

1930

The electron-sharing ability of organic radicals, ortho-chlorobenzyl radical

Frank E. Ware
Iowa State College

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THE ELECTRON-SHARING ABILITY OF ORGANIC RADICALS
ORTHOCHLORO BENZYL RADICAL

BY

Frank E. Ware

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Plant Chemistry

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1930

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INTRODUCTION

Hixon and Johns¹, and Johns² pointed out that the polar properties of any series of compounds containing only one polar group should be a function of the electron sharing ability of the radicals attached to the central group or atom. They also stated that the magnitude of the charge caused by substituting different central groups on the radicals would be an inverse function of the size and complexity of the central group. They showed that if they arranged the compounds of a series in order of their dissociation constants that the radicals were arranged in order of their electron-sharing ability. Representative values for the dissociation constants of the amines and acids found in the literature were plotted against an arbitrary abscissa termed "electron-sharing ability". An arbitrary curve $y = \log K = 20(e^{0.05x} - .75)$ was used for the amines, and the dissociation constants for the different amines were located on the curve, thus fixing the positions of the R radicals along the x axis. It was found that if the dissociation constants for other polar derivatives of the R radicals were plotted against the "electron-sharing ability" that a smooth curve could be drawn through the points. The curves were not erratic. They postulated that the equilibrium constants for any given reversible reaction of any series of

compounds would be a function of the electron-sharing ability of the radicals attached to the central atom or group. They extended this concept to the amines, carboxylic acids, organomercuric nitrates, organomercuric iodides as well as to the alcohols. Figure 1 shows these relationships.

On examining the literature no unsubstituted amines with dissociation constants between 5×10^{-5} and 1×10^{-9} were found. It was pointed out by Allison and Hixon³ that the carbohydrate radicals and terpenes, so important in plant chemistry, must have an electron-sharing ability in this range, values being given for glucosamine^{3,4}. Typical organic radicals were desired which would permit of a study of the chemical properties of compounds in this range without involving the complexity of specific reactions characteristic of these biological classes of compounds.

It was predicted by the use of the model, figure 2, that the value for o-chlorobenzyl amine came within this range 5×10^{-5} - 1×10^{-9} . The model was constructed to scale and shows the relationship between the dissociation constants of homologous series of acids and amines of various radicals. The method of predicting the constant for o-chlorobenzyl amine was the following:

The position of o-chloroaniline was located on the amine curves which fixed its position on the abscissa.

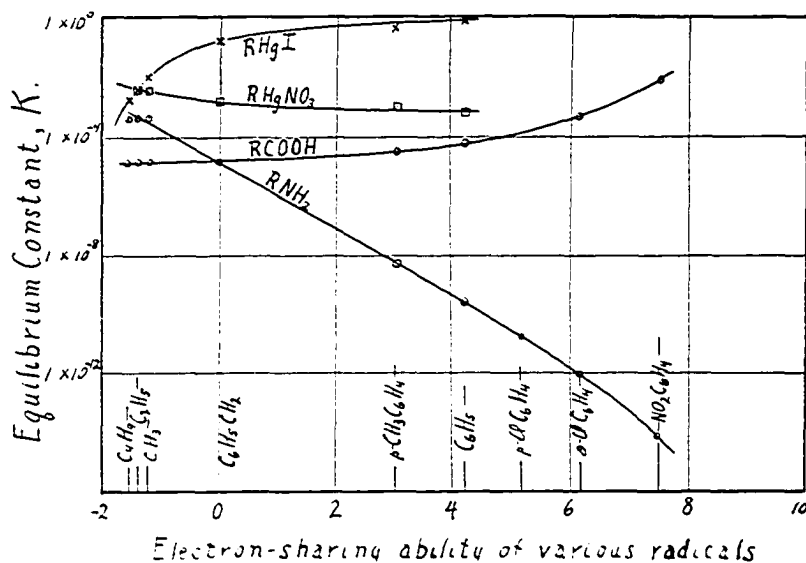
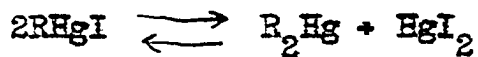


Figure 1. Relation between the equilibrium constants for the reaction



and the ionization constants of the type compounds



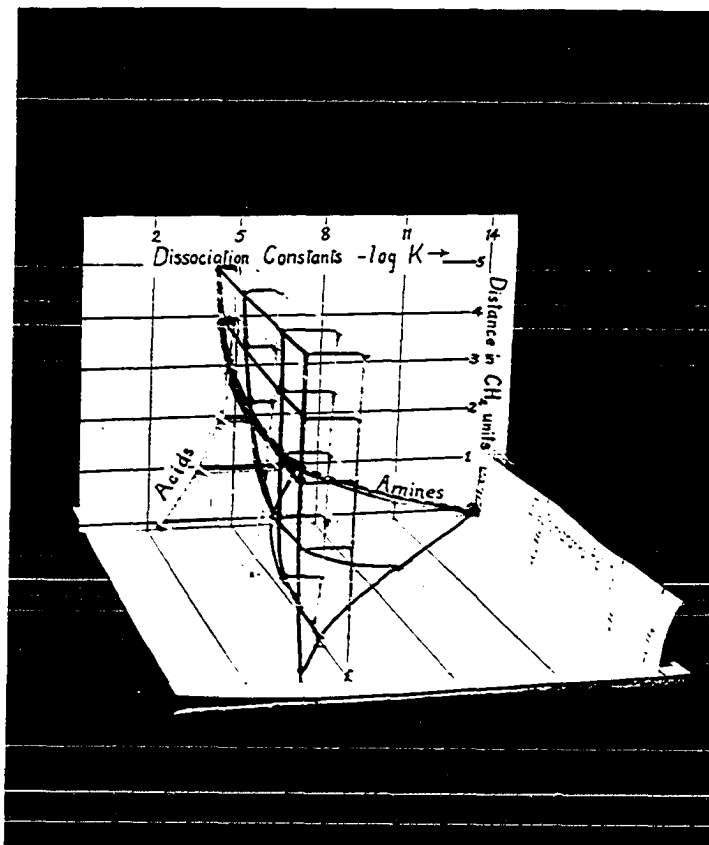


Figure 2. Photograph of a model, constructed to scale, showing the relationship between the dissociation constants of the acids and amines of radicals of different electron-sharing ability and the distance of radicals from the polar group in CH₂ units. This model was used in selecting an amine which had dissociation constant between 5×10^{-5} and 1×10^{-9} .

The position of o-chloroaniline was located on the amine curves which fixed its position on the abscissa. Since o-chlorobenzyl amine is removed by one CH_2 unit from o-chloroaniline its position was located on the amine curve removed by one CH_2 unit. Its constant was obtained from this curve. The predicted constant and its actual constant were not in good agreement since the dotted curve in the background has been located by only one point (o-nitroaniline). The position of the amine curve removed by one CH_2 units is dependent upon the slope of the dotted curve. The dotted curve should be fixed by more values. Values for o-nitrophenyl methyl, - ethyl, - propyl, - butyl and - amyl amines should be obtained or at least several of the above. This correction would also correct the slope of the amine curves removed by varying number of (CH_2) units from the radicals, whose electron-sharing ability is known.

STATEMENT OF THE PROBLEM

Johns and Hixon² have extended this concept of electron-sharing ability to several series of compounds namely, the amines, carboxylic acids, organomercuric nitrates, and organomercuric iodides. Osburn⁵ extended this idea to the arsonic acids. He used conductivity data for determining the dissociation constants of these acids. Another method of determining the dissociation constants of the arsonic acids is desired in order to calculate free-energy of ionization and to test further the validity of the electron-sharing ability concept. Also more radicals are needed which have an electron-sharing ability between $1\frac{1}{2}$ and $3\frac{1}{2}$.

The experimental work of this thesis concerns itself with:

1. Determination of the dissociation constants of the arsonic acids from E.M.F. data.
2. Determination of the electron-sharing ability of the o-chlorobenzyl radical.
 - (a) Dissociation constant of the amine.
 - (b) Preparation and determination of the constant for the arsonic acid.
 - (c) The preparation of some mercury derivative of o-chlorobenzyl radical.
 - (d) Determination of the equilibrium be-

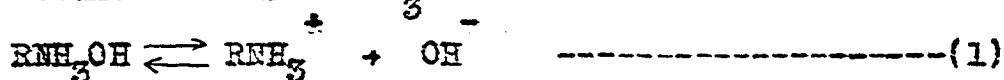
tween o-chlorobenzylmercuric iodide and mercury di-o-chlorobenzyl.

ELECTRON-SHARING ABILITY OF O-CHLOROBENZYL AMINE

In the introduction of this dissertation it was pointed out that there were no amines with dissociation constants between 5×10^{-5} and 1×10^{-9} with the exception of glucosamine^{3,4} whose constant was 4.6 to 6.0×10^{-7} and consequently we have no data concerning radicals which have an electron-sharing ability between $1\frac{1}{2}$ and $3\frac{1}{2}$. It was desired to find a radical which would fall in this range. It was shown how the o-chlorobenzyl radical was predicted to fall within this range by means of the diagram shown in Figure 2. This portion of the thesis concerns itself with the determination of the dissociation constant for o-chlorobenzyl amine as a test of this theory.

