DISSOCIATION CONSTANTS OF ISOMERIC HALOGENO-PHENOLS

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INTRODUCTION

The measurements of dissociation constants of organic acids and phenols have thrown much light on the polar effects of the substituent atoms or groups Ostwald classified the substituent groups or atoms as possessing the negative or positive properties according as they increased or decreased the dissociation constant of the acid In recent years many workers have attempted to correlate the changes in dissociation constants with the polar properties of the substituent groups Derrick (J Am Chem Soc, 1911, **33**, 1152) has expressed that the polar influence of the substituents can be represented by, $-\frac{1000}{\log K} \Big/ -\frac{1000}{\log K_u}$, where K is the dissociation constant of the substituted acid and K_u, that of the unsubstituted acid Waters (Phil Mag, 1929, **8**, 436) took the view that the change in free energy of ionization is a measure of the influence of the substituent group, and correlated the dissociation constants of substituted benzoic acids $X-C_6H_4$ COOH with the dipole moment of the corresponding substituted benzenes $X-C_6H_5$ He suggested, that in the absence of any electronic and steric effects, log K is a linear function of the dipole moment Smallwood (J Am Chem Soc, 1932, **54**, 3048) emphasized the relationship between the dissociation constants and dipole moments, and showed that changes in the ionization of an organic acid, are mainly determined by the magnitude of the orientation of the electric moment associated with the substituent group Kirkwood and Westheimer (J Chem Phys, 1938, **6**, 507, 513) have developed a mathematical relationship connecting K and the electrostatic influence due to substitution, which has been used by Westheimer and Shookhoff (J Am Chem Soc, 1939, **61**, 555) to account for the changes in the dissociation constants of a number of acids

Nathan and Watson (J Chem Soc 1933, 890) have derived an equation connecting the dissociation constants of substituted acetic acids with the dipole moments (μ) of the appropriate methane derivatives According to them $\log K = \log K_0 - x\ (\mu + a\mu^2)$ where 'x' and 'a' are the constants of the system This relationship has been extended to aromatic acid by Dippy and co-workers (Nature, 1937, **139**, 591 , J Chem Soc, 1938, 357) who found that a linear relationship existed between the dissociation constants of the meta-substituted benzoic acids and the dipole moments of the corresponding benzene derivatives Meta acids were chosen because they were free from any inductive or mesomeric effects Dippy and co-workers, however did not attempt to show any relationship to include the ortho and para substituted acids along with corresponding meta isomers In substituted phenols, no relationship of any kind has been suggested by any of the above authors

Jenkins (J Chem Soc, 1939, 640, 1137) has correlated the inductive effects due to substitution in various ortho, meta and para positions in benzoic acids with the dissociation constants of corresponding acids He has taken F, the field intensity at the carbon atom of C COOH group as a measure of inductive influence of the substituent group The group C COOH is regarded as more or less a perfect conductor and the carbon atom of the ring as the centre determining the free energy of ionization (–RT ln K). The field intensity at this carbon atom due to a dipole situated at a distance 'r' and inclined at an angle θ to 'r' is,

$$F = \mu \sqrt{1 + 3\cos^2\theta}/r^3$$

For isomeric halogeno-benzoic acids and halogeno-phenols a straight line relationship has been observed between log K and F and for the latter a proportionality between the mesomeric and the inductive effects has been assumed Jenkins in a recent paper (Nature, 1940, **145**, 149) has also pointed out a relationship between the degeneracy and the dissociation constants in a certain series of acids

The effect of substitution of various groups in organic acids has been studied in other ways also The study of Raman spectra and the infrared spectra of substituted acids, phenols and related compounds have thrown some light on the structure of the compound Kohlrausch and Stockman (Monatsch, 1935, **66**, 316) while studying the Raman spectra of a number of substituted benzoic acid esters observed that the substitution of groups or atoms effected the shift in CO frequency in the same manner, in which they increased the dissociation constants of the acids Pauling (J Am Chem Soc, 1936, **58**, 94) and Wulf, Liddel and Hendricks (Ibid, 1935, **57**, 1464, 1936, **58**, 2287) have measured the infrared spectra of many substituted phenols and explained their results on the assumptions of the existence of the resonance of *cis* and *trans* forms of the phenols, but no attempt has so far been made to apply this idea to the dissociation constants of the phenols

In the present investigation the dissociation constants of halogeno-phenols have been measured in pure water at 25°C and the results have been discussed in light of the above observations The previous data for the halogeno-phenols were obtained in 30% ethyl alcohol by Bennet, Brooks and Glasstone (J Chem Soc, 1935, 1821) and in 50% methyl alcohol by Kuhn and Wassermann (Helv Chim Acta, 1928, **11**, 3) by a potentiometric method, which involved complications due to the junction potential

The dissociation constants of organic acids and phenols have been measured by various methods Apart from the conductivity method, employed by Dippy and others (Chem Rev 1939, **25**, 151) other methods such as (1) the potentiometric titration method and (2) the electromotive force method of Harned and co-workers (J Am Chem Soc, 1932, **54**, 1350, ibid, 1930, **52**, 5079) have been developed The potentiometric titration method, which consists in measuring the pH of acid solution at various stages of neutralization, has been used by Abichandani and Jatkar (This Journal 1938, **21A**, 417) for computing the dissociation constants of various hydroxy benzoic acids and phenols, but the results obtained are not comparable with those by other methods, because of the complications involved due to the use of a liquid junction and low solubility of the acids

The method of Harned and co-workers (loc cit) has been successfully used for determining the dissociation constants of weak organic acids, and the results obtained are of high degree of accuracy The method avoids the use of a liquid junction and consists in measuring the electromotive forces of the cells of the type,

$H_2 \mid HAn(m_1), NaAn(m_2), NaCl(m_3) \mid AgCl\ Ag$

The hydrogen electrode in the above combination can be replaced by a quinhydrone electrode or a glass electrode, as the former gets invariably poisoned in certain salt solutions The glass electrode has been used in the above combination by MacInnes and Belcher (J. Am Chem Soc, 1933, **55**, 2630) for determining the first dissociation constant of carbonic acid

The authors in the present investigation have made use of a cell without junction potential in which the hydrogen electrode is replaced by a glass electrode for measuring the dissociation constants of isomeric halogeno-phenols, as the former was found to get poisoned in the phenol solutions

CALCULATION OF DISSOCIATION CONSTANT

The cell used for the measurements of dissociation constants was Ag–AgCl, (0 1N)HCl | glass | $HAn(m_1)$, NaAN (m_2) $NaCl(m_3)$ | AgCl–Ag Since the glass surface is reversible to H ion activity, the above cell is equivalent to the sum of two cells,

(1) Ag–AgCl, 0 1N HCl | H_2 and

(2) $H_2 \mid HAn(m_1), NaAn(m_2), NaCl(m_3) \mid AgCl\ Ag$

Therefore the potential of the original cell is

$$E = E_g + E_1,$$

where E_g is the potential of the cell (1) and has the value −0 3521 (Harned and co-workers, loc cit), and E_1 is the potential of the cell (2) E_1 is given by the equation,

$$E_1 = E_0 - \frac{RT}{F} \ln m_H \gamma_H m_{Cl} \gamma_{Cl} \qquad \ldots \quad I$$

where E_0 is the e m.f of the cell H_2 | HCl, AgCl–Ag at unit activity For the dissociation of a weak acid HAn, the thermodynamical dissociation constant K is given by

$$K = \frac{m_H\, m_{An}}{m_{HAn}} \, \frac{\gamma_H\, \gamma_{An}}{\gamma_{HAn}} \qquad \ldots \quad II$$

Combining this equation with equation I, we have

$$E_1 - E_0 + \frac{RT}{F} \ln \frac{m_{Cl}\, m_{HAn}}{m_{An}} = -\frac{RT}{F} \ln \frac{\gamma_{Cl}\, \gamma_{HAn}}{\gamma_{An}} - \frac{RT}{F} \ln K \quad . \qquad \text{III}$$

Therefore from the measurement of the original cell, we have

$$E - E_g - E_0 + \frac{RT}{F} \ln \frac{m_{Cl}\, m_{HAn}}{m_{An}} = -\frac{RT}{F} \ln \frac{\gamma_{Cl}\, \gamma_{HAn}}{\gamma_{An}} - \frac{RT}{F} \ln K$$

At zero ionic concentration the term involving the activity coefficients of ions becomes zero, so that a plot of the left hand side of the equation against the ionic concentration (μ) permits the determination of log K by an extrapolation to $\mu = 0$.

