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Acid–Base Equilibria in Glacial Acetic Acid. I. Spectrophotometric Determination of Acid and Base Strengths and of Some Dissociation Constants[1]

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The following constants are defined for an acid: ionization or ion-pair formation, $K_{\mathrm{i}}^{\mathrm{HX}} = [\mathrm{H^+X^-}]/[\mathrm{HX}]$; dissociation, $K_{\mathrm{d}}^{\mathrm{HX}} = ([\mathrm{H^+}][\mathrm{X^-}])/[\mathrm{H^+X^-}]$; and over-all dissociation, $K_{\mathrm{HX}} = ([\mathrm{H^+}][\mathrm{X^-}])/([\mathrm{HX}] + [\mathrm{H^+X^-}]) = K_{\mathrm{i}}^{\mathrm{HX}}K_{\mathrm{d}}^{\mathrm{HX}}/(1 + K_{\mathrm{i}}^{\mathrm{HX}})$. Similar constants are defined for bases. The formation constant of the salt of an (indicator) base, I, and an acid is given by $K_{\mathrm{i}}^{\mathrm{IHX}} = K_{\mathrm{HX}}K_{\mathrm{I}}/K_{\mathrm{d}}^{\mathrm{IHX}}K_{\mathrm{s}}$, where $K_{\mathrm{s}} = [\mathrm{H^+}][\mathrm{Ac^-}]$. The strength of an acid depends upon the kind of (indicator) base used for reference and *vice versa*. From spectrophotometric measurements at 25° with *p*-naphtholbenzein (PBN) as indicator base, the following constants have been derived: $K_{\mathrm{i}}^{\mathrm{PNB}} \leqq 0.0042$, $K_{\mathrm{HCl}} = 2.8 \times 10^{-9}$, $K_{\mathrm{HTs}} = 7.3 \times 10^{-9}$ (HTs = *p*-toluenesulfonic acid), $K_{\mathrm{i}}^{\mathrm{HClO_4}} = 1.0$, $K_{\mathrm{i}}^{\mathrm{IHCl}} = 1.3 \times 10^2$, $K_{\mathrm{i}}^{\mathrm{IHTs}} = 3.7 \times 10^2$, $K_{\mathrm{d}}^{\mathrm{IHCl}} = 3.9 \times 10^{-6}$, $K_{\mathrm{d}}^{\mathrm{IHTs}} = 4.0 \times 10^{-6}$, $K_{\mathrm{i}}^{\mathrm{UHClO_4}} = 1.6 \times 10^5$ (U = urea), $K_{\mathrm{i}}^{\mathrm{UHCl}} = 4.9 \times 10^2$, $K_{\mathrm{i}}^{\mathrm{UHTs}} = 1.2 \times 10^3$, $K_{\mathrm{i}}^{\mathrm{H_2O \cdot HClO_4}} = 6.8 \times 10^1$, $K_{\mathrm{i}}^{\mathrm{PHClO_4}} = 1.7 \times 10^1$ (P = 2-propanol), $K_{\mathrm{i}}^{\mathrm{EHClO_4}} = 1.5 \times 10^1$ (E = ethanol), and $K_{\mathrm{i}}^{\mathrm{MHClO_4}} = 8.8$ (M = methanol). The heat of reaction of I + HX $\rightleftarrows$ IH$^+$X$^-$ is -7 kcal./mole with HCl or HTs as HX and PNB as I.

Introduction

In defining acid and base strength in glacial acetic acid it must be considered that in this solvent even strong electrolytes are incompletely dissociated into ions, the largest dissociation constant being of the order of 10^{-5}. The "ionization" constant of an acid or a base in amphiprotic solvents of very low dielectric constant gives a more exact expression of acid or base strength than the "dissociation" constant, *e.g.*

$$\mathrm{HClO_4 + HAc \rightleftarrows H_2Ac^+ClO_4^- \rightleftarrows H_2Ac^+ + ClO_4^-} \quad (1)$$

$$\underset{\text{Ionization}}{\mathrm{B + HAc \rightleftarrows BH^+Ac^-}} \underset{\text{Dissociation}}{\rightleftarrows \mathrm{BH^+ + Ac^-}} \quad (2)$$

As in any other solvent the extent of solvation of the proton is unknown in acetic acid and equation 1 can be written conventionally

$$\mathrm{HClO_4 \rightleftarrows H^+ClO_4^- \rightleftarrows H^+ + ClO_4^-} \quad (3)$$

The "ionization" constants of an acid (HX) and a base (B) are

$$K_{\mathrm{i}}^{\mathrm{HX}} = \frac{a_{\mathrm{H^+X^-}}}{a_{\mathrm{HX}}} \quad (4)$$

and

$$K_{\mathrm{i}}^{\mathrm{B}} = \frac{a_{\mathrm{BH^+Ac^-}}}{a_{\mathrm{B}}} \quad (4a)$$

In these equations the activity of acetic acid is omitted since the activity of solvent may be considered constant in dilute solutions. The dissociation constants of the ion-pairs H$^+$X$^-$ and BH$^+$Ac$^-$ are

$$K_{\mathrm{d}}^{\mathrm{HX}} = \frac{a_{\mathrm{H^+}}a_{\mathrm{X^-}}}{a_{\mathrm{H^+X^-}}} \quad (5)$$

and

$$K_{\mathrm{d}}^{\mathrm{B}} = \frac{a_{\mathrm{BH^+}}a_{\mathrm{Ac^-}}}{a_{\mathrm{BH^+Ac^-}}} \quad (5a)$$

It is readily seen that the over-all dissociation constants K_{HX} and K_{B} are

$$K_{\mathrm{HX}} = \frac{a_{\mathrm{H^+}}a_{\mathrm{X^-}}}{a_{\mathrm{HX}} + a_{\mathrm{H^+X^-}}} = \frac{K_{\mathrm{i}}^{\mathrm{HX}}K_{\mathrm{d}}^{\mathrm{HX}}}{1 + K_{\mathrm{i}}^{\mathrm{HX}}} \quad (6)$$

and

$$K_{\mathrm{B}} = \frac{a_{\mathrm{BH^+}}a_{\mathrm{Ac}}^{-}}{a_{\mathrm{B}} + a_{\mathrm{BH^+Ac^-}}} = \frac{K_{\mathrm{i}}^{\mathrm{B}}K_{\mathrm{d}}^{\mathrm{B}}}{1 + K_{\mathrm{i}}^{\mathrm{B}}} \quad (6a)$$

Concentrations are substituted for activities for all species appearing in equations 4 through 6a. This approximation is justified by the facts that the dielectric constant of acetic acid is 6.13,[3] and

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[1] From a thesis submitted by S. Bruckenstein to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1954.

[2] Du Pont Teaching Fellow, 1953–1954.

[3] J. Timmermans, "Physico Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, N. Y., 1950.

the strongest electrolytes in this solvent have over-all dissociation constants of the order of only 10^{-5},[4,5] and that in all ionic equilibria considered in this paper the ionic strength was less than 1×10^{-5}. Assuming that the limiting Debye–Hückel expression ($-\log f = 22.8 \sqrt{\mu}$ at 25°, molar scale) holds, we calculate that $f = 0.83$ at an ionic strength of 10^{-5}. The limiting expression does not take into account the effect of ion size and gives the maximum possible correction. It was also assumed that activity coefficients of neutral molecules and ion-pairs was not significantly different from one in the range of concentrations studied.

The over-all dissociation constant does not give an exact relation of the relative strengths of bases or acids since K_d for all ion-pairs is not the same. On the other hand, K_i in acetic acid gives an exact expression of base (or acid) strength with reference to this solvent as an acid (or base). In a subsequent paper the results of the spectrophotometric determination of the ionization constant of the base, *p,p'*-dimethylaminoazobenzene, will be presented. Somewhat arbitrarily an acid or a base may be called strong in acetic acid when K_i is equal to or greater than one. Evidence is presented in this paper that perchloric acid is a strong acid in acetic acid, and a method has been developed for the estimation of its ionization constant.

