ELECTRON-SHARING ABILITY OF ORGANIC RADICALS: CONCENTRATION CELLS USING ORGANOMERCURIC IODIDES*

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The preceding paper[1] indicated that the ionization of the organomercuric nitrates could be correlated with the dissociation constants of the corresponding organic acids and amines as was to be expected if our modern concepts of valence[2] are correct. The ionization values of the organomercuric nitrates could not be used to calculate free energy of ionization due to incident acid hydrolysis and variation of the ionization constant with dilution. To obtain data which could be used to calculate free energy relationships and therefore interpreted in terms of chemical affinity, a study of the reversible reaction:

$$2\ RHgI \rightleftarrows R_2Hg + HgI_2 \qquad \text{Eq. I.}$$

was undertaken.

This reaction is general for the organomercury halides and the fact that it is used for the preparation of either the compounds of type RHgI or R_2Hg from the other demonstrates its reversibility. The reaction tends to go to the left with the aliphatic compounds and the complete removal of the mercuric iodide by reducing agents is necessary for the preparation of the dialkyl mercury compounds from the corresponding alkylmercury halides. With the aromatic mercury derivatives, the reaction is easily carried to the right, the removal of the mercuric halide by formation of the complex compound with potassium halide being sufficient for the preparation of some diaromatic mercury derivatives from the corresponding aromatic mercury halides.

These relationships which suggest a correlation with the positivity and negativity of the organic radicals, can be more readily observed if the mercuric iodide is qualitatively determined in the alcoholic solutions by means of diphenyl carbazide.[3] In alcoholic solutions of the alkylmercuric iodides, the blue color is very faint, its intensity increasing slowly on standing. With benzylmercuric iodide, the color develops quite quickly while with the tolyl- and phenylmercuric iodides, the color appears immediately on adding the reagent. The radicals are mentioned in the order of the dissociation constants of their amines and carboxylic acids and these color tests would indicate the same order in the formation of mercuric iodide according to reaction (I). This colorimetric method was found inadequate for the accurate determination

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[1] J. Phys. Chem., **34**, 2218 (1930).

[2] Hixon and Johns: J. Am. Chem. Soc., **49**, 1786 (1927).

[3] Skinner: J. Chem. Soc., **53**, 551 (1888). This compound has been suggested as a reagent for detecting mercury, a blue color being formed with very slightly basic solutions of mercury salts, a blue precipitate slowly forming as the solutions stand.

of the concentration of mercuric iodide since the compound formed with diphenyl carbazide soon precipitates displacing reaction (I) to the right. Also, the bis-organomercuric compounds produce colored compounds with the reagent.[4] These red shades of color interfere with the accurate estimation of the blue color produced by the mercuric halide. In very dilute solutions, the blue compound does not precipitate and in such a case the reaction can be reversed by adding a large excess of the type compound R_2Hg with resulting decrease of the blue color.

The equilibrium represented by Eq. I. is so labile that the use of precipitating reagents for the determination of the concentration of the constituents is out of the question. Since the R_2Hg compounds do not ionize to form the free mercury ion, as evidenced by the failure of hydrogen sulfide to precipitate mercuric sulfide from their solutions, and since the RHgI compounds have been shown to be very slightly ionized,[1] it seemed probable that the concentration of the mercuric iodide in the equilibrium could be determined by concentration cell methods. Preliminary experiments using 0.05 molal alcoholic potassium iodide as solvent showed that reproducible voltages could be obtained when known solutions of RHgI compounds where measured against a corresponding solution of HgI_2 in cells of the type.

$$\mathrm{Hg}\ \left|\ \begin{array}{ll} \mathrm{HgI_2} & 0.005\mathrm{M} \\ \mathrm{KI} & 0.05\ \mathrm{M} \end{array}\ \right\|\ \begin{array}{c} 2\mathrm{RHgI} \rightleftarrows \mathrm{R_2Hg} + \mathrm{HgI_{2C_1}} \\ \mathrm{KI}\ \ 0.05\ \mathrm{M} \end{array}\ \Big|\ \mathrm{Hg} \qquad \text{Eq. II.}$$

Furthermore, identical voltages could be obtained quite independent of whether the organomercury cell was made up by adding RHgI or equivalent quantities of $R_2Hg + HgI_2$ according to Eq. I. This experiment quantitatively demonstrates the reversibility of the reaction represented by Eq. I.

