pressure at the liquid surface is 17.8 mm.; the calculated oxygen concentrations at this point necessary to effect the known rates of oxygen transfer correspond to partial pressures of 2.6 to 11.8 mm.

V. Conclusions

The diffusion coefficients of peroxide into various permanent gases may be measured to an accuracy of ±2% by the method and apparatus described in this report. Peroxide decomposition does not interfere with diffusion measurement, for rates of decomposition which are not excessively high.

(An important diffusion coefficient, that of peroxide vapor into its decomposition products, is not however measurable by this method.)

VI. Summary

The diffusion coefficient of peroxide vapor into air has been measured at a temperature of 60°. A value of 0.188 ± 0.004 sq. cm./sec. was obtained. The method and apparatus used are applicable to the measurement of peroxide vapor diffusion rates into other permanent gases. An estimate of the coefficient, using the Edwin R. Gilliland formula[12] gives the number 0.1982.

(12) E. R. Gilliland, *Ind. Eng. Chem.*, **26**, 681 (1934).

RECEIVED JUNE 5, 1948

[CONTRIBUTION FROM THE DOW CORNING CORPORATION]

Organosilicon Polymers. IV. Infrared Studies on Cyclic Disubstituted Siloxanes[1]

BY C. W. YOUNG,[2] P. C. SERVAIS,[3] C. C. CURRIE[3] AND M. J. HUNTER[3]

Numerous reports[4] have appeared on cyclic disubstituted siloxanes, and it has been observed that the cyclic forms are often the prevalent structures obtained from the hydrolysis of R_2SiCl_2 type compounds in organic solutions. Most frequently the cyclics so obtained are the trimer and tetramer polymers. When the R group is relatively small, separation of the trimer and tetramer polymers is reasonably satisfactory by fractional distillation. In order to be certain of the molecular size, it has been necessary in the past to rely on molecular weight determinations. Difficulties in these determinations have been expressed by certain workers.[4e, 4g]

The purpose of this paper is to show how infrared absorption spectra may be used to distinguish between cyclic trimer and tetramer siloxane forms, and also to point out the characteristic bands for methyl, ethyl, and phenyl groups attached to silicon. The spectra of the cyclics used in this study are given in Figs. 1 and 2. Besides the dimethyl and diphenyl cyclic forms which are well known, this paper will present the spectra of the diethyl and new ethyl phenyl compounds. Included also are the two isomers of the methyl phenyl cyclic trimers recently described by Lewis,[5] and in addition, a new crystalline isomer of the cyclic tetramers in the same system.

Experimental

Source of Materials.—The dimethyl cyclic trimer and tetramer samples were identical with those used in the previous paper[6] and are described well in other reports.[4f,4g]

The diphenyl cyclosiloxane trimer and tetramer were prepared according to procedures well described in other articles.[4a,4b,4c,4d,4e]

Hexaethylcyclotrisiloxane–Octaethylcyclotetrasiloxane.—Diethyl siloxanes have been reported[7,4c] in rather general terms, but accurate physical properties of the cyclic trimer and tetramer forms have not been given. Hydrolysis of the $(C_2H_5)_2SiCl_2$ was carried out as follows: To a mixture of 478 g. of $(C_2H_5)_2SiCl_2$ in 700 cc. of diethyl ether was added 478 g. of ice. After all of the ice had melted, the mixture was refluxed for one hour with the hydrochloric acid solution so formed. The aqueous layer was separated and the ether solution washed with an equal volume of water. The solution was then refluxed for one hour with a 5% sodium hydroxide solution which served to remove any lingering chloride groups as well as to condense hydroxyl groups. Concentration of the siloxane by removal of the ether gave a clear white fluid which contained 62% of volatile cyclic polymers. Hydrolysis of dichlorodiethylsilane with ice using no ether gave 27% volatiles. In a third run, dropping the dichlorodiethylsilane into boiling water yielded only 22% of volatile $[(C_2H_5)_2SiO]_x$ polymers.

Fractional distillation of the accumulated volatiles gave 60–70% of cyclic trimer and 10–20% of cyclic tetramer. Redistillation of $[(C_2H_5)_2SiO]_3$ through a glass helices packed column (20 plates) yielded the pure trimer with the following properties: b. p. 156.7° (50 mm.), m. p. 9.9°, d^{20}_4 0.9549, $n^{20}D$ 1.4308, visc.[25] 3.6 centistokes. *Anal.* Calcd. for $(C_2H_5)_2SiO$: Si, 27.45; C, 47.06. Found: Si, 27.5; C, 46.95.

A much lower yield of higher boiling cyclic tetramer was found to have the following properties: visc.[25] 11.2 centistokes, b. p. 127° (1 mm.), f. p. −64°, d^{20}_4 0.964, $n^{20}D$ 1.4336.

