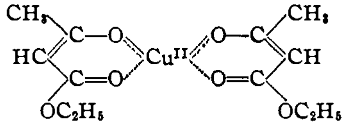
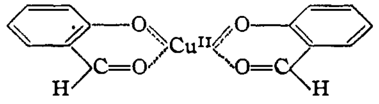


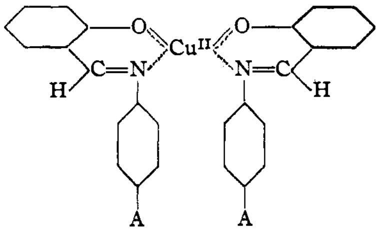
$\epsilon^{(1)}_{1/2} = -0.09$



$\epsilon^{(1)}_{1/2} = +0.01$

Here the result exactly parallels that reported in an earlier paper[2] in which the relative stabilities of these compounds were measured by a different method in another solvent. It is due in part to the contribution of a benzenoid resonance involving the copper atom and the interference with it by the ester resonance in the acetoacetic ester chelate and by the benzene resonance in the salicylaldehyde chelate.

The last series from which a definite conclusion may be drawn as yet is formed by the substituted anils of salicylaldehyde giving chelates of the type



where A may be varied. The values of $\epsilon^{(1)}_{1/2}$ for the series for the various structures of A are: NO_2, +0.03; SO_3Na, −0.09; , −0.10; H, −0.12; CH_3, −0.15; OH, −0.17; OCH_3, −0.21. This is just the order of increasing base strength of the corresponding aniline except for the inversion of the last two of the series, which inversion may be real or more likely is due to uncertainties in these measurements or inaccuracies in the base strength determination. Thus we are again[2] led to the conclusion that the more available the coördinating electron pair the stronger the coördination bond which it may form with a metal.

Summary

1. The reduction of 41 compounds, 37 of which are chelate compounds, at the dropping mercury electrode has been studied in 50% by volume aqueous pyridine.

2. It has been shown that the cuprous compounds of most of the chelating groups studied are unstable under these solvent conditions and that they dissociate, giving a cuprous pyridine ion.

3. Certain trends have been pointed out in the effect of the structure of the chelating group upon the relative stability of the copper chelates; among these, the effect of tieing together the coördinating groups is by far the largest and most important.

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Group and Bond Refractions in Organosilicon Liquids

BY ROBERT O. SAUER

Introduction

The use of the atomic refraction values computed by Eisenlohr[1] for a number of atoms frequently present in organic liquids has proved a convenient tool for confirming the identity and structure of new organic compounds.[2] This paper deals with the establishment and application of refractometric constants for organosilicon liquids.

Bygdén[3] has measured and discussed the refraction of silicon compounds. He concluded that the simple concept of additivity of atomic refractions did not give satisfactory results when applied to a wide variety of silicon compounds[3e,4] and states[5]: "It is therefore of interest to investigate whether (or not) the introduction of specific refraction values for the various types of silicon bonding permit at least an approximate calculation of the atom refraction of silicon in compounds where its valences are occupied by dissimilar radicals." From the refractions of the symmetrical molecules SiY_4, where Y was chlorine, bromine, ethoxyl or alkyl, Bygdén subtracted the sum of the Eisenlohr values for the four Y groups and the difference was then divided by four to give the (artificial) refraction of the Si–Y bonds. These figures when applied to the

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(1) Eisenlohr, *Z. physik. Chem.*, **75**, 585 (1911).

(2) See, for example, Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, 1940, p. 107.

(3) (a) Bygdén, *Ber.*, **44**, 2640 (1911); (b) *ibid.*, **45**, 707 (1912); (c) *ibid.*, **48**, 1236 (1915); (d) *Z. physik. Chem.*, **90**, 243 (1915); (e) Dissertation, Uppsala, 1916.

(4) This conclusion was aptly illustrated in our experience by attempting to calculate the atomic refraction of the oxygen atom in hexamethyldisiloxane. By subtracting the Eisenlohr atomic refractions for carbon and hydrogen from the observed molar refraction (30.33 mls.) of silicon tetramethyl we obtained the value 7.45 mls. for the atomic refraction of silicon. Using this value (and again the Eisenlohr values for carbon and hydrogen) we next calculated the refraction of two trimethylsilyl groups and found that this computed figure (49.22 mls.) was actually *larger* than the molar refraction of hexamethyldisiloxane (48.90 mls.). Thus, by the concept of atomic refractions the oxygen atom in hexamethyldisiloxane would have a *negative value*.

(5) Ref. 3e, p. 171.

various disilane derivatives gave fairly consistent values for the refraction of the silicon–silicon bond: 5.64, 5.78, 5.98. Using the four bond refraction values: silicon–carbon, 1.85; Si–Cl, 1.21; silicon–oxygen, 1.0; silicon–silicon, 5.7, so derived, Bygdén was able to give several examples in which good agreement resulted between the calculated and observed molar refractions. However, to the author's knowledge no extended treatment of the subject on this basis has been presented.

A list of organosilicon liquids, which, from the preparative methods used and the care exercised in their isolation, appear to be of high purity, has been compiled (Table I). As is generally the case a certain number of arbitrary decisions had to be made on the inclusion or exclusion in this table of certain reported compounds. In general, any one of the following was considered a legitimate barrier against inclusion: (a) *a priori* questionable purity or structure, (b) refractive index and density not reported at the same temperature, or (c) structure such that questionable assumptions must be made in writing the observation equations (see method of analysis of data below). In cases where two observations of equal *a priori* reliability exist, such as for methyl and ethyl silicates, both values have been included in Table I.

The molar refractions, *MR*, in all cases have been calculated by the n^2-formula (equation 1)

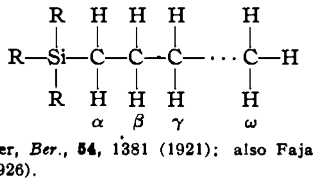
$$MR = \frac{n^2 - 1}{n^2 + 2} \cdot V \qquad (1)$$

(n = refractive index; V = molar volume)

and since, in general, the influence of temperature on *MR* is slight, a number of compounds have been included on which the data were measured at temperatures other than 20°. However, it will be seen that most of the measurements included in Table I were taken between 20 and 26°. In some cases the values of MR_D listed in Table I differ from the values originally reported. This is because modern atomic weights (1941) have been used in calculating the molecular weights.

In the present development use of the concept of the *additivity of bond refractions*[6] has been employed. Values for the refractions of methyl and phenyl groups bonded to silicon as well as the refractions of the silicon–oxygen, silicon–hydrogen and silicon–chlorine bonds have been established. In general, when the most probable values of two refractometric constants were sought simultaneously (as frequently happened) the least squares method of adjustment was employed.

