

Protonation constants of hydroxybenzenes in hydrochloric acid

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The absorption spectra of monohydroxybenzene (Fen), 1,3-dihydroxybenzene (Rez), 1,4-dihydroxybenzene (Hi), 1,2,3-trihydroxybenzene (Pg) and 1,3,5-trihydroxybenzene (Fg) in aqueous solutions of hydrochloric acid with different values of the Hammett acidity function (H_0) have two absorption bands in the region between 190–220 nm and 260–290 nm. This behavior is similar in another mineral acids (H_2SO_4 , H_3PO_4 , $HClO_4$). The absorbance decreases with increasing of acidity (with decreasing of H_0 values) because of O-protonation. The absorption maxima shift to longer wavelengths, and the graphic dependence of the absorption of the second band as a function of H_0 gives characteristic S-curves. These curves show the different effect of the acid on the form the protonation of the investigated hydroxybenzenes. The protonation constants of the hydroxybenzenes were calculated: $pK_{Fen} = -1.95$; $pK_{Rez} = -2.40$; $pK_{Hi} = -1.93$; $pK_{Pg} = -2.95$; $pK_{Fg} = -1.83$.

Key words: hydroxybenzenes, Hammett acidity function, hydrochloric acid, protonation, UV spectra, S-curve, protonation constant.

In aqueous solutions of strong mineral acids, hydroxybenzenes and their derivatives behave as weak bases and therefore can be protonated. Protonation of hydroxybenzenes causes some changes in UV/VIS spectra; maxima are shifted, the intensity of absorbances are decreased and new maxima occur. These changes are caused not only by protonation but also by the effect of the solvent. In acid media, protonation of this compounds can be expected to happen on *orto* and *para* carbon atom of the ring or on oxygen atom of the OH group. The position of protonation depends on the properties and concentration of the solvent, acidity of the solvent as well as on the kind of substituents groups. Very often the mixture of the O- and C-protonated species can be obtained. The O protonation is more exothermic. On the position of protonation the biggest effect has the solvent acidity. The protonation on the oxygen atom (formation of the π complex) happens more often in the less acid media. This is followed by the small shift of the absorption maxima as well as by the decrease of the absorbance intensity. If the acidity of the solvent is higher, the carbon protonation happens (formation of the δ complex). That leads to the formation of new products. This is followed by the appearance of the new bands in the absorption spectra.^{1–3}

In order to define the values of the acidity function H_0 , Hammett and Deyrup⁴ used 15 indicators (seven of them were primary amines). In the study of the ionisation equilibrium of this weak bases in H_2SO_4 and $HClO_4$ (acids were used as standards) they defined a new acidity function, H_0 , while the bases were called Hammetts bases. If the graphic dependence $\log ([BH^+]/[B]) - f(-H_0)$ of some other base with structure different from the primary amines, is the straight line with the value of the slope equal one. This compound is also a Hammett base or a Hammett indicator.

The literature data give values for protonation constants in H_2SO_4 , $HClO_4$ and H_3PO_4 for only a very small number of hydroxybenzenes. The protonation constants in H_3PO_4 were determined for the following hydroxybenzenes: Fen (−1.20), Rez (−2.20), Hi (−1.92) and Pg (−1.30).⁵ The pK values for Fen in H_2SO_4 ^{2,3} is −6.4,^{6,7} and −7.06,⁸ for Rez in $HClO_4$ −7.83⁹ and in H_2SO_4 −8.05⁹ and for Fg in H_2SO_4 −3.37⁹ and in $HClO_4$ −3.13.⁹ Some literature data show that the pK values of Fg in H_2SO_4 are from −3.73 to −3.96.¹⁰

There are no data in the literature about the behavior of hydroxybenzenes in HCl and therefore there are no data about protonation constants. The aim of this paper is determination of the protonation constants of this compounds in HCl and a comparison of the obtained results with pK values in other acids, in order to study a possibility of using hydroxybenzenes as Hammett bases.

EXPERIMENTAL

Monohydroxybenzene, 1,3-dihydroxybenzene, 1,4-dihydroxybenzene, 1,2,3-trihydroxybenzene, 1,3,5-trihydroxybenzene, HCl and $NaOH$, all p.a. were used in the experiments.

Solutions of HCl of different acidity (on the basis of available tables)⁴ were prepared by diluting concentrated acid and were pH-metric standardised.

The pH measurements were performed using a pH-meter Radiometer 2pH M-29 with a GK 2311 electrode. The solutions were thermostated at 25 ± 0.1 °C. UV spectra were obtained using a Perkin Elmer Lambda 15 UV/VIS spectrophotometer with a 1 cm quartz cell. Solutions of hydroxybenzenes, concentration 1×10^{-4} and 1×10^{-3} mol/dm³, were prepared by dissolving exact quantities of the corresponding substances in solutions of HCl of known H_0 value immediately before recording the absorption spectra. Spectra were recorded against the acid solution with the corresponding H_0 value.