2,4,6-Trimethyltriphenylcyclotrisiloxane (α and β Isomers); 2,4,6,8-Tetramethyltetraphenylcyclotetrasiloxane (α Isomer).—These two geometric isomers have recently been reported by Lewis,[5] but he did not describe the crystalline tetramer form which we have found in the same preparation. Five hundred grams of pure dichloromethylphenylsilane (b. p. 204° (760 mm.), d^{20}_4 1.1578, $n^{20}D$ 1.5190) was diluted with three volumes of ether and cooled in an ice-bath. To this solution was slowly added 370 cc. of water per mole of dichloromethylphenylsilane. The ether solution was then washed free of chloride with dis-

(1) Presented in part at the Chicago Meeting of the American Chemical Society, April, 1948.

(2) The Dow Chemical Company.

(3) Dow Corning Corporation.

(4) (a) Kipping, *J. Chem. Soc.*, **101**, 2125 (1912); (b) Kipping and Robinson, *ibid.*, **105**, 484 (1914); (c) Hyde and DeLong, THIS JOURNAL, **63**, 1194 (1941); (d) Burkhard, Decker and Harker, *ibid.*, **67**, 2174 (1945); (e) Hyde, Frevel, Nutting, Petrie and Purcell, *ibid.*, **69**, 488 (1947); (f) Patnode and Wilcock, *ibid.*, **68**, 358 (1946); (g) Hunter, Hyde, Warrick and Fletcher, *ibid.*, **68**, 667 (1946).

(5) Lewis, *ibid.*, **70**, 1115 (1948).

(6) Wright and Hunter, *ibid.*, **69**, 803 (1947).

(7) (a) Martin and Kipping, *J. Chem. Soc.*, **95**, 302 (1909); (b) Alfrey, Honn and Mark, *J. Polymer Sci.*, **1**, 102 (1946).

