Sample analysis data are given for two sets of the silicas. Each result shown in the table was a duplicate average from which was determined as absolute and relative range. The standard deviation and relative standard deviation (RSD) were calculated from the average relative ranges. The carbon analyses yielded RSD values of 0.286% and 0.341%. Adsorbed water determination data indicated RSD values of 2.26% and 4.35%. The RSD figures for total hydroxyl analyses were 1.72% and 1.87%. The precision of analyses in all instances was considered excellent and reflected the effectiveness of the new methods for this type of application. The speed, precision, and applicability of these methods are generally not possible with other methods. The silicas employed in this study were very consistently prepared, effectively treated, and reasonably uniform in surface character. The correlation obtained from this work probably does not hold for wet process or precipitated silicas in general. A correlation might exist for any silica of specific type but no one relationship should be completely effective.

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# Ion Pair Dissociation of Solvated Bases and Base Perchlorates in Anhydrous Acetic Acid

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**A simple potentiometric method was devised for the determination of ion pair dissociation constants for representative solvated bases and their perchlorate salts in anhydrous acetic acid as the solvent. Sodium acetate and sodium perchlorate were the reference solutes used in this procedure requiring emf measurements on separate solutions of the base and the half-neutralized base. Trends in the perchlorate salt dissociation constant as a function of the basicity constant were correlated with the Bruckenstein-Kolthoff theory of acid-base neutralization in anhydrous acetic acid. It was found that the value of the base perchlorate dissociation constant is always larger than the basicity constant, and their ratio ranges from 10:1 for strong bases to 10⁶:1 for very weak bases.**

THE PRECISE INTERPRETATION of potentiometric and spectrophotometric titration curves for acid-base reactions in anhydrous acetic acid requires a knowledge of four equilibrium constants; the ionization constants for the solvent and the protonic acid; the basicity constant for the solvated base; and the ion pair separation constant for the salt containing the protonated base. Although the complete quantitative treatment of neutralization equilibria in glacial acetic acid was developed a number of years ago by Bruckenstein and Kolthoff (*1*, *2*), the experimental verification of that theory, and particularly its simplifying assumptions, has rested upon a very restricted set of reliable constants. Also, more accurate ion pair dissociation constants for salts are needed in the examination of ionic strength effects in acetic acid as the solvent (*3*).

The present investigation was limited to the determination of basicity constants and ion pair dissociation constants for perchlorate salts, because perchloric acid is the most common titrant for bases and reasonably precise constants for the acid and the solvent have been established. A comparative method based upon the sodium acetate-sodium perchlorate equilibrium as a standard system and the half-neutralization potential measured with the glass-calomel electrode pair was used to determine constants for a representative range of strong to very weak bases in anhydrous acetic acid. General trends in the dissociation constants for nitrogen bases and their perchlorate salts were observed.

## THEORY

The defining equilibria for the dissociation of the solvated base and its perchlorate salt, together with the corresponding constants, are shown by Equations 1 and 2.

$$B\cdot HOAc \rightleftharpoons BH^+ + OAc^- \qquad K_B = \frac{[BH^+]\,[OAc^-]}{[BHOAc]} \tag{1}$$

$$B\cdot HOAc + HClO_4 \rightleftharpoons HOAc + BH^+ClO_4^- \rightleftharpoons BH^+ + ClO_4^-$$

$$K_{BClO_4} = \frac{[BH^+]\,[ClO_4^-]}{[BH^+ClO_4^-]} \tag{2}$$

Bruckenstein-Kolthoff notation is used throughout and the additional defined symbols required are $K_s$ for the autoprotolysis constant of the solvent and $C_i$ for the stoichiometric concentration ($M/L$) for the particular solute, $i$. Because the response of the glass electrode in acetic acid is identical to that of the chloranil electrode used by Bruckenstein and Kolthoff, their derived equations based upon the Nernst relationship can be applied without alteration (*1*).