As indicated above, it seems probable that no appreciable voltage would be exerted between RHgI and Hg_0 or between R_2Hg and Hg_0. Accordingly, the voltage of the organomercury half-cell in Eq. II. has been interpreted as due to the concentration of HgI_2 only. Concentration cells of the type:

$$\mathrm{Hg}\ \left|\ \frac{\mathrm{HgI_2}\ \ C_1}{\mathrm{KI}\ \ 0.05\mathrm{M}}\ \right\|\ \frac{\mathrm{HgI_2}\ \ C_2}{\mathrm{KI}\ \ 0.05\mathrm{M}}\ \Big|\ \mathrm{Hg} \qquad \text{Eq. III.}$$

have been measured to determine the relationship between concentration of HgI_2 and voltage. This relationship has then been used to translate the voltages obtained in the organomercury cells of Eg. II into concentrations of HgI_2. Knowing the total concentration of organic mercury added and the concentration of mercuric iodide at equilibrium the concentration of all the members in Eq. I can be calculated and the equilibrium constant for the various compounds derived. In the experimental studies reported in this paper, all solutions were made in absolute alcohol 0.05 molal in potassium iodide. The reference cell was in all cases 0.05 molal in potassium iodide and 0.005 molal in mercuric iodide.

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[4] Fiegel and Lederer: Monatsheft, **45**, 115-32 (1924).

Experimental

Absolute Alcohol.

The alcohol used was prepared by fractionating through a three-bulb distilling head, three gallons of 96% alcohol to which had been added 100 cc. of 50% sulfuric acid, rejecting the first and last half gallon. The middle fraction was refluxed for twenty-four hours with freshly dehydrated lime and distilled. It was then treated with a slight excess of metallic calcium and again distilled. The conductance of such alcohol varies from 3×10^{-7} to 8×10^{-8}. The conductance of a 0.05 molal solution of potassium iodide in such alcohol varied from 1.02×10^{-3} to 1.15×10^{-3}. This variation has not been accounted for. It cannot be due to water in the alcohol for with a solution whose conductance was 1.02×10^{-3}, the addition of 2.5% water by volume raised the conductance only to 1.07×10^{-3}. It cannot be due to variations of concentration for in preparing 1500 g. batches, the weighing of the alcohol was accurate to one part in thirty thousand, and the weighing of the potassium iodide to one part in fifty thousand. These variations in conductance produced no noticeable variation in the E.M.F. of the cells.

Potassium Iodide.

A c.p. grade of KI was recrystallized once from water and once from alcohol and dried at 200° for three hours. It was then powdered and dried again at 200° for three hours.

Mercuric Iodide.

The mother liquors from the purification of potassium iodide were added to a saturated mercuric chloride solution to precipitate mercuric iodide. The precipitate was washed several times by decantation and then boiled with water three times. It was then dried and distilled. The yellow lustrous crystals, which soon turn red, were finely powdered.

Organomercuric Derivatives.

These compounds,[5] all of which are described in the literature, were recrystallized several times from appropriate solvents, the last recrystallization being done in ethyl alcohol even for compounds limitedly soluble in this solvent. They were dried for twenty-four hours in vacuo, before using.

Apparatus and Method.

The potentiometer used was a Leeds and Northrup type K. with Galvanometer 2500-b with lamp and scale at 1 meter. The standard cell (Weston) and the concentration cells were kept in an air thermostat with temperature controlled to 25° ± 0.1. The half cells were a modification of the type used in this laboratory[6] in the studies on potassium and sodium amalgams.

At the beginning of the work, a great deal of trouble was experienced in getting satisfactory measurements, due to condensation of moisture on the

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[5] The compounds were prepared and purified by B. R. Daniel in this laboratory. These pure compounds were in every case carefully recrystallized and dried immediately before use.

[6] Bird and Hixon: J. Phys. Chem., **34**, 1412 (1930).

cells and consequent leakage of current. This was especially true in warm weather. This trouble was entirely eliminated by the cell construction shown in Fig. 1. All supports are of glass sufficiently far removed from metallic contacts to insure proper insulation. In use, the tips of two such cells are put together. The solutions join and drip from the tips into a beaker tall enough to surround both cells and covered by a card through which the cells pass.

