Among the first reactions is also the linear growth of small amounts of Cl_2 and $COCl_2$. As the reaction progresses the formation of chlorine (difference between oxidizing products and peroxide) continues at an accelerated rate at higher oxygen concentrations (see Figs. 2 and 3).

As the reaction progresses, it enters a second phase in which the peroxide and chlorine disappear to yield $COCl_2$, HCl and other products. The disappearance of chlorine can probably be accounted for by the chlorination of $CHCl_3$ to yield CCl_4 and HCl. Several features of the second stage seem of considerable interest. One is that the ratio of HCl/$COCl_2$ after long irradiation periods is much in excess of that corresponding to the net change

$$CHCl_3 + {}^1/_2O_2 \longrightarrow COCl_2 + HCl$$

Departures from this stoichiometry in the observed direction could be accounted for by the formation of other oxygen-containing products (*e.g.*, CO or CO_2) or some carbon–chlorine compounds which were not detected in this study. It should be noted that water has never been observed in the reaction products. A second point of interest is that oxygen remains in the system even during the second phase. Apparently the accumulation of some product explains the differing reactions in the first and second phases.

A. Mechanism.—One may regard the decomposition of chloroform by oxygen as proceeding mainly through intermediates which ultimately decompose to yield HCl, $COCl_2$ and chlorinated hydrocarbons. Of primary importance in this study was the formation of a peroxide, presumably CCl_3OOH. The net reaction for the production of this component can be considered as

$$CHCl_3 + O_2 \longrightarrow CCl_3OOH$$

No definite conclusions about complete mechanisms can be drawn from these studies. The radicals resulting from the interaction of the radiation and chloroform presumably generate a chain reaction for the combination of oxygen and chloroform. Since mass spectrograph studies of $CHCl_3$ give $CHCl_2^+$ and $CHCl_2^{++}$ as the most abundant fragments resulting from electron impact on $CHCl_3$ gas, it is not unreasonable that these same fragments would result in liquid $CHCl_3$ bombarded by gamma rays. The primary act in the production of the peroxide compound would therefore probably be

$$CHCl_3 \xrightarrow{\gamma\text{-rays}} CHCl_2 + Cl$$

The data indicate that of the products studied, the peroxide is the only compound produced by a chain reaction in the initial stages; chlorine, phosgene, hexachloroethane and hydrogen chloride apparently result principally from reactions generating the chain-carrying species or reactions which result in the net destruction of radicals.

B. Application to Dosimetry.—The excellent agreement obtained with Cl^- determinations suggests the use of the $CHCl_3$–O_2 system as a dosimeter for higher dosages. The analysis for total oxidizing agent can also be performed conveniently. However, it should be pointed out that even though the decomposition of $CHCl_3$ is a chain reaction, the quantities of products involved are still quite small. Consequently, for dosages less than 1000 r., micro-techniques would have to be employed even to determine Cl^- which represents not only the HCl and $COCl_2$ produced but also Cl_2 and CCl_3OOH. By irradiating 1 cc. of $CHCl_3$ in 0.014 millimole of O_2 one would expect only 4.5×10^{-4} meq. Cl^- to be produced by 10^3 r.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Physical Properties of Organosilicon Compounds. I. Hexamethylcyclotrisiloxane and Octamethylcyclotetrasiloxane

BY ROBERT C. OSTHOFF, W. T. GRUBB AND CHARLES A. BURKHARD

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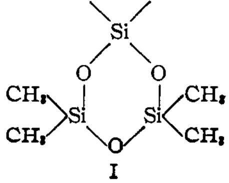
The vapor pressure of hexamethylcyclotrisiloxane as a function of temperature has been determined. The enthalpies of vaporization, fusion and sublimation are 9.5, 3.7 and 13.2 kcal./mole, respectively. For octamethylcyclotetrasiloxane the enthalpy of fusion is 4.4 kcal./mole. Octamethylcyclotetrasiloxane is well suited as a cryoscopic solvent.