The method used for determining the constant is that used by Carothers⁶ who published a paper on the preparation and basic strength of some amines. The method consists in half neutralizing the free amine with hydrochloric acid and then measuring the hydrogen ion concentration of the solution by the hydrogen electrode. From the theoretical consideration the hydrogen ion concentration is numerically equal to the dissociation constant for an acid so measured. For a base the hydroxyl ion concentration is numerically equal to the dissociation constant. The above method only applies to weak acids and bases.

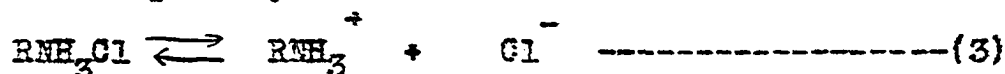
Assume the amine RNH_3OH and let it ionize



The ionization constant can be formulated as

$$\frac{C_{\text{RNH}_3^+} \times C_{\text{OH}^-}}{C_{\text{RNH}_3\text{OH}}} = K_a \text{-----(2)}$$

Since the amine was one-half neutralized with an acid such as hydrochloric acid the salt RNH_3Cl is formed, and is assumed to be completely ionized as



Then $C_{\text{RNH}_3\text{OH}} = C_{\text{RNH}_3^+} \text{-----(4)}$

Equation (3) then becomes

$$C_{\text{OH}^-} = K_B \text{-----(5)}$$

The hydroxyl ion concentration is not measured directly but the hydrogen ion concentration is. The relationship between C_{H^+} and C_{OH^-} is given by the equation

$$C_{\text{H}^+} \times C_{\text{OH}^-} = K_{\text{H}_2\text{O}} = 10^{-14} \text{-----(6)}$$

or $C_{\text{OH}^-} = \frac{10^{-14}}{C_{\text{H}^+}} \text{-----(7)}$

Preparation of o-Chlorobenzyl Amine

o-Chlorobenzyl amine was prepared by the method described by Franzen.⁷ o-Chlorobenzyl oxime was prepared from o-chlorobenzaldehyde and hydroxylamine. The oxime was then reduced by zinc dust in a solution of alcohol and

acetic acid. The amine hydrochloride was recrystallized from alcohol several times. The melting point is 216-17. Franzen gives 215-16.

The free amine was liberated from the amine hydrochloride by treating the salt with a potassium hydroxide solution and extracting with ether. The ether solution was dried over solid potassium hydroxide for several days. The ether solution of the amine was then placed in a Claisen flask which had been modified by having its neck and side arm extended eight inches. This modification prevented the vapors and liquid amine from coming in contact with the stoppers during the distillation. The ether was removed from the solution by evaporating on a water-bath while the last traces were removed under vacuum by means of an oil pump. During the removal of the ether and distillation of the amine a stream of dry, carbon dioxide free nitrogen bubbled through the liquid. The amine was then fractionally distilled, collected in weighed ampules, sealed, weighed and placed aside for use. Four different fractions were obtained.

The fractionation was carried out in a modified Brushl distilling receiver. See Figure 3. The carriage was suspended on a pivot so that it revolved freely. On the bottom of the carriage was placed an iron core made

from soft iron wire. The ends of the core extended nearly to the glass walls of the receiver. Space enough was allowed between the core and walls so that the ends of the core could not touch the wall when the carriage revolved. On a revolvable platform on the outside of the receiver were placed two electromagnets wired in series. These two magnets were placed at the same height as the iron core in the receiver. The carriage could be moved and held at any position desired by moving the platform carrying the electromagnets. Two dry cells were used to supply the current for the magnets. It was later found that two twelve inch bar magnets could be used instead of the electromagnets. The carriage carried five receivers for the distillate.

The purity of the amine was determined by titrating an ampoule from each fraction with a standard hydrochloric acid solution, using methyl red as an indicator. Its neutralization equivalent was then calculated. In Table I are found the results. The average of the neutralization equivalents checked the theoretical value very closely. The standard hydrochloric acid was made up from constant boiling acid and conductivity water. It was standardized by precipitating with silver nitrate and weighing the silver chloride.

TABLE I.

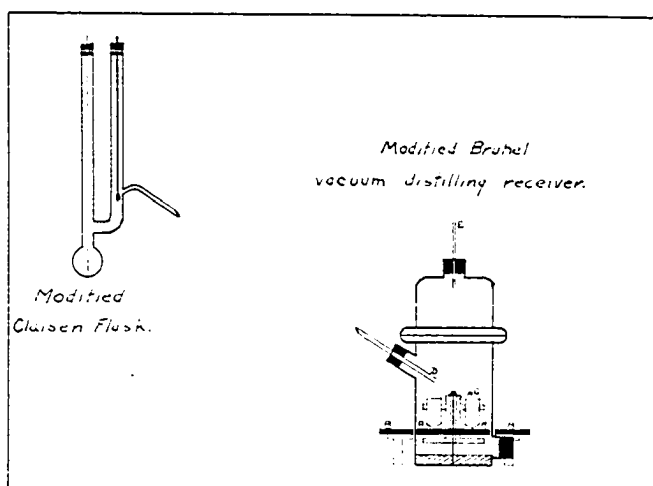
NEUTRALIZATION EQUIVALENT OF THE AMINE.

Fraction	Sample Number	Weight of Amine	Volume of 0.1327 N HCl	Neutralization equivalent
1	1	.7408	39.45	141.33
2	5	.5413	28.80	141.50
3	5	.2907	15.44	141.74
Average				141.52
Theoretical				141.57

Preparation of Electrodes and Half-cells

The calomel half-cells, both 0.1N, and saturated with potassium chloride, were prepared according to the directions given by Popoff⁸ in his book on Quantitative Analysis. The potassium chloride was recrystallized twice from conductivity water. The mercury was carefully washed with mercurous nitrate solution, water, and then carefully dried.

The platinum electrodes were plated with platinum black according to the method recommended by Popoff.⁹ The old deposit of platinum black was removed by electrolyzing as an anode in concentrated hydrochloric acid. Several of the new electrodes were cleaned in hot alkali. The clean electrode was then plated with gold by electrolyzing as a cathode in a dilute potassium cyanide solution of gold. It was then electrolyzed as a cathode for about five minutes



A vacuum distillation apparatus for amines.

Figure 3. A vacuum distillation apparatus used for fractionating and collecting the amine in vacuum.

- (a) Iron core
- (b) Electromagnet
- (c) Carriage on pivot

in a chloroplatinic acid solution. (Popoff's method was not strictly followed here since a chloroplatinic solution of unknown composition was on hand.) The electrode was then electrolyzed for a few seconds in a dilute solution of sodium hydroxide and for one minute in a dilute sulphuric acid solution. The electrodes were then kept in distilled water until ready for use.

Determination of Hydrogen Ion Concentration of the Solution

In measuring the C_{H^+} concentration of amines Carothers⁶ used palladized platinum foils. This electrode was tried but no results could be obtained. The platinized platinum foil was found more satisfactory.

The hydrogen electrode was connected to the calomel electrode by a saturated potassium chloride bridge. Both the 0.1N and the saturated potassium chloride calomel cells were used.

The C_{H^+} concentration of the solution was determined first with the saturated potassium chloride calomel cell and then with 0.1N calomel cell. Different hydrogen electrodes were used against these two calomel cells in separate solutions of the amine. The electrodes were checked against a 0.05M potassium acid phthalate solution

from time to time. Boundary potentials were disregarded since these corrections would be well within the experimental errors.

The amine solution was prepared by placing a weighed sealed amount of the amine in an ampoule in a 100 c.c. or a 200 c.c. volumetric flask. The calculated volume of dilute hydrochloric acid was added and then about 100 c.c. of recently boiled distilled water. The ampoule was then crushed with a stirring rod. The flask was agitated until the amine went into solution. The hydrogen ion concentration was determined by the method described above.

A Leeds and Northrup type K potentiometer with galvanometer 2500-b with lamp and scale at one meter was used. The determination was carried out at $25^{\circ}\text{C} \pm .1^{\circ}\text{C}$.

In order to check on the method before running the *o*-chlorobenzyl amine, the dissociation constant for benzyl amine was determined. A sample of Eastman's benzyl amine hydrochloride was used for the determination without further purification. The average constant obtained was 2.32×10^{-5} . The value reported by Carothers⁶ was 2.35×10^{-5} . Bredig¹⁰ reports 2.4×10^{-5} as obtained by conductivity. The results are found in Table II.

Position of *o*-Chlorobenzyl Amine on the Amine Curve

The amine curve Figure 4 is obtained from the

equation $y = \log K = -20(e^{0.5x} - .75)$. The positions of the various radicals on the electron-sharing ability axis were obtained by locating the dissociation constants of the various amines, Table III, on the curve thereby automatically determining their position on the axis.

In Table III are found representative values of the dissociation constants for various amines whose electron-sharing ability has been fixed in Figure 4. Values for the corresponding acids are also given.