In order to have a *p*H scale in acetic acid comparable to that in water it is necessary to know the over-all dissociation constant of some acid and some base. The autoprotolysis constant of acetic acid can then be found from potentiometric measurements. Values of K_{HX} and K_B of several acids, bases and salts are given in the literature. They have been derived from conductance data using the Fuoss and Kraus[6] graphical extrapolation method. In acetic acid the plot gives only an approximate value as is illustrated, for example, by the fact that two authors, Smith and Elliot,[4] and Jones,[7] using the same conductance data of Kolthoff and Willman[8] for perchloric acid, extrapolate *pK* values of 6.05 and 5.26. By using a spectrophotometric method described in the present paper the ionization and dissociation constants of the indicator salts *p*-naphtholbenzein hydrochloride and *p*-naphtholbenzein *p*-toluenesulfonate were derived. Simultaneously, the over-all dissociation constants of hydrochloric and *p*-toluenesulfonic acid were found.

In a subsequent paper the over-all dissociation constant of pyridine, as determined by spectrophotometric methods in the presence of *p,p'*-dimethylaminoazobenzene, will be reported.

The fact that strong electrolytes (ion-pairs) are so weakly dissociated in acetic acid is the cause of widely different behavior of indicator bases in this solvent than in water. Consider an indicator base with an ionization constant of 0.1 (equation 4A). Neglecting dissociation, a solution of the indicator in acetic acid is present 10% in the acid form. Addition of a strong base does not affect the equilibrium between B and BH^+Ac^-. Neglecting also secondary effects of triple and quadruple ion formation (*vide infra*), the addition of a strong base to a solution of the indicator should not affect the color. In water on the other hand, in which ion-pair formation as a rule is negligible, the addition of a strong base to a solution of a relatively strong indicator base causes the color to shift completely to the basic side.

Another major point of difference between the two solvents is that in water acid–base indicators are *p*H indicators, but in acetic acid they are not. The extent of the reaction between an indicator base I and acid HX is given by

$$\mathrm{I} + \mathrm{HX} \rightleftarrows \mathrm{IH^+X^-} \rightleftarrows \mathrm{IH^+} + \mathrm{X^-} \qquad (7)$$

in which IH^+X and IH^+ represent the acid forms of the indicator base.

Neglecting dissociation for the moment the extent of the reaction between an indicator base and a given acid is determined by the concentration of HX. However, there is no simple relationship between the alkaline and acid forms of the indicator and *p*H as exists in water. Quantitatively, the ionization (formation) constant of IH^+X^- of the first equilibrium of equation 7 is given by

$$K_i^{IHX} = \frac{[IH^+X^-]}{[I][HX]} \qquad (8)$$

K_i^{IHX} is determined by the over-all dissociation constants of the indicator base, (K_I), and the acid, (K_{HX}), the dissociation constant of the indicator salt, K_d^{IHX} and the autoprotolysis constant of acetic acid (K_s). It is easily derived that

$$K_i^{IHX} = \frac{K_{HX}K_I}{K_d^{IHX}K_s} \qquad (9)$$

Evidently the ratio of the acid strengths of two acids HX and HY with regards to the base I is not only determined by the ratio of their over-all dissociation constants, but also by the ratio of the dissociation constants of IH^+X^- and IH^+Y^-. In the classical potentiometric method the ratio of the over-all dissociation constants, K_{HX}/K_{HY}, is found which may therefore differ considerably from that found from their reactivity with a base I.

Usually we do not find the same relative acid strength of two acids with one (indicator) base, I, as with another base, B. Defining the ratio $K_i^{IHX}/K_i^{IHY} = R_1$ and the ratio $K_i^{BHX}/K_i^{BHY} = R_2$ we find that

$$\frac{R_1}{R_2} = \frac{K_d^{IHY}K_d^{BHX}}{K_d^{IHX}K_d^{BHY}} \qquad (10)$$

In general the ratio of all these constants will not be one. In reporting relative strengths of acids as found by the indicator method it is imperative to mention the reference base in solvents of low dielectric constant. The above makes clear that Hammett's acidity function[9] has no exact significance in acetic acid (and other low dielectric constant solvents) as for a given solution it varies somewhat with the indicator used. Hammett,[9] in fact, stated that the validity of the acidity function would be restricted to solvents of high dielectric constant.

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[4] T. L. Smith and J. H. Elliot, THIS JOURNAL, **75**, 3566 (1953).

[5] M. M. Jones and E. Griswold, *ibid.*, **76**, 3247 (1954).

[6] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 476 (1933).

[7] M. M. Jones, private communication.

[8] I. M. Kolthoff and A. Willman, THIS JOURNAL, **56**, 1007 (1934).

[9] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 264 ff.

Using the classical indicator method we find just as with Lewis acids and bases that in solvents with low dielectric constants the apparent strength of a Brönsted acid varies with the reference base used and *vice versa*.

Another phenomenon which occurs particularly in solvents of low dielectric constant and which may complicate expression of ionic equilibria is the ease of formation of higher ionic aggregates. This is indicated by the abnormally small freezing point depressions of electrolytes in glacial acetic acid. The cryoscopic work of Oddo and Anelli,[10] Turner and co-workers[11,12] and Walden[13] reveals that many compounds are extensively associated in acetic acid. For example, Turner and Pollard[12] found that tetrapropylammonium iodide has a molecular weight four times its formula weight in acetic acid.

Clear indications of ion triplet formation can be derived from conductance data.[14] The equivalent conductance of a "strong" electrolyte when plotted against the square root of the concentration decreases to a minimum and then increases as a result of the formation of ion triplets. Kolthoff and Willman[8] found the minimum to occur at a concentration of 0.04 to 0.05 molar in solutions of sulfuric acid, potassium acetate and pyridine. As is shown in the present paper the spectrophotometric method gives conclusive evidence of formation of higher ionic aggregates. In a subsequent paper examples of the determination by the spectrophotometric method of the formation constant of some ionic aggregates containing an indicator will be reported.

Evidence is found in the experimental part that all acid forms of an indicator base, IH^+, IH^+X^-, $X^-IH^+X^-$, etc., have the same absorption spectra and extinction coefficients.

In the experimental work *p*-naphtholbenzein (denoted by PNB) has been used as the indicator base. A given amount of indicator was added to a solution of an acid, HX, of known concentration. Spectrophotometrically, the sum of the concentration of the acid forms, $[IH^+X^-] + [IH^+] = \Sigma[IH^+]$, was measured and the concentration of the indicator base, [I], was found from the difference between the total concentration of indicator added and the sum of the concentration of the acid forms. The total concentration of acid added, $(C_{HX})_t$, is equal to the sum $\Sigma[IH^+] + C_{HX}$, where

$$C_{HX} = [HX] + [H^+X^-] + [H^+] \qquad (11)$$

so that C_{HX} may be found from the known amount of acid added to the solution, $(C_{HX})_t$, and the sum of the concentration of indicator acid forms $\Sigma[IH^+]$.

