STUDIES ON THE FORMATION OF HEXAMINE FROM FORMALDEHYDE AND AMMONIUM SALTS IN AQUEOUS SOLUTION

A Thesis

by

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Ph.D. Department of Chemistry

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STUDIES ON THE FORMATION OF HEXAMINE FROM FORMALDEHYDE AND AMMONIUM SALTS IN AQUEOUS SOLUTION

Hexamine was prepared from the reaction of formaldehyde with numerous ammonium salts, in both aqueous and glacial acetic acid media.

The rate of formation and the final yield of hexamine vary greatly with the different ammonium salts.

Both the rate of formation and the final yield of hexamine are increased by an increase in the pH of the solution.

When buffered at given pH, the various ammonium salts give approximately the same rates of formation and final yields of hexamine.

Rate curves have been determined for the reaction of formaldehyde with ammonium nitrate in aqueous solutions buffered at pH 8.0, 6.0 and 4.0, at temperatures of 0°C., 20°C. and 40°C. and over a range of initial mole ratios (formaldehyde: ammonium nitrate) of 0.75 to 3.0. For each set of conditions, three rate curves have been obtained on the basis of ammonia consumed, formaldehyde consumed and material precipitated with mercuric chloride.

In excess formaldehyde, a stable by-product is formed; its formation increases as the temperature is increased.

In excess ammonium nitrate, by-product formation is decreased.

A mechanism of hexamine formation has been proposed in accordance with the kinetic data.

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INTRODUCTION

Formaldehyde, which is prepared by the oxidation of methyl alcohol, was available only in limited quantities prior to 1923. In that year, however, a commercial method for the production of synthetic methyl alcohol by the catalytic reduction of carbon monoxide was discovered (1). This in turn made formaldehyde more plentiful, as a result of which it became possible to produce hexamine in large quantity by the evaporation of an aqueous solution of formaldehyde and ammonia.

Before World War II, hexamine was produced commercially for use in industry as a special form of anhydrous formaldehyde, for example, in the manufacture of synthetic resins. To a smaller extent, it was used in the preparation of certain pharmaceutical products. The production of hexamine and the study of its chemistry attained national importance, however, by its use as the starting material in the production of the explosive, RDX.

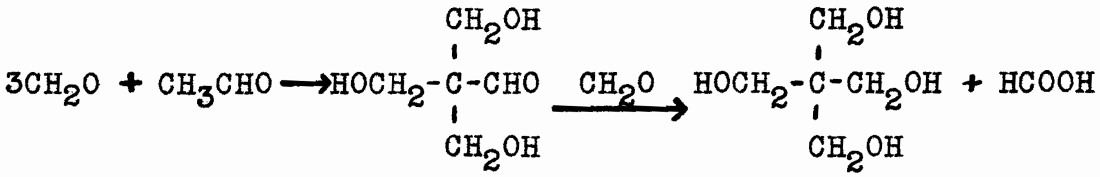
Although hexamine is still produced commercially by the evaporation of an aqueous formaldehyde-ammonia solution, it has also been isolated from the aqueous reaction of formaldehyde and ammonium chloride (2) or ammonium sulphate (3). In glacial acetic acid, it has been prepared by the reaction of paraformaldehyde with ammonium acetate (4) and with ammonium nitrate (5).

Although it has been shown that formaldehyde reacts not only with ammonia but also with various ammonium salts in water and in glacial acetic acid to form hexamine, other reactions must also be possible, in view of the well-known preparation of methylamine from formaldehyde and ammonium chloride.

Formaldehyde undergoes chemical reactions which may be broadly classified into three types: (1) addition or condensation reactions which lead to the formation of methylol or methylene derivatives, (2) oxidation-reduction reactions in which the formaldehyde acts as a reducing agent and is itself oxidized to formic acid, and (3) polymerization reactions resulting in the formation of polymethylene derivatives.

Formaldehyde reacts readily with many compounds containing active hydrogen atoms with the formation of methylol derivatives. The hydrogen atoms which are active in these additions are those which are in the α position with respect to a carbonyl, nitro or cyano group. After the addition reaction has taken place, a methylol group, $-CH_2OH$, occupies the position formerly held by the active hydrogen. Thus, when formaldehyde reacts with acetaldehyde, nitromethane, cyclopentanone and hydrogen cyanide, primary alcohols are formed. For example, consider the reaction of formaldehyde with acetaldehyde. Four equivalents of formaldehyde in warm aqueous solution in the presence of calcium hydroxide react with one equivalent of acetaldehyde to form pentaerythritol.

Three of the formaldehyde molecules react with the three α hydrogens of the acetaldehyde. The fourth formaldehyde molecule reduces the aldehyde group to $-CH_2OH$ and is itself oxidized to formic acid.



$$3CH_2O + CH_3CHO \longrightarrow HOCH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CHO \xrightarrow{CH_2O} HOCH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH + HCOOH$$

A reaction similar to that between formaldehyde and acetaldehyde occurs when formaldehyde reacts with nitromethane in the presence of potassium carbonate. In this reaction the intermediates were actually isolated (7).

$$CH_3NO_2 + CH_2O \longrightarrow HOCH_2CH_2NO_2 \longrightarrow (HOCH_2)_2CHNO_2 \longrightarrow (HOCH_2)_3CNO_2$$

Hydrogen cyanide combines with formaldehyde producing formaldehyde cyanohydrin (8).

$$CH_2O_{(aq.)} + HCN \longrightarrow HOCH_2CN$$

Another important methylol derivative is dimethylolurea produced from neutral or alkaline formaldehyde and urea:

$$NH_2CONH_2 + 2CH_2O_{(aq.)} \longrightarrow HOCH_2NHCONHCH_2OH$$

If water is eliminated in the course of the reaction, the reaction is a condensation reaction rather than a simple addition reaction. An example is the reaction of formaldehyde solution with phenylhydrazine:

$$C_6H_5NHNH_2 + CH_2O_{(aq.)} \longrightarrow C_6H_5NHN = CH_2 + H_2O$$

The formation of hexamine by the evaporation of an aqueous formaldehyde-ammonia solution is another example of a condensation reaction, as in:

$$6CH_2O + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$$

Many of the methylol derivatives, such as methylene glycol, $HOCH_2OH$, are unstable and decompose with regeneration of their original reactants or the formation of methylene derivatives or polymers, when their isolation in the pure state is attempted. Other methylol derivatives, such as pentaerythritol, are more stable and can be readily isolated. The formation of methylol derivatives usually proceeds most readily under neutral or alkaline conditions, whereas under acidic conditions, methylene derivatives are usually obtained. Methylol derivatives are considered to be the primary formaldehyde reaction products and it is probable that their formation is a part of the mechanism of all formaldehyde reactions (9).

In addition to the above typical addition and condensation reactions, formaldehyde also undergoes many reactions in which it functions as a reducing agent. Methylation, accomplished by heating formaldehyde or paraformaldehyde with ammonium chloride, is an example of this reducing action of formaldehyde (10,11).

$$NH_4Cl + CH_2O \longrightarrow CH_3NH_2\cdot HCl \longrightarrow (CH_3)_2NH\cdot HCl \longrightarrow (CH_3)_3N\cdot HCl + nHCOOH$$

In greater detail, the initial stages of this reaction might occur as follows:

$$CH_2O + NH_4Cl \longrightarrow HOCH_2NH_3Cl \quad \text{(addition)}$$

$$HOCH_2NH_3Cl + CH_2O \longrightarrow CH_3NH_3Cl + HCOOH \quad \text{(oxidation-reduction)}$$

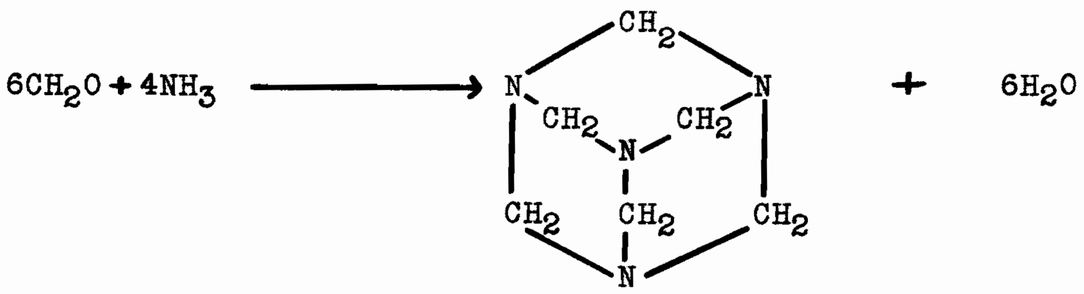
Simple aliphatic amines are smoothly methylated to the tertiary amines by warming them in formic acid with formaldehyde, the yield being over 80 per cent (12). Under these conditions, the more complex amine, hexamine, gave mainly ammonia and trimethylamine, with some monomethylamine and dimethylamine.

Formaldehyde solutions, when evaporated, yield a white polymeric residue known as paraformaldehyde. Following an exhaustive study of formaldehyde polymers, Delépine (13) concluded that paraformaldehyde was a mixture of polymeric hydrates and was formed by the condensation of methylene glycol, as indicated by the equation:

$$nCH_2(OH)_2 \longrightarrow (CH_2O)_n \cdot H_2O + (n-1)H_2O$$

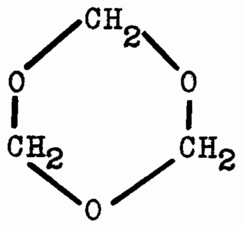
Commercial paraformaldehyde contains at least 95 per cent formaldehyde and is used in reactions as a source of anhydrous formaldehyde since formaldehyde is regenerated by depolymerization on dilution (14, 15).

Formaldehyde and ammonia react to form hexamethylenetetramine.



Hexamine

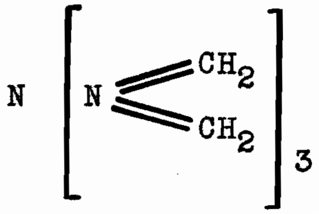
Hexamethylenetetramine (now commonly called hexamine) is the ammono-analog of trioxane, the cyclic trimer of formaldehyde.



Trioxane

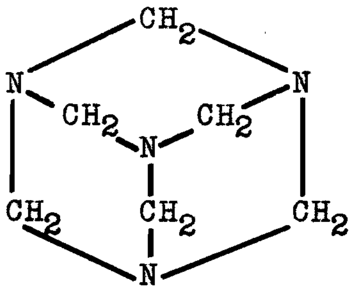
Hexamine is also a tertiary amine and shows the characteristic properties of such amines, forming numerous salts, addition compounds and complexes. In this it resembles pyridine and triethanolamine but differs in possessing a lower degree of basicity.

Hexamine was first prepared by Butlerov (16) in 1859 by the reaction of gaseous ammonia and paraformaldehyde. He determined the empirical formula to be $C_6H_{12}N_4$ and proposed the structural formula:



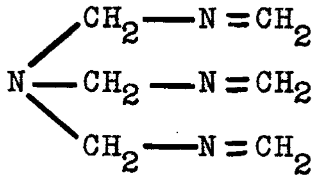
In 1869, Hofmann (17) obtained hexamine from the reaction of formaldehyde with ammonia in aqueous solution. This is still the commercial method for its preparation.

Various chemical structures have been proposed for hexamine by different investigators. Of these, the formula of Duden and Scharff (18) seems to be in best agreement with the facts and is now generally accepted as the probable structure:



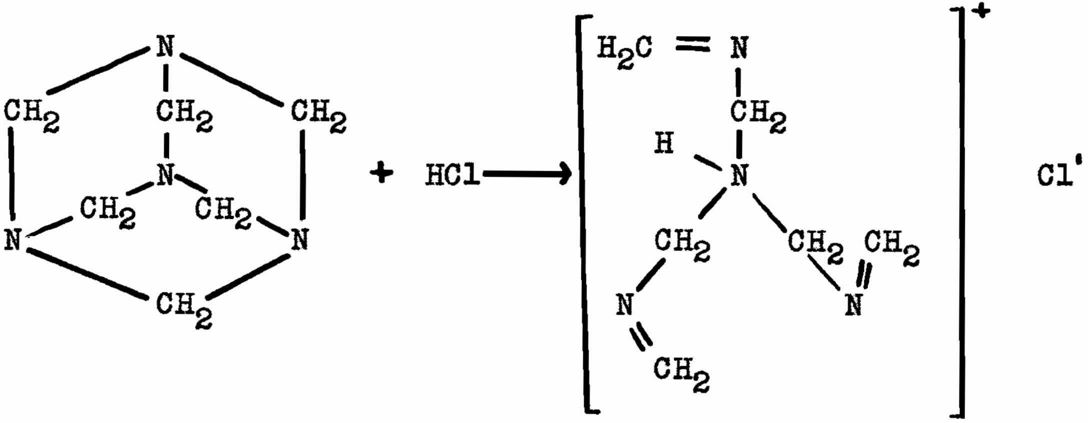
This structure is supported by the results of X-ray examinations (19,20) which indicate that the carbon atoms and the nitrogen atoms in the molecule are all equivalent. In space, the nitrogen atoms form a tetrahedron, whereas the carbon atoms form an octahedron.

Of the other structures advanced for hexamine, that of Lösekann (21) is of definite interest and is still accepted by some investigators.



Spatial models of this structure indicate that, although it is less symmetrical than that of Duden and Scharff (18), the general atomic configuration may be very similar to it. Since the symmetry of the Duden and Scharff structure is probably lost when one of the nitrogen atoms becomes coördinated, the

Lösekann structure may illustrate this change.



The first kinetic study of the formation of hexamine in an aqueous solution of formaldehyde and ammonia was made by Baur and Ruetschi (22) in 1941. They studied the reaction at 0°C. using solutions of concentrations 0.5 to 2.0 molar. They found that, in aqueous solution, an almost complete reaction took place between formaldehyde and ammonia and that the "overall" reactions could be represented by the equation:

$$6CH_2O + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$$

The course of the reaction was followed by an acid titration of the ammonia. On the basis of the rate constants calculated from the consumption of ammonia, Baur and Ruetschi concluded that the reaction was third order, with ammonia and formaldehyde in the stoichiometrical ratio of 1:2.

Two possible mechanisms for hexamine formation were proposed:

A. 1. $CH_2O + NH_3 \xrightarrow{\text{rapid}} CH_2 = NH + H_2O$

2. $CH_2 = NH + CH_2O \xrightarrow[\text{measured}]{\text{slow}} CH_2 = N\text{-}CH_2OH$

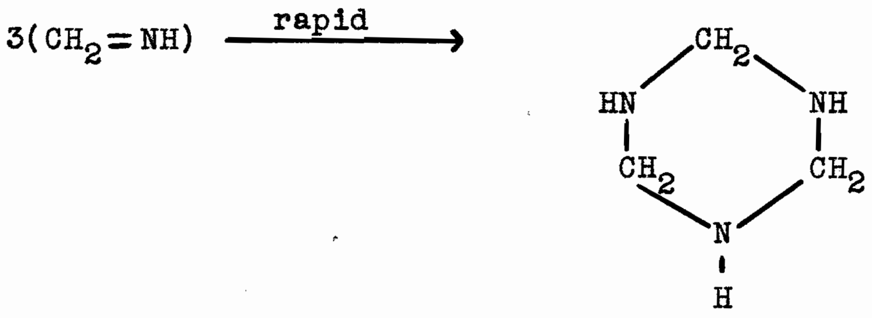
3. $CH_2=N-CH_2OH + HNH_2 + CH_2O \xrightarrow[\text{rapid}]{\text{slow}} CH_2=N-CH_2-N=CH_2 + 2H_2O$

4. $2(CH_2)_3N_2 \xrightarrow{\text{rapid}} (CH_2)_6N_4$

B. 1. $3CH_2O + 3NH_3 \xrightarrow{\text{rapid}} 3(CH_2=NH) + 3H_2O$

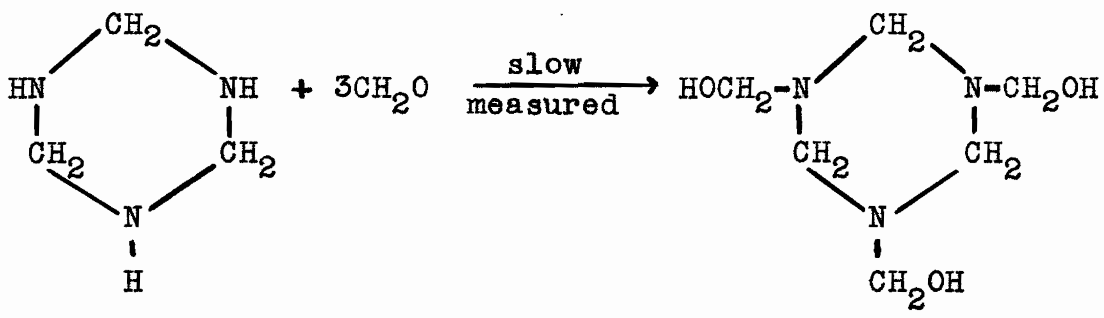
Methyleneimine

2.



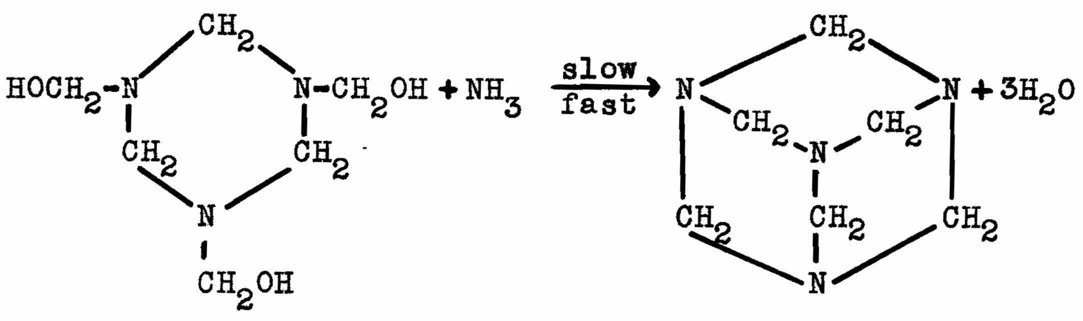
Trimethylenetriamine

3.



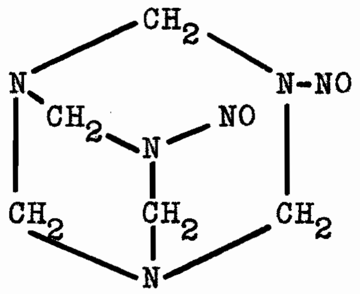
Trimethyloltrimethylenetriamine

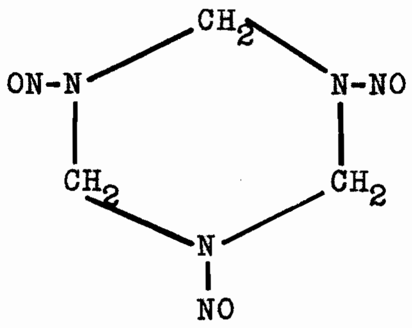
4.



Hexamine

Baur and Ruetschi (22) favoured mechanism B, in view of the fact that Griess and Harrow (23) and also Mayer (24) had previously isolated dinitrosopentamethylenetetramine and trinitrosotrimethylenetriamine from the reaction mixture. These nitroso compounds are derivatives of the postulated intermediate trimethylenetriamine.





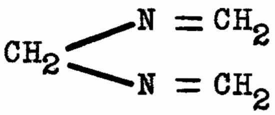
Dinitrosopentamethylenetetramine   Trinitrosotrimethylenetriamine

The formation of the above nitroso derivatives was confirmed by Duden and Scharff (18). They also isolated the tribenzoyl derivative of trimethylenetriamine by reacting benzoyl chloride with the mixture obtained by treating a cold solution of formaldehyde and ammonium chloride with sodium hydroxide. This benzoyl derivative is a crystalline product melting at 223°C. The isolation and identification of these derivatives was offered by these investigators as basic evidence for the presence of the postulated trimethylenetriamine.

Henry (25) dried an equimolar solution of aqueous ammonia and formaldehyde with potassium carbonate. He concluded that the liquid obtained was trimethylolamine. Wright (26), however, showed that Henry's solution was actually a

40-50 per cent aqueous solution of cyclotrimethylenetriamine in equilibrium with methyleneimine, $CH_2=NH$ or methylolamine $HOCH_2NH_2$.

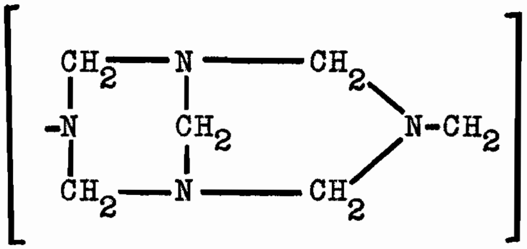
Investigators of the Research Department, Woolwich, (27, 28) concluded that the primary product of the reaction of formaldehyde and ammonia in aqueous solution was a hemihexamine molecule, from which hexamine can result by a dimerization.



Hexamine has also been prepared in the gas phase by Novotny and Vogelsang (29). They reacted anhydrous ammonia with vaporized aqueous formaldehyde. Kolosov (30) claims that hexamine of 98 per cent purity can be obtained by the reaction of gas containing 0.25 kilograms of formaldehyde per cubic metre with anhydrous ammonia.

Vroom and Winkler (31) investigated the reaction between formaldehyde and ammonia in the gas phase at temperatures of 110°-150°C. and molar ratios of formaldehyde:ammonia varying from 2:1 to 1:5. Hexamine was obtained and also a product giving the same analysis as hexamine but possessing different physical properties. It was insoluble in chloroform. This product yielded hexamine on sublimation and hexamine dinitrate when treated with dilute nitric acid. In boiling water, it decomposed into formaldehyde and ammonia.

When subjected to a direct nitrolysis reaction, RDX was formed. Vroom concluded that the new compound was a polymerized form of hexamine and suggested the following structure:



Ring closure between the ends would lead to hexamine.

Kinetic studies on the formation of hexamine were conducted by Boyd and Winkler (32) in 1945. Rate curves were determined for the reaction of ammonia and formaldehyde in aqueous solution at 0°C. and 35°C. over a range of initial mole ratios of formaldehyde:ammonia of 0.25 to 2.0. For each set of conditions, three curves were obtained on the basis of ammonia consumed, formaldehyde consumed and material precipitated with mercuric chloride. At 0°C. it was found that the three rate curves approximated one another in a large excess of ammonia but were widely separated in excess formaldehyde. The reverse was true at 35°C. Boyd concluded that a stable by-product existed in excess formaldehyde. This conclusion was based on the fact that there was a variation in final yields of hexamine when these were calculated on the basis of formaldehyde consumed, ammonia consumed and material precipitated by mercuric chloride. The results indicated that more formaldehyde and ammonia were consumed than appeared as hexamine.

A mechanism was suggested, having the following characteristics:

1) Formaldehyde and ammonia react to form a monomer, $HOCH_2NH_2$, and a dimer, $HOCH_2NHCH_2NH_2$. Alternative paths lead to hexamine from the dimer; one path being preferred in excess formaldehyde, the second in excess ammonia.

2) Rapid equilibrium exists between monomer and dimer.

3) Formaldehyde but not ammonia can be obtained from the monomer and the dimer.

4) The activation energy for the formation of the monomer is less than that for the reaction of the dimer with formaldehyde and greater than that for its reaction with ammonia.

The possible two-path mechanism was represented as follows:

$A = CH_2O \qquad B = NH_3$

$$\begin{tikzcd}
A + B \arrow[r] & AB \arrow[r] & (AB)_2 \arrow[r] \arrow[d, "+B"] & A_3B_2 \arrow[r, "2x"] & A_6B_4 \\
 & & A_2B_3 \arrow[d, "+A"] & \text{hemihexamine} & \text{hexamine} \\
 & & A_3B_3 \arrow[d, "+(3A+B)"] & \text{(cyclotrimethylenetriamine)} & \\
 & & A_6B_4 & \text{(hexamine)} &
\end{tikzcd}$$

Boyd considered that the path leading to hemihexamine formation was favoured in excess formaldehyde, while the path leading to the cyclotrimethylenetriamine was favoured in excess ammonia. It was found that the rate of formation of hexamine from formaldehyde and ammonium acetate was as rapid in glacial acetic acid as in water. It was also shown that the reaction of ammonium nitrate and formaldehyde was slow, compared with the reaction of ammonium acetate and formaldehyde, each in glacial acetic acid.

Both of the kinetic studies on hexamine formation made by Baur and Ruetschi (22) and by Boyd (32) involved the reaction in aqueous solution of formaldehyde with ammonia. Boyd also briefly studied the reaction of formaldehyde with ammonium acetate and ammonium nitrate in glacial acetic acid.

Hexamine has also been prepared by the reaction of formaldehyde with various ammonium salts, not only in aqueous solution but also in glacial acetic acid, nitromethane, hexane and heptane.

In glacial acetic acid, Williams and Winkler (5) isolated hexamine dinitrate from the reaction of ammonium nitrate with paraformaldehyde. They also succeeded in preparing hexamine dinitrate in nitromethane, hexane and heptane. In these solvents, however, the hexamine dinitrate was not actually isolated but was expressed in terms of the RDX equivalent, obtained by adding acetic anhydride and thereby converting the hexamine dinitrate to RDX, according to the equation:

$$\underset{\text{(Formaldehyde)}}{3CH_2O} + \underset{\substack{\text{(Ammonium}\\ \text{Nitrate)}}}{3NH_4NO_3} + \underset{\substack{\text{(Acetic}\\ \text{Anhydride)}}}{6(CH_3CO)_2O} \longrightarrow \underset{\text{RDX}}{C_3H_6O_6N_6} + \underset{\substack{\text{(Acetic}\\ \text{Acid)}}}{12CH_3COOH}$$

This is the Ross or McGill Reaction for the preparation of RDX.

The preparation of hexamine by the reaction of paraformaldehyde with ammonium acetate in glacial acetic acid was reported by Whitmore (33). He reacted 2.0 moles of ammonium acetate with 2.0 moles of paraformaldehyde. Half of the paraformaldehyde was added forty-three minutes after the start of the reaction. The mixture was heated to 70° C. for one and one-half hours. When cool, the acetic acid was removed by distillation at a reduced pressure of 12-15 mm. The residue, thus obtained, was washed with ether and then subjected to a direct nitrolysis reaction. Assuming that hexamine was converted to RDX in a 40 per cent yield, Whitmore estimated the hexamine yield to be 50 per cent, based on the formaldehyde.

In aqueous solution, hexamine has been prepared by slowly adding formaldehyde solution to a solution of ammonium chloride supersaturated with sodium bicarbonate (2). After evaporation, a mixture of sodium chloride and hexamine is obtained. This impure hexamine is produced under a British patent for use directly in resin manufacture. The hexamine can be purified by extraction with alcohol. Another procedure of a similar type involves the addition of formaldehyde to an aqueous solution of ammonium sulphate in the presence of the oxide, hydroxide or carbonate of an alkaline earth metal (3). The hexamine is obtained by concentrating the final solution and extracting the resulting precipitate with hot alcohol.

The addition of formaldehyde to an aqueous ammonium salt solution at room temperature results in the liberation of acid. If an excess of alkali be added to a solution containing the ammonium salt of a strong acid plus an excess of formaldehyde, the acid which was originally combined with the ammonia may be accurately determined by measuring the amount of alkali consumed. A volumetric method for the determination of ammonium nitrate is based on the reaction (35):

$$6CH_2O_{(aq.)} + 4NH_4NO_3 + 4NaOH \longrightarrow (CH_2)_6N_4 + 4NaNO_3 + 10H_2O$$

Although formaldehyde-ammonium salt reactions of the above type can be explained by assuming that hexamine is formed in the reaction solution, mechanism studies by Werner (36) indicated that this may not be true. According to his findings, a solution containing ammonium chloride and formaldehyde did not give the precipitate characteristic of polymethyleneamines when treated with picric acid. Werner concluded that weakly basic methyleneimine, the salts of which are almost completely dissociated in water, was the true reaction product. The mechanism of its formation was postulated as:

$$NH_4Cl + CH_2O_{(aq.)} \longrightarrow NH_2CH_2OH \cdot HCl \longrightarrow NH{=}CH_2 \cdot HCl + H_2O$$

According to this hypothesis, the methyleneimine is stable under acidic conditions and does not tend to polymerize, hexamine only being formed after the acid has been neutralized or otherwise removed, as in:

$$6NH{=}CH_2 \cdot HCl + 6NaOH \longrightarrow (CH_2)_6N_4 + 2NH_3 + 6NaCl + 6H_2O$$

As opposed to this hexamine formation in aqueous solutions at room temperature, heating solutions containing formaldehyde and ammonium salts gives rise to the salts of methylamines in good yield (37). This fact was illustrated by Knudsen (38) who isolated the salts of methylamine, dimethylamine and trimethylamine from the aqueous reactions of formaldehyde with ammonium chloride and ammonium sulphate. Werner's hypothesis (36) involving the primary formation of methyleneimine affords a possible interpretation of these reactions.

(1) $NH_3 \cdot HCl + CH_2O \longrightarrow CH_2{=}NH \cdot HCl + H_2O$

(2) $CH_2{=}NH \cdot HCl + CH_2O_{(aq)} + H_2O \longrightarrow CH_3NH_2 \cdot HCl + HCOOH$

(3) $CH_3NH_2 \cdot HCl + CH_2O_{(aq.)} \longrightarrow CH_3N{=}CH_2 \cdot HCl + H_2O$

(4) $CH_3N{=}CH_2 \cdot HCl + CH_2O_{(aq.)} + H_2O \longrightarrow (CH_3)_2NH \cdot HCl + HCOOH$

(5) $2(CH_3)_2NH \cdot HCl + CH_2O_{(aq.)} \longrightarrow CH_2(N(CH_3)_2)_2 \cdot 2HCl + H_2O$

(6) $CH_2(CH_3)_2)_2 \cdot 2HCl + CH_2O + H_2O \longrightarrow (CH_3)_3N \cdot HCl + (CH_3)_2NH \cdot HCl + HCOOH$

It is also possible, that, since aqueous formaldehyde probably is actually methylene glycol, $HOCH_2OH$, the intermediates in the above reactions are methylol derivatives rather than methylene compounds.

Thus $NH_3 \cdot HCl + HOCH_2OH \longrightarrow HOCH_2NH_2 \cdot HCl$

$HOCH_2NH_2 \cdot HCl + HOCH_2OH \text{ ——— } CH_3NH_2 \cdot HCl + HCOOH$

This reaction of formaldehyde with an ammonium salt to form methylamine salts involves the reducing action of formaldehyde. This reduction reaction was investigated by Emde and Hornemann (39). When they demonstrated that almost exactly one mole of formic acid was produced for every N-methyl radical formed in the reaction, they concluded that this reduction reaction was a Cannizzaro reaction.

At the present time, there are three main reactions for the preparation of RDX, although only two of these, the nitrolysis process and the Bachmann process, represent industrial methods.

Nitrolysis (Woolwich) Process:

$$(CH_2)_6N_4 + 4HNO_3 \longrightarrow (CH_2)_3(N\text{-}NO_2)_3 + 3CH_2O + NH_4NO_3$$

(Hexamine) (Nitric Acid) (RDX) (Formaldehyde) (Ammonium Nitrate)

Bachmann (Combination) Process:

$$(CH_2)_6N_4 + 4HNO_3 + 2NH_4NO_3 + 6(CH_3CO)_2O \longrightarrow 2(CH_2)_3(N\text{-}NO_2)_3 + 12CH_3COOH$$

(Hexamine) (Nitric Acid) (Ammonium Nitrate) (Acetic Anhydride) (RDX) (Acetic Acid)

Ross (McGill) Process:

$$3(CH_2O)_n + 3nNH_4NO_3 + 6n(CH_3CO)_2O \rightarrow n(CH_2)_3(N\text{-}NO_2)_3 + 12nCH_3COOH$$

(Paraform) (Ammonium Nitrate) (Acetic Anhydride) (RDX) (Acetic Acid)

Despite the fact that a vast amount of research has been conducted on the conversion of hexamine to RDX, both in the nitrolysis reaction and in the Bachmann reaction, this introduction illustrates how little has been done on the mechanism of hexamine formation. Few reports on the kinetic study of hexamine formation were found in the literature. The one by Baur and Ruetschi (22) and the other by Boyd and Winkler (32) involved the aqueous reaction of formaldehyde with ammonia. Although hexamine has also been prepared by the reaction of formaldehyde with certain ammonium salts, there has been no investigation of the kinetics of hexamine formation in the reaction of formaldehyde with ammonium salts, either in aqueous solution or in other solvents such as glacial acetic acid. As has been illustrated in these introductory remarks, at least two different reaction courses must be possible. When the formaldehyde functions as a condensing agent, hexamine (5) is formed as in:

$$6CH_2O + 4NH_4NO_3 \longrightarrow (CH_2)_6N_4 + 4HNO_3 + 6H_2O$$

When the formaldehyde acts as a reducing agent, in addition, the salts of methylamine (38) are formed as in:

$$CH_2O + NH_4Cl \longrightarrow CH_3NH_2 \cdot HCl \longrightarrow (CH_3)_2NH \cdot HCl \longrightarrow (CH_3)_3N \cdot HCl + nHCOOH$$

Moreover, Werner (36) has questioned the actual existence of hexamine in an aqueous solution of formaldehyde and an ammonium salt, suggesting that methyleneimine is the true reaction product.

From the foregoing, it is obvious that considerably more study is required on the reaction of formaldehyde with ammonium salts. A thorough understanding of this reaction would be of more than academic interest for it would presumably throw additional light on the reaction of paraformaldehyde with ammonium nitrate to form RDX, as in the McGill Reaction:

$$3(CH_2O)_n + 3nNH_4NO_3 + 6n(CH_3CO)_2O \longrightarrow n(CH_2)_3(N\text{-}NO_2)_3 + 12nCH_3COOH$$

A more detailed knowledge of the mechanism of hexamine formation became desirable, especially since hexamine has been suggested as an intermediate in the McGill Reaction (6). Also in the Bachmann process for RDX formation, one mole of RDX has been considered by some to arise by nitrolysis from the hexamine, whereas the second mole arises by synthesis from the remnants of the hexamine ring with ammonium nitrate (40).

It was therefore proposed in this work to (1) investigate the possibility of preparing hexamine from the reaction of formaldehyde with a number of different ammonium salts in both aqueous and glacial acetic acid media and (2) make a kinetic study of hexamine formation in the reaction of formaldehyde with ammonium salts.

