than 0.04 that of the corresponding Hg(II) complex if it is to be detectable potentiometrically.[19] Spectrophotometric detection requires ligands, the spectra of which change considerably on complexing. The high ultraviolet absorbance of Hg_2^{+2} and the absorbance of Hg(II) complexes increase the difficulty of observation.

Therefore, it is not surprising that more Hg(I)–nitrogen complexes have not been detected, even if they exist. However, neither Hg(I)–ammonia nor

(19) Reference 1, pp. 29–31.

Hg(I)–guanidine complexes are stable enough to be detected potentiometrically.[12a] Hg(I) complex stability may increase less strongly with increasing ligand basicity than the stability of Hg(II) complexes. It should then be possible to detect other Hg(I) complexes with amines of low basicity, but none with amines of high basicity.

The Mercuration of Aniline in Acidic Solution. Mercury(II) Complexes with Mercurated Aniline Derivatives[1,2]

By Thomas H. Wirth and Norman Davidson

Spectrophotometric studies of acidic $Hg(ClO_4)_2$ solutions containing small amounts of aniline or p-acetoxymercurianiline indicate that aniline is mercurated in such solutions, and that the mercuration products form labile complexes with Hg^{+2}. These complexes are characterized by an intense ultraviolet absorption band between 330 and 335 mμ, the molar absorptivity of which ranges from 10^3 to 10^4 l./mole-cm., depending on the degree of mercuration. The equilibrium constant of the reaction p-$^+HgC_6H_4NH_3^+$ + Hg^{+2} = p-^-Hg-$C_6H_4NH_3Hg^{+2}$ + H^+ is 1.5 at 27°, μ = 1.0 M ($NaClO_4$). The value of this constant changes only slightly as the number of mercury atoms on the ring varies. The molar absorptivity of the p-$^+HgC_6H_4NH_2Hg^{+2}$ complex is 1.1 × 10^3 l./mole-cm. at 331 mμ. An explosive, crystalline compound of simplest formula $C_6NH_3Hg_3$-$(ClO_4)_2 \cdot 4H_2O$ has been isolated from acidic solutions 2 F in $Hg(ClO_4)_2$ and 0.1 F in $C_6H_5NH_3ClO_4$.

Introduction

Potentiometric and spectrophotometric studies of $Hg(ClO_4)_2$–$C_6H_5NH_3ClO_4$ solutions in aqueous perchloric acid[3] reveal that slow reactions occur in such solutions and are accompanied by spectral changes, drifting potentials, and eventually by the formation of precipitates. These reactions can be distinguished sharply from the instantaneous formation of labile Hg–N complexes. The present paper deals with spectrophotometric studies and with the isolation of a crystalline aniline–mercury–perchlorate compound, which indicate that the slow reactions are aromatic mercuration.

Mercuration is a well-known example of electrophilic substitution.[4] Hg(II) salts, particularly mercuric acetate, react with aromatic substrates

$$C_6H_6 + Hg(Ac)_2 \longrightarrow C_6H_5HgAc + HAc \qquad (1)$$
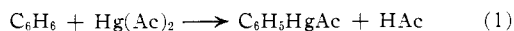
Carmack,[5] Westheimer,[6–9] and their co-workers have directed attention to mercuration by $Hg(NO_3)_2$ and $Hg(ClO_4)_2$ in aqueous solution.

Aromatic amines are easily mercurated; aniline is mercurated in aqueous solution at room temperature by mercuric acetate.[10] The voluminous early work on compounds of mercury with aromatic amines has been surveyed by Whitmore.[11] The effect of HAc,

NaAc, $HClO_4$, $NaClO_4$, and HNO_3 on the rate of mercuration of aniline by $Hg(Ac)_2$ in aqueous solution was recently studied by Wronski.[12] He found that the rate is decreased by acids. This is to be expected, since free aniline is a much better substrate in aromatic substitution than is the anilinium ion. Unfortunately, the studies were not sufficiently complete to permit quantitative interpretation, for the rate of mercuration is sensitive to salt concentration,[8,9] as well as to mercury(II)–acetate complex formation.

