MERCURY-AMINE COMPLEXES AND AROMATIC MERCURIALS-- A STUDY OF COMPOUNDS CONTAINING MERCURY-NITROGEN AND MERCURY-CARBON BONDS IN AQUEOUS SOLUTION

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ABSTRACT

The Hg(II) complexes of aniline, guanidine, and ammonia have been studied potentiometrically in aqueous solution with a mercury electrode. The stability of the HgR_2^{++} complexes of these compounds correlates well with their basicities. An $RHgOH^+$ complex (R = guanidine) has been identified potentiometrically and its stability determined.

Potentiometric evidence for the existence of a 1:1 Hg(I)-aniline complex was confirmed spectrophotometrically. The complex is less stable than the corresponding complex of Hg(II). No 2:1 complex ($Hg_2L_2^{++}$) was observed.

The 1:1 complexes of aniline and para-mercurated aniline with Hg(II) were studied spectrophotometrically. Cationic, ring mercurated anilines bind Hg(II) strongly; no decrease in complex stability occurs as $-Hg^+$ groups are added to the aromatic ring. Complexes of Hg(II) with mercurated anilines exhibit a unique ultraviolet absorption band at 330-335 mμ in aqueous solution.

Slow but pronounced spectral changes occur in aqueous $Hg(ClO_4)_2$-$HClO_4$ solutions containing small amounts of φNH_3ClO_4 which are allowed to stand. These changes have been interpreted in terms of mercuration of the aniline and the formation of Hg(II) complexes with the products.

Single crystals of an explosive Hg(II)-aniline compound $C_6NH_3Hg_3(ClO_4)_2 \cdot 4H_2O$ have been prepared.

Equilibrium in the mercuration of benzene and p-methoxy anisole has been studied at room temperature in aqueous $HClO_4$-$NaClO_4$ solution in the presence of excess organic. An analytical procedure utilizing the U.V. absorption of the $HgCl_4^{=}$ complex was used. The equilibrium quotient of the reaction $C_6H_6 + Hg^{++} = C_6H_5Hg^{+} + H^{+}$ lies in the range 70-500 .

CONTENTS

INTRODUCTION

Mercury (II) shows an extremely strong affinity for organic nitrogen ligands; in aqueous solution the Hg(II) ion forms stronger complexes with nitrogen bases than do the transition metal ions or even the other ions of the d-10 electronic configuration. Studies of the binding of Hg(II) by a variety of heterocyclic and aromatic nitrogen ligands have been carried out in this laboratory (1, 2, 3). Interest in the topic was stimulated in part by the role of Hg(II) in the study of biological systems which contain nitrogen compounds such as proteins and DNA. That work showed that the interaction of Hg(II) with such ligands is neither straightforward nor easily characterized.

The present rather diversified exploration of mercury complex ion chemistry began with the study of the Hg(II)-aniline complex. Aniline, the simplest aromatic amine, was chosen as a prototype to determine whether Hg(II) exhibits an unusually strong affinity for such compounds. But it was soon discovered that aqueous, acidic, Hg(II)-aniline solutions are not stable with time. In spite of this, it was possible to measure the stability constant of the complex φNH_2Hg^{++} spectrophotometrically and that of $(\varphi NH_2)_2Hg^{++}$ potentiometrically. (Throughout this thesis, φ represents C_6H_5-.) In the course of the latter measurements, a Hg(I)-aniline complex, $\varphi NH_2Hg_2^{++}$, was discovered. Spectrophotometric evidence confirmed the existence of this soluble mercurous-nitrogen complex. This is the first such complex to be investigated quantitatively.

A lengthy study of the solutions and solids produced by the slow reaction of Hg(II) with protonated aniline led to the conclusion that mercuration--electrophilic attack by mercury on the aromatic ring--occurs. The solid products and solutions resulting from the reaction are usually mixtures and are difficult to characterize. Under some conditions, however, a crystalline product can be obtained. The binding of Hg(II) ion by mercurated anilines was studied to help clarify the reactions which occur in Hg(II)-aniline solutions.

The work with aniline stimulated interest in the Hg-C bond, which, unlike most metal-carbon bonds, is stable in aqueous systems. One may think of aromatic mercurials as inert coordination compounds; the equilibrium constant of aromatic mercuration was investigated in order to compare aromatic carbon and aromatic nitrogen as ligands in binding mercury (II).

The stability constant of the $Hg(NH_3)_2^{++}$ complex was determined potentiometrically in order to obtain an accurate value. The binding of Hg(II) with guanidine was studied in order to test the correlation between complex stability and ligand basicity over a wider range of basicity and structure. It was found that in addition to the 2:1 guanidine-mercury(II) complex, R_2Hg^{++}, a mixed guanidine-hydroxide complex of mercury(II), $RHgOH^+$, forms.

CHAPTER I

MERCURY(I AND II) COMPLEXES OF ANILINE--POTENTIOMETRIC STUDIES. GENERAL EXPERIMENTAL PROCEDURES

Mercury(II) forms labile complexes with amines which are extremely stable in aqueous solution; the equilibrium

$$RH^{+} + Hg^{++} \rightleftarrows RHg^{++} + H^{+} , \qquad (I-1)$$

where RH^{+} is a protonated amine, lies far to the right except at low pH. The presence of significant concentrations of free H^{+} as the metal passes from the uncomplexed to the complexed form limits the usefulness of the glass-electrode method of determining stability constants (57). Therefore, potentiometric measurements with a mercury electrode and spectrophotometric methods were used.

Because of its low complexing tendency and transparency in the ultraviolet, perchlorate was chosen as the anion in these studies.

The Potentiometric Method--Principles

The mercury electrode. - Measurement of the concentration of Hg(II) ions in solution with a metallic mercury electrode differs from the ordinary potentiometric measurement in that the electrode reacts with the ion of interest:

$$Hg(liq) + Hg^{++} \rightleftharpoons Hg_2^{++} \quad . \tag{I-2}$$

The equilibrium constant $K = [Hg_2^{++}]/[Hg^{++}]$ is 88 at infinite dilution (5). It may require several hours for this reaction to attain equilibrium in the bulk of a solution. However, a mercury electrode placed in a Hg(II) solution takes on its equilibrium potential almost immediately except in very concentrated or rapidly stirred solutions (6). This shows that equilibrium is rapidly attained at the electrode surface.

Assuming only mononuclear complexes and recalling the stoichiometry of reaction I-2 , the equation for the conservation of Hg is

$$[Hg^{++}]_o = [Hg^{++}] + [Hg_2^{++}] + \Sigma_i [C_i] \ , \tag{I-3}$$

or

$$[Hg^{++}]_o = [Hg^{++}]\,(1 + K) + \Sigma_i [C_i] \tag{I-4}$$

at the electrode. The subscript o indicates total, formal concentration, and $[C_i]$ is the concentration of the i-th complex. Since accurate determination of K is difficult, equation I-3 is most useful if the concentration of Hg^{++} (and therefore of Hg_2^{++}) is small. Unless the

Hg^{++} ion is well complexed, HgO will precipitate at pH > 4-5. For these reasons, potentiometric measurements are made in the presence of excess ligand.

Calibration of the mercury electrode. - The cell used for potentiometric measurements can be represented in abbreviated form as

$$+ \text{S.C.E.} \parallel \text{Salt Bridge} \parallel Hg^{++} \mid Hg\ (\text{liq.}) - .$$

The potential E varies with the concentration of Hg(II) in the right hand compartment:

$$E = E_{02} + \frac{RT}{2F}\ \ell n\ [Hg^{++}]\ .$$

The empirical value of E_{02} cannot be determined directly, since Hg(II) added to the right hand compartment reacts to form Hg(I).

The potentials of the cells

$$+ \text{S.C.E.} \parallel \text{Salt Bridge} \parallel Hg_2^{++} \mid Hg(\text{liq.}) -$$

and

$$+ \text{S.C.E.} \parallel \text{Salt Bridge} \parallel Hg^{++}, Hg_2^{++} \mid Pt -$$

are

$$E = E_{01} + \frac{RT}{2F}\ \ell n\ [Hg_2^{++}]$$

and

$$E = E_{12} + \frac{RT}{2F}\,\ell n\left(\frac{[Hg^{++}]^2}{[Hg_2^{++}]}\right) .$$

The quantities E_{01} and E_{12} can be determined from the variation of the potential of these cells as the appropriate concentrations are varied. E_{02} can then be computed:

$$E_{02} = (E_{01} + E_{12})/2, \text{ and}$$

$$[Hg^{++}] = \exp\left[\frac{2F}{RT}(E - E_{02})\right] .$$

The equilibrium constant K is

$$K = \left(\frac{[Hg_2^{++}]}{[Hg^{++}]}\right)_{\text{at equil.}} = \exp\left[\frac{F}{RT}(E_{12} - E_{01})\right] .$$

Reference (7) reviews the principles from which these relationships are derived.

The glass electrode. - A glass electrode was used to measure $[H^+]$ simultaneously with the measurement of $[Hg^{++}]$. If the solution is unbuffered, the formation of Hg_2^{++} may change the pH by causing dissociation of complexes (e.g., $RHg^{++} + H^+ + Hg(\text{liq.}) \rightarrow RH^+ + Hg_2^{++}$). It is then necessary to wait for equilibrium to be attained in the bulk of the solution, when the pH measured by the glass electrode is equal to that at the mercury electrode. This was important in the guanidine measurements (Chapter V), where the ligand does not buffer the solution.

Calibration of the glass electrode. - Measurement of the apparent pH of solutions of known acidity and unit ionic strength ($NaClO_4$) in the cell

$$\text{S.C.E.} \,\Vert\, \text{Salt Bridge} \,\Vert\, H^+ \,|\, \text{Glass}$$

permitted calibration of the pH meter-glass electrode combination. Prior to calibration and each day's measurements, the pH meter was adjusted to read the pH of a standard buffer in which the calomel and glass electrodes were immersed (omitting the salt bridge). This assured that the calibration remained valid from day to day.

If the pH meter is calibrated with Beckman #3506 Buffer Solution (pH = 4.00) and a Beckman 40495 (type E-2) glass electrode is used, the following equation applies:

$$-\log [H^+] = (pH)_{obs} + 0.13 \, .$$

In this calibration, a 1.0 F $NaNO_3$ salt bridge was used. Assuming the junction potentials in the cell are zero, the activity coefficient of H^+ in 1 F $NaClO_4$ is $10^{0.13}$, or 1.35. The validity of neglecting the junction potentials here is discussed later in the chapter.

In some cases daily calibrations were performed on the actual reaction solutions prior to addition of Hg(II). For a given buffer, these calibrations fell within the range ± .02 pH.

The reference electrode and the salt bridge. Junction potentials. - A saturated calomel electrode was the reference. Because of the strong binding of Hg(I) and Hg(II) by chloride and the insolubility of $KClO_4$, it is necessary to isolate the reference electrode with a salt bridge. In full detail, the cell used was

$$\begin{gathered} -\mathrm{Hg(liq.)}\,|\,\mathrm{Hg_2Cl_2},\ \mathrm{KCl\ (sat.)}\ \underset{A}{\|}\ \mathrm{RHNO_3}(c'_1),\ \mathrm{HNO_3}\ (c_2), \\ \mathrm{NaNO_3}\ (1-c'_1-c_2)\ \underset{B}{\|}\ \mathrm{RHClO_4}\ (c_1),\ \mathrm{HClO_4}\ (c_3), \qquad \text{(I-5)} \\ \mathrm{Hg(ClO_4)_2}\ (c_4),\ \mathrm{NaClO_4}\ (1-c_1-c_3-3c_4)\,|\ \mathrm{Hg(liq.)}\ + . \end{gathered}$$

The concentrations c are formal concentrations. For pH measurements, a glass electrode replaced the Hg electrode on the right. This cell was chosen because the junction potentials at A and B are very nearly constant, and are close to zero. At A, the junction potential E_j is determined almost entirely by the very concentrated KCl regardless of the composition of the solution on the right, and the junction potential is small (8). If c_2, c_3, and c_4 are small, the E_j at B is essentially that of the junction $RHNO_3(c'_1)$, $NaNO_3(1-c'_1)\,|$ $RHClO_4\ (c_1)$, $NaClO_4\ (1-c_1)$. If $c_1 \cong c_1'$, this potential is due to the difference between the ionic mobility of

ClO_4^- and that of NO_3^-. But the limiting equivalent conductivities of these ions at 25°, which are proportional to the mobilities at infinite dilution, are 67.4 and 71.5 cm^2 ohm^{-1} (g. equiv.)$^{-1}$, respectively (9). This near equality causes E_j to be small. Insofar as E_j deviates from zero, it will be constant with variation of c_1 except for the very small effect on the mobilities of the anions which arises from changing the cations.

Small changes in the junction potential at B do arise from mismatch of acid concentrations, volume changes during titrations, and, in some cases, the reaction of RH^+ in the titration compartment to give free amine. But in all cases c_2, c_3, and c_4 are less than .01 M and $(c_1 - c'_1)$ never exceeds .05 M.

Activities vs. concentrations. - All constants reported in this thesis are quotients of concentrations, not activities. The glass and and mercury electrodes were calibrated to read the actual concentration of H^+ and Hg^{++} present in solution.

The Potentiometric Method--Mathematical Treatment of Data

The following equilibria occur in all cases:

$$Hg_0 + Hg^{++} \rightleftarrows Hg_2^{++}$$

$$RH^+ + Hg^{++} \rightleftarrows HgR^{++} + H^+$$

$$2RH^+ + Hg^{++} \rightleftarrows HgR_2^{++} + 2H^+ \qquad \text{(I-5a)}$$

$$RH^+ \rightleftarrows R + H^+$$

In what follows, we shall designate HgR^{++} as C_1 and HgR_2^{++} as C_2. The equilibrium constants for these reactions are

$$K = [Hg_2^{++}] \,/\, [Hg^{++}] \qquad \text{(I-6)}$$

$$K_1 = \frac{[C_1]\,[H^+]}{[Hg^{++}][RH^+]} \qquad \text{(I-7)}$$

$$K_2 = \frac{[C_2]\,[H^+]^2}{[Hg^{++}][RH^+]^2} \qquad \text{(I-8)}$$

$$K_A = \frac{[R]\,[H^+]}{[RH^+]} \qquad \text{(I-9)}$$

Solving for $[C_1]$, $[C_2]$, etc. and substituting into equation I-4 , we obtain

$$\frac{[\mathrm{Hg}^{++}]_0}{[\mathrm{Hg}^{++}]} = 1 + K + K_1 \frac{[\mathrm{RH}^+]}{[\mathrm{H}^+]} + K_2 \frac{[\mathrm{RH}^+]^2}{[\mathrm{H}^+]^2} \qquad \text{(I-10)}$$

which, on rearrangement, yields

$$\left(\frac{[\mathrm{Hg}^{++}]_0}{[\mathrm{Hg}^{++}]} - 1 - K \right) \frac{[\mathrm{H}^+]}{[\mathrm{RH}^+]} = K_1 + K_2 \frac{[\mathrm{RH}^+]}{[\mathrm{H}^+]} \; . \qquad \text{(I-11)}$$

$[\mathrm{H}^+]$ is determined from the glass electrode, and $[\mathrm{Hg}^{++}]$ from the potential of the cell (I-5). Since, from "conservation of protons,"

$$[\mathrm{H}^+]_0 - [\mathrm{OH}^-]_0 + [\mathrm{RH}^+]_0 = [\mathrm{RH}^+] + [\mathrm{H}^+],$$

where

$[\mathrm{H}^+]_0$ and $[\mathrm{OH}^-]_0$ are the formal concentrations of acid and base added, and

$[\mathrm{RH}^+]_0$ is the formal concentration of amine,

we can calculate $[\mathrm{RH}^+]$:

$$[\mathrm{RH}^+] = [\mathrm{RH}^+]_0 + [\mathrm{H}^+]_0 - [\mathrm{OH}^-]_0 - [\mathrm{H}^+] \; . \qquad \text{(I-12)}$$

In basic solution, this becomes

$$[\mathrm{RH}^+] = [\mathrm{RH}^+]_0 + [\mathrm{H}^+]_0 - [\mathrm{OH}^-]_0 + [\mathrm{OH}^-] \; . \qquad \text{(I-13)}$$

A plot of the quantity on the left of I-11 vs. $[\mathrm{RH}^+]/[\mathrm{H}^+]$

will yield a straight line of slope K_2 and intercept K_1. (We shall see later that we expect K_1 to be too small to determine accurately.)

In this general treatment we have omitted corrections for the hydrolysis of Hg^{++}. These corrections are negligible except when K_2 and $[RH^+]$ are small. Where necessary, they can be calculated from the values of K_{1H} and K_{2H} given by Hietanen and Sillén (10):

$$K_{1H} = \frac{[HgOH^+][H^+]}{[Hg^{++}]} = 10^{-3.7} \tag{I-14}$$

$$K_{2H} = \frac{[Hg(OH)_2][H^+]^2}{[Hg^{++}]} = 10^{-6.3} \tag{I-15}$$

at 25.0°C; $\mu = 0.5$ ($NaClO_4$). In all experiments where an elementary mercury electrode is present, $HgOH^+$ is negligible, for $[HgOH^+]$ never exceeds 12% of the sum of $[Hg(OH)_2] + [Hg^{++}] + [HgOH^+]$ (6). It is therefore an even smaller fraction of $[Hg^{++}]_0$, which includes $[Hg_2^{++}]$ as well.

Preparation of Standard Reagents

Many standard solutions were used in several different experiments. They were always prepared and standardized as described in this section unless otherwise noted. Comercially distilled water was redistilled in glass. Solutions of Hg(II), amines, and reaction mixtures were stored in the dark.

Sulfuric acid; potassium thiocyanate. - Standard solutions of these reagents were prepared by quantitatively diluting PH - Tamm concentrated volumetric solutions purchased from Biorad Laboratories.

Sodium perchlorate. - 5 F stock solutions were prepared from 60% perchloric acid (B & A or Mallinckrodt) and 50% sodium hydroxide solution which was made up from solid reagent grade NaOH and filtered through a carefully cleaned sintered glass funnel. The acid was standardized against standard base (see below). A large aliquot of acid was neutralized with 50% NaOH until neutral when tested with pH paper; the solution was quantitatively transferred to a volumetric flask and diluted. More dilute $NaClO_4$ solutions and other solutions containing $NaClO_4$ were prepared from aliquots of this stock solution. 1 F $NaClO_4$ solutions used in potentiometric experiments were carefully analyzed for excess acid or base by titration with a glass electrode using a salt bridge. In some cases, they were accurately neutralized.

Mercuric perchlorate. - Reagent grade HgO (J. T. Baker, Baker & Adamson) was weighed out and slurried with H_2O; 60% $HClO_4$ was quantitatively added in slight excess and the solution diluted. The slight residue was removed by filtration through a sintered glass funnel. The solutions were analyzed for Hg(II) by Volhard titration with KSCN using $FeNH_4(SO_4)_2$. The concentration of excess acid was determined by titration with standard base in the presence of a large excess of NaCl. A glass electrode was used as indicator. A sharp endpoint is obtained. Hg(II), complexed with chloride, does not react with hydroxide except at very high pH.

Perchloric acid. - 60% perchloric acid was diluted and standardized by titration with base using methyl red indicator.

Nitric acid. - Freshly opened concentrated HNO_3 was diluted and standardized with base.

Sodium chloride; sodium nitrate. - Reagent grade chemicals were weighed out, dissolved, and diluted to volume.

Sodium hydroxide. - Solutions were prepared by dilution of 50% NaOH which had been filtered to remove Na_2CO_3. They were standardized against sulfuric acid using methyl red indicator. Solutions of base for potentiometric experiments were 1.0 F in $NaClO_4$ to maintain the ionic strength. Standard solutions were stored in polyethylene bottles equipped with glass siphons; ascarite tubes protected the solutions from atmospheric CO_2. The air inlets were closed off when not in use. PH-Tamm commercial standard solutions were also employed.

General Experimental Procedures

Potentiometric measurements.- A four-necked, 200 ml titration flask with an additional inlet for nitrogen gas was immersed in a water bath, maintained at the desired temperature to within ± 0.05°C. A straight tube containing the salt bridge solution extended through one neck. At the lower end of the tube was a frit junction, kindly provided by Beckman Instruments, Inc. from their Reference Electrode 39071. A Beckman fiber type saturated calomel electrode (#39970) was inserted into the top of the salt bridge tube. A J-type mercury electrode and a glass electrode extended into the titration flask.

A switch connected the calomel electrode either to a potentiometer or a pH meter. The E.M.F. between the reference and mercury electrodes was measured with a Leeds & Northrup type K-2 potentiometer and a .02 μa/mm galvanometer.

The glass electrode used in each experimental series is described in the appropriate section. The pH's were measured with a Beckman Expanded Scale pH Meter; the mercury electrode was disconnected during pH readings.

Dry nitrogen from a cylinder was bubbled through two gas-washing bottles filled with distilled water and introduced into the titration flask. Flow was maintained throughout all experiments except when free volatile amines were present in significant quantities.

A magnetic stirrer mixed the contents of the titration flask. Unused necks of the flask were stoppered. Various components of solutions being investigated were added directly to the titration flask by pipette. Titrants were added by burette. No measurements were made with drops adhering to the burette tip. Solution volumes ranged from 75 to 150 ml. Exposure of solutions to daylight or fluorescent lights was avoided.

Ionic strength. - All potentiometric and spectrophotometric equilibrium and rate experiments were performed in solutions made up to ionic strength 1.0M with sodium perchlorate.

Calibration of the mercury electrode. - A $Hg(ClO_4)_2$ solution, .010 F in $HClO_4$, $\mu = 1.0$, was prepared from stock solutions and standardized. An identical solution was stirred with metallic mercury for 10 days in the dark at 25.0°C with a magnetic stirrer. The resulting $Hg_2(ClO_4)_2$ solution was analyzed for total mercury after oxidation with $KMnO_4$. The brown color in the solution, due to MnO_2, was removed with $FeSO_4$ solution. The Hg(II) was then titrated with KSCN in the usual way.

An aliquot of $Hg_2(ClO_4)_2$ solution was added to the titration flask at 25.0°C containing .99 F $NaClO_4$-.010 F $HClO_4$; the potential of a platinum electrode was recorded. The electrode was cleaned with concentrated HNO_3 before use. (Salt bridge: .99 F $NaNO_3$-.01 F HNO_3.) The salt bridge tube was jacketed and water from the bath was circulated around it. Aliquots of $Hg(ClO_4)_2$ solution were added by pipette and the potentials observed. From these data, the Hg(II) content of the $Hg_2(ClO_4)_2$ solution and E_{12} were calculated.

E_{01} was calculated from another experiment in which the potential of an Hg(0) electrode was observed as aliquots of the $Hg_2(ClO_4)_2$ solution were added. Salt bridge, temperature, acid concentration, and ionic strength were unchanged from the above.

The apparent E_{12} was corrected for the slight hydrolysis (2%) of Hg(II) at $[H^+] = .010$.

$$E_{12} = E_{12}\,(\text{apparent}) + \frac{RT}{F}\,\ell n\left(1 + \frac{K_{1H}}{[H^+]}\right)$$

(For the value of K_{1H}, see equation I-14.)

The calibration at 25°C was used in the ammonia experiments. The aniline and guanidine binding was studied at 27° ; the calibrations at that temperature were identical to those above except that the Hg(I) solution was made up from solid $Hg_2(NO_3)_2$ (Baker & Adamson reagent grade). The Hg(II) content of that solution did not correspond to equilibrium, but the very small corrections in concentration due to reaction with the mercury electrode were neglected. The salt bridge tube was not jacketed during the measurements at 27°C.

The results of the calibrations are given in Table I.

Spectrophotometric measurements. - Except where otherwise noted, all spectrophotometric measurements in this thesis were made on a Cary Model 14 Spectrophotometer using 1 cm quartz cells. As a rule, spectra were recorded with air in the reference beam, and a blank--pure solvent in the sample cell--was recorded during each period of use.

Melting points. - Melting points were determined on a thermistor-equipped micro hot stage (A. H. Thomas Co., 6887-C2 assembly).

TABLE I

Calibration of the Mercury Electrode:

The Values of E_{02}, E_{01}, E_{12}

$\mu = 1.0$ M ($NaClO_4$)

Salt Bridge: .99 F $NaNO_3$-.01 F HNO_3

Temperature		25.0°C	27.1°C
E_{01}	(volts)	.5395±.0005	.5400±.0013
E_{12}	(volts)	.6714±.0013	.6733±.0005
E_{02}	(volts)	.6054±.0009	.6066±.0009
K		169±12	172±12

The literature value of K in 1.0 F $NaClO_4$ at 25°C is about 170 (5).

The Aniline-Mercury Potentiometric Measurements

If a mercury electrode is introduced into a slightly acidic mercuric perchlorate solution containing aniline perchlorate in excess, a stable potential is not attained. The initial value of the potential, however, is reproducible and varies in a regular and predictable manner with composition of the solution. This potential accurately reflects the distribution of mercury among the components of a rapidly-established equilibrium at the electrode surface (see "The mercury electrode," above). From the initial potentials, the stabilities of labile Hg-aniline complexes can be determined.

Experimental details. - Although free aniline turns brown immediately on exposure to air, solutions of its salts are very stable if they contain excess acid and are stored in the dark. Stock solutions of φNH_3ClO_4 and φNH_3NO_3 were prepared by distilling aniline directly into a solution of the appropriate acid. An aliquot of standardized acid was added to the receiver flask containing water and a magnetic stirring bar. The flask was tared on a platform balance; aniline (freshly opened Baker & Adamson or J. T. Baker reagent grade) was distilled into it. The still was flushed with nitrogen and protected from ultraviolet light; the contents of the receiving flask were stirred continuously. After the distillation, the receiving flask was reweighed.

The solution was quantitatively transferred to a volumetric flask and diluted.

These solutions were 1.00 F in total acid. 1.00 F HNO_3 was added to the φNH_3NO_3 solution to match the φNH_3^+ concentration with that in the φNH_3ClO_4 solution. The aniline salt concentrations could be calculated to within .5% from the weighings.

The salt bridge tube was primed by boiling in 1 F $NaNO_3$. The glass electrode was a Beckman 40498 (general purpose). The standard buffer used in the glass electrode calibration was Beckman pH 4. 1 F $NaClO_4$ was titrated with $HClO_4$ in the calibration; a 1 F $NaNO_3$ salt bridge was used. Corrections were made for the small amount of carbonate in the $NaClO_4$ solution. The temperature in this series was 27.1° ± .5°C.

The following procedure was followed for each measurement. The calomel and glass electrodes were immersed in standard buffer; the pH meter was adjusted after standing for 30 min. Aliquots of $NaClO_4$ and φNH_3ClO_4 stock solutions were added to the clean, dry titration flask. The salt bridge was prepared from $NaNO_3$ and φNH_3NO_3 stock solutions; the salt bridge tube was filled and inserted into the titration flask. Nitrogen was bubbled through the flask to free the solution from CO_2 and O_2. Appropriate quantities of standard base were added; the glass and calomel electrodes were placed in the titration flask and salt bridge tube, respectively.

An aliquot of $Hg(ClO_4)_2$ was added; immediately the mercury electrode was inserted and the E.M.F. measured. The pH was then determined.

Results. - The results are presented in Table II. In Figure I, the plot of

$$\left(\frac{[Hg^{++}]_o}{[Hg^{++}]} - 1 - K \right) \frac{[H^+]}{[RH^+]} \quad \text{vs.} \quad \frac{[RH^+]}{[H^+]}$$

is shown (see equation I-11). Hydrolysis corrections are negligible in every case. The calculated values of K_1 and K_2 are 16 and 0.45. The reaction I-5a is composed of two steps, the equilibrium constants of which are K_1 and K_2/K_1. For most ligands, the magnitude of these two constants is similar (11). The high value of K_1 is very unexpected. The spectrophotometric determination of K_1 described in Chapter III leads to a much more reasonable value.

It seemed possible, though unlikely, that a Hg(I)-aniline complex was causing the effect. This indeed turned out to be the case; the unequivocal detection of the absorption spectrum of the $\varphi NH_2Hg_2^{++}$ complex is described in Chapter II. A reinterpretation of the potentiometric data is now required.

TABLE II. Potentiometric Experiments: Mercury-Aniline Composition of Solutions*

No.	Formal Concentrations			Salt Bridge	
	$[Hg(ClO_4)_2]$ x 10^2	$[\varphi NH_3ClO_4]$	$[HClO_4]^{**}$	$[\varphi NH_3NO_3]$	$[HNO_3]$ x 10
8	.121	.073	-.0030	.073	.004
9	.121	.073	.0041	.073	.004
10	.121	.290	.0174	.290	.018
11	.121	.290	-.0155	.290	.018
12	.121	.029	-.0089	.029	.018
13	.121	.029	.0015	.029	.002
14	.121	.029	-.0028	.029	.002
15	.121	.029	-.0071	.029	.002
16	.605	.073	-.0095	.073	.004
17	.061	.073	-.0102	.073	.004
18	.242	.145	-.0056	.145	.009
19	.121	.145	-.0057	.145	.009
20	.061	.145	-.0058	.145	.009
21	.121	.290	.0155	.290	.018
22	.121	.290	.0031	.290	.018
23	.121	.290	-.0155	.290	.018
24	.121	.073	-.0030	.073	.004
25	.121	.073	.0041	.073	.004

* In the reaction solutions, $[NaClO_4] = 1.00 - [\varphi NH_3ClO_4] - [HClO_4) - 3[Hg(ClO_4)_2]$. In the salt bridge, $[NaNO_3] = 1.00 - [HNO_3] - [\varphi NH_3NO_3]$.

**If this value is negative, a formal excess of base has been added. The solution remains acidic because φNH_3ClO_4 reacts with this excess.

TABLE II. (continued)

Potentiometric Experiments: Mercury-Aniline

Experimental Results. T = 27.1±.5°C, μ = 1.0 M

No.	$-\log[H^+]$	EMF vs. SCE (volts)	$[\varphi NH_3^+]/[H^+] \times 10^{-1}$	$Y \times 10^{-1}$*
8	3.09	.4090	8.5	6.0
9	2.19	.4423	1.1	2.1
10	1.68	.4400	1.4	2.2
11	3.37	.3568	64	46
12	3.09	.3723	35	26
13	2.46	.4448	0.78	2.0
14	3.37	.4169	6.1	4.4
15	4.17	.3793	32	16
16	2.87	.4490	4.6	2.2
17	3.99	.3550	61	28
18	2.97	.4113	13	6.6
19	3.26	.3855	25	13
20	3.37	.3703	33	16
21	3.45	.3575	77	36
22	2.23	.4237	4.9	3.1
23	3.46	.3565	79	38
24	3.10	.4097	8.7	5.5
25	2.21	.4423	1.14	2.0

$$* \; Y \equiv \left(\frac{[Hg^{++}]_o}{[Hg^{++}]} - 172 \right) \frac{[\varphi NH_3^+]}{[H^+]}$$

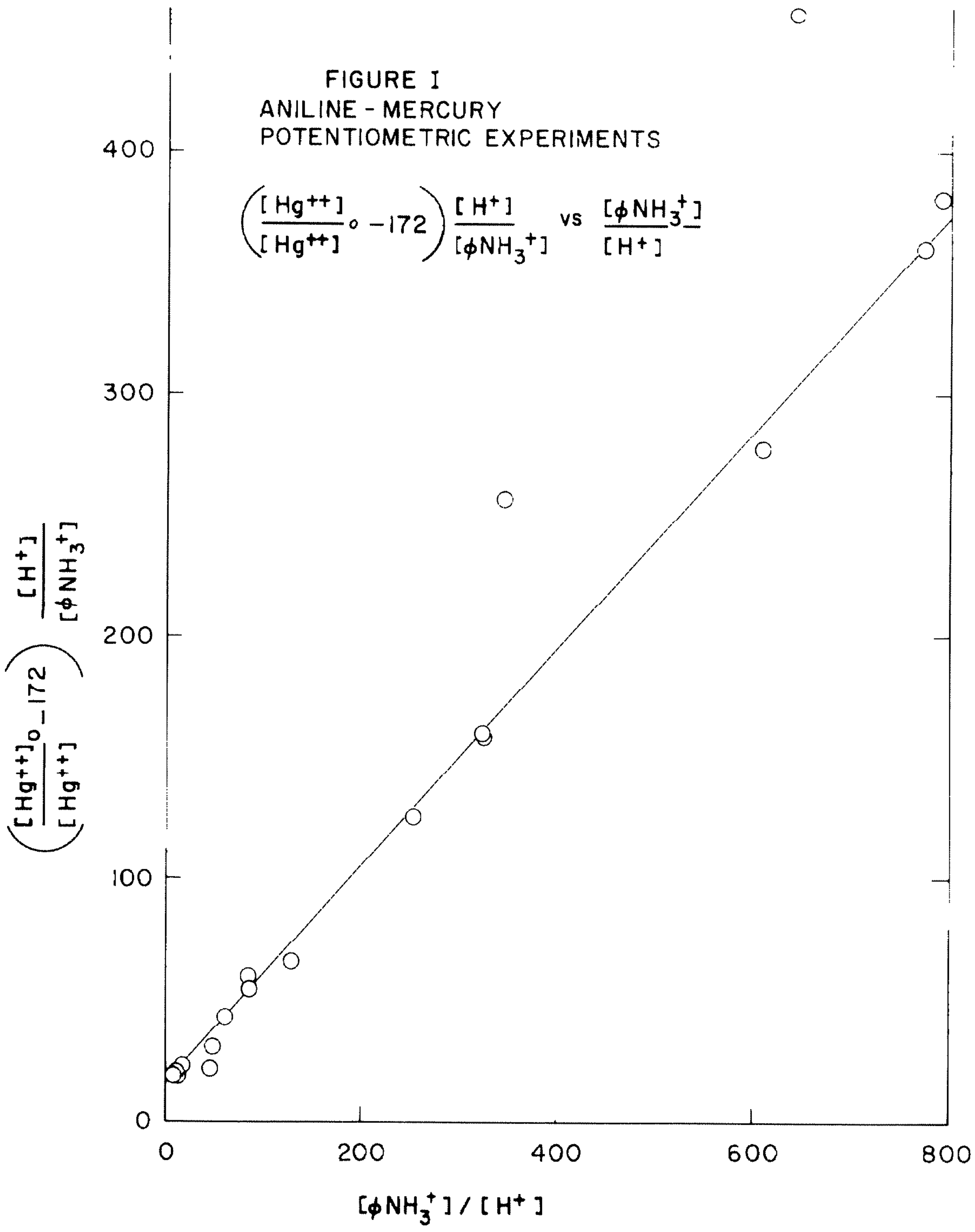


FIGURE I
ANILINE - MERCURY
POTENTIOMETRIC EXPERIMENTS

$$\left(\frac{[Hg^{++}]_o}{[Hg^{++}]} - 172\right)\frac{[H^+]}{[\phi NH_3^+]} \text{ vs } \frac{[\phi NH_3^+]}{[H^+]}$$

The Potentiometric Method and Hg (I) Complexes

Reinterpretation of the mercury-aniline data. - Since the $[Hg_2^{++}]/[Hg^{++}]$ ratio is constant at the surface of a mercury electrode, it will respond to complexing of either Hg_2^{++} or Hg^{++}. The functional form of the response is independent of the species being bound. Formation of any Hg(I) species, free or complexed, requires reduction of Hg(II):

$$Hg(II) + Hg(0) \rightarrow (Hg(I))_2 \ .$$

One might assume that two mercurous complexes are formed:

$$Hg_2^{++} + RH^+ \rightleftharpoons RHg_2^{++} + H^+$$

$$Hg_2^{++} + 2RH^+ \rightleftharpoons R_2Hg_2^{++} + 2H^+ \ .$$

Representing RHg_2^{++} by C_1^I and $R_2Hg_2^{++}$ by C_2^I,

$$K_1^I = \frac{[C_1^I]\,[H^+]}{[Hg_2^{++}][RH^+]} \qquad \text{(I-16)}$$

$$K_2^I = \frac{[C_2^I]\,[H^+]^2}{[Hg_2^{++}]\,[RH^+]^2} \ . \qquad \text{(I-17)}$$

Equation I-3 for the conservation of mercury(II) becomes

$$[Hg^{++}]_0 = [Hg^{++}] + [Hg_2^{++}] + [C_1] + [C_1^I] + [C_2] + [C_2^I]$$

$$[Hg^{++}]_0 = [Hg^{++}] + [Hg_2^{++}] + K_1 \frac{[Hg^{++}][RH^+]}{[H^+]} + K_1^I \frac{[Hg_2^{++}][RH^+]}{[H^+]} + K_2 \frac{[Hg^{++}][RH^+]^2}{[H^+]^2} + K_2^I \frac{[Hg_2^{++}][RH^+]^2}{[H^+]^2}$$

$$\left(\frac{[Hg^{++}]_0}{[Hg^{++}]} - K - 1 \right) \frac{[H^+]}{[RH^+]} = K_1 + KK_1^I + (K_2 + KK_2^I) \frac{[RH^+]}{[H^+]}$$

If, then, 1: 1 and 2: 1 mercurous-aniline complexes exist, the intercept of the plot in Figure I is $(K_1 + KK_1^I)$ and the slope is $(K_2 + KK_2^I)$.

