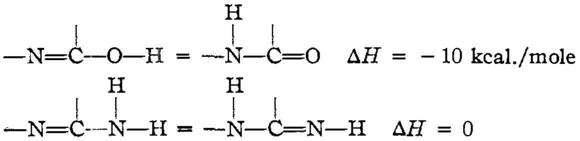
on addition of acid may be attributed to the binding of a hydrogen ion with consequent formation of a cation and the destruction of the symmetry of the neutral molecule. The reduced symmetry, by increasing the dipole strength, would increase the transition probability and hence the intensity of absorption.

It is of interest to note in passing that the acid pK of the melamine cation as determined from spectral variations (5.05) agrees well with the value calculated from direct titration experiments with a glass electrode (5.10).

Absorption spectra thus indicate that the most stable forms of cyanuric acid and melamine, respectively, in neutral aqueous solution are essentially the same as those in the solid state. It is of interest to observe that in both states, the carbonyl form (I) is the more stable structure for cyanuric acid, whereas the amide structure (IV) is the more stable for melamine. The basis of this difference is apparent when one considers the relative energies involved. Branch and Calvin[6] have pointed out that the transfer of a hydrogen atom is favored much more in enol-keto tautomerism than in amide-imide conversions, *i. e.*,



$$-N{=}\overset{|}{C}-O-H = -\overset{\overset{H}{|}}{N}-\overset{|}{C}{=}O \quad \Delta H = -10 \text{ kcal./mole}$$

$$-N{=}\overset{|}{C}-\overset{\overset{H}{|}}{N}-H = -\overset{\overset{H}{|}}{N}-\overset{|}{C}{=}N-H \quad \Delta H = 0$$

Thus in cyanuric acid, the keto formation is accompanied by a stabilization energy of 30 kilocalories/mole which is more than sufficient to overbalance the extra resonance energy which would be obtained from the conjugation within the ring in the enol form. In contrast in melamine, the conversion from the amide to the imide form merely trades one C=N for another and produces no net stabilization energy. In consequence the additional resonance energy obtained by conjugation within the ring is more than sufficient to stabilize the molecule in the amide form.

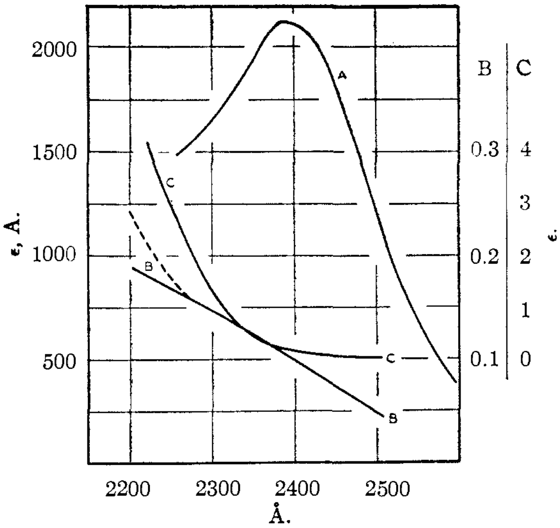


Fig. 4.—Absorption spectra of: A, cyanuric chloride in methyl alcohol; B, guanidine, —, pH 1.04. ----, pH 6.24; C, urea in 0.10 N NaOH.

Summary

The absorption spectra of cyanuric acid, melamine, cyanuric chloride, barbital, guanidine, and urea have been investigated in aqueous solutions at various pH's. From these observations it is concluded that cyanuric acid exists in the carbonyl form and melamine in the amide configuration in neutral solution, but that acid or base causes modifications in structure.

EVANSTON, ILLINOIS RECEIVED OCTOBER 28, 1946

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[6] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 289.

[CONTRIBUTION FROM DOW CORNING CORPORATION]

Organosilicon Polymers. III. Infrared Spectra of the Methylpolysiloxanes

BY NORMAN WRIGHT[1] AND MELVIN J. HUNTER[2]

In the study of a new class of compounds the infrared absorption spectra rank high in importance since these spectra are unquestionably among the most distinguishing of the physical properties of molecular substances. The frequencies of vibration and the absorption intensities depend directly upon the masses of the atoms, the strengths and electrical characters of the interatomic bonds, and the geometrical configuration of the molecule; hence, interpretation of the spectra often leads to fundamental information on molecular structure. Treated solely from an empirical point of view, the spectra are of considerable value for identification and quantitative analysis.

Literature reports on infrared spectra of silicon containing compounds include studies of silane,[3,4] halosilanes,[5,6] carborundum,[7] and a large number

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[1] The Dow Chemical Company, Midland, Michigan.

[2] Dow Corning Corporation, Midland, Michigan.