THE FORMATION OF HEXAMINE IN THE REACTION
OF
FORMALDEHYDE WITH AN AMMONIUM SALT

Hexamine has been prepared by the aqueous reaction of formaldehyde with ammonium chloride (2) and with ammonium sulphate (3). The presence of hexamine in an aqueous formaldehyde-ammonium acetate solution has been reported (32), although, in this case, the hexamine was not actually isolated. In glacial acetic acid, it has been isolated from the reaction of paraformaldehyde with ammonium nitrate (5) and with ammonium acetate (4). Consider, as an example, the reaction between formaldehyde and ammonium chloride:

$$6CH_2O + 4NH_3 \cdot HCl \longrightarrow (CH_2)_6N_4 + 4HCl + 6H_2O$$

In the patented process for hexamine production by this method, the reaction takes place in an aqueous solution supersaturated with sodium bicarbonate. The sodium bicarbonate neutralizes the hydrochloric acid as it is formed and the reaction equilibrium is thereby continually shifted in favour of hexamine formation. The hexamine is isolated from this reaction by first evaporating the solution and then extracting the hexamine from the solid residue by the use of hot alcohol. The hexamine is obtained as hexamine itself and not as a hexamine hydrochloride.

On the other hand, the reaction of paraformaldehyde with ammonium nitrate in glacial acetic acid yielded hexamine in the form of its dinitrate, since no attempt was made to neutralize the nitric acid formed.

$$6CH_2O + 4NH_3 \cdot HNO_3 \longrightarrow (CH_2)6N_4 + 4HNO_3 + 6H_2O$$

If the reaction of formaldehyde with an ammonium salt to form hexamine is a general one, the equation can be written in the general form:

$$6CH_2O + 4NH_3 \cdot HX \longrightarrow (CH_2)_6N_4 + 4HX + 6H_2O$$

It was proposed, in this first part of the work, to determine whether this is really a general reaction, by investigating the possibility of preparing hexamine by reacting formaldehyde with numerous ammonium salts, in both aqueous and glacial acetic acid media. If possible, the hexamine or hexamine salt would be isolated and identified. Because of the similarity in solubility behaviour of hexamine and its salts and the various ammonium salts with which it occurs in these preparations, the isolation of the hexamine in pure form is extremely difficult. An example of this is the attempt to separate in pure form, hexamine dinitrate from ammonium nitrate.

If, in any experiment, hexamine can not be isolated, its presence in the reaction solution can be detected by the addition of mercuric chloride to a sample of the acidified solution. This results in the precipitation of an insoluble hexamine-mercuric chloride complex (41). The solution to be tested for hexamine must be acidified before adding the mercuric chloride, since compounds such as ammonia and methylamine also form a precipitate with mercuric chloride in neutral or alkaline solutions but not in acidic solutions. It has been reported by Dobriner (42) that hexamine and mercuric chloride form two complexes, $C_6H_{12}N_4 \cdot 6HgCl_2$ and $2C_6H_{12}N_4 \cdot 3HgCl_2$, the composition depending on the ratio of mercuric chloride to hexamine. An excess of mercuric chloride favours the formation of the complex, $C_6H_{12}N_4 \cdot 6HgCl_2$. The fact that the complex formed in a given test is actually due to hexamine, can be further checked by an analysis of the complex for formaldehyde and ammonia. In hexamine, the molar ratio of formaldehyde: ammonia is 1.5. Numerous other compounds, such as ammonia and methylamine, which can also form a precipitate with mercuric chloride, obviously can not fulfil the hexamine requirement of formaldehyde:ammonia::1.5:1.

Analysis of the Hexamine-Mercuric Chloride Complex

For the determination of the molar ratio, formaldehyde: ammonia in the complex, the following method was used.

A sample of the complex of about 1.0 gram was placed in a Kjeldahl flask. To this was added 100 ml. of 5 per cent sulphuric acid. This was distilled until only about 10 ml. remained in the flask. The distillation was made at such a rate that it required about one hour to reduce the volume to 10 ml. The distillate was collected in a 125-ml. Erlenmeyer flask containing exactly 50.0 ml. of potassium cyanide (0.1N).

When the distillation was completed, the cyanide solution was acidified by the addition of 6 ml. of concentrated hydrochloric acid. Bromine was added dropwise until a permanent yellow colour remained. The excess bromine was then removed by the addition of a few drops of 5 per cent aqueous phenol solution until the solution became clear. About 0.3 gram of potassium iodide was added, the flask tightly stoppered and allowed to stand for one-half hour. The unreacted potassium cyanide was then titrated using 0.1N sodium thiosulphate solution. No indicator is required, since the yellow iodine colour disappears sharply at the end point. The amount of potassium cyanide solution equivalent to formaldehyde equals the volume of potassium cyanide originally added (50.0 ml.), minus one-half the titer of 0.1N thiosulphate. One ml. of 0.1N potassium cyanide is equivalent to 0.003002 g. of formaldehyde. The cyanide solution must be standardized iodimetrically against thiosulphate. This determination of formaldehyde is based on Schulek's (43) variation of the well-known potassium cyanide method of Romijn (44).

The residue in the flask was allowed to cool and 125 ml. of water was added. This solution was made alkaline by the addition of 50 per cent sodium hydroxide. A further 20 ml. of 50 per cent sodium hydroxide was then added. The mercury in the solution was precipitated as mercurous sulphide by the addition of 20 ml. of 4 per cent sodium sulphide solution and this precipitate removed by filtration. It is necessary to precipitate the mercury to prevent the formation of ammonia-mercury complexes. The ammonia was distilled into 50.0 ml. of nitric acid (0.1N) and this was then back titrated with sodium hydroxide (0.1N) to give the number of moles of ammonia present in the complex.

In addition, it was found experimentally here that, if the precipitation of hexamine were made under constant conditions and using an excess of saturated aqueous mercuric chloride solution, the complex formed always had the same definite melting point, 214°-216°C., and was the same multiple of the weight of hexamine used in the test.

Detection of Hexamine

The method used to detect hexamine was based on the formation of a precipitate when 0.1 gram of hexamine was dissolved in 40 ml. of nitric acid (1.0N) and then 30 ml. of saturated aqueous mercuric chloride added. The reason for using the nitric acid was to ensure the neutralization of any free ammonia or amine in a sample being tested, since these compounds also form a precipitate with mercuric chloride in neutral or alkaline solutions. It was found that under these conditions, the precipitate formed had a weight about ten times that of the hexamine present. The melting point of this complex was 214°-216°C. and the molar formaldehyde:ammonia ratio, determined by the method described above, was 1.50 ± 0.03.

To test a given solution for the presence of hexamine, a 1-ml. sample was added to 40 ml. of nitric acid (1.0N) and then 30 ml. of saturated aqueous mercuric chloride solution added. If a precipitate formed, hexamine was not concluded to be present until the melting point and the formaldehyde: ammonia ratio of the complex had been determined and shown to be identical to those for pure hexamine.

In this part of the work, the objective was to isolate and identify hexamine from the reaction of formaldehyde with numerous ammonium salts in both aqueous and glacial acetic acid media. In any experiment in which the isolation of hexamine was not successful, the reaction solution was tested for the presence of hexamine by the mercuric chloride method described above.

The ammonium salts used in these experiments were: chloride, nitrate, sulphate, phosphate (dibasic), carbonate, oxalate, acetate and propionate. The following different experimental methods were used to attempt the isolation of hexamine from formaldehyde-ammonium salt reactions.

(1) Into a 250-ml. distillation flask containing 100 ml. of distilled water were placed 0.125 mole of the ammonium salt and 15 ml. (0.188 mole) of 38 per cent reagent-grade neutral formaldehyde solution. The solution was evaporated under reduced pressure at 50°C. until only a solid residue or thick paste remained. This was washed out of the flask with absolute alcohol and the mixture added to an evaporating dish containing about 20 grams of barium carbonate. After evaporation to dryness in a vacuum desiccator, a 5-gram sample of the solid material was warmed with 20 ml. of distilled water and the mixture filtered. This filtrate was tested for

the presence of hexamine by the mercuric chloride method. The remainder of the solid material was extracted with hot 95 per cent ethyl alcohol. The mixture was filtered and the filtrate evaporated to dryness. The residue was extracted with 30 ml. of boiling chloroform and the chloroform then removed on the steam bath. The reason for this chloroform extraction is that although alcohol serves to separate hexamine from numerous inorganic salts, some of these salts, such as ammonium nitrate, are partially soluble in alcohol. The product obtained was recrystallized from 95 per cent ethyl alcohol. The melting point of a mixture of this recrystallized product and pure hexamine was then determined.

By the above procedure, hexamine was isolated and identified when ammonium carbonate, acetate and propionate were used. The mercuric chloride method indicated the presence of some hexamine in all the reactions, although the amount was very small with ammonium nitrate, sulphate, chloride and phosphate (dibasic).

(2) To 0.125 mole of the ammonium salt dissolved in 100 ml. of distilled water, was added 15 ml. (0.188 mole) of 38 per cent reagent-grade neutral formaldehyde solution. Sufficient sodium bicarbonate was added with stirring to make the solution barely alkaline. The water was then removed by distillation under reduced pressure at 50°C. until only a white solid residue remained in the flask. This material was boiled with 50 ml. of absolute alcohol and the mixture filtered. The filtrate was evaporated to dryness. A sample of

the solid was dissolved in a little distilled water and this solution tested for the presence of hexamine by the mercuric chloride method. The remainder of the solid residue was boiled with 30 ml. of chloroform and the mixture filtered. The filtrate was evaporated to dryness. The solid material thus obtained was recrystallized from a minimum amount of 95 per cent ethyl alcohol. The melting point of this crystalline product and also the melting point of a mixture of this material and pure hexamine were determined.

By this method, hexamine was isolated and identified in the reaction of formaldehyde with ammonium acetate, propionate, carbonate, chloride, nitrate, sulphate and phosphate. The results with ammonium benzoate were inconclusive. The mercuric chloride method indicated the presence of hexamine in all the reactions.

(3) To 0.125 mole of the ammonium salt dissolved in 100 ml. of distilled water, was added 15 ml. (0.188 mole) of 38 per cent reagent-grade neutral formaldehyde solution. This solution was added to a 500-ml. distillation flask containing 25 grams of barium carbonate. The solution was then distilled under reduced pressure until only a white solid remained. This residue in the flask was boiled with 50 ml. of absolute alcohol and the mixture filtered. The filtrate was evaporated to dryness. A sample of the solid was dissolved in a little distilled water and this solution tested for the presence of hexamine by the mercuric chloride method. The remainder of the solid was boiled with 30 ml. of chloroform and the mixture

filtered. The filtrate was evaporated to dryness. The residue was recrystallized from 95 per cent ethyl alcohol. The melting point of this recrystallized material and also the melting point of a mixture of this product and pure hexamine were determined.

Hexamine was isolated and identified from the reaction of formaldehyde with all the ammonium salts tested. The mercuric chloride method confirmed the formation of hexamine in all these reactions.

(4) To a 500-ml. distillation flask containing 150 ml. of glacial acetic acid, were added 0.125 mole of the ammonium salt and 5.64 g. (0.188 mole) of paraformaldehyde. The flask was heated until solution was attained. The glacial acetic acid was then removed by distillation under reduced pressure at 50° C. Distillation was continued until only a white solid residue or a thick paste (with the ammonium salt of a non-volatile acid) remained. The contents of the flask was washed out with 95 per cent alcohol into an evaporating dish containing about 25 g. of sodium bicarbonate. The 95 per cent alcohol was removed by evaporation to dryness in a vacuum desiccator. The solid residue was extracted with two 40-ml. portions of hot 95 per cent ethyl alcohol. After this mixture had been filtered, the filtrate was evaporated to dryness on a steam bath. Sufficient distilled water was added to dissolve all the residue. The pH of the solution was then adjusted to 7.0 - 7.3 by the addition of saturated sodium bicarbonate

solution. The reason for this step was that it was found that either considerable acid remained adsorbed on the solid material or strongly acidic salts were present. After the solution had been rendered neutral or faintly alkaline, it was again evaporated to dryness in a vacuum desiccator. A sample of this solid residue was dissolved in a little distilled water and this solution tested for the presence of hexamine by the mercuric chloride method. The remainder of the solid material was boiled with 25 ml. of absolute ethyl alcohol and the mixture filtered. Hexamine, being fairly soluble in hot alcohol, is thus separated from the inorganic salts. The filtrate was evaporated to dryness on a steam bath. The melting point of the product and the melting point of a mixture of this product and pure hexamine were determined.

By means of the mercuric chloride method, the presence of hexamine was demonstrated in all the residues remaining after the removal of the glacial acetic acid by distillation under reduced pressure. Hexamine was also detected after evaporation of the aqueous solution. The actual yield of hexamine, however, appeared to be very small except with ammonium acetate, carbonate and propionate.

Hexamine was isolated and identified readily from the reaction of paraformaldehyde with ammonium carbonate, acetate and propionate. With the other ammonium salts, material tentatively identified as impure hexamine was obtained but a conclusive isolation was not attained.

(5) To a 500-ml. distillation flask containing 150 ml. of glacial acetic acid, were added 0.125 mole of the ammonium salt and 5.64 g. (0.188 mole) of paraformaldehyde. The solution was distilled under reduced pressure at 50°C. until only about 20 ml. remained. An excess of barium carbonate was added to the flask and the contents then dried under reduced pressure at 50°C. The material was extracted three times with 30-ml. portions of hot 95 per cent ethyl alcohol. After filtration, the combined filtrates were evaporated to dryness. This residue was dissolved in a minimum of distilled water and neutralized with sodium bicarbonate. The solution was then evaporated to dryness. The residue was extracted with chloroform and the chloroform then removed by heating on a steam bath. The solid material remaining was boiled with 25 ml. of absolute alcohol and the mixture filtered. This filtrate was evaporated to dryness in a vacuum desiccator. The melting point and the melting point of a mixture of these crystals and pure hexamine were determined. A sample of these crystals was dissolved in about 5 ml. of distilled water and this solution tested for hexamine by the mercuric chloride method.

After following the above procedure, it was shown, by the use of mercuric chloride, that hexamine was formed in all of the paraformaldehyde-ammonium salt reactions investigated. A qualitative observation indicated that the hexamine yield by this method was considerably larger than that obtained by the previous method in which distillation was continued directly to dryness.

Hexamine was isolated and identified in all cases. The actual quantities obtained, however, were very small.

Since it has been shown that hexamine is formed in the reaction of formaldehyde with ammonium nitrate in both aqueous and glacial acetic acid media, it was decided to investigate whether hexamine was also formed in the reaction of formaldehyde with substituted ammonium nitrates such as monomethylammonium nitrate, dimethylammonium nitrate and trimethylammonium nitrate.

Thirty ml. (0.375 mole) of neutral reagent-grade formaldehyde solution (38 per cent) was added to 23.5 g. (0.25 mole) of monomethylammonium nitrate dissolved in 70 ml. of distilled water. This solution was allowed to stand for twenty-four hours and then a sample added to mercuric chloride solution. No precipitate was formed. The solution was then distilled under reduced pressure at 50°C. until only a thick syrup remained. This also failed to give a precipitate with mercuric chloride.

When tested in a similar manner, the other methyl-substituted ammonium nitrates also failed to yield any detectable hexamine.

To summarize these results, hexamine was isolated from the aqueous reactions of formaldehyde with nine different ammonium salts. The isolation of the hexamine was readily accomplished with ammonium carbonate, acetate and propionate by removal of the liquid by distillation under reduced pressure. The solid product remaining in the flask was shown to be almost pure hexamine. With the ammonium salt of a strong acid, distillation to dryness resulted in almost no hexamine being left in the flask. For example, in the aqueous formaldehyde-ammonium chloride solution, the presence of an appreciable amount of hexamine in the solution before distillation was demonstrated by means of mercuric chloride.

$$6CH_2O + 4NH_4Cl \longrightarrow (CH_2)_6N_4 + 4HCl + 6H_2O$$

Distillation of the solution evidently resulted in a destruction of the hexamine, probably by acid hydrolysis as the solution became more and more concentrated by the continual removal of the solvent.

$$(CH_2)_6N_4 + 4HCl + 6H_2O \longrightarrow 6CH_2O + 4NH_4Cl$$

This hexamine loss was overcome when the formaldehyde-ammonium salt reaction took place in the presence of an excess of sodium bicarbonate or barium carbonate. Hexamine was readily isolated by evaporating these solutions to dryness. The hexamine was removed from the solid residue by extraction with hot 95 per cent ethyl alcohol.

The results obtained in glacial acetic acid were analogous to those in aqueous solution. By means of the mercuric chloride method, hexamine was shown to be present in all the paraformaldehyde-ammonium salt solutions. When the solution was distilled to dryness, hexamine was obtained in good yield with ammonium carbonate, acetate and propionate. As in aqueous solution, however, this procedure was not successful when the ammonium salt of a strong acid was used. On the other hand, hexamine was isolated when the last quarter of the distillation was carried out in the presence of barium carbonate.

Furthermore, it has been shown that when a sample of an aqueous formaldehyde-ammonium salt solution or a glacial acetic acid solution of paraformaldehyde and an ammonium salt was added to an excess of mercuric chloride solution, an insoluble complex was formed. This complex had the same melting point, 214°-216°C., and the same molar formaldehyde-ammonia ratio as the complex formed between mercuric chloride and pure hexamine. Hence, either hexamine does actually exist in a formaldehyde-ammonium salt solution contrary to the view of Werner (36), who believed that methyleneimine was the true reaction product, or, hexamine, when in solution, is in equilibrium with some other structure. In this event, the characteristic mercuric chloride complex might be formed with this other structure or with methyleneimine itself. However, only in a complex of the type $(CH_2)_6N_4 \cdot 6HgCl_2$ is the molar formaldehyde:ammonia ratio 1.50. Actual analysis of the complex formed in these experiments showed this ratio to be 1.50 ± 0.03. In methyleneimine, $CH_2{=}NH$, or the postulated trimethylenetriamine intermediate of Baur and Ruetschi (23), the molar formaldehyde: ammonia ratio is seen to be 1.0. Thus, apparently, hexamine does actually exist in formaldehyde-ammonium salt solutions.

RATE OF HEXAMINE FORMATION

In the preceding experiments, the formation of a complex with mercuric chloride was used as a qualitative indication of the presence of hexamine in a solution. The formation of this complex has also been used for the quantitative estimation of hexamine by Hale (45) and by Garmaise (46), while Boyd (32) studied the rate of hexamine formation in aqueous formaldehyde-ammonia solutions by precipitation of the hexamine after given time intervals by the addition of mercuric chloride solution. The weight of hexamine was determined from a calibration curve between given weights of hexamine and the corresponding weight of the hexamine-mercuric chloride complex.

In the present work a study has been made of the rate of hexamine formation in aqueous solutions of formaldehyde with numerous ammonium salts.

Hexamine Analysis

To analyze the solutions for their hexamine content, a 1-ml. sample was added to 40 ml. of N/1 nitric acid and then 30 ml. of a saturated aqueous mercuric chloride solution was added. The precipitate was allowed to stand for one-half hour and was then collected on a tared, fine sintered-glass crucible. The precipitate was washed with 3 ml. of 3 per cent mercuric chloride solution (about 50 per cent saturated), since washing with water caused the fine precipitate to pass through the filter. The crucibles were dried for one hour in an oven at 100°C., allowed to cool, and then weighed. The hexamine content of this 1-ml. sample was determined from a hexamine-complex calibration curve which was established under these analytical conditions. The total hexamine content of the solution was then obtained by multiplying this value by the total volume of the formaldehyde-ammonium salt solution. The calibration curve determined for these analytical conditions is shown in Fig.1, the data for this curve being given in Table I. Also shown in Fig.1, for comparison, is the curve obtained when the hexamine was precipitated from distilled water instead of from 1.0N nitric acid.

Table I

Calibration Data for the Analysis of Hexamine

Weight of Hexamine (grams)	Weight of Complex (grams)
0.0264	0.2104
0.0350	0.3014
0.0516	0.4955
0.0632	0.6102
0.0782	0.7900
0.0907	0.9315

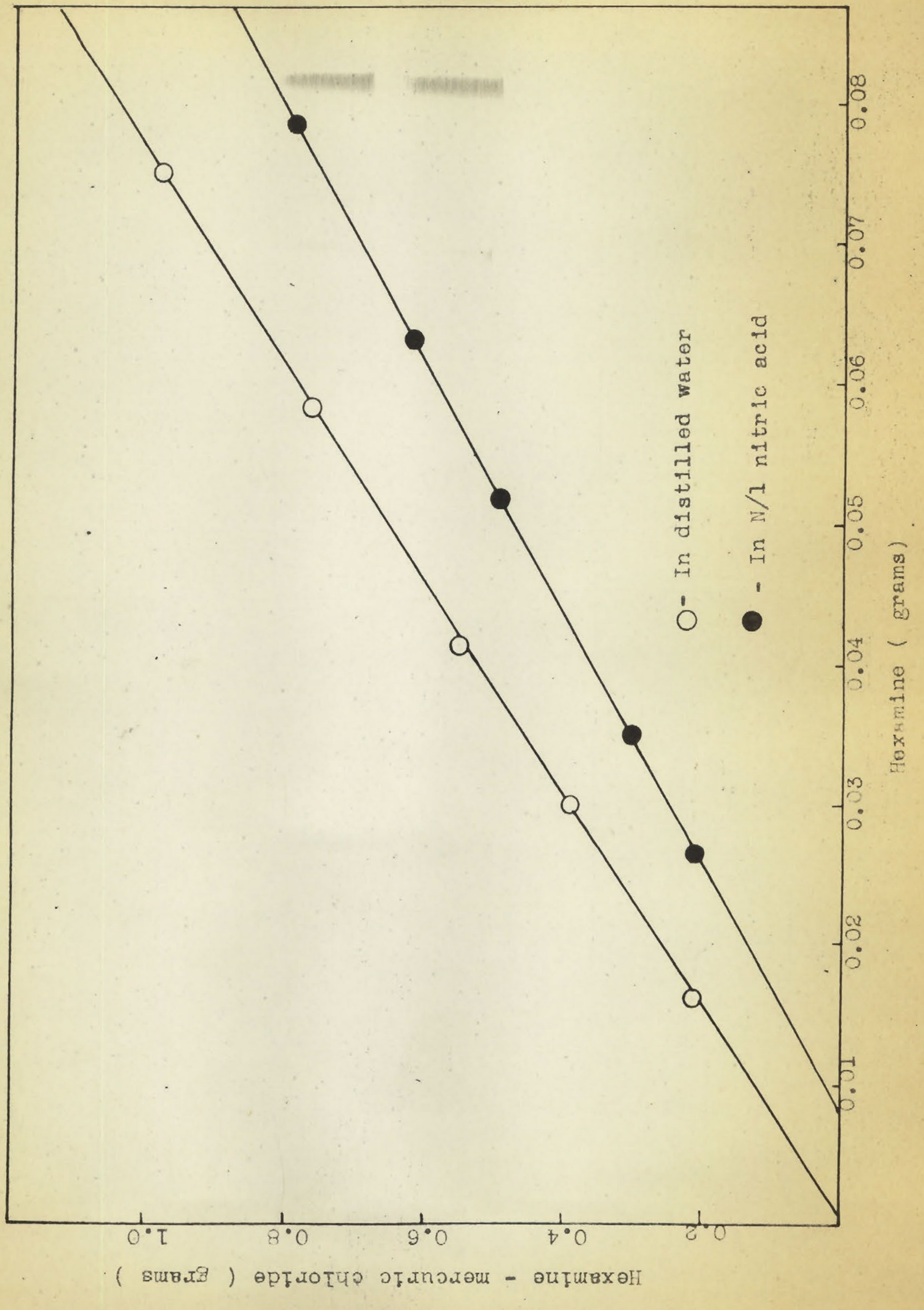
The precision of the hexamine values is within ± 1.5 per cent.

In the first series of experiments made, the molar ratio of formaldehyde:ammonia (as an ammonium salt) was 1.5, the ratio required by the equation (henceforth designated the theoretical ratio).

$$6CH_2O + 4NH_3 \cdot HX \longrightarrow (CH_2)_6N_4 + 6H_2O + 4HX$$

Fig.1

Calibration curve for the analysis of hexamine



The formaldehyde used in these experiments was added in the form of reagent-grade neutral formaldehyde solution (37.2 per cent by analysis).

To illustrate the procedure, a typical experiment is described below.

One-quarter (0.25) equivalent of the ammonium salt was dissolved in a minimum of distilled water and the volume then made to 70 ml. This solution was placed in a 125-ml. Erlenmeyer flask which was suspended in a water bath at 25°C. Thirty ml. (0.375 mole) of the formaldehyde solution was placed in a 125-ml. Erlenmeyer flask, also suspended in the water bath. When the temperature of both solutions became constant at 25°C., the formaldehyde solution was poured quickly into the ammonium salt solution and the time noted. The final solution was thus 2.5N with respect to the ammonium salt and 3.75N with respect to formaldehyde (molar ratio formaldehyde:ammonia::1.5:1). At different times, 1-ml. samples of the solution were analyzed for their hexamine content by the method described above, and the total hexamine content of the solution calculated after different time intervals. A graph was then plotted between time and hexamine formation.

The rate of hexamine formation from formaldehyde with a series of ammonium salts was investigated by this procedure. The effect of varying the formaldehyde:ammonium salt ratio on the rate of hexamine formation was also investigated. Using the method described above, the formaldehyde concentration was doubled in one series of experiments (mole ratio formaldehyde: ammonia::3:1), while in another series, the ammonium salt concentration was doubled (mole ratio formaldehyde:ammonia::1.5:2). The results are shown in Tables II - XIV and Figs. 2 - 5. In the tables, the ammonia concentrations are expressed in terms of the available ammonia (present as an ammonium salt).

Table II

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Chloride Solution

Mole ratio formaldehyde:available ammonia::1.5:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
9	0.57	6.5
20	0.67	7.7
40	0.97	11.1
60	1.13	12.9
100	1.42	16.2
150	1.82	20.8
200	1.94	22.2
360	2.32	26.5
420	2.34	26.7
600	2.39	27.3
1440	2.43	27.8

Table III

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Sulphate Solution

Mole ratio formaldehyde:available ammonia::1.5:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
2	0.65	7.4
5	0.67	7.7
10	0.95	10.9
20	1.42	16.2
30	1.94	22.2
50	2.30	26.3
70	2.68	30.6
110	3.40	38.9
160	3.97	45.4
210	4.25	48.6
240	4.54	51.9
315	4.70	53.7
450	5.06	57.9
1440	5.18	59.2

Table IV

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Nitrate Solution

Mole ratio formaldehyde:available ammonia::1.5:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
15	0.57	6.5
25	0.81	9.3
40	0.97	11.1
60	1.10	12.6
80	1.22	14.0
110	1.35	15.4
140	1.49	17.0
180	1.62	18.5
240	1.89	21.6
300	2.19	25.1
375	2.47	28.2
500	2.56	29.3
600	2.64	30.2
1440	2.68	30.7

Table V

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Acetate Solution

Mole ratio formaldehyde:available ammonia::1.5:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	(per cent)
2	7.16	81.9
5	7.65	87.4
15	7.89	90.2
30	7.94	90.7
120	7.87	90.0
240	7.85	89.7
480	7.90	90.3

Table VI

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Oxalate Solution

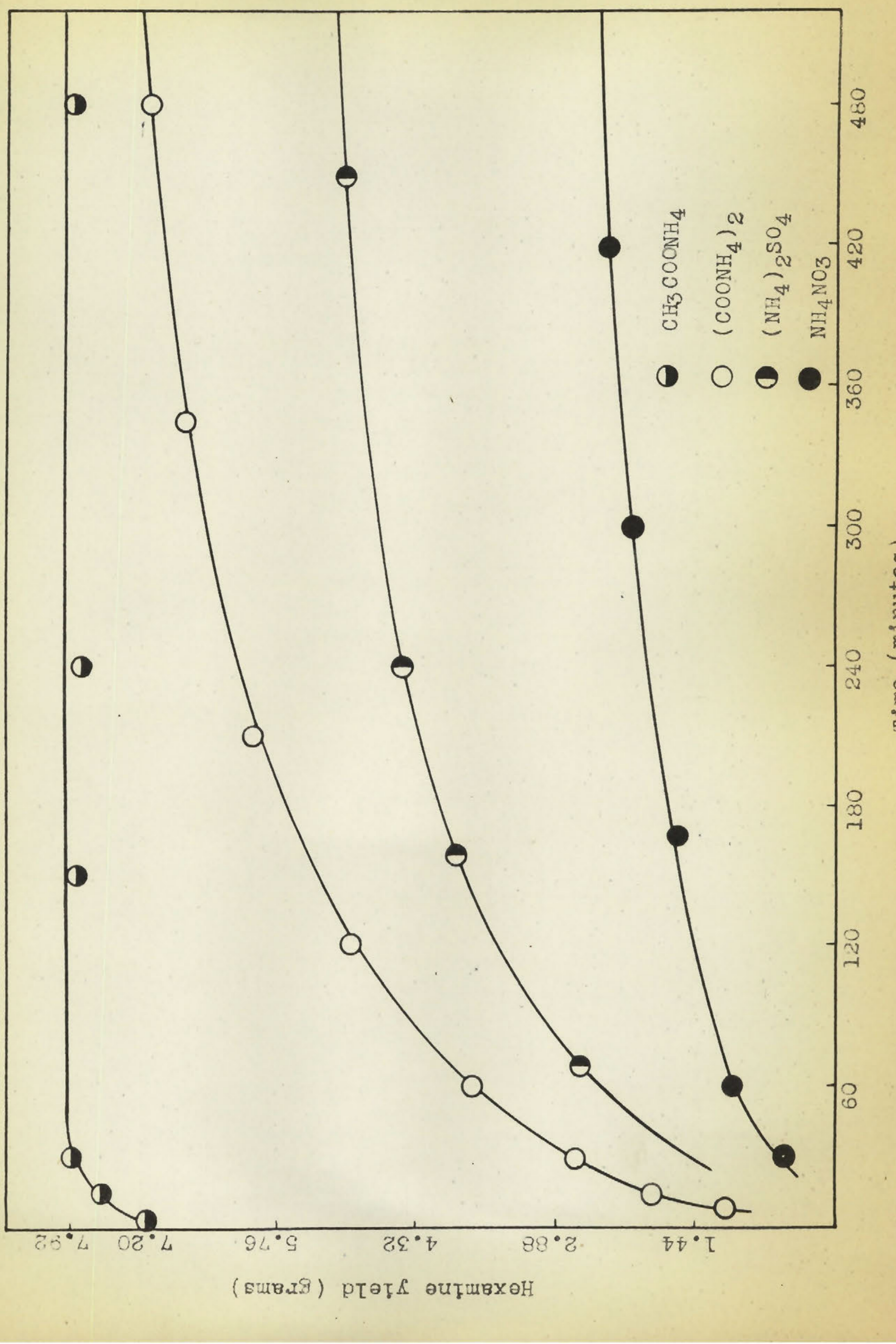
Mole ratio formaldehyde:available ammonia::1.5:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	(per cent)
6	1.17	13.4
15	1.91	21.9
60	3.77	43.1
210	6.02	68.9
480	7.12	81.4

Fig.2

Rate of hexamine formation with different ammonium salts



The theoretical yield of hexamine in these experiments is 8.75 grams. Since both the formaldehyde and the ammonium salt are present in the proportions required by the theoretical ratio, the theoretical yield can be calculated on the basis of either the formaldehyde or the ammonium salt.

From Fig.2 it can be seen that both the rate of hexamine formation and the total hexamine yield vary with the different ammonium salts. The rate is slowest and the yield smallest (about 30 per cent) with the ammonium salt of a strong acid, such as ammonium nitrate. The rate is fastest and the yield largest (about 90 per cent) with the ammonium salt of a weak acid, such as ammonium acetate.

The effect of the relative concentrations of the reactants was next investigated in a series of experiments in which the formaldehyde concentration was doubled (formaldehyde:ammonium salt ratio 7.50N:2.50N, mole ratio formaldehyde:available ammonia::3:1). The results are shown in Tables VII - X.

Table VII

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Acetate Solution

Mole ratio formaldehyde:available ammonia::3:1

Temperature 25°C.

Time (minutes)	Hexamine Yield	
	(grams)	(per cent)
3	8.33	95.2
6	8.57	97.9
30	8.62	98.5
210	8.66	99.0

Table VIII

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Chloride Solution

Mole ratio formaldehyde:available ammonia::3:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	 (per cent)
20	1.19	13.6
60	2.05	23.4
90	2.59	29.6
150	3.19	36.5
210	3.51	40.1
390	4.32	49.4
540	4.70	53.7
1440	4.81	55.0

Table IX

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Sulphate Solution

Mole ratio formaldehyde:available ammonia::3:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	 (per cent)
9	1.40	16.0
40	3.00	34.0
80	3.89	44.5
210	5.13	58.6
390	6.00	68.6
540	7.08	80.9
1440	7.13	81.5

Table X

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Nitrate Solution

Mole ratio formaldehyde:available ammonia::3:1

Temperature 25°C.

Time (minutes)	Hexamine Yield	
	(grams)	(per cent)
6	0.61	7.0
17	1.13	12.9
50	1.78	20.3
90	1.94	22.2
150	2.77	31.8
210	2.97	33.6
390	3.83	43.7
540	4.10	46.9
1440	4.27	48.9

Experiments were also made in which the concentration of the ammonium salt was doubled, so that the formaldehyde: ammonium salt ratio in these experiments was 3.75N:5.0N (mole ratio formaldehyde:available ammonia::1.5:2). The results are shown in Tables XI - XIV.

Table XI

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Sulphate Solution

Mole ratio formaldehyde:available ammonia::1.5:2

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
4	1.21	13.8
30	3.02	34.5
50	3.65	41.7
120	4.86	55.5
210	5.40	61.7
310	5.75	65.7
480	5.81	66.4
600	5.83	66.7

Table XII

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Chloride Solution

Mole ratio formaldehyde:available ammonia::1.5:2

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
30	0.81	9.3
60	2.21	25.3
120	2.57	29.4
210	2.89	33.1
480	3.11	35.5
600	3.06	35.0

Table XIII

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Nitrate Solution

Mole ratio formaldehyde:available ammonia::1.5:2

Temperature 25°C.

Time (minutes)	Hexamine Yield	
	(grams)	(per cent)
21	0.87	10.0
50	1.88	21.5
80	2.16	24.7
120	2.46	28.1
210	2.97	34.0
360	2.99	34.2
600	3.06	35.0
1440	3.04	34.7

Table XIV

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Acetate Solution

Mole ratio formaldehyde:available ammonia::1.5:2

Temperature 25°C.