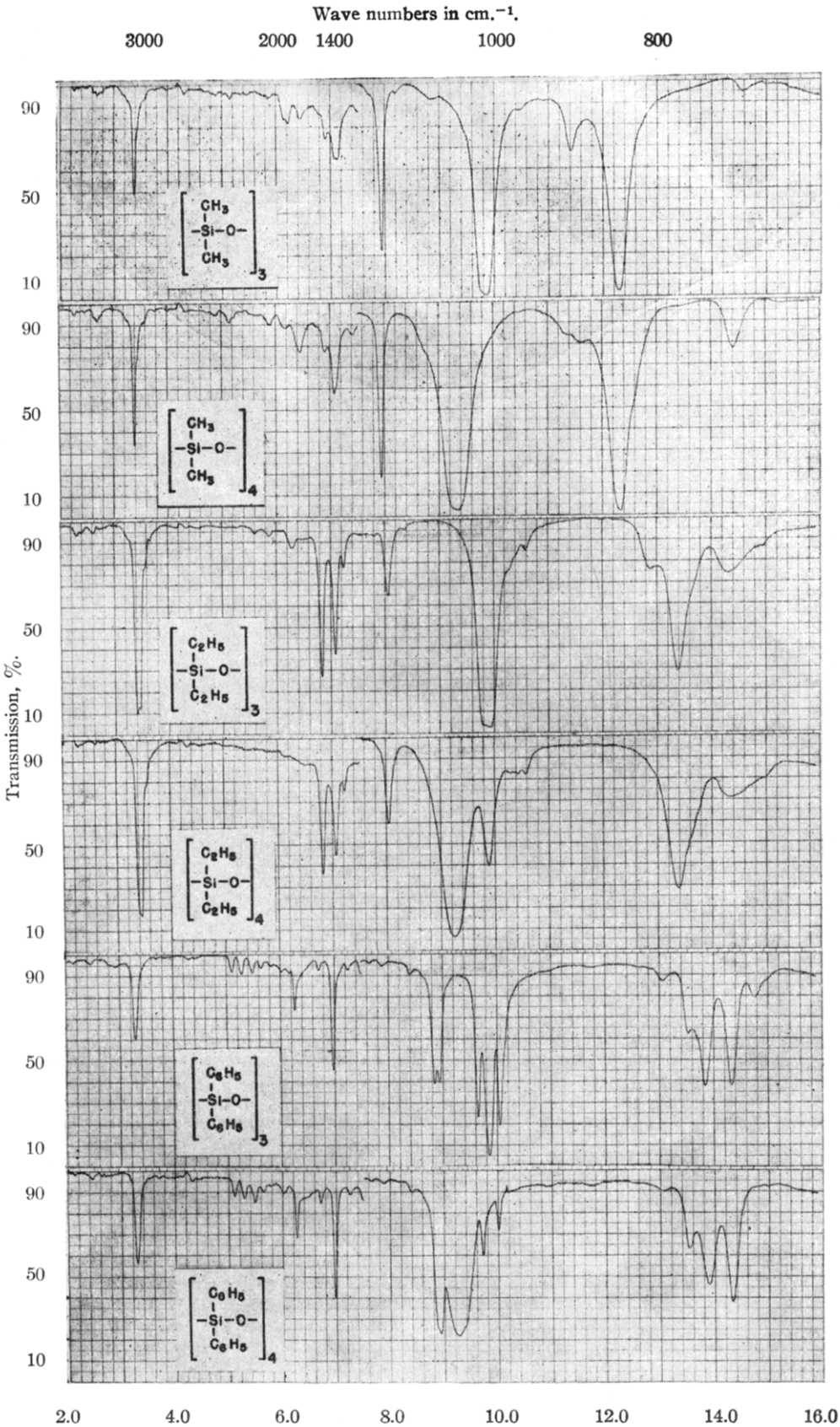


Fig. 1.—Infrared spectra of cyclosiloxanes with one type of substituent group.

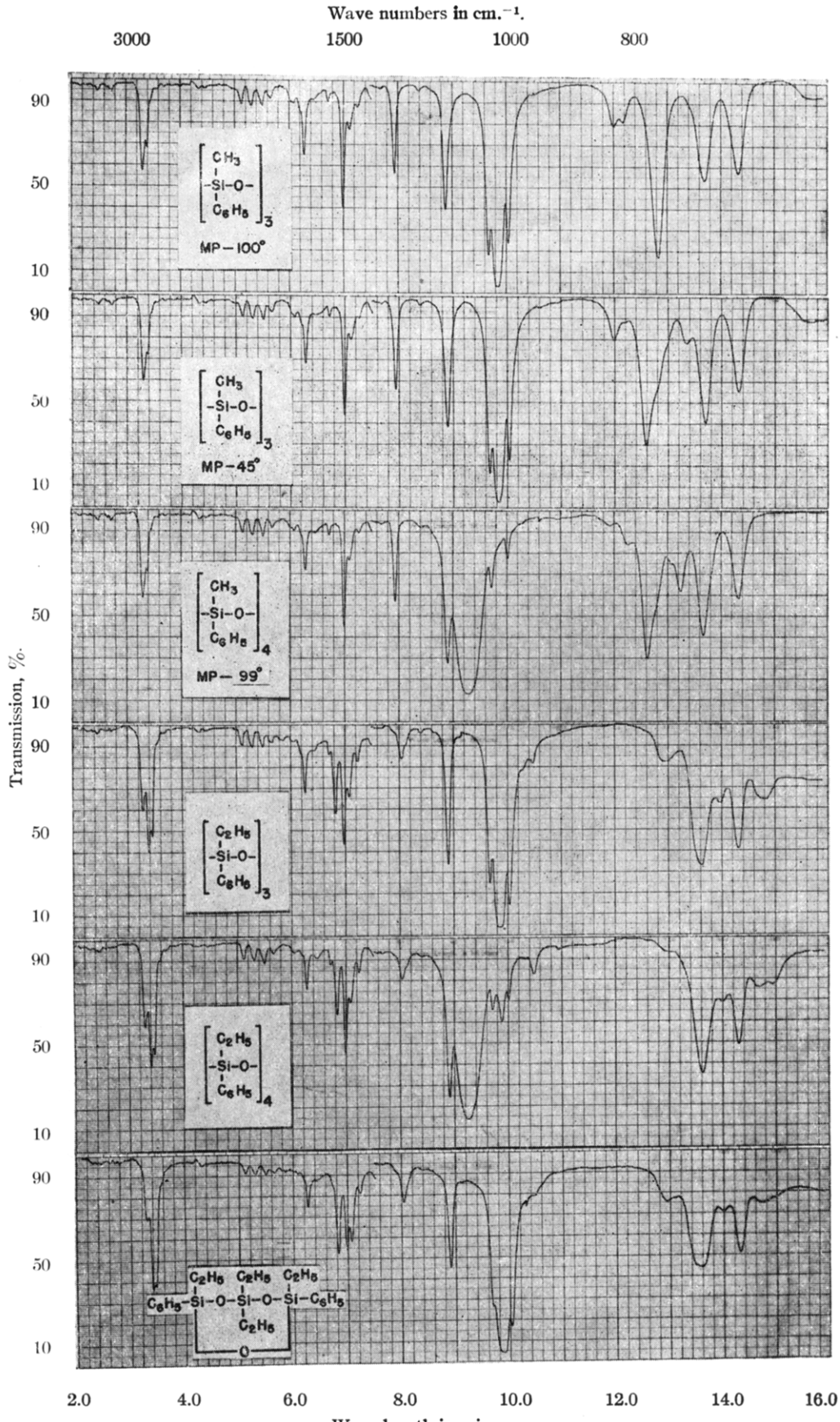


Fig. 2.—Infrared spectra of cyclosiloxanes with two kinds of substituent groups.

tilled water. After removal of ether under water vacuum at 20 mm. and 100°, the residue obtained was a water-white oil: visc.^{20} 203 centistokes, $n^{20}D$ 1.5451, d^{20}_4 1.125. *Anal.* Calcd. for $CH_3(C_6H_5SiO$: Si, 20.61; OH, 0.0. Found: Si, 20.02; OH, 1.21. Vacuum stripping in a short path still at 0.1 mm. and 300° yielded a volatile portion (76.7%): visc.^{20} 187 centistokes, $n^{20}D$ 1.5445, d^{20}_4 1.121. *Anal.* Si, 20.56; OH, 0.31.