We first consider experiments carried out in solutions of hydrochloric and *p*-toluenesulfonic acids which are such weak acids that $[H^+X^-]$ and $[H^+]$ are negligibly small as compared to [HX] therefore

$$C_{HX} = [HX] \qquad (11a)$$

The experimentally determined ratio of the total acid species to indicator species is given by

$$\frac{\Sigma[IH^+]}{[I]} = \frac{[IH^+] + [IH^+X^-]}{[I]} = \frac{[IH^+X^-]}{[I]}\left[1 + \frac{[IH^+]}{[IH^+X^-]}\right] \qquad (12)$$

Substituting K_i^{IHX} and K_d^{IHX} into equation 12, we obtain

$$\frac{\Sigma[IH^+]}{[I]} = K_i^{IHX}[HX]\left[1 + \frac{K_d^{IHX}}{[X^-]}\right] \qquad (12a)$$

In acid solution in which the concentration of acetate ion may be neglected, the rule of electroneutrality reduces to

$$[H^+] + [IH^+] = [X^-] \qquad (13)$$

Substituting K_{HX} and K_d^{IHX} into equation 13, yields

$$[X^-] = \sqrt{K_{HX}C_{HX} + K_d^{IHX}\,[IH^+X^-]} \qquad (13a)$$

In the case of a weak acid such as hydrochloric and *p*-toluenesulfonic acid, substitution of equations 11a and 8 into equation 13a gives

$$[X^-] = \sqrt{C_{HX}} \times \sqrt{K_{HX} + K_d^{IHX}K_i^{IHX}[I]} \qquad (13b)$$

Substituting the expression for $[X^-]$ in equation 13b into equation 12a and dividing both sides of the equation by $\sqrt{(HX)}$ yields

$$\frac{\Sigma[IH^+]}{[I]\sqrt{C_{HX}}} = K_i^{IHX}\sqrt{C_{HX}} + \frac{K_i^{IHX}K_d^{IHX}}{\sqrt{K_{HX} + K_i^{IHX}\,K_d^{IHX}\,[I]}} \qquad (14)$$

All the concentrations appearing in equation 14 are known in a given experiment and it is possible to evaluate the various equilibrium constants.

The problem of evaluating the various constants can be simplified considerably by proper design of the experiment. If varying amounts of PNB are added to a solution containing a fixed concentration of HX it is possible to construct a $\Sigma[IH^+]$ *vs.* [I] curve. Interpolating between experimental points on this curve values of $\Sigma[IH^+]$ at chosen values of [I] (such as 2.00, 3.00, 4.00, 5.00 and 6.00 × 10^{-6} molar) can be obtained. The above experiment can then be repeated at several different concentrations of HX and a table of data obtained which gives $\Sigma[IH^+]$ for a given concentration of indicator base, at the various concentrations of acid (*e.g.*, see Tables IV and V).

If [I] is held constant, eq. 14 can be represented by a straight line of the form $y = mx + b$ where $y = \Sigma[IH^+]/[I]\sqrt{C_{HX}}$, $x = \sqrt{C_{HX}}$, $m = K_i^{IHX}$ and $b = K_i^{IHX}K_d^{IHX}/\sqrt{K_{HX} + K_i^{IHX}K_d^{IHX}\,[I]}$. Thus a family of straight lines of the same slope are obtained for each given value of [I] when *different* constant values of [I] are chosen. The slope corresponds to K_i^{IHX}.

The value of the intercept, *b*, depends upon the value of [I] chosen. It is possible to obtain K_{HX} and K_d^{IHX} from this intercept since

$$b^2 = \frac{(K_i^{IHX}K_d^{IHX})^2}{K_{HX} + K_i^{IHX}K_d^{IHX}\,[I]} \qquad (15)$$

or

$$[I]b^2 = K_i^{IHX}K_d^{IHX} - \frac{K_{HX}}{K_i^{IHX}K_d^{IHX}}\,b^2 \qquad (15a)$$

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(10) G. Oddo and G. Anelli, *Gazz. chim. ital.*, **411**, 532 (1911).

(11) W. E. S. Turner and C. C. Bussett, *J. Chem. Soc.*, **105**, 1777 (1914).

(12) W. E. S. Turner and C. T. Pollard, *ibid.*, **105**, 1751 (1914).

(13) P. Walden, *Z. Elektrochem.*, **26**, 60 (1920).

(14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 194.

Equation 15a can be represented by a straight line of the form $y' = m'x' + b'$ where $y' = [\mathrm{I}]\, b^2$, $x' = b^2$, $m' = -K_{\mathrm{HX}}/K_{\mathrm{i}}^{\mathrm{IHX}}K_{\mathrm{d}}^{\mathrm{IHX}}$ and $b' = K_{\mathrm{i}}^{\mathrm{IHX}}K_{\mathrm{d}}^{\mathrm{IHX}}$. Since $K_{\mathrm{i}}^{\mathrm{IHX}}$ is known from the slope of equation 14 it is possible to determine $K_{\mathrm{d}}^{\mathrm{IHX}}$ and K_{HX} from the slope and intercept of equation 15a. The reliability of the constants derived in the above way was tested by a direct determination of $K_{\mathrm{i}}^{\mathrm{IHX}}$ in the presence of such a concentration of a salt of HX that dissociation of the acid and the indicator salt were completely repressed.

With a strong acid like perchloric, the experimental data must be treated differently. For a strong acid, C_{HX} is given by equation 11. Experimentally, the value of $\Sigma[\mathrm{IH}^+]/[\mathrm{I}]C_{\mathrm{HX}}$ was found to be constant at different concentrations of perchloric acid. In order to account for this we write equation 16, which is obtained by dividing equation 12a by 11.

$$\frac{\Sigma[\mathrm{IH}^+]}{[\mathrm{I}]C_{\mathrm{HX}}} = K_{\mathrm{i}}^{\mathrm{IHX}}\left[1 + \frac{K_{\mathrm{d}}^{\mathrm{IHX}}}{[\mathrm{X}^-]}\right] \times \left[\frac{[\mathrm{HX}]}{[\mathrm{HX}] + [\mathrm{H}^+\mathrm{X}^-] + [\mathrm{H}^+]}\right] \quad (16)$$

Substituting $K_{\mathrm{i}}^{\mathrm{HX}}$ and then $K_{\mathrm{d}}^{\mathrm{HX}}$ into equation 16 in order to express [HX], $[\mathrm{H}^+\mathrm{X}^-]$ and $[\mathrm{H}^+]$ in terms of $[\mathrm{X}^-]$, equation 16a is obtained. Substituting equation 6 into

$$\frac{\Sigma[\mathrm{IH}^+]}{[\mathrm{I}]C_{\mathrm{HX}}} = K_{\mathrm{i}}^{\mathrm{IHX}}\,\frac{K_{\mathrm{d}}^{\mathrm{IHX}} + [\mathrm{X}^-]}{K_{\mathrm{d}}^{\mathrm{HX}}K_{\mathrm{i}}^{\mathrm{HX}} + (1 + K_{\mathrm{i}}^{\mathrm{HX}})\,[\mathrm{X}^-]} \quad (16\mathrm{a})$$

equation 16a after factoring the term $(1 + K_{\mathrm{i}}^{\mathrm{HX}})$ out of the denominator, equation 16b is obtained.

$$\frac{\Sigma[\mathrm{IH}^+]}{[\mathrm{I}]\;C_{\mathrm{HX}}} = \frac{K_{\mathrm{i}}^{\mathrm{IHX}}(K_{\mathrm{d}}^{\mathrm{IHX}} + [\mathrm{X}^-])}{(1 + K_{\mathrm{i}}^{\mathrm{HX}})(K_{\mathrm{HX}} + [\mathrm{X}^-])} = K_{\mathrm{i.s.}}^{\mathrm{HX}} \quad (16\mathrm{b})$$

The experimental fact that the expression on the left-hand side of equation 16b is constant can be accounted for only when $K_{\mathrm{d}}^{\mathrm{IHX}} = K_{\mathrm{HX}}$. Under these conditions,

$$\frac{\Sigma[\mathrm{IH}^+]}{[\mathrm{I}]\;C_{\mathrm{HX}}} = \frac{K_{\mathrm{i}}^{\mathrm{IHX}}}{(1 + K_{\mathrm{i}}^{\mathrm{HX}})} \quad (16\mathrm{c})$$

equation 16b simplifies to equation 16c.

