linear, where the HL_{D_4} represents the half lifetime of D_4. When the reactions were run at similar molar ratios of $[O_3]_0$, the following relative disappearance rates were observed: D_4, $(Me_3Si)_2O$, n-octane, Me_4Si: 3.3, 1.4, 1.0, 0.55.

INTRODUCTION

Previous research conducted by research workers at Dow Corning has indicated that volatile cyclic silicon compounds such as hexamethylcyclotrisiloxane, 1 (D_3), octamethylcyclotetrasiloxane, 2 (D_4), and decamethylcyclopentasiloxane, 3 (D_5) can be formed by the action of clay-containing soils on nonvolatile polydimethylsiloxane [1]. Since these siloxanes have fairly high vapor pressures [2] and thus gain entry to atmosphere, it is of interest to investigate the degradation of these compounds relative to that of hydrocarbons which are intensively studied with regard to their atmospheric chemistry.

Although several reports have been published on ultraviolet little photodegradation of nonvolatile polydimethylsiloxane [1-7], no work has been carried out on that of volatile silicon compounds [8]. We therefore decided to investigate the gas-phase UV photodegradation of volatile silicon compounds such as (octamethylcyclotetrasiloxane, D_4). Initially, we attempted to study the UV photodegradation of D_4 in the presence of oxygen as a function of wavelength using GC/mass spectrometry. However, these measurements were not satisfactory due to the complexity of the photolysis products and the relatively slow photodegradation under these conditions.

An experiment was therefore devised to monitor the relative rates of disappearance of several volatile silicon compounds of various silicon oxidation states, i.e., D_4, D_3, and tetramethylsilane $Si(CH_3)_4$, as well as the much studied hydrocarbon n-octane using tropospheric UV wavelengths ($\lambda > 290$ nm) in the presence of a high O_3 concentration to accelerate the photodegradative processes. A reaction chamber was designed to allow convenient ozone generation, measurement of its concentration, and introduction of samples, as well as periodic gas sampling for GC determination upon irradiation with a UV source from which all light of wavelength shorter than 290 nm was filtered off.

EXPERIMENTAL

Design of the Reaction Vessel and Ozone Generation

Figure 1 shows the reaction vessel equipped with a 10 cm pathlength quartz cell (A), Swagelock valve (B) for sample injection and gas sampling, and side tube for ozone generation with copper wire (C) and Tessla coil (D). In a typical experiment the vessel attached to a vacuum line at joint (E) was evacuated at 350°C for 3 h under vacuum at 10^{-5}-10^{-6} mmHg to remove adsorbed water, after which dry oxygen was introduced into the vessel at 150 or 760 mmHg pressure, followed by sealing off at constriction (F). A discharge was sent through copper wire (C) while cooling with liquid nitrogen to

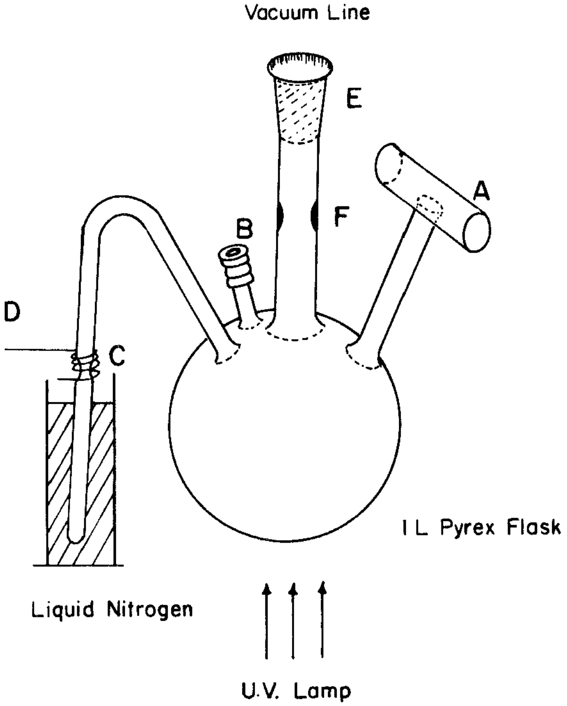


FIG. 1. Apparatus for generation of ozone and photolysis: (A) 10 cm quartz optical cell, (B) injection port, (C) copper wire, (D) Tessla coil, (E) ground joint, (F) constriction.

trap ozone (cool discharge). Ozone generation was observed by the formation of a blue liquid at the inside of the tube and was monitored at a wavelength of 255 nm using a 10-cm UV cell (A). Ozone concentrations were calculated using an extinction coefficient of 150 L^{-1} mol^{-1} cm^{-1} [9]. Figure 2 shows that ozone concentration increases linearly with discharge time.

