Spectrophotometric Determination of the Thermodynamic $pK$ Value of Picric Acid in Water at 25 °C

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The thermodynamic $pK$ value of picric acid was determined spectrophotometrically in water containing hydrochloric acid to repress the ionization. The $pK$ value 0.33 ($K = 0.46$) was obtained from data at 460 m.$\mu$. Attempts to determine the $pK$ value by potentiometric titrations of picric acid and by spectrophotometric measurements of picric acid solutions in the near-saturation range did not yield satisfactory results. The new $pK$ value is compared with previously published values.

1. Introduction

Because of the wide-ranging importance of picric acid, numerous attempts have been made to determine its ionization constant in water. Table I summarizes ionization constants or $pK$ values which have been reported in the literature, obtained by catalytic, conductance, distribution, or spectrophotometric methods. The values obtained for $K$ range from about 0.15 to 0.8, the corresponding $pK$ range being about 0.8 to 2.

The principle of additivity of substituent effects, which has been applied successfully in calculating approximate $pK$ values for some of the meta- and para-substituted benzoic acids (for example, see [1, 2]), cannot be used for a dependable estimate of the $pK$ values of di- and trinitrophenols, because the calculated acidic strengths are less than those determined experimentally—in some cases, very much less [3 to 5]. For picric acid, several different estimated $pK$ values are obtained on using different combinations of the following experimentally obtained $pK$ values: Phenol (10.90), m-cresol (10.08), 3,5-xylenol (10.19), o-nitrophenol (7.21), p-nitrophenol (7.15), 2,4-dinitrophenol (4.10), 2,6-dinitrophenol (3.71), 2,4,6-trinitro-m-cresol (0.91), and 3,5-dimethylpicric acid (1.35). The variability of the calculated $pK$ values is evident from the following examples:

(1) The $pK$ value 1.57 is obtained by using $pK$ values for phenol, o-nitrophenol and p-nitrophenol.

(2) By subtracting the numerical difference between the $pK$ values for phenol and o-nitrophenol from the $pK$ value for 2,4-dinitrophenol one obtains 1.31.

(3) Subtracting the numerical difference between the $pK$ values for phenol and p-nitrophenol from the $pK$ value for 2,6-dinitrophenol gives the value 0.86.

(4) Subtracting 0.09 from the experimental $pK$ value for trinitro-m-cresol gives 0.72.

### Table I. Ionization constants previously reported for picric acid

| Temp. °C | Range of sources | Method of measurement | $pK$ | Equiv. value of $pK$
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>0.00279 to 0.00262</td>
<td>Dist.</td>
<td>0.265</td>
<td>0.497</td>
</tr>
<tr>
<td>25</td>
<td>0.05 to 0.06</td>
<td>Cat.</td>
<td>0.32</td>
<td>0.265</td>
</tr>
<tr>
<td>20</td>
<td>0.0396 to 0.0424</td>
<td>Spee.</td>
<td>0.381</td>
<td>0.265</td>
</tr>
<tr>
<td>25</td>
<td>0.03978 to 0.04967</td>
<td>Cond.</td>
<td>0.51</td>
<td>0.265</td>
</tr>
<tr>
<td>25</td>
<td>Approx. 0.00035</td>
<td>Spec.</td>
<td>0.419</td>
<td>0.708</td>
</tr>
<tr>
<td>25</td>
<td>0.00358 to 0.00440</td>
<td>Cond.</td>
<td>0.51</td>
<td>0.265</td>
</tr>
</tbody>
</table>

All concentrations appear to have been in molar units.

Abbreviations used: "Cat." catalytic effect on the hydrolysis of ethyl ester as compared with that of HCl; "Cond." conductance; "Dist." distribution between water and benzene; "Spec." spectrophotometric.

An asterisk signifies that $K$ and $pK$ are claimed to be thermodynamic values.

$K$ of hydrochloric acid and C. Druecker, Phys. Chem. 40, 211 (1960). Dippy, Hughes and Laxton (see footnote k), who evidently recalculated $K_c$ cites this value as 0.29, which is equivalent to $pK$ of 0.60. R. Schreiner (see footnote C) obtained $pK$ of 4.06 at 25° from Rothmund and Drucker's data.

R. M. Neale, Trans. Faraday Soc. 17, 353 (1921). He used 0.37, and observed a trend from $K = 0.285$ for 0.0221 to 0.282 m.HCl.

E. Schreiner, Z. anorg. allgem. Chem. 285, 591 (1952). Assumptions made: HCl is completely dissociated; $K_c$ is associated with 11 H$_2$O; PI and HPI are unstable. In these cases, with $C_HCl = 0.06$, 0.26, he obtained for $K_c$ the respective values 0.666, 0.534, 0.547. Emf measurements at 18° yielded $pK = 0.580$.