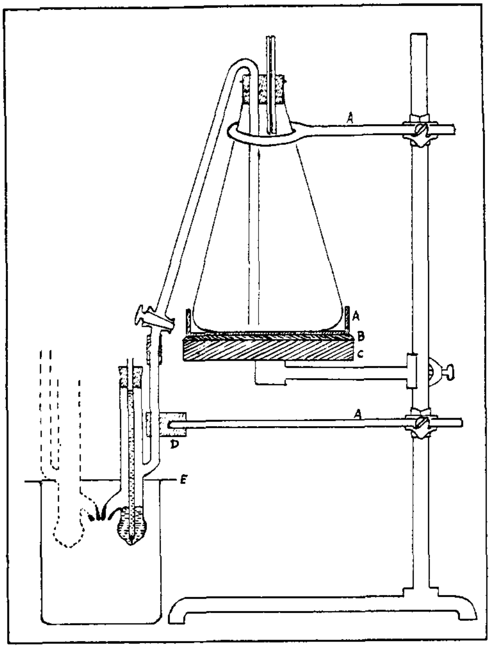

FIG. 1

Diagram of Cell with Flowing Junction
A, glass; B, paraffin; C, wood; D, rubber; E, card.

The electromotive force is independent of the flow of the solutions for all rates greater than two drops per second. At very low rates (one drop per second or less) the electromotive force becomes erratic but returns to a steady reproducible value on increasing the rate beyond two drops per second.

The resistance across two such half-cells is approximately 40,000 ohms when filled with alcohol 0.05 molal in potassium iodide. This high resistance forbids the use of the usual half-cells with long narrow limbs, when working with dilute alcoholic solutions.

Electromotive Force of Mercuric Iodide Concentration Cells.

In the study of the mercuric iodide concentration cells of the type shown in Eq. III, the concentration of mercuric iodide was varied from 0.0005 molal to saturation. In the absence of metallic mercury, an absolute alcohol solution .05 molal in potassium iodide will be 0.1136 molal in mercuric iodide when saturated with this salt. If metallic mercury is added, reduction takes place with the precipitation of mercurous iodide until the concentration is lowered to 0.05101 molal. If a solution is prepared from mercurous iodide, the concentration is 0.05101 molal (HgI_2) at saturation. At all concentrations of mercuric iodide lower than 0.05100 molal, no measurable reduction takes place as evidenced by the constancy of the weight of a globule of mercury placed in it. It is to be expected that an equilibrium will always exist between mercuric and mercurous iodides in the presence of metallic mercury, but the amount of the mercurous iodide in solution is too low to be determined. For this reason, in all the cells of this study, the mercury may be considered to be entirely in the higher valence form.

With all cells using solutions below saturation, a definite reproducible (to ± .0002 volts) E.M.F. was obtained immediately after solution was effected. With the saturated solutions, the voltage of the cell:

$$\begin{array}{c|l||l|l} \mathrm{Hg} & \mathrm{HgI_2},\ \ 0.005\ \mathrm{M} & \mathrm{HgI_2\ sat} & \mathrm{Hg.} \\ & \mathrm{KI}\ \ 0.05\ \mathrm{M} & \mathrm{KI}\ \ 0.05\ \mathrm{M} & \end{array}$$

becomes approximately -0.229 after fifteen days but could not be checked within five millivolts.

The E.M.F. of the cells measured are reported in Table I. The second column, headed "number of cells," gives the number of times the cells were prepared from entirely new solutions. The E.M.F. of each individual cell was measured at intervals over a period of time ranging from two days to one month. At least two reference cells were maintained at all times for checking.

TABLE I

E.M.F. of Alcoholic Concentration Cells of the Type:

$$\begin{array}{c|cc||cc|l} \mathrm{Hg} & \mathrm{HgI_2} & \mathrm{KI} & \mathrm{HgI_2} & \mathrm{KI} & \mathrm{Hg.} \\ & 0.005 & .05 & c & .05 & \end{array}$$

C	No. of cells	E.M.F.	Max. Variation
.025	5	+.04850	±.0002
.010	5	+.01455	±.0001
.0025	2	−.01150	±.0001
.0010	2	−.02260	±.0002
.0005	2	−.02905	±.0001

The relationship between voltage and concentration of HgI_2 is represented graphically in Fig. 2. It is evident that the relation between E and ln c_1/c_2 is far from linear. It is interesting to note that by plotting the data of M. S. Sherrill[7] for mercuric iodide in aqueous potassium iodide (1M) the same type of curve is obtained.