The residue (19.5%) had a viscosity of 614,000 centistokes at 20°, $n^{20}D$ 1.5472, d^{20}_4 1.133. *Anal.* Si, 22.07. The cold trap contained 1–3% of benzene.

The collected volatiles from three hydrolysis runs (973 g.) were placed in a fractionating still comprising a (24 × 1.25 in.) column containing one-fourth inch glass helices and a Corad head. The first plateau (150 cc.) was obtained at 10% reflux ratio with a head temperature of 157° and a pot temperature of 250°. McLeod gage reading of the distillation pressure showed 0.5 mm., but this is probably lower than the actual pressure in the flask. The head temperature then rose rapidly to 180° at 0.1 mm. When distillation rate was increased by application of more heat, the head temperature rose to 190°. If the column was placed on total reflux at any time, the head temperature would drop to 155–160°. Pot temperature readings during the distillation of the higher boiling plateau varied from 350–390°.

White crystals formed early in the distillation of the 157° plateau. These were filtered from the colorless liquid portion and recrystallized from methanol to a constant melting point of 100°. *Anal.* Calcd. for $[(CH_3)(C_6H_5)$-SiO]: C, 61.74; Si, 20.61. Found: C, 61.1; Si, 20.52.

The infrared spectra indicated that it was a cyclotrisiloxane. On standing at room temperature several days, no further crystallization was observed in the mother liquor (visc.^{20} 82.5 centistokes). It was then placed in a cold chest (−20°) to see if more 100° m. p. crystals could be obtained. This caused it to become very stiff, and on warming up to room temperature it crystallized to a completely solid mass. Recrystallization several times from methanol gave white crystals m. p. 45.5°. *Anal.* Calcd. C, 61.74; Si, 20.61. Found: C, 61.4; Si, 20.7. Infrared spectra of this compound indicated that it was also a cyclotrisiloxane and differed slightly, but distinctly, from the 100° melting isomer as seen in Fig. 2. Approximately 80 g. each of 100° and 45.5° compounds were isolated.

Crystals which formed in the head when the still was placed on total reflux, any time during the distillation of the 190° plateau, after the head temperature dropped to 155–160°, were always the 100° melting cyclic trimer.

The tetramer plateau (610 cc.) was collected in numerous cuts. On standing several weeks, fractions near the end of this plateau deposited 15–20% of white crystals which on recrystallization from methanol were found to melt at 99°. *Anal.* Calcd. for $CH_3(C_6H_5)SiO$: C, 61.74; Si, 20.61. Found: C, 61.4; Si, 20.2. A mixed melting point determination of these with the lower boiling 100° melting crystals was found to be 83°. An infrared spectrum showed the compound melting at 99° to be a pure cyclotetrasiloxane form. Spectra of the liquid tetramers were very similar, but somewhat different from the crystalline form. On standing three years, no new cyclic tetramer forms could be induced to crystallize from this liquid tetramer fraction.

2,4,6-Triethyltriphenylcyclotrisiloxane (Mixed Isomers); 2,4,6,8-Tetraethyltetraphenylcyclotetrasiloxane (α Isomer).—To 770 g. of crushed ice was slowly added 510 g. of dichloroethylphenylsilane, b. p. 94° (10 mm.), dissolved in three volumes of diethyl ether. The mixture was allowed to warm to room temperature and then refluxed for one hour. After washing the ether solution twice, it was refluxed a second time with an equal volume of 5% sodium hydroxide solution. This was washed first with 2% hydrochloric acid solution and then with distilled water until neutral. The ether solution was dried with calcium chloride and concentrated on a water pump at 50 mm. to 150°. The water-white oil was placed in a short path still and distilled to a pot temperature of 280° with 0.05–0.10 mm. pressure. The distillate (77.5%) had a viscosity of 81 centistokes at 25°. *Anal.* Calcd: Si, 18.76; C, 63.9; OH, 0.0. Found: Si, 18.29; C, 63.5; OH, 0.43.

Five hundred and thirty grams of distillate from three runs was placed in a fractionating still with a 12 × 1 in. Vigreux column and a Corad head. This distillation yielded 260 cc. of a fraction boiling at 170–175° (0.1 mm.) and 120 cc. boiling at 212° head temperature. Redistillation of each plateau through the same still gave a 230 cc. fraction of ethyl phenyl cyclic trimer boiling at 166° (0.025 mm. gauge reading); $n^{25}D$ 1.5402, d^{25}_4 1.0932, visc.^{25} 63.6 centistokes. *Anal.* Calcd. for $C_2H_5(C_6H_5)$-SiO: C, 63.96. Found: C, 63.95.