Experimental

Materials.—Solutions of acids, bases, inorganic salts, C_6H_5-NH_3ClO_4, and $Hg(ClO_4)_2$–$C_6H_5NH_3ClO_4$ solutions containing excess Hg(II) were prepared as in part I.[3]

p-Acetoxymercurianiline was prepared by the method of Dimroth.[10] It was recrystallized by dissolving it in an ammoniacal NH_4Ac solution, adding decolorizing charcoal, and filtering. After the solution was neutralized with HAc, the compound precipitated slowly. This method was adapted from that used by Vecchiotti for 2,4-diacetoxymercurianiline.[13] After drying in a vacuum desiccator, the crystals melted at 166–167.5°; lit. m.p. 167°.[10] A stock solution of *para*-mercurated aniline was prepared by dissolving a weighed sample in an $HClO_4$–$NaClO_4$ solution and diluting to known volume.

The p-$^+HgC_6H_4NH_2$ Complex with Hg(II).—The spectrophotometric procedure used to study the Hg(II) complex of aniline[3] was also employed here. The absorbance at 331.0 mμ, where the 1:1 complex is the only absorbing species initially present, was recorded as a function of time. Occasionally 10-cm. cells were used. Data were obtained at 27°, μ = 1.0 M.

The Crystalline Mercuration Product.—Several weeks after preparation, a yellow, crystalline compound precipitated copiously from a solution 2 F in $Hg(ClO_4)_2$, 0.1 F in $C_6H_5NH_3ClO_4$, and 0.5 F in $HClO_4$. (Single crystals can be obtained in 1–2.5 weeks if a small sample of the solution is seeded.) The solid was filtered off and washed, first with concentrated $Hg(ClO_4)_2$ solution, then with large amounts of water. If the supernatant is diluted by a factor of 2 or 3 with water, a yellowish white precipitate forms.

(1) Paper II in the series "Studies of the Chemistry of Mercury in Aqueous Solution."

(2) This work is described in more detail in the Ph.D. Thesis by T. H. W., California Institute of Technology, 1964.

(3) T. H. Wirth and N. Davidson, *J. Am. Chem. Soc.*, **86**, 4314 (1964).

(4) F. C. Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., New York, N. Y., 1921, pp. 34–37, 163 ff.

(5) M. Carmack, M. M. Bazier, G. R. Handrick, L. W. Kissinger, and E. H. Specht, *J. Am. Chem. Soc.*, **69**, 785 (1947).

(6) F. H. Westheimer, E. Segel, and R. Schramm, *ibid.*, **69**, 773 (1947).

(7) W. J. Klapproth and F. H. Westheimer, *ibid.*, **72**, 4461 (1950).

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

(9) C. Perrin and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 2773 (1963).

(10) O. Dimroth, *Ber.*, **35**, 2032 (1902).

(11) Reference 4, pp. 205–253.

(12) M. Wronski, *Roczniki Chem.*, **34**, 947 (1960).

(13) L. Vecchiotti, *Gazz. chim. ital.*, **II44**, 34 (1914).

The yellow crystalline precipitate is not significantly soluble in water, ethanol, or dilute $Hg(ClO_4)_2$. It turns white on treatment with HCl or H_2SO_4. If treated with 1 F HClO$_4$ soon after preparation, it dissolves easily, but after drying (at 50% humidity) it dissolves only with difficulty. The compound explodes with extraordinary violence if it is struck with a hammer. It does not deteriorate if stored in the dark.

The solid is closely related to aniline. A crystalline sample was digested for several hours at 70° in 3 F HCl, whereupon it finally dissolved. H_2S was bubbled through the solution and the black HgS precipitate filtered off. The solution was boiled to remove excess H_2S, made slightly basic with NaOH, and diluted with water. The ultraviolet spectrum showed an absorption band at 280 mμ; on acidification the characteristic anilinium band replaced it, confirming the presence of aniline. A substantial fraction of the carbon in the compound is accounted for by this spectrum; therefore, it is probable that no oxidation or degradation of the aniline has occurred.

Although the crystals do not dissolve completely in concentrated aqueous $Hg(ClO_4)_2$, a strong absorption at 335 mμ develops slowly in the solution. As we shall see, this is characteristic of the labile N–Hg complexes of C-mercurated aniline.

