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Acid-Base Equilibria in Acetonitrile. Spectrophotometric and Conductometric Determination of the Dissociation of Various Acids¹

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The indicators *o*-nitroaniline, *o*-nitro-*p*-chloroaniline and *o*-nitrodiphenylamine are about 5×10^4 as strong in acetonitrile as in water. Perchloric acid behaves as a strong acid, other acids denoted by HA are weak. Except in extremely dilute solutions hydrobromic, sulfuric, nitric and hydrochloric acids dissociate according to $2\text{HA} \rightleftharpoons \text{H}^+ + \text{AHA}^-$. The over-all dissociation constants of these acids have been determined spectrophotometrically with the aid of indicator bases and conductometrically for sulfuric and picric acids. By other suitable methods the stability constants $K_{\text{AHA}^-} = \frac{[\text{AHA}^-]}{[\text{HA}][\text{A}^-]}$ have been evaluated. The value of K_{AHA^-} decreases from 1.3×10^3 for sulfuric acid to 2.5×10^2 for hydrobromic, and 2×10^2 for nitric and hydrochloric acids at 25°. From the above data the simple dissociation constants $K_{\text{HA}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$ could be evaluated. These values for pK_{HA} are reported: hydrobromic, 5.5; sulfuric, 7.25; nitric and hydrochloric acids, 8.9. Picric acid at concentrations smaller than 0.1 *M* dissociates into H^+ and Pi^- , and $pK_{\text{HPi}} = 8.9$. At higher concentrations the data fit a dissociation $3\text{HPi} \rightleftharpoons \text{H}^+ + \text{Pi}(\text{HPi})_2^-$, $pK_{3(\text{HPi})} = 6.1$. The ion pair dissociation constants of tetraethylammonium bisulfate and of lithium nitrate were found to be 1.4×10^{-3} and 4.1×10^{-4} , respectively.

Introduction

No exact data on the dissociation of acids in acetonitrile (AN) as a solvent are found in the literature. In the present paper, quantitative data are presented on the kind and degree of dissociation of fresh solutions of various acids in AN. It has been observed in this Laboratory that a considerable decrease of hydrogen ion concentration occurs when fresh solutions of acids in AN are allowed to stand. Quantitative data and an interpretation of this aging effect will be described in a subsequent paper.

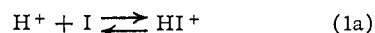
In the present work the hydrogen ion concentration has been determined spectrophotometrically using uncharged indicator bases in fresh solutions of hydrobromic, sulfuric, hydrochloric, nitric and picric acids and also in bisulfate-sulfuric acid mixtures. In picric acid solutions, picrate ion concentration was determined spectrophotometrically.

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(2) From the experimental part of the Ph.D. thesis submitted by M. K. Chantooni, Jr., to the University of Minnesota, December 1960.

Use of picric acid as indicator for hydrogen ion concentration in some buffer solutions has been made. Also, conductance data are presented for fresh solutions of picric and sulfuric acids.

Perchloric acid is completely dissociated in AN,³ a statement which has been confirmed in this work. Before applying some Hammett indicators to the determination of the hydrogen ion concentration in solutions of weak acids, it is necessary to determine their indicator constant K_I (eq. 1b) and to show that the reaction between the uncharged indicator base I and hydrogen ions is represented by the simple equation



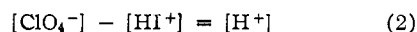
in which H^+ is the solvated proton. The equilibrium constant for this reaction is

$$K_I = \frac{[\text{HI}^+]f_{\text{HI}^+}}{[\text{I}][\text{H}^+]f_{\text{I}}f_{\text{H}^+}} \quad (1b)$$

where f denotes the conventional activity coefficient. In order to understand the kind of plots of our experimental data, we first consider equilibria involved in solutions containing various types of acid-base systems.

(3) J. F. Coetzee and I. M. Kolthoff, *J. Am. Chem. Soc.*, **79**, 6110 (1957).

Reaction of Perchloric Acid with Uncharged Indicator Bases.—In solutions of perchloric acid and indicator base



Substituting equation 1b into 2 yields

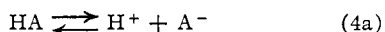
$$[\text{ClO}_4^-] - [\text{HI}^+] = \frac{[\text{HI}^+]f_{\text{HI}^+}}{K_1[\text{I}]f_{\text{I}}} \quad (3a)$$

In dilute solutions it is reasonable to assume that $f_{\text{HI}^+} = f_{\text{H}^+}$ and that $f_{\text{I}} = 1$. Thus

$$\log \{[\text{ClO}_4^-] - [\text{HI}^+]\} = \log \frac{[\text{HI}^+]}{[\text{I}]} - \log K_1 \quad (3b)$$

Experimentally [I] is determined directly by spectrophotometric measurement and $[\text{HI}^+]$ is found by difference from the known total analytical concentration of indicator, while $[\text{ClO}_4^-]$ is equal to the analytical concentration of perchloric acid. Thus a plot of the left hand side of equation 3b vs. $\log [\text{HI}^+]/[\text{I}]$ should be a straight line of slope one and intercept equal to $-\log K_1$. Actually, the straight line relation has been found to be obeyed with *o*-nitroaniline, *o*-nitro-*p*-chloroaniline and *o*-nitrodiphenylamine in perchloric acid solutions (Fig. 1).

Reaction of Hydrobromic, Sulfuric, Hydrochloric and Nitric Acids with Uncharged Indicator Bases.—Knowing the indicator constants, the hydrogen ion concentration of solutions of these weak acids was determined spectrophotometrically using the above indicators. It appeared that in not too dilute solutions the dissociation was not accounted for by the simple reaction



Acetonitrile is a poor solvating solvent and the A^- ions are stabilized by association with HA ^{4,5}



The constants corresponding to eq. 4a and 4b are

$$K_{\text{HA}} = \frac{[\text{H}^+][\text{A}^-]f_{\text{H}^+}f_{\text{A}^-}}{[\text{HA}]f_{\text{HA}}} \quad (5a)$$

$$K_{\text{AHA}^-} = \frac{[\text{AHA}^-]f_{\text{AHA}^-}}{[\text{A}^-][\text{HA}]f_{\text{A}^-}f_{\text{HA}}} \quad (5b)$$

The electroneutrality rule for a solution of a weak acid in presence of indicator base yields

$$[\text{H}^+] + [\text{HI}^+] = [\text{A}^-] + [\text{AHA}^-] \quad (6)$$

Neglecting activity coefficients (the ionic strength is very low), and substituting equations 1b, 5a and 5b into equation 6 yields

$$\frac{[\text{HI}^+]}{[\text{I}]} = K_1 \sqrt{K_{\text{HA}}[\text{HA}] \frac{\{1 + K_{\text{AHA}^-}[\text{HA}]\}}{\{1 + K_1[\text{I}]\}}} \quad (7)$$

when $1 \ll K_{\text{AHA}^-}[\text{HA}]$, equation 7 may be written

$$\log \frac{[\text{HI}^+]}{[\text{I}]} \sqrt{1 + K_1[\text{I}]} = \log K_1 \sqrt{K_{\text{HA}}K_{\text{AHA}^-}} + \log [\text{HA}] \quad (8)$$

With all weak acids investigated [HA] was practically equal to the analytical concentration of the acids. Thus, when equations 4a and 4b account quantitatively for the dissociation of weak acids, plots of $\log [\text{HI}^+]/[\text{I}] \sqrt{1 + K_1[\text{I}]}$ vs. $\log [\text{HA}]$

should be linear with slope one according to equation 8. As shown in the experimental part (Fig. 2) the linear relationship was obeyed by all weak acids investigated.

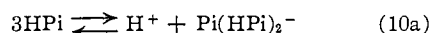
Picric Acid (HPi).—No indicator is needed for the determination of the simple or associated picrate ion concentration $[\text{Pi}^-]$, as this is determined directly by spectrophotometric measurement. It was found that in solutions more dilute than 0.1 *M*, equation 4a quantitatively accounts for the dissociation of the acid. Under these conditions

$$\log [\text{Pi}^-] = 1/2 \log K_{\text{HPi}} + 1/2 \log [\text{HPi}] \quad (9)$$

writing concentrations instead of activities.

A plot of $\log [\text{Pi}^-]$ vs. $\log [\text{HPi}]$ should yield a straight line of slope $1/2$ from which $1/2 \log K_{\text{HPi}}$ is the intercept. Such a straight line relationship has been found in Fig. 4.

