from equation 1 for nine substituted acetophenones are $\rho = 0.968$, $s = 0.055$, $r = 0.991$; for five substituted ethyl benzoates $\rho = 0.612$, $s = 0.038$, $r = 0.996$.[4] The excellent fit of the data to the Hammett equation may be taken as further evidence that the assumptions made in the above derivations are reasonable.

Few other determinations of pK's of conjugate acids of very weak bases are available for comparison.[5] The pK's of acetophenone,[6,7] of two of its substitution products,[6] of methyl benzoate,[7] and of nitrobenzene[7,8] have been reported. Relative values of these data, referred to acetophenone as standard, are compared in Table I with values calculated by use of equation 1 from the data of Pratt and Matsuda.[1] Although qualitatively the order of basicities of the compounds is the same, the ratios for benzene solution are much smaller than those obtained in the much more polar solvents sulfuric acid,[6,8] nitrobenzene[7] and acetophenone.[7]

[4] s is the standard deviation, approximately 1.5 times the probable error used by Hammett to estimate the fit of data; r is the correlation coefficient. *Cf.* H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[5] I am indebted to Dr. E. F. Pratt of the University of Maryland, and to one of the referees for calling my attention to these data.

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Dipole Moments of *t*-Butylperphthalic Acid and Di-*t*-butyldiperphthalate

BY STERLING E. VOLTZ[1]

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In the past decade an increased amount of interest has been given to studies of the properties of organic peroxides. This is due largely in part to the increased availability of these compounds and their subsequent uses in newly developed commercial processes. In particular, di-*t*-butyldiperphthalate is more effective than benzoyl peroxide in the polymerization of isoprene and isoprene–styrene.[2]

As part of a study of the dielectric properties of certain organic peroxides and solutions containing these peroxides, the dipole moments of a number of these compounds have been determined. Dielectric polarization data for *t*-butylperphthalic acid and di-*t*-butyldiperphthalate are given in Table I. Measurements of the benzene solutions of the acid were made at 50° and those of the ester at 30°. The molar polarizations of benzene at 50 and 30° were calculated to be 26.74 and 26.66 cc.$^{-1}$, respectively.[3,4] The extrapolated molar polarizations of *t*-butylperphthalic acid and di-*t*-butyldiperphthalate at infinite dilutions are about 323 and 285 cc.$^{-1}$, respectively. The polarization of *t*-butylperphthalic acid in benzene is practically independent of concentration, whereas the polarization of di-*t*-butyldiperphthalate decreases linearly with increasing dilution.

The molar refractions of these two compounds were calculated from appropriate atomic refractions; the atomic refraction of the peroxidic oxygen was taken to be 2.19.[5] The calculated molar refractions are 59.4 and 80.2 cc.$^{-1}$ for *t*-butylperphthalic acid and di-*t*-butyldiperphthalate, respectively. Thus, the dipole moment of *t*-butylperphthalic acid is 3.74 D and that of di-*t*-butyldiperphthalate is 3.20 D.

Experimental

The peroxides used in this work were obtained from commercial sources. They were recrystallized from ether solutions and dried over sulfuric acid.[6] Thiophene-free benzene was purified by standard procedures.

The dielectric constants were determined with a resonance apparatus.[7] Density measurements were made with a calibrated pycnometer.

TABLE I

DIELECTRIC POLARIZATION DATA

Mole fraction	Dielectric constant, D	Density (g./cc.)	Polarization (cc.$^{-1}$)
t-Butylperphthalic acid (50°)			
0.007692	2.373	0.8580	326
.01410	2.483	.8616	319
.01892	2.596	.8644	337
.02552	2.723	.8696	330
Di-*t*-butyldiperphthalate (30°)			
0.009437	2.413	0.8744	318
.01521	2.513	.8784	322
.02600	2.778	.8851	362
.03352	2.977	.8891	376

Acknowledgment.—The author wishes to express his appreciation to Dr. M. W. Rigg for his encouragement in this work and to Temple University for the research grant that made this investigation possible.

[1] Houdry Process Corp., Marcus Hook, Pa.

[2] L. H. Perry, *Ind. Eng. Chem.*, **41**, 1438 (1949).

[3] A. A. Maryott and E. R. Smith, *Natl. Bur. Standards, Circular*, **514**, 18 (1951).

