

The effect of Ionization on the Absorption Spectra of Hydroxy-benzene Derivatives

By G. L. SZEPESY

Introduction. In an earlier paper the effect of ionization on the absorption spectra of the organic compounds was interpreted by Kiss and Csetneky (1) on the basis of a fundamental theory. The object of the present investigation is to decide whether this theory is suitable for the interpretation of the influence exerted by acids and bases on phenolic compounds. The investigation in question was facilitated by the results of the quantum mechanical calculations carried out by Sándorffy (2).

Experimental part. The commercial phenolic compounds were purified by repeated recrystallization and distillation. Acid and basic solutions were made from Merck p. a. HClO_4 , H_2SO_4 , NaOH and KOH , respectively, in the following concentration: 0,01, 1,00 and 5,00 mol/liter. In the cases of resorcinol, orcinol, hydroquinone, pyrogallol and phloroglucinol owing to the fact that these compounds are readily oxidised in an alkaline medium, to avoid or to restrict this process, a Na_2SO_3 solution of 0,8% and 1,0%, respectively (3) was added to these solutions. At this concentration the absorption spectrum of this compound does not disturb the absorption spectrum of the examined compounds not causing errors until 230, 220 $\text{m}\mu$ (4). The measurements of the absorption spectra were carried out as previously described with the same apparatus (5, 6).

In each case, on interpreting the experimental results the obtained spectra were compared with the spectra of phenol (1) (curve 7, 8) and benzene obtained in acidic, alkaline and alcoholic mediums, respectively.

Experimental results. To abbreviate matters, instead of describing each curve in detail the data of table I. are referred to. The following changes are mentioned as being the more important ones.

In cases of pyrocatechol, hydroquinone and resorcinol the measurements were accomplished in more concentrated acids. In the case of resorcinol greater changes could be established at H_2SO_4 of 5 mol/liter, namely the spectra exhibits two smaller bands (276 and 263 $\text{m}\mu$) (curve 2). Owing to the oxidation of resorcinol and hydroquinone the spectra of these compounds obtained in alkaline medium were not taken into consideration.

At HClO_4 of 0,01 mol/liter the shape of the curve of pyrogallol is approximately equal to that of phenol (curve 7) while that of phenol shifts with 5 $\text{m}\mu$ towards the shorter wave lengths. At HClO_4 of 5 mol/liter the spectrum of pyrogallol (curve 1) exhibits three smaller bands at 276, 269 and 259 $\text{m}\mu$, respectively. Two bands were obtained for phloroglucinol (curve 6) at 272 and 266 $\text{m}\mu$ at HClO_4 of 1,0 mol/liter. Owing to the oxidation of pyrogallol only the

spectrum of phloroglucinol obtained in alkaline medium was taken into consideration.

Discussion of results. On the basis of quantum mechanical calculations (2) the conjugation between the hydroxyl group and the benzene ring is much greater than between the ring and the methoxyl group, on the other hand the conjugation between the methoxyl group and the ring is greater than that between the ring and the methyl group, therefore the bathochromic effect decreases in the m-, o-, and p-derivatives and that of the dihydroxy-benzene and cresols shift gradually towards longer wave lengths. The position of the bands obtained on the basis of quantum mechanical calculations is in good agreement with the experimental findings.

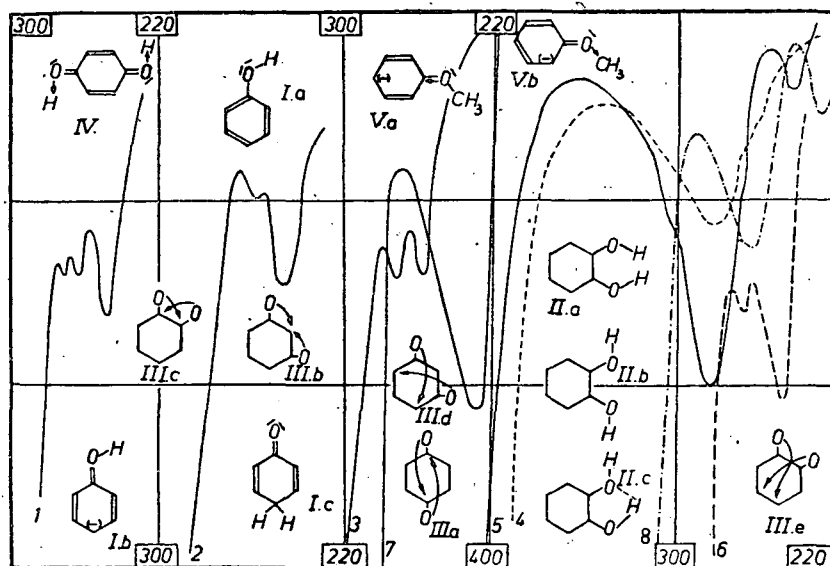
Table I.