In solutions more concentrated than 0.1 *M* the simple relationship no longer was observed. A set of equations was derived, taking equilibrium 4b into account. However, the experimental data did not fit the final relationship. It was then assumed that at higher concentrations of the acid, the simple picrate ion reacts with two molecules of undissociated picric acid, resulting in the over-all dissociation



with a corresponding constant

$$K_{3(\text{HPi})} = \frac{[\text{H}^+][\text{Pi}(\text{HPi})_2^-]f_{\text{H}^+}f_{\text{Pi}(\text{HPi})_2^-}}{[\text{HPi}]^3f_{\text{HPi}}^3} \quad (10b)$$

When $\text{Pi}(\text{HPi})_2^-$ is the predominant picrate species present

$$[\text{H}^+] = [\text{Pi}(\text{HPi})_2^-]$$

Neglecting activity coefficients, equation 11 is obtained

$$\log [\text{Pi}(\text{HPi})_2^-] = 1/2 \log K_{3(\text{HPi})} + 3/2 \log [\text{HPi}] \quad (11)$$

Under the specified conditions, a plot of $\log [\text{Pi}(\text{HPi})_2^-]$ vs. $\log [\text{HPi}]$ should yield a straight line with a slope of $3/2$. Equation 11 was found to be obeyed (Fig. 4) assuming the spectrum of $\text{Pi}(\text{HPi})_2^-$ to be the same as that of the picrate ion.

Conductance of Fresh Solutions of Weak Acids in Acetonitrile.—Dissociation constants of weak acids which dissociate in dilute solutions according to reaction 4a were determined by measuring the conductance as a function of weak acid concentration. Using the equation of Kraus and Bray⁶

$$\frac{1}{\Lambda} = \frac{C\Lambda}{K_{\text{HA}}\Lambda_0^2} + \frac{1}{\Lambda_0} \quad (12)$$

where Λ is the equivalent conductance and Λ_0 is the limiting equivalent conductance, a linear $1/\Lambda$ vs. $C\Lambda$ plot was obtained in picric acid solutions more dilute than 0.1 *M* (Fig. 5). Under our experimental conditions, the refined treatment of Fuoss and Kraus⁷ was unnecessary.

For acids that dissociate according to reaction 4b the conductance data were treated by the method proposed by French and Roe⁴ who plotted, in our notation, $\Lambda \sqrt{c[c + (1/K_{\text{AHA}^-})]}$ vs. c , according to equation 13. Plots according to equation 13

(4) C. M. French and I. G. Roe, *Trans. Faraday Soc.*, **49**, 314 (1953).

(5) E. Romberg and K. Cruse, *Z. Elektrochem.*, **63**, 404 (1959).

(6) C. A. Kraus and W. C. Bray, *J. Am. Chem. Soc.*, **35**, 1315 (1913).

(7) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 476, 2390 (1933).

$$\Lambda \sqrt{c \left[c + \frac{1}{K_{\text{AHA}^-}} \right]} = \Lambda_{0\text{HA}} \sqrt{\frac{K_{\text{HA}}}{K_{\text{AHA}^-}}} + c \Lambda_{\text{OH}^+(\text{AHA}^-)} \sqrt{K_{\text{HA}} K_{\text{AHA}^-}} \quad (13)$$

using various assumed values of K_{AHA^-} are entered in Fig. 3 for fresh solutions of sulfuric and hydrochloric acids. From spectrophotometric data we have found that in picric acid solutions more concentrated than 0.1 M the picrate ion is associated as $\text{Pi}(\text{HPi})_2^-$. French and Roe have derived a general conductivity expression applicable to systems containing "polymeric" ions of the type $(\text{HA})_r\text{A}^-$. When $r = 2$, their expression becomes, in our notation

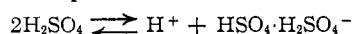
$$\Lambda \sqrt{c \left[\frac{1}{K_{\text{A}(\text{HA})_2^-}} \right]} = \Lambda_{0\text{HA}} \sqrt{\frac{K_{\text{HA}}}{K_{\text{A}(\text{HA})_2^-}}} + \Lambda_{\text{OH}^+[\text{A}(\text{HA})_2^-]} c^2 \sqrt{K_{\text{HA}} K_{\text{A}(\text{HA})_2^-}} \quad (14)$$

where

$$K_{\text{A}(\text{HA})_2^-} = [\text{A}(\text{HA})_2^-] / [\text{A}^-][\text{HA}]^2$$

Plots of $\Lambda \sqrt{c \left[\frac{1}{K_{\text{A}(\text{HA})_2^-}} + c^2 \right]}$ vs. c^2 at various assumed values of $K_{\text{A}(\text{HA})_2^-}$ are entered in Fig. 6. The plot becomes linear only at a certain value of $K_{\text{A}(\text{HA})_2^-}$.

Equilibria in Mixtures of Uncharged Acids and Singly Charged Anionic Bases. (a) **Sulfuric Acid-Bisulfate with Uncharged Indicator Base.**—In a mixture of tetraethylammonium bisulfate with a large excess of sulfuric acid, reaction 4b may be expected to occur quantitatively. The dissociation then corresponds to the over-all reaction



Equations 5a and 5b yield the relationship in

$$K_2(\text{HA}) = K_{\text{HA}} K_{\text{AHA}^-} = \frac{[\text{H}^+][\text{AHA}^-]}{[\text{HA}]^2} f_{\text{H}^+} f_{\text{AHA}^-} \quad (15)$$

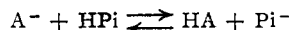
which f_{HA} has been assumed to be one. The solvated proton concentration has been determined in the mixtures with *o*-nitroaniline. Combining equations 1b and 15 yields

$$\frac{[\text{HA}]^2}{[\text{AHA}^-]} = \frac{f^2}{K_1 K_2(\text{HA})} \cdot \frac{[\text{HI}^+]}{[\text{I}]} \quad (16)$$

where $f = f_{\text{H}^+} = f_{\text{AHA}^-}$, calculated from the Debye-Hückel limiting law. Tetraethylammonium bisulfate in AN with an ion pair dissociation constant of 1.42×10^{-8} (Table IV) could be considered completely dissociated under our experimental conditions. Assuming that all the simple bisulfate ions react quantitatively with sulfuric acid, so that $[\text{HSO}_4 \cdot \text{H}_2\text{SO}_4^-]$ is the equilibrium salt concentration, the equilibrium concentration of sulfuric acid, $[\text{HA}]$, is the difference of the analytical concentration of sulfuric acid and simple bisulfate ion. According to equation 16 plots of $[\text{HA}]^2/[\text{AHA}^-]$ vs. $[\text{HI}^+]/[\text{I}]$ should be linear with a slope of $\frac{f^2}{K_1 K_2(\text{HA})}$. As is shown in Fig. 7, the above relationship was found to be obeyed. Since K_1 had been determined separately, the value of $K_2(\text{HA})$ became known.

(b) **Anionic Bases, Chloride and Nitrate, with Picric Acid.**—Simple dissociation of hydrochloric and nitric acids occurs in mixtures of picric acid ($c < 7 \times 10^{-5} M$) with very dilute solutions of

tetramethylammonium chloride ($0.4 \times 10^{-5} M < c < 2.8 \times 10^{-5} M$) or lithium nitrate ($2.8 \times 10^{-5} M < c < 2.8 \times 10^{-4} M$). Picric acid and the anionic base, A^- , react



In these systems, the equilibrium concentrations of both A^- and HA are so small that AHA^- formation is negligible. Substituting the relation $a_{\text{HPi}}/a_{\text{Pi}^-} \cdot K_{\text{HPi}} = a_{\text{H}^+}$ into equation 5a, and introducing the relation $[\text{HA}] = [\text{Pi}^-]$ from reaction 4a, equation 17 is obtained

$$\frac{[\text{Pi}^-]^2}{[\text{HPi}]} = \frac{K_{\text{HPi}}}{K_{\text{HA}}} [\text{A}^-] \quad (17)$$

Activities can be assumed equal to concentrations in these dilute solutions. The equilibrium concentration $[\text{A}^-]$ equals $\{\alpha_1 c_{\text{salt}} - [\text{Pi}^-]\}$ where α_1 is the degree of dissociation of lithium nitrate (or tetramethylammonium chloride) calculated from the appropriate ion pair dissociation constant. Linear plots of $[\text{A}^-]$ vs. $[\text{Pi}^-]^2/[\text{HPi}]$ as predicted from equation 17 were found and are presented in Fig. 8. From the slope of the plot and the value of $K_{\text{HPi}} = 1.3 \times 10^{-9}$, K_{HA} can be calculated.