The value of E_0 was taken to be –0 2224 at 25° due to Harned and co-workers (loc cit), and the ionic concentrations were taken to be $m_{Cl} = m_3$, $m_{HAn} = m_1 - m_H + m_{OH}$ and $m_{An} = m_2 + m_H - m_{OH}$ m_H was determined by a short series of successive approximations (Harned and Embree, J Am Chem Soc, 1934, **56**, 1042) and m_{OH} from a rough approximation of the hydrolysis constant (Harned, Chem Reviews, 1939, **25**, 31) In actual practice, however, it was found that m_H and m_{OH} could be neglected if the value of K is between 10^{-6} and 10^{-9}

EXPERIMENTAL

Materials—Pure recrystallized sodium chloride and pure phenols were used for the experiments The purity of the benzoic acid and halogeno-phenols was checked by determining their melting points. The solutions were made in conductivity water by adding to it a weighed quantity of sodium chloride and of phenol A weighed quantity of carbonate free sodium hydroxide solution was run in the above solution and amount of sodium salt formed was calculated For the determination of the dissociation constant of benzoic acid, however, pure sodium benzoate was used

Cell.—The electromotive force measurements were made with a glass electrode in a cell of the type shown in Fig 1 (This Journal 1941, **23-A,** 94) It consisted of a pyrex tubing about 2 cm in diameter and 20 cm long, with a silver–silver chloride electrode fused at the bottom The glass electrode used in the experiments was of the same type as described previously The silver-silver electrode was prepared according to the directions of Carmody (J Am. Chem Soc, 1929, **51**, 2901)

A clean piece of platinum gauze (1 5 × 1 cm) was silver plated in a solution of potassium silver cyanide, for 8 hours, at a current density of 6 m a per sq cm. The electrode was then washed in running water for about 48 hours and electrolysed, as an anode, in a dilute solution of hydrochloric acid for one hour at a current density of 2 m a per sq cm It was found to behave normally and showed no change of e m f with aging after keeping for about five days in distilled water

Procedure—The cell was kept in oil thermostat, maintained at 25°C ± 0 02, for about half an hour before making measurements The electrodes were checked against 0 1 N HCl solution, immediately before and after each set of experiments and the electromotive force recorded was zero Two cells were used and measurement with each solution was repeated twice

The push pull electrometer valve potentiometer described previously was used for recording the electromotive forces The values of ionic concentrations along with the observed electromotive forces are given in tables 1 to 11 for each acid

In Figs 1, 2, 3 and 4 the ionic concentrations μ have been plotted against the logarithm of the corresponding dissociation constants for each phenol This plot when extrapolated to zero ionic concentration gives the values of K, the true thermo-dynamical dissociation constant of each phenol in pure water at 25°C

TABLE 1

Benzoic acid

Composition of solutions and electromotive forces of cells

Solution	m_{HA}	m_{Cl}	m_A	μ	E 25°
I	0 00566	0 01045	0 00639	0 01692	0 2395
II	01302	01327	00981	02321	2234
III	00965	01886	00728	02624	2146
IV	00683	02328	00526	02864	2096
V	00962	04006	00546	04566	1882
VI	00795	07082	00823	07914	1899

Calculation of dissociation constant

Solution	m_H	$\frac{E+E_g-E_o}{0\ 0591}$	$\log \frac{m_{HA}\, m_{Cl}}{m_A}$	log K′	$K' \times 10^5$
I	0 00008	6 2521	−2 0337	−4 2184	6 047
II	00013	5 9797	−1 7543	−4 2254	5 951
III	00010	5 8308	−1 6021	−4 2287	5 906
IV	00010	5 7456	−1 5196	−4 2260	5 943
V	00014	5 3845	−1 1513	−4 2332	5 844
IV	00009	5 4128	−1 1648	−4 2480	5 649

Extrapolated value of $K' = K = 6\ 15 \times 10^{-5}$,

TABLE 2

Phenol

Composition of solutions and electromotive forces of cells

Solution	m_{HA}	m_{Cl}	m_A	μ	E(25°C)
I	0 00730	0 01002	0 00603	0 01598	0 5685
II	00880	01436	00848	02276	.5633
III	00847	01760	00765	02518	.5566
IV	01137	01714	01083	02790	5584
V	01624	03201	01679	04872	.5450
VI	01521	03598	01425	05017	.5395

Calculation of dissociation constant

Solution	$\frac{E+E_{c}-E_0}{0\ 0591}$	log $\frac{m_{HA}m_{Cl}}{m_A}$	log K'	K' × 10^{10}
I	11 8190	–1 9161	–9 9029	1 250
II	11 7310	–1 8268	–9 9042	1 247
III	11 6176	–1 7102	–9 9074	1 238
IV	11 6481	–1 7450	–9 9031	1 250
V	11 4213	–1 5092	–9 9121	1 225
VI	11 3283	–1 4157	–9 9126	1 223

Extrapolated value of $K' = K = 1.27 \times 10^{-10}$

TABLE 3

o-Chloro Phenol

Composition of solutions and electromotive forces of cells

Solution	m_{HA}	m_{Cl}	m_A	μ	E (25°C)
I	0 00855	0 00852	0 00734	0 01586	0.4683
II	01056	01300	00884	02184	4570
III	01168	02946	01223	04169	4423
IV	00687	03663	00831	04494	4406
V	01126	03335	01298	04633	4421
VI	01587	03359	01444	04803	4357
VII	01671	04455	01576	06031	4296
VIII	01873	04495	01886	06381	4314
IX	02152	04954	01839	06793	4246

Calculation of dissociation constant

Solution	$\frac{E+E_g-E_0}{0\ 0591}$	$\log\frac{m_{HA}\,m_{Cl}}{m_A}$	log K′	$K'\times10^{-9}$
I	10 1235	–2 0033	–8 1202	7 582
II	9 9323	–1 8088	–8 1235	7 525
III	9 6836	–1 5507	–8.1329	7 364
IV	9.6548	–1 5188	–8 1360	7 311
V	9 6802	–1 5386	–8 1416	7 218
VI	9 5719	1 4327	–8 1392	7 254
VII	9 4687	–1 3257	–8 1430	7 194
VIII	9 4992	–1 3503	–8 1489	7.098
IX	9 3841	–1.2368	–8 1473	7 124

Extrapolated value of $K'=K=7\ 73\times10^{-9}$.

