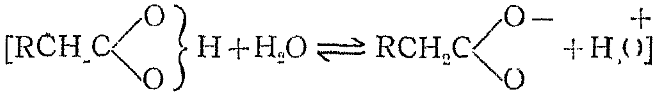
DISSOCIATION CONSTANTS OF ORTHO-HYDROXY BENZOIC ACID AND γ-RESORCYLIC ACID

By C T Abichandani and S K K Jatkar

INTRODUCTION

The work of Ostwald on the dissociation constants of substituted carboxylic acids has shown that the substitution of groups or atoms changes the strength of the acid Ostwald characterized the groups as possessing negative or positive properties, according as they increased or decreased the dissociation constant Such groups or atoms may be regarded as possessing electron attracting or electron repelling dipoles "In the dissociation of a substituted acid the influence of a substituent relative to hydrogen is expressed by the extent to which the equilibrium



$$[\mathrm{RCH_2C}\begin{matrix}\diagup \mathrm{O} \\ \diagdown \mathrm{O}\end{matrix}\Big\}\mathrm{H} + \mathrm{H_2O} \rightleftharpoons \mathrm{RCH_2C}\begin{matrix}\diagup \mathrm{O}^{-} \\ \diagdown \mathrm{O}\end{matrix} + \mathrm{H_3\overset{+}{O}}]$$

is displaced in one way or the other When a substituent brings about the electrons of the hydrogen-oxygen link more under the control of oxygen, the strength of the acid is increased, and conversely, when it causes an opposite movement of electrons, the strength of the acid decreased" (Dippy Chem Rev , 1935, **28**, 151)

In the substituted benzoic acids the dissociation constants vary with the nature and position of the substituent group with respect to the carboxyl The hydroxyl group, which possesses an electron attracting dipole, increases the strength of the acid abnormally when present in the ortho position In the course of a systematic research on the dissociation constants of hydroxy benzoic acids (Abichandani and Jatkar This Journal 1938, **21A**, 417) it has been shown that the order of strength of the first dissociation constants, is ortho> meta>H>para, while for the second dissociation constants, is the reverse Gallic acid, which has two hydroxyl groups in meta positions and one in para position, is a weaker acid than benzoic acid To explain these changes in the strength of the acids, it seemed interesting to study the dissociation constants of o hydroxy benzoic acid and γ and γ-resorcylic acids. The previous values of dissociation constants for these acids were determined by conductivity method and were not corrected for interionic attractions.

In a previous investigation (Abichandani and Jatkar, loc. cit.) the dissociation constants of various acids were determined by the potentiometric titration method. The pH at any point was computed from the electromotive forces of the cells,

Pt, H_2 | Solution x ‖ KCl (sat) | Sat. Calomel electrode

The junction potential in the above cell between solutions and saturated calomel was assumed to be negligible. Burton, Hammer and Acree (J. Bureau Standards, 1936, **16**, 575) have, however, shown that this assumption is not correct. Due to the uncertainties of junction potential involved in the use of a ground glass stoppered salt bridge in the previous investigation, it was thought necessary to use a method, in which junction potential can be avoided.

The method consists of measuring the electromotive forces of the cells of the type

H_2 | HAn (m_1), NaAn(m_2), NaCl(m_3) | AgCl–Ag

(Harned and co-workers. J. Amer. Chem. Soc. 1930, **52**, 5079; 1932, **54**, 350)

The dissociation constant K is calculated according to the equation

$$E - E_0 + \frac{RT}{F} \ln \frac{m_{HA} m_{Cl}}{m_{An}} = -\frac{RT}{F} \ln K'$$

$$= -\frac{RT}{F} \ln \frac{\gamma_{HAn} \gamma_{Cl}}{\gamma_{An}} - \frac{RT}{F} \ln K$$

where E is the electromotive force of the cell, the terms m represent the ionic concentrations of the salts in solution and γ is the activity coefficient of the ions. At zero ionic concentration, the term $\ln \frac{\gamma_{HAn} \gamma_{Cl}}{\gamma_{An}}$ becomes zero, so that K′ is equal to K the true thermodynamical dissociation constant in pure water at that temperature.