In agreement with this postulate is the fact that addition of alkali perchlorate to an indicator solution in very dilute perchloric acid does not change the value of the expression on the left hand side of equation 16b. Equation 16c can be written in a different form, equation 16d, since $K_{\mathrm{i}}^{\mathrm{IHClO_4}} = K_{\mathrm{HClO_4}}K_{\mathrm{I}}/K_{\mathrm{d}}^{\mathrm{IHClO_4}}K_{\mathrm{s}} = K_{\mathrm{I}}/K_{\mathrm{s}}$ in which K_{s} is the autoprotolysis constant $[\mathrm{H}^+][\mathrm{Ac}^-]$.

$$K_{\mathrm{i.s.}}^{\mathrm{IHClO_4}} = \frac{K_{\mathrm{I}}}{K_{\mathrm{s}}\,(1 + K_{\mathrm{i}}^{\mathrm{HClO_4}})} \quad (16\mathrm{d})$$

Dividing equation 16d by equation 9 and solving for $K_{\mathrm{i}}^{\mathrm{HClO_4}}$ yields equation 17

$$K_{\mathrm{i}}^{\mathrm{HClO_4}} = \frac{K_{\mathrm{i}}^{\mathrm{IHX}}K_{\mathrm{d}}^{\mathrm{IHX}}}{K_{\mathrm{i.s.}}^{\mathrm{IHClO_4}}K_{\mathrm{HX}}} - 1 \quad (17)$$

$K_{\mathrm{i}}^{\mathrm{IHX}}$, $K_{\mathrm{d}}^{\mathrm{IHX}}$ and K_{HX} are quantities which have been determined for hydrochloric and *p*-toluenesulfonic acids. Thus the ionization constant of perchloric acid can now be found from equation 17.

Hydrobromic acid, although approaching perchloric acid in strength, is definitely a weaker acid, and it is no longer justified to put $K_{\mathrm{HBr}} = K_{\mathrm{d}}^{\mathrm{IHBr}}$. Thus we write equation 17a

$$K_{\mathrm{i}}^{\mathrm{HBr}} = \frac{K_{\mathrm{i}}^{\mathrm{IHX}}K_{\mathrm{d}}^{\mathrm{IHX}}K_{\mathrm{HBr}}}{K_{\mathrm{i.s.}}^{\mathrm{IHBr}}K_{\mathrm{HX}}K_{\mathrm{d}}^{\mathrm{IHBr}}} - 1 \quad (17\mathrm{a})$$

Since $K_{\mathrm{i}}^{\mathrm{HBr}}$ must be greater than zero and less than $K_{\mathrm{i}}^{\mathrm{HClO_4}}$ we find that

$$\left[\frac{1}{1 + K_{\mathrm{i}}^{\mathrm{HClO_4}}}\right]\left[\frac{K_{\mathrm{i}}^{\mathrm{IHX}}K_{\mathrm{d}}^{\mathrm{IHX}}}{K_{\mathrm{i.s.}}^{\mathrm{IHBr}}K_{\mathrm{HX}}}\right] \leqq \frac{K_{\mathrm{d}}^{\mathrm{IHBr}}}{K_{\mathrm{HBr}}} \leqq \frac{K_{\mathrm{i}}^{\mathrm{IHX}}K_{\mathrm{d}}^{\mathrm{IHX}}}{K_{\mathrm{i.s.}}^{\mathrm{IHBr}}K_{\mathrm{HX}}} \quad (17\mathrm{b})$$

Equation 17b enables us to give limiting values of the ratio of $K_{\mathrm{d}}^{\mathrm{IHBr}}/K_{\mathrm{HBr}}$.

Experimental

Materials. Acetic Acid.—The method of Eichelberger and LaMer[15] which employs preliminary treatment of reagent grade acetic acid with chromium trioxide, followed by drying with boron triacetate and subsequent distillation, was used. The water content of the solvent was determined by titration with Karl Fischer reagent.

Acetic acid was distilled directly into one-liter Pyrex bottles fitted with No. 29 standard taper glass stoppers and stored until needed. The solvent was dispensed by introducing an automatic buret with a matching standard taper joint. It was found that if the buret was protected from atmospheric moisture with Drierite, there was no detectable increase in water content in the solvent over a period of several months.

Acetic Anhydride.—A reagent grade material was used.

Ethanol.—A reagent grade material was used. The Karl Fischer titration showed less than 0.1% water.

Hydrobromic Acid.—Bromine was dropped into dried tetralin and the resultant hydrogen bromide passed through two wash bottles with tetralin, over Drierite and then into acetic acid. The solution was standardized gravimetrically by weighing as silver bromide. It was frozen and stored at −20° since a 0.2 molar solution turned yellow after standing several days at room temperature.

Hydrochloric Acid.—Concentrated aqueous hydrochloric acid was dropped into concentrated sulfuric acid, and the gas dried by bubbling through concentrated sulfuric acid prior to saturating acetic acid. The solution was standardized gravimetrically by weighing as silver chloride.

Lithium Chloride.—A saturated solution of reagent grade lithium chloride was prepared in acetic acid just below the boiling point. After cooling to 50°, a twenty-fold excess of benzene was added and the precipitate washed thoroughly with benzene. The product was dried to constant weight at 50° *in vacuo*.

Methanol.—Reagent grade methanol was dried over magnesium and redistilled. The water content was less than 0.01% by Karl Fischer titration.

***p*-Naphtholbenzein** (PNB).—An Eastman Kodak White Label product was used.

2-Propanol.—A reagent grade material was used. The Karl Fischer titration showed less than 0.1% water.

Perchloric Acid.—A one molar stock solution was prepared by adding a known amount of analyzed reagent grade 72% aqueous perchloric acid to 750 ml. of chilled anhydrous acetic acid. The mixture was frozen and a calculated amount of acetic anhydride added cautiously. The mixture was found to contain 0.22% water (Karl Fischer method) and to be 0.975 *M* in perchloric acid at 25.5°. The standardization of the acid was conducted volumetrically using potassium acid phthalate as the primary standard and crystal violet as the indicator.

Sodium *p*-Toluenesulfonate.—In 200 ml. of acetic acid 0.099 mole of sodium acetate reacted with 0.100 mole of *p*-toluenesulfonic acid at 70°. The salt separated as a silky white precipitate on cooling. It was recrystallized once from acetic acid and washed thoroughly with ether before drying to constant weight in a vacuum oven at 50°.

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(15) W. C. Eichelberger and V. K. LaMer, THIS JOURNAL, **55**, 3633 (1933).

p-Toluenesulfonic Acid (HTS).—Eastman Kodak White Label product was dissolved in acetone and precipitated by adding a large excess of benzene. This procedure was repeated three more times until a colorless product was obtained. The product was dried overnight in a vacuum oven at 50°.

Urea.—Reagent grade material was recrystallized from acetic acid, washed with ethanol and dried to constant weight in a vacuum oven at 90°.

Methods. Spectrophotometric Measurements.—The Cary Recording Spectrophotometer, Model 11 was used to determine all absorption spectra, while all data taken at a given wave length were obtained with the Beckman model B spectrophotometer. Five centimeter cylindrical Pyrex cells fitted with ground glass stoppers were used in all measurements.

Whenever possible, a known amount of acetic acid was introduced into a dry spectrophotometer cell and increments of the appropriate reagent added directly to the cell. Usually a concentrated solution of the compound in question was prepared and a measured volume of this stock solution added with a Gilmont ultra-microburet of appropriate size. They are available in 1.0, 0.1 and 0.01 ml. capacities, and an accuracy of 0.1% absolute is easily obtained.

Normally the volume of reagent added was insignificant as compared to the total volume of solvent present initially. Otherwise the dilution was considered in reporting concentrations, assuming that the volumes of solvent and reagent solution are additive.

The spectrophotometer cells were filled directly from the automatic buret containing the solvent as were all other vessels. All the vessels in which solutions were prepared, primarily volumetric flasks, were dried at 180° for two days, cooled and stored in a desiccator until used. The long, narrow neck of the volumetric flasks minimized absorption of atmospheric moisture during transfer of solvent, and it was found that the above technique gave the same results as transferring in a sealed box dried with phosphorus pentoxide.

All spectrophotometric measurements were made at 25°, unless otherwise specified. The spectrophotometer cell was immersed in a water-bath held at 25.0 ± 0.1° and removed only to measure absorbances. An absorbance measurement could be made easily in 30 seconds so that no appreciable change could occur in the cell temperature.

