KINETICS AND MECHANISM OF THE BERTHELOT REACTION WITH PARTICULAR REFERENCE TO AMMONIA ANALYSIS

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ABSTRACT

KINETICS AND MECHANISM OF THE BERTHELOT REACTION WITH PARTICULAR REFERENCE TO AMMONIA ANALYSIS

By

Charles Johnston Patton

An investigation of the mechanism of the Berthelot reaction has led to an increased understanding of the many conflicts in the literature concerning the reaction's use for the analytical determination of ammonia. Monochloramine is shown to be the first intermediate, and the kinetics of its formation and decomposition is presented. The identical visible spectra obtained for a series of indophenols synthesized in the course of this research and the blue complexes formed when phenol or a substituted phenol was used in the Berthelot reaction has confirmed that indophenol is the final product of the reaction. Conditions which led to the formation of final products other than indophenol have been observed and are also discussed. Finally, a new procedure for ammonia analysis using the Berthelot reaction, which is superior in both sensitivity and precision to the best procedure found in the literature, is presented.

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Charles Johnston Patton

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DEDICATED TO

LEROY W. HAYNES

The blues ain't nothin' but a low-down shakin' chill.
If you ain't never had 'em, God knows I hope you never will.

Robert Johnson

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I. INTRODUCTION

Although a large number of analytical schemes for ammonia analysis have appeared in the literature, the method finding the most widespread application is the Berthelot reaction. In this reaction, indophenol, an intensely blue charge-transfer complex, is formed when an aqueous solution containing ammonia is treated with phenol and hypochlorous acid. Under controlled conditions, the amount of indophenol produced is proportional to the concentration of ammonia originally present in the solution. The method is specific for ammonia, and when sodium nitroprusside is used as a "catalyst," detection limits for ammonia concentrations as low at 10^{-7} M have been reported. The precision of such procedures is quite poor, however, and despite the many papers which have appeared in the literature describing "improved" procedures for the catalyzed Berthelot reaction, a truly satisfactory method has yet to appear.

The trouble with most of the work to date on the Berthelot reaction is that while reaction parameters have been wildly juggled to "optimize" various procedures, little attention has been paid to the mechanism which leads to indophenol formation. In this research, a mechanistic approach to the problem of poor precision in the Berthelot reaction was undertaken. The rate of formation of monochloramine, the first intermediate in the Berthelot reaction, was determined as a function of pH. The rate was maximum at pH 8.0 with an

observed second-order rate constant of $2.4 \times 10^4 \pm 0.4 \times 10^3$ ℓ $mole^{-1}$ sec^{-1}. It was also observed that dilute aqueous solutions of monochloramine decomposed extensively in the presence of hypochlorous acid if the pH was less than 10.0.

In other experiments, the actual catalyst for the Berthelot reaction was found to be sodium pentacyanoaquoferrate, rather than sodium pentacyanonitroferrate or sodium pentacyanonitritoferrate as reported by other workers. This observation has not been reported elsewhere. Also, a series of substituted indophenols was synthesized, and the details of their preparation, as well as their visible spectra, have been included. These data confirmed that indophenol was the final product of the Berthelot reaction.

The final outcome of this research was a new analytical procedure for ammonia which has a lower detection limit and higher precision than any published procedure for the catalyzed Berthelot reaction. This method could be easily automated and, with minor modifications, should be well-suited to the analysis of ammonia in natural waters.

II. HISTORICAL

Evolution of the Berthelot Reaction

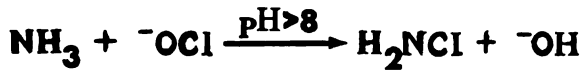
The blue color produced in alkaline solutions containing phenol, hypochlorite ions, and ammonia was first reported by Berthelot (4). This reaction was first used analytically by Thomas (42) to determine ammonia in blood. Although several other workers (6,43) modified Thomas's procedure, the first real improvement in ammonia analysis via the Berthelot reaction was reported by Russel (35). She found that the reaction was catalyzed by Mn(II) ions, and observed a three-fold increase in sensitivity relative to the uncatalyzed reaction.

Ten years later, two other catalysts more effective than Mn(II) ions were reported: acetone (10) and sodium nitroferricyanide (22). The use of these new catalysts, especially sodium nitropentacyanoferrate (nitroprusside), increased the sensitivity of the Berthelot reaction to the extent that concentration of the ammonia in biological fluids and natural waters prior to analysis was no longer necessary. This, coupled with the reaction's relative insensitivity to nitrogen-containing compounds other than ammonia, led to its widespread application. Over the past twenty years, literally scores of papers have appeared describing new applications or modified procedures for the catalyzed Berthelot reaction.

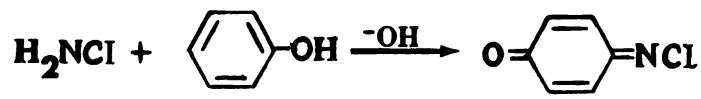
Unfortunately, few of these papers agree on such reaction parameters as reagent concentrations, pH, or order and timing of reagent additions. For example, a few papers (5,36) reported enhanced sensitivity when the chlorinating reagent was added first, while most other papers reported virtually no sensitivity unless the phenol reagent was added first. This led some researchers (15,37) to the erroneous conclusion that the phenol-hypochlorite and hypochlorite-phenol reactions were two distinct entities. Numerous conflicts in the literature give the impression that no single mechanism is operative in the catalyzed Berthelot reaction since the only thing most procedures have in common is extremely poor precision.

Kinetics and Mechanism of the Berthelot Reaction

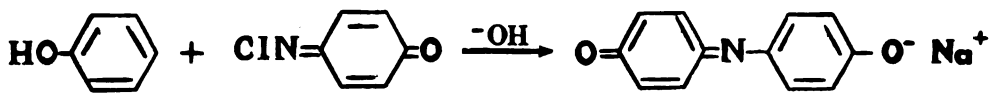
Very little has been published concerning the kinetics and mechanism of the Berthelot reaction. Russel (35) suggested that the end product of this reaction was indophenol or a closely related compound. Bolleter, et. al., (5) proposed a generalized mechanism (outlined below) in which monochloramine and quinone-N-chloroimine were intermediates and indophenol was the end product. The role of a catalyst was not considered.



monochloroimine



quinone-N-chloroimine



indophenol, sodium salt

There is substantial evidence in the literature (7,11,24) which supports the first step of Bolleter's proposed mechanism. At pH values greater than 8.5, monochloramine is the sole product in the reaction between equimolar concentrations of ammonia and hypochlorite ions. The fact that most papers in which reaction parameters for the Berthelot reaction were investigated reported a drastic reduction in sensitivity when the hypochlorite reagent was added first, however, led many workers to discount the proposed mechanism.

This conflict over the preferred order of reagent addition seems to have been resolved by Horn and Squire (18). They noted that all procedures in which the phenol reagent had to be added first in order to obtain satisfactory sensitivity used hypochlorite reagents in at least one thousand-fold excess of the stoichiometric amount

necessary to convert all the ammonia in the sample to monochloramine. They found, however, that the order of reagent addition could be reversed, affecting an increase in sensitivity and precision in these procedures if the concentration of the hypochlorite reagent was reduced by two orders of magnitude. This observation suggested that monochloramine was unstable in the presence of hypochlorite ions. It is interesting to note that Morris and Weil (27), who did extensive research on the products formed when waste water was chlorinated, reported that monochloramine was unstable in solutions containing a large excess of hypochlorite ions.

Role of Pentacyano Iron Complexes in the Berthelot Reaction

In a subsequent paper (19), Horn and Squire presented evidence that the catalyst for the Berthelot reaction was sodium nitritopentacyanoferrate which formed spontaneously when sodium nitroferricyanide, the assumed catalyst, was prepared in mildly alkaline solutions. They reported that conversion of the nitro complex to the nitrito complex prior to its use as a reagent increased both the sensitivity and precision of the Berthelot reaction. Later, Mark (23) confirmed this observation and suggested that the nitrito complex catalyzed the formation of monochloramine.

There is evidence in the literature not pertaining directly to the Berthelot reaction, however, which suggests that Mark's hypothesis concerning the catalytic role of sodium nitritopentacyanoferrate is in error. First, work of Weil and Morris (47) and of

Yagil and Anbar (49) has shown that the formation of monochloramine from ammonia and hypochlorous acid in the pH range of 7.5 to 11.5 is too rapid to be studied by conventional techniques. It does not seem likely that a reaction this rapid would require a catalyst. Second, work of Ohkuma (30) and of Swinehart and Rock (41) has shown that while sodium nitropentacyanoferrate is converted to sodium nitritopentacyanoferrate, the nitrito complex is in equilibrium with sodium aquopentacyanoferrate, as shown in the following scheme. For this

$$[Fe(CN)_5NO]^{2-} + 2^-OH \rightleftharpoons [Fe(CN)_5NO_2]^{4-} + H_2O$$

$$[Fe(CN)_5NO_2]^{4-} + H_2O \rightleftharpoons [Fe(CN)_5H_2O]^{3-} + NO_2^-$$

reason, it is possible that the real catalyst for the Berthelot reaction is the aquo complex rather than either the nitro or the nitrito complexes.

In another paper (29), Ohkuma reported that sodium nitroferricyanide is converted directly to sodium aquopentacyanoferrate by alkaline hydroxylamine. The aquoferrate thus formed incorporates a second molecule of hydroxylamine as a ligand, and in the presence of phenol, aminophenol was produced as shown below. The similarity be-

$$Na_2[Fe(CN)_5NO] + H_2NOH + NaOH \longrightarrow Na_3[Fe(CN)_5H_2O] + N_2 + {}^-OH$$

$$Na_3[Fe(CN)_5H_2O] + H_2NOH \xrightarrow{{}^-OH} Na_3[Fe(CN)_5H_2NOH] + H_2O$$

$$Na_3[Fe(CN)_5H_2NOH] + \langle O \rangle\!-\!OH \xrightarrow{{}^-OH} HO\!-\!\langle O \rangle\!-\!NH_2 + Na_3[Fe(CN)_5H_2O]$$

tween monochloramine and hydroxylamine suggests first that an

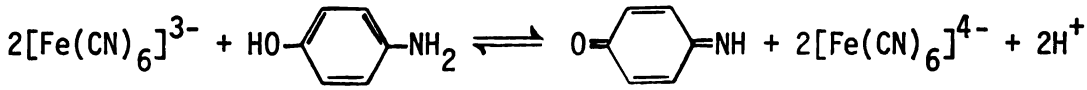
analogous mechanism may explain the catalytic role of sodium nitroferricyanide in the Berthelot reaction, and second that sodium aquopentacyanoferrate may be a better catalyst than either sodium nitropentacyanoferrate or sodium nitritopentacyanoferrate. To date, there has been no mention in the literature concerning the relevance of these works to the elucidation of the reaction mechanism for the catalyzed Berthelot reaction.

Use of Substituted Phenols in the Berthelot Reaction

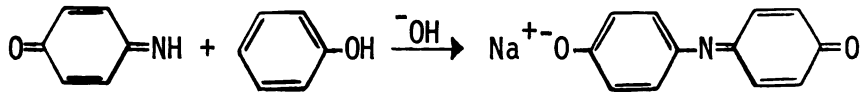
Another interesting development in the evolution of the Berthelot reaction as an analytical tool is the use of substituted phenols. Roskam and de Langen (34) reported a two-fold increase in sensitivity and more stable blanks when thymol (3-methyl-6-isopropylphenol) was used in place of phenol in the acetone-catalyzed Berthelot reaction. Procedures in which salicylic acid (33), 2-chlorophenol (51), 3-methylphenol (50), and 1-naphthol (26) were used have also been reported. Although no mention was made in these references concerning the mechanistic or kinetics implications of using substituted phenols in the Berthelot reaction, the work of several dye chemists is relevant.

Corbett (9) reported a synthesis for indophenols in solution as sodium salts by the ferricyanide oxidation of aminophenols to the corresponding quinone imines. The imines thus formed coupled spontaneously with phenol to give indophenolate ions when the pH range

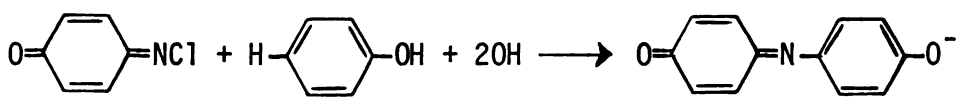
was between 8.5 and 11.5, as shown in the following scheme. Corbett



quinone imine



found that in the preparation of methyl substituted indophenolate ions, the use of the less methylated aminophenols and the more methylated phenols led to the fastest coupling rates. Thus when quinone monoimine was reacted with 2- and 3-methylphenol, for example, there was a thirty- and ten-fold increase, respectively, in the rate of indophenolate ion formation relative to phenol. In the case of chloroindophenolate ion synthesis, the use of the more chlorinated aminophenol and the less chlorinated phenol led to the fastest coupling rates. Gibbs, Hall, and Clark (14), in a much earlier work, made this same observation regarding the coupling rates of quinone-N-chloroimines and phenols although no quantitative data were given.



These observations suggest that there might be a kinetics advantage in using certain substituted phenols in the Berthelot reaction.

III. EXPERIMENTAL

Equipment and Instruments

Melting point data were obtained with an oil bath immersion apparatus (Thomas-Ashley). All pH data were obtained with a servo digital pH/volt meter (Heath EU-302A) and a combination reference and pH electrode (Beckman). All visible and ultraviolet spectra were obtained with a scanning spectrophotometer (Cary 17). Infrared spectra were obtained with a scanning infrared spectrophotometer (Beckman AccuLab 2). Data from kinetics experiments were obtained by using an automated stopped-flow spectrophotometer designed in these laboratories (2,3).