[4] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950, pp. 140–149.

[5] N. A. Milas, D. M. Surgenor and L. H. Perry, THIS JOURNAL, **68**, 1617 (1946).

[6] N. Milas and D. Surgenor, *ibid.*, **68**, 642 (1946).

[7] S. E. Voltz, Thesis, Temple University (1951).

Density of Liquid Hydrogen Bromide

BY W. G. STRUNK AND W. H. WINGATE

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The density of liquid hydrogen bromide has been determined over the range −75 to +60°. Results obtained in laboratory and plant-scale experiments agree very well and show the density of liquid hydrogen bromide to be substantially greater than values reported in the literature.

Figure 1 shows the agreement between all of the data obtained as a part of this work and the disagreement between these data and those previously published.[1] Since the present work utilized two entirely different techniques which are

[1] "International Critical Tables," Vol. III, 1st edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 228.

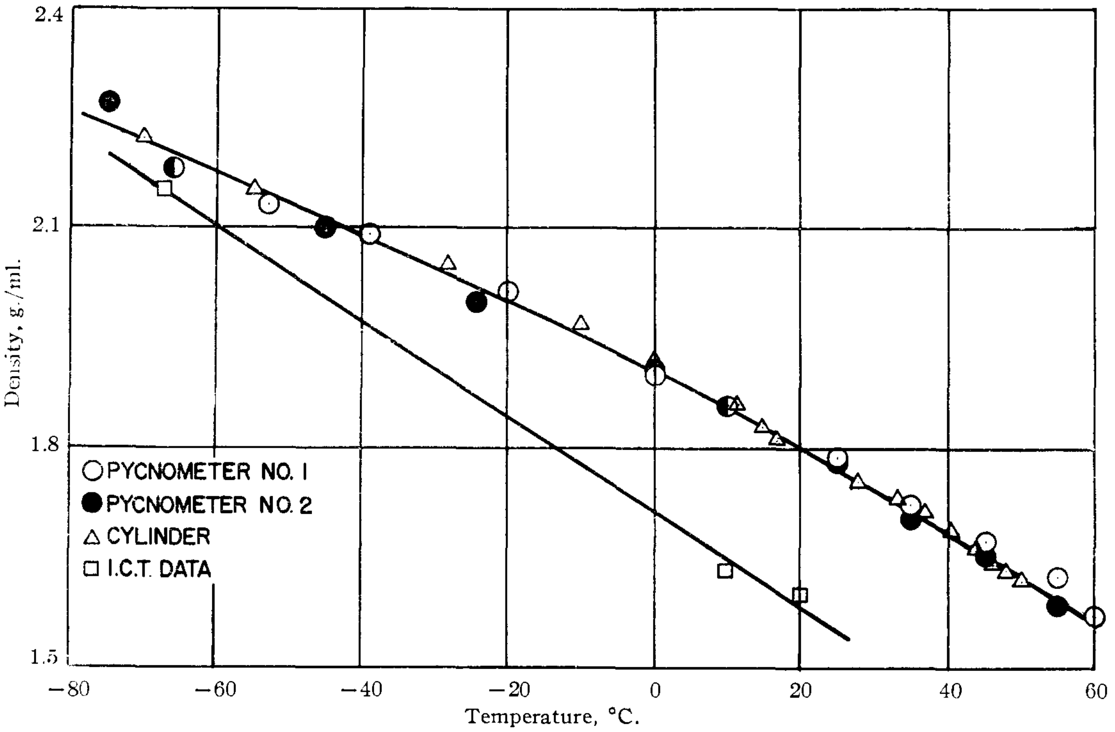

Fig. 1.—Density of liquid hydrogen bromide: ○, pycnometer no. 1; ●, pycnometer no. 2; △, cylinder; □, I.C.T. data.

subject to different sources of error, the agreement which was obtained is considered satisfactory. The maximum deviation of individual measurements from the curve is 0.04 g./ml., and the standard deviation of the data is ±0.02 g./ml. The density of liquid hydrogen bromide under an atmosphere of hydrogen bromide gas can be calculated by the equation

$$D = 2.757 - 1.238 \times 10^{-3}T - 7.01 \times 10^{-6}T^2$$

D = density, gram per ml.
T = abs. temp. (range 193 to 333T)

Experimental

Laboratory.—Pycnometers were made from about 12-inch sections of 4-mm. i.d., Pyrex, capillary tube. The bottom was sealed off and the volume of the capillary calibrated with water. The tared pycnometers were charged by passing a stream of hydrogen bromide gas into the capillary while the pycnometer was immersed in Dry Ice.

