

Ülo HALDNA, Marina GREBENKOVA and Arkadi EBBER

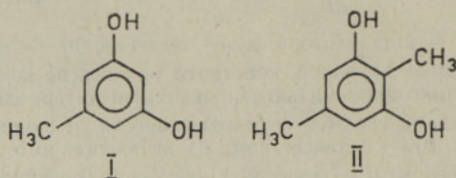
**PROTONATION OF 5-METHYLRESORCINOL AND  
2,5-DIMETHYLRESORCINOL IN AQUEOUS STRONG  
ACIDS STUDIED BY UV-ABSORPTION SPECTRA**

(Presented by J. Kann)

Few estimates of phenols basicity have been previously made [1-4]; this is probably due to a rather rapid sulfonation reaction of phenols in aqueous sulfuric acid solutions [5]. In some laboratories the use of alternative, i. e. perchloric acid solutions is considered dangerous. Nevertheless, our point of view is that the basicity of weak bases should be studied in both sulfuric and perchloric acid aqueous solutions. This enables us to detect the specific effects (if they exist) of the mineral acids used and estimate the corresponding influence on the  $pK_{BH^+}$  and solvation parameter ( $m^*$ ) values.

**Results and discussion**

For the bases studied



altogether four sets of spectra were measured:

1. 35 spectra of 5-methylresorcinol (I) in aqueous sulfuric acid solutions (0—94.90% (w/w)  $H_2SO_4$ );
2. 23 spectra of I in aqueous perchloric acid solutions (0—71.80% (w/w)  $HClO_4$ );
3. 44 spectra of 2,5-dimethylresorcinol (II) in aqueous sulfuric acid solutions (0—92.82% (w/w)  $H_2SO_4$ );
4. 37 spectra of II in aqueous perchloric acid solutions (0—72.03% (w/w)  $HClO_4$ ).

The most notable feature is the presence of three well-defined absorption bands in the spectral sets measured (see Figs. 1—4). The respective maxima are located at the frequencies shown in Table 1. The maxima of the bands B (I), C (I), B (II) and C (II) are practically not shifted with increasing acid concentration (see Table 1). This is not the case for the bands A (I) and A (II): with increasing acid concentration they first shift towards higher frequencies but when the percentage of  $H_2SO_4 > 70$  a distinctive shift to lower frequencies is observed.

We estimated  $pK_{BH^+}$  and  $m^*$  for I and II using all three absorption bands in the respective spectra. The excess acidity method was applied [6]. On each absorption band 4—5 frequencies were chosen for which the indicator ratio values,  $I = C_{BH^+}/C_B = (\epsilon - \epsilon_B)/(\epsilon_{BH^+} - \epsilon)$ , were calculated [7]. The  $\epsilon$  values for B and  $BH^+$  forms were obtained from the plots  $\epsilon$  vs. acid % (see Figs. 5 and 6). For the shifting bands A (I) and

A (II) only the values at the band maxima were used. The indicator ratios in the range of  $0.1 > I > 10$  were applied to estimate the  $pK_{BH^+}$  and  $m^*$  values [6, 7]:

$$\log I - \log C_{H^+} = m^* \cdot X + pK_{BH^+}. \quad (1)$$

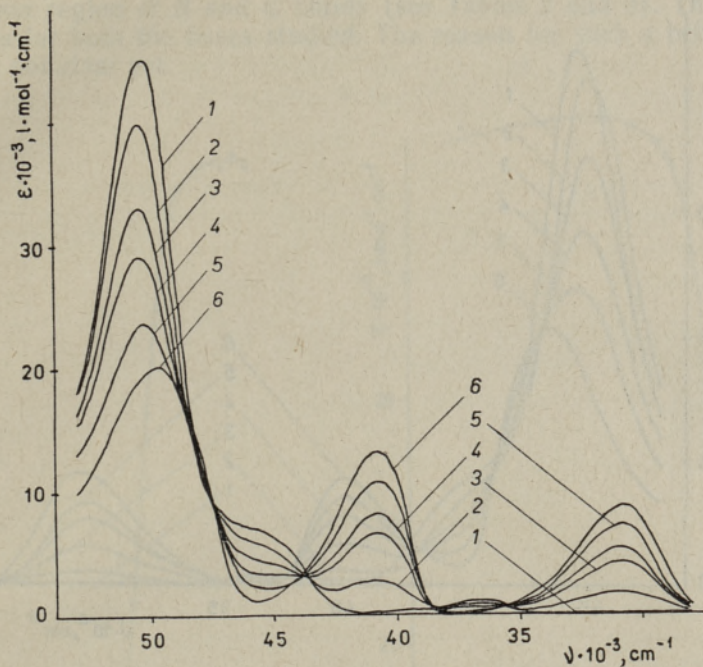


Fig. 1. UV-absorption spectra of 5-methylresorcinol in aqueous sulfuric acid solutions. Sulfuric acid %: 1 — 53.6, 2 — 62.1, 3 — 66.0, 4 — 67.4, 5 — 70.3, and 6 — 78.0.

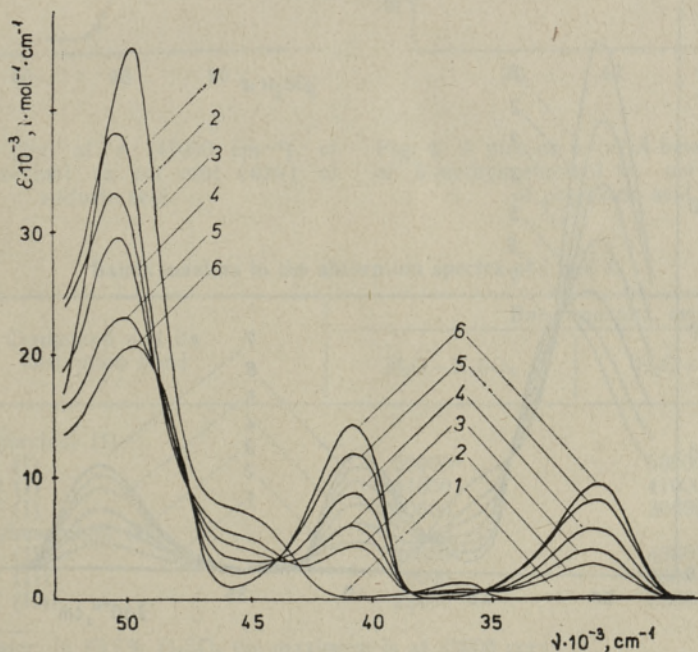


Fig. 2. UV-absorption spectra of 5-methylresorcinol in aqueous perchloric acid solutions. Perchloric acid %: 1 — 0.0, 2 — 59.3, 3 — 60.5, 4 — 62.0, 5 — 65.0, and 6 — 71.8.

In the regression analysis (1) statistical weights of the  $\log I$  values were taken into account [3, 7]. The results of the regression analysis are presented in Tables 2 and 3. The  $pK_{BH^+}$  and  $m^*$  values obtained for the regions of bands B and C (see Table 1) agree between themselves rather

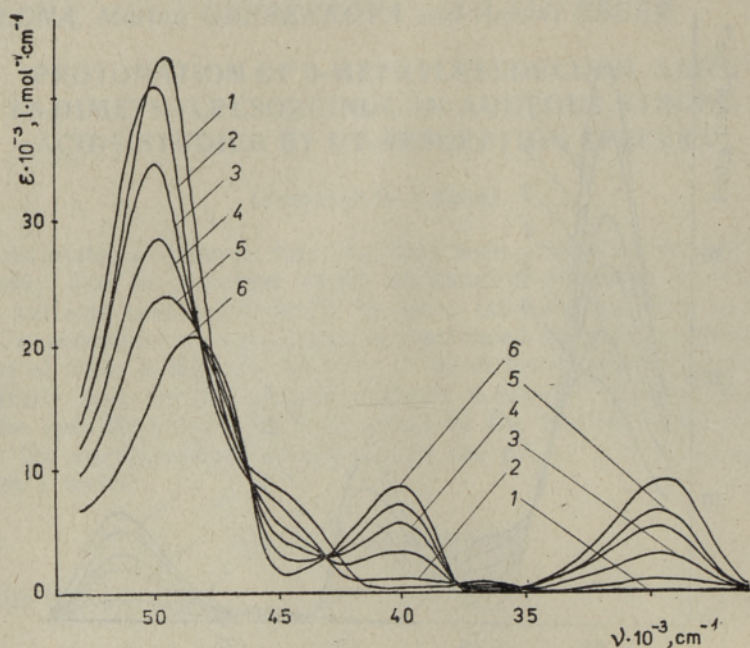


Fig. 3. UV-absorption spectra of 2,5-dimethylresorcinol in aqueous sulfuric acid solutions. Sulfuric acid %: 1 — 0.0, 2 — 56.0, 3 — 60.4, 4 — 63.1, 5 — 65.3, and 6 — 78.1.