For a solution of base alone, Equation 3 gives the potential for the glass-calomel electrode pair.

$$E_B = E^\circ_{GC} + E_j + \frac{RT}{F}\ln K_s - \frac{RT}{2F}\ln K_BC_B \tag{3}$$

($E_j$ is the liquid junction potential for the reference electrode and $E^\circ_{GC}$ is the total standard potential for the cell.) This equation forms the basis for determining the p$K_B$ of a base by direct comparison to a reference base having an identical concentration, provided $C_B$ is at a sufficiently low level that

(1) S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2974 (1956).
(2) I. M. Kolthoff and S. Bruckenstein, in "Treatise on Analytical Chemistry," Pt. I, Vol. 1, Interscience, New York, 1959, pp 499-511 and 524-31.
(3) O. W. Kolling, *Trans. Kansas Acad. Sci.*, **70**, 9 (1967).

higher ionic aggregates do not form. The complete Equation 4

$$pK_{B1} = pK_{B2} + \frac{2F}{RT}(E_{B1} - E_{B2}) \quad (4)$$

removes the need for evaluating the standard potential of the cell and for estimating the contribution from the junction potential. Sodium acetate has been used as the reference base (*4*).

In developing a comparative method for determining $K_{BClO_4}$ from potentiometric measurements two different approaches can be used. First, from the known value for $K_{HClO_4}$ and accurately measured concentrations, the hydrogen ion activity in a mixture of perchloric acid and the perchlorate salt can be applied to the calculation of $K_{BClO_4}$. Or, secondly, after the $K_B$ for the base has been obtained, potentiometric data for base–base perchlorate mixtures of known composition can be used to compute the desired constant. The second is the more suitable alternative, for it has been shown conclusively that the hydrogen ion activity of a perchlorate salt–perchloric acid mixture is highly dependent upon the water content of the solvent. By contrast, variations in water concentration in the acetic acid solvent well below the limit of $C_{H_2O} = 0.5M$ exert a negligible effect upon [H$^+$] in a base–base perchlorate mixture having $C_{BClO_4}$ similar to $C_B$ (*2*). Also, any acetolysis of the salt will be repressed in such a mixture.

For an acetic acid solution of a base and its perchlorate, the hydrogen ion activity has the function given in Equation 5 (*2*).

$$a_{H^+} = K_s \left[ \frac{K_B C_B + K_{BClO_4} C_{BClO_4}}{K_B C_B (K_s + K_B C_B)} \right]^{1/2} \quad (5)$$

Under the condition of half neutralization of the base by $HClO_4$, the Nernst relationship for $E_{HNP}$ assumes the form of Equation 6 at 25° C.

$$E_{HNP} = E^0_{GC} + E_j + 0.0591 \log K_s + 0.0295 \log (K_B + K_{BClO_4}) - 0.0295 \log K_B - 0.0295 \log (K_s + K_B C_B) \quad (6)$$

For weak bases, simplifying approximations cannot be made without *a priori* assumptions concerning the relative magnitudes of $K_s$ and $K_{BClO_4}$. On the other hand, for moderately dilute solutions ($C_B \simeq 0.001M$) of bases having $K_B \simeq 10^{-10}$ or greater, the term $(K_s + K_B C_B)$ becomes $K_B C_B$, and the suitability of such an approximation can be easily appraised after p$K_B$ is obtained by Equation 4. If the half-neutralization potential of a solution of a reference base (*B*1) and its perchlorate is compared to the $E_{HNP}$ of another base (*B*2) having $C_B$ different from that of the first base, but both with $K_B > 10^{-10}$, the difference in the two potentials will be given by Equation 7.

$$\frac{(E_{HNP})_2 - (E_{HNP})_1}{0.0295} = 2(pK_{B2} - pK_{B1}) + 2 \log \frac{C_{B1}}{C_{B2}} + \log \frac{(C_{BClO_4})_2}{(C_{BClO_4})_1} - \log (K_B + K_{BClO_4})_1 + \log (K_B + K_{BClO_4})_2 \quad (7)$$

Sodium acetate–sodium perchlorate can be used as the reference pair, and, by careful preparation of solutions having identical concentrations, the elimination of the concentration terms from Equation 7 (along with $E^0_{GC}$ and $E_j$) permits the simple calculation of $(K_{BClO_4})_2$ from two potential measurements. Perchlorate ion pair dissociation constants for the salts of very weak bases can be obtained by using the $(E_{HNP})_2 - (E_{HNP})_1$ difference with the more general Equation 6.

The application of reference solutes to the determination of both p$K_B$ and p$K_{BClO_4}$ has the added advantage of nullifying the differences in absolute potentials found with different glass indicator electrodes.

