DISSOCIATION CONSTANTS OF PARA SUBSTITUTED BENZOIC ACIDS IN ALCOHOLIC SOLUTIONS

by

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ABSTRACT

The dissociation constants for benzoic and p-chlorobenzoic acids were measured in aqueous solution, and the constants for benzoic, p-chlorobenzoic, p-bromobenzoic, p-iodobenzoic, p-toluic, p-ethyl benzoic, and p-cuminic acids were measured in 80% alcoholic solutions by means of a quinhydrone electrode.

A description of the electrode, and the vacuum tube amplifying circuit used in connection with the potentiometer, is given.

The synthesis of p-toluic, p-ethyl benzoic, and p-cuminic acids is described.

INTRODUCTION

The present research was undertaken in hope that the dissociation constants of a series of para substituted benzoic acids could be determined with sufficient accuracy to draw definite conclusions as to the relative inductive effects of the several substituent groups.

Early investigators were confronted with the fact that monosubstituted benzene derivatives fell into two classes, those that form meta disubstituted derivatives, and those forming ortho or para disubstituted derivatives. Groups such as the nitro, the sulfonic, and the carboxyl group, were found to be strongly meta-directing to the exclusion of the other positions whereas groups such as the hydroxyl and the amino groups directed ortho and para, but not meta.

The orientating effect of poles has shown that a positive pole is strongly meta-directing, even when removed from the benzene nucleus by a carbon atom in a side chain, cf. $C_6H_5.NMe_3^+$, 100% meta; $C_6H_5.CH_2.NMe_3^+$, 88% meta. On the other hand, negative poles are strongly ortho, para directing; witness, the rapid bromination of phenol in alkaline solution to symmetric tribromophenol.

For other groups, that are not definitely polar, a dipole is formed. These can be ortho,para-directing, or meta-directing depending on the electron-attraction of the group. Groups that attract electrons strongly are meta-directing, those that attract them weakly, or repell them, are ortho,para-directing to a lesser of greater extent.

The groups studied in the present research are weakly ortho, para-directing groups. They have not enough electron attraction to be meta-directing, nor enough electron repulsion to be strongly ortho,para-

directing. However, their effects are noticeable in the degree of dissociation of the substituted benzoic acids.

A group that attracts electrons, tends to shift the electron pair between the hydrogen and the oxygen atom in the carboxyl, away from the position they would assume in the unsubstituted acid, towards the oxygen, thus leaving the proton freer to pass into solution as an ion. Similarly, those that repell electrons, shift them away from the oxygen toward the proton, making it less free to ionize. The halogen groups exhibit a weak electron attraction, and the alkyl groups a weak electron repulsion.

On the above basis, it was thought that the increasing kernel charge in the series of halogen-substituted benzoic acids, might manifest itself in a distinguishable increase in the dissociation constants, passing from chlorine to iodine. A similar change might be exhibited in the alkyl-substituted acids passing from methyl, to ethyl, to isopropyl.

METHODS

Several general methods have been used in investigating the dissociation constants of weak acids: conductivity, colorometric and potentiometric measurements. For acids that are weak as benzoic acid, and as insoluble as the halogen substituted benzoic acids, conductivity measurements would be attended with such errors, due to the difficulty in technique required to measure so feebly conducting solutions, that accurately determined acid constants seemed unattainable. Similar difficulties attend colorometric determinations. The insolubility of the acids would rule out potentiometric titrations. The quinhydrone electrode had been used with success on benzoic acid, and was adopted as the most practicable means available.

ELECTRODE REACTION

The quinhydrone electrode furnishes a convenient oxidation-reduction potential, and may be used as a hydrogen-ion concentration cell:

(1) Pt, quinhydrone, $H^+(c_1) \,||\, H^+(c_2)$, quinhydrone, Pt

Considering the electrode reaction,

$$Q\,H_2 \rightleftharpoons Q + 2H^+(c) + 2\,e$$

the electrode potential is

$$E = E_o - \frac{RT}{2F} \ln \frac{(Q)}{(QH_2)} (c)^2$$

and since quinhydrone dissociates in solution to give equal parts of quinone and hydroquinone, the ratio $\frac{(Q)}{(QH_2)} = 1$ and

(2) $$E = E_o - \frac{RT}{F} \ln (c).$$

Thus the cell (1) has a potential given by

(3) $$-E = \frac{RT}{F} \ln \frac{c_1}{c_2}$$

c is written instead of a and it will be shown that the method is con-

cerned with the concentration rather than with the activity.

