

The solution from which zinc is to be deposited should always be neutral or slightly acid.

These experiments were made during 1897-1898 in the laboratory of the Koenigliches Polytechnikum in Munich, Germany.

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THE INFLUENCE OF SUBSTITUENTS ON THE ELECTRICAL CONDUCTIVITY OF BENZOIC ACID.¹

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INTRODUCTORY.

VICTOR MEYER and his pupils have shown that in a substituted aromatic acid, the rate of esterification is affected by the nature and position of the substituting atoms or groups. Kellas² proved that for monochlor-, monobrom-, and moniodobenzoic acids, the rate of esterification varies with the molecular weight of the acid, or in other words, with the atomic weight of the substituting halogen. Thus, graphically represented, when the molecular weight of the acid is taken as the abscissa, and the percentage of ester formed in a given time, as the ordinate, a straight line is obtained.

No attempt appears to have been made, even in view of this work, to examine the effect of the position and nature of a substituent on the electrical conductivity of the aromatic acids. The conductivities of substituted benzoic acids have been examined by many investigators, but usually with the view of determining their affinity coefficients, and with little regard for the nature of the substituting group.

The conductivities of salts of organic acids have also been investigated, notably by Ostwald, but never, as it would appear, with the view of finding any relation between the conductivities in question and the atomic weights of the metals forming these salts.

The present investigation was undertaken with the object of examining into the changes introduced in the conductivity of benzoic acid, by the substitution of various metals for the

¹ From author's thesis for the Ph.D. degree.

² Kellas: Inaugural Dissertation, Heidelberg, 1897.

hydrogen of the carboxyl group, and of halogens for the hydrogen of the benzene nucleus.

It was hoped that these substituting elements might be found to have an influence traceable to their position in the periodic table. It was further thought possible that some definite relationship might be disclosed between the conductivities of position-isomers.

With these objects in view, the elements substituting carboxylic hydrogen were entirely selected from Group I of the periodic table, while those entering the nucleus in the two chosen positions ortho and para were from Group VII.

We are thus in a position to see :

1. What is the effect on its electrical conductivity of introducing an alkali metal into the carboxyl group of benzoic acid, and how this effect varies with the atomic weight of the metal.

2. What effect is produced on its electrical conductivity when, in a salt so formed, a hydrogen atom is replaced in the ortho, or in the para position, by one of the heavier halogen atoms.

The work described in the pages which follow is of a purely preliminary nature, and no claim to extreme accuracy is made.

Several factors militate against any such claim, notably the small quantities of substance available in some cases, with a consequent absence of certainty that purification was thorough. Another objection, which may plausibly be made, is that the conductivity of the water employed was comparatively high, so rendering the correction to be applied somewhat uncertain.

Nevertheless it is believed that the approach to accuracy is sufficiently near to show certain points which merit further investigation. Some idea as to this degree of accuracy may be gained by noting the extent of agreement, where, for any reason, determinations of conductivity have been made from separately prepared samples of the same compound.

Perhaps it should be noted that many of the salts studied in this research have not hitherto been elsewhere described.

PRACTICAL.

Preparation of p-Brombenzoic Acid.—Commercial toluene was brominated in the usual manner. The resulting product was

repeatedly fractionated, those portions passing over between 130° and 190° being collected. The bromtoluene so obtained was heated with an excess of nitric acid (one part concentrated acid to three parts water) till oxidation to the corresponding acid was complete. The crystals which separated, on cooling, from a large volume of the acid liquid were found to have the melting-point 248° (melting-point of *p*-brombenzoic acid, 251°). They were purified by repeated extraction with hot water, and were finally recrystallized from alcohol till they possessed the constant melting-point of 251° - 252° .

*Preparation of o-Brombenzoic Acid.*¹—This acid was obtained from *o*-amidobenzoic acid by the Sandmeyer reaction. The crude product was repeatedly crystallized from water, converted into its barium salt, reobtained by treating this with hydrochloric acid, and finally crystallized from dilute alcohol until it possessed a constant melting-point.

Preparation of p-Iodobenzoic Acid.—*p*-Iodobenzoic acid was obtained by the oxidation of *p*-iodotoluene. Chromium trioxide and glacial acetic acid were at first used for this purpose; it was subsequently found that boiling with dilute nitric acid was a much preferable means of procedure. By the latter method the oxidation seems to be quite as rapid and as readily controlled. It is also much easier to obtain the product in a pure form. The products obtained by the above two methods were mixed together and carefully sublimed. The acid was then further purified by crystallization from slightly dilute alcohol; it then had the melting-point 267° - 268° .

