

ANTHRAQUINONE DYESTUFFS. XIV.*

PROTONATION OF 9,10-ANTHRAQUINONE DERIVATIVES

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pK_a Values and degree of protonation of 9,10-anthraquinone, 1-amino-, 2-amino-, 1-methylamino-, 1-phenylamino-, 1-chloro-, 2-chloro- and 1,8-dichloroanthraquinone have been determined spectrophotometrically.

We have been studying the problems of phthaloylcarbazole dyestuffs in our Institute for a longer period. In order to elucidate the mechanism of acid condensation reagents on 9,10-anthraquinone derivatives, it is necessary to know the structure of starting substances in the reaction state, particularly their degree of protonation in various media, if condensation reactions taking place in strong mineral acid media are concerned. In this connection we have occupied ourselves with pK_a value determination of 9,10-anthraquinone, 1-amino-, 2-amino-, 1-methylamino-, 1-phenylamino-, 1-chloro-, 2-chloro- and 1,8-dichloroanthraquinone.

In spite of the fact that 9,10-anthraquinone was one of the indicators used in the original study of Hammett and Deyrup¹ concerning the construction of H_0 acidity function of sulphuric acid, the pK_a values given in literature for anthraquinone differ from each other: Hammett and Deyrup¹ give a value -8.27 , Paul and Long² give -8.37 , Handa³ gives -7.5 and recently Greig and Johnson⁴ gave the so called half-protonation values -8.66 and -8.48 for λ 311 and 410 nm respectively. The differences between the results published can be explained by the fact that the influence of the solvent used (medium effect)⁴ was not sufficiently eliminated in the older pK_a values and various acidity functions of sulphuric acid were used in evaluating the results. It is necessary to see that most data concerning acidity functions of the system water-sulphuric acid are based on the study of Hammett and Deyrup, but the original values of the acidity function were confirmed by further authors⁵⁻⁷ only for 1-68% sulphuric acid. The values for the higher sulphuric acid concentrations were corrected recently by Jorgenson and Hartter⁸ and by other authors^{9,10}. The acidity function values of anhydrous fuming sulphuric acid were published¹¹, by various authors¹¹⁻¹³. Various explanations are given in literature for the behaviour of 9,10-anthraquinone in sulphuric acid. The original idea of gradual protonation of the both anthraquinone carbonyl groups^{14,15} was disproved by Ovčarenko and Vinogradova¹⁶. The occurrence of isosbestic points in electronic spectra of 9,10-anthraquinone solutions in sulphuric acid was explained by many authors^{1-3,16-20} to be a consequence of equilibrium between the protonated and unprotonated forms of anthraquinone.

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EXPERIMENTAL

Purity of all the substances was verified chromatographically. The melting points were determined with the use of a Kofler apparatus calibrated with standard substances, the heating velocity being 4°C per minute.

Reagents

9,10-Anthraquinone (Merck, Darmstadt) was purified by sublimation and crystallization from toluene. The product obtained melted at $287\text{--}288^{\circ}\text{C}$ (ref.²¹ 286°C). 1-Aminoanthraquinone, m.p. $256\text{--}257^{\circ}\text{C}$ (ref.²² $252\text{--}253^{\circ}\text{C}$), 2-aminoanthraquinone, m.p. $311\text{--}313^{\circ}\text{C}$ (ref.²³ 302°C) and 1-methylaminoanthraquinone, m.p. $172\text{--}172.5^{\circ}\text{C}$ (ref.²⁴ 170°C) were obtained from the respective commercial products by repeated crystallizations from 1-butanol. 1-Phenylaminoanthraquinone was prepared by a modified Ullmann synthesis from 1-aminoanthraquinone and bromobenzene in the presence of potassium carbonate²⁵. The product obtained was purified by crystallization from 1-butanol and had a m.p. $149.5\text{--}150^{\circ}\text{C}$ (ref.²⁴ 147.5°C). 1-Chloroanthraquinone, m.p. $162.5\text{--}163.5^{\circ}\text{C}$ (ref.²⁶ 162°C) and 2-chloroanthraquinone, m.p. $211\text{--}211.5^{\circ}\text{C}$ (ref.²⁷ 210°C) were obtained from the respective commercial samples by repeated crystallizations from toluene. 1,8-Dichloroanthraquinone was obtained from a commercial sample by repeated crystallization from glacial acetic acid and melted at $205\text{--}206^{\circ}\text{C}$ (ref.²⁷ 202°C).