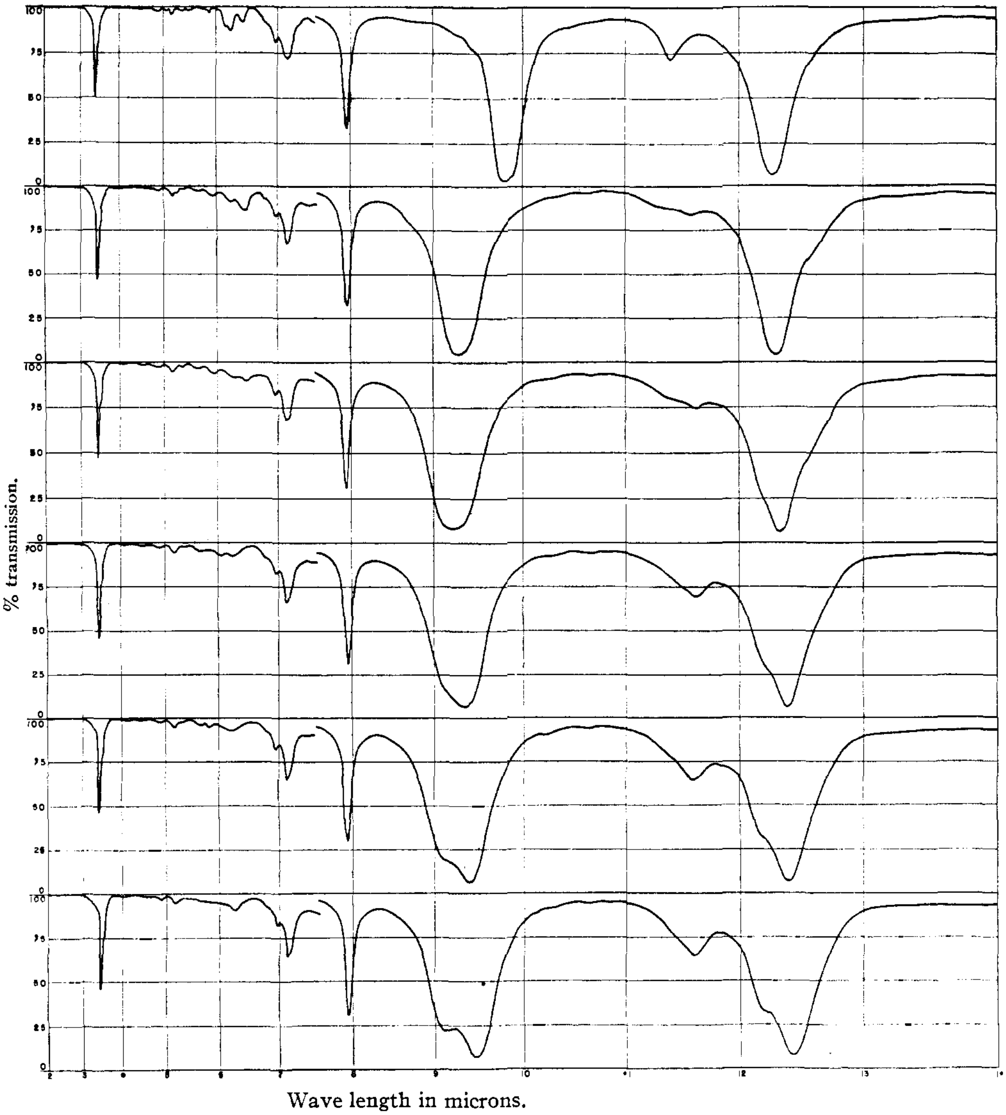
[3] W. B. Steward and H. H. Nielsen, *J. Chem. Phys.*, **2**, 712 (1934); *Phys. Rev.*, **47**, 828 (1935).

[4] C. H. Tindal, J. W. Straley and H. H. Nielsen, *Proc. Natl. Acad. Sci. U. S.*, **27**, 208 (1941); *Phys. Rev.*, **62**, 151 (1942).

[5] C. R. Bailey, J. B. Hale and H. W. Thompson, *Proc. Roy. Soc.* (London), **167**, 555 (1933).

[6] Clemens Schaefer, *Z. Physik*, **60**, 586 (1930).

[7] W. W. Coblentz, Publication No. 65, Carnegie Inst. of Wash. (1906).



Hexamethylcyclotrisiloxane: 10% soln. in CCl_4, 2.5 to 7.5μ, 2% soln. in CS_2, 7.5 to 14μ, cell thickness 0.102 mm.

Octamethylcyclotetrasiloxane: 10% soln. in CCl_4, 2.5 to 7.5μ, 2% soln. in CS_2, 7.5 to 14μ, cell thickness 0.102 mm.

Decamethylcyclopentasiloxane: 10% soln. in CCl_4, 2.5 to 7.5μ, 2% soln. in CS_2, 7.5 to 14μ, cell thickness 0.102 mm.

Dodecamethylcyclohexasiloxane: 10% soln. in CCl_4, 2.5 to 7.5μ, 2% soln. in CS_2, 7.5 to 14μ, cell thickness 0.102 mm.

Tetradecamethylcycloheptasiloxane: 10% soln. in CCl_4, 2.5 to 7.5μ, 2% soln. in CS_2, 7.5 to 14μ, cell thickness 0.102 mm.

Hexadecamethylcyclooctasiloxane: 10% soln. in CCl_4, 2.5 to 7.5μ, 2% soln. in CS_2, 7.5 to 14μ, cell thickness 0.102 mm.