The spectrophotometric determination of K_1 is described in Chapter III; a value of 0.68 was obtained at $\mu = 1.0$, T = 27°C. The intercept in Figure I is 16. Since K = 172, $K_1^I = .09$. This agrees with the spectrophotometrically determined value of 0.07 (Chapter II).

The question now arises: To what extent does the term KK_2^I contribute to the slope, $(K_2 + KK_2^I)$? It was mentioned earlier that as a rule K_2 for Hg(II) complexes is nearly equal to $(K_1)^2$. This is also true for Ag(I) complexes (12). If Hg(I) complexes behave similarly, one would predict that $K_2^I = (K_1^I)^2$, and that the slope

$$(K_2 + KK_2^I) = K_1^2 + K(K_1^I)^2 = 0.5 + 1.4 = 1.9 .$$

The observed slope is 0.45, nearly equal to the first term of the predicted value.

A spectrophotometric experiment was undertaken in an attempt to detect the complex $(\varphi NH_2)_2Hg_2^{++}$; it is described in Chapter II. No complex was detected; from the results, one can say that the concentration of $(\varphi NH_2)_2Hg_2^{++}$ is less than 10% of that of $(\varphi NH_2)_2Hg^{++}$ in the solutions under consideration. At worst, only a small error will be introduced by neglecting $K\,K_2^I$ and setting the slope equal to K_2.

$$K_2 \approx (K_2 + K\,K_2^I) = 0.45 .$$

The implications of the existence of the 1: 1 mercury(I)-aniline complex and the fact that $K_2^I << (K_1^I)^2$ are discussed in Chapter II.

Detection of Hg(I) complexes with a mercury electrode. - The unusual behavior of the Hg(0) electrode which led to the discovery of the Hg(I)-aniline complex requires that $K\,K_1^I$ be large compared to K_1. Since other Hg(I)-amine complexes may exist, it is useful to consider quantitatively the conditions under which the effect is detectable.

The fraction of the original mercury(II) which exists in the form of a 1: 1 Hg(I)-aniline complex is

$$f = \frac{[C_1^{I}]}{[Hg^{++}] + [Hg_2^{++}] + [C_1] + [C_1^{I}] + [C_2] + [C_2^{I}]} \qquad \text{(I-18)}$$

If the equilibrium constant expressions I-6, I-7, I-8, I-16, and I-17 are rearranged and substituted into equation I-18, the equation

$$f = \frac{K K_1^{I} x}{1 + K + (K_1 + K K_1^{I})x + (K_2 + K K_2^{I})x^2}$$

is obtained, where

$$x \equiv [RH^+] / [H^+] .$$

Setting df/dx equal to zero, one finds that the maximum value of f occurs when

$$x = \sqrt{(1 + K)/(K_2 + K K_2^{I})}$$

for which,

$$f_{max} = 1/ \left(\frac{1 + 2\sqrt{(K_2 + K K_2^{I})(1 + K)} + K_1}{K K_1^{I}} \right) . \qquad \text{(I-19)}$$

If the complex is to be detected with any certainty, f_{max} must be greater than ~0.2. We may note that $K >> 1$. In a typical case,

$K_2 \sim (K_1)^2$; we shall further assume that the 2: 1 Hg(I) complex is not stable (i.e., that $K K_2^I << K_2$). Then, inverting the inequality derived from I-19 ,

$$5 > 1 + \frac{2\sqrt{K K_1^2} + K_1}{K K_1^I}$$

Substituting 170 for K_1 and rearranging, we obtain the condition

$$K_1^I > .04 K_1 .$$

If this is not true, there is little hope of obtaining significant information about the Hg(I) complex potentiometrically. In the case of aniline, $K_1^I > 0.1 K_1$.

Determination of K_1 : a limitation of the mercury electrode technique. - One may invoke an argument exactly parallel to that just presented to show that in the general case, the determination of K_1 by the potentiometric method is not possible. If no Hg(I) complexes form, the fraction of initial Hg(II) present as the 1: 1 complex C_1 is

$$f = \frac{K_1 x}{1 + K + K_1 x + K_2 x^2}$$

where x is defined as before. In the same way, we find that

$$f_{max} = 1/\left(1 + \frac{2\sqrt{(1+K)\,K_2}}{K} \right)$$

when

$$x = \sqrt{(K+1)/K_2} \quad .$$

If $K_2 = (K_1)^2$ and $K = 170$,

$$f_{max} = \frac{1}{27} \quad .$$

Since f_{max} is much less than 0.2, K_1 cannot be determined.

The Basicity of Aniline

In order to correlate the basicity of aniline with the stability of its Hg(II) complexes, K_A of the anilinium ion in $NaClO_4$ ($\mu = 1.0M$) was determined.

This was done by titration of φNH_3ClO_4 solutions with standard base. The pH during the titration was measured in the same way as in the potentiometric experiments. The titration flask, temperature control, salt bridge arrangement, and principles of measurement were identical with those already described.

The experimental procedure was slightly modified. An aliquot of carefully neutralized 1.0 F $NaClO_4$ was introduced into the titration flask. A salt bridge solution was prepared from $NaNO_3$ and φNH_3NO_3 stock solutions. The φNH_3^+ concentration in the salt bridge was equal to that in the titration flask at half equivalence. A Beckman 41260 glass electrode (type E-2) was used. The pH meter was calibrated by pipetting aliquots of standard acid ($\mu = 1.0$) into the flask and observing the readings. During this procedure, the solution was flushed with N_2. An aliquot of φNH_3ClO_4 solution was then added and titrated with standard base containing 1.0 F $NaClO_4$. The nitrogen was turned off during the titration.

The apparent K_A was calculated at 15-20 points during the titration. In two different experiments, the total aniline concentrations were approximately .018 and .053 F. The average of the results were

$$K_A = 1.66 \pm .07 \times 10^{-5} \text{ moles}/\ell .$$

at T = 27.1° , μ = 1.0 M ($NaClO_4$). Thus,

$$pK_A = 4.78 \pm .02 .$$

Note that K_A is defined in terms of concentrations, not activities (equation I-9).

CHAPTER II

MERCURY(I)-ANILINE: SPECTROPHOTOMETRIC CONFIRMATION OF THE EXISTENCE OF A 1:1 COMPLEX IN AQUEOUS SOLUTION

As a rule, organic nitrogen bases cause Hg(I) salts to disproportionate. Instead of Hg(I) complexes, Hg(II) complexes and metallic mercury are formed (13, 14). Many workers have reported solid products from this type of reaction (15, 16, 17); in most cases, they are black, indicating the presence of Hg(0). Mercurous diacethydrazide is the only mercurous-nitrogen compound which has been characterized unequivocally (17). A soluble complex of triethanolamine with Hg(I) has been reported (18), but the conclusiveness of the work cannot be judged on the basis of available abstracts.

The potentiometric investigation of the binding of Hg(II) by aniline, however, strongly suggests that a Hg(I)-aniline complex exists. The study, described in Chapter I, produces a value for the association constant of the 1:1 Hg(II)-aniline complex which is both anomalously high and inconsistent with independent spectrophotometric measurements.

At the surface of a Hg(0) electrode in solutions containing Hg(II) ions, equilibrium with respect to the reaction

$$Hg^{++} + Hg(liq.) \rightleftharpoons Hg_2^{++}$$

exists. Since the ratio $[Hg_2^{++}]/[Hg^{++}]$ is therefore constant, the electrode responds to complexing of either Hg(I) or Hg(II) without distinction. Thus, it is possible to explain an apparently anomalous Hg(II) complex by postulating a corresponding Hg(I) complex.

Such a hypothesis demands independent confirmation. The U.V. absorption spectra of solutions of $Hg_2(ClO_4)_2$ and φNH_3ClO_4 in aqueous perchloric acid provide this confirmation. The spectrum can be interpreted only by postulating a $\varphi NH_2\text{-}Hg_2^{++}$ complex:

$$Hg_2^{++} + \varphi NH_3^{+} \rightleftharpoons \varphi NH_2Hg_2^{++} + H^{+} . \qquad \text{(II-1)}$$

The equilibrium constant for this reaction can be estimated from the spectral changes as acid is added to the solution; the value so derived is completely consistent with that obtained potentiometrically. There is no evidence for a 2: 1 complex.

Experimental Details

A $Hg_2(ClO_4)_2$ stock solution was prepared by adding metallic mercury to a $Hg_2(ClO_4)_2\text{-}HClO_4$ solution and allowing it to stand in the dark for several days with occasional shaking. The φNH_3ClO_4 stock solution was that prepared previously (Chapter I). Solution A, approximately equimolar in Hg(I) and aniline perchlorate, was prepared by adding an aliquot of each stock solution to a volumetric flask and diluting quantitatively with redistilled water. The absence of a precipitate indicated that no disproportionation occurred. Disproportionation would be expected if no Hg_2^{++} complex existed. A sample was transferred to a clean, dry spectrophotometer cell with an eyedropper. After recording the U.V. spectrum, the sample was returned to the flask. Small amounts of standardized 60% $HClO_4$ were added from a 0.2 ml micrometer burette to the volumetric, the solution mixed, the spectrophotometer cell rinsed with the same solution, and a new spectrum taken. Only minor amounts of liquid were lost during this procedure, which was repeated several times. The total dilution by $HClO_4$ was less than 1%. Repeated scanning revealed no slow changes in the spectrum.

On the same day, solution B was prepared from an identical aliquot of Hg(I) stock, but the aniline was omitted. The spectrum was recorded; it is unchanged by addition of acid. Solution B was later analyzed for total mercury by oxidation with permanganate and titration with KSCN.

On the following day, the Hg(I) stock solution was potentiometrically analyzed for Hg(II) with a platinum electrode, as described by Jonsson, Qvarfort and Sillén (6). Less than 1% of the Hg was present as Hg(II).

Solution C was prepared, containing $Hg(ClO_4)_2$ and φNH_3ClO_4 in the same concentration as Solution A, but with no Hg(I). A standard $Hg(ClO_4)_2$ solution was used. As before, the spectrum was repeatedly recorded during a titration with 60% $HClO_4$. The small absorbance in the region of interest (300-350 mμ) at acid concentrations of 1×10^{-3} M to 1×10^{-1} M is due to minute amounts of unprotonated aniline and the Hg(II)-aniline complex.

Results

In Figure II, the spectrum of Solution A is compared with those of the blanks, Solutions B and C . A strong increase in absorbance occurs as the reagents are combined. The acid concentration of a Hg(I)-aniline solution increases as the complex is formed. A strictly comparable φNH_3ClO_4 blank therefore absorbs even less than indicated, since the absorbance decreases with increasing acidity.

The absorbance of Solution A decreases during titration with acid. In Figure III, the absorbance of the solution is plotted as a function of the reciprocal of the formal acid concentration at four different wavelengths. The points on the y-axis are the absorbances of Solution B, the Hg(I) blank. The absorbances vary as one would expect for the formation of a 1: 1 complex liberating one proton; the nonlinearity at low acid concentration reflects the effect of complex formation on the initial concentrations.

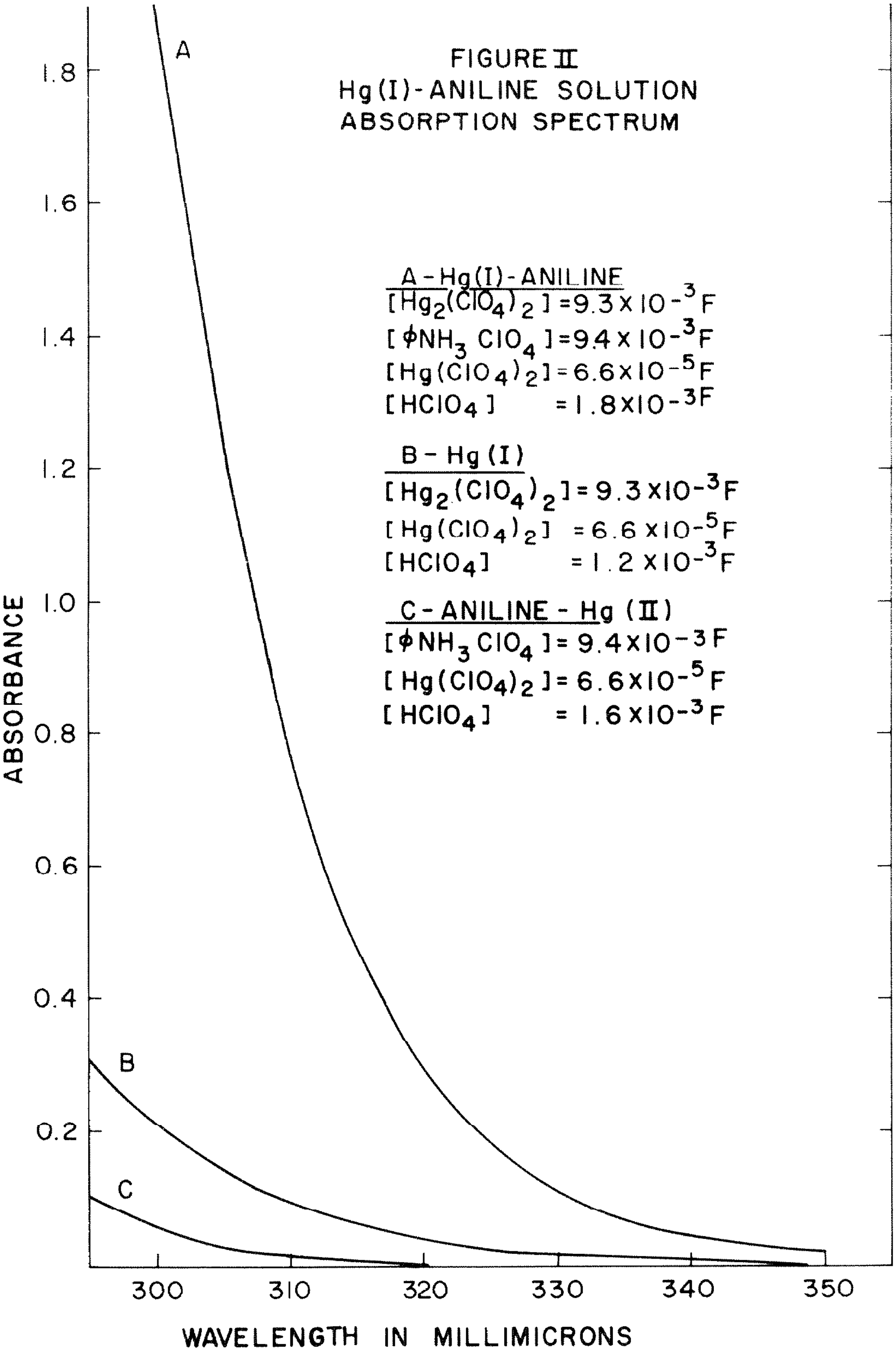


FIGURE II
Hg(I)-ANILINE SOLUTION
ABSORPTION SPECTRUM

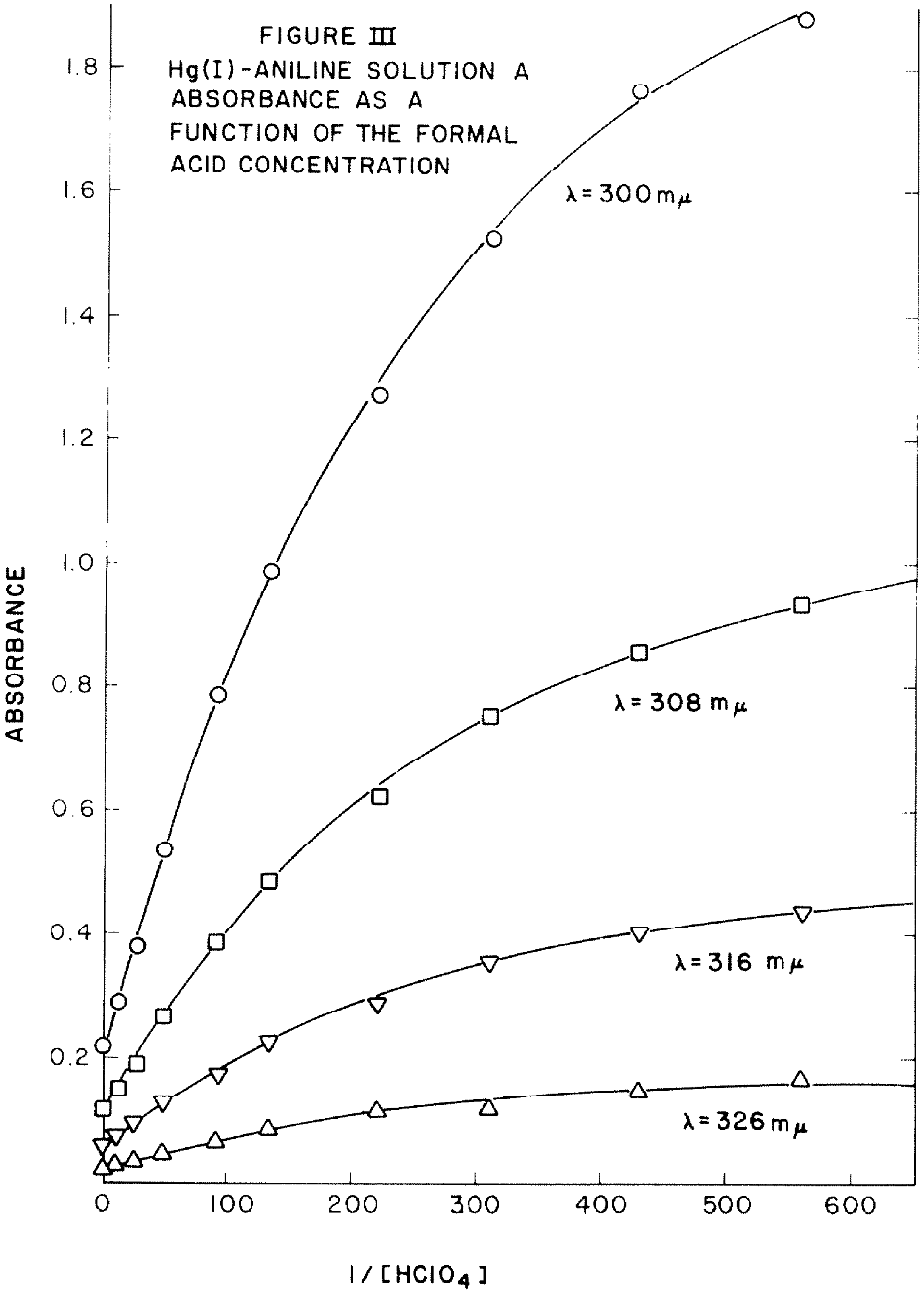


FIGURE III
Hg(I)-ANILINE SOLUTION A
ABSORBANCE AS A
FUNCTION OF THE FORMAL
ACID CONCENTRATION
λ = 300 mμ
λ = 308 mμ
λ = 316 mμ
λ = 326 mμ
ABSORBANCE
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
100
200
300
400
500
600
1/[HClO₄]

The data can be discussed quantitatively by assuming a value of K_1^I, the equilibrium constant of reaction II-1:

$$K_1^I = \frac{[\varphi NH_2Hg_2^{++}][H^+]}{[\varphi NH_3^+][Hg_2^{++}]} \quad .$$

For any value of K_1^I, the quadratic equation

$$K_1^I = \frac{[C_1^I]([H^+]_0 + [C_1^I])}{([\varphi NH_3^+]_0 - [C_1^I])([Hg_2^{++}]_0 - [C_1^I])}$$

can be solved for $[C_1^I]$, the concentration of complex. If the model is adequate and the trial K_1^I approximately correct, the absorbance of the solution (corrected for background) will be directly proportional to the calculated complex concentration. That this is indeed the case for a trial K_1^I of 0.07 is shown in Figure IV.

The corrections to the observed absorbance for a given K_1^I were determined from the spectra of the Hg(I) and aniline blank solutions and the calculated concentrations of free H^+, φNH_3^+, and Hg_2^{++} present at equilibrium. In no case did the aniline correction, which depends on acidity, exceed 5% of the total absorbance.

Noticeable deviations from linearity result from trial values of K_1^I = 0.075 or 0.060. Therefore,

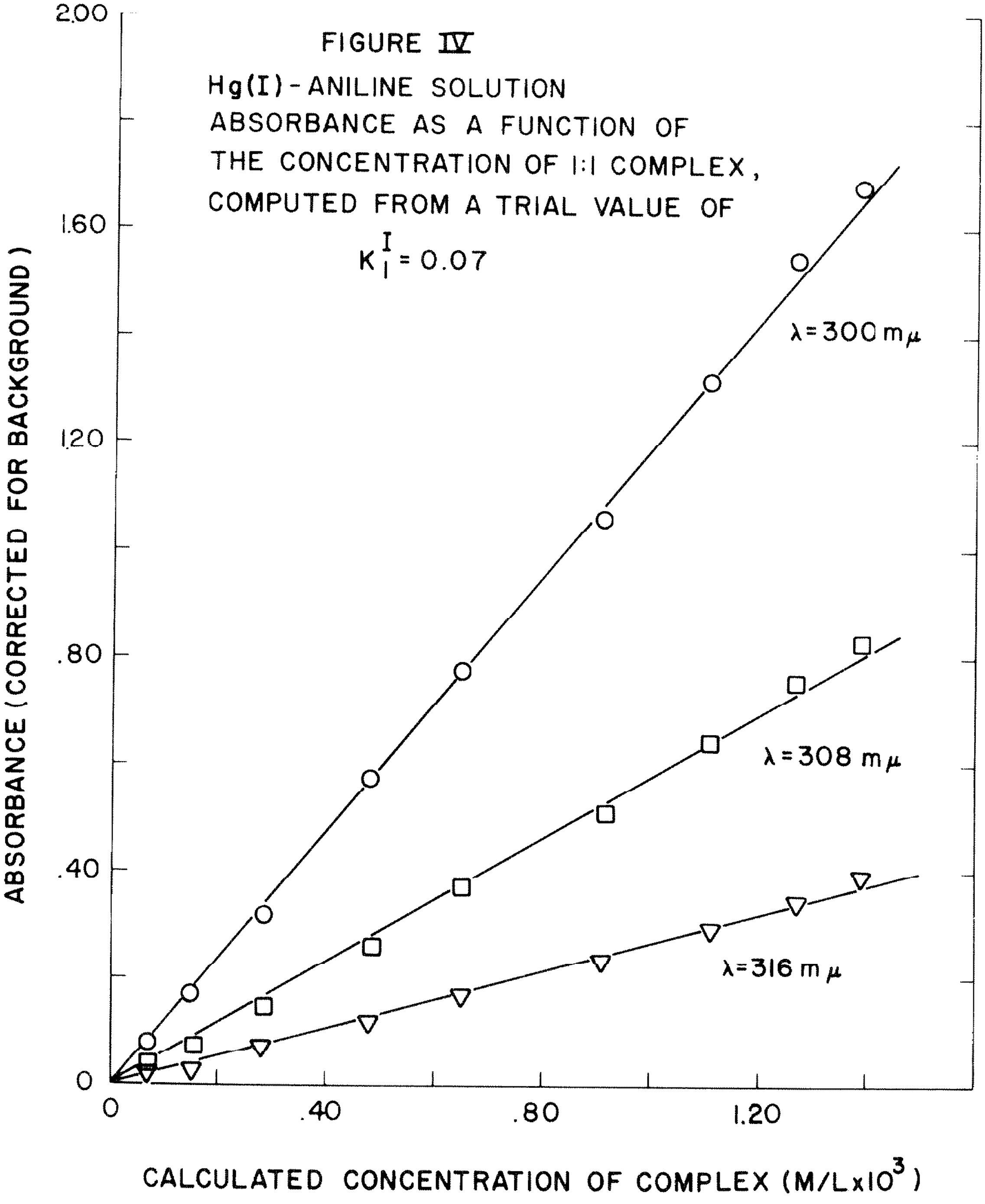


FIGURE IV
Hg(I)-ANILINE SOLUTION
ABSORBANCE AS A FUNCTION OF
THE CONCENTRATION OF 1:1 COMPLEX,
COMPUTED FROM A TRIAL VALUE OF
$K_1^I = 0.07$
λ=300 mμ
λ=308 mμ
λ=316 mμ
2.00
1.60
1.20
.80
.40
0
0
.40
.80
1.20
ABSORBANCE (CORRECTED FOR BACKGROUND)
CALCULATED CONCENTRATION OF COMPLEX (M/L x 10³)

$K_1^I = 0.07 \pm .01$.

No attempt was made to control the ionic strength or the temperature, which was about 23°C. This valuc K_1^I agrees well with that obtained potentiometrically,

$$K_1^I = 0.09 \pm .01 \qquad (T = 27°C, \qquad \mu = 1.0\ M\ (NaClO_4)).$$

A 2:1 Complex?

If the 2:1 aniline-Hg(I) complex were sufficiently stable, significant quantities of metallic Hg would react with Hg(II) in $(\varphi NH_2)_2Hg^{++}$ solutions to form $(\varphi NH_2)_2Hg_2^{++}$. Such a reaction in strongly complexing media would affect the U.V. spectra of acidified samples of the reaction mixture. (Upon acidification, both Hg(I) and Hg(II) complexes are decomposed.) The molar absorptivity of the Hg_2^{++} ion is 2.6×10^4 ℓ/mole-cm at the maximum, 237 mμ (19). That of Hg^{++} at the same wavelength is 2.3×10^1 (20). Therefore, any reduction of Hg(II) to Hg(I) is accompanied by an increase in the absorbance of the acidified solutions. No such increase was detected.

Two φNH_3ClO_4-$Hg(ClO_4)_2$ solutions, each identical with that of potentiometric experiment #21 (Table II), were prepared. Metallic mercury was added to one of these solutions and it was stirred for a few hours. Both solutions were stored in the dark for several days.

Immediately on preparation and periodically thereafter an aliquot of each solution was diluted by a factor of 200 into 0.100 F $HClO_4$. The spectra of the diluted solutions were recorded; they were characteristic of the anilinium ion, which does not absorb strongly at 237 mμ (Figure V). At this acidity, neither Hg(I) nor Hg(II) is complexed.

The spectra of the diluted samples changed slightly with time, but in an identical fashion. Even after 6 days, no consistent difference between the two solutions could be detected. The absorbances of the diluted solutions at 237 mμ were equal to within .005 absorbance units. A difference of .01 absorbance units could not have escaped detection. This corresponds to a $[Hg_2^{++}]$ of 8×10^{-5} M in the undiluted solutions, which were 1.21×10^{-3} F in $Hg[ClO_4]_2$. Under conditions where $(\varphi NH_2)_2Hg^{++}$ is the principal Hg(II) complex, then, less than 10% of the original Hg(II) is present as Hg(I).

Discussion

In Table III, the stability of the Hg(I) aniline complex is compared with that of other complexes of aniline. Although Hg(I) binds aniline less well than Hg(II), both oxidation states form far more stable complexes than Ag(I) or Ni(II). It appears, then, that the scarcity of mercurous complexes indeed results from the very high stability of Hg(II) complexes rather than lack of complexing tendency on the part of Hg(I). But the extra margin of stability seems to be smaller than was previously believed.

Failure to detect a 2: 1 complex means that $K\,K_2^{I} < 0.1\,K_2$. Since $K_2 = .45$ and $K = 120$ (Chapter I), $K_2^{I} < 3 \times 10^{-4}$. On the other hand, $K_1^{I} = 9 \times 10^{-2}$. It was mentioned before that for most complexes of Hg(II) and Ag(I), K_2 is generally equal to $(K_1)^2$. It is clear, however, that $K_2^{I} \ll (K_1^{I})^2$.

At this point it is instructive to consider the sequence of reactions

$$Hg_2^{++} \rightleftharpoons Hg^{++} + Hg(liq.)$$

$$\varphi NH_2Hg_2^{++} \rightleftharpoons \varphi NH_2Hg^{++} + Hg(liq.)$$

$$(\varphi NH_2)_2Hg_2^{++} \rightleftharpoons (\varphi NH_2)_2Hg^{++} + Hg(liq.)$$

TABLE III

Stability Constants of 1: 1 Metal-Aniline Complexes

M	$\log\beta_1^*$	Temperature	Medium	Method	Ref.
Hg^{++}	4.60	27°	1M $NaClO_4$	spectrophotometric	(21)
Hg_2^{++}	3.71	27°	1M $NaClO_4$	potentiometric	(21)
Ag^+	1.44	25°	1M KNO_3	distribution	(22)
Ni^{++}	.09	---	85% EtOH	spectrophotometric	(23)

$*\beta_1 = [\varphi NH_2M]/[\varphi NH_2][M]$ in ℓ./mole.

in which waters of hydration around the mercury ions are successively replaced by aniline. The nature of these reactions is very similar, and to a first approximation one might expect the equilibrium constants to be equal. The actual constants are $1/K$, $(1/K)(K_1/K_1^I)$, and $(1/K)(K_2/K_2^I)$; they are not equal. $K_1 = 0.68$ (Chapter III); $K_1^I \sim .08$. Therefore, the second constant is about eight times as large as the first. Since $K_2^I << (K_1^I)^2$ while $K_2 \approx (K_1)^2$, the constant of the third reaction is much greater than eight times that of the second. In such similar reactions, it is unlikely that differences in entropy or enthalpy of solvation contribute to the differences in ΔF. Rather, they are probably due to differences in bond stability within the complex.

If one assumes that a N-Hg or O-Hg bond is not affected by the other groups bound to Hg, then the increasing equilibrium constants must be attributed to destabilization of the Hg-Hg bond in Hg(I) complexes. Yamane and Davidson (19) have pointed out that the more strongly covalent the Hg-X bond, the longer is the Hg-Hg bond in Hg_2X_2 crystals (where X is a halogen). They interpret this to mean that strong covalent ligand-Hg bonds destabilize the Hg-Hg bond. From this point of view, the trend in ΔF and the very low stability of the 2:1 complex is understandable.

The assumption that N-Hg or O-Hg bond stability is independent of the other groups bound to Hg may well be invalid. But several such bonds are involved in each reaction and speculation as to their relative effects on the equilibria is not very informative.

It may be that the 1:1 Hg(I)-aniline complex owes its existence to the unique character of aniline as a ligand. But it seems likely that other Hg(I) complexes exist in solution and simply have not been observed. Few mercury electrode studies have been made on nitrogen ligands. The region of stability of such complexes is small. The value of the 1:1 stability constant cannot be less than 1/25 that of the corresponding Hg(II) complex if it is to be detectable potentiometrically (Chapter I). Spectrophotometric detection requires ligands, the spectra of which change considerably on complexing. The high U.V. absorbance of Hg_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. From the work described in Chapters V and VI, however, it is possible to say that if Hg(I)-ammonia or Hg(I)-guanidine complexes exist, they are not stable enough to be detected potentiometrically.