Time (minutes)	Hexamine Yield	
	(grams)	(per cent)
2	6.93	79.2
15	7.96	91.0
30	8.05	92.0
45	8.24	94.2
75	8.19	93.6
210	8.21	93.8

Fig.3

Rate of hexamine formation at 25°C. in formaldehyde-ammonium nitrate solutions

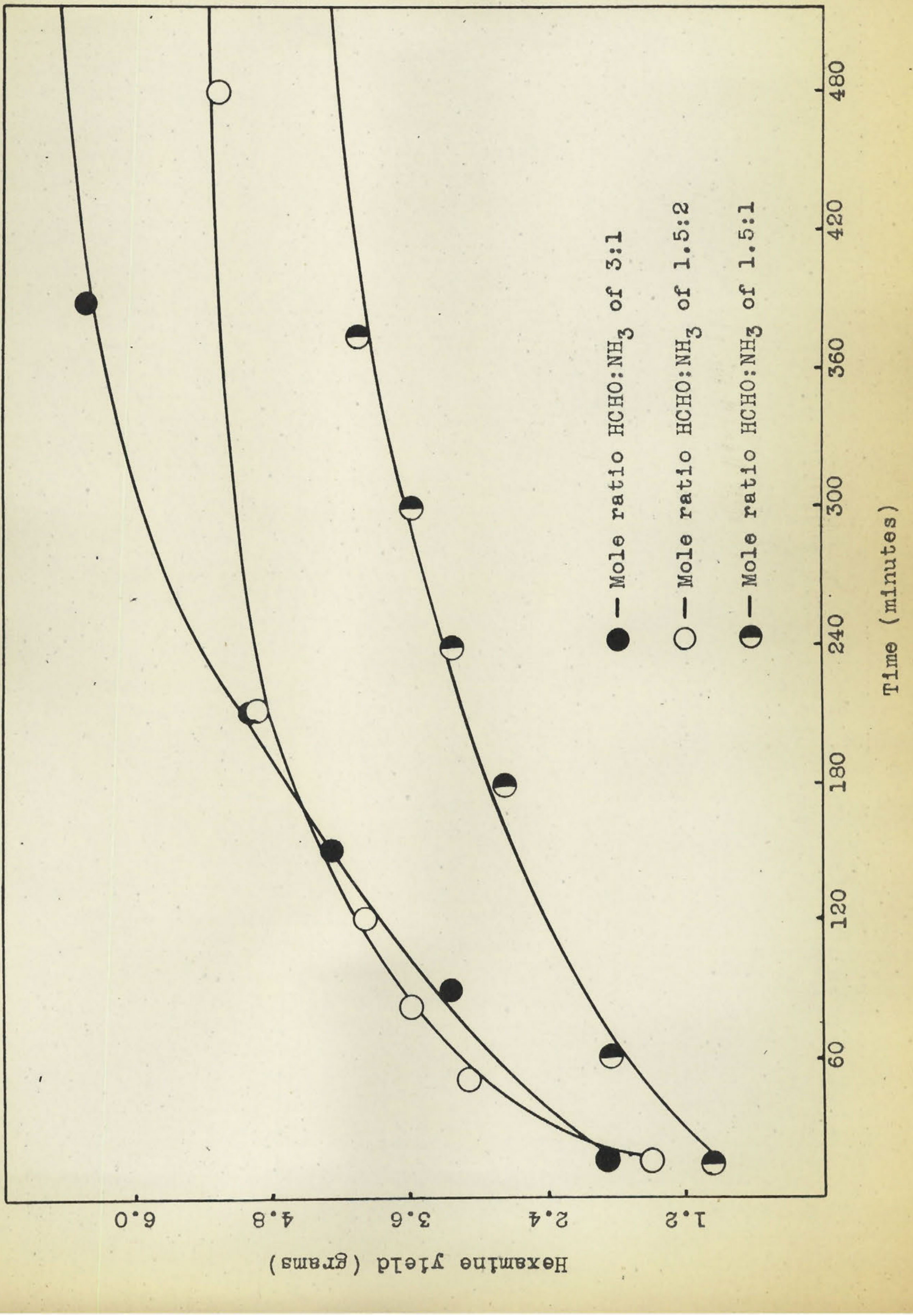


Fig.4

Rate of hexamine formation at 25°C. in formaldehyde-ammonium sulphate solutions

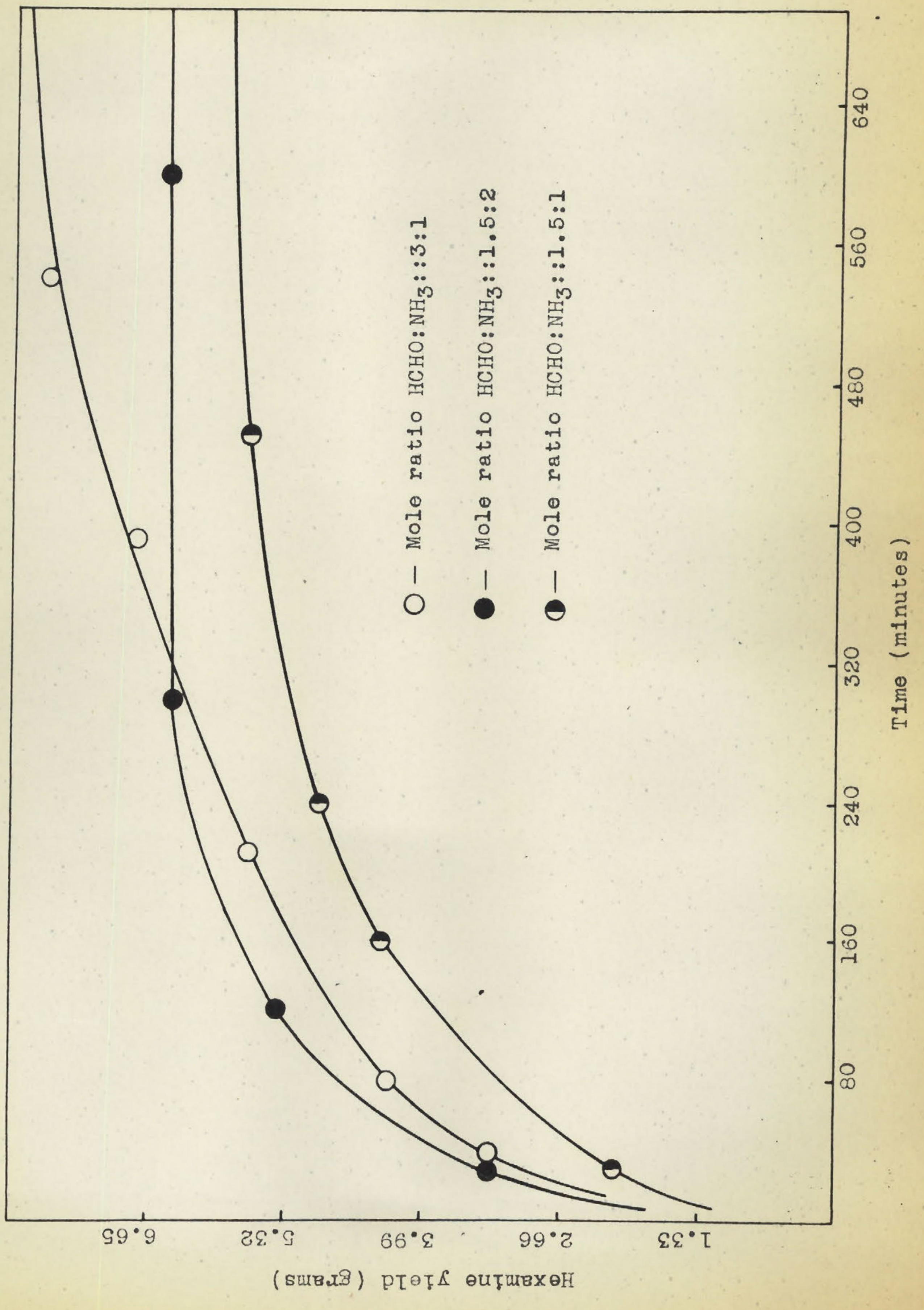
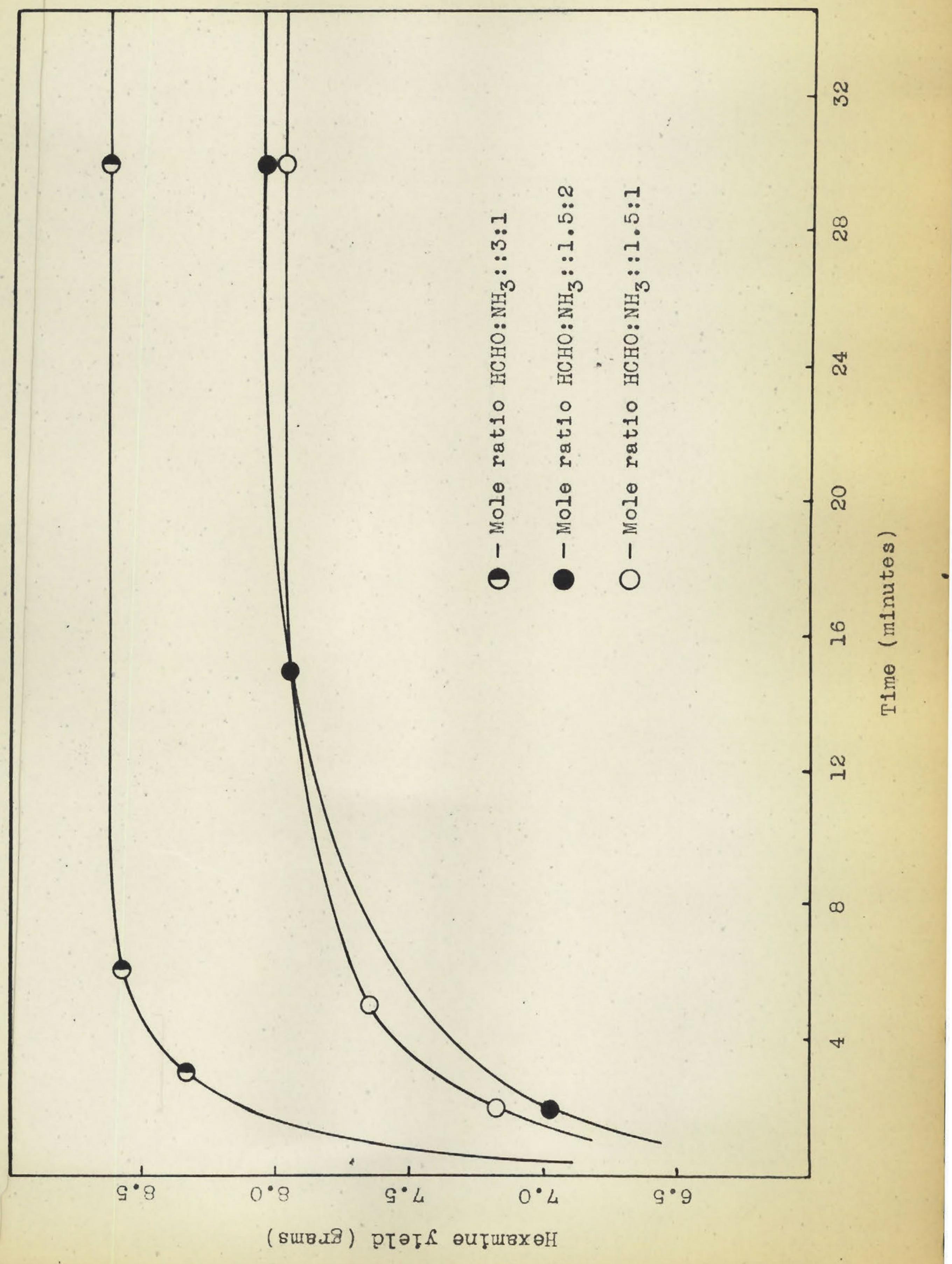


Fig.5

Rate of hexamine formation at 25°C. in formaldehyde-ammonium acetate solutions



While Fig.2 shows how the rate of hexamine formation and the final yield vary with different ammonium salts, Figs. 3, 4 and 5 show the effect of doubling the formaldehyde or ammonium salt concentration on the rate with a given ammonium salt. Both the rate of hexamine formation and the final yield are increased by an increase in either the formaldehyde or ammonium salt concentration beyond the theoretical ratio. Doubling the formaldehyde concentration is seen to result in an initial rate closely similar to that obtained by doubling the ammonium salt concentration, but the hexamine yield is increased.

In the experiments described above, the rate of hexamine formation was studied in relatively concentrated aqueous formaldehyde-ammonium salt solutions. More reliable kinetic data were obtained by using solutions 0.5N in ammonia and 0.75N in formaldehyde, retaining a molar ratio formaldehyde: ammonia of 1.5, with a theoretical yield of hexamine of 2.62 grams based on either the formaldehyde or the ammonium salt. The experimental technique was similar in essential respects to that described previously. The results are shown in Tables XV - XX and Fig.6.

Table XV

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Oxalate Solution

Mole ratio formaldehyde:available ammonia::1.5:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
6	1.65	62.9
22	1.72	65.6
55	1.87	71.3
90	2.13	81.3
150	2.25	86.0
240	2.47	94.3
450	2.52	96.2
700	2.50	95.4

Table XVI

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Sulphate Solution

Mole ratio formaldehyde:available ammonia::1.5:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
30	0.45	17.2
120	0.61	23.3
180	0.63	24.1
240	0.64	24.4
360	0.65	24.8
450	0.69	26.3
570	0.72	27.5

Table XVII

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Chloride Solution

Mole ratio formaldehyde:available ammonia::1.5:1

Temperature 25°C.

Time (minutes)	Hexamine Yield	
	(grams)	(per cent)
25	0.32	12.2
90	0.37	14.1
150	0.41	15.6
240	0.44	16.8
360	0.46	17.6
450	0.47	17.9
570	0.47	17.9
700	0.47	17.9

Table XVIII

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Nitrate Solution

Mole ratio formaldehyde:available ammonia::1.5:1

Temperature 25°C.

Time (minutes)	Hexamine Yield	
	(grams)	(per cent)
25	0.32	12.2
90	0.36	13.7
150	0.39	14.9
240	0.42	16.0
360	0.44	16.8
570	0.45	17.1
700	0.46	17.6

Table XIX

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Acetate Solution

Mole ratio formaldehyde:available ammonia::1.5:1

Temperature 25°C.

Time (minutes)	Hexamine Yield	
	(grams)	(per cent)
2	1.30	49.6
10	2.34	89.3
15	2.40	91.6
25	2.50	95.4
40	2.59	98.8
120	2.61	99.6
240	2.61	99.6

Table XX

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Phosphate (dibasic) Solution

Mole ratio formaldehyde:available ammonia::1.5:1

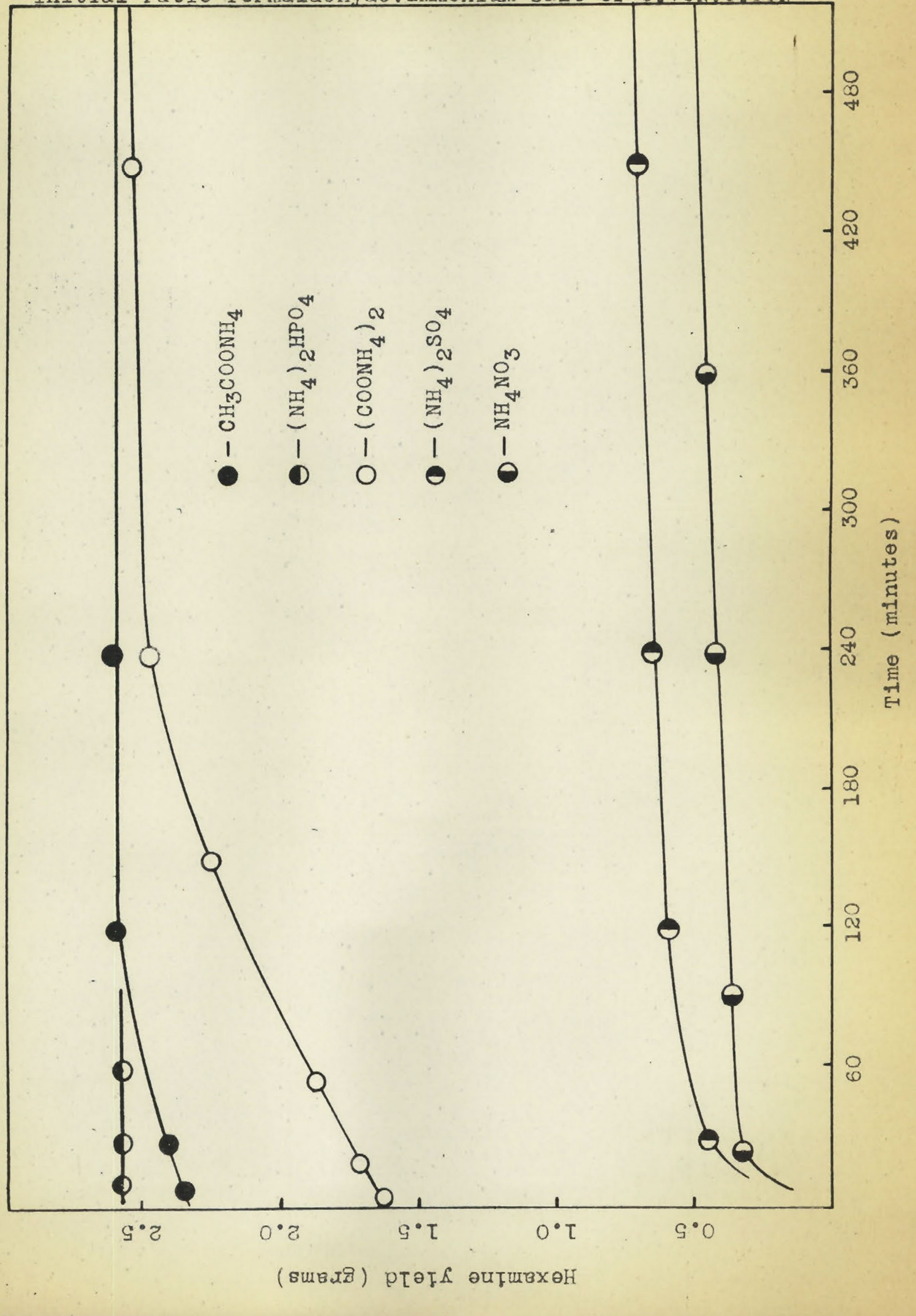
Temperature 25°C.

Time (minutes)	Hexamine Yield	
	(grams)	(per cent)
4	2.49	95.0
11	2.59	98.8
16	2.59	98.8
30	2.58	98.5
45	2.58	98.5
60	2.58	98.5
120	2.58	98.5

Fig.6

Rate of hexamine formation at 25°C. in formaldehyde-ammonium salt solutions

Initial ratio formaldehyde:ammonium salt of 0.75N:0.50N



The results from Tables XIV - XX are shown in Fig.6. As was observed with concentrated aqueous formaldehyde-ammonium salt solutions, Fig.2 (p.43), here also the rate of hexamine formation and the final yield vary with different ammonium salts.

This series of experiments was repeated, but in this new series, the formaldehyde concentration was doubled. The formaldehyde:ammonium salt ratio in this series was 1.50N:0.50N (mole ratio formaldehyde:available ammonia::3:1). The results are shown in Tables XXI - XXVI.

Table XXI

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Oxalate Solution

Mole ratio formaldehyde:available ammonia::3:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
3	1.42	54.2
10	1.57	60.0
15	1.92	73.3
25	2.11	80.5
40	2.26	86.2
60	2.47	94.3
150	2.60	99.2
390	2.60	99.2

Table XXII

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Sulphate Solution

Mole ratio formaldehyde:available ammonia::3:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
20	0.43	16.4
60	0.62	23.7
120	0.73	28.0
180	0.76	29.0
240	0.83	31.7
390	0.98	37.4
510	0.99	37.8

Table XXIII

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Phosphate (dibasic) Solution

Mole ratio formaldehyde:available ammonia::3:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
0.5	2.25	86.0
1	2.41	92.0
2	2.58	98.5
4	2.60	99.2
10	2.61	99.6
60	2.60	99.2

Table XXIV

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Acetate Solution

Mole ratio formaldehyde:available ammonia::3:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
0.5	1.15	43.9
1.5	1.74	66.4
3	2.10	80.1
6	2.58	98.5
10	2.60	99.2
60	2.60	99.2
120	2.60	99.2

Table XXV

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Nitrate Solution

Mole ratio formaldehyde:available ammonia::3:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
30	0.30	11.4
60	0.37	14.1
120	0.42	16.0
180	0.48	18.3
240	0.53	20.2
510	0.57	21.7

Table XXVI

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Chloride Solution

Mole ratio formaldehyde:available ammonia::3:1

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
30	0.33	12.6
60	0.37	14.1
120	0.46	17.5
180	0.49	18.7
240	0.54	20.6
390	0.56	21.4
510	0.58	22.1

This series of experiments was repeated, but this time the concentration of the ammonium salt was doubled. These solutions were thus 1.0N with respect to the ammonium salt and 0.75N with respect to the formaldehyde. The results are shown in Tables XXVII - XXXII.

Table XXVII

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Chloride Solution

Mole ratio formaldehyde:available ammonia::1.5:2

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
40	0.33	12.6
60	0.35	13.4
90	0.37	14.1
150	0.42	16.0
240	0.48	18.3
450	0.50	19.1
540	0.53	20.2

Table XXVIII

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Nitrate Solution

Mole ratio formaldehyde:available ammonia::1.5:2

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
40	0.32	12.2
60	0.35	13.4
90	0.37	14.1
150	0.39	14.9
240	0.46	17.5
300	0.47	18.0
540	0.50	19.1

Table XXIX

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Sulphate Solution

Mole ratio formaldehyde:available ammonia::1.5:2

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
20	0.44	16.8
40	0.49	18.7
60	0.56	21.4
90	0.64	24.4
120	0.73	28.0
240	0.77	29.4
300	0.82	31.3
540	0.87	33.2

Table XXX

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Oxalate Solution

Mole ratio formaldehyde:available ammonia::1.5:2.

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
6	1.16	44.3
25	1.80	68.7
60	2.24	85.5
120	2.42	92.4
210	2.50	95.4
540	2.52	96.2

Table XXXI

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Acetate Solution

Mole ratio formaldehyde:available ammonia::1.5:2

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
1	1.02	38.9
4	1.80	68.7
11	2.05	78.2
17	2.30	87.8
30	2.50	95.4
60	2.61	99.6
90	2.61	99.6

Table XXXII

Rate of Hexamine Formation in Aqueous Formaldehyde-Ammonium Phosphate (dibasic) Solution

Mole ratio formaldehyde:available ammonia::1.5:2

Temperature 25°C.

Time (minutes)	Hexamine Yield (grams)	Hexamine Yield (per cent)
1	2.17	82.8
3	2.35	89.7
10	2.47	94.3
15	2.55	97.3
60	2.61	99.6
90	2.62	100.0

Fig.7

Rate of hexamine formation at 25°C. in dilute formaldehyde-ammonium nitrate solutions

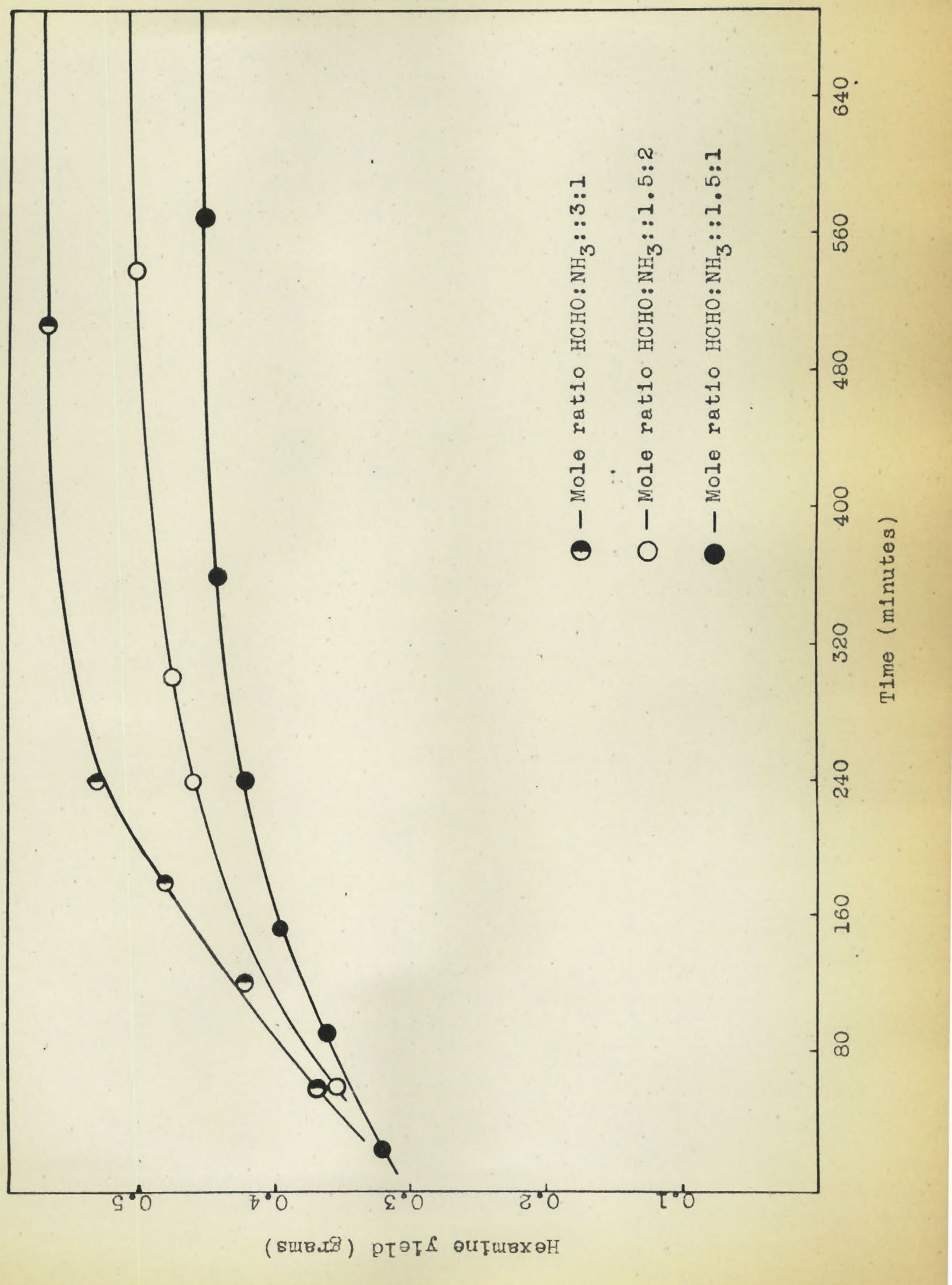


Fig.8

Rate of hexamine formation at 25°C. in dilute formaldehyde-ammonium oxalate solutions

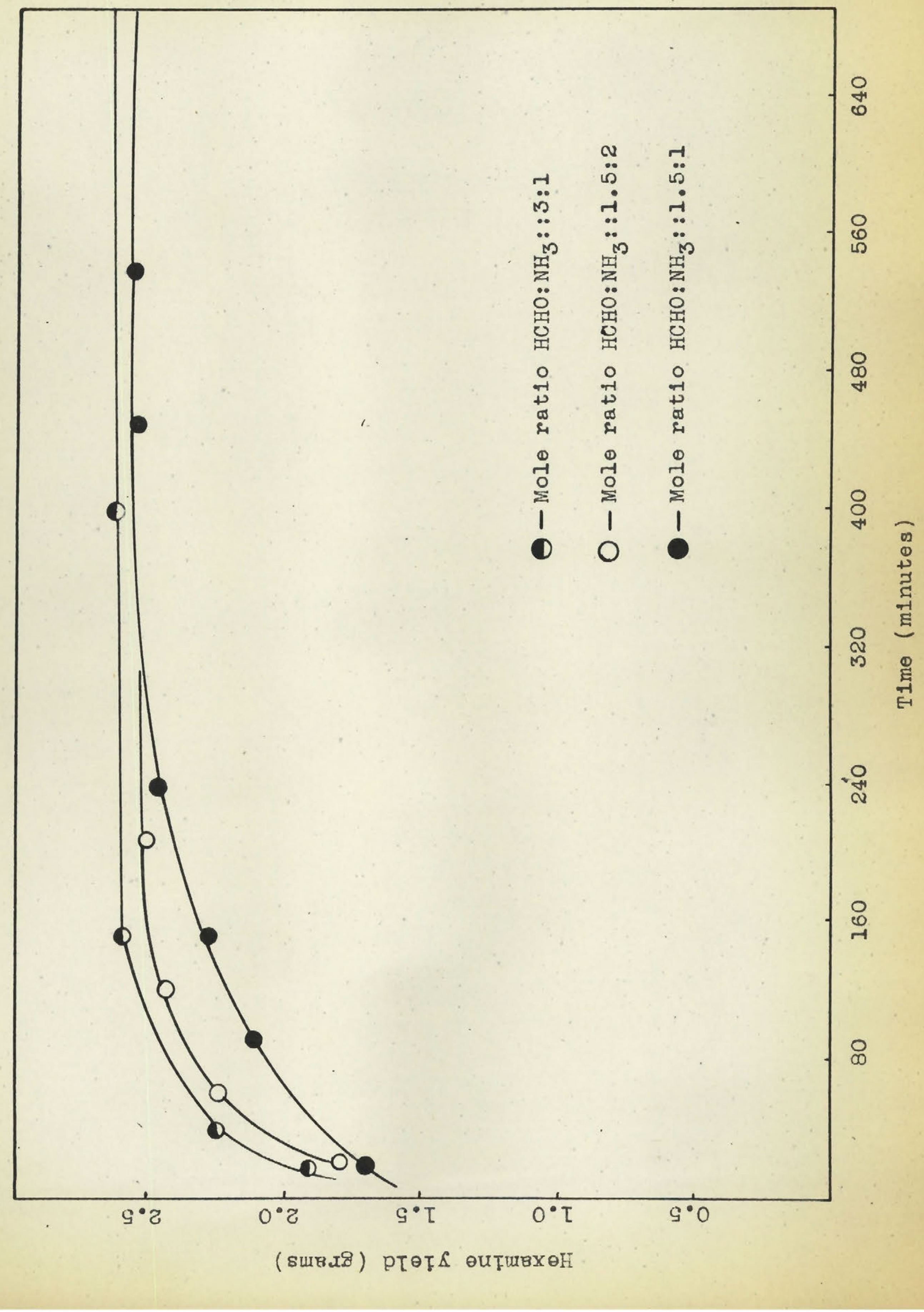
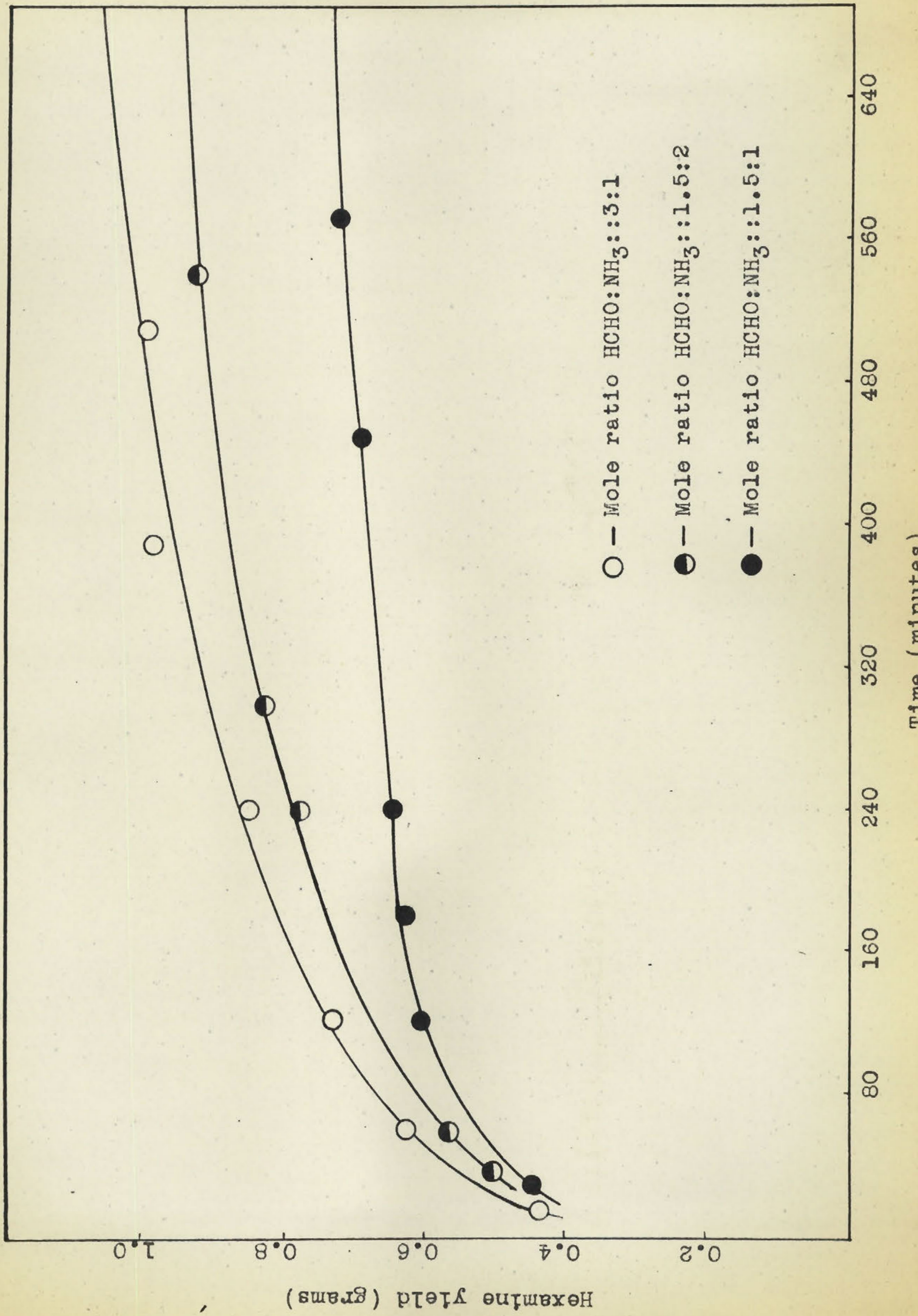


Fig.9

Rate of hexamine formation at 25°C. in dilute formaldehyde-ammonium sulphate solutions



In Fig.6 (p.56) are shown the rate curves of hexamine formation in dilute aqueous formaldehyde-ammonium salt solutions. In Figs. 7,8 and 9 is shown the effect of doubling the formaldehyde or ammonium salt concentration on the rate of hexamine formation in the reaction of formaldehyde with a given ammonium salt. These curves are seen to be analogous to those obtained with concentrated solutions. In both concentrated and dilute solutions, it is seen that doubling the formaldehyde concentration beyond that required by the theoretical ratio produces a larger increase in the rate of formation and final yield of hexamine than is observed when the ammonium salt concentration is doubled. Furthermore, in both concentrated and dilute solutions, the slower rates and smaller hexamine yields are associated with the ammonium salts of strong acids, such as ammonium chloride, whereas the rates are faster and the yields greater with ammonium salts of weaker acids, such as ammonium acetate.

