

THE BASICITY OF MONOHALOGENO DERIVATIVES
OF 9,10-ANTHRAQUINONE AND THEIR CHROMATOGRAPHY
ON A THIN LAYER OF SILICA GEL*

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The degree of protonation was determined spectrophotometrically; pK_a values of monohalogeno derivatives of 9,10-anthraquinone were also determined and their behaviour during thin-layer chromatography on silica gel studied.

Monohalogeno derivatives of 9,10-anthraquinone are important intermediates in the production of anthrimides and carbazole vat dyes. Electron absorption spectra of these substances were studied recently¹ at 295 and 77 K. The spectra at 295 K are characterised by three bands which differ by the position of their maxima in dependence on the nature and the position of the halogen in the anthraquinone. For the spectra of all monohalogeno derivatives in n-hexane a broad and weak $s_n \rightarrow \pi^*$ band in the 360–480 nm region is characteristic. In ethanolic solutions this band is without a vibrational structure and shifted weakly hypsochromically. Chromatography on paper of 1- and 2-halogeno anthraquinones was investigated by Franc and Wurst² who found that these substances differ in their chromatographic mobility even though having equal dipole moments. They explained this fact by the possibility of the 1-isomer to form hydrogen bonds. Dokunichin and Kolokolov³ suppose the existence of a polar six-membered cycle closed between the halogen atom in the position 1 and carbonyl oxygen by mediation of a hydrogen from a molecule of water or from hydroxonium ion. The ability to form this polar cycle decreases in the sequence $F \gg -Cl > Br > J$ -derivatives in accordance with the decreasing electroaffinity and the ability to form hydrogen bonds. Paper chromatography of a series of mono- and dichloroanthraquinones in the system 1-bromonaphthalene-90% acetic acid was described by Nepraš and coworkers⁴.

In this paper the results of a spectrophotometric determination of the degree of protonation, pK_a values, and chromatography on a thin layer of silica gel, as well as the correlation of the experimental data with some HMO indexes of reactivity are presented.

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EXPERIMENTAL

Chemicals used: 1-Chloroanthraquinone, m.p. 162.5–163.5°C (lit.⁴ 163°C) and 2-chloroanthraquinone, m.p. 211–211.5°C (lit.⁴ 211°C) were obtained by repeated crystallisation of the technical product from toluene. 1-Bromoanthraquinone, m.p. 191–192°C (lit.⁵ 188°C), 2-bromoanthraquinone, m.p. 210–211°C (lit.⁶ 210°C), 1-iodoanthraquinone, m.p. 208–209°C (lit.⁷ 204–205°C) and 2-iodoanthraquinone, m.p. 175.5–177°C (lit.⁸ 175–176°C) were obtained by repeated crystallisation of the technical product, purified chromatographically on an alumina column (activity II), from glacial acetic acid. 1-Fluoroanthraquinone, m.p. 233.5–236°C (lit.⁹ 234–236°C) was prepared according to Valkanas and Hopff⁹, purified by sublimation and crystallisation from chlorobenzene. 2-Fluoroanthraquinone, m.p. 203.5–204.5°C (lit.⁹ 203–204°C) was obtained by purification of the technical product by sublimation and recrystallisation from chlorobenzene. The purity of all substances was controlled chromatographically. The melting points were determined on a Kofler block calibrated with standards, at 4°C/min heating rate. Cyclohexane (Lachema, Brno) was purified for spectral purposes by filtration through a column of adsorbent¹⁰ and distillation.

Apparatus: Recording spectrophotometer Unicam SP 700. Single-beam spectrophotometer Hilger Uvispek with a photomultiplier adapter. Quartz cells with optical layer thickness 10 mm. A glass chamber of 19 × 5 cm basis and 18 cm high, with ground upper edges, closed with a glass lid.

The determination of pK_a was carried out by the procedure described earlier¹¹. The exact concentration of sulfuric acid in the solutions of the investigated substances was determined acidimetrically under the utilisation of mixed Tashiro indicator. The H_0 values of the sulfuric acid solutions and of fuming sulfuric acid are taken from the paper by Vinnik¹².

Chromatography on a thin layer of silica gel containing a luminescent indicator: On the start (2 cm from the edge) of a plate of Silufol UV 254 (Kavalier, Czechoslovakia), 15 × 15 cm, 4% solutions (1 μ l) of halogenoanthraquinone solutions in glacial acetic acid were applied and chromatography was carried out by ascending technique with toluene as the mobile phase. After evaporation of the solvent detection was carried out by inspection under short-wave UV light (254 nm; Miniuis, Desaga, G.F.R.). Halogenoanthraquinones appear first as dark violet spots on a light background. After prolonged irradiation the spots give a pink fluorescence.