The acid whose strength is to be measured is dissolved at a definite molality in a 0.09 molal solution of KCl. This forms a half cell, which is measured against a standard half cell containing HCl 0.01 molal, KCl 0.09 molal. (All solutions were made 0.09 molal in KCl to eliminate liquid junction potentials.) Consider now the hydrogen ion activities in the two half cells. To a first approximation, $-\log \gamma$ is proportional to the $\sqrt{\mu}$ where μ is the ionic strength and γ is the activity coefficient:

Thus $$-\log \gamma_1 = \alpha\sqrt{\mu_1}$$
$$-\log \gamma_2 = \alpha\sqrt{\mu_2}$$

$$\alpha = \frac{e^3(2\pi n)^{1/2}}{2.306(DkT)^{3/2}} = 0.5066$$

and $$\log \frac{\gamma_1}{\gamma_2} = \alpha(\sqrt{\mu_2} - \sqrt{\mu_1})$$

So rewriting (3) substituting activities for concentrations

$$-E = 59.15 \log \frac{a_1}{a_2} \text{ millivolts}$$

$$= 59.15 \left(\log \frac{c_1}{c_2} + \log \frac{\gamma_1}{\gamma_2}\right)$$

$$= 59.15 \log \frac{c_1}{c_2} + 59.15 \times \alpha(\sqrt{\mu_2} - \sqrt{\mu_1})$$

$$= 59.15 \log \frac{c_1}{c_2} + \Delta E$$

here

$\mu_1 = 0.1000$ $\qquad$ $\sqrt{\mu_1} = 0.3162$

$\mu_2 = 0.0900$ $\qquad$ $\sqrt{\mu_2} = 0.3000$

whence $\Delta E = -59.15 \times 0.5066 \times 0.0162 = -0.48$ mv.

Since this value is of the order of magnitude of the reproducibility

of the experiments, it can be neglected, and concentrations may be used in place of activities.

From equation (3) we find

$$\log c_2 = \frac{EF}{RT} + \log c_1 = \frac{E}{59.15} + \log c_1$$

$$= E \times 0.010907 + \log c_1$$

But in all our runs E is negative and $\log c_1 = -2.0000$;

so taking the absolute value of E,

(4) $$-\log c_2 = E \times 0.016907 + 2.0000$$

where c_2 is the hydrogen ion concentration from the organic acid.

The Acid Dissociation Constant

To calculate the dissociation constant of the acid, we take as our definition

$$k_a = \frac{(c_2)^2}{c - c_2}$$

where c is the molal concentration of the acid and c_2 is the hydrogen ion concentration determined by equation (4).

The dissociation constant of an acid is the equilibrium constant for the reaction

(5) $$HA = H^+ + A^-$$

Before the concept of activities, the constant was written according to the usual mass action calculation

(6) $$\frac{(H^+)(A^-)}{(HA)} = k_a;$$

and since $(H^+) = (A^-)$, and $(HA) = c_{HA} - c_{H^+}$

where c_{HA} = molality of acid assuming no dissociation

$c_{H^+} = (H^+)$ = molality of H^+ ions

expression (6) may be written

$$(7) \qquad k_a = \frac{(c_{H^+})^2}{c_{HA} - c_{H^+}}$$

With the advent of the concept of activity, the acid dissociation constant was written

$$(8) \qquad K_A = \frac{(a_{H^+})(a_{A^-})}{a_{HA}}$$

$$= \frac{(c_H)^2 \gamma^2}{(c_{HA} - c_{H^+})} = \gamma^2 k_a$$

where a_H and a_A are respectively the activities of the hydrogen ion and the anion, and a_{HA} is the activity of the undissociated portion of the acid. If γ is taken as the mean ion activity coefficient, and the activity of the undissociated acid is taken equal to its concentration, expression (8) holds. In the case of aqueous solutions of benzoic acid where γ can be determined, K_A is calculated as well as k_a. In alcoholic solutions where γ is not known, only k_a is given.