When the O_2 (20%)-N_2 (80%) and O_2 (20%)-He (80%) gas systems were used, oxygen was first introduced at 150 mmHg pressure followed by ozone generation, and introduction of helium or nitrogen at 610 mmHg pressure.

Sample Injection and Measurement of the Disappearance Rate of Sample with GC

Sample and perfluoroheptane as an internal standard were injected into the vessel with a microsyringe and the gas system was equilibrated at room temperature (25°C) by warming and cooling to 25°C.

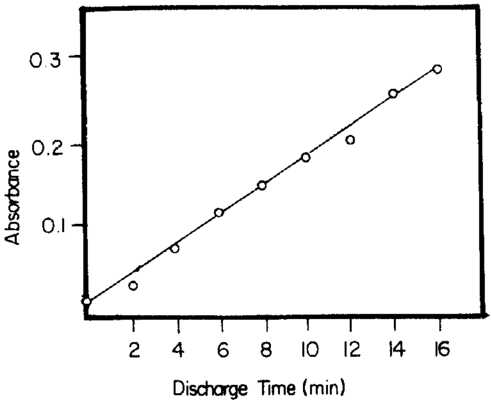


FIG. 2. Ozone generation by discharge with copper electrode and Tessla coil.

After measurement of the initial concentration of ozone and sample using UV spectrophotometry and GC, respectively, the whole vessel was irradiated from the distance of ~6 cm using a 150-W xenon-mercury lamp with wide range wavelength in the manner shown in Fig. 1. By periodic sampling of a gas sample by syringe and injection into GC, the disappearance rate of sample was measured. It was confirmed that perfluoroheptane was not decomposed during the time period of irradiation. An example of a typical run is shown in Fig. 3. The disappearance rate of a sample is indicated in terms of its half-lifetimes.

RESULTS AND DISCUSSION

Degradation of Ozone

Using the vessel shown in Fig. 1, pure ozone was conveniently generated in fairly high concentrations up to about 10^{-2} mol/L. Figure 2 shows the increase of ozone concentration with discharge time. In this case, pressure of the vessel was kept at 150 mmHg (O_2) and equilibrium was easily attained. At atmospheric pressure, prompt equilibration was attained by cooling and warming the vessel.

Ozone has UV adsorptions at 255 (strong), 305 (weak), and 340 (weak) nm, and also at higher wavelengths (760, 670, 615, 510 nm), indicating ozone may be degradable by adsorption at several of these wavelengths [10]. In this experiment the gasses such as He, N_2, and O_2 were added to keep the vessel at atmospheric pressure. The

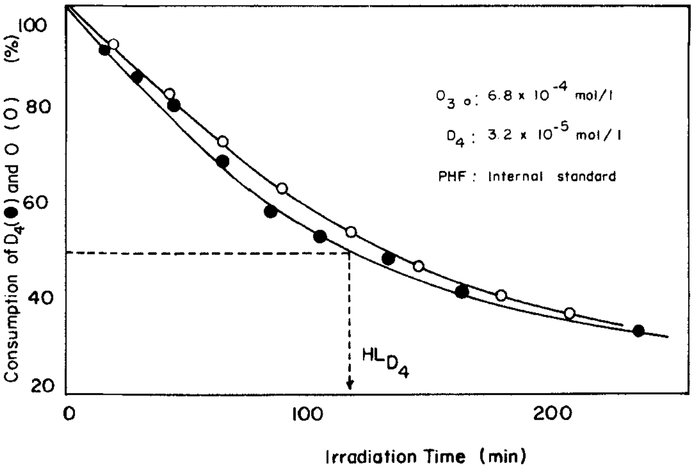


FIG. 3. Photolysis of D_4 in the presence of O_3.

disappearance rate of O_3 upon photolysis is also shown in Fig. 3. The degradation in the O_2-He gas system is faster than in pure O_2 or O_2-N_2 mixtures. Figure 4 shows that removal of adsorbed water by flaming the vessel makes no appreciable difference, but addition of water accelerates the degradation of O_3.