It was also noted that the pH of ammonium chloride-formaldehyde solution was lower than that of ammonium acetate-formaldehyde solution, both at the beginning of the reaction and at the end point. Likewise, dibasic ammonium phosphate, which formed the solution of highest pH when dissolved in water, also showed the most rapid rate of hexamine formation. These observations suggested that the pH of the medium might be one of the most important factors governing the rate of reaction.

EFFECT OF pH ON THE RATE OF FORMATION AND YIELD OF HEXAMINE

The effect of the pH on both the rate of hexamine formation and the final yield was studied in aqueous formaldehyde-ammonium salt solutions buffered at pH 4.0, 6.0 and 8.0.

The formaldehyde-ammonium salt solutions used in these experiments were 0.375N in formaldehyde and 0.25N in the ammonium salt (mole ratio formaldehyde:available ammonia of 1.5:1), with a theoretical hexamine yield of 1.31 gram. These solutions were more dilute than those used in the previous rate studies, which made it easier to maintain constant pH. The experimental procedure was identical with that previously used, except that here the ammonium salt was dissolved in buffered solution instead of in distilled water. Since these solutions were so dilute, 4-ml. samples were used for the hexamine analysis instead of the previous 1-ml. samples. The buffers were of the type recommended by McIlvaine but were five times as concentrated as those used by him.

The results of the reactions in buffered solutions are shown in Tables XXXIII - XXXVIII.

Table XXXIII

Rate of Hexamine Formation in Buffered Formaldehyde-Ammonium Acetate Solution

Mole ratio formaldehyde:ammonia::1.5:1

Temperature 25°C.

Time (min.)	pH 8.0		pH 6.0		pH 4.0	
	% Hexamine Yield	pH of Solution	% Hexamine Yield	pH of Solution	% Hexamine Yield	pH of Solution
0.5	81.7	7.1	66.4	5.9	-	-
1	85.5	-	83.2	-	-	-
5	97.7	6.7	92.3	5.8	-	-
10	97.0	-	93.9	-	34.3	3.9
20	-	-	93.9	5.6	-	-
30	97.7	6.7	93.9	5.5	44.2	3.8
60	97.7	6.7	96.2	5.4	51.1	3.7
120	-	-	-	-	55.0	3.7
150	-	-	-	-	57.2	3.7
240	-	-	-	-	65.1	3.5

Fig.10

Rate of hexamine formation at 25°C. in buffered formaldehyde-ammonium acetate solutions

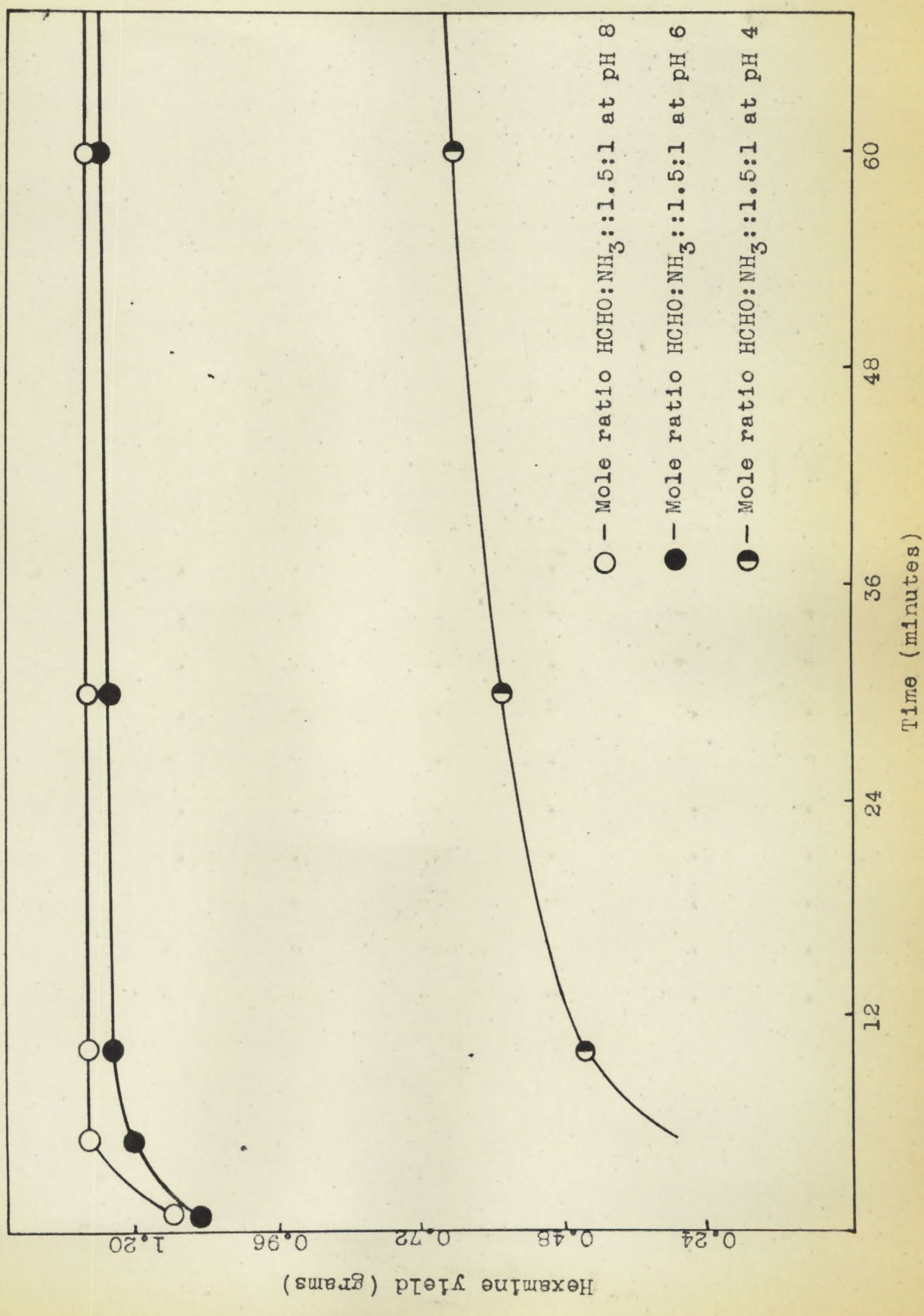


Table XXXIV

Rate of Hexamine Formation in Buffered
Formaldehyde-Ammonium Chloride Solution
Mole ratio formaldehyde:ammonia::1.5:1
Temperature 25° C.

Time (min.)	pH 8.0		pH 6.0		pH 4.0	
	% Hexamine Yield	pH of Solution	% Hexamine Yield	pH of Solution	% Hexamine Yield	pH of Solution
0.5	67.9	7.0	45.0	5.6	-	-
1	76.3	-	61.8	-	-	-
5	87.8	6.6	77.1	5.3	-	-
10	-	-	77.8	5.2	29.8	3.7
15	88.6	-	-	-	-	-
20	-	-	80.1	5.0	-	-
30	89.3	6.3	80.9	5.0	40.4	3.6
60	89.3	6.2	80.9	5.0	48.9	3.5
120	-	-	-	-	52.7	3.4
150	-	-	-	-	53.4	3.4
240	-	-	-	-	58.8	3.3
300	-	-	-	-	59.5	3.2

Table XXXV

Rate of Hexamine Formation in Buffered
Formaldehyde-Ammonium Nitrate Solution
Mole ratio formaldehyde:ammonia::1.5:1
Temperature 25°C.

Time (min.)	pH 8.0		pH 6.0		pH 4.0	
	% Hexamine Yield	pH of Solution	% Hexamine Yield	pH of Solution	% Hexamine Yield	pH of Solution
0.5	66.4	7.0	46.6	5.7	-	-
1	74.0	-	61.8	-	-	-
5	87.0	6.7	77.8	5.3	-	-
10	-	-	80.9	5.2	29.8	3.7
20	-	-	80.9	5.1	-	-
30	88.6	6.4	81.7	5.0	39.7	3.6
60	87.8	6.2	81.7	5.0	47.3	3.5
120	-	-	-	-	52.7	3.4
150	-	-	-	-	54.2	3.4
240	-	-	-	-	60.3	3.3

Fig.11

Rate of hexamine formation at 25°C. in buffered formaldehyde-ammonium nitrate solutions

Mole ratio $HCHO:NH_3::1.5:1$

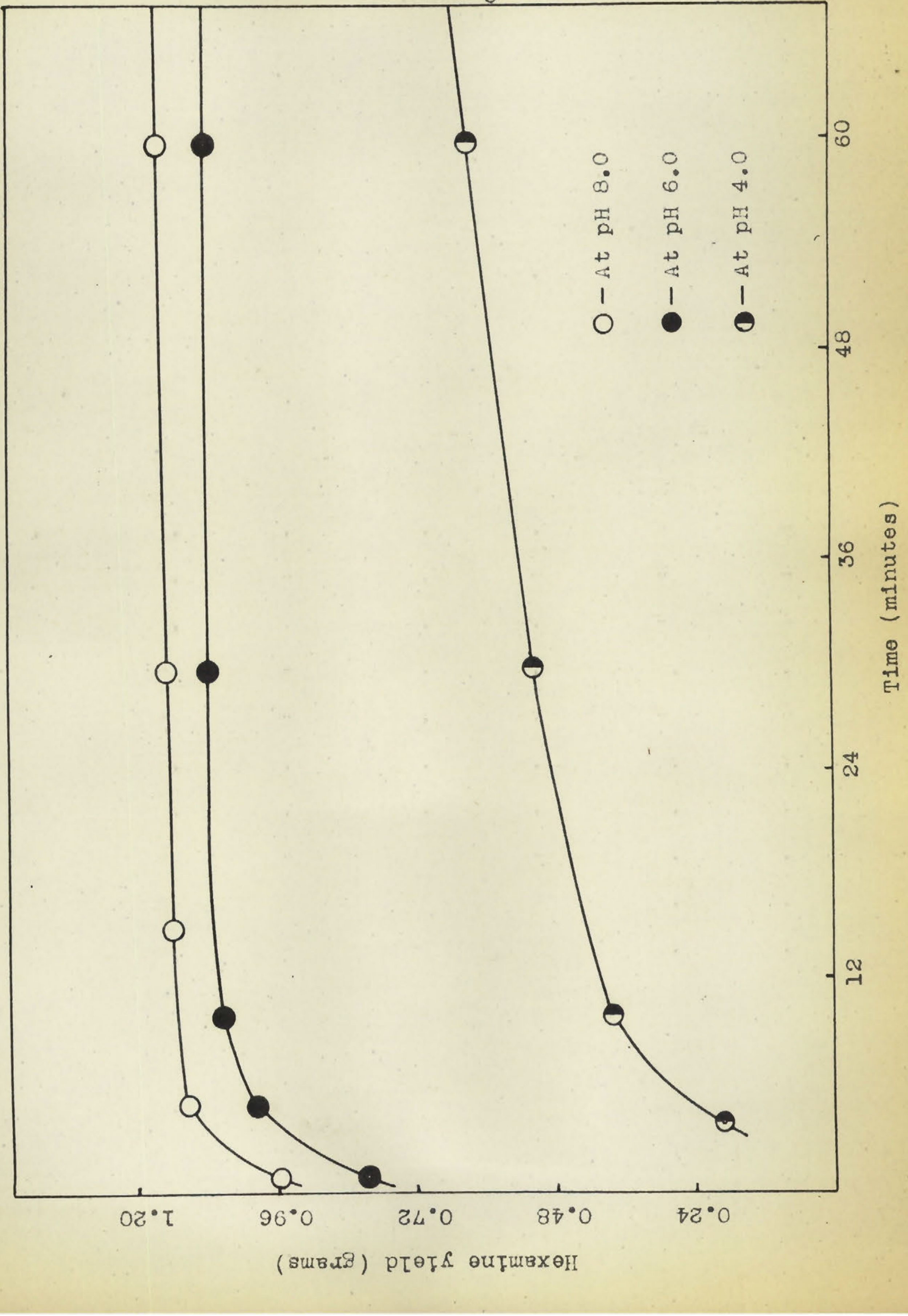


Table XXXVI

Rate of Hexamine Formation in Buffered

Formaldehyde-Ammonium Sulphate Solution

Mole ratio formaldehyde:ammonia::1.5:1

Temperature 25°C.

Time (min.)	pH 8.0		pH 6.0		pH 4.0	
	% Hexamine Yield	pH of Solution	% Hexamine Yield	pH of Solution	% Hexamine Yield	pH of Solution
0.5	72.5	7.1	56.5	5.8	-	-
1	77.9	-	71.0	5.6	-	-
5	90.9	6.8	80.9	5.4	-	-
10	-	-	83.2	5.2	31.3	3.8
20	-	-	84.0	5.1	-	-
30	90.1	6.4	84.0	5.0	42.7	3.7
60	90.9	6.4	83.2	5.0	48.1	3.6
120	-	-	-	-	53.4	3.5
150	-	-	-	-	55.0	3.5
240	-	-	-	-	59.5	3.4

Table XXXVII

Rate of Hexamine Formation in Buffered Formaldehyde-Ammonium Phosphate (dibasic) Solution

Mole ratio formaldehyde:ammonia::1.5:1

Temperature 25° C.

Time (min.)	pH 8.0		pH 6.0		pH 4.0	
	% Hexamine Yield	pH of Solution	% Hexamine Yield	pH of Solution	% Hexamine Yield	pH of Solution
0.5	86.2	7.4	74.0	5.8	-	-
1	89.3	-	87.0	-	-	-
5	98.5	7.2	93.1	5.7	-	-
10	98.5	7.1	95.4	5.6	35.9	3.9
20	-	-	97.0	5.6	-	-
30	98.5	7.0	97.7	5.5	47.3	3.8
60	97.7	7.0	97.0	5.4	52.7	3.6
120	-	-	-	-	56.5	3.5
150	-	-	-	-	58.0	3.5
240	-	-	-	-	63.3	3.5

Table XXXVIII

Rate of Hexamine Formation in Buffered Formaldehyde-Ammonium Oxalate Solution

Mole ratio formaldehyde:ammonia::1.5:1

Temperature 25°C.

Time (min.)	pH 8.0		pH 6.0		pH 4.0	
	% Hexamine Yield	pH of Solution	% Hexamine Yield	pH of Solution	% Hexamine Yield	pH of Solution
0.5	74.8	6.8	56.5	5.7	-	-
1	78.6	-	71.7	-	-	-
5	92.3	6.6	84.0	5.4	-	-
10	93.1	-	87.0	5.3	30.5	3.8
20	92.9	6.5	89.3	5.2	-	-
30	92.3	6.4	89.3	5.2	42.0	3.7
60	93.1	6.4	90.1	5.2	49.6	3.7
120	-	-	-	-	55.7	3.6
150	-	-	-	-	57.2	3.5
240	-	-	-	-	61.8	3.5

Fig.12

Rate of hexamine formation at 25°C. in buffered formaldehyde-ammonium oxalate solutions

Mole ratio $HCHO:NH_3::1.5:1$

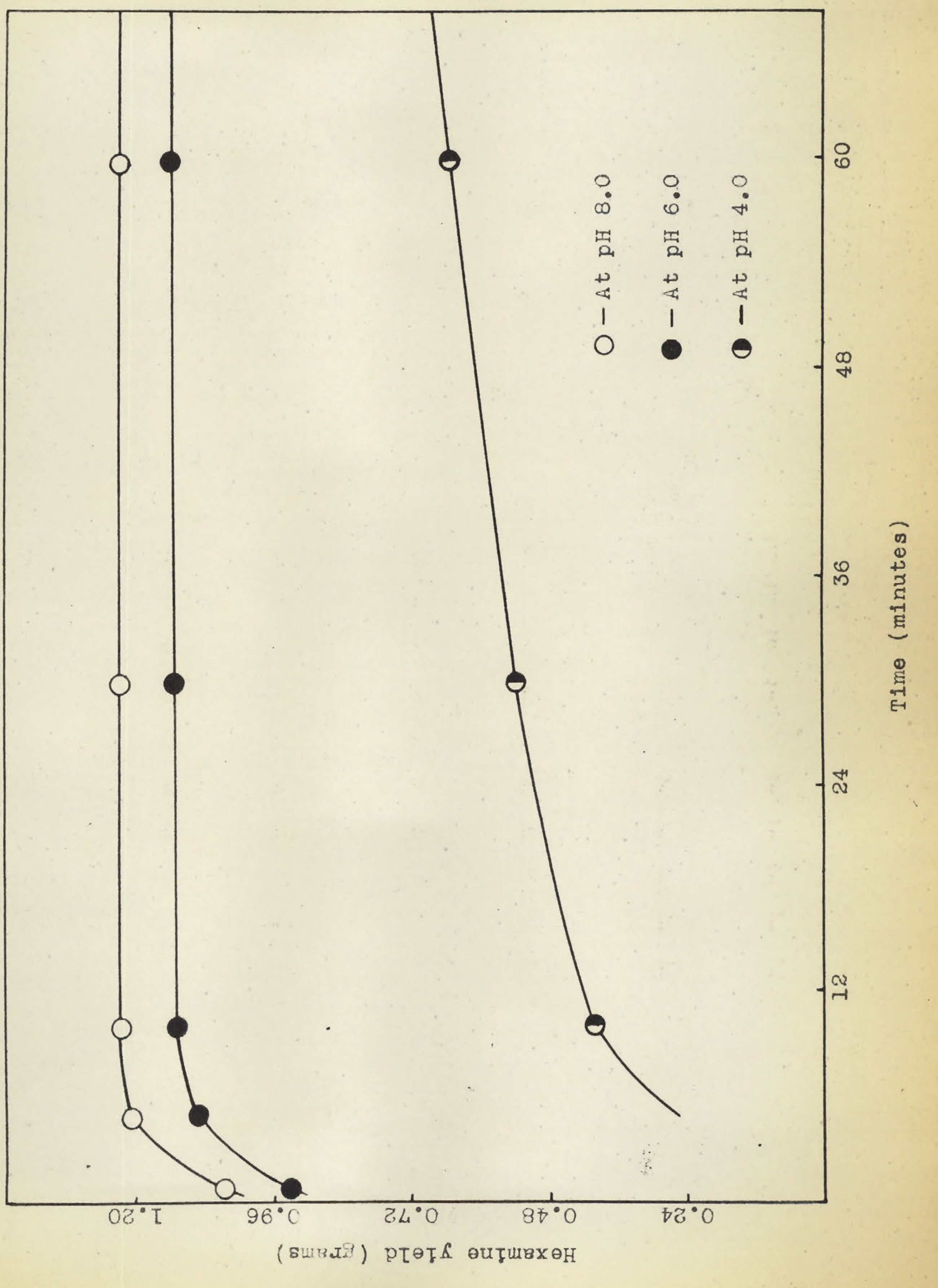
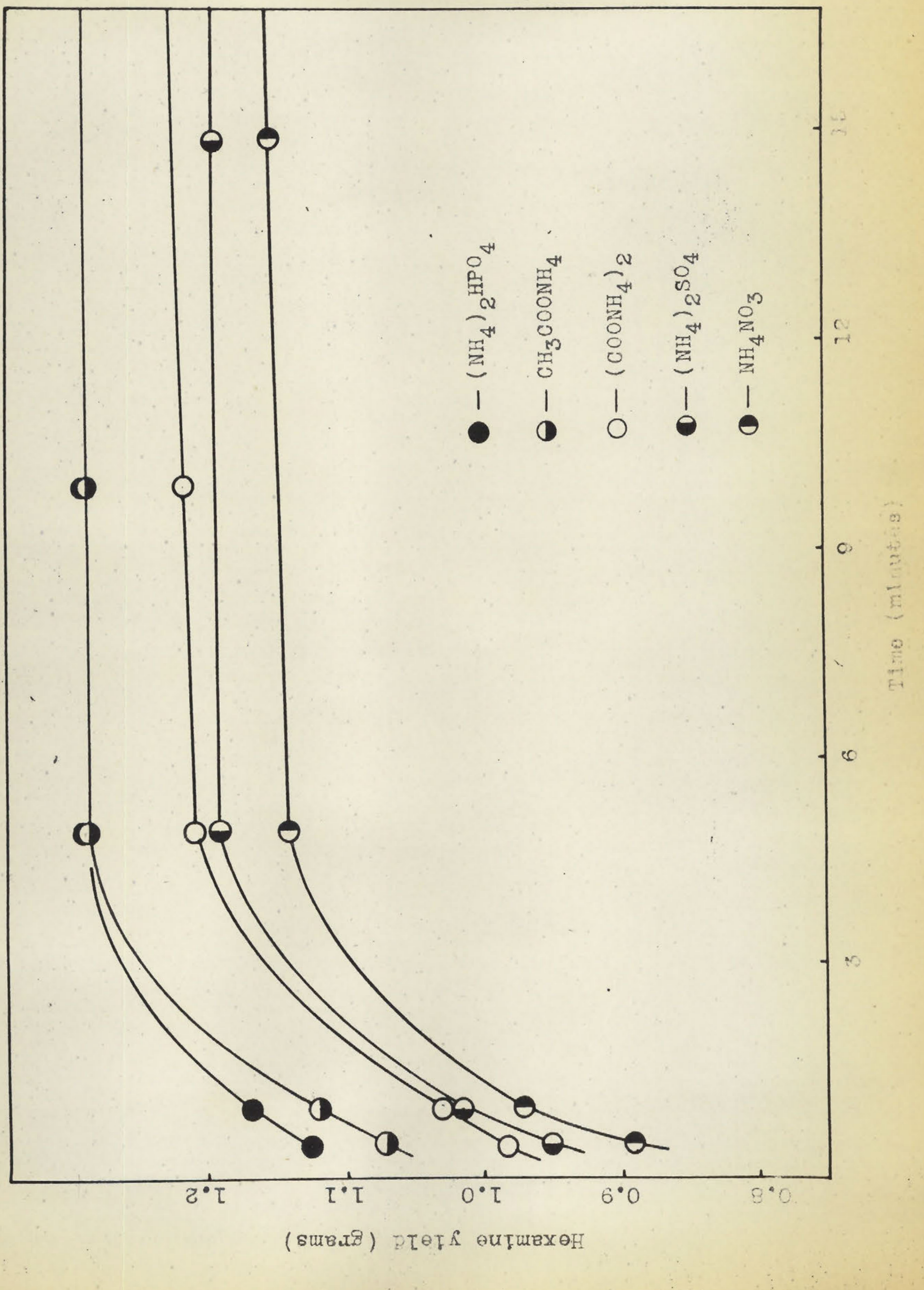


Fig.13

Rate of hexamine formation at 25°C. in various formaldehyde-ammonium salt solutions buffered at pH 8.0



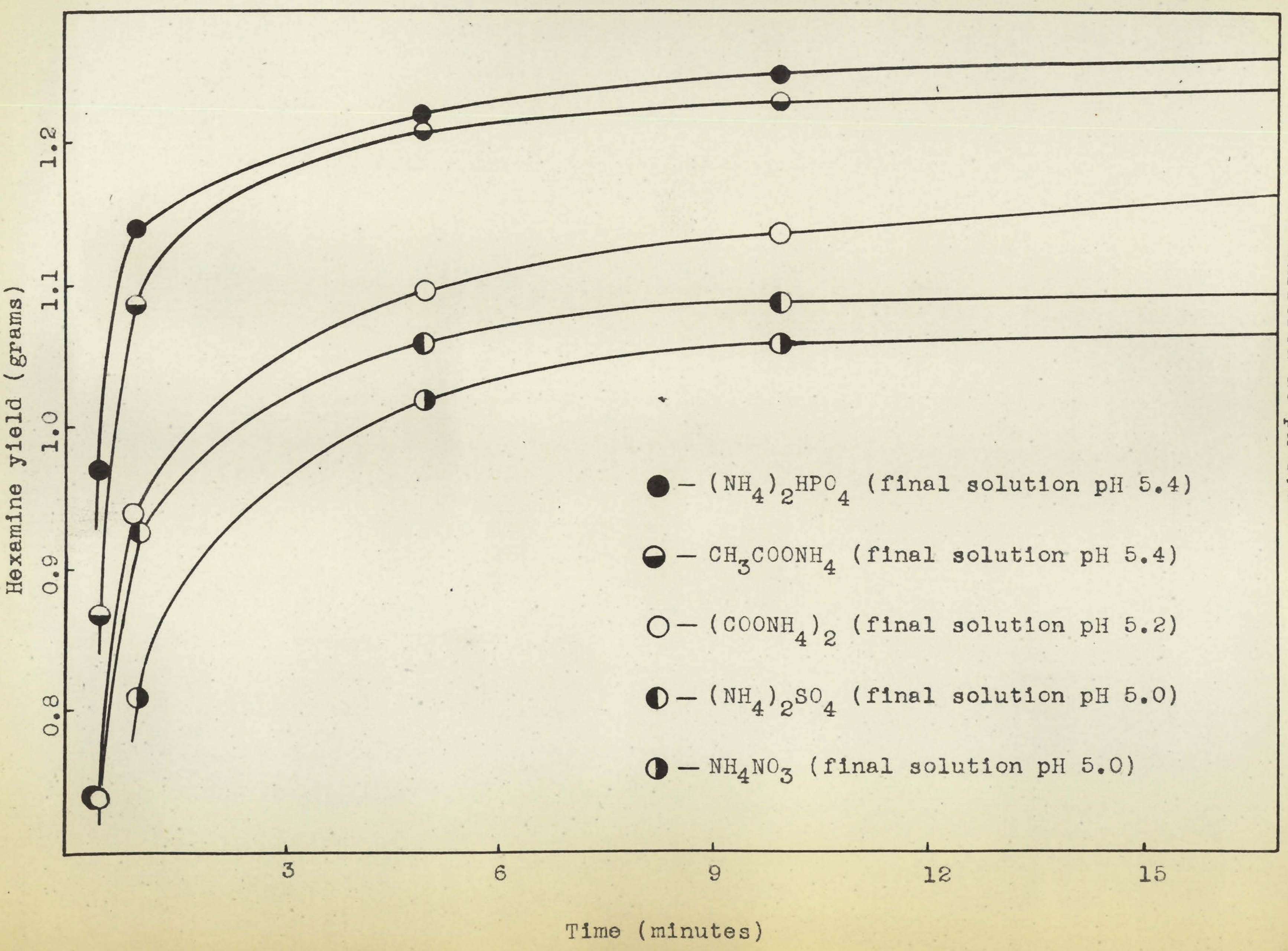
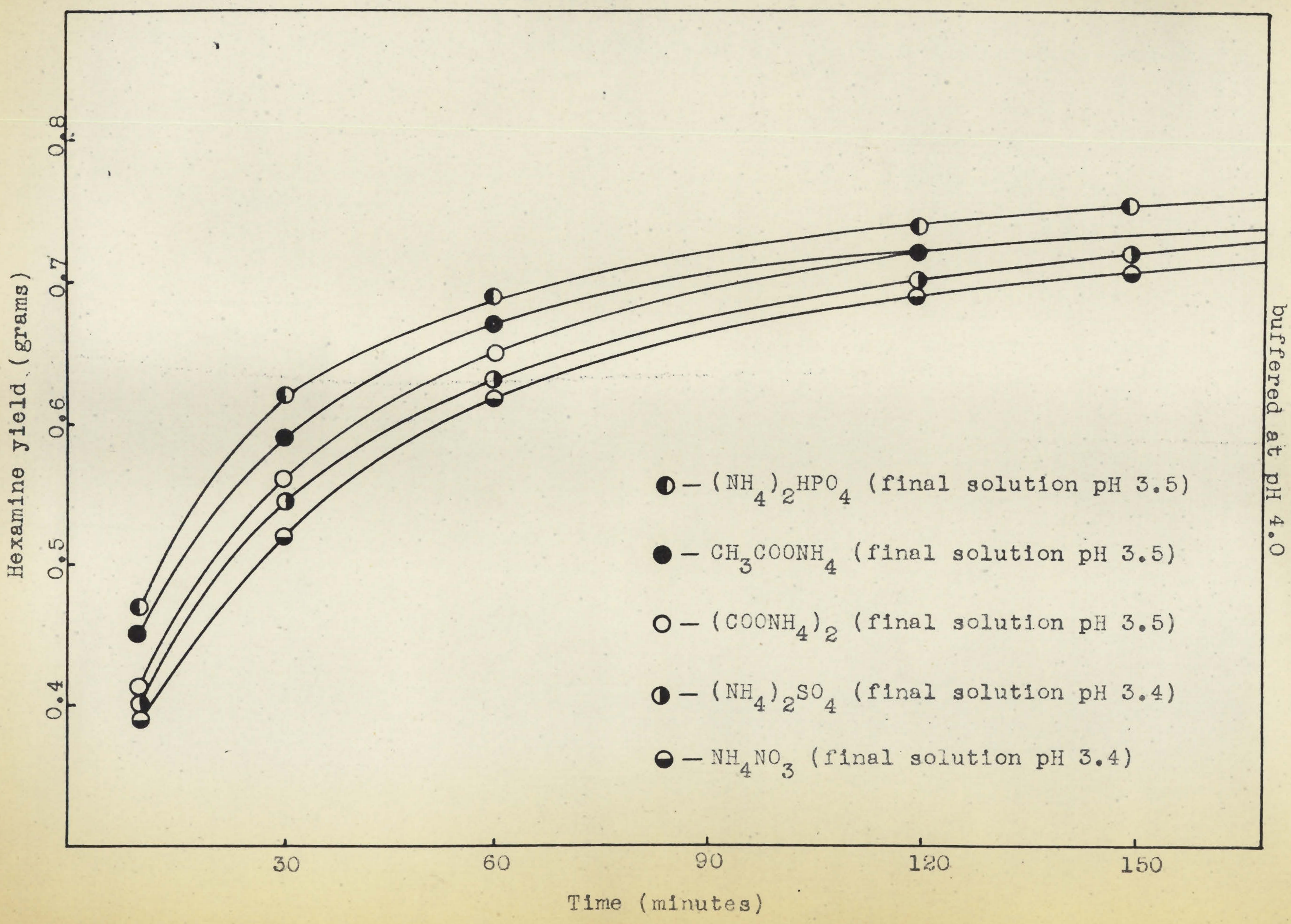


Fig.14

Rate of hexamine formation at 25°C. in various formaldehyde-ammonium salt solutions buffered at pH 6.0

Fig.15

Rate of hexamine formation at 25°C. in various formaldehyde-ammonium salt solutions buffered at pH 4.0



An examination of the results in Tables XXXIII - XXXVIII shows that the pH did not remain constant throughout the reactions. These data, however, present a striking illustration of the effect of pH on both the rate of hexamine formation and the final yield. In buffered solution, the rates are closely similar for the different ammonium salts used, and the final yields differ by only about 15 per cent (Figs. 13, 14 and 15), whereas in unbuffered solutions, the yields differ by about 60 per cent (Fig. 6). Furthermore, although the pH of the reaction solutions decreased from their initial buffered value, the faster rates and larger final yields are associated with the solutions having the higher final pH, while the slower rates and smaller final yields are associated with the lower pH.

Probably the best illustration of the effect of the pH of the formaldehyde-ammonium salt solution on the rate of hexamine formation and the final yield can be obtained by considering a given ammonium salt, such as ammonium nitrate. From Table XVIII (p.54), it is seen that the final yield of hexamine in the unbuffered formaldehyde-ammonium nitrate solution is only 18 per cent of the theoretical. When buffered, however, the final yield was 61 per cent at pH 4.0, 81 per cent at pH 6.0 and 88 per cent at pH 8.0. Thus, raising the pH of the formaldehyde-ammonium nitrate solution above that existing in the unbuffered solution results in increased hexamine yield and an increased rate. On the other hand, with ammonium acetate in unbuffered solution, the yield was 99 per cent. When buffered at pH 8.0, the yield was 97.7 per cent, at pH 6.0 it was 96.2 per cent and at pH 4.0 it was 65 per cent.

From the data presented, it is seen that, at a given pH, all the ammonium salts investigated give approximately the same rates of formation and final yields of hexamine, indicating that at given pH, different ammonium salts lose their individuality and become merely sources of ammonium ions or available ammonia as far as hexamine formation is concerned.

A KINETIC STUDY OF THE FORMATION OF HEXAMINE IN BUFFERED FORMALDEHYDE-AMMONIUM NITRATE SOLUTIONS

In the preceding experiments, the rate of hexamine formation was studied in both unbuffered and buffered aqueous formaldehyde-ammonium salt solutions. It was shown that the rate of hexamine formation and the final yield increase with an increase in the pH of the solution and also that at given pH, the different ammonium salts exhibit similar rates of hexamine formation. The point of interest was the rate of appearance of hexamine in the various ammonium salt solutions at 25°C. under different pH conditions, no attempt being made to follow simultaneously the rate of disappearance of the formaldehyde and the ammonia, nor to investigate the effect of temperature and relative reagent concentrations on the rate of hexamine formation at controlled pH levels.

A kinetic study of the formation of hexamine in an aqueous formaldehyde-ammonium salt solution was then made, the rate of disappearance of formaldehyde and ammonia being followed, as well as the rate of appearance of hexamine. Since it was shown that at given pH the various ammonium salts show similar rates of hexamine formation, these new experiments were made using ammonium nitrate as a representative ammonium salt.

Formaldehyde-ammonium nitrate solutions buffered at pH 4.0, 6.0 and 8.0 were used. To facilitate buffering these reactions, the ammonium nitrate concentration was reduced to 0.20N and the formaldehyde concentration to 0.30N. The buffer solutions were prepared according to McIlvaine, but five times the recommended concentrations were used to ensure an adequate alkali reserve in the buffered solutions.

The rate of hexamine formation and the rates of formaldehyde and ammonia disappearance were determined in the buffered solutions at temperatures of 0°C., 20°C. and 40°C.

The effect on the rate of formation and the final yield of hexamine, of doubling the concentration of the formaldehyde and the ammonium nitrate beyond the theoretical ratio was also studied in the solutions at the pH levels and temperatures indicated above.

To illustrate the experimental procedure, a typical experiment is described below.

To prepare the 0.20N ammonium nitrate solution, 2.4 g. of ammonium nitrate was dissolved in a little of the buffer solution. When necessary, the pH was adjusted to exactly that desired by the addition of finely powdered dibasic sodium phosphate. The volume of the solution was then made to exactly 130 ml. by the addition of buffer solution. This solution was placed in a 250-ml. Erlenmeyer flask suspended in a water bath at the required temperature. Into a 125-ml. Erlenmeyer flask was placed 3.6 ml. of reagent-grade neutral formaldehyde solution (37.2% by analysis) and the volume made to 20 ml. by the addition of buffer solution. This flask was also suspended in the water bath. When both solutions were at the temperature of the bath, the reaction was started by quickly pouring the formaldehyde solution into the flask containing the buffered ammonium nitrate solution and the time noted. This resulted in 150 ml. of solution which was 0.20N in respect to ammonium nitrate and 0.30N in respect to formaldehyde. The pH of the reaction solution was tested from time to time and if any decrease in the pH was observed, the pH was adjusted by the addition of a few drops of N/10 sodium hydroxide solution.