1. Tetraalkylsilanes.—Let us consider the bond refractions in a n-alkyl group attached to silicon



$$\begin{array}{ccccccccc} & R & & H & H & H & & H & \\ & | & & | & | & | & & | & \\ R- & Si & - & C - & C - & C - & \cdots & C & -H \\ & | & & | & | & | & & | & \\ & R & & H & H & H & & H & \\ & & & \alpha & \beta & \gamma & & \omega & \end{array}$$

At a sufficient distance from the silicon atom along the alkyl chain, for example, at the γ-carbon atom, the refractions of the carbon–carbon and carbon–hydrogen bonds should approach closely those of similar bonds farther removed from the silicon atom. Also, these bond refractions beyond the γ-carbon atom should be identical with the values found in paraffinic hydrocarbons and other aliphatic compounds. In the present treatment we use van der Hulst's values[7]: $r_D(CH_2—) = 4.640$ and $r_D(H—) = 1.025$ which, *on a bond refraction basis*, reduce to $r_D(C–C) = 1.295$ and $r_D(C–H) = 1.673$.

It is to be expected that the refraction of the silicon–carbon bond, $r(Si–C')$, will differ considerably from $r(C–C)$ or $r(Si–Si)$ and that probably $r(C'–H)$, where the prime denotes the α-carbon atom, differs from $r(C–H)$, the refraction of the paraffinic carbon–hydrogen bond. In fact, it is to be expected that all bonds on the α-carbon atom will exhibit "abnormal" refractions. We shall assume, however, that the refraction of all bonds on the β-carbon atom except the C'–C bond are "normal" and equivalent to like bonds in the more familiar aliphatic compounds. This assumption appears to hold within the limits of experimental error.

The refraction of the methyl group bonded to silicon, that is, the sum: $r(Si–C') + 3r(C'–H)$, is of particular interest to us. In order to obtain a more reliable figure than the one given by silicon tetramethyl alone and to test the assumptions expressed above an analysis of the molar refractions of the tetraalkylsilanes listed in Table I has been made in the manner described below. The refraction of an ethyl group attached to silicon may be written as

$$r(Si\text{–}C_2H_5) = r(Si\text{–}C') + 2r(C'\text{–}H) + r(C'\text{–}C) + 3r(C\text{–}H)$$

Let us now subtract from this the refraction of a methyl group bonded to silicon giving

$$\begin{aligned} r(Si\text{–}C_2H_5) - r(Si\text{–}CH_3) &= r(C\text{–}C) + 2r(C\text{–}H) + \\ &[r(C\text{–}H) - r(C'\text{–}H) - r(C\text{–}C) + r(C'\text{–}C)] = \\ &r(CH_2—) + b \qquad (2) \end{aligned}$$

where b represents the term in the brackets and $r(CH_2—)$ is the "normal" refraction (4.640 ml.) of the methylene group in an alkyl chain. The significance of the term b is clear: it allows for the possible (and probable) non-equivalence of C'–H with C–H bonds and of C'–C with C–C bonds; its introduction simplifies the algebraic expression of molar refraction in organosilicon compounds having alkyl groups larger than methyl.

The refractometric constants desired for the tetraalkylsilanes are $r_D(Si–CH_3)$ and b. To reduce the size of the numbers involved in the least squares reduction let us define

$$A \equiv 4r_D(Si\text{–}CH_3) \equiv 4r_D(Si\text{–}C') + 12r_D(C'\text{–}H) \qquad (3)$$

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[6] von Steiger, *Ber.*, **54**, 1381 (1921); also Fajans and Knorr, *ibid.*, **59**, 249 (1926).

[7] van der Hulst, *Rec. trav. chim.*, **54**, 518 (1935). In addition to Eisenlohr's values (ref. 1) of $r_D(CH_2—) = 4.618$ and $r_D(H—) = 1.100$, compare those of Swientoslawski: $r_D(CH_2—) = 4.622$ and $r_D(H—) = 1.066$ [THIS JOURNAL, **42**, 1945 (1920)].