The position of o-chlorobenzyl radical on the electron-sharing ability axis is between that of benzyl, and glucosamine.

TABLE II.

DISSOCIATION CONSTANT FOR O-CHLOROBENZYL AMINE IN WATER SOLUTION

AT 25°C.

Block Number	Fraction	Set Number	Weight of Amine	Vol. HCl added	N. of HCl	E.M.F. at 737 m.m.	$K_B \times 10^{-6}$ at 737 m.m.	$K_B \times 10^{-6}$ corrected at 760 m.m.
4	2	2	.3107	59.36	.0185	.8576	7.0x	6.49
5	2	3	.3881	74.14	.0185	.8576	7.0x	6.49
6	2	4	.5284	14.05	.1328	.8560	6.6	6.10
13	4	1	.6252	16.62	.1328	.8560	6.6	6.10
							Aver: 6.8	6.30

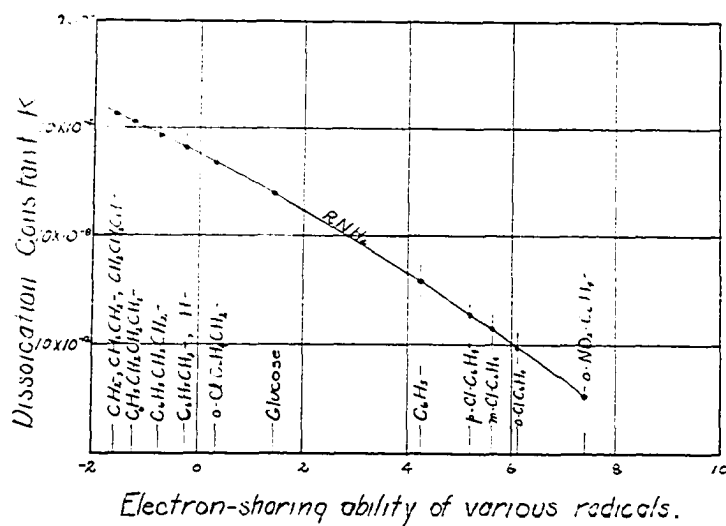


Figure 4. The position of *o*-chlorobenzyl amine on the electron-sharing ability axis and various other organic radicals.

TABLE III.

DISSOCIATION CONSTANTS OF SOME AMINES AND CORRESPONDING ACIDS IN WATER AT 25°C.

Radical	Amine R.NH ₂ .H ₂ O	Acid R.COOH
CH ₂ -	5. x 10 ⁻⁵	1. x 10 ⁻⁵
C ₂ H ₅ -	5. x 10 ⁻⁵	1 x 10 ⁻⁵
C ₃ H ₅ -	5 x 10 ⁻⁵	1 x 10 ⁻⁵
C ₄ H ₇ -		1 x 10 ⁻⁵
C ₆ H ₅ CH ₂ CH ₂ CH ₂ -	1.6 x 10 ⁻⁴	
C ₆ H ₅ CH ₂ CH ₂ -	6.8 x 10 ⁻⁵	
H -	2. x 10 ⁻⁵	
C ₆ H ₅ CH ₂	2.3 x 10 ⁻⁵	5 x 10 ⁻⁵
o-C ₆ H ₄ CH ₂ -	6.8 x 10 ⁻⁶	
Glucose	5.3 x 10 ⁻⁶	
C ₆ H ₅	3 x 10 ⁻¹⁰	7 x 10 ⁻⁵
p - Cl-C ₆ H ₄ -	1 x 10 ⁻¹¹	9 x 10 ⁻⁵
m - Cl-C ₆ H ₄ -	6 x 10 ⁻¹²	2 x 10 ⁻⁴
o - Cl-C ₆ H ₄ -	9 x 10 ⁻¹³	1 x 10 ⁻³
o - NO ₂ -C ₆ H ₄ -	1 x 10 ⁻¹⁴	6 x 10 ⁻³

DISSOCIATION CONSTANTS OF THE ARSONIC ACIDS

o-CHLOROBENZYL ARSONIC ACID

Introduction

⁵
Osburn prepared and determined the dissociation constants of a number of arsonic acids by the conductivity method. He showed that the polar properties of the arsonic acids were a function of the electron-sharing ability of the R radicals or that the differences in the degree of ionization of these acids were brought about by the differences in the electron-sharing ability of the different R radicals combined with the arsonic radical. To avoid the introduction of further assumptions he showed this by a "purely statistical" method, that is by plotting conductances against concentrations. The curves for the various arsonic acids are all very nearly parallel and do not cross each other. The arsonic acids which have the more negative R radical combined with the arsonic acid radical have greater conductances than those with less negative groups. The aromatic arsonic acid derivatives have greater conductances than those of the aliphatics. A summary of the conductivity data obtained by Osburn and myself is presented in Table IV. The concentration of the acid at which the conductances are determined is expressed in millimols. \wedge is the conductances of two or more determinations. K_2 was calculated by the Washburn¹¹ method.

TABLE IV.

CONDUCTANCES AND DISSOCIATION CONSTANTS OF ARSONIC ACIDS.

Methyl	C	5.000	2.500	1.250	.625	.312	.156	.000
	Λ	43.5	59.2	80.6	107.9	140.2	175.6	310.
	$K_a \times 10^{-4}$	1.05	1.06	1.06	1.06	1.06	1.03	1.00
Ethyl	C	7.810	3.905	1.952	.976	.488		.000
	Λ	34.8	46.7	62.8	83.7	110		320
	$K_a \times 10^{-5}$	1.04	9.8	9.3	9.1	8.8		9.0
Propyl	C	5.000	2.500	1.250	.625	.312	.156	.000
	Λ	34.5	47.4	64.5	86.6	113.6	146.6	295
	$K_a \times 10^{-5}$	7.75	7.70	7.60	7.50	7.50	7.35	7.60
Butyl	C	7.810	3.905	1.952	.976	.488		.000
	Λ	27.6	38.2	52.4	71.4	95.8		300
	$K \times 10^{-5}$	7.30	7.30	7.20	7.20	7.30		7.30
Phenylpropyl *	C	5.000	2.500	1.250	.625	.312	.156	.000
	Λ	35.2	49.2	65.8	90.0	117.8		300
	$K_a \times 10^{-5}$	7.80	8.00	7.70	8.00	7.90		7.90
Benzyl	C	7.810	3.905	1.952	.976	.488		.000
	Λ	40.6	55.7	75.6	100.0	133.3		345
	$K_a \times 10^{-4}$	1.22	1.22	1.19	1.17	1.19		1.2
o-Chlorobenzyl * *	C	5.000	2.500	1.250	.625	.312	.156	.000
	Λ	54.6	74.7	99.8	131.5	170.2	210.6	342
	$K_a \times 10^{-4}$	1.44	1.45	1.42	1.42	1.44	1.42	1.40
Phenyl * * *	C	7.810	3.905	1.952	.976	.488		.000
	Λ	59.0	84.9	111.8	142.0			350
	$K_a \times 10^{-4}$	2.67	3.05	2.83	2.69			2.7
o-Nitrophenyl	C	7.810	3.905	1.952	.976	.488		.000
	Λ	71.3	96.1	128.2	163.9	202.1		335
	$K_a \times 10^{-4}$	4.51	4.51	4.64	4.53	4.52		4.5

* Determined by the author:

** The compound was prepared and the conductance determined by the author.

*** Data for compounds obtained from Fichter^{1,2}.

TABLE IV. (Concluded)

	: C	: 7.81	: 3.905	: 1.952	: .976	: .488	: .000
o-Nitrophenyl ***	: $K_a \times 10^{-4}$: 71.3	: 95.1	: 124.5	: 157.9	: .	: 335
	: C	: 4.61	: 4.40	: 4.30	: 4.10	: .	: 4.3
	: $K_a \times 10^{-4}$: 5.000	: 2.500	: 1.250	: .625	: .312	: .156
p-Chlorophenyl *	: C	: 94.0	: 124.9	: 162.2	: 202.4	: 247.4	: 286.8
	: $K_a \times 10^{-4}$: 4.58	: 4.59	: 4.55	: 4.54	: 4.55	: 4.51
	: C	: 5.000	: 2.500	: 1.250	: .625	: .312	: .156
o-Chlorophenyl *	: C	: 94.1	: 124.6	: 162.1	: 203.4	: 244.8	: 283.0
	: $K_a \times 10^{-4}$: 4.78	: 4.82	: 4.79	: 4.78	: 4.77	: 4.76
	: C	: 5.000	: 2.500	: 1.250	: 0.625	: 0.312	: 0.156
M-Chlorophenyl *	: C	: 104.2	: 137.6	: 176.1	: 219.8	: 261.4	: 297.1
	: $K_a \times 10^{-4}$: 5.52	: 5.51	: 5.41	: 5.35	: 5.37	: 5.40

*Determined by the author.
 ***Data for compounds obtained from Fichter¹⁸.

The conductances of compounds marked with a star * were determined by the author. Two stars ** indicated the compound was prepared and the conductance determined by the author also. Those data for compounds marked with three stars *** was obtained from Fichter¹².