The hydrogen bromide gas was obtained by vaporizing liquid hydrogen bromide from regular Westvaco Chemical Division production. The assay of Westvaco hydrogen bromide is usually above 99.9%. The open end of the pycnometer was then sealed off with a flame and the charged pycnometer weighed on an analytical balance. An appreciable vapor space was left in the pycnometer to permit liquid expansion. The weight of hydrogen bromide in the vapor phase was estimated from the perfect gas laws.

The pycnometer was immersed in a liquid bath and the height of the column of liquid hydrogen bromide noted at various temperatures. The density of the liquid was then calculated from the observed liquid volume and the weight of hydrogen bromide present in the liquid phase. Density determinations made using two different pycnometers were in substantial agreement (Fig. 1).

Plant.—The density was determined on a larger scale by observing the weight of anhydrous hydrogen bromide in a cylinder of known volume at various temperatures.

Two ICC No. 3AA 1800 hydrogen bromide cylinders were used for the large-scale test. The test cylinder, which was full of hydrogen bromide at all times, was fitted with a Schedule 80 cross containing an 800 p.s.i.g. pressure-vacuum gage, a thermocouple well extending about eight inches into a body of the cylinder, and a high-pressure cylinder valve. The second cylinder, which acted as a receiver, was fitted with a Schedule 80 tee containing a thermocouple well extending about eight inches into the body of the cylinder, and a high-pressure cylinder valve. Copper–constantan thermocouples connected to a direct-reading potentiometer were used to measure the temperature. The test cylinder was positioned on dial scales. To be certain that there would be no strain that would affect the weight readings of the test cylinder, the two cylinders were interconnected by means of a loop of flexible copper tubing. The connecting tubing was provided with a vacuum connection for evacuating the line after making the necessary connections. The volume of the test cylinder was calculated from its weight when filled with water.

Both of the cylinders were washed and dried immediately before starting the actual test. The receiver cylinder was evacuated and then filled with hydrogen bromide vapors at room temperature. The test cylinder was chilled in a Dry Ice bath, evacuated and filled at −70° with liquid anhydrous hydrogen bromide, placed on scales and the tubing connected and evacuated. The valves connecting the cylinders were opened; as the liquid temperature increased, it expanded and overflowed into the receiver. Temperature, weight and pressure were recorded at regular intervals. When the test cylinder had warmed to room temperature, both of the cylinders were wrapped with lead-covered heating wire and covered with asbestos insulation. After applying the heating wire and insulation, a new tare was obtained for the test cylinder and the heating cycle started. The rate of heating was controlled through individual variable transformers. Since each of the cylinders contained two 70° fusible plugs, no attempt was made to exceed 50°.

Care was taken to ensure that the receiver was always at a higher temperature than the test cylinder to prevent vaporization of liquid in the full cylinder. Since the entire wall of both cylinders was heated and the temperature was raised at a rate of one degree every 10 to 15 minutes, it was felt that the over-all liquid temperature was uniform at all times.

The effects of the volumetric change of the cylinder due to thermal expansion and pressure were studied and found to be of small consequence; however, the density figures have been corrected for this error.

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The Si–C Bond Energy in Alkylsilanes

BY STANLEY TANNENBAUM

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There is considerable discrepancy in the reported values for the Si–C bond energy. Pauling[1] gives a value of 57.6 kcal./mole for crystalline carborundum, whereas Gilman and Dunn[2] calculate a value of 75.0 kcal./mole using newer heats of atomization for carbon and silicon. Thompson[3] found an average value of 64 kcal./mole for the Si–C bond in polydimethylsiloxanes. In order to add to the information available, it was considered worthwhile to calculate the Si–C bond energy in some alkylsilanes from heats of combustion recently obtained at this Laboratory.[4]

Table I lists the heats of formation for the alkylsilanes and the energies calculated for the Si–C bond[5] using the elemental heats of atomization and other required bond energies given by Gilman and Dunn[2] and by Thompson.[3] Except for vinylsilane, the values in the last two columns of Table I agree very well. The heats of formation differ slightly from those originally reported by Tannenbaum, *et al.*[4] Corrections were made for the newer value of the heat of formation of amorphous SiO_2 (−208.14 kcal./mole) formed in the combustion process as calculated by Thompson from the data of Humphrey and King.[6] The heats of vaporization of triethylsilane and dimethyldi-*n*-propylsilane, not previously measured, were estimated from Trouton's rule.