In order to facilitate computation, curves were plotted of k_a against E. In all the final runs, the acid concentration was 0.02 molal. Preliminary work showed that too dilute solutions were attended by unsatisfactory results due, possibly, to adsorption of hydrogen ions on the glass of the containers. Because of the insolubility of the halogen substituted benzoic acids, it was necessary to change from aqueous solutions to alcoholic solutions. These will be discussed later.

Apparatus

The cell used consisted of an inner and an outer half connected through

a ground glass joint, which was wetted with saturated KCl solution when the cell was being assembled. The inner cell held 3 cc. of the standard HCl, KCl solution; the outer cell, 17 cc. of the organic acid, KCl solution. These amounts gave the same liquid level in both containers, thus reducing diffusion across the ground glass joint to a minimum. The inner electrode was a rectangular platinum foil 8 mm. by 5 mm. The two outer electrodes were coiled platinum wires. These proved more reproducible than platinum foil.

Due to the relatively high resistance of the cell, it was necessary to use an amplifying circuit in conjunction with the potentiometer. The circuit used consisted of two vacuum tubes balanced one against the other by varying the grid bias. The description of the electrical circuit is given below.

Potentiometric Circuit

The diagram shows the insertion of the amplifier into the potentiometer circuit. This was accomplished by removing the wires a, b, from the switch posts a', b', and soldering them together. The switch was then connected to the plates of the amplifying circuit.

After the potentiometer is adjusted to the standard cell in the ordinary manner, the single-pole double-throw switch, S, is turned so as to short out the potentiometer-cell circuit. The two tubes are then brought into balance by means of the subsidiary potential (tapped off resistances R_3 and R_4) applied to the grid of the floating tube. The switch is then thrown, applying to the grid of the other tube the electromotive force of the cell, which is counterbalanced by the potentiometer. This method has the advantage of

having the D.C. resistance of the vacuum tube always in series with the electrolytic cell. The high resistance reduces the current drawn during a reading to a negligible value, thus preventing polarization errors.

Solutions

The alcoholic solutions were made up to 80% alcohol by volume. This value was chosen in order that their molality in KCl might be 0.09 and still permit the organic acids to be sufficiently soluble.

If the original volume percent alcohol is s, and the desired volume percent is t, dilute a cc. of the original to 100 cc. by adding b cc. of water, thus obtaining 100 cc. of alcohol t percent by volume. Let d_1 be the density of the original alcohol; d_2, of the final alcohol; d_a, of absolute alcohol.

Then $$a\,s = 100\,t$$

$$a = 100\,\frac{t}{s}$$

The amount of water in 100 cc. of final alcohol $= 100\,d_2 - t\,d_a$ grms.

" " " " a cc. of original " $= \frac{a}{100}(100d_1 - sd_a)$ "

" " " " to be added $= bd = 100(d_2 - \frac{t}{s}d_1)$ grms.

$$b = \frac{100}{d}(d_2 - \frac{t}{s}d_1) \text{ cc.}$$

where d is the density of water.

If the final solution is to be m molal in some constituent, an aqueous solution is made lm molal in that constituent, where $l = \frac{100}{b}$. Then b cc. of this solution diluted to 100 cc. with alcohol will be m molal

in the constituent, and t percent alcohol by volume.

So in making up alcoholic solutions, three solutions are necessary:

Solution I	alcohol s percent by volume
Solution II	HCl ($\frac{1}{a}$ x 0.01 molal), KCl ($\frac{1}{a}$ x 0.09 molal)
Solution III	KCl ($\frac{1}{a}$ x 0.09 molal)

To make standard reference solution, dilute b cc. of II to 100 cc. with I.

To make standard organic acid solution, dissolve sample of acid in less than a cc. of I, add b cc. of III, and dilute to 100 cc. with I.

Preparation of Materials

The alkyl substituted benzoic acids, with the exception of the toluic acids, are not obtainable from any chemical supply house. Two methods of synthesis presented themselves: 1. the introduction of a CHO group para to an alkyl group by the Gatterman reaction, followed by oxidation to the acid; 2. the replacement of an amino group by a CN group by the Sandmeyer reaction, followed by hydrolysis to the acid.

The preparation of p. toluic aldehyde is described in Organic Syntheses Vol. XII, p. 80. The procedure was followed, using carefully dried toluene, freshly prepared Cu_2Cl_2 (Org.Syn.), and freshly opened $AlCl_3$. The absorption of CO was good, and after 4.5 hours, the reaction mixture had thickened to the consistency of butter. The yield of aldehyde was 51.5% of the theoretical.