Experimental Results and Discussion

Absorption Spectrum of PNB.—The indicator is orange-brown in pure acetic acid and more alkaline solutions, while it is green in acid solutions. The basic form has one absorption maximum (454 mμ) and the acid form two absorption maxima (464 and 625 mμ). The spectra of both forms are shown in Fig. 1. All spectrophotometric measurements were made at 625 mμ because of the overlap of spectra in the 454–464 mμ range. The molar absorptivity[16] of the acid form of PNB was determined and found to be 2.86 × 10⁴ liters/(mole cm.) in perchloric acid (0.02 *M*).

The molar absorptivity and wave length at the absorption maximum differ from those reported by Smith and Elliot[4] who found, respectively, 1.06 × 10⁴ at 640 mμ. We found the spectra and absorptivities of the acid form of PNB as determined by three different spectrophotometers (Beckman Models B and DU and Cary Recording Model 11) to be in good agreement.

The complete spectrum of PNB was determined in the presence of a large excess of four different acids, perchloric (0.02 *M*), hydrobromic (0.2 *M*), hydrochloric (1.2 *M*) and p-toluenesulfonic (1.0 *M*), and was found to be quantitatively identical in all respects in these four solutions, indicating that the nature of X^- in the ion-pair IH^+X^- does not affect the spectrum of the IH^+ unit. At the concentrations of acid used, undoubtedly there exist appreciable amounts of $IH^+X^-H^+$, $X^-IH^+X^-$, and possibly $\overset{IH^+X^-}{X^-H^+}$ so that there is considerable justification to extend the above statement to include all ionic aggregates rather than limiting it to ion-pairs.

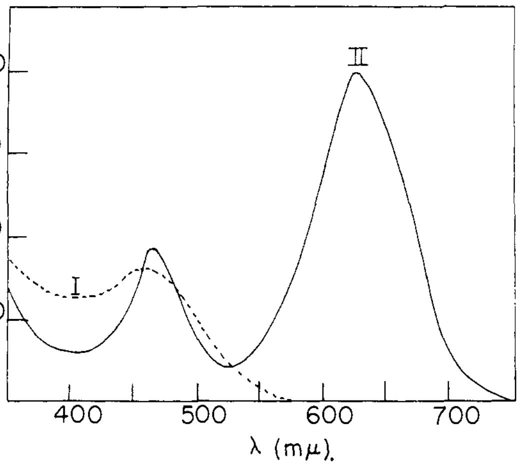

Fig. 1.—Absorption spectrum of PNB: I, basic spectrum in acetic acid; II, acid spectrum in acetic acid containing excess perchloric acid; $(C_{PNB})_t = 1.30 \times 10^{-5}$ *M*, cell length = 50 mm.

PNB is such a weak base in acetic acid that in the normal concentration ranges used (up to 1.3 × 10^{-5}) the species IH^+Ac^- is not detectable. An estimate of K_i^I was obtained by measuring the absorbance of more concentrated solutions of PNB at 625 mμ in the presence of enough pyridine to quantitatively suppress the dissociation of IH^+Ac^-. At this wave length, the absorbance can be caused by I and/or IH^+Ac^-. Assuming that I absorbs negligibly at 625 mμ, the maximum possible concentration of IH^+Ac^- is calculated and, thus, the maximum value of K_i^I is obtained. The results of six experiments in Table I reveal that $K_i^I \leqq 0.0042$. In pure acetic acid considerably less than 1% is present in the acid form.

TABLE I

MAXIMUM IONIZATION CONSTANT OF PNB

Molar concn. of pyridine	Max. molarity of IH^+Ac^- at molar concn. of PNB 3.63×10^{-4}	Max. molarity of IH^+Ac^- at molar concn. of PNB 9.07×10^{-4}	Max. K_i^I at molar concn. of PNB 3.63×10^{-4}	Max. K_i^I at molar concn. of PNB 9.07×10^{-4}
0.0005	1.51×10^{-6}	3.73×10^{-6}	0.00419	0.00413
.0008	1.52	3.73	.00421	.00413
.0011	1.52	3.74	.00421	.00414

The Reaction of PNB with Weak Acids.—The reaction of PNB with hydrochloric acid and p-toluenesulfonic acid (hereafter designated as HTs) was studied and some experimental results are presented in Fig. 2, where $\log \Sigma[IH^+]/[I]$ is plotted against pC_{HX}, the latter denoting the negative logarithm of C_{HX} (defined by equation 11). Straight lines were obtained, with slopes of −0.71 for HTs and −0.54 for hydrochloric acid. The large deviation from −1.00 of the slopes proves that appreciable dissociation of the indicator salts, IH^+Cl^- and IH^+Ts^-, occurs under our experimental conditions.

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[16] H. K. Hughes, *Anal. Chem.*, **24**, 1349 (1952).

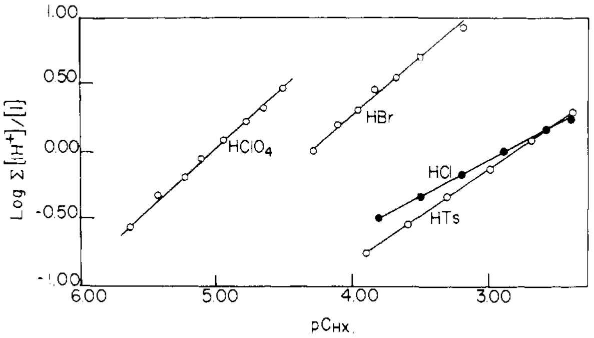

Fig. 2.—The reaction of PNB with acids: $(C_{PNB})_t$ = 3.7 × 10^{-6} *M*. The slopes are: $HClO_4$ = −1.00, HBr = −0.93, HTs = −0.71, and HCl = −0.54.

More experiments were performed with solutions of PNB and hydrochloric acid, and PNB and HTS, to determine K_{HX}, K_i^{IHX} and K_d^{IHX} by means of equations 14 and 15a. Tables II and III contain the experimental data. These data were used to construct graphs of [I] *vs.* Σ[IH$^+$] for each acid solution. Values of Σ[IH$^+$] were obtained at [I] of 2.00, 3.00, 4.00, 5.00 and 6.00 × 10^{-6} molar. The interpolated values of Σ[IH$^+$] are in Tables IV and V. The data in Tables IV and V were used to calculate $\Sigma[IH^+]/[I]\sqrt{C_{HX}}$. Figures 3 and 4 give plots of this expression *vs.* $\sqrt{C_{HX}}$. In accordance with equation 14, a family of parallel straight lines was obtained for both acids, the slopes and intercepts being presented in Table VI.

Table II

Reaction of Hydrochloric Acid with PNB

The water content was 0.035%.

Total concn. of PNB, $M \times 10^6$	Σ(IH$^+$) × 10^6 at *M* concn. of hydrochloric acid 0.663 × 10^{-3}	1.326 × 10^{-3}	2.05 × 10^{-3}	5.31 × 10^{-3}
1.82	0.427	0.596	0.792	1.07
3.64	0.798	1.16	1.56	2.07
5.46	1.11	1.66	2.26	3.05
7.28	1.44	2.11	2.98	4.00
9.08	1.73	2.58	3.61	4.92
10.87	2.00	2.98	4.24	5.81

Table III

Reaction of *p*-Toluenesulfonic Acid with PNB

The water content was 0.035%.