TABLE 4

m-*Chloro Phenol*

Composition of solutions and electromotive forces of cells

Solution	m_{HA}	m_{Cl}	m_A	μ	E(25°C)
I	0 00704	0 01141	0 00616	0 01757	0 5014
II	01534	01598	01423	03021	4944
III	01234	02091	00968	03059	4835
IV	01431	01827	01261	03088	4896
V	01306	02544	01388	03932	4861
VI	01471	03061	01217	04278	4753
VII	01722	04538	01516	06054	4674
VIII	01314	05624	01000	06624	4585
IX	01750	06217	01581	07798	4606

Calculation of dissociation constants

Solution	$\frac{E+E_g-E_c}{0\ 591}$	$\log \frac{m_{HA}m_{Cl}}{m_A}$	log K′	$K' \times 10^{-9}$
I	10 6836	−1 8848	−8 7988	1 623
II	10 5651	−1.7638	−8 8013	1 581
III	10.3807	−1 5741	−8 8066	1 561
IV	10 4839	−1.6834	−8 8005	1 583
V	10 4247	−1 6209	−8 8038	1 571
VI	10 2420	−1 4318	−8 8102	1 548
VII	10 1083	−1 2878	−8 8205	1 512
VIII	9 9577	−1 1314	−8 8263	1 491
IX	9 9932	−1 1623	−8 8309	1 476

Extrapolated value of $K' = K = 1\ 64 \times 10^{-9}$

TABLE 5

p-*Chloro Phenol*

Composition of solutions and electromotive forces of cells

Solution	m_{HA}	m_{Cl}	m_A	μ	E(25°C)
I	0 01249	0 01224	0 01008	0 02230	0 5226
II	01279	01727	01049	02774	5138
III	01387	02009	01015	03022	5068
IV	01560	02163	01378	03539	5102
V	01554	02724	01370	04092	5043
VI	01680	03037	01420	04455	5006
VII	01653	03758	01340	05096	4940
VIII	02201	04305	01904	06207	4931
IX	02764	06876	02246	09120	4802

Calculation of dissociation constant

Solution	$\frac{E+E_g-E_o}{0\ 0591}$	$\log \frac{m_{HA}\, m_{Cl}}{m_A}$	log K′	$K' \times 10^{-10}$
I	11 0355	–1 8190	–9 2165	6 074
II	10 8934	–1 6766	–9 2168	6 070
III	10 7750	–1 5612	–9 2138	6 112
IV	10 8325	–1 6110	9 2215	6 005
V	10 7327	–1 5100	–9 2227	5 988
VI	10 6701	–1 4445	–9 2256	5 948
VII	10 5584	–1 338	–9 2246	5 962
VIII	10 5431	–1 3029	–9 2402	5 751
IX	10 3249	–1 0725	–9 2524	5 593

Extrapolated value of $K' = K = 6\ 28 \times 10^{10}$

TABLE 6

o-*Bromo Phenol*

Composition of solutions and electromotive forces of cells

Solution	m_{HA}	m_{Cl}	m_A	μ	E (25°C)
I	0 00744	0.00963	0 00801	0.01764	0 4874
II	.00800	0 1400	.00769	02169	4750
III	01010	02553	00892	.03445	4576
IV	.00848	02426	01085	03511	4690
V	00843	03179	00767	03946	4530
VI	01284	04264	01235	05499	4480
VII	01293	05055	01328	06383	4427
VIII	01738	06043	01533	07576	4373
IX	01867	06673	01839	.08512	4379

Calculation of dissociation constant

Solution	$\frac{E+E_g-E_o}{0\ 0591}$	$\log \frac{m_{HA}\, m_{Cl}}{m_A}$	log K′	$K' \times 10^{-9}$
I	10 4467	−2 0485	−8 3982	3.997
II	10 2369	−1 8368	−8 4001	3 980
III	9 9425	−1 5389	−8 4036	3 949
IV	10 1354	−1 7221	−8 4133	3.861
V	9 8646	−1 4567	−8 4079	3 909
VI	9 7800	−1 3533	−8 4267	3 744
VII	9 7327	−1 3078	−8 4249	3 759
VIII	9 5990	−1 1642	−8 4348	3.675
IX	9.6091	−1 6191	−8 4400	3.631

Extrapolated value of $K' = K = 4\ 10 \times 10^{-9}$.

TABLE 7

m-*Bromo Phenol*

Composition of solutions and electromotive forces of cells

Solution	m_{HA}	m_{Cl}	m_A	μ	E(25°C)
I	0 00544	0 01663	0 00568	0 02231	0 5011
II	00537	01971	00576	02547	4960
III	00971	02618	00799	03417	4840
IV	00902	02541	01010	03551	4923
V	01081	03625	01088	04713	4814
VI	00742	04076	00785	04861	4800
VII	01004	04979	01031	06010	4746
VIII	0 1155	06021	01140	07161	4688

Calculation of dissociation constant

Solution	$\frac{E+E_g-E_o}{0\ 0591}$	$\log\frac{m_{HA}m_{Cl}}{m_A}$	log K′	$K'\times10^{-9}$
I	10 6785	–1 7978	–8 8807	1 316
II	10 5922	–1 7075	–8 8847	1.304
III	10 3892	–1 4973	–8 8919	1 282
IV	10 5296	–1 6442	–8 8854	1 302
V	10 3452	–1 4435	–8 9017	1 254
VI	10 3215	–1 4142	–8 9073	1 238
VII	10 2301	–1 3144	–8 9157	1.214
VIII	10 1320	–1 2147	–8 9173	1 210

Extrapolated value of $K'=K=1\ 36\times10^{-9}$

TABLE 8

p-*Bromo Phenol*

Composition of solutions and electromotive forces of cells

Solutions	m_{HA}	m_{Cl}	m_A	μ	E(25°C)
I	0.00919	0.00934	0.00992	0.01924	0.5391
II	00759	01215	00764	01977	5304
III	00911	01845	00866	02709	5183
IV	01031	02166	00983	.03147	5147
V	01076	02863	01003	03864	5071
VI	01006	03666	01018	04682	5035
VII	01213	04564	01121	05683	4951
VIII	01229	04569	01201	05768	4968
IX	01477	05628	01386	07012	4911

Calculation of dissociation constant

Solution	$\frac{E+E_g-E_0}{0.0591}$	$\log \frac{m_{HA}\,m_{Cl}}{m_A}$	log K′	$K' \times 10^{-10}$
I	11.3215	−2.0628	−9.2587	5.512
II	11.1743	−1.9183	−9.2568	5.537
III	10.9695	−1.7120	−9.2575	5.527
IV	10.9086	−1.6436	−9.2650	5.433
V	10.7800	−1.5128	−9.2672	5.405
VI	10.7191	−1.4409	−9.2782	5.270
VII	10.5770	−1.3064	−9.2706	5.363
VIII	10.6058	−1.3301	−9.2757	5.301
IX	10.5093	−1.2219	−9.2874	5.159

Extrapolated value of $K' = K = 5.65 \times 10^{-10}$

TABLE 9

o-Iodo Phenol

Composition of solutions and electromotive forces of cell

Solution	m_{HA}	m_{Cl}	m_A	μ	E(25°C)
I	0.00516	0.01068	0.0544	0.01612	0.4885
II	.00489	.01156	.00508	.01664	.4863
III	.00809	.02363	.00816	.03179	.4673
IV	.00719	.02484	.00765	.03249	.4664
V	.00808	.02850	.00881	.03731	.4649
VI	.00726	.03186	.00863	.04049	.4643
VII	.00978	.04314	.01082	.05396	.4551
VIII	.01013	.05062	.01113	.06175	.4511

Calculation of dissociation constants

Solution	$\frac{E+E_g-E_0}{0.0591}$	$\log\frac{m_{HA}m_{Cl}}{m_A}$	log K′	K′ × 10^9
I	10.4653	−1.9944	−8.4707	3.383
II	10.4281	−1.9535	−8.4746	3.353
III	10.1049	−1.6302	−8.4747	3.352
IV	10.0914	−1.6140	−8.4774	3.332
V	10.0660	−1.5827	−8.4833	3.286
VI	10.0558	−1.5719	−8.4839	3.282
VII	9.9002	−1.4091	−8.4911	3.228
VIII	9.8325	−1.3365	−8.4960	3.192

