provided that (a) the rate of demercuration is negligible, and (b) the molar absorptivity of the Hg(II) complex of the product is much greater than that of the reactant. The plot analogous to Fig. 5 for *para*-mercurated aniline-Hg(II) solutions is in fact also linear.²⁰

Since ϵ_1^V is not known, the empirical spectral changes cannot be translated into rate constants. Thus, the main result of these kinetic studies is to confirm the basic rate equation (17), which leads to eq. 21 when account is taken of all the labile equilibria. Furthermore, the ratio of intercept to slope in Fig. 5 gives K_1^V as 0.95. This equilibrium constant refers to the formation of the N-Hg+2 complex of monomercurated aniline, which is probably a mixture of ortho and para species. The direct equilibrium measurements already described give for K_1^{P} , the equilibrium constant for formation of the N-Hg+2 complex of para-mercurated aniline, 1.5. For the dimercurated species formed from *para*-mercurated aniline, the corresponding equilibrium constant for the N-Hg⁺² complex, as determined from kinetic data, is $K_1^{V'} = 0.8$.

The isolation of a crystalline product provides direct analytical evidence that aniline is mercurated in aqueous, acidic solution by $Hg(ClO_4)_2$. The results of analysis of this compound were: 7.75 \pm 0.07% C, 60.7 \pm 1.3% Hg, 22.3 \pm 0.1% ClO₄, and 8.3% H₂O. This suggests that the empirical formula is C₆NH₃Hg₃(ClO₄)₂·4H₂O, for which the calculated composition is: 7.50% C, 62.6% Hg, 20.7% ClO₄, and 7.5% H₂O.

The composition of this compound requires that it contain Hg-C bonds. It is inconceivable that all three Hg atoms per aromatic ring be exclusively bound to $N.^{21}$ The low ClO₄ analysis requires either hydroxyl anions or, more likely, extensive -Hg-bridging between aromatic groups. Thus, the structure is probably polymeric.

Summary and Discussion

The phenomena which occur in aqueous, acidic solutions of mercuric perchlorate containing aniline or pacetoxymercurianiline can be explained as follows. (a) Rapid equilibria of the type shown in eq. 22 occur, with n ranging from 0 to probably 3 or 4. The

(20) Reference 2, p. 86.

(21) A referee has remarked that it is improbable but not inconceivable that the high mercury to carbon ratio is due to double salt formation with, say, $Hg(OH)_2$. We agree, but this is surely unlikely in acid solution.

equilibrium constants of this reaction range between 0.6 and 3. (b) Slow, reversible reactions

$$\underbrace{\operatorname{NH}_{3}^{+}}_{\mathrm{S}}(\mathrm{Hg}^{+})_{n} + \mathrm{Hg}^{+2} \rightleftharpoons \underbrace{\operatorname{NH}_{3}^{+}}_{\mathrm{S}}(\mathrm{Hg}^{+})_{n+2} + \mathrm{H}^{+}(23)$$

lead to the formation of several mercurated species in solution. (c) Species of type r with n > 0 are responsible for ultraviolet light absorption at wave lengths > 300 m μ . They have a characteristic band centered at 330-335 m μ . The molar absorptivities range between 1 × 10³ and 1 × 10⁴ l./mole-cm. (d) The rate of reaction 23 is proportional to the $[C_6H_3NH_2][Hg^{+2}]$ product, most probably because the free amine is attacked by Hg⁺² ions in a bimolecular reaction.

It is surprising that ions so highly charged should readily form complexes which have still higher charge. However, in a study of the mercuration of benzene, Perrin and Westheimer.^{9,22} found that the rate of the reaction is not decreased by $-Hg^-$ substituents nearly as much as one would expect for a charged group. This lack of deactivation was attributed to the effective dispersion of the ionic charge by solvation. The same effect may be invoked here to explain the continued stability of these complexes as the number of charged groups on the ring increases.

The characteristic ultraviolet band of the mercurated Hg complexes at $330-335 \text{ m}\mu$ is very curious. It lies $50-55 \text{ m}\mu$ to the red of the long wave-length band of free aniline itself. Thus, a species containing a Hg atom on both ring and amino groups develops an absorption band which is not present if a Hg is bound only to the nitrogen or only to carbon. This fact implies an interaction between the Hg atoms, at least in the excited state, the nature of which is not clear.

Acknowledgment.—This research has been supported by the Atomic Energy Commission under Contract AT(11-1)-188. T. H. W. was a Woodrow Wilson Fellow in 1959–1960.