The value of E_0, the standard potential of the cell Ag–AgCl(s) | HCl | H_2(Pt) is determined by measuring the electromotive force of the cell containing hydrochloric acid of different concentrations, E_0

being given by the equation $E = E_0 - \frac{RT}{F} \ln m^2\gamma^2$,
where all the terms have their usual significance The value of γ at 30°C can be calculated by the method of Sheldlovsky and *MacInnes* (J Amer Chem Soc 1936, **58**, 1970) The results are given in (Table A) The value obtained is in good agreement with that reported (0 21912 volts) by Harned and Ehlers (J Amer Chem Soc 1933, **55**, 2179)

The results for β resorcylic acid are published by the authors elsewhere (Jour Ind Chem Soc *1939*, **16**, 385)

EXPERIMENTAL

Materials—Ortho-hydroxy benzoic acid (M P 149°), [β-resorcylic acid (M P 213°)] and γ-resorcylic acid (M P 166°-167°) were purified by two crystallisation of the pure salts from distilled water Sodium chloride of A R quality was recrystallized The solutions were prepared in resistance (Jena) glass bottles by adding a weighed quantity of the materials to conductivity water A weighed quantity of standard sodium hydroxide solution (prepared by the action of the water vapour on metallic sodium) was run into the above solution and the quantity of sodium salt formed was calculated

Cell —The Cell (cf authors loc cit) used for measurements was made of pyrex glass The silver—silver chloride electrode sealed to the bottom of the cell was prepared according to the directions of Carmody (J Am Chem Soc 1929, **51**, 2901) The hydrogen electrode was prepared according to the method of Branch, Yabroff and Bettman (J Amer Chem Soc, 1934, **56**, 937) A clean platinum foil (1 5 × 2 cm) was first electrolysed in 10% sulphuric acid and was then platinized in 3% platinic chloride solution for five minutes, using a current density of 0 03 amperes per sq cm Hydrogen was prepared by the electrolysis of 10% caustic soda solution with nickel electrodes and was purified by passing it through a stainless steel tube (three feet long and one inch in diameter) containing paladinized asbestos and heated to about 230°C It was found to be 99 9% pure The gas before admitting to the cell, was bubbled through water kept at the same temperature as the cell to insure against concentration changes

Before each experiment the electrodes and the cells were rinsed with the solution to be used and the hydrogen was allowed to bubble through it for about three hours Two cells were used and the measurements with each solution were repeated twice The cells were kept in a thermostat maintained at 30° ± 0 02 and the electromotive force measurements were taken on a Tinsley's Vernier Potentiometer, using a mirror galvanometer as a null instrument

The hydrogen ion concentration (m_H) of each solution was determined from the electromotive force readings of the cell H_2| Solution ||KCl (sat) |HgCl−Hg at 30°C The high strength of the acids did not warrant the use of method advocated by Harned and Embree (J Amer Chem Soc, 1934, **56**, 1042)

The values of E_0, as determined by the measurement of the cell H_2|HCl(m), AgCl- Ag at 30°C are given in the following Table A m the concentration of hydrochloric acid solutions was determined by the electrometric titration of the each acid solution

TABLE A

m	γ	E	E_0 30°
0 0030	0 961	0 52457	0 21914
0061	943	48840	21910
0080	937	47565	21912
0120	918	45448	21905
0212	890	42637	21904
0375	863	39876	21916
0612	837	37432	21915
0824	.820	35988	21918
0925	814	35414	21908
1201	805	34113	21912
		Mean	−0 21911

The values of ionic concentrations of various salts along with the observed electromotive forces of cells are given in the following tables 1 and 2 for each acid.

