The expression for the change in standard free energy, $\Delta F°$, in the reaction,

$$\mathrm{C\ (graphite)} \rightleftarrows \mathrm{C\ (in\ Bi)}$$

was calculated to be

$$\Delta F^0 = 1640 + 14.5T \text{ in calories per mole}$$

The heat of solution of carbon in bismuth is 1640 ± 200 calories per mole.

Discussion

Oxygen reacts with liquid bismuth to form the stable compound, bismuth trioxide. Therefore, the solubility of oxygen in liquid bismuth is determined by the oxide–metal equilibrium and is practically independent of the partial pressure of oxygen over the melt.[7] Chipman[8] in his investigation of a similar metal–oxide system (Fe–FeO) found that the oxygen solubility was not only independent of the pressure of an oxygen atmosphere but also was virtually independent of the character of the ambient atmosphere. In the present investigation, the melts were made in a vacuum to prevent excessive oxidation of the metal. The temperatures fluctuated only about ±5° during equilibration.

The oxygen (or carbon) content of the samples represented equilibrium values only if the following conditions were fulfilled: (1) the liquid bismuth was saturated with the solute element, (2) this saturation amount of solute was retained quantitatively during quenching, and (3) no undissolved solute element was mechanically entrapped in the metal at the end of the holding period.

In general, the results obtained on a few exploratory melts heated for one hour and for three hours, agreed. The three hours holding period was, therefore, undoubtedly more than long enough to establish equilibrium.

Equilibrium was approached from a higher temperature (supersaturated condition) in all cases except for the melts quenched from 750°. The data show a reasonable internal consistency whether equilibrium was approached from a higher or lower temperature.

The molten bismuth solidified within one minute after cooling started. Microscopic examination of the resulting ingots showed that the precipitated solute element was present as fine dendrites and not as large agglomerates as would be the case in slow-cooled melts, or melts in which the excess solute was incompletely liquated during equilibration. As a further precaution each analytical sample was composed of the entire portion of the ingot remaining after cleaning off surface contamination.

COLUMBUS 1, OHIO

(7) C. J. Smithells, "Metals Reference Book," Interscience Publishers, Inc., New York, N. Y., 1949, p. 379.

(8) J. Chipman and K. L. Fetters, *Trans. Am. Soc. Metals*, **29**, 953 (1941).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Acid Strength of Iodine Monochloride, Antimony Trichloride and Picric Acid with Reference to the Bases Pyridine and Aniline in Nitrobenzene

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The dissociation constants in nitrobenzene of picric acid, pyridinium picrate, pyridine–iodine monochloride, pyridine–antimony trichloride and aniline–antimony trichloride have been determined spectrophotometrically. These constants, together with others available in the chemical literature, allow a comparison of strengths of a series of Lewis acids and bases in nitrobenzene. The magnitude and in some instances even the order, of the strengths of a series of acids depends on the base chosen as reference, and *vice versa*.

In the Brønsted–Lowry theory of acidity and basicity the strength of a base is a measure of its affinity for the proton. In the Lewis theory, which recognizes as acids other electrophilic substances in addition to the proton, the term base strength is ambiguous unless a reference acid is specified. If we consider the simplest type of acid–base reaction

$$\mathrm{A + B \rightleftarrows AB}$$

one in which a soluble Lewis acid of any charge type reacts with a soluble base of any charge type to form a soluble addition compound ("neutralization product"), we may suppose on theoretical grounds that no simple relationship exists between the strengths of a series of bases toward one acid and the strengths of the same series of bases toward another acid. This supposition is based chiefly on the consideration that the energy of the bond between A and B, and also the solvation energy of AB, are in general not related in a simple or known way to the individual properties of A and B. Similarly the term acid strength might be expected to have meaning only if a reference base is specified.

An experimental comparison of the strengths of the bases, pyridine, aniline and picrate ion, and of the acids iodine monochloride, antimony trichloride, picric acid, pyridinium ion and anilinium ion was possible after the approximate determination of the dissociation constants of several addition products. The constants were calculated from results of spectrophotometric measurement of equilibrium concentrations in appropriate solutions. Nitrobenzene, which has a dielectric constant of 34.5, was used as solvent. Preliminary experiments were carried out in chloroform; however, the results of experiments involving ionic species were difficult to interpret because of the low dielectric constant (about 5) of this solvent.