(22) C. Perrin, Ph.D. Thesis, Harvard University, 1963; Dissertation Abstr., 24, 1836 (1963).

[CONTRIBUTION NO. 3116 FROM THE GATES, CRELLIN, AND CHURCH LABORATORIES OF CHEMISTRY, PASADENA, CALIFORNIA]

Studies of the Chemistry of Mercury in Aqueous Solution. III. The Equilibrium Quotient of Aromatic Mercuration for Benzene and *p*-Methoxyanisole

By Thomas H. Wirth and Norman Davidson

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The equilibrium quotients for the mercuration of benzene and *p*-methoxyanisole have been measured in dilute aqueous HClO₄-NaClO₄ solutions ($\mu \sim 1 M$). The results are that, for the reaction ArH + Hg⁺² \rightleftharpoons ArHg⁺ + H⁻, $K = 300 \pm 230$ if Ar = C₆H₅ (22 $\pm 3^{\circ}$, $\mu = 1.0$ -1.2 M) and $K = 470 \pm 360$ if Ar = 2,5-(H₃CO)₂C₆H₃ (26.1°, $\mu = 1.0$ -2.0 M).

Introduction

Aromatic mercuration is a reversible electrophilic substitution reaction.¹ The products are usually classi-(1) F. H. Westheimer, E. Segel, and R. Schramm, J. Am. Chem. Soc., 69, 773 (1947). fied as substituted aromatic compounds. It is also possible, however, to regard them as inert coordination compounds of Hg(II). In this context it is interesting to compare the mercury-carbon bonds of these compounds with the mercury-nitrogen bonds of the labile amine complexes of Hg(II). In particular, the equilibrium constant of the mercuration reaction

$$\bigcirc C - H + Hg^{+2} \rightleftharpoons \bigcirc C - Hg^{+} + H^{+} (1)$$

might be compared with that of

$$\begin{array}{c} \begin{array}{c} & \\ & \\ \end{array}^{+} H + Hg^{+2} \end{array} \begin{array}{c} \end{array} \begin{array}{c} \\ & \\ \end{array} \begin{array}{c} \\ \\ & \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \end{array} \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \end{array} \end{array} \end{array}$$
 \end{array}

The latter equilibrium constant is 0.8 at 25° in 0.5 F pyridine nitrate.² Mercuration does occur in aqueous solution; it has been studied under these conditions by Westheimer,^{1,3-6} Carmack,⁶ Wright,⁷ and their respective co-workers. Westheimer, Segel, and Schramm¹ determined the concentrations of phenylmercuric nitrate and mercuric nitrate present at equilibrium in 20-50% nitric acid solutions containing benzene. They expressed their results as an "apparent equilibrium constant"

$$K_{\rm M}' \equiv [{\rm Hg}({\rm NO}_3)_2] [{\rm C}_6 {\rm H}_6] / [{\rm C}_6 {\rm H}_5 {\rm Hg} {\rm NO}_3]$$
 (3)

This quotient was characteristic of a given acid concentration regardless of whether mercuric nitrate or phenylmercuric nitrate was used as the starting material, proving that equilibrium was reached and that mercuration is reversible. In Table I, Westheimer's

TABLE I				
Approximate Equilibrium Quotients for the				
Mercuration of Benzene at 50° in HNO_3				
% HNO₃	20	30	40	50
$K_{M}{}^{a}$	90	80	90	100

 $^{a}K_{M} = [HNO_{3}]/K_{M}$ '. [HNO₃] in moles/liter was computed from the densities of HNO₃ in the International Critical Tables.

data are recast into the form of the conventional equilibrium constant of the reaction

$$C_6H_6 + Hg(NO_3)_2 = C_6H_5HgNO_3 + HNO_3$$
 (4)

The values of $K_{\rm M}$ have been calculated making the very crude assumption that all the species in eq. 4 are un-ionized and have activity coefficients of unity. The same numerical value would be calculated if it were assumed that all species were completely ionized and the reaction was eq. 1. Neither extreme assumption is true. Nevertheless, the results suggest that the equilibrium constant of eq. 1 is greater than that for eq. 2.

The present research is an attempt to obtain equilibrium data at 1.0 M ionic strength in aqueous solution—conditions which are comparable with those usually encountered in the investigation of complex ion equilibria. We chose to study *p*-methoxyanisole because this substance has only one monomercuration product, has some solubility in water, and was expected to come to equilibrium fairly rapidly. It was also possible, by waiting for a period of 1 year, to come close to equilibrium for the mercuration of benzene itself at room temperature. An effort was made to suppress the formation of dimercuration products by working at high ArH/Hg⁺² ratios.