The idea that aniline is a unique type of ligand gains some support from the U.V. absorption of its Hg(II) complexes and those of its mercurated derivatives. These spectra are difficult to understand in terms of an N-Hg bond with strictly "σ" character (see p. 102). But the Hg(II)-aniline association constants correlate well with the basicity of aniline. So there is no consistent indication that the aromatic amino group is special in its interaction with mercury.

It may well be that Hg(I) complex stability increases 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.

CHAPTER III

MERCURY(II) COMPLEXES OF ANILINE AND ITS MERCURATED DERIVATIVES--SPECTROPHOTOMETRIC STUDIES. MERCURATION OF ANILINE IN ACIDIC SOLUTION CONTAINING AN EXCESS OF MERCURY(II).

The 1:1 Aniline-Mercury(II) Complex

K_1, the equilibrium constant of the reaction

$$\varphi NH_3^+ + Hg^{++} \rightleftarrows \varphi NH_2Hg^{++} + H^+ ,$$

cannot be determined by potentiometric means. However, the formation of the complex, C_1, produces a pronounced change in the spectra of $Hg(ClO_4)_2$-$HClO_4$ solutions containing small amounts of φNH_3ClO_4. The solutions are not stable with time, but the spectral changes are moderately slow, and the absorbance can be easily extrapolated to the time of mixing. In this way, the rapidly formed complex C_1 can be studied.

In Figure V, the spectrum of an acidic φNH_3ClO_4-$Hg(ClO_4)_2$ solution is compared with the sum of the individual spectra of the components. In this particular solution, the spectrum changes only slowly with time. It is clear that a complex exists. The formation

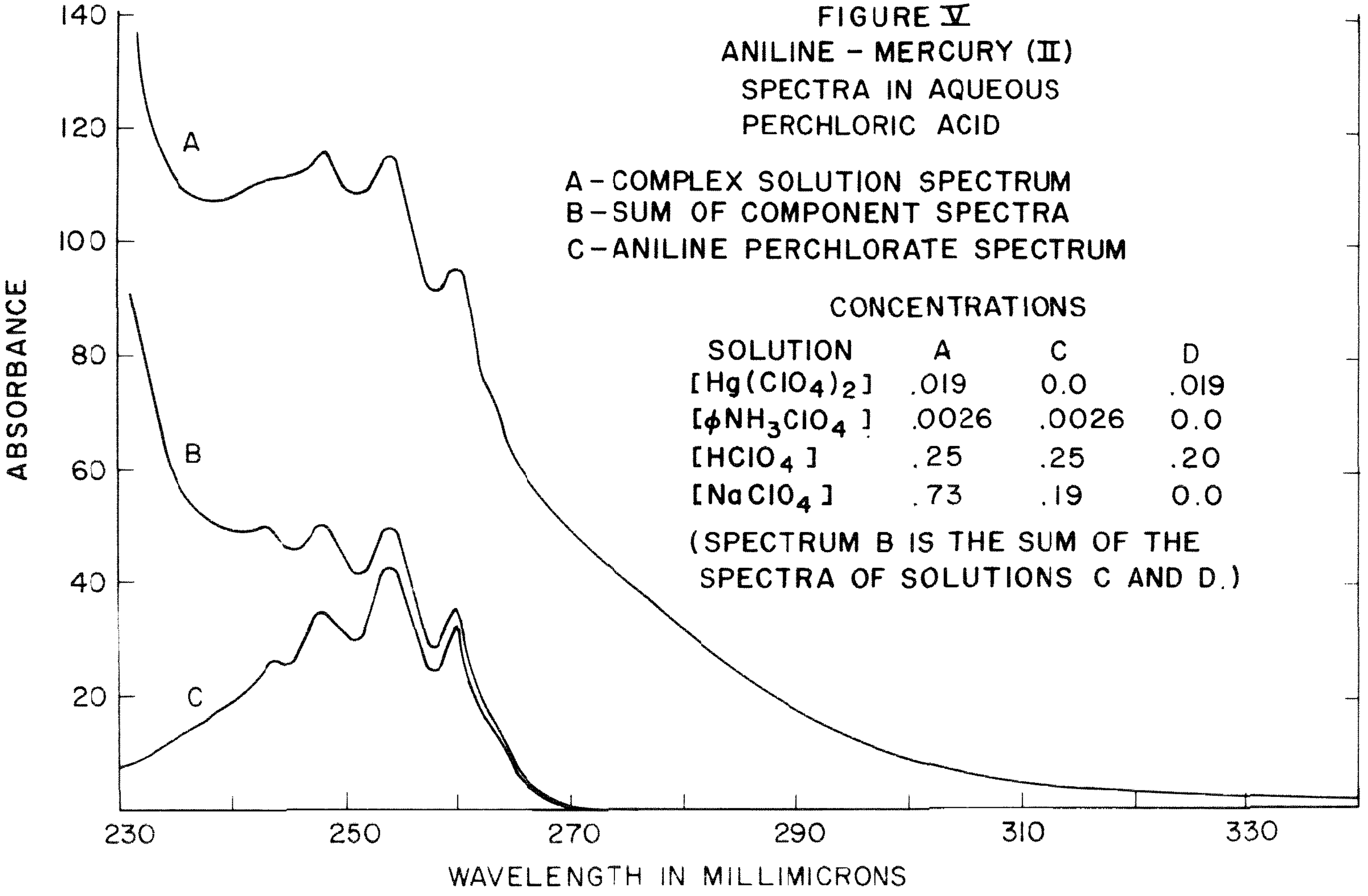


FIGURE V
ANILINE - MERCURY (II)
SPECTRA IN AQUEOUS
PERCHLORIC ACID

A - COMPLEX SOLUTION SPECTRUM
B - SUM OF COMPONENT SPECTRA
C - ANILINE PERCHLORATE SPECTRUM

CONCENTRATIONS

SOLUTION	A	C	D
$[Hg(ClO_4)_2]$	.019	0.0	.019
$[\phi NH_3ClO_4]$	.0026	.0026	0.0
$[HClO_4]$	.25	.25	.20
$[NaClO_4]$	.73	.19	0.0

(SPECTRUM B IS THE SUM OF THE SPECTRA OF SOLUTIONS C AND D.)

of the complex was studied quantitatively by observing the absorbance of a series of solutions at 276.0 millimicrons. At this wavelength, the absorption is almost entirely due to the complex.

Experimental details. - The aniline perchlorate stock solution used in the spectrophotometric experiments was prepared from the solid compound. Reagent grade aniline (J. T. Baker) was added to excess 30% $HClO_4$, cooled, and filtered. φNH_3ClO_4 is very soluble in ethanol, acetone, and water. The crude solid was dissolved in hot acetone. Chloroform was added until the solution became cloudy; it was then cooled and filtered. The solid was washed with cold 15% acetone-85% chloroform. The recrystallization was repeated three times. The pure white product was dried in a vacuum dessicator. A carefully weighed sample was dissolved in a known volume of standardized perchloric acid. Other stock solutions were prepared from this one by dilution.

The technique for preparing solutions of the complex was designed to permit the spectrum to be observed as rapidly as possible after mixing the components. This allowed accurate compensation for the slow spectral changes.

Both halves of a ₮ 24/40 ground joint were sealed to form test tubes. Into one half, aliquots of $Hg(ClO_4)_2$, $HClO_4$, and $NaClO_4$ stock solutions were introduced. All stock solutions were of unit ionic strength. An aliquot of φNH_3ClO_4 was added to the other. The tubes were individually stoppered and placed in a constant temperature bath at 26.9°C for at least one-half hour. Water from the bath circulated around the spectrophotometer cell compartment.

The quartz cell was cleaned and dried, and the spectrophotometer was set on the desired wavelength. The tubes were taken from the bath and the stoppers removed. As the contents of one were poured into the other, a stopclock was started. The tubes were joined and shaken vigorously; a sample was quickly transferred to the spectrophotometer cell, and the absorbance at 276 mμ was continuously recorded. Thus the recorder produced a graph of absorbance vs. time. The spectral changes were linear with time in every case, greatly facilitating extrapolation.

The absorbance at 332 mμ was also of interest, as will become evident later in the discussion. The spectrophotometer was set alternately on each wavelength for several minutes(without stopping the chart). The remainder of the solution (total volume-- 25 ml) was transferred to a glass-stoppered flask and stored in the dark.

Analysis of the data. - If the complex C_1 has a molar absorptivity ε_1 at a given wavelength,

$$[C_1] = Y/\varepsilon_1 , \tag{III-1}$$

where Y is the absorbance at that wavelength. If C_1 is the only complex formed,

$$[\varphi NH_2]_0 = [\varphi NH_3^+] + [C_1] \; . \qquad \text{(III-2)}$$

Equation I-7, with $[RH^+] \equiv [\varphi NH_3^+]$, can be solved for $[\varphi NH_3^+]$. If this expression and equation III-1 are introduced into III-2,

$$\frac{[\varphi NH_2]_0}{Y} = \frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_1 K_1} \frac{[H^+]}{[Hg^{++}]} \; . \qquad \text{(III-3)}$$

In these particular experiments, $[\varphi NH_2]_0 << [Hg^{++}]_0$ and $[H^+]_0$. Therefore, $[H^+]_0$ and $[Hg^{++}]_0$ can be substituted for $[H^+]$ and $[Hg^{++}]$, respectively. A plot of $[\varphi NH_2]_0/Y$ vs. $[H^+]_0/[Hg^{++}]_0$, then, has intercept $1/\varepsilon_1$ and slope $1/\varepsilon_1 K_1$.

Experimental results. - One expects a complex like φNH_2Hg^{++} to be rapidly formed; therefore, the absorbance at the time of mixing is the appropriate Y. The composition of the solutions and the extrapolated absorbance at 276.0 mμ are presented in Table IV. In Figure VI, $[\varphi NH_2]_0/Y$ is plotted against $[H^+]_0/[Hg^{++}]_0$. From the slope and intercept,

$$\varepsilon_1 = 2.4^4 \times 10^3 \; \ell\text{/mole-cm. at } \lambda = 276.0 \text{ m}\mu$$

$$K_1 = 0.68 \qquad (T = 27°C, \; \mu = 1.0 M).$$

TABLE IV. The 1:1 Aniline-Mercury(II) Complex. Absorbance of Mercury(II)-Aniline Solutions at 276 mμ

$T = 27°C$; $\mu = 1.0$ M ($NaClO_4$)

No.	$[\varphi NH_3ClO_4]$ x 10^2	$[Hg(ClO_4)_2]$	$[HClO_4]$	Absorbance at t=0 $\lambda = 276.0$	Corrected* Absorbance (Y)	$\frac{[\varphi NH_2]_0}{Y}$ x 10^2	$\frac{[H^+]_0}{[Hg^{++}]_0}$
42	.050	.178	.089	.773	.719	.070	0.50
43	.050	.178	.089	.783	.729	.069	0.50
44	.050	.178	.129	.657	.603	.083	0.72
45	.050	.178	.129	.657	.603	.083	0.72
46	.050	.178	.230	.466	.412	.121	1.29
47	.050	.178	.230	.473	.419	.119	1.29
48	.050	.178	.331	.379	.325	.154	1.86
50	.096	.171	.399	.577	.525	.183	2.34
51	.050	.178	.413	.324	.270	.185	2.34
52	.050	.0186	.104	.140	.134	.373	5.6
53	.050	.0186	.104	.143	.137	.365	5.6
54	.050	.037	.107	.247	.236	.212	2.87
55	.050	.074	.113	.405	.382	.131	1.52
56	.050	.074	.113	.406	.383	.131	1.52
57	.050	.149	.124	.608	.563	.089	.84
59	.050	.261	.141	.768	.701	.071	.54
60	.050	.178	.054	.928	.874	.057	.31
61	.050	.178	.054	.915	.861	.058	.31
62	.050	.148	.124	.590	.545	.092	.84
63	.050	.037	.107	.239	.228	.219	2.87
64	.050	.0186	.104	.136	.130	.385	5.6
65	.150	.178	.331	1.024	.970	.155	1.86
66	.100	.178	.331	.691	.637	.157	1.86
67	.070	.178	.331	.499	.445	.157	1.86
68	.030	.178	.331	.235	.181	.166	1.86

*Corrected for the absorption of Hg^{++}: $\varepsilon(Hg^{++}, \lambda = 276) = .30$ ℓ/mole-cm.

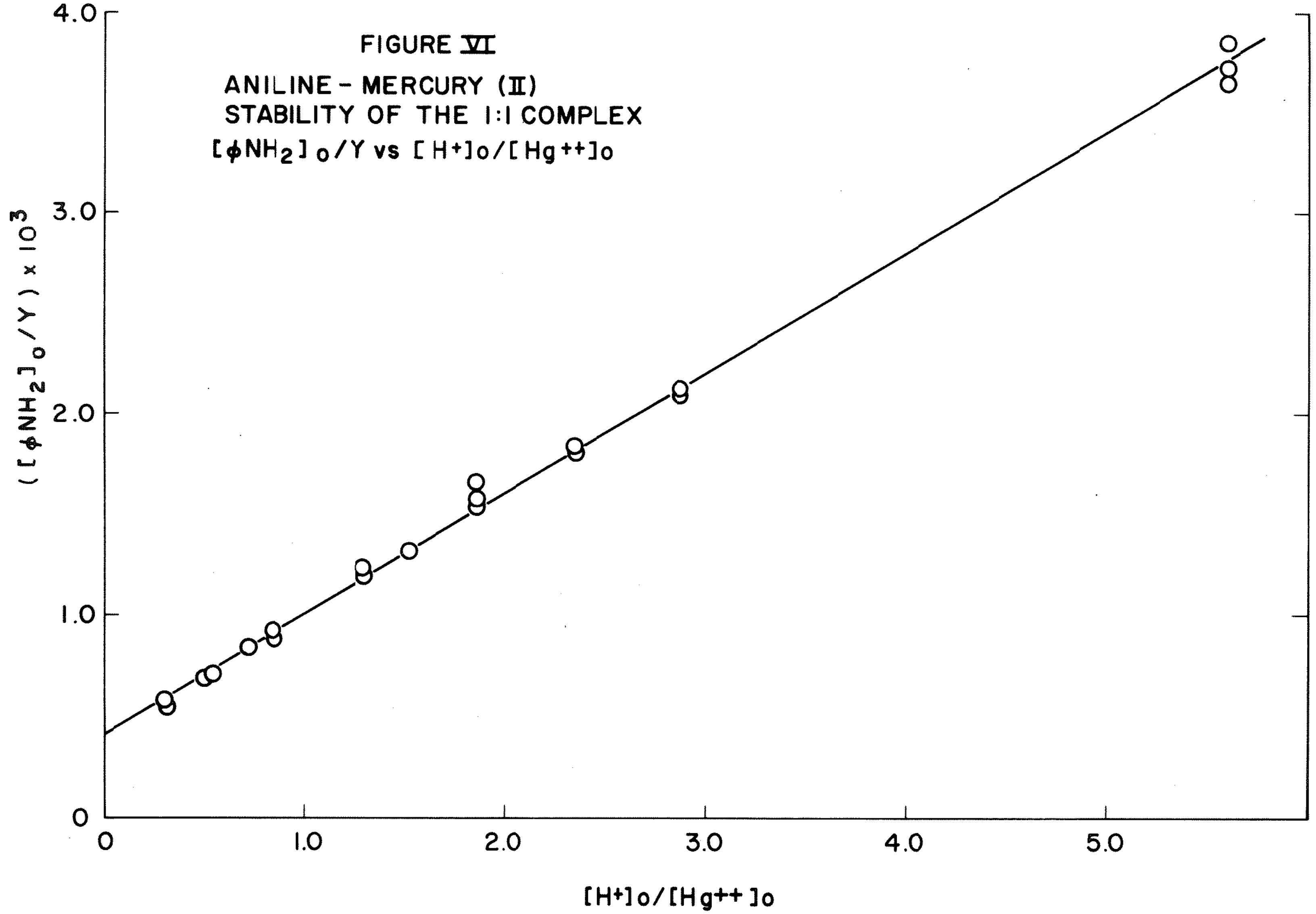


FIGURE VI

ANILINE - MERCURY (II)
STABILITY OF THE 1:1 COMPLEX
$[\phi NH_2]_o/Y$ vs $[H^+]_o/[Hg^{++}]_o$

Knowledge of ε_1 allows us to determine the concentration of C_1 responsible for the spectrum in Figure V. The absorption due to unreacted φNH_3^+ and Hg^{++} can be subtracted out and the spectrum of C_1 computed. The spectrum of C_1 is displayed in Figure VII.

The Mercuration of Aniline--An Introduction

The slow reactions between $Hg(ClO_4)_2$ and φNH_3ClO_4 in aqueous perchloric acid are accompanied by spectral changes and eventually by the formation of precipitates. They can be sharply distinguished from the formation of complexes C_1 and C_2, which is instantaneous. We have not succeeded in isolating or purifying the products eventually formed under the conditions where complex formation was studied. Nonetheless, a variety of indirect evidence--including a crystalline aniline-mercury-perchlorate compound prepared from more concentrated solutions--leads to the conclusion that the slow reaction is mercuration.

The literature.- Mercuration, a reaction of mercury(II) salts with aromatic compounds, is a well known example of electrophilic substitution (24). The salt, usually mercuric acetatate, reacts directly with the substrate; occasionally a solvent is used. A proton is displaced from the ring:

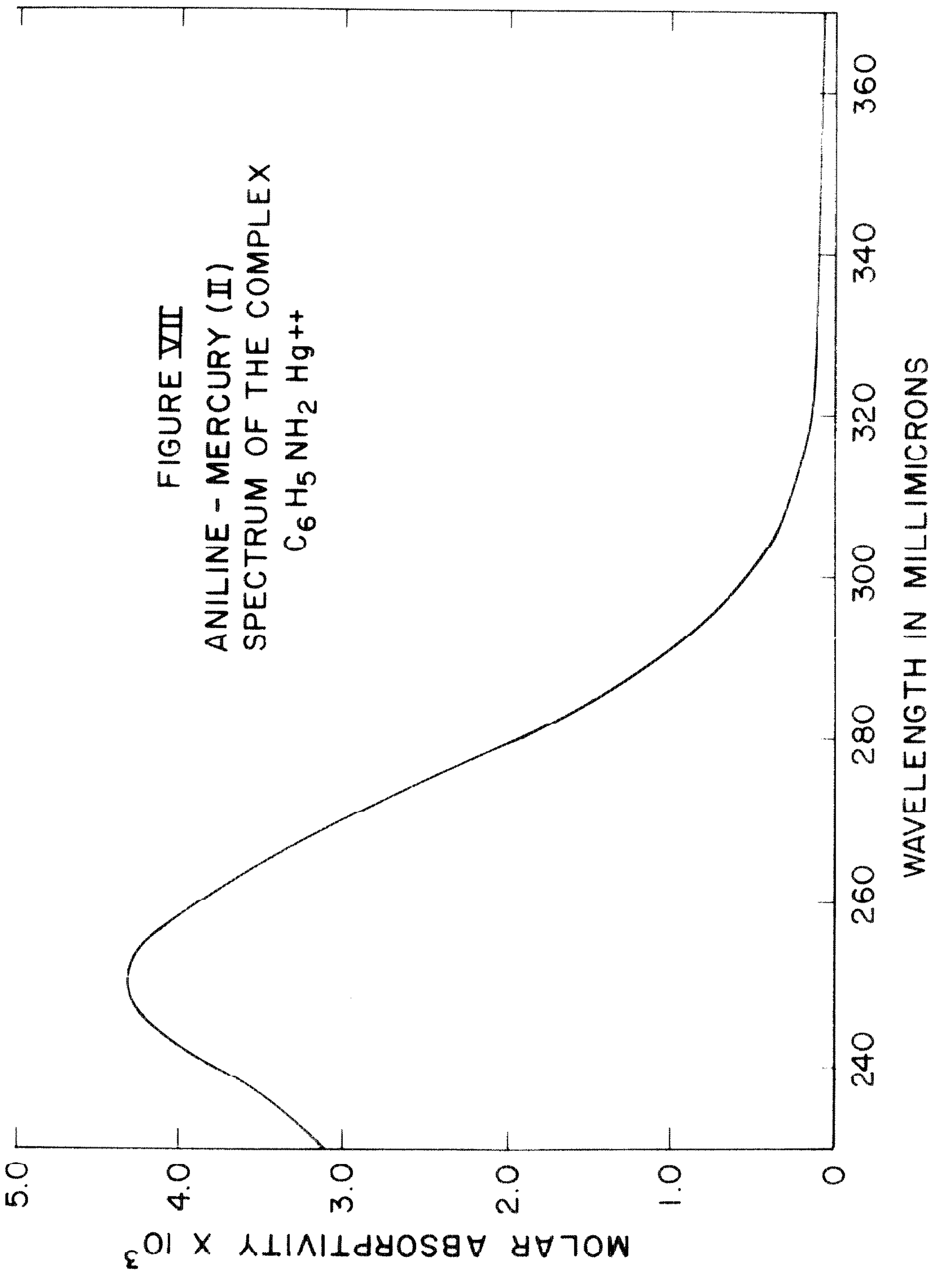


FIGURE VIII

ANILINE - MERCURY (II)
SPECTRUM OF THE COMPLEX
$C_6H_5NH_2\ Hg^{++}$

$$C_6H_6 + Hg(OAc)_2 \xrightarrow[\varphi NO_2 \text{ solvent}]{130°} C_6H_5HgOAc + HOAc$$

(25). More recently, Carmack (26), Westheimer (27, 28, 29, 30), and their coworkers 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 (31). The voluminous early work on compounds of mercury and its salts with aromatic amines has been surveyed by Whitmore (32). The situation was confused by the existence of HgX_2-amine double salts (X = halide), as well as by complex compounds containing only Hg-N bonds--$Hg(NHC_6H_5)_2$, for example. Dimroth (31) was the first to recognize mercuration as a general type of reaction, similar to other aromatic substitutions such as nitration and halogenation. He showed that in most cases the reaction of $Hg(OAc)_2$ with aromatic amines is fully analogous to the mercuration of other aromatic substrates. Pesci (33) studied the mercuration of a vast number of amines, but he remained convinced that Hg-N bonds, as well as Hg-C bonds, exist in the products (34). The views of Dimroth prevailed, but the duration and intensity of the controversy reflected the difficulty of proving directly whether mercury in a given compound is bound to N, C, or both.

The effect of acetic acid, NaOAc, $HClO_4$, $NaClO_4$, and HNO_3 on the rate of mercuration of aniline by mercuric acetate in aqueous solution was recently studied by Wronski (35). 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 reaction conditions were not varied systematically. Since the rate of mercuration is sensitive to salt concentration (29, 30), as well as to mercury(II)-acetate complex formation, no quantitative interpretation of Wronski's data is possible.

Some experimental observations. - Successive spectra of a φNH_3ClO_4-$Hg(ClO_4)_2$ solution are shown in Figure VIII. The most characteristic feature of the slow spectral change is the appearance of a strong absorption band at 330 mμ.

In solutions of low acidity or high concentrations of Hg(II), precipitates appear after periods ranging from a few hours to several weeks. The nature of the solids varies with the composition of the solution. Some solids are yellow, others white; some crystalline, others amorphous. In most cases, they are mixtures, insoluble in common solvents, and difficult to purify.

The key to understanding these reactions and the spectral changes accompanying them was the spectrum of an independently

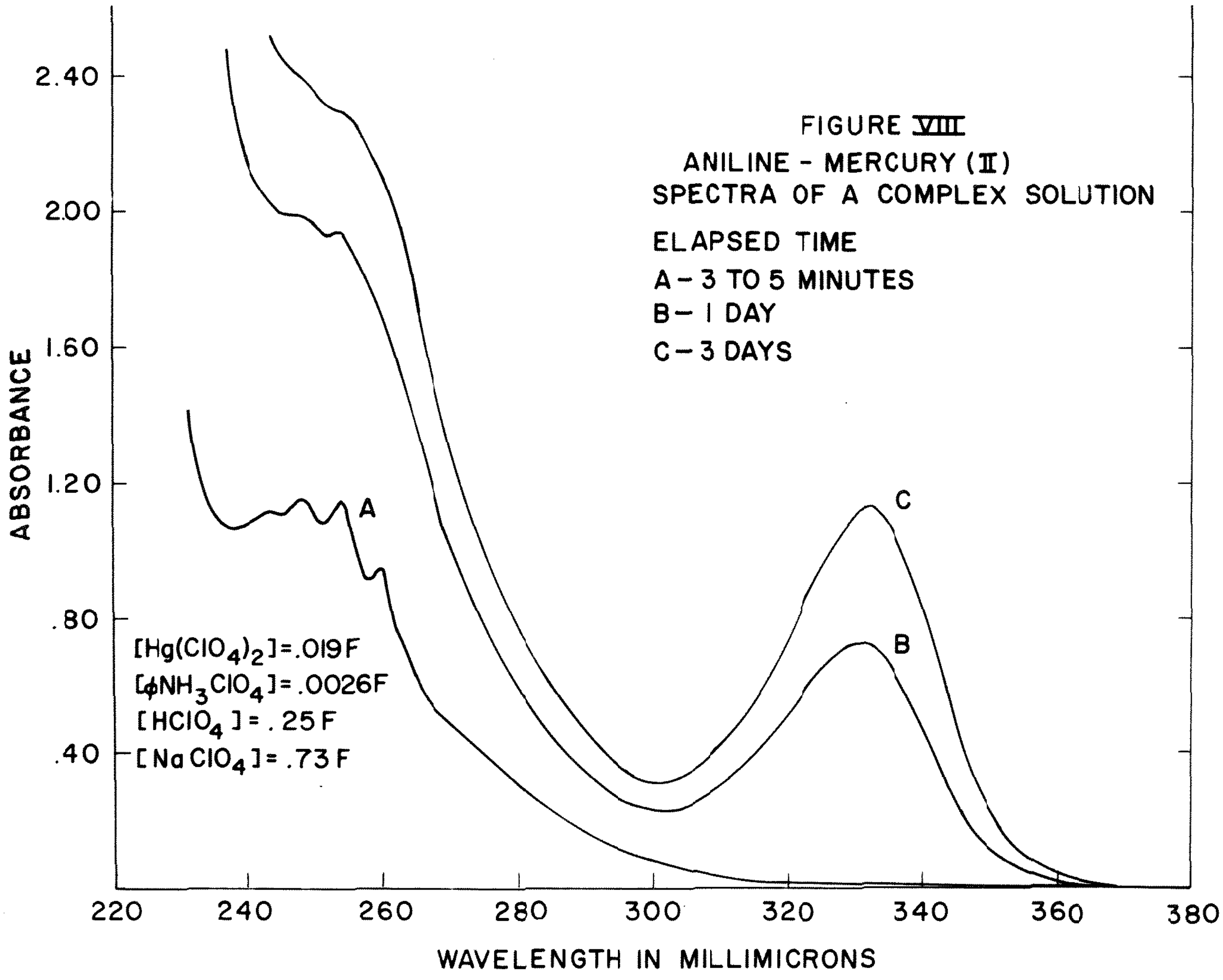


FIGURE VIII

ANILINE - MERCURY (II)
SPECTRA OF A COMPLEX SOLUTION

ELAPSED TIME
A – 3 TO 5 MINUTES
B – 1 DAY
C – 3 DAYS

$[Hg(ClO_4)_2] = .019F$
$[\phi NH_3ClO_4] = .0026F$
$[HClO_4] = .25F$
$[NaClO_4] = .73F$

synthesized sample of p-mercurated aniline in $HClO_4$-$Hg(ClO_4)_2$ solution. If no Hg(II) is present, the spectrum resembles the sum of the spectra of φNH_3^+ and Hg^{++}. No absorption occurs at wavelengths greater than 300 mμ. Addition of Hg(II), however, results in the immediate formation of a band in the 330 mμ region. As in the case of aniline itself, the absorbance increases slowly on standing. This is shown in Figure IX.

The experiment strongly suggests that mercuration occurs in $Hg(ClO_4)_2$-φNH_3ClO_4 solutions and that the distinctive band at wavelengths greater than 300 mμ is characteristic of Hg(II) complexes with the reaction products. In the following sections a number of studies are described which were suggested by this hypothesis. The results consistently support it.

(1) The 1:1 complex of p-mercurated aniline with Hg(II) ion was studied quantitatively.

(2) The spectra of the solutions of both aniline and p-mercurated aniline were determined after spectral changes had ceased. The results in the two cases were compared.

(3) The spectral behavior of these solutions on addition of acid, base, and $Hg(ClO_4)_2$ was determined.

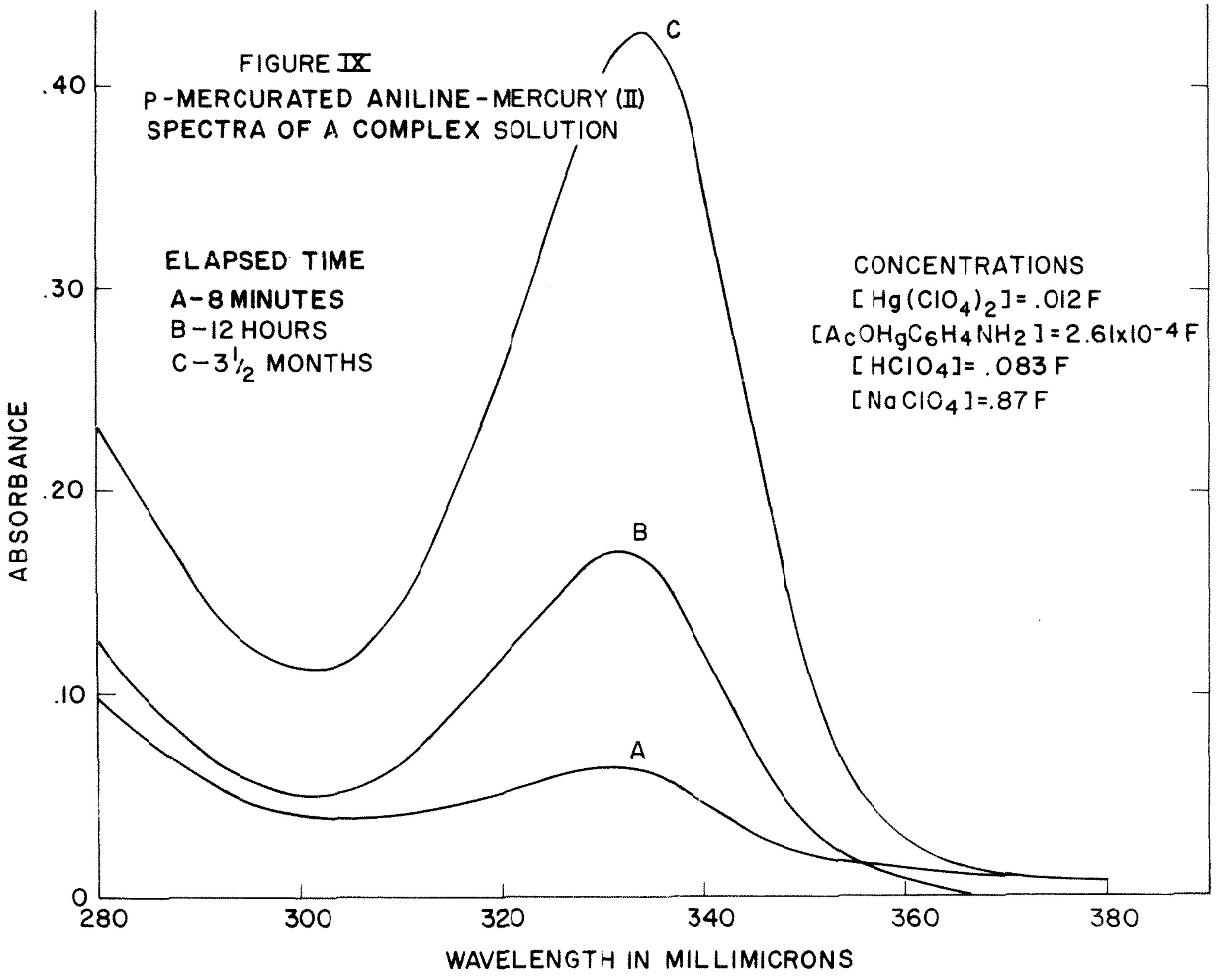


FIGURE IX
P-MERCURATED ANILINE-MERCURY (II) SPECTRA OF A COMPLEX SOLUTION

(4) The variation of the initial reaction rate
with solution composition was studied.

It is well to state at the onset that a complete quantitative interpretation of the spectra of the reaction solutions in terms of rate and equilibrium constants and molar absorptivities was not possible. This was due to the large number of product isomers and to the multiplicity of species in any given solution. The functional form of the quantitative relationships remains significant, however.

The 1:1 Complex of the p-$^{+}HgC_6H_4NH_2$ Ion with Hg(II)

The determination of the association constant of this complex is very similar to the determination of K_1.

Experimental details.- p-Acetoxymercurianiline was prepared by the method of Dimroth (31). The compound was recrystallized by dissolving it in an ammoniacal NH_4OAc solution, adding decolorizing charcoal, and filtering. After the solution is neutralized with acetic acid, the compound precipitates slowly. This method was adapted from that used by Vecchiotti for 2,4-diacetoxymercurianiline (36). Dried in a vacuum dessicator, the crystals melted at 166-167.5°C. Literature value: 167° (31).