Experimental

Nitrobenzene was purified by washing it successively with 1:1 sulfuric acid, water, concentrated sodium hydroxide (until washings were colorless), and finally with several portions of water. The product was dried over calcium chloride and then distilled under reduced pressure over barium oxide. **Pyridine** of analytical reagent grade was dried over sodium hydroxide. **Picric acid** of melting point 121–121.5°

was used. **Iodine monochloride** of Eastman Practical Grade was tested for free chlorine or free iodine as described elsewhere.[1] If free chlorine was found, an equivalent quantity of pure iodine was added.

Pyridinium picrate was prepared by adding pyridine to a saturated solution of picric acid in ethanol. The precipitate was dried, recrystallized from absolute alcohol, and dried *in vacuo* over magnesium perchlorate 24 hours. **Sodium picrate** was prepared by a method similar to pyridinium picrate except that concentrated sodium hydroxide was used instead of pyridine. **Antimony trichloride** was of reagent grade quality.

Equilibrium mixtures were prepared and allowed to come to equilibrium in a water-bath at 25 ± 0.2°. Spectrophotometric measurements were made at room temperature on a portion of the mixture with a Beckman model DU spectrophotometer, the optical path through the solution being exactly one centimeter. The maximum change in temperature of solution during measurement was estimated to be ±3°.

Results and Interpretation

Dissociation of Picric Acid.—Figure 1 shows the absorption at 430 mμ of picric acid at various concentrations in nitrobenzene. The absorption of light at this wave length by undissociated picric acid is negligible,[2] but the absorption by the picrate ion (yellow) is considerable. The dissociation of picric acid can be represented as

$$\mathrm{HPi} \rightleftarrows \mathrm{H}^+ + \mathrm{Pi}^-;\ K_1 = [\mathrm{H}^+][\mathrm{Pi}^-]/[\mathrm{HPi}] \quad (1)$$

where $[\mathrm{H}^+]$ denotes the concentration of solvated hydrogen ion, and [HPi] denotes the total concentration of undissociated picric acid, whether combined with nitrobenzene or uncombined (see below). Picric acid picrate ion, PiHPi^-, exists but need not be considered in reaction (1) because it is not formed in appreciable quantity in solutions of pure picric acid (see below). Dimerization of picric acid also need not be considered in nitrobenzene solutions[3,4] because of the relatively strong intramolecular hydrogen bond of picric acid[5] and because of its partial association with the solvent.[3]

The value of the dissociation constant K_1 can be calculated from the equation

$$K_1 = [\mathrm{Pi}^-]^2/C - [\mathrm{Pi}^-] = \frac{(E/\epsilon)^2}{C - (E/\epsilon)}$$

where C is the total, analytical concentration of picric acid, E is the extinction of the solution (log I_0/I), and ϵ is the molar extinction coefficient of the picrate ion. The value of ϵ was found to be 1.05×10^4 l./mole cm. at 430 mμ from measurements of the extinction of solutions of pure tetramethylammonium picrate (see below). A test of the validity of the equation above is provided by a plot of the *square* of the extinction *vs.* the concentration of picric acid. Since the concentration of picrate ion is negligible compared with the total concentration of picric acid, the plot should be a straight line with zero intercept. It is seen from line II of Fig. 1 that the experimental points fall on a nearly straight line but that the intercept is not zero. This is thought to be due to a small amount of water absorbed from the air during the experiment. Water is a much stronger base than nitrobenzene and would cause in these solutions the formation of an equivalent amount of picrate ion. Line III was obtained by assuming that the concentration of water was 10^{-5} M and by correcting line II for its effect on the dissociation of picric acid. The slope of line III corresponds to a value of K_1 of 3.5×10^{-8} at 25°.

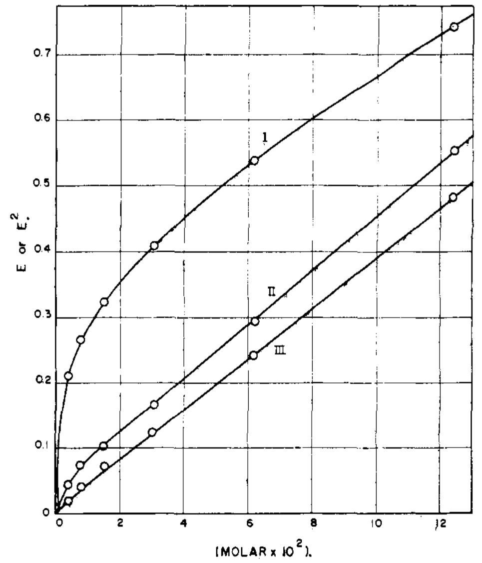

Fig. 1.—Absorption of light of 430 mμ by picric acid in nitrobenzene: I, extinction *vs.* concentration; II, square of extinction *vs.* concentration; III, same as II after correction for 10^{-5} M water.