Chemicals

The phenols used as starting materials for indophenol synthesis were obtained from three sources: Aldrich, Eastman Kodak, and K and K. All were marketed as ≃ 97% purity and were used as received. All other chemicals used in this research were reagent grade, and no attempt was made to purify them further.

Standardization Procedures

Solutions of sodium hypochlorite and monochloramine were standardized by thiosulfate titration. Two grams of potassium

iodide and 5 ml of glacial acetic acid were added to an aliquot of the solution to be analyzed. The sample was immediately titrated to a starch end point with ≃ 0.1 N sodium thiosulfate, which had been previously standardized against primary standard grade potassium iodate.

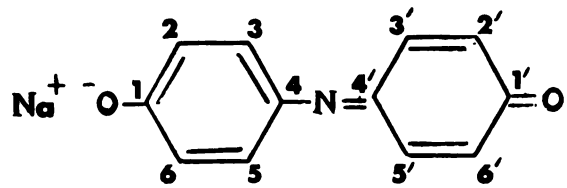
Phosphate and borax buffers in the pH range of 4.0 to 12.5 were prepared as described in the "Handbook of Chemistry and Physics" (46). These were referenced relative to commercial standard buffers of pH 4.00, 7.00, and 10.00.

Data Analysis

General calculations, including standard deviation and linear regression analysis, were performed on an SR-51 calculator (Texas Instruments). Control of the stopped-flow spectrophotometer, data acquisition, and formating was performed by a PDP/8e minicomputer (Digital Equipment Corporation). Data from kinetics runs were analyzed with the aid of KINFIT, a generalized curve-fitting routine developed by Dye and Nicely (13).

IV. SYNTHESIS

Many of the compounds and reagents used in this research were not commercially available. The details of their preparation are included in this chapter. The first section covers the synthesis of symmetric indophenols, where the word symmetric implies that the identity and position of substituents are identical on both rings of the indophenol. The numbering system used for naming indophenols is shown below. The second section covers the synthesis of sodium



hypochlorite, monochloramine, and sodium aquopentacyanoferrate, which are participants in the Berthelot reaction.

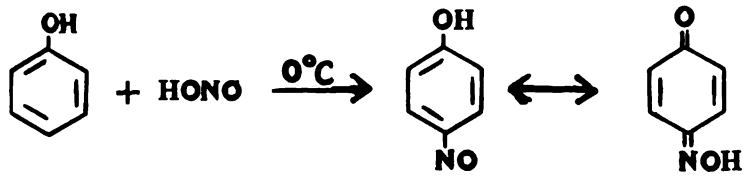
All yields reported for compounds synthesized were calculated on the basis of total dry weight of the crude product recovered. Generally, only a small portion of the crude product was recrystallized or sublimed for melting point and spectra determination, while the rest was used as recovered for succeeding syntheses. Any significant details for a particular synthesis not included in the general

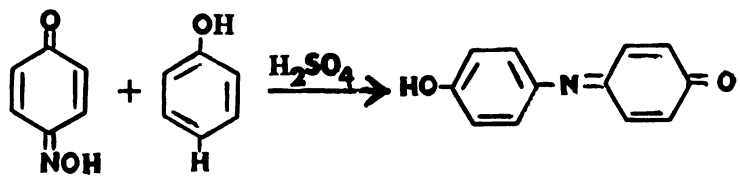
procedures for each class of compounds can be found at the end of each section.

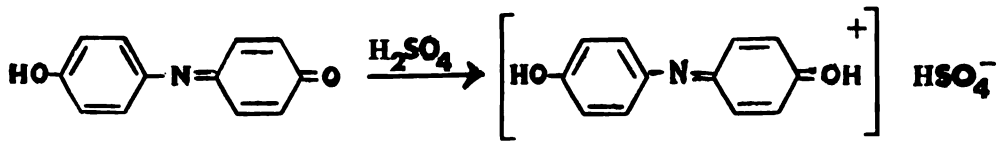
Preparation of Indophenol and Related Compounds

Since the end product of the Berthelot reaction is generally assumed to be an indophenol dye, a series of these compounds was synthesized. Two pathways for indophenol synthesis were investigated: the Liebermann nitroso reaction and the procedure outlined by Gibbs, et. al.

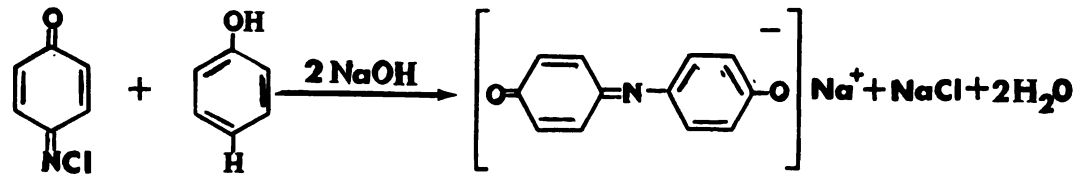
In the Liebermann nitroso reaction, a phenol is reacted with nitrous acid in the cold to produce the nitrosophenol. In the presence of excess phenol and strong mineral acid, the nitrosophenol and phenol couple to form the acid sulfate of indophenol, as shown below. Dilution with cold water precipitates the free indophenol.







In the Gibbs procedure, a phenol is reacted with a quinone-N-chloroimine in basic media to form an indophenol as the sodium salt.



Since the sodium salts of indophenols were found to be much more stable than the free indophenols from the Liebermann nitroso reaction, the Gibbs procedure proved to be the most satisfactory method for indophenol synthesis.

In general, the 4-aminophenols necessary as starting material for indophenol synthesis were not available, and so a series of commercially available substituted phenols were 4-nitrosated and then reduced to the desired 4-amino compounds. Nitration of phenols and subsequent reduction to the amine proved less satisfactory for two reasons. First, nitration gives several products which must be separated, while nitrosation yields the 4-substituted products almost exclusively. Second, the nitrosophenols are reduced under much milder conditions than the corresponding nitrophenols.

Synthesis of 4-nitroso alkylphenols

For synthesis of 4-nitroso alkylphenols, 0.20 mole of the alkylphenol was added to a 400 ml beaker containing 50 ml of ethanol and 50 ml of concentrated hydrochloric acid. An off-white slurry

formed after the reaction mixture was cooled to -2°C in a salt-ice bath. Next, 0.25 mole of pulverized sodium nitrite was added gradually while the reaction mixture was hand stirred with a glass rod. After about half of the sodium nitrite was added, the reaction mixture thickened considerably and a yellow-green sheen was observed on the sides of the reaction vessel. Fifteen minutes after the addition of sodium nitrite was complete, the reaction mixture was poured into a 1 ℓ beaker containing 700 ml of ice cold water. A copious, fluffy precipitate developed, which was suction filtered and washed well with cold water.

Synthesis of 4-nitroso chlorophenols

A 500 ml beaker containing a solution of 0.03 mole of the chlorophenol, 2 g of sodium hydroxide, and 10 g of sodium nitrite in 300 ml of water was cooled to 15°C in an ice bath. Next, 25 ml of 33% v/v sulfuric acid, cooled to 4°C, were added gradually. When the addition of sulfuric acid was complete, the reaction mixture was transferred to a refrigerator. After two hours, a large mass of burnt-orange needles had formed, which were filtered and washed with a little ice cold water. The mother liquor was returned to the refrigerator, and after eight hours, a second crop of needles was recovered.

2-methyl-4-nitrosophenol

The reaction of 22.0 g (0.20 mole) of 2-methylphenol gave 22.0 g (80.2%) of the crude nitroso-phenol. Recrystallization from water gave white needles, MP = 134-135°C-d [lit (12): 134-135°C-d].

2,6-dimethyl-4-nitrosophenol

The reaction of 24.5 g (0.20 mole) of 2,6-dimethylphenol gave 18.7 g (61.8%) of the crude nitrosophenol. Recrystallization from benzene gave gold plates, MP = 171-173°C-d [lit (44): 171°C-d].

3,5-dimethyl-4-nitrosophenol

The reaction of 10.0 g (0.08 mole) of 3,5-dimethylphenol gave 6.5 g (53.7%) of the crude nitrosophenol. Recrystallization from benzene gave yellow plates, MP = 184-185°C-d [lit (28): 185-186°C-d].

3-methyl-6-isopropyl-4-nitrosophenol

The reaction of 10.0 g (0.07 mole) of 3-methyl-6-isopropylphenol gave 8.6 g (68.6%) of the crude nitrosophenol. Recrystallization from benzene gave white needles, MP = 162-163°C-d [lit (12): 160-164°C-d].

2,3,5,6-tetramethyl-4-nitrosophenol

The reaction of 30.0 g (0.20 mole) 2,3,5,6-tetramethylphenol gave 27.2 g (75.9%) of the nitrosophenol. Recrystallization from 50% ethanol gave yellow needles, MP = 88-89°C-d [lit (40): 89°C-d].

2-chloro-4-nitrosophenol

The reaction of 4.0 g (0.03 mole) of 2-chlorophenol gave 2.5 g (52.9%) of the nitrosophenol. Recrystallization from 50% ethanol gave burnt-orange needles, MP = 147°C-d [lit (16): 148°C-d].

2,6-dichloro-4-nitrosophenol

The reaction of 4.0 g (0.02 mole) of 2,6-dichlorophenol gave 2.7 g (57.4%) of the crude nitrosophenol. Recrystallization from benzene gave orange needles, MP = 162-164°C-d [lit (8): 160-164°C-d].

Synthesis of 5-nitroso-N-methylanthranilic acid

N-methylanthranilic acid (0.07 mole) was dissolved in 75 ml of concentrated hydrochloric acid. The solution was cooled to 0°C in a salt-ice bath, and 5 g of sodium nitrite were added gradually. The reaction mixture was transferred to a refrigerator, and after twelve hours the hydrochloride of 5-nitroso-N-methalanthranilic acid had separated as a bright gold precipitate, which was filtered and washed successively with 5 ml of cold ethanol and 40 ml of ether. The hydrochloride was transformed into the free base by trituration with 0.05 mole of sodium bicarbonate and 300 ml of water. The blue-green precipitate which formed was filtered and dried. The yield was 9.5 g (75.4%). The crude product was recrystallized from 50% ethanol to give emerald green crystals, MP = 191-192°C-d [lit (20): 191°C-d].

Synthesis of 2-hydroxy-5-nitrosobenzoic acid

Crude 5-nitroso-N-methylanthranilac acid (0.025 mole) was added to 25 ml ice cold 10 N sodium hydroxide. To this 150 ml of ice cold water were then added slowly. The temperature of the reaction mixture was always less than 5°C. After twelve hours in a refrigerator at 0°C, the reaction mixture had a deep redish-blue color. The

temperature was maintained at 0°C in a salt-ice bath, and ice cold concentrated sulfuric acid was added drop-wise until a pH of 1 was obtained. The blue-green precipitate which formed was filtered, washed with several small portions of ice cold water, and dried in a vacuum desiccator. The yield was 4.1 g (98.1%). The crude product was recrystallized from benzene to give blue-green needles, MP = 161-162°C-d [lit (20): 162-163°C-d].

Synthesis of substituted 4-aminophenols

The 4-nitrosophenol (0.1 mole) was dissolved in 250 ml of ammonium hydroxide solution prepared from 160 ml of water and 90 ml of concentrated ammonium hydroxide. The deep yellow-brown solution was suction filtered and transferred to a 400 ml beaker. Next, tank hydrogen sulfide diffused through a sintered glass frit was vigorously passed through the solution. After five minutes, the reaction mixture turned clear orange and a precipitate began to form. After twenty minutes, the precipitate was copious and the hydrogen sulfide was turned off. The reaction mixture was cooled to 0°C and filtered.

2-methyl-4-aminophenol

The reaction of 10 g (0.07 mole) of crude 2-methyl-4-nitrosophenol gave 6.4 g (71.3%) of the amine. Recrystallization from benzene gave white plates, MP = 174-176°C [lit (12): 175°C].

2,6-dimethyl-4-aminophenol

The reaction of 5 g (0.03 mole) of recrystallized 2,6-dimethyl-4-nitrosophenol gave 3 g (66.3%) of the amine.

Recrystallization from benzene gave tan needles, MP = 138°C-d [lit (44): 137-138°C-d].

3,5-dimethyl-4-aminophenol

The reaction of 6 g (0.04 mole) of crude 3,5-dimethyl-4-nitrosophenol gave 5 g (91.1%) of the amine. Recrystallization from benzene gave white plates, MP = 182-183°C-d [lit (44): 181.8-183°C-d].

3-methyl-6-isopropyl-4-aminophenol

The reaction of 9 g (0.05 mole) of crude 3-methyl-6-isopropyl-4-nitrosophenol gave 8 g (96.8%) of the amine. Recrystallization from benzene gave white needles, MP = 178-179°C [lit (12): 178-179°C].

2,3,5,6-tetramethyl-4-aminophenol

The reaction of 6 g (0.03 mole) of crude 2,3,5,6-tetramethyl-4-nitrosophenol gave 4.7 g (86.2%) of the amine. Sublimation gave a white powder, MP = 179°C-d [lit (38): 177-178.5°C-d].

2-chloro-4-aminophenol

The reaction of 5.1 g (0.03 mole) of crude 2-chloro-4-nitrosophenol gave 2.9 g (67.3%) of the amine. Recrystallization from benzene gave white needles, MP = 151°C-d [lit (12): 153°C-d].

2,6-dichloro-4-aminophenol

The reaction of 2.4 g (0.01 mole) of crude 2,6-dichloro-4-nitrosophenol gave 1.6 g (71.9%) of the amine. Recrystallization

from benzene gave tan needles, MP = 168-170°C-d [lit (12): 165-166°C-d].

2-hydroxy-5-amino benzoic acid

When 2.3 g (0.02 mole) of 2-hydroxy-5-nitroso benzoic acid was reacted, no product was isolated.