Osburn pointed out in his Thesis that Washburn's¹¹ method of extrapolation for μ . was developed for strong electrolytes and does not give such sharply defined results when applied to organic acids as it does with salts. The values calculated for μ_0 are perhaps not exact but are at least a close approximation. Since free-energy calculations from this data will retain all of the errors of the experimental procedure another method was desired for checking the constants. The following studies were made for this purpose.

Description of Method for Determining Dissociation Constants of the Arsonic Acids

The hydrogen ion concentration of a one-half neutralized arsonic acid solution was determined by the quinhydrone electrode against a saturated calomel cell. The theoretical consideration as applied to acids and bases has already been discussed on page 16.

This method is based on the assumption that only one of the hydrogens of the arsonic acid is ionized. It is as-

sumed that the second hydrogen is only ionized to a very slight extent. This assumption is justified when one compares the constants for the first, second and third hydrogens for several inorganic acids, such as H_3PO_4 , H_3PO_3 and H_2SO_3 . Such a comparison is made in Table V. From this data one would expect the K_a for the second hydrogen for the arsonic acids to be about 1×10^{-7} or 1×10^{-8} or even smaller.

TABLE V.

A COMPARISON OF THE DISSOCIATION CONSTANTS FOR THE FIRST, SECOND AND THIRD HYDROGENS IN SEVERAL INORGANIC ACIDS.¹³

Acid	K_a	1st H.	K_a	2nd H.	K_a	3rd H.
H_3PO_4	1.1×10^{-2}		2×10^{-7}		3.6×10^{-13}	
H_3PO_3	$5. \times 10^{-2}$		2×10^{-5}			
H_2SO_3	1.7×10^{-2}		5×10^{-6}			

Determination of Hydrogen Ion Concentration
By the Quinhydrone Electrode

For these measurements 0.01 moles of the carefully purified arsonic acid, free from chlorides, was weighed into a clean, dry 100 c.c. volumetric flask. A few cubic centimeters of freshly boiled distilled water was added. The calculated volume of 0.02025 N potassium hydroxide solution

was added. When solution had resulted the flasks were filled to the mark with more water. A definite volume of solution was used to avoid any differences in hydrogen ion concentration caused by dilution should there be any.

The pH of the solutions were determined with the quinhydrone electrode and the saturated calomel half-cell. A Leeds and Northrup student potentiometer was used for the measurements. The voltage was determined at room temperature and the pH calculated for a temperature of 25° from the formula

$$p_H = \frac{.4526 - 0.00009(t - 25) - \pi}{0.0591 + 0.002(t - 25)}$$

given by Clark¹⁴ and Collins. π is the observed voltage at t temperature. The electrodes were checked against an 0.05N potassium acid phthalate solution from time to time during the determinations. The determinations were made in duplicate. The two sets of solutions were made up and determined at two different times. In each case the pH of the two similar solutions checked within 0.03 of a pH unit.

The data are found in Table VI. The last column gives the average values for K_a . The values have been rounded off.

TABLE VI.

pH AND DISSOCIATION CONSTANTS FOR VARIOUS ARSONIC ACIDS IN WATER AT 25°C.

AS DETERMINED BY E.M.F. METHOD

Radical	Trial 1 - 2700.			Trial 2 - 2900.			Average K _a
	Obs. E.M.F.	Corrected: pH	K _a	Obs. E.M.F.	Corrected: pH	K _a	
Methyl	.208	4.11	7.76 x 10 ⁻⁵	.208	4.08	8.32 x 10 ⁻⁵	8.0 x 10 ⁻⁵
Propyl	.199	4.26	5.50 x 10 ⁻⁵	.197	4.26	5.50 x 10 ⁻⁵	5.5 x 10 ⁻⁵
Butyl	.198	4.28	5.25 x 10 ⁻⁵	.197	4.26	5.50 x 10 ⁻⁵	5.4 x 10 ⁻⁵
Phenylpropyl	.203	4.19	6.46 x 10 ⁻⁵	.201	4.19	6.46 x 10 ⁻⁵	5.5 x 10 ⁻⁵
Benzyl	.218	3.94	1.15 x 10 ⁻⁴	.216	3.94	1.15 x 10 ⁻⁴	1.2 x 10 ⁻⁴
o-Chlorobenzyl	.223	3.86	1.33 x 10 ⁻⁴	.220	3.88	1.33 x 10 ⁻⁴	1.4 x 10 ⁻⁴
Phenyl	.239	3.59	2.57 x 10 ⁻⁴	.237	3.59	2.57 x 10 ⁻⁴	2.6 x 10 ⁻⁴
m-Chlorophenyl	.257	3.28	5.25 x 10 ⁻⁴	.255	3.29	5.13 x 10 ⁻⁴	5.2 x 10 ⁻⁴
o-Chlorophenyl	.251	3.39	4.07 x 10 ⁻⁴	.249	3.39	4.07 x 10 ⁻⁴	4.1 x 10 ⁻⁴
p-Chlorophenyl	.251	3.39	4.07 x 10 ⁻⁴	.251	3.36	4.37 x 10 ⁻⁴	4.2 x 10 ⁻⁴

In Table VII the values of the dissociation constants as obtained by conductivity and E.M.F. are compared. The agreement is quite well considering that a slight change in the calculation of K_a by Washburn's¹¹ method changes K_a considerable. It is to be noted that the two values check very closely in the case of the stronger acids of this series.

In the column "average E.M.F." are found the average E.M.F.s at 25°C. of the quinhydrone half-cell. They were calculated from the average P_H at 25°C. by the formula

$$P_H = \frac{E}{.0591} \quad ,$$

In the last column are found values for the free-energy of ionization. These values have been calculated from the formulae

$$-\Delta F = E.N.F.$$

$$-\Delta F = -E \times 1 \times 96500 \times .2387$$

The values of $-\Delta F$ for ethyl arsonic acid and o-nitrophenyl were calculated from K_a by the formula

$$-\Delta F = RT \ln K. \quad -\Delta F = 2.3025 \times 1.98 \times 298 \log K_a.$$

The free-energy of ionization of the arsonic acids represents the work required to separate one mole of the undissociated arsonic acid into the normal solutions of its

TABLE VII.

COMPARISON OF THE VALUES FOR K_2 AS OBTAINED BY THE
E.M.F. METHOD AND CONDUCTIVITY METHOD

Radical	K_2 Conductivity	K_2 E.M.F.	Average E.M.F.	$-\Delta F$ Calculated
Methyl	$10. \times 10^{-5}$	8.0×10^{-5}	-.242	-5574 cal.
Ethyl	9.0×10^{-5}			-5498 "
Propyl	7.6×10^{-5}	5.5×10^{-5}	-.252	-5805 "
Butyl	7.3×10^{-5}	5.4×10^{-5}	-.252	-5805 "
Phenylpropyl	7.9×10^{-5}	5.5×10^{-5}	-.248	-5713 "
Benzyl	1.2×10^{-4}	1.2×10^{-4}	-.233	-5367 "
o-Chlorobenzyl	1.4×10^{-4}	1.4×10^{-4}	-.228	-5252 "
Phenyl	2.7×10^{-4}	2.6×10^{-4}	-.212	-4883 "
o-Nitrophenyl	4.5×10^{-4}			-4548 "
m-Chlorophenyl	5.4×10^{-4}	5.2×10^{-4}	-.194	-4469 "
o-Chlorophenyl	4.8×10^{-4}	4.1×10^{-4}	-.200	-4607 "
p-Chlorophenyl	4.5×10^{-4}	4.2×10^{-4}	-.199	-4584 "

two ions $RAsO(OH)O^-$ and H^+ by means of the hypothetical equilibrium box.

The values for $-\Delta F$ increase as the strength of the arsonic acid increase. This means that it requires less work to separate a strong acid into its respective ions than it does a weak acid.

As stated before, Hixon and Johns presumed that if our present concepts of valence are correct, that the polar properties of any series of compounds such as ROH , $RCOOH$, RSH , $RAsO(OH)_2$, RNH_2 should be a function of the electron-sharing ability of R. They showed that this generalization held for all the available data for the dissociation constants of the organic acids and amines. Later Johns extended this generalization to include the mercury derivatives $RHgNO_3$ and $RHgI$.

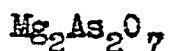
In Figure 5 the electron-sharing ability of various radicals have been fixed from the amine curve. The dissociation constants for the arsonic acids have been plotted against the electron-sharing ability of the various radicals. The curve obtained is a fairly smooth curve. The change in R which is expressed by the electron-sharing ability and which causes the progressive changes in the ionization of the amines also causes an equally orderly change in the ionization constants of the arsonic acids. This then extends

the concept of electron-sharing ability of Johns and Hixon to the arsonic acids.

