

ACID-BASE STRENGTHS IN PYRIDINE

M. BOS AND E. A. M. F. DAHMEN

Department of Chemical Technology, Twente University of Technology, Enschede (The Netherlands)

(Received July 21st, 1970)

Pyridine is an important solvent for acid-base titrations, but there are few systematic investigations about the equilibria that play a part in neutralization reactions in pyridine. It is generally accepted that ion pairs occur as intermediates in the dissociation of acids in solvents like pyridine¹⁻³. Only overall dissociation constants of some acids have been measured in pyridine^{1,2}.

When ion-pair formation occurs these overall dissociation constants are not suitable for the comparison of the acid strengths of a compound in different solvents⁴. For this comparison the so-called ionization constants are needed. If the dissociation of an acid in pyridine is represented by the following equilibria



this ionization constant is defined as

$$K_i^{\text{HX}} = [\text{H}^+\text{X}^-]/[\text{HX}] \quad (2)$$

The dissociation constant of the ion pair is given by

$$K_d^{\text{H}^+\text{X}^-} = [\text{H}^+][\text{X}^-]/[\text{H}^+\text{X}^-] \quad (3)$$

For acids of the ammonium type the dissociation can be represented by



Here the dissociation constant can be defined as

$$K_d^{\text{BH}^+} = [\text{B}][\text{H}^+]/[\text{BH}^+] \quad (5)$$

In order to determine the ionization constant of an indicator acid, the method proposed by Kolthoff and Bruckenstein⁴ can be used.

In this paper, besides the application of the method by Kolthoff and Bruckenstein, a method for the determination of dissociation constants of acids of the ammonium type from titration curves is discussed.

EXPERIMENTAL

Chemicals

Pyridine. Pyridine (Merck, reagent grade) was kept over an activated molecular sieve 3A for 48 h and was afterwards distilled over barium oxide. The pyridine (b.p. 115°) was collected and stored in an automatic burette. From this burette it was

dispensed under pressure of carbon dioxide-free nitrogen. The water content was below 0.05% (Karl Fischer titration).

Perchloric acid. This was used as its pyridinium salt, which was prepared as described by Mukherjee *et al.*¹.

Hydrochloric acid. Solutions of hydrochloric acid in pyridine were prepared by passing a stream of dry hydrogen chloride gas through pyridine.

Sulfonphthaleins. The sulfonphthaleins, bromophenol blue, bromocresol purple, bromocresol green and chlorophenol red (indicator grade, Merck) were used as received.

Nitrophenols. The following samples were used: picric acid (Merck, reagent grade), 3-nitrophenol (Merck, indicator grade), 2,4-dinitrophenol (Merck and dried *in vacuo* at 40°), 2,5-dinitrophenol (Merck, indicator grade), 2,6-dinitrophenol (Merck, indicator grade). All the dinitrophenols were recrystallized twice from ether and dried *in vacuo* at 40°.

Bases. The bases used were *n*-butylamine, triethylamine and morpholine, all of which were reagent grade (Fluka).

Spectrophotometric technique

All measurements were carried out with a Zeiss spectrophotometer, type PMQ II, at a temperature of $20 \pm 2^\circ$ in quartz cells with a light path of 1 cm.

Differential vapour pressure measurements

A Mechrolab model 301A osmometer was used for the differential vapour pressure measurements at 37°. The osmometer was calibrated for pyridine with benzil.

Potentiometric measurements

A Knick pH-meter, type 260, was used for the potentiometric measurements. The glass electrode was a Radiometer G222c electrode. As reference electrode an Ag/AgCl electrode filled with a saturated solution of tetramethylammonium chloride in pyridine was used. When not in use the glass electrode was kept in an aqueous buffer pH of 7. With this set of electrodes each potential measurement was continued until its change within 5 min became less than 2 mV. This took about 30 min. The resulting values are reproducible within ± 2 mV. The glass electrode was calibrated regularly in standard solutions of perchloric acid in pyridine.

Potentiometric titrations

The potentiometric titrations were recorded automatically with a Radiometer titration assembly composed of pH-meter PHM 28, burette ABU 2, recorder SBRC, and titrator TT 11. The electrode set was the same as the one described above. Titration curves were reproducible within ± 5 mV.