Introduction

Hexamethylcyclotrisiloxane (I) is unique among cyclic dimethylsiloxanes because it possesses a planar, strained ring structure[1,2] and unusual physical properties, *e.g.*, a comparatively high melting point and short liquid range.[3] Thus it was of interest to determine its vapor pressure as a function of temperature, and its enthalpies of vaporization, sublimation and fusion. In order to compare the properties of I with those of a typical non-planar homolog, the enthalpy of fusion of octamethylcyclotetrasiloxane (II) was deter-



I

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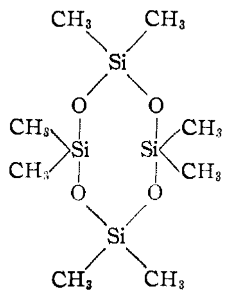
[1] W. L. Roth and D. Harker, *Acta Cryst.*, **1**, 34 (1948).

[2] D. W. Scott, THIS JOURNAL, **68**, 2294 (1946).

[3] W. I. Patnode and D. F. Wilcock, *ibid.*, **68**, 358 (1946).

mined also. The enthalpy of vaporization of II has been reported previously.[4]



II

Wilcock[4] has evaluated the vapor pressures of a number of linear and cyclic polysiloxanes; however, he did not determine the vapor pressure of I. Hunter, *et al.*,[5] have used the empirical method of Cox[6] to estimate the vapor pressure of I as a function of temperature. Selected values of the vapor pressure of the liquid compound have been compiled from this Cox chart but evidently no direct determinations of the vapor pressure have been reported.[7]

Experimental

The measurements of the vapor pressure of I were conducted in a modified isoteniscope of Smith and Menzies.[8,9] Conventional methods of operation of the isoteniscope were employed. Temperature was controlled by immersion of the isoteniscope into a rapidly stirred silicone oil-bath, the temperature of which was controlled to ±0.1° (the temperature was determined with an 0.1° Bureau of Standards calibrated partial immersion thermometer).

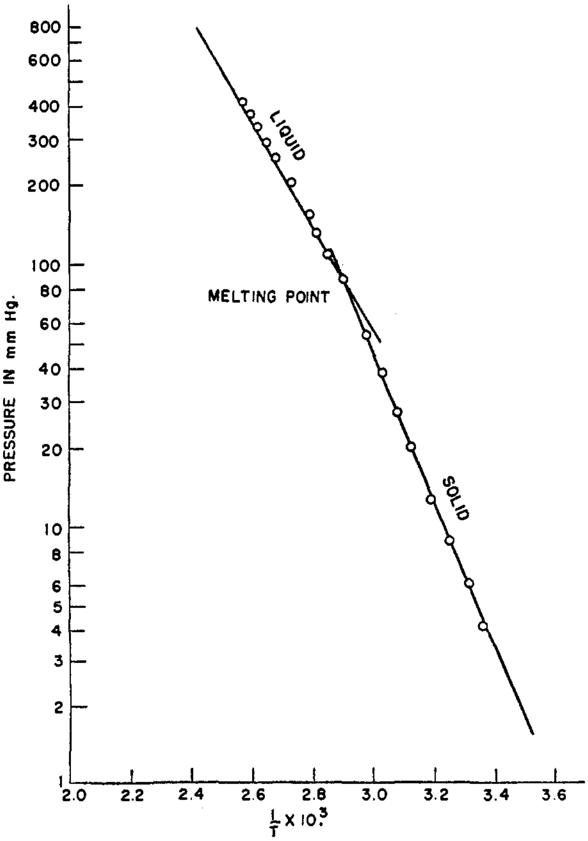


Fig. 1.—Log vapor pressure *vs.* the reciprocal of the absolute temperature for $[(CH_3)_2SiO]_3$.

Resublimed samples of I (m.p. 65°) were introduced into the isoteniscope by vacuum sublimation.

In Table I are presented the calculated and observed vapor pressures of I (solid) at various temperatures.