(c) **Bisulfate and Bromide with Picric Acid as Indicator.**—In mixtures of picric acid ($c < 7 \times 10^{-5} M$) with either dilute solutions of tetraethylammonium bisulfate ($10^{-4} M < c < 10^{-3} M$) or bromide ($0.002 M < c < 0.008 M$), picric acid and the anionic base react



where A^- represents either bisulfate or bromide. The equilibrium constant for reaction 18 is obtained by dividing equation 5a by 5b and substituting $\frac{a_{\text{HPi}}}{a_{\text{Pi}^-}} \cdot K_{\text{HPi}}$ for a_{H^+} yielding

$$\frac{K_{\text{AHA}^-}}{K_{\text{HA}}} = \frac{a_{\text{AHA}^-} a_{\text{Pi}^-}}{a_{\text{A}^-}^2 a_{\text{HPi}} K_{\text{HPi}}} \quad (18b)$$

According to equation 18a $[\text{AHA}^-] = [\text{Pi}^-]$. It is seen that ionic activity coefficients cancel assuming f_{Pi^-} , f_{AHA^-} , and f_{A^-} are all equal. Thus we obtain

$$\frac{[\text{Pi}^-]^2}{[\text{HPi}]} = \frac{K_{\text{AHA}^-} K_{\text{HPi}}}{K_{\text{HA}}} [\text{A}^-]^2 \quad (18c)$$

immediately, assuming f_{HPi} is one. The equilibrium concentration of bisulfate or bromide is $\{\alpha c_s - 2[\text{Pi}^-]\}$ where α is the degree of dissociation of the ion pair $\text{Et}_4\text{N}^+ \cdot \text{HSO}_4^-$ or $\text{Et}_4\text{N}^+ \cdot \text{Br}^-$ as calculated from the ion pair dissociation constant determined from conductance data (Table IV) and c_s is the analytical salt concentration. $[\text{Pi}^-]^2/[\text{HPi}]$ was found from spectrophotometric measurements as described above. Plots of $[\text{Pi}^-]^2/[\text{HPi}]$ vs. $[\text{HSO}_4^-]$ and $[\text{Br}^-]$, respectively, should yield straight lines passing through the origin with a slope $K_{\text{AHA}^-} K_{\text{HPi}}/K_{\text{HA}}$. The straight line relationship has been found as illustrated in Fig. 9. Since K_{HPi} and $K_{\text{HA}} K_{\text{AHA}^-}$ had been found by independent methods, the above method permitted us to find the individual values of K_{HA} and K_{AHA^-} .

Experimental

Solvent.—For our purposes the solvent AN should be very pure and free of ammonia and water. Commercial

grade AN is usually contaminated with water, which slowly hydrolyzes the solvent with the formation of acetamide, ammonium acetate and ammonia. Recommended procedures⁸ for purification start by shaking for less than 15 seconds ten parts of solvent with three parts of saturated potassium hydroxide and collecting the acetonitrile layer. The solvent thus obtained is about 0.01 *M* in potassium hydroxide and 5% in water. We found that acetic acid could be removed by shaking three liters of solvent for 24 hr. with 200 g. of freshly reactivated alumina (Alcoa product). The alumina was reactivated by heating at 250° for 4 hr. The solvent was decanted and the shaking repeated with reactivated alumina. The solvent was decanted and then shaken with 100–150 g. of anhydrous reagent grade calcium chloride, and this was repeated four times until the water content was less than 0.2%. This was followed by shaking the acetonitrile for 24 hr. with 100 to 150 g. of anhydrous magnesium sulfate and then for 1 hr. with 10 g. of Mallinckrodt reagent grade phosphorus pentoxide. The shaking with fresh phosphorus pentoxide was repeated.

The solvent was distilled at atmospheric pressure (b.p. 80.4° at 760 mm.) using a column 1 m. long and 2 cm. i.d., packed with stainless steel wool. The contents of the flask and the distillate were protected from atmospheric moisture with drying tubes filled with calcium chloride. The first and last 100 ml. of distillate were discarded. A 50–60% yield of pure solvent was obtained. The water content was determined by titrating a weighed portion of the solvent in pure methanol with Karl Fischer reagent.⁹ In various batches the water content varied from 0.7 to 2.0 millimolar (1 millimolar water corresponds to 0.0018%).

Traces of ammonia are formed in a solvent 1 to 2 millimolar in water after standing for a few months. Ammonia in a concentration of 10⁻⁶ *M* can be detected from the increase in absorption of 10⁻⁴ *M* picric acid at 420 m μ . The effect of 10⁻⁶ *M* ammonia was found equal to that of 7 \times 10⁻³ *M* water. Various batches of purified solvent contained less than 10⁻⁸ *M* ammonia. Ammonia in AN yields an anodic wave with half-wave potential of +0.25 volt *vs.* aqueous saturated calomel electrode (s.c.e.).³ Polarographically 10⁻⁴ *M* ammonia could be estimated. The picric acid test is more sensitive. The magnitude of the residual current at the d.m.e. in tetraethylammonium perchlorate serves as an indicator for the presence of acetic acid, which yields a wave at -2.3 volt *vs.* s.c.e.³ Our purified solvent gave a continuous curve for residual current until -2.8 volts *vs.* s.c.e., which is the cathodic limit in AN. The residual current was 0.04 μ a. at -0.2 volt, 0.2 μ amp. at -1.0 volt and 0.6 μ amp. at -2.4 volt. Polarographically it was found that the acetic acid content of various batches of purified solvent was less than 2 \times 10⁻⁴ *M*, and usually less than 1 \times 10⁻⁴ *M*.

The specific conductivity of various batches of purified solvent varied between 0.7 \times 10⁻⁷ and 1.5 \times 10⁻⁷ ohm⁻¹ cm.⁻¹.

The solvent was stored in one-liter Pyrex bottles with F 29 stoppers. When ready for use, an all glass siphon with a male F 29 joint was installed. The pressure within the system was equalized with that of the atmosphere by an opening in the siphon joint, protected from atmospheric moisture with a calcium chloride drying tube. The tip of the siphon was covered with a plug of Tygon tubing with a tight-fitting piece of glass rod inserted at the open end. The solvent was stored in the dark.

Chemicals. **Anhydrous Sulfuric Acid.**—The method described by Kuntzler¹⁰ was used to prepare anhydrous sulfuric acid. Analysis of samples of this acid dispensed from a stoppered weight buret into water gave 100.00 \pm 0.02% H₂SO₄ by alkalimetric titration and 100.00 \pm 0.05% H₂SO₄ by gravimetric determination as BaSO₄.

Anhydrous Hydrochloric Acid.—Matheson anhydrous hydrochloric acid from a tank was used without further purification. The gas was bubbled directly into the solvent through a capillary. Solutions of hydrochloric acid in AN were analyzed after flooding one volume of the solution in AN with twenty volumes of water and titrating with stand-

ard sodium hydroxide to a phenolphthalein end point. After acidifying the neutralized solution with nitric acid, chloride was determined by the Volhard titration. Good agreement between the alkalimetric and Volhard titration end points was obtained.

Solutions of Anhydrous Perchloric Acid in Acetonitrile.—Solutions of perchloric acid in anhydrous acetic acid were prepared as described by Coetzee⁸ and diluted with pure acetonitrile to the desired concentration of perchloric acid.

Anhydrous Hydrobromic Acid.—Anhydrous hydrobromic acid (Matheson product) from a tank was used without further purification. The acid content in acetonitrile solutions was determined by flooding one volume of solution with twenty volumes of water and titrated amperometrically at zero volt *vs.* s.c.e. with 0.1 *M* aqueous silver nitrate using the rotated platinum wire as indicator electrode.

Anhydrous Picric Acid.—Eastman Kodak White Label picric acid was recrystallized once from Merck Reagent Grade acetone and dried in a vacuum oven at 80° for 2 hr. Obsd. m.p. 121.5°, lit. value¹¹ 121.8°.

Anhydrous Nitric Acid.—This was obtained by mixing equivalent amounts of lithium nitrate (see below) and anhydrous perchloric acid, prepared as previously described.

Tetraethylammonium Bromide.—An Eastman Kodak White Label product was recrystallized from water and dried at 110° at atmospheric pressure.

Tetraethylammonium Bisulfate.—An aqueous solution of tetraethylammonium hydroxide (*ca.* 1 *M*) was prepared by shaking an aqueous tetraethylammonium bromide solution (Eastman Kodak White Label tetraethylammonium bromide) with an excess of silver oxide (Fisher Purified Grade) and filtering. The filtrate was neutralized to a phenolphthalein end-point with aqueous sulfuric acid. An equal volume of sulfuric acid solution then was added and the resulting solution evaporated to incipient dryness, the residue recrystallized from ethanol and dried at 110° and atmospheric pressure. Analysis of the salt gave 100.0% of the theoretical by alkalimetric titration and 99.8% gravimetrically as BaSO₄.

Tetramethylammonium Chloride.—Eastman Kodak White Label product was recrystallized once from ethanol and dried at atmospheric pressure at 80°.