TABLE 1

o-Hydroxy Benzoic Acid

Composition of solutions and electromotive forces of cells

Solution	m_{HA}	m_{Cl}	m_A	μ	E(30°C)
I	0.00522	0.00170	0.00416	0.00805	0.5548
II	00654	00621	00538	01354	5221
III	00672	01335	00631	02104	5067
IV	01210	01723	00902	02780	4942
V	00659	02287	00764	03109	4950
VI	00945	02360	01092	03562	4982
VII	00788	03497	00889	04527	4882
VIII	00489	04301	00828	05227	4941

Calculation of dissociation constant

Solution	m_H	$\frac{E-E_0}{0.06012}$	$\log \frac{m_{HA} m_{Cl}}{m_A}$	log K′	$K' \times 10^3$
I	0.00219	5.5838	−2.6710	−2.9128	1.223
II	.00195	5.0149	2.1221	−2.9228	1.195
III	00138	4.7837	−1.8471	−2.9365	1.156
IV	00155	4.5759	−1.6360	−2.9399	1.148
V	00148	4.5892	−1.6505	−2.9387	1.152
VI	00110	4.6424	−1.6900	−2.9524	1.116
VII	.00141	4.4760	−1.5086	−2.9674	1.077
VIII	00098	4.5742	−1.5925	−2.9790	1.050

Extrapolated value of $K' = K = 1.25 \times 10^{-3}$

TABLE 2

γ-*Resorcylic Acid*

Composition of solutions and electromotive forces of cells

Solution	m_{HA}	m_{Cl}	m_A	μ	E (30°C)
I	0 00070	0 00415	0 01089	0 02012	0 5088
II	00121	00718	01187	02572	4827
III	00127	01862	01363	02876	1607
IV	00074	02295	00933	03673	4599
V	00315	02046	01906	04907	1448
VI	00299	03690	01887	06489	4318
VII	00222	06522	01818	09090	4255

Calculation of dissociation constant

Solution	m_H	$\frac{E-E_0}{0\ 06012}$	$\log\frac{m_{HA}m_{Cl}}{m_A}$	log K′	K′ × 10²
I	0 00508	4 8187	–3 5740	–1 2447	5 693
II	00667	4 3846	–3 1355	–1 2491	5 633
III	00651	4 0186	–2 7607	–1 2579	5 522
IV	00545	4 0053	–2 7399	–1 2654	5 428
V	00955	3 7542	–2 4710	–1 2832	5 210
VI	00912	3 5379	–2 2331	–1 3048	4 957
VII	00750	3 4331	–2 0989	–1 3342	4 633

Extrapolated value of $K' = K = 6\ 00 \times 10^{-2}$.