This was converted to the acid by the Cannizzaro reaction, with a 72%

yield.

The same method was employed with other hydrocarbons. Two runs with n. butyl benzene, two with cumene, and one with ethyl benzene. In all these cases, the absorption of CO was poor, and the yields of aldehyde were nil or very small.

Two more runs were made with ethyl benzene, each yielding a low percentage of an aldehyde. The aldehyde from the first was oxidized with alkaline permanganate and converted entirely to phthalic acid. The aldehyde from the second was converted by a Cannizzaro reaction to an impure ethyl benzoic acid. Repeated recrystalizations failed to raise the melting point above 87°. The contaminant was probably o. ethyl benzoic acid. This difference in behavior between toluene and ethyl benzene, viz: that the toluene directs the entering CO entirely to the para position, whereas the ethyl benzene seems to favor the ortho position as well, might prove worthy of future investigation.

The failure of this method, except in the case of toluic acid, (which was available from Eastman), led to the adoption of alternatives. For Cuminic acid, p. cuminic aldehyde was obtainable from Eimer and Amend. This was oxidized by alkaline permanganate to p. cuminic acid, in almost quantitative yield.

Para aminoethylbezene was prepared by a molecular rearrangement of ethyl aniline in the presence of zinc chloride. (Hickenbottom J.C.S. p.64 (1927)). The method used was a slight modification of the one there described.

90 grms. of freshly distilled ethyl aniline were heated with 45 grms.

of fused zinc chloride in a 300 cc. Erlenmeyer flask on a sand bath. The flask was fitted with a short air reflux condenser (14 inches long), and heating was adjusted to keep the mixture boiling gently. After 10.5 hours, the hot, red mixture was poured into a porcelain dish, where it solidified. The solid zincichloride salt of the primary amine was triturated in a mortar with ether to remove any of the unchanged ethyl aniline. The ether was filtered off; the product pressed between sheets of filter paper, and decomposed with 200 cc. of 50% NaOH solution to the free amine, which was separated by steam distillation. This was extracted with ether, dried over $CaCl_2$, and the ether was evaporated off. The yield of p. amino ethyl benzene was 50 grms, 54.5% of the theoretical.

In converting this to the nitrile, standard procedure was followed; except that after forming the cuprous cyanide complex, enough sodium carbonate was added to neutralize the acid from the diazo-mixture. This prevented the evolution of HCN, which being undesirable from the standpoint of general comfort, tends also to reduce the yield of the nitrile.

37.5 grams of the neutral sulfate of the amine was diazotized, by dissolving it in a mixture of 40 grams of sulfuric acid in 100 cc. of water. This was cooled in a pan of ice, and to it was added, with constant stirring, 18 grms. of sodium nitrite in 50 cc. of water.

The diazo solution was added to the warm cuprous cyanide solution slowly over a period of about 10 minutes. This solution had been prepared previously by 65 grms. of copper sulfate dissolved in 200 cc.

of water, heated on a water bath. To this was added, cautiously in the fume hood, 55 grms. of NaCN in 100 cc. of water. After the evolution of cyanogen had ceased, and the entire amount of cyanide had been added, 60 grms. of sodium carbonate was added. The reaction was done in a 3 litre balloon flask.

The mixture was heated 15 minutes after the diazo solution had been added, and was then steam distilled. The nitrile was taken up in ether, the ether evaporated and the product was shaken with 4 grms. of stannous chloride in 10 cc. of HCl to remove isocyanide. It was then poured into water, extracted with ether, dried over $CaCl_2$, and ether evaporated off. Yield of purified nitrile, 13.4 grms; 59.5% of the theoretical.

This was hydrolysed with 40 grms. of sulfuric acid in 20 grms. of water, heating for 10 hours in an oil bath at 155°. Yield of crude acid 7.5 grms., 48.5% of the theoretical. This was purified by dissolving in sodium carbonate, reprecipitating with HCl, twice recrystallizing from 50% alcohol, and finally subliming. Yield of purified acid, 5.5 grms.

The remaining acids, p. chloro benzoic, p. bromo benzoic, and p.iodo benzoic, were from Eastman. The first two were purified by twice recrystallizing from 50% alcohol, while the p. iodo benzoic was sublimed just before using.