Synthesis of quinone-N-chloroimines

The aminophenol to be reacted was dissolved in 100 ml of 5% v/v hydrochloric acid (≃ 0.6 N) and cooled to)°C. This solution was then added gradually to a three- to five-fold excess of sodium hypochlorite solution also cooled to 0°C and containing a few pieces of crushed ice. A bright yellow to orange precipitate formed immediately. After five minutes, this precipitate was filtered, washed with cold water, and dried in a vacuum desiccator.

Quinone-N-chloroimine

The reaction of 5.5 g (0.05 mole) of commercial 4-aminophenol gave 5.7 g (81.4%) of the N-chloroimine. Recrystallization from ether gave yellow needles, MP = 87-89°C-d [lit (45): 88°C-d].

2-methylquinone-N-chloroimine

The reaction of 1.2 g (0.01 mole) of 2-methyl-4-aminophenol gave 1.4 g (90%) of the N-chloroimine. Recrystallization from ether gave yellow needles, MP = 99-100°C-d [lit: no data].

2,6-dimethylquinone-N-chloroimine

The reaction of 2.4 g (0.2 mole) of 2,6-dimethyl-4-aminophenol gave 2.1 g (61.9%) of the N-chloroimine. Recrystallization from benzene gave bright yellow needles, MP = 69.5-71°C-d [lit: no data].

3,5-dimethylquinone-N-chloroimine

The reaction of 4.6 g (0.03 mole) of 3,5-dimethyl-4-aminophenol gave 3.9 g (69.7%) of the N-chloroimine. Recrystallization from ether gave yellow needles, MP = 175-177°C-d [lit: no data].

3-methyl-6-isopropylquinone-N-chloroimine

The reaction of 5.0 g (0.03 mole) of 3-methyl-6-isopropyl-4-aminophenol gave a bright orange oil. Repeated attempts to crystallize the product failed.

2,3,5,6-tetramethylquinone-N-chloroimine

The reaction of 1 g (0.06 mole) of 2,3,5,6-tetramethyl-4-aminophenol gave 0.7 g (59.0%) of the N-chloroimine. The product appeared dirty and no suitable recrystallization solvent was found, MP = 77-80°C-d [lit: no data].

2-chloroquinone-N-chloroimine

The reaction of 5.5 g (0.04 mole) of 2-chloro-4-aminophenol gave 3.5 g (52.3%) of the N-chloroimine. Recrystallization from ether gave orange needles, MP = 85-86°C-d [lit (24): 86-87°C-d].

2,6-dichloroquinone-N-chloroimine

The reaction of 8 g (0.04 mole) of commercial 2,6-dichloro-4-aminophenol gave 3.3 g (35.2%) of the N-chloroimine. Recrystallization from ether gave gold needles, MP = 64-45°C-d [lit (25): 66-67°C-d].

Synthesis of indophenols

A 100 ml beaker containing 30 ml of water and a few pieces of ice was cooled to 0°C in a salt-ice bath. Next equimolar quantities of phenol and quinone-N-chloroimine were added. Then enough 3 N sodium hydroxide to provide a 2:1 molar ratio plus 10% was added slowly while the temperature of the reaction mixture was maintained at 0°C. The reaction mixture immediately darkened and passed through several shades of green before finally attaining a deep blue color. The calculated amount of sodium chloride necessary to give a near saturated solution was added, and the reaction mixture was transferred to a refrigerator. After approximately four hours, the irradescent sodium salt of the indophenol had precipitated. The precipitate was suction filtered and dried in a vacuum desiccator over calcium chloride.

Indophenol, sodium salt

The reaction of 4.7 g (0.05 mole) of phenol, 7.1 g (0.05 mole) of quinone-N-chloroimine, and 38 ml of 3 N sodium hydroxide solution gave 12.2 g (109.4%) of the crude indophenol salt.

2,2'-dimethylindophenol, sodium salt

The reaction of 1.0 g (0.009 mole) of 2-methylphenol, 1.4 g (0.009 mole) of 2-methylquinone-N-chlorimine, and 7 ml of 3 N sodium hydroxide solution gave 3.5 g (156.1%) of the crude indophenol salt.

2,6,2',6'-tetramethylindophenol, sodium salt

The reaction of 1.4 g (0.012 mole) of 2,6-dimethylphenol, 2.0 g (0.012 mole) of 2,6-dimethylquinone-N-chloroimine, and 8 ml of 3 N sodium hydroxide solution gave 3.6 g (108.3%) of the crude indophenol salt.

3,3'-dimethyl-6,6'-diisopropylindophenol, sodium salt

The reaction of 0.8 g (0.005 mole) of thymol, 1.0 g (0.005 mole) of the orange oil thought to be 3-methyl-6-isopropylquinone-N-chloroimine, and 4 ml of 3 N sodium hydroxide solution gave a sticky, purple solid which could not be further purified.

3,5,3',5'-tetramethylindophenol, sodium salt

When 1.4 g (0.012 mole) of 3,5-dimethylphenol, 2.0 g (0.012 mole) of 3,5-dimethylquinone-N-chloroimine and 8 ml of 3 N sodium hydroxide were reacted, the charactersitic blue color did not develop and no product was recovered.

2,3,5,6,2',3',5',6'-octamethylindophenol

When 0.46 g (0.003 mole) of 2,3,5,6-tetramethylphenol, 0.60 g (0.003 mole) of the crude 2,3,5,6-tetramethylquinone-N-chloroimine and 2 ml of 3 N sodium hydroxide solution were reacted, the characteristic blue color did not develop and no product was recovered.

2,2'-dichloroindophenol, sodium salt

The reaction of 2.3 g (0.018 mole) of 2-chlorophenol, 3.2 g (0.018 mole) of 2-chloroquinone-N-chloroimine, and 13 ml of 3 N sodium hydroxide solution gave 6.1 g (116.8%) of the crude indophenol salt.

2,6,2',6'-tetrachloroindophenol, sodium salt

The reaction of 2.8 g (0.013 mole) of 2,6-dichloroquinone-N-chloroimine and 8.5 ml of 3 N sodium hydroxide solution gave 4.9 g (105.10%) of the crude indophenol salt.

Discussion

4-nitroso alkylphenols and 4-aminophenols were prepared by the Kremers and Wakeman procedure (31), and 4-nitroso chlorophenols by the Hodgson procedure (16). The synthesis of 5-nitroso-N-methylanthranilic acid and 2-hydroxy-5-nitrosobenzoic acid followed the procedure of Houben (20). Quinone-N-chloroimines and sodium salts of indophenols were prepared by the procedures of Gibbs, et. al. (14).

Generally, reduction of nitrosophenols to aminophenols with hydrogen sulfide proceded smoothly. It proved essential, however, to filter the ammoniacal nitrosophenol solutions prior to hydrogen sulfide reduction in order to obtain the aminophenols in high purity. Due to the insolubility of 2,3,5,6-tetramethyl-4-nitrosophenol in water, it was necessary to dilute the concentrated ammonium hydroxide with ethanol rather than with water. After this reaction was

complete, addition of 50 ml of water enhanced the precipitation of the aminophenol.

The oxidation of aminophenols to quinone-N-chloroimines also proceded smoothly. Precooling both the hypochlorite and acidic aminophenol solutions to 0°C and maintaining that temperature in the reaction mixture was essential. The fact that some of the aminophenols were not completely soluble in 5% v/v hydrochloric acid solution did not seem to hinder their complete reaction. For all 4-amino alkylphenols reacted, a commercial sodium hypochlorite solution, Chlorox^{R}, was a satisfactory reagent. For 4-amino chlorophenols, however, Rashig's hypochlorite, prepared as described in the next section, was a better reagent.

The difficulty in synthesizing symmetrical indophenols arose in their separation and purification. In all cases, sodium chloride had to be added to "salt out" the product, and invariably the sodium salts of indophenols thus obtained were contaminated with sodium chloride. This accounts for the greater than 100% yields reported for the indophenols synthesized. Two purification procedures were investigated. In one procedure, the crude product was dissolved in water and resalted with about half the calculated amount of sodium chloride necessary to give a saturated solution. This procedure was fairly efficient, but of course some sodium chloride was still a contaminant. In a second procedure, the crude product was dissolved in a small amount of anhydrous methanol and filtered to remove any insoluble material, including sodium chloride. A

fifteen-fold volume of ether was then added to reprecipitate the indophenol. This procedure was not satisfactory, however, because in many cases decomposition of the indophenol occurred in non-aqueous solutions. No truly satisfactory method for isolating high purity sodium salts of indophenols was devised. In the only published values for the visible spectra of indophenols as their sodium salts, the indophenols were prepared in solution by the reduction of a 4-aminophenol with ferricyanide to the quinone monoimine, which then coupled with phenol in basic media to form the indophenol salt. Indophenols prepared in this research have absorption maxima in good agreement with the published values, but their molar absorptivities are 10-15% lower. This difference may well be accounted for by contamination of the indophenols with sodium chloride.

It was observed that when both the quinone-N-chloroimine and phenol were 3,5-disubstituted, no indophenol was produced. Both 3,5-dimethyl and 2,3,5,6-tetramethylquinone-N-chloroimines produced the blue color charactersitic of indophenols when added to alkaline phenol, so steric hinderance, rather than a lack of reactivity, was assumed to inhibit the formation of these symmetric indophenols.

Preparation of Other Materials

Synthesis of sodium hypochlorite

Sixty-three grams of sodium hydroxide were dissolved in 100 ml of water, cooled, and poured onto enough crushed ice to give a total weight of 1 kg. Next, tank chlorine diffused through a

glass frit was bubbled through the solution until the weight had increased by 75 g. The resulting solution was pale yellow and still contained a large amount of ice.

Synthesis of monochloramine

Twenty grams of ice, 70 ml of Chlorox^{R} (≃ 0.7 M NaOCl) and 100 ml of ether were combined in a 500 ml separatory funnel. After about ten minutes, the contents of the separatory funnel had cooled to 2°C, and 7.5 ml of concentrated (≃ 7.4 M) ammonium hydroxide were added. The reaction mixture was gently shaken, after which the aqueous phase was discarded. Then 100 ml of ice cold distilled water were added. After gentle shaking, the aqueous phase was transferred to a brown bottle and refrigerated.

Synthesis of sodium aquopentacyanoferrate

Solutions containing 20 g of sodium nitroferricyanide in 60 ml of distilled water, 8 g of sodium hydroxide in 20 ml of distilled water, and 7 g of hydroxylamine hydrochloride in 20 ml distilled water were prepared individually and cooled to -2°C in a salt-ice bath. The sodium hydroxide solution was added to the sodium nitroprusside solution, and then the hydroxylamine solution was added drop-wise. The reaction mixture turned brownish-green and gas was evolved. At no time did the temperature of the reaction mixture rise above 0°C. After one hour, 300 ml of ice cold ethanol was added, and the aquoferrate precipitated as a brown resinous mass. The liquid was decanted, and the solid was redissolved in about 60

ml of ice cold distilled water. The aquoferrate was again precipitated by the addition of 200 ml of ice cold methanol and suction filtered through a medium glass frit. After several more dissolutions with distilled water and reprecipitations with methanol, the aquoferrate was filtered, washed with a little ether, and transferred to a vacuum desiccator over concentrated sulfuric acid. The dry product was a gold powder.

Discussion

Sodium hypochlorite was prepared by the procedure of Raschig (32). The procedure was straightforward but required a rather cumbersome, large-capacity, double-pan balance to monitor the weight changes in the reaction mixture. When used for qunione-N-chloroimine synthesis, this reagent was prepared just prior to its use and still contained some crushed ice.

Monochloramine was prepared by the procedure of Kleinberg, et. al. (21). The concentration of each batch, as determined by thiosulfate titration, varied slightly but was usually about 0.06 M. Due to the instability of this solution, it had to be prepared freshly every few days.

Sodium aquopentacyanoferrate was prepared by the procedure of Hofmann (17) as modified by Asperger, et. al. (1). The temperature had to be maintained at or below 0°C throughout the synthesis and for the first few recrystallizations to prevent the formation of iron oxides. Due to the resinous nature of the product in preliminary precipitations, decantation, rather than filtration, for the removal of the supernatant liquid was more expedient.

V. NON-KINETICS EXPERIMENTS

UV Spectrum of Hypochlorous Acid

The ultraviolet absorption spectrum of hypochlorous acid as a function of pH is shown in Figure 1. Free hypochlorous acid is characterized by a single band at 233 nm with a molar absorptivity of 134 ℓ mole^{-1}cm^{-1}. Hypochlorite ions display a broad band with maximum absorption at 293 nm and a molar absorptivity (above pH 11) of 358 ℓ mole^{-1}cm^{-1}. Under conditions of constant pH, solutions of hypochlorite ions obey Beer's Law in the concentration range of 10^{-5} to 10^{-3} molar. The ultraviolet absorption spectrum of sodium hypochlorite buffered at pH 11.5 is shown in Figure 2.

UV Spectrum of Monochloramine

Solutions of monochloramine display a broad absorption band between 200 and 300 nm with λ_{max} at 243 nm and a molar absorptivity of 460 ℓ mole^{-1}cm^{-1}. Dilute solutions of monochloramine decompose slowly but are relatively stable in the pH range of 7.5 to 11.5. The ultraviolet absorption spectrum of monochloramine buffered at pH 10.0 is shown in Figure 3.