H. von Halban and L. Eber, Z. physikal. Chem. 113, 399 (1924). From measurements at 450 m.$\mu$. HPI solutions of three concentrations were used, as well as data in 0.136 N HCl, and the results were extrapolated by the method of least squares.

H. von Halban and M. Seiler, Helv. chim. acta 21, 285 (1938). From measurements at 438 m.$\mu$. Percent measurements were made with Cu$_2$O ranging from 0.5 to 5. Cu$_2$O ranging from 0.5 to 5. When the data are treated as in this paper, the average $pK$ value obtained is 0.585.


G. Kortum, Z. Elektrochem. 47, 433 (1933). They used $K_{HCl} = 0.500$, consider optical results to be acute.

R. G. Bates and O. Schwarzenbach, Experientia 1, 482 (1945). From data at 529 m.$\mu$. As in this work, hydrochloric acid was added to repress ionization of picric acid, but larger amounts were added (C$_{HCl} = 0.1$ molar to 4 molar). The same equation (eq (1)) was used to calculating $pK'$. Because of uncertainty about the value of $D_p$, $pK$ values were calculated with eight assumed values of $D_p$, then plotted against the mobility of the hydrochloric acid. The best $D_p$ value was considered to be the one providing the best linear relation between $pK$ and the mobility of HCl.

J. F. J. Dippy, S. R. C. Hughes, and J. W. Laxton, J. Chem. Soc. (London) 1966, 3572. Solutions of five concentrations were measured. They used $K_{HCl} = 0.43$, 0.58, calculated by the extrapolation method of R. M. Fosse (J. Am. Chem. Soc. 47, 468 (1935)).

2. Experimental Procedures

2.1. Materials

A commercial high grade of picric acid was recrystallized several times from benzene-cyclohexane or water, the final time from water, forming long needles. Preliminary drying to constant weight at room temperature was accomplished by leaving the crystals for approximately four hours in a desiccator through which dried air passed continuously. No further measurable loss in weight occurred on heating for an hour at 100 to 110 °C. The melting point was 121.5 to 122.0 °C. The values for percent purity obtained by potentiometric weight-titrations of two samples were 99.97 and 100.02.

The hydrochloric acid and sodium hydroxide were commercial materials of highest grade, stated to meet A.C.S. specifications.

2.2. Attempt to Determine pH by Potentiometric Titrations

Solutions of picric acid about 0.004 M or 0.044 M were titrated with approximately 0.40-M sodium hydroxide, using glass and sleeve-type calomel electrodes. The method of calculation was the same as in the titrimetric determination of the pH of 2,6-dichlorobenzoic acid [2]. Before the titrations the electrode system was checked with NBS 0.05-M potassium acid phthalate buffer (pH 4.01) and 0.05-M potassium tetroxalate buffer (pH 1.65). The initial pH values ranged from 1.50 to 1.54, and the average pH values from three experiments were 0.78, 0.86, and 0.74. These are not considered reliable values. In the first place, pH values calculated by this method are highly sensitive to the magnitude of the experimental pH values, and these were not reproducible enough. There was evidence of a tendency for picrate to crystallize near the sleeve of the calomel electrode during titrations.

A second difficulty concerns the standardization of the instrument with buffer solutions before the titrations. The pH range near 1.50, which is vital for this method of determining the pH of picric acid, is outside the range of pH values in which the Hitchcock and Taylor scale of pH values (obtained with buffer solutions using cells with liquid junction) and the NBS scale (obtained using cells without liquid junction) are in excellent agreement [6]. Near pH 1.50, the two scales differ by 0.04 pH unit.

2.3. Determination of the pH Value by Spectrophotometry

Absorbances were obtained with a Beckman Model DU quartz spectrophotometer, equipped with a thermostated cell compartment [7]. The absorption cells were the same accurately made, demountable cells of various lengths used in other spectrophotometric studies [8]. When solutions contained hydrochloric acid or sodium hydroxide, the same concentration of acid or alkali was present in the sample cell and the reference cell. To increase the precision of wavelength settings, the spectrophotometer is provided with an auxiliary indicator line, as recommended in [9]. The absorbance values used are the average of at least five independent settings, which were highly reproducible, even on a steep slope of an absorption curve.

a. Determination of pH in Hydrochloric Acid Solutions of Picric Acid

In picric acid solutions as dilute as 5×10⁻⁵ M the concentration of nonionized molecules is negligibly small unless a stronger acid is added to repress the ionization. The pH value was calculated from the equation

\[
\text{pH} = -\log [H^+] - 2 \log \gamma_+ - \log [(D-D^s)/(D_1-D)].
\]  