Name of the compounds.	Medium	λ maximum		λ minimum	
		m μ	log. E	m μ	log. E
o-cresol	0,01 M HClO ₄	270	3,40	242	2,00
	0,01 M KOH	288	3,42	261	2,94
m-cresol		256	3,90	224	3,56
	0,01 M HClO ₄	273	3,00	243	1,68
	0,01 M KOH	290	3,42	261	2,66
		237	3,80	222	3,50
p-cresol	0,01 M HClO ₄	278	3,34	243	1,98
	1,00 M HClO ₄	279	3,10	247	1,74
	0,01 M KOH	308	3,34	265	2,68
		238	3,80	217	3,40
thymol	1,50 M HClO ₄	279	3,15	243	1,96
	0,01 M NaOH	283	3,25	259	2,99
		240	3,42	232	3,38
o-cresol-methyl-ether	0,01 M HClO ₄	273	3,22	238	2,03
pyrocatechin	2,00 M HClO ₄	273	3,13	241	2,12
	0,01 M KOH	291	3,43	267	2,96
		233	3,82	220	3,54
orcin	0,01 M HClO ₄	271	3,00	246	1,94
hydroquinone	5,00 M H ₂ SO ₄	285	3,14	244	1,94

In the ground state the resonance forms of phenol may be Ia-Ic. Through proton transition the resonance form Ib turns into resonance form Ic on the ceasing of the polarization of the molecule in the ground state. The possibility of proton transition ceases as the ionization is restricted on the action of acid, and the Ia. form becomes the prominent resonance form. Therefore it is obvious that the vibrational structure of the spectrum occurs especially in cases when effects hindering mesomerism (e. g. at polyphenols) take place. The vibrational structures of the spectrum of phenol obtained in a solution of hexane, in which case ionization cannot occur, also support this observation. In the case of concentrated acids the experiments did not account for the role of the H⁺ ions in the formation of the vibrational structure of the spectrum. The vibrational spectrum is probably caused by the predominance of the resonance form Ia.

In principle the spectrum of a neutral molecule ought to be obtained which would be similar to that obtained in a solution of hexane. This has neither been found in the case of phenol at HClO_4 of 0.01 mol/liter (1), nor in that of p-cresol in a solution of 1.0 mol/liter. As the concentration of acid used is sufficient to restrict the ionization, the lack of vibrational structure must be caused by complex, difficultly revealable disturbing influences (7). The conditions do not change in acidic medium through methylation (Va-Vb), e.g. in the case of o-cresol-methyl-ether. An attempt was made to establish whether thymol belongs to the group of hindered phenols, or to that of crypto-phenols (8). However, the hindering effect of the isopropyl group in ortho position is small owing to the slight shift.

In the case of two, or more, identical substituents the resonance effects are limited owing to their sending an electron to cer-



tain positions only (2) (cf. IIIa-IIIe.) Therefore, in these cases a mesomerism hindering effect of the identical radicals can also occur. Thus in the case of resorcinol, pyrogallol and phloroglucinol, respectively, the vibrational bands of benzene are obtained, pointing to the fact that the elimination of the mesomerism is due to the complete restriction of the dissociation of the hydroxyl group. The hindering effect exerted by the hydroxyl groups in meta positions on each other contributes to this too. In the case of pyrogallol the mesomerism of the middle hydroxyl group is sterically hindered by the two hydroxyl groups in o-position. The elimination of the mesomerization by means of etherization of the hydroxyl groups is proved by the absorption spectra of phloroglucinol-trimethyl-ether obtained in a solvent of dipole character (curve 3).

Both groups are able of mesomerism in the case of pyrocatechol as a quinoidal mesomeric structure may form. In more con-

centrated acid the spectrum shifted to shorter wave lengths, namely the energy of excitation increased in the neutral state. On the basis of the infra red spectrum (9, 10), three kinds of structures are possible (IIa-IIc), of which IIc is the most stable. Because of the oxygen-hydrogen interaction (11) this structure can be considered as having the smallest energy, but the greatest energy is needed for its excitation.