Lithium Nitrate.—Mallinckrodt Reagent Grade product was recrystallized from ethanol and dried at 110°.

***n*-Butylamine.**—Matheson Practical Grade product was shaken over potassium hydroxide (Merck Reagent Grade), allowed to stand for one week and distilled at atmospheric pressure; b.p. 75–76° (735 mm.), lit. value¹¹ 77.8° (760 mm.).

***o*-Nitroaniline.**—A Matheson product was recrystallized from ethanol and dried 3 hr. at 60° at atmospheric pressure; m.p. 71°; lit. value¹¹ 71.5°.

***o*-Nitro-*p*-chloroaniline.**—An Eastman Kodak Yellow Label product was recrystallized from water and dried for 10 hr. at 60° *in vacuo*; m.p. 108°, lit. value¹¹ 107–108°.

***o*-Nitrodiphenylamine.**—A student preparation from the Organic Chemistry Division, University of Minnesota was recrystallized from ethanol and dried 10 hr. at 60° *in vacuo*; m.p. 75°, lit. value¹¹ 75.5°.

Spectrophotometry.—A Beckman Model B spectrophotometer was used with a slit width of 0.05 mm. at sensitivity 4 with the nitroaniline indicators. Absorbances of *o*-nitroaniline, *o*-nitro-*p*-chloroaniline and *o*-nitrodiphenylamine in AN were measured at 410, 410 and 430 m μ , respectively, corresponding to maximum absorptivity. At these wave lengths the molar absorptivities were 2.76 \times 10⁴, 2.71 \times 10⁴ and 3.68 \times 10⁴, respectively. Beer's law was obeyed in solutions of all three indicators from 2 \times 10⁻⁶ to at least 3 \times 10⁻⁵ *M*. Since the spectrum of 1.85 \times 10⁻⁵ *M* *o*-nitroaniline is the same in 0.056 *M* *n*-butylamine solutions as in pure solvent, it is concluded that the indicator is present entirely in its basic form in pure solvent. No detectable absorbance of *o*-nitroaniline and *o*-nitro-*p*-chloroaniline was found in 0.01 *M* and 0.05 *M* perchloric acid solutions, respectively, indicating complete conversion to the acid form. In 0.10 *M* perchloric acid 5 \times 10⁻⁵ *M* *o*-nitrodiphenylamine had an absorbance of 0.020. A Beckman DU spectrophotometer was used at 410–430 m μ with a slit width less than 0.01 mm. at photomultiplier sensitivity 4 for studying picrate spectra.

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(9) M. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 127.

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(11) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1958.

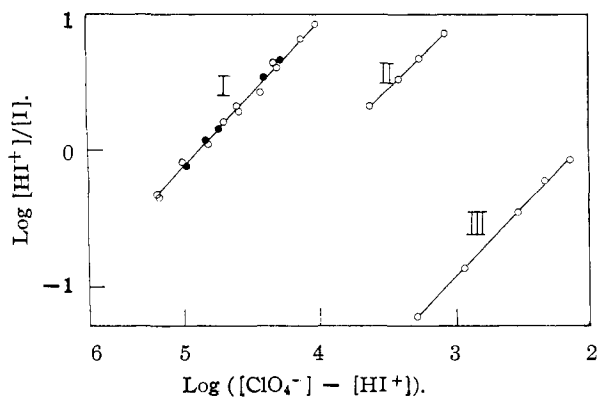


Fig. 1.—Nitroanilines in fresh solutions of perchloric acid. I, O, with $2.20 \times 10^{-5} M$ *o*-NA and ●, with $1.36 \times 10^{-5} M$ *o*-NA, slope = 1.04; II, $1.66 \times 10^{-5} M$ *o*-Np-ClA, slope = 0.920; III, $1.23 \times 10^{-5} M$ *o*-nitrodiphenylamine, slope = 1.06.

Stopped cylindrical Pyrex cells of 4.97 cm. path length were used with nitroaniline indicators and 1.75 cm. stopped cylindrical Pyrex cells with picric acid. In all cases water served as reference liquid. Cell path lengths were determined from the absorbance of cells filled with National Bureau of Standards potassium dichromate solution.¹² Each cell used had a mark etched on its neck. The cell volume of each cell was determined by weighing the cell filled to the mark with conductivity water. Experiments were run at room temperature, which was $25 \pm 1^\circ$.

Conductivity.—A Leeds and Northrup Jones Conductivity Bridge List No. 4666 operated at 1000 cycles/sec. in conjunction with a Heathkit 51 oscilloscope and Leeds and Northrup oscillator set at 1000 cycles/sec. were used for resistance measurements accurate to 0.01%. It was rarely necessary to use a 1000 μf . external capacitance.

Cell constants of 0.0175, 0.112 and 1.272, respectively, were determined with $10^{-3} M$ aqueous potassium chloride solution in the conventional way for three conductivity cells with leads 2 to 8 cm. apart and lightly platinized electrodes. The cells were placed in a light kerosene oil thermostat which was maintained at $25.0 \pm 0.005^\circ$. Acetonitrile in volumetric flasks was brought to constant temperature in the bath before preparation of solutions. The solution was transferred immediately to the cell, immersed in the bath. A series of measurements was taken at 5 to 10-minute intervals for the first 40 minutes after preparation and the specific conductances extrapolated to zero time.

Experimental Results

Values of $[\text{HI}^+]/[\text{I}]$ were determined in dilute perchloric acid solutions for the uncharged indicator bases *o*-nitroaniline, *o*-nitro-*p*-chloroaniline and *o*-nitrodiphenylamine. Plots of $\log [\text{HI}^+]/[\text{I}]$ vs. $\log \{[\text{ClO}_4^-] - [\text{HI}^+]\}$ according to equation 3b are presented in Fig. 1. Values of $-\log K_1 = pK_1$ are given in Table I.

TABLE I

ACIDITY CONSTANTS OF UNCHARGED INDICATOR BASES IN WATER AND ACETONITRILE^a

Indicator	$(pK_1)_{\text{H}_2\text{O}}^a$	$(pK_1)_{\text{AN}}$	$[(pK_1)_{\text{H}_2\text{O}} - (pK_1)_{\text{AN}}]$
<i>o</i> -Nitroaniline	-0.29	-4.85	5.14
<i>o</i> -Nitro- <i>p</i> -chloroaniline	1.03	-3.88	4.91
<i>o</i> -Nitrodiphenylamine	2.94	-2.01 ^b	4.95

^a Values taken from M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957). ^b Determined in 45-59% by weight H_2SO_4 in water using H_0 values reported by Paul and Long.

Spectrophotometric data for the reaction between the uncharged weak acids hydrochloric, hydrobromic, sulfuric and nitric acid, respectively, with the uncharged indicator bases *o*-nitroaniline and *o*-nitro-*p*-chloroaniline are given in

(12) G. W. Haupt, *J. Research Natl. Bureau Standards*, **48**, 414 (1952).

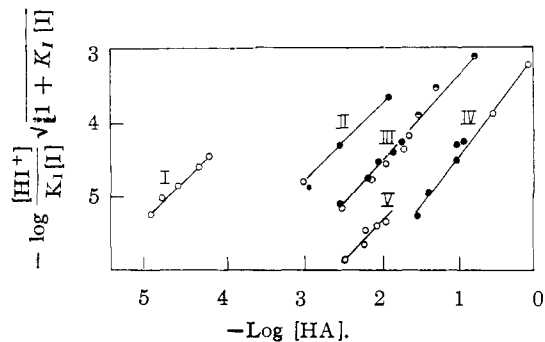


Fig. 2.—Weak acids with nitroaniline indicator bases. I, HClO_4 with $2.20 \times 10^{-5} M$ *o*-NA, ordinate in this case $-\log [\text{HI}^+]/[\text{I}]$, slope = 1.09; II, HBr , ●, with $4.08 \times 10^{-5} M$ *o*-N *p*-ClA, and ○, with $6.20 \times 10^{-5} M$ *o*-NA, slope = 1.04; III, H_2SO_4 , ●, with $1.68 \times 10^{-5} M$ *o*-NA, ○, with $4.85 \times 10^{-5} M$ *o*-NA, and ●, with $2.15 \times 10^{-5} M$ *o*-N *p*-ClA, slope = 1.09; IV, HCl , ●, with $6.15 \times 10^{-5} M$ *o*-NA, and ○, with $4.64 \times 10^{-5} M$ *o*-N *p*-ClA, slope = 1.28; V, HNO_3 with $8.7 \times 10^{-5} M$ *o*-NA, slope = 1.02.

Table II. Data for nitric acid were taken from a paper by Kolthoff and Ikeda¹³ and are incorporated in Fig. 2.