RESULTS AND DISCUSSION

From a detailed study of absorption electronic spectra in cyclohexane, ethanol, and sulfuric acid of various concentrations we found that in monohalogeno-9,10-anthraquinones protonation takes place only on one carbonyl group. By protonation of one oxygen atom the basicity of the other oxygen atom is decreased to such an extent that it cannot be protonated even in fuming sulfuric acid. In Table I the obtained results are given including the values of factor m , which is the gradient of the plot of $\log(C_{BH^+}/C_B)$ on H_0 and a criterion of the validity of the H_0 function for the base investigated. The values of factor m were obtained by the method of smallest squares. From the results given in Table I it is evident that the values of half protonation H'_0 of the investigated substances differ very little from one another and that the substitution of hydrogen by one halogen atom in the position 1 decreases the pK_a

TABLE I
 pK_a Values and R_F Values of Monohalogeno Derivatives of 9,10-Anthraquinone

Substituent	H'_0 ^a	λ , nm	m	pK_a	R_F ^b
1-F	-9.05	308	1.05	- 9.51	0.21
	-9.09	422	1.05	- 9.55	
2-F	-8.99	313	1.06	- 9.53	0.37
	-9.01	410	0.96	- 8.66	
1-Cl	-9.09	313	1.04	- 9.45	0.32
	-9.07	429	1.06	- 9.61	
2-Cl	-9.12	323	1.00	- 9.12	0.46
	-9.03	418	1.02	- 9.21	
1-Br	-9.04	313	1.15	-10.40	0.36
	-9.14	435	1.06	- 9.69	
2-Br	-9.10	422	0.95	- 8.65	0.47
1-I	-9.02	317	1.08	- 9.74	0.41
	-8.97	461	1.00	- 8.97	
2-I	-9.21	495	0.96	- 8.84	0.48

^a H'_0 means half protonation; ^b chromatography was carried out on Silufol sheets, toluene was the mobile phase.

value more than the substitution in the position 2 in comparison with 9,10-anthraquinone ($pK_a = -8.40$) (ref.¹¹). From the absorption spectra it is evident that monohalogeno derivatives of 9,10 anthraquinone are characterised by a small "medium effect" in sulfuric acid which also becomes evident in the values of the gradient m which is close to one in these substances.

Monohalogeno derivatives of 9,10 anthraquinone behave on thin-layer chromatography in non-polar systems in the same way as in paper chromatography in systems with water as the stationary phase. The mobility of 1-halogenoanthraquinones is here probably affected by the formation of intermolecular hydrogen bonds with the anchored polar phase, *i.e.* with the water of the aqueous envelope of silica gel globules, or also with the hydroxyls of the $-\text{Si}-\text{OH}$ bonds. 2-Halogenoanthraquinones are not capable of forming such bonds, their molecule is more hydrophobic and therefore they move in the unpolar phase better.

Even in chromatography on silica gel the exceptional behaviour of fluoroanthraquinones was confirmed. Their interaction with the stationary phase is stronger than in other halogenoanthraquinones. While in the series with the substituents in the

position 1 the polarity decreases in the following sequence: $F \gg Cl > Br > J$, in the case of substituents in the position 2 the sequence may be expressed as follows: $F > Cl \doteq Br \doteq J$. Among 2-halogenoanthraquinones it is only 2-fluoroanthraquinone that behaves differently, while 2-chloro, bromo and iodoanthraquinones practically do not separate. The R_F values of 1- and 2-halogenoanthraquinones are given in Table I.

On the basis of the results obtained we made an attempt at the formation of a theoretical model of the investigated substances within the frame of one-electron HMO method. The values of half protonation H'_0 were correlated with the localisation energies and superdelocalisabilities obtained with the HMO method ($\alpha_F = \alpha + 2.5\beta$, $\beta_{CF} = 0.8\beta$; $\alpha_{Cl} = \alpha + 2.0\beta$, $\beta_{CCl} = 0.7\beta$; $\alpha_{Br} = \alpha + 1.5\beta$, $\beta_{CBr} = 0.4\beta$; $\alpha_J = \alpha + 1.5\beta$, $\beta_{CJ} = 0.25\beta$). In view of the small differences between the experimental values of H'_0 for 1- and 2-monohalogeno derivatives of 9,10-anthraquinone we could not expect a correlation. Negligible differences in the values of both indexes of reactivity for the series of the substances investigated confirm the suitability of the parameters for heteroatoms which we used for HMO calculations.

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