The alkaline medium facilitates the formation of the quinoidal mesomeric structure. In an alkaline medium the dissociation of the benzene nucleus takes place (cf. Ib) causing the rise of the extinction in the area of the long wave lengths. The results prove the principles described above. Not only the first, but the second band of the spectrum was also shifted to longer wave lengths. The latter band also exists for the neutral molecule in the region of the far ultraviolet (12). It was pointed out by Klingsted (13) that the shift to longer wave lengths takes place, if the carbonyl groups have double bonds in a conjugal position. The assignment of the diketonic formula (14, 15, 16) e.g. to p-quinone has been favored by evidence obtained by Garner and Sugden (17) from parachor measurements, by Pascal (18) from magnetic susceptibility measurements, this might also explain the appearance of the second band due to the presence of a greater percentage of the quinoidal mesomeric formula (cf. 5b) in the case of ionization this structure can occur more easily because of the lack of the energy of proton transition.

However, the cause of resorcinol, orcinol and phloroglucinol is interesting, because the occurrence of quinoidal structure is less probable owing to the position of substituents, yet the greatest shift was found towards the longer wave lengths. The interpretation of this phenomenon has not yet succeeded.

In the case of dihydro-resorcinol the taking place of a keto-enol tautomerism was proved by the alkylation reaction (19) and by bromine titrational examinations accomplished by Sonn and Winsor (20). It is known that an alkaline medium shifts the balance towards enol, though methylation of phloroglucinol by methyl iodide in a sodium methylate medium, namely in an alkaline medium, leads to a keto form (21).

On the basis of the most recent investigations ionization is a process in which the ions are attached to the phenolic hydroxyl group or closely approach it, although the possibility of intermolecular forces is smaller than in solvents of dipole character (22), as the spectrum has not been diminished by the increase in temperature (23).

Analysis of curves. The curves obtained at HClO_4 of 0.01 mol/liter were analysed for resorcinol, orcinol and pyrogallol, respectively. The analysis of the curves was carried out as previously described (24). The results are shown in table II.

On the basis of the analysis (2) of the spectra of the various phenolic derivatives obtained in alcoholic solutions the phenolic band is dissolved into three bands. The spectra of resorcinol and pyrogallol on the contrary may only be dissolved into two bands.

in acidic medium. Theoretically the number of transitions would be accounted for by the number of bands. According to classic electrodynamics and experience the number of the transitions and resonators is in proportion to the region of the bands. Therefore, the region of the bands of the spectra was determined and the diminution of the former in the order described above could be established. This fact again supports the hindering effect exerted on each other of the mesomerisable radicals in meta position.

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Summary. In several attempts the effect exerted by acid and base on mono-, di-, tri-hydroxy-benzene derivatives was examined. It is assumed that the spectrum of the neutral molecule is obtained in a suitable acid concentration, however, complex ion effects may also occur. In the case of pyrogallol it could be shown that the hydroxyl groups may also have a sterically hindering effect in a suitable position. The accomplished analysis of the curves again proved the mesomerism hindering effect of identical radicals.

It is obvious on the basis of the enumerated data that the hydroxyl groups are more strongly mesomerised in a dissociated condition because of the greater probability of the mesomeric limit cases. Quinoidal mesomeric structures form particularly readily, especially for o- and p-derivatives, respectively.

Table II.

Name of the compounds	log. E_{\max}	γ cm ⁻¹	log. E of obt. bands	ϑ	area of obt. bands	summarised area
resorcin	3,20	3620	3,20	1000	5616800	8713400
		3800	2,90	1100	3096600	
orcin	3,00	3660	3,00	1400	4961600	6167740
		3840	2,65	600	949820	
		3960	2,16	500	256320	
pyrogallol	2,87	3710	2,87	1500	3940600	5018500
		3920	2,58	800	1077900	
		3770	2,48	1000	1070260	
phloroglucinol	2,48	3340	2,24	600	369520	2034540
		3940	2,10	1000	594760	

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The preparation of p-acetamino benzaldehyde thiosemicarbazone

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In a previous communication Fodor (1) mentions Domagk's observation (2), that benzaldehyde thiosemicarbazone and p-acetamino benzaldehyde thiosemicarbazone have a tuberculostatic effect. But Domagk did not describe the compound, only its effect. I was entrusted by Prof. Fodor to prepare under his direction the compound mentioned above, as for medical purposes larger amounts of this drug were needed. The experiments were successful. From easily available starting materials I was able to realise the preparation of the compound with good yields. P-nitrotoluene (I) reacted on the effect of sodium sulphide according to Hodgson (3) furnishing p-aminobenzaldehyde (II). On removing, however, from the reaction mixture containing sodium sulphide the p-toluidine, which