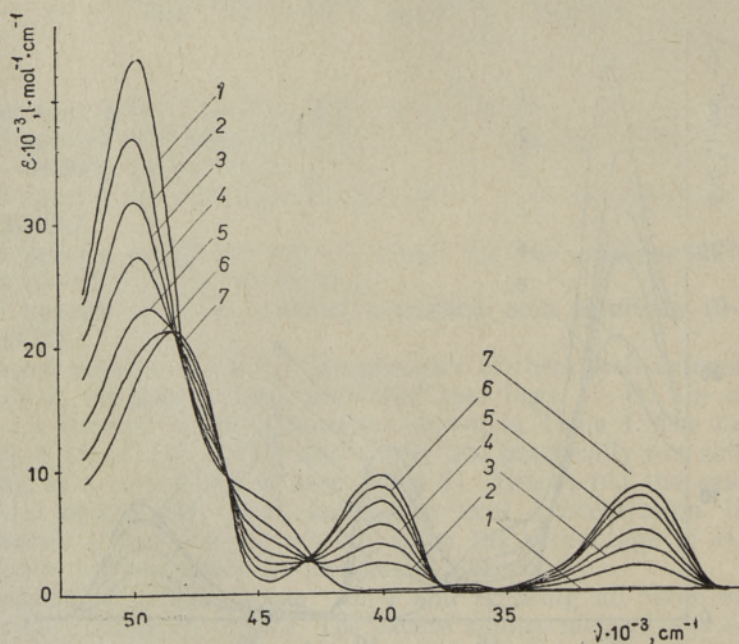


Fig. 4. UV-absorption spectra of 2,5-dimethylresorcinol in aqueous perchloric acid solutions. Perchloric acid %: 1 — 39.9, 2 — 55.3, 3 — 57.1, 4 — 58.6, 5 — 60.4, 6 — 62.7, and 7 — 70.3.

well. Therefore we are suggesting the use of mean  $pK_{BH^+}$  and  $m^*$  values in the region of 29600–42000  $cm^{-1}$  as the best estimates for  $pK_{BH^+}$  and  $m^*$  of the bases studied (see Tables 2 and 3).

It should be pointed out that the shifting A-band (see Table 1) yields the  $pK_{BH^+}$  and  $m^*$  values which remarkably differ from those obtained in the common region of B and C bands (see Tables 2 and 3). This conclusion holds for both the bases studied. The reason for such a behaviour of band A is not clear yet.

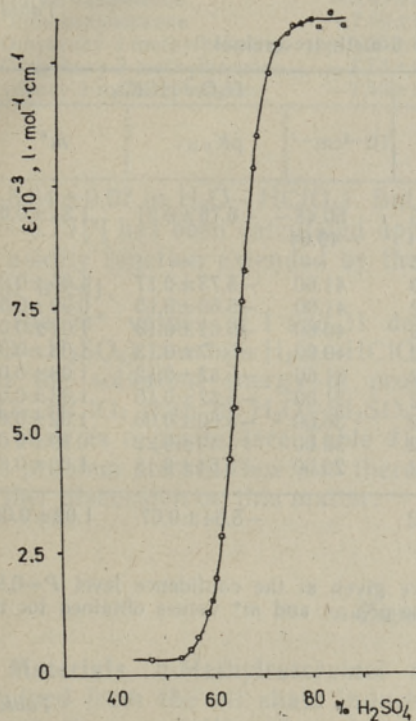


Fig. 5. A plot of  $\epsilon$  (41000  $cm^{-1}$ ) of 5-methylresorcinol vs. per cent (w/w) of sulfuric acid.