After standing four years no crystalline trimers were observed to separate from this fraction. Infrared examination indicated that it was pure ethyl phenyl cyclic trimer (1,3,5-triethyltriphenylcyclotrisiloxane) free from cyclic tetramer.

The higher boiling fraction (120 cc.) was thought to be quite pure ethyl phenyl cyclic tetramer with a visc.^{25} of 220 centistokes; $n^{25}D$ 1.5430, d^{25}_4 1.1000. *Anal.* Calcd. for (EtPhSiO): C, 63.96. Found: C, 63.85.

On standing for three weeks at room temperature fine white crystals began to separate from the high boiling fraction. These were filtered off and recrystallized twice from anhydrous methanol, m.p. 106° (yield, 10-11 g., about 10%). *Anal.* Calcd. for $[C_2H_5(C_6H_5)SiO]_4$: Si, 18.68; C, 63.96. Found: Si, 18.5; C, 63.6. The infrared spectrum of this compound indicated that it was a cyclic tetrasiloxane. The mother liquor was also pure cyclic tetrasiloxane.

Tetraethyl-2,4-diphenylcyclotrisiloxane.—Cohydrolysis of a mixture of two moles of dichlorodiethylsilane and one mole of dichloroethylphenylsilane by the procedure described above yielded a highly complex mixture of cyclic trimer and tetramer cyclosiloxane structures. Fractional distillation of 3089 g. of hydrolysate distilling above 150° (15 mm.) gave 460 cc. of tetraethyl-2,4-diphenylcyclotrisiloxane, b. p. 150° (0.5 mm.), $n^{20}D$ 1.5008, d^{20}_4 1.0561. *Anal.* Calcd. for $(C_2H_5)_4(C_6H_5)_2Si_3O_3$: C, 59.7; Si, 20.9. Found: C, 59.8; Si, 21.1.

Pentaethylphenylcyclotrisiloxane.—In the above preparation a smaller fraction 240 cc. distilling at 165° (12 mm.) was taken off before the tetraethyl-2,4-diphenylcyclotrisiloxane fraction. This compound was pentaethylphenylcyclotrisiloxane $n^{20}D$ 1.4734, d^{20}_4 1.0096. *Anal.* Calcd. for $(C_2H_5)_5(C_6H_5)Si_3O_3$: C, 54.2; Si, 23.4. Found: C, 54.6; Si, 23.5.

Apparatus and Techniques.—The infrared spectra shown here are photographic reproductions of records obtained on the Baird Associates double-beam spectrometer of The Dow Chemical Company. For the most part, the samples were observed in solution, 500 mg. made up to 5 cc. in carbon tetrachloride from 2–7.5 μ, 100 mg. made up to 5 cc. in carbon disulfide from 7.5–16 μ. The sample cell was approximately 0.13 mm. thick; a compensating cell containing pure solvent of sufficient thickness to eliminate solvent bands was placed in the second beam of the spectrometer.

Because of lower solubility, the diphenyl trimer was made up to 5% solution in carbon tetrachloride, using an 0.2 mm. cell in the 2–7.5 μ range.

In order to conserve space a table containing the list of wave lengths of the absorption bands is not included here.[8] This table includes more accurate and better resolved measurements from a lithium fluoride spectrometer, as well as bands measured at longer wave lengths with a potassium bromide spectrometer.

The spectra of the dimethyl compounds have been given before,[6] but are here for direct comparison in the series since a change in scale is involved and a slightly greater wave length range is included.

Discussion of Spectra

Wright and Hunter[6] have presented the infra-

(8) Copies of these tables, Document 2534, may be obtained from the American Documentation Institute (Science Service), 1719 N Street, N. W., Washington, D. C. Photoprints $0.50; microfilm $0.50.

red spectra of a number of methylpolysiloxanes, both chain and cyclic, and have discussed the salient features of these spectra. The present series of cyclic trimers and tetramers, variously substituted with methyl, ethyl, and phenyl groups, afford new features of interest in their infrared spectra in terms of the "inner" vibrations of the substituent groups linked to silicon, besides showing the special frequencies associated with the siloxane rings.

Characteristic bands for methyl, ethyl and phenyl linked to silicon are remarkably constant in all the compounds for wave lengths shorter than about 11.0 μ, and allow a ready determination of the presence of these groups. The methyl group always shows at 3.38 μ, 7.08 μ, 7.94 μ; the ethyl group at 6.84, 7.08, 7.26, 8.05, 9.9, 10.4; the phenyl group at 6.28, 6.7, 6.98, 8.4, 8.9, 9.7, 10.04. These bands vary only by a few hundredths of a micron and show but slight variations in relative intensities from compound to compound.