A stock solution of p-acetoxymercurianiline was prepared by dissolving a weighed sample in an $HClO_4$-$NaClO_4$ solution and diluting to known volume. The procedure was the same as that used to determine K_1. The absorbance at $\lambda = 331.0$ mμ was determined as a function of time. Neither Hg^{++} nor the p-$^{+}HgC_6H_4NH_3^{+}$ ion absorbs at this wavelength. In some cases, a 10 cm spectrophotometer cell was used. On these occasions, a larger volume of solution was prepared, and a 100 ml R.B. flask was used in conjunction with the sealed male joint for mixing.

The results.- The analysis of the data is the same as before, and equation III-3 becomes

$$\frac{[RP]_0}{Z} = \frac{1}{\varepsilon_1^P} + \frac{1}{\varepsilon_1^P K_1^P} \frac{[H^+]}{[Hg^{++}]} \qquad \text{(III-4)}$$

In this equation, $[RP]_0$ is the total amount of p-acetoxymercuri-aniline added, ε_1^P is the molar absorptivity of the complex, Z is the absorbance at 331.0 mμ, and K_1^P is the equilibrium constant of the reaction

$$p\text{-}^{+}HgC_6H_4NH_3^{+} + Hg^{++} \rightleftharpoons p\text{-}^{+}HgC_6H_4NH_2Hg^{++} + H^{+} .$$

(III-5)

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_3HgOAc, is 3×10^3 ℓ/mole (37). Taking the pK_A of acetic acid as 4.76 (38), we can calculate the ratio $[CH_3HgOAc]/[CH_3Hg^+]$ under the conditions most unfavorable to dissociation ($[H^+] = .03\,M$, $[RP]_0 = 4 \times 10^{-4}$ F). The result is $10^{-3.1}$. Certainly, then, the acetate salt is completely dissociated. Acetic acid does not contribute to the absorbance at 331 mμ.

The rate of increase of absorbance decreased with time, but it was relatively easy to perform a valid extrapolation to the time of mixing. To obtain $[H^+]$, the initial acid concentration was corrected for reaction with the mercurated amine (2 equiv./mole). Additional corrections for complex formation were not made, since $[RP]_0 \leq .01[H^+]_0$.

The data are presented in Table V, and in Figure X $[RP]_0/Z$ is plotted against $[H^+]/[Hg^{++}]_0$. From this,

$$\epsilon_1^P = 1.1 \times 10^3 \ \ell/\text{mole-cm at } \lambda = 331.0 \text{ m}\mu$$

$$K_1^P = 1.5 \qquad (T = 27°C, \ \mu = 1.0 M) .$$

It is interesting to note that K_1^P is greater than K_1.

The para-mercurated complex is clearly not the ultimate product formed in the reaction system. If a single mercurated compound and its Hg(II) complex are the ultimate products, no slow reaction would occur when that compound was introduced into an $Hg(ClO_4)_2$-$HClO_4$ solution.

2,4-Bis(acetoxymercuri)aniline. -Dimercurated aniline forms a similar complex with Hg(II). A slow absorbance increase also occurs in this case; therefore, the equilibrium was not systematically studied. The molar absorptivity of the complex was roughly estimated, however.

2,4-Bisacetoxymercurianiline, prepared by the method of Bruice (39), was purified by the method of Vecchiotti (36). The compound melted at 205-207°C; literature value: 206° (36), 209° (39). A stock solution was prepared by dissolving a weighed sample in

TABLE V. The 1: 1 Complex of Mercury(II) with Monomercurated Aniline ($p\text{-}{}^{+}HgC_6H_4NH_2Hg^{++}$)

$T = 27°C$; $\mu = 1.0\,M$ ($NaClO_4$)

No.	$[RP]_0$ x 10^3	$[Hg(ClO_4)_2]$	$[HClO_4]$	Z*	$\frac{[RP]_0}{Z}$ x 10^3	$\frac{[H^+]^{**}}{[Hg^{++}]_0}$
C-1	.261	.118	.055	.231	1.13	.46
C-2	.261	.118	.095	.194	1.34	.80
C-3	.261	.118	.116	.176	1.48	.97
C-4	.261	.118	.136	.162	1.61	1.14
C-5	.261	.118	.176	.142	1.84	1.48
C-6	.261	.118	.217	.121	2.16	1.83
C-7	.261	.148	.083	.219	1.19	.56
C-8	.261	.118	.083	.210	1.24	.70
C-9	.261	.095	.083	.195	1.34	.87
C-10	.261	.047	.083	.137	1.90	1.75
C-11	.261	.024	.083	.093	2.81	3.5
C-12	.261	.0118	.083	.058	4.50	7.0
C-13	.261	.154	.065	.244	1.07	.42
C-14	.38	.0178	.033	$\underline{.192}$	1.99	1.80
C-15	.38	.0178	.073	$\underline{.111}$	3.44	4.1
C-16	.38	.0178	.114	$\underline{.079}$	4.83	6.3
C-17	.38	.0178	.154	$\underline{.062}$	6.14	8.6
C-18	.38	.0178	.194	$\underline{.051}$	7.55	10.9
C-19	.38	.0178	.235	$\underline{.045}$	8.56	13.2
C-20	.38	.0178	.275	$\underline{.042}$	8.99	15.5

* Z = absorbance at $\lambda = 331.0$ mμ, t = 0. Underlined values were determined in 10 cm cells and the results divided by 10.

** $[H^+] = [H^+]_0 - 2[RP]_0$.

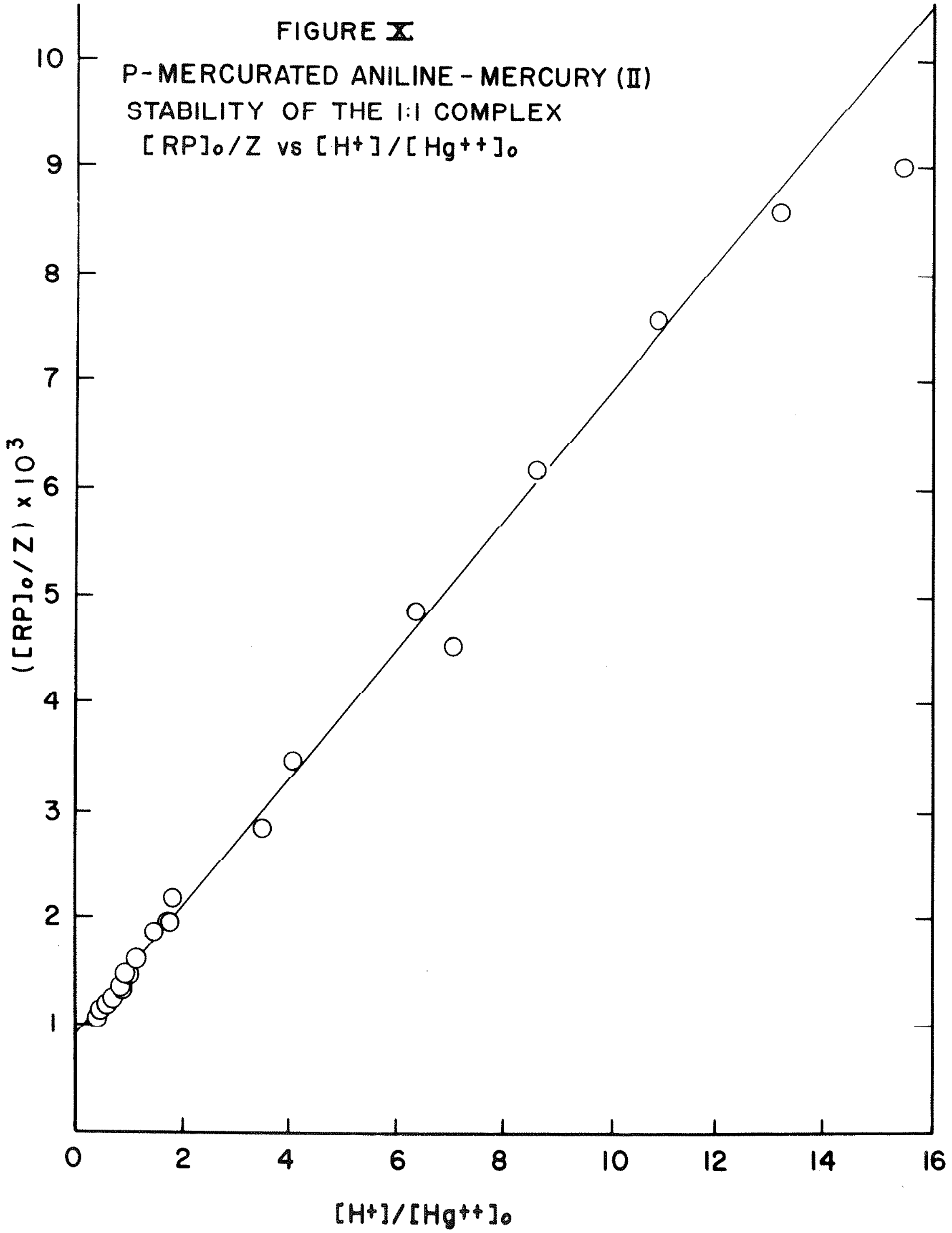


FIGURE X
P-MERCURATED ANILINE - MERCURY (II)
STABILITY OF THE 1:1 COMPLEX
[RP]o/Z vs [H+]/[Hg++]o
$([RP]_0/Z) \times 10^3$
1
2
3
4
5
6
7
8
9
10
0
2
4
6
8
10
12
14
16
$[H^+]/[Hg^{++}]_0$

0.16 F $HClO_4$-0.84 F $NaClO_4$.

This 0.01 F solution of 2,4-dimercurated aniline exhibited a band at 333 mμ with an intensity of .28 absorbance units in a 0.1 cm cell. However, the solution does not absorb at wavelengths greater than 300 mμ if diluted into acid. The band is probably due to intermolecular C-Hg-N complexing.

1.00 ml of this solution was added to 50.0 ml of a solution .32 F in $Hg(ClO_4)_2$ and .04 F in $HClO_4$. Under these strongly complexing conditions, most of the amine is complexed, and the absorbance is a rough measure of the absorptivity of the complex. By extrapolation to the time of mixing, the molar absorptivity $\epsilon_1^{2,4}$ of the complex 2,4-$({}^{+}Hg)_2C_6H_3NH_2Hg^{++}$ is

$$\epsilon_1^{2,4} \sim 4 \times 10^3 \ \ell/\text{mole-cm} \quad (\lambda = 333 \text{ m}\mu)$$

This is a factor of 4 greater than ϵ_1^P, which indicates that the molar absorptivity of these 1:1 complexes tends to increase with the degree of ring mercuration.

Spectrophotometric Study of Solutions of Aniline Derivatives and Mercury(II) after the Termination of Slow Reactions

The solutions themselves. - The foregoing sections describe some rather detailed spectral studies of the complexes of mercury(II) with aniline and para-mercurated aniline. These studies were complicated by slow reactions which cause the appearance of a band in the 330 mμ region or an increase in its intensity. It has been suggested that in both cases the slow reaction is mercuration of the aromatic ring, and that the absorption band is due to Hg(II) complexes with the products.

Eventually, the spectral changes in these solutions cease. It is likely that equilibrium among the various possible ring-mercurated anilines has then been attained. If so, the final absorbance should not depend on whether aniline or p-mercurated aniline was the original starting material.

This is indeed the case. The spectra of the aniline-Hg(II) solutions were taken after standing four months in glass-stoppered erlenmeyer flasks. The spectra of p-mercurated aniline-Hg(II) solutions were recorded three-and-one-half months after preparation. All solutions had been stored in the dark. Neutral density filters made measurement of high absorbances possible. In Table VI, the

TABLE VI. Spectra of Aniline and p-Acetoxymercurianiline Solutions at Equilibrium in the Presence of Excess $Hg(ClO_4)_2$ and $HClO_4$

$T \sim 22°C$; $\mu = 1.0$ ($NaClO_4$)
(For concentrations, see Tables IV and V)

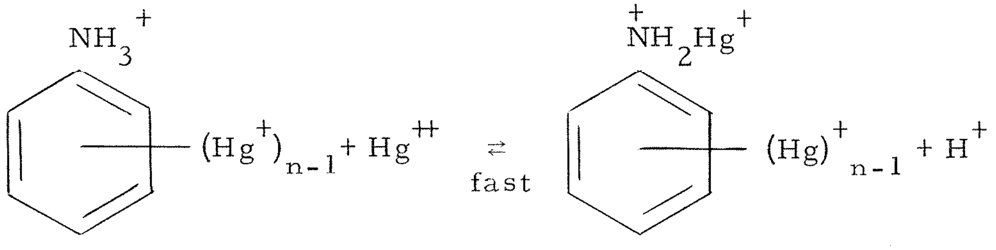
No.	λ_{max}	Z_{max}	$\frac{[R]_0}{Z_{max}} \times 10^4$	No.	λ_{max}	Z_{max}	$\frac{[R]_0}{Z_{max}} \times 10^4$
			Aniline Solutions				
43	334.1	4.51	1.11	55	335.0	2.91	1.72
44	334.6	3.84	1.30	56	335.0	2.92	1.71
45	334.7	3.87	1.29	57	334.3	3.68	1.36
46	334.6	3.31	1.51	59	335.2	3.93	1.27
47	334.3	3.17	1.58	61	334.9	4.41	1.13
48	334.4	3.35	1.49	62	334.9	3.80	1.32
49	334.7	2.57	1.95	63	334.5	1.91	2.62
50	334.3	4.44	2.16	64	333.8	1.01	4.94
51	334.1	2.39	2.09	65	329.7	5.65	2.66
52	333.9	1.05	4.78	66	334.3	5.01	2.00
53	333.9	1.00	4.99	67	334.7	3.55	1.97
54	334.2	1.93	2.59	68	334.5	1.54	1.95
			p-Acetoxymercurianiline Solutions				
C-2	334.8	1.94	1.35	C-11	334.5	.894	2.92
C-3	334.8	1.73	1.51	C-12	334.0	.428	6.10
C-4	334.6	1.69	1.54	C-13	334.8	2.20	1.19
C-5	334.5	1.54	1.70	C-15	334.2	1.08	3.53
C-6	334.5	1.49	1.76	C-16	334.0	.684	5.57
C-7	334.8	2.16	1.21	C-17	334.0	.480	7.94
C-8	334.8	2.00	1.31	C-18	333.0	.355	10.7
C-9	334.7	1.91	1.37	C-19	333.2	.288	13.2
C-10	334.5	1.45	1.80	C-20	332.6	.231	16.5

wavelength of maximum absorption and the absorbance at that wavelength (Z_{max}) are presented. Solutions in which precipitates developed are omitted.

In Figure XI, $[R]_0/Z_{max}$ is plotted as a function of $[H^+]/[Hg^{++}]_0$. (If $R = \varphi NH_2$, $[H^+] = [H^+]_0$. For p-acetoxymercurianiline, where $R = RP$, $[H^+] = [H^+]_0 - 2[R]_0$. See previous section.) It is clear that the functional behavior is independent of the starting material.

Interpretation of the results. - The model predicts that at equilibrium, the products are ring-mercurated aniline derivatives and their complexes with Hg(II) . It is possible that a single stage of mercuration is strongly favored under these conditions--that is, that only tri- or tetra-mercurated species are present at equilibrium. However, the data suggest that the products are distributed between two different stages of mercuration.

If this is true, the following principal equilibria exist:



(HRW)

(CW_1)

(III-6)

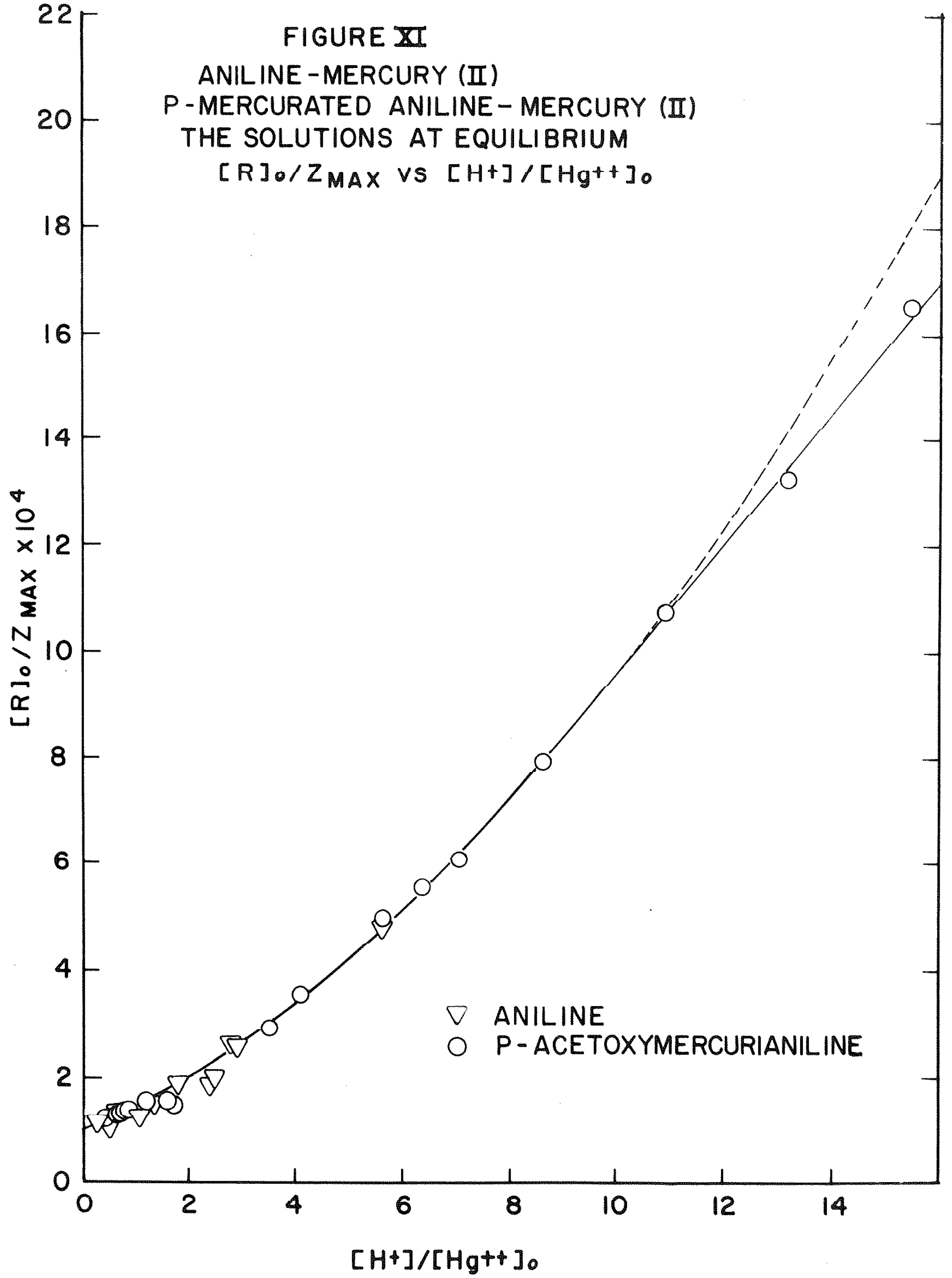
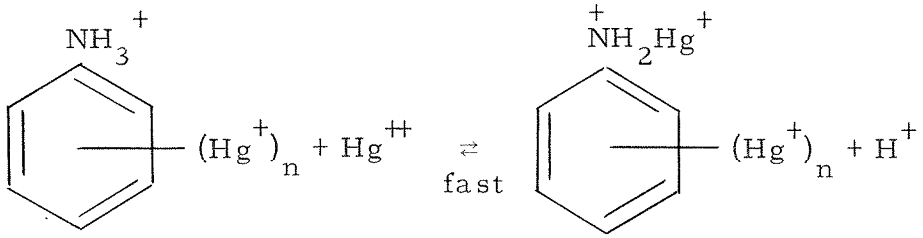


FIGURE XI
ANILINE-MERCURY (II)
P-MERCURATED ANILINE-MERCURY (II)
THE SOLUTIONS AT EQUILIBRIUM
[R]o/ZMAX VS [H+]/[Hg++]o
[R]o/Z MAX X 10^4
[H+]/[Hg++]o
0
2
4
6
8
10
12
14
16
18
20
22
▽ ANILINE
○ P-ACETOXYMERCURIANILINE



(HRX) (CX$_1$)

(III-7)

$$CW_1 + Hg^{++} \underset{\text{slow}}{\rightleftarrows} CX_1 + H^+ \ . \qquad \text{(III-8)}$$

Abbreviated symbols for the four major species are given in parentheses below their formulae. The equilibrium constants for these reactions are:

$$K_1^W = \frac{[CW_1]\,[H^+]}{[HRW]\,[Hg^{++}]}$$

$$K_1^X = \frac{[CX_1]\,[H^+]}{[HRX]\,[Hg^{++}]}$$

$$K_{WX} = \frac{[CX_1]\,[H^+]}{[CW_1]\,[Hg^{++}]}$$

An equilibrium analogous to III-8 exists between HRW and HRX, but the constant is not independent of the other three.

At equilibrium, then,

$$[R]_0 = [HRW] + [CW_1] + [HRX] + [CX_1] .$$

Rearranging the equilibrium constant expressions and substituting, we obtain

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

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

$$Z = \epsilon_1^W[CW_1] + \epsilon_1^X[CX_1] ,$$

from which

$$Z = [CX_1]\left(\epsilon_1^X + \frac{\epsilon_1^W}{K_{WX}}\frac{[H^+]}{[Hg^{++}]}\right) . \tag{III-10}$$

Dividing III-9 by III-10, we obtain

$$\frac{[R]_0}{Z_{max}} = \frac{1 + \left(\frac{1}{K_1^X} + \frac{1}{K_{WX}}\right) x + \left(\frac{1}{K_1^W K_{WX}}\right) x^2}{\epsilon_1^X + \left(\frac{\epsilon_1^W}{K_{WX}}\right) x} , \tag{III-11}$$

where x is $[H^+]/[Hg^{++}]$. (Z, the absorbance at a particular wavelength, can be replaced by Z_{max} because λ_{max} is very nearly constant.) We correctly predict, then, that $[R]_0/Z$ is a function of $[H^+]/[Hg^{++}]$. The function would be linear in the absence of HRW and CW_1 .

It is difficult to distinguish a function like III-10 from a simple quadratic unless extensive data at high values of the independent variable are available. Although our data in this range are limited, Figure XI indicates that the $[R]_0/Z$ function is most likely of the form III-11. A parabola was fit to the data for which $[H^+]/[Hg^{++}]_0 < 10$ by the method of least squares. The result is the dotted line in the figure, which is the function

$$[R]_0/Z_{max} = (0.94 + 0.46x + 0.42x^2) \times 10^{-4} . \qquad \text{(III-12)}$$

This represents the data excellently if $x < 10$, but the points for which $x > 10$ lie much more nearly on a straight line tangent to the parabola as indicated. The asymptotic form of the function III-10 is linear.

At this point, we are faced with a difficulty which makes more extensive interpretation rather futile--namely, the likelihood that HRW, HRX, etc. are not really single species at all. Rather, one expects them to be mixtures of isomers present in an equilibrium ratio which is independent of $[H^+]$ and $[Hg^{++}]$. As such, they have an apparent molar absorptivity and exhibit an apparent K_1. These quantities, while perfectly well defined, are not as interesting as those characteristic of a single compound.

In spite of this, it is useful to point out that the y-intercept in Figure XI is $1/\varepsilon_1^X$, where ε_1^X is the apparent molar absorptivity of the most highly mercurated aniline-Hg(II) complex existing in these solutions. From III-12,

$$\varepsilon_1^X = 1.1 \times 10^4 \ \ell/\text{mole-cm} ,$$

which exceeds ε_1^P by a factor of ten and $\varepsilon_1^{2,4}$ by a factor of 2.5.

Addition of $HClO_4$, NaOH, and $Hg(ClO_4)_2$. - If the model developed above is correct, addition of acids, bases, or $Hg(ClO_4)_2$ should produce immediate and pronounced changes in the spectra of the equilibrated solutions. This effect indeed occurs. Samples of aniline-Hg(II) solutions which had equilibrated 3 to 4 months were measured into spectrophotometer cells. Concentrated perchloric acid, sodium hydroxide, or $Hg(ClO_4)_2$ was added by micropipette. The solutions were mixed by bubbling N_2 through the cell; every attempt was made to avoid loss of sample. The absorbance was immediately recorded at the equilibrium λ_{max}.

This procedure caused immediate and marked changes in absorbance; slower and much smaller changes followed. Various concentrated reagents were added successively in random order. The absorbance after each addition was extrapolated to the time of mixing.

Perchloric acid caused a decrease in intensity; base and $Hg(ClO_4)_2$ caused an increase. A more quantitative interpretation is rendered somewhat inaccurate by the slow reactions. Furthermore, quantitative interpretation is not feasible if the products exist in more than one stage of mercuration. However, if $[H^+]/[Hg^{++}]$ is sufficiently small, only products of the type HRX and CX_1 are present in significant concentration.

Quantitatively, then,

$$[\varphi NH_2]_0 = [HRX] + [CX_1] .$$

If V_1 is the initial volume of the sample, and V_2 the volume after addition of concentrated reagent, this equation must be modified:

$$V_1[\varphi NH_2]_0/V_2 = [HRX] + [CX_1]$$

$$\frac{V_1[\varphi NH_2]_0}{V_2} = [CX_1]\left(1 + \frac{1}{K_1^X}\ \frac{[H^+]}{[Hg^{++}]}\right) \qquad \text{(III - 13)}$$

If

$$Z_{max} = \varepsilon_1^X [CX_1] ,$$

$$\frac{V_1 [\phi NH_2]_0}{V_2 Z_{max}} = \frac{1}{\varepsilon_1^X} + \frac{1}{\varepsilon_1^X K_1^X} \left(\frac{[H^+]}{[Hg^{++}]} \right) . \qquad \text{(III-14)}$$

It must be emphasized again that this equation is valid only if $[H^+]/[Hg^{++}]$ in the equilibrated solution is small. The results for all solutions in which $[H]/[Hg]_0 < 1$ are presented in Figure XII. The range of variation is somewhat small because a very large amount of concentrated $HClO_4$ was necessary to suppress more than 50% of the absorbance. It is clear, however, that equation III-14 is obeyed. The intercept of the line is 0.99×10^{-4}, leading to a value of ε_1^X of 1.0×10^4 ℓ/mole-cm. This agrees with the previous value. In addition, the ratio of intercept to slope is an estimate of K_1^X. From the graph, $K_1^X = 3$; this is slightly larger than either K_1 or K_1^P.

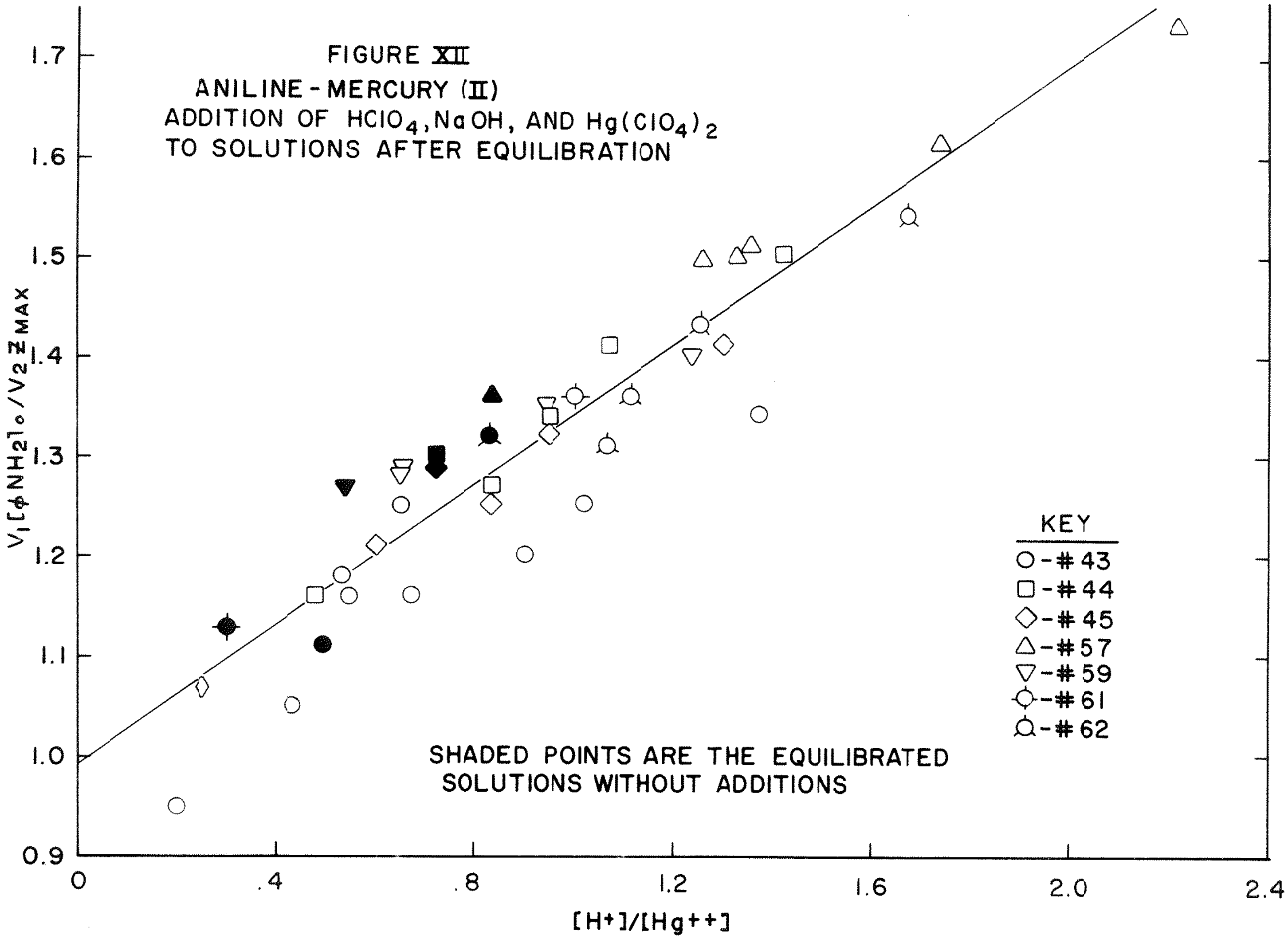


FIGURE XII

ANILINE - MERCURY (II)

ADDITION OF $HClO_4$, NaOH, AND $Hg(ClO_4)_2$ TO SOLUTIONS AFTER EQUILIBRATION

Reaction of Aniline and p-Acetoxymercurianiline with Excess Mercury(II): The Initial Rate

In conjunction with the determination of K_1 and K_1^P, the absorbance of the complex solutions in the 330 mμ region was recorded as a function of time. The slow increase in intensity is linear with time, or nearly so. The initial rate V_λ (in absorbance units/minute at wavelength λ) is related to $[H^+]$, $[Hg^{++}]$, and the concentration of 1: 1 complex in a very interesting way:

$$\frac{[C_1]}{V_\lambda} = a + b\,\frac{[H^+]}{[Hg^{++}]} \quad . \tag{III-15}$$

This empirical equation applies to both aniline and p-acetoxymercurianiline.

For each solution, V_λ was obtained by finding the slope of the line drawn tangent to the absorbance vs. time curve. The curve is linear for aniline solutions; the slight deviation from linearity exhibited by mercurated aniline solutions decreases the accuracy of those measurements slightly. The data are recorded in Table VII. Figures XIII and XIV show that equation III-15 applies to both cases. The rate law (III-15) is of unusual form, but it is the one predicted by the hypotheses already presented. Mercuration of benzene obeys a second order rate law (29); there is no reason to

TABLE VII. Spectral Changes at 331-332 mμ in Aqueous, Acidic Solutions of Aniline or p-Acetoxymercurianiline and Excess Mercuric Perchlorate: The Initial Rate

T = 27°C; μ = 1.0 M ($NaClO_4$)

Aniline Solutions*

No.	V_{332} x 10 (abs.units/min)	$[C_1]/V_{332}$** x 10 (mole-min/ℓ)	No.	V_{332} x 10 (abs.units/min)	$[C_1]/V_{332}$ x 10 (mole-min/ℓ)
42	.089	.33	56	.032	.49
43	.090	.33	57	.066	.35
44	.063	.39	59	.084	.34
45	.068	.36	60	.109	.33
46	.035	.48	61	.134	.26
47	.037	.46	62	.064	.35
48	.021	.62	63	$.013^8$	.67
50	.029	.73	64	$.003^6$	1.47
51	$.015^5$	.71	65	.072	.55
52	$.003^6$	1.53	66	.046	.56
53	$.004^5$	1.25	67	.033	.55
54	$.001^2$	.81	68	$.012^9$	.57
55	$.030^5$	.52			

p-Acetoxymercurianiline Solutions

No.	V_{331} x 10^2 (abs.units/min)	$[C_1^P]/V_{331}$*** x 10 (mole-min/ℓ)	No.	V_{331} x 10^2 (abs.units/min)	$[C_1^P]/V_{331}$ x 10 (mole-min/ℓ)
C-1	.94	.220	C-11	$.10^5$	.79
C-2	.62	.279	C-12	$.03^4$	1.52
C-3	.50	.314	C-13	1.09	.20
C-4	.41	.353	C-14	.34	.51
C-5	.32	.396	C-15	.083	1.19
C-6	.28	.386	C-16	.061	1.15
C-7	.76	.258	C-17	.035	1.61
C-8	.70	.268	C-18	.021	2.14
C-9	.55	.317	C-19	.017	2.38
C-10	.31	.402	C-20	.016	2.32

TABLE VII (continued) --Footnotes

* For $[H^+]$, $[Hg^{++}]$, and $[H^+]/[Hg^{++}]$, see Tables IV and V.

