99. *The Absorption Spectra of Some* m-*Substituted Phenols, and the Influence of Nucleophilic Substituents on Electronic Mobility.*

By Herbert H. Hodgson.

The ultra-violet aborption spectra of phenol and of eight *m*-substituted phenols have been measured in aqueous neutral, acid, and alkaline solution. The substituents were all *op*-directing, *i.e.*, electron-repelling, and their considerable effects on the electronic mobility are compared.

The ultra-violet aborption spectra of *m*-substituted phenols, $R\cdot C_6H_4\cdot OH$, where R = F, Cl, Br, I, OH, Me, OMe, OEt, have been measured in neutral, acid, and alkaline aqueous solution, and compared with the spectrum of phenol to ascertain the effect of electron-repelling substituents on the electronic mobility of phenol. Between 2200 A. and 3200 A. all nine compounds afforded only one absorption band (see graphs), and this is ascribed to the un-ionised molecule in each case, since the 3-halogeno-4-nitrosophenols (except 3-fluoro-4-nitrosophenol), owing to their more pronounced ionisations, afford two bands (Hodgson, J., 1937, 520), one at *ca.* 3000 A. corresponding to the un-ionised molecule, and the other at *ca.* 4000 A. due to the anion. 3-Fluoro-4-nitrosophenol has only band, due to the anion (Hodgson, this vol., p. 89).

The bands are really the envelopes of the fine structures not revealed in aqueous solution, and the peak displacements of all the *m*-substituted phenols (except *m*-fluorophenol) relative to that of phenol are towards the longer wave-lengths in neutral and acid solution. The peak of the *m*-fluorophenol band envelope is shifted by 30 A. towards a shorter wave-length. These shifts indicate a loosening of the electronic structure of phenol by the substituent except in the case of fluorine, which imposes a restraint. In alkaline solution, however, *m*-fluorophenol comes into line, owing to the increased ionisation and therefore decreased restraint in the un-ionised molecule.

The four *m*-halogenophenols have their shifts in the order, $F < Cl < Br < I$, *i.e.*, exactly the reverse of that of the total effects of the halogens as indicated by the ionisations of the phenols, except that *m*-fluorophenol is anomalous (Baddeley, Bennett, Glasstone, and Jones, J., **1935**, 1827; Hodgson and Smith, J., **1939**, 154).

In neutral and in acid solution the shifts for the remaining substituents are in the order, O > Me = OH = OMe, but in alkaline solution the order becomes OH > OEt > OMe > Me> H, which was to be anticipated, the second phenolic group in resorcinol being now more ionised and the structure of the molecule correspondingly loosened. This order illustrates clearly the differences in *op*-directing power of the groups, and is in accord with that established by their effects on chemical reactivity.

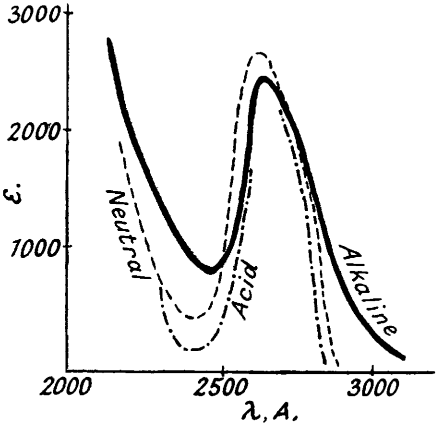
A comparison of the band-envelope shifts of all nine compounds gives : In neutral and in acid solutions, F < H< OH,Me,OMe,Cl < OEt < Br < I; in alkaline solution, H< F < Me < OMe < OEt < OH < Cl< Br < I.

EXPERIMENTAL.

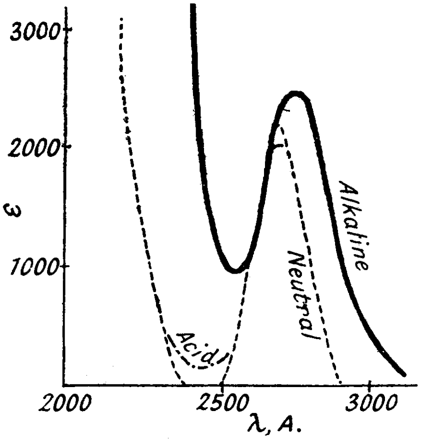
Apparatus and Measurements.—All measurements were made by means of a Hilger U.-V. Spekker Spectrophotometer, the absorption due to 1, 2, or 4 cm. paths being compared photographically with a blank cell filled with the solvent used. All the solutions were aqueous, in some cases with a trace of alcohol. Acidity was produced by hydrochloric acid, and alkalinity by sodium hydroxide. The pH measurements were made on a standard Cambridge pH meter.

Absorption Data.