A second sample was prepared from an essentially similar $Hg(ClO_4)_2$ solution (1.6 F $Hg(ClO_4)_2$, 0.07 F $C_6H_5NH_3ClO_4$, 0.3 F HClO$_4$); the sample was dried at 50% relative humidity over a saturated $Mg(NO_3)_2 \cdot 6H_2O$ solution. If dried more exhaustively in a vacuum desiccator over anhydrous $CaCl_2$, the crystals lose 8.30% of their weight and are converted to a yellow powder. On exposure to the air, this weight loss is reversed.

Mercury and carbon analyses of the material dried at 50% humidity were performed by Schwarzkopf Microanalytical Laboratories. In their Hg analysis, the compound is decomposed in a sealed tube at 400° and titrated for Hg(II) with sodium diethyl dithiocarbamate.[14]

The compound was analyzed for perchlorate in this laboratory using tetraphenylarsonium chloride in a modification of the procedure of Willard and Perkins.[15] Weighed samples of the compound were digested in 25 ml. of 3 F HCl on a steam bath at 90–100° until they dissolved. This required 8 hr. Each warm sample was saturated with H_2S and filtered through a sintered glass funnel; the funnel was rinsed and the washings were combined with the filtrate. The combined solutions were boiled for 15 min. to expel excess H_2S. Each sample was neutralized with 50% NaOH, then made slightly acidic with HCl. $(C_6H_5)_4AsCl$ solution (60 ml.) was added (0.011 F, prepared from solid $(C_6H_5)_4AsCl$ purchased from G. Frederick Smith). The samples were allowed to stand overnight and filtered into tared crucibles; the precipitates were dried and weighed.

The compound was also analyzed for mercury by the method of Schulek and Floderer.[16]

Results and Discussion

Successive spectra of a $C_6H_5NH_3ClO_4$–$Hg(ClO_4)_2$ solution are shown in Fig. 1. The most characteristic feature of the slow spectral change is the appearance of a strong absorption band at 330 mμ. A very similar band, which is due to the labile p-$^+HgC_6H_4NH_2Hg^{+2}$ complex, appears instantaneously if $Hg(ClO_4)_2$ solution is added to an acidic solution of $para$-mercurated aniline. This band intensity increases on standing, however, indicating, we believe, that further mercuration is occurring.

The absorbance at 331.0 mμ of $para$-mercurated aniline solutions containing excess Hg(II) was extrapolated to the time of mixing. The initial components do not absorb at this wave length. If the absorbance is due to a 1 : 1 complex

$$\frac{[RP]_0}{Z} = \frac{1}{\epsilon_1^P} + \frac{1}{\epsilon_1^P K_1^P} \frac{[H^+]}{[Hg^{+2}]} \qquad (2)$$

$[RP]_0$ is the total amount of p-acetoxymercurianiline added, ϵ_1^P is the molar absorptivity of the complex, Z
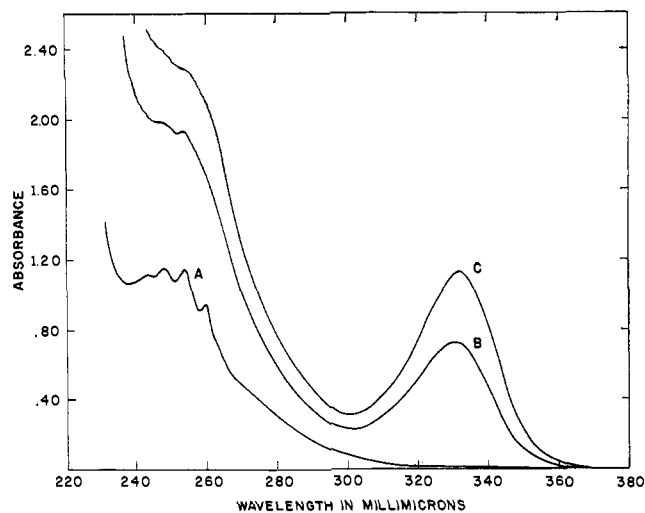
(14) R. Wickbold, Z. Anal. Chem., **152**, 261 (1956).
(15) H. H. Willard and L. R. Perkins, Anal. Chem., **25**, 1634 (1953).
(16) E. Schulek and I. Floderer, Z. Anal. Chem., **96**, 388 (1934).