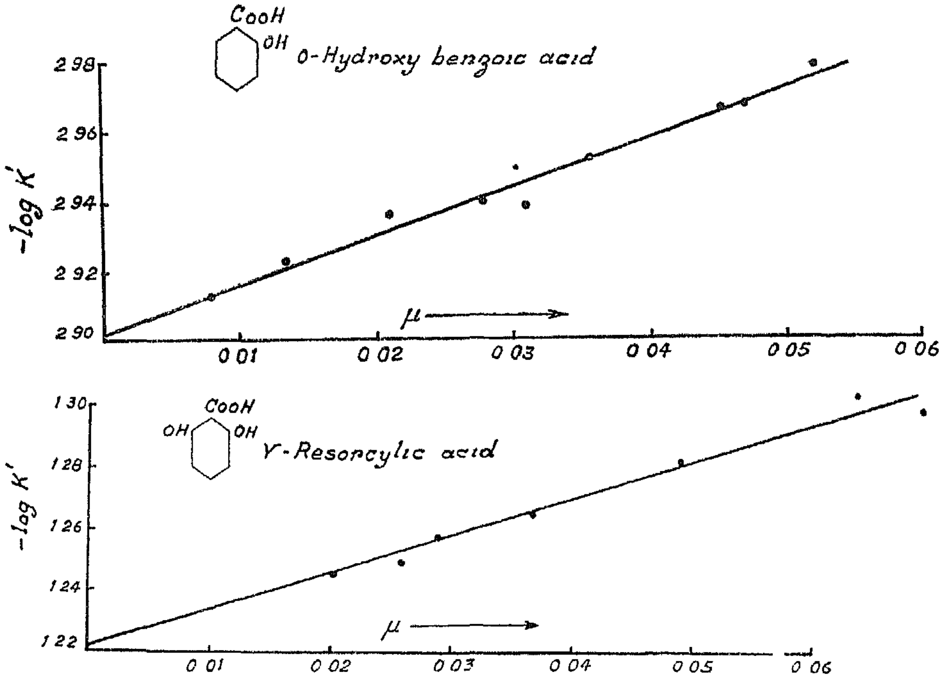


FIG 1

In Fig 1 the ionic concentrations μ have been plotted against the corresponding dissociation constant of each acid This plot when extrapolated for zero ionic concentration gives the value of K, the true thermodynamical dissociation constant of each acid in pure water at 30°C Following values of K have been obtained

Acid	K Authors (30°C)	Others (25°C)
o–Hydroxy benzoic acid .	$1\ 25 \times 10^{-3}$	$1\ 06 \times 10^{-3}$ (a)
β–Resorcylic acid .	$6\ 07 \times 10^{-4}$	$5\ 16 \times 10^{-4}$ (b) $4\ 96 \times 10^{-4}$ (c)
γ–Resorcylic acid	$6\ 00 \times 10^{-2}$	$5\ 0 \times 10^{-2}$ (b)

(a) Thiel and Roemer, Z Physikal Chem, 1908, **63**, 731

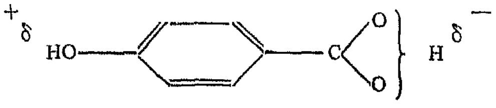
(b) Ostwald, ibid , 1889, **3**, 249

(c) Suss, Monatsh 1905, **26**, 1331,

The lower values obtained by previous workers are due principally to (1) the assumption of incomplete dissociation of sodium salt, a view prevelant at the time of their determinations and (2) the use of Siemens unit of resistance, according to which the value of Λ in older literature is lower than that calculated from the present definition of ohm The old results have not been corrected for the effect of interionic attractions.

DISCUSSION

The values of dissociation constants of various hydroxy carboxylic acids show that the hydroxyl group owing to its electron attracting dipole increases the strength of the acid This electrostatic induction (–I) is transmitted through the molecule and also through space (cf Ingold J Chem Soc, 1933, 1120) In saturated conjugate systems, along with the electronic displacement of the inductive type, a migration of the electrons, bringing about covalency changes, takes place (cf Lowry J Chem Soc 1923, 822) This electronic migration is the outcome of resonance, and is called the mesomeric effect (M) In *ortho-* and *para*-hydroxy benzoic acids, the presence of an unshared electron pair on the oxygen atom brings about a resonance which in the latter compound is expressed by the structure



This resonance decreases the strength of the *para* acid The effect in the *ortho* acid being counter-acted by the electrostatic induction (–I) In *m*-hydroxy benzoic acid, there being no possibility of a resonating structure, the only factor which contributes towards the increase in acid strength, is the electrostatic induction (–I).

Jenkins (J Chem Soc, 1939, 640) has calculated this factor (I) in the case of *o*–, *m*– and *p*–halogeno benzoic acids and has shown that for these acids, F the field strength at the carbon atom of C COOH group, due to a small dipole situated at a distance r, is proportional to the logarithm of the dissociation constant The value of F is given by the expression, $F = \mu \sqrt{1+3\cos^2\theta}/r^3$

The values of F calculated for the three hydroxy benzoic acids are given in the following table and are plotted against log K in Fig 2

Substituent	$K \times 10^5$	log K	$F \times 10^{-6}$
H	6 31	–4 200	± 0 000
o–OH	125 0	–2 902	488
m–OH	8 3	–4.081	124
p–OH	2 9	–4 538	084