Hexamine Analysis

The course of hexamine formation in the reaction solutions was followed by removing 4-ml. samples after different times with a pipette and adding them to 20 ml. of N/1 nitric acid, followed immediately by the addition of 25 ml. of saturated aqueous mercuric chloride solution. The purpose of this procedure was to neutralize any free ammonia before the addition of the mercuric chloride. It was shown that no significant reaction of formaldehyde with ammonium nitrate occurred in N/1 nitric acid in the time required for the analysis, by adding some 0.20N ammonium nitrate solution to N/1 nitric acid, followed by the addition of an equivalent amount of 0.30N formaldehyde solution. No hexamine was detected, even after one hour. After one-half hour, the hexamine-mercuric chloride complex precipitate from the analysis was collected on a tared, fine sintered-glass crucible, dried for one hour at 100 $^{\circ}$C., allowed to cool and then weighed. The hexamine content of the sample was determined from a hexamine-mercuric chloride complex calibration curve established for these analytical conditions.

The hexamine-mercuric chloride complex calibration curve was established for each pH of the reaction mixture investigated (pH 4.0, 6.0 and 8.0). This was necessary, since the addition of 4-ml. samples of these different buffered solutions to the 20 ml. N/1 nitric acid resulted in slightly different pH of the medium from which the hexamine was precipitated. It was found that the calibration curve was shifted by a change in the pH of the medium from which the hexamine was precipitated. For example, when a 0.100 gram sample of hexamine was precipitated from distilled water, the resulting complex weighed 13.0 times the weight of the hexamine sample. When precipitated from N/1 nitric acid, however, the complex weighed only 11.6 times the weight of the hexamine sample. This demonstrated the necessity of conducting the hexamine precipitations at a constant pH and using a calibration curve established at that pH.

Preliminary experiments demonstrated that the precision of the hexamine values may be taken to be within ± 1.5 per cent.

Formaldehyde Analysis.

The method used was developed by Schulek (43) and is a variant of the well-known potassium cyanide method of Romijn (44). The procedure is based on the quantitative formation of cyanohydrin when formaldehyde is treated with a solution containing a known excess of potassium cyanide.

$$CH_2O_{(aq.)} + KCN + H_2O \longrightarrow CNCH_2OH + KOH$$

The method involves determining the unreacted cyanide by iodimetry as follows: a 3-ml. sample of the reaction solution was removed with a pipette after different times and added to a glass-stoppered Erlenmeyer flask containing exactly 20.0 ml. of N/10 potassium cyanide solution. This was allowed to stand for ten minutes and then 6 ml. of concentrated hydrochloric acid added. Bromine was then added dropwise until a permanent yellow colour developed. The excess bromine was removed by the addition of a few drops of 5 per cent phenol solution. Approximately 0.3 g. of potassium iodide was added and the free iodine titrated after one-half hour with N/10 sodium thiosulphate solution. No indicator was necessary in this titration, since the yellow iodine colour disappeared sharply at the end point. The amount of potassium cyanide solution equivalent to formaldehyde equals the volume of N/10 potassium cyanide solution originally added (20.0 ml.) minus one-half the titer of N/10 sodium thiosulphate solution. One ml. of N/10 potassium cyanide is equivalent to 0.003002 g. of formaldehyde. The potassium cyanide solution was standardized iodimetrically against the sodium thiosulphate solution.

The precision of the formaldehyde analysis was found to be within ± 0.5 per cent and the values were not influenced by the presence of hexamine or ammonium nitrate.

Analysis for Residual Ammonia

The residual ammonia, as ammonium nitrate, at any given time in the reaction solution could not be determined directly by the Kjeldahl method, since hexamine was also present. Therefore, the method used involved the determination of the ammonia present in a sample from which the hexamine had been removed by precipitation with mercuric chloride.

When the 4-ml. sample of the reaction solution was removed after different times for a hexamine determination, the hexamine-mercuric chloride complex was collected on a tared, sintered-glass crucible. The filtrate was carefully collected for a determination of the residual ammonia. To this filtrate was added 10 per cent sodium sulphide solution until no further precipitate was formed. It was necessary to precipitate the excess mercury as mercurous sulphide to prevent the formation of mercury-ammonia complexes. After removing the mercurous sulphide precipitate by filtration, the solution was placed in a 125-ml. Kjeldahl flask and 10 ml. of 50 per cent sulphuric acid added. This was distilled until only about 10 ml. remained in the flask. When cool, 50 per cent sodium hydroxide was added until the solution became alkaline and then a further 20 ml. added. The ammonia was distilled into 50.0 ml. of N/10 sulphuric acid. This was then back titrated with N/10 sodium hydroxide.

The results obtained in this kinetic study are shown in Tables XXXIX - LXV and Figures 16 - 43.

Table XXXIX

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.30N

Temperature 0° C. pH 8.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	14.3	16.1	17.9
3	42.0	39.3	44.2
10	75.0	71.4	71.0
20	80.3	80.3	78.8
40	83.9	83.9	85.0
60	86.6	86.6	87.4
90	89.3	90.2	91.9

Table XL

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.40N Formaldehyde - 0.30N

Temperature 0° C. pH 8.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	17.0	16.1	19.4
5	81.2	76.8	77.8
15	89.3	86.6	90.2
30	94.7	88.4	92.3
60	96.4	90.2	95.9

Fig.16

Rate curves for reaction at pH 8.0 and 0°C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:1

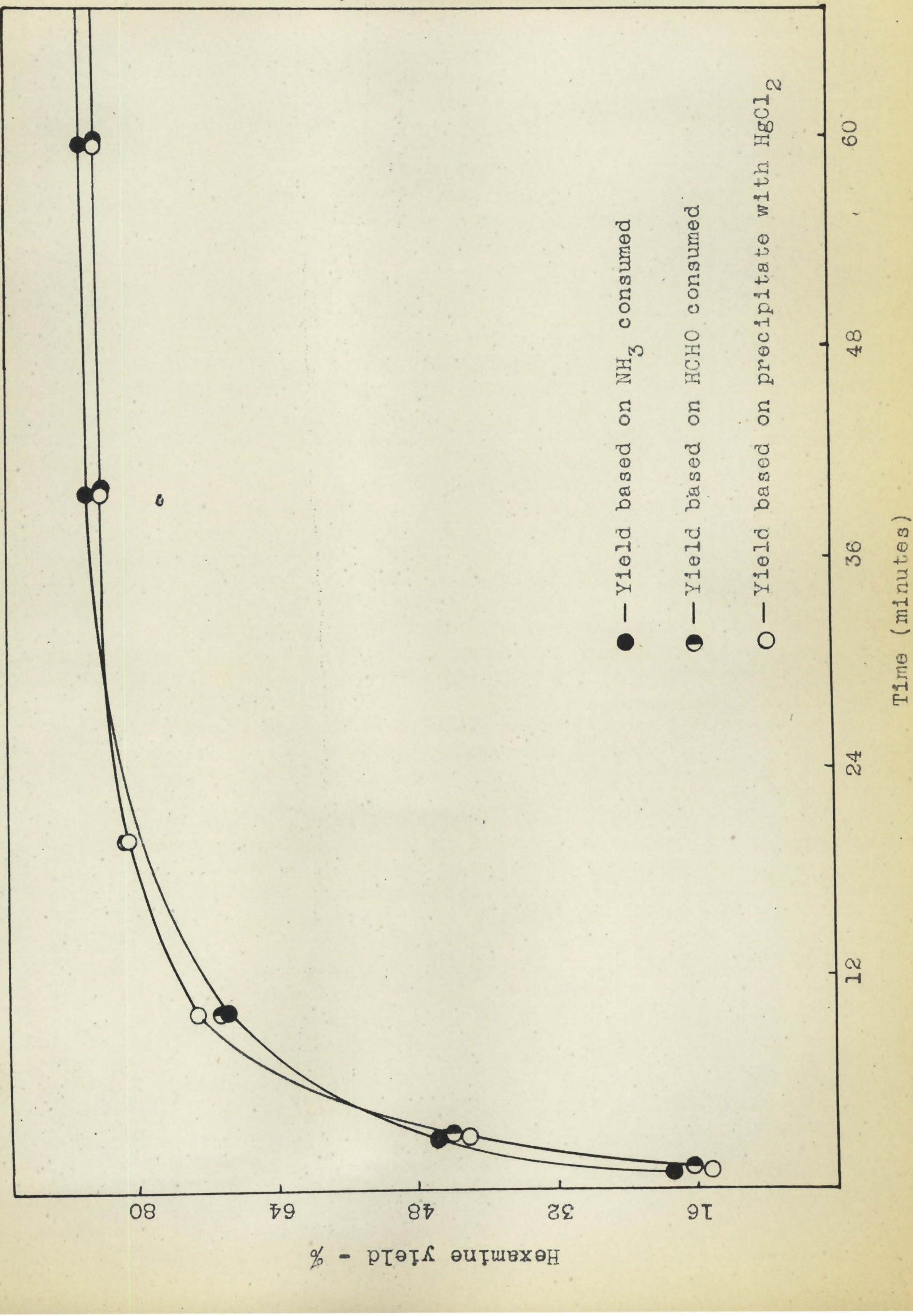


Fig.17

Rate curves for reaction at pH 8.0 and 0°C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:2

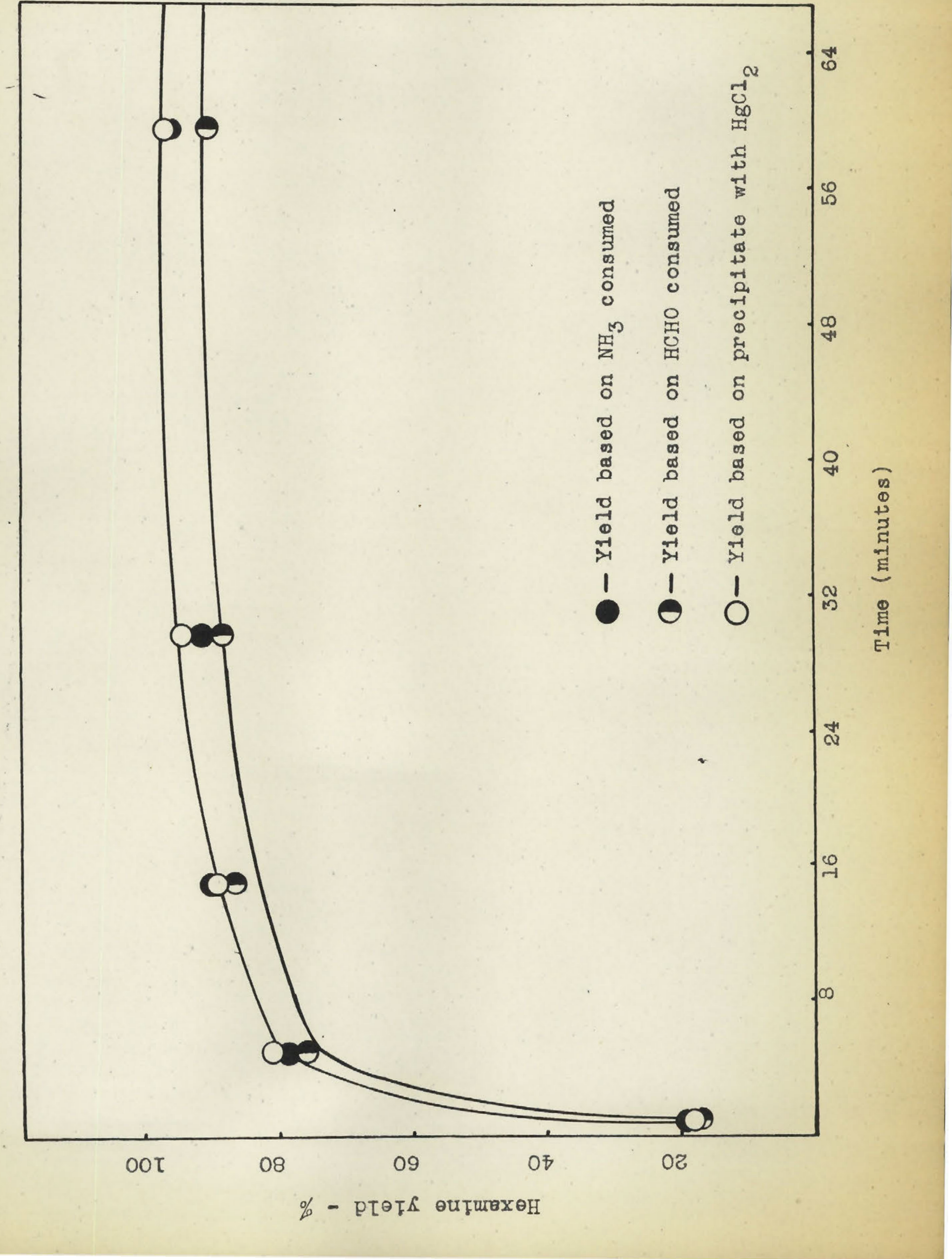


Table XLI

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.60N

Temperature 0°C. pH 8.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	18.8	17.9	22.2
3	42.9	40.2	45.0
10	80.4	87.5	91.2
30	83.9	92.9	95.9
60	86.6	95.5	98.0
90	88.4	96.4	98.2

Table XLII

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.30N

Temperature 20°C. pH 8.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	63.4	60.2	64.2
3	71.0	67.0	70.5
6	76.1	72.3	-
10	79.4	75.0	78.0
20	83.4	78.8	81.8
60	86.9	84.4	85.8

Fig.18

Rate curves for reaction at pH 8.0 and 0°C.

Mole ratio formaldehyde:ammonium nitrate of 3:1

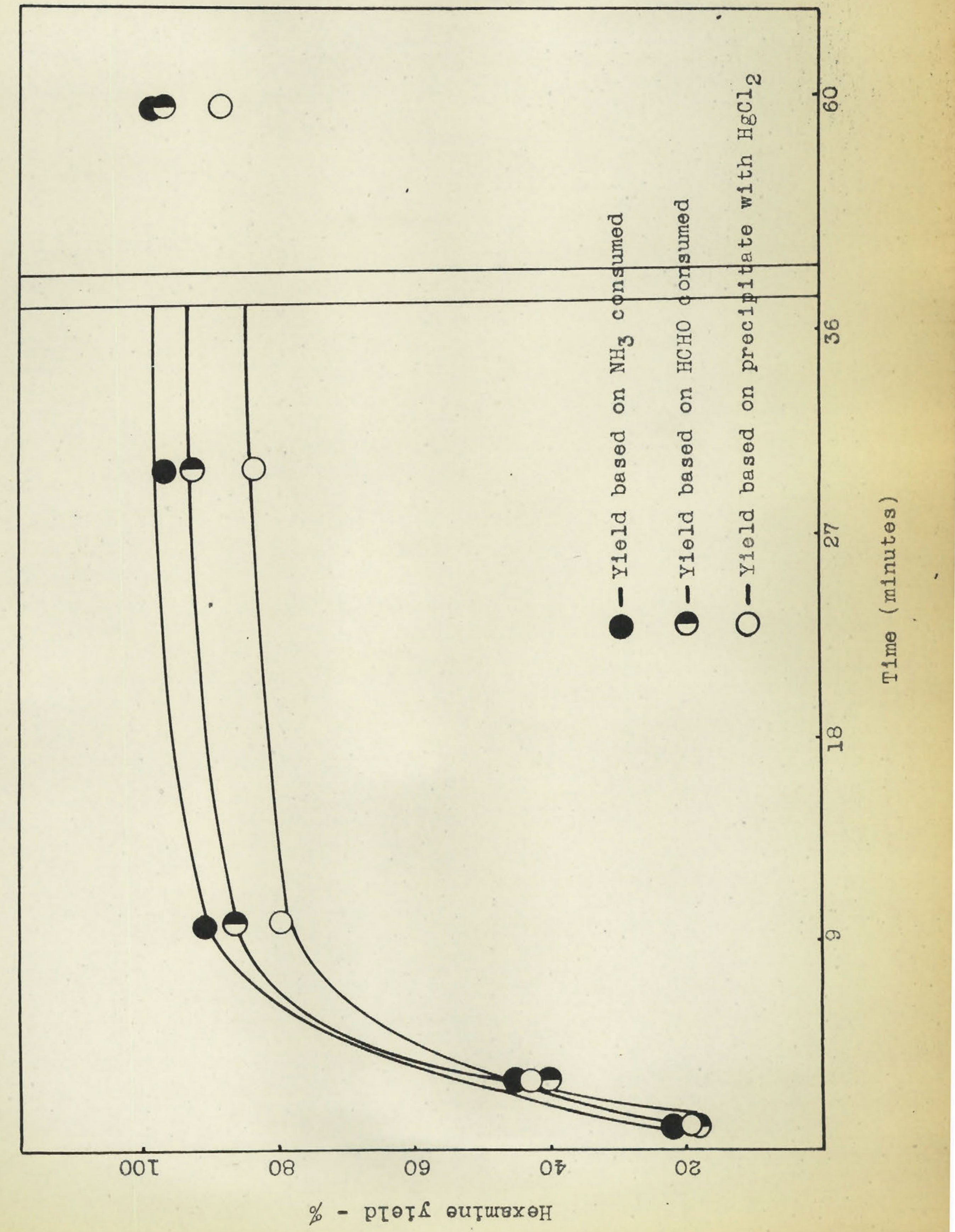


Fig.19

Rate curves for reaction at pH 8.0 and 20°C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:1

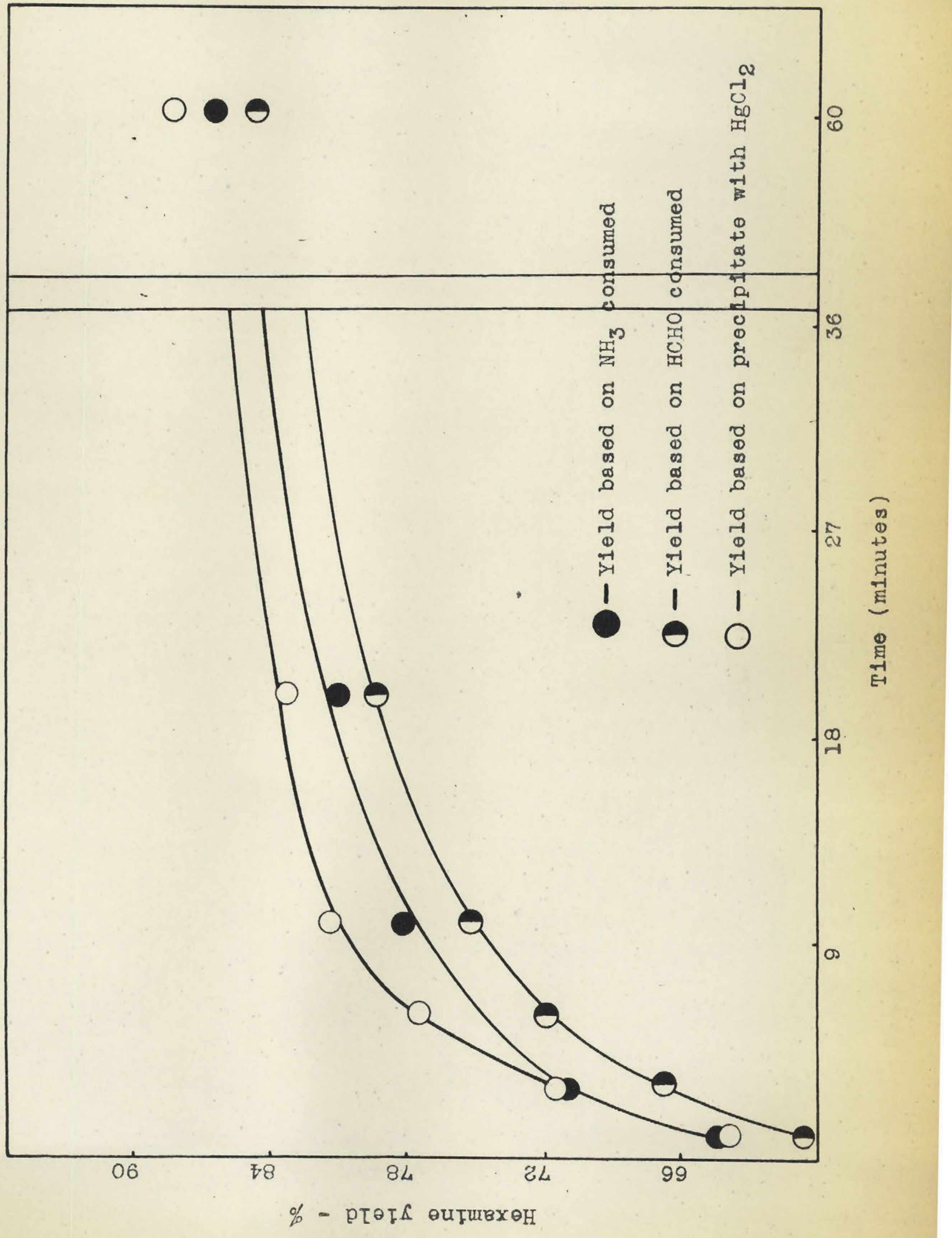


Table XLIII

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.40N Formaldehyde - 0.30N

Temperature 20°C. pH 8.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	82.1	77.8	-
3	89.3	84.9	88.4
6	96.4	92.0	95.9
10	96.4	95.5	97.0
30	96.4	97.3	98.7
60	96.4	97.3	98.1

Table XLIV

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.60N

Temperature 20°C. pH 8.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	89.3	89.3	-
3	92.9	94.6	95.7
6	96.4	98.2	97.2
30	96.4	98.2	97.0
60	96.4	98.2	97.7

Fig.20

Rate curves for reaction at pH 8.0 and 20°C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:2

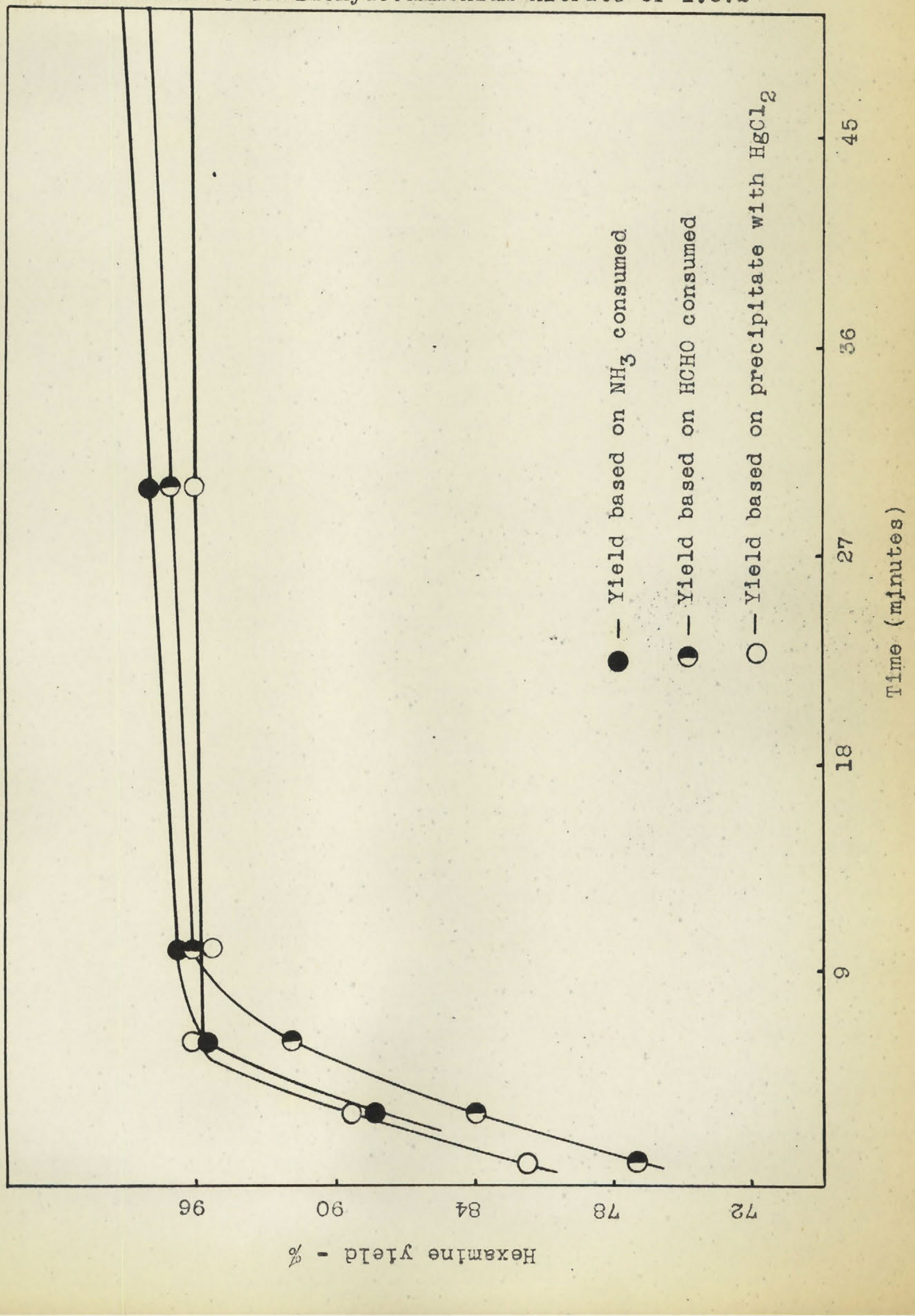


Fig.21

Rate curves for reaction at pH 8.0 and 20°C.

Mole ratio formaldehyde:ammonium nitrate of 3:1

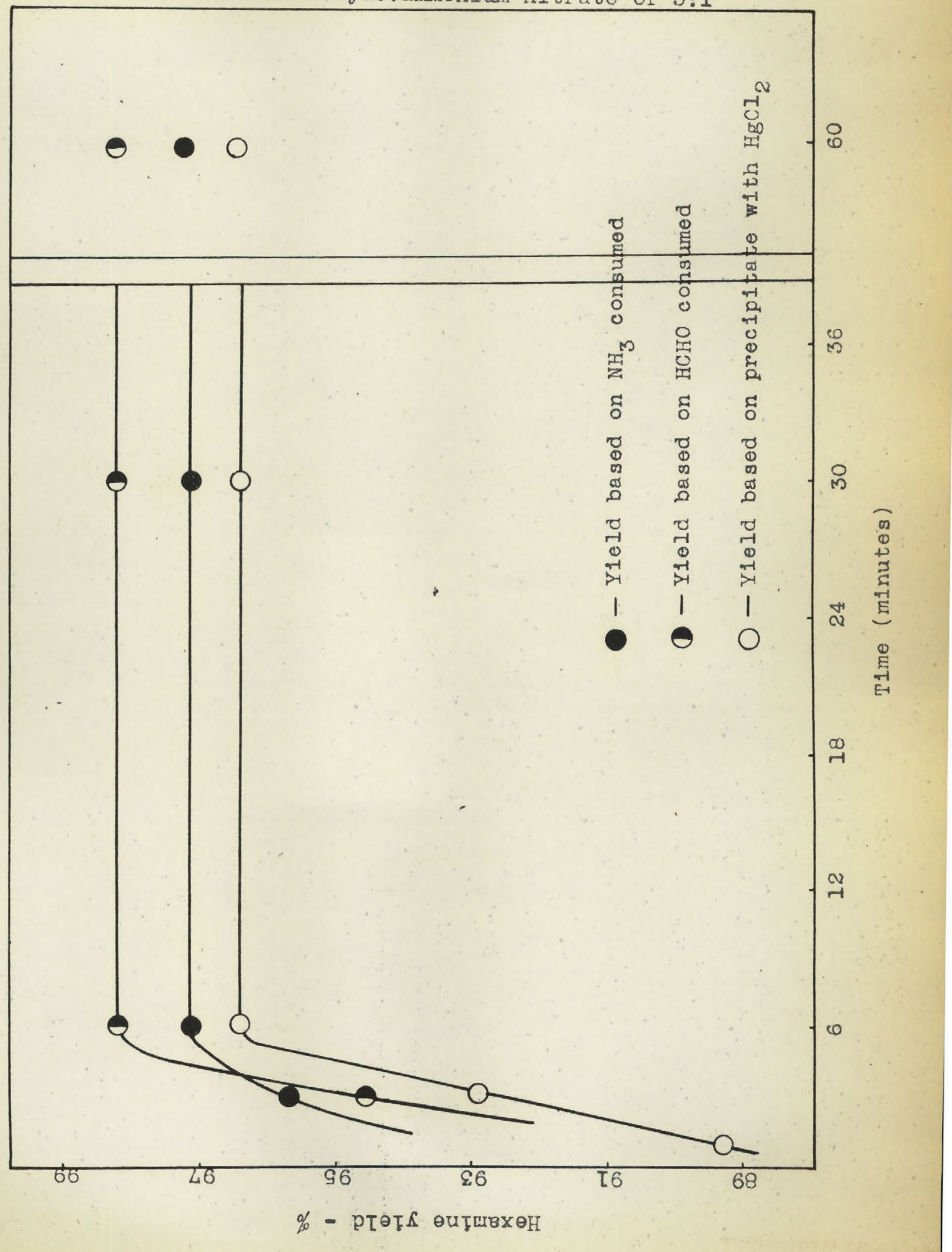


Table XLV

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.30N

Temperature 40°C. pH 8.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	67.9	63.4	67.4
3	79.5	75.0	78.3
10	87.5	82.1	85.1
30	89.5	86.1	88.0
60	90.4	85.7	88.7
180	91.0	88.4	91.4

Table XLVI

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.40N Formaldehyde - 0.30N

Temperature 40°C. pH 8.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	87.5	83.0	84.3
3	90.4	88.4	89.7
10	95.5	97.3	95.7
30	99.1	98.2	99.4
60	99.1	99.1	99.5

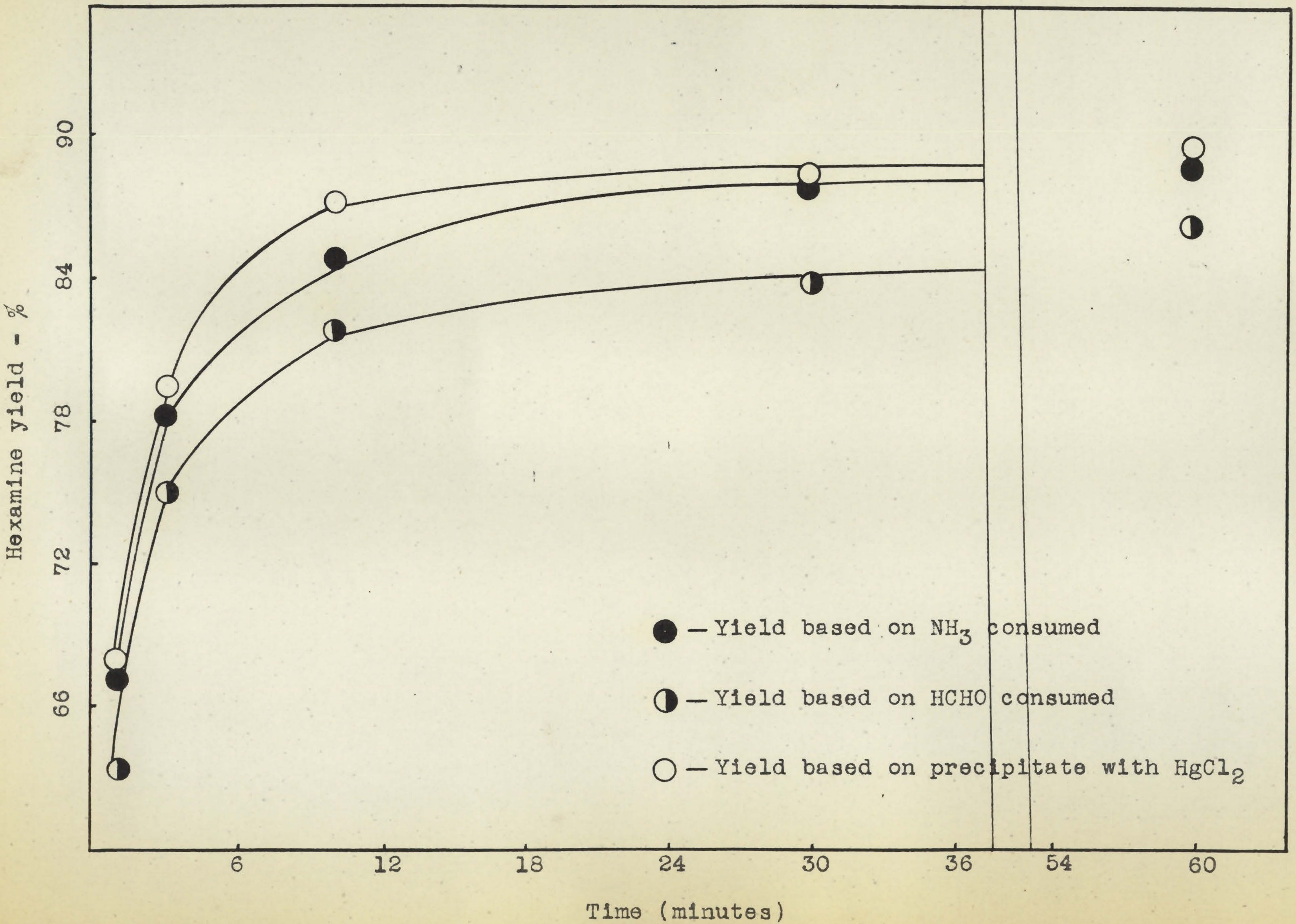


Fig. 22

Rate curves for reaction at pH 8.0 and 40°C.
Mole ratio formaldehyde:ammonium nitrate of 1.5:1

Fig.23

Rate curves for reaction at pH 8.0 and 40°C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:2

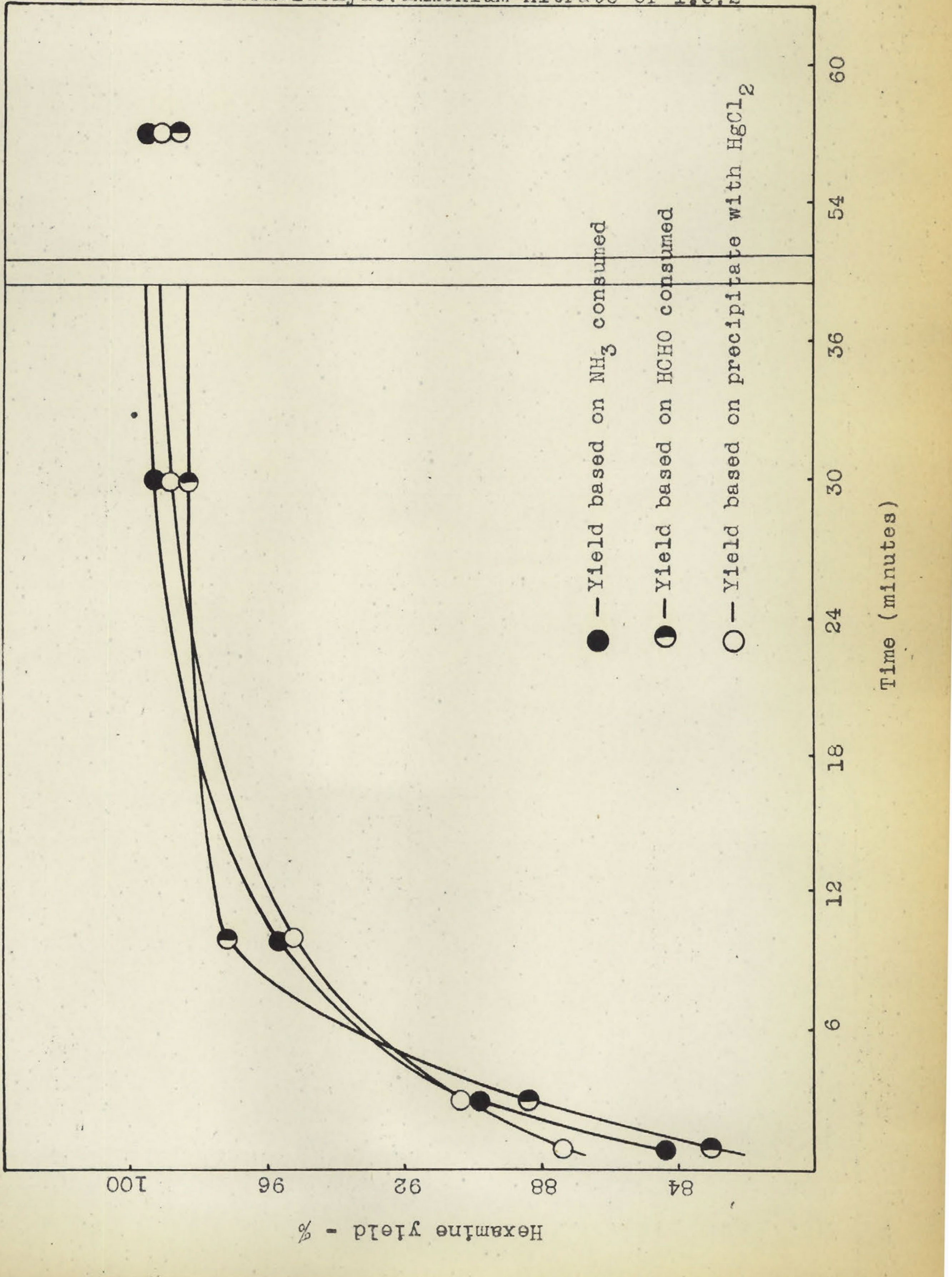


Table XLVII

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate 0.20N Formaldehyde - 0.60N

Temperature 40°C. pH 8.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	90.4	91.0	91.4
3	91.0	92.9	93.6
10	91.0	98.2	99.3
30	91.0	98.4	98.9
60	91.2	98.0	99.4

Table XLVIII

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.30N

Temperature 0°C. pH 6.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
5	6.3	7.1	-
10	8.0	8.9	7.6
30	12.0	9.8	14.0
60	20.5	20.5	22.0
120	28.6	29.5	30.2
300	38.4	39.3	42.3

Fig.24

Rate curves for reaction at pH 8.0 and 40 °C.

