

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} nitrobenzene⁷ 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.

(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 271.

(7) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940); cf. also L. P. Hammett, *ibid.*, **8**, 644 (1940).

(8) J. C. D. Brand, W. C. Horning and M. B. Thornley, *J. Chem. Soc.*, 1374 (1952).

VENEREAL DISEASE EXPERIMENTAL LABORATORY
U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, N. C.

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

By STERLING E. VOLTZ¹

RECEIVED NOVEMBER 11, 1953

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*-butyldiperphthal-

(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.

ate 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, <i>D</i>	Density (g./cc.)	Polarization (cc. ⁻¹)
<i>t</i> -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- <i>t</i> -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.

(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

RECEIVED NOVEMBER 2, 1953

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. 225.