Table I

Acid	m.p. ° C.
* Benzoic	121
p. Chloro benzoic	237-238
p. Bromobenzoic	251-252
* p. Iodobenzoic	265-268
* p. Toluic	177-178.5
* p. Ethylbenzoic	112-112.5
* p. Cuminic	115.5-116.5

*Sublimed.

Preparation of Alcohol

The alcohol for the final runs was refluxed with KOH and granular aluminum for two hours to render it aldehyde free. (Stout and Schuette I.& E. Ch. Vol. 5, No.2, p. 100 (1933)). It was distilled into a nitrogen filled container, and forced out by nitrogen when used. It gave no test for aldehyde with Schiff's reagent. Its density at 25° was determined pyknometrically.

Density 25°		0.80064 grms./cc.
Vol. percent alcohol		97.114
Density 80.00% alcohol 25°		0.83904 grms./cc.
s = 97.11%		b = 18.00 cc.
t = 80.00%		l = 5.5556
whence Solution I	alcohol	97.114%
Solution II	HCl	0.055556 molal
	KCl	0.50000 "
Solution III	KCl	0.50000 "

The HCl solutions were made up by weighing out constant boiling HCl prepared after the method of Faulk and Hollingsworth (F & H, J.A.C.S. 45, 1220 (1923)). The KCl used was twice recrystallized, fused, and powdered.

Technique of E.M.F. Measurements

Solutions of the acids under investigation were made up to 0.02000 molal strength in 100 cc. samples. These, with the reference HCl solution, were kept in a thermostated oil bath at $25.00^{\circ} \pm 0.01^{\circ}$. In making a run, the ground glass connection between the inner and outer half cell was wetted with saturated KCl solution; a pinch of quinhydrone (prepared method Bijlmann Bul. Soc. Ch. 41, 245) was added to each half from a knife blade; the electrodes were inserted in the outer half cell, and the cell was mounted on a shaker in the thermostatic bath. The solutions were then added by means of pipettes so built that the liquid level in the two half cells was the same. The electrode for the reference solution was then inserted, and the shaker started. Potentiometric measurements were made on the average of every two minutes over a period of ten minutes.

Between runs, the cell was carefully washed and dried. The electrodes were kept in the same solution that they were surrounded by in the cell. This treatment gave, by far, the most reproducible and consistent results. It might be noted that treating the electrodes with cleaning solution is disastrous; subsequent runs fail to agree, by wide variations, with those previous to such treatment, and new electrodes must be made.

In the case of runs with aqueous solutions, shaking was not necessary; identical results were obtained with or without. But for the alcoholic solutions, wide discrepancies occurred which were eliminated by shaking continuously throughout a run.

Experimental Results

Preliminary runs in aqueous solutions 0.09 molal in KCl of various molalities of HCl against the standard reference concentration of 0.01 molal HCl, showed that for not too dilute solutions, the hydrogen ion concentration could be determined to a few percent. When the acid concentration was less than 0.0001 molal, the determinations gave invariably too low a concentration. This could be explained by assuming that hydrogen ions were adsorbed on the walls of the cell and containing vessel. A very slight molal adsorption per unit area of surface would account satisfactorily for the discrepancy. It was due to this that alcoholic solutions were employed.

Table II

HCl solutions in 0.09 molal KCl against standard reference solution HCl 0.01 molal, KCl 0.09 molal.

Run	molality HCl	-E calculated	-E observed	c_H calculated
1	1.000×10^{-3}	59.15 mv.	59.30	0.9949×10^{-3}
2	"	"	59.10	1.003
3	"	"	59.41	0.9905
4	"	"	59.40	0.9909
5	"	"	58.60	1.022

Table II - Continued

Run	molality HCl	-E calculated	-E observed	c_H calculated
6	1.000×10^{-3}	59.15	58.94	1.009
7	"	"	58.90	1.010
8	"	"	59.23	0.9975
9	"	"	57.70	1.059
10	"	"	57.05	1.086
11	1.000×10^{-4}	118.30	120.52	0.9185×10^{-4}
12	"	"	120.45	0.9210
13	"	"	124.62	0.6157
14	"	"	119.41	0.9591
15	"	"	126.62	0.7244

Measurements were made with aqueous solutions of benzoic acid at 2.000×10^{-2} molal and 2.000×10^{-3} molal concentrations. The results appear in Table III.