RESULTS AND DISCUSSION

It is evident from the absorption spectra of Fen in a solution of HCl ($H_0 = -0.20$) (Fig. 1), that two absorption bands are present, one at 204.6 nm and the other at 269.0 nm. With increasing acidity, $H_0 = -1.58$ and -2.86 , the absorption maxima are shifted to longer wavelengths, with decreasing of absorbancy. The absorption spectra of another hydroxybenzenes show similar behavior, which was noticed earlier in other mineral acids (H_2SO_4 , $HClO_4$, H_3PO_4), and which is characteristic for O-protonation.^{1,2}

The absorption spectra of the investigated hydroxybenzenes (Fen, Rez, Hi, Pg and Fg) in aqueous solutions of HCl of different acidity (H_0 from -0.20 to -3.99) were recorded. Nonprotonated base B and protonated BH^+ have different ab-

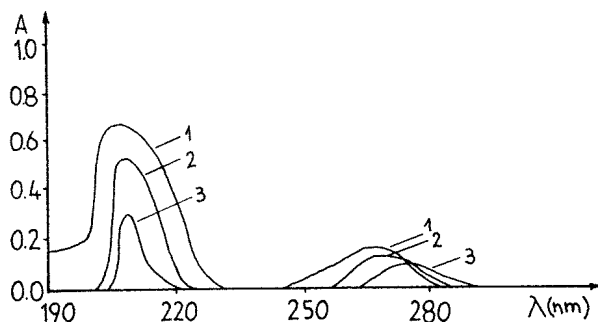


Fig. 1. Absorption spectra of monohydroxybenzene ($c = 1 \times 10^{-4}$ mol/dm³) in hydrochloric acid solutions: 1. $H_0 = -0.20$; 2. $H_0 = -1.58$ and 3. $H_0 = -2.86$.

sorptions, therefore, it is possible to determine the protonation constants by following the changes of absorbancy with changing concentration of acid or with a changing Hammett acidity function H_0 . The graphs of the dependence of absorbancy as a function of $-H_0$ give characteristic curves, from which the values of protonation constants can be determined. The values of the absorbance at λ_{\max} of the hydroxybenzene solutions in HCl solutions of different acidity are shown in Table I. The protonation constants, determined at λ_{\max} and at another wavelength, show a mutual deviation of ± 0.05 . However, Fen has a specific behavior. The dependence of absorbance on the specific λ does not show the typical S curve with an inflection point because it rapidly decreases. The behavior of the Fen in HClO_4 is the same.⁸ Namely, the maximum intensities in the area of 260–270 nm decrease in the wide range from diluted HClO_4 up to the 70%. At the same time, the dependence of the A on the H_0 is not a typical S-curve. The authors think that the decrease of the maximum intensity is not the consequence of the protonation. The possibility of specific influence of HClO_4 and HCl on the behavior of Fen can be considered.

Using the equation:^{11,12}

$$\log I = \log \frac{[BH^+]}{[B]} = \log \frac{A_B - A}{A - A_{BH^+}} = mH_0 + pK \quad (1)$$

the protonation constants were determined as the intercept on the ordinate and m (the number of hydrogen ions participating in protonation) were calculated as the slope of the linear dependence of $\log I$ on H_0 . In Eq. (1) A_B is the absorbance of the base (initial part of the S-curve), A_{BH^+} is the absorbance of the protonated base (final part of the curve) and A is the absorbance obtained for the corresponding H_0 value.

On the basis of the results presented in Table I, S-curves were constructed (Fig. 2) from which the values of A_B , A_{BH^+} and A were determined. The S-curves show that HCl is a solvent which has a significant effect on the protonated base of Fen, Hi and Pg (Fig. 2a for Fen as an example) whereas this is not the case for Rez

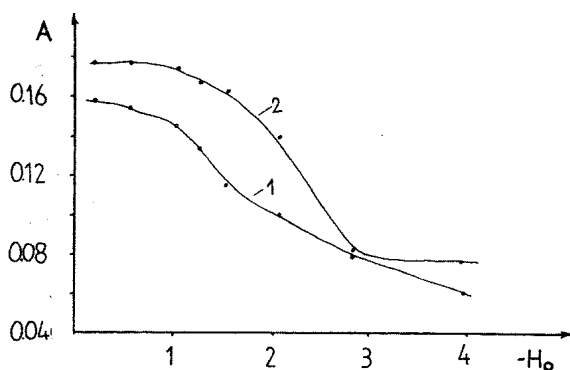


Fig. 2. Absorbance changes of hydroxybenzenes as a function of the hydrochloric acid H_0 value: a. Fen ($c = 1 \times 10^{-4}$ mol/dm³, λ_{\max}); b. Rez ($c = 1 \times 10^{-4}$ mol/dm³, $\lambda = 272.8$ nm).

and Fg (Fig. 2b for Rez). From the given linear dependence of the calculated ionization ratio as a function of $-H_0$ (Fig. 3), the protonation constants, pK , and m were determined which are given in Table II.