(2) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," Part I. The Chemical Society, London, 1957, p. 28.

(5) C. Perrin and F. H. Westheimer, J. Am. Chem. Soc., 85, 2773 (1963).
(6) M. Carmack, M. M. Bazier, G. R. Hendrick, L. W. Kissinger, and E. H. Specht, *ibid.*, 69, 785 (1947).

(7) M. Malaiyandi, H. Sawatzky, and G. F. Wright, Can. J. Chem., 39, 1827 (1961).

Experimental

Materials.—The preparation of solutions of $Hg(ClO_4)_2$, HClO₄, NaClO₄, and NaOH is described elsewhere.⁸ Spectrograde benzene (Eastman) and cyclohexane (Matheson Coleman and Bell) were used. Solutions of 5 *F* NaCl were prepared from reagent grade material. *p*-Methoxyanisole (Matheson Coleman and Bell) was sublimed before use. Phenylmercuric hydroxide (from the same supplier) melted at 234–235° after recrystallization from aqueous NaOH (lit. m.p. 226–228°.⁹ A stock solution was prepared from a weighed sample, which dissolved in a known volume of redistilled H₂O over a period of several days.

2-Chloromercuri-4-methoxyanisole was synthesized as follows: 0.2 mole (27.6 g.) of *p*-methoxyanisole and 0.1 mole (31.9 g.) of mercuric acetate (Merck, C.P.) were added to 175 ml. of glacial acetic acid and heated to 65° for 2 hr. The mixture was poured into 600 ml. of dilute NaCl solution (25 g./600 ml.). The copious white precipitate was filtered with suction and washed twice with water and twice with cold 95% ethanol. The precipitate was heated in 1.2 l. of 95% ethanol and filtered hot; a considerable fraction of the solid was not soluble. The filtrate was cooled on ice and filtered, and the precipitate was recrystallized again from 700 ml. of 95% ethanol; this time only a small amount was insoluble. The product was filtered and dried in air. The yield was 13.0 g. (35% based on $Hg(OAc)_2$), m.p. 176–180°.

Mercuration Solutions.—Solutions of $Hg(ClO_4)_2$, $HClO_4$, and NaClO₄ in glass-stoppered conical flasks were made up at $\mu =$ 1.0 *M* over wide concentration ranges. Excess benzene or *p*-methoxyanisole was added, and the flasks were shaken so that the aqueous phase was saturated with organic material at all times. To study the reverse reaction, phenylmercuric hydroxide was substituted for mercuric perchlorate. In the case of *p*-methoxyanisole, the reverse reaction was studied by diluting into acid samples in which considerable forward reaction had already occurred, as determined by analysis for Hg^{+2} . The Hg^{+2} concentration then increased to a new equilibrium value.

All benzene solutions were allowed to stand for at least 1 year. The temperature was not controlled, but the temperature of a closed flask of water adjacent to the solutions was read from time to time. The thirty readings lay in the range 19.5-25.3° and averaged 22°. The *p*-methoxyanisole solutions were placed in a constant temperature bath maintained at 26.1 \pm 0.1° for at least 3.5 months.

Analytical Procedures.—Since some evaporation occurred, each component of the solutions was determined independently.¹⁰ The concentration of hydrogen ion was determined by titration with NaOH in the presence of excess NaCl (thus complexing all the mercury species) using a glass electrode indicator.

The solubility of benzene in the aqueous phase was determined by extracting aliquots of the reaction solution with cyclohexane and recording the ultraviolet spectrum of the organic phase. The molar absorptivity of benzene in cyclohexane was measured to be 235 1./mole-cm. at 254.6 m μ and 186 1./mole-cm. at 248.8 m μ .

p-Methoxyanisole was determined in the same way; solid *p*-methoxyanisole was first removed from the reaction solution by forcing the solution through a clean, dry sintered glass funnel. The mola: absorptivity of *p*-methoxyanisole in cyclohexane, determined from the spectrum of a solution prepared from a weighed sample of compound, is 3.17×10^3 l./mole-cm. at 289.1 m μ .

The concentration of $C_6H_5Hg^+$ at equilibrium was determined from the ultraviolet spectrum of each benzene reaction solution after the benzene had been extracted with cyclohexane.