Preparation of o-Iodobenzoic Acid.—This was obtained by two processes. A part of the acid employed was made by oxidizing *o*-iodotoluene with boiling dilute nitric acid. This seems to be the best method, even the crude product being very nearly pure. It was necessary, however, to obtain the greater part of the acid used in these experiments from *o*-amidobenzoic acid by the Griess reaction. The acid obtained in this way was purified by repeated crystallization from hot water, till it possessed the correct melting-point. It was mixed with the portion of acid obtained by oxidizing *o*-iodotoluene, and the whole was then twice recrystallized.

¹For the preparation of this and of the similarly obtained *o*-iodobenzoic acid, I am indebted to my fellow-student, Mr. T. M. Taylor.

Purification of Benzoic Acid.—"Chemically pure" benzoic acid was dissolved in hot water, the solution filtered, and allowed to crystallize. The product was again crystallized from water, when its melting-point remained unaltered and correct.

Preparation of Pure Water.—The method adopted was a slight modification of that suggested by H. C. Jones and Mackay.¹ The only change made, at first, was that of substituting a well-steamed hard glass condenser for the block-tin condenser employed by these workers. The water so obtained was, of course, inferior in purity to that obtained by them, but was considered to be sufficiently pure in view of certain other sources of error. It was of fairly uniform quality, the average conductivity being 4.4×10^6 mercury units. In every case a correction has been applied, based upon a determination of the particular sample of water employed. It was later found that much time could be saved by refilling the washing retort, after each occasion on which the apparatus was cleaned, with an alkaline solution made from previously purified water. In this way it was possible to dispense with the use of potassium permanganate in the washing retort without the least danger of ammonia passing over, even in the first portions.

Method of Operation.—These conductivities were determined, by the method of Kohlrausch, at a temperature of 25°. The resistance capacity of the electrode vessel was found by using a solution of pure potassium chloride.

The bridge wire was one meter in length, and was not calibrated. In making up the solutions to be determined, a calculated quantity of the salt, dried at 120°–130°, was accurately weighed out, dissolved in water, and the solution brought up to the proper volume. Except where otherwise stated, the solution so obtained was $\frac{n}{4}$, the solution $\frac{n}{128}$ being generally prepared by diluting the stronger solution in the electrode vessel.

SALTS OF *p*-IODOBENZOIC ACID.

The method by which these salts were prepared is typical of that employed with all except the benzoates. The dry alkaline carbonates were accurately weighed and dissolved in water. To these solutions a calculated quantity of *p*-iodobenzoic acid was

¹ *Am. Chem. J.*, 19, 90.

added. The quantity of acid employed was about five-tenths milligram more than was necessary exactly to neutralize the alkali; it was considered impossible on account of adherent moisture, etc., to weigh out exact equivalents of acid and carbonate, but more easy to afterwards remove this slight excess of acid than a possibly unforeseen trace of alkali. The mixture so obtained was warmed on the water-bath till no further reaction could be observed to take place. It was then cooled and filtered (the acid being almost insoluble in cold water). The clear solution so obtained was evaporated to dryness on the water-bath, and the residue then crystallized from its most convenient solvent. The salt was next air dried, and finally dried at 120° – 130° as mentioned above.

Sodium p-Iodobenzoate.—This salt crystallized from water in needles.

Conductivity determination:

v	μ
64	66.04
128	67.39

Potassium p-Iodobenzoate.—The salt employed was crystallized from alcohol, and the crystals very thoroughly washed with ether.

Conductivity determination:

v	μ
64	74.66
128	77.05

Rubidium p-Iodobenzoate.—This salt crystallized in beautiful plates and needles from a mixture of alcohol and ether.¹

Conductivity determination:

v	μ
64	93.53
128	97.19

Cesium p-Iodobenzoate.—Crystallized from alcohol and ether, in needles.

¹A mixture of alcohol and ether is not commonly employed, it is believed, in the crystallization of the alkali salts of organic acids. In the course of this work it has been frequently used with the best results, giving good, and very pure crystals. By the use of this solvent the waste incidental to recrystallizations was reduced to a minimum, while it was eminently calculated to remove any trace of acid. The method of handling the medium is to dissolve the salt in a little hot alcohol, allow this to cool somewhat, and add about five times its volume of ether.