Mole ratio formaldehyde:ammonium nitrate of 3:1

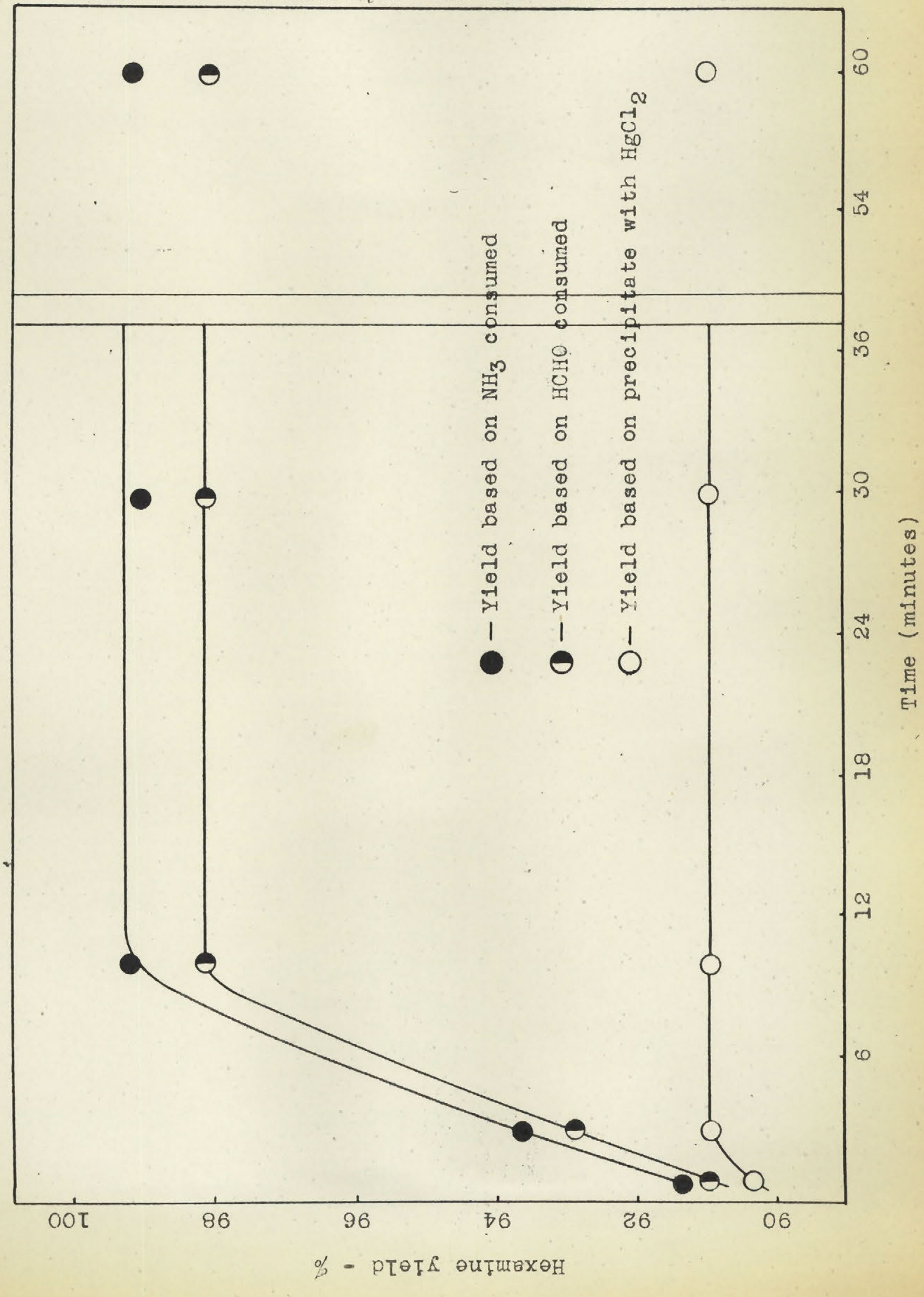


Fig.25

Rate curves for reaction at pH 6.0 and 0°C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:1

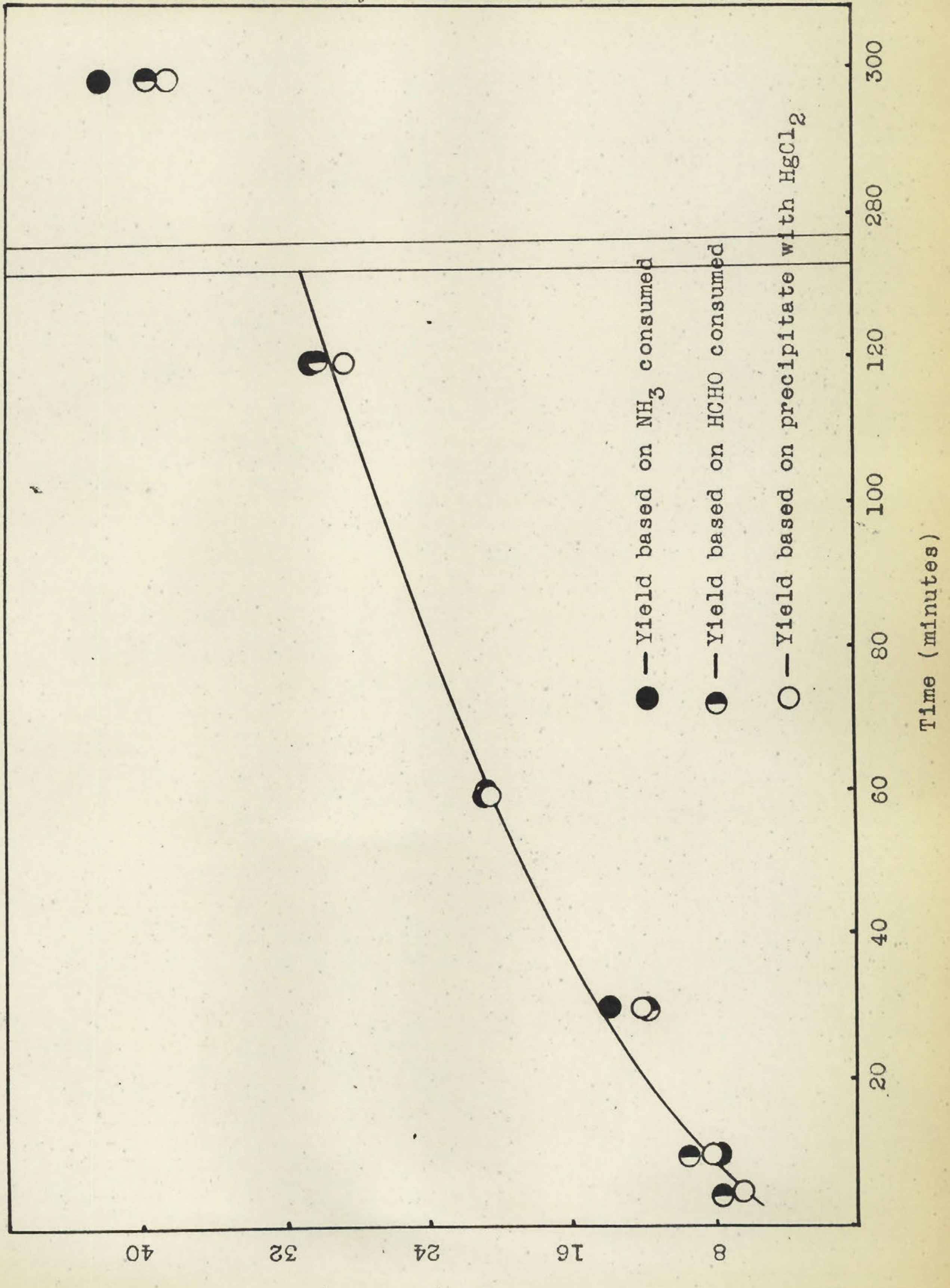


Table XLIX

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.40N Formaldehyde - 0.30N

Temperature 0°C. pH 6.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
3	12.0	11.6	13.6
10	16.9	20.5	21.7
30	33.0	33.9	37.1
60	43.8	45.5	48.7
120	55.3	55.3	56.2

Table L

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.60N

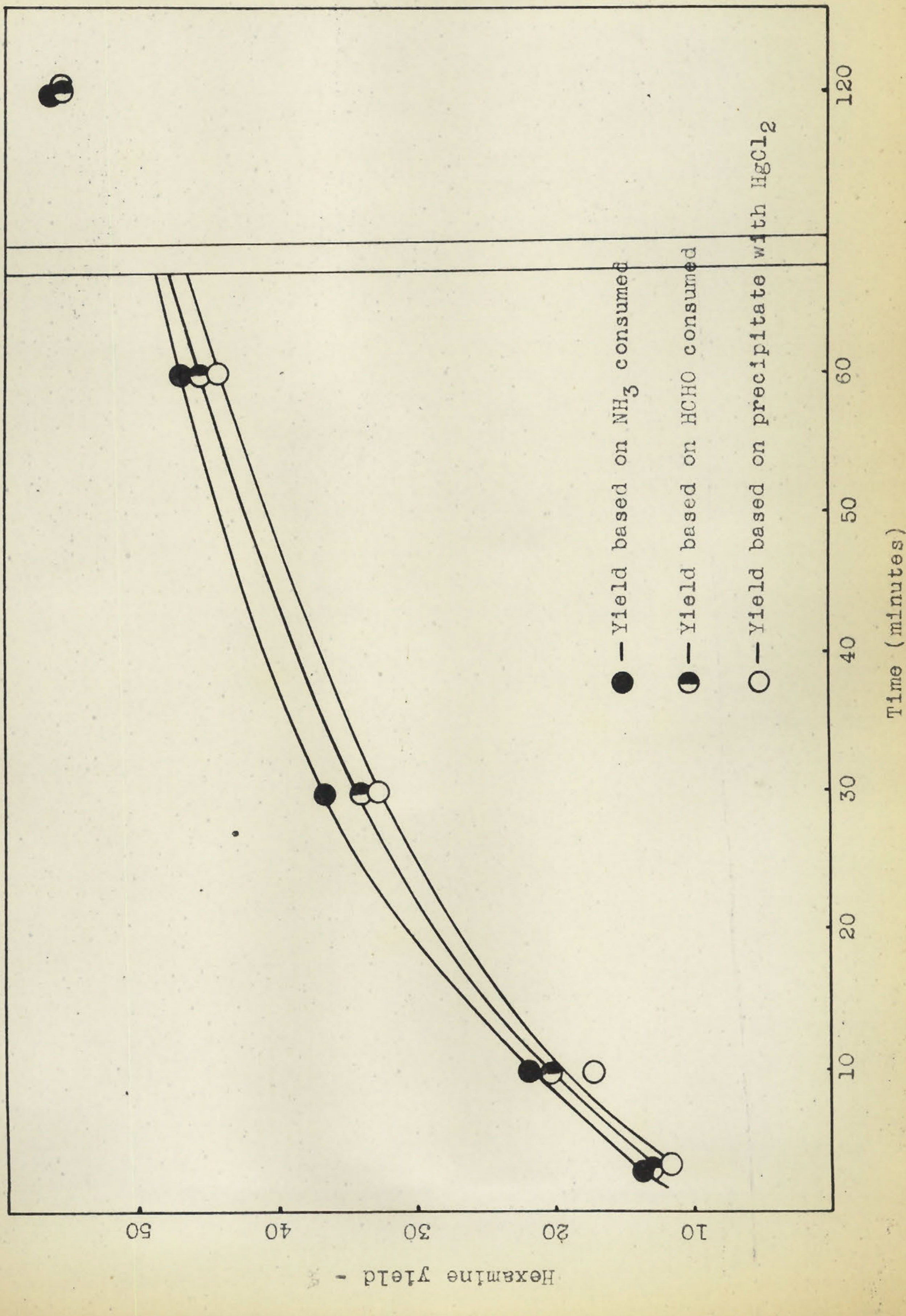
Temperature 0°C. pH 6.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
4	15.2	12.5	11.1
10	20.5	20.5	19.3
30	38.4	42.0	44.4
60	52.7	55.3	56.4
120	62.5	67.8	69.3

Fig.26

Rate curves for reaction at pH 6.0 and 0°C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:2



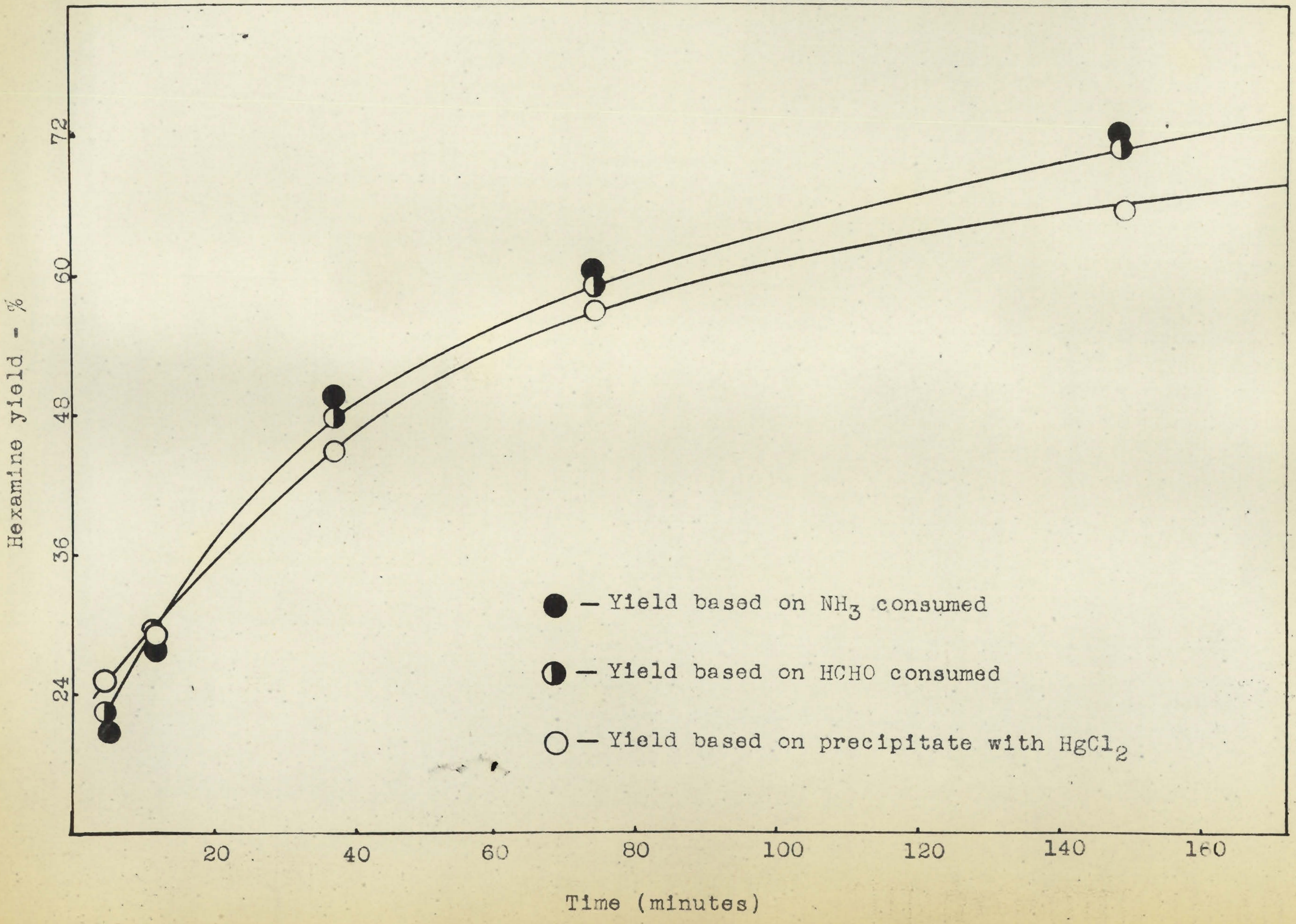


Fig.27

Rate curves for reaction at pH 6.0 and 0°C.
Mole ratio formaldehyde:ammonium nitrate of 3:1

Table LI

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.30N

Temperature 20° C. pH 6.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	13.4	-	-
3	22.3	20.5	18.5
10	41.0	42.9	46.0
30	50.0	50.9	52.0
60	60.7	57.1	56.5
90	61.8	59.0	60.5
480	74.9	70.0	72.2

Table LII

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.40N Formaldehyde - 0.30N

Temperature 20° C. pH 6.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	26.8	-	31.5
3	50.9	53.6	56.4
10	71.4	67.0	69.0
30	75.9	73.2	77.5
60	83.9	80.3	85.6
300	83.9	84.8	84.1

Fig.28

Rate curves for reaction at pH 6.0 and 20°C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:1

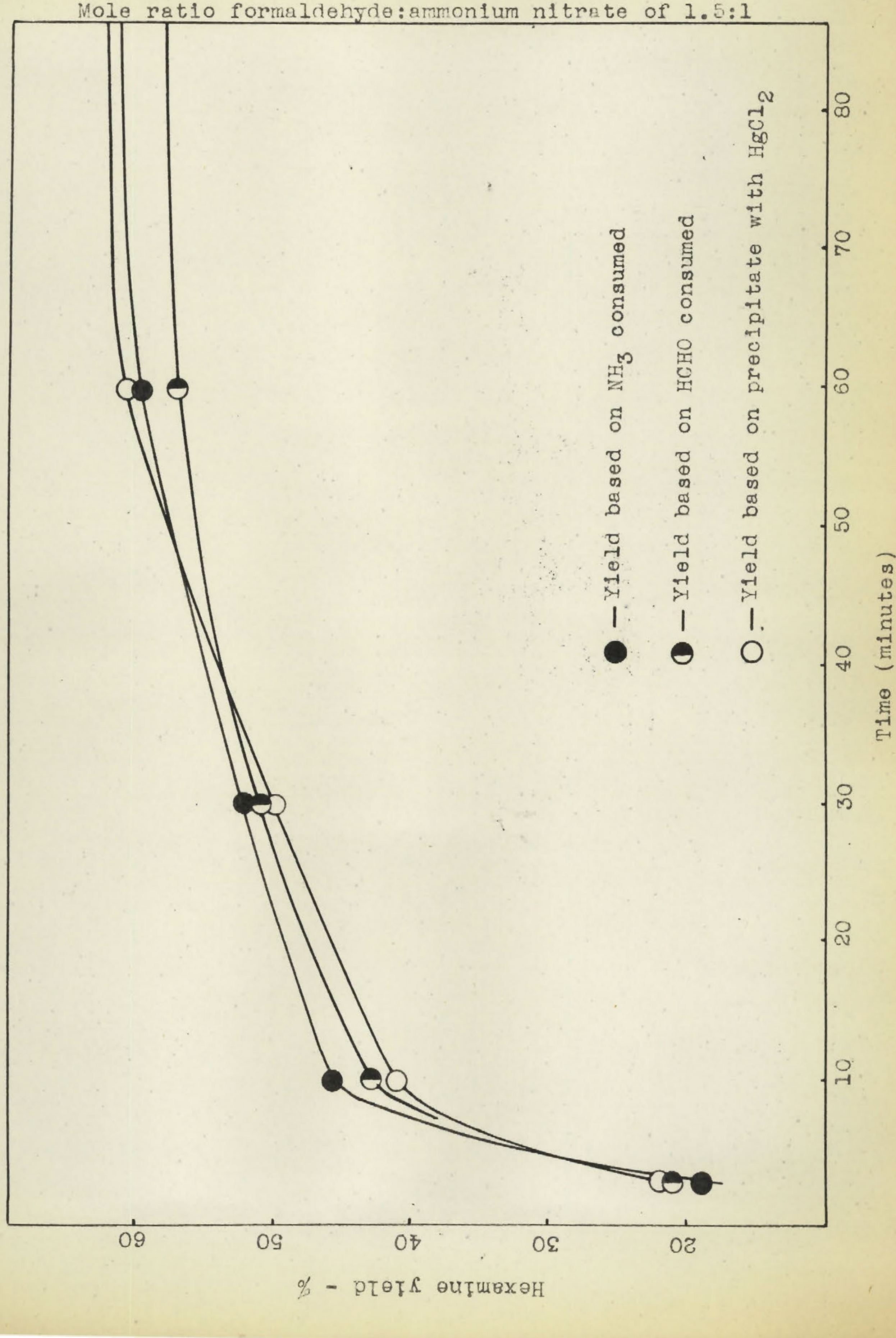


Fig.29

Rate curves for reaction at pH 6.0 and 20°C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:2

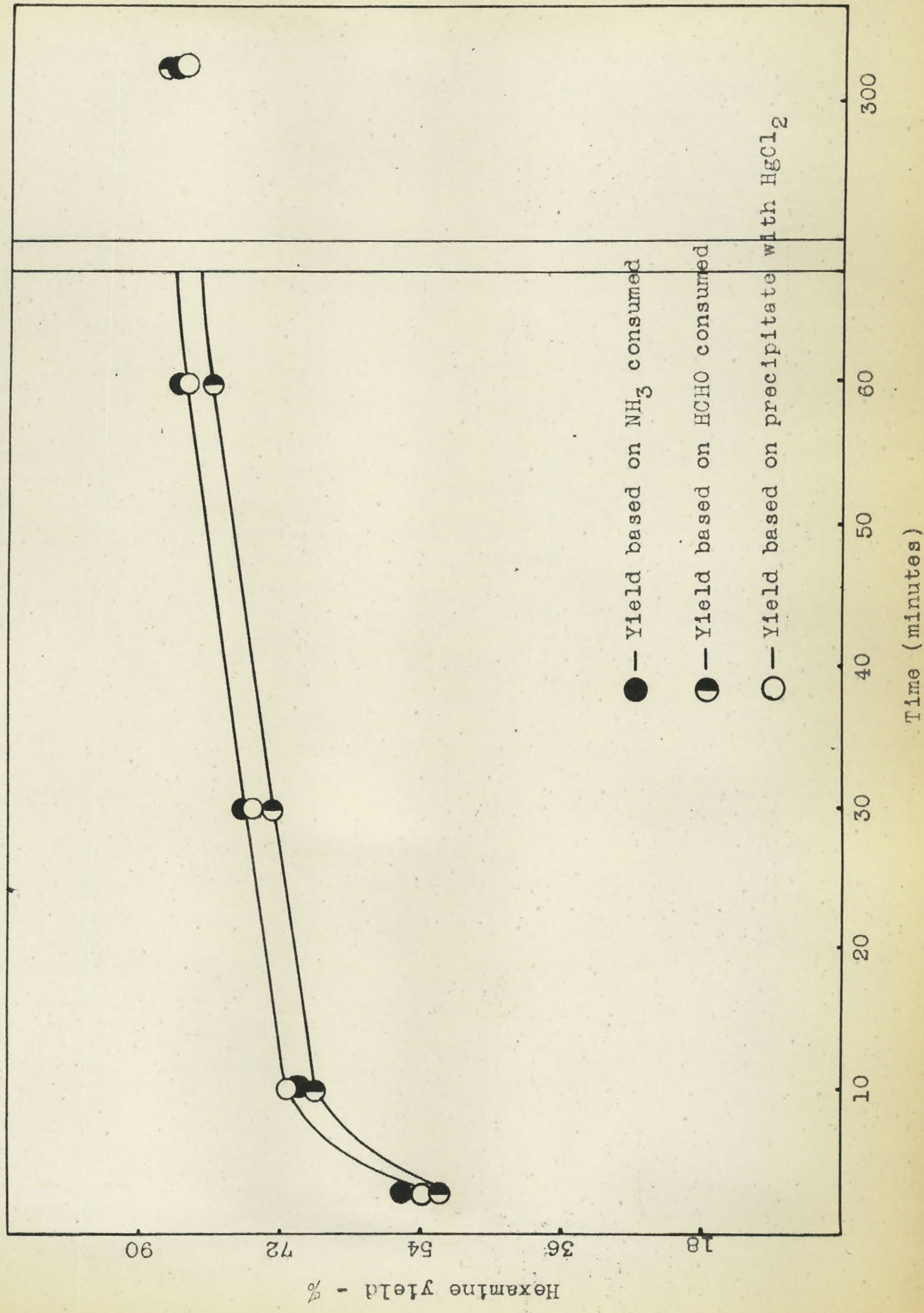


Table LIII

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.60N

Temperature 20°C. pH 6.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	30.4	-	38.1
3	65.2	67.8	70.2
6	75.9	75.9	78.2
10	83.9	81.2	85.3
30	89.3	86.6	89.0
60	96.4	93.8	97.5
120	96.4	97.3	98.5

Table LIV

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.30N

Temperature 40°C. pH 6.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	30.4	-	33.3
5	47.3	49.1	50.3
10	53.6	55.4	54.6
30	62.5	61.6	63.4
60	66.1	65.2	67.7
300	69.7	72.3	74.1

Fig.30

Rate curves for reaction at pH 6.0 and 20°C.

Mole ratio formaldehyde:ammonium nitrate of 3:1

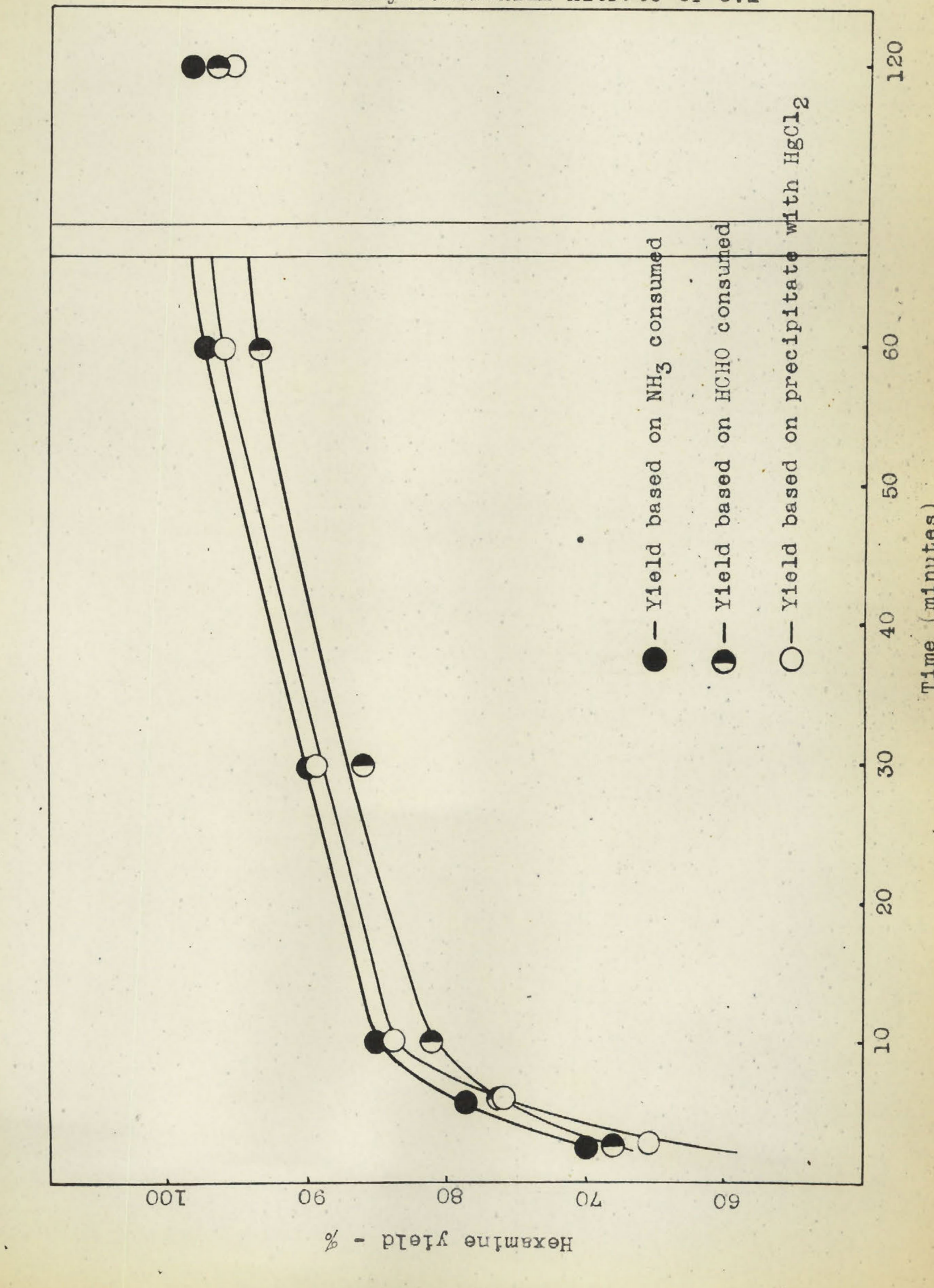


Fig.31

Rate curves for reaction at pH 6.0 and 40°C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:1

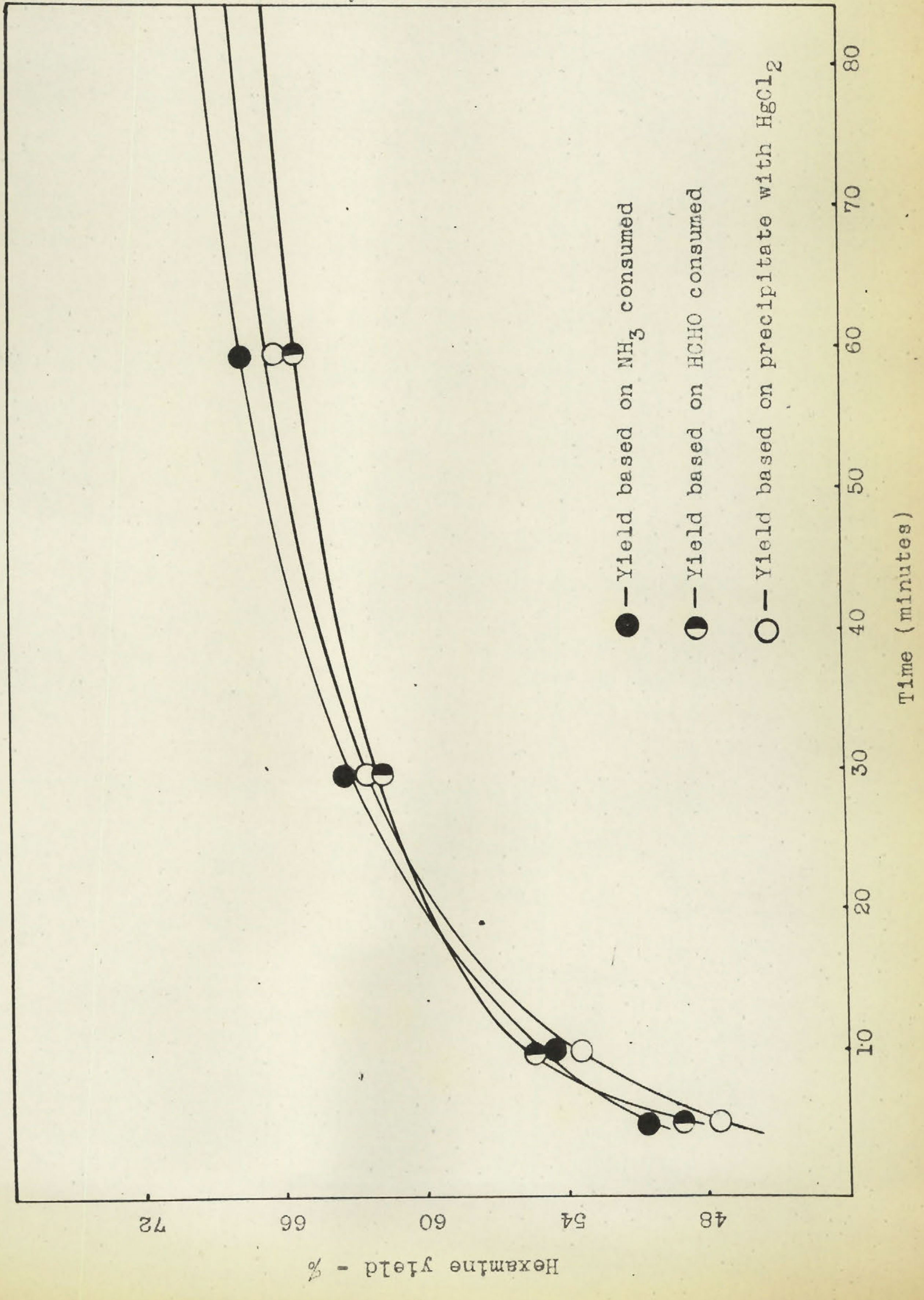


Table LV

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.40N　　Formaldehyde - 0.30N

Temperature 40°C.　　pH 6.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	47.3	-	54.0
3	64.3	66.9	68.0
6	68.8	72.3	74.4
10	71.7	76.8	79.2
30	80.3	83.0	85.2
60	83.0	86.6	89.0
180	87.5	91.0	92.0