Fig. 1.—Infrared spectra of cyclic dimethylsiloxanes.

of works on quartz[7,8,9] and inorganic silicates.[9] Raman spectra of silane, disilane and hexachlordisilane,[10] the halosilanes,[11,12] tetramethylsilane,[13,14] and quartz[15] have been measured. The present paper reports the infrared absorption spectra (2–14 μ) of the first six polymers of the cyclic dimethylsiloxanes,[16,17] the first seven members of the dimethylsiloxane polymer series end blocked with trimethylsiloxy groups[18] and the two branched compounds, 3-(trimethylsiloxy)-heptamethyltrisiloxane[16] and 3,3-di-(trimethylsiloxy)-hexamethyltrisiloxane.

Experimental

Apparatus and Technique

The infrared spectra were obtained using a rock-salt prism spectrometer identical in internal optics with that described in an earlier publication.[19] In the present case, however, the external optics consists of two beams of radiation from the same source which alternately (at six times per second) pass into the spectrometer. One of these beams passes through the sample while the second passes through a cell containing the blank solvent. An automatically controlled shutter moving in the second beam keeps its intensity equal to that transmitted by the sample.

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[8] H. Rubens and E. F. Nichols, *Wied. Ann.*, **60**, 418 (1897).

[9] Barnes, Gore, Liddel and Williams, "Infrared Spectroscopy," Reinhold Publishing Corp., New York, N. Y., 1944 (bibliography).

[10] F. Stitt and D. M. Yost, *J. Chem. Phys.*, **4**, 82 (1936); **5**, 90 (1937).

[11] D. M. Yost, E. N. Lassettre and S. T. Gross, *ibid.*, **4**, 325 (1936).

[12] K. W. F. Kohlrausch, "Der Smekal-Raman Effekt (1931–1937)," J. Springer, Berlin, 1938.

[13] D. H. Rank and E. R. Bordner, *J. Chem. Phys.*, **3**, 248 (1935).

[14] F. T. Wall and C. R. Eddy, *ibid.*, **6**, 107 (1938).

[15] B. D. Saksena, *Proc. Ind. Acad. Sci.*, **16A**, 270 (1942).

[16] W. Patnode and D. F. Wilcock, THIS JOURNAL, **68**, 358 (1946).

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

[18] M. J. Hunter, E. L. Warrick, J. F. Hyde and C. C. Currie, *ibid.*, **68**, 2284 (1946).

[19] N. Wright, *Ind. Eng. Chem., Anal. Ed.*, **13**, 1 (1941).