The absorption spectrum of the phenylmercuric cation is presented in Fig. 1. It was obtained from the spectrum of an aliquot of $C_{6}H_{5}HgOH$ stock solution diluted into excess dilute perchloric acid. The spectrum of benzene in water is presented in Fig. 1 for comparison. Care was taken to avoid evaporation during preparation of the aqueous benzene solution of known concentration.

(9) R. M. Schramm, ibid., 69, 1831 (1947).

(10) A detailed description of these experimental procedures is contained in the Ph.D. Thesis of T. H. W., California Institute of Technology, 1964, along with numerical tabulation of the results on pp. 116 and 127.

⁽³⁾ W. J. Klapproth and F. H. Westheimer, J. Am. Chem. Soc., 72, 4461 (1950).

⁽⁴⁾ R. M. Schramm, W. Klapproth, and F. H. Westheimer, J. Phys. Colloid Chem., 55, 843 (1951).

⁽⁸⁾ Part I of this series: T. H. Wirth and N. Davidson, J. Am. Chem. Soc., 86, 4314 (1964).



Fig. 1.—Absorption spectra in aqueous solution: A, phenylmercuric perchlorate, $[HClO_4] = 0.19 F$; B, C_6H_6 .

In order to compensate for background absorbance due to other species, the concentration of $C_6H_6Hg^+$ was calculated from the difference in absorbance between the maximum at 256.2 m μ and a base line connecting the two adjacent minima. The $\Delta\epsilon$ indicated by the dashed line in Fig. 1 is 66.5; the total molar absorptivity is 268 at 256.2 m μ . The background was usually fairly small, but in some cases as much as 70% of the absorbance at 256 m μ was not due to $C_6H_6Hg^+$. We believe the background is mainly due to dimercurated products; it was more pronounced in solutions where some dimercuration was expected.¹¹

The spectrophotometric analysis for the product of the monomercuration of *p*-methoxyanisole (2-perchloratomercuri-4-methoxyanisole) was accomplished in the same general fashion. That this is indeed the major product was confirmed by treatment of a reaction solution with NaCl and purification of the precipitate. The product was recrystallized from EtOH and melted at 175–178°, which agrees with the synthetic sample.

Anal.¹² Calcd. for C₈H₉HgClO₂: C, 25.74; H, 2.43; Hg, 53.75; Cl, 9.50. Found: C, 25.55; H, 2.47; Hg, 55.18; Cl, 9.50.

The spectrum of 2-perchloratomercuri-4-methoxyanisole was determined in the following way. A water suspension of the synthetic sample of 2-chloromercuri-4-methoxyanisole was treated with freshly precipitated, thoroughly washed Ag₂O, shaken, and allowed to staud 24 hr. The solution was filtered through sintered glass and standardized by titration with 0.1000 M KSCN in dilute HNO₃ below 10° using FeNH₄SO₄ indicator. A sample was quantitatively diluted into aqueous perchloric acid-sodium perchlorate and the ultraviolet spectrum recorded. In Fig. 2, this spectrum is presented along with that of *p*-methoxyanisole in water for comparison. The concentration of 2,5-(H₃CO)₂C₆H₃Hg⁻ in the reaction solutions was then determined from the absorbance at 295.0 m μ (ϵ = 3.58 × 10³ 1./mole-cm.).

Unfortunately, the spectrum of the monomercurated product contains no fine structure to permit elimination of background due to polymercuration. If excess $Hg(ClO_4)_2$ reacts with the substrate, both the wave length and the intensity of the absorption increase beyond those of the monomercurated product. In all the reaction solutions, 295 m μ was the wave length of maximum absorbance. However, the peak is broad enough that moderate contamination might escape detection.

If the equilibrium constant for the second step of mercuration were the same as that of the first, then the ratio of concentration of dimercurated product to monomercurated product would equal that of monomercurated product to substrate. In some solutions, the latter ratio is as high as 0.5. Taking the greater molar absorptivity of dimercurated material into account, then, polymercuration might cause an error as large as a factor of two. We believe the actual error due to polymercuration to be less than this, however, since there was no systematic trend in the results that could be attributed to polymercuration. Determination of $[Hg^{-2}]$ at 10^{-3} to 10^{-5} M in the presence of

Determination of $[Hg^{-2}]$ at 10^{-3} to 10^{-5} M in the presence of 10 to 100-fold excess of mercurated products was performed spectrophotometrically. The method takes advantage of the ultraviolet absorption of the $HgCl_4^{-2}$ complex and the fact that