TABLE I

SELECTED LIST OF ORGANOSILICON LIQUIDS USED IN DERIVING REFRACTOMETRIC CONSTANTS

No.	Formula	Mol. wt.	d^{t}_{4}(vac.)	n^{t}_{D}	t, °C.	*MR* (obs.)	Ref.
1	$(CH_3)_4Si$	88.20	0.6495	1.3648	10.0	30.33	[a]
2	$(CH_3)_3SiC_2H_5$	102.22	.6837	1.38277	20.2	34.86	[b]
3	$(CH_3)_3SiC_3H_7$-*n*	116.25	.6972	1.39079	25.0	39.60	[b]
4	$(CH_3)_2Si(C_2H_5)_2$	116.25	.7129	1.39819	24.8	39.37	[b]
5	$(CH_3)_2Si(CH_2)_5$	128.26	.8039	1.43940	20.1	42.00	[b]
6	$(CH_3)_3SiC_4H_9$-*n*	130.27	.7141	1.40035	24.8	44.26	[b]
7	$(CH_3)_2Si(C_2H_5)C_3H_7$-*n*	130.27	.7259	1.40624	25.2	44.10	[b]
8	$(CH_3)_3SiC_5H_{11}$-*i*	144.30	.7240	1.40571	24.9	48.92	[b]
9	$(CH_3)_2Si(C_2H_5)C_4H_9$-*i*	144.30	.7378	1.41296	25.4	48.76	[b]
10	$(CH_3)_2Si(C_3H_7$-*n*$)_2$	144.30	.7350	1.41193	25.8	48.84	[b]
11	$(C_2H_5)_4Si$	144.30	.7620	1.42463	25.1	48.38	[b]
12	$(C_2H_5)_3SiC_3H_7$-*n*	158.33	.7683	1.42886	25.2	53.11	[b]
13	$(C_2H_5)_3SiC_4H_9$-*n*	172.35	.7742	1.43223	25.4	57.77	[b]
14	$(C_2H_5)_3SiC_4H_9$-*i*	172.35	.7758	1.43333	25.5	57.78	[b]
15	$(C_2H_5)_3SiC_5H_{11}$-*i*	186.38	.7766	1.43361	25.7	62.45	[b]
16[k]	$[(CH_3)_2SiO]_4$	296.51	.9558	1.3968	20.0	74.67	[c]
17[k]	$[(CH_3)_2SiO]_5$	370.64	.9593	1.3982	20.0	93.29	[c]
18[k]	$[(CH_3)_2SiO]_6$	444.77	.9672	1.4015	20.0	111.85	[c]
19[k]	$[(CH_3)_2SiO]_7$	518.90	.9730	1.4040	20.0	130.43	[c]
20[k]	$(CH_3)_3SiOSi(CH_3)_3$	162.32	.7638	1.3772	20.0	48.90	[d]
21[k]	$(CH_3)_3Si[OSi(CH_3)_2]_2CH_3$	236.45	.8200	1.3848	20.0	67.54	[c]
22[k]	$(CH_3)_3Si[OSi(CH_3)_2]_3CH_3$	310.58	.8536	1.3895	20.0	86.15	[c]
23[k]	$(CH_3)_3Si[OSi(CH_3)_2]_4CH_3$	384.71	.8755	1.3925	20.0	104.76	[c]
24[k]	$(CH_3)_3Si[OSi(CH_3)_2]_5CH_3$	458.84	.8910	1.3948	20.0	123.40	[c]
25[k]	$CH_3Si[OSi(CH_3)_3]_3$	310.58	.8499	1.3880	20.0	86.23	[c]
26[k]	$(CH_3)_3SiOC_2H_5$	118.22	.7573	1.3743	20.0	35.68	[d]
27[k]	$(CH_3)_3SiOC_4H_9$-*n*	146.27	.7774	1.3925	20.0	44.85	[d]
28[k]	$(CH_3)_2Si(OC_4H_9$-*n*$)_2$	204.35	.8434	1.4058	20.0	59.49	[e]
29[k]	*n*-$C_4H_9O[(CH_3)_2SiO]_2C_4H_9$-*n*	278.48	.8733	1.4051	20.0	78.17	[e]
30[k]	*n*-$C_4H_9O[(CH_3)_2SiO]_3C_4H_9$-*n*	352.61	.8932	1.4053	20.0	96.82	[e]
31	$Si(OCH_3)_4$	152.20	1.02804	1.36773	22.0	33.30	[b]
		152.20	1.0232	1.3683	20.0	33.51	[f]
32	$Si(OC_2H_5)_4$	208.34	0.93975	1.3862	15.0	52.10	[g]
		208.34	.9320	1.3821	20.0	52.04	[b,h]
33	$Si(OC_3H_7$-*n*$)_4$	264.40	.91580	1.40159	22.7	70.24	[b]
34	$C_6H_5Si(CH_3)_3$	150.26	.8651	1.48830	24.7	50.07	[b]
35	$C_6H_5Si(CH_3)_2C_2H_5$	164.27	.8729	1.49281	25.3	54.67	[b]
36	$C_6H_5Si(C_2H_5)_3$	192.34	.8874	1.50035	25.1	63.79	[b]
37[k]	$[CH_3SiHO]_4$	240.40	.9912	1.3870	20.0	57.10	[i]
38[k]	$[CH_3SiHO]_5$	300.50	.9985	1.3912	20.0	71.54	[i]
39[k]	$[CH_3SiHO]_6$	360.60	1.0060	1.3944	20.0	85.82	[i]
40[k]	$(CH_3)_3SiOSiH(CH_3)OSi(CH_3)_3$	222.42	0.8194	1.3818	20.0	63.14	[i]
41[k]	$(CH_3)_3Si[OSiH(CH_3)]_2OSi(CH_3)_3$	282.52	.8559	1.3854	20.0	77.42	[i]
42[k]	$(CH_3)_3Si[OSiH(CH_3)]_3OSi(CH_3)_3$	342.62	.8806	1.3878	20.0	91.77	[i]
43	$SiCl_4$	169.89	1.4745	1.41156	25.0	28.64	[j]
44	$C_2H_5SiCl_3$	163.49	1.2381	1.42573	19.8	33.82	[b]
45	*n*-$C_3H_7SiCl_3$	177.51	1.1963	1.43121	20.3	38.42	[b]
46	*n*-$C_4H_9SiCl_3$	191.54	1.1606	1.43630	20.2	43.18	[b]
47	*n*-$C_3H_7(C_2H_5)SiCl_2$	171.13	1.0429	1.43587	19.9	42.89	[b]
48	*i*-$C_4H_9(C_2H_5)SiCl_2$	185.15	1.0235	1.44037	20.0	47.71	[b]
49	$(CH_2)_5SiCl_2$	169.10	1.1558	1.46973	20.2	40.80	[b]

[a] G. H. Fleming and J. G. Aston, private communication, July 22, 1943. [b] Refs. 3d, e. [c] Patnode and Wilcock, THIS JOURNAL, **68**, 358 (1946). [d] Sauer, THIS JOURNAL, **66**, 1707 (1944). [e] Sauer, *ibid.*, **68**, 138 (1946). [f] Holzapfel, *Z. Elektrochem.*, **47**, 327 (1941); *C. A.*, **35**, 5377 (1941). [g] Solana and Moles, *Anales. soc. espan. fis. quim.*, **30**, 886 (1932); *C. A.*, **27**, 1252 (1933). [h] Kannonikoff, *J. prakt. Chem.*, (2) **31**, 359 (1885). [i] Sauer, Scheiber and Brewer, THIS JOURNAL, **68**, 962 (1946). [j] Holleman, *Z. physik. Chem.*, **B32**, 353 (1936). [k] Compounds prepared and properties measured in this Laboratory.

The molar refractions of the tetraalkylsilanes can then be written

$$MR_D = A + xb + yr_D(\mathrm{CH_2}—) \qquad (4)$$

where x is the number of C′–C bonds in the molecule and y is the number of methylene groups not included in A. Assigning the value 4.640 ml. to $r_D(\mathrm{CH_2}—)$ the observation equations in A and b assume the form

$$A + xb = MR_D(\text{obs.}) - yr_D(\mathrm{CH_2}—) \qquad (5)$$

Least squares analysis of the fifteen observation equations of the form based on the first fifteen compounds of Table I yields the values: A = 30.41 mls., b = −0.12 ml. Substitution of these values in the observation equations gives a standard deviation of ±0.06 ml.

If b were set equal to zero in the observation equations (5) A would be given by the arithmetical average of the right-hand terms, namely, 30.15 mls. In Fig. 1 the deviation ΔMR_D of the values of MR_D calculated on the basis: A = 30.15 mls., b = 0 from the observed values ($\Delta MR_D = MR_D$ (calcd.) − MR_D (obs.)) has been plotted against the number of b terms per molecule (x). It is apparent that either $r_D(\mathrm{CH_2}—)$ is not constant beyond the α-carbon atom as assumed or that the non-equivalence

$$r(\text{C–H}) - r(\text{C}'\text{–H}) \neq r(\text{C–C}) - r(\text{C}'\text{–C})$$

exists. From the approximate linear relation of ΔMR_D to the number of b terms we prefer the latter alternative.

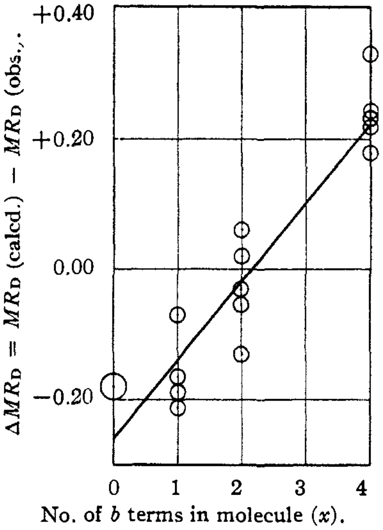

Fig. 1.—ΔMR_D *vs.* the number of b terms per tetraalkylsilane molecule.

A similar analysis of the forty-nine lead tetraalkyls reported by Grüttner and Krause[8] (using, however, modern atomic weights in computing the molar refractions) gave $r_D[\mathrm{Pb(CH_3)}]_4$ = 40.37 mls. and b = +0.26 ml.