## EXPERIMENTAL

**Apparatus and Procedures.** Potentials were measured with a Leeds and Northrup 7401 pH meter equipped with the standard glass and calomel electrodes. Equilibrium potentials for intermittently stirred solutions were obtained after 30 to 60 minutes within the temperature interval of 25 ± 1° C. The emf for the electrode pair is negative in acetic acid as the solvent.

All potentials reported in Tables I and II are mean values from three separate solutions of each base and a minimum of four emf readings on each solution. Measurements on the sodium acetate–sodium perchlorate reference solution were redetermined for each new batch of anhydrous acetic acid prepared. The maximum experimental uncertainty in these emf values is ±2 mV, although most are reproducible within ±1 mV. The cumulative effect from this source alone upon the computed p*K*'s gives an uncertainty in the derived result of ±0.03 to 0.04 for p$K_B$ and ±0.04 to 0.08 for p$K_{BClO_4}$. These experimental deviations are quite similar in magnitude to the uncertainties contributed by the constants from the reference compounds listed in the tables.

The basicity constants for sodium acetate and lithium acetate were used to calculate the revised result for urea. All other p$K_B$ values were determined graphically from a calibration plot of mV *vs.* p$K_B$ for which NaOAc, LiOAc, KOAc, and urea were standards.

**Reagents and Solutions.** The nitrogen bases were Eastman Organic Chemicals, White Label grade, with the exceptions of *N,N*-diethylaniline (special mono-free) and pyridine (Spectroanalyzed). The particular bases were selected from representative compounds as ones likely to be of high purity, judged by the comparative mp or bp of possible basic contaminants.

Anhydrous acetic acid, standard perchloric acid in acetic acid, and stock solutions of the bases and half-neutralized bases were prepared as reported earlier (*5*). Stock solutions of those bases having $K_B$'s greater than urea were standardized by potentiometric titration in acetic acid with perchloric acid. Solutions of the weaker bases were prepared determinately. Volumes of solvent required for the exact dilution of the bases to a final concentration of 0.00400*M* and the half-neutralized base-perchlorate mixtures to 0.00667*M* were measured from burets protected with drying tubes.

## RESULTS AND DISCUSSION

**Basic Constants.** The bases listed in Table I include a representative range of base strengths for nitrogen bases in anhydrous acetic acid. The strongest bases have p$K_B$ values approaching 5.00, and are exemplified by the tertiary alkylamines and the *N,N*-dialkylanilines. At the other extreme are the amides and nitroanilines which are far too weak to be titrated potentiometrically, with constants near 11. In general the overall order of decreasing dissociation for the solvated bases in acetic acid parallels that for the aquated

(4) O. Kolling and J. Lambert, *Inorg. Chem.*, **3**, 202 (1964).

(5) O. Kolling and D. Garber, ANAL. CHEM., **39**, 1562 (1967).

Table I. Dissociation Constants ($pK_B$) for Bases in Acetic Acid at 25° C. ($C_B = 0.0040M$)

| Base | $E_B$, mV | $pK_B$ (HOAc) Calcd | $pK_B$ ($H_2O$) Literature[a] |
|---|---|---|---|
| Acetamide | 491 | 10.50 | 14.5 |
| Acetanilide | 500 | 10.96 | ... |
| *p*-Acetophenetidide | 499 | 10.90 | ... |
| *o*-Anisidine | 486 | 10.25 | ... |
| *p*-Anisidine | 493 | 10.60 | 8.71 |
| Benzylamine | 406 | 6.12 | 4.70 |
| *n*-Butylamine | 401 | 5.86 | 3.39 |
| Isobutylamine | 397 | 5.68 | 3.58 |
| *tert*-Butylamine | 398 | 5.70 | 3.55 |
| 2,5-Dichloroaniline | 486 | 10.25 | ... |
| Diethylamine | 395 | 5.55 | 3.00 |
| *N,N*-Diethylaniline | 388 | 5.20 | 7.44 |
| *N,N*-Dimethylaniline | 395 | 5.55 | 8.94 |
| Diphenylamine | 485 | 10.20 | ... |
| 1,3-Diphenylguanidine | 387 | 5.15 | 4.00 |
| *N*-Ethylaniline | 463 | 9.10 | ... |
| Lithium acetate | 420 | 6.79 ± 0.03[b] | ... |
| *o*-Nitroaniline | 502 | 11.05 | 14.0 |
| *N*-Phenylbenzylamine | 476 | 9.73 | ... |
| Pyridine | 403 | 5.97 | 8.78 |
| Sodium acetate | 415 | 6.58 ± 0.02[b] | ... |
| Thiourea | 478 | 9.84 | ... |
| *m*-Toluidine | 491 | 10.50 | ... |
| Tri-*n*-butylamine | 387 | 5.15 | 3.11 |
| Triethylamine | 384 | 5.00 | 3.26 |
| Urea | 485 | 10.18 | 13.8 |

[a] Obtained from $pK_a$ values in Tables I–VII of the summary by Hall (*6*).
[b] Constants used as standards and reported by Bruckenstein and Kolthoff (*1*).