Extrapolated value of $K' = K = 3.44 \times 10^{-9}$

TABLE 10

m-Iodo Phenol

Composition of solutions and electromotive forces of cells

Solutions	m_{HA}	m_{Cl}	m_A	μ	E(25°C)
I	0 00479	0 01050	0 00476	0 01526	0 5121
II	00703	01715	00678	02393	4989
III	.00518	02143	00505	02658	.4942
IV	00724	02511	00704	03215	4900
V	01024	02944	01065	04009	4877
VI	.00907	03477	00966	04443	4840
VII	01169	04482	01141	.05623	4763
VIII	01049	.05417	01088	06505	4731

Calculation of dissociation constant

Solution	$\frac{E+E_g-E_o}{0\ 0591}$	$\log\frac{m_{HA}m_{Cl}}{m_A}$	log K'	$K' \times 10^{-9}$
I	10 8646	–1 9760	–8 8886	1 292
II	10 6413	–1 7500	–8 8913	1 284
III	10 5618	–1 6666	–8 8952	1.273
IV	10 4907	–1 5881	–8 9026	1 251
V	10 4518	–1 5480	–8 9038	1 248
VI	10.3892	–1 4861	–8 9031	1 250
VII	10 2589	–1 3380	–8 9209	1 199
VIII	10 2047	–1 2821	–8 9226	1.195

Extrapolated value of $K' = K = 1.32 \times 10^{-9}$

TABLE 11

p-*Iodo Phenol*

Composition of Solutions and Electromotive forces of cells

Solution	m_{HA}	m_{Cl}	m_{A}	μ	E (25°C)
I	0.00470	0.00939	0.00459	0.01396	0.5334
II	00655	01679	00633	02310	5181
III	00651	01839	00663	02560	.5167
IV	00831	02467	00801	03266	5089
V	00850	03094	00878	03970	5054
VI	00939	03988	00991	04977	4992
VII	01027	04055	01014	05067	4973
VIII	01463	05417	01427	06842	4900

Calculation of dissociation constant

Solution	$\frac{E+E_g-E_0}{0.0591}$	$\log \frac{m_{HA}m_{Cl}}{m_A}$	log K′	$K' + 10^{-10}$
I	11.2250	−2.0171	-9.2079	6.195
II	10.9662	−1.7602	-9.2060	6.223
III	10.9425	−1.7293	-9.2132	6.120
IV	10.8105	−1.5920	-9.2185	6.046
V	10.7513	−1.5236	-9.2277	6.920
VI	10.6464	−1.4227	-9.2237	6.974
VII	10.6142	−1.3869	-9.2273	5.924
VIII	10.4907	−1.2553	-9.2354	5.315

Extrapolated value of $K' = K = 6.30 \times 10^{-10}$

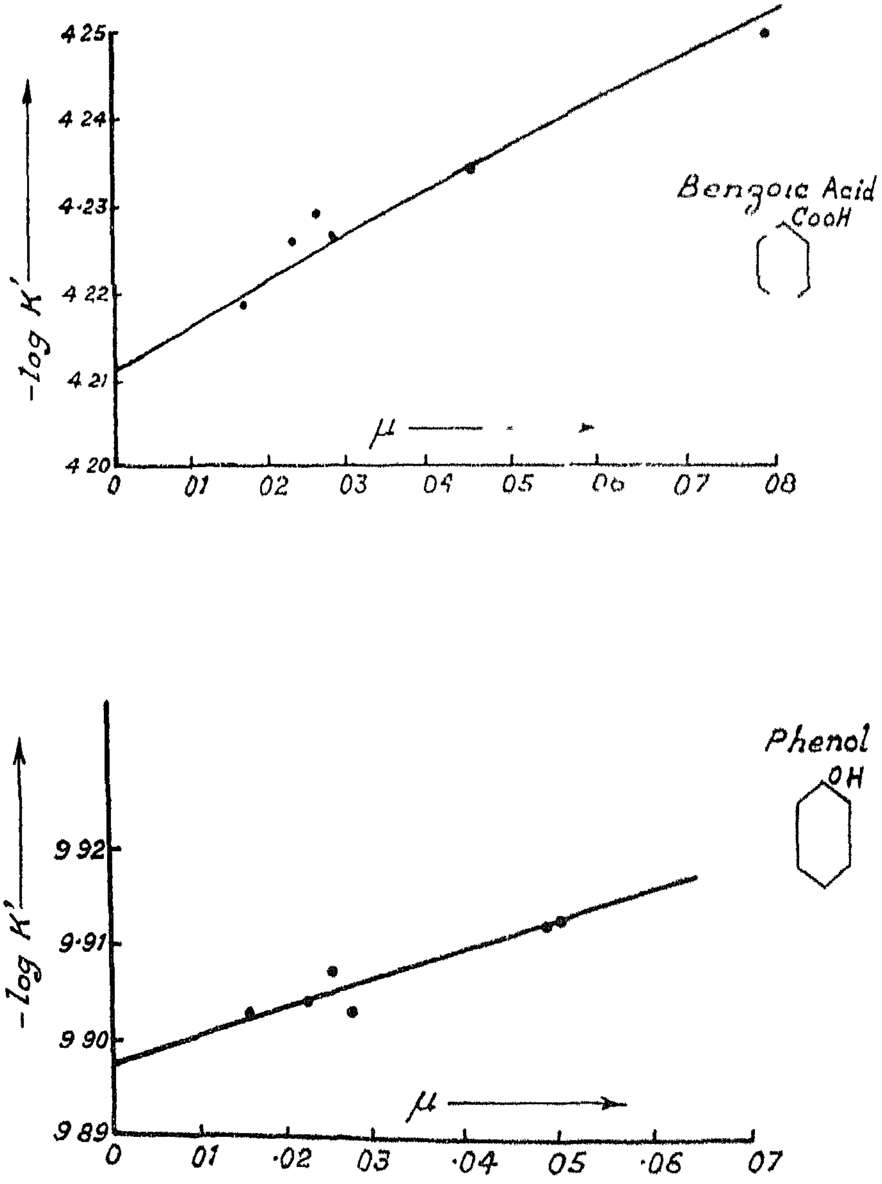

-log K′
4 25
4 24
4·23
4 22
4 21
4 20
0
01
02
03
04
05
06
07
08
μ
Benzoic Acid
CooH
-log K′
9 92
9·91
9 90
9 89
0
01
·02
03
·04
05
·06
07
μ
Phenol
OH

