[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF MIAMI AND TULANE UNIVERSITY]

The Application of Bond Parachors to Organosilicon Chemistry

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Using the system of organic bond parachors developed by Vogel and co-workers as a basis, the following set of silicon bond parachors has been developed: Si–C, 11.8 (no F, O or Cl bonded to Si), 9.2 (C is aryl), 12.6 (one O or up to 3 Cl's bonded to Si), 14.2 (2 O's bonded to Si); Si–O, 12.7; Si–Cl, 60.3; Si–I, 107.9; Si–H, 25.0 (no F, O or Cl bonded to Si); 29.1 (1 to 3 O's or Cl's bonded to Si); C–C, 3.0 (SiEt or SiPr except SiR_4 cpd.), 2.3 ($SiEt_4$ and $SiPr_4$), 2.6 (SiOEt or SiOPr); C–O, 16.0 (SiOR). The probable 50% deviation based on the 20 measured parachors used in deriving this system is 0.43%. An average deviation of 0.56% is obtained when this system is applied to 34 measured parachors not used in deriving this system.

Introduction

The use of atomic parachor values for the prediction of parachors has served along with molar refraction as a convenient tool for confirming the structure of new organic compounds. The first atomic parachor system was developed by Sugden[1] in 1924; one of the most recent systems was published by Vogel[2] in 1948.

When attempts were made to extend the system to silicon compounds the same difficulties were encountered as with atomic refractions.[3,4] In the compounds studied by Warrick[4] the range of the atomic refraction for silicon as calculated from the observed molar refraction was 3.23 to 8.54. Similar calculations of atomic parachor for the compounds listed in Tables III and IV yielded values ranging from 9.0 to 54.4. In the case of molar refractions this difficulty was overcome by Sauer,[3] who used a mixed system of group and bond refractions, and by Warrick,[4] who extended Denbigh's[5] bond refraction system to organosilicon compounds.

In 1950 Vogel and co-workers[6] published a set of 34 bond parachors based on the investigation of 700 liquid compounds of high purity. Some of these values are listed in Table II.

TABLE I

PHYSICAL PROPERTIES OF ORGANOSILICON COMPOUNDS

Compound	B.p. °C.	B.p. Mm.	d^t_4	t, °C.	n^t_D	t, °C.	γ_t (dynes/cm.)	t, °C.	MR_D Obsd.	MR_D Calcd.[a]
$Si(OC_2H_5)_4$	73.3	20	0.9334	20.0	1.3829	20.2	21.67 ± 0.12[b]	20.0	52.11	51.84
			.9227	30.0	1.3777	32.5	20.75 ± .09	29.4		
$Si(OC_3H_7\text{-}n)_4$	120	20	.9176	20.0	1.4019	18.3	23.58 ± .12	20.0	70.10	70.36
			.9097	28.7	1.3967	31.7	22.73 ± .12	29.8		
$[(CH_3)_3Si]_2O$	99.4	760	.7640	20.0	1.3769	21.8	15.48 ± .09	20.0	49.01	48.92
			.7542	29.2	1.3712	31.8	14.77 ± .09	29.3		
$[(CH_3)_2SiO]_4$	174.5	760	.9558	20.0	1.3964	19.3	18.57 ± .16	20.0	74.70	74.56
			.9451	29.3	1.3912	31.6	17.80 ± .10	29.5		
$[(CH_3)_2SiO]_5$	102	20	.9584	20.0	1.3976	20.0	18.43 ± .13	20.0	93.39	93.20
			.9500	28.1	1.3937	30.0	17.95 ± .08	28.5		
$(CH_3)_4Si$	25.5	760	.6399	20.0	1.3588	20.0	12.85 ± .07	20.0	30.34	30.28
$(C_2H_5)_4Si$	152.7	760			1.4259	21.2	23.04 ± .13	20.0[c]	48.39[c]	48.80
					1.4216	31.8	21.90 ± .10	31.2		
					1.4174	41.0	20.75 ± .11	41.2		
$(CH_3)_3SiCl$	57.2	760	.8528	25.5	1.3837	27.5	17.25 ± .11	25.8	29.85	29.91
			.8327	41.4			15.92 ± .09	41.0		

[a] System of Warrick.[4] [b] Technical probable 50% error. [c] Calcd. based on densities from Sugden and Wilkins, *J. Chem. Soc.*, 126 (1931) (d^{20}_4 0.7660, d^{30}_4 0.7579).