2. Cyclic and Linear Polymethylpolysiloxanes.—Definition of the refractometric constant

$$C \equiv 4r_D(\text{Si–O}) \qquad (6)$$

enables the expression of the molar refractions of the polymethylpolysiloxanes $\left[(\mathrm{CH_3})_N\mathrm{SiO}_{\frac{4-N}{2}}\right]_s$, where N is the methyl-to-silicon ratio and s is the number of silicon atoms per molecule, in terms of the group refractions A and C. Thus

$$MR_D = (Ns/4)A + s(1 - N/4)C \qquad (7)$$

where the coefficients of A and C are readily determined by inspection of a structural formula. Least squares analysis of ten such observation equations based on the data for compounds 16–25, inclusive, of Table I gave: A = 30.235 mls., C = 7.051 mls. Substitution of these values in the observation equations indicates a standard deviation of ±0.06 ml. in MR_D.

3. Ethers of the Silanes and Siloxanes.—In order to extend the scope of the analysis appreciably below a methyl-to-silicon ratio of two it became necessary to include carbon ethers of the silanes and polysiloxanes. In these compounds it appeared desirable to apportion the refraction between the following group or bond refractions: A, b, C, $r(\mathrm{CH_2}—)$ and $r(\mathrm{CH_3OCH_3})$. We have analyzed the molar refraction data (15 observations) for eleven dialkyl ethers; by setting $r_D(\mathrm{CH_2}—)$ = 4.640 mls. in these ethers we found the mean value for $r_D(\mathrm{CH_3OCH_3})$ to be 13.07 ± 0.15 mls. Using this value we may write the molar refraction of dimethyldi-n-butoxysilane, for example, as

$$MR_D = 0.5A + 0.5C + 6r_D(\mathrm{CH_2}—) + r_D(\mathrm{CH_3OCH_3}) = 0.5(A + C) + 6 \cdot 4.640 + 13.07$$

In this way observation equations in A and C were established for compounds 26–33, inclusive, of Table I. Least squares adjustment of these equations gave: A = 30.066 mls., C = 7.233 mls. Substitution of these values in the observation equations indicates a standard deviation of ±0.13 ml. in the value of MR_D.

4. The Final Values of A and C.—A simultaneous least squares adjustment for the values of A and C was made using the 33 observation equations described above in which the following values were *assumed:* b = −0.12 ml.; $r_D(\mathrm{CH_2}—)$ = 4.640 ml.; r_D $(\mathrm{CH_3OCH_3})$ = 13.07 mls. The values so obtained were

$$\left.\begin{aligned} A &= 30.293 \text{ mls.} \\ \text{and} \quad C &= 7.005 \text{ mls.} \end{aligned}\right\} \qquad (8)$$

giving $r_D(\mathrm{Si–CH_3})$ = 7.573 mls., r_D(Si–O) = 1.751 mls. and $A + C$ = 37.298 mls. Substituting these final values in the observation equations indicated a standard deviation of ±0.15 ml. The deviations are plotted in Fig. 2 against MR_D.

It is interesting to compare the values of A obtained in sections 1, 2 and 3, that is, 30.41, 30.256 and 30.066 mls., respectively, as well as the corresponding values of C established in sections 2 and 3, that is, 7.051 and 7.233 mls., respectively.

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(8) Grüttner and Krause, *Ann.*, **415**, 338 (1918).

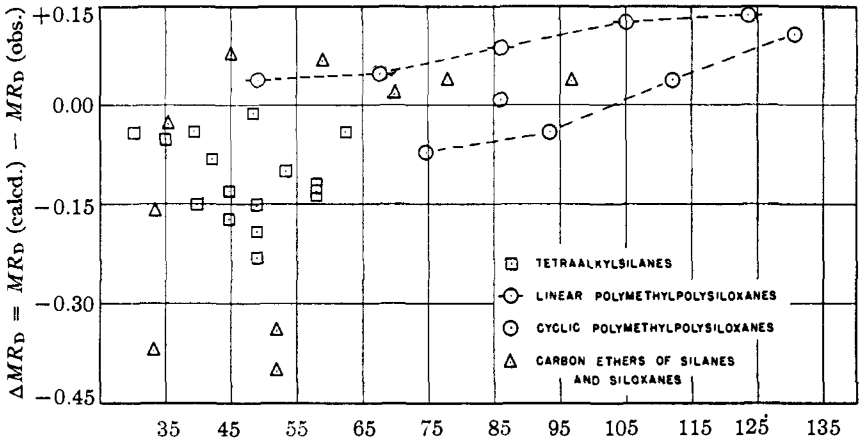

Fig. 2.—Deviation of calculated molar refractions *vs.* MR_D.

The apparent decrease in A and the increase in C with decreasing alkyl-to-silicon ratio appear to compensate each other in a manner such that $A + C$ remains approximately constant. A decision as to whether the apparent changes in the individual values is real or not will have to be deferred until a larger amount of reliable work is available.

TABLE II

THE REFRACTOMETRIC CONSTANTS: D, E AND F

Compounds	Constant derived	Value of constant (mls.)
34-36[a]	D ≡ $4r_D$(Si-C_6H_5)	109.72
37-42[a]	E ≡ $4r_D$(Si-H)	12.87[b]
43-49[a]	F ≡ $4r_D$(Si-Cl)	28.72

[a] These numbers refer to Table I. [b] Compare the value P_E = 11.95 mls. found for gaseous silane [Watson and Ramaswamy, *Proc. Roy. Soc. London*, **A156**, 156 (1936)].

5. **Other Group and Bond Refractions.**—In computing r_D(Si–C_6H_5), r_D(Si–H) and r_D(Si–Cl) from the remaining compounds of Table I the values already established for A, b and C and the value of r_D(CH_2—) assumed were used directly because of the paucity of reliable data on compounds containing the desired groupings. Table II gives the results of these calculations.

There are insufficient data on the molar refractions of alkylfluorosilanes[9] to warrant calculation of the corresponding value of $4r_D$(Si–F).

6. **Application of the Constants to Molar Refraction.**—The utility of the values derived is apparent upon inspection of Table III which lists the observed and calculated molar refractions for a number of organosilicon liquids not included in Table I. The average deviation without regard to sign is 0.56 (excluding the four values of ΔMR_D indicated by the daggers).