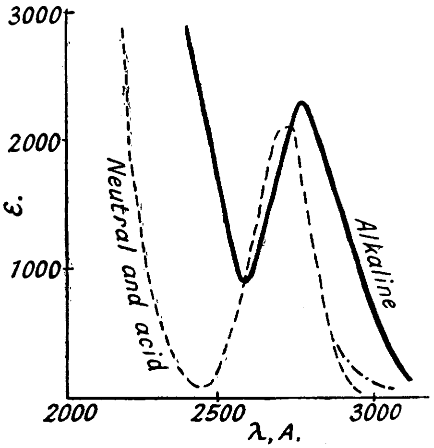
Compound.	Concn.		pH Values.			Acid and neutral solution.		Alk. soln.	
	Mg./l.	$4N \times 10^{-4}$.	Acid.	Neutral.	Alk.	λ max., A.	λ min., A.	λ max., A.	λ min., A.
m-Fluorophenol	54·2	1·21	3·21	7·61	9·03	2680	2410	2755	2540
m-Chlorophenol	60·8	1·18	3·12	7·69	9·10	2740	2475	2880	2605
m-Bromophenol	62·8	0·91	3·11	7·70	10·17	2760	2475	2925	2690
m-Iodophenol	64·4	0·73	3·06	7·55	10·00	2770	2525	2970	2645
m-Cresol	54·6	1·27	2·64	7·61	9·93	2740	2450	2790	2570
m-Methoxyphenol	62·2	1·25	2·38	7·22	9·96	2740	2450	2825	2580
m-Ethoxyphenol	63·8	1·15	2·68	6·95	10·11	2755	2450	2847	2593
Phenol	33·5	0·81	3·75	7·00	9·21	2710	2410	2720	2490
Resorcinol	44·7	1·02	2·38	7·16	11·00	2740	2450	2870	2600



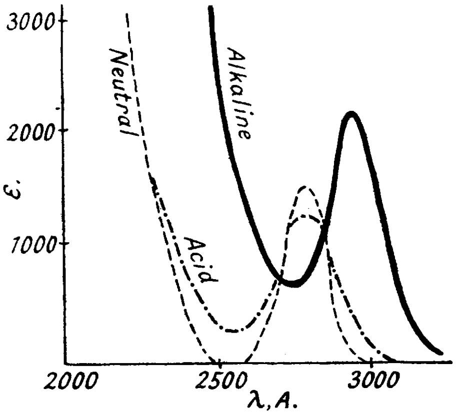
Absorption spectra of phenol.



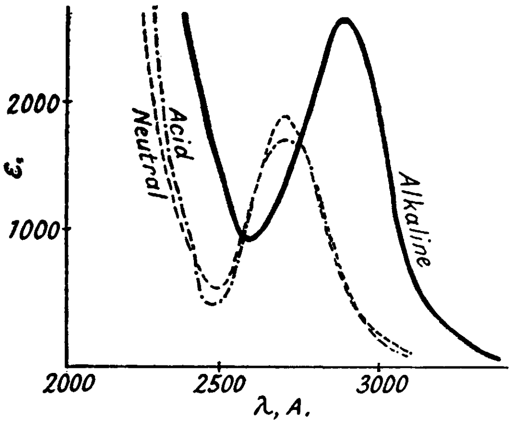
Absorption spectra of m-*fluorophenol.*



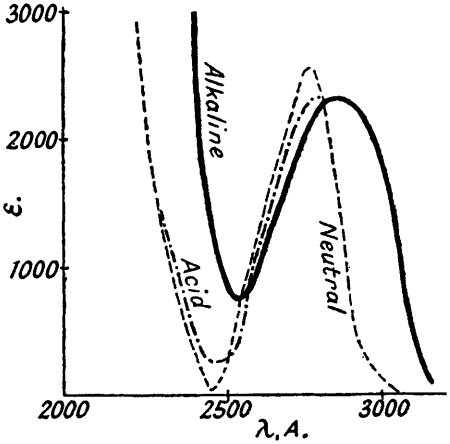
Absorption spectra of m-*cresol*



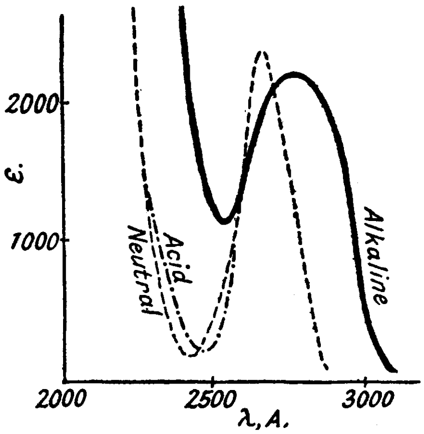
Absorption spectra of m-*bromophenol.*



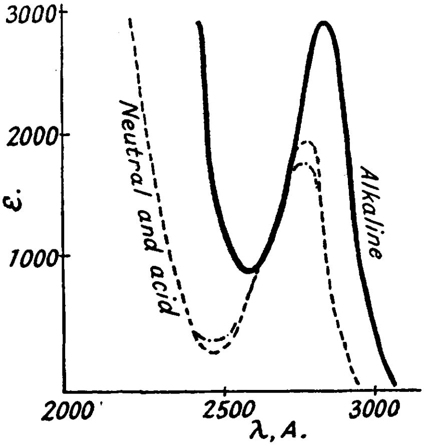
Absorption spectra of m-*iodophenol.*



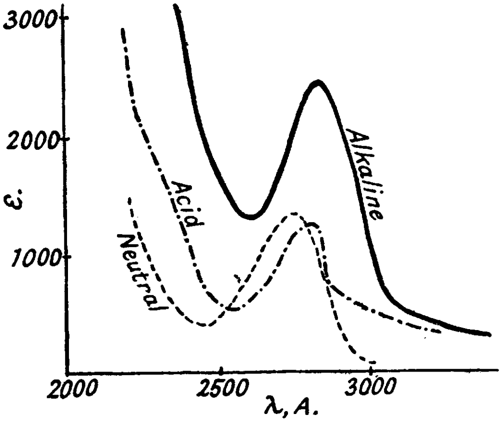
Absorption spectra of m-*chlorophenol.*



Absorption spectra of m-*methoxyphenol.*



Absorption spectra of m-*ethoxyphenol.*



Absorption spectra of resorcinol.

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