Fig. 1.—Spectra of an aniline–Hg(II) solution (0.019 F Hg-$(ClO_4)_2$, 0.0026 F $C_6H_5NH_3ClO_4$, 0.25 F HClO$_4$, 0.73 F NaClO$_4$): elapsed times (A) 3 to 5 min.; (B) 1 day; (C) 3 days.

is the absorbance at 331.0 mμ extrapolated to zero time, and K_1^P is the equilibrium constant of the reaction

$$p\text{-}^+HgC_6H_4NH_3^+ + Hg^{+2} \rightleftharpoons$$
$$p\text{-}^+HgC_6H_4NH_2Hg^{+2} + H^+ \qquad (3)$$
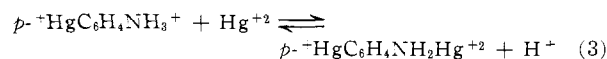
We assume here that the moderately high acidity of these solutions dissociates the acetate salt into acetic acid and a mercurated cation. The association constant of a similar salt, CH_3HgAc, is 3×10^3 l./mole.[17] This suggests that under the conditions of our experiments most unfavorable to dissociation ($[H^+] = 0.03$ M, $[RP]_0 = 4 \times 10^{-4}$ F), the ratio $[RHgAc]/[RHg^+]$ is $10^{-3.1}$. Certainly, then, the acetate salt is completely dissociated. Acetic acid does not contribute to the absorbance at 331 mμ.

To obtain $[H^+]$, the formal acid concentration was corrected for reaction with the mercurated amine (2 equiv./mole). Additional corrections for complex formation were not made, since $[RP]_0 \leq 0.01[H^+]_0$.

In Fig. 2, $[RP]_0/Z$ is plotted against $[H^+]/[Hg^{+2}]$.[18] From this plot, $\epsilon_1^P = 1.1 \times 10^3$ l./mole-cm. at λ 331.0 mμ; $K_1^P = 1.5$ (27°, $\mu = 1.0$ M). It is interesting that the mercurated complex is slightly more stable than the nonmercurated one ($K = 0.68$).

2,4-Dimercurated aniline also forms a Hg(II) complex with an intense ultraviolet absorption band in the 330–335 mμ region. The absorbance increases slowly here as well, and the equilibrium was not studied systematically. However, the molar absorptivity of the complex with Hg^{+2} was roughly estimated to be $\epsilon_1^{2.4}$ $\sim 4 \times 10^3$ l./mole-cm. at λ 333 mμ.[19]

An intense band in the 330–335 mμ region appears to be characteristic of the ultraviolet absorption spectra of ring-mercurated anilines when the amino group is bound to Hg(II). It is believed, therefore, that the appearance of this band in $Hg(ClO_4)_2$ solutions containing small amounts of aniline is due to mercuration of the aniline and formation of Hg(II) complexes with the products.

Eventually, the spectral changes in these solutions cease. If equilibrium among the various possible ring-mercurated anilines has then been attained, the final

(17) R. B. Simpson, J. Am. Chem. Soc., **83**, 4711 (1961).
(18) The numerical data in this paper are tabulated in ref. 2.
(19) For details, see ref. 2, pp. 67, 70.