Conductivity determination :

v	μ
64	88.18
128	90.48

SALTS OF *p*-BROMBENZOIC ACID.

The general method employed in preparing these salts was identical with that given under the salts of *p*-iodobenzoic acid.

Sodium p-Brombenzoate.—This salt did not readily crystallize from water. It was purified by the use of alcohol. In this medium it dissolved with some difficulty, separating when cool as a gelatinous precipitate, which dried to a somewhat horn-like mass.

Conductivity determination :

v	μ
64	65.14
128	67.10

Potassium p-Brombenzoate.—Crystallized from alcohol, in large plates somewhat resembling mica in general appearance. The crystals were washed first with a little alcohol, and then with much ether. In this case the two solutions employed were prepared independently, and from samples of the salt made at different times.

Conductivity determination :

v	μ
64	86.74
128	87.58

Rubidium p-Brombenzoate.—Crystallized from a mixture of ether and alcohol, in needles.

Conductivity determination :

v	μ
64	86.21
128	88.93

Cesium p-Brombenzoate.—Crystallized in needles, from a mixture of ether and alcohol.

Conductivity determination :

v	μ
64	83.71
128	88.03

SALTS OF *o*-IODOBENZOIC ACID.

The method applied to the preparation of the foregoing salts was also used here. The greater solubility of the ortho acid, however, made it necessary to use a small quantity of water in the first stages of these preparations.

Sodium o-Iodobenzoate.—Crystallized from alcohol-ether mixture.

Conductivity determination :

v	μ
64	64.21
128	67.35

Potassium o-Iodobenzoate.—Crystallized from alcohol-ether mixture.

Conductivity determination :

v	μ
64	78.94
128	83.36

SALTS OF *o*-BROMBENZOIC ACID.

The remarks on the preparation of *o*-iodobenzoates apply equally to these salts.

Sodium o-Brombenzoate.—Crystallized in magnificent feathery needles from a mixture of ether and alcohol. The two solutions ($v = 64$ and $v = 128$) employed were from different samples of the salt, and were made independently of one another.

Conductivity determination :

v	μ
64	66.11
128	68.02

Potassium o-Brombenzoate.—The purification of this salt offered some slight difficulty on account of its great solubility and the small quantity available for the work. It refused to crystallize from alcohol, with which it formed a somewhat oily solution. On the addition of ether to this, the ether quickly separated as a distinct layer, and failed to induce crystallization. The whole was therefore evaporated to dryness, and the dry salt so obtained quickly washed on the filter with a mixture of ether and a little alcohol.

Conductivity determination :

v	μ
64	86.92
128	90.92

SALTS OF BENZOIC ACID.

In preparing the benzoates in pure condition, the comparatively great solubility of benzoic acid offered a difficulty. This was, it is believed, overcome by prolonged gentle heating of the aqueous solutions on the water-bath, and the use of considerable volumes of alcohol in the later crystallizations.

Lithium Benzoate.—In this case advantage was taken of the comparative insolubility of lithium carbonate: this was weighed out in slightly greater quantity than that calculated for the previously weighed benzoic acid. The two were mixed in the presence of alcohol and warmed. On the reaction ceasing, the excess of lithium carbonate was filtered out, the solution evaporated to dryness and the residue dissolved in a little water. The solution was again filtered, and again evaporated to dryness. The salt was finally crystallized from a mixture of alcohol and ether.

Conductivity determination :

v	μ
64	57.30
128	59.67

Sodium Benzoate.—This salt did not crystallize at all well from water, but merely dried out on the sides of the beaker. It showed little tendency to dissolve in alcohol, and from this medium it was deposited in gelatinous form. The attempt at crystallization was therefore abandoned; the salt solution was evaporated to dryness, the solid mass repeatedly extracted with hot alcohol, and finally washed on the filter by the same liquid. From the foregoing it is evident that the purity of this sample of the salt must remain doubtful.

Conductivity determination :

v	μ
64	67.93
128	70.66

Potassium Benzoate.—This salt was crystallized from alcohol, in which it is very soluble, and was subsequently washed with ether.