TABLE I

VAPOR PRESSURE OF SOLID HEXAMETHYLCYCLOTRISILOXANE

t, °C.	P_{mm} Obsd.	P_{mm} Calcd.	t, °C.	P_{mm} Obsd.	P_{mm} Calcd.
24.2	4.2	4.4	45.9	20.1	19.8
27.8	6.1	5.7	51.0	27.1	27.5
34.1	8.9	8.7	56.0	39.2	37.5
39.8	12.6	13.2	62.4	54.1	55.2

By application of the method of least squares to the observed data the constants of equation 1 below were evaluated.

$$\log_{10} P_{mm}\,(\text{solid}) = 10.3347 - \frac{2883.6}{T} \qquad (1)$$

It is seen from an examination of the data of Table I that the observed values of the vapor pressure are reproduced with a mean deviation of 0.6 mm. by means of equation 1. From the slope given by the equation, the enthalpy of sublimation, ΔH_s, of I was found to be 13.2 ± 0.1 kcal./mole.

Vapor pressure data for liquid I have been determined and analyzed in the same manner. Observed and calculated values of the vapor pressure of the liquid are given in Table II.

TABLE II

VAPOR PRESSURE OF LIQUID HEXAMETHYLCYCLOTRISILOXANE[a]

t, °C.	P_{mm} Obsd.	P_{mm} Calcd.	t, °C.	P_{mm} Obsd.	P_{mm} Calcd.
69.8	82.2	83.1	99.0	251.1	247.9
76.9	110.0	110.3	103.8	293.5	291.7
81.4	131.0	131.2	108.4	338.6	339.0
85.0	150.6	149.9	111.4	375.7	376.1
92.8	203.2	199.8	114.8	412.7	419.9

[a] The observed values of the vapor pressure above 80° were corrected by subtraction of the vapor pressure of mercury.

The constants of equation 2 were determined by applying the method of least squares to the observed data.

$$\log_{10} P_{mm}\,(\text{liquid}) = 7.9839 - \frac{2080.2}{T} \qquad (2)$$

Equation 2 reproduces the observed values of the vapor pressure with a mean deviation of 1.9 mm. The enthalpy of vaporization was calculated to be 9.5 ± 0.1 kcal./mole from equation 2 and the extrapolated b.p. was calculated to be 134.4° (obsd. value is 135°[3]). The logarithm of the vapor pressure of solid and liquid I is plotted against the reciprocal of the absolute temperature in Fig. 1. Employing equations 1 and 2 the melting point was calculated to be 68° (obsd. value is 64°[3]).

The enthalpy of fusion, ΔH_f, of I was calculated to be 3.7 ± 0.1 kcal./mole by means of the relation $\Delta H_f = \Delta H_s - \Delta H_v$. This value of ΔH_f yields a molal freezing point depression constant of 13.7 deg. 10^3 g. mole^{-1}.

In order to determine the enthalpy of fusion of II, a cryoscopic method was employed because the vapor pressure of solid II is very small (vapor pressure of II at its melting point is 0.8 mm. Hg[4]). Purified II was obtained by repeated fractionations of the hydrolysate of pure dimethyldichlorosilane until a sample having a melting point of 17.51°

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[4] D. F. Wilcock, THIS JOURNAL, **68**, 691 (1946).

[5] M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, *ibid.*, **68**, 667 (1946).

[6] E. R. Cox, *Ind. Eng. Chem.*, **15**, 592 (1923).

[7] D. R. Stull, *ibid.*, **39**, 517 (1947).

[8] A. Smith and A. W. C. Menzies, THIS JOURNAL, **32**, 1412 (1910).

[9] H. S. Booth and H. S. Halbedel, *ibid.*, **68**, 2652 (1946).

resulted.[10] The enthalpy of fusion was determined by using a modification of the freezing curve technique of Mair, Glasgow and Rossini.[11] In Table III are recorded for each case the solute employed, the mole fraction of the solute in II, the observed freezing point depression, ΔT, and the calculated values of the enthalpy of fusion, ΔH_f.