Table II. Dissociation Constants ($pK_{BClO_4}$) for Base Perchlorates in Acetic Acid at 25° C. ($C_{BClO_4} = 0.0067M$)

| Base perchlorate | $E_{HNP}$, mV | $pK_{BClO_4}$ Calcd | $pK_{BClO_4}$ Literature |
|---|---|---|---|
| 1 Acetamide | 674 | 5.25 | 5.95[a] |
| 2 Acetanilide | 722 | 4.53 | 3.34[a] |
| 3 *p*-Acetophenetidide | 713 | 4.73 | ... |
| 4 *o*-Anisidine | 643 | 5.79 | ... |
| 5 *p*-Anisidine | 683 | 5.14 | ... |
| 6 Benzylamine | 419 | 5.18 | ... |
| 7 *n*-Butylamine | 411 | 4.93 | ... |
| 8 Isobutylamine | 402 | 4.89 | ... |
| 9 *tert*-Butylamine | 403 | 4.89 | ... |
| 10 2,5-Dichloroaniline | 645 | 5.73 | ... |
| 11 Diethylamine | 400 | 4.59 | ... |
| 12 *N,N*-Diethylaniline | 391 | 4.28 | 5.75 and 5.80[b] |
| 13 *N,N*-Dimethylaniline | 407 | 4.44 | ... |
| 14 Diphenylamine | 638 | 5.85 | ... |
| 15 1,3-Diphenylguanidine | 398 | 3.92 | ... |
| 16 Lithium perchlorate | 454 | 5.31 | 5.80[c] |
| 17 *o*-Nitroaniline | 737 | 4.51 | ... |
| 18 *N*-Phenylbenzylamine | 595 | 6.38 | ... |
| 19 Sodium perchlorate | 437 | ... | 5.48 ± 0.06[b] |
| 20 Thiourea | 605 | 6.26 | 5.43[a] |
| 21 *m*-Toluidine | 672 | 5.31 | ... |
| 22 Tri-*n*-butylamine | 392 | 4.14 | ... |
| 23 Triethylamine | 391 | 3.81 | ... |
| 24 Urea | 636 | 5.90 | 5.58[a] |

[a] Calculated from $K_f$ data reported by Higuchi and Connors (*7*)
[b] Value obtained by Bruckenstein and Kolthoff (*1*).
[c] Obtained from conductance measurements by Winstein, Klinedinst, and Robinson (*8*).

bases, although exceptions occur for a few having close-lying constants—*i.e.*, *n*-butylamine and isobutylamine. Likewise, it will be noted that several of the solvated weak bases are more extensively ionized in acetic acid than in aqueous media; however, there are a sufficient number of bases for which the opposite trend is observed to exclude any statement concerning a general solvent influence upon $pK_B$.

The usual shifts in the basicity constant which are anticipated by the introduction of alkyl groups onto the nitrogen are found in acetic acid as the solvent. For aromatic amines, the order of the degree of dissociation is $R_2N$-Ar > RHN-Ar and among aliphatic amines, $R_3N > R_2NH > RNH_2$. Subtile changes in $pK_B$ with *ortho*-to-*para* shifts of a given substituent on the aromatic amine are discernible, as is the increased basicity of thiourea compared to urea. By contrast, Hall (*6*) has concluded that the order of relative base strengths of *N*-substituted amines is not always clearly defined in aqueous and alcoholic solvents; however, such sequences in basicity do appear in aprotic media—*i.e.*, ethyl acetate with a dielectric constant very similar to that of HOAc.

Four of the bases in Table I were included in the investigation by Bruckenstein and Kolthoff (*1*). Their results for the computed $pK_B$'s are: urea 10.24; pyridine 6.10; 2,5-dichloroaniline 9.48; and *N,N*-diethylaniline 5.78. The first two values are in close agreement with the data in Table I; however, the disagreement for *N,N*-diethylaniline is significant and may reflect differences in the purity of samples of the base. It was found experimentally that the addition of small amounts of ethylaniline causes the apparent $pK_B$ of the diethyl derivative to shift toward 6.