Total concn. of PNB, $M \times 10^6$	Σ[IH$^+$] × 10^6 at *M* concn. of *p*-toluenesulfonic acid 0.270 × 10^{-3}	0.538 × 10^{-3}	1.075 × 10^{-3}	2.15 × 10^{-3}
1.82	0.477	0.680	0.896	1.14
3.64	0.911	1.29	1.13	2.19
5.46	1.30	1.84	2.51	3.27
7.28	1.64	2.38	3.28	4.29
9.08	1.99	2.88	4.02	5.29
10.87	2.32	3.39	4.71	6.25

Table IV

Interpolated Values of Σ[IH$^+$] × 10^6 *M* in Hydrochloric Acid Solutions

Concn. acid $M \times 10^3$	Σ[IH$^+$] × 10^6 at *M* concn. of I 2.00 × 10^{-6}	3.00 × 10^{-6}	4.00 × 10^{-6}	5.00 × 10^{-6}	6.00 × 10^{-6}
5.31	2.55	3.70	4.75	5.75	
2.65	1.51	2.17	2.80	3.38	3.91
1.33	0.94	1.35	1.71	2.05	2.40
0.663	0.58	0.83	1.06	1.28	1.48

Table V

Interpolated Values of Σ[IH$^+$] × 10^6*M* in *p*-Toluenesulfonic Acid Solution

Concn. of acid, $M \times 10^3$	Σ[IH$^+$] × 10^6 *M* concn. of I 2.00 × 10^{-6}	3.00 × 10^{-6}	4.00 × 10^{-6}	5.00 × 10^{-6}	6.00 × 10^{-6}
2.15	3.00	4.32	5.54	6.76	
1.075	1.79	2.57	3.28	3.98	4.61
0.538	1.10	1.55	2.00	2.42	2.80
0.270	0.69	0.98	1.25	1.50	1.74

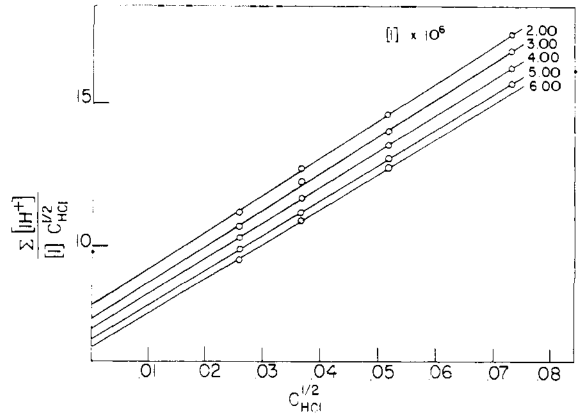

Fig. 3.—Test of equation 14 for hydrochloric acid.

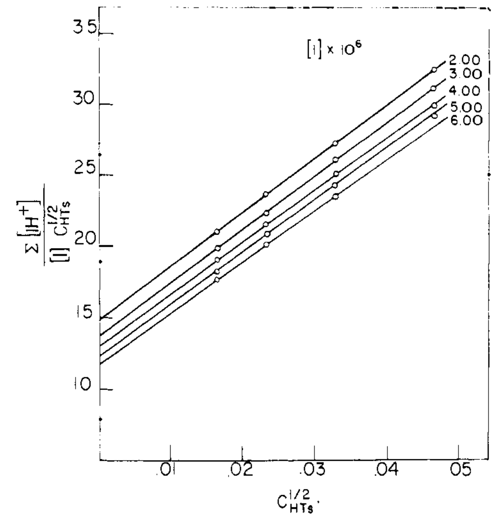

Fig. 4.—Test of equation 14 for *p*-toluenesulfonic acid.

Table VI

The Slopes and Intercepts of Equation 14

[I] × 10^6	Hydrochloric acid Slope (K_i^{IHX})	Intercept	*p*-Toluenesulfonic acid Slope (K_i^{IHX})	Intercept
2.00	128	9.00	380	14.75
3.00	128	7.50	376	13.65
4.00	125	7.15	365	12.95
5.00	124	6.80	369	12.15
6.00	124	6.45	361	11.65

Figure 5 is a graph of equation 15a, using the data in Table VI to compute b^2 and $[I]b^2$. Plotting these two quantities against each other yielded straight lines for each acid with a slope of −5.72 × 10^{-6} and an intercept of 4.95 × 10^{-4} for hydrochloric acid, and a slope of −4.91 × 10^{-6} with an intercept of 1.49 × 10^{-3} for HTs.

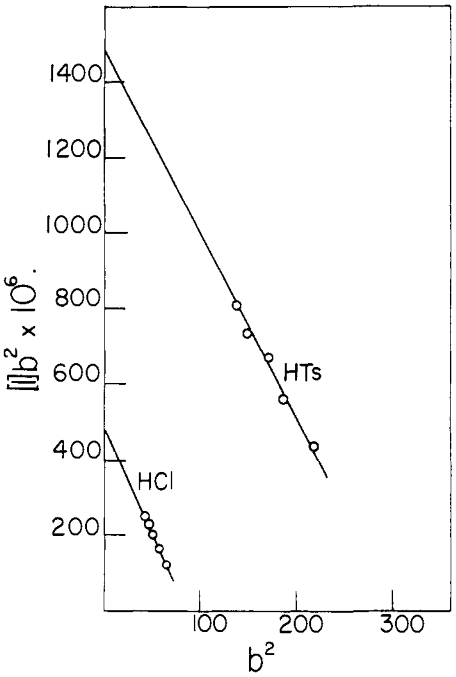

Fig. 5.—Test of equation 15a.

Table VII contains K_{HX}, K_i^{IHX} and K_d^{IHX} obtained from Figs. 3, 4 and 5 using equations 14 and 15a. These data show that the dissociation constants of IH^+Cl^- and IH^+Ts^- are identical.

TABLE VII

EQUILIBRIUM CONSTANTS DERIVED FOR THE SYSTEM PNB-HX

Equilibrium constant	Hydrochloric acid	*p*-Toluenesulfonic acid
K_{HX}	2.8×10^{-9}	7.3×10^{-9}
K_i^{IHX}	1.3×10^2	3.7×10^2
K_d^{IHX}	3.9×10^{-6}	4.0×10^{-6}

In order to provide independent support for the reliability of these data we derive from equation 9 that

$$\frac{K_i^{IHTs}}{K_i^{IHCl}} = \frac{K_{HTs}K_d^{IHCl}}{K_{HCl}K_d^{IHTs}} \quad (18)$$

From the data in Table VII it appears that the left-hand side of equation 18 is equal to 2.9, in satisfactory agreement with the value of 2.5 for the right-hand side of this equation.

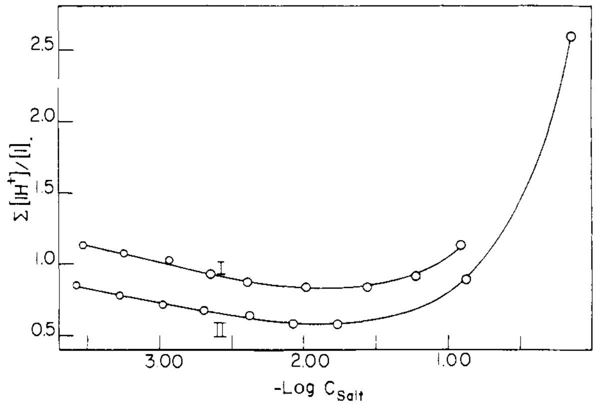

Fig. 6.—Repression of the dissociation of IH^+X^-: I, 2.15×10^{-3} *M* *p*-toluenesulfonic acid and sodium *p*-toluenesulfonate; II, 5.30×10^{-3} *M* hydrochloric acid and lithium chloride; $(C_{PNB})_t = 1.08 \times 10^{-5}$ *M*.

Upon addition of lithium chloride to a solution of PNB and hydrochloric acid the ratio of $\Sigma[IH^+]/[I]$ decreased. Similar results were obtained with sodium *p*-toluenesulfonate (NaTs) and HTs, as is shown in Fig. 6. The initial decrease is caused by repression of the dissociation of IH^+X^- by the salt containing the common ion, X^-, while the subsequent increase is caused by formation of ionic aggregates involving more than two ions. The minimum value of $\Sigma[IH^+]/[I]$ corresponds to those solutions of salt in which negligible dissociation of IH^+X^- and little or no formation of higher ionic aggregates occurs, so that $\Sigma[IH^+] = [IH^+X^-]$. Hence, the graph of $\log \Sigma[IH^+]/[I]$ against pC_{HX} in solutions of PNB containing just enough salt to reach the minimum in the $\Sigma[IH^+]/[I]$ *vs.* salt curve should be a straight line of slope −1.00. This was experimentally verified for hydrochloric acid in 0.01 *M* lithium chloride solutions and HTs in 0.025 *M* NaTs solutions, figure 7 depicting the experimental results, K_i^{IHCl} was found to equal 1.2×10^2 and K_i^{IHTs} was found to be 4.0×10^2. These values agree well with those in Table VII.