** $[C_1] = Y/\varepsilon_1$, with ε_1 taken as 2.44×10^3 ℓ/mole-cm. For Y, see Table IV.

*** $[C_1^P] = Z/\varepsilon_1^P$, with ε_1^P taken as 1.12×10^3 ℓ/mole-cm. For Z, see Table V.

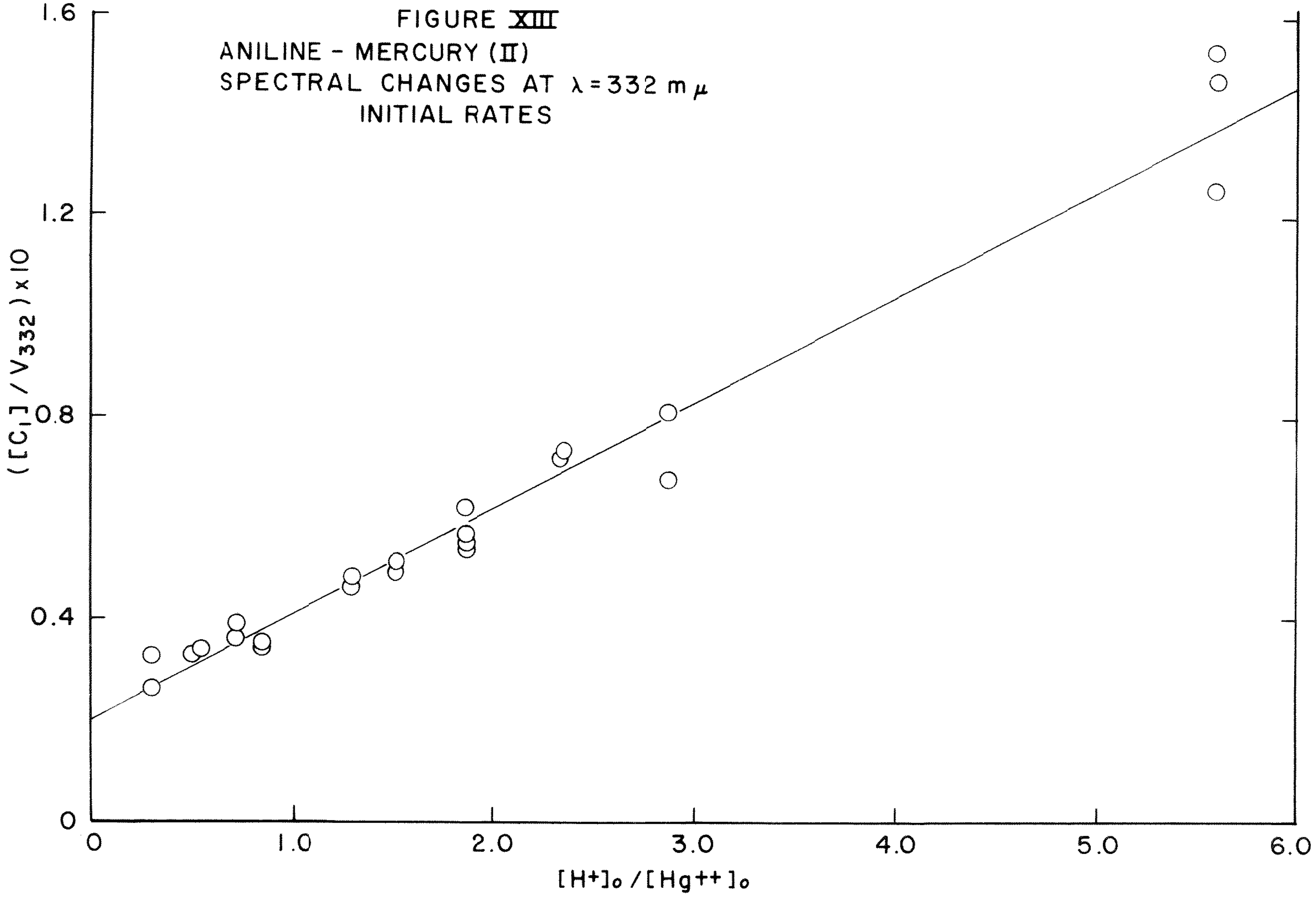


FIGURE XIII

ANILINE - MERCURY (II)

SPECTRAL CHANGES AT $\lambda = 332$ mμ

INITIAL RATES

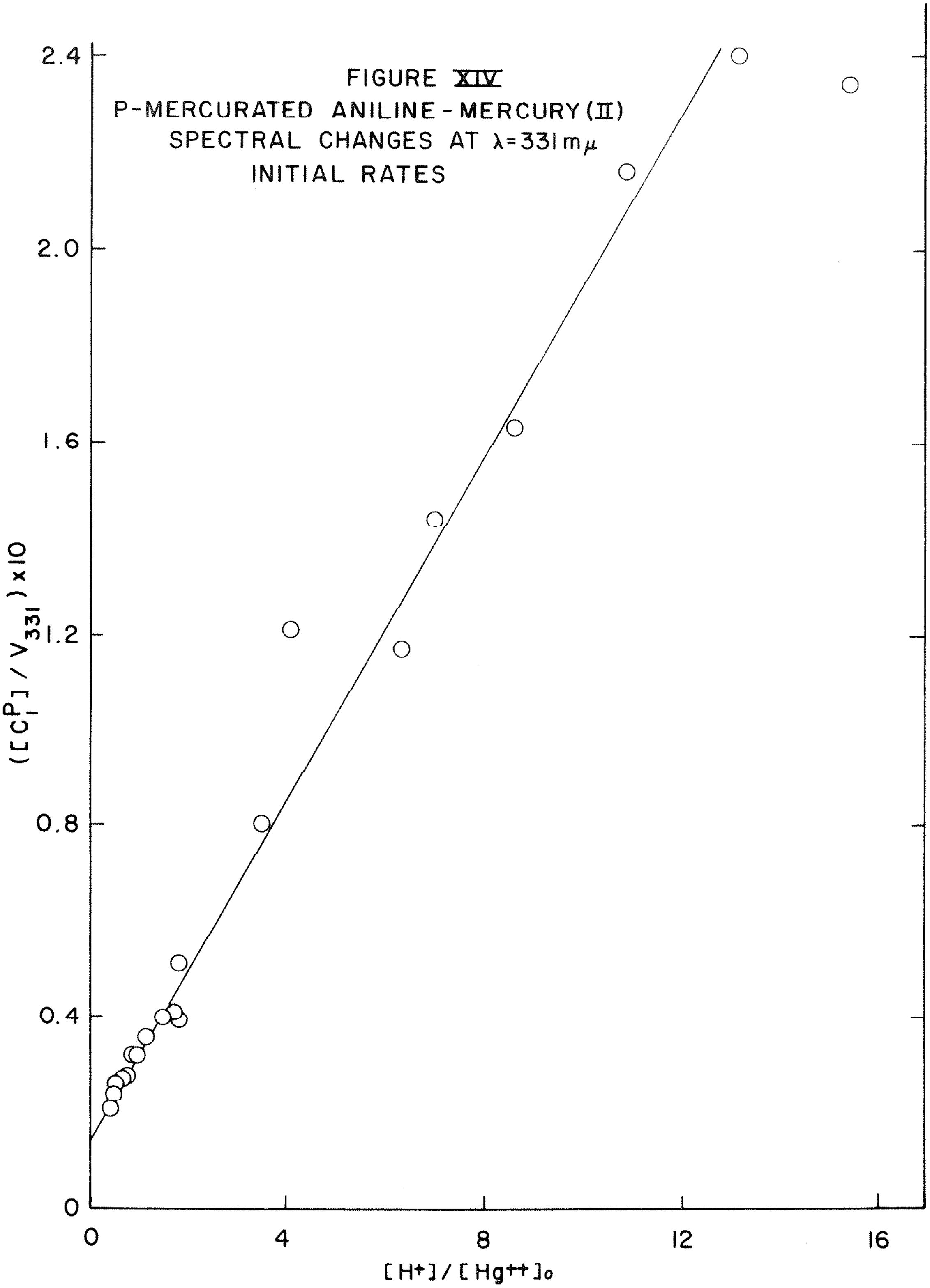


FIGURE XIV
P-MERCURATED ANILINE-MERCURY(II)
SPECTRAL CHANGES AT λ=331mμ
INITIAL RATES
$([C_1^P]/V_{331})\times 10$
$[H^+]/[Hg^{++}]_0$
0
0.4
0.8
1.2
1.6
2.0
2.4
0
4
8
12
16

suppose that aniline behaves differently. The reaction rate v is then

$$v = k[Hg^{++}]\,[\varphi NH_2]\,. \tag{III-16}$$

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

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

where [HRV] is the product (which is probably monomercurated), and $[CV_1]$ is the corresponding Hg(II) complex. But

$$K_1^V = \frac{[CV_1][H^+]}{[HRV][Hg^{++}]}\ .$$

Then

$$v = \left(1 + \frac{1}{K_1^V}\ \frac{[H^+]}{[Hg^{++}]}\right)\frac{d[CV_1]}{dt}\ . \tag{III-17}$$

In line with the supposition that CV_1 absorbs but that HRV does not, the absorbance Z_λ at the wavelength under consideration is equal to $[CV_1]\,\varepsilon_1^V$. Further, we may note that

$$[\varphi NH_2] = K_A\frac{[\varphi NH_3^{\ +}]}{[H^+]} = \frac{K_A}{K_1}\ \frac{[C_1]}{[Hg^{++}]}\ .$$

From all of this, III-16 becomes

$$\left(1 + \frac{1}{K_1^V} \frac{[H^+]}{[Hg^{++}]}\right) \frac{1}{\varepsilon_1^V} \frac{dZ_\lambda}{dt} = \frac{k\,K_A}{K_1}\,[C_1]\,.$$

Since $dZ_\lambda/dt = V_\lambda$ and $k\,K_A/K_1$ can be represented by k_C, we have

$$\frac{[C_1]}{V_\lambda} = \frac{1}{\varepsilon_1^V\,k_C} + \frac{1}{\varepsilon_1^V\,k_C\,K_1^V} \frac{[H^+]}{[Hg^{++}]}\,. \qquad \text{(III-18)}$$

This equation has the same form as the empirical relationship III-15. It is valid only for the initial rate; the complete rate expression is very complex and is of little use in evaluating the many parameters which appear therein.

Substitution of p-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.

From what has already been said, these seem to be realistic conditions.

Since ε_1^V is not known, the empirical spectral changes cannot be translated into rate constants. However, the ratio of intercept to slope in Figures XIII and XIV gives K_1^V. For aniline,

$K_1^V = 0.9^5$. For p-mercurated aniline, $K_1^{V'} = 0.8$. One does not expect the constants to be the same, since the first products are certainly different.

The fact that $K_1^V = 0.9^5$, while $K_1^P = 1.5$, indicates that isomers other than para are produced when aniline is monomercurated. There is no reason to believe that K_1^V is characteristic of di- or tri-mercurated species, for this would require that the second step of mercuration be much faster than the first.

This concludes the presentation of the spectrophotometric studies. The internal consistency of the results lends strong support to the interpretation which has been developed. In the following section, several less fruitful approaches are summarized. The final sections of the chapter contain a description of the isolation of a mercuration product and a general summary.

Additional Experimentation

Halide precipitation. - Addition of halide salts to the equilibrated solutions causes precipitation. Because the aniline concentration in the solutions prepared for spectrophotometric study was too small for preparative purposes, solutions of higher aniline concentration were prepared and allowed to stand. Halide precipitates of these were amorphous and clearly mixtures; usually white, the solids often turn yellow when washed free of supernatant. The products are only slightly soluble in the usual solvents; this is characteristic of aromatic mercurials.

The development of an analysis to differentiate between C- and N-bound Hg(II) was attempted. Treatment with concentrated halide solutions is expected to complex all labile Hg(II) and precipitate mercury bound to aromatic rings. This principle was successfully used in the study of the mercuration of benzene (Chapter IV), where the spectrum of the $HgCl_4^{=}$ complex was used in the analysis. Unfortunately, in this case it was not possible to remove the many compounds which absorb at 230 mμ. $HgI_4^{=}$ has a distinctive spectrum at much longer wavelengths. However, analytical procedures utilizing iodide gave erratic results which indicated that significant demercuration occurs when so strong a complexing agent is present. Experiments with bromide produced similar results.

Dimroth (31) distinguished between carbon- and nitrogen-bound Hg(II) by treatment of a compound with cold $(NH_4)_2S$. p-Acetoxymercurianiline and 2,4-bis(acetoxymercuri)aniline do not form HgS for at least 5 minutes, whereas a compound like $(\varphi NH_2)_2HgCl_2$ turns black immediately. However, many compounds tested exhibited intermediate behavior, turning black after 15-45 seconds, so clear-cut conclusions could not be drawn.

It was thought that the crude halide precipitates might be investigated by acetylation and subsequent treatment with bromine. This procedure was used by Dimroth to determine the structure of the products he isolated from the mercuration of aniline (31). Klapproth and Westheimer (28) used a bromination technique in the study of isomer distribution in the mercuration of nitrobenzene and toluene. The products, in which Br replaces Hg on the aromatic ring, are much easier to separate and analyze than the mercury compounds.

However, it was found that acetanilide itself is brominated, even under the very mild conditions used here (dilute aqueous Br_2-KBr). Therefore, the method is not useful for analysis of crude acetanilides, although structure determination of a pure, analyzed compound by bromination is not necessarily discredited. Toluene and nitrobenzene are much less reactive than acetanilide.

Ion exchange. - The components of the equilibrated solutions are cations; one might expect that they could be separated on a cation exchange column. Preliminary experiments were performed on purified Dowex 50 resins of different degrees of cross-linking. Acidic solutions of Hg^{++} and 2,4-bis(acetoxymercuri)aniline were chromatographed, as well as samples of concentrated reaction solutions of Hg(II) and aniline. Columns were developed with acidic .1-1.0 F $Ca(ClO_4)_2$, $Ba(ClO_4)_2$, or $La(ClO_4)_3$ solutions; Ti(IV) oxidizes aniline derivatives under these conditions. Eluent fractions were assayed spectrophotometrically; mercury-containing material on the columns was detected by treatment with H_2S at the end of the elutions.

The experiments showed that separations are indeed possible. However, the very large and highly charged mercurated cations adhere so strongly to the column that even $La(ClO_4)_3$ elutes them only in very dilute condition. It appears that moderately concentrated Hg^{++} reacts with the resin to some degree; in some cases, H_2S assay produced a uniform gray. In no case where complete separations were achieved was all the material removed from the column.

It is almost impossible to draw any conclusions from the detailed behavior of the various species on the column (elution times, etc.). The presence of H^+ in the eluent, necessary to solublize the mercurated compounds, makes the theoretical treatment intractable.

Although the method showed some promise, it was not pursued, inasmuch as little information can be gained from very dilute solutions of these mercurated products in so overwhelming an excess of salt.

Isolation of a Crystalline Mercurated Product

Most of the aniline-Hg(II) solutions were intended for spectrophotometric study; consequently, they contained aniline in small concentrations (5×10^{-4} - 5×10^{-3} F). Precipitates formed in these solutions at acid concentrations in the range $1\text{-}5 \times 10^{-2}$ F. The tendency to precipitate increased with increasing $Hg(ClO_4)_2$ concentration and/or decreasing acidity. Formed only in small amounts, these yellowish-white solids were amorphous, insoluble in organic solvents, and not amenable to purification.

In concentrated $Hg(ClO_4)_2$ solutions of higher acidity and φNH_3ClO_4 concentration, a yellow crystalline compound forms. A solution was prepared of the following composition:

2 F $Hg(ClO_4)_2$
0.1 F φNH_3ClO_4
0.5 F $HClO_4$.

Five weeks after preparation, a copious yellow precipitate appeared over the course of a few days. 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.

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 was kept always in the dark, and does not deteriorate under these conditions.

The solid is closely related to aniline. A crystalline sample was digested for several hours at 70°C 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 U.V. 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, no oxidation or degradation of the aniline has occurred.

The solid is related to the products formed in more dilute solutions. 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.

A second sample was prepared from an essentially similar $Hg(ClO_4)_2$ solution (1.6 F $Hg(ClO_4)_2$; .07 F φNH_3ClO_4; .3 F $HClO_4$).

Seed crystals were added to the solution; precipitation began within 3 days and was allowed to continue for two weeks. The crystals were washed with concentrated $Hg(ClO_4)_2$ and water as before, and dried over a saturated solution of $Mg(NO_3)_2 \cdot 6H_2O$. (This maintains 50% relative humidity.)

If a weighed sample of these crystals is dried further in a vacuum desiccator over anhydrous $CaCl_2$, 8.30% of the weight is lost. The compound turns to a yellow powder. If exposed to the air, it regains this weight.

Elemental analysis. - Three samples of the compound were sent to Schwarzkopf Microanalytical Laboratories for C and Hg analyses after drying at 50% humidity. In their Hg analytical procedure, the compound is decomposed in a sealed tube at 400°C and titrated for Hg(II) with sodium diethyl dithiocarbamate (40).

The compound was analyzed for perchlorate in this laboratory using tetraphenylarsonium chloride in a modification of the procedure of Willard and Perkins (41). Weighed samples of the compound were digested in 25 ml of 3 F HCl on a steam bath at 90-100°C until they dissolved. This required eight hours. Each warm sample was saturated with H_2S. The solutions were filtered through a sintered glass funnel; the funnel was rinsed and the washings combined with the filtrate. The combined solutions were boiled for fifteen minutes to expel excess H_2S. Each sample was neutralized with 50% NaOH, then made slightly acidic with HCl. 60 ml of φ_4AsCl solution was added (.011 F, prepared from solid φ_4AsCl purchased from G. Fredrick Smith). The samples were allowed to stand overnight, filtered into tared crucibles, dried, and weighed.

The compound was also analyzed for mercury by the method of Schulek and Floderer (42). These results were consistently lower than those obtained commercially.

On the basis of these analyses, the compound can be assigned the following formula: $C_6NH_3Hg_3(ClO_4)_2 \cdot 4H_2O$. One nitrogen was assumed per six carbons; the hydrogen content was assigned on the basis of charge balance.

The composition of this compound can be explained only on the basis of the following:

(a) It must contain Hg-C bonds. It is inconceivable that all 3 Hg atoms per aromatic ring be exclusively bound to N.

(b) The low ClO_4 analysis requires either hydroxyl anions or, more likely, extensive -Hg- bridging between aromatic groups.

No further speculation will be attempted, except to say that the structure is probably polymeric.

TABLE VIII. Calculated and Observed Composition of the Crystalline Hg(II)-Aniline Compound Isolated from Concentrated Aqueous Perchlorate Solution

Group	C	Hg	ClO_4	H_2O
Calculated % by wt. $(C_6NH_3Hg_3(ClO_4)_2 \cdot 4H_2O)$	7.50	62.6	20.7	7.50
Found	7.68	59.6[a]	22.43	8.30
	7.75	59.7[a]	22.40	
	7.82	59.8[a]	22.36	
		61.8[b]	22.25	
		62.0[b]		
		61.4[b]		

[a] Schulek and Floderer method

[b] Wickbold method

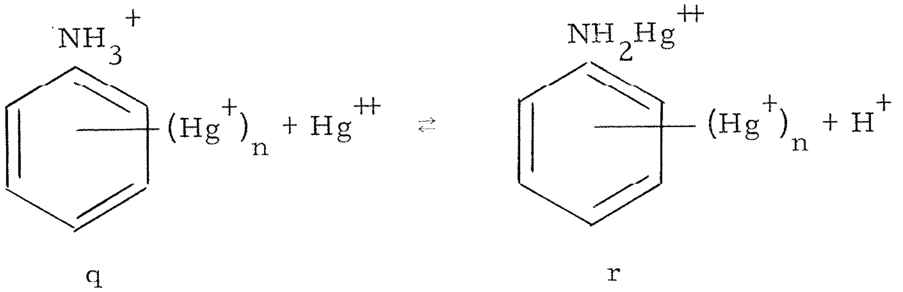
Single crystals. - A small sample of $Hg(ClO_4)_2$-φNH_3ClO_4 solution identical to the one first described was placed in a weighing bottle and seeded. After 2½ weeks, excellent single crystals had formed. Preliminary crystallographic data were kindly taken by Mr. D. Duchamp.

The crystals are monoclinic; the space group is $P2_1/C$. The dimensions of the unit cell are a = 10.66 Å, b = 17.22 Å, c = 13.27 Å; β = 105.6°. The approximate density of 5.45 g/cm^3 corresponds to 8 monomer units per unit cell.

Summary and Discussion

A hypothesis has been developed to account for the interesting and complicated phenomena which occur in aqueous, acidic solutions of mercuric perchlorate and aniline. It consists of the following elements:

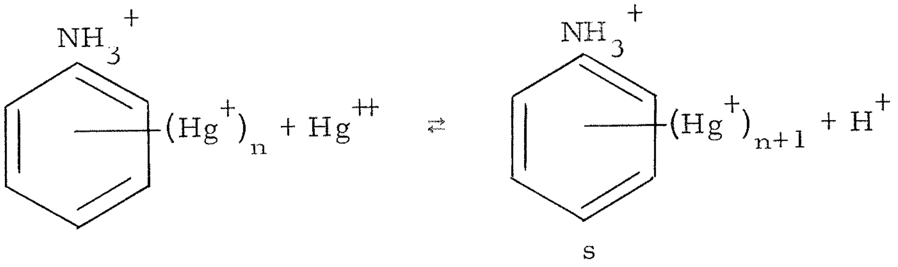
(a) Rapid equilibria of the type



(III-19)

occur, with n ranging from 0 to probably 3 or 4.

(b) Slow, reversible reactions



(III-20)

lead to the formation of several mercurated species in solution.

(c) Species of types r and s with $n > 0$ are responsible for U.V. light absorption at wavelengths > 300 mμ. They have a characteristic band centered at 330-335 mμ.

(d) The rate of reaction III-20 is proportional to the $[\varphi NH_2][Hg^{++}]$ product, most probably because the free amine is attacked by Hg^{++} ion in a bimolecular reaction.

The results of the study of the spectra of the solutions at the time of mixing, the rate of subsequent slow spectral changes, the absorption spectra of the equilibrated solutions, the response of the equilibrated solutions to changes in acidity and $[Hg^{++}]$ --all these consistently support this interpretation. A pure crystalline solid has been isolated, the composition of which cannot be interpreted reasonably without invoking Hg-C bonds. This shows that mercuration occurs under these general conditions.

A number of equilibrium constants have been determined. For reaction III-19,

K_1	$= 0.68$	(27°C, $\mu = 1.0$) if $n = 0$ (aniline)
K_1^P	$= 1.5$	(27°C, $\mu = 1.0$) if $n = 1$ (para-mercurated aniline)
K_1^V	$= 0.95$	(27°C, $\mu = 1.0$)--initial product(s) of the mercuration of aniline, probably mono-mercurated
$K_1^{V'}$	$= 0.8$	(27°C, $\mu = 1.0$)--initial product(s) of the mercuration of p-mercurated aniline, probably dimercurated

$K_1^X = 3$ (~ 22°C, $\mu = 1.0$)--most highly mercurated products.

From the study of the mercurous complex with aniline in Chapters I and II,

$K_1^I = 0.09$ (27°C, $\mu = 1.0$)-- $n = 0$, Hg_2^{++} complex.

In addition,

$K_2 = 0.45$ (27°C, $\mu = 1.0$)

for the reaction

$$2\varphi NH_3^+ + Hg^{++} \rightleftarrows (\varphi NH_2)_2Hg^{++} + 2H^+ .$$

Pertinent molar absorptivities of 1: 1 complexes such as r and s are (in ℓ/mole-cm):

$\epsilon_1 = 2.44 \times 10^3$ ($\lambda = 276.0$) if $n = 0$

$\epsilon_1^P = 1.1 \times 10^3$ ($\lambda = 331.0$) if $n = 1$, para isomer

$\epsilon_1^X = 1.1 \times 10^4$ ($\lambda \sim 334$)-- most highly mercurated product .

Several items deserve further comment. One is the charge on these species. It is surprising that ions so highly charged should readily form complexes which have still higher charge. However, the mercuration of benzene with $Hg(NO_3)_2$ in aqueous solution results in some tetramercurated product, which is also highly charged (43). In their study of the mercuration of benzene, Perrin and

Westheimer (30, 44) 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 they 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 increase.

The characteristic U.V. band of the mercurated Hg-complexes at 330-335 mμ is very curious. It lies 50-55 mμ to the red of the long wavelength band of free aniline itself. Reaction of N,N-dimethylaniline results in the slow appearance of a peak at 350 mμ in $Hg(ClO_4)_2$ solution; this is equally unexpected. Thus, a species containing a Hg atom on both ring and amino group possesses a critical factor 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.

From these studies we can see that the chemistry of mercury-aniline systems is rich in unusual and interesting effects. In one respect, however, aniline behaves as a typical ligand. The stabilities of the simple 1:1 and 2:1 aniline-mercury(II) complexes are in line with those predicted from the basicity of aniline and the stability of other mercury(II)-amine complexes (see Chapter VII and Figure XXIII).

Study of the binding of D.N.A. and the nucleotides by Hg(II) is an interesting method of investigating the physical properties of these biologically important molecules (2, 45). These compounds contain several different types of basic sites where a metal ion might bind. Determination of the site of binding is very difficult. The compounds contain aromatic amino groups in which the unshared electrons are part of a pi system. The question arises whether such groups bind Hg(II) more strongly than their basicity would indicate. It is now possible to say that aromatic amines show no such enhanced tendency to bind Hg(II).

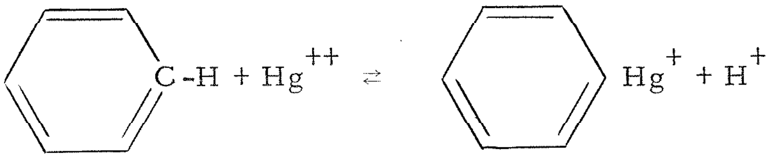
CHAPTER IV

THE EQUILIBRIUM QUOTIENT OF AROMATIC MERCURATION: BENZENE AND p-METHOXYANISOLE

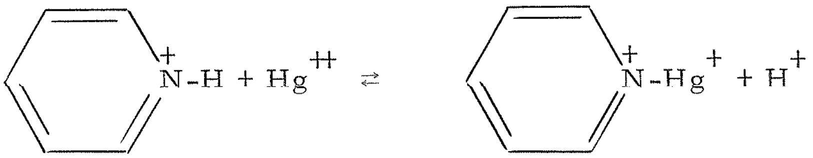
Research on the mercuration of aniline stimulated interest in the more general aspects of this reaction. Mercury(II) salts of oxygen acids--mercuric perchlorate or mercuric acetate, for example--attack aromatic compounds. Mercuric halides, in which the mercury is covalently bound, do not. Mercuric acetate produces a smaller multiplicity of products and higher yields than do the salts of strong acids. This has been attributed to the reversibility of the reaction: if mercuric acetate is the reactant the product is acetic acid, a weak acid (46).

The mercuration products are solids, usually amorphous; they are not easily decomposed by water or atmospheric oxygen. In this respect, mercury compounds are unique among organometallics.

Mercuration products--C_6H_5HgOAc, for example--are usually classified 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, it would be interesting to compare the equilibrium constant of the reaction



with that of



The latter equilibrium constant is 0.8 at 25°C in 0.5 F pyridine nitrate (47). Mercuration has been studied under comparable conditions (i.e., in aqueous solution) by Westheimer (27, 28, 29, 30), Carmack (43), Wright (48), and their respective coworkers. Westheimer, Segel, and Schramm (27) determined the concentrations of phenylmercuric nitrate and mercuric nitrate present at equilibrium in 20-25% nitric acid solutions containing benzene. A very small amount of urea was added to suppress oxynitration. They expressed their results as an "apparent equilibrium constant" :

$$K'_M \equiv \frac{[Hg(NO_3)_2]\,[C_6H_6]}{[C_6H_5HgNO_3]} .$$

This number was characteristic of a given acid concentration regardless of whether mercuric nitrate or phenylmercuric nitrate was used as the starting material--which proves that equilibrium was reached and that mercuration is reversible. The data can be recast into the form of the conventional equilibrium constant of the reaction

$$C_6H_6 + Hg(NO_3)_2 \rightleftarrows C_6H_5HgNO_3 + HNO_3 .$$

But one does not necessarily expect the observed concentration product,

$$K_M = \frac{[C_6H_5HgNO_3]\,[HNO_3]}{[C_6H_6]\,[Hg(NO_3)_2]}$$

to remain constant as the acidity of the medium is changed, because in these concentrated solutions, the gross nature of the medium and the degree of dissociation of nitric acid must change along with the acidity. Westheimer's results are summarized in Table IX.

The present research is an attempt to obtain equilibrium data on mercuration under conditions more comparable with those usually encountered in the investigation of complex ion equilibria. Aqueous solutions of mercuric perchlorate and perchloric acid, made

TABLE IX. Approximate Equilibrium Constants for the Mercuration of Benzene at 50°C

% HNO_3 *	K'_M(m/liter)	$[HNO_3]$ **	K_M ***
20	$0.04 \pm .02$	3.5	90
30	$0.07 \pm .03$	5.5	80
40	$0.09 \pm .02$	7.7	90
50	$0.10 \pm .01$	10	100

* From which the solution was made up.

** In m/ℓ, computed from the densities at 50°C in the Int. Crit. Tables.

*** $K_M = [HNO_3]/K'_M$

up to unit ionic strength with sodium perchlorate, were equilibrated with a benzene phase. This system is similar to that used by Schramm, Klapproth, and Westheimer (29) in their investigations of the kinetics of mercuration. The measurement of an equilibrium constant is difficult, however, because (a) the reaction is very slow in dilute solution, and (b) the ionic strength of 1.0 determines the maximum concentration of acid, so the reaction goes at least 90% to completion.

The first difficulty was not overcome; we simply waited for equilibrium. The problem of analyzing solutions for Hg^{++} at 10^{-3} to 10^{-5} M in the presence of a 10 to 100-fold excess of mercurated products was solved with a spectrophotometric method. The method takes advantage of the ultraviolet absorption of the $HgCl_4^=$ complex and the fact that aryl mercuric cations cannot form complexes of this type.

The Reaction Solutions--Mercuration of Benzene

Mercuric perchlorate, perchloric acid, and sodium perchlorate stock solutions were prepared and standardized as described earlier. Reaction solutions were made up over wide concentration ranges and placed in 500 ml glass-stoppered erlenmeyer flasks.

Eastman spectro grade benzene was added, and the flasks were shaken and allowed to stand.

In order to prove attainment of equilibrium, it was approached from both directions. Phenylmercuric hydroxide--purchased from Matheson, Coleman & Bell--melted at 234-235° after recrystallization from aqueous NaOH. The literature value is 226-228° (49). A weighed sample was dissolved in a known volume of redistilled water. The process of solution takes several days. Reaction solutions were then made up using this stock solution instead of mercuric perchlorate, and benzene was added.

All reaction solutions were allowed to stand for at least one 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 30 readings lay in the range 19.5-25.3°C, and averaged 22°C.

The Analyses

Since some evaporation occurred, each component of the solutions was determined independently:

(A) H^+.- An aliquot of reaction solution and another of concentrated NaCl were added to a beaker containing distilled water. The sample was titrated with standard, carbonate-free NaOH using a glass electrode as indicator. The excess chloride, present at 0.5-1.0 M during the titration, complexes or precipitates the mercury compounds and prevents their reaction with base. A sharp endpoint at pH = 6.5 is obtained.

(B) Benzene.- The solubility of benzene in each solution was determined spectrophotometrically. Samples of distilled water and spectro grade cyclohexane (Matheson, Coleman & Bell) were added to a glass-stoppered erlenmeyer flask by pipette. An aliquot was withdrawn from the reaction flask, carefully avoiding uptake of any benzene. The benzene was wiped from the pipette tip and the sample delivered into the erlenmeyer. The flask was shaken and allowed to stand for about an hour. The U.V. spectrum of the cyclohexane phase was recorded, and the concentration of benzene was computed from the absorption of the maxima at λ = 248.8 and 254.6 mμ. A second extraction reveals no residual benzene in the aqueous phase.

The molar absorptivity of benzene in cyclohexane at these wavelengths was determined as follows: the weight of benzene delivered by a 1 ml pipette was measured, and found to be constant to within 1 mg. Aliquots of spectro grade benzene from this pipette were diluted into spectro cyclohexane, the resulting solutions diluted again, and the spectra recorded. The molar absorptivities--235 ℓ/mole-cm.

at 254.6 mμ and 186 ℓ/mole-cm. at 248.8 mμ--are probably accurate to ± 1% in spite of the pipetting error in the dilution of the cyclohexane solution. The analytical results were reproducible to within ± 1.5%.

(C) $\underline{C_6H_5Hg^+}$. - The concentration of mercurated product at equilibrium was determined from the spectrum of each reaction solution after the benzene had been extracted. Samples of the aqueous phase remaining from the procedure above were carefully withdrawn with a pipette and their U.V. spectra were recorded.

The absorption spectrum of the phenylmercuric cation is presented in Figure XV. It was obtained by diluting an aliquot of the phenylmercuric hydroxide stock solution already described into excess dilute perchloric acid and recording the spectrum. Its similarity to that of benzene, as well as to that of the anilinium ion (Figure V), is worthy of note.*

The concentration of φHg^+ in the reaction solutions was determined from the local maximum at 256.2 mμ. A base line was drawn tangent to the minima on either side, and the absorbance indicated by the dotted line (Figure XV) was measured. The "partial

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* The spectrum of benzene in water is also presented in Figure XV. Aliquots of benzene were delivered from the calibrated 1 ml pipette into 2 ℓ volumetrics filled with water. Liquid had been quantitatively added above the mark to minimize the air space. The benzene required 2-3 hours to dissolve. Spectra of 3 solutions are averaged in the figure.