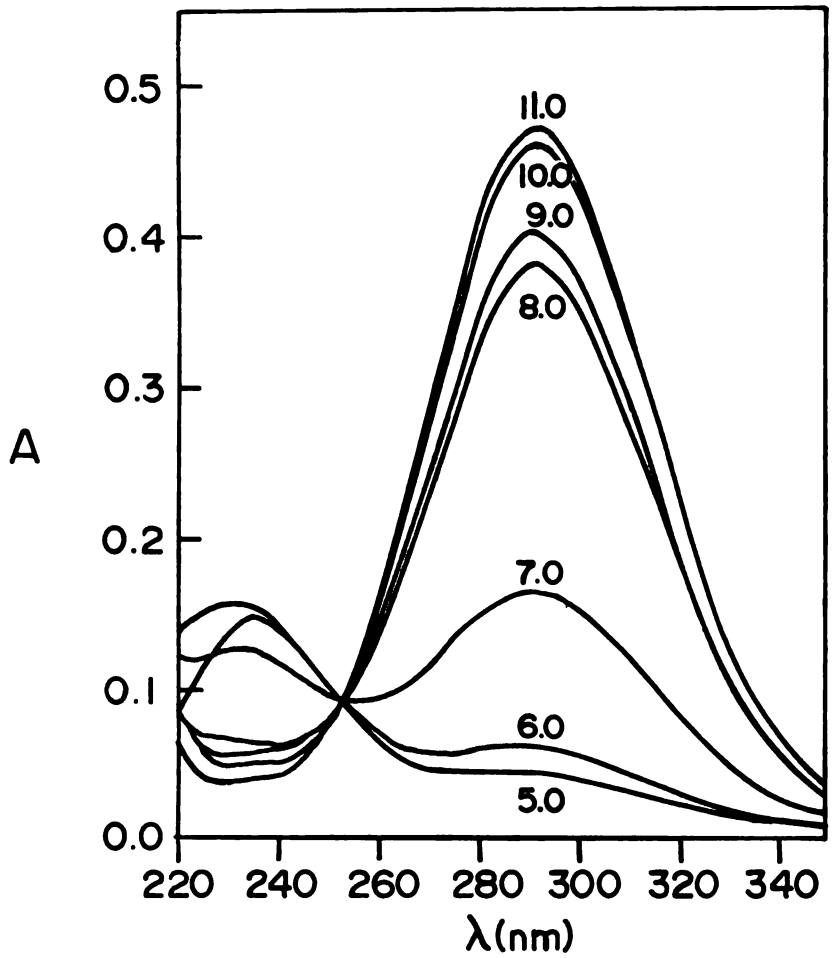


Figure 1: UV Spectrum of Hypochlorous Acid as a Function of pH.

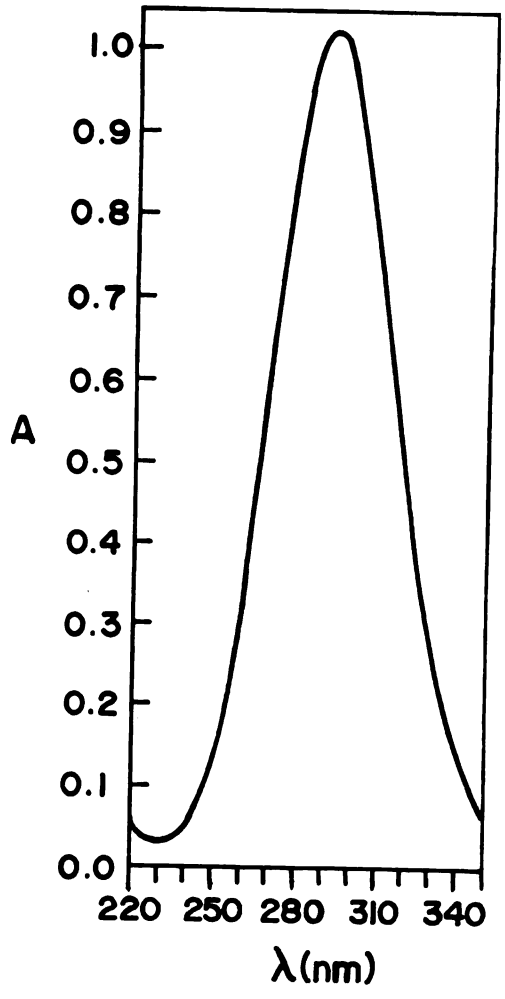


Figure 2: UV Spectrum of Hypochlorite Ions

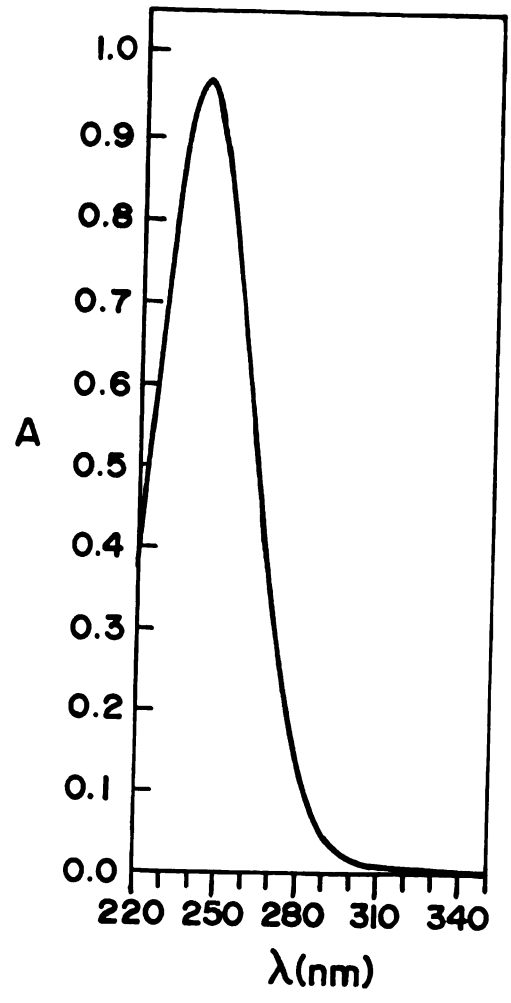


Figure 3: UV Spectrum of Monochloramine

Visible Spectra of Pentacyano Iron Complexes

The absorption maxima of the pentacyano iron complexes used in this research are listed in Table 1. When monochloramine is added to aqueous solutions of any of these complexes, a rapid shift in the wavelength of maximum absorption to 392 nm occurs. An identical shift occurs when hypochlorous acid is added to any of these complexes. Literature values for λ_{max} and log ε_{max} are shown in parentheses.

TABLE 1

Absorption Maxima and Molar Absorptivities of Some Pentacyano Iron Complexes

Compound	λ_{max}(nm)	log ε_{max}
$Na_2[Fe(CN)_5NO]$	398 (398)	1.30 (1.31)
$Na_4[Fe(CN)_5NO_2]$	398 (398)	2.92 (2.99)
$Na_3[Fe(CN)_5H_2O]$	415 (428)	2.29 (2.40)

Visible Spectra of Indophenols

The visible absorption spectrum of 2,6,2',6'-tetramethylindophenol as a function of pH is shown in Figure 4 and

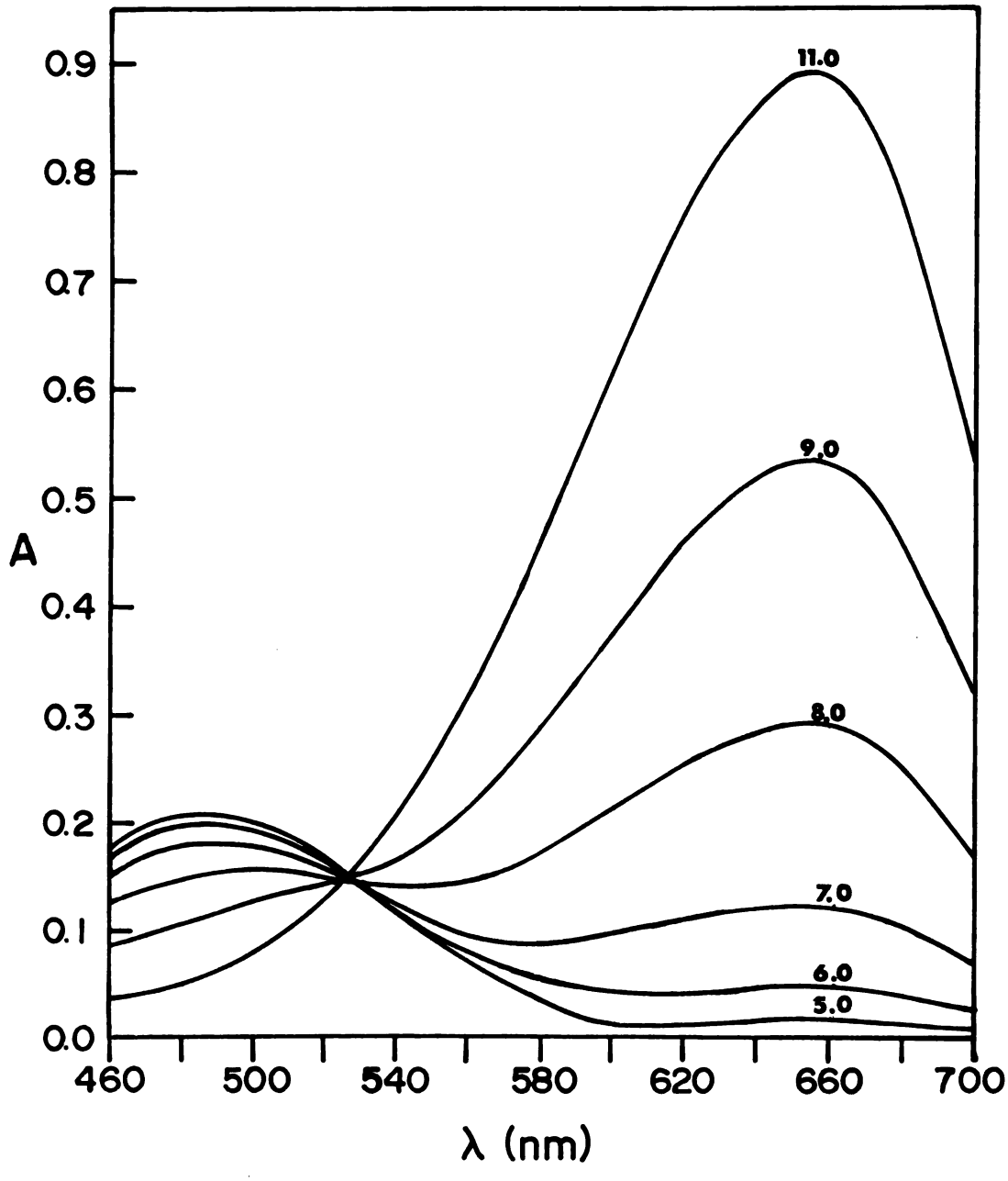


Figure 4: Visible Spectrum of 2,6,2',6'-tetramethylindophenol as a Function of pH.

is typical of indophenols. The free indophenol which predominates in acidic solutions is characterized by a broad band between 400 and 500 nm, while the indophenolate ion, which predominates in basic solutions, displays a more intense band between 600 and 700 nm. The wavelengths of maximum absorption and the molar absorptivities of indophenols synthesized in this research are listed in Table 2 along with the literature values, which are shown in parentheses. Values of λ_{max} agree quite favorably with the literature, and the approximately 10% lower values for ε_{max} are attributable to sodium chloride impurities, as discussed in Chapter IV.

TABLE 2

Absorption Maxima and Molar Absorptivities of

Some Indophenols and Their Sodium Salts

Substituents	Indophenol		Indophenolate	
	λ_{max}	log ε_{max}	λ_{max}	log ε_{max}
none	495 (496)	3.40 (3.83)	635 (637)	3.95 (4.50)
2,2'-dimethyl	495 (495)	3.64 (3.97)	648 (648)	4.15 (4.52)
2,6,2',6'-tetramethyl	493 (494)	3.50 (3.82)	658 (662)	4.14 (4.47)
2,2'-dichloro	508 (no data)	3.04 (no data)	650 (662)	4.41 (4.47)
2,6,2',6'-tetrachloro	515 (no data)	3.15 (no data)	668 (no data)	4.02 (no data)

Formation of Indophenols in Aqueous Solution

When solutions of monochloramine, pentacyanoaquoferrate, and phenol buffered at pH 11.5 were mixed, the blue complex which formed displayed a visible absorption spectrum identical to that of indophenol. As the molar ratio of pentacyanoaquoferrate to monochloramine approached 1:1, the wavelength of maximum absorption remained constant while the absorbance approached a maximum. Molar ratios of pentacyanoaquoferrate to monochloramine exceeding 1:1, however, resulted in progressively increasing hypsochromic shifts in the wavelengths of maximum absorption which approached 700 nm. The same trends were observed when phenol in the reaction mixture was replaced with methyl- or chloro-substituted phenols. The data from this experiment are presented in Table 3. A similar experiment was performed in which ammonia and a five-fold molar excess of sodium hypochlorite was used in place of the monochloramine solution. Data from this experiment are presented in Table 4. Both data sets are in excellent agreement.