TABLE I. Absorbances at λ_{\max} for Fen, Rez, Hi ($c = 1 \times 10^{-4}$ mol/dm³) and for Pg and Fg ($c = 1 \times 10^{-3}$ mol/dm³) in hydrochloric acid solutions of different H_0 values

$-H_0$	Fen	Rez	Hi	Pg	Fg
0.20	0.158	0.176	0.285	0.658	0.624
0.47	0.154	0.178	0.255	0.663	0.610
1.05	0.147	0.160	0.244	0.651	0.515
1.23	0.135	0.172	0.242	0.654	0.513
1.58	0.110	0.170	0.211	0.623	0.464
2.12	0.100	0.193	0.206	0.642	0.448
2.86	0.079	0.081	0.226	0.602	0.454
2.99	0.057	0.079	0.255	0.581	0.440

TABLE II. Protonation constants (pK) and number of H^+ ions (m) participating in the protonation of hydroxybenzenes in hydrochloric acid

	Fen	Rez	Hi	Pg	Fg
$-pK$	1.95	2.40	1.93	2.95	1.83
m	1.60	1.07	1.40	2.07	1.75

The graphic dependence $\log ([BH^+]/[B]) - f(-H_0)$ should, according to Eq. (1), give a straight line for all the investigated hydroxybenzenes. However, this dependence has a slope with the value one only for Rez. The literature data show that some compounds are Hammett bases if this dependence is linear with a slope with the value one.⁴ Therefore, only the protonation constant for Rez is a thermodynamic constant of the protonation reaction (*i.e.*, pK).

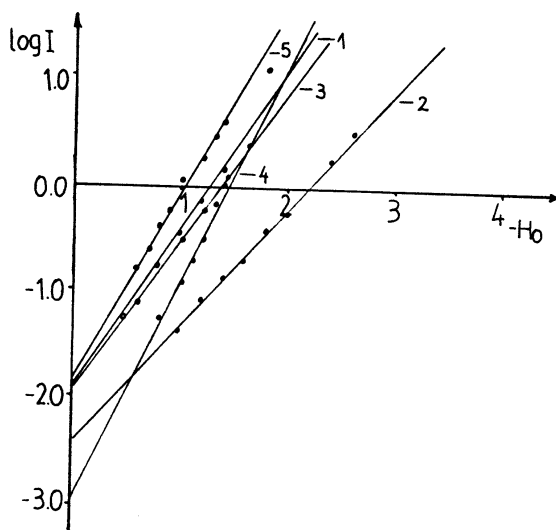


Fig. 3. Dependence of $\log I$ on the hydrochloric acid H_0 value: 1. Fen, 2. Rez, 3. Hi, 4. Pg and 5. Fg.

Comparing the results given in this work with literature data⁵⁻¹⁰ concerning the protonation constants of hydroxybenzene in H_2SO_4 , $HClO_4$ and H_3PO_4 , it can be concluded that differences exist. Considering the fact that the same values of pK in different acids are condition for some compound to be Hammett base, it can be concluded that hydroxybenzenes do not follow this rule and therefore do not belong to the Hammett bases.

ИЗВОД

КОНСТАНТЕ ПРОТОНАЦИЈЕ ХИДРОКСИБЕНЗЕНА У ХЛОРОВОДОНИЧНОЈ КИСЕЛИНИ

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У раду су дати резултати одређивања константи протонације, pK , испитиваних хидроксibenzena (монохидроксibenzen (Fen), 1,3-дихидроксibenzen (Rez), 1,4-дихидроксibenzen (Hi), 1,2,3-трихидроксibenzen (Pg) и 1,3,5-трихидроксibenzen (Fg)), као и број просечно везаних протона (m). Резултати су добијени снимањем апсорпционих спектра испитиваних хидроксibenzena у растворима хлороводоничне киселине различите киселости изражене Hammett-овом киселинском функцијом H_0 . Из карактеристичних S-кривих одређене су константе протонације: $pK_{Fen} = -1,95$; $pK_{Rez} = -2,40$; $pK_{Hi} = -1,93$; $pK_{Pg} = -2,95$; $pK_{Fg} = -1,83$.

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