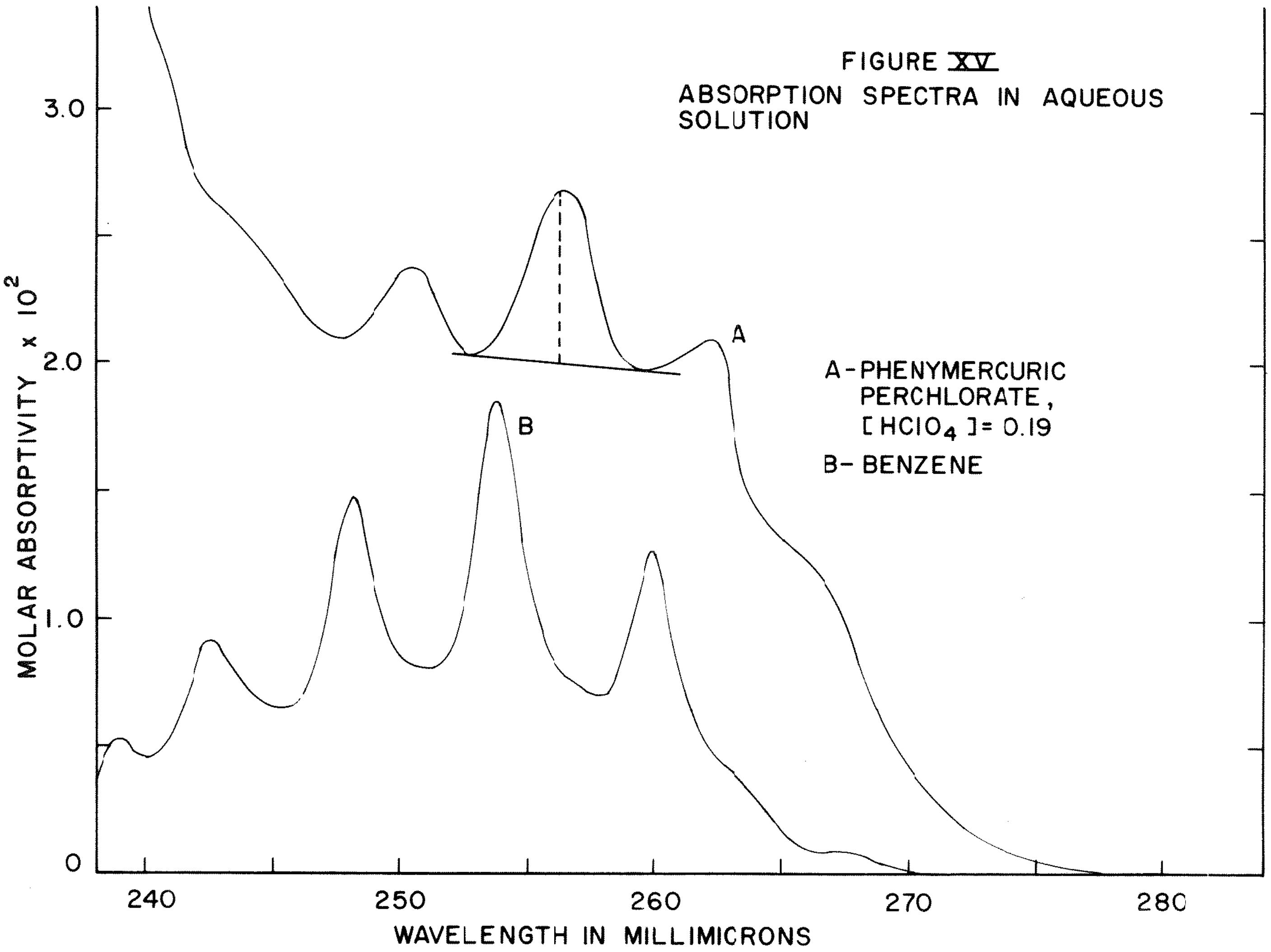

FIGURE XV

ABSORPTION SPECTRA IN AQUEOUS SOLUTION

molar absorptivity" of φHg^+ measured in this way is 66.5 at 256.2 mμ; the total molar absorptivity is 268. The concentrations of φHg^+ in the reaction solutions so computed are independent of sample dilution. This method compensates for background absorbance which results from polymercuration. It is valid as long as the background is nearly linear over the range in question.*

(D) $\underline{Hg^{++}}$. - Aliquots of reaction solution were treated with concentrated NaCl and extracted successively with benzene and ether. The partially precipitated arylmercuric chlorides are covalent compounds and fairly soluble in these solvents. Free Hg^{++} ion, on the other hand, is converted to $HgCl_4^=$, 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^{++} concentration in the reaction solutions.

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* Note on polymercuration: As much as 70% of the absorbance in some solutions at 256 mμ was background. Calculation of $[\varphi Hg^+]$ as described above allows one to subtract its absorbance from the observed spectrum. The result is an absorbance which increases monotonically with decreasing wavelength.

Correcting for evaporation, it is possible to determine the concentration of Hg(II) in the reaction solutions which is not accounted for by Hg^{++} or $C_6H_5Hg^+$; the background absorbance at 256 is roughly proportional to this quantity. It is also roughly proportional to the quantity $[\varphi Hg^+][Hg^{++}]/[H^+]$. The ratio of these proportionality constants is about 200, a reasonable value for the average equilibrium constant of the mercuration of phenylmercuric perchlorate. Therefore, it is reasonable to ascribe the background absorbance to dimercurated compounds.

5F NaCl was prepared by weighing out solid NaCl (Mallinckrodt AR), dissolving it in redistilled H_2O, and diluting to volume. A 6 ml aliquot of this solution was added to a 50 ml glass-stoppered erlenmeyer along with about 25 ml of spectro grade benzene (M. C. & B.). A 4 ml aliquot of reaction solution (quantitatively diluted with water if necessary) was added; the flask was stoppered and shaken vigorously. The aqueous phase was withdrawn with a pipette as soon as the phases separated. A maximum of 1 ml of aqueous phase remained behind. The sample was delivered into another erlenmeyer containing 25 ml of anhydrous ether (Mallinckrodt AR) and shaken. A final extraction with 25 ml of ether was then performed and the spectrum of the aqueous chloride solution was recorded. The amount of $HgCl_4^=$ present was determined from the absorption maximum at 230 mμ.

The procedure was calibrated with repeated analyses of $Hg(ClO_4)_2$ solutions of two different (known) concentrations. The extracted aqueous phase was .005 M in $HClO_4$ in the calibrations. If the phase is not acidic, the analytical results decrease by ~ 30% and become quite erratic. It appears that basic mercury salts are extracted from neutral solutions into the organic phase. This in spite of the overwhelming excess of chloride. All reaction solutions were acidic.

The procedure is very sensitive to interference from unextracted compounds. A blank of pure water gives a negligible absorbance at 230 mμ; phenylmercuric chloride is completely extracted from aqueous solution by ether. Polymercurated products are a potential source of interference, but the spectra of the chloride solutions after extraction correspond closely to that of $HgCl_4^{=}$ at all wavelengths. The absorbance to be expected at 216 and 248 mμ in these solutions was calculated from that at 230 and the spectrum of $HgCl_4^{=}$. In only one case did an observed value deviate from the calculated one by more than .016 absorbance units.

Results and Discussion

The analytical results for each solution and the calculated values of K_M are presented in Table X. The average is

$$K_M = (3.0 \pm 2.3) \times 10^2 .$$

In Figure XVI, K is displayed as a function of acid concentration. There is a distinct increase in K with increasing acid concentration, but the scatter is high. The scatter can be explained in terms of temperature and ionic strength variations, analytical inaccuracies, and perhaps a moderate background in the $HgCl_4^{=}$ spectra which was not detected. The variation of the equilibrium

TABLE X. The Equilibrium Quotient for the Mercuration of Benzene in Aqueous Perchloric Acid-Sodium Perchlorate Solutions Saturated with Benzene

$T = 22 \pm 3°C$; $\mu = 1.0\text{-}1.2$ M[a]

Solution No.	$[Hg^{++}]$ x 10^4	$[C_6H_5Hg^+]$ x 10^2	$[H^+]$	Solubility[b] of Benzene (m/ℓ)	K_M x 10^{-2} [c]
		Forward Reaction			
D-1	6.3	1.22	.293	.0185	3.1[d]
D-2	4.1	1.18	.242	.0183	3.8[d]
D-3	3.4	1.23	.228	.0180	4.6
D-4	2.0	0.67	.219	.0177	4.1
D-5	2.0	0.26	.225	.0173	1.7
D-6	0.59	0.14	.207	.0176	2.8
D-8	0.13	0.027	.209	.0176	2.5
D-9	0.07^5	0.012	.206	.0175	1.9
D-10	4.8	0.64	.797	.0215	4.9
D-11	5.8	0.64	.462	.0187	2.8
D-12	1.9	0.67	.216	.0176	4.3
D-13	1.0^3	0.67	.0921	.0175	3.4
D-14	0.82	0.66	.0547	.0169	2.6
D-15	0.74	0.43	.0334	.0168	1.2[d]
D-16	0.66	0.38	.0253	.0167	0.9[d]
D-17	0.46	0.32	.0173	.0168	0.7[d]
		Reverse Reaction			
D-18	0.06^3	0.094	.0088	.0168	0.8
D-19	0.19^5	0.098	.0944	.0169	2.8
D-20	0.85	0.089	.998	.0226	4.6
D-21	0.12	0.018	.477	.0194	3.7
D-22	1.9	0.36	.480	.0193	4.8

[a] The solutions were made up at $\mu = 1.0$. The degree of evaporation was calculated from the measured $[H^+]$ and the initial concentrations.

[b] All concentrations are expressed in moles/liter.

[c] $K = [C_6H_5Hg^+][H^+]/([Hg^{++}][C_6H_6]$.

[d] Precipitate observed in the solution.

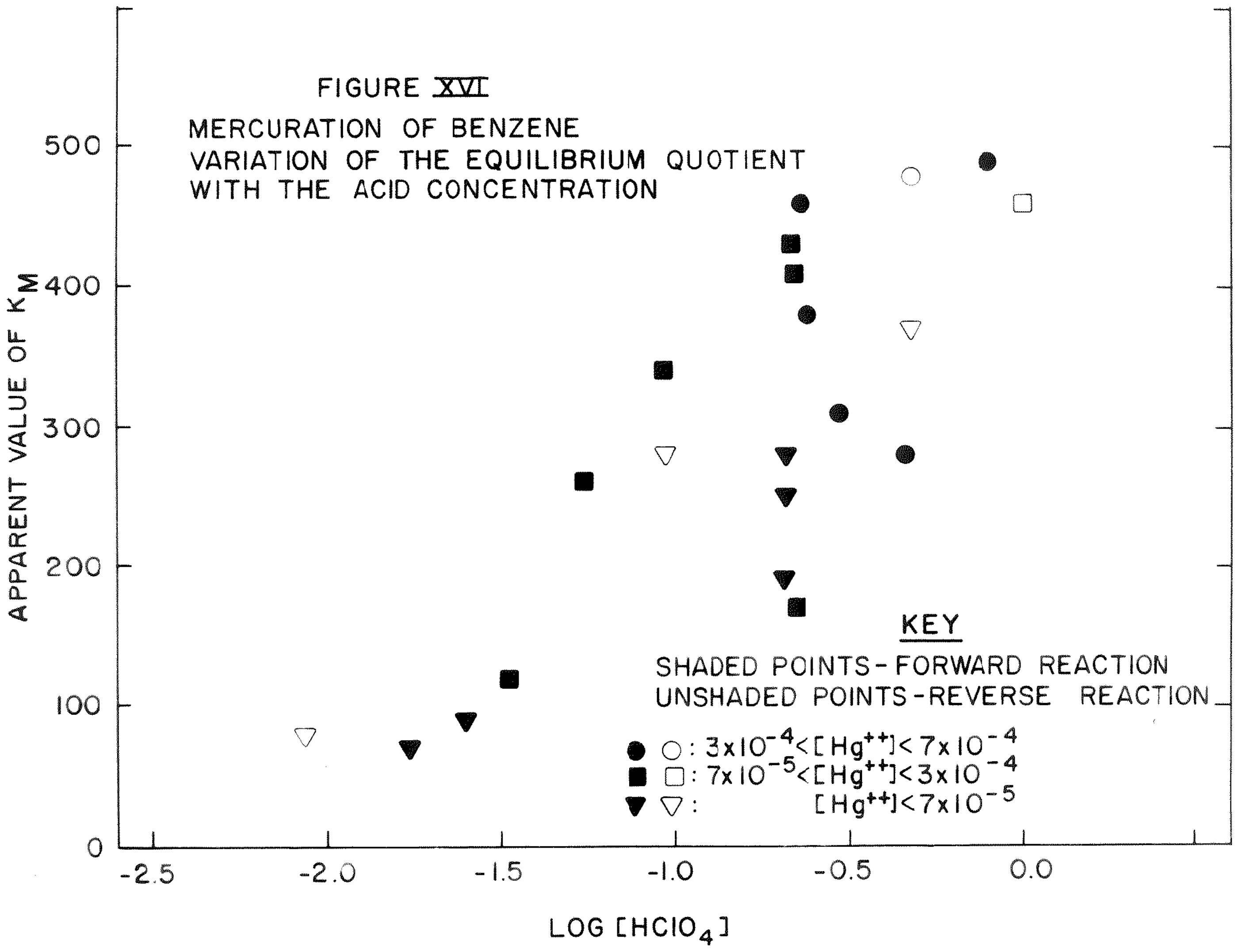


FIGURE XVI

MERCURATION OF BENZENE
VARIATION OF THE EQUILIBRIUM QUOTIENT
WITH THE ACID CONCENTRATION

quotient with acid is more mysterious. It may be due to a strong decrease in the activity coefficient of φHg^+ as protons replace sodium ions in the medium, or perhaps even to a labile H^+-φHg^+ complex. The fact that benzene itself is 30% more soluble in 1 F $HClO_4$ than in 1 F $NaClO_4$ lends credence to these possibilities.

If either of the explanations is correct, the lower values of K correspond most closely to the conventional equilibrium constant. In the absence of more accurate data or independent evidence, however, it seems preferable to accept the average value.

We have determined, then, that the equilibrium quotient of the reaction

$$C_6H_6 + Hg^{++} \rightleftarrows C_6H_5Hg^+ + H^+$$

is two orders of magnitude greater than that of

$$C_5H_5NH^+ + Hg^{++} \rightleftarrows C_5H_5N^+Hg^+ + H^+$$

Therefore, equilibrium in the reaction

$$C_5H_5N^+Hg^+ + C_6H_6 \rightleftarrows C_5H_5NH^+ + C_6H_5Hg^+$$

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).

The Mercuration of p-Methoxyanisole

A similar series of experiments was performed with p-methoxyanisole as substrate. Only one monosubstitution isomer exists, as is the case with benzene. But the activating effect of methoxy substituents in electrophilic substitution increases the rate of mercuration considerably. The results were similar to those just described; the equilibrium quotient increases with increasing acid concentration. There was less scatter in the results; yet in some respects the data are less firm.

The reaction solutions were prepared from mercuric perchlorate, perchloric acid, and sodium perchlorate stock solutions and placed in 125 ml glass-stoppered flasks. p-Methoxyanisole, purchased from Matheson, Coleman & Bell, was sublimed and a few grams of solid added to each flask. The solutions were shaken and placed in a constant-temperature bath maintained at 26.1 ± .1°C. The reverse reaction was studied by diluting into acid samples in which considerable reaction had already occurred, as determined by analysis for Hg^{++}. The Hg^{++} concentration increased to a new equilibrium value. All solutions were allowed to stand for at least $3\frac{1}{2}$ months; on one occasion, they were shaken for 12 hrs on a mechanical shaker.

The analytical procedures were slightly modified from those described earlier. The titration for H^+ was identical except that it was carried out in .05 M NaCl and smaller samples were used.

The determinations of the solubility of unreacted p-methoxyanisole and the concentration of reaction product were also the same in principle. A sample of reaction solution was forced under pressure through a sintered glass funnel which had been cleaned with redistilled water and reagent grade acetone, and dried by applying suction. This procedure removed undissolved p-methoxyanisole. An aliquot of the solution was then added to a centrifuge tube containing measured volumes of spectro cyclohexane and water. The tube was stoppered with a polyethylene cap, shaken, and centrifuged. The spectrum of both phases was taken; p-methoxyanisole was determined from the cyclohexane spectrum, and the mercurated product (2, 5-dimethoxyphenylmercuric perchlorate) from the spectrum of the aqueous phase.

The molar absorptivity of p-methoxyanisole in cyclohexane was determined as follows: a weighed sample of the compound, purified by sublimation, was dissolved in cyclohexane. The solution was diluted quantitatively, and the spectrum of the dilute solution recorded. The molar absorptivity at 289.1 mμ

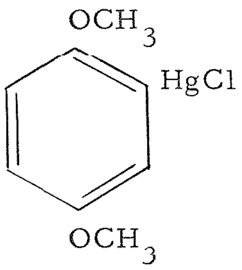
(3.17×10^3 ℓ/mole-cm) was used to compute concentrations.

Spectrophotometric determination of the mercurated product has two aspects--confirmation of the identity of the compound and preparation of a standard solution thereof.

Synthesis of 2-chloromercuri-4-methoxyanisole.- 0.2 moles (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 hours. A white precipitate formed on cooling. 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, 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° .

Isolation of the mercurated product from an equilibrium solution.- Solution E-15 was treated with NaCl and the precipitate extracted into ether, which was washed with NaCl solution and water. The small amount of undissolved precipitate in the ether was filtered off. The ether was evaporated, and the residue was recrystallized twice from small portions of absolute ethanol. The compound melted at 175-178°C. Its composition was: 25.55% C, 2.47% H, 55.18% Hg, 9.50% Cl. Calculated for $C_8H_9HgClO_2$: 25.74% C, 2.43% H, 53.75% Hg, 9.50% Cl.*

Both compounds, then, are



<u>The spectrum of 2-perchloratomercuri-4-methoxyanisole.</u> - A water suspension of the chloride salt prepared by the first method was treated with freshly precipitated and thoroughly washed Ag_2O, shaken, and allowed to stand 24 hours. The solution was filtered through exhaustively rinsed sintered glass. It was standardized by titration with 0.1000 KSCN in dilute HNO_3 at less than 10°C using $FeNH_4SO_4$ indicator. A sample was quantitatively diluted into aqueous perchloric acid-sodium perchlorate, and the U.V. spectrum was recorded (Figure XVII).** The molar absorptivity of the

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* Analysis by Schwarzkopf Microanalytical Laboratory.

** The spectrum of p-methoxyanisole in water is also presented in Figure XVII. It differs from that in cyclohexane. Stock solutions were prepared by dissolving weighed quantities of sublimed p-methoxyanisole in water; several days of mechanical shaking were required. Spectra were taken of solutions prepared from these by dilution.

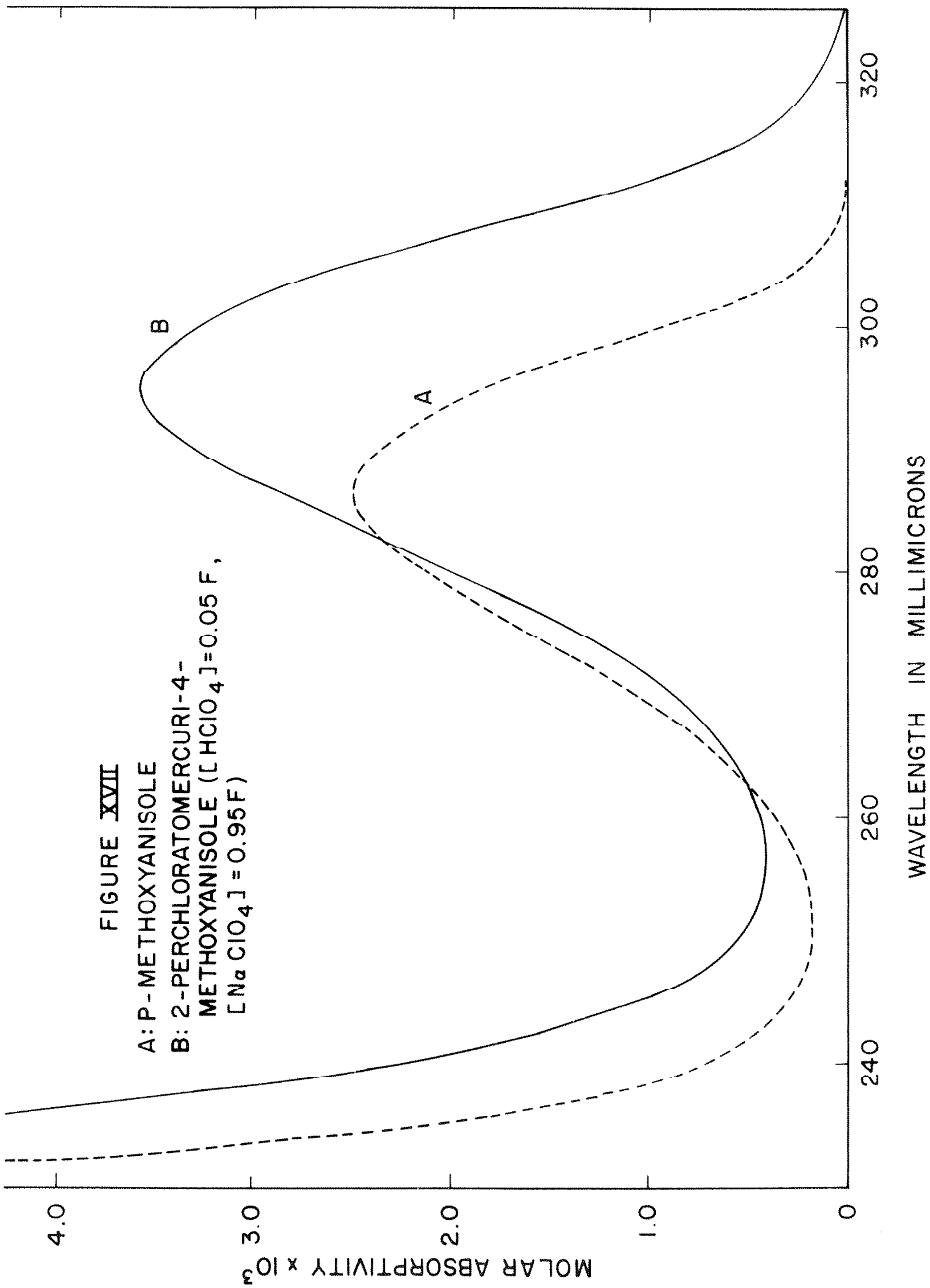


FIGURE XVIII

peak at 295.0 mμ is 3.58×10^3 ℓ/mole-cm. The wavelength of maximum absorbance of the equilibrium solutions after extraction is also 295.0 mμ; the concentration of 2,5-$(H_3CO)_2C_6H_3Hg^+$ was determined from this absorbance.

Unfortunately, the spectrum of the monomercurated product contains no fine structure to permit elimination of background due to polymercuration. In Figure XVII, the spectrum of monomercurated product in aqueous solution is compared with that of unreacted p-methoxyanisole. If excess $Hg(ClO_4)_2$ reacts with the substrate, both the hyperchromic effect and the bathochromic shift increase beyond those shown. Thus, severe contamination would probably shift the wavelength of the maximum. In all the reaction solutions, 295 mμ was the wavelength 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 concentrations 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.

So great an error is unlikely, however, because the two solutions which would be particularly suspect (E-14 and 18, Table XI) do not stand out.

The analysis for free Hg^{++} was the same as that employed to study the benzene equilibrium except that only two extractions were employed. The 10 ml aqueous phase was extracted with 25 ml of ether, then with 10 ml of ether. The procedure was calibrated with good precision (± .5%) using standard, acidic $Hg(ClO_4)_2$ solutions. There was a slight tendency for the results to increase when the extractions were performed slowly; they were therefore performed as rapidly as possible.

The presence of solid 2-chloromercuri-4-methoxyanisole causes no increase in background. However, a small but significant $HgCl_4^{=}$ spectrum appears if the analysis is performed on a slurry of product from a reaction solution freshly precipitated with NaCl and washed with water. This may be due to adsorbed $HgCl_2$, however. Such adsorption is eliminated in the procedure itself, since most of the chloride precipitate dissolves in the ether phase. The results at small Hg^{++} concentrations are somewhat suspect, however.

The results. - The results are presented in Table XI, and the values of the equilibrium quotient are displayed as a function of acid concentration in Figure XVIII. We can see the same type of behavior here as was displayed by benzene; in spite of the analytical uncertainties, the same comments apply. K_M falls in the range 110-810, with an average value of 470.

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

TABLE XI. The Equilibrium Quotient for the Mercuration of p-Methoxyanisole in Aqueous Perchloric Acid-Sodium Perchlorate Solutions Saturated with p-Methoxyanisole

$T = 27.2°C$; $\mu = 1.0\text{-}2.0$ M[a]

Solution No.	$[Hg^{++}]$ x 10^4	$[2,5\text{-}(H_3CO)_2\text{-}C_6H_3Hg^+]$ x 10^3	$[H^+]$	Solubility of $p(H_3CO)_2\text{-}C_6H_4$ x 10^3 (m/ℓ)	K_M x 10^{-2} [b]
E-3	0.78	1.72	0.043	5.42	1.8
E-4	0.90	1.70	0.085	5.37	3.0
E-5	0.99	1.34	0.152	5.94	3.5
E-6	1.04	1.27	0.278	6.42	5.3
E-7	1.25	1.20	0.400	6.92	5.6
E-8	1.32	1.07	0.711	8.01	7.2
E-9	2.02	1.21	1.389	10.23	8.1
E-10	0.11^5	0.036	0.599	7.70	2.4
E-11	0.26	0.111	0.579	7.61	3.3
E-12	0.60	0.44	0.603	7.57	5.8
E-13	2.08	1.76	0.615	7.74	6.7
E-14	4.4	3.78	0.581	7.70	6.5
E-17	0.62	0.38	0.544	7.69	4.4
E-18	4.5	3.81	0.572	7.78	6.3
E-23a	0.91	0.51	1.093	8.64	7.0
E-24	0.82	0.57	0.653	7.71	5.8
E-25	0.80	0.58	0.696	7.97	6.4
E-26	0.17^4	0.96	0.0127	6.04	1.2
E-27	0.18	0.94	0.023	6.08	2.0
E-28	0.28	0.99	0.046	6.07	2.6

[a] See note "a" to Table X.

[b] $K = [2,5\text{-}(H_3CO)_2C_6H_3Hg^+][H^+]/([Hg^{++}][p\text{-}(H_3CO)_2C_6H_4])$

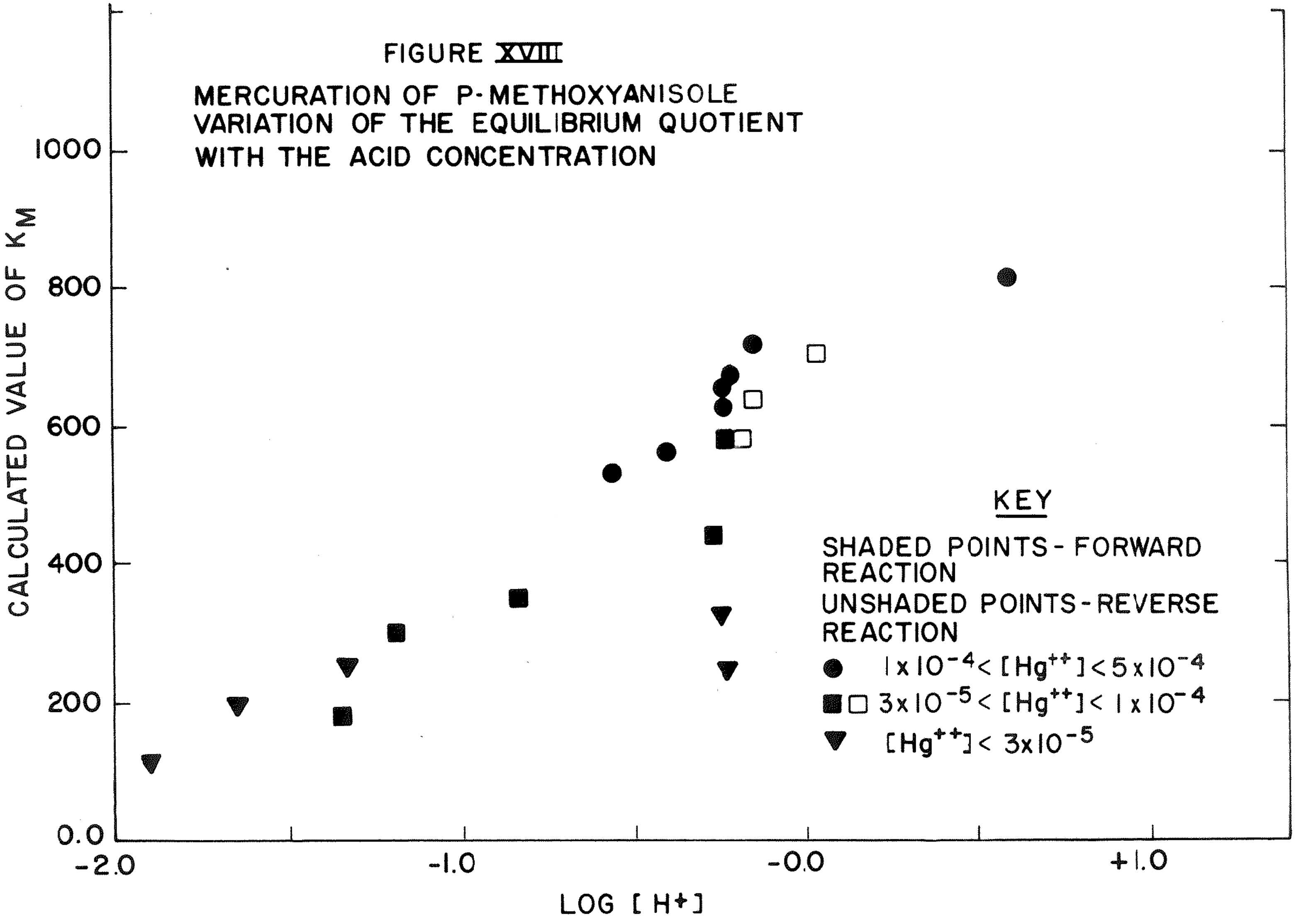


FIGURE XVIII

MERCURATION OF P-METHOXYANISOLE
VARIATION OF THE EQUILIBRIUM QUOTIENT
WITH THE ACID CONCENTRATION

CHAPTER V

MERCURY(II) COMPLEXES OF GUANIDINE

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 (Chapter VII). Guanidine is among the strongest organic bases known (50). It is therefore of interest to study its binding with metal ions in order to test this relationship over the widest possible range. Few solid guanidine complexes have been prepared, however. Wormser (51) studied the formation of the guanidine-Ag(I) complex in solution, but calculated no stability constants. Very little, then, is known about the characteristics of guanidine as a ligand.

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. The stability of the complex does not deviate from that which one would predict on the basis of guanidine's basicity (see Chapter VII). Evidence for a mixed complex, RHgOH, was obtained (R ≡ guanidine).

Experimental

In all but a few details, the experimental procedure was identical to that employed in the study of the aniline-Hg(II) complex (Chapter I). All measurements were carried out at 27.2°C.

Preparation of guanidine perchlorate and nitrate. - These guanidine salts 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°C for 1 hour produced no weight loss. The melting point was 252-255°C; literature value: 240° (52).

The nitrate was recrystallized from water. It was then dried and dissolved in hot absolute methanol. This solution was evaporated to half its original volume and filtered. Dried in a vacuum dessicator over $CaSO_4$, the compound melted at 216-218°C, which compares with literature values of 214.2° (53) and 217° (54).

1 F stock solutions were prepared by dissolving weighed amounts of these salts in water and diluting to volume.

Calibration of the pH meter. The apparent ion product constant of water. - A Beckman 40495 Type E-2 glass electrode was used in this series. Beckman pH 4 buffer was the standard on which the pH meter was set prior to each experiment. To calibrate the meter, an aliquot of standard acid was added to 1 F $NaClO_4$ in the titration flask; the solution was flushed with nitrogen and titrated with standard base. A 1 F $NaNO_3$ salt bridge was used. From the pH in acid solution, the pH meter was calibrated; from that in basic solution, the apparent ion product constant of water was determined.

$$pK_W = 13.68 \pm .04 \quad (T = 27.2°, \mu = 1.0)$$

K_W is defined here as the concentration product $[H^+][OH^-]$. It was used to compute the K_A of the guanidinium ion from the K_B of guanidine.

The potentiometric measurements. - Aliquots of $NaClO_4$, $C(NH_2)_3ClO_4$, $Hg(ClO_4)_2$, and $HClO_4$ or NaOH were added to the clean, dry titration flask. The salt bridge was prepared from 1 F $NaNO_3$ and 1 F $C(NH_2)_3NO_3$ to match the $C(NH_2)_3^+$ concentration in the titration solution. The salt bridge tube was filled and inserted into the flask. The calomel and glass electrodes were removed from standard buffer and put in place. Nitrogen was bubbled through the titration solution for at least 10 minutes. The mercury electrode was inserted, metallic mercury added to the flask, and the solution was allowed to stand for up to 1 hour while the pH and EMF became constant. This was necessary because the pH of the unbuffered solutions is sensitive to the formation of Hg_2^{++}. The solutions were then titrated with standard acid or base. At least 10 minutes elapsed after each addition before pH and EMF were recorded. Frequent checks assured that no significant change occurred thereafter. Nitrogen was bubbled through the solution throughout the titrations; the solution was protected from fluorescent lights and daylight.