These data indicate that only one mole of pentacyanoaquoferrate is required for each mole of indophenol produced. Furthermore, pentacyanoaquoferrate in excess of this stoichiometric concentration reacts with indophenol or one of its intermediates to form an unidentified complex. This complex is not stable, however, and after several days its green color fades into blue, and the visible absorption spectrum again corresponds to that of indophenol. The fate

TABLE 3

Effect of Aquopentacyanoferrate Concentration on the End Product of the Berthelot Reaction

$[Fe(CN)_5H_2O]^{3-}$	$[H_2NCl]$	$\frac{[Fe(CN)_5H_2O]^{3-}}{[H_2NCl]}$	λ_{max}	A* at λ_{max}
1.05×10^{-5}	8.52×10^{-5}	1.23×10^{-1}	635	1.076
5.26×10^{-5}	8.52×10^{-5}	6.17×10^{-1}	635	1.680
1.05×10^{-4}	8.52×10^{-5}	1.23	641	1.520
5.26×10^{-4}	8.52×10^{-5}	6.17	688	1.348
1.05×10^{-3}	3.52×10^{-5}	1.23×10^{1}	700	1.426

*1 cm cells

TABLE 4

Effect of Aquopentacyanoferrate Concentration on the End Product of the Berthelot Reaction in the Presence of Hypochlorite Ions

$[Fe(CN)_5H_2O]^{3-}$	$[NH_3]$	$[^-OCl]$	$\frac{[Fe(CN)_5H_2O]^{3-}}{[H_2NCl]^*}$	λ_{max}	A^+ at λ_{max}
1.05×10^{-5}	2.47×10^{-4}	1.49×10^{-3}	4.25×10^{-2}	633	1.596
5.26×10^{-5}	2.47×10^{-4}	1.49×10^{-3}	2.13×10^{-1}	635	3.266
1.05×10^{-4}	2.47×10^{-4}	1.49×10^{-3}	4.25×10^{-3}	635	3.560
5.26×10^{-4}	2.47×10^{-4}	1.49×10^{-3}	2.13	675	2.614
1.05×10^{-3}	2.47×10^{-4}	1.49×10^{-3}	4.25	695	2.926

*Total conversion of ammonia in solution to monochloramine is assumed.

+1 cm cells

of pentacyanoaquoferrate in this process was not investigated. It should be noted, however, that when solutions containing synthetic indophenol and a large excess of pentacyanoaquoferrate were mixed, no shift in wavelength was observed.

Identity of the "Catalyst" for the Berthelot Reaction

Methods of ammonia analysis in which sodium nitropentacyanoferrate (nitroprusside) or sodium nitritopentacyanoferrate is used to catalyze the Berthelot reaction often produce colors with a greenish tint, rather than the clear blues characteristic of indophenols. No clear-cut correlation for the stoichiometric amounts of these compounds necessary to produce the hypsochromic shift observed for sodium aquopentacyanoferrate could be made, but in general, 100 to 150 times as much was required. This led to the hypothesis that sodium nitropentacyanoferrate and sodium nitritopentacyanoferrate were in equilibrium with sodium aquopentacyanoferrate. This hypothesis was confirmed by the work of Swinehart and Rock (41), who reported rapid conversion of the nitro complex to the nitrito complex in alkaline solutions. After this initial reaction (I), they observed that a second equilibrium (II) was established between the

$$[Fe(CN)_5NO]^{2-} + 2OH^- \rightleftharpoons [Fe(CN)_5NO_2]^{4-} + H_2O, \quad K_{eq} = 1.5 \times 10^6 \quad (I)$$

$$[Fe(CN)_5NO_2]^{4-} + H_2O \rightleftharpoons [Fe(CN)_5H_2O]^{3-} + NO_2^-, \quad K_{eq} = 3 \times 10^{-4} \quad (II)$$

nitrito and the aquo complexes. These observations compled with the simple 1:1 stoichiometry observed between monochloramine and sodium aquopentacyanoferrate in indophenol formation support the hypothesis that the aquo complex is the actual catalyst for indophenol formation in the Berthelot reaction.

VI. KINETICS EXPERIMENTS

Formation of Monochloramine

The rate of formation of monochloramine as a function of pH were obtained by mixing buffered, equimolar aqueous solutions of ammonium chloride and sodium hypochlorite in the stopped-flow spectrophotometer and recording the change in absorbance with time at either 243 nm or 292 nm, which are the wavelengths of maximum absorption for monochloramine and hypochlorite ions, respectively. At both wavelengths, the reaction was found to be second-order overall and first-order each in hypochlorous acid and ammonia. The maximum observed rate constant occurred at pH 8.0. The magnitude of the observed rate constants calculated from data collected at 243 nm was approximately twice as large as those calculated from data collected at 292 nm for pH $\leq$ 10.0. This is because the band for monochloramine at 243 nm is overlapped by the hypochlorous acid band at 233 nm, the dichloramine band at 230 nm, and the tailing edge of the hypochlorite ion band, while the hypochlorite ion band at 292 nm is not overlapped by any other species present in the reaction mixture. For this reason, the data collected at 292 nm should give the best estimate for observed rate constants. Data for the formation of monochloramine when the molar ratio of ammonia to hypochlorous acid was 1:5 and 1:10 were also collected at 292 nm over the same pH

range. Computer plots of data collected at pH 8.0 when solutions of ammonia and hypochlorous acid with molar ratios of 1:1, 1:5, and 1:10 were mixed in the stopped-flow spectrophotometer are presented in Figures 5, 6, and 7, respectively. On the plots, "x" represents experimental points, "o" represents points calculated from the data assuming general second-order kinetics, and "=" represents the overlap of experimental and calculated points. Each point plotted is the average of ten separate determinations. Values for the observed second-order rate constant agree within 10%. Data from these experiments are presented in Figure 8, where the log of the observed second-order rate constant is plotted against pH.

As indicated in Figure 8, the observed second-order rate constants for monochloramine formation are highly pH dependent. The fact that the maximum rate occurs at pH 8.0 indicates that the species involved in monochloramine formation are ammonia and hypochlorous acid rather than ammonium ions and hypochlorite ions. This is most easily visualized with the aid of a distribution diagram for ammonia, ammonium ions, hypochlorous acid, and hypochlorite ions as a function of pH, such as the one presented in Figure 9. As can be seen in Figure 9, pH 8.0 corresponds to the maximum concentrations of ammonia and hypochlorous acid relative to each other. If the reaction involved ammonium ions and hypochlorite ions, the maximum observed rate constant would occur at pH 9.5.

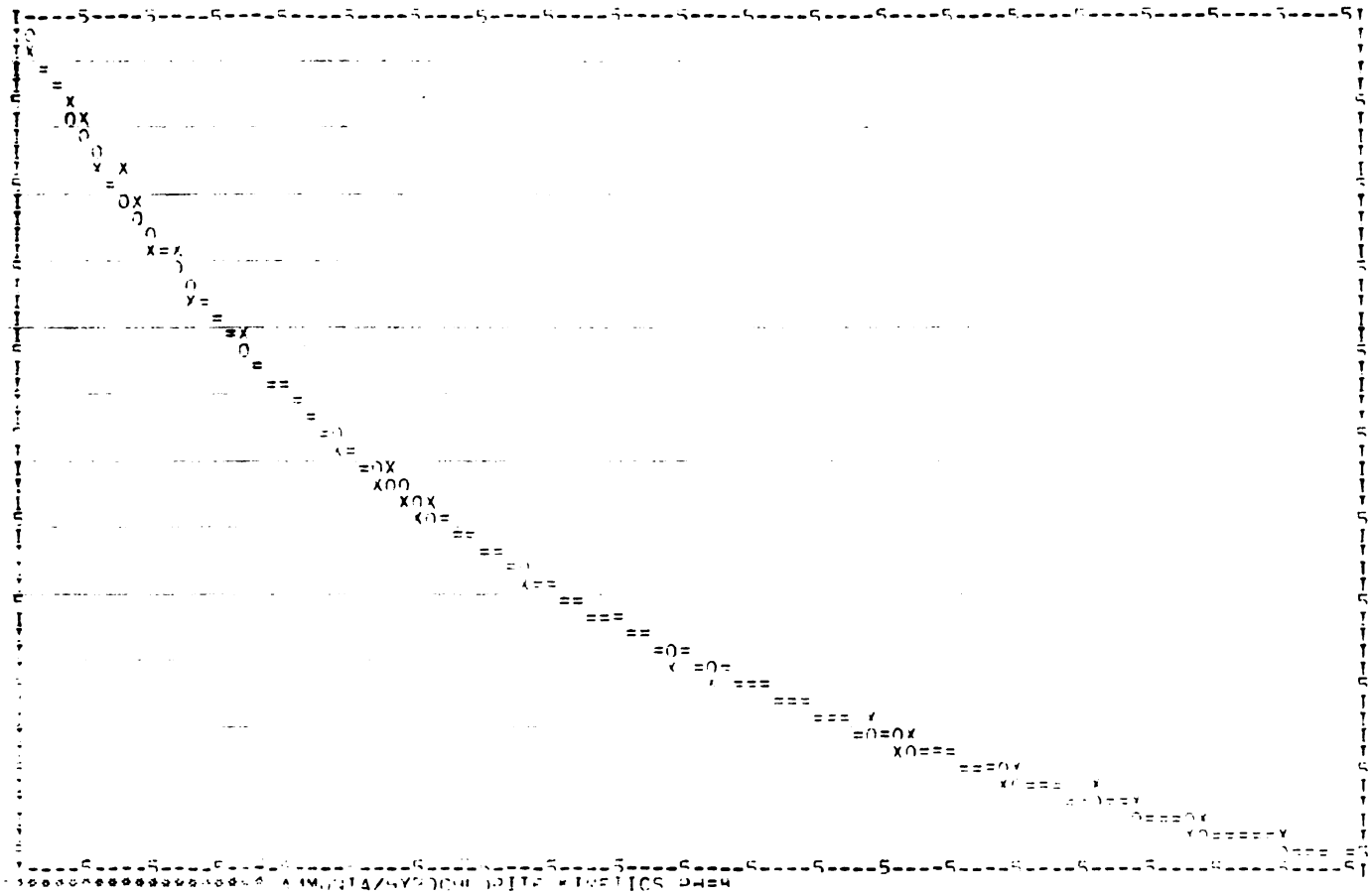


Figure 5: Formation of Monochloramine from Ammonia and Hypochlorous Acid in 1:1 Molar Ratio. pH = 8.0, λ = 292 nm. $[NH_3]_o$ = 1.49 x 10^{-4} F, and $[OCl^-]_o$ = 1.49 x 10^{-4} F. Horizontal axis is time (s). Value at left = 6.30 x 10^{-3}; value at right = 5.94 x 10^{-1}; increment = 5.94 x 10^{-3}. Vertical axis is absorbance at 292 nm. Value at top = 7.64 x 10^{-1}; value at bottom = 2.44 x 10^{-2}; increment = 1.06 x 10^{-3}.

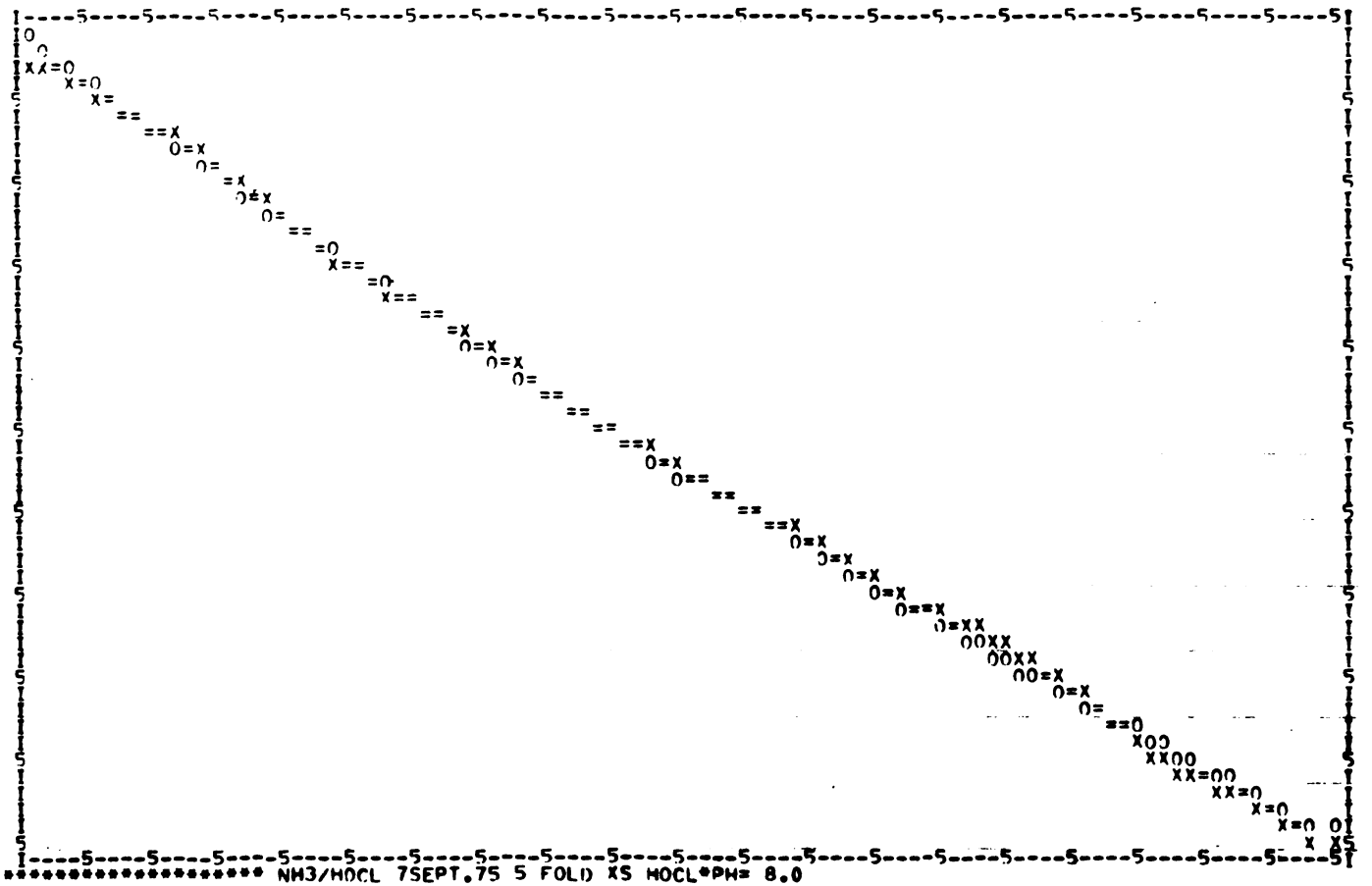


Figure 6: Formation of Monochloramine from Ammonia and Hypochlorous Acid in 1:5 Molar Ratio. pH = 8.0, λ = 292 nm, $[NH_3]_o$ = 1.49 x 10^{-4} F, and $[OCl^-]_o$ = 7.44 x 10^{-4} F. Horizontal axis is time (s). Value at left = 6.50 x 10^{-3}; value at right = 2.61 x 10^{-2}; increment = 1.98 x 10^{-4}. Vertical axis is absorbance at 292 nm. Value at top = 4.06 x 10^{-1}; value at bottom = 3.87 x 10^{-1}; increment = 4.04 x 10^{-4}.

