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BASICITY OF 5-METHYLRESORCINOL STUDIED BY CARBON-13 NMR AND UV-ABSORPTION SPECTROSCOPY

The protonation of 5-methylresorcinol (5 MR) in aqueous sulfuric acid solutions has been studied by ^{13}C NMR spectroscopy [1] and UV-absorption spectrophotometry [2]. A remarkable disagreement between the protonation parameters ($\text{p}K_{\text{BH}^+}$, m^*) estimated applying these two spectroscopic methods was established (see Table 1). In this paper search for the explanation of these conflicting results is proceeded. Previously we have paid attention to the ^{13}C NMR spectra of 5 MR in aqueous sulfuric acid solutions [1]. These spectra indicate that in $<70\%$ H_2SO_4 (w/w) the O-protonation of 5 MR is predominant. In more concentrated sulfuric acid solutions, the C-protonated form of 5 MR appears [1]. This point of view is also indirectly supported by UV-spectrophotometry. It has been shown that the UV-absorption maximum of 5 MR in the region of 50000 cm^{-1} shifts along the frequency axis when the sulfuric acid concentration is increased [2]. This shift consists of two curves A and B having a sharp joint around the 70% H_2SO_4 solutions (see Fig. 1). Curve A may be attributed to the blue shift in the absorption maximum caused by the O-protonation of 5 MR. On the other hand, curve B, demonstrating quite a different behaviour as compared to curve A, may be due to the red shift caused by the C-protonation of 5 MR. The turning point between these two curves at ca 70% H_2SO_4 is in good agreement with ^{13}C NMR results.

Table 1

Protonation parameters of 5-methylresorcinol in aqueous sulphuric acid solutions estimated from ^{13}C NMR and UV-absorption spectra

Data and method used	$\text{p}K_{\text{BH}^+}$	m^*
^{13}C NMR chemical shifts		
δ (C-1, C-3)		
plot ($\log I - \log C_{\text{H}^+}$) vs. X -function ($-0.2 \leq \log I \leq 0.75$)	-3.65	0.63
nonlinear regression procedure [1]	-4.25	0.78
δ (C-5)		
plot ($\log I - \log C_{\text{H}^+}$) vs. X -function ($-0.2 \leq \log I \leq 0.75$)	-3.63	0.63
nonlinear regression procedure [1]	-4.17	0.76
UV-absorption spectra ($30\,000\text{--}42\,000\text{ cm}^{-1}$)		
plot ($\log I - \log C_{\text{H}^+}$) vs. X -function [2]	-5.84 ± 0.05	1.21 ± 0.02

Note: All the $\text{p}K_{\text{BH}^+}$ and m^* values in this Table were obtained assuming that only one BH^+ form of the base under study exists.

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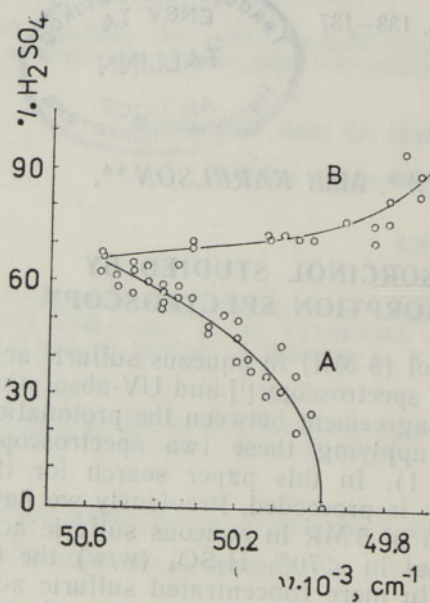


Fig. 1. Far-UV band's maximum of 5-methylresorcinol vs. % H_2SO_4 (w/w). A is the region where O-protonation prevails, B is that with C-protonation predominance.

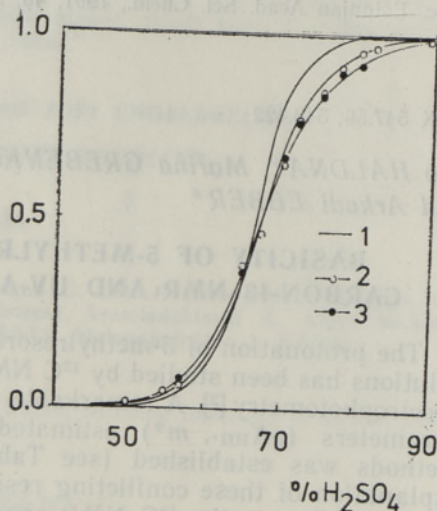


Fig. 2. Protonation curves for 5-methylresorcinol vs. % H_2SO_4 : $\alpha = (p - p_B) \times (p_{BH^+} - p_B)^{-1}$, where p is the parameter measured. For UV-spectra [2] $p = \epsilon$ (1) and for NMR-spectra $p = \delta$ (2 and 3). Curve 2 — δ (C-1, C-3), curve 3 — δ (C-5).