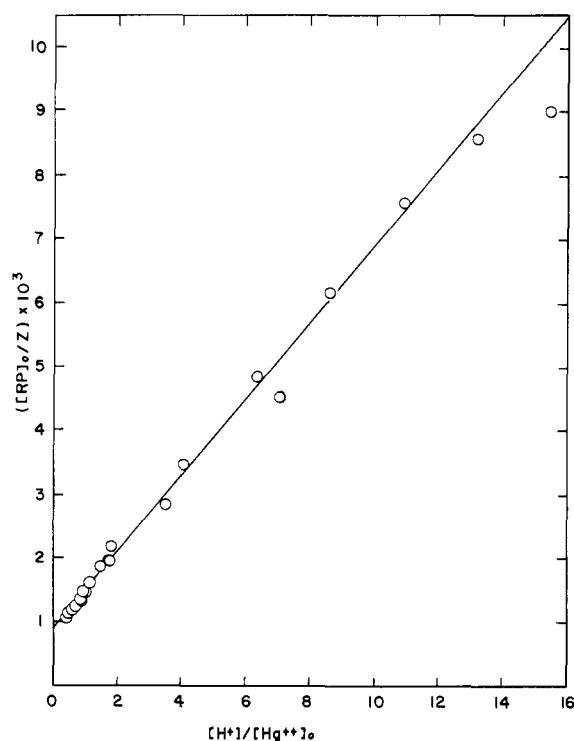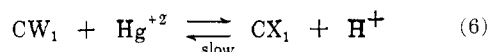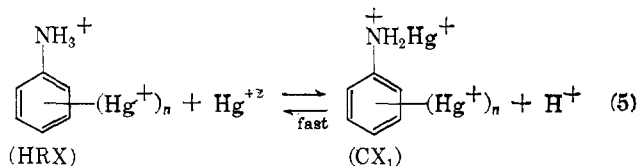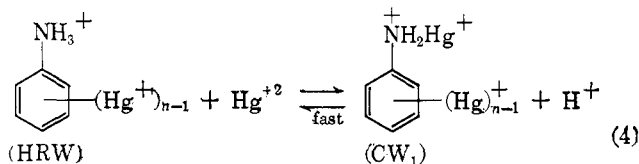Fig. 2.—Formation constant of the p-$^+HgC_6H_4NH_2Hg^{+2}$ complex.

absorbance should not depend on whether aniline or *para*-mercurated aniline was the original starting material.

This is indeed the case. The spectra of the aniline–Hg(II) and *para*-mercurated aniline–Hg(II) solutions were taken after standing about 4 months in the dark. In Fig. 3, $[R]_0/Z$ is plotted as a function of $[H^+]/[Hg^{+2}]$.[18] $[R]_0$ is the formal concentration of amine; Z is here the absorbance at the maximum in the 330–335 region. Solutions in which precipitates developed are omitted. It is clear that the functional behavior is independent of the starting material.

The data suggest that the products are distributed principally between two different stages of mercuration, and that the following principal equilibria exist.

$$\underset{(HRW)}{\overset{NH_3^+}{\underset{}{\bigcirc}}\!\!-(Hg^+)_{n-1} + Hg^{+2}} \underset{\text{fast}}{\rightleftharpoons} \underset{(CW_1)}{\overset{\overset{+}{N}H_2Hg^+}{\underset{}{\bigcirc}}\!\!-(Hg)_{n-1}^+ + H^+} \quad (4)$$

$$\underset{(HRX)}{\overset{NH_3^+}{\underset{}{\bigcirc}}\!\!-(Hg^+)_n + Hg^{+2}} \underset{\text{fast}}{\rightleftharpoons} \underset{(CX_1)}{\overset{\overset{+}{N}H_2Hg^+}{\underset{}{\bigcirc}}\!\!-(Hg^+)_n + H^+} \quad (5)$$

$$CW_1 + Hg^{+2} \underset{\text{slow}}{\rightleftharpoons} CX_1 + H^+ \quad (6)$$

Abbreviated symbols for the four major species are given in parentheses below their formulas. The equilibrium constant of reaction 4 is

$$K_1^W = \frac{[CW_1][H^+]}{[HRW][Hg^{+2}]} \quad (7)$$

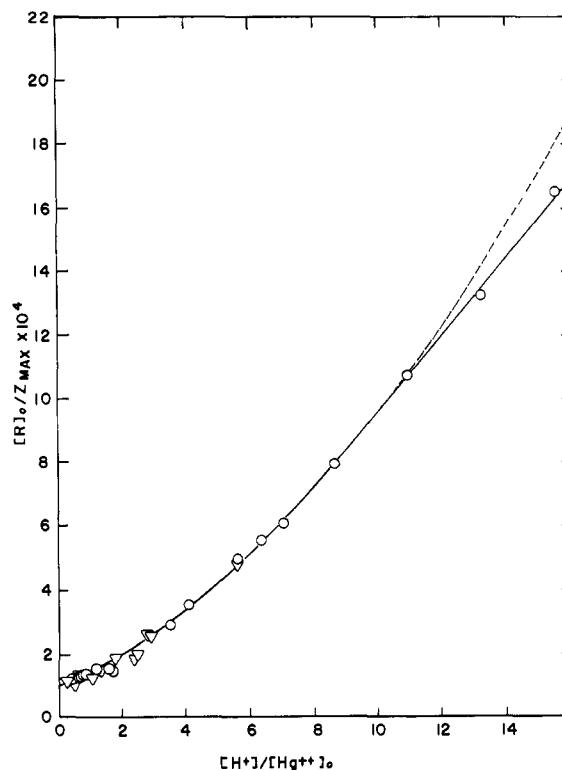K_1^X and K_{WX} are the analogous constants for reactions 5 and 6.