Acid Solvents

Concentrated sulphuric acid p.a. and c. 99% pure sulphuric acid were commercial products (Lachema, Brno). Anhydrous (100%) sulphuric acid was prepared from 97.9% H_2SO_4 and 10% fuming sulphuric acid. The latter was prepared from redistilled sulphur trioxide and 99% H_2SO_4 in a glass apparatus. Anhydrous acetic acid (100%) was prepared by azeotropic distillation of the glacial acetic acid (rid of aldehydes according to the method of Petránek and Večeřa²⁸) with ethyl acetate in a rectification column of about 10 theoretical plates. Its quality was checked by determination of freezing point and water content according to Fischér. The solutions of sulphuric acid in anhydrous acetic acid were prepared by direct weighing of the two anhydrous acids in a calibrated flask. 90% Acetic acid was prepared from the glacial acetic acid free of aldehydes and deionized water. The solutions of sulphuric acid in 90% acetic acid were prepared by direct weighing of 90.0% H_2SO_4 and 90.0% acetic acid in calibrated flask.

 pK_a Measurements

a) *Protonation at oxygen.* The pK_a values of 9,10-anthraquinone and its derivatives were determined spectrophotometrically at 20°C in the system water-sulphuric acid, anhydrous sulphuric acid, eventually fuming sulphuric acid if necessary. The stock solutions of 9,10-anthraquinone and its derivatives ($2 \cdot 10^{-4}$ or $4 \cdot 10^{-4}\text{M}$) were prepared in 96% sulphuric acid. Therefrom 1 ml samples were withdrawn by means of a pipette into 10 ml calibrated flasks and the volume was adjusted with sulphuric acid of the requested concentration. After mixing and tempering at 20°C , the absorption spectrum was measured against the reference solution using a Unicam SP 700 recording spectrophotometer. The reference solution was prepared by mixing 1 ml 96% H_2SO_4 and the sulphuric acid solution used, up to the total volume of 10 ml. Usually, absorption spectra of 10–14 solutions of the substance studied were measured. The system of absorption curves showed always at least one or even several isobestic points. At the same time, the course of protonation was followed with the use of a single-beam spectrophotometer Hilger Uvispek at the wavelengths chosen (Table I) in such a way that the extinction of the protonated form BH^+ was maximum and that of free base was minimum. Accurate concentration

of sulphuric acid in the solutions of a substance studied was determined acidimetrically using the mixed Tashiro indicator.

From the spectral data obtained pK_a values were calculated according to the known relation (1) (ref.^{1,2}), where E , E_B and E_{BH^+} are the extinctions of the solution measured, unprotonated

$$pK_{BH^+} = H_0 + \log((E - E_B)/(E_{BH^+} - E)). \quad (1)$$

form and protonated form (conjugate acid) respectively. The H_0 values of sulphuric acid and fuming sulphuric acid solutions were taken from the paper by Vinnik¹⁰.

b) *Monoprotonation of aminoanthraquinone derivatives (i.e. at nitrogen)*. The measurements of monoprotation of 1-amino-, 2-amino- and 1-methylaminoanthraquinone were carried out in the systems sulphuric acid–90% acetic acid, and the respective H_0 values were taken from the paper by Roček²⁹. Stock solutions of the substances mentioned were prepared in 90% acetic acid. The measurement was carried out at the wavelength of absorption maximum of the unprotonated form (Table I). In the case of 1-phenylaminoanthraquinone the measurements were carried out in the system anhydrous (100%) acetic acid–anhydrous (100%) sulphuric acid, and the respective H_0 values were taken from the paper by Hall and Spengemann³⁰. Accurate concentration of sulphuric acid in the reaction media was checked by gravimetric analysis or potentiometric titration with 0.1N sodium acetate in glacial acetic acid medium using a low-resistance glass and a saturated calomel electrodes and a Master-type pH meter (Pye, Cambridge).

RESULTS AND DISCUSSION

Exact determination of a thermodynamic pK_a value necessitates the values calculated from Eq. (1) to be independent of the acidity of medium and the dependence of $\log(C_{BH^+}/C_B)$ (i.e. $\log I$) on H_0 to be linear with the angular coefficient equal unity^{4,31}. Exact determination of the thermodynamic pK_a value is possible only in the case of protonation region of the base studied falling within the region of exact validity of Eq. (2). In the case of half protonation, $pK = m \cdot H_0$

$$pH = pK_a - \log I \quad (2)$$

for m being equal or very near to unity (m is the angular coefficient of the dependence of $\log I$ on H_0). The value m is thus a criterion of validity of H_0 function for the base studied and a measure of influence of the solvent used (so called medium effect) which makes itself felt especially in the case of very weak bases in media of high sulphuric acid concentrations. A shift of absorption bands of the base or its conjugate acid is observed in spectrum depending on the concentration of the mineral acid used, and the system of absorption curves does not show any isosbestic points characteristic for system with one equilibrium. It can be presumed that Eq. (3) applies

$$H_0 = pK_{BH^+} - \log I \quad (3)$$

only in that case if the base studied and the indicator used are of the same chemical type and if the protonation takes place at the same group.