(1)

In this equation \([H^+]\) denotes the total hydrogen ion concentration in moles per liter, and \(\gamma_+\) is taken as the mean activity coefficient of aqueous hydro-
chloric acid of equivalent molarity (see [4], footnote 4). The symbols $D_1$, $D_2$, and $D$ apply to any picric acid solution of a given stoichiometric concentration, $D_1$ being the spectral absorbance (optical density) when the acid is present entirely as HPi, $D_2$, the absorbance when it is present entirely as Pi$^-$, and $D$, the absorbance when conversion of HPi to Pi$^-$ or vice versa is only partial. The use of eq (1) involves the usual convention that $Y_+ = Y^- = Y_0^+$ for hydrochloric acid, as well as the assumptions that $7HPI=1$ and $7P1^-$ is the same as $y_+^-$ for hydrochloric acid.

A recognized problem in determining spectrophotometrically the $pK$ values of acids as strong as picric acid is the difficulty in determining $D_1$ values. In the high concentrations of mineral acid needed for repressing the ionization, additional effects on the spectral absorption seem prone to occur. In the hope of meeting this difficulty, measurements were made not only at 355 m$\mu$, which is near the wavelength of maximum absorption of Pi$^-$, and at 400 m$\mu$, which is on a shoulder of the absorption curve for Pi$^-$, but also at 450 m$\mu$, where it seemed fairly certain that $D_1$ would equal zero.

b. Attempt to Determine $pK$ Using More Concentrated Aqueous Solutions

Using the shortest available absorption cells (0.01-cm), absorbance measurements were made at 450 m$\mu$ for five picric acid solutions ranging from 0.025 $M$ to 0.50 $M$, with and without additions of sodium hydroxide. The absorbance values indicated that in all of these solutions more than 90 percent of the solute was present as Pi$^-$. An attempt was made to calculate $pK$ by eq (1) (with the same assumptions as before). These calculations, which indicated that $pK$ may be about 0.4 or less, cannot be considered reliable, both because of experimental uncertainties and because of the uncertainty as to how much the assumed activity coefficients differ from the true values.

3. Results and Discussion

3.1. Spectral Absorption Curves

Figure 1 shows a series of absorption curves obtained with $5 \times 10^{-5}$-M picric acid in water, in 0.023-$M$ sodium hydroxide, and in aqueous hydrochloric acid ranging from 0.145 $M$ to 8 $M$. The faintly dotted line shows the spectral absorption of picric acid in cyclohexane [10]. The arrows indicate the three wavelengths used in determining $pK$.

It is generally accepted that ionization of picric acid is essentially complete in solutions as dilute as $5 \times 10^{-5} M$. This belief finds support in our experiments, in which the absorption curves obtained in water and in 0.023-$M$ sodium hydroxide ($pH>12$)
agreed very closely. It was thought desirable to limit the excess of alkali, as a large concentration causes an irreversible deepening of the color. The alkali was added slowly, with stirring, to avoid momentary large excesses.

For all the aqueous solutions containing 0.724-M hydrochloric acid or less, there is a well-marked isosbestic point at approximately 307 m\(\mu\), \(\epsilon \approx 50500\). The curves for the three highest concentrations of hydrochloric acid do not pass through this isosbestic point, but appear to be shifted toward the ultraviolet. The curves obtained with 6-M and 8-M hydrochloric acid are very similar at wavelengths longer than about 250 m\(\mu\), but in the region from about 320 m\(\mu\) to 350 m\(\mu\) there is a suggestion of the kind of behavior observed in determining the \(pK\) of dimethylpicric acid [4], when progressive decreases in the absorption on the first additions of hydrochloric acid were followed by increases in the absorption at high concentrations of hydrochloric acid.

As is well known, in the near ultraviolet and visible regions the absorption curve for aqueous picrate appears to be the envelope of at least two overlapping bands, one near 355 m\(\mu\) and the other in the vicinity of 400 m\(\mu\). In some solvents, these bands are more clearly distinguishable and, moreover, their positions vary with the nature of the cation (for example, [14, 15]). The absorption of the nonionized acid is also affected by the nature of the medium (see fig. 1 and [14, 15]). Physical constants determined from absorbance measurements in a region of overlapping bands could be in error if, for example, one component band were a "blue-shift" band and another, a "red-shift" band, or if both were "red-shift" bands not equally affected by a changing medium. In recent years attempts have been made to account theoretically for strong absorption bands of nitroaromatic compounds, including mono- and dinitrophenols and picric acid. For example, it has been suggested that the absorption band of picrate ion near 353 m\(\mu\) and the band showing as a shoulder near 400 m\(\mu\) are intramolecular charge-transfer bands, in which the phenyl and nitro groups act as electron-donor and electron-acceptor groups, respectively (see [19] and references cited). This is recognized as being only a partial interpretation, which does not take into account such factors as inter- and intramolecular hydrogen bonding and steric inhibition of resonance of substituent groups with the benzene ring.