TABLE II

REACTION OF WEAK ACIDS WITH UNCHARGED INDICATOR BASES

c_{acid}	Indicator	$[\text{I}] \times 10^5$	$\frac{[\text{HI}^+]}{[\text{I}]} \times \sqrt{1 + K_1[\text{I}]}$	
Sulfuric acid				
1.18×10^{-3}	$1.68 \times 10^{-5} M$ <i>o</i> -NA ^a	1.17	0.66	
3.27×10^{-3}		0.915	1.08	
4.73×10^{-3}		.781	1.31	
6.90×10^{-3}		.621	2.10	
9.80×10^{-3}		.490	2.86	
13.8×10^{-3}		.370	4.04	
1.74×10^{-3}	$4.85 \times 10^{-5} M$ <i>o</i> -NA	3.90	0.48	
3.49×10^{-3}		3.22	0.93	
5.24×10^{-3}		2.74	1.32	
8.74×10^{-3}		2.09	2.10	
14.0×10^{-3}		1.46	3.34	
20.9×10^{-3}		1.00	4.96	
1.84×10^{-3}	$12.2 \times 10^{-5} M$ <i>o</i> -NA	7.96	1.36	
3.68×10^{-3}		6.55	2.08	
5.52×10^{-3}		5.39	2.71	
9.20×10^{-3}		3.85	4.22	
14.7×10^{-3}		2.50	5.07	
2.50×10^{-2}		1.00	4.96	
1.84×10^{-3}	$6.11 \times 10^{-5} M$ <i>o</i> -Np-ClA ^b	2.95	1.12	
4.02×10^{-3}		1.91	2.35	
15.5×10^{-3}		0.93	6.31	
Hydrochloric acid				
1.055×10^{-2}		$6.48 \times 10^{-5} M$ <i>o</i> -NA	5.43	0.43
3.01×10^{-2}			4.86	0.79
6.45×10^{-2}	3.15		2.32	
8.12×10^{-2}	2.07		3.84	
0.243×10^{-2}	1.78		1.15	
0.996×10^{-2}	0.68		4.73	
Hydrobromic acid				
5.45×10^{-4}	$6.21 \times 10^{-5} M$ <i>o</i> -NA	3.54	1.41	
7.48×10^{-4}		3.46	0.15	
19.1×10^{-4}		2.80	0.50	
82.0×10^{-4}		0.72	3.58	
Sulfuric acid				
1.18×10^{-3}		$1.68 \times 10^{-5} M$ <i>o</i> -NA ^a	1.17	0.66
3.27×10^{-3}	0.915		1.08	
4.73×10^{-3}	.781		1.31	
6.90×10^{-3}	.621		2.10	
9.80×10^{-3}	.490		2.86	
13.8×10^{-3}	.370		4.04	
1.74×10^{-3}	$4.85 \times 10^{-5} M$ <i>o</i> -NA	3.90	0.48	
3.49×10^{-3}		3.22	0.93	
5.24×10^{-3}		2.74	1.32	
8.74×10^{-3}		2.09	2.10	
14.0×10^{-3}		1.46	3.34	
20.9×10^{-3}		1.00	4.96	
1.84×10^{-3}	$12.2 \times 10^{-5} M$ <i>o</i> -NA	7.96	1.36	
3.68×10^{-3}		6.55	2.08	
5.52×10^{-3}		5.39	2.71	
9.20×10^{-3}		3.85	4.22	
14.7×10^{-3}		2.50	5.07	
2.50×10^{-2}		1.00	4.96	
1.84×10^{-3}	$6.11 \times 10^{-5} M$ <i>o</i> -Np-ClA ^b	2.95	1.12	
4.02×10^{-3}		1.91	2.35	
15.5×10^{-3}		0.93	6.31	

^a *o*-Nitroaniline; ^b *o*-nitro-*p*-chloroaniline.

Plots of $\log [\text{HI}^+]/[\text{I}] \sqrt{1 + K_1[\text{I}]}$ vs. $\log [\text{HA}]$, according to equation 8, are entered in Fig. 2. These plots are linear with slopes of 0.8 to 1.3. When $\log [\text{HI}^+]/[\text{I}] \sqrt{1 + K_1[\text{I}]} = 0$, $\log [\text{HA}] = -\log K_1 \sqrt{K_{\text{HA}} K_{\text{AHA}^-}}$. Knowing K_1 from the reaction of nitroaniline indicator bases with perchloric acid, the values of $K_{\text{HA}} K_{\text{AHA}^-}$ were found for the

(13) I. M. Kolthoff and S. Ikeda, *J. Phys. Chem.*, **65**, 1020 (1961).

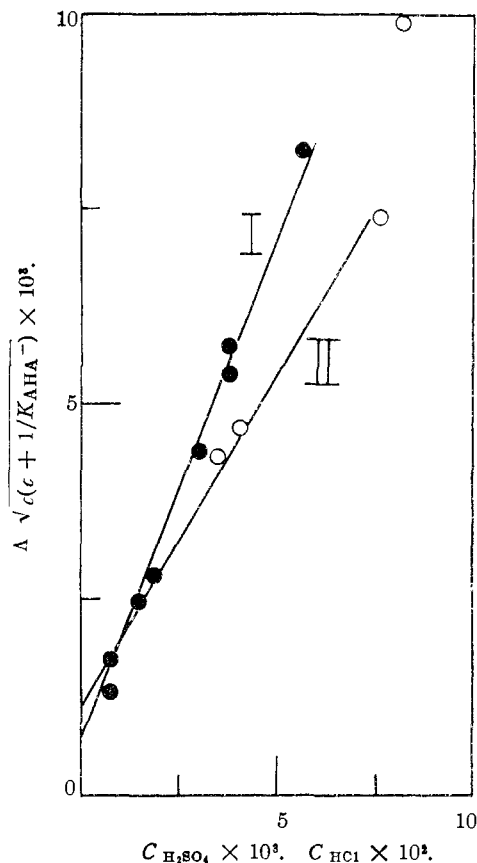


Fig. 3.— $\Lambda \sqrt{c(c + 1/K_{AHA^-})}$ vs. c_{HA} plots for sulfuric and hydrochloric acids: I, H_2SO_4 , $1/K_{AHA^-} = 0.4 \times 10^{-3}$; intercept = 0.70×10^{-3} , slope = 1.04; II, HCl , $1/K_{AHA^-} = 0.58 \times 10^{-3}$, intercept = 1.17×10^{-3} , slope = 0.107.

above weak acids. Their negative logarithms, $-\log K_{HA}$, $K_{AHA^-} = pK_{2(HA)}$, are listed in Table III.

TABLE III

DISSOCIATION CONSTANTS OF WEAK ACIDS IN ACETONITRILE

Acid	pK_{HA}	pK_{AHA^-}	$pK_{2(HA)}$	$[pK_{AHA^-} - pK_{HA}]^d$	$pK_{A(HA)_2}$	$-pK_{3(HA)}$
H ₃ r	5.51 ^{c,d}	-2.43 ^{c,d}	3.08	-7.95
H ₂ SO ₄	7.32 ^{c,d}	-3.06 ^{c,d}	4.26	-10.38
	7.21 ^e	-3.40 ^e
HNO ₂	8.89 ^b	-2.30 ^{b,c}	6.60
HCl	8.94 ^b	-2.23 ^{b,c}	6.71
	(8.1 ^e)	-2.2 ^e
HPi	8.87 ^f	-2.6 ^{f,h}	6.4 ^h
	8.91 ^a	-3.1 ^g	5.8 ^a

^a pK_{HA} , conductometric (Fig. 5). ^b pK_{HA} , spectrophotometric (Fig. 8). ^c $pK_{2(HA)}$, spectrophotometric (Fig. 2). ^d $pK_{AHA^-} - pK_{HA}$, spectrophotometric (Fig. 9). ^e pK_{HA} , pK_{AHA^-} , conductometric (Fig. 3, curves I and II), hydrochloric acid data from Janz and Danyluk¹⁴. ^f pK_{HA} , spectrophotometric (Fig. 4). ^g $pK_{A(HA)_2}$, conductometric (Fig. 3, curves I and II). ^h $pK_{3(HA)}$, spectrophotometric (Fig. 4). ⁱ $pK_{3(HA)}$, conductometric (Fig. 6).

Plots of $\Lambda \sqrt{c \left(\frac{1}{K_{AHA^-}} + c \right)}$ vs. c , according to equation 13, of conductivity data for sulfuric and hydrochloric acids are given in Fig. 3, curves I and II, respectively. The data for hydrochloric acid were taken from a publication by Janz and Danyluk.¹⁴

Linear plots are obtained only when $1/K_{AHA^-}$ is taken between 5×10^{-4} and zero for sulfuric acid and between 10^{-3} and zero for hydrochloric acid. However, only one of the

(14) G. J. Janz and S. Danyluk, *J. Am. Chem. Soc.*, **81**, 3854 (1959).