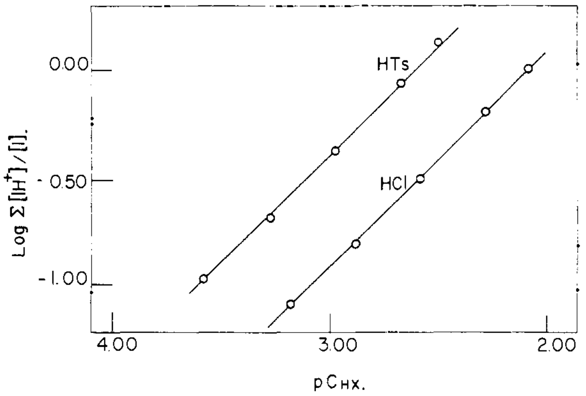

Fig. 7.—Determination of K_i^{IHX}: $(C_{PNB})_t = 1.08 \times 10^{-5}$ *M* HCl in presence of 0.0104 *M* LiCl; HTs in presence of 0.0252 *M* NaTs. Lines of slope −1.00 have been drawn through the experimental points.

The Reaction of PNB with Strong Acids.—The reaction of PNB with perchloric and hydrobromic acid was studied. The experimental results are presented in Fig. 2 where $\log \Sigma[IH^+]/[I]$ is plotted against pC_{HX}. Straight lines were obtained with slopes of −1.00 for perchloric and −0.93 for hydrobromic acid. In a previous section, equation 16d has been derived for a strong acid which on plotting as in Fig. 2 should give a straight line of slope −1.00, provided K_d^{IHX} were equal to K_{HX}. This equation is satisfied by perchloric acid and nearly so by hydrobromic acid, but not by HTs or hydrochloric acid for which K_{HX} is much smaller than K_d^{IHX}.

The observed ratio of $\Sigma[IH^+]/[I]$ for PNB in a 3.12×10^{-5} *M* solution of perchloric acid was 3.00. The addition of sufficient sodium perchlorate to make the solution 0.01 *M* in this compound did not alter the ratio. Also, addition of lithium bromide to a 3.25×10^{-4} *M* solution of hydrobromic acid to make the solution 0.02 *M* in lithium bromide did not alter the observed ratio of $\Sigma[\mathrm{IH}^+]/[\mathrm{I}]$ from the value of 5.35. The over-all dissociation constants of perchloric and hydrobromic acid are in the range of 10^{-5} to 10^{-6} and of the same order of magnitude as the concentration of the acids in the reported experiments. Thus in solutions of the acids without alkali salt, there is appreciable dissociation into ions (and also of indicator salt). The dissociation of both acid and salt are suppressed by addition of an alkali salt of the acid without affecting the ratio of acid to alkaline species of the indicator. Again, this behavior is quantitatively accounted for by equation 16b if $K_{\mathrm{HX}} = K_{\mathrm{d}}^{\mathrm{IHX}}$.

The value of $K_{\mathrm{i.s.}}^{\mathrm{IHX}}$ (defined by equation 16b) is 1.0×10^5 for perchloric acid from the data in Fig. 2. Using this value, and the data in Table VII the ionization constant of perchloric acid was calculated using equation 17. $K_{\mathrm{i}}^{\mathrm{HClO_4}}$ was calculated to be 0.8 using the hydrochloric acid data of Table VII and 1.0 using the HTs data. No estimate of $K_{\mathrm{i}}^{\mathrm{HBr}}$ can be made since the value of $K_{\mathrm{HBr}}/{}_{\mathrm{d}}^{\mathrm{KIHBr}}$ is sufficiently different from 1.00 to rule out the use of equation 17. Using equation 17b, the maximum value of the ratio $K_{\mathrm{d}}^{\mathrm{IHBr}}/K_{\mathrm{HBr}}$ can be estimated. From Fig. 2, $K_{\mathrm{i.s.}}^{\mathrm{IHBr}}$ is approximately 1.7×10^4, so that $5 \leqq K_{\mathrm{d}}^{\mathrm{IHBr}}/K_{\mathrm{HBr}} \leqq 10$ according to the hydrochloric acid data in Table VII or $6 \leqq K_{\mathrm{d}}^{\mathrm{IHBr}}/K_{\mathrm{HBr}} \leqq 12$ according to the HTs data.

Reaction of Colorless Bases with Acids.—The indicator PNB is suitable for the determination of $K_{\mathrm{i}}^{\mathrm{BHX}}$ of bases of suitable strength. With HX as perchloric acid, we know $\Sigma[\mathrm{IH}^+]/[\mathrm{I}]C_{\mathrm{HClO_4}}$, thus from the experimentally determined value of $\Sigma[\mathrm{IH}^+]/[\mathrm{I}]$ in the presence of a colorless base, B, with total concentration C_{B} we can find $C_{\mathrm{HClO_4}}$. Denoting $(C_{\mathrm{HX}})_{\mathrm{t}}$ as the total concentration of acid in equation 19

$$[\mathrm{BHX}] + [\mathrm{BH}^+] = \Sigma[\mathrm{BH}^+] = (C_{\mathrm{HX}})_{\mathrm{t}} - C_{\mathrm{HX}} - \Sigma[\mathrm{IH}^+] \qquad (19)$$

$$[\mathrm{B}] = C_{\mathrm{b}} - \Sigma[\mathrm{BH}^+] \qquad (19a)$$

$$K_{\mathrm{i.s.}}^{\mathrm{BHClO_4}} = \frac{\Sigma[\mathrm{BH}^+]}{[\mathrm{B}]C_{\mathrm{HClO_4}}} \qquad (19b)$$

Equation 19 and 19a give the values of $\Sigma[\mathrm{BH}^+]$ and [B], while $K_{\mathrm{i.s.}}^{\mathrm{BHClO_4}}$ is calculated from equation 19b.

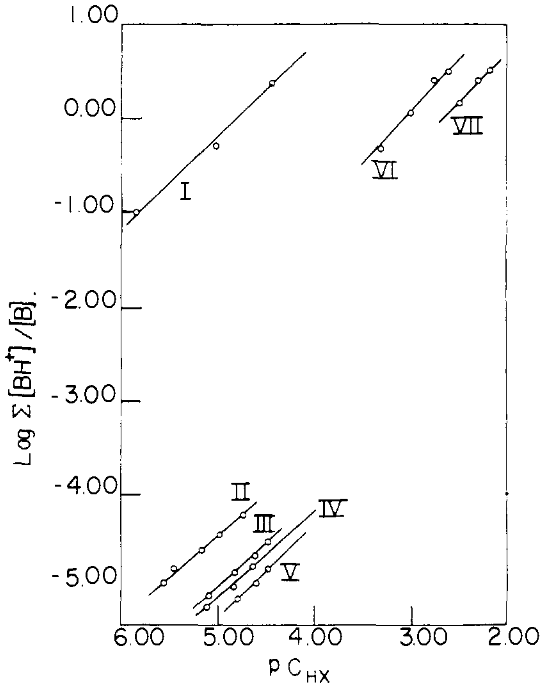

Fig. 8.—Determination of $K_{\mathrm{i}}^{\mathrm{BHX}}$ for colorless bases: I, urea and $\mathrm{HClO_4}$; II, water and $\mathrm{HClO_4}$; III, 2-propanol and $\mathrm{HClO_4}$; IV, ethanol and $\mathrm{HClO_4}$; V, methanol and $\mathrm{HClO_4}$; VI, urea and HTs; VII, urea and HCl. The slopes of these lines are given in Table VIII.