The centre of the dipole in these acids has been taken mid-way between C and O, and the OH group has been assumed to be more or less a perfect conductor The value of μ for phenol which has been determined in benzene solution is corrected for the vapour by multiplying by a factor $\frac{\mu \text{ vapour}}{\mu \text{ solution}}$ for chlorobenzene (cf Groves and Sugden J Chem Soc, 1937, 1992) 'r' and θ have been calculated trignometrically from the values of interionic distances given by Pauling and Huggins (Z Krist, 1934, **84**, 205)

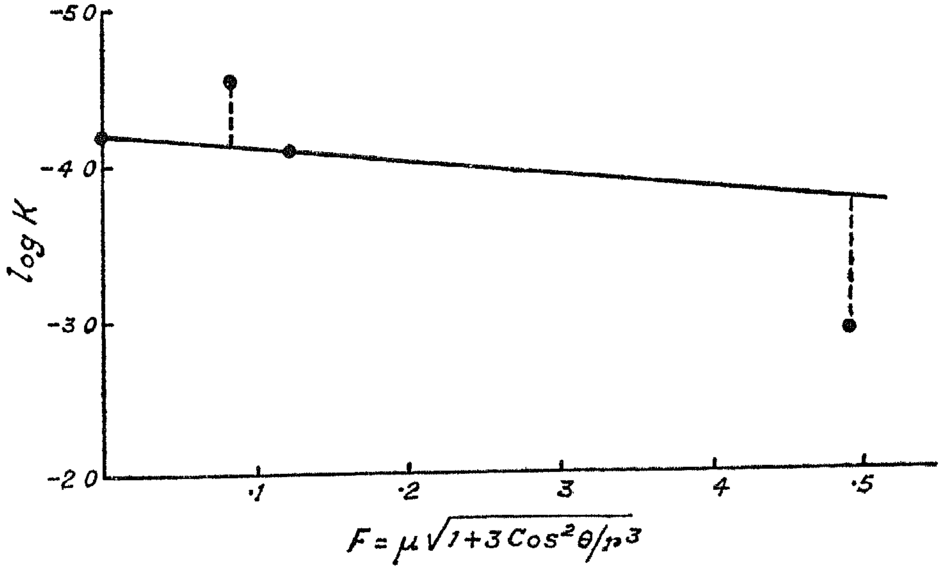
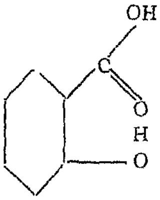
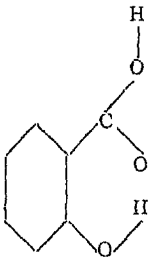


FIG 2

Since the *m*- acid has been taken as an ideal case in which only electrostatic induction is responsible for increased acid strength, a straight line (Fig 2) has been drawn passing through benzoic acid and *m*-hydroxy benzoic acid The deviation of *o*- and *p*- acids from the straight line relationship is also shown in the diagram

The abnormally high dissociation constant of *o*-hydroxy benzoic acid, however cannot be entirely accounted for on the inductive (–I) and mesomeric (+M) effects Branch and Yabroff (J Amer Chem. Soc, 1934, **56**, 2568) have pointed out that this anomalous behaviour of the ortho substituted acid is due to the resonance, which results in the formation of the chelate ring The acid may be considered to exist as a tautomeric equilibrium between the classical and chelate structures

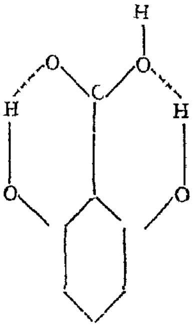




Baker (Nature, 1936, **137**, 236) has suggested that it is the chelation of the anion, which hinders the return of the proton and increases the acid strength He has suggested a presence of an internal hydrogen bond in the molecule