Conductivity determination:

v	μ
64	88.05
128	92.02

Rubidium Benzoate.—The salt is readily soluble in hot, but rather insoluble in cold, water, a property which rendered it all the more difficult to remove benzoic acid; in this case, therefore, the steaming of the salt on the water-bath was prolonged. It was ultimately crystallized from a mixture of ether and alcohol. From this medium it deposited in beautiful plates, but from water it appeared in the form of needles. Two preparations were made and their conductivities determined separately.

Conductivity determination:

v	μ
64	92.04 (1st preparation)
64	91.48 (2d ")
128	94.33 (3d ")

Cesium Benzoate.—This salt appears to be more soluble in cold water than the foregoing. It was crystallized from alcohol and ether. The two solutions employed were made independently, from different samples of the salt.

Conductivity determination:

v	μ
64	91.85
128	94.66

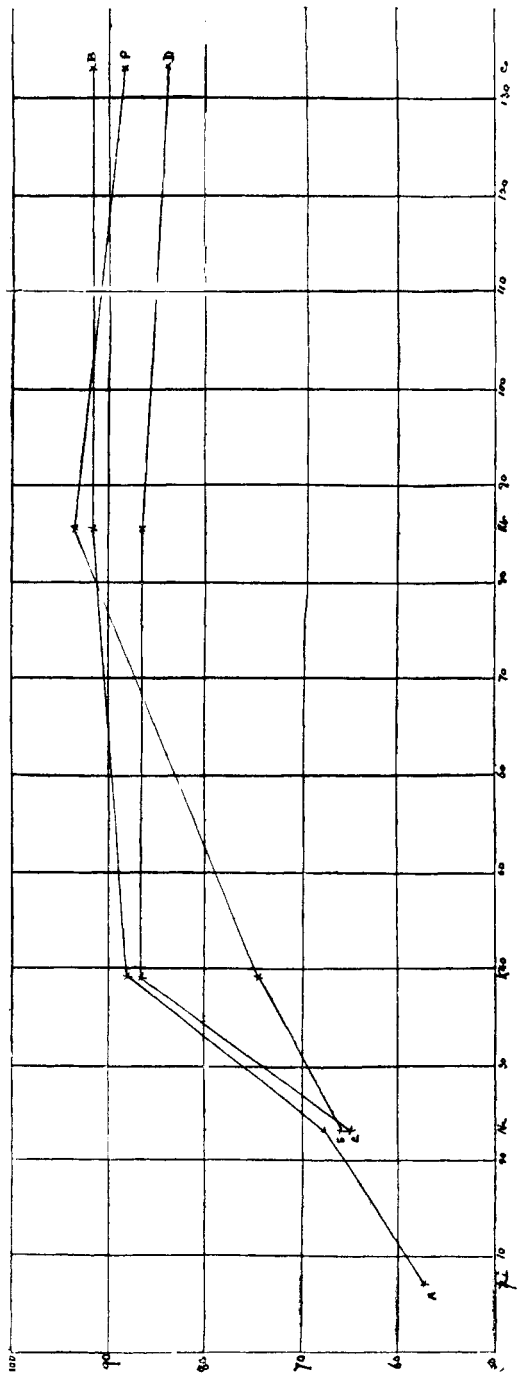
An attempt was made to determine the conductivity of lithium *p*-brombenzoate. The pure salt was obtained in solid form with difficulty, as it is very soluble in alcohol and appears to be somewhat soluble even in ether alone. On being placed between filter-paper and left over night, the crystals deliquesced completely. No further preparation of the salt was made. Lithium *o*-iodobenzoate was also prepared. It was obtained as a gummy mass, which, on long standing, became permeated with stellate groups of needles. On the addition of ether it immediately reassumed its original gummy form, and the attempt to purify it was abandoned.

CONCLUSION.