Fig 1

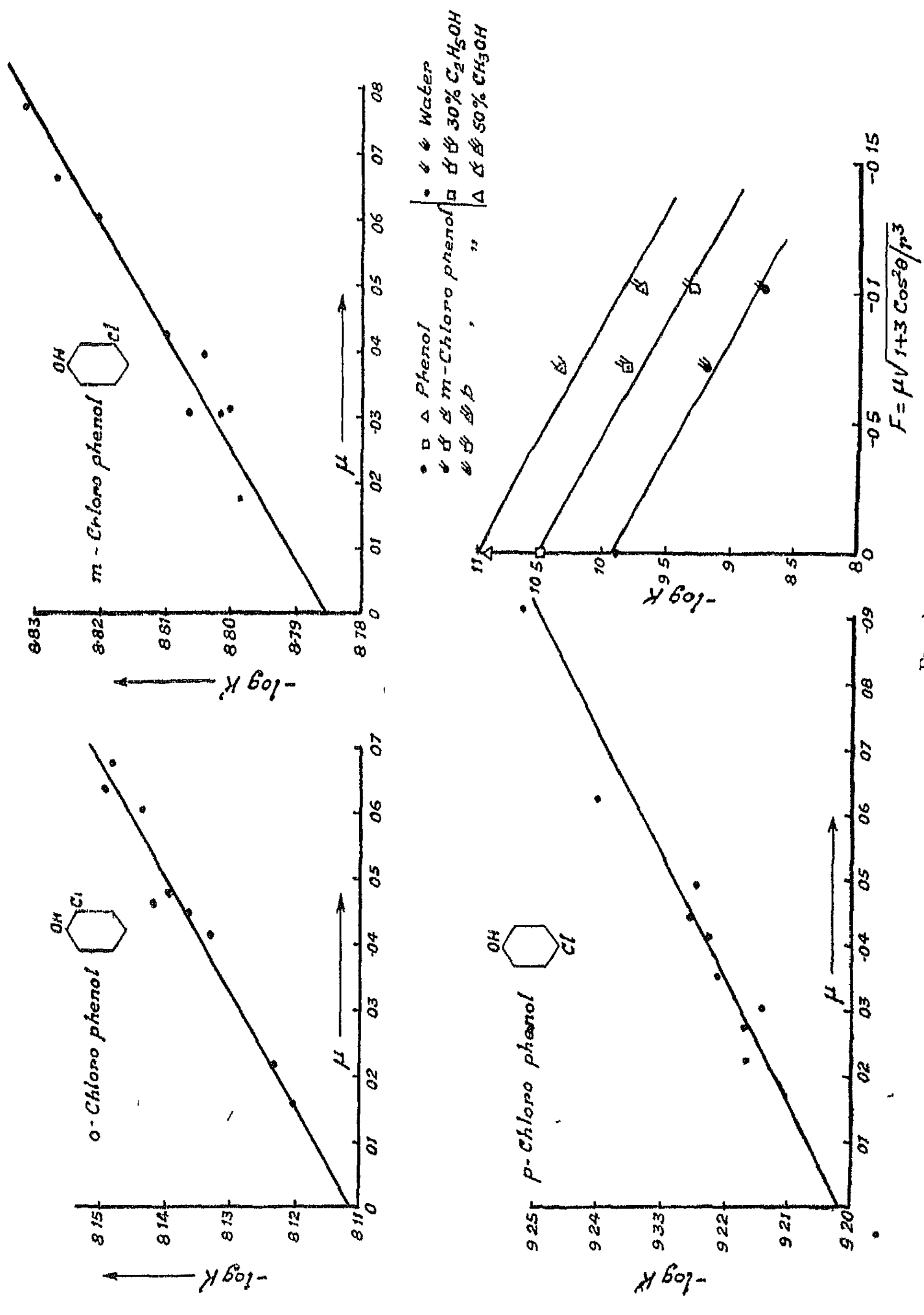
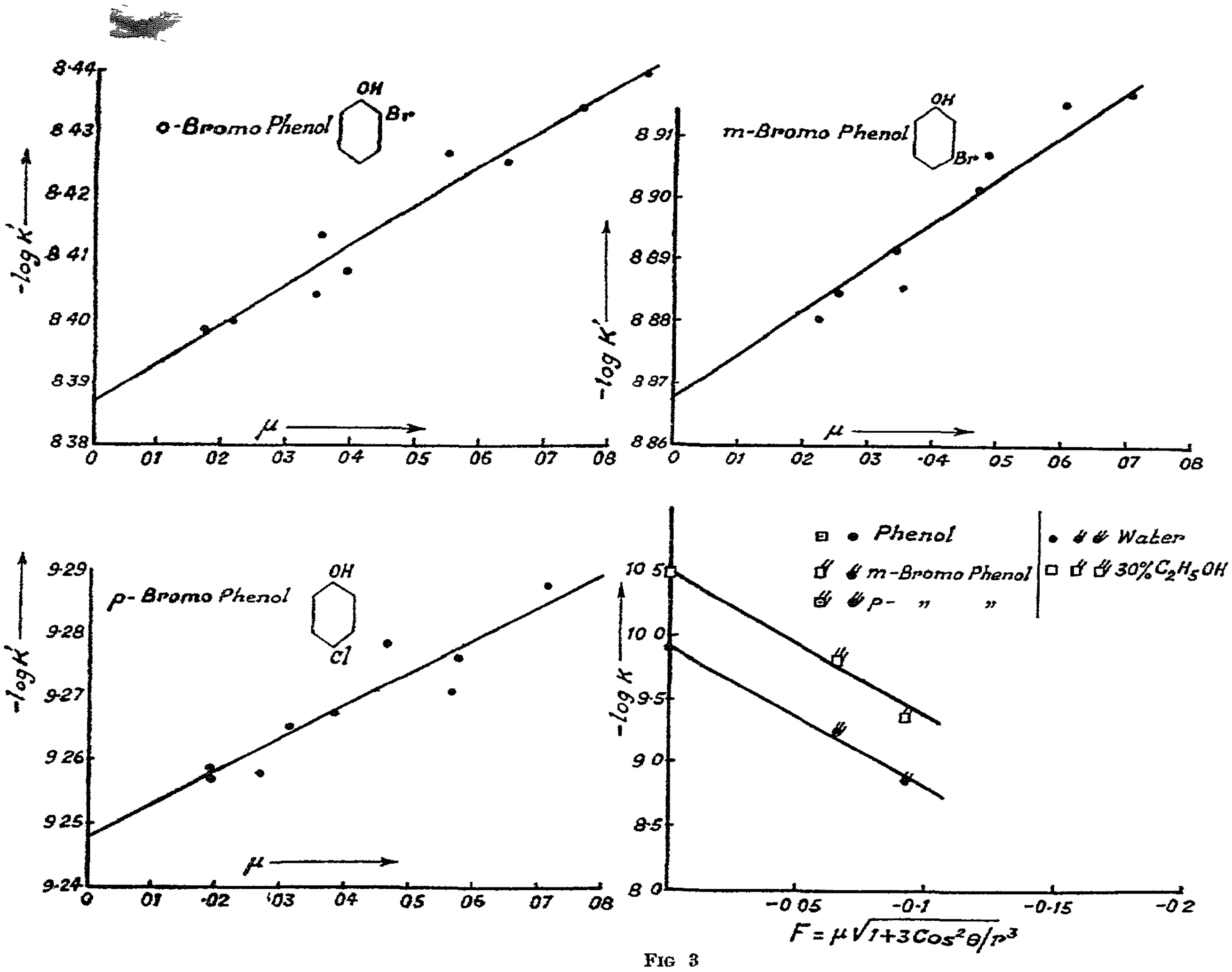
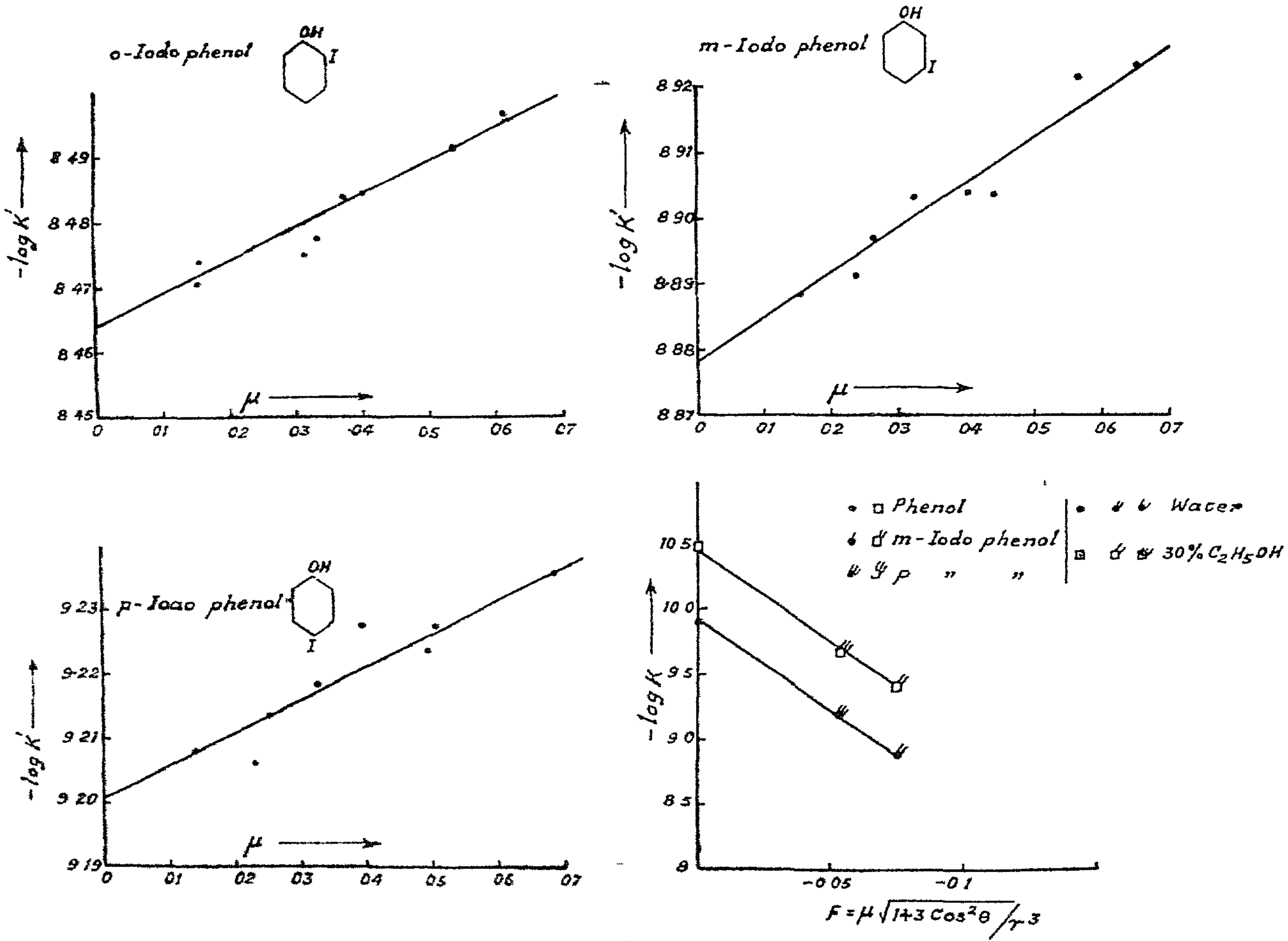