Wright and Hunter have characterized the above three bands for methyl as being due to C–H stretching, CH bending, and CH_3 rocking. Another strong band between 12 and 13 μ has been attributed by them to the Si–C stretching mode. This latter is at a less definitely fixed wave length than the three shorter wave length bands. Presumably interaction with ring vibrations has more effect on a CH_3 mode of lower frequency than on those CH_3 modes having higher frequencies.

It is true in general, of course, that lower vibration frequencies in large molecules cannot usually be successfully attributed to the vibrations of attached groups.

The band at 7.94 for dimethylsiloxane may be due to the symmetrical deformation mode as suggested for tetramethylsilane by Young, Koehler and McKinney.[9] If this assignment is the correct one, the methyl rocking would be identified with the longer wave length band between 12 and 13 μ.

A tentative assignment of the C_2H_5–Si system is suggested as follows: 6.84 μ, CH_3 unsymmetrical deformation; 7.08 μ, CH_2 deformation; 7.26 μ, CH_3 symmetrical deformation; 8.05 μ, CH_2Si deformation; 9.9 μ, C–C stretching. A further band, again not well defined in the long wavelength region, at about 13.4 μ, may possibly be assigned to methyl rocking. While the 9.9 μ ethyl band in the cyclic trimers is not easily differentiated from the 9.8 μ SiO band in the reproduced spectra, in the unreduced original spectra there is always very clear evidence for two overlapping bands at this wave length.

The phenyl bands cannot as yet be very closely characterized. Although there is a rough correspondence between the phenyl bands in the siloxanes and, for example, those of the phenyl halides, there is no great similarity either in relative intensities or wave length between the phenyl bands of phenyl siloxanes and phenyl halides in the two systems. We have not attempted to assign the phenyl bands of siloxane systems to definite modes of vibration. The 7.0 μ band is very characteristic of unsubstituted phenyl groups attached to silicon while the band near 9.0 μ is less constant in wave length but equally prominent. Of the phenyl bands longer than 11.0 μ, the pair of bands at about 13.5–13.6 μ and 14.3 μ are very similar to a pair often found with monosubstituted benzenes, and appear to be reasonably characteristic.

Similarities in spectra between 13 and 15 μ will be noted between dimethyl trimer and tetramer, between diphenyl trimer and tetramer, and between diethyl trimer and tetramer, respectively, although in general the various substituting groups do not appear to contribute to the spectra in any very characteristic fashion in this region. In the two isomeric forms of phenyl methyl trimer, a noteworthy point is the shift from 12.6 μ of the methyl band in the 45.5° m. p. isomer to 12.84 μ in the 100° m. p. isomer.

An interesting feature is the doubling of the 8.9 μ band in the systems containing two phenyl groups on silicon, and the doubling of the 7.1 μ band in the dimethyl siloxane compounds.

In an infrared survey of a wide variety of cyclic structures, it was observed that there was a marked and consistent difference between certain bands of trimer structures on one hand and cyclic tetramers on the other. All cyclic trimers were observed to have a strong absorption band at 9.8–9.9 μ while all cyclic tetramers have a strong band at 9.15–9.25 μ. It is thought that this band is associated with stretch vibrations of the Si–O–Si configuration. The spectra of the disubstituted systems of methyl, ethyl and phenyl are shown in Fig. 1. The problem involving isomorphic crystalline structures encountered by Hyde[4e] is completely eliminated since the infrared spectra are made from solutions. More rigorous methods of structure proof have been carried out on some of the trimer–tetramer pairs shown above and nice correlation is now demonstrated that infrared can be relied upon to distinguish accurately between trimers and tetramers of any pair of disubstituted organocyclosiloxanes. All systems encountered up to this time have been easily resolved by use of this method.

Stereoisomerism of Cyclosiloxanes

Stereoisomerism of cyclic compounds has been studied extensively as reported by Gilman.[10] The preparation of isomeric cyclic hydrocarbon systems often demands special types of synthesis, but in organosiloxane preparations it is possible to obtain these stereoisomeric forms very readily in high yields.

When all of the groups attached to disubstituted siloxane cyclic polymers are the same radical, no isomeric forms have been observed. Theo-

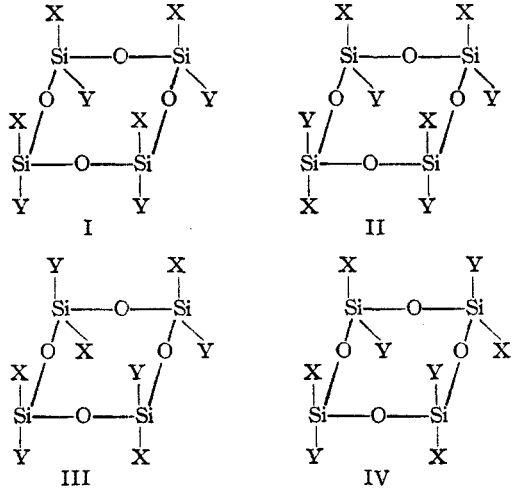
(9) Young, Koehler and McKinney, THIS JOURNAL, **69**, 1410 (1947).

