

PROTONATION OF MONOSUBSTITUTED 9,10-ANTHRAQUINONE DERIVATIVES

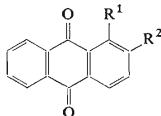
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Protonation of monosubstituted 9,10-anthraquinone derivatives has been studied spectrophotometrically in sulphuric acid. The substituents of anthraquinone nucleus have much higher effect on the basicity of carbonyl group, if they are in *ortho* event. *para* position with respect to the carbonyl group.

Different explanations of behaviour of anthraquinone in sulphuric acid are given in literature. The original idea of Battegay¹ and Hawke², *viz.* that of gradual protonation of the both carbonyl groups of anthraquinone nucleus, was replaced by the theory of Lukin and Zavarichina³ suggesting a formation of a complex of anthraquinone and sulphuric acid or sulphur trioxide. This opinion was disproved by the UV and IR spectral studies carried out by Ovčarenko and Vinogradova⁴. The theory of an equilibrium between anthraquinone and dihydroanthraquinone in sulphuric acid solutions⁵ was disproved by UV spectral studies⁶. The erroneous explanation of isosbestic points in UV spectra by a formation of associates between molecules of the protonated form⁴ was discussed by Handa⁷ who suggested that the isosbestic points were due to the equilibrium between the non-protonated and protonated forms of anthraquinone⁸⁻¹², whereas the association made itself felt in the dependence of molar extinction coefficients on the initial anthraquinone concentration. Greig and Johnson¹³ give the value -8.48 for the H_0 of half-protonation of anthraquinone based on H_0 function of Jorgenson and Hartter¹⁴. Greig and Johnson recommended to give the H_0 value of half-protonation instead of pK_A value with respect to the fact that the increasing acidity of sulphuric acid causes a further increase of molar extinction coefficients of the protonated form of anthraquinone.



	R ¹	R ²		R ¹	R ²		R ¹	R ²
I,	NO ₂	H	V,	Br	H	XI,	H	F
II,	SO ₃ Na	H	VI,	I	H	XII,	H	CH ₃
III,	F	H	VII,	H	H	XIII,	H	OCH ₃
IV,	Cl	H	VIII,	CH ₃	H	IX,	OCH ₃	H
						X,	H	NO ₂

1-Nitroanthraquinone and 1,5-dinitroanthraquinone are far less basic than anthraquinone¹⁵, and 9,10-anthraquinone-1-sulfonic acid is reported not to undergo protonation up to 100% sulphuric acid¹⁶.

Within the framework of our kinetic studies of nitration of anthraquinone derivatives in sulphuric acid, we have measured the protonation of 9,10-anthraquinone derivatives *I* – *XIII*.

EXPERIMENTAL

Reagents

The substances used were prepared by known methods and purified by chromatography on an alumina column (activity II according to Brockman, neutral) using cyclohexane-acetone mixture 3 : 1 as eluent. A commercial sample of sodium anthraquinone-1-sulfonate (VCHZ, Synthesia) was purified by crystallization from distilled water with charcoal. Its purity was checked by paper (Whatman No 3) chromatography using butanol-acetic acid-water mixture 75 : 15 : 20 as eluent. The melting points were determined by means of a Kofler apparatus and are corrected.

Spectral Measurements

96% Sulphuric acid p.a. was used for preparation of solutions of the anthraquinone derivatives. The solutions of higher sulphuric acid concentrations were prepared by distillation of sulphur trioxide from 65% oleum into 96% sulphuric acid. The solutions of sulphuric acid and oleum did not absorb in the range of wavelengths used. The stock solutions of $5 \cdot 10^{-4}$ mol/l anthraquinone and its derivatives in 90% sulphuric acid were prepared. Therefrom 2.5 ml samples were withdrawn into 25 ml calibrated flasks and the volume was adjusted with sulphuric acid of the requested concentration. The final concentration of the samples measured was $5 \cdot 10^{-5}$ mol/l. The analytical wavelength was determined by means of a Unicam SP 800 apparatus using 1 cm quartz cells at 25°C. The course of protonation was followed by means of a VSU-1 spectrophotometer using 1 cm quartz cells at the wavelength chosen and at 25°C. The concentration of sulphuric acid or oleum was determined alkalimetrically²⁷ after the electrophotometric measurements. The samples were weighed in the Lunge pipette and, after dilution with distilled water, titrated with 0.5M-NaOH using methyl orange as indicator. The molar extinction coefficients measured were evaluated according to the equation²⁸ (*I*) where ϵ_B , ϵ_{BH^+} and ϵ are the molar