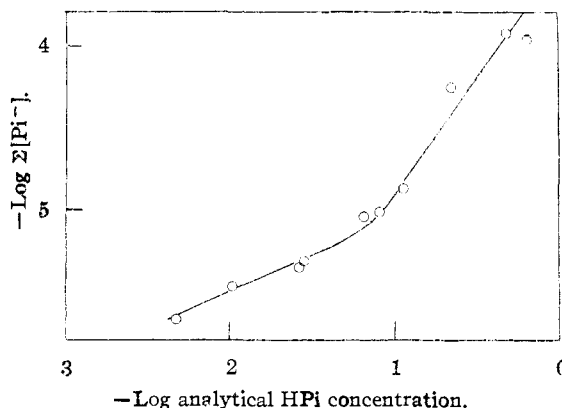


Fig. 4.— $[\text{Pi}^-]$ as function of analytical picric acid concentration: 1.75 cm. cell, except 0.096 cm. cell used at three highest HPi concentrations. Slope = 0.48 in solutions when $c < 0.08 M$ and 1.45 when $c > 0.12 M$.

linear plots for each acid yields a value of K_{AHA^-} as calculated from the intercept, $\Lambda_{0HA} \sqrt{\frac{K_{HA}}{K_{AHA^-}}}$, and from the slope,

$\Lambda_{0H^+}(\text{AHA}^-) \sqrt{K_{HA} K_{AHA^-}}$, which agrees with the assumed value of K_{AHA^-} . The values of K_{AHA^-} and K_{HA} thus found are listed in Table III. $\Lambda_{0H_2SO_4}$ and Λ_{0HCl} were calculated from the expressions $\Lambda_{0H_2SO_4} = \Lambda_{0HClO_4}^3 - \Lambda_{0Et_4NClO_4}^{15} + \Lambda_{0Et_4NH_2SO_4} = 169.4$ and $\Lambda_{0HCl} = \Lambda_{0HClO_4}^3 - \Lambda_{0Et_4NClO_4}^{15} + \Lambda_{0Et_4NCl}^{15} = 168.8$, assuming Kohlrausch's law to hold. $\Lambda_{0H^+}(\text{AHA}^-)$ is taken as one half that of Λ_{0HA} .⁴ Agreement between the conductometrically and spectrophotometrically determined dissociation constant of sulfuric acid is obtained, using this value of $\Lambda_{0H^+}(\text{AHA}^-)$. Because there is no experimentally determined value of $\Lambda_{0H^+}(\text{AHA}^-)$, the values of K_{HA} and K_{AHA^-} involve the uncertainties in the estimate of $\Lambda_{0H^+}(\text{AHA}^-)$. For example, if $\Lambda_{0H^+}(\text{AHA}^-)$ is chosen equal to $\Lambda_{0H^+} + 1/2\Lambda_{0A^-}$, pK_{HA} increases 0.11 unit for hydrochloric acid and 0.26 unit for sulfuric acid while pK_{AHA^-} increases 0.10 unit for both acids. Choosing $\Lambda_{0H^+}(\text{AHA}^-)$ equal to Λ_{0HA} produces approximately twice the above difference.

A spectrophotometric study of solutions of picric acid in AN was made at 415 m μ , the wave length at which the molar absorptivities of picrate ion and picric acid have their maximum difference. The molar absorptivity of picrate ion, 1.36×10^4 was determined by adding picric acid to 0.01 M diphenylguanidine, while the molar absorptivity of picric acid, 5.95, was determined in 0.01 M perchloric acid. The total concentration of picrate ion species, $\Sigma[\text{Pi}^-]$, at a given analytical picric acid concentration was calculated from the change in absorbance at 415 m μ on making the solution 0.01 M in perchloric acid. A plot of the logarithm of $\Sigma[\text{Pi}^-]$ vs. the logarithm of the picric acid concentration is given in Fig. 4.

A Kraus and Bray plot⁶ of the conductance data of picric acid in dilute solutions ($c < 4 \times 10^{-2} M$) is given in Fig. 5.

The constant K_{HA} calculated from the slope of the $1/\Lambda$ vs. $c\Lambda$ plot and Λ_{0HA} is given in Table III. Λ_{0HPi} was taken equal to $\Lambda_{0HClO_4}^3 + \Lambda_{0Et_4N}^{15} - \Lambda_{0Et_4NClO_4}^{15} = 160.0$.

In more concentrated solutions the value of $1/K_{A(HA)_2} = 8 \times 10^{-4}$ results in a linear plot of $\Lambda \sqrt{c \left(\frac{1}{K_{A(HA)_2}} + c \right)}$ vs. c^2 according to equation 14 (Fig. 6). From the intercept

$\sqrt{\frac{K_{HA}}{K_{A(HA)_2}}} \Lambda_{0HA}$, (equation 14) and previously determined values of K_{HPi} and Λ_{0HPi} , a value of $1/K_{A(HA)_2} = 8 \times 10^{-4}$ was calculated, in agreement with the assumed value. From equations 5a, 14 and 10b, $K_{3(HA)} = K_{A(HA)_2} K_{HA}$. Since $K_{3(HA)} = 3.5 \times 10^{-7}$ and $K_{HA} = 1.3 \times 10^{-9}$ from spectrophotometric data, $1/K_{A(HA)_2}$ was calculated to be 4×10^{-3} .

Conductivity data of the salts tetraethylammonium bisulfate and lithium nitrate are given in Table IV. Dissociation constants of these salts calculated from Kraus and Bray

(15) P. Walden and E. J. Birr, *Z. physik. Chem.*, **144**, 269 (1929).

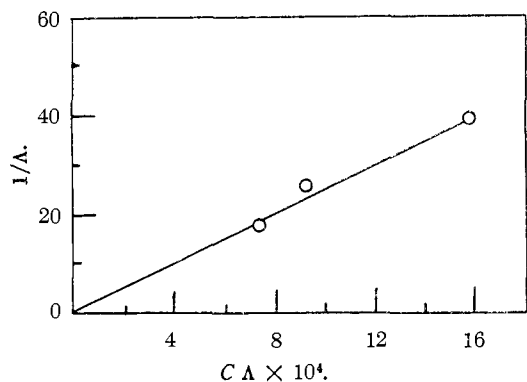


Fig. 5.—Kraus and Bray plot of picric acid; slope = 2.4×10^4 .

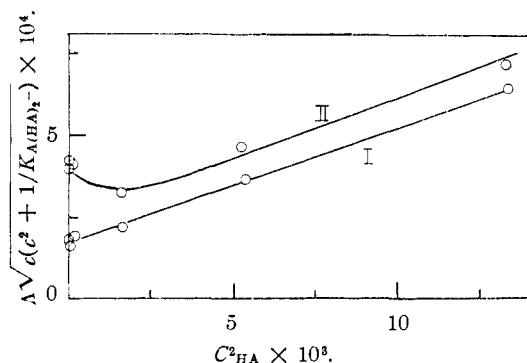


Fig. 6.— $\sqrt{c^2 + 1/K_{A(HA)_2^-}}$ vs. c^2_{HA} plot of picric acid: I, value of $1/K_{A(HA)_2^-}$ taken as that giving the best linear plot, *i.e.*, 8×10^{-4} . Intercept = 1.7×10^{-4} , slope = 0.039. II, assuming spectrophotometric value of $1/K_{A(HA)_2^-} = 4 \times 10^{-3}$.

plots are also given in Table IV. From data of Walden and Birr¹⁶ a dissociation constant of 1.8×10^{-2} was calculated for tetraethylammonium bromide. For tetramethylammonium chloride a dissociation constant of 1.3×10^{-2} was reported by Popov and Skelly.¹⁶

TABLE IV
CONDUCTANCE OF SALTS IN ACETONITRILE AT 25.00°

Lithium nitrate ^a		Tetraethylammonium bisulfate ^b	
LiNO_3	Λ	Et_4NHSO_4	Λ
2.83×10^{-4}	109.0	0.272×10^{-4}	174
5.86×10^{-4}	85.4	0.652×10^{-4}	167
8.49×10^{-4}	78.5	1.418×10^{-4}	160
14.15×10^{-4}	66.6	2.264×10^{-4}	155
21.20×10^{-4}	58.1	5.91×10^{-4}	142
28.3×10^{-4}	46.3		

^a From Kraus and Bray plot $\Lambda_0 = 159$, $K_{\text{dissoc.}} = 4.1 \times 10^{-4}$. ^b From Kraus and Bray plot $\Lambda_0 = 176$, $K_{\text{dissoc.}} = 1.4 \times 10^{-3}$.