TABLE III

OBSERVED AND CALCULATED VALUES OF THE MOLAR REFRACTION OF MISCELLANEOUS ORGANOSILICON LIQUIDS

Formula	Observer	t, °C.	MR_D (obs.)	MR_D (calcd.)	ΔMR_D
$(CH_3)_4Si$	[a]	18.7	29.97	30.29	+ .32
$(CH_3)_3SiC_4H_9$-*i*	[a]	25.6	44.29	44.09	− .20
(*n*-$C_4H_9)_4Si$	[b]	22	81.12	85.49	+4.37†
(*n*-$C_4H_9)_3SiOC_2H_5$	[b]	22	(77.27)	77.05	− .22
*(*n*-$C_4H_9)_2Si(OC_2H_5)_2$	[c]	20.0	68.96	68.60	− .36
p-$(C_2H_5)_3SiC_6H_4CH(OH)CH_3$	[d]	20.0	74.53[e]	74.64[f]	+ .11
p-$(C_2H_5)_3SiC_6H_4CH(OH)C_2H_5$	[d]	17.0	78.89[e]	79.28	+ .39
p-$(C_2H_5)_3SiC_6H_4CH(OH)C_3H_7$-*i*	[d]	17.5	83.33[e]	83.95	+ .62
$(C_2H_5)_3SiC_6H_4C_2H_5$-*p*	[d]	20.7	73.30	72.99[g]	− .31
$(C_2H_5)_3SiC_6H_4Cl$-*p*	[h]	9.6	68.78	68.61[i]	− .17
$(C_2H_5)_3SiC_6H_4Br$-*p*	[h]	20.0	72.27	71.50[j]	− .77
$(C_2H_5)_3SiC_6H_4I$-*p*	[h]	20.0	77.61	76.54[k]	−1.07
(*n*-$C_3H_7)_3SiC_6H_4Cl$-*p*	[h]	9.0	83.15	82.53	−0.62
*$(CH_3)_3SiOH$	[l]	20.0	26.23	26.33[m]	+ .10
$(C_2H_5)_3SiOH$	[d]	20.0	39.90[e]	39.89	− .01
*$(CH_3)_3SiOC_2H_4Cl$	[n]	20.0	40.40	40.55[o]	+ .15
*$(CH_3)_3SiOSi(C_2H_5)_3$	[p]	20.0	62.42	62.50	+ .08
*$(CH_3)_3Si[OSiH(CH_3)]_4OSi(CH_3)_3$	[q]	20.0	106.06	106.11	+ .05
*$(CH_3)_3SiOSi(CH_3)_2CH_2Cl$	[r]	20.0	53.61	53.84	+ .23
*$[ClCH_2(CH_3)_2Si]_2O$	[r]	20.0	58.20	58.74	+ .54
*$[(CH_3)_2SiO]_8$	[s]	20.0	148.73	149.19	+ .46
*$CH_3SiH(OCH_2CH_2Cl)_2$	[n]	20.0	46.26	46.44[t]	+ .18
*$(CH_3)_2Si(OCH_2CH_2Cl)_2$	[n]	20.0	50.62	50.79	+ .17
*$(CH_3)_2Si(OCH_2CH_2Br)_2$	[u]	20.0	56.17	56.59	+ .42

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(9) See, however, Gierut, Sowa and Niewland, THIS JOURNAL, **58**, 897 (1936).

TABLE III (*Concluded*)

Formula	Observer	t, °C.	MR_D (obs.)	MR_D (calcd.)	ΔMR_D
*$(CH_3)_2Si(OC_2H_5)_2$	v	20	41.16	41.00	− .16
*$(CH_3)_2Si(OC_2H_5)_2$	b	20	38.96	41.00	+2.04†
*$(C_6H_5)_2Si(OCH_2CH_2Cl)_2$	n	20.0	90.53	90.50	− .03
$p\text{-}BrC_6H_4(C_6H_5)SiCl_2$	d	19.0	76.60	77.00	+ .40
$p\text{-}BrC_6H_4(C_6H_5)Si(OC_2H_5)_2$	d	19.0	89.59	88.51	−1.08
*$(CH_3)_{12}Si_7O_8$	x	20.0	119.03	118.90	− .13
*$(CH_3)_{14}Si_8O_9$	x	20.0	137.74	137.55	− .19
*$HSi(OCH_2CH_2Cl)_3$	n	20.0	56.63	56.70	+ .07
$CH_3Si(OC_2H_5)_3$	b	20	44.74	46.35	+1.61
*$CH_3Si(OCH_2CH_2Cl)_3$	n	20.0	60.93	61.05	+ .12
*$CH_3Si(OCH_2CH_2Br)_3$	u	20.0	69.22	69.75	+ .53
*$CH_3Si(OC_4H_9\text{-}n)_3$	y	20.0	74.19	74.19	± .00
$C_2H_5Si(OC_2H_5)_3$	z	20.0	51.55	50.87	− .68
$C_2H_5Si(OC_2H_5)_3$	w	22	48.59	50.87	+2.28†
$C_2H_5Si(OC_3H_7\text{-}n)_3$	w	23	63.66	64.79	+1.13
$C_2H_5Si(OC_4H_9\text{-}n)_3$	w	24	78.49	78.71	+ .22
$C_2H_5Si(OC_4H_9\text{-}i)_3$	z	20.0	78.92	78.71	− .21
$C_2H_5Si(OC_5H_{11}\text{-}n)_3$	w	23?	90.66	92.63	+1.97
$C_2H_5Si(OC_5H_{11}\text{-}i)_3$	z	20.0	93.38	92.63	− .75
$C_2H_5Si(OC_5H_{11}\text{-}i)_3$	w	24?	89.91	92.63	+2.72†
$n\text{-}C_3H_7Si(OC_2H_5)_3$	w	26	59.68	55.51	−4.17
$C_4H_9Si(OC_2H_5)_3$	b	29	59.35	60.15	+ .80
$C_6H_5Si(OC_2H_5)_3$	z	20.0	67.54	66.21	−1.33
*$C_6H_5Si(OC_2H_4Cl)_3$	n	20.0	80.76	80.91	+ .15
$C_6H_5Si(OC_3H_7\text{-}n)_3$	w	20	80.52	80.13	− .39
$C_6H_5Si(OC_4H_9\text{-}i)_3$	z	20.0	94.76	94.05	− .71
$C_6H_5Si(OC_5H_{11}\text{-}i)_3$	z	20.0	106.90	107.97	+1.07
$p\text{-}BrC_6H_4Si(OCH_3)_3$	d	16.5	61.50	60.09	−1.41
$p\text{-}BrC_6H_4Si(OC_2H_5)_3$	d	16.6	75.46[e]	74.01	−1.45
*$Si(OCH_2CH_2Cl)_4$	n	20.0	71.07	71.30	+ .23
$(C_2H_5O)_3SiOC_4H_9\text{-}n$	b	20	61.40	60.98	− .42
$(C_2H_5O)_2Si(OC_4H_9\text{-}n)_2$	b	20	70.64	70.26	− .38
$Si(OC_4H_9\text{-}n)_4$	b	20	88.86	88.83	− .03
$Si(OC_5H_{11}\text{-}i)_4$	aa	20.0	107.23	107.39	+ .16
$Si(OC_7H_{15}\text{-}n)_4$	w	29	144.13	144.51	+ .38
$(n\text{-}C_3H_7O)_3SiOSi(OC_3H_7\text{-}n)_3$	a	22.6	107.63	108.90	+1.17
$(i\text{-}C_4H_9O)_3SiCl$	z	20.0	74.62	73.80	− .82
$(i\text{-}C_5H_{11}O)_3SiCl$	z	20.0	87.94	87.72	− .22