o-Chloro phenol
OH
Cl
-log K
8.15
8.14
8.13
8.12
8.11
0
01
02
03
04
05
06
07
μ
m-Chloro phenol
OH
Cl
8.83
8.82
8.61
8.80
8.79
8.78
01
02
03
04
05
06
07
08
p-Chloro phenol
9.25
9.24
9.33
9.22
9.21
9.20
09
08
• □ △ Phenol
m-Chloro phenol
p
Water
30% C_2H_5OH
50% CH_3OH
11
10.5
10
9.5
9
8.5
8
-0.5
-01
-0.15
$F = \mu\sqrt{1+3\cos^2\theta/r^3}$

FIG. 2



o-Bromo Phenol
OH
Br
-log K′
8·44
8 43
8·42
8 41
8 40
8 39
8 38
μ
0
01
02
03
04
05
06
07
08
m-Bromo Phenol
OH
Br
-log K′
8 91
8 90
8 89
8 88
8 87
8 86
μ
0
01
02
03
·04
05
06
07
08
p-Bromo Phenol
OH
Cl
-log K′
9·29
9·28
9·27
9 26
9 25
9·24
μ
0
01
·02
·03
04
05
06
07
08
Phenol
m-Bromo Phenol
p- " "
Water
30% C_2H_5OH
-log K
10 5
10 0
9·5
9 0
8·5
8 0
-0 05
-0·1
-0·15
-0 2
$F = \mu\sqrt{1+3\cos^2\theta}/r^3$

FIG 3



o-Iodo phenol
OH
I
-log K′
8 49
8 48
8 47
8 46
8 45
μ
0
01
02
03
·04
05
06
07
m-Iodo phenol
OH
I
-log K′
8 92
8 91
8 90
8·89
8 88
8 87
μ
0
01
02
03
04
05
06
07
p-Iodo phenol
OH
I
-log K′
9 23
9·22
9 21
9 20
9 19
μ
0
01
02
03
04
05
06
07
Phenol
m-Iodo phenol
p " "
Water
30% C_2H_5OH
-log K
10 5
10 0
9 5
9 0
8 5
8
-0 05
-0 1
$F = \mu\sqrt{1+3\cos^2\theta}/r^3$

FIG 4

TABLE 12

Dissociation constants of phenols

	In pure water (a)	In 30% C_2H_5OH (b)	In 50% CH_3OH (c)	In 25% C_2H_5OH (d)	(e)	Other authors
Phenol	1.27×10^{-10}	$0.32 \times 10^{-1[illegible]}$	0.123×10^{-10}		1.7×10^{-10}	$1.25 \times 10^{-[illegible]}$ (f) 1.05×10^{-10} $1.30 \times 10^{-1[illegible]}$ (g) $1.2 \times 10^{-[illegible]}$ (h)
o-Chloro phenol	7.73×10^{-9}	1.02×10^{-9}	$3.2 \times 10^{-[illegible]}$	7.97×10^{-10}	$3.2 \times 10^{-[illegible]}$	
m-Chloro phenol	1.64×10^{-9}	4.9×10^{-10}	$1.95 \times 10^{-[illegible]}$	$3.[illegible]0 \times 10^{-[illegible]}$	$1.4 \times 10^{-[illegible]}$	
p-Chloro phenol	6.28×10^{-10}	1.32×10^{-10}	$0.47 \times 10^{-[illegible]}$	$1.46 \times 10^{-[illegible]}$	$6.6 \times 10^{-[illegible]}$	
o-Bromo phenol	4.10×10^{-9}	$9.78 \times 10^{-[illegible]}$				
m-Bromo phenol	$1.[illegible]6 \times 10^{-[illegible]}$	$4.[illegible]7 \times 10^{-[illegible]}$				
p-Bromo phenol	5.65×10^{-10}	$1.55 \times 10^{-[illegible]}$				
o-Iodo phenol	3.44×10^{-9}	$9.12 \times 10^{-[illegible]}$				
m-Iodo phenol	1.32×10^{-9}	$3.86 \times 10^{-[illegible]}$				
p-Iodo phenol	6.30×10^{-10}	$2.19 \times 10^{-[illegible]}$				

(a) The present investigation

(b) Bennet Brooks and Glasstone loc. cit.

(c) Kuhn and Wassermann loc. cit.