$$H_0 = pK_A - \log \left(\frac{\epsilon - \epsilon_B}{\epsilon_{BH^+} - \epsilon} \right) \quad (I)$$

extinction coefficients of the non-protonated form, protonated form and the mixture of the both forms respectively at the wavelength chosen. The acidity function H_0 determined by Vinik²⁹ was used for the calculation which was carried out by the least squares method.

RESULTS AND DISCUSSION

From the study of the UV spectra of the anthraquinone derivatives given it follows that they behave as weak bases in sulphuric acid medium and undergo protonation. The H_0 values of half-protonation are effective values because the monoprotonation may take place at the both carbonyl groups, the basicities of which are not equal due to the different position with respect to the substituent. The H_0 values of half-

TABLE I
Half-protonation H_0 Values of Some Monosubstituted 9,10-Anthraquinone Derivatives

Com- pound	Prep. (ref.)	M.p., °C	λ_{\max}	$-H_{0(1/2)}$	m^a	% H_2SO_4	σ_m	σ_0	σ_p
I	17	236	406	10.67 ± 0.05	0.96	99.19	0.70	0.80	—
II	—	—	420	10.66 ± 0.12	1.06	99.17	—	—	—
III	18	128 — 129	420	9.00 ± 0.04	0.97	89.80	0.36	0.24	—
IV	19	161 — 162	423	9.04 ± 0.04	1.01	90.08	0.39	0.21	—
V	20	187.5 — 188.5	428	8.97 ± 0.04	0.98	89.60	0.39	0.21	—
VI	21	204 — 205	430	8.83 ± 0.08	0.96	88.64	0.34	0.21	—
VII	—	286	410	8.58 ± 0.03	0.99	87.00	0.00	0.00	0.00
VIII	22	171 — 172	423	8.16 ± 0.18	0.85	84.16	—0.10	—0.17	—
IX	23	169	464	5.27 ± 0.04	0.97	65.58	—	—	—
X	24	184.5 — 185	402	10.67 ± 0.12	1.02	99.19	0.70	—	0.80
XI	18	203 — 204	410	9.06 ± 0.13	0.97	90.22	0.36	—	0.05
XII	25	177	415	8.32 ± 0.07	1.01	85.20	—0.10	—	—0.14
XIII	26	194.5 — 195.5	492	7.45 ± 0.06	1.02	79.55	0.12	—	—0.26

^aThe angular coefficient of the dependence of H_0 on $\log ([BH^+]/[B])$.

protonation represent a pK_A in those cases when the angular coefficient m of the straight line representing the dependence of H_0 on $\log ([BH^+]/[B])$ is unity or almost unity. The values H_0 of half-protonation given in Table I were correlated with σ_m (ref.³⁰), σ_p (ref.³⁰) and σ_0 (ref.³¹) constants using the two-parameter Jaffé equation (2)

$$\log K = \log K_0 + \varrho_1 \sigma_1 + \varrho_2 \sigma_2, \quad (2)$$

where σ_m were used for σ_1 , and σ_0 (in the case of 1-substituted anthraquinone derivatives) or σ_p (in the case of 2-substituted anthraquinone derivatives) were used for σ_2 . The following values of constants were obtained by the least squares method: $\log K_0 = -8.58$, $\varrho_1 = 0.48 \pm 0.043$, $\varrho_2 = -3.04 \pm 0.035$, correlation coefficient $r = 0.972$. The markedly higher value of ϱ_2 constant means that the basicity of the carbonyl group in *ortho* eventually *para* position to a substituent is much more affected by the substituent than the basicity of the carbonyl group in *meta* position.

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