3.2. Results of \(pK\) Determinations in Aqueous Hydrochloric Acid

\(a\), \(pK\) Value Determined at 480 m\(\mu\)

Table 2 summarizes the results obtained by calculating \(pK\) from absorbance data at 450 m\(\mu\). The equation used and the assumptions made about activity coefficients were discussed in section 2.3a. At 450 m\(\mu\) the additional assumption was made that \(D_1 = 0\), justification for which is as follows:

1. The absorbance of picric acid in 6-M and 8-M hydrochloric acid is negligibly small at 450 m\(\mu\) and even shorter wavelengths (fig. 1).

2. Under comparable experimental conditions picric acid dissolved in cyclohexane (see fig. 1) or benzene [15] has negligibly small absorbance in this region.

3. Nonionized 2,4-dinitrophenol does not absorb measurably at wavelengths as long as 450 m\(\mu\); the close similarity of the absorption curves of 2,4-dinitrophenol and picric acid in both acidic and alkaline solutions has been pointed out [11].

Averaging of the results from three independent experiments gives 0.33 as the \(pK\) value of picric acid. (The average obtained by including only the \(pK\) values obtained for \(C_{\text{HCl}} = 0.241 \text{M}\) or greater, where the values of \(\log [D/(D_1 - D_2)]\) are in the best range, is not significantly different from the average based on all 26 values.)

Table 2. \(\text{pK}\) of picric acid in water at 25 °C from data at 450 m\(\mu\)

<table>
<thead>
<tr>
<th>Molar concentration of HCl</th>
<th>(D)</th>
<th>(\log D)</th>
<th>(-\log [1 + 1] - 2 \log y_{\pm})</th>
<th>(pK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. 1. (C_{\text{HCl}} = 5.005 \times 10^{-5} \text{M}), (b = 5 \text{cm})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td>0.430</td>
<td>0.620</td>
<td>0.149</td>
<td>0.044</td>
</tr>
<tr>
<td>0.0050</td>
<td>0.419</td>
<td>0.605</td>
<td>0.138</td>
<td>0.042</td>
</tr>
<tr>
<td>0.0100</td>
<td>0.398</td>
<td>0.590</td>
<td>0.127</td>
<td>0.040</td>
</tr>
<tr>
<td>0.0200</td>
<td>0.382</td>
<td>0.574</td>
<td>0.116</td>
<td>0.038</td>
</tr>
<tr>
<td>0.0500</td>
<td>0.365</td>
<td>0.555</td>
<td>0.104</td>
<td>0.035</td>
</tr>
<tr>
<td>0.100</td>
<td>0.353</td>
<td>0.541</td>
<td>0.094</td>
<td>0.033</td>
</tr>
<tr>
<td>0.200</td>
<td>0.338</td>
<td>0.518</td>
<td>0.073</td>
<td>0.033</td>
</tr>
<tr>
<td>0.500</td>
<td>0.327</td>
<td>0.491</td>
<td>0.054</td>
<td>0.033</td>
</tr>
<tr>
<td>1.00</td>
<td>0.320</td>
<td>0.475</td>
<td>0.045</td>
<td>0.033</td>
</tr>
</tbody>
</table>

| Exp. 2. \(C_{\text{HCl}} = 5.005 \times 10^{-5} \text{M}\), \(b = 5 \text{cm}\) |
|---------------------------|---------|---------|-----------------------------|-------|
| 0.083 | 0.452 | 1.100 | 1.276 | 0.164 | 0.300 |
| 0.086 | 0.450 | 1.090 | 1.266 | 0.162 | 0.300 |
| 0.107 | 0.445 | 1.040 | 1.099 | 0.160 | 0.300 |
| 0.171 | 0.411 | 0.964 | 0.777 | 0.319 |
| 0.241 | 0.375 | 0.915 | 0.611 | 0.330 |
| 0.321 | 0.348 | 0.880 | 0.488 | 0.350 |
| 0.435 | 0.328 | 0.838 | 0.434 | 0.370 |
| 0.576 | 0.284 | 0.753 | 0.316 | 0.390 |
| 0.676 | 0.251 | 0.681 | 0.258 | 0.410 |

| Exp. 3. \(C_{\text{HCl}} = 5.005 \times 10^{-4} \text{M}\), \(b = 5 \text{cm}\) |
|---------------------------|---------|---------|-----------------------------|-------|
| 0.240 | 0.452 | 1.100 | 1.276 | 0.164 | 0.300 |
| 0.240 | 0.450 | 1.090 | 1.266 | 0.162 | 0.300 |

Average \(pK\) \(= 0.334\), \(K = 0.46\), Relative standard deviation, % \(= 2.1\).