(d) Bra[illegible] Yaor et. Bettmorn J. Am. Chem. Soc. [illegible] 56, [illegible]

(e) M[illegible] and Gordon J. Am. C. S. 19[illegible] 57, [illegible]

(f) Holm and Kirckman Z. Physikal. Chem. [illegible] 157 [illegible]

(g) W[illegible]ke Ibid. [illegible] 32, [illegible]

(h) M[illegible]atan, Ibid. 192[illegible] 118, [illegible]

The value of dissociation constant for benzoic acid obtained by this method is $6\,15 \times 10^{-5}$, which is slightly higher than $6\,05 \times 10^{-5}$ obtained by Briscoe and Peake (J Phys Chem, 1938, **43**, 637) from e m f measurements of the cells without junction potential, and lower than $6\,312 \times 10^{-5}$ by Brockman and Kilpatrick (J Am Chem Soc, 1934, **56**, 1483) and 6.295×10^{-5} by Saxton and Meier (ibid 1934, **56**, 1918), by the conductivity method The difference is due to the fact that the electromotive force method is not as accurate as the conductivity method, the electromotive force being reproducible only to 0 1 millivolt, on account of the use of a glass electrode and the low acid concentrations used

In the values of dissociation constants of Table 12 isomeric phenols in pure water are recorded and compared with the values obtained by other workers

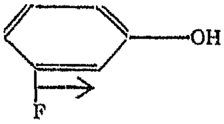
Murray and Gordon have measured the dissociation constants in 50% methyl alcohol and corrected them for aqueous solutions by multiplying all the values by a factor, K aqueous/K 50% CH_3OH for phenol Their results for *o*-chloro phenol are very low, while the values for *p*- and *m*-chloro phenols, are in agreement with those obtained in the present investigation

DISCUSSION

The introduction of a substituent group or atom in phenol in various positions, increases the dissociation constant There are at least two influences the inductive influence (I) and the mesomeric influence (M), which the substituent groups of atoms exert on the dissociating hydrogen. The inductive influence which arises from the electric dipole of the substituent, increases or decreases the dissociation constant, according as the substituents possess the electron attracting or electron repelling dipole respectively The halogen atoms due to strong electron attracting dipole (--I) increase the dissociation constant of substituted phenols The inductive influence of halogen atoms can be best studied from the data for the *meta* substituted compounds, as this influence in *ortho* and *para* compounds is modified by the mesomeric disturbances

Substituent	m–F	m–Cl	m Br	m -I
–log K	9 280	8.785	8 868	8 878

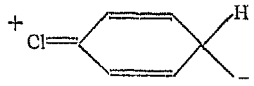
The above results show that the magnitude of inductive influence due to the substitution of halogen atoms is in the order Cl > Br > I, which is identical with that indicated by the study of velocity coefficients of reactions of *m*-halogen-benzyl chlorides (Bennet and Jones, J Chem Soc, 1935, 1815) The *meta*-fluorophenol, however, shows a lower dissociation constant, which is probably due to inductive influence, being affected by the relayed modified influences of the mesomeric type, by the following mechanism.



(Dippy and Lewis, J Chem. Soc, 1936, 644)

The mesomeric influence (M), which is also known as the permanent electrometric influence, is the outcome of the resonance in the molecule In saturated conjugate system a migration of electrons involving co-valency changes, takes place, which results in resonance. According to Ingold (Chem Rev, 1934, **15**, 244) and Branch and co-workers (J Am Chem Soc, 1934, **56**, 1850), the mesomeric influence in *p*-halogeno phenols is due to the resonance between the two forms.

I



II

The substitution of halogen atoms, in *ortho* and *para* positions to the hydroxyl, brings about practically the same kind of resonance as the hydroxyl group, due to the presence of a pair of unshared electrons on the carbon atom attached to the benzene ring This resonance has a tendency to decrease the dissociation constant The magnitude of the mesomeric influence (as will be shown later) diminishes in the order F>Cl>Br>I

Jenkins (loc cit) has calculated the inductive influence in the substituted halogeno-benzoic acids and halogeno-phenols in terms of F, the field intensity and ψ, the electrostatic potential at the carbon atom to which the carboxyl or hydroxyl group is attached A plot of F or ψ against log K for these acids shows that the inductive influence of the substituent is largely responsible for the observed acid strengths F, the field intensity has been calculated from the equation $F=\mu\sqrt{1+\text{Cos}^2\theta}/r^3$ and the electrostatic potential from the equation $\psi=\mu\,\text{Cos}\,\theta/r^2$, by taking the latest vapour values of dipole moments (μ, the dipole moments of corresponding mono halogeno-benzenes) due to Groves and Sugden (J Chem Soc, 1937, 1992) The values of r (the distance between the carbon atom and the centre of the dipole) are calculated from the values of interionic distances by Pauling and Huggins (Z Krist, 1934, **87**, 205) and θ (the angle at which r is inclined to the direction of the dipole) in each case was calculated trignometrically The values of F for halogeno-phenols are given in the following table along with the log of corresponding dissociation constants

	$-\log K$	F
Phenol	9 897	±0 000
o—Fluorophenol	8 810*	419
m— ,,	9.280*	106
p— ,,	9 951*	075

---

* Bennet, Brooks, and Glasstone (loc cit)

		log K	F
o -Chlorophenol	.	8 112	381
m - ,,		8 785	101
p - ,,		9 [illegible]	071
o Bromophenol	.	8 387	34[illegible]
m – ,,		8 868	092
p - ,,		9 258	065
o --Iodophenol	.	8 461	269
m – ,,	.	8 878	071
p ,,	...	9 [illegible]	053

Since the interionic distances are expressed in Angstrom units and dipole moments in Debye units, the absolute value of field intensity is $F \times 10^8$.

The values of log K, in pure water, 30% ethyl alcohol and 50% methyl alcohol are plotted against F in Figs 2, 3 and 4, which show that for chloro, bromo and iodo-phenols, the points for unsubstituted phenol and for *meta* and *para* isomers lie on the same straight line. The graphs indicate that the mesomeric influence in *para* isomers is very small The change in dissociation constant is thus mainly due to the inductive influence The small mesomeric influence in these compounds, however, diminishes in the order F > Cl > Br and disappears totally in the iodo-compound, as seen from the exceedingly small deviation of the points for the *para* isomers In *p*-fluorophenol, the inductive influence is completely modified by strong mesomeric influence which is very much in excess of that existing in other halogeno-phenols A comparative data for the hydrolysis of *p*-halogenated benzyl chloride (Bennet and Jones, loc cit) shows that the velocity coefficient of reaction for fluoro-compound is very much larger than for other halogenated compounds, revealing a strong mesomeric effect The equation for the relationship of log K with F, after converting the common logarithms to the Napierian logarithms, is given by, $\ln K_s = \ln K_u - \beta F$ (1)

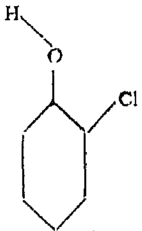
where K_s is the dissociation constant of the substituted phenol, K_u that of the unsubstituted phenol and β is the slope of line, which is constant for any particular series The value of β for chloro- bromo- and iodo-phenols are as follows

Substituent	Cl	Br	I
β. .	24 6	25 3	31 1

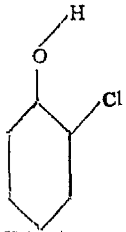
The slope of the line increases with the diminished electro-negativity of the substituent atom Since the absolute value of field intensity is $F \times 10^6$, the absolute value of the slope is $\beta \times 10^{-6}$

Jenkins (loc cit) plotted the electrostatic potential (ψ) against log K for the halogeno-phenols and observed that only *meta* compounds showed a deviation from the straight line relationship This was attributed by him to the existence of inductive influence (–I) only in *meta* compounds, and inductive and mesomeric (–I + M) influences in *ortho* and *para* compounds This view is based on the assumed proportionality between the mesomeric and inductive influences in *ortho* and *para* positions, for which no evidence has been given In the present investigation, the plot of log K against F (Fig 2, 3 and 4), reveals a deviation of the *ortho* compound from the relationship given by equation (1) This deviation of the *ortho* compound, however, cannot be accounted for on the inductive and mesomeric influences only Even if a proportionality is assumed to exist between the mesomeric and inductive influences in *ortho* and *para* positions, the dissociation constant will decrease to a slight extent, since the mesomeric influence in *para* compounds is very small compared with the inductive influence

The abnormal behaviour of the *ortho* compound can be satisfactorily explained, if it is assumed that compound has two resonating structures as follows



I (*trans*)



II (*cis*)

