[Contribution from the Richardson Chemical Laboratories, Tulane University]

Physical Properties of Trichlorosilane and Some of Its Derivatives[1]

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Although a number of derivatives of trichlorosilane have been reported, there is a paucity of information about their physical properties. Quite often only boiling points and densities are recorded. We have determined boiling points, densities, refractive indices, surface tensions, viscosities and melting points for trichlorosilane, *n*-butyldichlorosilane, ethyldichlorosilane, diethylchlorosilane, triethylsilane and triethoxysilane.

Experimental

Materials.—*n*-Butyldichlorosilane, ethyldichlorosilane, diethylchlorosilane and triethylsilane were prepared by the addition of the appropriate Grignard reagent to trichlorosilane. Triethoxysilane was prepared by the addition of absolute ethanol to a solution of trichlorosilane in heptane.[3] The compounds were purified by fractionation using a column packed with glass helices and having about 15 theoretical plates. The boiling point ranges of the samples used for the physical measurements were: trichlorosilane, 31.6–32.0°; ethyldichlorosilane, 74.7–75.0°; diethylchlorosilane, 99.6–99.9°; triethylsilane, 107.5–107.9°; triethoxysilane, 131.2–131.8°; and *n*-butyldichlorosilane, 128.7–129.5°. The benzene used for calibration in the density, surface tension and viscosity measurements was purified by distilling, freezing and discarding the first liquid to melt, and finally by distilling from phosphorus pentoxide.

Density.—The densities of trichlorosilane, ethyldichlorosilane and diethylchlorosilane were measured using the following method. The apparatus consisted of a $^7/_{25}$ S. T. female joint with a 15-cm. length of 6 mm. Pyrex glass tubing sealed to a bulb of about 10-ml. capacity. Three thin scratches, spaced 3 to 4 cm. apart, were made on the capillary perpendicular to its length. The distances between these scratches were measured with a traveling microscope.

Calibration of the capillary and the bulb was accomplished by filling the bulb twice with distilled water; the first filling bringing the meniscus up into the lower part, the second bringing it up near the top of the capillary tube. In the calibration the density tube was closed with a $^7/_{25}$ S. T. stopper. The density bottle was clamped in a vertical position and immersed in a constant temperature bath at 20°. After attainment of thermal equilibrium the distance of the meniscus from the nearest scratch was measured with a traveling microscope.

The bulb was dried and filled by distilling the liquid, *e. g.*, trichlorosilane, directly into the density tube through a small drawn out capillary. After chilling, the capillary of the density bottle was sealed off between the top scratch and the female ground glass joint. The bulb, clamped in a vertical position, was completely immersed in a constant temperature bath. The height of the meniscus was measured at 20° and at least two other temperatures. The volumes of the bulb and capillary at other temperatures were calculated using the formula given by Crumpler and Yoe,[4] $V_t = V_{20}/1 + 0.000025(20 - t)$. In taking readings at different temperatures it was assumed that the gas above the liquid in the bulb had a negligible effect on the volume of the liquid. All weights were corrected to *in vacuo*.

Refractive Index.—The refractive indices were measured with an Abbe refractometer using a sodium vapor lamp for the light source.

Surface Tension.—The surface tensions were measured by the capillary rise method with a modified Richards and Coombs apparatus.[5] The large tube, 15 cm. in length, had an internal diameter of 30 mm.; the capillary tube had an internal diameter of 0.5 mm. A 5-liter beaker of water was used for a constant temperature bath. A traveling microscope was used to measure the capillary rise both in calibration with purified benzene and in all other measurements.

Viscosity.—The viscosities were measured with a Drucker viscometer calibrated with benzene.[6] Samples of 3 ml. each were used for the determinations.

Melting Point.—The melting points were measured with a chromel–alumel thermocouple connected to a type K-2 potentiometer and a wall galvanometer. The liquid was placed in the inner tube of two concentric test-tubes and cooled by immersing in liquid nitrogen. The rate of cooling was not regulated closely enough to obtain significant cooling curves for the freezing liquids. Since interest in the melting points did not justify the effort required to obtain accurate values the temperature at which the liquid changed to a solid is given as an approximate melting point.