Fig. 2.—Spectra in aqueous solution: A, p-methoxyanisole; B, 2-perchloratomercuri-4-methoxyanisole (in 0.05 F HClO₄-0.95 F NaClO₄).

arylmercuric cations cannot form such complexes. Aliquots of reaction solution were treated with concentrated NaCl and extracted successively with benzene and ether (with *p*-methoxyanisole, only ether was used). The partially precipitated arylmercuric chlorides are covalent compounds and fairly soluble in these solvents. Free Hg⁺² ion, on the other hand, is converted to HgCl₄⁻², which remains in the aqueous phase. After extraction of the interfering mercuration products, the absorbance of the aqueous phase at 230 mµ was used to determine the free Hg⁺² concentration in the reaction solutions. The procedure was calibrated with repeated analyses of acidic Hg(ClO₄)₂ solutions of two different (known) concentrations.

This procedure is very sensitive to interference from unextracted compounds. Although phenylmercuric chloride is completely extracted from aqueous solution by ether, polymercurated products are a potential source of interference. However, the spectra of the chloride solutions after extraction correspond closely to that of $HgCl_4^{-2}$ at all wave lengths. It is not believed that this type of interference was significant except perhaps at very low Hg^{-2} concentrations.

Results and Discussion

From the concentrations of Hg^{+2} , H^+ , unreacted aromatic compound, and mercurated product in the aqueous phase, $K_{\rm M}$ was calculated for each solution.¹⁰

$$K_{\rm M} = \frac{[{\rm ArHg^+}][{\rm H^+}]}{[{\rm ArH}][{\rm Hg^{+2}}]}$$
(5)

The average value was

$$K_{\rm M} = 300 \pm 230 \tag{6}$$

for Ar = C_6H_5 (22 ± 3°, μ = 1.0-1.2 M).¹³ For *p*-methoxyanisole (Ar = 2,5-(H₃CO)₂C₆H₃)

$$K_{\rm M} = 470 \pm 360 \tag{7}$$

 $(26.1^{\circ}, \mu = 1.0-2.0 M)$. In both cases $K_{\rm M}$ increases distinctly with increasing acid concentration, but the scatter is high. Figure 3 shows the results for the mercuration of *p*-methoxyanisole, which are typical.

The scatter can be explained in terms of temperature and ionic strength variations, and analytical inaccuracies. The apparent systematic variation of the equilibrium quotient with acid is more mysterious. It may be due to a strong decrease in the activity coefficient of $C_6H_5Hg^+$ as protons replace sodium ions in the medium, or perhaps even to a labile $H^+-C_6H_5Hg^+$ complex. The fact that benzene itself is 30% more

⁽¹¹⁾ Reference 10, p. 113.

⁽¹²⁾ By Schwarzkopf Microanalytical Laboratory.

⁽¹³⁾ The solutions were prepared at $\mu = 1.0 \ M_{\odot}$ Evaporation, the amount of which was computed from the measured [H⁺] and the initial concentrations, caused an increase in ionic strength.

soluble in 1 F HClO₄ than in 1 F NaClO₄ lends credence to these possibilities.

If either of the explanations is correct, the lower values of $K_{\rm M}$ correspond most closely to the conventional equilibrium constant. In the absence of more accurate data or independent evidence, however, it seems preferable to propose the average value.

We have determined, then, that the equilibrium quotient of reaction 1 is two orders of magnitude greater than that of reaction 2.

Therefore, equilibrium in the reaction

 $C_5H_5N^-Hg^+ + C_6H_6 \Longrightarrow C_5H_5NH^+ + C_6H_6Hg^+$ (8)

favors the products. While solvation effects have a strong influence on equilibria in aqueous solution, it seems likely the position of this equilibrium reflects relative strengths of aromatic carbon and aromatic nitrogen bonds with Hg(II).

From a practical point of view, this work points out that in aqueous solution, nonacidic aromatic hydrogens may in fact be replaced by Hg^{+2} . This is important in the study of the interaction of Hg(II) with complex nitrogen heterocycles, including those of biological significance.



Fig. 3.— Variation of the equilibrium quotient for the mercuration of p-methoxyanisole with $[H^+]$: solid points, forward reaction; open points, reverse reaction; circles, squares, and triangles represent solutions of decreasing $[Hg^{-2}]$ $(1 \times 10^{-5} \times 10^{-4} M)$.