TABLE III

ENTHALPY OF FUSION OF OCTAMETHYLCYCLOTETRASILOXANE

Solute	Mole fraction	ΔT^a	ΔH_f, kcal./mole
$BrCH_2CH_2Br$	0.00277	0.109	4.3
$(CH_3)_6Si_2O$	.00126	.051	4.1
$(CH_3)_6Si_2O$	.00373	.140	4.5
$(CH_3)_6Si_2O$	.00607	.221	4.6
$[(CH_3)_2SiO]_5$	.00207	.080	4.3

Mean value $\Delta H_f = 4.4 \pm 0.3$

[a] The freezing temperature depressions were obtained using a Beckmann thermometer.

Using the value of enthalpy of fusion of II, the molal freezing point depression constant was found to be 11.3 deg. 10^3 g. mole^{-1} of solvent.

It was possible to estimate the heat capacity of II at 18° by comparison with the rate of cooling of glacial acetic acid. This value was found to be 0.4 cal. g.$^{-1}$ deg.$^{-1}$ or 120 cal. mole^{-1} deg.$^{-1}$.

As an extension of this work, the solubility of I in II at approximately 20° was found to be 55 g. of I per 100 g. of II.

TABLE IV

THERMOPHYSICAL PROPERTIES OF HEXAMETHYLCYCLOTRISILOXANE (I) AND OCTAMETHYLCYCLOTETRASILOXANE (II)

	I	II
V.p. of solid	$\log_{10} P_{mm}(\text{solid}) = 10.3347 - (2883.6/T)$	......
V.p. of liquid	$\log_{10} P_{mm}(\text{liq.}) = 7.9839 - (2080.2/T)$	$\log_{10} P_{mm}(\text{liq.}) = 8.13 - (2366^4/T)$
ΔH_s, kcal./mole	13.2 ± 0.1	15.3 ± 0.5^a
ΔH_v, kcal./mole	9.5 ± 0.1	10.9 ± 0.2
ΔH_f, kcal./mole	3.7 ± 0.1	4.4 ± 0.3
$\Delta H_v/T_b$, e.u.	23.3	24.3[4]
$\Delta H_f/T_m$, e.u.	10.9	14.8
$K_f = RT_m^2/\Delta H_f$, deg.	61.6	38.0
$K_f^\circ = RT_m^2M/1000\ \Delta H_f$, deg. 10^3 g. mole^{-1}	13.7	11.3
t_m, °C.	65	17.51

[a] This value of ΔH_s was calculated from Wilcock's value of the enthalpy of vaporization and the value of the enthalpy of fusion reported in this paper.

Discussion

For the purpose of comparing the physical properties of I and II, the observed and derived thermodynamic quantities for these compounds are listed in Table IV in which T_b represents the boiling point, T_m represents the melting point, and M is the molecular weight of the particular species.

The vapor pressure equations for solid and liquid hexamethylcyclotrisiloxane (I) have been used to calculate the solubility of I in II assuming ideal mixing of II with supercooled liquid I at 20°.[12] From these calculations a solubility value of 54 g. of I per 100 g. of II is obtained which is in close agreement with that obtained experimentally (55 g. I per 100 g. of II). This indicates that in all probability cyclic dimethylsiloxanes of varying ring sizes form almost ideal solutions with each other.

It is of interest to compare the enthalpies and entropies of fusion per $(CH_3)_2SiO$ unit for I and II. These quantities have the values 1.2 kcal. and 3.6 e.u. for I and 1.1 kcal. and 3.8 e.u. for II. Such close agreement of these values suggests that I possesses interaction energies and a degree of free rotation in the solid state which are not significantly different from II. The enthalpy of vaporization of I calculated from the equation of Wilcock[4] is 9.5 kcal./mole (experimental value, 9.5 ± 0.1 kcal./mole). It may be concluded that liquid I shows no anomalous behavior compared to other cyclic siloxanes.

The high values of the freezing point depression constants of these compounds suggest their use as solvents for cryoscopic measurements of molecular weight. The high volatility of I in the vicinity of its melting point might limit its use. On the other hand, II appears to be well suited for cryoscopic determinations due to its water immiscibility, stability on storage and its convenient freezing point.

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(10) The melting point was determined with a calibrated 0.01° partial immersion thermometer.

(11) B. J. Mair, A. R. Glasgow and F. D. Rossini, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).

(12) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 26.

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