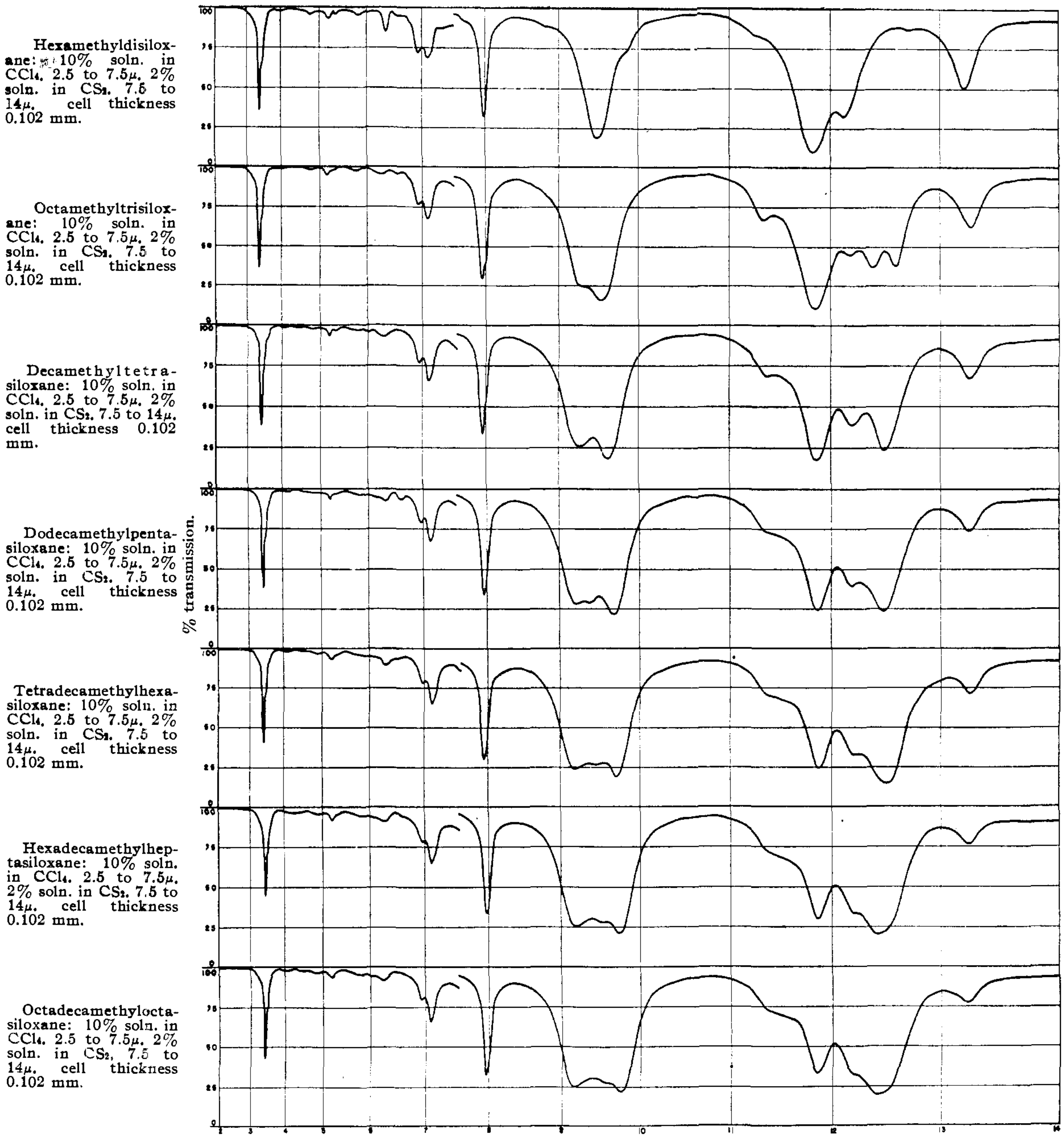

Fig. 2.—Infrared spectra of linear polymethylsiloxanes.

Recording of the shutter motion thus gives an automatic graph of the per cent. of radiation transmitted *versus* wave length. A detailed description of this infrared spectrophotometer is to appear elsewhere.[20]

The curves of Figs. 1–3 are contact tracings of the automatically recorded spectra. Values of per cent. transmitted are believed to be accurate to within ±2%. Efforts to replot these spectra manually from earlier type records[19] on a linear wave length scale were abandoned because of inability to reproduce with sufficient fidelity the gradually changing details to be noted in the two homologous series shown.

All samples were observed as solutions, 10% in carbon tetrachloride (10 g./100 cc. solution) being used in the range 2–7.5μ and 2% in carbon sulfide from 7.5 to 14μ. In all cases the cell was 0.10 mm. thick.

The wave lengths of the absorption bands are listed in Table I. Those near 3μ were also measured with a lithium fluoride prism replacing the rock salt to obtain more accurate supplementary data in this region. Relative intensities are indicated by S—strong, M—medium, and W—weak; more accurate values can be obtained by reference to the curves.

Source of Materials

The cyclic dimethylsiloxanes employed in this study were identical samples previously reported,[17] and the open chain polymers are portions of the materials described later.[18]

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[20] N. Wright and L. W. Herscher, to be published in the *J. Opt. Soc. Am.*, Mar. (1947).

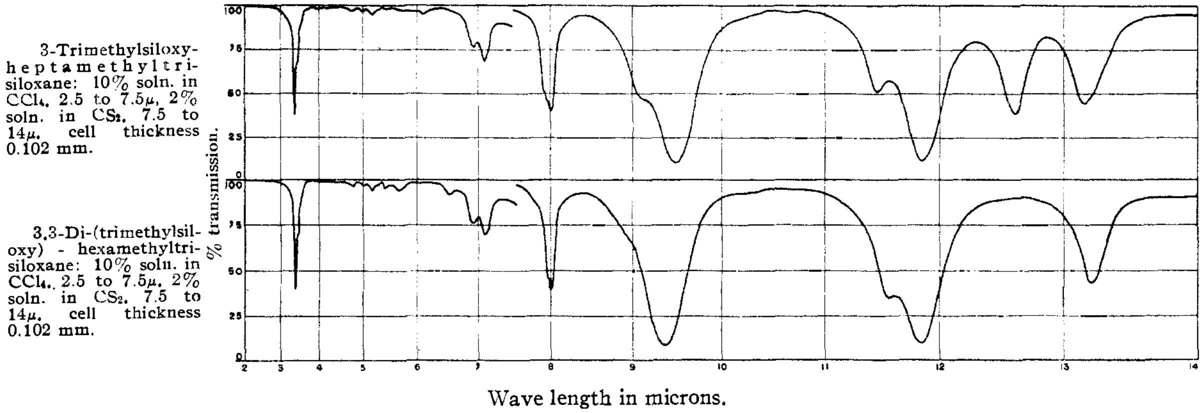

Fig. 3.—Infrared spectra of branched polymethylsiloxanes.