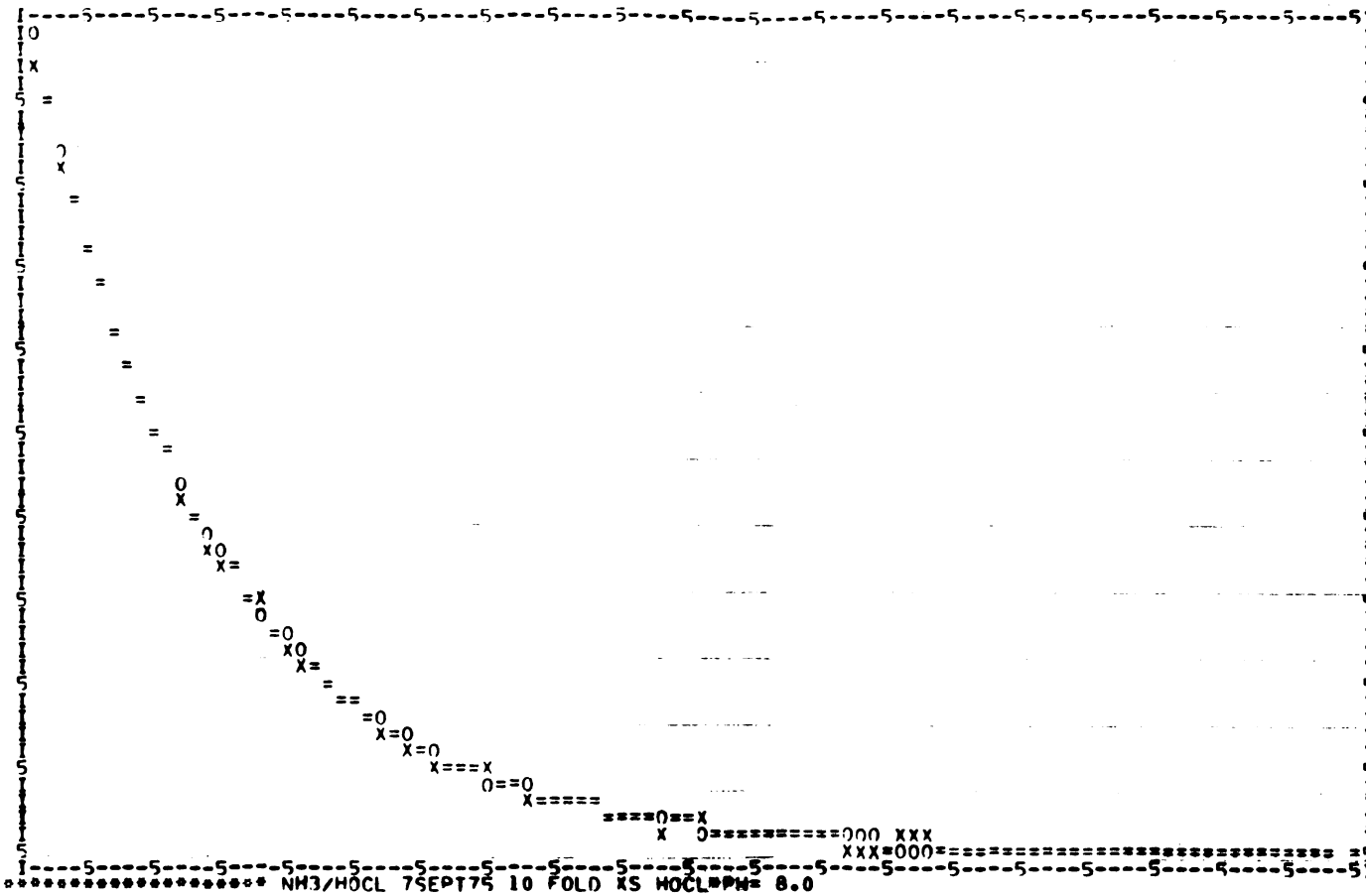


Figure 7: Formation of Monochloramine from Ammonia and Hypochlorous Acid in 1:10 Molar Ratio. pH = 8.0, λ = 292 nm, $[NH_3]_o$ = 1.49 x 10^{-4} F, and $[OCl^-]_o$ = 1.49 x 10^{-3} F. Horizontal axis is time (s). Value at left = 6.50 x 10^{-3}; value at right = 2.02 x 10^{-1}; increment = 1.98 x 10^{-3}. Vertical axis is absorbance at 292 nm. Value at top = 8.03 x 10^{-1}; value at bottom = 7.38 x 10^{-1}; increment = 1.32 x 10^{-3}.

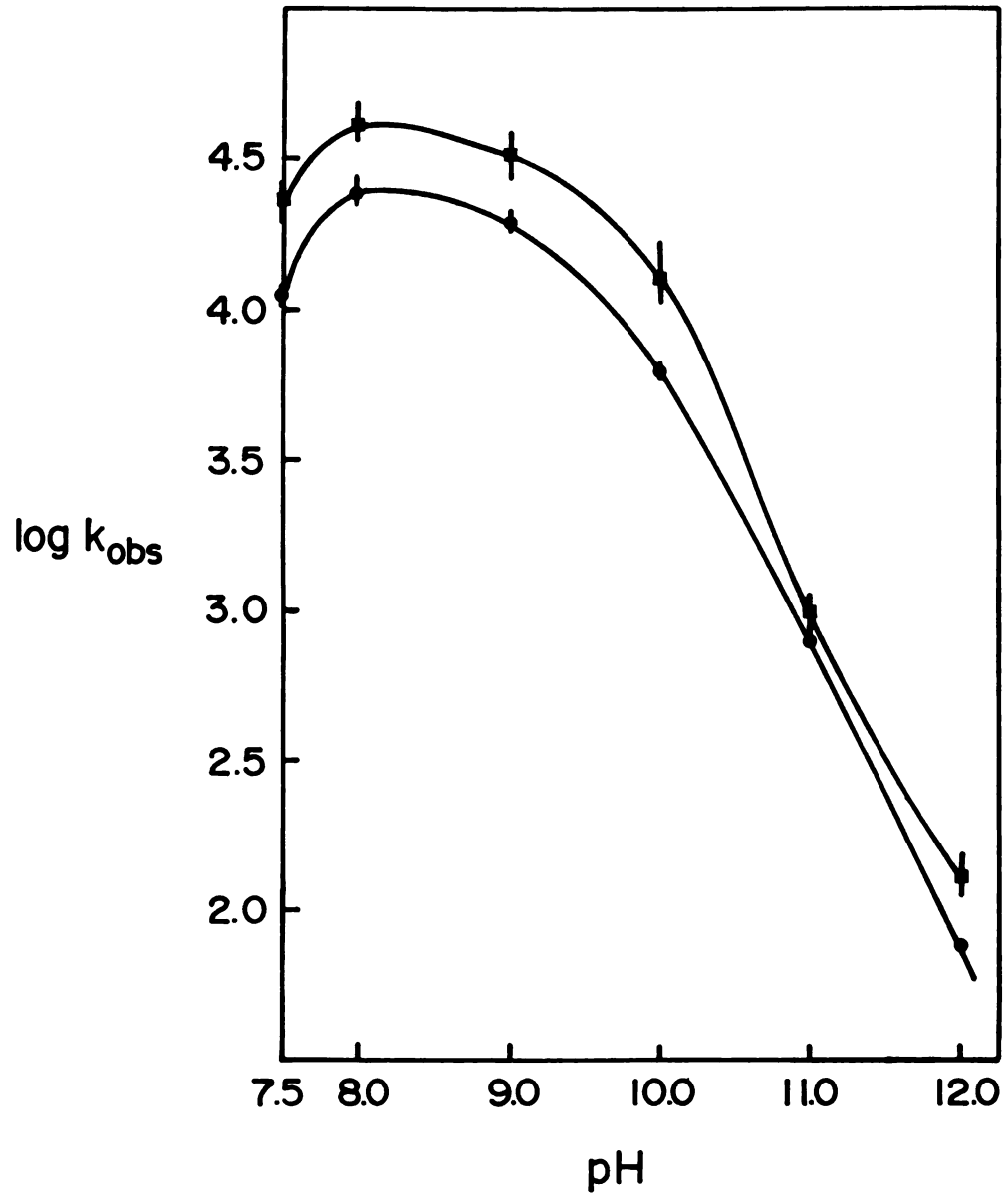


Figure 8: Log of observed Second-order Rate Constants for the Formation of Monochloramine versus pH at 292 nm (•) and 243 nm (■).

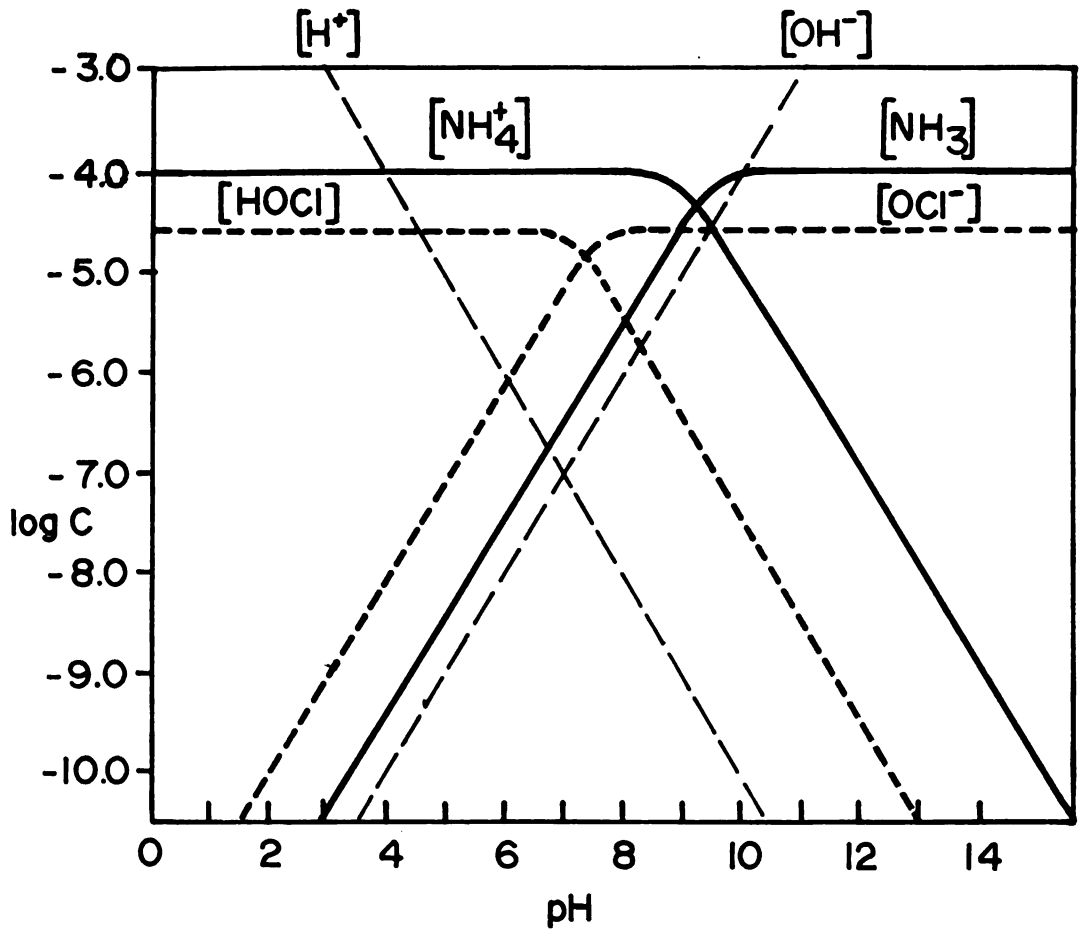


Figure 9: Distribution Diagrams for Hypochlorous Acid-Hypochlorite Ions and Ammonia-Ammonium Ions as a Function of pH.

Decomposition of Monochloramine

Monochloramine and hypochlorous acid are mutually unstable, as evidenced by the decrease in absorbance at 243 nm and 292 nm when their dilute aqueous solutions are mixed. The effect of pH on the stability of these species was determined by mixing 1.45×10^{-4} M monochloramine and 1.49×10^{-3} F hypochlorous acid, buffered at the same pH, in the stopped-flow spectrophotometer. The pH values chosen for these experiments were 8.5, 10.5, and 12.0. All experimental data presented are the average of four runs.

In the first set of experiments, the change in absorbance at 243 nm with time was recorded. A "blank" in which buffered hypochlorous acid was mixed with buffer containing no monochloramine was also performed at this wavelength so that the contribution of hypochlorous acid and hypochlorite ions to the absorbance could be subtracted. In the second set of experiments, the change in absorbance at 292 nm with time was recorded for identical solutions. No blank was necessary for these experiments since hypochlorite is the only species in solution which absorbs significantly at this wavelength.