Table III

Dissociation Constant of Benzoic Acid in Aqueous Solution

Run	Molality	-E	$k_a \times 10^5$	$K_A \times 10^5$
1	2.000×10^{-2}	52.35	9.10	5.96
2	"	52.05	9.31	6.16
3	"	52.10	9.08	5.95
4	"	52.60	8.94	5.85
5	"	52.50	8.99	5.88
6	"	52.45	9.02	5.91
		mean:	9.11	5.98

Table III - Continued

Run	Molality	-E	$k_a \times 10^5$	$K_A \times 10^5$
7	2.000×10^{-3}	84.00	8.92	5.84
8	"	84.20	8.74	5.72
9	"	84.50	8.52	5.58
10	"	84.30	8.68	5.68
11	"	84.65	8.40	5.50
12	"	84.45	8.56	5.61
		mean:	8.64	5.66

note: $K_A = k_a \gamma^2$ $\gamma = 0.81$ (Kilpatrick and Chase J.A.C.S. 53, 1732 (1931)).

Runs were also made with aqueous solutions of p. chlorobenzoic acid. Due to its low solubility, no solution could be stronger than 4×10^{-4} molal.

Table IV

Dissociation Constant of p. Chlorobenzoic Acid in Aqueous Solutions

Run	Molality	-E	$k_a \times 10^5$	$K_A \times 10^5$
1	3.9540×10^{-4}	106.29	10.8	7.10
2	"	106.36	10.7	7.01
3	"	106.18	10.9	7.14
4	"	106.89	8.05	5.28
5	"	107.31	9.72	6.45
6	"	105.26	12.0	7.85
7	"	106.15	11.0	7.21
		mean:	10.5	6.86

Table IV - Continued

Run	Molality	-E	$k_a \times 10^5$	$K_A \times 10^5$
8	1.9770×10^{-4}	120.44	8.19	5.38
9	"	122.43	6.43	4.24
		mean:	7.31	4.81

The final runs in 80% alcoholic solutions are given in Table V.

Table V

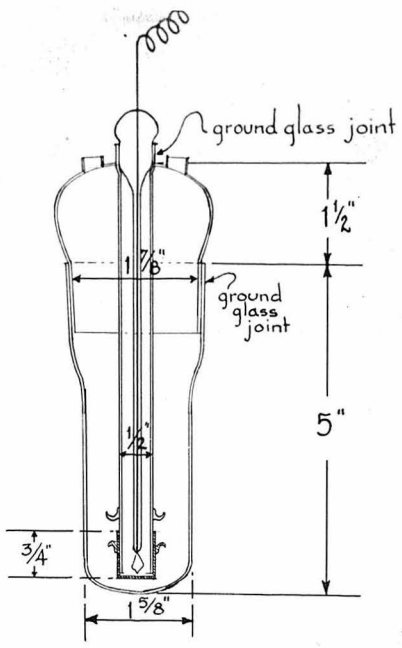
Dissociation Constants of 0.02000 Molal Acids in 80% Alcohol 0.09 Molal in KCl.

Acid	-E mv.	$k_a \times 10^7$	Acid	-E mv.	$k_a \times 10^7$
p. Iodobenzoic	92.99	36.5	p. Bromobenzoic	92.41	38.0
	93.41	35.5		97.01	26.5
	94.40	32.5		94.24	33.0
	93.42	35.2		91.30	41.5
	97.23	26.1		93.18	36.0
mean:	94.36	33.2		93.63	35.0
p. Chlorobenzoic	92.77	37.2	Benzoic	105.29	13.5
	96.64	27.5		105.91	13.0
	96.06	29.0		106.14	12.7
	95.30	30.5		107.08	12.0
	96.50	27.8			
mean:	95.45	30.4		106.11	12.8