Preparation of 3,3-Di-(trimethylsiloxy)-hexamethyltrisiloxane.—In a 12-liter flask fitted with an agitator and a reflux condenser were placed 1269 g. (6.1 moles) of ethyl orthosilicate, 2880 g. (24.4 moles) of ethoxytrimethyl silane, and 750 g. of ethanol. To this mixture was added 439 g. of water containing 6.2 g. of sodium hydroxide, over

TABLE I

INFRARED ABSORPTION BANDS OF METHYLPOLYSILOXANES

Cyclic Dimethylsiloxanes

(Bands common to all polymers in this series occur at 3.375(S), 3.445(M), 6.92(W), 7.10(M), 7.16(W). and 7.95(S))

Di	Tri	Tetra	Penta	Hexa	Hepta	Octa
				9.11(W)	9.09(W)	9.11(M)
	9.82(S)	9.29(S)	9.25(S)	9.36(S)	9.43(S)	9.47(S)
	11.41(W)	11.66(W)	11.68(W)	11.66(W)	11.65(W)	11.64(M)
			12.19(W)	12.19(W)	12.19(W)	12.18(W)
	12.29(S)	12.33(S)	12.37(S)	12.42(S)	12.44(S)	12.45(S)

Open Chain Polymers

Di	Tri	Tetra	Penta	Hexa	Hepta	Octa
3.380(S)	3.380(S)	3.377(S)	3.375(S)	3.375(S)	3.375(S)	3.375(S)
3.450(M)	3.450(M)	3.448(M)	3.445(M)	3.445(M)	3.445(M)	3.445(M)
6.34(M)						
6.94(W)	6.93(W)	6.94(W)	6.93(W)	6.94(W)	6.94(W)	6.93(W)
7.09(M)	7.08(M)	7.09(M)	7.09(M)	7.09(M)	7.09(M)	7.08(M)
7.14(W)	7.14(W)	7.15(W)	7.15(W)	7.16(W)	7.15(W)	7.15(W)
	7.96(S)	7.96(S)	7.95(S)	7.95(S)	7.95(S)	7.95(S)
7.99(S)	8.00(M)	8.00(W)				
	9.29(M)	9.26(S)	9.21(S)	9.19(S)	9.16(S)	9.15(S)
			9.40(M)	9.47(M)	9.53(W)	9.57(W)
9.48(S)	9.56(S)	9.63(S)	9.68(S)	9.72(S)	9.74(S)	9.77(S)
	11.36(W)	11.39(W)	11.40(W)	11.38(W)	11.41(W)	11.39(W)
11.85(S)	11.87(S)	11.88(S)	11.88(S)	11.89(S)	11.88(S)	11.88(S)
12.14(M)	12.20(W)	12.23(W)	12.22(W)	12.21(W)	12.21(W)	12.21(W)
	12.42(M)					
	12.62(M)	12.52(S)	12.52(S)	12.50(S)	12.49(S)	12.48(S)
13.22(M)	13.27(M)	13.27(M)	13.27(M)	13.26(M)	13.25(W)	13.26(W)

Branched Polymers

(Bands common to both polymers occur at 3.38(S), 3.450(M), 6.94(W), 7.09(M) and 7.15(W))

Isotetra[a]	Neopenta[b]
7.92(M)	
7.96(M)	7.96(M)
8.00(S)	8.00(S)
9.06(W)	
9.47(S)	9.36(S)
11.47(M)	11.55(M)
11.85(S)	11.84(S)
12.62(M)	
13.17(M)	13.21(M)

[a] 3-(Trimethylsiloxy)-heptamethyltrisiloxane. [b] 3,3-Di-(trimethylsiloxy)-hexamethyltrisiloxane.

a period of one hour. On stirring one and one-half hours more, the temperature reached 50°. The resulting product was poured into several volumes of water and washed twice to remove as much alcohol as possible. The oil layer was placed back in the original flask and refluxed for two hours with an equal volume of 20% hydrochloric acid. The resulting siloxane fluid was washed free from hydrochloric acid and dried with calcium chloride. On distillation of the mixture through four feet of quarter inch glass helices there was obtained 346 g. of hexamethyldisiloxane, 635 g. of 3,3-di-(trimethylsiloxy)-hexamethyltrisiloxane (27%), and 536 g. of high boiling residue. The residue contained a white crystalline solid which readily sublimed before melting under vacuum.

The following properties were obtained on the 3,3-di-(trimethylsiloxy)-hexamethyltrisiloxane: b. p. (9 mm.) 91°; d^{25} 0.875; f. p., −54°; visc.^{25} 2.97 centistokes; $n^{25}\text{D}$ 1.3865. Found: C, 37.1; Si, 36.4. Calcd.: C, 37.3; Si, 36.5.

3-(Trimethylsiloxy)-heptamethyltrisiloxane.—3-(Trimethylsiloxy)-heptamethyltrisiloxane has been previously reported by Patnode and Wilcock.[16] The material used for this investigation was prepared in a manner similar to that described for 3,3-di-(trimethylsiloxy)-hexamethyltrisiloxane from the reaction of three moles of ethoxytrimethylsilane with one mole of triethoxymethylsilane: b. p. (6 mm.) 60°; visc.^{25} 1.57 centistokes; f. p. −74°; d^{25} 0.853; $n^{25}\text{D}$ 1.3851. Calcd.: C, 38.7; Si, 36.1. Found: C, 38.5; Si, 36.2.