Reaction (1) is a simplified representation of the dissociation of picric acid. Inasmuch as nitrobenzene is a weak base,[6] undissociated picric acid probably exists in these solutions largely as NbHPi[3] and the hydrogen ion as NbH^+ and NbHNb^+, where Nb represents the nitrobenzene molecule. Reaction (1) is, however, a valid representation, and K_1 is a true constant, because the activity of nitrobenzene in the dilute solutions under investigation was always essentially the same. Similar comments apply to the equilibria discussed below. It may also be mentioned that in all of the solutions investigated the ionic strength was less than 10^{-4}. Inasmuch as the dielectric constant of nitrobenzene is high (34.5), the activities of solutes were assumed to be equal to the concentrations.

Formation and Dissociation of Picric Acid Picrate Ion.—Because of the possibility of hydrogen bond formation, the ion PiHPi^- would be expected to exist in solutions containing sufficiently high concentrations of picrate ion and picric acid.

$$\mathrm{PiHPi}^- \rightleftarrows \mathrm{Pi}^- + \mathrm{HPi};$$
$$K_2 = [\mathrm{Pi}^-][\mathrm{HPi}]/[\mathrm{PiHPi}^-] \quad (2)$$

In order to evaluate K_2 the following experiment was performed. The solubility of sodium picrate in nitrobenzene was determined and found to be 8.5×10^{-4} M at room temperature. The solubility of sodium picrate in nitrobenzene containing 0.001 M picric acid was, under identical experimental conditions, the same within experimental

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[1] T. S. Lee, I. M. Kolthoff and M. A. Mairs, *J. Polymer Sci.*, **3**, 66 (1948).

[2] H. v. Halban and M. Seiler, *Helv. Chim. Acta*, **21**, 385 (1938).

[3] T. S. Moore, E. Shepard and E. Goodall, *J. Chem. Soc.*, 1931, 1447.

[4] J. N. Brønsted and R. P. Bell, THIS JOURNAL, **53**, 2478 (1931).

[5] G. E. Hilbert, O. R. Wulf, S. B. Hendricks and U. Liddel, *ibid.*, **58**, 548 (1936).

[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 47.

error. Quantitative interpretation of these results, together with the value of 2.8×10^{-5} for the dissociation constant of dissolved sodium picrate[7] leads to the conclusion that K_2 is greater than 10^{-2}. This value is so large that the presence of PiHPi^- could be neglected in all of the equilibrium mixtures described below.

Formation and Dissociation of Pyridinium Picrate.—As shown by Elliot and Fuoss[8] and others,[7,9] pyridinium picrate in various solvents undergoes both molecular and ionic dissociation

$$\mathrm{PyHPi} \rightleftarrows \mathrm{Py} + \mathrm{HPi};\ K_3 = [\mathrm{Py}][\mathrm{HPi}]/[\mathrm{PyHPi}] \quad (3)$$

$$\mathrm{PyHPi} \rightleftarrows \mathrm{PyH}^+ + \mathrm{Pi}^-;$$
$$K_4 = [\mathrm{PyH}^+][\mathrm{Pi}^-]/[\mathrm{PyHPi}] \quad (4)$$

where Py represents the pyridine molecule.

The absorption of light of 430 mμ by nitrobenzene solutions containing pyridine and picric acid is shown in Fig. 2. The molar ratio of pyridine to picric acid was 1000, thus assuring that all of the picric acid would be present as PyHPi, or as Pi^- with PyH^+ or PyHPy^+ as cations. The linear relationship between extinction and initial picric acid concentration indicates that undissociated pyridinium picrate and picrate ion have about the same molar extinction coefficient. The slope of the line of Fig. 2 corresponds to a molar extinction coefficient of 1.05×10^4 l./mole cm. The same value was obtained for solutions of tetramethylammonium picrate, a compound that is completely dissociated into ions in dilute nitrobenzene solutions.[7]

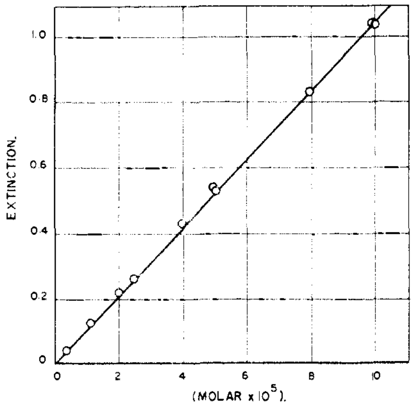
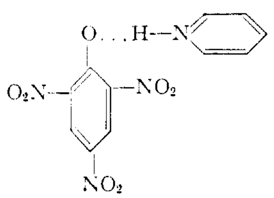