Fig. 3.—Aniline–Hg(II) and *para*-mercurated aniline–Hg(II) solutions at equilibrium: triangles, aniline solutions; circles, p-acetoxymercurianiline solutions.

At equilibrium

$$[R]_0 = [HRW] + [CW_1] + [HRX] + [CX_1] \quad (8)$$

Rearranging the equilibrium constant expressions and substituting, we obtain

$$[R]_0 = [CX_1]\left\{1 + \left(\frac{1}{K_1^X} + \frac{1}{K_{WX}}\right)\frac{[H^+]}{[Hg^{+2}]} + \frac{1}{K_1^W K_{WX}}\left(\frac{[H^+]}{[Hg^{+2}]}\right)^2\right\} \quad (9)$$

We expect both CW_1 and CX_1 to contribute to the intensity of the 330-mμ band. Therefore

$$Z = \epsilon_1^W[CW_1] + \epsilon_1^X[CX_1] \quad (10)$$

from which

$$Z = [CX_1]\left(\epsilon_1^X + \frac{\epsilon_1^W}{K_{WX}}\frac{[H^+]}{[Hg^{+2}]}\right) \quad (11)$$

Dividing eq. 9 by eq. 11, we obtain

$$\frac{[R]_0}{Z} = \frac{1 + \left(\frac{1}{K_1^X} + \frac{1}{K_{WX}}\right)x + \left(\frac{1}{K_1^W K_{WX}}\right)x^2}{\epsilon_1^X + \left(\frac{\epsilon_1^W}{K_{WX}}\right)x} \quad (12)$$

where x is $[H^+]/[Hg^{+2}]$. We correctly predict, then, that $[R]_0/Z$ is a function of $[H^+]/[Hg^{+2}]$. The function would be linear in the absence of HRW and CW_1.

A parabola was fit to the data for which $[H^+]/[Hg^{+2}] < 10$ by the method of least squares. The result is the dashed line in Fig. 3 which is the function

$$[R]_0/Z = (0.94 + 0.46x + 0.042x^2) \times 10^{-4} \quad (13)$$

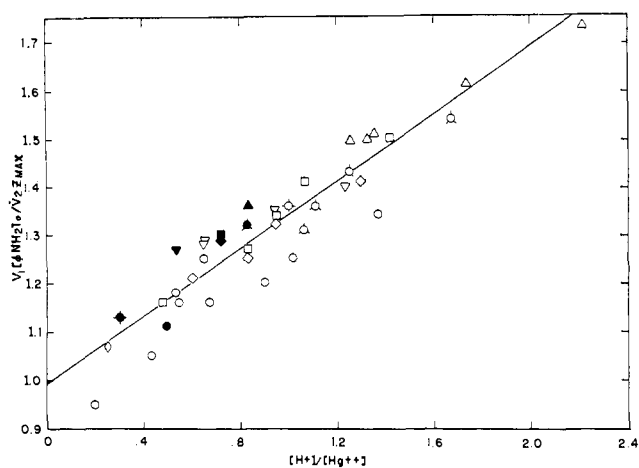This represents the data excellently if $x < 10$, but the points for which $x > 10$ lie much more nearly on a

Fig. 4.—Addition of $HClO_4$, NaOH, or $Hg(ClO_4)_2$ to aniline–Hg(II) solutions after equilibration; the solid points represent the original equilibrated solutions, and the open points of the same shape the solutions immediately after addition of $HClO_4$, NaOH, or $Hg(ClO_4)_2$.

straight line tangent to the parabola, in agreement with the form of eq. 12.