Discussion of the Spectra

Perhaps the most arresting feature of the infrared absorption spectra of the organosiloxane compounds is the great intensity of the bands lying in the region 8 to 14 μ, which necessitated the use of cell thickness or sample concentration one-fifth that normally required for the corresponding carbon compounds. The strong absorption in this region is another of the properties placing the "silicones" in an intermediate position between the carbon–oxygen compounds and the inorganic silicates. The bands due to the C–H linkage lying at shorter wave lengths are almost equally spectacular because of their weakness relative to the corresponding bands of carbon compounds. A further difference between the spectra of organosilicon compounds in general and the corresponding carbon compounds is the lack of any evidence of an absorption band due to Si═O group. Reasoning by analogy with the C═O bond, which in ketones produces a strong absorption band near 5.8 μ, one would expect the Si═O band to appear near 6.5 μ with very great intensity. No such band has been noted in the hydrolysis products from a large number of R_2SiX_2 type compounds having alkyl or aromatic substituent groups. Chemical evidence[16,17,21] has also ruled against the existence of this group.

Although at first glance the spectra of the two homologous series shown in Figs. 1 and 2 appear extraordinarily similar, closer inspection reveals many significant differences. Particularly the first member of each series differs more from the second than do adjacent higher members. In the higher members the changes become more gradual, and it is noticeable that the spectra of the two series, cyclic and open chain, approach congruence as the polymer size increases. The types of vibration responsible for the stronger bands are discussed in the following sections.

Vibrations Involving the Si–O Bond.—The strong bands near 9.5 μ are unquestionably due to the stretch vibration of the Si–O linkage. This vibration appears in the reflection spectrum of crystalline quartz[7] as the strong "restrahlen" bands at 8.48 and 9.02 μ. Corresponding to this in the carbon compounds is the C–O stretch vibration of ethers near 9.0 μ. As already mentioned the intensity of the Si–O bands is roughly five times that of the C–O bands.

Valence bending vibrations involving the Si–O linkage occur in the vicinity of 20 to 30 μ as shown[15] in the Raman spectrum of crystalline quartz and by the presence of a reflection band of quartz[8] at 20.75 μ (center of gravity of a residual ray using multiple reflections of black-body radiation). Furthermore, the absorption spectra of a few of the compounds of this report were observed in the 14–24 μ region using a potassium bromide prism, all of which showed powerful bands extending from the vicinity of 23 μ to beyond 25 μ (limit of the potassium bromide prism). A harmonic of this band probably falls in the 12–13 μ region, possibly corresponding to the reflection band of quartz[7] at 12.6 μ, but this is not readily differentiated in the present spectra because of the presence in this region of strong Si–C stretch vibration bands as noted later.

Vibration Involving the Si–C Bonds.—Vibration involving stretch of the Si–C bond gives rise to bands in the region 11.6 to 14 μ or greater. In the reflection spectrum of carborundum[7] this band occurs at 12.0 μ. Tetramethylsilane exhibits this band at 11.63 μ (860 cm.$^{-1}$) in absorption and at 863 cm.$^{-1}$ in the Raman spectrum,[13] while in tetraethylsilane the absorption band of Si–C appears at 13.65 μ. In the compounds of this report the Si–C stretch band of the group O–Si–$(CH_3)_3$, the trimethyl end group, lies uniformly at 11.88 μ (Figs. 2 and 3). It is to be noticed in Fig. 2 that this band decreases in strength with the decreasing concentration of end group as the polymer size increases. A less intense band of the same group falls at 13.27 μ and exhibits the same behavior as the 11.88 μ band. In the group [–Si$(CH_3)_2$–] of the cyclic polymer (Fig. 1), the Si–C band gradually shifts from 12.29 μ to 12.45 μ, while in the open chain series (Fig. 2) this band appears at about 12.50 μ and simply increases in intensity as polymer size, or concentration of the group, increases.

Vibrations Involving Methyl Group of Si–CH_3.—Under this heading are discussed the bands involving the C–H bond in stretch and bending vibrations and the so-called "methyl rocking" vibration in which the methyl group rocks as a unit about the Si–C axis. The C–H stretch vibration band lies at 3.38 μ, exactly the position characteristic of methyl group in hydrocarbons. How-

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(21) F. S. Kipping, *J. Chem. Soc.*, **101**, 2108, 2125 (1912).

ever, the intensity of this band is of the order of only one-third to one-fourth that observed when carbon replaces the silicon.

The C–H bending vibrations of the Si–CH$_3$, group lie near 7.0 μ, close to those of the hydrocarbons. The very strong band near 7.95 μ noted in all the compounds of this report is interpreted as the methyl rocking vibration. There is no doubt that this band is associated with the Si–CH$_3$ group since the band is absent in the spectra of all compounds not having this grouping so far observed: *e.g.*, tetraethylsilane, tetraethoxysilane, dichlordiphenylsilane and others. In the carbon compounds this vibration usually occurs in the range 8 to 9 μ, but it is many times weaker than in the Si–CH$_3$ group.

In the series of open chain compounds (Fig. 2) it will be noted that the methyl rocking vibration of the trimethyl end group occurs at 8.00 μ, while that of O–Si(CH$_3$)$_2$–O occurs at 7.95 μ, producing a double band. The 8.00 μ band decreases in intensity with increasing polymer size and consequent decrease in end group concentration. In the compounds of Fig. 3 the methyl rocking band is multiple, three components appearing in 3-(trimethylsiloxy)-heptamethyltrisiloxane, and two appearing in the case of 3,3-di-(trimethylsiloxy)-hexamethyltrisiloxane. In both cases, however, the 8.0 μ trimethyl end group band predominates.