The observed increase in the rate of ozone degradation in the presence of H_2, He, Ar, etc. [10] suggests that O_3 may be subject to catalytic degradation rather than simple photolysis, according to the Eq. (1). The slower degradation observed in the O_2 and O_2-N_2 systems may imply the following mechanism (Eqs. 2 and 3) in addition to Eq. (1). Furthermore, the accelerating effect on the photolysis due to H_2O may be caused by the formation of hydroxy radicals (Eq. 4).

$$O_3 \rightleftharpoons O_2 + O(^1D) \quad (1)$$

$$2O(^1D) \longrightarrow O_2 \quad (2)$$

$$xO(^1D) + \tfrac{1}{2}N_2 \rightleftharpoons NO_x \quad (3)$$

$$O(^1D) + H_2O \longrightarrow 2OH^\circ \quad (4)$$

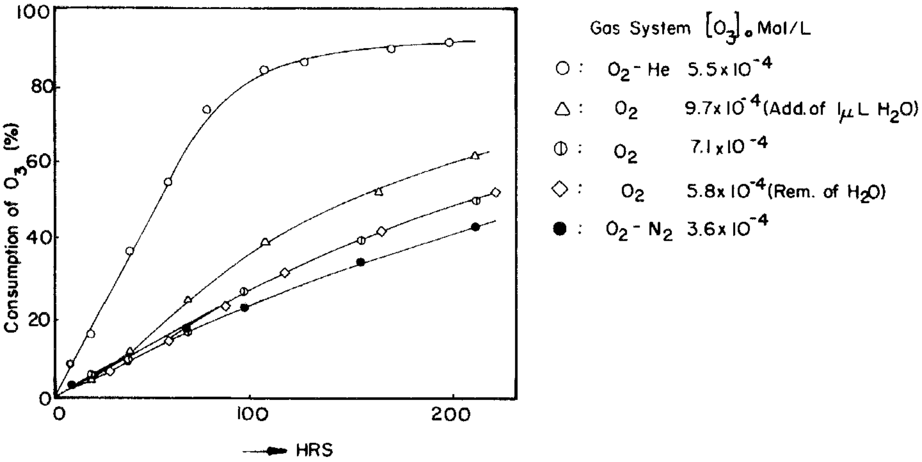


FIG. 4. Photolysis of O_3 under various conditions.

Degradation of D_4

Degradation of D_4 upon irradiation by UV light as measured by GC/mass spectrometry in the absence of O_3 is negligible and was very small (~2%) in pure O_2 after 2 days. In oxygen in the presence of moderate concentrations of ozone (~10^{-3} M), however, degradation is much faster with half lifetimes in the order of 0.5-2 h (Table 1).

Degradation of D_4 in the O_2 and O_2/He (20/80) proceeded at essentially the same rate (Table 1), the difference being the faster rate of ozone decomposition in the O_2/He system. These results allowed us to substitute the O_2 system for the O_2/He and O_2/N_2 systems. Complications in the latter system arise because of the formation of nitrogen oxides NO_x generated according to Eq (3) that possibly may affect the photolysis of D_4. The effect of the presence of a small quantity of water is of considerable interest. Removal of H_2O adsorbed on the wall of the vessel by annealing at 350°C for several hours at 10^{-6} mmHg decreased the rate of D_4 decomposition by about 50%. Furthermore, addition of small quantities of H_2O to the annealed vessel increased the D_4 degradation rate significantly (Table 1). This acceleration in rate is probably due to the formation of the highly reactive hydroxyl radical (Eq. 4).

The above observations support the view that the degradation of D_4 under the above conditions is probably caused by the formation of $O(^1D)$ from excited O_3. This is consistent with the absence of UV absorptions of D_4 in the wavelength range examined [11].

TABLE 1. Effect of Gas System, Adsorbed, and Added Water on Photolysis of D_4[a]

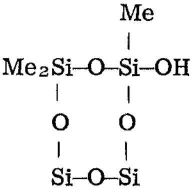
Gas system	Molar ratio H_2O/D_4	$[O_3]$ (mol/L)	Molar ratio $[O_3]_0/D_4$	HL_{D_4} (min)
O_2-He	-	6.80×10^{-4}	21	120[b]
O_2-He	-	6.20×10^{-4}	19	120-130[b]
O_2	-	6.20×10^{-4}	19	120-130[b]
O_2	-	1.70×10^{-3}	53	65-70[c]
O_2	-	1.70×10^{-3}	53	37[b]
O_2	-	1.15×10^{-3}	36	60[b]
O_2	1.7	1.20×10^{-3}	37	50-55[c]
O_2	5.2	1.10×10^{-3}	34	37-40[b]

[a] $D_4 \approx 3.2 \times 10^{-5}$ mol/L.

[b] Adsorbed water was not removed.

[c] Adsorbed water was removed by evacuation at 350°C for 3 h under vacuum at 10^{-6} mmHg.