Fig. 2.—Extinction of solutions of pyridinium picrate (circles) and of sodium picrate (circles with tails). The calculated ratio $[\mathrm{PyHPi}]/[\mathrm{Pi}^-]$ was 0.04 at the lowest concentration and 0.22 at the highest. The ratio $[\mathrm{NaPi}]/[\mathrm{Pi}^-]$ was 0.30 at the lowest concentration and 1.4 at the highest.

Figure 2 also shows the extinction of sodium picrate. This compound is a weak electrolyte in nitrobenzene, the dissociation constant being 2.8×10^{-5} at 25°.[7] From the results of Fig. 2 it can be concluded that neither hydrogen bond formation (in I) nor ion pair formation (in II) appreciably affects the absorption of visible light, at least at 430 mμ, by the picrate ion.



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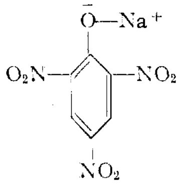

II

As a consequence, the ionic dissociation of pyridinium picrate cannot be determined spectrophotometrically. It should be mentioned that Davis and MacDonald found that the absorption spectra, in the visible region, of tribenzylammonium picrate, which contains a hydrogen bond, and of tetramethylammonium picrate, which exists as an ion pair, were slightly different in the solvent benzene.[10]

The molecular dissociation constant of pyridinium picrate was calculated from the extinctions of solutions of pure pyridinium picrate. In these solutions the formation of pyridinium pyridine (see below) and the formation of solvated proton (by reaction 1) can be neglected. The principal equilibria are therefore reactions (3) and (4). It is apparent that

$$E/\epsilon = [\mathrm{PyHPi}] + [\mathrm{Pi}^-] \quad (4a)$$

and

$$[\mathrm{HPi}] = C - E/\epsilon$$

where C is the total concentration of pyridinium picrate. Combination of equation (4a) with (4) yields the following equation from which the picrate ion concentration can be calculated

$$[\mathrm{Pi}^-] = -K_4/2 + \sqrt{K_4^2/4 + K_4E/\epsilon}$$

where the value 5.5×10^{-5} given by Witschonke and Kraus[7] is used for K_4. The value of K_3 can be calculated by means of the following equation, which is obtained by dividing (3) by (4).

$$[\mathrm{Py}][\mathrm{HPi}]/[\mathrm{PyH}^+][\mathrm{Pi}^-] = [\mathrm{HPi}]^2/[\mathrm{Pi}^-]^2 = K_3/K_4$$

The experimental results are given in Fig. 3. Ac-

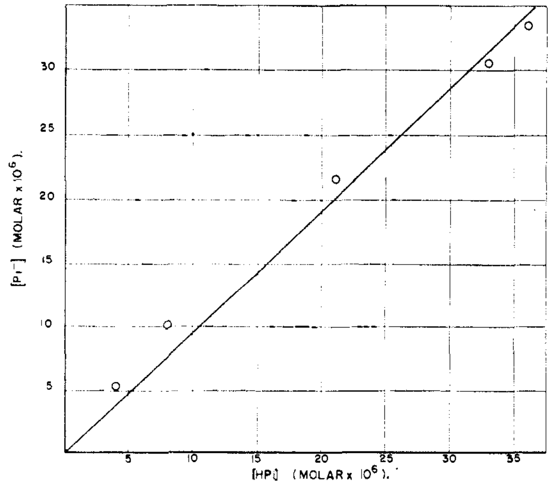

Fig. 3.—Determination of molecular dissociation constant of pyridinum picrate. Total analytical concentrations of pyridinium picrate, 1, 2, 5, 8 and 9 $\times 10^{-5}$ *M*. Measured extinctions, 0.063, 0.126, 0.315, 0.493 and 0.567, respectively.

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(7) C. R. Witschonke and C. A. Kraus, THIS JOURNAL, **69**, 2472 (1947).

(8) M. A. Elliot and R. M. Fuoss, *ibid.*, **61**, 294 (1939).

(9) E. G. Taylor and C. A. Kraus, *ibid.*, **69**, 1731 (1947).