Experimental

Materials.—Tetraethylsilane was prepared by the addition of ethylmagnesium bromide in triethylchlorosilane. The remaining compounds were obtained from Anderson Laboratories, Inc. All of the above compounds were purified by fractionation using a column packed with glass helices and having about 15 theoretical plates.

Density.—The densities were determined in sealed or stoppered density bulbs by the method of MacKenzie, Mills and Scott,[7] a cathetometer being used for the measurements.

Refractive Index.—The refractive indices were measured with an Abbe refractometer. Measurements were made rapidly in order to minimize errors due to oxidation and hydrolysis.

Surface Tension.—The surface tensions were determined by the capillary rise method in the double capillary type of apparatus, the two capillaries having internal diameters of 0.3 and 0.55 mm., respectively. A cathetometer was used to measure the capillary rise.

The experimental data are listed in Table I.

Results and Discussion

In this research the Si–C, Si–O, Si–Cl, Si–I, Si–H, C–C and C–O bond parachors were calculated. The resulting values are given in Table II.

The parachors used in deriving this system are listed in Table III. The probable 50% deviation based on these 20 observed parachors is 0.43%.

In Table IV are listed the observed and calculated parachors for a number of organosilicon liquids not included in Table III. The average deviation without regard to sign is 0.56%; the median deviation is 0.485%.

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(1) S. Sugden, *J. Chem. Soc.*, 1177 (1924).

(2) A. I. Vogel, *ibid.*, 1842 (1948).

(3) R. O. Sauer, THIS JOURNAL, **68**, 954 (1946).

(4) E. L. Warrick, *ibid.*, **68**, 2455 (1946).

(5) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(6) A. I. Vogel, W. T. Cresswell, G. J. Jeffery and J. Leicester, *Chemistry and Industry*, 358 (1950).

(7) C. A. MacKenzie, A. P. Mills and J. M. Scott, THIS JOURNAL, **72**, 2032 (1950).

TABLE II

BOND PARACHORS

Bond	Parachor, ml./mole	Bond	Parachor, ml./mole
	Vogel[6]		
C–H	17.85	C–Cl	57.4
C–C	4.30	C–O(ethers)	12.2
C=C	28.5		
	This research		
Si–Car	9.2	Si–H(non-polar)[a]	25.0
Si–C(non-polar)[a]	11.8	Si–H(polar)[d]	29.1
Si–C(polar)[b]	12.6	C–C(Si–R)[e]	3.0
Si–C(R_2SiO)[c]	14.2	C–C(SiR_4)[e]	2.3
Si–O	12.7	C–C(SiOR)[e]	2.6
Si–Cl	60.3	C–O(SiOR)	16.0
Si–I	107.9		

[a] No F, O or Cl bonded to Si. [b] One O or up to 3 Cl's bonded to Si. [c] 2 O's bonded to Si. [d] 1 to 3 O's or Cl's bonded to Si. [e] Only for C–C bonds in Et and Pr; use Vogel's value for other C–C bonds in longer chains.

TABLE III

SELECTED LIST OF OBSERVED PARACHORS USED IN DERIVING BOND PARACHOR SYSTEM

No.	Formula	Observer	P_{obs}	P_{pred}	Dev., %
1	$Si(OCH_3)_4$	[b]	330.9	329.0	−0.57
2	$Si(OC_2H_5)_4$	[a]	481.6	482.2	+ .12
3	$Si(OC_3H_7\text{-}n)_4$	[a]	635.2	635.4	+ .03
4	$[(CH_3)_3Si]_2O$	[a]	422.1	422.3	+ .05
5	$[(CH_3)_2SiO]_4$	[a]	644.5	643.6	− .14
6	$[(CH_3)_2SiO]_5$	[a]	802.7	804.5	+ .22
7	$(CH_3)_4Si$	[a]	262.2	261.4	− .30
8	$(C_2H_5)_4Si$	[a]	412.7	413.4	+ .17
9	$(n\text{-}C_3H_7)_4Si$	[b]	565.3	565.4	+ .02
10	$(C_6H_5)_4Si$	[b]	787.5	787.4	− .01
11	$(CH_3)_3SiCl$	[a]	260.7	258.8	− .73
12	$(C_2H_5)_2SiHCl$	[c]	299.8	299.1	− .23
13	$C_2H_5SiHCl_2$	[c]	255.0	254.6	− .16
14	$HSiCl_3$	[c]	209.0	210.0	+ .48
15	$HSi(OC_2H_5)_3$	[c]	394.0	390.8	− .81
16	$(C_2H_5)_3SiH$	[c]	339.4	337.2	− .65
17	$SiCl_4$	[b]	242.2	241.2	− .41
18	SiH_4	[d]	99.7	100.0	+ .30
19	SiH_3I	[e]	182.5	182.9	+ .22
20	SiH_2I_2	[e]	266.4	265.8	− .23

[a] This research. [b] S. Sugden and H. Wilkins, *J. Chem. Soc.*, 126 (1931). [c] C. A. MacKenzie, A. P. Mills and J. M. Scott, THIS JOURNAL, **72**, 2032 (1950). [d] T. G. Pearson and P. L. Robinson, *J. Chem. Soc.*, 736 (1934). [e] H. J. Emeleus, A. G. Maddock and C. Reid, *ibid.*, 353 (1941).