Ionic Character of Silicon Bonds.—The amount of electric charge which can be considered as residing on the nuclei of two atoms connected by a chemical bond is a measure of the ionic character, as distinct from the covalent character, of the bond. Pauling[22] defines the "per cent. ionic character" in the case of the hydrogen halides as $[\mu/eR_0]$ (100), where μ is the observed permanent electric dipole moment, e is the electron charge, and R_0 is the equilibrium internuclear distance. In the case of hydrogen chloride this expression has the value 17.0%. Thus a charge equal to 17.0% of the electronic charge residing on each of the two nuclei, positive and negative, respectively, would produce the observed permanent dipole moment. Intensities of infrared absorption bands also depend on an effective vibrating charge and hence afford another means of evaluating ionic character of bonds.

For example, measurements[23,24] of the absorption coefficient of the hydrogen chloride fundamental vibration band at 3.46 μ give for this effective charge the value 19.9% e, in this case nearly equal to that calculated from the dipole moment. Unfortunately such measurements of absolute intensity of absorption in the infrared are very difficult to make, results having been reported only in the case of simple molecules. Relative intensities, however, are an easier matter, and ratios of amount of ionic character can be approximated using the proportionality between absorption coefficient and $\epsilon^2\nu^2/k$, where ϵ is the effective charge, ν is the frequency of the absorption band and k is the bond force constant.

The ratio of ionic character of the Si–O bond to that of C–O was estimated in this manner to have the value of 2.3. For this calculation were chosen the 9.48 μ Si–O stretch band of hexamethyldisiloxane and the 8.97 μ C–O stretch band of diethyl ether, which have intensities in the ratio of 4.6 to 1 when the materials are in dilute solution in CS$_2$. The values of k are 5.0×10^5 dynes/cm. for Si–O and 4.7×10^5 dynes/cm. for C–O.[25] Pauling's relationship between electronegativity difference and per cent. ionic character gives for the Si–O bond 51% ionic character while that for C–O is 22%. The ratio, $51/22 = 2.3$, agrees with the infrared value more closely than would be expected in view of the experimental error of the relative intensity measurement. Thus the great intensity of the absorption bands involving the Si–O bond furnishes direct confirmation of the large ionic character predicted for this bond.

Some ionic character is also indicated for the Si–C bond since the Si–C stretch vibration bands near 12 μ are fairly intense. The electronegativity difference relation ascribes 12% ionic character to this bond. That the Si–C bond has a dipole moment of considerable size is revealed also by the intensity of the methyl rocking vibration (near 8.0 μ) in which an angular motion of the Si–C group (pivoting on the silicon) is involved. A progressive increase in the absorption coefficient of this band (per methyl group) in the compounds tetramethylsilane, hexamethyldisiloxane, and hexamethylcyclotrisiloxane, in the order named, reveals that the Si–C dipole moment increases as the number of oxygen atoms attached to the silicon increases from 0 to 2. The weaknesss of the C–H bands at 3.38 μ and near 7.0 μ of the methyl group in Si–CH$_3$, relative to those in C–CH$_3$, is explainable as due to the inductive effect of the strong Si$^+$–C$^-$ dipole which causes a lessening of the C–H dipole moment. Agreeing with this is the fact that increasing the Si–C dipole moment by successive attachment of one and two oxygen atoms to the silicon (as in the above mentioned three compounds) results in a progressive weakening of the methyl C–H band absorption coefficients. Other evidence of this lessening of the C–H dipole moment of methyl group in Si–CH$_3$ as compared with C–CH$_3$ is the smaller contribution to molar cohesion which has been previously discussed.[16,18]

Summary

1. The infrared absorption spectra of 15 polymethylsiloxanes have been recorded in the range 2–14 μ.

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[22] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

[23] D. G. Bourgin, *Phys. Rev.*, **29**, 794 (1927).

[24] D. M. Dennison, *ibid.*, **31**, 503 (1928).

[25] These values of k were calculated assuming the above-mentioned bands to be the antisymmetrical stretch vibration of Si–O and C–O, respectively, and assuming the oxygen bond angle to be 120° as determined by X-ray diffraction for hexamethylcyclotrisiloxane (L. K. Frevel and M. J. Hunter, THIS JOURNAL, **67**, 2275 (1945)).

2. A rough classification has been made of the types of vibration involved in the stronger bands.

3. It has been pointed out that the great intensity of the bands involving the Si–O linkage confirms the large ionic character predicted from electronegativity difference.

4. Comparatively weak C–H vibration bands of the group Si–CH_3 indicate a dipole moment of the methyl group considerably smaller than in compounds where carbon replaces the silicon.

