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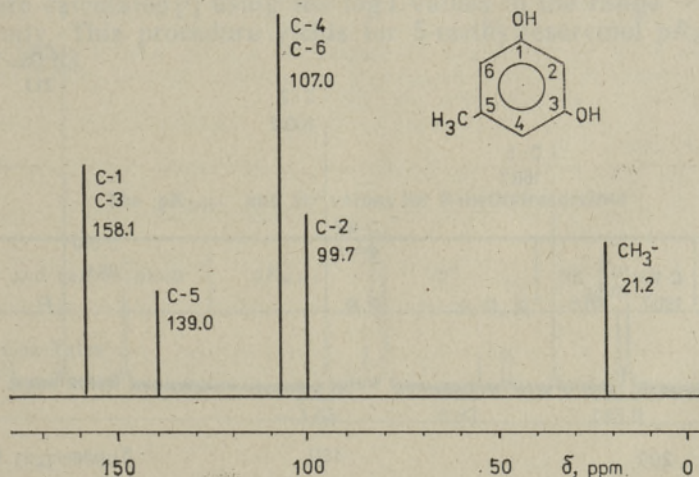
Ülo HALDNA, Kalle LINASK, Helle KUURA, Marina GREBENKOVA,
Arkadi EBBER and Mati KARELSON**A CARBON-13 NUCLEAR MAGNETIC RESONANCE STUDY
OF THE PROTONATION OF 5-METHYLRESORCINOL
IN SULFURIC ACID SOLUTIONS***(Presented by O. Kirret)*

The basicity of some hydroxybenzenes and alkoxybenzenes has already been studied [1-3]. These bases are half-protonated in 75—82% (w/w) aqueous sulfuric acid [4]. Besides a considerable amount of data are available about the protonation sites in hydroxybenzenes and alkoxybenzenes obtained by ^1H and ^{13}C NMR spectroscopy [5, 6].

Results and discussion

We wish to report the ^{13}C NMR observation of protonation of 5-methylresorcinol (5MR) in aqueous sulfuric acid solutions. The ^{13}C NMR spectrum of 5MR in DMSO is shown in Fig. 1. The assignment of the observed ^{13}C resonances to carbon atoms in 5MR is based on the equation and increments given by D. F. Ewing [7, 8]. The following chemical shifts (ppm) were calculated by this equation (in brackets the respective chemical shifts measured in DMSO are presented): C-1,3 156.7 (158.1), C-2 99.9 (99.7), C-4,6 109.0 (107.0), C-5 140.5 (139.0), CH_3 - 21.5 (21.2).

The ^{13}C chemical shifts (δ) of 5MR in water-sulfuric acid mixtures are presented in Table 1. It is evident that the protonation of 5MR causes remarkable changes only in C-1,3 and C-5 chemical shifts (about 35 and 26 ppm to the lower field or frequencies, respectively). The chemical shifts of C-2 and CH_3 - are practically not changed when the sulfuric acid

Fig. 1. ^{13}C NMR spectrum of 5-methylresorcinol dissolved in DMSO (2% w/w).

^{13}C chemical shifts of 5-methylresorcinol
in aqueous sulfuric acid solutions

% H_2SO_4 w/w	Chemical shifts δ (ppm) relative to TMS				
	C-1,C-3	C-5	C-4,C-6	C-2	C in CH_3 -
50.0	156.7	143.0	109.4	100.5	21.2
55.0	157.3	144.0	109.2	100.5	21.2
57.0	158.9	144.4	109.3	100.7	21.2
60.0	a	a	109.2	100.3	21.2
65.0	169.0	153.0	109.2	100.4	21.2
67.5	a	155.0	108.9	100.3	21.2
70.0	179.5	160.0	a	100.2	21.2
72.0	183.0	163.0	a	100.1	21.2
75.0	185.5	165.0	a	100.0	21.2
77.6	187.6	166.8	118.0	100.0	21.2
80.0	188.6	167.9	117.8	100.0	21.2
82.5	188.8	168.2	118.0	100.0	21.2
90.0	190.9	168.9	118.0	100.4	21.2
95.7	190.8	168.9	118.0	100.3	21.2

a — the chemical shift is uncertain because the respective line is broad (more than 15 ppm).

concentration is increased from 0 to 95.7%. The chemical shift of C-4,6 (δ (C-4,6)) is not changed in the range of 0–75% H_2SO_4 . In more concentrated acid solutions δ (C-4,6) is split into two lines: δ' (C-4,6) \approx 118 ppm and δ'' (C-4,6) \approx 40 ppm. In 75–80% H_2SO_4 , the respective components δ' and δ'' are rather broad (10–15 ppm) becoming narrower in more concentrated acid solutions. The appearance of this dublet indicates that in these solutions 5MR becomes C-protonated in position 4,6 (see Fig. 2). As a result, the carbon atoms in positions 1 and 3 become unequal, one being closer to the protonation site than the other, and line C-1,3 is also split into a dublet (Fig. 2). The absence of this dublet in δ (C-4,6) at sulfuric acid concentrations lower than 75% allows us to conclude that in these solutions 5MR are presumably protonated on oxygen. A similar conclusion has been drawn about some other phenols [5].