II (*cis*) being distinctly acid weakening in character

Pauling (J Am Chem Soc, 1936 **58**, 94) has pointed out that in phenol the C O bond has a double bond character and the hydrogen atom lies in the plane of the ring On this assumption phenol molecule can be assumed to have two different configurations, which however are identical In ortho substituted mono halogenophenols the two structures I and II are not identical The form in which the hydrogen of the hydroxyl group is turned towards the substituent atom has been termed by Pauling, as the *cis* form and the other in which it is turned away from the substituted atom as the *trans* form

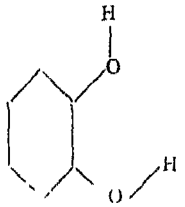
The study of infrared spectra of the phenol and *ortho* halogenated phenols in carbon-tetrachloride solutions by Wulf, Liddel and Hendricks (J Am Chem Soc, 1936, **58**, 2287) revealed a single absorption peak at 7050 cm^{-1} for phenol and two absorption peaks one at 6890 cm^{-1} and other at 7050 $^{-1}$ for the halogenophenols These absorption peaks are due to the vibration of the stretching of O-H bond in molecules and are the first overtones of the main frequency at 3500 cm^{-1} Pauling (loc cit) has explained the occurrence of these peaks on the assumption that there are two forms, *cis* and *trans*, of the halogenated phenols in carbon tetrachloride solutions The peak at 7050 cm^{-1}, has been attributed to the *trans* form and at 6890 cm^{-1}, to *cis* form From the area of peaks it has been assumed that the *cis* form outnumbers the *trans* form Errera and Mollet (J de Physique et le Radium, 1935, **6**, 281) have observed the second absorption peak in the case of pure compounds at 6620 cm^{-1} instead of at 6890 cm^{-1} and the decrease has been attributed by Pauling to the presence of a intramolecular bond in pure compounds From the study of infrared spectra it is obvious that the two peaks are due to the degeneracy of the frequency 7050 cm^{-1}, due to the two (*cis* and *trans*) resonance forms of the molecule of which the *cis* is predominant

In the *cis* form of o-chloro, o bromo and o iodo phenols, the attraction of the partially shielded proton (hydrogen atom with some positive charge) by a negative atom, involves a weak hydrogen bond due to the stabilizing influence of the OH . Cl interaction This internal bonding decreases the positive charge on dissociating hydrogen and decreases the dissociation constant Thus in the case of *ortho* substituted compounds the effect due to OH Cl interaction is superimposed on the inductive and mesomeric influences This effect decreases in the order Cl, Br, I as shown by the decrease in log K from the relationship $\ln K_s = \ln K_u - \beta F$

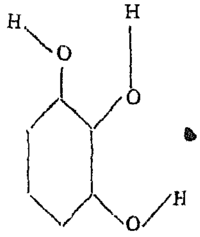
Substituent	Cl	Br	I
decrease in $-\log K$	2·4	2·3	2 2

This order is in accordance with the decreasing OH halogen interaction of the halogen atoms

The existence of internal OH bonding is also shown by catechol and pyrogallol, the infrared spectra of which are in agreement with the following configurations (Pauling loc cit)



Catechol



Pyrogallol

In these compounds (as in the case of *ortho* halogenated phenols) the attraction of the partially shielded proton by the negative oxygen of the adjoining hydroxyl group stabilizes the configuration and involves a weak hydrogen bond This internal OH O bond decreases the ionising character of the hydrogen, and results in a decrease in the second dissociation constant of the phenol

	K_1	K_2
Catechol	$7\ 5 \times 10^{-10}$	$8\ 37 \times 10^{-13}$
Pyrogallol	$9\ 67 \times 10^{-10}$	$2\ 30 \times 10^{-12}$

cf Abichandani and Jatkar (loc cit)

Since the energy of internal OH O bond is four times the energy OH. .Cl bond (Pauling, Nature of the Chemical Bond, Cornel University Press, 1939, Page 303) the OH.. O bond should depress the dissociation constant more than the OH...Cl bond does. The existence of OH...O bond has also been propounded by Baker (Nature, 1936, **137**, 236) in ortho-hydroxy benzoic acid to account for its anomalous first dissociation constant (K). It should be expected that the second dissociation constant of this acid would be very small and of the same order as that of catechol. The second dissociation constant of this acid has been actually found to be $1\cdot20 \times 10^{-13}$ (Abichandani and Jatkar, loc. cit.)

The lower dissociation constant of *o*-fluorophenol is, however, due to a strong mesomeric effect, and not to an internal OH...F bonding. The infrared spectra of this compound shows only single peak at 7010 cm^{-1}, corresponding only to the *trans* structure of the compound.

SOLVENT EFFECT

The dissociation constants of the halogeno-phenols have been measured by many workers in aqueous alcohol solutions and the values obtained are substantially lower than in water, due to the lower dielectric constant of the medium. From the graph of log K against F it is seen that the slopes of lines for a particular series in different alcoholic solution and in water, are the same. This does not seem to bear out the suggestion of Wynne Jones (Chemistry and Industry, 1933, **52**, 273), that the organic acids of similar type do not give the same order of strength in all solvents.

The results of the dissociation constants in different dielectric media, show that for the isomeric halogenophenols the value of logarithm of dissociation constants is inversely proportional to logarithm of the dielectric constant of the medium. The values in 25% ethyl alcohol by Branch, Yabroff and Bettman, however, do not follow this relationship, though the order of strength for various, *ortho*, *meta* and *para* isomers is maintained.

SUMMARY

The dissociation constants of benzoic acid, phenol and isomeric chloro, bromo and iodo phenols were determined in water at 25°C by means of cells without junction potential using a glass electrode.

The cells used for the measurement were of the type, Ag-AgCl, (0.1N) HCl | glass | HAn(m_1), NaAn(m_2), NaCl(m_3) | AgCl–Ag. Following values of K are obtained.

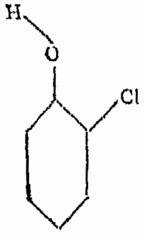
Benzoic acid	6.15×10^{-5}
Phenol	1.27×10^{-10}
o-Chlorophenol	7.73×10^{-9}
m– ,, ,,	1.64×10^{-9}
p– ,, ,,	6.28×10^{-10}
o–Bromophenol	4.10×10^{-9}
m– ,, ,,	1.36×10^{-9}
p– ,, ,,	5.65×10^{-10}
o-Iodophenol	3.44×10^{-9}
m– ,, ,,	1.32×10^{-9}
p– ,, ,,	6.30×10^{-10}

The values for benzoic acid and phenol are in fair agreement with those obtained previously by the conductivity method. The values of the dissociation constants of isomeric halogeno-phenols in water are substantially higher than those in aqueous alcoholic solution found by other workers because of the high dielectric constant of the medium. From the values in different dielectric media, it is observed that log K is inversly proportional to log D.

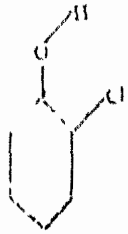
The inductive and mesomeric influences on dissociation constant due to the introduction of halogen atoms in phenol, have been discussed. Both the influences are in the order Cl>Br>I, the former increasing the dissociation constant and the latter decreasing it.

The value of F, the field intensity at the carbon atom (to which the hydroxyl group is attached) due to the electric dipole of the substituent group has been calculated for all halogeno-phenols. The increase in the dissociation constants of *meta* and *para* substituted compounds has been shown to be due to the predominant inductive influence, the mesomeric influence being almost negligible.

The anomalous dissociation constant of the *ortho* compound has been explained on the basis of the two resonance forms.



I (*trans*)



II (*cis*)

the existence of which has been discussed by Pauling from the study of infrared spectra of *ortho* compounds The *cis* form has been found to be predominant and involves an internal OH Cl bonding which is acid weakening in character, due to the attraction of the partially shielded proton by the negative atom

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Received 23-9-1940

Printed at the Hosali Press, Ulsoor, Bangalore, by D N Hosali, Proprietor