Under our GC conditions the D_4 degradation product(s) was detected as a single peak at an early stage of irradiation, but at a later stage of the photolysis two or three peaks were evident (Fig. 5a). After a 4-h irradiation of this sample, the mixture was trapped at -78°C and was analyzed by GC/mass spectrometry. More than 30 degradation products were present with molecular weights ranging from 300 to 623. In another run using a longer irradiation time, the product was found to contain a substantial (~50%) volume fraction of water. This suggests that the attack of $O(^1D)$ on D_4 may result in compounds containing hydroxy groups which, in turn, condense to form siloxanes and water. Compounds 4-5 were identified in preliminary GC/mass spectrometry experiments.



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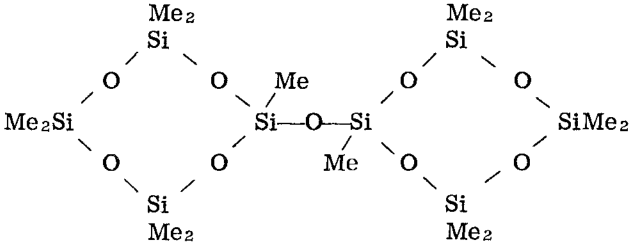

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The participation of the OH° radical and faster degradation rate observed in the $O_2/O_3/H_2O$ system might be expected to lead to a

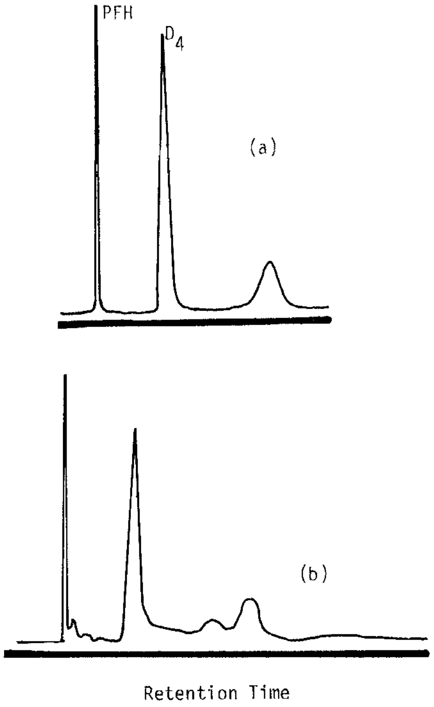

FIG. 5. Gas chromatographs of UV irradiated D_4 samples in the absence (a) and presence (b) of water.

greater variety of decomposition products. This indeed appears to be the case. Under similar conditions the number and concentration of D_4 decomposition products appear to be much larger in the system containing water (Fig. 5). This, in turn, may again indicate a rather unselective attack of the hydroxyl radical on D_4.

The Dependence of the Disappearance Rate of D_4 on Initial Ozone Concentrations

It is reported that the ozone concentration is at most a few tenths ppm in typical urban areas which is equivalent to 10^{-9} mol/L [12]. Under our experimental conditions it is possible to compute the rate of disappearance of D_4 at relatively high ($>10^{-4}$ M) ozone concentrations, but this becomes difficult at concentrations lower than 10^{-6} mol/L. It was thought, therefore, that it may be possible to estimate the half lifetime of $D_4HL_{D_4}$ at lower ozone concentrations if some

TABLE 2. Photolysis of D_4 under Various Ozone Concentrations

Molar ratio $[O_3]_0/D_4$[a]	$[O_3]_0$ (mol/L)	$-\text{Log}\,[O_3]_0$	HL_{D_4}	
			Minutes	Log HL_{D_4}
50.0	1.60×10^{-3}	2.80	40	1.60
21.2	6.80×10^{-4}	3.17	120	2.08
19.4	6.20×10^{-4}	3.21	240	2.38
6.0	1.90×10^{-4}	3.71	480	2.68
5.4	1.73×10^{-4}	3.86	720	2.86
2.5	8.00×10^{-5}	4.10	1800	3.26
1.7	5.46×10^{-5}	4.26	2700	3.43

[a] $D_4 = 3.20 \times 10^{-5}$ mol/L.