It is probable that HRW, HRX, etc., are not single species at all, but are mixtures of isomers present in an equilibrium ratio which is independent of $[H^+]$ and $[Hg^{+2}]$. Such mixtures would exhibit apparent molar absorptivities and apparent K_1's. It is useful to note that the y-intercept in Fig. 3 is $1/\epsilon_1^X$, where ϵ_1^X is the apparent molar absorptivity of the most highly mercurated aniline–H (II) complex(es) existing in these solutions. From eq. 13, $\epsilon_1^X = 1.1 \times 10^4$ l./mole-cm., which exceeds ϵ_1^P by a factor of 10 and $\epsilon_1^{2,4}$ by a factor of 2.5.

The above hypothesis requires that addition of acids, bases, or $Hg(ClO_4)_2$ produces immediate and pronounced changes in the spectra of the equilibrated solutions. This indeed occurs. Concentrated perchloric acid, sodium hydroxide, or $Hg(ClO_4)_2$ was added by micropipet to samples of aniline–Hg(II) solutions which had equilibrated 3 to 4 months. The absorbance was immediately recorded at the equilibrium λ_{max}.

Immediate and marked changes in absorbance occurred; slower and much smaller changes followed. Perchloric acid caused a decrease in intensity; base and $Hg(ClO_4)_2$ caused an increase. Concentrated reagents were added successively in random order. The absorbance after each addition was extrapolated to the time of mixing.

A quantitative interpretation is not feasible if the products exist in more than one stage of mercuration. However, if $[H^+]/[Hg^{+2}]$ in the original equilibrated solution is sufficiently small, only products of the type HRX and CX_1 are present in significant concentration. If V_1 is the initial volume of the sample, and V_2 the volume after addition of concentrated reagent

$$V_1[C_6H_5NH_2]_0/V_2 = [HRX] + [CX_1] \quad (14)$$

If

$$Z = \epsilon_1^X[CX_1] \quad (15)$$

$$\frac{V_1[C_6H_5NH_2]_0}{V_2Z} = \frac{1}{\epsilon_1^X} + \frac{1}{\epsilon_1^X K_1^X}\left(\frac{[H^+]}{[Hg^{+2}]}\right) \quad (16)$$

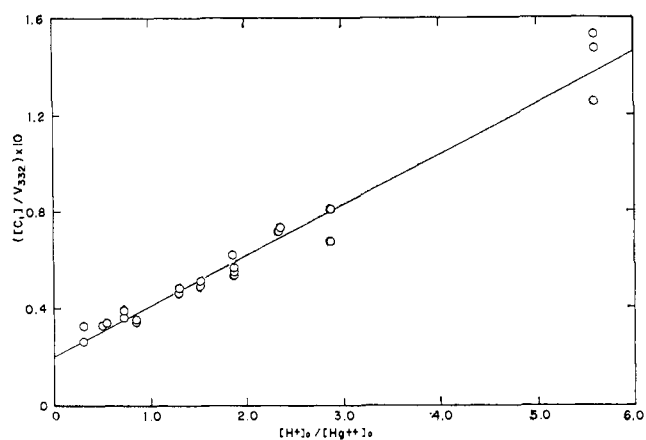The results for all solutions in which $[H^+][Hg^{+2}]_0 < 1$ are presented in Fig. 4. From the intercept of the

Fig. 5.—Aniline–Hg(II): initial rates of spectral changes at λ 332 mμ.

line, ϵ_1^X is 1.0×10^4 l./mole-cm. This agrees with the previous value. From the ratio of intercept to slope, $K_1^X = 3$; this is slightly larger than either K_1 or K_1^P.

In conjunction with the previous[3] determination of K_1 and the present determination of K_1^P, the absorbance of the complex solutions in the 330-mμ region was recorded as a function of time. The initial rate of increase in absorbance, V_λ (in absorbance units per minute at wave length λ), was obtained for each solution from the slope of the tangent to the absorbance $vs.$ time curve. The curves are all nearly linear.