* These compounds prepared and their properties measured in this Laboratory. [a] Refs. 3d, e. [b] Post and Hofrichter, *J. Org. Chem.*, **5**, 572 (1940). The "tetrabutylsilane" was prepared from ethyl silicate and *n*-butylmagnesium bromide. It is quite possible that all the ethoxy groups were not replaced so the molar refraction has been recomputed on the assumption that the product reported was tri-*n*-butylethoxysilane. [c] Ethyl silicate (0.73 mole) was treated with 3.44 moles of *n*-butylmagnesium chloride. The principal product was di-*n*-butyldiethoxysilane (55 g.), b. p. 80–84° (4 mm.), n^{20}_D 1.4189, d^{20}_4 (vac.) 0.8508. *Anal.* Calcd. for $C_{12}H_{28}SiO_2$: C, 62.01; H, 12.14. Found: C, 61.94, 61.91; H, 12.13, 12.17. [d] Grüttner and Cauer, *Ber.*, **51**, 1283 (1918). [e] The value of n_D used in this calculation was interpolated or extrapolated from values given at a temperature differing from t by not more than 3.5°. [f] The calculated value of MR_D was obtained as follows: $MR_D = [0.75A - 3b + 3r(CH_2—)] + 0.25D + 2r(C–C) + 3r(C–H) + r(C–O–H)$. The refraction of the two bonds in the group COH is readily given by subtracting van der Hulst's value for three C–H bonds (5.02 mls.) from the molar refraction of methanol (8.34 ml.) calculated from Eisenlohr's atomic values; this gives r(C–O–H) = 3.32 mls. [g] Calculated assuming $r(Si–C_6H_4–C_2H_5) = r(Si–C_6H_5) + 2r(CH_2—)$. As in *f* this assumes that a phenyl–hydrogen bond is equivalent to the alkyl–hydrogen bond. [h] Grüttner and Krause, *Ber.*, **50**, 1559 (1917). [i] Calculated assuming $r(Si–C_6H_4Cl) = r(Si–C_6H_5) - r(C–H) + r(C–Cl)$; r(C–Cl) was assumed to be 6.57 mls. [Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, 1940, p. 527.] [j] Calculated as in *i* assuming r(C–Br) = 9.47 mls. [k] Calculated as in *i* assuming r(C–I) = 14.50 ml. [l] Sauer, THIS JOURNAL, **66**, 1707 (1944). [m] Calculated as $MR_D = 0.75A + 0.25C + 0.5r(H_2O)$ in which $r(H_2O)$ was calculated from Eisenlohr's atomic values for alcoholic oxygen and hydrogen. [n] Sauer and Patnode, THIS JOURNAL, **67**, 1548 (1945). [o] Calculated as $MR_D = 0.75A + 0.25C + r(CH_2—) + 0.5r(CH_3OCH_3) - r(C–H) + r(C–Cl)$. See [h] for r(C–Cl). [p] Hexaethyldisiloxane (27 g.) was equilibrated with hexamethyldisiloxane (80 g.) in the presence of concentrated sulfuric acid (4.0 cc.) [compare Patnode and Wilcock, THIS JOURNAL, **68**, 358 (1946)]. From the reaction mixture there was obtained 18.5 g. of crude product. Redistillation gave 12.4 g. of 1,1,1-trimethyl-3,3,3-triethyldisiloxane, b. p. 173.6–173.9° (751 mm.), n^{20}_D 1.4098, d^{20}_4 (vac.) 0.8110. *Anal.* Calcd. for $C_9H_{24}Si_2O$: C, 52.88; H, 11.83. Found: C, 53.0; H, 11.8. [q] Sauer, Scheiber and Brewer, work in publication. [r] Elliott and Krieble, work in publication. [s] Patnode and Wilcock, THIS JOURNAL, **68**, 358 (1946). [t] Calculated as $MR_D = 0.25A + 0.50C + 0.25E + 2r(CH_2—) + r(CH_3OCH_3) - 2r(C–H) + 2r(C–Cl)$. Compare with [o]. [u] Gilliam, Meals and Sauer, work in publication. [v] R. H. Krieble, private communication. [w] Post and Hofrichter, *J. Org. Chem.*, **4**, 363 (1939). [x] Scott, THIS JOURNAL, **68**, 356 (1946). [y] Sauer, *ibid.*, **68**, 138 (1946). [z] Kalinin, *Compt. rend. Acad. Sci. U. S. S. R.*, **26**, 368 (1940). [aa] Holzapfel, *Z. Elektrochem.*, **47**, 327 (1941).

The refraction of the silicon–silicon bond may be calculated from the molar refraction of hexamethyldisilane (51.29 mls.[3e]) and hexachlorodisilane (48.65 mls.[3e]). By the subtraction of 1.5*A* from the former, r_D(Si–Si) = 5.85 mls.; subtracting 1.5*F* from the latter gives r_D(Si–Si) = 5.60 mls. (*cf.* Bygdén's value[5] of 5.7). The agreement is only fair.

7. Specific Refraction and the Composition of Liquid Polymethylpolysiloxanes.—The refraction values for methyl groups bonded to silicon and for silicon–oxygen bonds now established can be applied to the analysis of liquid polymethylpolysiloxanes and their mixtures. For those materials described by the formula $(CH_3)_NSiO_{\frac{4-N}{2}}$ the value of MR_D, the average refraction per formula weight, is given by the expression

$$MR_D = Nr_D(\text{Si-CH}_3) + (4 - N)r_D(\text{Si-O}) \quad (9)$$

MR_D is also the product of the Lorentz–Lorenz specific refraction and the average formula weight (per silicon atom) which can be written in terms of *N*; thus

$$M = 60.06 + 7.034N \quad (10)$$

Since the values of $4r_D$(Si–CH$_3$) and of $4r_D$(Si–O) are known to be 30.293 mls. and 7.005 mls., respectively, we obtain, upon substitution in equation 9

$$(60.06 + 7.034N)R_D = 7.005 + 5.822N \quad (11)$$

which may be rewritten separating R_D and *N*. Thus, we have

$$R_D \equiv \frac{n^2_D - 1}{n^2_D + 1}\cdot\frac{1}{d} = \frac{7.005 + 5.822N}{60.06 + 7.034N} \quad (12)$$

or

$$N = \frac{60.06R_D - 7.005}{5.822 - 7.034R_D} \quad (13)$$

We are particularly concerned with the values of *N* computed by means of equation 13 from the experimentally determined values of R_D; this quantity will be designated in the following discussion by the symbol $N(R_D)$.

By an analysis of the above equations it can readily be shown that at an *N*-value of 2.00 (a) the error in $N(R_D)$ computed from a refractive index measurement which is in error by Δn is roughly $10\cdot\Delta n$, and (b) the error in $N(R_D)$ computed from a density value which is in error by Δd is roughly $-5\cdot\Delta d$. Since the refractive index can be measured easily with a probable error of less than ±0.0003 and the density can be determined by the pycnometer method with a probable error of less than ±0.0001 g./ml., the expected probable error in a determination of *N* based on these measurements is ±0.003 in the neighborhood of $N = 2.00$. This estimate, of course, assumes *complete confidence in the validity of equation 13* and *the absence of any material other than that described by the formula* $(CH_3)_NSiO_{(4-N)/2}$.