(10) H. Gilman, "Organic Chemistry," Vol. I, sec. ed., John Wiley and Sons, New York, N. Y., 1943, p. 315.

ries indicating[11] that cyclotrisiloxane rings are planar have been postulated. Similar work on cyclotetrasiloxane rings has not been reported, but it does not seem probable that this eight membered siloxane ring would be planar also. Since more than one form has not been observed for the $[R_2SiO]_4$ compounds, one would conclude, in agreement with Gilman, that such rings may exist in different geometric forms, but that they are all readily interconvertible. Only by X-ray analysis would it be possible to determine whether the different crystalline forms of $[Ph_2SiO]_x$[4e] are different polymorphs of the same isomer or different ring forms, chair or boat forms for example. In solution, no distinction is found among the infrared spectra of any of the forms.

When two substituent groups R_1 and R_2 are attached to the same silicon atom, interesting geometric isomers are possible as demonstrated by the trimer forms of the methylphenylsiloxane compounds. We predict that the ethylphenyl trimer liquid is also comprised of two similar geometric forms even though it has not been possible to induce either of them to crystallize up to the present time.

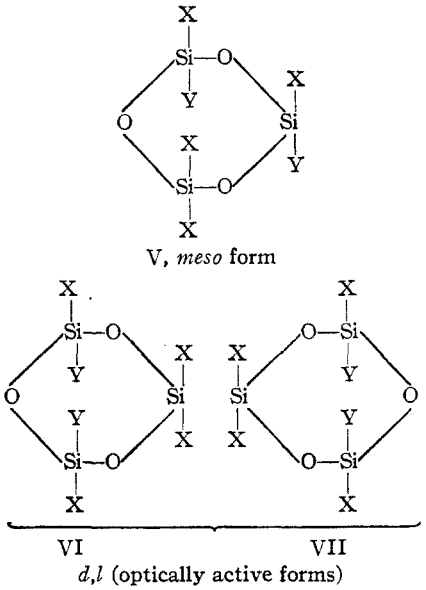
Lewis[5] predicted four forms of the methylphenyl cyclic tetramer polymers, but was unable to resolve any crystalline forms. The compound melting at 99° was easily obtained by crystallization from numerous mixtures of methylphenylsiloxane polymers by seeding with crystals from the original batch. Both trimers and the single tetramer could be obtained fairly pure in this manner without distillation by careful seeding techniques. It is thought that the liquid tetramer portion (approximately 80%) contains three more isomers as shown



Present knowledge is thought insufficient to say which of the above stereoisomers is the crystalline form.

The crystalline ethyl phenyl cyclic tetramer (m. p. 106°) is thought to be the same structural isomer as the 99° methyl phenyl tetramer with ethyl and methyl groups being in similar positions with relation to the phenyl groups. Liquid ethyl phenyl cyclic tetramer from which the 106° form had been completely crystallized showed a similar infrared spectrum to the crystalline form separated, but with slight variations in the 12–26 μ regions which indicate minor differences similar to those observed for two methyl phenyl cyclic trimer forms.

The preparation of copolymer cyclics containing two types of disubstituted silicon atoms allows for the formation of optically active molecules with asymmetric silicon atoms. Kipping[12] prepared optically active compounds with asymmetric silicon atoms by classical resolution procedures. The copolymer liquid tetraethyl-2,4-diphenylcyclotrisiloxane was prepared, but could not be resolved into the three isomeric structures which it is predicted to contain as shown



Resolution of cyclic tetramers in this system would be considerably more difficult and was not attempted. Many complex cyclosiloxane polymer systems are possible, and careful selection of groups which aid crystallization would make possible the demonstration of numerous types of cyclic isomers which would be considerably more difficult to obtain for cyclic hydrocarbon ring systems. The infrared techniques demonstrated here would greatly simplify the characterization of these cyclotri- and cyclotetra-siloxane compounds.

Summary

1. Infrared spectra for twelve disubstituted cyclosiloxane compounds are presented.

2. Characteristic bands for methyl, ethyl and phenyl groups attached to silicon are shown.

3. All trimeric and tetrameric cyclosiloxanes

(11) Frevel and Hunter, THIS JOURNAL, 67, 2275 (1945).

(12) Challenger and Kipping, *J. Chem. Soc.*, 97, 755 (1910).

are readily distinguishable by characteristic infrared bands for each ring structure.