Neither set of data could be fitted to overall second-order kinetics. Furthermore, the data could not be fitted to either second-order in monochloramine, or second-order in monochloramine and first-order in hypochlorous acid. This indicates that the decomposition of monochloramine is a multi-step process. Some possible pathways for monochloramine are outlined below. Reaction (I) is not expected to occur above pH 7.5 (7). Reactions (II) and (III),

$$H_2NCl + HOCl \longrightarrow HNCl_2 + H_2O \qquad (I)$$

$$H_2NCl + HOCl \longrightarrow H_2NOH + 2Cl^- \qquad (II)$$

$$H_2NCl + H_2NOH \xrightarrow{^-OH} .5\ N_2O + NH_3 + 1.5\ H_2O + Cl^- \qquad (III)$$

however, were reported by Yagil and Anbar (49) as side-reactions in synthesis of hydrazine when the concentration of monochloramine was less than 10^{-3} M. The ammonia formed in reaction (III) would react with any hypochlorous acid remaining in the solution to form additional monochloramine, which would further complicate the kinetics of the overall decomposition reaction.

Plots of absorbance at 243 nm (corrected for absorbance of hypochlorous acid and hypochlorite ions) and 292 nm versus time are presented in Figures 10 and 11, respectively. Both data sets are in excellent agreement. The sharp rise in absorbance in Figure 10 with a maximum occurring at 3s, 6s, and 30s for pH values of 8.5, 10.5, and 12.0, respectively, are corresponded by sharp decreases in absorbance in Figure 10 at the same time intervals. Initial changes in absorbance indicate the formation of monochloramine from small quantities of ammonia in the monochloramine solution. The steepness of these changes reflects the effect of pH on the rate of monochloramine formation reported in the previous section. Furthermore, the data show that monochloramine and hypochlorous acid are relatively stable in the pH range of 10.5 to 12.0.

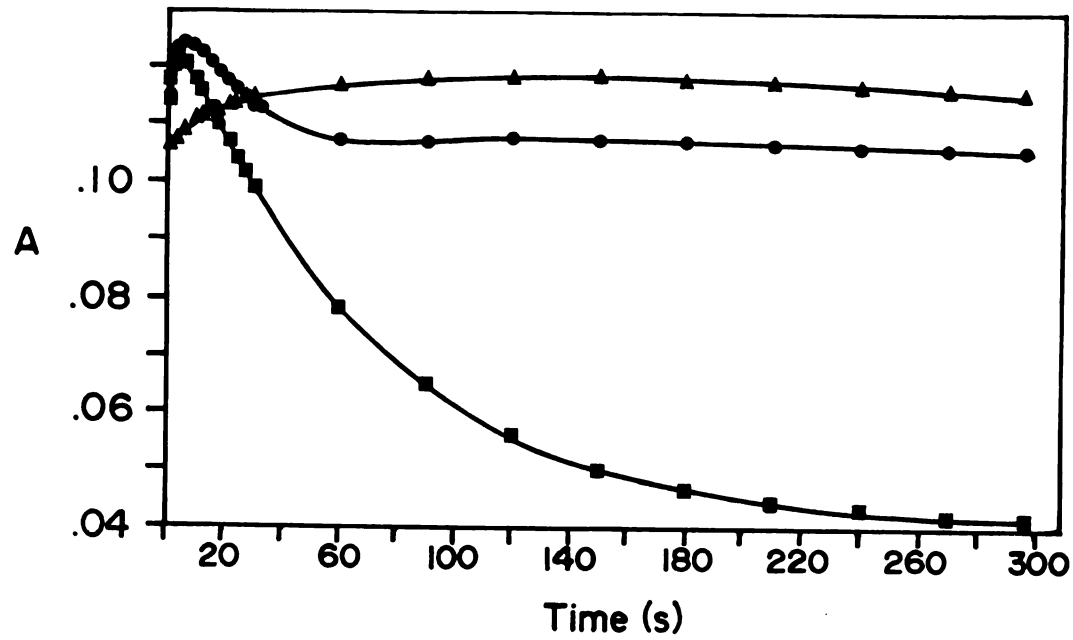


Figure 10: Decomposition of Monochloramine as a Function of Absorbance at 243 nm and Time at pH Values of 8.5 (■), 10.5 (●), and 12.0 (▲).

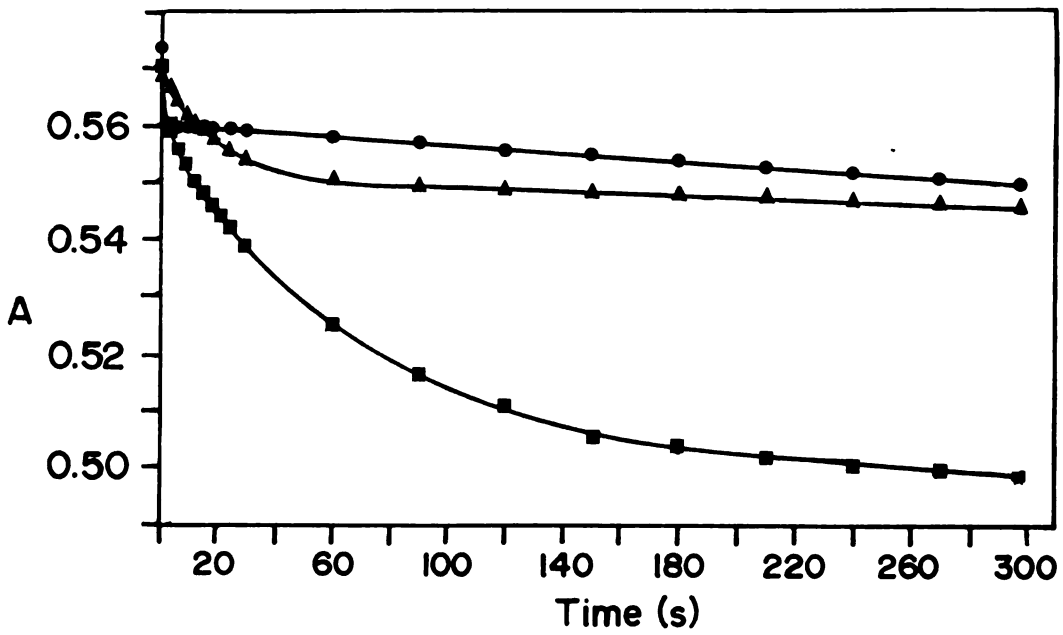
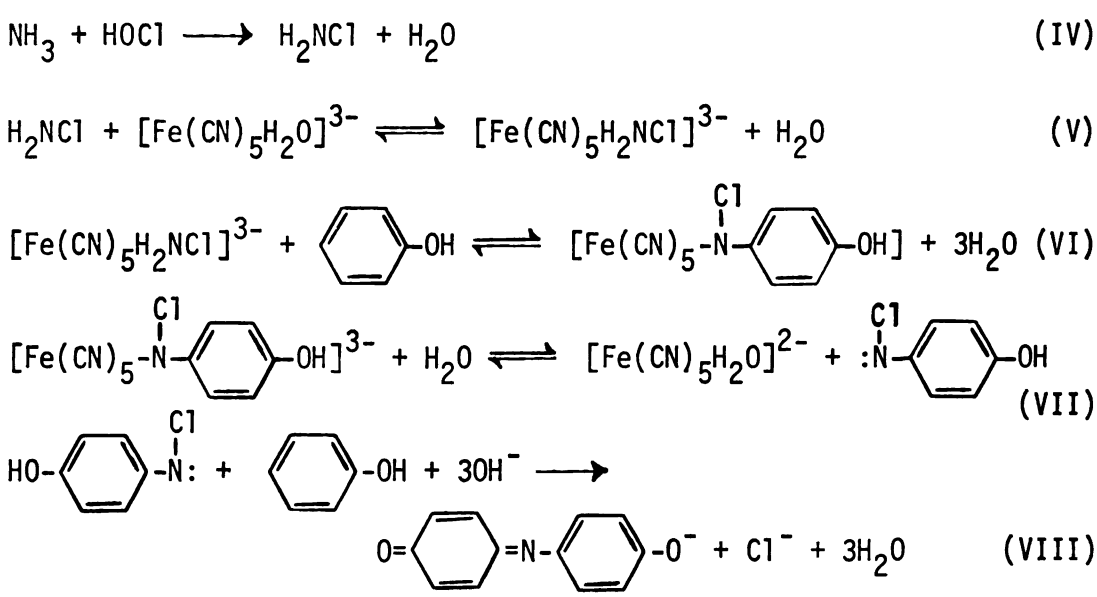


Figure 11: Decomposition of Monochloramine as a Function of Absorbance at 292 nm and Time at pH Values of 8.5 (■), 10.5 (●), and 12.0 (▲).

Mechanism and Kinetics of Indophenol Formation

The mechanism and kinetics of indophenol formation from ammonia, hypochlorous acid, sodium aquopentacyanoferrate, and phenol are complex. Experiments in which buffered solutions containing phenol, 2-methylphenol, or 2-chlorophenol plus sodium aquopentacyanoferrate and monochloramine were mixed in the stopped-flow spectrophotometer were performed. The change in absorbance with time was recorded at 635 nm and 650 nm, which corresponds to the wavelengths of maximum absorption for indophenol, 2,2'-dimethyl-, and 2,2'-dichloraoindophenol. Representative data are presented in Figure 12. Brief attempts to fit these data to rate laws were unsuccessful. Despite this fact, the following mechanism is proposed. It is based on the results of this research, related research of other workers, and a fair measure of intuition and speculation.



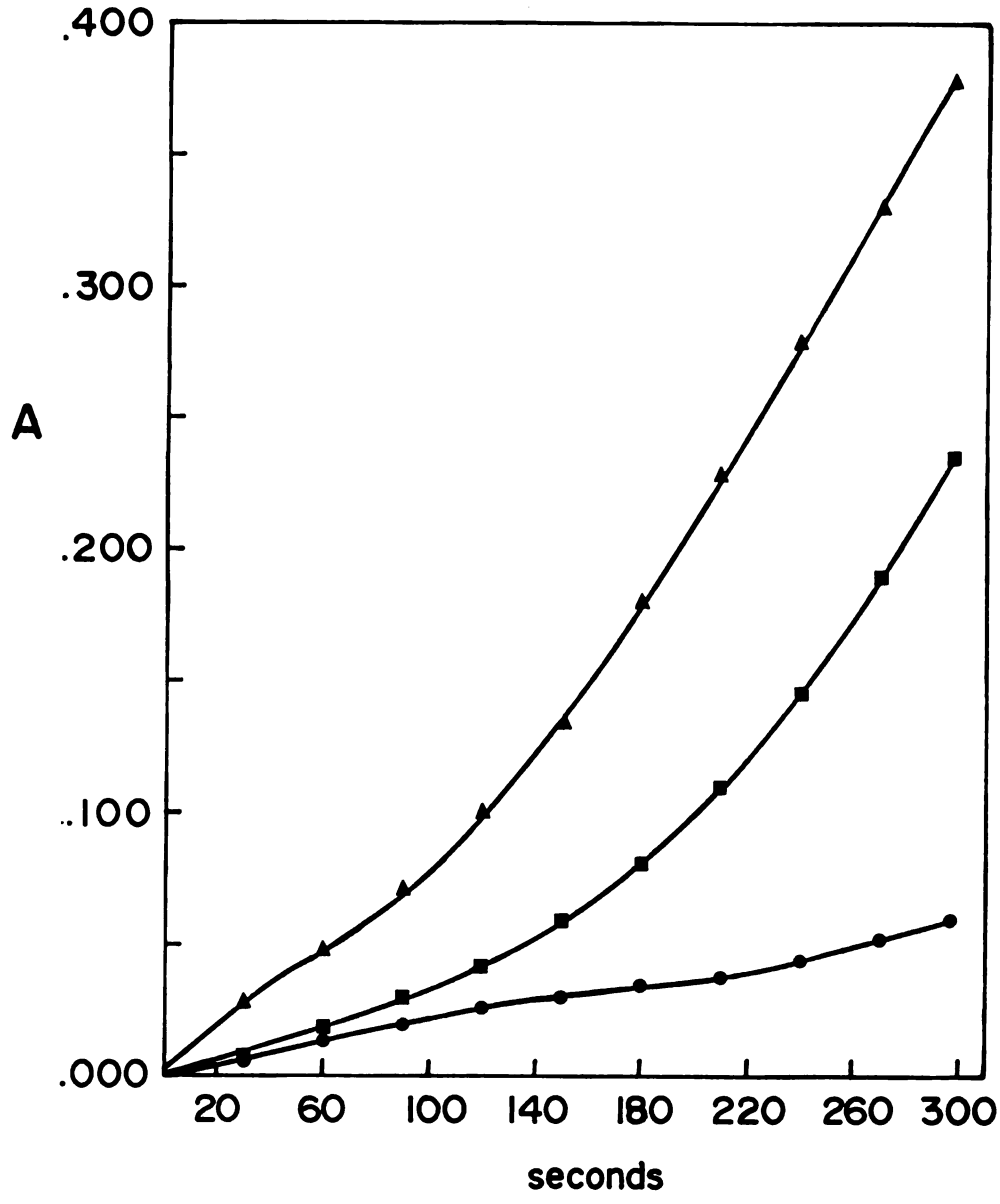


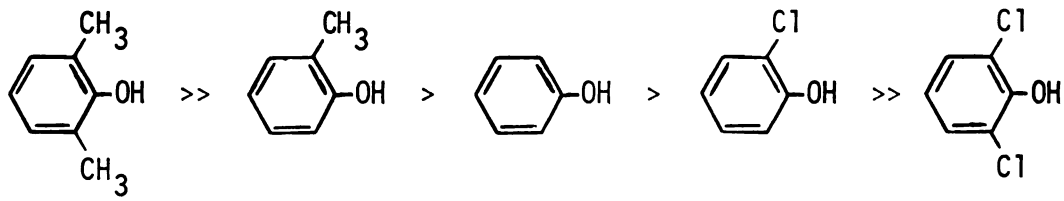
Figure 12: Rate of Formation of 2,2'-dimethylindophenol (▲), Indophenol (■), and 2,2'-chloroindophenol (●).