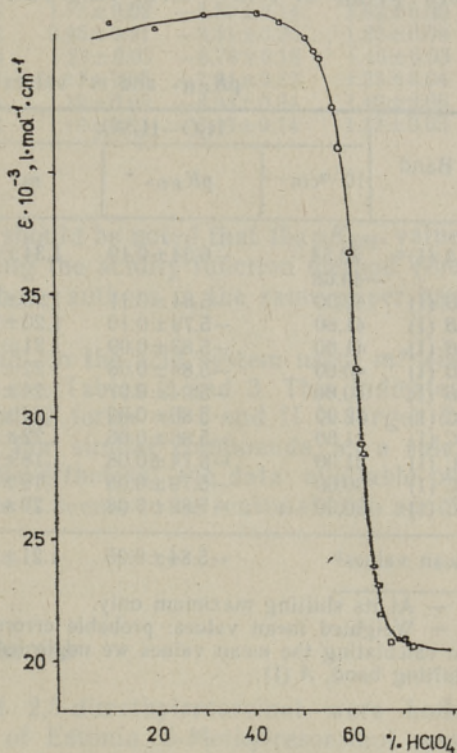


Fig. 6. A plot of  $\epsilon$  (at A-band maximum) of 5-methylresorcinol vs. per cent (w/w) of perchloric acid.

Bands maxima in the absorption spectra of I and II

Table 1

Compound and its absorption band	Band maxima, $cm^{-1}$	
	$H_2O-H_2SO_4$	$H_2O-HClO_4$
5-Methylresorcinol (I)		
A (I)	50000 <sup>a</sup>	50000 <sup>b</sup>
B (I)	41000	41000
C (I)	30600	30600
2,5-Dimethylresorcinol (II)		
A (II)	49600 <sup>c</sup>	49600 <sup>d</sup>
B (II)	40000	40000
C (II)	29600	29600

<sup>a</sup> — In water; in 85.7%  $H_2SO_4$  the maximum is at 49600  $cm^{-1}$ .

<sup>b</sup> — In water; in 71.8%  $HClO_4$  the maximum is at 49600  $cm^{-1}$ .

<sup>c</sup> — In water; in 81.7%  $H_2SO_4$  the maximum is at 48600  $cm^{-1}$ .

<sup>d</sup> — In water; in 70.3%  $HClO_4$  the maximum is at 48600  $cm^{-1}$ .

The  $pK_{BH^+}$  values of I and II obtained in the systems  $H_2O-H_2SO_4$  and  $H_2O-HClO_4$  are almost equal. The difference between the expected  $pK_{BH^+}$  values is approximately as large as the sum of probable errors (see Tables 2 and 3). Such a closeness of  $pK_{BH^+}$  values calculated by the X-function method [6] for the bases similar to I and II in aqueous  $H_2SO_4$  and  $HClO_4$  solutions is not a rule: Table 4 shows that in some cases the differences between the respective  $pK_{BH^+}$  values are in the range of 1–2  $pK_{BH^+}$  units. Other authors [3] have reported that in aqueous perchloric acid  $pK_{BH^+}$  of I is  $-5.75$ . This value is close to that of our estimations

Table 2

Band	$H_2O-H_2SO_4$			$H_2O-HClO_4$		
	$10^{-3}cm^{-1}$	$pK_{BH^+}$	$m^*$	$10^{-3}cm^{-1}$	$pK_{BH^+}$	$m^*$
A (I) <sup>a</sup>	50.54– –49.68	$-6.34 \pm 0.19$	$1.34 \pm 0.05$	50.48– –49.64	$-6.75 \pm 0.21$	$1.31 \pm 0.05$
B (I)	42.00	$-5.84 \pm 0.11$	$1.20 \pm 0.03$	—	—	—
B (I)	41.60	$-5.79 \pm 0.10$	$1.20 \pm 0.10$	41.60	$-5.73 \pm 0.17$	$1.05 \pm 0.04$
B (I)	41.00	$-5.83 \pm 0.09$	$1.21 \pm 0.02$	41.00	$-5.50 \pm 0.15$	$0.99 \pm 0.03$
B (I)	40.60	$-5.89 \pm 0.08$	$1.22 \pm 0.02$	40.60	$-5.62 \pm 0.13$	$1.02 \pm 0.03$
B (I)	40.00	$-5.94 \pm 0.07$	$1.24 \pm 0.02$	40.00	$-5.67 \pm 0.13$	$1.03 \pm 0.03$
C (I)	32.00	$-5.86 \pm 0.06$	$1.22 \pm 0.02$	31.60	$-5.82 \pm 0.12$	$1.08 \pm 0.05$
C (I)	31.60	$-5.86 \pm 0.06$	$1.22 \pm 0.02$	31.00	$-5.62 \pm 0.15$	$1.03 \pm 0.03$
C (I)	31.00	$-5.74 \pm 0.08$	$1.18 \pm 0.02$	30.60	$-5.60 \pm 0.09$	$1.02 \pm 0.02$
C (I)	30.60	$-5.79 \pm 0.08$	$1.19 \pm 0.02$	30.00	$-5.49 \pm 0.22$	$0.99 \pm 0.05$
C (I)	30.00	$-5.82 \pm 0.08$	$1.20 \pm 0.02$	29.60	$-5.54 \pm 0.18$	$1.00 \pm 0.04$
Mean values <sup>b</sup>		$-5.84 \pm 0.05$	$1.21 \pm 0.02$		$-5.64 \pm 0.07$	$1.02 \pm 0.02$

