An Emf Study on the Protonation of p-Aminophenol

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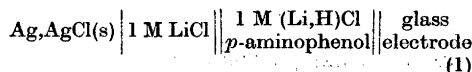
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Recently Chuchani et al.[1] suggested the possible formation of a 1:1 complex between p-aminophenol and its acid form in water. In order to investigate this possibility further we decided to study the protonation of p-aminophenol (B) by performing coulometric titrations of the hydrochloride in 1 M (Li,H)Cl medium in nitrogen atmosphere at 25.00°C using the automatic emf-titration equipment developed by Biedermann and Wallin.[2] The pure p-aminophenol hydrochloride (BHCl) was prepared by adding HCl to the alcoholic solution of the base (Kebo, *puriss.*). The salt was recrystallized twice from distilled water and dried in air. A certain amount of salt (~20 to ~200 mg) was weighed out in a small glass cup on an analytical balance to within ±0.02 mg and titrated coulometrically as described elsewhere.[2,3]

Experimental. The cell employed can be described schematically by

$$Ag,AgCl(s) \left| 1 \text{ M LiCl} \right\| \left. \begin{array}{c} 1 \text{ M (Li,H)Cl} \\ p\text{-aminophenol} \end{array} \right\| \begin{array}{c} \text{glass} \\ \text{electrode} \end{array} \quad (1)$$

The titrations were carried out at hydrogen ion concentrations such that the influence of H^+ on the diffusion potential can be shown to be negligible within 0.02 mV, so that the relation between the measured emf (E) in mV and the hydrogen ion concentration $[H^+]$ at 25°C is described by

$$E = E_0 + 59.157 \log [H^+] \quad (2)$$

The constant E_0 comprises the asymmetry potential and the diffusion potential as well as the activity coefficient term. Before the addition of salt the constant E_0 was determined coulometrically (H^+ consumed) by titration of a known amount of HCl. The acid had been standardized coulometrically employing the method of Gran.[4] In Table 1 are given the results of a typical E_0-titration. Titrations were performed with three different concentrations of BHCl: 2.467 mM, 6.585 mM, and 21.02 mM (mmole·l⁻¹).

Δn_{OH^-} was computed from Faraday's law

$$\Delta n_{OH^-} = \frac{10^3}{96\ 487} \cdot It \quad (3)$$

Results. The experimental results have been tabulated as $\log[H^+]$, for each experimental point at the three different concentrations. Z is defined by,

$$Z = [BHCl]/[BHCl] + [B]) \quad (4)$$

The results * are consistent with a simple protonation, *i.e.*

* The data are available upon request from the Dept. of Inorganic Chemistry, KTH.

Table 1. E_0-titration. 50.06 ml 1.00 M LiCl +10.02 ml 9.90 mM HCl +990 mM LiCl titrated coulometrically at $I = 4.991$ mA. temp. $= 25.000 \pm 0.003$°C.

Time sec t	Δn_{OH^-} mmol	n_{H^+} mmol	$[H^+]$ M	$59.157 \log[H^+]$	E mV	E_0 mV
0	—	0.09900	1.6478×10^{-3}	−164.64	357.49	522.13
300.323	0.01553	0.08347	1.3893×10^{-3}	−162.02	353.13	522.15
300.450	0.01554	0.06793	1.1307×10^{-3}	−174.31	347.84	522.15
300.704	0.01555	0.05238	8.7184×10^{-4}	−181.00	341.16	522.16
300.345	0.01554	0.03684	6.1318×10^{-4}	−190.04	332.12	522.16
300.070	0.01552	0.02132	3.5486×10^{-4}	−204.09	318.09	522.18
				Average:		522.15 ± 0.02

$$B + H^+ \rightleftharpoons BH^+ \qquad (5)$$

with $k = (5.621 \pm 0.008) \times 10^5 \; M^{-1}$

$$\log k = pk_a = 5.7498 \pm 0.0019$$

The calculations have been performed using a digital computer and the program LETAGROPVRID.[5] The possibility of a small constant error, δZ, in Z in each titration was accounted for, leading to the following results

2.467 mM BHCl $\delta Z = 0.00104 \pm 0.00031$
6.585 mM BHCl $\delta Z = 0.00131 \pm 0.00033$
21.02 mM BHCl $\delta Z = 0.00347 \pm 0.00032$

Neglecting the possibility of a constant error in Z the following results are obtained

$$k = (5.605 \pm 0.009) \times 10^5 \; M^{-1}$$

$$\log k = pk_a = 5.7486 \pm 0.0021$$

The value of k is practically independent of a small error in Z. The correction to Z is small, always less than 0.4 %.