RESULTS

Spectrophotometric measurements

If an ion pair occurs as an intermediate in the dissociation of an indicator acid, the ionization and dissociation constant of this acid can be determined spectro-

photometrically by means of the method developed by Kolthoff and Bruckenstein⁴. This method is based on the equation

$$[\text{HIn}]/\{\Sigma [\text{base}] - K_i[\text{HI}]\}^2 = (K_i K_d)^{-1} \quad (6)$$

where $[\text{HIn}]$ is the concentration of the indicator in the acid colour, and $\Sigma [\text{base}]$ is the spectrophotometrically determined concentration of the indicator in the basic colour; K_i and K_d are the ionization and the dissociation constants, respectively.

In the case of the polynitrophenols and sulfonphthaleins application of eqn. (6) did not result in a single value for K_i . Instead, the results of the experiments, plotted according to eqn. (6) gave straight lines for a wide range of values for K_i . The results did, however, follow the equation for simple dissociation:

$$\{\Sigma [\text{base}]\}^2/[\text{HIn}]^1 = K_{\text{HX}} \quad (7)$$

For the determination of the dissociation constants of sulfonphthaleins, solutions of these compounds were used in which the first step of the acid was neutralized with tetramethylguanidine. Molar extinction coefficients were determined in solutions of the indicators to which an excess of tetramethylammonium hydroxide had been added.

The dissociation constants calculated from eqn. (7) are given in Table I.

TABLE I

SPECTROPHOTOMETRIC DETERMINATION OF K_{HX} FROM DILUTION SERIES OF INDICATOR ACIDS^a

Indicator	$\lambda_{\text{max, base}}$ (nm)	ϵ_{base}	K_{HX}	pK_{HX}
Picric acid	380	$1.91 \cdot 10^{4b}$	$1.1 \cdot 10^{-3}$	3.0
2,6-Dinitrophenol	462	$1.07 \cdot 10^{4b}$	$5.9 \cdot 10^{-5}$	4.2
2,5-Dinitrophenol	470	$5.77 \cdot 10^{3b}$	$9.8 \cdot 10^{-6}$	5.0
Bromophenol blue ²	607	$1.17 \cdot 10^5$	$5.6 \cdot 10^{-6}$	5.3
Bromocresol green ²	633	$6.59 \cdot 10^4$	$3.4 \cdot 10^{-6}$	5.5
Bromocresol purple ²	610	$1.09 \cdot 10^5$	$3.1 \cdot 10^{-8}$	7.5
Chlorophenol red ²	597	$8.03 \cdot 10^4$	$8.4 \cdot 10^{-11}$	10.1

^a Activity coefficients for ionic species were calculated from $-\log f = 8.191 \mu^{1/2}$, while the activity coefficients for non-ionic species were assumed to be unity.

^b It was assumed that the acid is non-absorbing at this wavelength.

Differential vapour pressure measurements

The overall dissociation constant of an acid HX can be found by means of differential vapour pressure (DVP) measurements with the equation¹

$$K_{\text{HX}} = (m_d - m_s)^2 / (2m_s - m_d) \quad (8)$$

where m_d is the molarity measured by the DVP method and m_s is the stoichiometric concentration of HX.

The same equation can be applied in the determination of the dissociation constant of salts by this method (assuming that no acid-base dissociation occurs).

The results of the DVP measurements are given in Table II (acids) and Table III (salts).

TABLE II

DETERMINATION OF K_{HX} BY THE DIFFERENTIAL VAPOUR PRESSURE METHOD AT 37°

Acid	K_{HX}	pK_{HX}
Perchloric acid	$9.3 \cdot 10^{-4}$	3.0
Picric acid	$1.3 \cdot 10^{-3}$	2.9
2,5-Dinitrophenol	$2.8 \cdot 10^{-3}$	4.6
2,6-Dinitrophenol	$2.1 \cdot 10^{-4}$	3.7
2,4-Dinitrophenol	$1.0 \cdot 10^{-4}$	4.0