Electron-Sharing Ability of o-Chlorobenzyl
Arsonic Acid

Preparation of o-chlorobenzyl arsonic acid

o-Chlorobenzyl arsonic acid was prepared by the general method described by Quick and Adams¹⁵. One-tenth of a mole of o-chlorobenzyl bromide was added dropwise, refluxed and stirred in a three necked flask with 35 cc. of 10 N sodium hydroxide until all the halide had been used up. The acid was liberated from the sodium salt by adding concentrated hydrochloric acid, until acid to Congo Red paper. The arsonic acid precipitated as a thick pasty mass. After recrystallizing three times from distilled water the melting point is 154°. Mr. E. H. C. Fang analyzed the compound for Cl by the Carius method and for As by weighing the As as



Analysis calculated for $\text{C}_7\text{H}_8\text{ClAsO}_3$

Cl, 14.16; Found 14.23, 14.20

As, 29.92; Found 29.50*, 29.93

* Loss of precipitate due to creeping.

Dissociation constant of acid

The conductivity and E.M.F. data were obtained on a

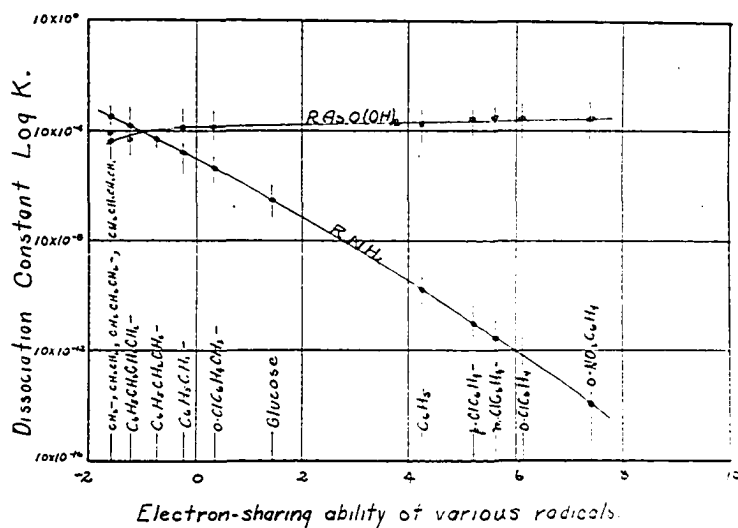


Figure 5. The relationship between the dissociation constants of the arsenic acids and the amines.

sample of acid free from chlorides. The constant obtained by the conductivity method was 1.4×10^{-4} . This checked exactly the dissociation constant as secured from the E.M.F. data.

The constant plotted against the electron-sharing ability of the o-chlorobenzyl radical falls on the arsonic acid curve.

Oxidation-Reduction Potentials of the Arsonic Acids

The general formula given by Clark¹⁶ for calculating oxidation-reduction potentials is

$$E_h = E'_0 - \frac{RT}{nF} \ln \frac{(\text{Red})}{(\text{Ox.})}$$

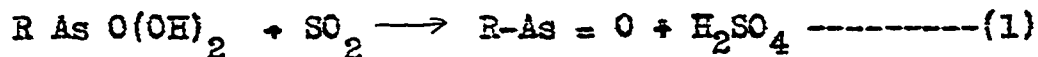
E_h is the observed potential difference between the electrode, platinum, gold, or other inert metal, and the standard normal hydrogen electrode. E'_0 is a constant characteristic for that particular oxidation-reduction equilibrium. (Red) and (Ox) represent the concentrations of the reductant and the oxidant respectively.

The oxidation-reduction potential of the arsenic atom of the arsonic acids would be expected to depend upon the R radical attached to it. The oxidation-reduction of any atom would be expected to be a function of its substituents just as degree of ionization of such an atom has been found to be a function of the electron-sharing ability of the or-

ganic radicals.

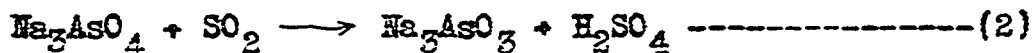
From the data at hand there is no way of calculating the oxidation-reduction potentials of the arsenic in the arsonic acids.

The arsonic acids are readily reduced to the arsine-oxides according to the equation

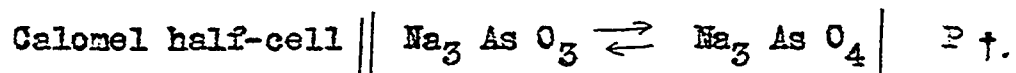


$R \text{ As (OH)}_2$ is formed first, but is unstable and loses water immediately.

A similar reaction is the reduction of Na_3AsO_4 to Na_3AsO_3 . However Na_3AsO_3 is stable.



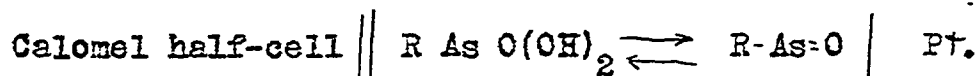
In order to determine E_0 for equation No. 2 it would be necessary to set up a cell



$$E_h - E_{\text{calomel}} = E_0 - \frac{RT}{2F} \ln \frac{(\text{As}^{+++})}{(\text{As}^{++++})}$$

$$E_h = E_0 \text{ when } (\text{As}^{+++}) = (\text{As}^{++++})$$

Similarly in order to determine E_0 for equation 1, the following cell should be set up and measured



$$E_0 = E_h \text{ when } (As^{+++}) = (As^{++++}).$$

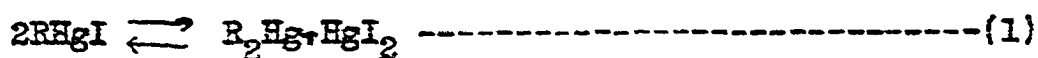
Equal molecular quantities of the arsonic acid and the organo-arsineoxide should be dissolved in the calculated amount of some alkali solution such as sodium or potassium hydroxide. This half-cell formed by placing a metal such as platinum or gold could be measured against the calomel half-cell.

The voltage produced by such a cell, E_0 , may or may not be the true oxidation-reduction potential since the effective concentrations of (As^{+++}) may not be equal to (As^{++++}) . However this value obtained for the various arsonic acids would be comparative and would be expected to be a function of the R radical.

The above is a suggested method of determining the oxidation-reduction potentials of the arsonic acids. However, much depends upon the solubility and properties of the $RAsO$ compound formed.

EQUILIBRIUM CONSTANT FOR EQUILIBRIUM BETWEEN
o-CHLOROBEZYL MERCURIC IODIDE AND MERCURY DI-
o-CHLOROBEZYL

The work of Johns² indicates the reversibility of the reaction

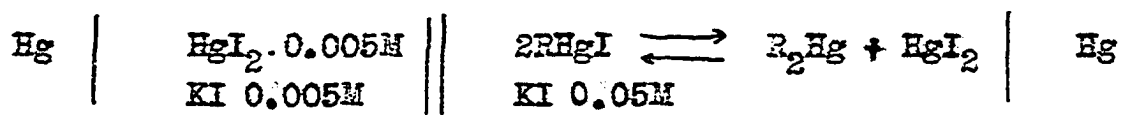


$RHgI$ may be prepared from R_2Hg and HgI_2 or R_2Hg may be prepared from $RHgI$. This reaction tends to form $RHgI$ with the aliphatic series of compounds while with the aromatic series there is more of a tendency to form the bis-organomercury compounds. In order to prepare the bis-organo-mercury compounds from the aliphatic mercury iodides it is necessary to completely remove the mercuric iodide formed by a reducing agent. Some of the bis-organomercury compounds may be prepared quite readily from the aromatic mercury iodides by removing the mercuric iodide in the form of a complex compound such as K_2HgI_4 .

In several qualitative experiments Johns² followed the course of the reaction in an alcoholic solution by the use of diphenyl carbazide. Skinner¹⁷ suggested the use of this compound for detecting mercury. In a slightly basic solution of mercury salts a blue color is formed with the reagent and on standing a blue precipitate is formed. In an

alcoholic solution of the aliphatic mercury iodides a faint blue color is formed and becomes more intense on standing. With benzylmercury iodide the color is developed quite quickly, while with tolyl and phenylmercuric iodide the color is developed immediately. Since the radicals are mentioned in the order of the dissociation constants of their amines the above qualitative experiments of Johns' indicate the same order in the formation of mercuric iodide. He, however, found these color tests inadequate for the quantitative determination of mercury iodide formed in the reaction.

After performing a few preliminary experiments Johns found that the concentration of mercuric iodide in alcoholic solutions formed in equation 1 could be accurately determined by means of concentration cells of the type



He found that identical voltages could be obtained no matter whether the organo-mercury cell was made up from the RHgI compound or from equivalent quantities of R₂Hg and HgI₂. These experiments demonstrated the reversibility of equation 1.

In order to translate the voltages produced by the cell equation (2) in concentration of mercuric iodide it was necessary to determine the voltages produced by cells of

the type



Consequently Johns determined the voltages produced by various concentrations of mercuric iodide in 0.05 M alcoholic KI solution against 0.005 M HgI_2 half-cell. These voltages thus produced are given in Table VIII taken from Johns' thesis.

TABLE VIII.