**Base Perchlorate Dissociation Constants.** Linear correlations between the $pK_a(H_2O)$ and half-neutralization potentials for nitrogen bases in aprotic solvents have been found with perchloric acid as the titrant and the glass electrode (*6*, *9*). However, data for amines and amides fall on noncoincident lines in nitromethane, and results for periodic group Ia metal salts in acetic anhydride form a nonlinear curve isolated from the nitrogen bases (*9*). Separate correlation lines are formed for amines and heterocyclic nitrogen bases in ethyl acetate and acetonitrile (*6*). Although the slope of $E_{HNP}$ *vs.* $pK_a(H_2O)$ is negative in all aprotic solvents, the numerical value is only roughly constant.

Bruckenstein and Kolthoff (*2*) have demonstrated that the hydrogen ion activities of pairs of half-neutralized bases in anhydrous acetic acid cannot be used as reliable quantitative measures of their relative basicities. Likewise, Equation 6 predicts that $E_{HNP}$ will not be a linear function of $pK_B$ alone, but instead is related to $\log (K_B + K_{BClO_4})^{1/2}/K_B$. If a plot of $E_{HNP}$ *vs.* $pK_B$ is made (not included herein), the smooth curve of increasing positive slope illustrates this dependence; and a linearity in the curve is approached only by the weak bases. Such a curve indicated an internal consistency for the set of data with no unique behavior exhibited by the various functional types of nitrogen bases included in this study.

The calculated ion pair dissociation constants for the base perchlorates are listed in Table II. Equation 7 was used for the bases having $pK_B$'s less than 9, whereas the $pK_{BClO_4}$ values for the salts of the weak bases were obtained using Equation 6 without approximations. It should be noted that the error which would be introduced by applying Equation 7 to the weak bases is not large; the maximum difference be-

(6) H. K. Hall, Jr., *J. Phys. Chem.*, **60**, 63 (1956).
(7) T. Higuchi and K. Connors, *J. Phys. Chem.*, **64**, 179 (1960).
(8) S. Winstein, P. Klinedinst, and G. Robinson, *J. Am. Chem. Soc.*, **83**, 885 (1961).
(9) C. A. Streuli, Anal. Chem., **31**, 1652 (1959).

tween the values obtained with and without the approximation is only 0.04 unit for *o*-nitroanilinium perchlorate, and no difference is found for perchlorates of bases stronger than *o*-anisidine—p$K_B$ = 10.25.

Literature values included in Table II are not in close agreement with the new experimental results. At best these confirm the order of magnitude figures. A serious disagreement is found for *N,N*-diethylanilinium perchlorate reported by Bruckenstein and Kolthoff (*1*), and this reflects the higher value of p$K_B$ used in their calculations. The literature value for lithium perchlorate was derived from conductance measurements, a procedure not characterized by high precision in low dielectric constant media. The remaining constants for previously recorded perchlorate dissociations were calculated from Equation 8, using the data of Higuchi and Connors (*7*).

$$pK_{BClO_4} = \log \frac{K_s K_f}{K_B K_{HClO_4}} \quad (8)$$

Here, $K_f$ is the perchlorate salt formation constant obtained by spectrophotometric titration, and the fundamental relationship among the constants was derived by Kolthoff and Bruckenstein (*2*). (The numerical values used for the other constants in Equation 8 are: $K_s = 3.5 \times 10^{-15}$; $K_{HClO_4} = 1.35 \times 10^{-5}$; and the $K_B$ for the base is that in Table I.) The maximum cumulative uncertainty in the p$K_{BClO_4}$ computed from the four constants is of the order of $\pm$ 0.20 unit. However, Higuchi and Connors stated that their $K_f$ results for the perchlorates from weak bases are only rough estimates. Therefore, the absolute differences between the literature and new experimental results for acetamide, acetanilide, thiourea, and urea are not statistically meaningful, and the general agreement is reasonably satisfactory.