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[CONTRIBUTION NO. 3117 FROM THE GATES, CRELLIN, AND CHURCH LABORATORIES OF CHEMISTRY, PASADENA, CALIFORNIA]

Mercury(II) Complexes of Guanidine and Ammonia, and a General Discussion of the Complexing of Mercury(II) by Nitrogen Bases¹

By Thomas H. Wirth and Norman Davidson

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The stability constants of guanidine and ammonia complexes of Hg(II) have been measured potentiometrically. For guanidine, the reactions and equilibrium constants at 27°, $\mu = 1.0 \ M$ (NaClO₄), are: 2RH⁺ + Hg⁺² = R₂Hg⁺² + 2H⁺, $K_2 = 7.4 \times 10^{-3}$; RH⁺ + Hg⁺² + H₂O = RHgOH + 2H⁺, $K_1^{\rm H} = 2.7 \times 10^{-4} \text{ mole/l}$. [R = (H₂N)₂CNH]. The pK_A of the guanidinium ion was determined pectrophotometrically to be 13.54 at 27°, $\mu = 1.0 \ M$ (NaClO₄), 2NH₄⁺ + Hg⁺² = (NH₃)₂. Hg⁺² + 2H⁺, $K_2 = 0.08 \pm 0.02$. The ammonia [25°, $\mu = 1.0 \ M$ NaClO₄)], 2NH₄⁺ + Hg⁺² = (NH₃)₂. Hg⁺² + 2H⁺, $K_2 = 0.08 \pm 0.02$. The ammonia results are in good agreement with the classic measurements of Bjerrum. An extensive tabulation of the binding constants of nitrogen bases for Hg⁺² and H⁺ is presented and the approximate linear free energy relationship is discussed.

Introduction

For many organic nitrogen ligands and metal ions, a parallel exists between the basicity of the ligand and the stability of the metal-ligand complex.^{2,3} Guanidine is among the strongest organic bases known.⁴ It is therefore of interest to study its binding with metal ions in order to test this relationship over the widest possible range. Very little is known about the characteristics of guanidine as a ligand, however. Few solid guanidine complexes have been prepared. Wormser⁵ studied the formation of the guanidine-Ag(I) complex in solution, but calculated no stability constants.

In this work, the potentiometric method was employed to study complexes of guanidine with Hg(II). The 2:1 complex was found to be stable enough that HgO does not precipitate in basic solutions containing guanidinium ion in excess. Evidence for a mixed complex, RHgOH, was obtained ($R \equiv$ guanidine).

(5) Y. Wormser, J. Chim. Phys., 46, 658 (1949).

The complexes of Hg(II) with ammonia were also studied potentiometrically. This system has already been studied by Bjerrum⁶ in his classical investigations of ammine complexes. Bjeruum himself pointed out, however, that his glass electrode method is less suitable for studying this system than the many other systems he investigated. Hg(II) is so strongly bound by amines—including ammonia—that the pH is not a sensitive measure of complex formation at the high acidities necessary to partially dissociate the complexes.

Experimental

Materials.—Guanidine perchlorate and nitrate were prepared by neutralizing a slurry of guanidine carbonate (Eastman Organic Chemicals) with the appropriate concentrated acid. The resulting mixtures were cooled and filtered. The perchlorate was recrystallized twice from absolute ethanol and dried in a vacuum desiccator using a Dry Ice-acetone trap. Heating at 105° for 1 hr. produced no weight loss. The melting point was 252- 255° ; lit. m.p. 240° .⁷ The nitrate was recrystallized from water, dried, and dissolved in hot absolute methanol. The solution was evaporated to half its original volume and filtered. After drying in a vacuum desiccator over CaSO₄, the compound melted at 216- 218° , which compared with literature values of

⁽¹⁾ This is the fourth and final paper in the series "Studies of the Chemistry of Mercury in Aqueous Solution."

⁽²⁾ J. Bjerrum, Chem. Rev., 46, 381 (1950)

⁽³⁾ R. J. Bruehlman and F. H. Verhoek, J. Am. Chem. Soc., 70, 1401 (1948).

 ⁽⁴⁾ D. J. Cram and G. S. Hammond, "Organic Chemistry," 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 173-174.

⁽⁶⁾ J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," Thesis, P. Haase and Son, Copenhagen, 1941, pp. 164-173.

⁽⁷⁾ A. Glasner and A. Makovsky, J. Chem. Soc., 182 (1953).