Ostwald¹ has experimentally shown, in a large number of cases, that where two metals form salts with the same acids, the

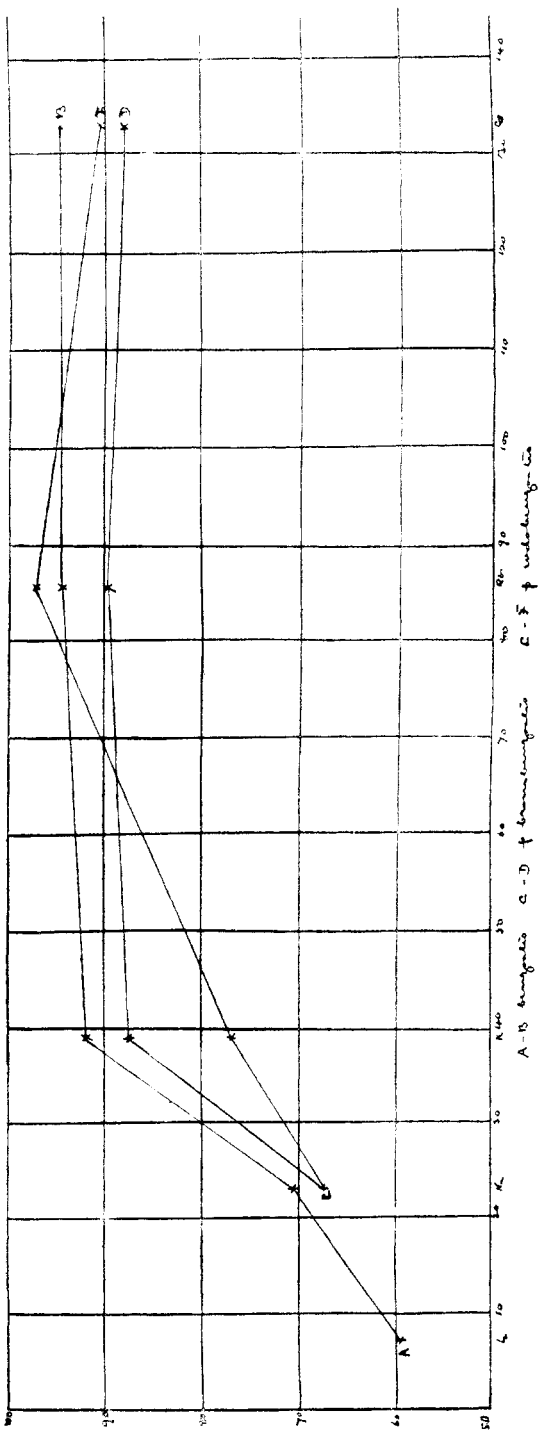
¹ *Ztschr. phys. Chem.*, 1, 74 and subsequent papers.

I v-64.



A-B benzol
C-D f. benzol
E-F f. indol

II $\sigma = 128$.



difference in conductivity of the same salts of the two metals is constant, and independent of the nature of the acids. He has also pointed out that this phenomenon is directly deducible from Kohlrausch's law of conductivity. A glance at the appended table of conductivities ($\nu = 64$), obtained in this research, will show that the variations from this rule are very marked in some cases, and are far in excess of what is believed to be the experimental error.

A graphic representation of the same table is given on Plate I, while Plate II shows the results when $\nu = 128$. The ordinates represent μ , and the abscissae the atomic weight of the metal. According to the law previously referred to, the curves, whatever their form, should be parallel, or at least approximately so, a condition which these do not fulfil.

In view of these variations, it seems necessary to refrain, for the present, from any attempt to draw theoretical conclusions from the results obtained. They are not final, but show that this series of salts requires further investigation. Perhaps, however, it may be allowable to point out that the departure from theory is much greater in the case of the potassium and sodium iodobenzoates than in those salts which the same metals form with acids of smaller molecular weight.

TABLE OF CONDUCTIVITIES.

($\nu = 64$.)

Salts of <i>p</i> -iodobenzoic acid.			Salts of <i>p</i> -brombenzoic acid.		
Metal.	μ .	Difference.	Metal.	μ .	Difference.
Cs.....	88.18		Cs.....	83.71	
		5.35			2.50
Rb.....	93.53		Rb.....	86.21	
		18.87			0.53
K.....	74.66		K.....	86.74	
		8.6			21.60
Na.....	66.04		Na.....	65.14	
Salts of benzoic acid.			Salts of <i>o</i> -iodobenzoic acid.		
Metal.	μ .	Difference	Metal.	μ .	Difference.
Cs.....	91.85		K.....	78.94	
		0.99			14.73
Rb.....	91.76		Na.....	64.21	
		3.71			
K.....	88.05		Salts of <i>o</i> -brombenzoic acid.		
		20.12	Metal.	μ .	Difference.
Na.....	67.93		K.....	86.92	
		10.63			20.81
Li.....	57.30		Na.....	66.11	