Recently, Greig and Johnson⁴ verified protonation of a series of aromatic carbonyl compounds inclusive of anthraquinone in the system water–sulphuric acid and found that these compounds did not follow the acidity function H_A (ref.³²) based on primary amides as indicators (which, before, several authors believed to be the case); they⁴ also stated that the corrected H_0 acidity function⁸ applied to these compounds except for anthraquinone.

In the present paper, the H_0 values of the system water-sulphuric acid were taken from the papers by Vinnik^{10,13}. The half-protonation values of anthraquinone found by us, *viz.* -8.67 and -8.69 for λ 315 and 413 nm respectively (Table I), stand in very good accord with the values given by Greig and Johnson⁴. Vinnik's H_0 values are satisfactory for other anthraquinone derivatives, too.

In the case of 9,10-anthraquinone, the protonation takes place at one carbonyl group only¹⁶. If one hydrogen is substituted by amino group, another basic centre capable of being protonated is formed in the molecule of 9,10-anthraquinone. From the absorption spectra of aminoanthraquinones it is obvious that the colour of these

TABLE I
pK_a Values of 9,10-Anthraquinone Derivatives

Derivatives	Degree of protonation	H' ₀ ^a	λ , nm	<i>m</i>	pK _a
Unsubstituted	1	- 8.64	313	0.98	- 8.47
		- 8.69	413	0.96	- 8.34
1-Amino	1	+ 0.59	470	0.98	+ 0.58
	2	-10.39	306	0.85	- 8.83
		-10.29	403	0.84	- 8.64
2-Amino	1	+ 1.29	440	0.93	+ 1.19
	2	-10.04	305	0.89	- 9.03
		-10.03	407	0.85	- 8.61
1-Methylamino	1	+ 0.38	505	1.02	+ 0.39
	2	-10.46	306	0.94	- 9.83
		-10.38	405	0.89	- 9.24
1-Phenylamino	1	- 2.78	505	0.99	- 2.75
	2	-10.20	306	1.06	-10.81
		-10.16	407	1.02	-10.36
1-Chloro	1	- 9.09	313	1.04	- 9.45
		- 9.07	429	1.06	- 9.61
2-Chloro	1	- 9.12	323	1.00	- 9.12
		- 9.03	418	1.02	- 9.21
1,8-Dichloro	1	- 9.63	312	1.10	-10.59
		- 9.50	427	1.12	-10.56

^a H'₀ Concerning half protonation.

compounds is due to the absorption band in visible region having a charge-transfer character, and it is caused by the electron transfer from the free electron pair at nitrogen into the anthraquinone skeleton. Protonation at nitrogen, *i.e.* binding of the free electron pair, should result in decolourization of solutions of these substances and in disappearing of the long-wave absorption band. This is really the case with 1-amino-, 1-methylamino-, 1-phenylamino- and 2-aminoanthraquinone. Their unprotonated forms (*e.g.* in 90% acetic acid) are deeply coloured, with increasing sulphuric acid concentration in reaction medium, however, the decolourization of the solutions of these compounds takes place, the protonated form being colourless and its absorption spectrum in ultraviolet region being very similar to the spectrum of anthraquinone itself in the same medium. The inductive influence of NH_3^+ group is not substantial.

The presence of a positive centre in the molecule, however, decreases the basicity of quinone oxygen, and, consequently, the half protonation (H'_0) of 1-aminoanthraquinone to the second degree is -10.34 (H'_0 of 9,10-anthraquinone is -8.68). Similar behaviour is encountered with the other amino derivatives of 9,10-anthraquinone, too. The values found are presented in Table I. The solution of 1-phenylaminoanthraquinone in 100% sulphuric acid turns blue with time (formation of a band at $1.7 \mu\text{m}^{-1}$) and therefore, the measurements had to be carried out with fresh solution in the case of determination of $\text{p}K_a$ of diprotonation. In the case of 2-phenylaminoanthraquinone the analogous colour change was so rapid that the $\text{p}K_a$ determination of this compound was impossible. An explanation of this behaviour is given in another paper³³.

Substitution of hydrogen by chloride in the position 1 and 2 of 9,10-anthraquinone lowers the basicity of oxygen by about 1.1 and 0.8 $\text{p}K_a$ units respectively. Two chlorine atoms in 1,8-dichloroanthraquinone lower the basicity of oxygen by about 2.2 $\text{p}K_a$ units as compared to 9,10-anthraquinone. From the absorption spectra it is obvious that chloroanthraquinones, in contrast to the other 9,10-anthraquinone derivatives studied, show a substantially lower "medium effect" in the sulphuric acid medium which can also be seen in the values of the angular coefficients m approaching unity in the case of these compounds (Table I).

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