heterogeneity¹⁸⁻²⁰ at low pH our investigation was confined to the homogeneous region at $pH \ge 4.0$. Thus, the conclusions of previous investigators,^{8,10} based on hydrodynamic data, are open to question. For this reason, also, we cannot confirm or deny the idea of an α - β transformation at pH's below 4 proposed by Yang and Foster,¹⁰ and discussed recently by Hill.⁵⁹ It may be pointed out that the heterogeneous sedimentation patterns of Fig. 3 are compatible with the existence of two forms. However, our sedimentation observations are too meager to identify these as α - and β -forms. It is our opinion that the nature of the configurational changes below pH 4 is still an unsettled matter. However, insofar as these changes already manifest themselves to a small extent as the pH is lowered from 5.13 to 4.0, we may conjecture at this time that the combined effects of reversible formation and breakage of hydrogen bonds be-

(59) T. L. Hill, THIS JOURNAL, 60, 358 (1956).

tween side chain polar R groups of BSA, and the concomitant penetration of solvent into the molecular domain (i.e., swelling), will account for the abnormal steepening of the titration curve in the pH region of the ionization of carboxyl groups. However, it must be emphasized that, without a determination of β for each species present below pH 4, we have no assurance that a sphere is a good model at the low pH. Therefore, conclusions drawn from only one hydrodynamic quantity (*i.e.*, viscosity) plus the assumption of spherical symmetry^{8,10,60} could be erroneous. It is quite conceivable that the changes taking place below pH 4 would require the use of asymmetrical equivalent ellipsoids to account for the hydrodynamic properties of BSA. In fact recent experiments of Harrington, Johnson and Ottewill⁴⁴ indicate that such may be the case.

(60) The lack of flow birefringence in a molecule as small as BSA is no guarantee of spherical symmetry.

THE SILICON-BROMINE AND SILICON-CARBON(ARYL) BOND PARACHORS AND THE SILICON-BROMINE BOND REFRACTION¹

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Trimethylphenylsilane, dimethyldiphenylsilane, trimethylbromosilane, dimethylphenylbromosilane, dimethyldibromosilane and methyldiethylbromosilane were prepared and purified and their refractive indices, densities, surface tensions and viscosities were measured. Using the bond parachor system of Mills and MacKenzie as a basis, values of 74.1 and 1.8 were derived for the silicon-bromine and silicon-carbon(aryl) bond parachors, respectively. Using the system of Vogel and coworkers as a basis, a new value of 10.24 was derived for the silicon-bromine bond refraction from data on 14 compounds. For the six compounds listed above, values of Trouton's constant were found to range from 21.1 to 25.5 and the ratio $\Delta E_{\rm vap}/\Delta E_{\rm vis}$ ranged from 2.96 to 3.86.

The organosilicon bond parachor system developed by Mills and MacKenzie² did not contain a value for the Si-Br bond and the value for the Si-C-(aryl) bond was based on a high temperature measurement of only one compound. Since most parachors change slightly with temperature it was considered desirable to obtain a new value based on measurements made at 25°.

The Si-Br bond refraction in Vogel's system³ was based on only three compounds. A new value was obtained by also considering the molar refractions of four compounds measured in this research and eight compounds measured by McCusker and Reilly.⁴

Experimental

Materials.—Trimethylphenylsilane and dimethyldiphenylsilane were prepared by the addition of phenylmagnesium bromide to trimethylchlorosilane and dimethyldichlorosilane, respectively. The silicon-phenyl bonds were then cleaved with bromine by the method of McBride and

(3) A. I. Vogel, W. T. Cresswell and J. Leicester, This Journal, 58, 177 (1954).

(4) P. A. McCusker and E. L. Reilly, J. Am. Chem. Soc., 75, 1583 (1953).