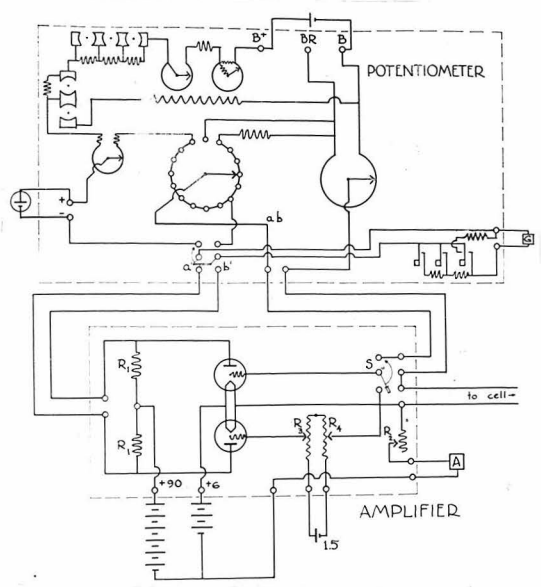
Table V - Continued

Acid	-E mv.	$k_a \times 10^7$	Acid	-E mv.	$k_a \times 10^7$
p. Toluic	115.67	6.1	p. Ethylbenzoic	109.59	9.9
	111.68	8.4		113.45	7.4
	113.60	7.2		111.77	8.4
	112.42	8.0		113.28	7.5
	116.60	5.9		110.78	9.0
mean:	113.99	7.1		111.77	8.4
p. Cuminic	108.66	10.5			
	108.41	10.7			
	109.49	10.0			
	108.77	10.5			
	111.65	8.5			
mean:	109.39	10.0			

Electrolytic Cell



Electric Circuit



Description of Amplifying Circuit

R_1 : Super Davohm wire-wound resistance, 100,000 ohms.

R_2 : Ordinary filament rheostat.

R_3 : 20 ohms.

R_4 : 50 ohms.

Tubes: Western Electric, 102 D.

Potentiometer: Leeds and Northrup, Type K.

Standard Cell: Weston, No. 6915 E M F = 1.01870

Galvanometer: Leeds and Northrup, No. 200334.

Cat. 2420 A Sens. 31 meg. Res. 340 ohms.

SUMMARY

I Dissociation Constants in Aqueous Solutions

Acid	Observer	Molality	$K_A \times 10^5$
Benzoic	Ostwald (1)	0.02	5.98
	Euler(2)	"	6.68
	Schaller (3)	"	6.80
	Kortwright (4)	"	6.19
	White and Jones (5)	"	6.70
	Kirschman,Wingfield and Lucas (6)	"	6.63
	Present paper	"	5.98
p-chloro-benzoic	Ostwald (1)	-	9.3
	Present paper	3.954×10^{-4}	7.3

II Dissociation Constants in Alcoholic Solutions

Acid	Molality	$k_a \times 10^7$
benzoic	0.02	12.8
p.chlorobenzoic	"	30.4
p.bromobenzoic	"	35.0
p-iodobenzoic	"	33.2
p.toluic	"	7.1
p.ethylbenzoic	"	8.4
p.cuminic	"	10.0

(1) Ostwald, Z.physik.Chem., 3, 241 (1889).
(2) Euler, ibid., 21, 257 (1896).
(3) Schaller, ibid., 25, 497 (1898).
(4) Kortwright, ibid., 21, 311 (1896).
(5) White and Jones, Am.Ch.J., 44, 159 (1910).
(6) Kirshman, Wingfield and Lucas, J.A.C.S., 52, 23 (1930).

Conclusions

Runs with 0.02000 molal benzoic acid in aqueous solutions give values for K_A with a maximum deviation of 2% from the mean; and at the dilution, 0.002000 molal, a maximum deviation of 3%.

In the case of p. chlorobenzoic acid, the aqueous solutions gave values for K_A varying 8% from the mean. This was thought excessive, especially when the determinations at half the original concentration fell considerably lower. The low value for k_a in both cases, raises doubt as to its validity.

The runs in alcoholic solutions, although consistent only to 20% of the mean values, show a much better spread from the halogen-substituted benzoic acids to benzoic, and from benzoic to the alkyl substituted benzoic acids.

In the case of the halogen-substituted acids, no distinction can be drawn between the strengths of the three. The same can be said for the alkyl-substituted acids, although there is a slight indication that p. cuminic acid is stronger than p. ethyl benzoic is stronger than p. toluic.

Since the research hoped to show definite distinctions between the three halogen-substituted acids, and between the three alkyl-substituted acids, the results are negative. However, it was shown that there is a definite distinction between the influence of an halogen group, and an alkyl group; and that the differences in influence between the members of these two classes are of a much lower order of magnitude.

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