With regard to both the spectra discussed above we made a conclusion that 5MR yields two monoprotonated species in aqueous sulfuric acid solutions, one of them being O-protonated (${}_1\text{BH}^+$) and the other C-protonated (${}_2\text{BH}^+$). The C-protonation sites of 5MR have been discussed in our previous paper [1] on the basis of NMR spectral data. The appearance of a doublet in respective spectral peaks indicates the formation of C-4 (C-6) protonated species. The dependence of the measured parameter (the ^{13}C NMR chemical shift δ or molar extinction coefficient ϵ) on the sulfuric acid concentration in the presence of those two monoprotonated forms is given by the following set of equations [3, 4]:

$$p = \frac{1}{1 + I_1 + I_2} \cdot p_0 + \frac{I_1}{1 + I_1 + I_2} \cdot p_1 + \frac{I_2}{1 + I_1 + I_2} \cdot p_2 = \alpha_0 p_0 + \alpha_1 p_1 + \alpha_2 p_2, \quad (1)$$

$$I_1 = C_{{}_1\text{BH}^+} / C_B = 10.0^{(\log C_{\text{H}^+} + m_1^* X + pK_{{}_1\text{BH}^+})}, \quad (2)$$

$$I_2 = C_{{}_2\text{BH}^+} / C_B = 10.0^{(\log C_{\text{H}^+} + m_2^* X + pK_{{}_2\text{BH}^+})}, \quad (3)$$

where p_0 , p_1 , and p_2 are the characteristic values of the measured parameter (p) for the unionized (B), O-protonated (${}_1\text{BH}^+$), and C-protonated forms (${}_2\text{BH}^+$), respectively. In the case described above, two pairs of protonation parameters ($pK_{{}_1\text{BH}^+}$, m_1^* and $pK_{{}_2\text{BH}^+}$, m_2^*) are needed to characterize the protonation process observed [3]. Provided that in the UV and NMR spectra the relative contribution of O- and C-protonation to the measured dependences $p = \varphi$ (% acid) are not exactly the same, the values of $pK_{{}_1\text{BH}^+}$, m_1^* , $pK_{{}_2\text{BH}^+}$, and m_2^* may be estimated using simultaneous nonlinear regression treatment of both experimental data. Equal statistical weights have been ascribed to the chemical shift (δ) in the ^{13}C NMR spectra and to the molar extinction coefficient (ϵ) in the UV-absorption spectra. This may be done by a linear transformation

$$b = \frac{1}{\rho_{\text{BH}^+} - \rho_{\text{B}}} \cdot p - \frac{\rho_{\text{B}}}{\rho_{\text{BH}^+} - \rho_{\text{B}}}, \quad (4)$$

where ρ_{B} and ρ_{BH^+} are the measured p values (δ or ε): ρ_{B} at low acid concentrations, where the base studied is in the B-form, and ρ_{BH^+} in concentrated acid solutions, where the base is practically completely protonated. It is obvious that at low acid concentrations $b \approx 0$ and in highly concentrated acid solutions $b \approx 1.0$ (see Fig. 2). It should be noted that in the classical case where only one BH^+ form is considered, b (Eq. 4) has the meaning of the protonation degree $\alpha = C_{\text{BH}^+} / (C_{\text{B}} + C_{\text{BH}^+})$. We used this to calculate the b (Eq. 4) values for UV-absorption spectra because the respective protonation parameters (pK_{BH^+} , m^*) in Table 1 are the classical mean values for the region of 30000—42000 cm^{-1} .

Performing a transformation of Eq. (4), parameters ρ_0 , ρ_1 , and ρ_2 in (1) may be presented as follows:

$$\rho_0 = (b_0 - A)/B, \quad (5)$$

$$\rho_1 = (b_1 - A)/B, \quad (6)$$

$$\rho_2 = (b_2 - A)/B, \quad (7)$$

where b_0 , b_1 , and b_2 are equivalents for ρ_0 , ρ_1 , and ρ_2 in the b -scale, respectively; $A = (\rho_{\text{B}} - \rho_{\text{BH}^+})^{-1} \cdot \rho_{\text{B}}$, and $B = (\rho_{\text{B}} - \rho_{\text{BH}^+})^{-1}$. By substituting ρ_0 (Eq. 5), ρ_1 (Eq. 6), and ρ_2 (Eq. 7) into Eq. (1), we obtain