(10) M. M. Davis and E. A. MacDonald, *J. Research Natl. Bur. Standards*, **42**, 595 (1949).

cording to the equation above a plot of [Pi$^-$] *vs.* [HPi] should be a straight line with slope $\sqrt{K_3/K_4}$. From the slope of the line of Fig. 3 the value of K_3 is calculated to be 6 × 10^{-5} at 25° as compared to the value 1.6 × 10^{-5} obtained by Witschonke and Kraus from conductivity measurements.[7] The latter value is probably more accurate and is used in the calculations that follow.

Formation and Dissociation of Pyridinium Pyridine.—Because of the possibility of hydrogen bond formation, the ion PyHPy$^+$ would be expected to be stable in solutions containing a Brønsted acid and a sufficiently high concentration of pyridine.

$$\text{PyHPy}^+ = \text{PyH}^+ + \text{Py};$$
$$K_5 = [\text{PyH}^+][\text{Py}]/[\text{PyHPy}^+] \quad (5)$$

The value of K_5 cannot be found from spectrophotometric measurements in the visible region but fortunately can be calculated from conductivity data reported by Witschonke and Kraus.[7]

In a solution containing pyridinium picrate and a relatively large concentration of pyridine the principal equilibria are reaction (5) and the ionic dissociation of pyridinium picrate, reaction (4). The molecular dissociation, reaction (3), is suppressed by excess pyridine and can be neglected. It is convenient to define a new quantity, K_{app}, by the equation

$$K_{\text{app}} = \frac{([\text{PyH}^+] + [\text{PyHPy}^+])[\text{Pi}^-]}{[\text{PyHPi}]} \quad (6)$$

If PyHPy$^+$ is considered to have properties similar to those of PyH$^+$, K_{app} is the *apparent* ionic dissociation constant of pyridinium picrate. The dependence of K_{app} on the concentration of pyridine is found by combining equations (4), (5) and (6)

$$K_{\text{app}} = K_4[1 + [\text{Py}]/K_5]$$

If the ratio of concentrations of pyridine and pyridinium picrate is much greater than unity, [Py] is approximately equal to the total concentration of free pyridine. The values of K_{app} given by Witschonke and Kraus were plotted against initial pyridine concentration. A straight line was obtained from which the value of K_5 was found, by dividing intercept by slope, to be 1.8 × 10^{-2} at 25°.

It should be noted that this value is based on the assumption that the specific conductance of the pyridinium pyridine ion and that of the solvated pyridinium ion are equal. From the conductivity data[7] it is concluded that the incorrectness of this assumption cannot introduce an error in K_5 greater than about 20%.

Reaction of Iodine Monochloride and Pyridine.—Although iodine monochloride can be considered, in the Lewis sense, to be a neutralization product of the unipositively charged iodine ion and the chloride ion, it can also be regarded as a Lewis acid since the iodine atom in iodine monochloride can share a pair of electrons provided by a suitable base. An equivalent statement is that the uni-positively charged iodine atom is a dibasic Lewis acid.

Carlsohn[11] has demonstrated that under suitable experimental conditions compounds of the type Py–I–X and also of the type Py–I–Py$^+$ X$^-$ are relatively stable in acetone and methanol solutions, the symbol X$^-$ representing the anion of a Brønsted acid (*i.e.*, an "acid radical"). We have studied the reaction of iodine monochloride with pyridine in both nitrobenzene and chloroform as solvents. The extinction coefficient of iodine monochloride in chloroform is shown by curve I, Fig. 4. Curve II represents a mixture of pyridine and iodine monochloride in the molar ratio 25:1. Figure 5 shows the result of a titration of iodine monochloride in chloroform with pyridine. Line I is the extinction of the titration mixture at 330 mμ, a wave length at which the absorption by the iodine monochloride–pyridine complex is strong, and line II is the extinction at 460 mμ, the wave length of maximum absorption by uncombined iodine monochloride. It is evident from the figure that the complex contains equimolar amounts of the two compounds and is PyICl.

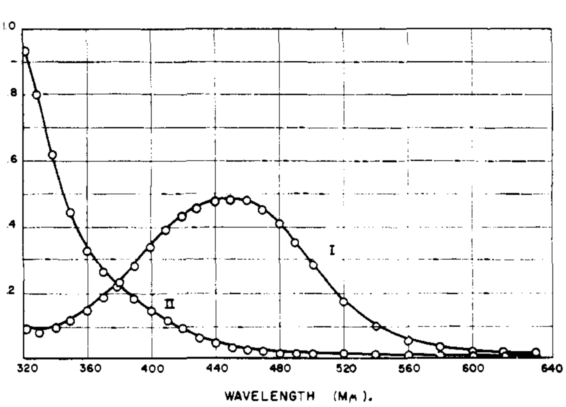

Fig. 4.—Absorption spectra of 0.004 *M* iodine monochloride (I) and of mixture of 0.1 *M* pyridine and 0.004 *M* iodine monochloride (II) in chloroform.