Reaction (IV) corresponds to the formation of the first intermediate in the overall reaction. The rate of this step is governed primarily by the pH of the reaction medium, as shown in the previous section. Reaction (V), which corresponds to the formation of the second intermediate, is supported by experiments discussed in Chapter V. Reactions (VI) and (VII) are speculative, but similar reactions between sodium nitropentacyanoferrate and acetophenone reported by Wolfe and Swinehart (48) lend some support. Reaction (VIII) corresponds to the formation of indophenol and is supported by the work of Corbett (9) and of Gibbs and Clark (14).

Rates of Formation of Several Indophenols

Referring again to Figure 12, it can be seen that the rate of formation of 2,2'-dimethylindophenol is greater than that of indophenol and that the rate of formation of 2,2'-dichloroindophenol is less than that of indophenol. These observations are easily rationalized in terms of the inductive effects discussed in Chapter II. Despite the fact that the rate of formation for 2,2'-dichloroindophenol was the slowest, its equilibrium value for absorbance was always the highest. This is probably because its molar absorptivity is the highest of the three. As an aside, 2,6-dimethylphenol coupled much faster than 2-methylphenol, and 2,6-dichlorophenol coupled much slower than 2-chlorophenol. The use of these phenols was hindered, however, due to their low solubility in

water. Furthermore, 2,6-dimethylphenol was rapidly chlorinated by hypochlorous acid, which resulted in yellow-orange oils. It was interesting to note that two ortho substituents on a phenol exerted effects greater than would be predicted by simply doubling the effect of one ortho substiuent. The relative rates of coupling for these phenols are as follows:



VII. A NEW AMMONIA METHOD

In this chapter, a method for ammonia analysis which evolved from a mechanistic consideration of the Berthelot reaction is presented. The order of reagent addition has been reversed relative to most procedures, and 2-chlorophenol was used in place of phenol. Sodium aquopentacyanoferrate was used to catalyze the reaction.

Reagents

Ammonia standards

(A) 7.44×10^{-1} M: Dissolve 3.9797 g of ammonium chloride (dried for two hours at 120°C) in 100 ml deionized distilled water.

(B) 7.44×10^{-4} M: Dilute 1 ml of A to 1 ℓ with deionized distilled water.

(C) 7.44×10^{-6} M: Dilute 1 ml of B to 100 ml with deionized distilled water.

(D) 7.44×10^{-5} M: Dilute 10 ml of B to 100 ml with deionized distilled water.

When 1 ml, 3 ml, and 5 ml of solution C were diluted to 25 ml, the concentrations of ammonia were 2.98×10^{-7} M, 8.93×10^{-7} M, and 1.49×10^{-6} M, respectively. When 1 ml, 3 ml, and 5 ml of solution D were diluted to 25 ml, the final concentrations of ammonia were 2.98×10^{-6} M, 8.93×10^{-6} M, and 1.49×10^{-5} M, respectively.

Sodium hypochlorite

(E) 7.44×10^{-2} M: Dilute 10 ml of 0.744 M sodium hypochlorite (Chlorox^{R}) to 100 ml with deionized distilled water.

(F) 1.49×10^{-2} M: Dilute 10 ml of solution E to 50 ml with deionized distilled water.

Sodium aquopentacyanoferrate

(G) 4.14×10^{-3} M: Dissolve 0.03 g of $Na_3[Fe(CN)_5H_2O]\cdot H_2O$ 25 ml of deionized distilled water.

(H) 1.66×10^{-4} M: Dilute 1 ml of solution G to 25 ml with deionized distilled water.

2-chlorophenol

(I) 1.06 M: Dissolve 2.3 g of 2-chlorophenol in 20 ml of 95% ethanol.

(J) 1.06×10^{-1} M: Dilute 5 ml of solution I to 50 ml with deionized distilled water.

When 1 ml each of reagents F, H, and J were diluted to 25 ml, their final concentrations were 5.95×10^{-4} M, 6.62×10^{-6} M, and 4.24×10^{-3} M, respectively.

The Method

Into twelve 25 ml volumetric flasks, which had been rinsed with 10% HCl and deionized distilled water just prior to use, were pipetted the required amount of standards C and D to give ammonia concentrations of 2.98×10^{-7} M, 8.93×10^{-7} M, 1.49×10^{-6} M,

2.98×10^{-6} M, 8.93×10^{-6} M, and 1.49×10^{-5} M when diluted to 25 ml. Next, 15 ml of pH 10.5 buffer was pipetted into each flask, as well as two other 25 ml volumetric flasks containing no ammonia, which served as reagent blanks. Then 1 ml of reagent F was added and the flask was swirled. After one minute, 1 ml each of H and J were added in rapid succession, and the mixture was swirled, diluted to the mark with deionized distilled water, and shaken. This procedure was repeated for each flask. The flasks were allowed to stand for two hours at room temperature after which the absorbance of each solution was measured in 5 cm cells at 650 nm against pH 10.5 buffer. The results are presented in Table 5.

The method for ammonia analysis described by Solorzano (39), which is in widespread use in water chemistry laboratories in this country because of its high sensitivity, was used for comparison with the proposed method. Solorzano's procedure used sodium nitropentacyanoferrate as the catalyst. Standard solutions were prepared identically to those used for the proposed method except 15 ml of deionized distilled water was added to each flask instead of buffer. After addition of reagents, the solutions were allowed to stand for two hours, after which the absorbance of each solution was measured in 5 cm cells at 640 nm. The results are presented in Table 6.

Discussion

The calibration curves for the Solorzano and the proposed method are presented in Figure 13. Both obey Beer's Law in the ammonia concentration range of 10^{-7} M to 10^{-5} M. The slope and

TABLE 5

Data Obtained When Ammonia Was Analyzed

by the Proposed Method

$[NH_3]$	A^{650}	$\bar{A}^{std} - \bar{A}^{blk} \pm$ SD (% REL. SD)
0.00	.032	-
0.00	.034	-
2.98×10^{-7}	.070	0.034 ± .002 (5.98)
2.98×10^{-7}	.067	
8.93×10^{-7}	.126	0.096 ± .005 (4.77)
8.93×10^{-7}	.128	
1.49×10^{-6}	.191	0.162 ± .006 (3.92)
1.49×10^{-6}	.200	
2.98×10^{-6}	.382	0.344 ± .007 (2.06)
2.98×10^{-6}	.372	
8.93×10^{-6}	1.022	0.086 ± .004 (0.36)
8.93×10^{-6}	1.017	
1.49×10^{-5}	1.533	1.494 ± .008 (0.52)
1.49×10^{-5}	1.522	

TABLE 6

Data Obtained When Ammonia Was Analyzed

by the Solorzano Method

$[NH_3]$	A^{640}	$\bar{A}^{std} - \bar{A}^{blk} \pm$ SD (% REL. SD)
0.00	.048	-
0.00	.048	-
2.98×10^{-7}	.073	0.024 ± .002 (9.03)
2.98×10^{-7}	.070	
8.93×10^{-7}	.139	0.093 ± .003 (3.04)
8.93×10^{-7}	.143	
1.49×10^{-6}	.202	0.144 ± .014 (9.82)
1.49×10^{-6}	.182	
2.98×10^{-6}	.306	0.274 ± .023 (8.39)
2.98×10^{-6}	.339	
8.93×10^{-6}	.885	0.865 ± .040 (4.58)
8.93×10^{-6}	.941	
1.49×10^{-5}	1.326	1.344 ± .093 (6.89)
1.49×10^{-5}	1.456	

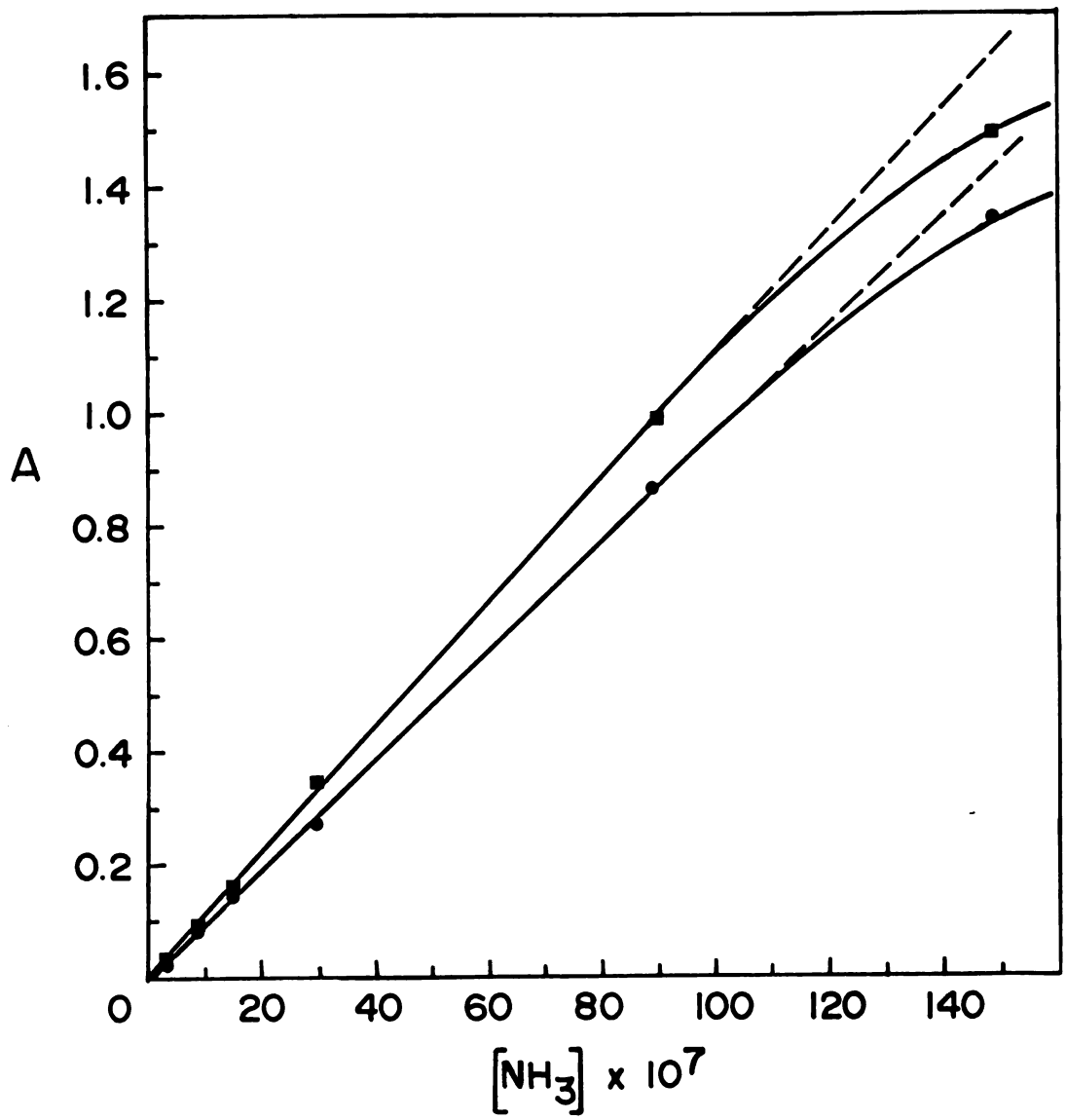


Figure 13: Calibration Curves for Ammonia as Determined by the Solorzano (•) and Proposed (■) Methods

intercept obtained from a linear least squares fit of the data from the Solorzano and proposed methods are 9.69×10^{4} and -2.43×10^{-3}, and 1.11×10^{5} and 2.28×10^{-3}, respectively. This corresponds to a 12.7% increase in sensitivity of the proposed method over the Solorzano method. An examination of Tables 5 and 6, in which the average and standard deviation of absorbance for each set of standards, shows that the precision of the proposed method is as much as ten times better than the Solorzano method, especially at higher concentration ranges. The precision of the proposed method increases with increasing ammonia concentration, while the precision of the Solorzano method is low and random for all concentrations. It is interesting to note that the color produced in the Solorzano method fades to green or yellow after twelve hours, while the color produced in the proposed method is stable for at least four days.

The small increase in sensitivity for the proposed method relative to the Solorzano method may be largely due to the fact that the molar absorptivity of 2,2'-dichloroindophenol is slightly higher than that of indophenol. The large increase in precision of the proposed method relative to the Solorzano method, however, is attributable to the fact that side reactions have been minimized in the proposed method. For example, in the Solorzano method, reagents used are in several thousand-fold excess of their stoichiometric concentrations, and the hypochlorite reagent is added last. Under these conditions, ammonia must compete for hypochlorous acid with phenol and catalyst molecules, which are present in very large

excess. In addition, both the first intermediate and the final product of the Berthelot reaction, monochloramine and indophenol, are unstable in the large excess of sodium hypochlorite recommended by Solorzano. In the proposed method, the hypochlorite reagent is added first and in only five-fold excess of the stoichiometric amount necessary to convert all the ammonia in the highest standard to monochloramine.

In the concentration range of 10^{-7} M to 10^{-5} M, the time required to convert 99.5% of ammonia present in solution to monochloramine was calculated as forty to fifty seconds when an observed second-order rate constant of 2×10^{3} ℓ $mole^{-1}sec^{-1}$ was assumed and the initial concentration of the hypochlorite reagent was 5.95×10^{-4} M. This means that the first intermediate in the Berthelot reaction is formed before the other reagents are added so side reactions are minimized.

Although the proposed method offers increased sensitivity and precision, it is important to stress that real samples were not analyzed. Calcium, iron, and magnesium present in fresh- and seawater would be precipitated at pH 10.5 causing serious interference. The addition of sodium citrate or EDTA to the buffer, however, should alleviate this problem. The proposed method could be easily automated and after minor modification could become the preferred method for trace ammonia analysis.

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