$$b = \alpha_0 b_0 + \alpha_1 b_1 + \alpha_2 b_2, \quad (8)$$

where the term

$$\alpha_0 b_0 = 0$$

because in the limit $\alpha_0 = 1$, $\alpha_1 = \alpha_2 = 0$, and we have $b = b_0 = 0$. Now the calculated values of b (Eq. 4) are given by

$$b_{\text{calc. UV}} = \alpha_1 b_{1, \text{UV}} + \alpha_2 b_{2, \text{UV}}, \quad (9)$$

$$b_{\text{calc. NMR}} = \alpha_1 b_{1, \text{NMR}} + \alpha_2 b_{2, \text{NMR}}, \quad (10)$$

where the subindices UV and NMR refer to the respective spectral data considered. To estimate the values of pK_{BH^+} , m^* , $pK_{2\text{BH}^+}$, m_2^* , $b_{1, \text{UV}}$, $b_{2, \text{UV}}$, $b_{1, \text{NMR}}$, and $b_{2, \text{NMR}}$ the following error function was minimized

$$S = \frac{1}{m} \sum_{i=1}^m (b_{\text{NMR}} - b_{\text{calc. NMR}})^2 + \frac{1}{n} \sum_{j=1}^n (b_{\text{UV}} - b_{\text{calc. UV}})^2, \quad (11)$$

where b_{NMR} and b_{UV} were obtained from experimental data by Eq. (4), substituting $p = \delta$ and $p = \varepsilon$, respectively. The values of $b_{2, \text{NMR}}$ and $b_{2, \text{UV}}$ were fixed to 1.00 and were not iterated in nonlinear regression analysis because in concentrated sulfuric acid solutions the C-protonated form (2BH^+) predominates no matter what kind of spectra are considered ($I_{\text{H}^+} \gg (1 + I_1)$).

The nonlinear regression analysis was performed applying an iterative nonderivative algorithm [5]. The respective computer program was written in FORTRAN IV. The number of spectral points used was $m + n = 14 + 12 = 26$ and that of estimated parameters was 6. It should be pointed out that the initial data for the nonlinear regression analysis consisted of

- (i) — experimental chemical shift values for carbon atoms C-1, C-3 ($\delta(\text{C}-1, \text{C}-3)$), and C-5 ($\delta(\text{C}-5)$), taken from our previous report [1]; these two shifts were treated separately in combination with UV-spectra (see Table 2);
- (ii) — calculated values for UV assuming that only one BH^+ form is present [2] with $pK_{\text{BH}^+} = -5.84$, $m^* = 1.21$; in this case we could calculate $b_{\text{UV}} = \alpha$.

Protonation parameters estimated for 5-methylresorcinol

Protonation site and parameters	δ used in combination with UV-spectra		Mean values
	δ (C-1, C-3)	δ (C-5)	
O-protonation			
pK_{1,BH^+}	-5.69	-5.70	-5.70
m_1^*	1.17	1.18	1.18
$b_{1, NMR}$	0.82	0.77	0.80
$b_{1, UV}$	0.99	0.97	0.98
C-protonation			
pK_{2,BH^+}^a	-10.2 ± 0.2	-10.2 ± 0.2	-10.2 ± 0.2
m_2^*	1.92	2.00	1.96
$b_{2, NMR}^b$	1.00	1.00	1.00
$b_{2, UV}^b$	1.00	1.00	1.00

a — Along the pK_{2,BH^+} -axis the minimum of the *S*-function (11) is not sharp but rather flat so that it is not possible to estimate the precise value of pK_{2,BH^+} . *b* — Prefixed at 1.00 (not iterated).

The b_{UV} values were calculated for the following sulfuric acid concentrations (% w/w): 45, 51, 57, 61, 63, 65, 67, 69, 71, 73, 75, 79, 83, and 85. The nonlinear regression procedure applied does not require that the δ and ϵ values should be given at the same sulfuric acid concentrations.

The values of the parameters obtained by the nonlinear regression analysis are listed in Table 2. They allow us to reproduce the initial data with a relative square root mean error of $\pm 2\%$ (in the *b*-scale). As expected, both the chemical shifts, δ (C-1, C-3) and δ (C-5), yielded practically the same values of parameters (see Table 1 and Fig. 2). It is obvious that C-protonation occurs in concentrated sulfuric acid solutions only: $pK_{2,BH^+} < pK_{1,BH^+}$ (see Table 2 and [1]). The C-protonation leads to much larger delocalization of the positive charge than the O-protonation: $m_2^* > m_1^*$ (see Table 2 and [6]). The relationship between the relative fractions of O- and C-protonated forms (α_1 and α_2) of 5MR is presented in Fig. 3. It can be seen from Fig. 3 that with increasing sulfuric acid concentration C-protonation starts to play the major role only when the acid concentration exceeds 70% H_2SO_4 as found in [1] on the basis of the NMR-spectra of 5MR. The contributions arising from O- (α_1) and C-protonation (α_2) to the UV- ($p = \epsilon$ in (1)) and NMR-spectra ($p = \delta$ in (1))