Results

It was shown in Chapter I that in general K_1 is too small to measure potentiometrically. After rearrangement, equation I-11 then becomes

$$K_2 = \left(\frac{[H^+]}{[RH^+]} \right)^2 \left(\frac{[Hg^{++}]_o}{[Hg^{++}]} - 1 - K \right) \qquad (V-1)$$

However, the K_2 for guanidine calculated in this manner is not constant, but is proportional to $1/[RH^+]$. This behavior indicates the existence of a species which releases two protons but consumes only one guanidinium ion when it forms from Hg^{++} and $C(NH_2)_3^+$. A likely species of this type is

$(H_2N)_2\,C\text{-}NH\text{-}HgOH^+$,

which will be designated C_1^H.

$$K_1^H = \frac{[C_1^H]\,[H^+]^2}{[Hg^{++}][RH^+]} \qquad (V\text{-}2)$$

Equation I-4 for the conservation of Hg(II) becomes

$$[Hg^{++}]_o = [Hg^{++}]\,(1 + K) + [Hg(OH)_2] + [C_2] + [C_1^H]. \quad (V\text{-}3)$$

In these experiments, hydrolysis was not always negligible. Therefore, $[Hg(OH)_2]$ is included in V-3. Using equations V-2, I-8, and I-15,

$$\frac{[Hg^{++}]_o}{[Hg^{++}]} = 1 + K + \frac{K_{2H}}{[H^+]^2} + K_2\,\frac{[RH^+]^2}{[H^+]^2} + K_1^H\,\frac{[RH^+]}{[H^+]^2} \quad (V\text{-}4)$$

from which

$$\left(\frac{[Hg^{++}]_o}{[Hg^{++}]} - 1 - K - \frac{K_{2H}}{[H^+]^2}\right)\left(\frac{[H^+]}{[RH^+]}\right)^2 = K_2 + \frac{K_1^H}{[RH^+]}\,. \quad (V\text{-}5)$$

The quantity on the left of V-5 will be designated Q_1. In Figure XIX, the experimental results are presented in the form of a plot of Q_1 vs. $1/[RH^+]$. These results represent variation over wide concentration ranges. ($[RH^+]_o$ = .015 - .38 F; $[Hg^{++}]_o = 1 \times 10^{-4}$ - 6×10^{-3} F; pH = 2.6 - 5.1).

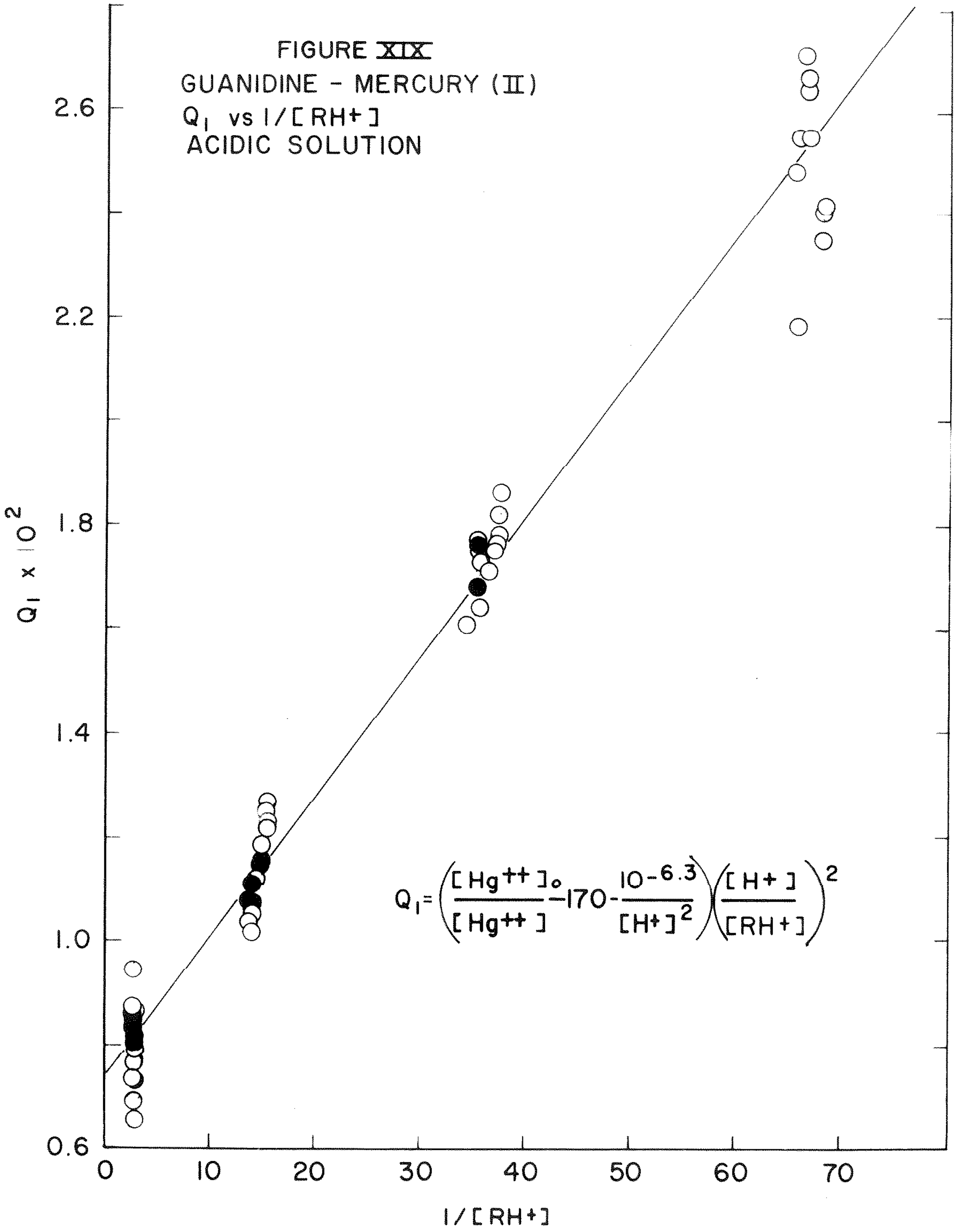


FIGURE XIX
GUANIDINE - MERCURY (II)
Q_1 vs $1/[RH^+]$
ACIDIC SOLUTION

Excluded were points for which $[Hg^{++}]_o/[Hg^{++}]$ was less than 300. Inspection of equation V-4 shows that $[Hg^{++}]_o/[Hg^{++}]$ equals the sum of a number of terms, each of which is proportional to the concentration of a particular species. One of these--K, proportional to $[Hg_2^{++}]$--is constant. The difference between $[Hg^{++}]_o/[Hg^{++}]$ and 1 + K is proportional to the total concentration of Hg(II) complexes. This is the critical parameter in determining stability constants. When

$$[Hg^{++}]_o/[Hg^{++}] = 300 ,$$

$$[Hg^{++}]_o/[Hg^{++}] - (1 + K) = 300 - (170 \pm 12) = 130 \pm 12.$$

Because of the uncertainty in K, then, the total concentration of complexed Hg(II) is uncertain by 10%. This relative uncertainty increases sharply as $[Hg^{++}]_o/[Hg^{++}]$ falls below 300.

The experiments in Figure XIX were conducted in acidic solution. The pH-EMF behavior is essentially similar in basic solution, as can be seen from Figure XX. There is no evidence for the formation of additional complexes. Irreversible changes in the solutions occur at high basicity, however. Since the results in basic solution are also less precise, they were not included in the equilibrium constant calculations. From Figure XIX,

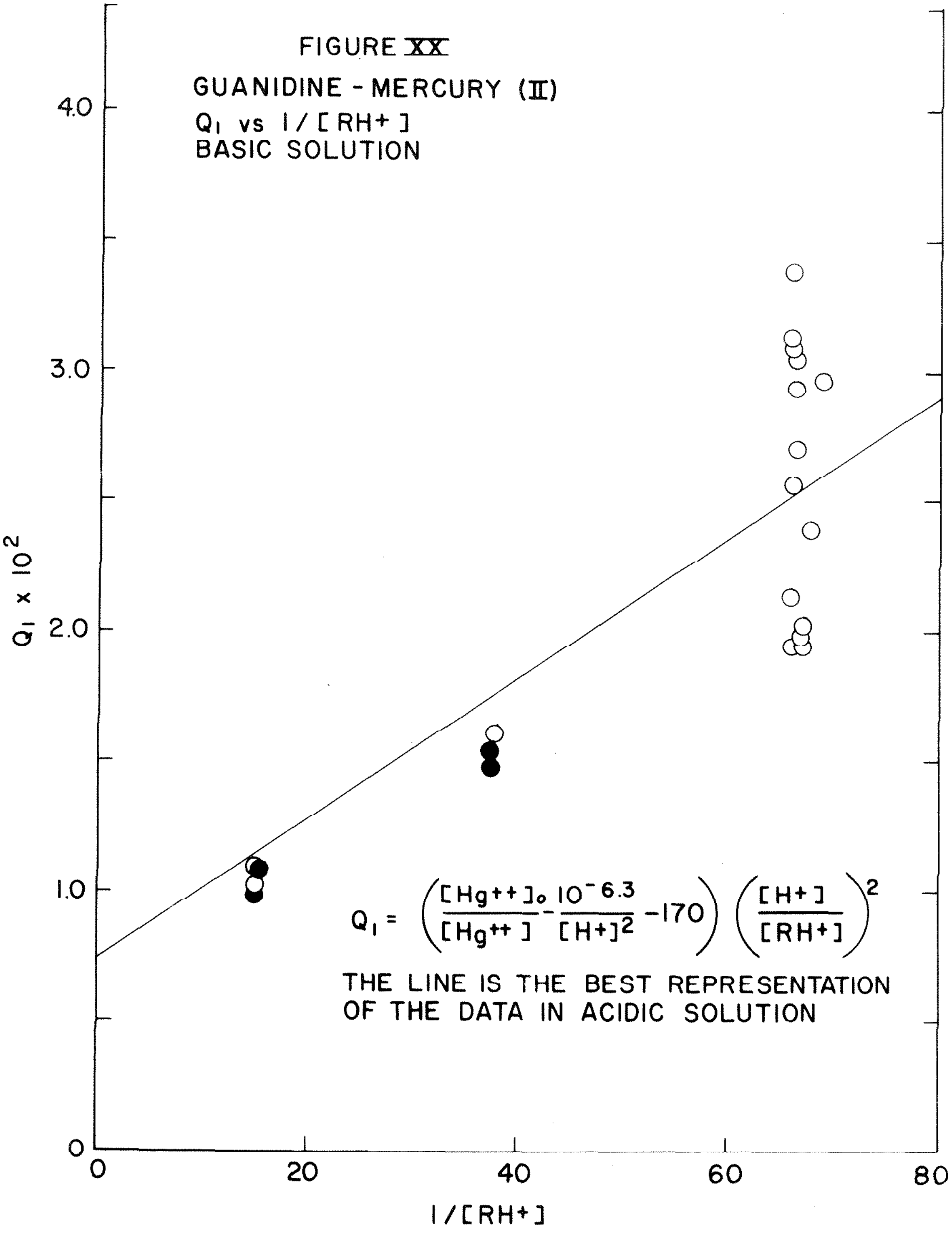


FIGURE XX

GUANIDINE - MERCURY (II)
Q_1 vs $1/[RH^+]$
BASIC SOLUTION

$$Q_1 = \left(\frac{[Hg^{++}]_0}{[Hg^{++}]} - \frac{10^{-6.3}}{[H^+]^2} - 170\right)\left(\frac{[H^+]}{[RH^+]}\right)^2$$

THE LINE IS THE BEST REPRESENTATION
OF THE DATA IN ACIDIC SOLUTION

$K_2 = 7.4 \times 10^{-3}$

$K_1^H = 2.7 \times 10^{-4}$ moles/ℓ

at T = 27.2°C, $\mu = 1.0$ M.

The Basicity of Guanidine

Hall and Sprinkle (55) found the pK_a of the guanidinium ion to be 13.59 $\pm$ .05 in 2 N KCl, T = 24.2°C. They used a hydrogen electrode. Since neither the temperature nor the medium corresponds to the present experimental conditions, a redetermination was desirable. A spectrophotometric method was chosen to avoid the difficulties of measuring pH in strong base.

The intensity of the absorption of the guanidinium ion between 220 and 250 mμ increases greatly in strong base. In both neutral and basic solution, the absorption maximum occurs at wavelengths shorter than 225 mμ. The absorption of the hydroxide ion itself makes observation of the spectrum of free guanidine at shorter wavelengths very difficult. The concentration of free guanidine can be determined from the absorbance in the 225-235 mμ region, however, even though the absorbance does not reach a maximum.

Solutions containing guanidine perchlorate (.006-.02 F), sodium perchlorate (.03-.87 F), and sodium hydroxide (.12-.96 F) at unit ionic strength were prepared. They were placed in a constant temperature bath for at least three hours. The spectra of three successive samples of each solution were recorded with air in the reference beam. Water from the bath circulated around the cell compartment. The spectra of fresh samples were identical; however, absorption of CO_2 changed the spectra of solutions exposed to the air. Blank solutions containing only NaOH were prepared and their spectra recorded; all unnecessary exposure to the air was avoided.

The concentration of free guanidine in each solution was determined from the absorbance at 227.0, 229.0, and 231.0 millimicrons. At the concentrations used, protonated guanidine does not absorb at these wavelengths. The absorbances were corrected for NaOH background. The concentration of guanidine never exceeded 5% of that of NaOH; therefore, corrections to [NaOH] for reaction were not made. Under these conditions,

$$\frac{[RH^+]_o}{X} = \frac{1}{\varepsilon_X} + \frac{K_B}{\varepsilon_X} \left(\frac{1}{[OH^-]} \right)$$

where X is the corrected absorbance, ε_X the molar absorptivity of $(H_2N)_2C = NH$ at that wavelength, $[RH^+]_o$ the formal guanidine concentration, and

$$K_B = \frac{[RH^+]\,[OH^-]}{[R]} \quad .$$

RH and R represent $C(NH_2)_3^+$ and $(H_2N)_2C = NH$, respectively.

The average K_B, independently determined at each wavelength, is

$$K_B = 0.72 \pm .06 \quad (T = 27.2°, \mu = 1.0 \text{ M})$$

The molar absorptivities of free guanidine are 54, 92, and 150 ℓ/mole-cm at 231.0, 229.0, and 227.0 mμ, respectively.

Using the value of pK_W which was determined earlier, (13.68),

$$pK_A = 13.54 \pm .06 \quad (T = 27.2°, \mu = 1.0 \text{ M})$$

Summary and Discussion

The following constants for guanidine have been determined at $T = 27.2°$, $\mu = 1.0$ M ($NaClO_4$):

$$K_B = \frac{[RH^+][OH^-]}{[R]} = 0.72 \pm .06 \text{ moles}/\ell$$

$$K_1^H = \frac{[C_1^H][H^+]^2}{[Hg^{++}][RH^+]} = 2.7 \times 10^{-4} \text{ moles}/\ell$$

$$K_2 = \frac{[C_2][H^+]^2}{[Hg^{++}][RH^+]^2} = 7.4 \times 10^{-3}$$

$$K_A = \frac{[R][H^+]}{[RH^+]} = 10^{-13.54 \pm .06} \text{ moles}/\ell$$

From K_2 and K_A,

$$\beta_2 = \frac{[C_2]}{[Hg^{++}][R]^2} = K_2/K_A^{\ 2} = 10^{24.95}\ \ell^2/\text{mole}^2 \ .$$

In Figure XXIII (Chapter VII), the relationship between Hg(II) complex stability and ligand basicity is presented. If all ligands are considered together, the correlation is not good. However, within the group which includes aniline, guanidine, ammonia, pyridine, and several others, the variation of $\frac{1}{2}\log\beta_2$ with pK_A is linear and the scatter is small.

It is useful to consider the equilibrium constant of the reaction

$$HgR_2^{++} + Hg(OH)_2 \rightleftharpoons 2R\,HgOH^+ \ .$$

This can be approximately computed using Hietanen's value of K_{2H} (in 0.5 F $NaClO_4$):

$$K^H = \frac{[C_1^{\ H}]^2}{[C_2][Hg(OH)_2]} = \frac{(K_1^{\ H})^2}{K_{2H}\ K_2} = 20 \ .$$

This is greater than the statistical value of 4, but it corresponds to an equilibrium value of $[C_1^{\ H}]$ only about twice as great as the statistical. Marcus (56) observed a similar stabilization of mixed complexes in his study of the mixed halides of mercury(II).

This study, then, has uncovered no unusual effects in the binding of Hg(II) by guanidine which are not reflected in its proton basicity. Yet the structure of guanidine differs greatly from that of other amines; the protonated form is highly symmetric, and the charge delocalized. An unusual effect would not have been surprising.

CHAPTER VI

MERCURY(II) COMPLEXES OF AMMONIA

Metal Ammine Formation in Aqueous Solution, the thesis of J. Bjerrum (4), is a classic in the field of complex ion chemistry. He determined the stepwise formation constants of a large number of metal ion-ammonia complexes using a glass electrode. From the pH and composition of a solution, the fraction of the metal ion which is complexed can be determined. Among the many metals ions he studied was Hg(II) (58).

Bjerrum himself pointed out, however, that the glass electrode method is less suitable for study of K_1 and K_2 in this system than in the many others he investigated. Hg(II) is so strongly bound by amines--including ammonia--that the reaction

$$Hg^{++} + 2NH_4^{+} \rightleftarrows Hg(NH_3)_2^{++} + 2H^{+}$$

is essentially complete even in quite acid solution, where the pH is not a sensitive measure of complex formation. Therefore, it was decided to study the system potentiometrically.

Experimental

Ammonium perchlorate and ammonium nitrate stock solutions were prepared by roughly neutralizing aliquots of standardized acid with ammonium hydroxide (duPont). 1.0 F solutions were prepared by appropriate dilution. Aliquots of these solutions were titrated with acid using a glass electrode and a 1 F $NaNO_3$ salt bridge. Using these results, the 1 F solutions remaining were accurately neutralized with standard acid. They were then analyzed by evaporating aliquots of solution and weighing the residues.

The titrations were carried out in the apparatus described in Chapter I. All measurements in this series were at 25.0°C. The salt bridge tube was jacketed and water from the constant temperature bath circulated around it.

A citrate buffer, $[H^+] = 10^{-2.75}$, was prepared from sodium citrate (B & A reagent grade), nitric acid, and sodium nitrate. The final concentrations were approximately 0.95 M $NaNO_3$, 0.05 M H_3Cit, and .05 M NaH_2Cit; $\mu = 1.0$ M. Between experiments, the glass and calomel electrodes were immersed in a sample of this buffer maintained at 25°C. Prior to each experiment, the pH meter was set with the electrodes in the buffer. A Beckman 41260 (type

E-2) glass electrode was used. In this series, the pH meter was independently calibrated before each titration.

The procedure was as follows: aliquots of $NaClO_4$ and NH_4ClO_4 stock solutions, both accurately neutralized, were added to the titration flask. Aliquots of standard acid were then added and the pH was read after each addition. The salt bridge was that of the titration which followed.

After the calibration, an aliquot of $Hg(ClO_4)_2$ stock solution was added along with standardized base if desired. The Hg(O) electrode was inserted and the salt solution was titrated with standard acid and/or base; the pH and EMF were measured after each addition.

The salt bridge was prepared from 1 F NH_4NO_3 and 1 F $NaNO_3$ to match the NH_4ClO_4 concentration at the beginning of the titration, but after addition of $Hg(ClO_4)_2$. Nitrogen was bubbled through the solution at all times except when it was basic. Solutions containing ammonia in low concentration were carefully observed to detect traces of turbidity.

The pK_A of ammonia was determined by titrating an NH_4ClO_4 solution with base directly after a pH meter calibration without adding $Hg(ClO_4)_2$. The salt bridge was made up to match the NH_4^+ concentration at half equivalence. The titration was performed at .09 and .029 F NH_4ClO_4.

Results and Discussion

The pK_A of the ammonium ion is 9.47 ± .02 at $\mu = 1.0$ M ($NaClO_4$), T = 25.0°C.

In the range of pH and ammonia concentration where $Hg(NH_3)_2^{++}$ is expected to be the only significant complex, K_2 was computed from the potentiometric data and equation V-5. If $Hg(NH_3)_2^{++}$ is the only ammonia complex, $K_2 = Q_1$.

$$Q_1 = \left(\frac{[Hg^{++}]_o}{[Hg^{++}]} - \frac{10^{-6.3}}{[H^+]^2} - (1 + K) \right) \left(\frac{[H^+]}{[RH^+]} \right)^2$$

K_2 is defined as in the previous chapters:

$$K_2 = \frac{[Hg(NH_3)_2^{++}][H^+]}{[Hg^{++}][NH_4^+]} .$$

As is true with guanidine, this value of K_2 is not constant as the total ligand concentration is changed. However, the relationship between $[NH_4^+]$ and Q_1 is not simple; indeed, Q_1 goes through a minimum.

In Table XII, the average value of K_2 from each of six separate titrations is given. Excluded from these averages are values where $[Hg^{++}]_o/[Hg^{++}] < 300$ (see Chapter V discussion). Also excluded are values where $[NH_4^+]/[H^+] > 10^7$. From the stability constants

TABLE XII

No.	$[NH_4^+]$	$[Hg(ClO_4)_2]_o$	Average K_2	$1/[NH_4^+]$
6	0.74	2.9×10^{-3}	$.098 \pm .005$	1.35
1	0.38-0.42	5×10^{-3}	$.089 \pm .012$	2.4-2.6
2	0.185-0.189	1.2×10^{-4}	$.066 \pm .006$	5.3-5.4
4	0.075-0.078	6.1×10^{-4}	$.080 \pm .007$	12.9-13.4
5	0.019-0.023	1.2×10^{-4}	$.101 \pm .006$	44-52
7	0.0066-0.0072	1.2×10^{-4}	$.15 \pm .01$	138-152

determined by Bjerrum, it is possible to calculate that if this ratio exceeds 10^7, $Hg(NH_3)_3^{++}$ begins to form in significant concentration. Q_1 does indeed increase above this point. Each average represents a wide variation of pH (between 3 and 7) at approximately constant $[NH_4^+]$. The indicated error is the maximum spread, not the standard error. The variation in K_2 is small but significant. It is clearly related to $[NH_4ClO_4]$, not to $[Hg(ClO_4)_2]_o$.

The increase in K_2 as $[NH_4ClO_4]$ decreases below 0.2 M might be attributed to a $HOHgNH_3^+$ complex similar to that formed in the Hg(II)-guanidine system. However, information on this possible complex must be obtained at low ammonia concentrations. In order to avoid precipitation of basic mercury salts, it is necessary to keep $[Hg^{++}]_o$ low as well. The potentials are stable under these conditions and no significant drift in K_2 occurred which might be due to oxidation of the electrode. Nonetheless, one prefers to work at total Hg(II) concentrations greater than 1×10^{-4} F. Although the solutions at low $[NH_4^+]$ were carefully inspected for precipitates, it is possible that some very slight turbidity might have escaped detection. Therefore, the critical Experiment #7 is not entirely decisive.

At high total ammonia concentrations, the apparent K_2 also increases. It is reasonable to attribute this to the effect of NH_4^+

ion on activity coefficients. The ionic strength principle has remained remarkably valid throughout this work. We have replaced Na^+ almost completely with Hg^{++}, $C(NH_2)_3^+$, and φNH_3^+ without any apparent effect on equilibrium constants. That this is not universally possible is perhaps unfortunate, but not surprising.

Rather than obtaining a value of K_2 by extrapolating a graph of Q_1 vs. $1/[RH^+]$ to $1/[RH^+] = 0$ and ignoring the experiments where $[NH_4^+] > 0.2$, it seems preferable to adopt an appropriate mean. The median of the average K_2's seems suitable. Experiment #7 can be excluded from the group of acceptable estimates of K_2, however. We have, then,

$$K_2 = .08 \pm .02 \quad (T = 26.0°,\ \mu = 1.0) .$$

From the pK_A of ammonia,

$$\beta_2 = \frac{[Hg(NH_3)_2^{++}]}{[Hg^{++}][NH_3]^2} = K_2/K_A^{\,2} = 10^{\,17.8 \pm 0.1}\ (\ell/\text{mole})^2$$

The value obtained by Bjerrum was: $\log \beta_2 = 17.5$ in 2 M NH_4NO_3 at approximately 22°C.

In more basic solution the complexes $Hg(NH_3)_3^{++}$ and $Hg(NH_3)_4^{++}$ form. The presence of free ammonia in such solutions makes a number of changes in procedure necessary in order to obtain accurate constants. Titration with acid or base is no longer useful, because large changes in [NH_4^+] result. The method of Bjerrum is suitable for study of these complexes; therefore, the constants were not redetermined.

These results confirm those of Bjerrum. It is somewhat disappointing that K_2 is so sensitive to the nature of the medium. Such variations make it difficult to define a constant of general validity. A constant useful in all 1 F perchlorate solutions cannot be more precisely determined than the K_2 given here.

CHAPTER VII

COMPLEX STABILITY AND LIGAND BASICITY

The base strength of an electron donor can be discussed in terms of its tendency to bind protons, metal ions, or any other Lewis acid. For a series of sufficiently similar donors, one expects a correlation to exist between basicities measured on different scales. Bruehlman and Verhoek (12) showed that the equation

$$\log K_{Ag} = a \log K_H + b$$

is obeyed for several amines. K_{Ag} is the equilibrium constant of the reaction

$$Ag^+ + R \rightleftarrows AgR^+$$

and K_H that of

$$H^+ + R \rightleftarrows HR^+ ,$$

R being an amine. The known stability constants of Hg(II) complexes with nitrogen bases are collected in Table XIII.

The listed value of K_{Hg} is a "mean complexity constant"--the square root of the overall association constant of the 2:1 complex

TABLE XIII. Association Constants of Nitrogen-Containing Ligands with Hg(II)

Ligand	Complex^a	log K_H^{a}	log K_{Hg}^{a}	Temp.	Method	Medium	Ref.
ammonia (L)	HgL_2^{+2}	9.61	8.75	22	pH	2M NH_4NO_3	(4)
	HgL_2^{+2}	9.47	8.9	25	Hg	1M $NaClO_4$	(21)
methylamine (L)	HgL_2^{+2}	10.72	8.95	25	pH	.5M $HLNO_3$	(11)
n-butylamine (L)	HgL_2^{+2}	10.71	9.05	25	pH	.5M $HLNO_3$	(11)
ethylene diamine (L)	HgL_2^{+2}	10.18	11.71	25	pH	1M KNO_3	(11)
	HgL_2^{+2}	10.00	11.65	25	Hg	.1M $NaClO_4$	(59)
	HgL_2^{+2}	10.00	11.59	25	Polarog	.1M KNO_3	(60)
	$Hg(HL)_2^{+4}$	7.20	6.45	25	Hg	.1M $NaClO_4$	(59)
2-methoxyethyl-amine (L)	HgL_2^{+2}	9.30	8.92	30	pH	1M $NaClO_4$	(61)
aminoacetic acid (HL)	HgL_2	9.76	9.6	20	pH	.5M KNO_3	(62)
ethanolamine (L)	HgL_2^{+2}	9.60	8.66	25	pH	.4M KNO_3	(11)
2-amino-2'-hydroxy-diethyl sulfide (L)	HgL_2^{+2}	9.18	9.13	30	pH	1M $NaClO_4$	(61)
pyridine (L)	HgL_2^{+2}	5.21	5.0	25	pH	.5M $HLNO_3$	(11)
aniline (L)	HgL_2^{+2}	4.78	4.60	27	Hg	1M $NaClO_4$	(21)
piperidine (L)	HgL_2^{+2}	11.12	8.72	25	pH	.5M KNO_3	(11)

TABLE XIII (continued)

Ligand	Complex[a]	$\log K_H^{2}$	$\log K_{Hg}$[a]	Temp.	Method	Medium	Ref.
diethanolamine (L)	HgL_2^{+2}	9.00	7.83	25	pH	.5M KNO_3	(63)
triethylamine (L)	HgL_2^{+2}	10.77	7.80	25	pH	.4M $HLNO_3$	(11)
triethanolamine (L)	HgL_2^{+2}	7.90	6.54	25	pH	.5M KNO_3	(11)
guanidine (L)	HgL_2^{+2}	13.54	12.48	27	Hg	1M $NaClO_4$	(21)
d-cycloserine (HL)	$Hg(HL)_2^{+2}$	4.57	7.04	25	Hg	.4M KNO_3	(64)
	HgL_2	7.40	8.77	25	Hg	.4M KNO_3	(64)
imidazole (L)	HgL_2^{+2}	7.12	8.37	27	Hg	.15M $NaClO_4$	(1)
histidine (HL)	$Hg(HL)_2^{+2}$	6.08	7.50	27	Hg	.15M $NaClO_4$	(1)
	HgL_2	9.12	10.61	27	Hg	.15M $NaClO_4$	(1)
adenosine (L)	HgL_2^{+2}	3.5	4.25	27	Hg	.1M $NaClO_4$	(2)
cytosine (L)	HgL_2^{+2}	4.5	5.45	27	Hg	.1M $NaClO_4$	(2)
thymidine (HL)	HgL_2	9.6	10.6	27	Hg	.1M $NaClO_4$	(2)
thymine (HL)	HgL_2	9.8	10.6	27	Hg	.1M $NaClO_4$	(2)

---

[a] If the complex is HgR_2,

$$K_H \equiv [HR^{+}]/[H^{+}][R]$$
$$\beta_2 \equiv [HgR_2^{++}]/[Hg^{++}][R]^2$$
$$K_{Hg} \equiv \sqrt{\beta_2}$$

(HgL_2^{++}). The first and second stepwise formation constants are usually similar (11). Therefore, K_{Hg} approximates β_1, the association constant of the 1:1 complex, which is not always reported separately from the overall constant. The β_1 of many mercury complexes is particularly difficult to determine.

The structure of several of the ligands is shown in Figures XXI and XXII. In Figure XXIII, log K_{Hg} is presented as a function of log K_H.

If all ligands are considered simultaneously, Figure XXIII shows that the stability of Hg(II) complexes only roughly parallels the basicity of the ligand. However, the data can be divided into three groups--simple alkylamines such as $(CH_3)_2NH$, complex cyclic amines such as imidazole, and the remaining amines.

One must be cautious in interpreting correlations such as this, because scatter due to different conditions of measurement, lack of accuracy, and the unique nature of each compound is inevitable. If, as here, more than one class of compounds exists, different groupings can result in very different recursion lines and consequently in different interpretations.