Mercuration of benzene obeys a second-order rate law.[8] If the same is true of aniline, the reaction rate v is

$$v = k[Hg^{+2}][C_6H_5NH_2] \quad (17)$$

But the product is in labile equilibrium with its Hg(II) complex. Therefore

$$v = \frac{d}{dt}([HRV] + [CV_1])$$

where HRV is the product (which is probably mono-mercurated), and CV_1 is the corresponding Hg(II) complex. If $K_1^V \equiv [CV_1][H^+]/[HRV][Hg^{+2}]$

$$v = \left(1 + \left(\frac{1}{K_1^V}\frac{[H^+]}{[Hg^{+2}]}\right)\right)\frac{d[CV_1]}{dt} \quad (18)$$

If the complex CV_1 absorbs but HRV does not, the absorbance Z at the wave length under consideration equals $[CV_1]\epsilon_1^V$. Further

$$[C_6H_5NH_2] = K_A\frac{[C_6H_5NH_3^+]}{[H^+]} = \frac{K_A}{K_1}\frac{[C_1]}{[Hg^{+2}]} \quad (19)$$

where K_A is the acid dissociation constant of C_6H_5–NH_3^+. From all of this, eq. 17 becomes

$$\left(1 + \frac{1}{K_1^V}\frac{[H^+]}{[Hg^{+2}]}\right)\frac{1}{\epsilon_1^V}\frac{dZ}{dt} = \frac{kK_A}{K_1}[C_1] \quad (20)$$

Since $dZ/dt = V_\lambda$ and kK_A/K_1 can be represented by k_C, we have

$$\frac{[C_1]}{V_\lambda} = \frac{1}{\epsilon_1^V k_C} + \frac{1}{\epsilon_1^V k_C K_1^V}\frac{[H^+]}{[Hg^{+2}]} \quad (21)$$

This equation is valid only for the initial rate; the complete rate expression is very complex. It can be seen from Fig. 5 that eq. 21 is obeyed.

Substitution of $para$-mercurated aniline for aniline as starting material does not change the argument,

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 ± 0.07% C, 60.7 ± 1.3% Hg, 22.3 ± 0.1% ClO$_4$, and 8.3% H$_2$O. This suggests that the empirical formula is C$_6$NH$_3$Hg$_3$(ClO$_4$)$_2$·4H$_2$O, for which the calculated composition is: 7.50% C, 62.6% Hg, 20.7% ClO$_4$, and 7.5% H$_2$O.

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 ClO$_4$ 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 *p*-acetoxymercurianiline 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.

$$\text{q} + Hg^{+2} \rightleftharpoons \text{r} + H^+ \quad (22)$$
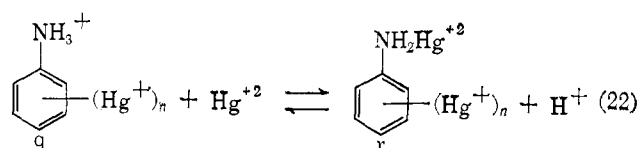
equilibrium constants of this reaction range between 0.6 and 3. (b) Slow, reversible reactions

$$\text{(Hg}^+)_n + Hg^{+2} \rightleftharpoons \text{(Hg}^+)_{n+1} + H^+ \quad (23)$$
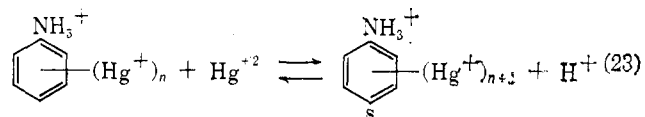
lead to the formation of several mercurated species in solution. (c) Species of type r with $n > 0$ are responsible for ultraviolet light absorption at wave lengths > 300 mμ. They have a characteristic band centered at 330–335 mμ. The molar absorptivities range between 1×10^3 and 1×10^4 l./mole-cm. (d) The rate of reaction 23 is proportional to the [C$_6$H$_5$NH$_2$][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 mμ is very curious. It lies 50–55 mμ 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.

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

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

The equilibrium quotients for the mercuration of benzene and *p*-methoxyanisole have been measured in dilute aqueous HClO$_4$–NaClO$_4$ solutions ($\mu \sim 1$ M). The results are that, for the reaction ArH + Hg^{+2} ⇌ ArHg$^+$ + H$^+$, $K = 300 \pm 230$ if Ar = C$_6$H$_5$ (22 ± 3°, $\mu = 1.0$–1.2 M) and $K = 470 \pm 360$ if Ar = 2,5-(H$_3$CO)$_2$C$_6$H$_3$ (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