Discussion. Although the spread in k is small, systematic errors have not been taken into account. Measurements on high impedance cells, such as cells with glass electrodes, are likely to be accompanied by systematic errors that vary with the emf measured. Measurements in the emf-range encountered here with impendances up to 10^3 MΩ give an error with an upper limit less than $+0.05$ mV for all experimental points. Another source of systematic error might be impurities in the chemicals

used. Due to the good fit ($\sigma(Z) = \pm 0.0024$), however, it can be shown that protolytic and nonprotolytic impurities cannot exceed 0.1—0.2 %.

In Table 2 our results are compared with others given in the literature. No direct comparison can be made between our value for pk_a obtained at high ionic strength and the literature data referring to low ionic strengths, where the measurements are considered to be rather uncertain.[6]

As seen from Table 2 there is a considerable spread in the values given for pk_a. We believe this is partly due to the extreme sensitivity of p-aminophenol towards oxidation.[12,13] All experiments have to be carried out in an oxygen free atmosphere. Fieser[12] is the only worker who deals explicitly with this problem. The value obtained by Chuchani *et al.* probably deviates so much from all the others because of partial oxidation of the base during titration. This is likely to be the reason why their results lead them to suppose the formation of a 1:1 complex between base and acid forms. However, a computer analysis of their data shows no evidence of such a complex but, instead, a very large scatter in data relating to the simple protonation reaction given by eqn. 5, found by us to be valid in the concentration range 2.5 mM — 21 mM.

Recently Joanna Los at this department performed a preliminary titration on a solution containing 228.8 mM of p-aminophenol hydrochloride. Her results indicate

Table 2. pk_a for p-aminophenol hydrochloride at room temperature.

pk_a	Method	temp.°C	Ionic strength (M)	
5.32	emf	24.5	0.004	7
5.68 ± 0.02 [a]	emf, buffer solutions	21	0.37	8
5.5	spectrophotometry	23?		9
5.65	spectrophotometry	25	≤ 0.01	10
5.55	emf, glass electrode	25	≤ 0.01	10
5.41	emf, glass electrode	Not stated	≤ 0.01	11
5.75 [b]	pH-dependence of redox potentials	25	0.2 (buffer solutions)	12
4.86 ± 0.20	emf, glass electrode	30	Not stated	1
5.749 ± 0.002	emf, glass electrode	25	1.00	This work
6.2	spectrophotometry	15	Not stated	13

[a] The average of the stoichiometric equilibrium constants as reported in Ref. 8.
[b] In the calculations modern values for pk_w have been used.[14]

that there is no deviation from eqn. 5 even at this relatively high concentration.

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Received January 15, 1970.

Chemical Studies on Lichens

28.* The Pigments of Some Foliicolous Lichens

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Nine species of obligately foliicolous lichens have been studied with regard to their content of coloured secondary metabolic products. Three anthraquinones, three pulvinic acid derivatives, three chlorinated xanthones, and usnic acid were identified by lichen mass spectrometry and thin layer co-chromatography.

The secondary metabolic products of obligately foliicolous lichens (*i.e.* lichens only occurring on living leaves)[1] are virtually unknown. Only one substantiated report on their constituents has appeared in the literature: the occurrence of 2,5,7-trichloronorlichexanthone in *Sporopodium phyllocharis* (Mont.) Mass. and of 3-O-methyl-2,5,7-trichloronorlichexanthone in *S. phyllocharis* var. *flavescens* R. Sant.[2]

By means of lichen mass spectrometry (LMS)[3] and instant thin layer co-chromatography (ITLC)[4] the pigments of nine foliicolous lichens have been studied. All investigated species belong to the family Lecideaceae.

The impossibility of obtaining more than a few milligrammes of lichen material (in advantageous cases!) has precluded isolation of the substances present and has
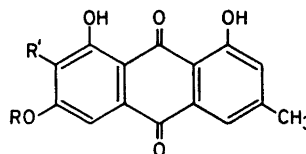
	R	R'
I:	H	H
II:	H	Cl
III:	CH$_3$	Cl
IV:	CH$_3$	H

* Part 27: Persson, B. and Santesson, J. *Acta Chem. Scand.* **24** (1970) 345.