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[7] M. S. Sherrill: Z. physik. Chem., 43, 721 (1903). In particular, cells 5 to 11, Table V, p. 721.

E.M.F. of Cells containing Organomercuric Iodides.

The solutions for the organomercuric iodide half-cells were prepared by adding to the alcoholic potassium iodide the calculated amount of the organomercuric iodide, or equivalent quantities of the bisorganomercuric compound and mercuric iodide. With the higher concentrations, the amount of mercuric iodide present when equilibrium is reached is sufficient to give a characteristic greenish yellow tint to the solutions. The E.M.F. of the organomercuric iodide half-cells against the reference mercuric iodide half-cell as shown in Eq. II was determined. No difficulties were encountered in obtaining electromotive force measurements reproducible to ±.0003 volt over a period of from two to twelve days with any of the compounds except methylmercuric iodide, which is discussed below as a special case.

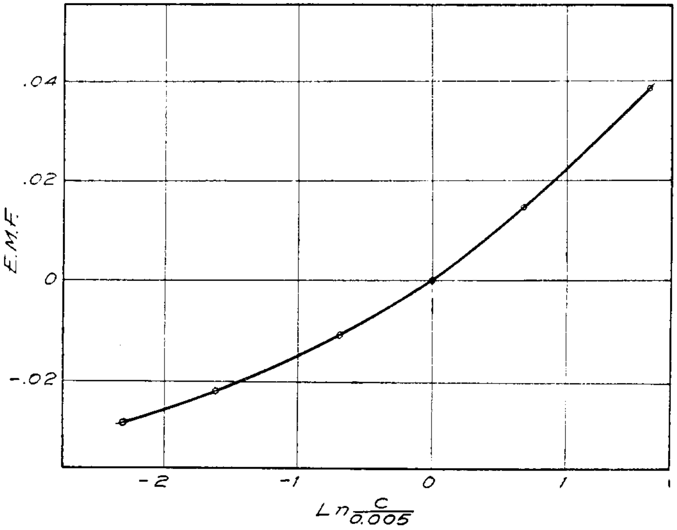

FIG. 2
E.M.F. of HgI_2 Concentration Cells

From the measured E.M.F., the concentration of mercuric iodide in the cells was found from the curve, Fig. 2. From this, and the initial concentration of organomercuric compound, the concentrations of all the constituents of Reaction I were calculated. These data, with the equilibrium constants and free energy calculated from them, are presented in Table II.

Irregularities of the Methylmercuric Iodide Cells.

Solutions of methylmercuric iodide in alcoholic potassium iodide deposit small quantities of metallic mercury on standing at 25°. After one week, the amount deposited is very noticeable and during this time the E.M.F. of the cell changes slowly in the direction of increasing concentration of mercuric iodide. This change is not complete in two weeks.

TABLE II

Study of the Reaction $2RHgI \rightleftarrows R_2Hg + HgI_2$, from E.M.F.

Measurements of Concentration Cells of the Type:

$$Hg \left| \begin{matrix} HgI_2 .005M \\ KI .05M \end{matrix} \right\| \begin{matrix} 2RHgI \rightleftarrows R_2Hg + HgI_2\ C_1 \\ KI .05M \end{matrix} \left| \ Hg \right.$$