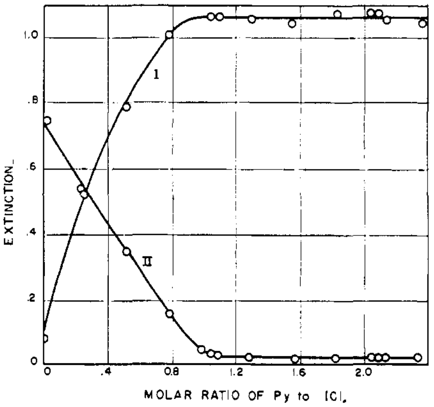

Fig. 5.—Titration of iodine monochloride (5 × 10^{-3} *M*) with pyridine in chloroform: I, at 330 mμ; II, at 260 mμ.

The results of a similar titration, in which nitrobenzene was used as solvent, are given in Fig. 6. The formation of PyICl is so nearly quantitative at all stages of titration that the dissociation constant, K_7, cannot be evaluated from the titration curve.

$$\text{PyICl} \rightleftharpoons \text{Py} + \text{ICl};\ K_7 = [\text{Py}][\text{ICl}]/[\text{PyICl}] \quad (7)$$

Competition of Iodine Monochloride and Picric Acid for Pyridine.—The dissociation constant of PyICl can be determined by measuring spectro-

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[11] H. Carlsohn, "Uber eine neue Klasse von Verbindungen des positiv einwertigen Iods," S. Hirzel, Leipzig, 1932, p. 57; *Ber.*, **68**, 2209 (1935). See also J. Kleinberg, *J. Chem. Education*, **23**, 559 (1946).

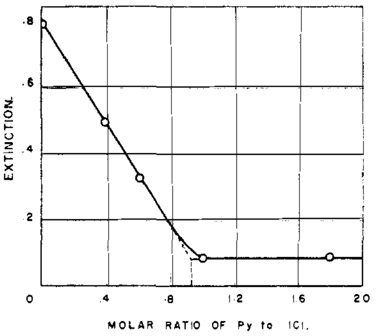

Fig. 6.—Titration of iodine monochloride (5×10^{-3} *M*) with pyridine in nitrobenzene (430 mμ).

photometrically the equilibrium concentration of PyHPi in a mixture containing pyridine, picric acid, and iodine monochloride. The latter two acids compete for the pyridine provided that an excess of pyridine is not used.

$$\mathrm{PyICl + HPi \rightleftarrows ICl + PyHPi;}$$
$$K_8 = [\mathrm{ICl}][\mathrm{PyHPi}]/[\mathrm{PyICl}][\mathrm{HPi}] \quad (8)$$

In addition to reaction (8), the molecular and ionic dissociations of PyHPi, reactions (3) and (4), must be taken into account. The formation of solvated proton (by reaction 1) and the formation of $\mathrm{PyHPy^+}$ and $\mathrm{PiHPi^-}$ can be neglected. The absorption of light of 430 mμ by ICl and PyICl in the equilibrium mixtures is negligible.

From the fact that the concentrations of pyridinium and picrate ions are equal and from equations (4) and (4a), the following equation is derived

$$[\mathrm{PyHPi}] = K_4/2 + E/\epsilon - \sqrt{K_4^2/4 + K_4E/\epsilon}$$

The concentrations of the other species in equation (8) were calculated from the relations

$$[\mathrm{HPi}] = C - E/\epsilon$$
$$[\mathrm{PyICl}] = B - E/\epsilon - K_3[\mathrm{PyHPi}]/[\mathrm{HPi}]$$
$$[\mathrm{ICl}] = A - [\mathrm{PyICl}]$$

where *A*, *B* and *C* are the total, analytical concentrations of iodine monochloride, pyridine and picric acid, respectively. From the results given in Table I it is concluded that K_8 is approximately 5×10^{-2} and K_7, which is equal to K_3K_8, is approximately 9×10^{-7} at 25°.