4. The properties of hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane are given.

5. New crystalline isomers of methyl phenyl and ethyl phenyl cyclotetrasiloxane systems are presented.

6. Optical as well as geometrical stereoisomeric cyclosiloxane compounds are postulated.

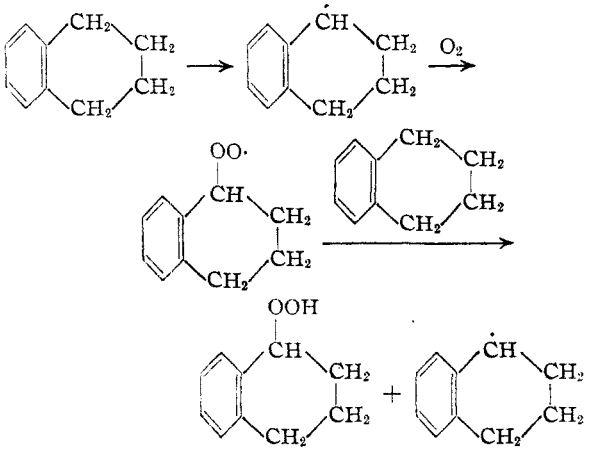
MIDLAND, MICHIGAN RECEIVED JUNE 7, 1948

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

The Liquid Phase Oxidation of Ethylbenzene

BY WILLIAM S. EMERSON, JOSEF W. HEYD, VICTOR E. LUCAS,[1] WILLIAM B. COOK,[2] WARREN I. LYNESS[3] AND JAMES K. STEVENSON[4]

The catalytic liquid phase oxidation of tetralin to α-tetralone has been shown to proceed through tetralin hydroperoxide by a free radical mechanism.[5] The formation of the hydroperoxide is a simple chain reaction.[6] The exact process by



which the peroxide decomposes is not known, although a mechanism involving the formation of hydroxyl free radicals has been suggested.[5]

The catalytic, liquid phase oxidation of ethylbenzene by air to give acetophenone probably proceeds by a similar mechanism.

$$C_6H_5CH_2CH_3 + \text{Catalyst} \longrightarrow C_6H_5\dot{C}HCH_3 + \text{Catalyst H}\cdot$$

$$C_6H_5\dot{C}HCH_3 + O_2 \longrightarrow C_6H_5CH(OO\cdot)CH_3$$

$$C_6H_5CH_2CH_3 + C_6H_5CH(OO\cdot)CH_3 \longrightarrow C_6H_5CH(OOH)CH_3 + C_6H_5\dot{C}HCH_3$$

That the first step is the loss of a hydrogen atom to give an α-phenylethyl free radical is shown by the fact that Sully[7] isolated its dimer, 2,3-diphenylbutane, from the higher boiling by-products of the oxidation. We also have isolated and identified 2,3-diphenylbutane.

$$2C_6H_5\dot{C}HCH_3 \longrightarrow C_6H_5CH(CH_3)-CH(CH_3)C_6H_5$$

The decomposition of α-phenylethyl hydroperoxide may occur by a number of mechanisms of which two seem the most probable. At 140° it could decompose thermally into two free radicals. Dialkyl peroxides

$$C_6H_5CH(OOH)CH_3 \xrightarrow{140^\circ} C_6H_5CH(O\cdot)CH_3 + HO\cdot$$

are known to decompose at 130–160°.[8] The hydroxyl free radicals thus generated could either attack an ethylbenzene molecule or assist in the decomposition of the hydroperoxide.

(1) $C_6H_5CH_2CH_3 + HO\cdot \longrightarrow H_2O + C_6H_5\dot{C}HCH_3$

(2) $C_6H_5CH(OOH)CH_3 + HO\cdot \longrightarrow H_2O + [C_6H_5C(OOH)CH_3] \longrightarrow C_6H_5COCH_3 + HO\cdot$

This last reaction is the same as that suggested by Robertson and Waters[5] in the case of tetralin hydroperoxide, except that they generated their initial hydroxyl free radicals by reaction between the catalyst and the hydroperoxide. This type of hydroxyl free radical generation also could occur in the case of α-phenylethyl hydroperoxide.

The α-phenylethoxy free radicals, from the thermal decomposition of the hydroperoxide, would undergo the same reactions as the hydroxyl free radicals.

(3) $C_6H_5CH(O\cdot)CH_3 + C_6H_5CH_2CH_3 \longrightarrow C_6H_5CH(OH)CH_3 + C_6H_5\dot{C}HCH_3$

(1) Present address: Firestone Tire and Rubber Company, Akron, Ohio.

(2) Present address: University of Wyoming, Laramie, Wyoming.

(3) Present address: Purdue University, Lafayette, Indiana.

(4) Present address: Battelle Memorial Institute, Columbus, Ohio.

(5) Robertson and Waters, *Trans. Faraday Soc.*, **42**, 201 (1946).

(6) George and Robertson, *ibid.*, **42**, 217 (1946).

(7) Sully, *ibid.*, **42**, 260 (1946).

(8) Raley, Rust and Vaughan, THIS JOURNAL, **70**, 88 (1948).