It appears, however, that alkylamines consistently bind Hg(II) less well relative to protons than do other nitrogen bases. A similar effect was observed by Bruehlman and Verhoek (12) in

FIGURE XXI

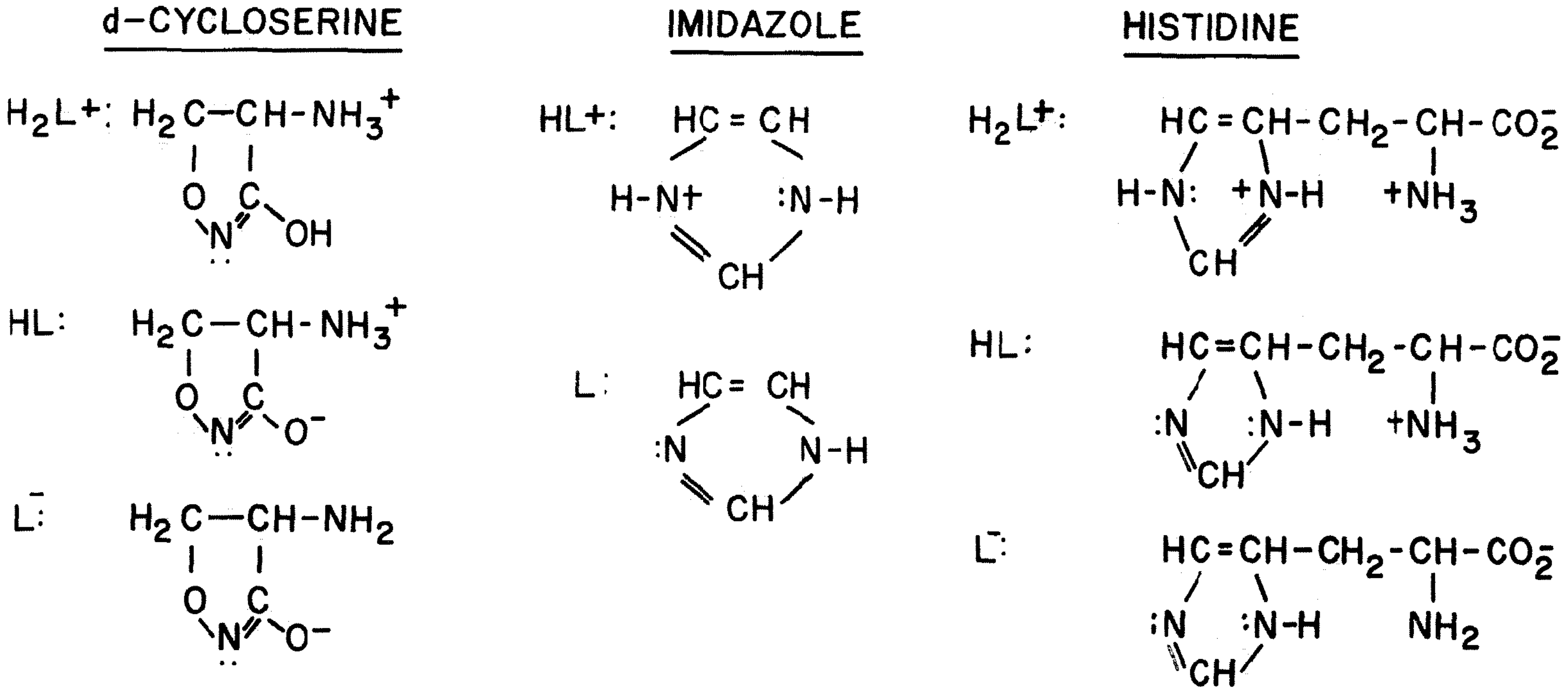
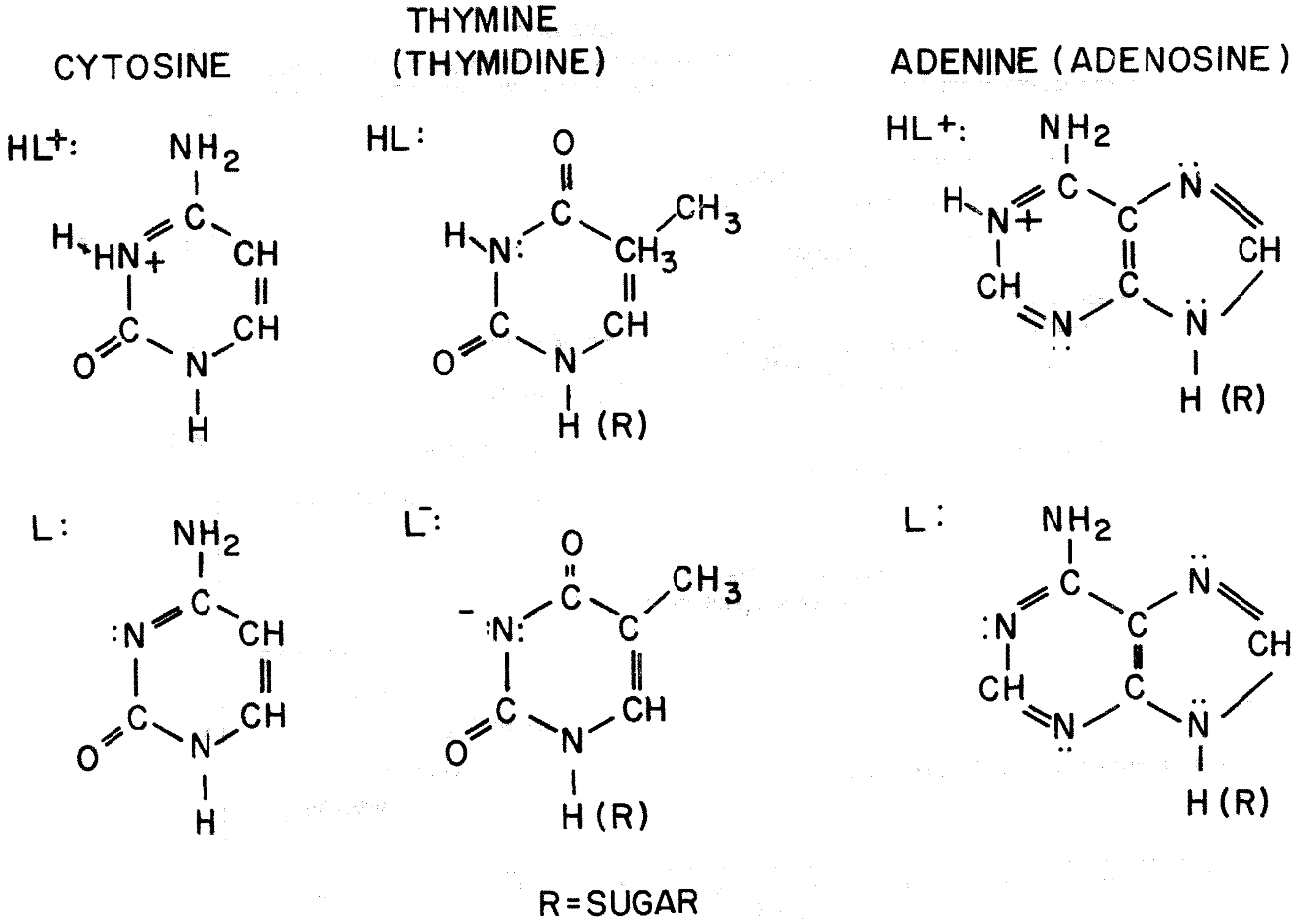


FIGURE XXII


CYTOSINE
THYMINE (THYMIDINE)
ADENINE (ADENOSINE)
HL+:
HL:
HL+:
L:
L⁻:
L:
R=SUGAR

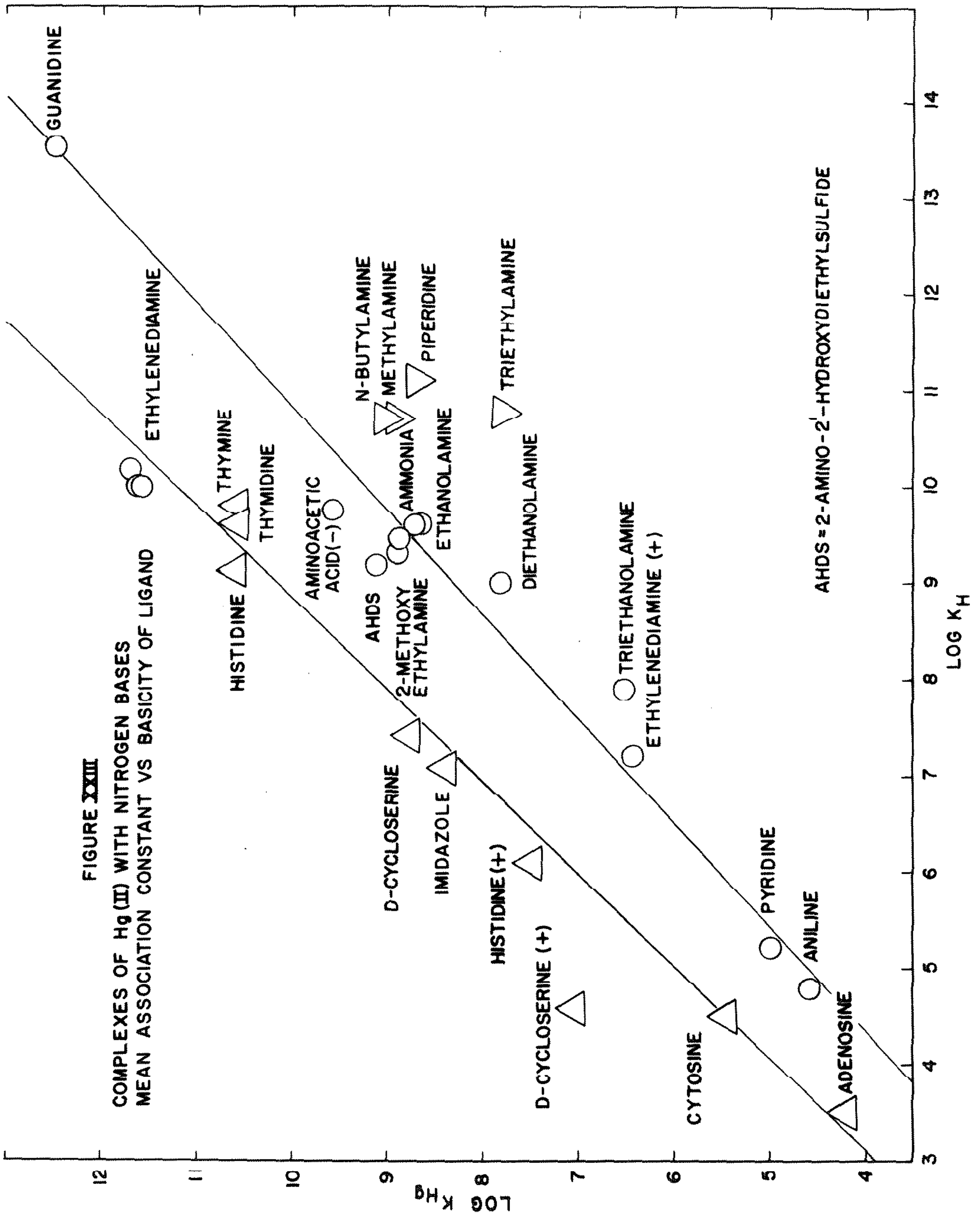


FIGURE XXIII
COMPLEXES OF Hg (II) WITH NITROGEN BASES
MEAN ASSOCIATION CONSTANT VS BASICITY OF LIGAND

AHDS = 2-AMINO-2'-HYDROXYDIETHYLSULFIDE

their work with Ag(I) complexes, but it was more closely associated with secondary and tertiary rather than primary amines.

The important effects of ionic hydration on the rate of mercuration of benzene discovered by Perrin and Westheimer (30, 44) have already been mentioned. They found that the rate of mercuration is very sensitive to the activity of water. They also attributed the ease with which the phenylmercuric cation is mercurated to charge dispersal by the solvent. Hydration may also affect complex stability--introduction of hydrophobic groups into a ligand may interfere with solvation and decrease the stability of a complex. The magnitude of such an effect would depend on the size and configuration of the hydrophobic groups, their steric relation to the metal ion, and the solvation requirements of the latter. Since the solvation of the proton is unique, such an effect would introduce irregularity into a correlation of complex stability with tendency to bind protons.

Bjerrum (11) pointed out that the stability of Hg(II) complexes is unusually sensitive to ligand basicity. This is evident from Figure XXIII. The slope of the lower line in the figure is 0.9. A corresponding plot for Ag(I)-amine complexes yields a slope of about 0.3 (12).

There remain a substantial number of ligands--compounds characterized by complicated heterocyclic rings--which bind Hg(II) more strongly than one would predict from their basicity. The effect is quite regular, and a second recursion line has been drawn to illustrate it. Yet the compounds in this group are very diverse. Speculation in terms of resonance or solvation effects seems unconvincing; the origin of this interesting enhanced stability remains obscure.

APPENDIX

SUMMARY OF U.V. ABSORPTION SPECTRA

Compound	Solvent	Wave-length (mμ)	Type (max, min, etc.)	Molar Absorptivity (ℓ/mole-cm)
p-methoxyanisole	cyclohexane	289.0	maximum	3.17×10^3
		293.0	"	3.14×10^3
		300.1	"	2.52×10^3
p-methoxyanisole	water	286.1	"	2.50×10^3
		252	minimum	1.81×10^2
2,5-dimethoxyphenylmercuric perchlorate	water (.95F $NaClO_4$-.05F $HClO_4$)	294.9	maximum	3.58×10^3
		257	minimum	4.2×10^2
phenylmercuric perchlorate	water (.19F $HClO_4$)	247.6	minimum	210
		250.4	maximum	238
		256.2	"	268
		262.2	"	210
benzene	cyclohexane	237.8	"	51.5
		238.9	"	53.4
		243.1	"	104
		248.8	"	186
		254.6	"	235
		260.7	"	162
		268.6	"	9.2
benzene	water	223.3	"	8.9
		228.5	"	16
		233.4	"	31
		238.0	"	53
		242.7	"	92
		248.1	"	148
		253.7	"	186
		259.8	"	128

Compound	Solvent	Wave-length (mμ)	Type (max, (min, etc.)	Molar absorptivity (ℓ/mole-cm)
anilinium perchlorate	aqueous perchloric acid	243.9	maximum	100
		248.3	"	133
		253.8	"	163
		259.9	"	124

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PROPOSITION I

The development of a cation exchange technique to analyze and purify the products of aromatic mercuration is proposed. In addition, it is proposed to study the behavior of phenylmercuric salts as substrates in the common electrophilic substitution reactions.

The separation and purification of the products of most mercuration reactions is a difficult problem. Many aromatic mercurials of the type RHgX (X = acetoxy, halide, etc.) are insoluble in the common solvents. In other cases, the solubility characteristics of various isomers are so similar that separations are impossible. These difficulties increase greatly if compounds are polymercurated, and conditions where polymercuration occurs are avoided in preparative work (1).

Arylmercuric salts of non-complexing anions--perchlorate in particular--are moderately soluble in acidic aqueous solution, however. Perrin (2) studied the mercuration of benzene at 40°C in $HClO_4$-$NaClO_4$ solutions; he observed no precipitation except in solutions of high salt or low acid. Since his reaction solutions were 0.2 M in Hg(II) (3), and he routinely carried the reaction to 50% completion, the mercurated products are soluble to ca. 0.1 M. The mixtures contained mono-, di-, and tri-mercurated species.

Presumably arylmercuric perchlorates are completely dissociated in aqueous solution. This suggests the possibility that they can be separated by chromatography on a cation exchange resin. Preliminary attempts to separate the products of the mercuration of aniline indicated that such separations are probably possible (4). 2,4-Dimercurated aniline is reversibly absorbed by a column of Dowex 50W in acidic solution. The principal difficulty to be overcome is the strong affinity of the column for such large, multi-charged cations which are probably capable of interacting directly with more than one sulfonic acid group. This causes the eluent to be unreasonably dilute; highly mercurated compounds are difficult to remove from the column at all.

Mercurated anilines, however, are protonated in acidic solution, which adds to their charge and increases their affinity for the column. If the mercurated cation possesses no basic group, the situation is more favorable. From the preliminary work, there is every reason to believe that successful separations of mono-, di-, and tri-positive mercurated aromatic cations can be successfully developed. One would expect the resins to be fairly selective toward various isomers for steric reasons, particularly in the case of poly charged cations, where the charge distribution on the ion changes greatly from isomer to isomer.

Such separation procedures would permit quantitative determination of isomeric distribution in mercuration reactions. In particular, it would be possible to study the distribution of products at equilibrium in the mercuration of benzene or other substrates and to study the equilibrium constant for the mercuration of the phenylmercuric ion.

It may also be possible to use this technique to study the directive effects of the $-Hg^+$ substituent. Electrophiles such as Br_2 react with mercurated substrate to replace the orienting group itself. Therefore, mercuration is about the only reaction in which the orienting effect of $-Hg^+$ can be studied. Isomer distribution in this system was studied by Malaiyandi, Sawatzky, and Wright (5). Their analytical procedure consisted of reaction of the products with bromine and I.R. analysis of the dibrominated products. The procedure contained many phase separations and even a distillation; it is therefore possible that it produced artifacts. The difficulties inherent in this problem are increased by the reversibility of mercuration. If the reaction is performed under reversible conditions, the observed products are those thermodynamically rather than kinetically favored.

An enticing possibility is that preparative separations using displacement development on ion exchange columns may be possible.

This requires a cation in the eluent with greater affinity for the resin than the ions to be separated (6). It is reasonable to presume that La^{+++} is such an ion if the products are monomercurated. Polymercurated cations may require an eluent of still higher affinity for the resin, such as Zr(IV) (7).

It might be pointed out that the proposed technique is applicable to products of conventional mercuration with mercuric acetate. Arylmercuric acetates are ionized in acid solution to the cation and acetic acid (8).

Arylmercuric compounds are useful synthetic intermediates, particularly if they are pure (1). The mercury atom is replaced in electrophilic substitution exceedingly readily. Bromination under mild conditions has long been a technique for determining the position of Hg atoms on the ring (9). It has been shown that in the course of the oxynitration reaction, oxides of nitrogen (N_2O_4) attack phenylmercuric nitrate and the $-Hg^+$ group is replaced by -NO (10).

It is proposed that the behavior of mercurated compounds as substrates in nitration and sulfonation be studied. It seems likely that substitution will occur very readily. It would be particularly useful if it were possible to introduce several sulfonic acid groups into an aromatic ring in one step. The strong deactivating effect of the sulfonic acid group ordinarily makes the introduction of a second such substituent very difficult (11). Non-acidic media (vis-a-vis protons) should be chosen, since proton acids demercurate aromatic compounds.

Summary

1. It is proposed that an analytical ion exchange chromatographic technique be developed for separation and quantitative analysis of mono-, di-, and perhaps tri-positive arylmercuric cations. A suggested procedure consists of chromatography on polystyrene-sulfonic acid cation exchange resins in aqueous solutions 0.5-1.0 M in $HClO_4$. The most promising eluents are solutions of concentrated salts, the cations of which have high affinity for the resin, such as $Ba(ClO_4)_2$ and $La(ClO_4)_3$. La(III) is transparent in the ultraviolet, and the effluent can be analyzed spectrophotometrically.

2. It is proposed that this technique be applied to the study of isomer distribution in the mercuration of phenylmercuric perchlorate and to the study of the equilibrium among mercurated species in aqueous perchloric acid solution.

3. It is proposed that the technique of displacement development in cation exchange chromatography is a possible general method

for preparation of pure isomers of aromatic mercurials. Suggested eluents are solutions of La(III) or Zr(IV).

4. It is proposed that the sulfonation and nitration of phenylmercuric chloride be studied. In nitration, it is proposed to effect reaction by treatment with nitryl chloride. Anhydrous silver tetrafluoroborate is usually added (12), but it may not be necessary in this case.

$$ArHgCl + NO_2Cl \rightarrow ArNO_2 + HgCl_2$$

It is proposed to sulfonate phenylmercuric chloride and its polymercurated analogs by reaction with the sulfur trioxide-pyridine complex in carbon tetrachloride (13).

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PROPOSITION II

The equilibrium constant of the reversible, first order reaction

$$A \underset{k_r}{\overset{k_f}{\rightleftarrows}} B$$

is

$$K = [B]_{eq}/[A]_{eq} = k_f/k_r ,$$

where $[A]_{eq}$ and $[B]_{eq}$ are the concentrations of reactant and product at equilibrium. The rate equations for this system can be solved in closed form, and have been discussed by many authors (1, 2, 3). However, no discussion of the rate at which the apparent equilibrium constant, $[B]/[A]$, approaches the true one seems to have appeared. A quantitative treatment of this question is useful in experimental planning, in estimating error, and in establishing that equilibrium has indeed been attained.

The rate equation is

$$-\frac{d[A]}{dt} = k_f [A] - k_r [B]$$

with the condition that

$$[A] + [B] = [A]_o + [B]_o ,$$

where $[A]_o$ and $[B]_o$ are the initial concentrations at $t = 0$. The solutions to these equations are:

$$[A] = a[1 + b e^{-(k_f+k_r)t}]$$

$$[B] = a[K - b e^{-(k_f+k_r)t}]$$

where

$$a = \frac{[B]_o + [A]_o}{1 + K}$$

$$b = \frac{[A]_o (1 + K)}{[A]_o + [B]_o} - 1 .$$

Therefore,

$$K_{obs} = \frac{[B]}{[A]} = \frac{K - b e^{-(k_f+k_r)t}}{1 + b e^{-(k_f+k_r)t}} ,$$

which approaches K as t becomes large.

The parameter of interest is actually the relative error in K,

$$D = \frac{| K_{obs} - K|}{K}$$

Computing this quantity from the formula for K_{obs}, we obtain

$$D = \frac{1 + K}{K} \left| \frac{1}{b^{-1} e^{(k_f+k_r)t} + 1} \right|$$

If $[B]_o = 0$, then $b = K$, and

$$D = \frac{1 + K}{e^{(k_f + k_r)t} + K} \qquad \text{(PII-1)}$$

while if $[A]_o = 0$, $b = -1$, and

$$D = \left(\frac{1 + K}{K}\right)\left(\frac{1}{e^{(k_f + k_r)t} - 1}\right) \qquad \text{(PII-2)}$$

If an approximate equilibrium and rate constant are known, then, an estimate of error can be computed. Only the rate in one direction need be known. Since the expotential term contains the sum of the rate constants, the actual error will always be less than that calculated when one of the rate constants is neglected.

For a given permissible error D, equations PII-1 and PII-2 can be solved for the minimum equilibration time in terms of K and $(k_f + k_r)$. In Figure XXIV, plots of $(k_f + k_r)t$ vs. log K are shown for various values of D.

It is clear from the figure that extra time is required if the equilibrium is approached from the "wrong" direction. For $K > 1$, the "wrong" direction is that of the forward reaction; the "right" direction that of the reverse. If K exceeds 10, the time required to approach equilibrium from the reverse direction is essentially

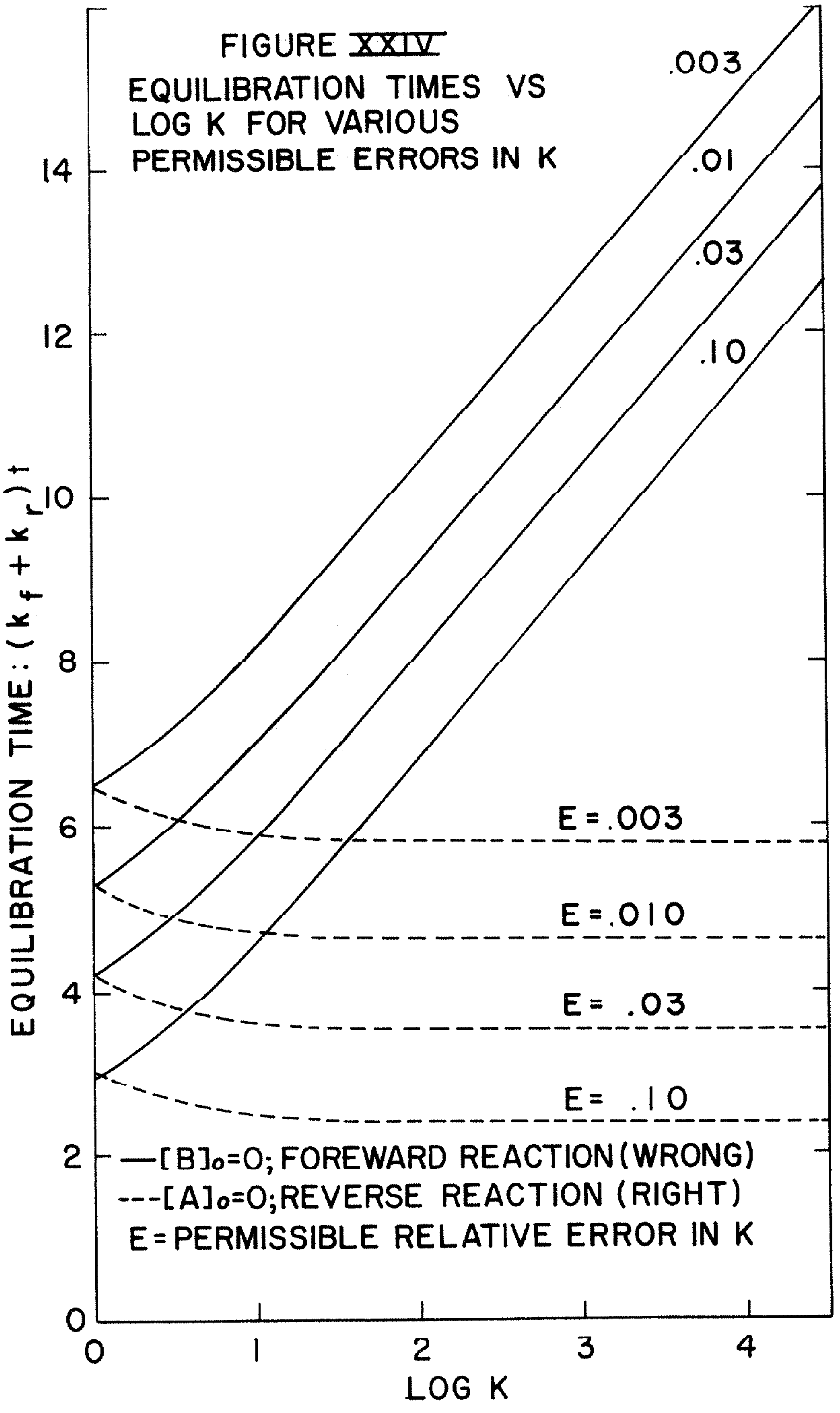

FIGURE XXIV
EQUILIBRATION TIMES VS LOG K FOR VARIOUS PERMISSIBLE ERRORS IN K

independent of K for a given permissible error. On the other hand, the equilibration time required in the forward direction increases linearly with the logarithm of K. Therefore, if K is large, a much greater time is required to reach equilibrium from one direction than from the other.

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PROPOSITION III

A search for a π-type complex of mercuric ion with aromatic compounds is proposed.

In 1922, Hill isolated $AgClO_4 \cdot C_6H_6$ during his investigation of the system: $AgClO_4$-H_2O-C_6H_6 (1). Below 140°C, it is the solid phase at equilibrium. He later discovered that toluene forms an analogous compound (2), and that $AgClO_4$ is soluble in toluene to a spectacular degree (50% by weight at 25°C). Rundle and his coworkers have analyzed the X-ray diffraction of single crystals of $AgClO_4 \cdot C_6H_6$ (3,4). The results affirm that the silver(I) ions are π-bonded to the aromatic ring. Two cations are bound to each ring. They are asymmetrically placed; one above and one below the plane of the ring; each interacts most strongly with two carbon atoms. The ring is slightly distorted with C-C bond distances of 1.35 Å if the bond is close to a silver atom and 1.43 Å if it is not.

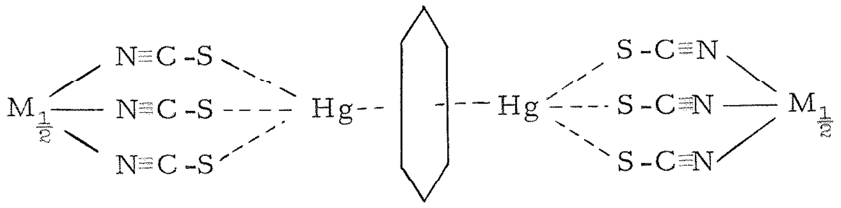
Complex formation between silver nitrate and a large number of aromatic compounds has been studied in aqueous solution (5,6,7). The 1:1 formation constants, which fall in the range 1-10 ℓ/mole at $\mu = 1$ M, were determined by the increase in solubility of aromatic in the aqueous phase as the silver nitrate concentration is increased. For large aromatic molecules, a 50 mole per cent solution of methanol-water has been employed (8,9).

The ultraviolet absorption spectrum of the toluene-$AgClO_4$ complex at wavelengths greater than 245 mμ has been observed by Keefer and Andrews in aqueous solution (10). The intensity of the toluene band in the 260 mμ region increases by about a factor of two on complexing, and the complex absorbs considerably more intensely at wavelengths greater than 280 mμ. This is a rather small change in spectrum, however, considering the distortion of the ring. Mullikan has indicated that a $C_6H_6 \rightarrow Ag^+$ charge transfer band is to be expected at roughly 230 mμ (12), although his earlier estimates placed the transition at longer wavelength (11).

Both Ag^+ and Hg^{++} are known to form strong complexes with olefins, those of Hg^{++} usually being more stable. K_1 for the Hg^{++} complex of cyclohexene is 2.2×10^4 ℓ/mole (13), while that for Ag^+ is 1.91×10^2 (14).

$$K_1 = \frac{[Ag\,R]^+}{[Ag^+][R]} \quad .$$

Thus, there appears to be ample reason to expect Hg^{++} complexes with aromatic compounds. But the only such species yet observed is possibly $MHg_2(SCN)_6 \cdot C_6H_6$, where M is Co(II), Ni(II), or Cd(II) (15). On the basis of indirect ultraviolet and infrared data and X-ray powder patterns, the authors postulate the following structure for these rather unstable compounds:



Aromatic

Dewar has proposed that the formation of π-complexes is the first step in many aromatic substitutions (16). The Hg(II) analogs of the known Ag(I) complexes with aromatic compounds are species of this type,and they are possible intermediates in aromatic mercuration. The isolation of such intermediates would be of great interest. Therefore, the following experiments are proposed:

1. A determination of the solubility of mercuric perchlorate in benzene, toluene, and m-xylene, and an attempt to prepare solid mercuric perchlorate-benzene compounds in the same fashion as the silver compounds are obtained. In this and the following proposed experiments, it may be necessary to operate at temperatures as low as possible to avoid mercuration of the aromatic material.

2. An investigation of the absorption spectra of solutions of mercuric perchlorate and mercuric acetate in benzene, toluene, and xylene. Although the solvent absorption interferes at wavelengths

less than 280 millimicrons, the formation of complexes should significantly intensify the long wavelength edge of the absorption band.

3. A study of the spectra of solutions of benzene, toluene, and xylene in aqueous mercuric perchlorate solution (.02-1 M). Even at 5-10°C, it will probably be necessary to correct for slow changes in the spectrum due to mercuration.

4. Solubility studies of the type performed by Andrews and Keefer, but utilizing mercuric perchlorate. The formation of mercurated products will not interfere with the determination of the solubility of benzene, and corrections can be applied for changes in mercuric ion concentration. Spectrophotometric determination of the benzene concentration in cyclohexane extracts of the reaction solutions is the recommended analytical procedure.

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PROPOSITION IV

A study of the AgF and TlF complexes of aromatic compounds in anhydrous HF is proposed. Of particular interest are the ultraviolet absorption and proton N.M.R. spectra of the complexes. It is also proposed to observe the changes in the F^{19} chemical shift which accompany complex formation.

In 1937, Klatt (1) found that certain metal salts greatly increase the solubility of aromatic compounds in anhydrous HF. Particularly effective were silver and mercuric azides, silver and thallous fluorides, and mercuric cyanide. Addition of these salts changes the colors of the aromatic hydrocarbon-HF solutions dramatically. Increases in solubility of up to four moles of aromatic per mole of metal salt could be obtained.

McCaulay and Lien (2) studied the effect of AgF on the solubility of arenes in HF in somewhat greater detail. They found that aromatic compounds could be selectively extracted from hydrocarbon mixtures with HF-AgF solutions. Benzene as well as toluene, m-xylene, and p-xylene are strongly complexed. Three moles of aromatic are complexed per mole of silver; the authors attribute this descrepancy from the earlier work to physical solubility of aromatic in the HF phase. Complex stability did not seem sensitive to number or position of methyl substituents.

These characteristics contrast sharply with those of the protonated aromatic cations which form in HF-BF_3 solutions (3, 4). Strongly stabilized by introduction of alkyl substituents, the latter complexes are also sensitive to substituent orientation (5). They are believed to be sigma-type complexes, in which the extra proton is bonded to a single carbon atom in the ring. Benzene and toluene are only very weakly bound.

The wide differences between the properties of Ag^+ and H^+ complexes of arenes led McCaulay and Lien to suggest that the former are pi-complexes. However, no further work has been undertaken to explore the structure and properties of metal ion-aromatic hydrocarbon complexes in HF solution. On the other hand, the proton N.M.R. and the ultraviolet absorption of aromatic carbonium ions have been extensively studied (6).

It is therefore proposed to undertake a study of the optical absorption spectra of the TlF and AgF complexes with aromatic compounds in anhydrous HF solution. If these are pi-type complexes, their spectra will differ considerably from those of protonated hydrocarbons. The color of the aromatic-metal salt solutions (1) may be due to an $Ar \rightarrow Ag^+$ charge-transfer band in the visible.

Gold-plated nickel or poly-chlorotrifluoroethylene cells with sapphire windows have been successfully used for U.V. absorbance measurements on HF solutions (7).

A proton N.M.R. study of these complexes is proposed. Such studies have been very useful in clarifying the structure of aromatic carbonium ions (8, 9). Comparison of the results for the two types of complex should be most informative. Low temperature experiments should be undertaken in an attempt to slow down the inter- and/or intra-molecular exchange rates and observe any asymmetry introduced by complex formation.

The F^{19} chemical shift in liquid HF is surely affected significantly by the introduction of metal ions into the solution. The magnetic resonance of this nucleus is therefore a possible probe for study of ionic solvation in such solutions. In this case an F^{19} N.M.R. study might elucidate the changes in solvation which occur as Ag(I) or Tl(I) ions are complexed by aromatic hydrocarbons.

Study of the variation of F^{19} solvent shifts when exchange rates are high requires high concentrations of metal ion. The observed shift is the average of all F^{19} shifts in the sample; if only a small fraction of nucleii participate in ion solvation, no effect can be detected. However, AgF and TlF are very soluble in anhydrous HF: the solubility of AgF is 44g per 100 g of HF at

-10° C; that of TlF is about 450g per 100g of HF (10). One also expects the shifts to be large; the chemical shifts of the F^{19} nucleus are an order of magnitude greater than those of H^1 (11). The sensitivity of detection for equal numbers of nucleii is 0.83 relative to H^1 in constant frequency work (12).

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PROPOSITION V

The existence of the monomeric mercurous ion has been a matter of some speculation (1). It has been postulated as an intermediate in a number of oxidation-reduction reactions of mercury as a mechanism of one-electron transfer (2). Direct evidence for the existence of this species would therefore be of great interest. Inasmuch as the monomeric mercurous ion possesses an unpaired spin, electron paramagnetic resonance suggests itself as a means of detection.

The Hg_2^{++} ion possesses a strong U.V. absorption band at 236.5 millimicrons, which deviates from Beer's law in very dilute solution. Higgenson (3) believed that this was due to the reaction

$$Hg_2^{++} \rightleftharpoons 2\,Hg^+ \quad , \qquad K = [Hg^+]^2/\,[Hg_2^{++}],$$

and that K is about 10^{-7}. Moser and Voigt (4) pointed out, however, that the effect may be due to disproportionation into Hg(II) and Hg(0). They determined the solubility of Hg(0) in water and the disproportionation constant in the absence of a metallic phase using Hg^{203} as a tracer. They found no evidence for a K greater than 10^{-7}, their lower limit of detection.

About 10^{13} unpaired spins can be detected in an E.P.R.

experiment. The available volume is 0.1 ml; therefore Hg^+ concentrations of 10^{-5} to 10^{-6} M are detectable. In a 1 M solution of Hg_2^{++} this corresponds to a K of 10^{-11}.

It must be anticipated that no signal will be observed, for the value of K has been estimated as low as 10^{-30} (2). However, U.V. irradiation would probably enhance the dissociation considerably. No quantum-mechanical treatment of the Hg_2^{++} absorption spectrum has appeared in the literature. In the crudest approximation, the ion is analogous to the H_2 molecule, and one would assign the 236.5 millimicron band to the ${}^1\Sigma_u \leftarrow {}^1\Sigma_g$ transition, which corresponds essentially to promotion of one electron from a bonding to an antibonding molecular orbital, both constructed from 6s atomic orbitals. Thus it is probable that light absorption at this wavelength causes dissociation, and observation of an electron spin resonance signal due to Hg^+ may be possible.

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