The calculated value of K_8 is very sensitive to errors in the initial concentrations of reactants. In the first experiment of Table I, for example, if the value of *A* (total concentration of iodine monochloride) is assumed to be 2% larger than the value given, and if *B* (total concentration of pyridine) is assumed to be 2% smaller, the calculated value of K_8 is 0.053 instead of 0.035. Small amounts of impurities, such as water, which cause shifts in the equilibria, or which cause the extinction to change (*e.g.*, by reaction with iodine monochloride and consequent formation of iodine) also influence the calculated constant. In the first experiment of Table I a 3% increase in extinction would cause the calculated value of K_8 to change from 0.035 to 0.047. The variations observed in the values of K_8 of Table I are therefore considered to be within the experimental limits of error.

Competition of Antimony Trichloride and Picric Acid for Pyridine.—Equilibrium constants of reactions involving pyridine antimony trichloride, $\mathrm{PySbCl_3}$, were determined by the method described for PyICl.

$$K_9 = [\mathrm{SbCl_3}][\mathrm{PyHPi}]/[\mathrm{PySbCl_3}][\mathrm{HPi}];$$
$$K_{10} = [\mathrm{Py}][\mathrm{SbCl_3}]/[\mathrm{PySbCl_3}]$$

The values of K_9 and K_{10} were found to be approximately 5×10^{-2} and 8×10^{-7}, respectively, at 25°. The variation in the values of K_9 obtained from different reaction mixtures was somewhat larger than the variation of K_8 of Table I. Because of these discrepancies the values of K_9 and K_{10} are considered provisional.

Table I

Competition of Iodine Monochloride and Picric Acid for Pyridine[a]

A	*B*	*C*	*E*	[Py-HPi]	[HPi]	[Py-ICl]	[ICl]	K_8
60	100	100	0.451	14.6	57	52.7	7.2	0.035
100	100	100	.325	8.9	69	66.9	33.1	.064
140	100	100	.189	3.7	82	81.3	58.7	.033
200	200	250	.609	22.6	192	140.1	59.9	.050
200	200	100	.461	15.1	56	151.6	48.4	.086
200	200	50	.283	7.1	23	168.5	32.0	.059
							Average	0.05

[a] All concentrations expressed as molar $\times 10^6$.

Competition of Antimony Trichloride and Picric Acid for Aniline.—It is not possible to study the acid–base reaction between aniline and iodine monochloride, because the aniline readily undergoes substitution. However, the acid–base reaction between aniline and antimony trichloride can be investigated by the method described in the last section.

$$K_{11} = [\mathrm{SbCl_3}][\mathrm{AnHPi}]/[\mathrm{AnSbCl_3}][\mathrm{HPi}];$$
$$K_{13} = [\mathrm{An}][\mathrm{SbCl_3}]/[\mathrm{AnSbCl_3}]$$

The values of the molecular and ionic dissociation constants, K_{13} and K_{14}, of anilinium picrate were found by Witschonke and Kraus to be 8.0×10^{-3} and 2.0×10^{-5}, respectively.[7] The constants K_{11} and K_{12} were found to have the approximate values 3×10^{-3} and 2×10^{-5}, respectively, at 25°.

Discussion

In the present work it was found convenient to extend Lewis' original concept of acid–base reactions to include reactions in which hydrogen bonds are formed as well as reactions in which the newly created bonds are largely covalent (see also reference[12]). Thus, undissociated picric acid, pyridinium ion and anilinium ion are, for convenience, considered to be Lewis acids. The proton is regarded as a divalent acid: it can, for example, combine with a pyridine molecule to form $\mathrm{PyH^+}$ or with two pyridine molecules to form $\mathrm{PyHPy^+}$ (compare with $\mathrm{HF_2^-}$). The proton is therefore considered to be analogous to the unipositively charged iodine ion.

The acid strengths, with respect to a given base in a given solvent, of a series of Lewis acids bear the same ratios to one another as do the reciprocals of the dissociation constants of the corresponding neutralization products. Likewise, base strengths

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(12) M. M. Davis, This Journal, **71**, 3544 (1949).

with respect to a given acid are in the ratio of the reciprocals of the dissociation constants of corresponding neutralization products. The values of the dissociation constants of the compounds investigated are summarized in Table II and the logarithms of the reciprocals of these constants, denoted by pK, are represented graphically in Fig. 7.