Beachell⁵ to form trimethylbromosilane, dimethylphenylbromosilane and dimethyldibromosilane. Methyldiethylbromosilane was prepared by the addition of appropriate quantities of ethylmagnesium bromide and p-tolylmagnesium bromide to methyltrichlorosilane to form methyldiethyl-p-tolylsilane (b.p. 132° at 20 mm. and 143° at 30 mm.) which was then cleaved with bromine. All of the above compounds were purified by reduced pressure fractionation⁶ using a column packed with glass helices and having about 15 theoretical plates. Density.—The densities were determined in stoppered density but he to be method of MostKearie Wills and

Density.—The densities were determined in 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.

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.

Viscosity.—The viscosities were measured with a Drucker viscometer.

The experimental data are listed in Table I.

Results and Discussion

Bond Parachors.—Using the bond parachor

(5) J. J. McBride, Jr., and H. C. Beachell, *ibid.*, 74, 5247 (1952).
(6) We wish to thank Louis H. Dunlop (McKeesport High School, McKeesport, Pa.) Future Scientists of America Summer Fellow, for his help with some of the fractionations.

(7) C. A. MacKenzie, A. P. Mills and J. M. Scott, J. Am. Chem. Soc., 72, 2032 (1950).

⁽¹⁾ Presented in part at the Meeting-in-Miniature of the Florida Section of the American Chemical Society, Orlando, Florida, May, 1955. Abstracted in part from the M.S. Thesis of Warren E. Becker, University of Miami, May, 1955.

⁽²⁾ A. P. Mills and C. A. MacKenzie, J. Am. Chem. Soc., 76, 2673 (1954).

		n								
Compound	۰C	. Б.р.	Mm.	n ^t D	<i>ŧ</i> , °C.		d 254	d ³⁵ 4	đ	2454
Me₃SiPh	67	.3	20	1.4879	25.0	0.	8646	0.8561	0.	8474
Me_2SiPh_2	137		9	1.5644	20.0	0.	9880	0.9797	0.	9719
Me_3SiBr	40	.5	200	1.4228	28.6	1.	1805	1.1656	1.	1507
Me ₂ PhSiBr ^a	102	.2	20	1.5294	25.0	1.	2666	1.2558	1.	2449
Me_2SiBr_2	51	.9	100	1.4713	25.0	1.	7177	1.6992	1.	6807
MeEt ₂ SiBr ^a	41	.0	20	1.4464	25.0	1.	1515	1.1397	1.	1277
~ .	γ	(dynes/or	n.)	V	iscosity (m.p.))	M	RD	Br	, %
Compound	255	35	45°	250	35	45°	Obsd.	Calcd. b	Ubsd.	Calcd.
Me₃SiPh	24.29	23.49	22.72	8.55	7.42	6.53	50.07	50.08		
$Me_{2}SiPh_{2}$	32.47	31.59	30.71	35.72	27.80	22.35	69.65	67.97		
Me ₃ SiBr	19.87	18.75	17.73	5.60	5.00	4.55	33.16	32.72	50.8	52.2
$Me_2PhSiBr^a$	28.30	27.59	26.88	17.64	14.74	12.55	52.43	52.61	36.9	37.2
Me ₂ SiBr ₂	24.57	23.63	22.80	8.83	7.96	7.14	35.49	35.26	73.6	73.4
$MeEt_2SiBr^a$	23.55	22.71	21.87	7.86	6.93	6.13	41.99	42.02	44.5	44.1

TABLE I PHYSICAL PROPERTIES OF BROMO- AND PHENYLSILANES

^a Previously unpurified compounds. ^b System of Vogel and co-workers.³

systems of Mills and MacKenzie² and Vogel⁸ as a basis, the following bond parachors (ml./mole) were derived: Si-Br 74.1, Si-C(aryl) 1.8. This latter, when used with Vogel's⁸ values of 17.85 for C-H and 16.5 for C_{ar} - C_{ar} gives a value of 190.0 for the Si-Ph bond-group. The parachors used in deriving these values are listed in Table II. The probable 50% deviation based on these six observed parachors is 0.72%.