VOLTAGES OF ALCOHOLIC CONCENTRATION CELLS OF THE TYPE

Hg	HgI_2	0.005 M	$\text{HgI}_2 \text{ C}_2$	Hg
	KI	0.05 M	KI 0.05	
Concentration		E.M.F.		
0.0250		+0.04850		
0.0100		+0.01455		
0.0025		-0.01150		
0.0010		-0.02260		
0.0005		-0.02905		

He represented graphically the relationship between voltage and concentration in Figure 6. From this curve the concentration of mercuric iodide produced by concentration cells, equation 2, could be read off. From the concentration

of mercuric iodide present it was an easy matter to calculate the concentration of RHgI and R_2Hg at equilibrium and calculate the equilibrium constant.

The equilibrium constants obtained by Johns for the reaction $2\text{RHgI} \rightleftharpoons \text{R}_2\text{Hg} + \text{HgI}_2$ using different R radicals are given in Table IX.

The relation between the equilibrium constants for the reaction $2\text{RHgI} \rightleftharpoons \text{R}_2\text{Hg} + \text{HgI}_2$ and the ionization constants of the type compounds RHgNO_3 , RCOOH , $\text{RAsO}(\text{OH})_2$ is given in Figure 7.

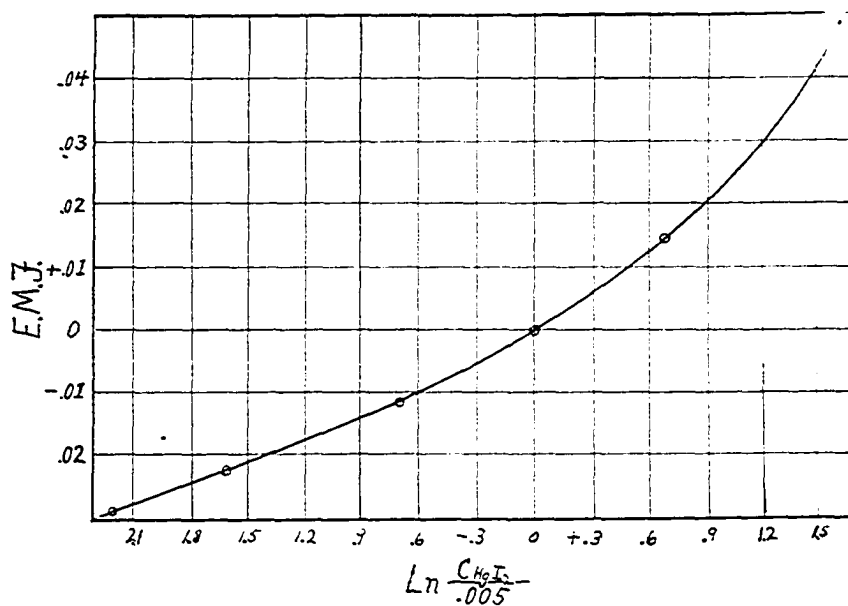
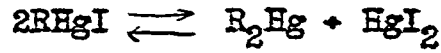


Figure 6. Relation between E.M.F. and $\ln \frac{C_1}{C_2}$ for mercuric iodide concentration cells in absolute alcohol.

TABLE IX.

EQUILIBRIUM CONSTANTS FOR THE REACTION



Radical	Concentration	$K = \frac{(R_2Hg)(HgI_2)}{(RHgI)^2}$
CH ₃	.06	1.4×10^{-2}
	.03	1.0×10^{-2}
C ₂ H ₅	.02	5.87×10^{-3}
	.02593	$6. \times 10^{-3}$
C ₄ H ₉	.02	2.87×10^{-3}
	.025	3.54×10^{-3}
	.030	3.04×10^{-3}
C ₆ H ₅ CH ₂	.01	2.84×10^{-1}
	.01	2.58×10^{-1}
CH ₃ C ₆ H ₄	.0025*	6.9×10^{-1}
	.0025	4.9×10^{-1}
	.003	10×10^{-1}
C ₆ H ₅	.0025	6.9×10^{-1}
	.0035	$13. \times 10^{-1}$

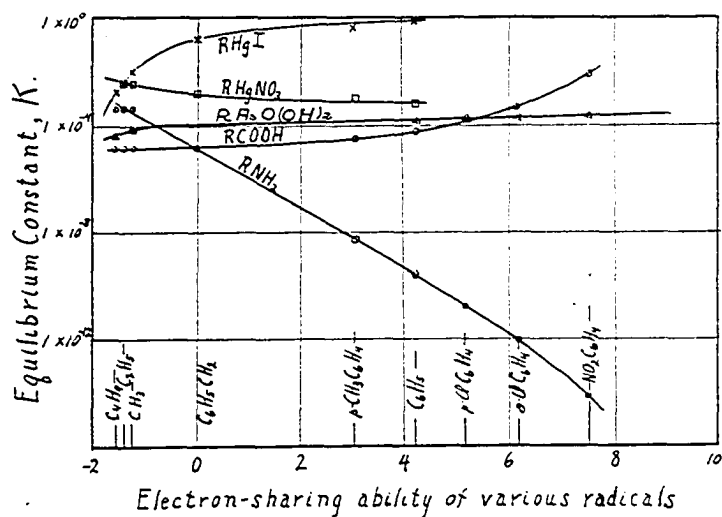


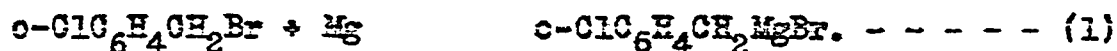
Figure 7. Relation between the equilibrium constants for the reaction $2RHgI \rightleftharpoons R_2Hg + HgI_2$ and the ionization constants for the type compounds $RHgNO_3$, $RCOOH$, $RAsO(OH)_2$, RNH_2 .

Preparation of Compounds

Mercury derivatives of the o-chlorobenzyl radical.

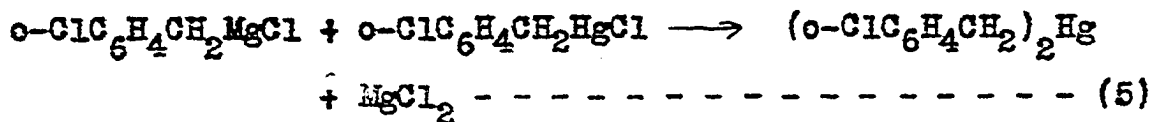
In studying the "electron-sharing ability of organic radicals", the o-chlorobenzylmercuric nitrate, the iodide as well as mercury di-o-chlorobenzyl were desired. It was found that none of the derivatives of this radical had been reported. In order to extend the literature on the mercury derivatives of this radical the chloride, bromide, acetate and benzoate as well as the above mentioned compounds were prepared.

The bromide and chloride were prepared by the reaction of the Grignard derivative of o-chlorobenzyl with the corresponding halides according to equations 2 and 3.

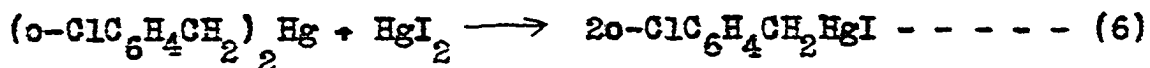


The mercury di-o-chlorobenzyl was prepared by treating mercuric chloride with an excess of Grignard reagent and also by treating the o-chlorobenzylmercuric chloride with an excess of the Grignard reagent according to equations 4 and 5.



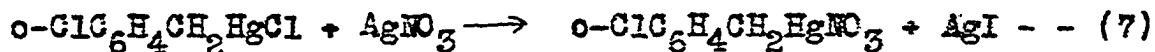


The iodide was prepared by treating mercury di-*o*-chlorobenzyl with calculated quantity of mercuric iodide, equation 6

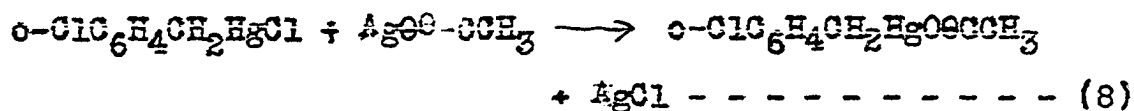


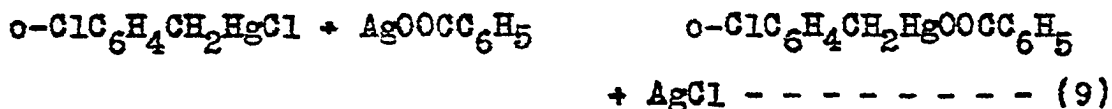
In order to check the acetate, bromide and chloride they were also prepared from the bis-compound and the corresponding mercury salts. The equations are analogous to equation 6. Mercury di-*o*-chlorobenzyl reacts quantitatively with mercuric bromide, chloride and iodide.

The nitrate was prepared by treating an alcoholic solution of *o*-chlorobenzyl mercuric chloride with the calculated weight of silver nitrate. The reaction goes quantitatively and was used for determining the percentage of iodine in *o*-chlorobenzyl iodide.



The acetate and benzoate derivatives were prepared by refluxing an alcoholic solution of the chloride with silver acetate and silver benzoate respectively.