In the Kolthoff–Bruckenstein theoretical treatment of base–perchloric acid neutralization curves approximations involving three relationships between the basicity constant and the perchlorate ion pair dissociation constant were considered: $K_B = K_{BClO_4}$; $K_{BClO_4} \neq K_B$; and $K_{BClO_4} \gg K_B$. Figure 1 correlating experimental p$K_B$ and p$K_{BClO_4}$ values was constructed from the data in the two tables in order to identify those instances for which these restrictions are found. It is clear that the first condition (equality of the constants) does not occur for any of the representative bases included, and, for the stronger bases, $K_{BClO_4}$ is about 10 times larger than $K_B$. On the other hand, for the weak bases, the third condition proposed by Kolthoff and Bruckenstein is confirmed; generally, $K_{BClO_4}$ is of the order of $10^4$ to $10^6$ times greater than the dissociation constant for the solvated base.

The completely opposite trends in p$K_B$ *vs.* p$K_{BClO_4}$ for the strong and weak bases is not fully anticipated. The limiting slope of the nearly linear weak base–perchlorate salt plot is $-0.60$, while the approximate linearity shown for the strong base function has a slope of 0.79 for nitrogen bases. (The LiOAc–$LiClO_4$ and NaOAc–$NaClO_4$ data lie off the curve, although conforming to the characteristic condition for the stronger bases in which $K_{BClO_4}$ increases with $K_B$.) It is

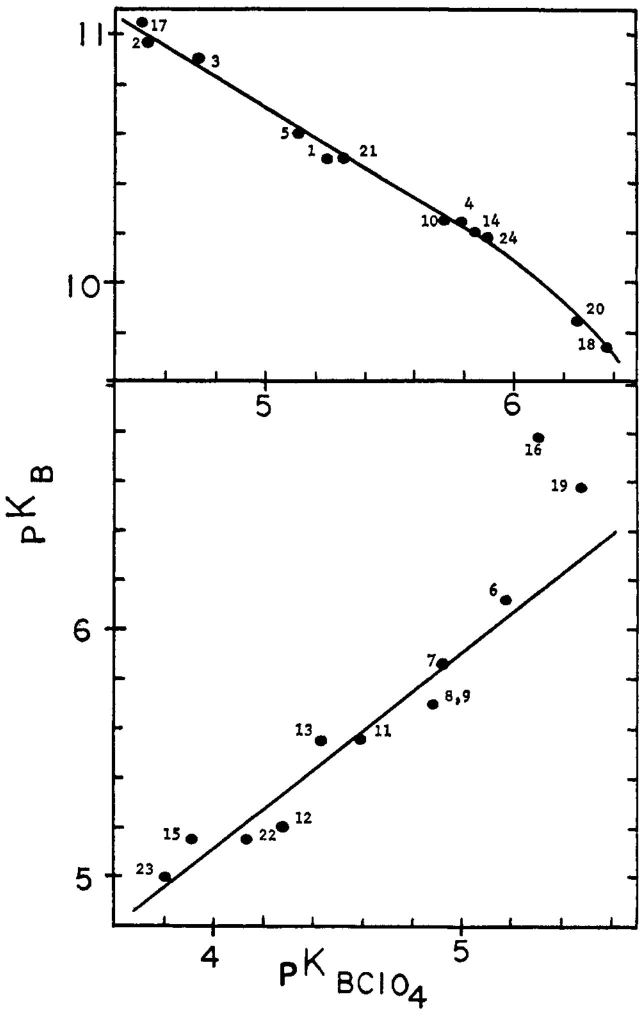


**Figure 1. The relationship of p$K_B$ for a given base to its perchlorate salt dissociation constant (as p$K_{BClO_4}$)**

**The numbered points correspond to the compounds listed in Table II**

noteworthy that the *B*-*B*HCl constants obtained by Bruckenstein and Kolthoff (*1*) for tribenzylamine, potassium acetate, and lithium acetate follow the same trend of p$K_{BHCl}$, increasing with increasing p$K_B$ although the slope is much steeper. Also, the data on the weak bases, acetanilide, acetamide, and urea, reported by Higuchi and Connors (*7*) confirm a negative slope for the upper function shown in Figure 1.

It appears that the ion pair dissociation constant for a given base perchlorate is larger than that for the base hydrochloride. This is illustrated by pairs of salts derived from urea and lithium acetate: p$K_{UHClO_4}$ = 5.90 and p$K_{UHCl}$, = 6.96; p$K_{LiClO_4}$ = 5.31 and p$K_{LiCl}$ = 7.08 (*1*).

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