In order to be certain, in the ultimate (combustion or digestion) analysis of a polymethylpolysiloxane in which *N* is roughly two, that the error in *N* be less than 0.02 it is required that both the percentage carbon and the percentage silicon be known to within 0.20. It is readily seen that if the accuracy of the specific refraction method approaches the value estimated in the preceding paragraph then the specific refraction method will give appreciably more accurate results than an ordinary ultimate analysis.

A sufficient number of pure monomeric polymethylpolysiloxanes are available to test the validity of equation 13. These examples are summarized in Table IV. Although the agreement between $N(R_D)$ and the value of N computed from the formula is in all cases within 0.7%, the deviations are generally about twice those estimated assuming normal experimental errors in refractive index and density. These deviations as well as their trend in the D_q compounds appear to be due, at least in part, to the influence of molecular structure on R_D. In other words, there appears to be a small *constitutive* deviation, for the listed compounds containing *small rings*, *i. e.*, eight atoms or less, give somewhat higher values of R_D than predicted by equation 13.

TABLE IV

SPECIFIC REFRACTIONS AND $N(R_D)$ FOR THE PURE COMPOUNDS

Formula[a]	R_D[b]	$N(R_D)$	*N* (formula)
$[(CH_3)_2SiO]_q$			
q = 4, D_4	0.2518	2.005	2.000
5, D_5	.2517	2.002	2.000
6, D_6	.2515	1.998	2.000
7, D_7	.25135	1.996	2.000
8, D_8	.2508	1.986	2.000
$CH_3[(CH_3)_2SiO]_qSi(CH_3)_3$			
q = 1, M–M	.3013	2.995	3.000
2, M–D–M	.2857	2.663	2.667
3, M–D_2–M	.2774	2.494	2.500
4, M–D_3–M	.2723	2.394	2.400
5, M–D_4–M	.26895	2.328	2.333
$(CH_3)_{12}Si_7O_8$, D_3–Q–D_3	.2358	1.719	1.714
$(CH_3)_{14}Si_8O_9$, D_3–Q–D_4	.23795	1.757	1.750
$CH_3Si[OSi(CH_3)_3]_3$, TM_3	.2777	2.501	2.500

[a] The abbreviated formulas D_4, M-M, etc. are based on the functionalities of the four units: $(CH_3)_3SiO_{1/2}$, M; $(CH_3)_2SiO$, D; $CH_3SiO_{3/2}$, T; SiO_2, Q. [b] These figures are computed from the values of MR_D compiled in Tables I and III for these compounds.

Values of R_D observed for the compounds of Table IV are plotted against *N* in Fig. 3. Also included for comparison are the corresponding values for silicon tetramethyl and for vitreous silica.[10] The solid line is a plot of equation 12.

We have seen that the pure individual polymethylpolysiloxanes give values of R_D which approximate quite closely the values predicted by equation 13. It would next appear of interest

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[10] "International Critical Tables," Vol. 6, p. 431 (n_D); *ibid.*, Vol. 4, p. 20 (density).

to apply this method to mixtures of simple polymethylpolysiloxanes by testing the validity of the expression

$$R(\text{mix}) = w_1R_1 + w_2R_2 + \cdots w_iR_i \qquad (14)$$

in which w_1, w_2, · · ·, w_i are the *weight fractions*, respectively, of the pure components 1, 2, · · ·, i, the specific refractions of which are R_1, R_2, · · ·, R_i. This check has been made on two binary systems: I, decamethyltetrasiloxane–tetradecamethylhexasiloxane[11]; and II, tetradecamethylhexasiloxane – dodecamethylcyclohexasiloxane. The deviations in the found values of R_D (at w_1-values near 0.5) from those calculated by equation 14 correspond to errors in N of +0.004 for system I and −0.004 for system II. It is to be concluded that equation 14, and consequently equation 13, is valid for simple mixtures of the pure compounds.

Patnode and Wilcock[12] have recently described the products of hydrolysis of pure dimethyldichlorosilane. Although the chief products isolated were the cyclic molecules D_q there appears to be little doubt that in certain cases a small amount of incompletely condensed material of the general formula HO—D_q—H is present in freshly prepared hydrolyzates of this type. Should such polysiloxanediols be present the specific refraction of the gross product would be lowered below the value 0.25158 given by equation 12 for pure "D" units since the specific refraction of the additional oxygen and two hydrogen atoms in the polysiloxanediol formula is approximately 0.207.

In order to verify the probable applicability of the present analytical method to the hydrolysis products of the methylchlorosilanes and their mixtures, three batches of pure dimethyldichlorosilane (A, B, C), one batch of dimethyldichlorosilane containing 5.0 mole per cent. of methyltrichlorosilane (D), and one batch of dimethyldichlorosilane containing 10.0 mole per cent. of methyltrichlorosilane (E) have been hydrolyzed individually by slowly adding the chlorosilanes without solvent to water or water–ice mixtures. The specific refraction of the oily products, the value of $N(R_D)$ computed by equation 13, and the difference between $N(R_D)$ and value of N based on the known composition of the chlorosilane mixture before hydrolysis are given in Table V.

TABLE V

SPECIFIC REFRACTIONS OF METHYLCHLOROSILANE HYDROLYZATES

Batch	N	R^{20}_D	$N(R_D)$	$N(R_D) - N$
A	2.000	0.2515	1.999	−0.001
B	2.000	.2514	1.997	− .003
C	2.000	.2518	2.003	+ .003
D	1.950	.2490	1.954	+ .004
E	1.900	.2463	1.904	+ .004

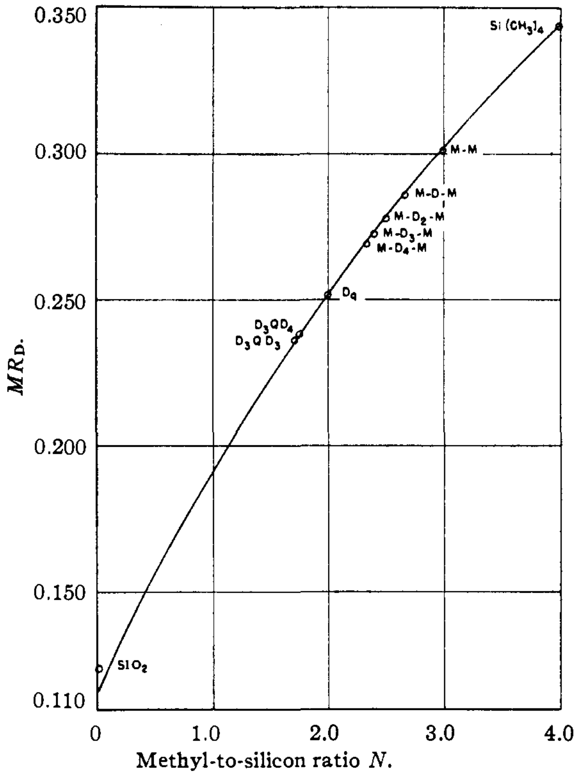

Fig. 3.—Specific refraction as a function of methyl-to-silicon ratio in polymethylpolysiloxanes.