a — At its shifting maximum only.

b — Weighted mean values: probable errors are given at the confidence level  $P=0.95$ . In calculating the mean values we neglected the  $pK_{BH^+}$  and  $m^*$  values obtained for the shifting band, A (I).

Table 3

Band	$H_2O-H_2SO_4$			$H_2O-HClO_4$		
	$10^{-3}cm^{-1}$	$pK_{BH^+}$	$m^*$	$10^{-3}cm^{-1}$	$pK_{BH^+}$	$m^*$
A (II) <sup>a</sup>	50.00– –48.44	$-6.80 \pm 0.02$	$1.69 \pm 0.02$	50.00– –48.48	$-7.01 \pm 0.19$	$1.58 \pm 0.05$
B (II)	41.00	$-6.06 \pm 0.08$	$1.47 \pm 0.02$	41.00	$-5.88 \pm 0.06$	$1.25 \pm 0.02$
B (II)	40.60	$-6.09 \pm 0.07$	$1.47 \pm 0.02$	40.60	$-5.77 \pm 0.05$	$1.22 \pm 0.01$
B (II)	40.00	$-6.06 \pm 0.07$	$1.46 \pm 0.02$	40.00	$-5.68 \pm 0.06$	$1.19 \pm 0.02$
B (II)	39.60	$-6.10 \pm 0.08$	$1.48 \pm 0.03$	39.60	$-5.63 \pm 0.06$	$1.18 \pm 0.02$
B (II)	39.00	$-6.15 \pm 0.09$	$1.50 \pm 0.03$	39.00	$-5.65 \pm 0.06$	$1.18 \pm 0.02$
C (II)	30.60	$-5.76 \pm 0.13$	$1.37 \pm 0.04$	30.60	$-5.88 \pm 0.04$	$1.26 \pm 0.01$
C (II)	30.00	$-5.66 \pm 0.10$	$1.33 \pm 0.03$	30.00	$-5.81 \pm 0.04$	$1.23 \pm 0.01$
C (II)	29.60	$-5.44 \pm 0.11$	$1.27 \pm 0.03$	29.60	$-5.69 \pm 0.05$	$1.20 \pm 0.01$
C (II)	29.00	$-5.23 \pm 0.16$	$1.20 \pm 0.05$	29.00	$-5.65 \pm 0.05$	$1.18 \pm 0.01$
C (II)	28.60	$-5.12 \pm 0.17$	$1.16 \pm 0.05$	28.60	$-5.50 \pm 0.06$	$1.14 \pm 0.02$
Mean values <sup>b</sup>		$-5.93 \pm 0.20$	$1.42 \pm 0.07$		$-5.74 \pm 0.09$	$1.21 \pm 0.02$

a — At its shifting maximum only.

b — Weighted mean values: probable errors are given at the confidence level  $P=0.95$ . In calculating the mean values we neglected the  $pK_{BH^+}$  and  $m^*$  values obtained for the shifting band, A (I).