Plots of $\log \Sigma[\mathrm{BH}^+]/[\mathrm{B}]$ against $pC_{\mathrm{HClO_4}}$ yielded straight lines with slopes near -1.00 as shown in Fig. 8. As has been shown with PNB, a slope of -1.00 can be obtained only when

$$K_{\mathrm{i.s.}}^{\mathrm{BHClO_4}} = K_{\mathrm{i}}^{\mathrm{BHClO_4}}/1 + K_{\mathrm{i}}^{\mathrm{HClO_4}} \qquad (19c)$$

in which $K_{\mathrm{i}}^{\mathrm{HClO_4}}$ is equal to 1.

With the weak acids, hydrochloric and HTs, the dissociation of the acid and of the salt of the base is suppressed quantitatively by carrying out the experiment in 0.01 *M* lithium chloride with hydrochloric acid, and in 0.025 molar NaTs with HTs. From the ratio $\Sigma[\mathrm{IH}^+]/[\mathrm{I}]$ we obtain [HX] and $K_{\mathrm{i}}^{\mathrm{BHX}} = [\mathrm{BHX}]/([\mathrm{B}]\,[\mathrm{HX}])$ is readily calculated. The plots of $\log \Sigma[\mathrm{BH}^+]/[\mathrm{B}]$ against pC_{HX} in Fig. 8 have slopes near -1.00. The results are given in Table VIII.

Table VIII

Reaction of HX with B[a]

Acid	Base	Slope	$\frac{[\mathrm{BH}^+]}{[\mathrm{B}]C_{\mathrm{HX}}}$	$K_{\mathrm{i}}^{\mathrm{BHX}}$
Perchloric	PNB	−1.00	1.0×10^5	2.0×10^5
Perchloric	Urea	−0.97	8.2×10^4	1.6×10^5
Perchloric	Water	−0.92	3.4×10^{1}[b]	6.8×10^1
Perchloric	2-Propanol	−0.90	8.6	1.7×10^1
Perchloric	Ethanol	−0.90	7.4	1.5×10^1
Perchloric	Methanol	−1.00	4.4	8.8
HTs	PNB	−1.00	3.7×10^2	3.7×10^2
HTs	Urea	−1.12	1.2×10^3	1.2×10^3
Hydro-	PNB	−1.00	1.3×10^2	1.3×10^2
chloric	Urea	−1.00	4.9×10^2	4.9×10^2

[a] The water content of the acetic acid used in solutions containing perchloric acid was less than 0.001%, and was 0.0023% in hydrochloric and HTs solutions of urea. No corrections for these traces of water are necessary. [b] Smith and Elliott's[4] data give a value of 2.8×10^1.

In the introductory section of this paper it has been mentioned that the relative strength of an acid generally varies with the base used for reference. With reference to PNB we find that $K_{\mathrm{i}}^{\mathrm{IHClO_4}}$ is 540 times greater than $K_{\mathrm{i}}^{\mathrm{IHTs}}$, while with reference to the base urea, $K_{\mathrm{i}}^{\mathrm{BHClO_4}}$ is only 140 times greater than $K_{\mathrm{i}}^{\mathrm{IHTs}}$ corresponding R_1/R_2 in equation 10 of 3.9. Also, we find that $K_{\mathrm{i}}^{\mathrm{IHClO_4}}$ is 1500 times greater than $K_{\mathrm{i}}^{\mathrm{IHCl}}$ while $K_{\mathrm{i}}^{\mathrm{BHClO_4}}$ is 330 times greater than $K_{\mathrm{i}}^{\mathrm{BHCl}}$ and $R_1/R_2 = 4.6$.

Even more striking is the result that the order of base strength of PNB and urea is reversed when the reference acid is changed from perchloric to hydrochloric or HTs. PNB is 1.3 times as strong a base as urea with reference to perchloric acid, but 0.27 as strong with regard to hydrochloric acid and 0.32 as strong with reference to HTs.

An attempt to study the reaction between water and hydrochloric acid was unsuccessful. In a range of water contents up to 0.05% (0.028 *M*), $\Sigma[IH^+]$ remained constant, while at higher water concentrations it increased gradually. The lack of sensitivity to water at low concentrations is in accord with the weak acid character of hydrochloric acid, while the abnormal effect of water resulting in an increase in acid color has been reported previously[17] for other indicators.

It is of interest to compare the basic strength of water and some alcohols with regard to perchloric acid. From Table VIII it is seen that water is the strongest base ($K_i^{H_2O\cdot HClO_4} = 68$), followed by 2-propanol ($K_i^{PHClO_4} = 17$), then ethanol ($K_i^{EHClO_4} = 15$), while methanol is the weakest base ($K_i^{MHClO_4} = 8.8$).

Effect of Temperature on K_i^{IHX}.—The ratio $\Sigma[IH^+]/[I]$ was determined as a function of temperature in solutions of hydrochloric acid being 0.01 *M* in lithium chloride, and HTs being 0.02 *M* in NaTs. The concentration of acid colored species decreased as the temperature increased. The results are presented in Fig. 9 where $\log_e[(K_i^{IHX})_T/(K_i^{IHX})_{25}]$ is plotted against the reciprocal of the absolute temperature. The subscripts refer to the temperature at which K_i^{IHX} was determined.

One straight line fits the data for both acids, the slope corresponding to a heat of reaction of −7 kcal./mole for the reaction $I + HX \rightleftarrows I^+HX^-$. Jolly[18] determined the heat of solution of sodium acetate in acetic acid and in acetic acid containing perchloric acid and calculated the heat of ionization of acetic acid on the assumption the sodium acetate, sodium perchlorate and perchloric acid are completely dissociated. His data correspond to −5.7 kcal./mole for the reaction $HClO_4 + NaAc \rightleftarrows NaClO_4 + HAc$. This result combined with the above indicates that the heat of reaction for $B + HX \rightleftarrows BHX$ is of the order of 6–7 kcal./mole, and is little affected by the strength of acid or base.

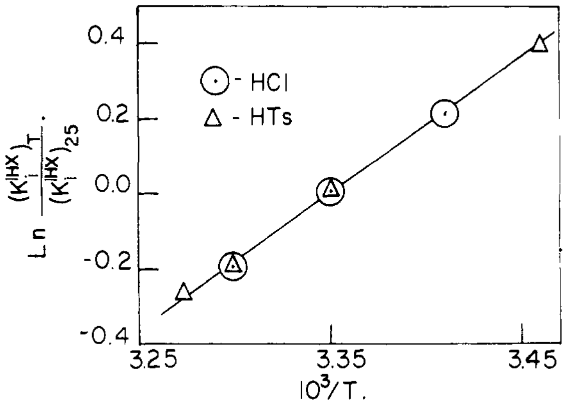

Fig. 9.—Effect of temperature on K_i^{IHX}.

Formation of Ionic Aggregates.—Addition of large amounts of lithium chloride gives rise to formation of the acid-colored species of PNB which must be a higher ionic aggregate containing IH^+. The exact nature of the acid species is unknown; experimentally it was found that $\Sigma[IH^+]/[I]\,[LiCl]$ is constant and equal to 1.25 in the concentration range of 1 to 11 × 10^{-6} *M* PNB and 0.1 to 1.3 *M* lithium chloride. The addition of base, such as lithium acetate or pyridine, causes the green (acid) color to disappear, indicating that the over-all reaction leading to the formation of the ionic aggregate' $\Sigma[IH^+]$, involves acetate (or hydrogen) ions. Addition of lithium chloride to hydrochloric acid solutions of PNB produces an increase in the concentration of acid-colored indicator species, as shown in Fig. 6, but no quantitative interpretation is possible until the exact formula of the ionic aggregate formed is known.

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[17] A. Willman, Ph.D. Thesis, University of Minnesota, 1933.

[18] W. L. Jolly, THIS JOURNAL, **74**, 6199 (1952).