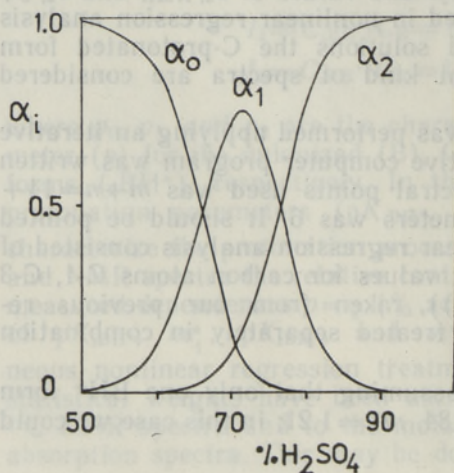


Fig. 3. Relative fractions of protonated forms (α) of 5-methylresorcinol vs. % H_2SO_4 . The meaning of α is given by Eq. (1): α_0 — unprotonated form, α_1 — O-protonated form, and α_2 — C-protonated form, α -s were calculated using $pK_{1,BH^+} = -5.70$, $pK_{2,BH^+} = -10.20$; $m_1^* = 1.18$, $m_2^* = 1.96$ (see Table 2).

depend also on p_0 (5), p_1 (6), and p_2 (7). The respective values $b_{1,UV}$, $b_{2,UV}$, $b_{1,NMR}$, and $b_{2,NMR}$ are listed in Table 2. The values of p_0 , p_1 , p_2 , and the respective a_0 , a_1 , a_2 calculated by (5)—(7) allow us to reproduce the measured dependences $\varepsilon = \varphi_1$ (% acid), $\delta = \varphi_2$ (% acid) shown in Fig. 2 with a relative square root mean error $\pm 2\%$ (as in the b-scale).

To sum it up, if we accept the existence of two protonated forms (O- and C-protonated ones) with the respective values of pK_{BH^+} , m^* , b_1 , and b_2 for each of them, then both the UV and NMR spectra may be handled together from a common point of view and pairs of protonation parameters (pK_{BH^+} , pK_{BH^+} , etc.) may be obtained which are valid for both the spectra involved.

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5-METÜÜLRESORTSIINI ALUSELISUSE UURIMINE SÜSINIK-13 TUUMAMAGNETRESONANTS- JA UV-ABSORPTSIOONSPEKTROSKOOPA ABIL

5-metüülresortsiiini aluselise uurimine süsinik-13 tuumamagnetresonantspektrite (TMR) ja UV-neeldumisspektrite abil on nende spektrite klassikalisel käsitlemisel andnud vastuolulisi tulemusi. Rakendades aga uut käsitusviisi, mis baseerub kahe erineva monoprotoneeritud vormi moodustumisel, on see vastuolu kõrvaldatud. Nendeks eristatavateks monoprotoneeritud vormideks on O-protoneerunud vorm (${}_1BH^+$) ja C-protoneerunud vorm (${}_2BH^+$). Artiklis on leitud, et erisugusel protoneerunud vormidel on erinevad protonisatsiooni parameetrid (${}_1BH^+ : pK_{BH^+} = -5,70$; $m^* = 1,18$ ja ${}_2BH^+ : pK_{BH^+} = -10,20$; $m^* = 1,96$). Kasutatud lähenemisviis lubas anda ühese, vastuoludeta seletuse 5-metüülresortsiiini aluselise uurimise tulemustele, mis on saadud TMR- ja UV-spektritelt.

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ИССЛЕДОВАНИЕ ОСНОВНОСТИ 5-МЕТИЛРЕЗОРЦИНА С ИСПОЛЬЗОВАНИЕМ ЕГО ^{13}C ЯМР- И УФ-СПЕКТРОВ

В рамках классического подхода использование ^{13}C ЯМР- и УФ-спектров 5-метилрезорцина привело к противоречивым результатам о его протонировании в водных растворах серной кислоты. В работе применен новый подход к обработке указанных спектров, предполагающий образование двух, отличных друг от друга протонированных форм: O-протонированной (${}_1BH^+$) и C-протонированной (${}_2BH^+$). Найдено, что эти формы характеризуются разными параметрами основности (${}_1BH^+ : pK_{BH^+} = -5,70$, $m^* = 1,18$; ${}_2BH^+ : pK_{BH^+} = -10,20$, $m^* = 1,96$). Использованный в работе подход позволил дать единую, без каких-либо противоречий трактовку результатов исследования основности 5-метилрезорцина по его ^{13}C ЯМР- и УФ-спектрам.