$pK_{BH^+}$  and  $m^*$  values of some hydroxy- and alkoxybenzenes  
in aqueous sulfuric and perchloric acid solutions [10]

Base	H <sub>2</sub> O—H <sub>2</sub> SO <sub>4</sub>		H <sub>2</sub> O—HClO <sub>4</sub>	
	$pK_{BH^+}$	$m^*$	$pK_{BH^+}$	$m^*$
1,3,5-Trihydroxybenzene	-4.08±0.03	1.21±0.01	-3.62±0.03	0.89±0.01
1,3,5-Trimethoxybenzene	-5.71±0.06	1.78±0.02	-5.59±0.14	1.62±0.05
1,3-Dihydroxybenzene	-6.49±0.08	0.95±0.01	-8.51±0.26	1.25±0.04
1,3-Dimethoxybenzene	-7.60±0.14	1.23±0.03	-8.78±0.18	1.45±0.03
1,3-Dihydroxy-2-methylbenzene	-6.65±0.23	1.11±0.05	-7.64±0.22	1.23±0.04
1,3-Dimethoxy-2-methylbenzene	-7.53±0.14	1.19±0.03	-8.94±0.34	1.46±0.06
1-Hydroxy-3-methoxybenzene	-7.50±0.22	1.19±0.04	-8.49±0.14	1.33±0.03

(-5.64±0.07 in H<sub>2</sub>O—HClO<sub>4</sub>). But it should be noted that the  $pK_{BH^+}$  value of -5.75 [3] has been calculated applying the acidity function method (the  $H_c$  acidity function extended by the above authors in the same paper has been used).

The  $m^*$  values of I and II depend on the acid system used:  $m^*$  (in H<sub>2</sub>O—H<sub>2</sub>SO<sub>4</sub>) >  $m^*$  (in H<sub>2</sub>O—HClO<sub>4</sub>), see Tables 2 and 3. This indicates that the solvation energy of protonated forms of I and II is larger in H<sub>2</sub>O—HClO<sub>4</sub> than in H<sub>2</sub>O—H<sub>2</sub>SO<sub>4</sub> [8]. For similar compounds, as a rule, the case is opposite (see Table 4). Nevertheless, the data available on this problem are still few and therefore it seems to be reasonable to avoid further discussion on this matter.

### Experimental

**Materials.** 5-Methylresorcinol and 2,5-dimethylresorcinol were both obtained from the oil shale industry of Estonia. 5-Methylresorcinol was repeatedly recrystallized from benzene. 2,5-Dimethylresorcinol was purified by extraction and finally recrystallized from water. The purity of both the compounds was checked by gas chromatography which showed that the total concentration of impurities in the samples used was less than 1%.

The acids used were purchased from Sojuzreaktiv. Sulfuric acid (c. p.) was used as supplied. The commercial aqueous perchloric acid (c. p. ca 57% (w/w) HClO<sub>4</sub>) was concentrated by distillation under reduced pressure (30 mm Hg). In this way 73% (w/w) HClO<sub>4</sub> was obtained. The concentrations of acids stock solutions were determined from their densities, by comparison with known densities from the literature [9]. The solutions of sulfuric and perchloric acids were prepared by diluting the concentrated stock solutions of acids with distilled water (using the weighing method).

**Spectral measurements.** The absorption spectra were measured on a SPECORD M 40 spectrophotometer (Karl Zeiss Jena) in the range of 53000—26000 cm<sup>-1</sup> (188.7—384.6 nm) in thermostated cells (path length 2 and 10 mm) at 25.0±0.2°C. The samples for absorption determination (concentration in the range of (1÷3) · 10<sup>-4</sup> moles per liter) were prepared from standard solutions in water. The absorbance of sample solutions was measured against references consisting of acid of the same concentration

as the sample. All the sample solutions were prepared immediately before running the spectra: each spectrum was run in 10–15 minutes. Special care was taken to check whether the changes in the spectra in concentrated acid solutions were reversible, i. e. a sample solution in concentrated acid (96% H<sub>2</sub>SO<sub>4</sub>, for instance) was prepared and after 10–15 minutes pieces of ice were added to obtain the acid concentration of about 25–30%; the spectrum of this sample was compared to that of the sample prepared in more diluted acid (25–30%) directly. The discrepancies between the molar extinction coefficient values obtained this way were not large (about 2%, relative).