TABLE III

SALT DISSOCIATION CONSTANTS DETERMINED BY THE DIFFERENTIAL VAPOUR PRESSURE METHOD AT 37°

	Tetra- methyl- guanidine	n-Butyl- amine	Morpho- line	Triethyl- amine
Perchloric acid	$1.5 \cdot 10^{-3}$	$9.5 \cdot 10^{-4}$	$6.1 \cdot 10^{-3}$	$5.3 \cdot 10^{-4}$
Hydrochloric acid	$1.5 \cdot 10^{-4}$	$6.3 \cdot 10^{-5}$	$3.4 \cdot 10^{-5}$	$2.8 \cdot 10^{-6}$
Picric acid	$3.9 \cdot 10^{-4}$	$6.7 \cdot 10^{-4}$	$2.0 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$
2,5-Dinitrophenol	$2.6 \cdot 10^{-4}$			
2,6-Dinitrophenol	$4.0 \cdot 10^{-4}$			
2,4-Dinitrophenol	$5.2 \cdot 10^{-4}$			

Potentiometric measurements. Calibration of the glass electrode

At 25° the e.m.f. of the cell

glass electrode | solution HX | ref. electrode

is given by

$$E_{(mV)} = E_{ref} + E_{l.j.} + 29.5 \log K_{HX} + 29.5 \log C_{HX} \quad (9)$$

By measuring an acid with a known overall dissociation constant, one can find $E_{ref} + E_{l.j.}$. If it is assumed that $E_{ref} + E_{l.j.}$ is constant, one can determine pH values of unknown solutions from

$$pH = \frac{1}{59} (E_{ref} + E_{l.j.} - E) \quad (10)$$

The behaviour of the glass electrode used can be represented by

$$E_{(mV)} = 29.4 \log C_{HClO_4} + 155$$

or, with $pK_{HClO_4} = 3.2^1$:

$$E_{(mV)} = 250 + 59 \log [H^+]$$

This calibration with perchloric acid solutions was repeated for each set of potentiometric determinations. The results of the potentiometric determinations, calculated according to the equation for simple dissociation, are given in Table IV.

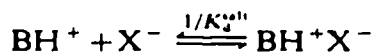
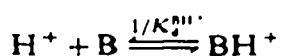
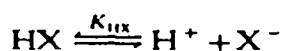
TABLE IV

 K_{HX} DETERMINED POTENTIOMETRICALLY

Acid	K_{HX}	pK_{HX}
Picric acid	$2.8 \cdot 10^{-4}$	3.5
2,6-Dinitrophenol	$1.9 \cdot 10^{-5}$	4.7
2,5-Dinitrophenol	$5.1 \cdot 10^{-6}$	5.3
3-Nitrophenol	$1.4 \cdot 10^{-13}$	12.5
2,4-Dinitrophenol	$4.1 \cdot 10^{-5}$	4.4

Potentiometric titrations

The following equilibria can be assumed to play a part in the titration of an acid HX with a nitrogen base B:



If the equilibrium constants are known, the titration curve can be calculated by general methods of equilibrium calculations⁵ with the aid of a fast digital computer. On the other hand equilibrium constants can be calculated from experimental titration curves by repeatedly entering the calculation procedure with various values for the constant to be determined until for one value of this constant, the experimental and the calculation curves give the best fit. In this way, the value of $K_d^{BH^+}$ for nitrogen bases can be determined when they are titrated with an acid of a known dissociation constant.

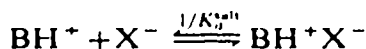
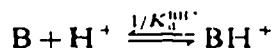
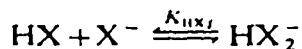
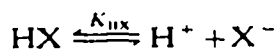
With the dissociation constants of the salts measured by the DVP method, $K_d^{BH^+}$ values were determined for tetramethylguanidine- H^+ , morpholine- H^+ , triethylamine- H^+ and *n*-butylamine- H^+ from the titrations of hydrochloric acid, perchloric acid and picric acid with the corresponding bases. The following pK values were used for the acids in the calculations: $pK_{HCl} = 5.66^1$, $pK_{HClO_4} = 3.2^1$, $pK_{picric\ acid} = 3.0$. The results are summarized in Table V.