TABLE II

Parachors Used in Deriving Si-Br and Si-Ph Bond Parachors

	j	Р	
Compound	Obsd.	Calcd.	Dev., %
Me₃SiPh	385.9	386.1	+0.05
Me_2SiPh_2	513.1	510.7	-0.47
Me _s SiBr	275.9	272.6	-1.19
$Me_2PhSiBr$	391.8	396.4	+1.17
Me_2SiBr_2	282.6	280.5	-0.74
$MeEt_{2}SiBr$	346.6	350.0	+0.98

Bond Refraction.—Using the bond refraction system of Vogel and co-workers⁸ as a basis, a value of 10.24 was derived for the Si-Br bond refraction. The molar refractions used in deriving this value are listed in Table III. The probable 50% deviation based on these 14 observed molar refractions is 0.38%.

Vapor Pressure and Viscosity.—The normal boiling points of the six compounds used in this research were obtained by a critical evaluation of literature data. Values of $\Delta H_{\rm vap}$ were then calculated from these normal boiling points and the reduced pressure boiling points measured in this research. The Trouton's constants were found to range from 21.1 to 25.5. Values of $\Delta E_{\rm vis}$ were calculated from the viscosity data and the ratio $\Delta E_{\rm vap}/$

(8) A. I. Vogel, W. T. Cresswell, G. J. Jeffery and J. Leicester, J. Chem. Soc., 531 (1952).

REFRACTION						
	Ob-	M	De	Dev.,		
Compound	server	Obsd.	Calcd.		76	
Me ₃ SiBr	a	33.16	32.88	-0).84	
Me_2SiBr_2	a	35.49	35.58	+	.25	
MeEt ₂ SiBr	a	41.99	42.18	+	.45	
Me ₂ PhSiBr	a	52.43	52.77	+	.65	
MeSiBr ₃	ь	38.56	38.27		.75	
EtSiBr ₃	ь	43.35	42.92	-	.99	
Et_2SiBr_2	ь	44.72	44.87	4	.34	
PhSiBr ₃	ь	58.10	58.16	+	.10	
PhSiHBr ₂	ь	51.04	51.09	+	.10	
PhSiH₂Br	ь	44.09	44.02		. 16	
Et ₃ SiBr	Ь	46.67	46.83	+	.34	
Ph ₂ SiBr ₂	Ь	75.52	75.36		.21	
$Et_2(ClCH_2CH_2)SiBr$	с	51.37	51.66	+	. 56	
SiBr ₄	d	40.74	40.96	+	.54	
^a This research. ^b	See ref.	4. °D.	L. Bailey	, L.	H.	
Sommer and F. C. W	hitmore.	, J. Am. (Chem. Soc.,	70,	436	
(1948). ^d E. L. Warrick, <i>ibid.</i> , 68, 2455 (1956).						

TABLE III

MOLAR REFRACTIONS USED IN DERIVING THE SI-Br BOND

 $\Delta E_{\rm vis}$ was calculated using the approximation, $\Delta E_{\rm vap} = \Delta H_{\rm vap} - RT$. The latter ratio ranged from 2.96 to 3.86, which is quite reasonable for this type of compound. These results are summarized in Table IV.

TABLE IV VAPOR PRESSURE AND VISCOSITY RELATIONSHIPS

			$\Delta H_{\rm vap}/$	vap/		
Com- pound	B.p., °C. (760 mm.)	$\Delta H_{\rm vap}$ (kcal./ mole)	(cal./ mole deg.)	$\Delta E_{\rm vis}$ (kcal./ mole)	$\Delta E_{ m vap}/\Delta E_{ m vis}$	
Me₃SiPh	171.3	10.49	23.6	2.54	3.82	
Me_2SiPh_2	277.4	14.03	25.5	4.42	2.96	
Me₃SiBr	79.9	7.46	21.1	1.95	3.48	
Me ₂ PhSiBr	215	11.77	24.1	3. 21	3.40	
Me ₂ SiBr ₂ .	111.6	8.45	22.0	2.00	3.86	
MeEt ₂ SiBr	139.5	9.51	23.1	2.34	3.75	