The small values of $N(R_D) - N$ tabulated in the last column appear to indicate the validity of equation 13 when applied to the complex molecular mixtures obtained by the hydrolysis of dimethyldichlorosilane and its mixtures with small amounts of methyltrichlorosilane. However, because of the possible presence of small amounts of silanolic groups (polysiloxanediols) and their effect on the value of R_D it would seem preferable to postpone a definite statement on the validity of eq. 13 in these complex systems until, for such hydrolysis products, "active hydrogen" analyses and specific refraction values can be reported on the same samples.

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Summary

1. Refraction data on a number of organosilicon liquids have been analyzed, and the refractions of the following groups or bonds have been established: Si–CH_3, Si–O, Si–C_6H_5, Si–H and Si–Cl.

2. The established refractometric constants have been applied to the computation of the molar

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[11] The nomenclature used in this paper has been discussed [Sauer, *J. Chem. Ed.*, **21**, 303 (1944)].

[12] Patnode and Wilcock, THIS JOURNAL, **68**, 358 (1946). Compare also Hyde and DeLong, *ibid.*, **63**, 1194 (1941).

refractions of a large number of reported organosilicon liquids.

3. A method requiring only refractive index and density measurements has been developed for determining the average composition of polymethylpolysiloxane systems.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Derivatives of the Methylchlorosilanes. V. Polysiloxanes from Methyldichlorosilane

BY ROBERT O. SAUER, W. J. SCHEIBER AND STUART D. BREWER

In view of the ready availability[1] of methyldichlorosilane it appeared of some interest to prepare the cyclic and linear polymethylpolysiloxanes of the general formulas $(CH_3SiHO)_n$ and $(CH_3)_3Si[OSiH(CH_3)]_nOSi(CH_3)_3$, analogous to those reported recently by Patnode and Wilcock[2] from dimethyldichlorosilane. In general we have utilized the methods of preparation and of characterization already described.[2]

Experimental

To obtain the cyclic compounds methyldichlorosilane has been hydrolyzed in ether solution; the organic phase was then fractionally distilled. The linear polysiloxanes were prepared by "equilibration" of such a hydrolyzate with a relatively large amount of hexamethyldisiloxane.

Starting Materials.—The methyldichlorosilane used in our experiments was prepared by the reaction of methyl chloride with copper-silicon.[1]

After rigorous purification by fractional distillation this substance had the following properties: b. p. 41.0° (748 mm.), d^{27}_{27} 1.105, m. p. −92.5°. Analysis for hydrolyzable chlorine by hydrolysis in ice-ether mixture and titration of the liberated acid indicated that our sample was substantially pure methyldichlorosilane.

Anal. Calcd. for CH_4SiCl_2: Cl, 61.66. Found: Cl, 61.61, 61.59, 61.60.

Stock and Somieski,[3] who first reported this compound, give d^0 *ca.* 0.93 g./cc. and m. p. −93°.

The hexamethyldisiloxane was prepared by the hydrolysis of trimethylchlorosilane.

TABLE I

Value of n	n^{20}_D	d^{20}_4 (vac.)	R_D	M. p., °C.	Mol. wt. Calcd.	Mol. wt. Found[a]	%H(–Si)[b] Found
4	1.3870	0.9912	0.2375	− 69 ± 3	240.4	239, 241, 244	1.64, 1.64
5	1.3912	.9985	.2381	−108 ± 3	300.5	298, 297, 297	1.65
6	1.3944	1.006	.2380	− 79 ± 2	360.6	360	1.67

[a] Cryoscopic in cyclohexane; maximum concentration of solute in weight per cent.: 0.56, 0.72, 0.78, respectively. Theoretical for CH_3SiHO, 1.68.

The Cyclic Polysiloxanes, $(CH_3SiHO)_n$.—Although an oil of about 20–25 centistokes viscosity usually results when dimethyldichlorosilane is hydrolyzed by adding it directly to water or to a mixture of ice and water, a somewhat different result is obtained under these conditions with methyldichlorosilane. The product first formed is a highly viscous oil which in a few minutes is transformed into an opalescent, sticky, rubbery gel. However, the formation of this high polymer can be obviated by employing a water-insoluble diluent which apparently increases the proportion of low-molecular weight cyclic polymers originally formed and suppresses their polymerization by reducing the concentration of hydrochloric acid.

Four moles (460 g.) of methyldichlorosilane was added with vigorous stirring to a mixture of 1 liter of diethyl ether and 2 kg. of cracked ice over a half-hour period. The temperature of the hydrolyzing mixture dropped from 0 to −10°, but rose finally to 7°. After stirring an additional half hour the aqueous layer was separated and the organic phase washed repeatedly with water until neutral to methyl orange. Distillation of the ethereal solution gave: (a) 2,4,6,8-tetramethylcyclotetrasiloxane, b. p. 134.5–134.9° (755 mm.), 85.4 g. (35.6%); (b) 2,4,6,8,10-pentamethylcyclopentasiloxane, b. p. 168.6–168.9° (755 mm.), 40.1 g. (16.7%); and (c) 2,4,6,8,10,12-hexamethylcyclohexasiloxane, b. p. 92.6–93.0° (21 mm.), 10.6 g. (4.4%). Intermediate fractions totaling 34.9 g. were collected, but there was no indication of the expected 2,4,6-trimethylcyclotrisiloxane; the residue amounted to 66.5 g. Pure 2,4,6,8,10,12-hexamethylcyclohexasiloxane, b. p. 76–77° (10 mm.), was obtained from fraction (c) by redistillation in a small glass-packed column. The refractive indices, densities and melting points of these new compounds are given in Table I.

The expected composition of these compounds was confirmed by determining the percentage hydrogen attached to silicon, %H(–Si), according to the equation $Si–H + KOH \rightarrow H_2 + Si–OK$.

The samples (0.15–0.20 g.) were decomposed with 40% aqueous potassium hydroxide solution in a Zerewitinoff apparatus, modified in such a way that the reaction mixture could be vigorously agitated by means of a solenoid-actuated plunger. The results are given in Table I. The lower-than-theoretical values for %H(–Si) obtained for the more volatile members is attributed to partial evaporation of unreacted sample into the gas buret. The residue from the distillation of the lower cyclic compounds was analyzed by the same procedure giving 1.68% H(–Si).

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[1] Rochow, THIS JOURNAL, **67**, 963 (1945).

[2] Patnode and Wilcock, *ibid.*, **68**, 358 (1946).

[3] Stock and Somieski, *Ber.*, **52**, 695 (1919).