MIDLAND, MICHIGAN RECEIVED SEPTEMBER 20, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

Polarographic Studies on Extracted Chlorophylls[1]

BY PIERRE VAN RYSSELBERGHE, JOHN M. MCGEE, ARMIN H. GROPP AND RALPH W. LANE

Complete and final elucidation of the mechanism of photosynthesis will require the accumulation of as much information as possible concerning oxidation–reduction reactions involving the chlorophylls. The present situation of the problem is admirably presented in Rabinowitch's[2] recent book. The investigations reported in the present paper were started before the publication of this book, but it seems to us that they are partial answers to certain questions posed by Rabinowitch. At an early date in our study of the polarographic reduction of carbon dioxide[3,4,5] we felt that results of significance would probably be obtained if extracted chlorophylls could be submitted to polarographic reduction. A comparison between the reduction potential of carbon dioxide and possible reduction potentials of the chlorophylls was considered as very desirable information. Two highly interesting phenomena were observed in our work: a reduction at a high cathodic potential which we have been able to ascribe to the double bond in the phytol chain, and another one at a very low cathodic potential which we have tentatively ascribed to the vinyl group. In mixtures of the chlorophylls with carbon dioxide a merging of the high potential reduction of chlorophyll with that of carbon dioxide was observed, a fact which may have some direct or indirect bearing on the establishment of possible mechanisms of photosynthesis.

Experimental

Chlorophyll was extracted in exact accordance with Zscheile and Comar's[6] latest method from several kinds of green leaves: lilac, Virginia creeper, grass, spinach and pine needles (this last source is unsatisfactory). Chlorophyll a was also extracted from *Vaucheria sp.* which does not contain any chlorophyll b.[7] A few extractions were carried out on smaller amounts of green material by the method of Strain and Manning.[8] The a and b components of the chlorophyll mixtures were separated in chromatographic columns packed with powdered sucrose. The final fractions were kept either in highly purified ethyl ether or, more frequently and with more satisfactory results, in highly purified dioxane. Whenever possible polarograms were taken immediately after extraction and separation. In a number of cases the polarograms were repeated at intervals of a few days in order to follow possible effects of aging of the chlorophylls or of their solvents. The chlorophyll solutions were kept in the dark in an ice box, the solutions in dioxane being then actually congealed. A Heyrovsky polarograph of the Sargent Company with photographic recording was used. Carefully recrystallized tetramethylammonium bromide was used as supporting electrolyte. Blanks were recorded with samples of 10 ml. of 0.1 molar solution. After passage of a stream of nitrogen to remove any dissolved oxygen a few drops of ether solution of chlorophyll were added. Stirring and further removal of oxygen were accomplished by a stream of nitrogen. In all cases enough chlorophyll was transferred to the aqueous solution to obtain good reduction waves. When a dioxane solution of the chlorophyll was used known volumes of up to 2 ml. were added to the 10 ml. of supporting electrolyte solution, the mixture was stirred with nitrogen and enough of the chlorophyll of the original dioxane solution stayed in solution in the resulting water–dioxane solvents to give suitable waves at sensitivities 50 and 100 of the Sargent polarograph. In all cases it had been previously established that the purified ether or dioxane alone had no disturbing effect on the polarograms. In a few cases the chlorophylls (several a + b mixtures, some samples of a from *Vaucheria*, as well as a commercial preparation obtained from the American Chlorophyll Co., Inc.) were saponified by a slight modification of the method of Willstätter and Stoll[9] using as alkali lithium or tetramethylammonium hydroxide in order to obtain chlorophyllins with positive ions having as high a polarographic reduction potential as possible.

The saponifications were carried out at 20° using methyl alcohol solutions of the respective bases. The required amount of each base was calculated and a slight excess taken to ensure complete conversion of the chlorophylls to chlorophyllin salts. The saponification proceeded rapidly as indicated by the complete solubility of the green product in water and the absence of any green ether-soluble residue.

After saponification the methanol was removed under reduced pressure at 20° and the chlorophyllin was extracted repeatedly with petroleum ether (b. p. 35–50°) to remove the phytyl alcohol released by the reaction. This phytol was transferred to ether or dioxane solutions for polarographic examination, while the lithium and tetramethyl-

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[1] Presented in part under the title "Polarographic Studies on Carbon Dioxide and Chlorophyll" by Pierre Van Rysselberghe and John M. McGee at the Pacific Northwest Regional Meeting of the American Chemical Society in Seattle, Wash., October 20, 1945.

[2] E. I. Rabinowitch, "Photosynthesis and Related Processes," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945.

[3] P. Van Rysselberghe and G. J. Alkire, THIS JOURNAL, **66**, 1801 (1944).

[4] P. Van Rysselberghe, *ibid.*, **68**, 2047 (1946).

[5] P. Van Rysselberghe, G. J. Alkire and J. M. McGee, *ibid.*, **68**, 2050 (1946).

[6] F. P. Zscheile and C. L. Comar, *Botanical Gazette*, **102**, 463 (1941).

[7] E. I. Rabinowitch, ref. 2, p. 405.

[8] H. H. Strain and W. M. Manning, *J. Biol. Chem.*, **144**, 625 (1942).

[9] R. Willstätter and A. Stoll, "Investigations on Chlorophyll," English translation by F. M. Schertz and A. R. Merz, Science Press Co., New York, N. Y., 1928; see pp. 288–290.