There appears to be a definite dependence of Si–C bond energy on the nature of the alkyl group joined to the silicon. The maximum estimated uncertainty in the measurement of the heat of combustion was −1.5 to +0.5%. This could result in a maximum error in the heats of formation of from 12 to 30 kcal./mole depending on the heat of combustion of the alkylsilane.[4] However, either the data are considerably more accurate than the uncertainty indicates, or the same relative error was involved in each determination, for there is little scatter within the methyl and ethyl series. It therefore appears that the trend observed in Table I is too large to be dismissed as within the experimental error.

Although no simple propylsilanes were investigated, a value of 57 kcal./mole for the Si–propyl bond was obtained from a plot of the average Si–C bond energy *vs.* type of alkyl group. Using this value along with the value of 74 kcal./mole for Si–methyl, the average Si–C bond energy in dimethyldi-*n*-propylsilane would be 65 kcal./mole compared to a value of 61 kcal./mole actually found.

TABLE I

HEATS OF FORMATION AND Si–C BOND ENERGY OF ALKYL SILANES

Compound	ΔH_{form}, kcal./mole		Si–C bond energy, kcal./mole	
	Liquid	Gas	Calcd. from values Gilman and Dunn[a]	Calcd. from values of Thompson[b]
$(CH_3)_2SiH_2$	−47	−42	76	72
$(CH_3)_3SiH$	−66	−60	76	74
$(CH_3)_4Si$	−75	−69	74	72
			Av. 75	Av. 73
$C_2H_5SiH_3$	−26	−21	64	61
$(C_2H_5)_2SiH_2$	−43	−36	66	65
$(C_2H_5)_3SiH$	−47	−39	62	63
$(C_2H_5)_4Si$	−47	−37	59	60
			Av. 62	Av. 62
i-$C_4H_9SiH_3$	−31	−24	52	56
n-$C_4H_9SiH_3$	−32	−14	52	56
$CH_2{=}CHSiH_3$	+ 1	+ 6	71	63
$(CH_3)_2Si(n\text{-}C_3H_7)_2$	−50	−41	60	61

[a] The C=C value was calculated from ΔH_{form} C_2H_4 (g) = −12.5[7] kcal./mole, C–H energy = 98.1 kcal./mole, and heat of atomization of C = 170 kcal./mole. [b] The Si–H value was calculated from ΔH_{form} SiH_4 (g) = −14.8[7] kcal./mole and heat of atomization of Si = 88.0 kcal./mole.

These results are similar to those obtained in studies of the bond dissociation energies of tetraalkylsilanes. The activation energy for the thermal decomposition of tetramethylsilane was found to be 79 kcal./mole,[8] whereas the values for tetraethylsilane and tetrapropylsilane were 50.5 and 46.0 kcal./mole, respectively.[9]

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(2) H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953).

(3) R. Thompson, *J. Chem. Soc.*, 1908 (1953).

(4) S. Tannenbaum, S. Kaye and G. F. Lewenz, THIS JOURNAL, **75**, 3753 (1953).

(5) A recent article by M. L. Huggins, *ibid.*, **75**, 4125 (1953), lists values for bond energies based on a heat of atomization of C = 137 kcal./mole. Calculations of the Si–C bond energy using these data result in values about 10 kcal./mole less than those in Table I; however, the same type of dependence on alkyl group is found.

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The Solubility of Phosphine in Aqueous Solutions[1]

BY RALPH E. WESTON, JR.

RECEIVED OCTOBER 27, 1953

In the course of recent work[2] it became necessary to determine the solubility of phosphine in water and aqueous solutions. Because of the low solubility, the solubility coefficient was determined by measuring directly the concentration of gas in a saturated solution, rather than by the usual procedure of measuring the pressure decrease upon

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] R. E. Weston, Jr., and J. Bigeleisen, THIS JOURNAL, to be published.