Spectrophotometric data with *o*-nitroaniline as indicator in sulfuric acid-tetraethylammonium bisulfate mixtures are presented in Table V. Plots of $[\text{H}_2\text{SO}_4]^2/[\text{H}_2\text{SO}_4 \cdot \text{HSO}_4^-]$ vs. $f^2 [\text{HI}^+]/[\text{I}]$ according to equation 16 are entered in Fig. 7.

Spectrophotometric data of the reaction of the relatively strong anionic bases, chloride and nitrate, with picric acid as indicator gave the equilibrium concentration of picrate ions. Plots of $[\text{A}^-]$ vs. $\frac{[\text{Pi}^-]^2}{[\text{HPi}]}$ according to equation 17 are given in Fig. 8. Values calculated for K_{HA} are presented in Table III. From the spectrophotometrically determined

(16) A. I. Popov and N. E. Skelly, *J. Am. Chem. Soc.*, **76**, 5309 (1954).

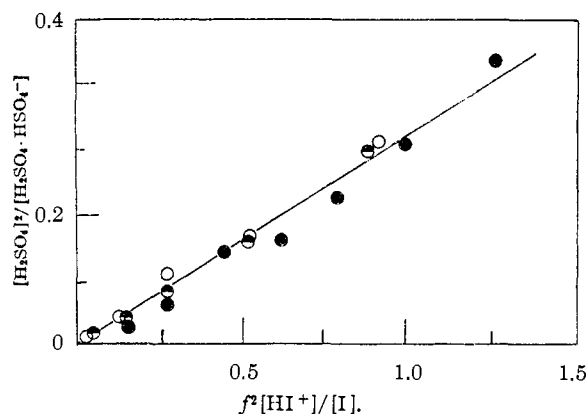


Fig. 7.—Sulfuric acid-tetraethylammonium bisulfate buffers at fixed analytical concentration of sulfuric acid, *o*-NA as indicator: ●, 0.0138 *M* in H_2SO_4 and 1.68×10^{-5} *M* *o*-NA; ○, 0.0221 *M* H_2SO_4 and 9.14×10^{-5} *M* *o*-NA; ◐, 0.0209 *M* H_2SO_4 and 4.88×10^{-5} *M* *o*-NA; slope = 0.33.

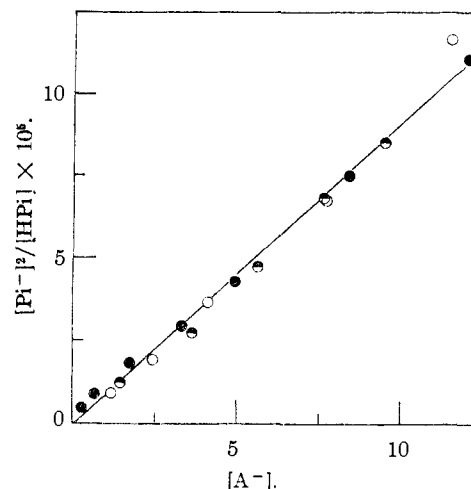


Fig. 8.—Chloride and nitrate with fresh picric acid. Me_4NCl , ●, 4.58×10^{-5} *M* HPi ; ○, 2.45×10^{-5} *M* HPi ; LiNO_3 , ◐, 2.38×10^{-5} *M* HPi , slope = 1.00, 1.75 cm. cell, 410 m μ ; $[\text{A}^-] = \{\alpha_{\text{LiNO}_3} - [\text{Pi}^-]\} \times 10^5$ for LiNO_3 ; $[\text{A}^-] = \{\alpha_{\text{Me}_4\text{NCl}} - [\text{Pi}^-]\} \times 10^5$ for Me_4NCl .

concentration of picrate ions in mixtures of the weak anionic bases bisulfate (as Et_4NHSO_4) and bromide (as Et_4NBr) with picric acid plots were made of $[\text{A}^-]^2$ vs. $[\text{Pi}^-]^2/[\text{HPi}]$ in accordance with equation 18c. These plots are presented in Fig. 9. Values of $K_{\text{HA}}/K_{\text{A}^-\text{HA}^-}$ calculated with the aid of equation 17 are given in Table III.

Discussion

Acetonitrile is a sufficiently strong basic solvent to cause complete dissociation of perchloric acid. There is a considerable difference in strength between perchloric and hydrobromic acid, hydrobromic acid having a K_{HA} of only 3×10^{-6} . From the second column in Table III it appears that the acid strength decreases in the order: $\text{HBr} > \text{H}_2\text{SO}_4 > \text{HNO}_3, \text{HCl}, \text{HPi}$. It is peculiar that picric acid has the same strength as hydrochloric acid in AN, although in water it is a considerably weaker acid.

Our conductance data in fresh solutions of picric acid are not in agreement with those of French and Roe⁴ and Romberg and Cruse,⁵ who used aged solutions of picric acid. Their con-

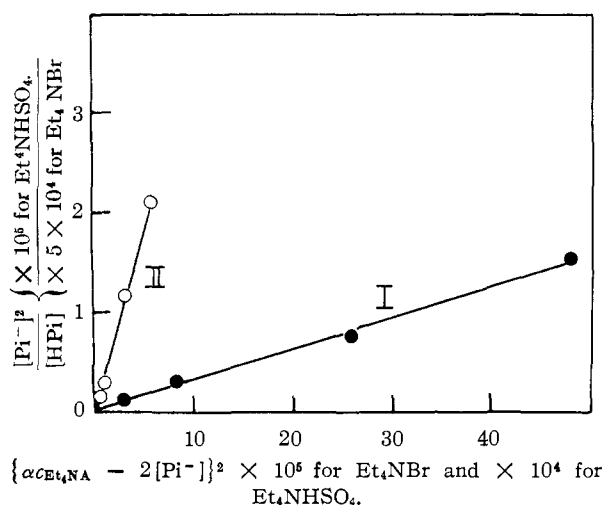


Fig. 9.—Bromide and bisulfate with picric acid: I, Et_4NHSO_4 with $6.81 \times 10^{-5} M$ HPi, slope = 28.6; II, Et_4NBr with $3.30 \times 10^{-5} M$ HPi, slope = 8.2×10^4 , 1.75 cm. cell, 410 m μ .

ductance data indicate dissociation into solvated protons and simple picrate ions in solutions 10^{-4} to $10^{-3} M$. Romberg and Cruse reported a dissociation constant of 2.5×10^{-7} as compared to our value of 1.5×10^{-9} . In a subsequent paper it will be shown that the dissociation of weak acids increases markedly upon aging of the solutions. Furthermore, the solvent used by Romberg and Cruse contained 0.05% water (0.021 M). Water is a fairly strong base in acetonitrile¹⁷ and promotes dissociation of weak acids. In solutions more concentrated than $10^{-3} M$ both French and Roe as well as Romberg and Cruse concluded from conductance data that dissociation into solvated protons and $\text{Pi} \cdot \text{HPi}^-$ occurs. It is remarkable that in our work no indication of $\text{Pi} \cdot \text{HPi}^-$ was found; simple dissociation was observed to 0.1 M and at higher concentrations $\text{Pi}(\text{HPi})_2^-$ was found with a constant $K_{3(\text{HA})}$ of 7×10^{-7} . In the transition range near 0.1 M , $\text{Pi}(\text{HPi})^-$ ions may be present, but their stability must be considerably less than that of $\text{Pi}(\text{HPi})_2^-$.

It is of interest to compare some dissociation constants in anhydrous acetic acid and AN. In acetic acid perchloric acid¹⁸ has a pK of 4.87, while in AN this acid is completely dissociated into the ions. On the basis of this relation one would expect that the simple dissociation constants of sulfuric and hydrochloric acids in acetic acid¹⁸ would be much smaller than those in AN. Actually, for either acid K_{HA} is the same in both solvents. In an interpretation of differences in acid strength in various solvents, formation and dissociation of ion pairs and degree of solvation of anions must be considered in addition to basic character of the solvent and its dielectric constant.

Acetic acid is strong enough a base to ionize perchloric acid practically completely.¹⁸ Because of the small dielectric constant ($D = 6.1$) of the solvent, the degree of dissociation of the ion pair

(17) I. M. Kolthoff and S. Ikeda, *J. Phys. Chem.*, unpublished.

(18) S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2974 (1956).