The experimental data are listed in Table I.

Discussion

Boiling Point Prediction.—Lewis and Newkirk[7] have suggested a system of boiling point predictions applicable to alkyl and aryldichlorosilanes and to dialkyl and diarylchlorosilanes. For compounds such as methyldichlorosilane these authors used a group boiling point number for methyl based on the formula $RSi\equiv$. For a compound such as dimethylchlorosilane they used $R_2Si=$. Calculations based on such values have been given poor results. Better values are obtained if it is assumed that a single hydrogen attached to silicon has an effect on the boiling point number of the alkyl group similar to that produced when the hydrogen is replaced by another alkyl group. Using this system the value for the methyl group in methyldichlorosilane is based on the formula $R_2Si=$ and the values for the methyl groups in dimethylchlorosilane are based on the formula R_3Si-. A second hydrogen attached to silicon does not appear to have this effect. For example, the boiling point of methylchlorosilane must be calculated on the basis of the formula $R_2Si=$ and not R_3Si-. A comparison of the two methods for prediction of boiling points is shown in Table II.

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[1] Based upon a part of the thesis submitted by A. P. Mills to the Department of Chemistry of Tulane University in April, 1949, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] For the use of benzene as a solvent see M. Havill, I. Jeffe and H. Post, *J. Org. Chem.*, **13**, 280 (1948).

[4] T. Crumpler and J. Yoe, "Chemical Computations and Errors," John Wiley & Sons, Inc., New York, N. Y., 1940, p. 113.

[5] T. W. Richards and L. Coombs, This Journal, **37**, 1657 (1915).

[6] Data for calibration were taken from the "International Critical Tables"; density, Vol. III, p. 29; surface tension, Vol. IV, p. 454; viscosity, Vol. V, p. 12.

[7] R. Lewis and A. Newkirk, This Journal, **69**, 710 (1947).

TABLE I

PHYSICAL CONSTANTS OF TRICHLOROSILANE AND SOME OF ITS DERIVATIVES

Compound	B. p. (760 mm.), °C.	M. p., °C.	Temp., °C.	Density, g./ml.	n^t_D	Sur. tens., dynes/cm.	Viscosity, mp.
$HSiCl_3$	31.8[a,b]	...	0.0	1.3830[a,h]	.....	20.43	3.97
			20.0	1.3417	1.4020	18.27	3.32
			25.0	1.3313	1.3983	17.74	3.16
$EtSiHCl_2$	74.9[c,d]	−107	0.0	1.1144	.....	...	..
			20.0	1.0926	1.4148	21.70	5.27
			25.0	1.0872	1.4120	21.09	5.09
Et_2SiHCl	99.7[d,e]	−143	0.0	0.9104	.....	...	..
			20.0	.8895	.....	22.30	4.90
			25.0	.8842	1.4133	21.77	4.64
Et_3SiH	107.7[c,e,]	...	20.0	.7316[e,i]	1.4109[e]	20.71	4.12
			25.0	.7269	1.4085[c]	20.32	3.92
$HSi(OEt)_3$	131.5[g]	−170	20.0	......	1.3767	21.25	..
			25.0	0.8903[g]	1.3744	20.80	5.12
n-$BuSiHCl_2$	129.0	...	20.0	1.0466	1.4272	...	..
			25.0	1.0397	1.4244	...	..