β–Resorcylic acid has two hydroxyl groups, in ortho and para positions The dissociation constant of the acid shows that both the groups exert an influence on the strength of the acid, independently of each other, one increasing the dissociation while the other decreasing it The effect of chelation or the internal hydrogen bond in ortho position is similar to that in *o*-hydroxy benzoic acid This effect is still more pronounced in *γ*–resorcylic acid, which has two hydroxyl groups in ortho positions to the carboxyl

This compound has two internal hydrogen bonds and has the following structure



According to Smallwood (J. Amer. Chem. Soc., 1932, **54**, 3048) the increased acidity of the ortho substituted acid is due to the diminished free rotation of the carboxyl with respect to the substituent group. It may however be pointed out that, this diminished free rotation is mainly due to the internal O H bond present in the molecule, which makes the oxygen of the carboxyl group directed towards the phenolic OH.

The factors which change the strength of the hydroxy substituted benzoic acids can be summarized as (1) electrostatic induction (2) mesomeric effect due to resonance and (3) inter atomic O H bonding present in the molecule. The factors for all these three effects as calculated from the graph of F against log K are given below

Substituent	Induction effect	Mesomeric effect	Internal bond effect	Total effect
o–OH	3.9	0.4	13.4	21.0
m–OH	1.3	—	—	1.3
p–OH	1.3	0.4	—	0.5

The values of K for various di- and tri-hydroxy benzoic acids, calculated on the basis of the above factors, are tabulated along with the observed values in the following table

Acid strength of di- and tri-hydroxy benzoic acids

Number of groups			Calculated K	Observed K	Acid
Ortho	Meta	Para			
1	1	–	1.7×10^{-3}	1.14×10^{-3} (c)	2.3 dihydroxy benzoic acid
1	–	1	6.6×10^{-4}	6.07×10^{-4} (a)	2.4 ,, ,,
1	1	–	1.7×10^{-3}	1.08×10^{-3} (c)	2.5 ,, ,,
2	–	–	2.8×10^{-2}	6.00×10^{-2} (a)	2.6 ,, ,,
–	1	1	4.1×10^{-5}	3.3×10^{-5} (c)	3.4 ,, ,,
–	2	–	10.6×10^{-5}	9.1×10^{-5} (c)	3.5 ,, ,,
1	1	1	8.5×10^{-4}	5.5×10^{-4} (c)	2.3.4 tri-
–	2	1	5.3×10^{-5}	4.6×10^{-5} (b) 3.8×10^{-5} (c)	3.4.5 ,, ,,
2	–	1	1.3×10^{-2}	2.2×10^{-2} (c)	2.4.6 ,, ,,

(a) Present investigation

(b) Abichandani and Jatkar (loc cit)

(c) Values from Landolt Bornstein

A scrutiny of the various experimental values of dissociation constants of di- and tri-hydroxy benzoic acids, given in the above table shows that the effect of substitution by hydroxyl group depends on the position and number of groups. The observed values of dissociation constants for 2.6 hydroxy and 2.4.6 tri-hydroxy benzoic acids are approximately twice the calculated values. This is significant in view of the fact that both the acids possess the two ortho groups, and have the same structural configuration, possessing two internal O....H bondings. Thus for an acid containing a number of internal O....H bondings the calculated value of the dissociation constant must be multiplied by the number of O....H bonds present in the molecule. On this assumption, we have for ortho hydroxy benzoic acid $K = 1 \times 1.253 \times 10^{-2}$ and for 2.6 di-hydroxy benzoic acid $K = 2 \times 2.8 \times 10^{-3}$ and for 2.4.6 tri-hydroxy benzoic acid $K = 2 \times 1.3 \times 10^{-2}$

The calculated values for rest of the acids are in fair agreement with those determined experimentally, the slight differences being due to the mutual influence, which the groups exert on each other and on carboxyl group

Recently Jenkins (Nature, 1940, **145**, 149) has shown the influence of degeneracy n, (which is defined in terms of number of possible resonating structures) on the strength of the acids in which the inductive effect is small or can be calculated He has shown that in the case of acetic acid (n = 2), phenyl acetic acid (n = 4) and diphenyl acetic acid (n = 8), a straight line relationship exists between n the degeneracy and the dissociation constant