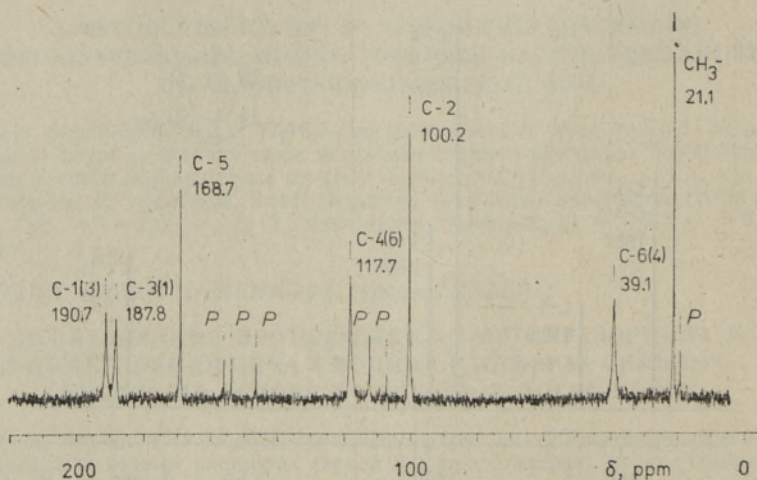


Fig. 2. ^{13}C NMR spectrum of 5-methylresorcinol (5MR) in 90% H_2SO_4 . The low intensity signals denoted by *P* are due to the sulfonation products of 5MR.

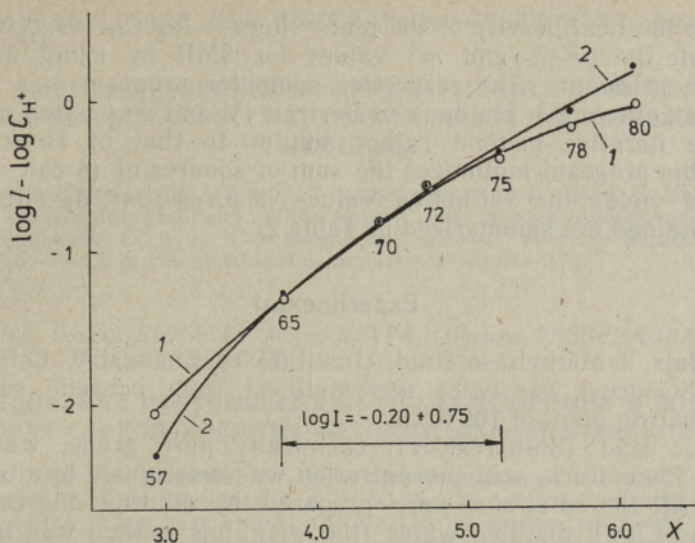


Fig. 3. The plots $\log I - \log C_{H^+}$ vs. X -function [9]: 1 — C-1,3; 2 — C-5. The numbers at points indicate the sulfuric acid concentrations (% w/w).

The dependences of δ (C-1,3) and δ (C-5) on the sulfuric acid concentration (see Table 1) may formally be used to estimate the pK_{BH^+} and m^* values of 5MR by the Cox-Yates excess acidity method [9]. The indicator ratio $I = C_{BH^+}/C_B$ values were calculated by

$$I = \frac{\delta_B - \delta}{\delta - \delta_{BH^+}},$$

where δ_B and δ_{BH^+} are the δ values for B and BH^+ forms of the base, respectively. The values of I were calculated taking C-1, C-3 $\delta_B = 156$ ppm, $\delta_{BH^+} = 191$ ppm and C-5 $\delta_B = 143$ ppm, $\delta_{BH^+} = 168.9$ ppm. The plots $\log I - \log C_{H^+}$ vs. X -function [9] show (see Fig. 3) the carbon atoms C-1, C-3 and C-5 to exhibit practically the same dependence $\log I - \log C_{H^+}$ vs. X . But except the region 65–75% H_2SO_4 ($-0.2 \leq \log I \leq 0.75$), these plots are not linear as expected. Therefore, the pK_{BH^+} and m^* values of 5MR were calculated [9] using the $\log I$ values in the range $-0.2 \leq \log I \leq 0.75$ only. This procedure yields for 5-methylresorcinol $pK_{BH^+} = -3.64$ and $m^* = 0.63$.