TABLE V
SULFURIC ACID-TETRAETHYLAMMONIUM BISULFATE MIXTURES WITH *o*-NITROANILINE

$c_{\text{Et}_4\text{NHSO}_4}$	$\frac{[c_{\text{H}_2\text{SO}_4} - c_{\text{Et}_4\text{NHSO}_4}]}{c_{\text{Et}_4\text{NHSO}_4}}$	A_{410}	$\frac{[\text{HI}^+]}{[\text{I}]}$	$f^2 \frac{[\text{HI}^+]}{[\text{I}]}$
Sulfuric acid, 0.0138 M				
<i>o</i> -Nitroaniline, $1.68 \times 10^{-5} M$				
1.90×10^{-4}	0.975	0.053	2.19	2.07
2.85×10^{-4}	.640	.059	1.87	1.72
4.18×10^{-4}	.430	.069	1.45	1.28
5.70×10^{-4}	.306	.078	1.165	1.00
7.61×10^{-4}	.222	.086	0.965	0.798
10.45×10^{-4}	.157	.095	.780	.620
14.3×10^{-4}	.143	.106	.594	.451
35.2×10^{-4}	.030	.136	.242	.158
Sulfuric acid, 0.0209 M				
<i>o</i> -Nitroaniline, $4.88 \times 10^{-5} M$				
1.82×10^{-4}	2.36	0.114	3.39	3.22
3.64×10^{-4}	1.156	.138	2.62	2.34
7.28×10^{-4}	0.562	.186	1.66	1.38
12.74×10^{-4}	.296	.229	1.15	0.886
21.83×10^{-4}	.160	.284	0.725	.518
36.42×10^{-4}	.0820	.338	.428	.276
54.5×10^{-4}	.0436	.379	.250	.146
90.9×10^{-4}	.0153	.421	.087	.044
Sulfuric acid, 0.0221 M				
<i>o</i> -Nitroaniline, $9.14 \times 10^{-5} M$				
7.89×10^{-4}	0.576	0.361	1.83	1.514
13.8×10^{-4}	.310	.462	1.20	0.915
23.5×10^{-4}	.165	.576	0.746	.525
31.4×10^{-4}	.115	.694	.417	.278
59.1×10^{-4}	.0443	.794	.225	.129
98.5×10^{-4}	.0151	.890	.051	.0251

^a f^2 was calculated using the limiting Debye-Hückel expression $-\log f = 1.53 \sqrt{\mu}$.

is small and the dissociation constant is only 1.8×10^{-5} . Even if AN were a somewhat weaker base than acetic acid, perchloric acid could be completely ionized because of the much greater dielectric constant of AN ($D = 46$).

Acetic acid is a strong hydrogen bonder and stabilizes anions like bisulfate, chloride, etc., thus promoting the dissociation of ion pairs of the ionized acid, while AN cannot stabilize these anions. Thus, the dissociation of the weaker acids into their (solvated) ions in acetic acid is promoted by hydrogen bonding, while in AN the lack of hydrogen bonding of the anions by the solvent counteracts the dielectric effect on the dissociation. The great effect of the hydrogen bonding in AN is evident from the fact that the over-all dissociation constant $K_{2(\text{HA})}$, which involves the hydrogen bonding between A^- and HA, is more than 100 times as great as K_{HA} (Table III). Thus the over-all dissociation constants of the above acids in AN are considerably greater than those in acetic acid. The values of pK_{AHA^-} in Table III refer to the stability constant of anions associated with HA as AHA^- (equation 5b). For the four acids listed in Table III, K_{AHA^-} varies approximately from 300 to 1000.

The formation of AHA^- in solvents which are poor hydrogen bonders for anions has been considered in some recent publications^{19,20} and also

its effect on the characteristics of conductometric,²¹⁻²³ potentiometric,^{5,23,24} and spectrophotometric²⁵ neutralization curves. Romberg and Cruse⁵ accounted quantitatively for the shape of their potentiometric titration curves on the basis of associated anions.

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The Thermal Decomposition of *cis*-1,2-Dimethylcyclobutane¹

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The gas-phase thermal decomposition of *cis*-1,2-dimethylcyclobutane has been investigated for pressures near 15 mm. over the temperature region 380–430° and for initial pressures from 5.8 to 393 mm. at 420°. The products which were analyzed qualitatively by infrared absorption and quantitatively by gas chromatography indicated that the main decomposition process is a ring cleavage to yield two molecules of propylene. A second ring cleavage of lesser importance produces ethylene and a mixture of *cis*-2-butene and *trans*-2-butene. Both processes were found to be first order decompositions which could not be inhibited by nitric oxide or propylene. The first order rate constant for the reaction forming propylene can be expressed as $k_1 = 3.0 \times 10^{15} \exp(-60400/RT)$ sec.⁻¹ and the rate constant for the cleavage into ethylene and 2-butene, $k_2 = 3.7 \times 10^{15} \exp(-63000/RT)$ sec.⁻¹. The ring cleavage is accompanied by a slower isomerization yielding *trans*-1,2-dimethylcyclobutane.

Earlier studies have shown that cyclobutane² and its monoalkyl substituted derivatives³ decompose thermally into ethylene and a substituted ethylene. The ring cleavages are first order homogeneous reactions and are unaffected by the addition of nitric oxide, propylene or toluene. An investigation of *cis*-1,2-dimethylcyclobutane was of interest because there was the possibility of one ring cleavage process yielding two molecules of propylene and another reaction forming 2-butene and ethylene. This study was undertaken to determine the relative importance of two types of ring cleavage and to compare the pyrolysis of a *cis*-disubstituted cyclobutane with those of the monosubstituted cyclobutanes. The consideration of the isomerization of the *cis*-isomer into *trans*-1,2-dimethylcyclobutane will be given in a subsequent paper.

Experimental

Materials and Apparatus.—*cis*-1,2-Dimethylcyclobutane was synthesized in a three-step process starting from the anhydride of *cis*-1,2-cyclobutanedicarboxylic acid.⁴ The procedure⁵ consisted in reduction of the anhydride to the diol with lithium aluminum hydride, followed by esterification with *p*-toluenesulfonyl chloride and subsequent reduction of the di-tosyl ester to the hydrocarbon with lithium aluminum hydride. The crude material was fractionated in a 75-cm. column with Lecky-Ewell packing while a 10 to 1 reflux ratio was maintained. Five fractions (~4 ml. each) which distilled over the range 66.3–67.1° at 748 mm. were taken, and for use in rate studies each of these fractions was subjected to further purification in a Perkin-Elmer 154B Vapor Fractometer. The infrared

spectra of the five purified samples were essentially identical. Quantitative analysis by gas chromatography indicated a purity of at least 99.7%. Carbon-hydrogen analysis⁶ of the purified material yielded: C, 85.44, 85.59; H, 14.55, 14.50 (theor. C, 85.62; H, 14.38). The refractive index was n_D^{20} 1.403. A second sample⁷ of *cis*-1,2-dimethylcyclobutane was obtained by the reduction of 2-methylcyclobutanecarboxylic acid by a procedure similar to that mentioned above. In this case both *trans* and *cis* isomers were formed and the higher boiling *cis* isomer was separated by fractional distillation and gas chromatography. The infrared spectrum and the kinetic behavior of this second sample of the *cis* isomer were essentially identical with the sample prepared from the anhydride of *cis*-1,2-cyclobutanedicarboxylic acid.

Propylene (99.5%, Ohio), ethylene (99.5%, Ohio), *trans*-2-butene (99%, Matheson), *cis*-2-butene (99%, Matheson) and nitric oxide (98.7%, Matheson) were distilled from trap to trap under vacuum and degassed thoroughly before use.

The vacuum system, furnace and temperature control were of a relatively conventional type. The temperature which was regulated to within $\pm 0.1^\circ$ during an experiment was measured with a platinum, platinum-13% rhodium thermocouple standardized regularly at the melting point of zinc (419.5°). The Pyrex glass reaction vessels used in the various phases of this investigation were cylindrical in shape and had these characteristics: vessel (A) 487 ml. capacity, low pressure experiments (below 40 mm. initial pressure); vessel (B), 319 ml. capacity, high pressure experiments (90–400 mm.); vessel (C), 430 ml. free volume, packed with thin-walled Pyrex tubing, surface-to-volume ratio about 35 times that of vessel (A).

The reaction system was one of almost constant volume. The pressure increase during a low pressure experiment was measured to ± 0.01 mm. on a wide bore manometer with the aid of a Gaertner M930-300 cathetometer. The pressure increase during a high pressure experiment was read directly from an ordinary mercury manometer. In all experiments the pressure data were corrected for the small "dead space" external to the reaction zone. Subsequent to the kinetic experiment the unreacted *cis*-1,2-dimethylcyclobutane and products were removed rapidly from the reaction vessel by expansion through a series of three cold traps, the coldest of which was at -196° .

Analysis of the Products.—The products of the reaction were separated by their differences in volatility and analyzed by infrared spectroscopy, gas chromatography and

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