This idea can be extended to benzoic acid, *o*-hydroxy benzoic acid and 2 6 dihydroxy benzoic acid (γ-resorcylic acid), if the inductive and mesomeric influences (page 85) are allowed for According to Branch Yabroff and Bettman (loc cit) the anomalous dissociation constant of *o*-hydroxy benzoic acid is due to the resonance between the classical and chelate structures On this basis and taking into account the Pauling's resonating structures for a acid, the value of n is 2 for benzoic acid, 4 for *o*-hydroxy benzoic acid and 8 for 2 6 dihydroxy benzoic acid, after neglecting the resonance structures due to the mesomeric influence

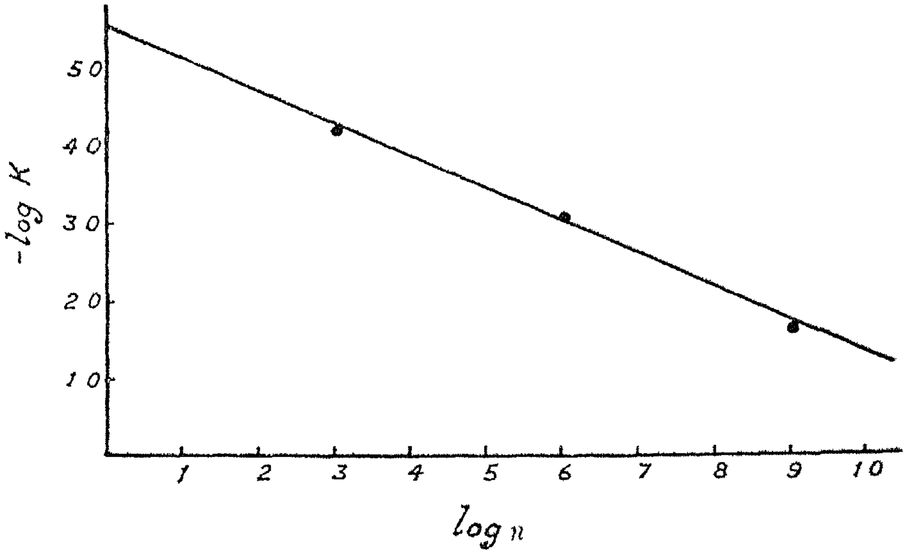


Fig [illegible]

Fig 3 shows the relationship between log n and log K after allowing for the inductive and mesomeric influences

SUMMARY

The dissociation constants of *o*–hydroxy benzoic acid and γ–resorcylic acid have been determined at 30°C, by the measurement of the electromotive force of the cells without liquid junction of the type

H_2 | H An, NaAn, NaCl | AgCl–Ag

The values of K for various acids in pure water are found to be as follows

o–Hydroxy benzoic acid $K = 1\ 25 \times 10^{-3}$
γ– Resorcylic acid $K = 6\ 0 \times 10^{-2}$

F, the field intensity at the carbon atom due to the substitution of hydroxyl groups in various *ortho*, *meta*, and *para* positions has been calculated The effect of various factors, such as inductive effect, mesomeric effect and internal bond effect, on the strength of the acid has been determined

The dissociation constants of the *di*-and *tri*-hydroxy benzoic acids have been calculated on the assumption that the change in dissociation constant depends on the position and number of the hydroxyl groups The experimentally observed values for all acids are in good agreement with the calculated values, except for 2 6 *di*-hydroxy and 2 4 6 *tri*-hydroxy benzoic acids, for which the observed values are approximately twice the calculated values This is significant in view of the fact that both the acids possess two *ortho* groups, and have the same structural configuration, possessing two internal O H bondings

The existence of OH O bonding in catechol and pyrogallol is also acid weakening in character as the second dissociation constant of these compounds is of the order of 10^{-13} In *o*-hydroxybenzoic acid also this OH O bonding is responsible for the remarkably low value of the second dissociation constant

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