Table LVI

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N　　Formaldehyde - 0.60N

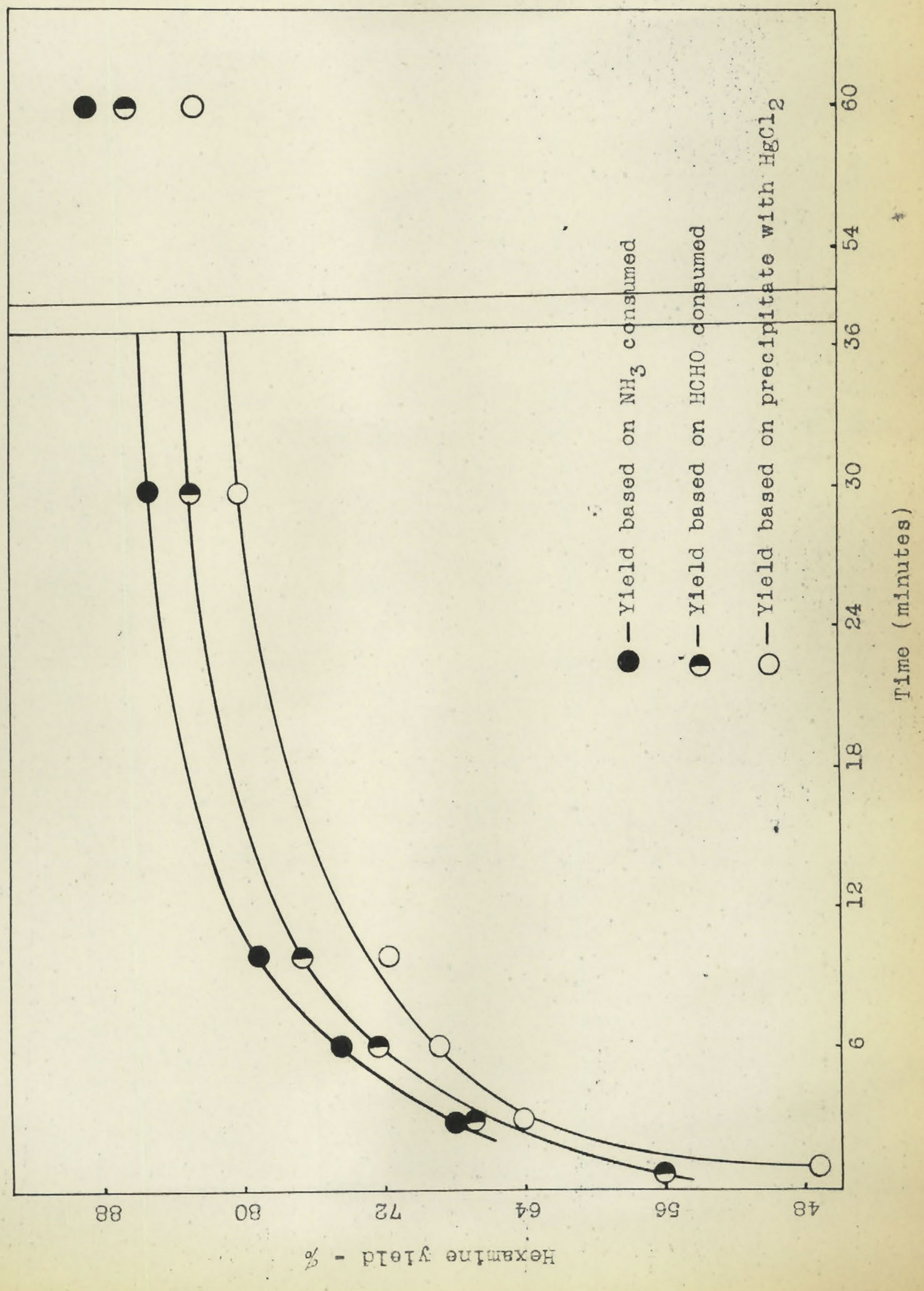
Temperature 40°C.　　pH 6.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
1	62.5	-	70.2
3	77.7	82.1	84.6
6	79.5	88.4	90.0
10	80.3	89.3	92.0
30	82.1	93.8	96.3
60	83.0	95.5	98.0

Fig.32

Rate curves for reaction at pH 6.0 and 40°C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:2



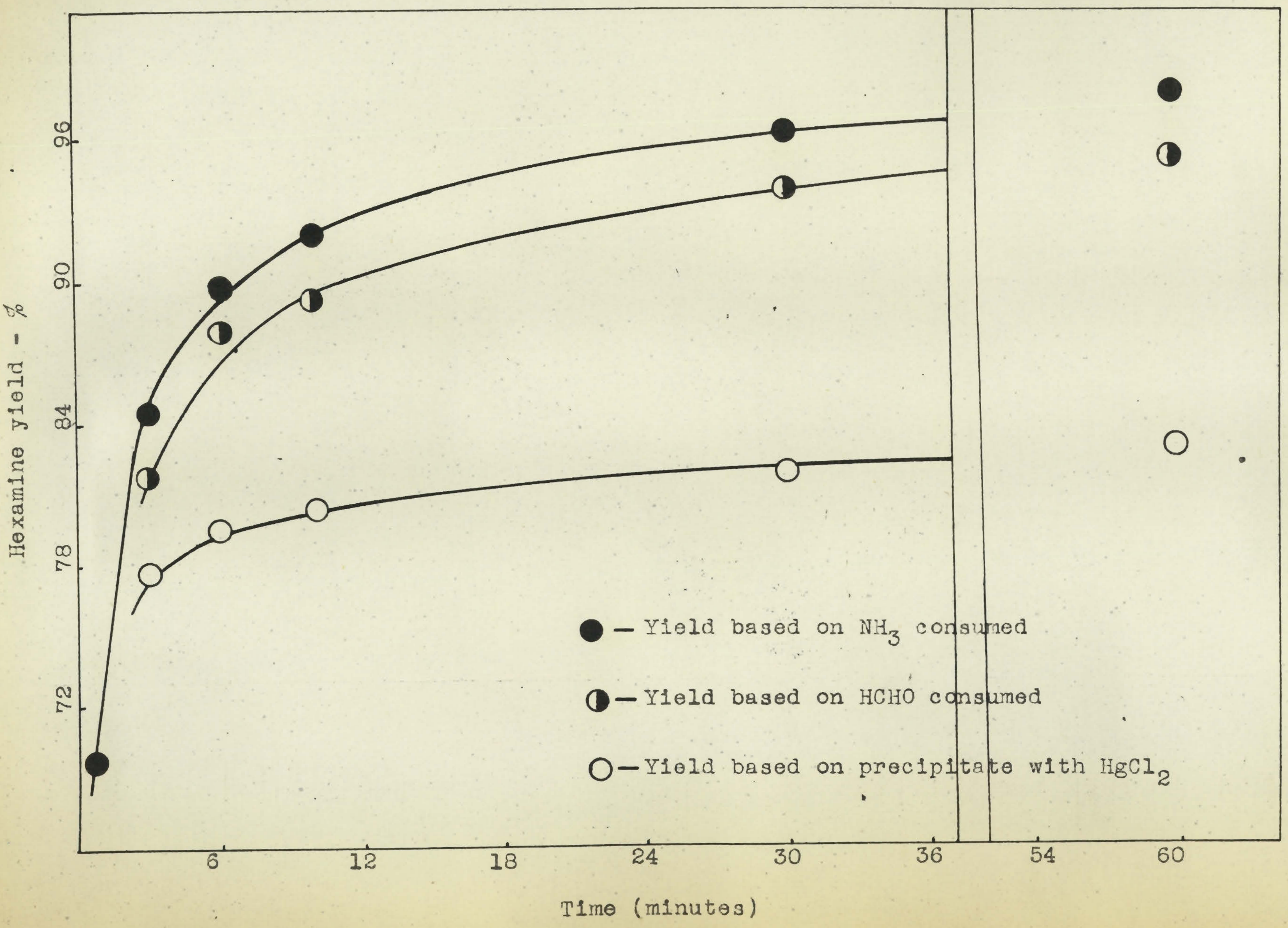


Fig. 33

Rate curves for reaction at pH 6.0 and 40°C.
Mole ratio formaldehyde:ammonium nitrate 3:1

Table LVII

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N   Formaldehyde - 0.30N

Temperature 0°C.   pH 4.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
150	0	0	0
240	0.9	0.9	1.3
300	1.8	1.8	2.0
390	2.7	2.7	3.0
480	3.0	3.0	3.4
600	5.4	5.4	5.1

Table LVIII

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.40N   Formaldehyde - 0.30N

Temperature 0°C.   pH 4.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
120	4.5	5.4	6.2
240	6.3	6.3	8.3
300	7.1	9.0	9.5
480	12.5	12.5	13.2
540	14.3	14.3	13.7
1440	30.3	32.1	31.7

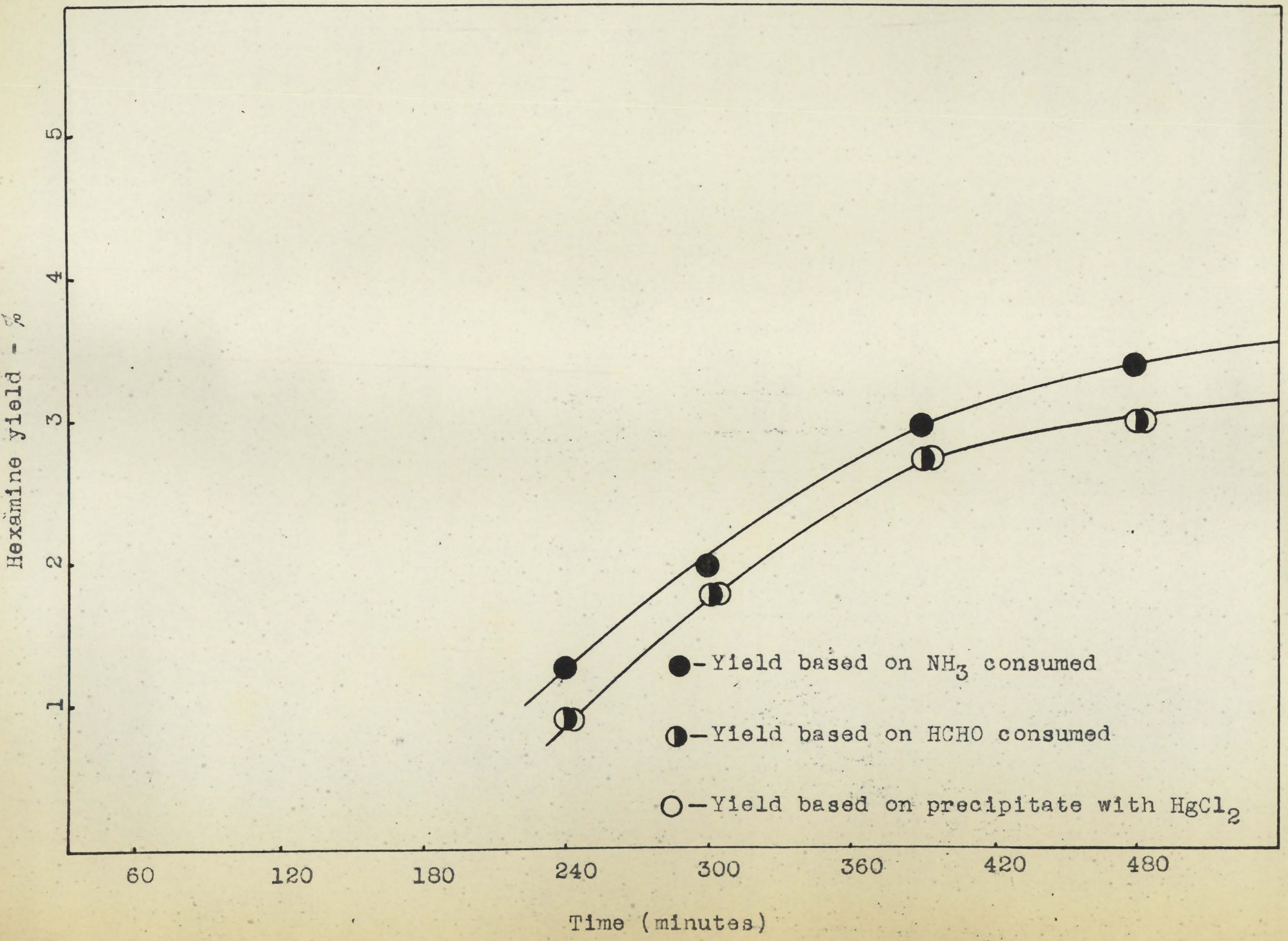


Fig.34

Rate curves for reaction at pH 4.0 and 0° C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:1

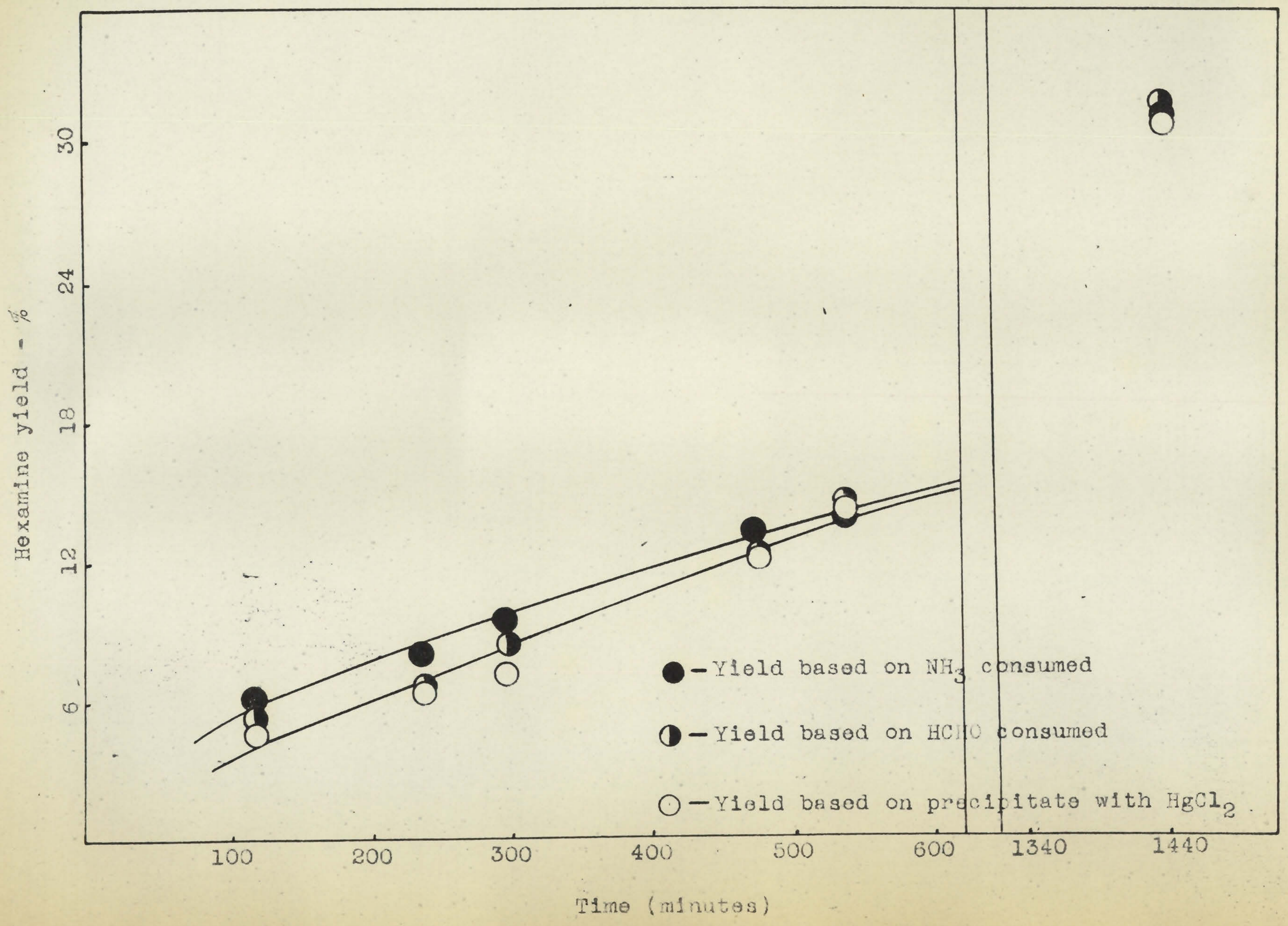


Fig. 35

Rate curves for reaction at pH 4.0 and 0°C.
Mole ratio formaldehyde:ammonium nitrate of 1.5:2

Table LIX

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.60N

Temperature 0°C. pH 4.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
150	4.5	5.4	6.1
240	9.0	9.8	10.4
300	12.5	12.5	13.2
480	16.0	18.8	17.8
600	18.8	20.5	20.8
1440	30.3	30.3	31.6

Table LX

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.30N

Temperature 20°C. pH 4.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
120	4.5	5.4	4.0
210	9.8	9.0	8.2
300	11.6	11.6	10.6
480	12.5	11.9	12.0
540	13.4	12.5	11.4
1440	16.9	16.0	15.1

Fig.36

Rate curves for reaction at pH 4.0 and 0° C.

Mole ratio formaldehyde:ammonium nitrate of 3:1

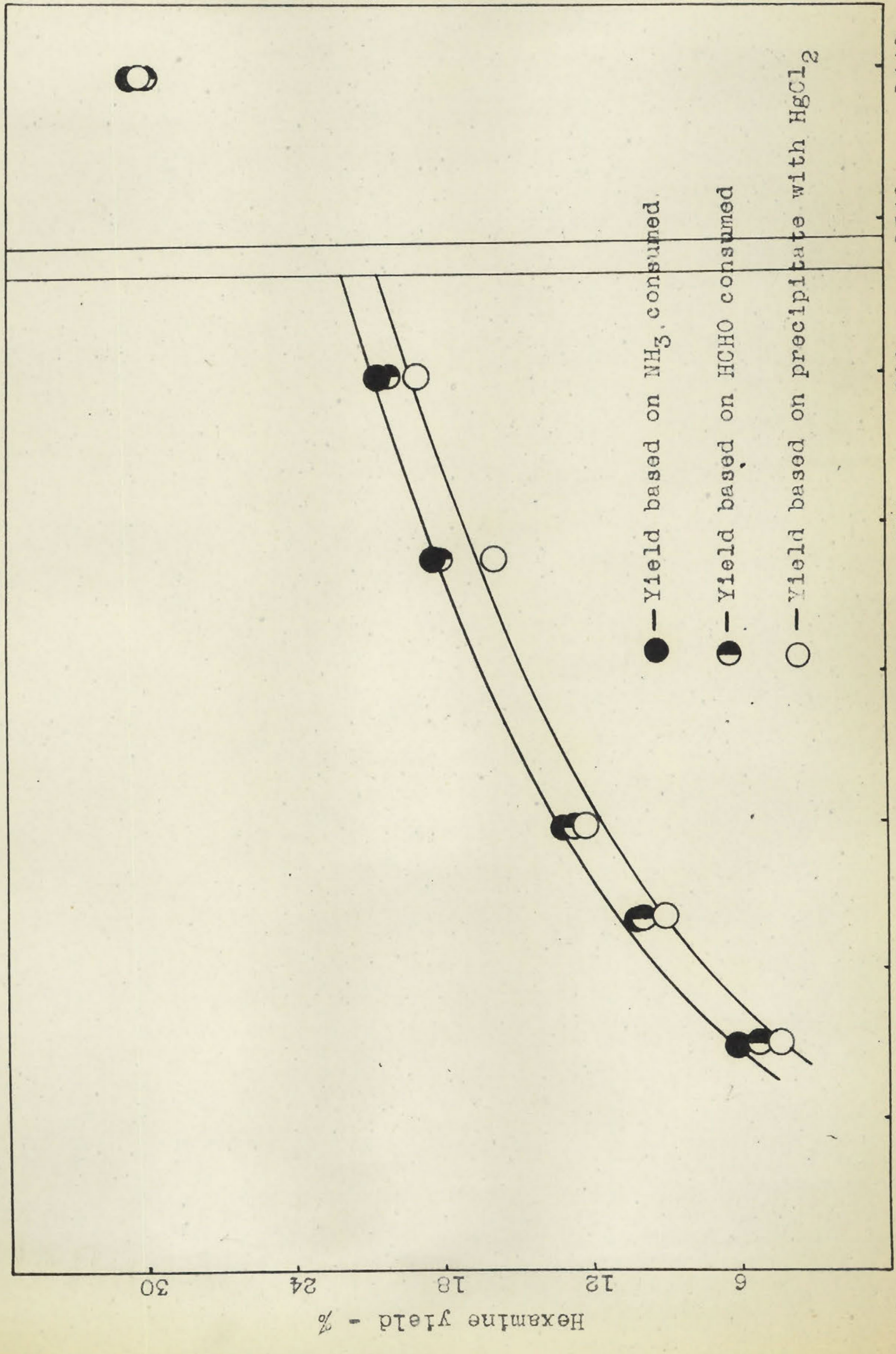


Fig.37

Rate curves for reaction at pH 4.0 and 20° C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:1

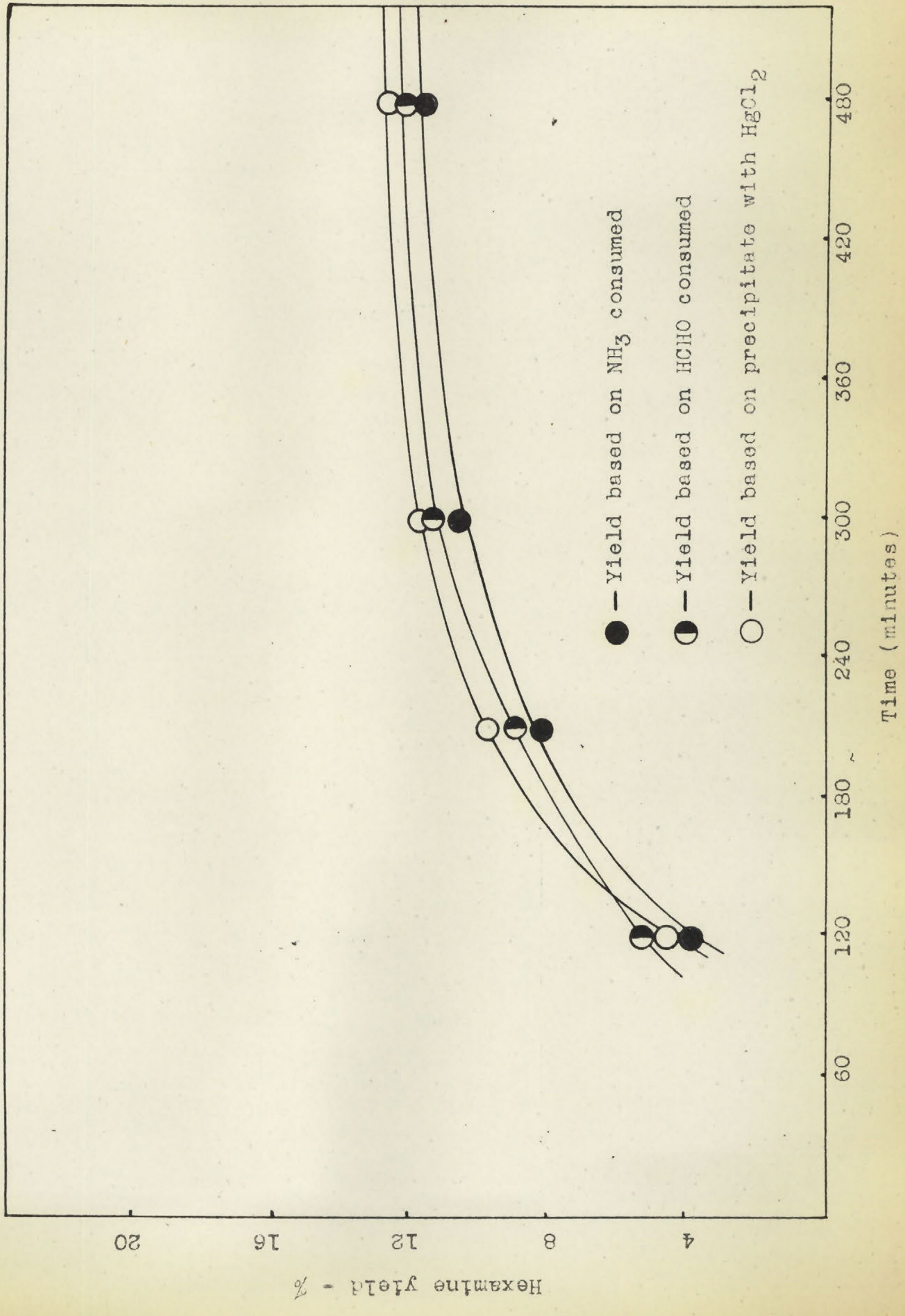


Table LXI

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.40N Formaldehyde - 0.30N

Temperature 20°C. pH 4.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
20	7.1	3.6	7.8
40	13.4	9.8	11.1
60	16.9	14.3	13.7
120	19.6	18.8	20.3
240	25.0	24.1	26.6
480	28.6	29.5	30.1
1440	33.0	34.0	35.2

Table LXII

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.60N

Temperature 20°C. pH 4.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
15	6.3	9.0	8.8
30	13.4	16.0	19.8
60	16.9	24.1	25.4
150	26.8	36.6	39.4
480	33.0	39.3	42.6
1440	43.7	48.2	51.3

Fig.38

Rate curves for reaction at pH 4.0 and 20°C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:2

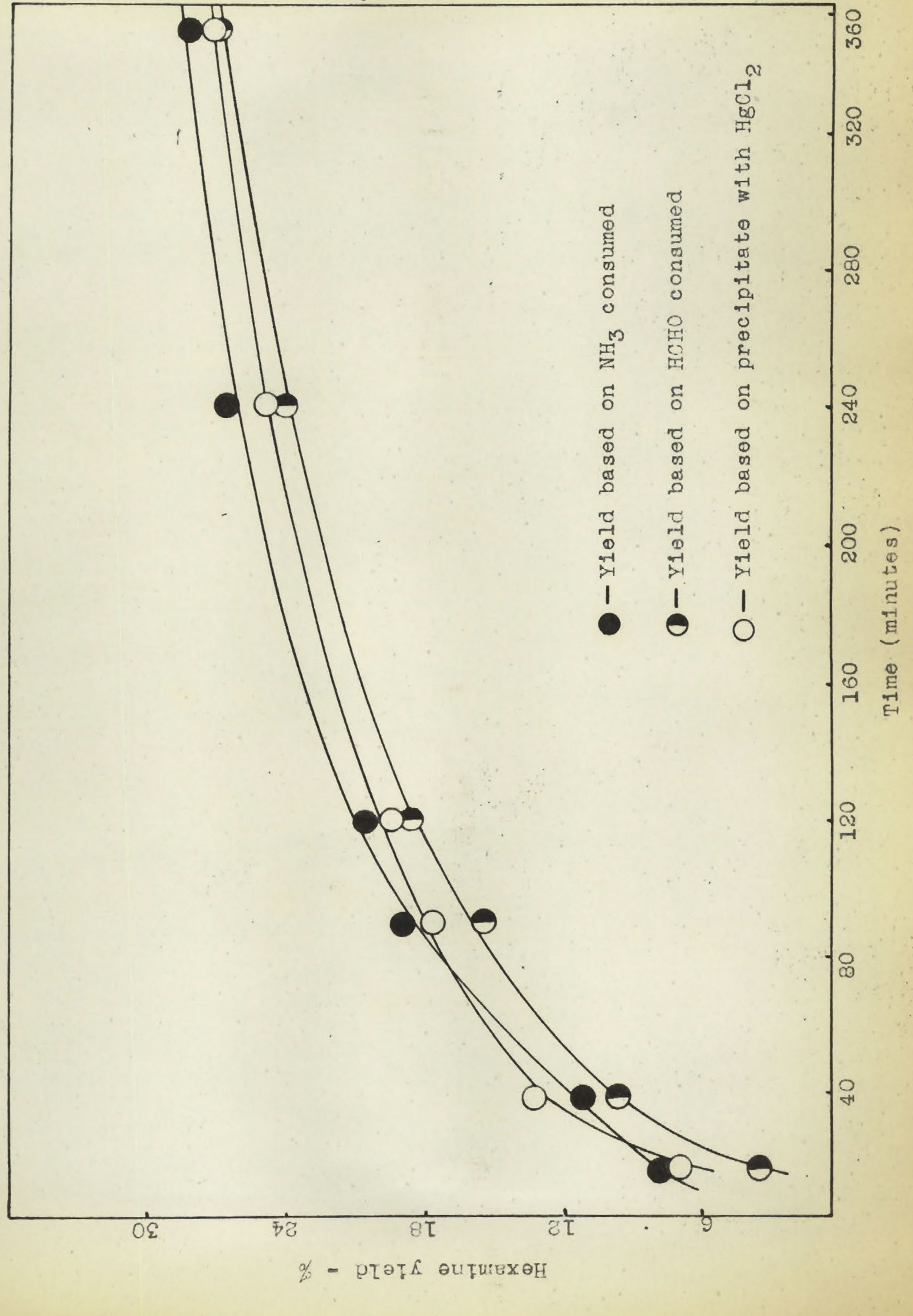


Fig.39

Rate curves for reaction at pH 4.0 and 20°C.