If homoconjugation does occur, the following set of equilibria must be used in the calculations:

TABLE V

 $K_d^{BH^+}$ DETERMINED FROM POTENTIOMETRIC TITRATIONS

Acid used	$K_d^{BH^+}$			
	<i>n</i> -Butylamine	Morpholine	Triethylamine	TMG
Perchloric acid	$1.7 \cdot 10^{-6}$	$2.9 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$	$4.2 \cdot 10^{-10}$
Picric acid	$6.0 \cdot 10^{-6}$	$5.0 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$	$1.0 \cdot 10^{-10}$
Hydrochloric acid	$2.5 \cdot 10^{-6}$	$1.5 \cdot 10^{-4}$		$2.1 \cdot 10^{-10}$
Average	$3.5 \cdot 10^{-6}$	$3.1 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$2.4 \cdot 10^{-10}$



With known values for $K_{\text{B}}^{\text{BH}^+}$ and $K_{\text{B}}^{\text{BH}^+}$, the dissociation constant, K_{HX} , as well as the homoconjugation constant, K_{HX_2} , can be determined from the curves of the potentiometric titrations of 2,4-dinitrophenol, 2,5-dinitrophenol and 2,6-dinitrophenol with tetramethylguanidine. Here, it is necessary to vary both K_{HX} and K_{HX_2} until the best fit between experimental and calculated titration curve occurs. The results of these determinations are summarized in Table VI.

DISCUSSION

The results of the spectrophotometric determinations of the dissociation constants of polynitrophenols and sulfonphthaleins can be explained on the basis of

TABLE VI

K_{HX} AND K_{HX_2} FOR POLYINITROPHENOLS DETERMINED FROM POTENTIOMETRIC TITRATION CURVES^a

Compound	K_{HX}	K_{HX_2}
2,4-Dinitrophenol	$5 \cdot 10^{-5}$	10
2,5-Dinitrophenol	$2.8 \cdot 10^{-7}$	100
2,6-Dinitrophenol	$1.1 \cdot 10^{-5}$	10^{-1}

^a Calculations based on concentrations, not on activities.

TABLE VII

pK VALUES IN PYRIDINE

Compound	pK			
	Spectrophotom.	DVP	Potentiom.	Titration
Picric acid	3.0	2.9	3.5	
2,6-Dinitrophenol	4.2	3.7	4.8	4.7
2,4-Dinitrophenol		4.0	4.4	4.3
2,5-Dinitrophenol	5.0	4.6	5.3	6.5
Bromophenol blue ²	5.3			
Bromocresol purple ²	7.5			
Bromocresol green ²	5.5			
Chlorophenol red ²	10.1			
3-Nitrophenol			12.5	
n-Butylamine-H ⁺				5.5
Morpholine-H ⁺				3.5
Triethylamine-H ⁺				3.8
Tetramethylguanidine-H ⁺				9.6

simple dissociation. This indicates that no ion pairs occur as intermediates in the dissociation of these compounds in pyridine, although the dielectric constant of this solvent is rather low.

Homoconjugation can explain the typical form of the curves for the titrations of 2,4-dinitrophenol, 2,5-dinitrophenol and 2,6-dinitrophenol with tetramethylguanidine. It also explains the discrepancies in the pK values determined from the titration curves on the one hand and from spectrophotometric and potentiometric measurements on the other, for the latter are calculated on the basis of simple dissociation only.

The differences found by Mukherjee *et al.*¹ between pK values determined spectrophotometrically in solutions of pure 2,5-dinitrophenol and in mixtures of 2,5-dinitrophenol and a non-absorbing acid can be explained in the same way.

The pK values, determined in different ways, are summarized in Table VII. A comparison of the pK values in water and in pyridine is given in Table VIII.

TABLE VIII

 pK_a VALUES IN PYRIDINE COMPARED WITH pK_a VALUES IN WATER

Compound	$pK_{(pyr)}$	$pK_{(water)}$	ΔpK
Picric acid	3.0	0.4	2.6
2,6-Dinitrophenol	3.7	3.0	0.7
2,4-Dinitrophenol	4.2	3.5	0.7
2,5-Dinitrophenol	5.0	4.7	0.3
Bromophenol blue ²	5.3	4.0	1.3
Bromocresol green ²	5.5	4.7	0.6
Bromocresol purple ²	7.5	6.1	1.4
Chlorophenol red ²	10.1	6.1	4.0
3-Nitrophenol	12.5	7.2	5.3
<i>n</i> -Butylamine-H ⁺	5.5	10.6	-5.1
Morpholine-H ⁺	3.5	9.6	-6.1
Triethylamine-H ⁺	3.8	10.8	-7.0
Tetramethylguanidine-H ⁺	9.6	12.3	-2.7

It is interesting to note that the pK values for the protonated nitrogen bases are much lower in pyridine than in water. Undoubtedly, this is due to the greater basicity of pyridine compared with water. With uncharged or negatively charged acids the dielectric constant of the solvent has great influence on the dissociation. This could explain why for these acids $pK_{(pyridine)}$ is greater than $pK_{(water)}$.