R.	RHgI Conc	No of Cells	E in millivolts *Max.*	E in millivolts *Min.*	Av. Conc $HgI_7 = C_1$	Av. Conc RHgI at Equil	K = $\frac{R_2Hg)(HgI_2)}{(RHgI)^2}$	ΔF. cal.	
CH_3-	.06	1	+ 2.7	†	.00575	.0485	1.4×10^{-2}	−2540	Av.
	.03	1	−11.5	†	.0025	.025	1×10^{-2}	−2710	−2620
C_2H_5-	.02	1	−19.6,	−19.3	.00134	.01732	5.97×10^{-3}	−3020	−3020
	.02593	1	−16.4,	−16.0	.00174	.02245	6×10^{-3}	−3030	
C_4H_9-	.02	2	−23.0,	−22.8	.000983	.01803	2.97×10^{-3}	−3430	
	.025	1	−19.6,	−19.4	.00133	.02234	3.54×10^{-3}	−3330	−3390
	.03	1	−18.1,	−18.0	.00149	.02702	3.04×10^{-3}	−3420	
$C_6H_5CH_2$-	.01*	1	−11.0,	−10.9	.00258	.00484	2.84×10^{-1}	−742	−768
	.01	1	−11.4,	−11.3	.00252	.00496	2.58×10^{-1}	−800	
$CH_3C_6H_4$-	.0025*	1	−25.4,	−25.3	.00078	.00094	6.9×10^{-1}	−219	
	.0025	1	−26.0,	−25.9	.00073	.00104	4.92×10^{-1}	−418	−212
	.003	1	−22.7,	−22.6	.0010	.0010	$10.\times10^{-1}$	0.	
C_6H_5-	.001*	1	−36.8,	−36.4					
	.001	1	−36.8,	−36.4					
	.0025*	1	−25.4,	−25.3	.00078	.00094	6.9×10^{-1}	−219.	
	.0025	1	−25.5,	−25.1	.00078	.00094	6.9×10^{-1}	−219.	Av.
	.0035*	1	−20.6,	−19.9	.00122	.00106	13.2×10^{-1}	+164.	−28
	.0035	1	−20.5,	−19.9	.00122	.00106	13.2×10^{-1}	+164.	

†Initial voltage of these cells is given, due to slow decomp. of compound.

*Cell prepared from equiv. quantities of R_2Hg and HgI_2, reported conc. calculated on basis of RHgI.

Thus, a cell of .06 molal methylmercuric iodide had an initial voltage of 0.0027, two days later the E.M.F. was .0062, and at the end of ten days the E.M.F. was 0.0158. Because of this change, only the initial values of the E.M.F. of the cells containing methyl mercuric iodide are included in Table II.

The methyl mercuric iodide is the only compound studied that has been found to decompose at 25° within the usual time of observation. Samples of all the solutions have been kept for two months without any visible separation of mercury and the original compound was removed and identified (by melting point) after evaporation of the alcohol and removal of potassium iodide with water. However, after six months at room temperature, solutions of ethyl mercuric iodide were found to have deposited minute quantities of mercury, and solutions of benzylmercuric iodide had deposited mercury in quantity sufficient to be easily observed in the flasks.

This decomposition can be brought about quickly with all the compounds studied by heating them to 130°-160° in a saturated alcoholic potassium iodide solution in sealed tubes. The literature[8] reports that dibenzylmercury when decomposed by heat yields metallic mercury and dibenzyl. This can be represented by the equation

$$R_2Hg \longrightarrow R-R + Hg \qquad \text{Eq. IV.}$$

In an alcoholic potassium iodide solution of an organomercuric iodide this would be a secondary reaction added to the reaction shown in Eq. I or the combined equations could be written:

$$\begin{tikzcd} 2RHgI \arrow[r, rightleftarrows] & R_2Hg + HgI_2 \arrow[d] & \\ & R_2 + Hg & \text{Eq. V.} \end{tikzcd}$$

The formation of metallic mercury and a hydrocarbon would render this reaction irreversible and if allowed to go to completion, one-half of the mercury in the organomercuric iodide should separate as metallic mercury. This conclusion was tested by heating 4.8296 g. benzylmercuric iodide in alcoholic potassium iodide to 160° for two hours in a sealed tube. The metallic mercury liberated weighed 1.1542 g. which is within 0.3% of the theoretical according to Eq. V.

Methylmercuric iodide shows the shortest time factor for this side reaction of any of the compounds studied. The constancy of K calculated for Eq. I from E.M.F. measurements on cells of varying concentration would indicate that even in this case, the speed of the side reaction is so slow that a reliable measure of the concentrations of the first equilibrium can be obtained.

Discussion of Results

The data presented in Table II shows that K is independent of concentration over the range of dilutions employed, with the possible exception of the cells containing totyl- and phenyl-mercuric iodides. Even in these cases the

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[8] Whitmore: "Organic Compounds of Mercury," 185 (1921).

variation in E.M.F. equivalent to the variation of K is only ±.0004 volts which is not much greater than the actual experimental error. The marked variations in K produced by such slight variations in E.M.F. results from the flatness of the curve in Fig. I. from which the concentration of HgI_2 is determined and from the smallness of the concentration of RHgI, which enters the denominator in the calculation of K. The cells cannot be measured at higher concentrations so as to employ the part of the curve with greater slope, due to the limited solubility of these compounds.