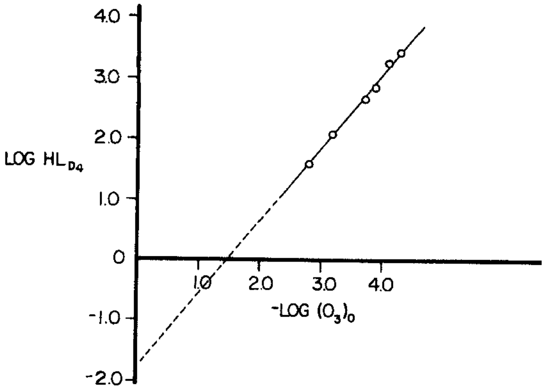

FIG. 6. Rate of decomposition of D_4 as a function of initial ozone concentration ($[O_3]_0$).

relationship between ozone concentrations on HL_{D_4} could be found. Table 2 shows the effect of initial ozone concentrations on HL_{D_4}, and illustrates that the HL_{D_4} values are linearly dependent upon $[O_3]_0$. Figure 6 is obtained by plotting the results of Table 2. The linear relationship between log HL_{D_4} and log $[O_3]_0$ leads to

$$\log HL_{D_4} = -1.21 \log [O_3]_0 - 1.75 \qquad (5)$$

TABLE 3. Relative Disappearance Rate of D_4 and Related Compounds

Compound	Mol/L	$[O_3]_0$ (mol/L)	Molar ratio $[O_3]_0$/compound	$HL_{compound}$ (h)
D_4	3.2×10^{-5}	1.70×10^{-3}	53	0.62
	3.2×10^{-5}	1.60×10^{-3}	50	0.67
	3.2×10^{-5}	1.15×10^{-3}	36	1.02
$(Me_3Si)_2O$	3.6×10^{-5}	1.79×10^{-3}	50	1.58
	4.7×10^{-5}	1.70×10^{-3}	36	3.83
Me_4Si	3.7×10^{-5}	1.93×10^{-3}	52	4.0
	3.7×10^{-5}	1.65×10^{-3}	44	6.0
n-Octane	3.1×10^{-5}	2.40×10^{-3}	76	1.66
	3.1×10^{-3}	1.71×10^{-3}	55	2.25

This relationship may allow an estimation of HL_{D_4} under the above experimental conditions at lower ozone concentration.

Degradation Rate of Volatile Methylsilicon Compounds Relative to n-Octane

Since the atmospheric fate of hydrocarbons is extensively studied, the relative environmental persistence of these silicon compounds would be known by comparing them with a well-known hydrocarbon such as n-octane. Table 3 shows the degradation rate of three silicon compounds and n-octane. When the half-lifetimes of these are compared at a comparable molar ratio of O_3, the following disappearance rates of the silicon compounds, relative to n-octane, were obtained: D_4, $(Me_3Si)_2O$, n-octane, Me_4Si: 3.3, 1.4, 1.0, 0.55. Provided that the relative rates of decomposition of these compounds approximate those prevalent under actual atmospheric conditions, it would appear that such products are not expected to accumulate in the atmosphere.

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REFERENCES

[1] R. R. Buch and D. N. Ingebrigtson, Env. Sci. and Techn., 13, 676 (1979).
[2] D. F. Wilcock, J. Am. Chem. Soc., 68, 691 (1946).
[3] A. D. Delman, M. Landy, and B. S. Simms, J. Polym. Sci., Part A-1, 7, 3375 (1969).
[4] S. Siegel and T. Stewart, J. Phys. Chem., 73, 823 (1969).
[5] E. L. Zhuzhgov, N. N. Bulnov, and V. V. Voevodskii, Kinet. Katal., 9, 773 (1968).
[6] F. A. Bovey, Effect of Ionizing Radiation on Natural and Synthetic High Polymers, Interscience, New York, (1958).
[7] A. A. Miller, J. Am. Chem. Soc., 82, 3519 (1960).
[8] A. G. Alexander and O. P. Strausz, J. Phys. Chem., 80(23), 2531 (1976) and papers therein; H. P. Schuchmann, A. Ritter and C. Von Sonntag, J. Organomet. Chem., 148, 213 (1978).
[9] G. K. Rellefson and M. Barton, Photochemistry and the Mechanism of Chemical Reaction, Prentice-Hall, Englewood Cliffs, New Jersey, (1939), pp. 143-145.
[10] Ozone Chemistry and Technology, Advances in Chemistry Series No. 21, American Chemical Society, H. A. Leedy Ed., Washington, D.C., 1959; J. G. Calvert and J. N. Pitts, Advances in Photochemistry, Wiley, New York, Vol. 11, 1979.
[11] C. A. Burkhard and E. H. Winslow, J. Am. Chem. Soc., 72, 3276 (1950).
[12] Physical and Chemical Nature of Photochemical Oxidants, AP-63, U.S. Department of Health, Education and Welfare Public Health Service, National Air Pollution Control Administration, Washington, D.C., March 1970, Chap. 2.

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