TABLE IV

OBSERVED PARACHORS NOT LISTED IN TABLE III

No.	Formula	Observer	P_{obs}	P_{pred}	Dev., %
		$Si(OR)_4$			
1	CH_3[a]	[c]	328.0	329.0	+0.30
2	C_2H_5[a]	[b]	487.6	482.2	−1.11
3	C_2H_5[a]	[c]	485.3	482.2	−0.64
4	CH_2CH_2Cl	[d]	647.9	640.4	−1.15
5	$n\text{-}C_3H_7$[a]	[c]	639.9	635.4	−0.70
6	$CH(CH_2Cl)_2$	[d]	947.0	951.8	+0.51
7	$n\text{-}C_4H_9$	[c]	799.3	795.4	−0.49
8	$n\text{-}C_6H_{13}$	[c]	1114.1	1115.4	+0.12
9	$n\text{-}C_7H_{15}$	[c]	1273.8	1275.4	+0.13
10	$n\text{-}C_8H_{17}$	[c]	1434.8	1435.4	+0.04
11	$n\text{-}C_9H_{19}$	[c]	1591.8	1595.4	+0.23
12	$n\text{-}C_{10}H_{21}$	[c]	1755.4	1755.4	0
		$Me_3Si(Me_2SiO)_nOSiMe_3$			
13	$n = 0$[a]	[e]	420.2	422.3	+0.50
14	0[a]	[f]	423.1	422.3	−0.19
15	1	[e]	580.1	583.2	+0.53
16	1	[f]	585.2	583.2	−0.34
17	2	[e]	737.4	744.1	+0.91
18	2	[f]	745.3	744.1	−0.16
19	3	[e]	900.1	905.0	+0.54
20	3	[f]	906.3	905.0	−0.14
21	4	[c]	1059.5	1065.9	+0.60
22	4	[f]	1067.3	1065.9	−0.13
23	5	[e]	1217.3	1226.8	+0.78
24	5	[f]	1223.5	1226.8	+0.27
25	6	[e]	1381.1	1387.7	+0.48
26	6	[f]	1385.6	1387.7	+0.15
27	7	[f]	1555.4	1548.6	−0.44
28	10	[f]	2040.3	2031.3	−0.44
29	15	[f]	2853.7	2835.8	−0.63
		$(Me_2SiO)_n$			
30	$n = 4$[a]	[g]	634.5	643.6	+1.43
31	5[a]	[g]	794.5	804.5	+1.26
32	6	[g]	947.8	965.4	+1.85
33	7	[g]	1110.6	1126.3	+1.41
34	$Si(C_2H_5)_4$[a]	[b]	412.2	413.4	+0.29

[a] Other measurements on compounds listed in Table III. [b] S. Sugden and H. Wilkins, *J. Chem. Soc.*, 126 (1931). [c] B. A. Arbuzov and V. S. Vinogradova, *Doklady Akad. Nauk. S.S.S.R.*, **60**, 799 (1948). [d] W. J. Jones, L. H. Thomas, E. H. Pritchard and S. T. Bowden, *J. Chem. Soc.*, 824 (1946). [e] M. J. Hunter, E. L. Warrick, J. F. Hyde and C. C. Currie, THIS JOURNAL, **68**, 2284 (1946). [f] H. W. Fox, P. W. Taylor and W. A. Zisman, *Ind. Eng. Chem.*, **39**, 1401 (1947). [g] M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, THIS JOURNAL, **68**, 667 (1946).

The predictability obtained with the above system compares favorably with that obtained using bond refractions; although the above system is somewhat more cumbersome and restricted than the bond refraction system of Warrick.[4] Due to the simplicity and high accuracy of refractive index measurements, the molar refraction system will usually be chosen for structure proof when a refractometer is available. In difficult or questionable cases, however, the use of both systems may prove advantageous.

Since accurate determinations of surface tensions are rather difficult, this system will have considerable value for calculating the surface tension of silicon compounds whose densities are known.

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