drift to a new 0.004° interval. After 3–4 drifts to higher or lower temperatures the crystal would settle to a 0.004° interval over which 6–8 reversals could be obtained. It was this final interval that determined the suspension temperatures listed in Table I.

If the $CoCl_2 \cdot 6H_2O$ crystals were exposed to the atmosphere and examined under a low power microscope, one could observe the formation of the pink anhydrous cobaltous chloride on the surface of the crystal. If a crystal were placed in the suspension media for about 15 minutes, and then withdrawn and examined in a humid atmosphere under the microscope, one observed an initial faint layer of the anhydrous material which would disappear within five minutes.

It would appear that a dehydration of $CoCl_2 \cdot 6H_2O$ was occurring during suspensions which would tend to increase the measured densities. However, the wide spread in suspension temperatures indicates crystal imperfections such as microscopic cracks and occlusions of solution which would tend to decrease measured densities. Differing from previous work[4] it is impossible to exclude crystals with small defects and all suspension temperatures must be included and given equal weight when obtaining the final most probable values of density and errors in density.

The probable errors of the crystal densities obtained from the individual suspension media are approximately one hundredth as large as the probable error computed from the three crystal densities corrected to 25°. Hence, the latter was used in stating the final error to the average of the three densities. Apparently the differences in the three values of the densities at 25°, *i.e.*, (a) 1.91080, (b) 1.90992 and (c) 1.90969, may be explained by the differences in the interactions of the suspension media with the $CoCl_2 \cdot 6H_2O$.

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Determination of the Basicity of Very Weak Bases

BY H. H. JAFFÉ

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Pratt and Matsuda have recently described a technique for the determination of the order of basicities of such weak bases as ketones, esters, ethers and alcohols.[1] The basicities were expressed in terms of the rate constants (k) of the self-etherification of benzhydrol in the presence of *p*-toluenesulfonic acid and of the base under a set of rigidly defined conditions. It appears desirable to attempt to derive, from these rate constants, relative values of the equilibrium constants (K_{BH^+}) for the reaction $BH^+ \rightleftharpoons B + H^+$, where B is the base.

Pratt and Draper have examined the self-etherification of benzhydrol in the presence of a small amount of *p*-toluenesulfonic acid, and have found the reaction to be of first order in benzhydrol.[2] These authors also suggested that the reaction is first order in the acid, and that the deviations from this order, which were observed, are due to salt effects.[2] The following arguments are based on the assumption that the reaction is first order in both alcohol and acid. It will further be assumed that all of the strong acid (HA), which is present in low concentration, transfers its protons to the base B or to benzhydrol (C) present in much higher concentration.[3]

We desire to calculate the acid dissociation constant of the conjugate acid of the base (B)

$$K_{BH^+} = [B][H^+]/[BH^+]$$

where the quantities in brackets represent concentrations. $[H^+]$ is given by

$$[H^+] = K_{CH^+}[CH^+]/[C]$$

where K_{CH^+} is the acid dissociation constant of the conjugate acid of C. $[BH^+]$ is given by

$$[BH^+] = [CH^+]^0 - [CH^+]$$

where $[CH^+]^0$ is the concentration of $[CH^+]$ in the absence of the base B. The rate law for the self-etherification is

$$-d[C]/dt = k'[CH^+][C] = k[C]$$

and hence $[CH^+]$ and $[BH^+]$ are proportional to k and $(k^0 - k)$, respectively, where k^0 is the rate in the absence of B, the blank in the notation of Pratt and Matsuda.[1] Then

$$K_{BH^+} = K_{CH^+} \frac{[B]}{[C]} \cdot \frac{k}{k^0 - k} \qquad (1)$$

Since B and C are present in large concentration compared to the other quantities involved in the calculations, $[B]/[C]$ is constant, and equals $^1/_2$ under the conditions of reference 1. Thus, Pratt and Matsuda's method combined with equation 1 permits evaluation of relative values of the acid dissociation constants of the conjugate acids of very weak bases in benzene solution.

Pratt and Matsuda[1] have shown that a correlation exists between Hammett's substituent constants (σ) and the relative basicities of substituted acetophenones and ethyl benzoates, as expressed by the rate constants of the self-etherification reaction. It is of interest to note that the relative values of K_{BH^+} obtained by use of equation 1 are much better represented by the Hammett equation than the rate constants of reference 1. The reaction constants calculated from the K_{BH^+}-values obtained

TABLE I

COMPARISON OF LITERATURE VALUES OF RELATIVE ACID DISSOCIATION CONSTANTS WITH VALUES CALCULATED BY USE OF EQUATION 1

Compound	$K/K_{C_6H_5COCH_3}$ From eq. 1	$K/K_{C_6H_5COCH_3}$ From lit.
p-$CH_3C_6H_4COCH_3$	0.79	0.21[a]
p-$BrC_6H_4COCH_3$	1.5	4.3[a]
$C_6H_5COOCH_3$	2.0	18[b]
$C_6H_5NO_2$	24[c]	25,000[d], 180,000[b]

[a] From reference 6. [b] From reference 7. [c] Too much significance should not be attached to this value. The denominator in equation 1 is about 3% of k^0, and both k and k^0 are known only to ±2%. [d] From reference 8.

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[1] E. F. Pratt and K. Matsuda, THIS JOURNAL, **75**, 3739 (1953).

[2] E. F. Pratt and J. D. Draper, *ibid.*, **71**, 2846 (1949).

(3) The same conclusions would be reached on the basis of the alternate assumption that all of the acid HA is involved in formation of complexes with the base B and benzhydrol (C), which appears more reasonable for solutions in the non-polar solvent benzene.

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.

[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).

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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

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[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.