[a] Stock and Zeidler, *Ber.*, **56**, 986 (1923), give b. p. 31.8°, d_0 1.35. [b] Booth and Stillwell, THIS JOURNAL, **56**, 1529 (1934), give b. p. 31.5°. [c] Meals, *ibid.*, **68**, 1880 (1946), gives b. p. 75.4° for $EtSiHCl_2$ and b. p. 109°, $d_{26.5}$ 0.744 and n_{25} 1.4092 for Et_3SiH. [d] Emeleus and Robinson, *J. Chem. Soc.*, 1592 (1947), give b. p. 74.2° for $EtSiHCl_2$ and b. p. 99.2° for Et_2SiHCl. [e] Whitmore, Pietrusza and Sommer, THIS JOURNAL, **69**, 2108 (1947), give b. p. 99° for Et_2SiHCl and b. p. 107°, d_{22} 0.7302 and n_{20} 1.4117 for Et_3SiH. [f] Krause and Nelson, *ibid.*, **56**, 195 (1934), give b. p. 107–110°. [g] Havill, Joffe and Post, *J. Org. Chem.*, **13**, 280 (1948), give b. p. 132–135° and d_{25} 0.8745. [h] Ruff and Albert, *Ber.*, **38**, 53, 2222 (1905), give 1.3438. [i] Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1946, gives d_0 0.751.

TABLE II

THE PREDICTION OF BOILING POINTS

			Lewis and Newkirk		Our method	
Compound	B. p. (obs.), °C.	Ref.	B. p. (calcd.), °C.	Δ[a]	B. p. (calcd.), °C.	Δ[a]
$MeSiHCl_2$	41.5	[b]	43.9	+2.4	40.6	−0.9
Me_2SiHCl	...	[b]	39.1	...	35.5	...
$MeSiH_2Cl$	7	[b]	10.1	+3.1	7.7	+0.7
$EtSiHCl_2$	74.2	[c,d]	81.4	+7.2	74.4	+ .2
n-$BuSiHCl_2$	129.0	[d]	133.6	+4.6	129.1	+ .1
$PhSiHCl_2$	184	[b]	187.8	+3.8	186.9	+2.9
Et_2SiHCl	99.2	[c,d]	103.7	+4.5	98.6	−0.6

[a] Δ = b. p. (calcd.) − b. p. (obs.). [b] Ref. 7. [c] Ref. *d*, Table I. [d] Our values, Table I.

TABLE III

PARACHORS AND MOLAR REFRACTIONS

Compound	Parachor detd.	P_{Si}, calcd.	*MR*, detd.	Compound	Parachor detd.	P_{Si}, calcd.	*MR* detd.
$HSiCl_3$	209.0	29.0	24.57	Et_3SiH	339.4	37.4	39.49
$EtSiHCl_2$	255.0	33.7	29.53	$HSi(OEt)_3$	394.0	31.6	42.15
Et_2SiHCl	299.8	38.2	34.61	n-$BuSiHCl_2$	...	..	38.63

Parachors.—The atomic parachor of silicon as shown in Table III was calculated from the measured values and the atomic parachors of the other atoms listed by Sugden.[8] Equally poor values were obtained when the systems of Mumford and Philips[9] and Bayliss[10] were used. It is obvious that this method of attack does not give a satisfactory value for the atomic parachor of silicon. A system of bond parachors might prove far more satisfactory in the study of structures.

Molar Refractions.—The molar refractions calculated for the six compounds checked quite well with those predicted by both Sauer[11] and Warrick.[12] Sauer's system gave an average deviation of 0.11 while Warrick's system gave one of 0.25 from the experimental values.

Summary

The boiling points, densities, refractive indices, surface tensions, viscosities and melting points have been measured for trichlorosilane, *n*-butyldichlorosilane, ethyldichlorosilane, diethylchlorosilane, triethylsilane and triethoxysilane. A modification is suggested for the application of Lewis and Newkirk's system of boiling point prediction to alkyl- and aryldichlorosilanes and to dialkyl- and diarylchlorosilanes. The molar refractions were calculated and were found to check quite satisfactorily with those predicted by the methods of Sauer and Warrick. The atomic parachor for silicon was found to vary from 29 to 38.

NEW ORLEANS, LA. RECEIVED NOVEMBER 29, 1949

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(8) S. Sugden and H. Wilkins, *J. Chem. Soc.*, 126 (1931).

(9) S. Mumford and J. Philips, *ibid.*, 2112 (1929).

(10) N. Bayliss, THIS JOURNAL, **59**, 444 (1937).

(11) R. Sauer, *ibid.*, **68**, 954 (1946).

(12) E. Warrick, *ibid.*, **68**, 2455 (1946).