Table 2

The pK_{BH^+} and m^* values for 5-methylresorcinol

Method and carbon atom	pK_{BH^+}	m^*	δ_B , ppm	δ_{BH^+} , ppm
Classical Cox-Yates method [9]				
C-1, C-3	-3.65	0.63	156.0	191.0
C-5	-3.63	0.63	143.0	168.9
Nonlinear regression procedure				
C-1, C-3	-4.25	0.78	155.7	189.7
C-5	-4.17	0.76	142.3	168.5

Due to the nonlinearity of the plots $\log I - \log C_{H^+}$ vs. X we decided to calculate the pK_{BH^+} and m^* values for 5MR by using a nonlinear regression procedure. The respective computer program was written by one of the authors (Ü. Haldna) in Fortran IV and was based on the non-derivative iterative method rather similar to that of Hook and Jeeves^[10]. This program minimizes the sum of squares of (δ calc. — δ experim.) and yields the estimated values of pK_{BH^+} , m^* , δ_B and δ_{BH^+} . The results obtained are summarized in Table 2.

Experimental

Materials. 5-Methylresorcinol (Institute of Chemistry, Estonian Academy of Sciences) was twice recrystallized from benzene solution and had the melting point of 106.5°C.

Sulfuric acid (Sojuzreaktiv), chemically pure grade, was used as supplied. The sulfuric acid concentration was determined by titration with Na_2CO_3 . All the solutions were prepared by diluting the concentrated sulfuric acid with distilled water (the weighing method was used).

The solutions of 5-methylresorcinol were prepared by dissolving this compound in aqueous sulfuric acid. The concentrations of 5-methylresorcinol were in the 0.5—2.5% (w/w) range.

Chemical shift measurements. ^{13}C magnetic resonance spectra were run on a Bruker AC-200 spectrometer operating in the pulsed Fourier transform mode. In order to obtain the NMR spectrum of 5-methylresorcinol from its 0.5—2.5% (w/w) solution in aqueous sulfuric acid, about 30000 pulses were used (the total time for obtaining a spectrum was 12.5 hours). 5-Methylresorcinol with the natural abundance of ^{13}C was used. The chemical shifts, represented in Table 1, were measured relative to the shift of the CH_3 -group carbon atom taking $\delta(CH_3) = 21.2$ ppm (i. e. its value in DMSO).

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Estonian Academy of Sciences,
Institute of Chemistry

Tartu University

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Ülo HALDNA, Kalle LINASK, Helle KUURA, Marina GREBENKOVA, Arkadi EBBER,
Mati KARELSON

**5-METÜÜLRESORTSIINI PROTONISATSIOONI UURIMINE
VÄÄVELHAPPE VESILAHUSTES SÜSINIK-13 TUUMA MAGNETRESONANTSI
MEETODIL**

Mõõdeti 5-metüülresortsiini süsinik-13 tuumade keemilised nihked 0—95,7-protsendi-
listes H_2SO_4 vesilahustes, kasutades selleks Fourier' teisendusega tuumamagnetresonantsi
meetodit. Süsinikkude C-1,3 ja C-5 keemilistest nihetest arvutati 5-metüülresortsiini
 $pK_{\text{вн}^+} = -3,6 - -4,2$ ja solvatatsiooni parameeter $m^* = 0,63 - 0,78$.

Юло ХАЛДНА, Калле ЛИНАСК, Хелле КУУРА, Марина ГРЕБЕНКОВА,
Аркадий ЭББЕР, Мати КАРЕЛЬСОН

**ИССЛЕДОВАНИЕ ПРОТОНИЗАЦИИ 5-МЕТИЛРЕЗОРЦИНА В ВОДНЫХ
РАСТВОРАХ СЕРНОЙ КИСЛОТЫ МЕТОДОМ ЯМР-СПЕКТРОСКОПИИ ^{13}C**

Методом ЯМР-спектроскопии (с фурье-преобразованием) измерены химические
сдвиги всех ядер ^{13}C 5-метилрезорцина в 0—95,7%-ной серной кислоте. Исходя из
химических сдвигов углеродных атомов C-1,3 и C-5 вычислены константа основности
($pK_{\text{вн}^+} = -3,6 - -4,2$) и сольватационный параметр ($m^* = 0,63 - 0,78$) 5-метилрезор-
цина.