#### REFERENCES

1. Koeberg-Telder, A., Lambrechts, H. J. A., Cerfontain, H. Solutes in sulfuric acid. Part VIII. Protonation of phenol, 4-fluorophenol and 2- and 4-sulfonates in concentrated aqueous sulfuric acid: determination of  $pK_a$  values by means of carbon-13 NMR // J. R. Neth. Chem. Soc., 1983, **102**, 293–298.
2. Lambrechts, H. J. A., Cerfontain, H. Solutes in sulfuric acid. Part IX. Effect of para-substitution on the ionization of the oxonium ions of phenol and anisole // J. R. Neth. Chem. Soc., 1983, **102**, 299–301.
3. Kresge, A. J., Chen, H. J., Hakka, L. E., Kouba, J. E. Aromatic protonation 8. The equilibrium protonation of hydroxy- and alkoxybenzenes // J. Am. Chem. Soc., 1971, **93**, 6174–6181.
4. Stewart, R. The Proton: Application to Organic Chemistry. New York; London; Toronto, 1985, 124.
5. Kresge, A. J., Chiang, Y., Hakka, L. E. Aromatic protonation 7. The structure of the conjugated acids of hydroxy- and alkoxybenzenes // J. Am. Chem. Soc., 1971, **93**, 6167–6173.
6. Cox, R. A., Yates, K. Excess acidities. A general method for the determination of basicities in aqueous acid mixtures // J. Am. Chem. Soc., 1978, **100**, 3861–3865.
7. Haldna, U. The methods of  $pK_{BH^+}$  calculations for weak organic bases // Russ. Chem. Rev., 1980, **49**, 693.
8. Bagno, A., Scorrano, G., More O'Ferral, R. A. Stability and solvation of organic cations // Rev. Chem. Intermediates, 1987, **7**, N 4, 313–352.
9. International Critical Tables, Vol. 3. New York, 1930, 56.
10. Cox, R. A., Yates, K. Excess acidities. A general method for the determination of basicities in aqueous acid mixtures // J. Am. Chem. Soc., 1978, **100**, 3861–3865. Supplementary data to this paper, obtained from the J. Am. Chem. Soc., Tables 8 and 18.

Estonian Academy of Sciences,  
Institute of Chemistry

Received  
April 19, 1990

Ülo HALDNA, Marina GREBENKOVA, Arkadi EBBER

#### 5-METUÜLRESORTSIINI JA 2,5-DIMETUÜLRESORTSIINI PROTONISATSIIONI UURIMINE TUGEVATE HAPETE VESILAHUSTES UV-ABSORPTSIOONISPEKTRITE ABIL

Möödeti 5-metuülresortsiiini ja 2,5-dimetuülresortsiiini ultravioletsed absorptsiooni-spektrid väävelhappe ja perkloorhappe vesilahustes spektri piirkonnas 53000–26000 cm<sup>-1</sup>. Tulemustest arvutati liighappelisuse meetodil uuritud nõrkade aluste  $pK_{BH^+}$  ja solvatatsiooni parameetri  $m^*$  väärtused. Saadi järgmised tulemused: 5-metuülresortsiiini  $pK_{BH^+} = -5,6$  —  $-5,8$ ,  $m^* = 1,0$  —  $1,2$ ; 2,5-dimetuülresortsiiini  $pK_{BH^+} = -5,7$  —  $-5,9$ ,  $m^* = 1,2$  —  $1,4$ .

Юло ХАЛДНА, Марина ГРЕБЕНКОВА, Аркадий ЭББЕР

#### ИССЛЕДОВАНИЕ ПРОТОНИЗАЦИИ 5-МЕТИЛРЕЗОРЦИНА И 2,5-ДИМЕТИЛРЕЗОРЦИНА В ВОДНЫХ РАСТВОРАХ СИЛЬНЫХ КИСЛОТ НА ОСНОВЕ УФ-СПЕКТРОВ ПОГЛОЩЕНИЯ

Измерены УФ-спектры поглощения (53000–26000 см<sup>-1</sup>) 5-метилрезорцина и 2,5-диметилрезорцина в водных растворах серной и хлорной кислот. Из полученных данных методом избыточной кислотности вычислены значения  $pK_{BH^+}$  и сольватационного параметра  $m^*$  для 5-метилрезорцина ( $pK_{BH^+} = -5,6$  —  $-5,8$ ,  $m^* = 1,0$ – $1,2$ ) и 2,5-диметилрезорцина ( $pK_{BH^+} = -5,7$  —  $-5,9$ ,  $m^* = 1,2$ – $1,4$ ).