\(1\) The log dissociation constant was derived using the equation:

\[
pK = -\log [1 + 1] - 2 \log y_{\pm} - \log [(D - D_1)/(D_1 - D)].
\]

See the text for discussion of assumptions made about activity coefficients. The symbols \(D_1\), \(D_2\), and \(D\) denote the spectral absorbances (optical densities) of solutions containing the same nonionized concentration of picric acid present as nonionized molecules, ionized molecules, or mixtures of the two, respectively. At 450 m\(\mu\), \(D_1\) was found to have the value 0.466 and \(D_2\) was assumed to be zero. The symbol \(D\) denotes the optical cell length.
The good agreement of the results was unexpected, considering the uncertain validity of assumptions made in applying eq (1) and the fact that the wavelength of measurement was on a steep slope instead of on or close to the head of an absorption band (which is generally considered desirable, when feasible). However, as noted in section 2.3, no difficulty was experienced in obtaining absorbance values of high precision.

As table 2 shows, the stoichiometric concentration of picric acid was varied 100-fold in a dilute range, and the concentration of hydrochloric acid extended from about 0.05-M to 0.97-M. Since the pK values obtained under these conditions show no perceptible trend, it seems justifiable to conclude that the pK value adopted is valid at zero ionic strength.

b. pK Values Obtained From Data at 355 μM and 400 μM

The spectral shifts in the most highly concentrated hydrochloric acid solutions (see sec. 3.1) interfere with experimental determination of D values at 355 μM and 400 μM. A general idea of their probable magnitudes can be obtained from the appearance of the curves and the comparative absorbance values at all three wavelengths. pK values were calculated assuming two different values of D which were thought to cover the most likely range of values. The results are presented in table 3.

While the values of pK obtained from the absorbance data at 355 μM and 400 μM are in the vicinity of 0.3, in agreement with the results obtained at 450 μM, the values in table 3 show a gradual increase in magnitude with increasing concentration of the hydrochloric acid. Conceivably this behavior occurred for one or more of the following reasons:

1. Adoption of values for D that were a little too low. The values adopted were believed to be close to the correct values, but, as table 3 shows, at 355 μM an increase of only 0.005 in the value of D can bring the pK values into fairly good agreement with the series obtained at 450 μM (see values enclosed in brackets).

2. Overlapping absorption bands of picrate ion that are not equally affected by the progressive changes in the medium (see sec. 3.1).

3. The gradual hypsochromic ("blue") shift in the absorption curve of ionized picric acid.

4. Slight changes in the spectral absorption resulting from interaction of picric acid with trace impurities in the hydrochloric acid.

3.3. Concluding Discussion

As indicated above, attempts to determine the pK of picric acid in water by potentiometric titration (sec. 2.2) or by applying spectrophotometry to nearly saturated solutions (sec. 2.3b) did not yield results that were considered reliable.

However, the consistent spectrophotometric results obtained at 450 μM with picric acid solutions covering the range 5×10⁻³ M to 5×10⁻³ M, in the presence of approximately 0.05-M to 1-M hydrochloric acid, point to the pK value 0.33 at 25 °C. The results obtained at 355 μM and 400 μM, though less consistent, support this choice. The pK value 0.33 is fairly close to three spectrophotometric values obtained earlier at 20° (table 1, footnote h) and at 25° (table 1, footnotes j and l).

It would be gratifying if this value agreed closely with the latest reported value (pK approx. 0.71), obtained from accurate conductance measurements (table 1, footnote k). One may speculate as to whether spectrophotometry and conductometry will always yield the same pK value, in view of recent reports ([30] and references cited) that flash photolysis of certain derivatives of phenol produces shortlived excited states of considerably enhanced acidity. However, one of the pK values obtained by conductance (table 1, footnote j) is not far from the spectrophotometric value obtained in this work, and, as shown in table 1, pK values calculated from conductance measurements depend on assumptions made (for example, table 1, footnote d). Moreover, the latest conductance measurements covered a rather restricted range of concentrations of picric acid (2.355×10⁻³ M to 4.410×10⁻³ M)