In all of this work, the electromotive force has been interpreted as being due to and a measure of the concentration of mercuric iodide resulting from the reaction represented in Eq. I. This assumption seems justified in view of the approximate constancy of K with varying concentrations. If the series were extended to the more negative radicals, compounds would be reached which would not form an unionizable radical RHg^+. This would be expected in the case of the extremely negative radicals such as $-NO_3$ or -Cl. Such compounds as NO_3HgI or ClHgI, if obtainable would undergo reaction I to give

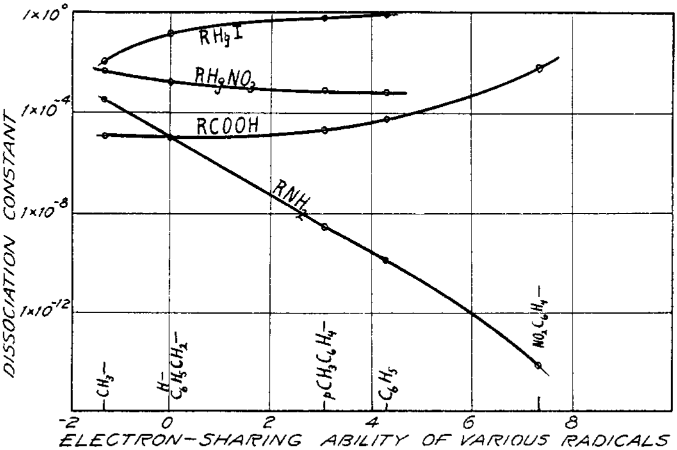

FIG. 3

Equlibrium constants for Eq. I compared with ionization constants of type compounds RNH_2, RCOOH, $RHgNO_3$.

$$2NO_3HgI \rightleftarrows Hg(NO_3)_2 + HgI_2$$

and in such a case both of the products of the reaction, as well as the initial compound NO_3HgI, would be expected to contribute to the total E.M.F. of the cell containing this equilibrium mixture. As mentioned earlier, it does not seem likely that any of the organomercuric iodides or bisorganomercury compounds used in this work would contribute measurably to the E.M.F. of the cells though even a slight effect of this kind might be a factor influencing the change in K with dilution, found with the cells using tolyl- and phenylmercuric iodides.

If these conclusions be true, one would expect that the more negative radicals in the series, such as NO_3, Cl, Br. would cause Reaction I to proceed even more completely to the right. This is supported by the work of Reinders[9] on mixed halides of mercury.

In the first paper of this series,[2] the available data was collected and a mathematical relationship pointed out between the dissociation constants and between the free energies of ionization of the five series $R\cdot(NH_2)$, $R\cdot(COOH)$, $R(CH_2COOH)$, $R\cdot(CH_2\cdot CH_2COOH)$ and $R\cdot(OH)$. The curves used in this former publication for showing the relationship between the dissociation constants of the RNH_2 and RCOOH derivatives are reproduced in Fig. 3. Since the equilibrium constants K derived in Table II are found to plot a smooth curve in Fig. 3, it is apparent that these mathematical relationships can also be extended to the type derivatives RHgI and R_2Hg. The approximate ionization constants for the $RHgNO_3$ derivatives as reported in the preceding paper have also been plotted in Fig. 3 to show that the mathematical relationship can be extended to cases in which the chemical factors do not permit the calculation of free energy. As in the preceding papers, the mechanistic theories of valence have been intentionally avoided; the data being offered as a further demonstration of the fact that the organic radicals can be arranged in a series analogous to the electrochemical series of the inorganic elements.

Summary

1. Mercuric iodide concentration cells in alcoholic potassium iodide are described and their E.M.F. reported.

2. The reaction of organomercury derivatives: $2RHgI \rightleftarrows R_2Hg + HgI_2$ has been shown to be reversible. Concentration cells containing this equilibrium mixture have been measured and the concentration of mercuric iodide has been derived from this data on the assumption that the organomercury ions will give no voltage with metallic mercury since they do not form free Hg^{++} ions. The equilibrium constants for the reaction at different concentrations justify this interpretation.

3. The equilibrium constants of the above reaction for six organic radicals are shown to correlate with the dissociation constants of the acid and amine derivatives of the same radicals.

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[9] Reinders: Z. physik. Chem., **32**, 494 (1900).