TABLE II

DISSOCIATION CONSTANTS AT 25 ± 3°

Acids	Bases Py	 An	 Pi$^-$
ICl	$K_7 = 9 \times 10^{-7}$	....	....
SbCl$_3$	$K_{10} = 8 \times 10^{-7}$	$K_{12} = 2 \times 10^{-5}$	....
HPi	$K_3 = 1.6 \times 10^{-5\,a}$	$K_{13} = 8.0 \times 10^{-3\,a}$	$K_2 > 10^{-2}$
PyH$^+$	$K_5 = 1.8 \times 10^{-2}$	....	$K_4 = 5.5 \times 10^{-5\,a}$
AnH$^+$	....	....	$K_{14} = 2.0 \times 10^{-5\,a}$
H$^+$	$K_{15} = 1.0 \times 10^{-8}$	$K_{16} = 1.4 \times 10^{-5}$	$K_1 = 3.5 \times 10^{-8}$
H$^+$ (in water)	$K'_{15} = 4.5 \times 10^{-6}$	$K'_{16} = 2.1 \times 10^{-5}$	$K'_1 = 2.9 \times 10^{-1\,b}$

[a] Values given by Witschonke and Kraus.[7] [b] Value given by v. Halban and Seiler.[2]

The dissociation constants of the pyridinium and anilinium ions in nitrobenzene were computed from the values of other dissociation constants.

$$K_{15} = [H^+][Py]/[PyH^+]; \quad K_{16} = [H^+][An]/[AnH^+]$$

It is easily demonstrated that K_{15} is equal to K_1K_3/K_4 and that K_{16} is equal to K_1K_{13}/K_{14}.

It must be kept in mind that the values of pK are not dependent solely on the decrease in free energy of formation of the bond between acid and base. Significant changes in solvation energy of the acid, base and neutralization product are also involved. In the case of the hydrogen acids the energy changes occurring when acid and base react may include an additional term. When picric acid, for example, reacts with pyridine a covalent bond is formed between the hydrogen atom of picric acid and the nitrogen atom of pyridine, and, simultaneously, the covalent bond between that same hydrogen atom and the picrate radical is replaced by an electrostatic bond (hydrogen bond).[13] The terms acid strength and base strength as commonly used refer to the free energy change of the over-all acid–base reaction and consequently pK or $1/K$, rather than a particular bond energy, is the proper measure of acid and base strength.

From Fig. 7 it is seen that antimony trichloride is about 20 times stronger than picric acid with respect to the base pyridine but about 400 times stronger with respect to aniline. The same comparison may be made in another way: pyridine is about 25 times stronger than aniline with respect to the acid antimony trichloride but with respect to picric acid, pyridine is 500 times stronger than aniline.

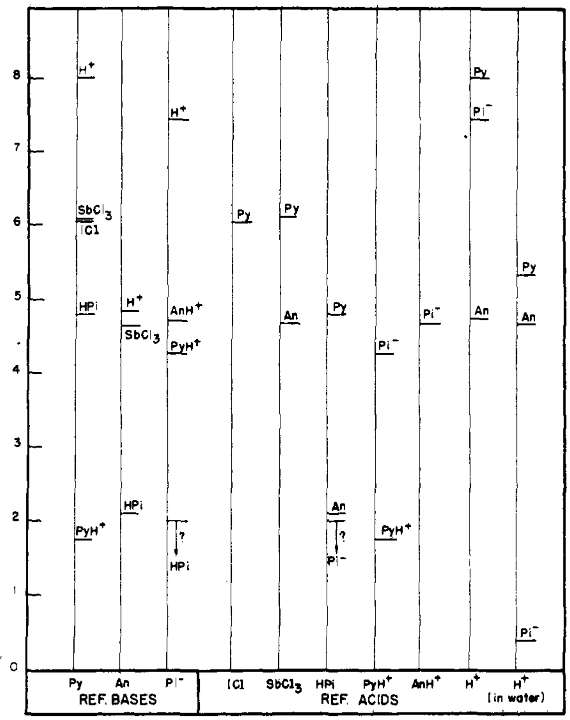

Fig. 7.—Comparison of strengths of acids and bases in nitrobenzene at 25°.

The order of acid strengths of picric acid and pyridinium ion changes if the reference base is changed from pyridine to picrate ion. This particular reversal of order is reasonable in view of the charge types of the acids and bases involved.

The order of base strength, toward the solvated hydrogen ion, of picrate ion and aniline is reversed if the solvent is changed from nitrobenzene to water. This reversal is ascribed chiefly to the charge types involved and to the high dielectric constant of water.

It may be concluded that the magnitude, and in some instances even the order, of strengths of a series of acids in a given solvent depends on the base chosen as reference, and *vice versa.*

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(13) C. A. Kraus, *J. Phys. Chem.*, **43**, 231 (1939).