The Grignard reagent was prepared in the usual manner. No difficulty was experienced in getting the reaction started. A crystal of iodine was used as a catalyst. The reaction started on the addition of a few drops of the ether solution of the halide on being warmed.

The yield of the Grignard reagent was determined by the method developed by Gilman and students¹⁸. The method consists in dissolving 5 c.c. of the ether solution containing the Grignard reagent in 200 c.c. of water containing 50 c.c. of a standard acid and back titrating with a standard base. Determinations made on several runs gave yields between 75-76% of Grignard. No attempt was made to obtain a maximum yield of Grignard reagent. This yield compared favorably with those obtained on a series of different halides by Gilman and McCracken¹⁹. However, for benzyl chloride they obtained their highest yield of Grignard which was 94.28%. For the o-chlorobenzyl chloride considerable di-o-chlorobenzyl was obtained.

Mercury di-o-chlorobenzyl.

To the Grignard reagent prepared from .5 M of o-chlorobenzyl chloride, .15 M of powdered dry mercuric

chloride was added in small portions, the mixture being refluxed with stirring for three hours. The excess Grignard reagent was hydrolyzed, the ether layer separated and evaporated, leaving the impure mercury di-*o*-chlorobenzyl, which was recrystallized from alcohol. M.P. 101°, Yield 18.3 gm. The mercury was determined by the method described by Johns, Peterson and Hixon²⁰.

The compound is very soluble in ether, fairly soluble in hot alcohol, quite soluble in cold benzene, fairly soluble in cold chloroform and carbontetrachloride, slightly soluble in cold or hot petroleum ether and cold alcohol.

o-Chlorobenzylmercuric iodide.

This compound is easily prepared by adding the theoretical quantities of mercury di-*o*-chlorobenzyl and mercuric iodide to a small volume of alcohol. The alcohol is brought to boiling and additional quantities of alcohol are added until complete solution results. On cooling, the iodide crystallizes out in white needles in practically a pure state. A few minutes exposure of the crystals to light turns them yellow. M.P. 148°.

The percentage of iodine was determined by dissolving the compound in the minimum quantity of hot alcohol and precipitating the iodide with alcoholic silver nitrate and weighing the silver iodide. The reason for determining the

iodide content instead of the mercury was because the percentage of mercury in mercuric di-o-chlorobenzyl and o-chlorobenzylmercuric iodide is practically the same, 451.62 and 453.05 respectively. The compound as stated above was prepared by treating the mercury di-o-chlorobenzyl with the calculated weight of mercuric iodide. The percentage of mercury in each of the two compounds is 44.42 and 44.28 respectively. The percentage of mercury in a mixture of the two would be between 44.42 and 44.28. And furthermore the molecular weight of mercuric iodide is 454.47 and percentage of mercury is 44.14. Therefore a mercury analysis would be valueless since a mixture of any two or three of the above compounds would give practically the theoretically percentage of mercury for the bis-compound. The determination of carbon and hydrogen in the presence of mercury and iodine by the combustion method is more or less complicated. The determination of the iodide in presence of mercury by the Carius method appeared unsatisfactory since the mercury must be removed before the halogen can be determined²¹.

Since the above methods appeared unsatisfactory the following method was used:

The sample, weighed by difference (since it has a tendency to adhere to the watch glass) was put in solution in just enough absolute alcohol to dissolve it. The iodide

was precipitated by adding with stirring the calculated weight plus .03 to .04 g. in excess of AgNO_3 to the hot RHgI solution. The precipitate was heated gently for a few minutes and then allowed to stand several hours. Then, it was again heated and the clear liquid was decanted through a weighed gooch. The precipitate was washed three times with a few c.c. of hot absolute alcohol by decantation. The sides of crucible were then washed with the hot alcohol. The precipitate was transferred to the gooch by the usual method with hot water instead of alcohol. The gooch was then dried in the oven and weighed. No correction was made for the solubility of AgI in alcohol.

Anal. Calc. for $\text{C}_7\text{H}_4\text{Cl}_1\text{HgI}$, I., 28.01

Found 27.92, 27.78

The compound is fairly soluble in hot alcohol, quite soluble in cold benzene, chloroform and carbon tetrachloride, slightly soluble in cold or hot petroleum ether and ethyl ether. Solubility in alcohol at 27°C , .56 gm. per 100 grams solutions.

o-Chlorobenzylmercuric chloride.

To the Grignard reagent prepared from .1 M. of o-chlorobenzyl chloride, .185 M. of dry powdered mercuric chloride was added in small amounts, refluxed and stirred for several hours, the ether evaporated off and the crude

material washed several times with 250 c.c. portions of a one percent acetic acid solution. The crude compound was extracted with hot alcohol (or hot benzene.) It melted at 111°C . after being recrystallized from hot alcohol. The crystals have a marked pyramidal habit; prismatic faces not common. Pyramidal forms seem to be 3-sided indicating the hexagonal system.

+Anal. Calc. for $\text{C}_7\text{H}_6\text{Cl}_2\text{Hg}$, Hg., 55.27
 Found Hg., 55.48, 55.27

+Analyzed by E.H.C.Fang.

The compound was also prepared by boiling .0025 M. of mercury di-*o*-chlorobenzyl with .0025 M. of mercuric chloride in 25 cc. of alcohol for a few minutes. Almost a quantitative yield of crystals, melting at 111°C ., was obtained on cooling.

The compound is slightly soluble in cold alcohol and carbontetrachloride but fairly soluble in the hot, quite soluble in cold benzene and chloroform but very soluble in the hot, slightly soluble in cold and hot ethyl and petroleum ethers.

o-Chlorobenzylmercuric bromide.

The same method of preparation was used for this compound as that used for the chloride, excepting that benzene is more suitable for extraction of the bromide from the

crude preparation. From .2 M. of O-chlorobenzyl bromide, 25 grams of the crude compound was obtained. After being recrystallized from hot alcohol, the compound melted at 128°. After being filtered, the crystals sometimes changed to a cubical form similar to those of the chloride while at other times they remained needle shaped. No difference was observed in the melting points of the two crystals.

The compound was also prepared by boiling .0025 M. of mercury di-o-chlorobenzyl with .0025 M. of mercuric bromide in 20 cc. of absolute alcohol. A quantitative yield of the crystals was obtained when the solvent was evaporated off at room temperature.

Anal. Calc. for $C_7H_6ClHgBr$; Hg, 49.41.

Found 49.29, 49.55

The compound is slightly soluble in cold benzene, alcohol, chloroform, carbontetrachloride, hot and cold ethyl and petroleum ethers, moderately soluble in hot alcohol while very soluble in hot benzene, chloroform and carbon-tetrachloride.

o-Chlorobenzylmercuric nitrate.

o-Chlorobenzylmercuric chloride (.02 M) was dissolved in the minimum volume of hot absolute alcohol to which was added with stirring, a hot alcoholic solution of silver

nitrate. The silver nitrate solution was prepared by dissolving .02 M. of silver nitrate crystals in 5 cc. of water, then add 50 cc. of absolute alcohol. The solution and precipitate was heated on a water bath at 55° to 60°. Any traces of chlorides were removed by dropping in alcoholic silver nitrate after heating a couple of hours. The filtrate, after filtering through an asbestos filter, was evaporated in an electrically heated vacuum dessicator to about 30 cc. The nitrate crystallized in clear transparent plate-like crystals. After recrystallizing from ether, the white needle-like crystals melted at 96°. They are not affected by diffused sunlight and do not blister the skin.

⁺
Anal. Calc. for $C_7H_6ClHgNO_3$; Hg., 52.25
Found Hg. 52.08, 52.39

+ Analyzed by E.H.C. Fang.

The compound is very soluble in hot alcohol, fairly soluble in cold alcohol, hot and cold chloroform, slightly soluble in cold and hot carbontetrachloride and only very slightly in water.

o-Chlorobenzylmercuric acetate.

o-Chlorobenzylmercuric chloride (.01 M) and silver acetate (.012 M) were refluxed in 50 cc. of alcohol until a few drops of the clear solution gave no test for chloride

with alcoholic silver nitrate. The solution was filtered. To the filtrate was added 100 cc. of warm distilled water and allowed to crystallize as small white needles. Melting point was 101.5°C. after being recrystallized from hot water. The yield was practically quantitative.

The compound was also prepared by boiling the mercury di-*o*-chlorobenzyl with mercuric acetate in alcohol.

Anal. Calc. for $C_7H_6ClHgO_2C_2H_2$ Hg, 52.03.

Found Hg. 52.35, 52.21

The compound is very soluble in chloroform, carbon-tetrachloride and benzene, quite soluble in alcohol and fairly soluble in hot water and ether, slightly soluble in petroleum ether. Besides hot water, it may be recrystallized from a mixture of carbontetrachloride and petroleum ether.

o-Chlorobenzylmercuric benzoate.