The authors wish to thank Mr. H. Hof who carried out most of the potentiometric determinations and Miss A. L. Dekkers who prepared the manuscript.

SUMMARY

Although pyridine is a solvent with a low dielectric constant, spectrophoto-

metric determinations show simple dissociation without ion pairs as intermediates for some sulfonphthaleins and polynitrophenols in pyridine.

The salts of a number of amines and hydrochloric acid, perchloric acid and picric acid are not completely dissociated in pyridine. Dissociation constants of these salts were determined from differential vapour pressure measurements. For the titrations in pyridine of an acid with an amine, calculations were based on the following reactions: $HX \rightleftharpoons H^+ + X^-$; $B + H^+ \rightleftharpoons BH^+$; $BH^+ + X^- \rightleftharpoons BH^+X^-$. With this reaction scheme it was possible to determine pK_a values for protonated amines in pyridine from the curves of titrations carried out with a calibrated glass electrode. Evidence for the occurrence of homoconjugation of some polynitrophenols in pyridine was found in the titration of these compounds with tetramethylguanidine. Homoconjugation constants were estimated from the titration curves.

RÉSUMÉ

Bien que la pyridine soit un solvant à faible constante diélectrique, des dosages spectrophotométriques montrent une dissociation simple pour quelques sulfophtaléines et polynitrophénols dans la pyridine. Les sels d'un certain nombre d'amines et acides chlorhydrique, perchlorique et picrique ne sont pas complètement dissociés dans la pyridine. Les constantes de dissociation de ces sels sont déterminées par des mesures de pression de vapeur différentielle. Pour les titrages d'un acide par une amine, dans la pyridine, des réactions sont données, permettent de déterminer les valeurs de pK_a .

ZUSAMMENFASSUNG

Obwohl Pyridin ein Lösungsmittel mit einer niedrigen Dielektrizitätskonstante ist, weisen spektrophotometrische Untersuchungen einiger Sulfonphthaleine und Polynitrophenole in Pyridin auf einfache Dissoziation ohne Ionenpaare als Zwischenstufen hin. Die Salze von einer Anzahl Amine und Salzsäure, Perchlorsäure und Pikrinsäure sind in Pyridin nicht vollständig dissoziiert. Dissoziationskonstanten dieser Salze wurden aus Differentialdampfdruckmessungen bestimmt. Berechnungen für die Titrationskurven einer Säure mit einem Amin in Pyridin gründeten sich auf folgende Reaktionen: $HX \rightleftharpoons H^+ + X^-$; $B + H^+ \rightleftharpoons BH^+$; $BH^+ + X^- \rightleftharpoons BH^+X^-$. Mit diesem Reaktionsschema konnten die pK_a -Werte für protonierte Amine in Pyridin aus den Titrationskurven bestimmt werden, die mit einer geeichten Glaselektrode erhalten wurden. Für einige Polynitrophenole in Pyridin wurden bei der Titration dieser Verbindungen Beweise für das Auftreten von Homokonjugation gefunden. Aus den Titrationskurven wurden Homokonjugationskonstanten ermittelt.

REFERENCES

- 1 L. M. MUKHERJEE, J. J. KELLY, W. BARANETZKY AND J. SICA, *J. Phys. Chem.*, 72 (1968) 3410.
- 2 L. M. MUKHERJEE AND J. J. KELLY, *J. Phys. Chem.*, 71 (1967) 2348.
- 3 S. BRUCKENSTEIN AND I. M. KOLTHOFF, *J. Amer. Chem. Soc.*, 78 (1956) 10.
- 4 I. M. KOLTHOFF AND S. BRUCKENSTEIN, *J. Amer. Chem. Soc.*, 78 (1956) 1.
- 5 D. F. DETAR, *Computer Programs for Chemistry, Vol. II*, 1969, pp. 65-67.