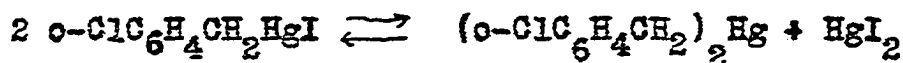
o-Chlorobenzylmercuric chloride (.01 M) and silver benzoate (.012 M) were refluxed in 100 cc. of alcohol until a test portion gave no precipitate with alcoholic silver nitrate. After the silver chloride was filtered off, the solution was evaporated to one-half its volume and a small amount of brown precipitate (Ag_2O) was filtered off. The solution was then concentrated to 25 or 30 cc. and on cooling a heavy dark liquid separated which finally crystallized

after considerable time. Yield 4.0 grams. For the purpose of recrystallization, it was placed in 80 cc. of petroleum ether, sufficient carbontetrachloride being added to dissolve it in the hot. On cooling, white needles separated, the melting point being somewhat indefinite, the crystals softening at 56° and apparently melting between 58-59°.

Anal. Calc. for $C_7H_6ClHgO_2C_2H_2$ Hg. 44.86
Found Hg. 45.11, 45.16

The compound is very soluble in ether benzene, alcohol, chloroform and carbontetrachloride, and is slightly soluble in hot and cold petroleum ether and water.

Determination of the Equilibrium Constant
for the Reaction



The concentration of mercuric iodide was determined by means of concentration cells by the method described above. A Leeds and Northrup type K potentiometer with galvanometer 2500-b with lamp and scale at one meter was used to determine the voltage produced in the concentration cells. The half-cells were those developed by Johns which were a modified type used in this laboratory by Bird and Hixon²². These cells are shown in figure 8. The measurements were

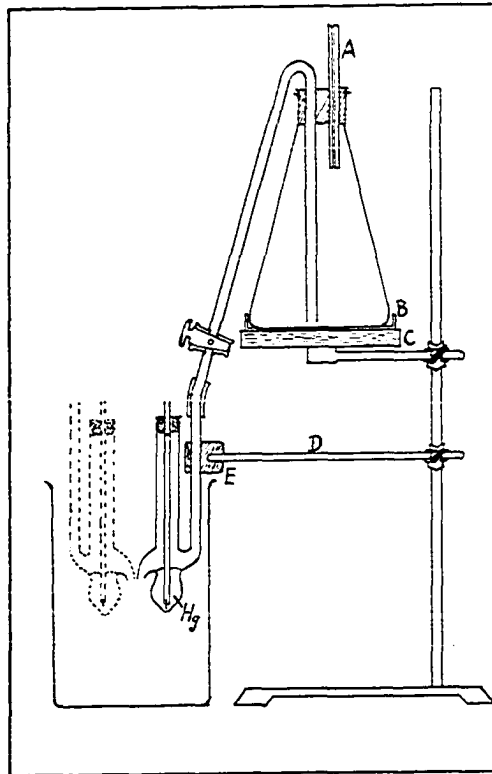


Figure 8. Type of concentration cells used.

carried out in a constant temperature air bath at $25^{\circ} \pm .1^{\circ}\text{C}$.

Solutions 0.005 and 0.01 molar in *o*-chlorobenzylmercuric iodide were made up by dissolving the calculated quantity of the compound in absolute alcoholic solution 0.05 molar in potassium iodide. Solutions 0.0025 and 0.005 molar in mercury di-*o*-chlorobenzyl and mercuric iodide were prepared in a similar manner. The 0.005 molar mercuric iodide standard half-cell was used as a reference cell. This half-cell was checked at each reading of the cells against the 0.0025 molar mercuric iodide half-cell and the voltages produced checked admirably with those obtained by Johns.

The voltages produced by the organomercury half-cells against the reference half-cell at various times are given in Tables X, and XI.

Irregularities of the di-*o*-chlorobenzyl mercury half-cell.

It will be noticed from the Tables that the voltages produced by the half-cells made up from organomercuric iodides do not check those made up from the bis-organomercury compounds. Since the voltages of the R_2Hg cells are not constant the equilibrium constants have not been calculated. The equilibrium constant calculated on the RHgI cells fall on the curve determined by Johns. In the R_2Hg cells a very small amount of HgI_2 is used up over a long period of time, however, the voltages do increase with time

TABLE X.

E.M.F. OF THE o-CHLOROBENZYL MERCURY IODIDE CON-
CENTRATION CELLS AGAINST 0.005 MOLAR REFER-
ENCES CELL.

Com- pound	Conc.	Days	E.M.F.	Conc. HgI ₂	$\frac{(R_2Hg)(HgI_2)}{(RHgI)^2}$
RHgI	0.005	10	0.0212	0.00133	3.24×10^{-1}
		12	0.0195		
		13	0.0194		
		15	0.0191		
RHgI	0.010	10	0.0040	0.00319	7.77×10^{-1}
		12	0.0079		
		13	0.0078		
		15	0.0074		
RHgI	0.005	8	0.0238	0.00133	3.24×10^{-1}
		11	0.0208		
		13	0.0197		
		14	0.0194 ^a		
RHgI	0.010	8	0.0106	0.00319	7.77×10^{-1}
		11	0.0078		
		13	0.0079		
		14	0.0065 ^c		

(a) New reference half-cell.

TABLE XI.

E.M.F. OF THE MERCURY DI-O-CHLOROBENZYL CONCENTRATION CELLS AGAINST 0.005 MOLAR

REFERENCE CELL

Compound	Conc.	Days	E.M.F.
R ₂ Hg	0.005 ^b	3	0.0121
		5	0.0122
		7	0.0126
		9	0.0123
		12	0.0127
		14	0.0133
R ₂ Hg	0.010 ^b	3	0.0011
		5	0.0017
		7	0.0029
		9	0.0024
		12	0.0041
		14	0.0041
R ₂ Hg	0.005 ^b	3	0.0103
		4	0.0119
		7	0.0119
		9	0.0122
R ₂ Hg	0.005 ^b	2	0.0108
		3	0.0119
		6	0.0119
		8	0.0119
R ₂ Hg	0.010 ^b	3	0.0014
		4	0.0024
		7	0.0038
		9	0.0038
		28	0.0047
R ₂ Hg	0.010 ^b	2	0.0012
		3	0.0013
		6	0.0025
		8	0.0035

(b) Concentration given on basis of RHgI.

indicating the rate of reaction to be very slow. However, on the other hand, starting with the RHgI compound an equilibrium is soon reached. After a few days the voltages drop very slowly with these cells indicating a shift of the reaction with the formation of more HgI_2 as was also found by Johns in his work with cells of this type.

Since the rate of reaction between mercury di-*o*-chlorobenzyl appeared to be very slow there was some doubt as to whether the bis-organo compound was in reality R_2Hg or some other inert compound. In his work Johns found that the equilibrium was soon reached in similar reactions. In order to determine the actuality of the bis-organomercury compound several experiments were tried. First, a reanalysis was made for mercury. The analysis checked the theoretical within the experimental errors. Secondly, calculated quantities of R_2Hg and HgI_2 were sealed in a tube with a small quantity of alcohol and shaken on a machine for a number of days. The mercuric iodide was used up. In a third experiment, calculated quantities of R_2Hg and HgI_2 were boiled together in a small amount of absolute alcohol. On cooling a compound precipitated out, presumably RHgI since all traces of HgI_2 had disappeared. These experiments show that compound was undoubtedly the bis-organomercury compound.

In order to show more conclusively that the dis-

crepancy between the RHgI and R_2Hg cell was due mainly to the slowness of the rate of reaction between mercury di-*o*-chlorobenzyl and mercury iodide the calculated quantities of potassium iodide and absolute alcohol necessary to make the solution 0.0025 molar, were added to the precipitated RHgI in the last experiment mentioned above. The voltage produced against the 0.005 molar HgI_2 reference cell was measured. At the end of one day the voltage was 0.0181; two days 0.0170; nineteen days 0.0168. These voltages are about three millivolts lower than the voltages produced by the 0.005 molar RHgI cells given in the Table. The calculated constant was 10.0×10^{-1} . This voltage and constant is in fair agreement with cells prepared from the isolated RHgI compound.

SUMMARY

- (1) The dissociation constant for o-chlorobenzyl amine has been determined.
- (2) The ionization constants for a number of the arsonic acids have been determined by the conductivity method and from E.M.F. data. Free-energy of ionization for these acids has been calculated. The concept of electron-sharing ability has been extended to include the arsonic acids series.
- (3) The ionization constant for o-chlorobenzyl arsonic acid has been determined.
- (4) The mercury di-o-chlorobenzyl, and the chloride, bromide, iodide, acetate and benzoate of the o-chlorobenzyl mercury radical have been prepared and described.
- (5) An attempt has been made to determine the equilibrium constant for the equilibrium between o-chlorobenzyl-mercuric iodide and mercury di-o-chlorobenzyl plus mercuric iodide in absolute alcoholic potassium iodide solution. The voltage obtained from cells made up from RHgI checked the values predicted by means of the dissociation constants of the corresponding amines and arsonic acids. The cells prepared from $\text{R}_2\text{Hg} + \text{HgI}_2$ did not come to equilibrium within the period of observation. By boiling these latter constituents in a

small volume of alcohol so that practically complete conversion to RHgI was accomplished before the cell was actually prepared, voltages in fair agreement with cells prepared from the isolated RHgI could be obtained.

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