Mole ratio formaldehyde:ammonium nitrate of 3:1

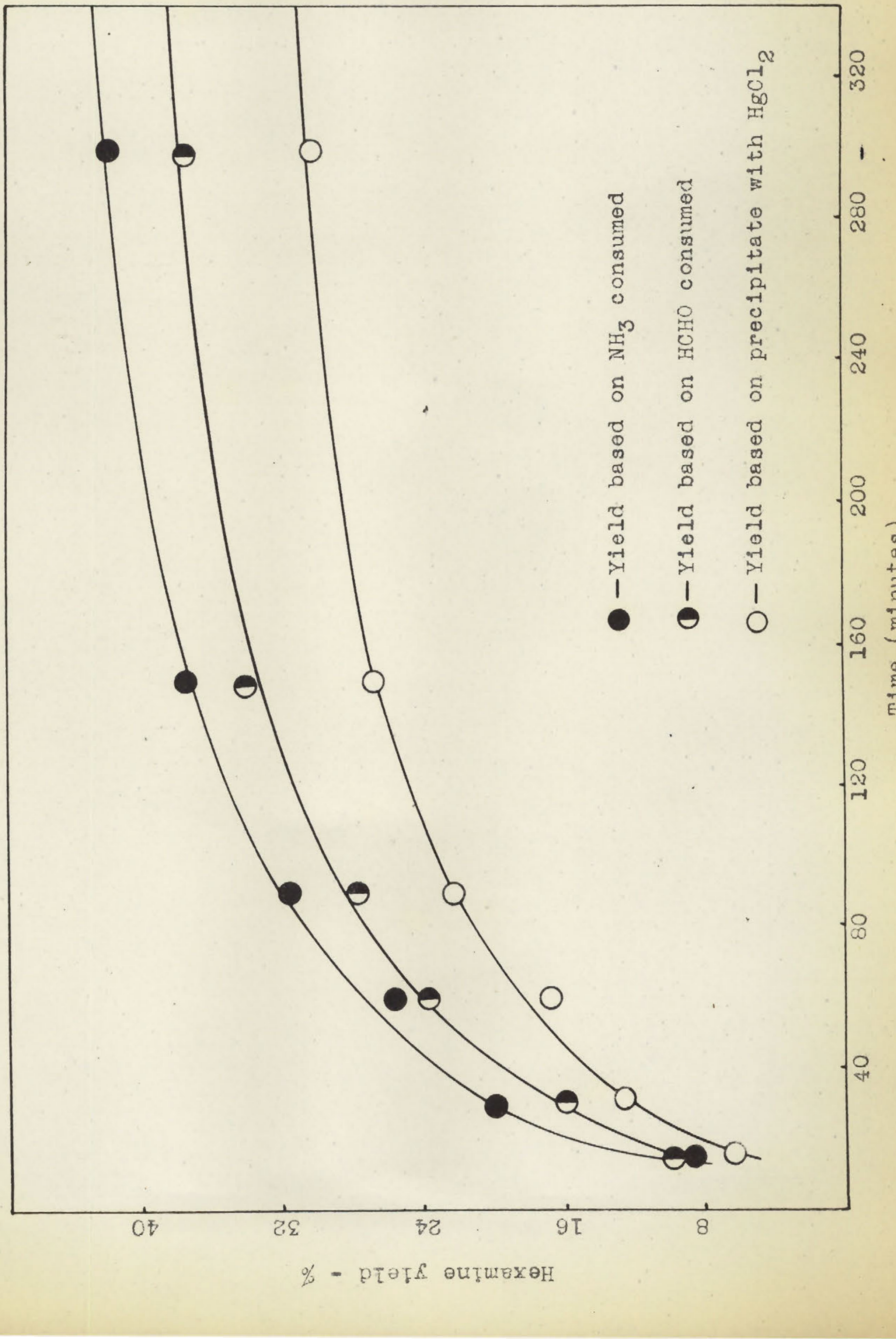


Table LXIII

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.30N

Temperature 40°C. pH 4.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
60	5.4	10.5	7.3
90	7.1	14.3	12.2
180	14.3	25.0	18.7
240	17.0	26.8	23.4
300	18.7	27.7	26.3
480	19.6	28.6	29.2

Table LXIV

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.40N Formaldehyde - 0.30N

Temperature 40°C. pH 4.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
5	7.1	5.4	-
15	13.4	12.5	14.6
30	19.6	18.8	21.1
60	26.8	25.0	28.6
180	28.6	27.7	29.2
240	29.5	30.3	28.6
480	30.3	31.2	29.1

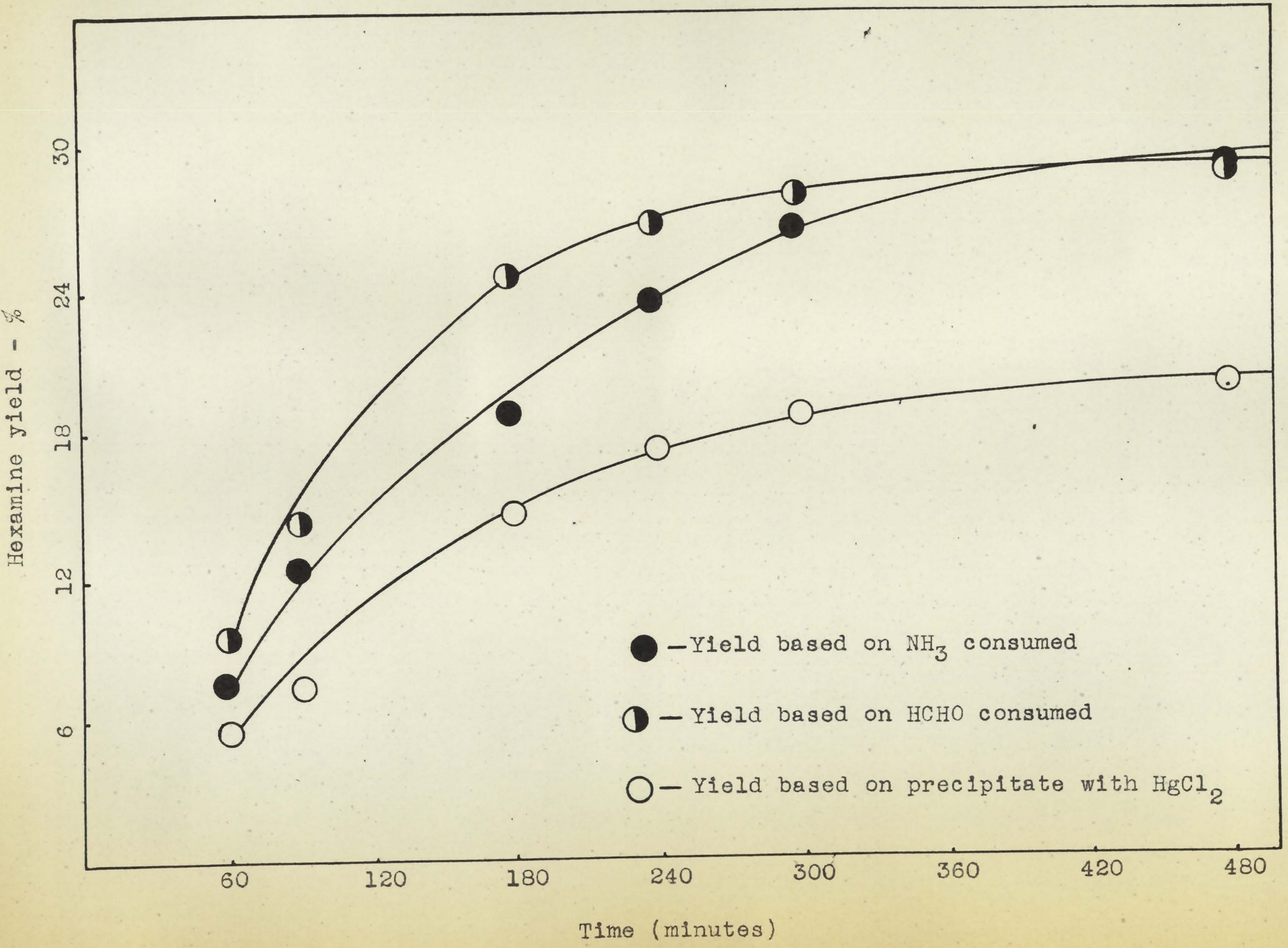


Fig.40

Rate curves for reaction at pH 4.0 and 40°C.
Mole ratio formaldehyde:ammonium nitrate of 1.5:1

Fig.41

Rate curves for reaction at pH 4.0 and 40°C.

Mole ratio formaldehyde:ammonium nitrate of 1.5:2

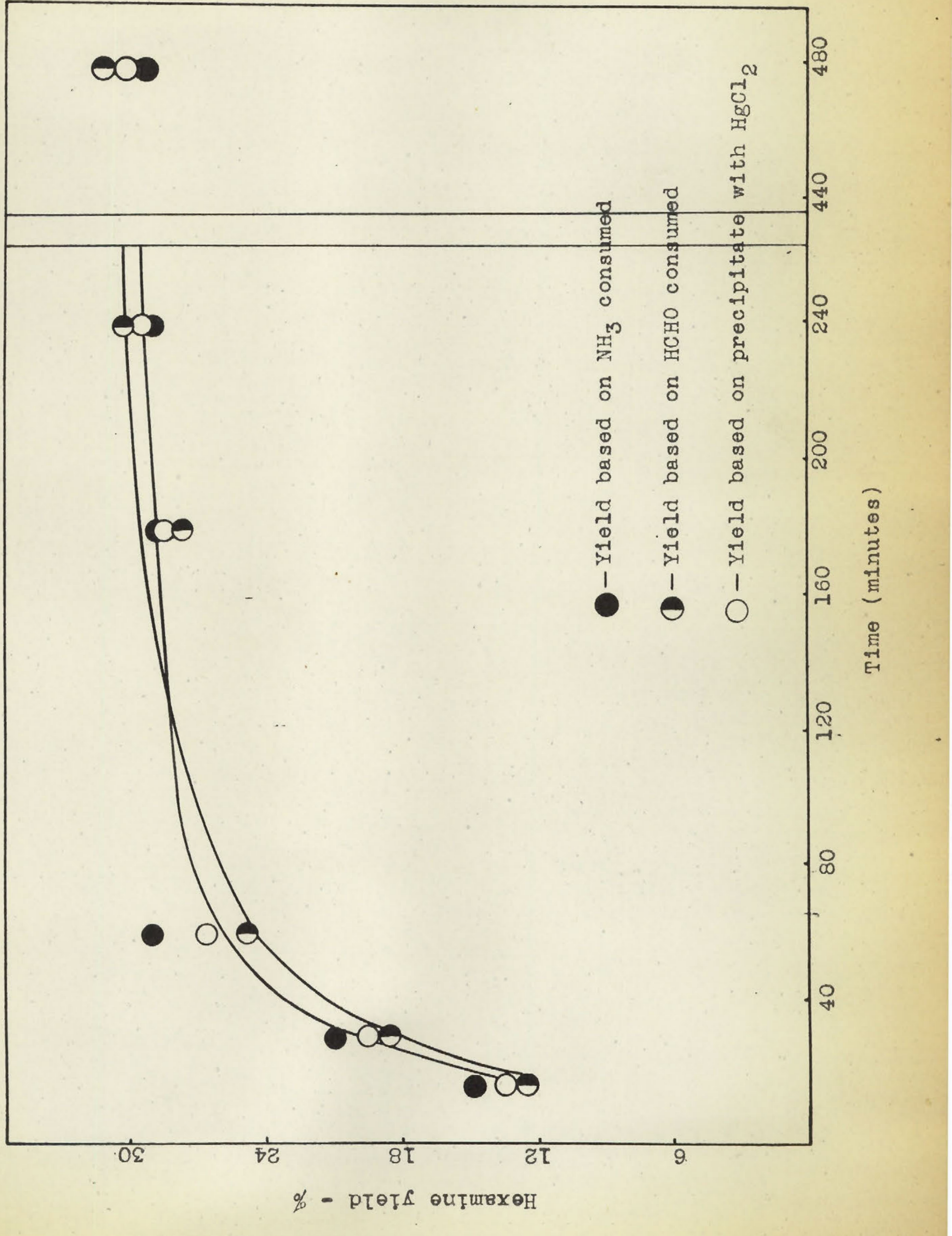


Table LXV

Rate of Hexamine Formation and Disappearance of Formaldehyde and Ammonia in Formaldehyde-Ammonium Nitrate Solution

Ammonium nitrate - 0.20N Formaldehyde - 0.60N

Temperature 40°C. pH 4.0

Time (min.)	Hexamine Yield - %		
	Based on $HgCl_2$ ppt.	Based on CH_2O consumed	Based on NH_3 consumed
5	12.5	20.5	22.9
15	24.1	28.6	30.5
30	26.8	36.6	35.0
60	33.0	41.9	43.0
90	36.6	44.6	47.5
120	37.5	48.2	52.6
210	44.6	58.0	60.9
300	47.8	62.5	65.1
600	53.6	66.2	69.8

Fig.42

Rate curves for reaction at pH 4.0 and 40°C.

Mole ratio formaldehyde:ammonium nitrate of 3:1

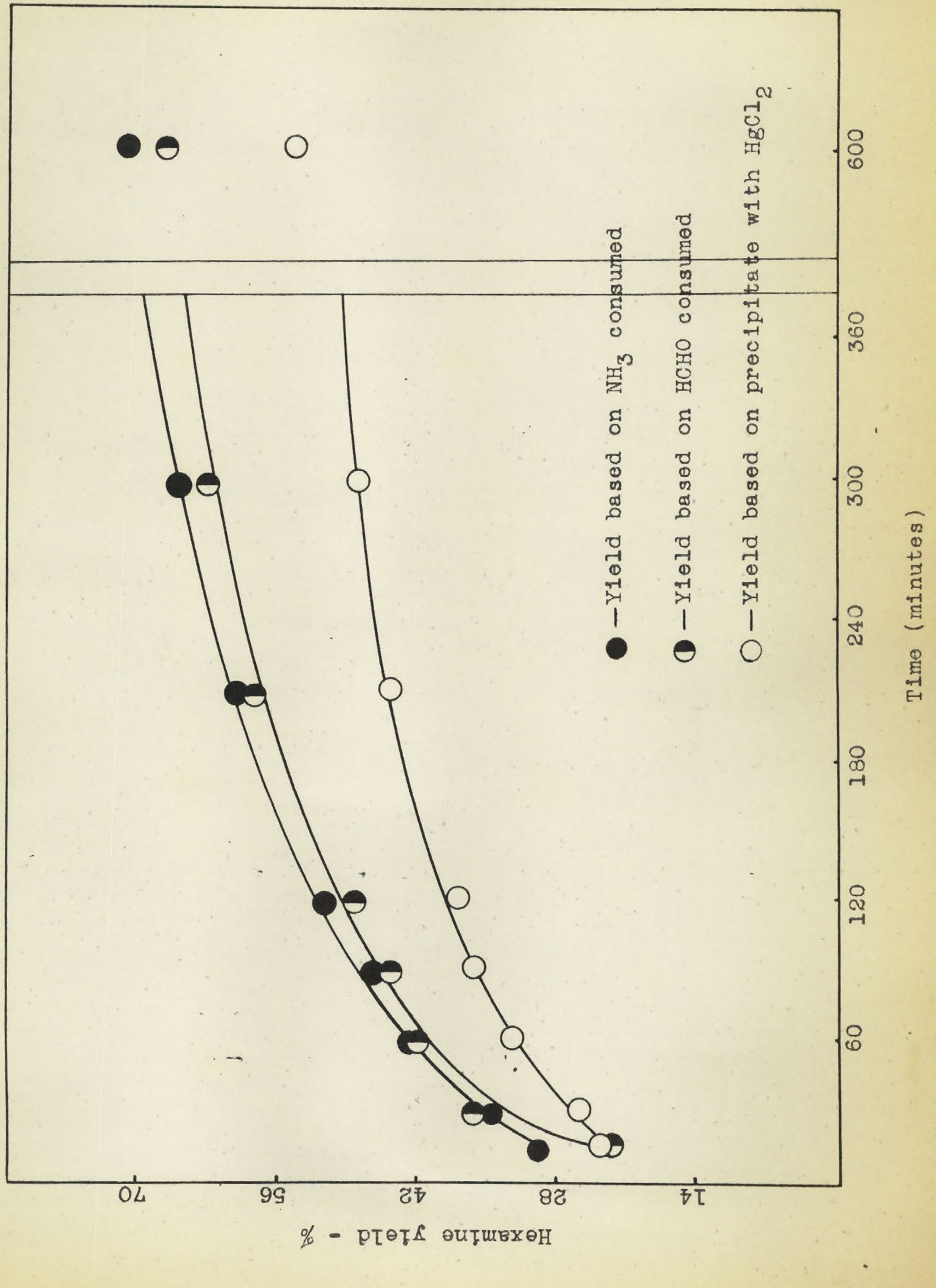
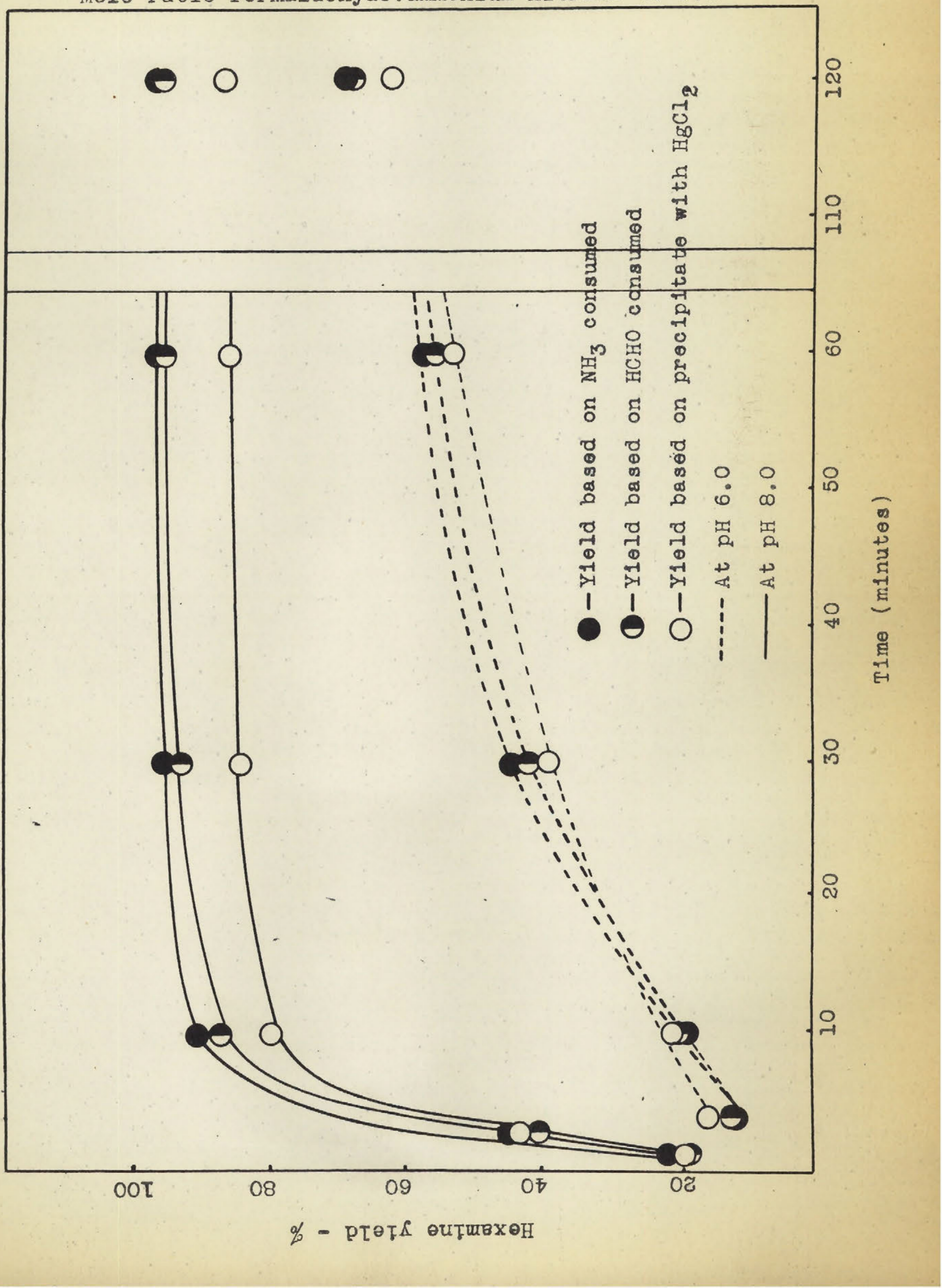


Fig.43

Comparison of rate curves at 0°C. in excess formaldehyde

Mole ratio formaldehyde:ammonium nitrate of 3:1



pH 8.0 and 0°C.

When the mole ratio formaldehyde:ammonium nitrate is 1.5:1, the three rate curves of hexamine formation based on material precipitated with mercuric chloride, formaldehyde consumed and ammonia consumed are seen to be closely similar throughout. Henceforth, for convenience, these curves are referred to as the mercuric chloride curve, the formaldehyde curve and the ammonia curve respectively.

In excess ammonium nitrate, the end point yields are increased by a very small extent. The three curves are about 5 per cent apart, with the mercuric chloride curve being the highest and the formaldehyde curve the lowest.

In excess formaldehyde, the three rate curves are increased slightly, over those for the 1.5:1 ratio. The mercuric chloride curve is 8 per cent below the formaldehyde curve at the end point, although the curves are in close agreement initially. The ammonia curve is about 3-5 per cent above the formaldehyde curve throughout. The fact that both the formaldehyde and ammonia curves lie at least 8 per cent above the mercuric chloride curve suggests that more formaldehyde and ammonium nitrate are consumed than appear as hexamine. In view of the manner in which the data are expressed, this behaviour can correspond only to formation of a by-product.

pH 8.0 and 20°C.

With the mole ratio formaldehyde:ammonium nitrate of 1.5:1, an increase in the temperature from 0°C. to 20°C. results in a 100 per cent increase in the initial rate. The mercuric chloride curve lies about 3 per cent above the ammonia curve and about 7 per cent above the formaldehyde curve.

In excess ammonium nitrate at 20°C., the initial rates are increased by about 20 per cent, whereas they are increased by only 3 per cent at 0°C. The three rate curves agree within 2 per cent at the end point, this time the mercuric chloride curve being the lowest. Initially, the formaldehyde curve lies about 5 per cent below the mercuric chloride and ammonia curves, but is between them at the end point. The final hexamine yield is about 8 per cent greater in excess ammonium nitrate.

In excess formaldehyde, the initial rates are increased by about 25 per cent but the final hexamine yields are nearly identical to those obtained in excess ammonium nitrate. The three rate curves agree within 2 per cent, with the mercuric chloride curve again the lowest.

pH 8.0 and 40°C.

An increase in the temperature from 20°C. to 40°C. is seen to produce only a 3-5 per cent increase in the initial rate and final hexamine yield.

When the mole ratio formaldehyde:ammonium nitrate is 1.5:1, the three rate curves differ by about 5 per cent initially but by less than 3 per cent at the end point. The mercuric chloride curve is the highest, closely parallelled by the ammonia curve, while the formaldehyde curve is 3-5 per cent lower.

In excess ammonium nitrate, the rate curves are in close agreement throughout.

In excess formaldehyde, the three rate curves are very similar at first, but at the end point, the formaldehyde and ammonia curves are close together and about 8 per cent above the mercuric chloride curve. This suggests that more formaldehyde and ammonium nitrate are consumed than appear as hexamine and this effect becomes more pronounced with increasing time.

An examination of the results obtained at pH 8.0 shows that hexamine formation is favoured at 40°C. by excess ammonium nitrate, at 20°C. by both excess formaldehyde and ammonium nitrate and at 0°C. by excess ammonium nitrate or by the theoretical proportions of the two reactants. At 0°C. and at 40°C., but not at 20°C., excess formaldehyde is seen to result in the formation of a stable by-product.

When the mole ratio formaldehyde:ammonia is 1.5:1, an increase in the temperature from 0°C. to 20°C. results in a large increase in the initial rate, but an increase from 20°C. to 40°C. produces only a small increase. The final hexamine yields agree within 3 per cent at 0°C., 20°C. and 40°C.

In excess ammonium nitrate, an increase in the temperature from 0°C. to 20°C. results in a large increase in the initial rate but raising the temperature from 20°C. to 40°C. produces only a small increase in the rate. The three rate curves are almost identical at 40°C.; they agree within 2 per cent at 20°C., but at 0°C., the formaldehyde curve is about 6 per cent below the mercuric chloride and ammonia curves.

In excess formaldehyde, an increase in the temperature from 0°C. to 20°C. results in a large increase in the initial rate but an increase from 20°C. to 40°C. has little effect on the rate which is already very rapid. At 40°C., the mercuric chloride curve is 7 per cent below the formaldehyde and ammonia curves; at 20°C., the three rate curves differ by only 2 per cent, but at 0°C., the mercuric chloride curve is 8 per cent below the formaldehyde and ammonia curves.

pH 6.0 and 0°C.

With the formaldehyde:ammonium nitrate ratio of 1.5:1, the three rate curves are in close agreement throughout.

When the ammonium nitrate is in excess, the initial rate is doubled and the hexamine yield at the end point is increased by about 15 per cent. The three rate curves are in close agreement throughout.

In excess formaldehyde, the initial rate is increased to a slightly greater extent than in excess ammonium nitrate. The final hexamine yield is about 10 per cent greater than in excess ammonium nitrate. The three rate curves differ by about 7 per cent, with the mercuric chloride curve being the lowest.

pH 6.0 and 20°C.

At 20°C., the initial rates are about five times as great as at 0°C. The final hexamine yields are increased by 30-40 per cent.

With the mole ratio formaldehyde:ammonium nitrate of 1.5:1, the three rate curves agree within 4 per cent, with the mercuric chloride curve being the highest.

In excess ammonium nitrate, the initial rate is doubled. The three rate curves differ initially by about 5 per cent, with the formaldehyde curve lying below the other two rate curves, but at the end point, they agree within 1 per cent. The final hexamine yield is increased by 10 per cent.

In excess formaldehyde, there is a still greater increase in the initial rate of hexamine formation. The three rate curves are in close agreement throughout. The final hexamine yields are about 10 per cent greater than in excess ammonium nitrate.

pH 6.0 and 40°C.

When the mole ratio formaldehyde:ammonium nitrate is 1.5:1, increasing the temperature from 20°C. to 40°C. results in doubling the initial rate. The final hexamine yields, however, are closely similar to those obtained at 20°C. The three rate curves agree within 4 per cent throughout, with the ammonia curve being highest and the mercuric chloride curve lowest.

In excess ammonium nitrate, the initial rate is increased by about 18 per cent, this increase being continued to final hexamine yields 18 per cent greater. The three rate curves agree within 5 per cent throughout, with the mercuric chloride curve being lowest.

In excess formaldehyde, the initial rate is about 15 per cent greater than in excess ammonium nitrate. Initially, the three rate curves differ by only 8 per cent, but at the end point, the difference is 15 per cent. The formaldehyde and ammonia curves are in close agreement but 15 per cent above the mercuric chloride curve. Evidently, the excess formaldehyde results in the formation of a stable by-product.

An examination of the results at pH 6.0 shows that the reaction of formaldehyde with ammonium nitrate leads almost exclusively to hexamine formation when the mole ratio formaldehyde:ammonium nitrate is 1.5:1 and also in excess ammonium nitrate at 0°C., 20°C. and 40°C. When the formaldehyde is in excess, the hexamine yield is increased but there is a much greater formation of by-products.

When the mole ratio formaldehyde:ammonium nitrate is 1.5:1, an increase in the temperature from 0°C. to 20°C. results in a five-fold increase in the initial rate and the final hexamine yield is doubled. Increasing the temperature from 20°C. to 40°C. results in an increased initial rate but the final hexamine yield is similar to that obtained at 20°C. The three rate curves agree within 4 per cent at the three temperatures investigated, 0°C., 20°C. and 40°C.

In excess ammonium nitrate, the initial rate is increased as is the final hexamine yield. At 0°C. and 20°C., the three rate curves agree within about 3 per cent. At 40°C., they agree within about 5 per cent, the mercuric chloride curve being the lowest, suggesting that there is some by-product formation.

In excess formaldehyde, the initial rate is increased and to a greater extent than in excess ammonium nitrate. The final hexamine yield, however, is increased by 7 per cent at 0°C., by 12 per cent at 20°C. and at 40°C., is actually 4 per cent less. At 0°C. and 40°C., it can be seen that more formaldehyde and ammonia are consumed than appear as hexamine. On the other hand, the optimum for hexamine formation at pH 6.0 is in excess formaldehyde at 20°C.

The hexamine yields at pH 6.0 are lower than at pH 8.0, except in excess formaldehyde at 20°C.

pH 4.0 and 0°C.

When the mole ratio formaldehyde:ammonium nitrate is 1.5:1, the three rate curves are very similar throughout.

In excess ammonium nitrate, the rate is increased about seven-fold, the final hexamine yield being about six times as large. The three rate curves agree within 3 per cent throughout.

In excess formaldehyde, the initial rate is increased to a still greater extent, but the final hexamine yield is closely similar to that obtained in excess ammonium nitrate. Here also, the three rate curves are in close agreement throughout.

pH 4.0 and 20°C.

The increase in the temperature from 0°C. to 20°C.

results in a ten-fold increase in the initial rate of hexamine formation.

When the mole ratio formaldehyde:ammonium nitrate is 1.5:1, the three rate curves are closely similar throughout.

In excess ammonium nitrate, the initial rate is about five times faster, the final hexamine yield being doubled. The three rate curves agree within 3 per cent throughout.

In excess formaldehyde, the initial rate is increased to a slightly greater extent than in excess ammonium nitrate, and the final hexamine yield is about 10 per cent greater. The three rate curves differ by about 10 per cent, with the mercuric chloride curve being the lowest. Evidently, in excess formaldehyde, there is by-product formation.

pH 4.0 and 40°C.

The initial rate is about four times faster at 40°C. than at 20°C. The final hexamine yields, however, are little increased, except in excess formaldehyde, when the increase is about 10 per cent.

When the mole ratio formaldehyde:ammonium nitrate is 1.5:1, the three rate curves differ by about 10 per cent throughout. The ammonia and formaldehyde curves are in close agreement and lie about 10 per cent above the mercuric chloride curve, indicating that more ammonium nitrate and formaldehyde are consumed than appear as hexamine.

In excess ammonium nitrate, the initial rate is at least five times faster, accompanied by about 10 per cent increase in the final hexamine yield. The three rate curves agree within 3 per cent. Thus, it is evident that excess ammonium nitrate favours the formation of hexamine and decreases by-product formation at this pH.

In excess formaldehyde, the initial rate is increased to a greater extent than in excess ammonium nitrate. The final hexamine yield is 20 per cent greater. The three rate curves differ by 10-15 per cent throughout, the mercuric chloride curve being the lowest. Evidently, the excess formaldehyde results in considerable by-product formation.

An examination of the results at pH 4.0 shows that the rate of formation and the final yields of hexamine are much lower than those observed at pH 6.0.

With the mole ratio formaldehyde:ammonium nitrate of 1.5:1, an increase in the temperature from 0°C. to 20°C. results in a large increase in the initial rate of hexamine formation. The final hexamine yield is about three times greater, although still only 16 per cent of the theoretical. Increasing the temperature from 20°C. to 40°C. produces a further increase in the initial rate but the final hexamine yield is only 3 per cent greater. At 0°C. and 20°C., the three rate curves are in close agreement throughout. At 40°C., however, the formaldehyde and ammonia curves are similar and they lie about 10 per cent above the mercuric chloride curve, indicating that more formaldehyde and ammonium nitrate are consumed than appear as hexamine.

In excess ammonium nitrate, the initial rates are about five times faster and the final hexamine yields are at least doubled. At 0°C., 20°C. and 40°C., the three rate curves are in close agreement throughout.

In excess formaldehyde, the initial rate is increased to a greater extent than in excess ammonium nitrate. At 0°C., the final hexamine yield is similar to that in excess ammonium nitrate and the three rate curves are in close agreement. At 20°C. and 40°C., the final hexamine yields are greater than in excess ammonium nitrate, but there is also an increased tendency for by-product formation, especially at 40°C.

General Analysis of Results

An examination of the kinetic data obtained in buffered solutions discloses the following relationships.

An increase in the temperature produces an increase in the initial rate of hexamine formation. This increase in the initial rate is greater when the temperature is raised from 0°C. to 20°C. than when it is raised from 20°C. to 40°C. At pH 8.0, although the initial rates are increased by a rise in the temperature, the final hexamine yields are almost unchanged. At pH 4.0 and 6.0, the final hexamine yields are also increased by a rise in the temperature, but this increase is more pronounced from 0°C. to 20°C. than from 20°C. to 40°C.

At a given temperature, an increase in the pH causes an increase in the initial rate of hexamine formation. An increase in the pH from 4.0 to 6.0 produces a much greater increase in the initial rate and final hexamine yield than an increase from 6.0 to 8.0. Since an increase in both pH and temperature result in an increased rate of formation and final yield of hexamine, the effect of increased temperature is less at higher than at lower pH. Similarly, at higher temperature, the effect of increased pH is less pronounced.

When the mole ratio formaldehyde:ammonium nitrate is 1.5:1, the mercuric chloride, formaldehyde and ammonia curves agree within 5 per cent at pH 8.0 at each of the temperatures investigated. This means that under these experimental conditions, the reaction of formaldehyde with ammonium nitrate leads almost exclusively to hexamine formation. The difference which does exist between the three rate curves is due to the fact that the ammonia and mercuric chloride curves are closely similar and both lie about 4 per cent above the formaldehyde curve. If there were by-product formation, the ammonia and formaldehyde curves would lie above the mercuric chloride curve, as is observed in excess formaldehyde. Similarly, at pH 6.0, the three rate curves agree within 5 per cent, whether at 0°C., 20°C. or 40°C. However, whereas at 0°C. and at 40°C., the mercuric chloride curve is the lowest of the three, indicating that more formaldehyde and ammonium nitrate are consumed than appear as hexamine, at 20°C., the mercuric chloride curve lies about 5 per cent above the formaldehyde curve and 3 per cent above the ammonia curve. At pH 4.0, the three rate curves are in close agreement at 0°C. and 20°C. At 40°C., the formaldehyde and ammonia curves are in close agreement, but both lie about 10 per cent above the mercuric chloride curve, indicating that there is by-product formation, since more formaldehyde and ammonia are consumed than appear as hexamine. Evidently this tendency for by-product formation increases with time, since the curves initially differ only slightly but become increasingly divergent with increasing time.

Thus, when the mole ratio formaldehyde:ammonium nitrate is 1.5:1, hexamine formation is favoured at the higher pH and lower temperature; by-product formation increases at higher temperatures, especially as the pH is decreased.

In excess ammonium nitrate, the initial rate of hexamine formation is increased. The per cent increase in the initial rate at a given temperature is greater at the lower pH. It is also seen that in excess ammonium nitrate, the formation of hexamine is favoured and the formation of by-products is decreased. This effect is most pronounced at 40°C. and pH 4.0, where otherwise by-product formation is quite large. In a given experiment, it is seen that the three rate curves are in close agreement, showing that the formaldehyde and ammonium nitrate consumed are converted almost entirely to hexamine. With the ammonium nitrate in excess, it is noted that there is a tendency for the ammonia and mercuric chloride curves to be in close agreement and to lie slightly above the formaldehyde curve. Apparently, under these conditions, the mercuric chloride complex is contaminated with some ammonia or a compound containing ammonia and formaldehyde but which gives up its formaldehyde content on analysis. This effect was also observed by Boyd (32).

In excess formaldehyde, the initial rate of hexamine formation is increased, the per cent increase being greater at the lower pH. It is also observed that in excess formaldehyde, a stable by-product is formed. This is indicated by the fact that the formaldehyde and ammonia curves lie above the mercuric chloride curve. At pH 8.0, there is by-product formation at 0°C., 20°C. and 40°C. but it is most pronounced at 40°C. At pH 6.0, there is less by-product formation at 0°C. and 20°C. than at pH 8.0. At 40°C., however, it is again extensive. At pH 4.0, the three rate curves agree within about 2 per cent at 0°C. but by-product formation becomes increasingly great as the temperature is raised to 20°C. and then to 40°C.

DISCUSSION OF RESULTS

There are several general characteristics of the reaction of formaldehyde with an ammonium salt which must be taken into account by any proposed mechanism of hexamine formation.

It has been shown that hexamine is formed in the reaction of formaldehyde with a variety of ammonium salts, in both aqueous and glacial acetic acid media. The successful isolation of the hexamine in good yield depends upon the neutralization of acid formed in the reaction before the solution is evaporated to dryness.

When the rate of hexamine formation was investigated in the reaction of formaldehyde with various ammonium salts in aqueous solution, it was found that both the rates of formation and the final yields of hexamine vary greatly with the different ammonium salts. The slower rates and smaller hexamine yields are associated with the ammonium salts which, when dissolved in water, form the solutions of lower pH, such as ammonium nitrate. The rates are faster and the yields greater with the ammonium salts which form solutions of higher pH, such as ammonium acetate and dibasic ammonium phosphate.

When the formaldehyde-ammonium salt reactions took place in buffered solution, however, the different ammonium salts showed approximately similar rates of formation and final yields of hexamine. This suggests that at given pH, the different ammonium salts become merely sources of ammonium ions or available ammonia as far as hexamine formation is concerned.

The pH of the reaction solution is an important factor governing both the rate of formation and the final yield of hexamine. An increase in the pH results in an increased rate of formation and final yield. When the pH is decreased from 8.0 to 6.0, the rate and the yield are also decreased, but to a smaller extent than is caused by a decrease in the pH from 6.0 to 4.0. Apparently the pH of the reaction solution becomes increasingly important as a rate-determining factor as the solution becomes more acidic. An examination of the kinetic data, however, shows that the relations of the three rate curves at given temperature and relative reactant concentration are not affected by a change in the pH of the reaction solution. For example, excess formaldehyde favours by-product formation at pH 8.0, 6.0 and 4.0. Similarly, excess ammonium nitrate decreases by-product formation at each reaction solution pH. That is, the effect observed at pH 8.0 is also observed at pH 4.0. This does not mean that the pH is without effect, but rather that the pH increases or decreases a reaction tendency governed primarily by whether the formaldehyde or ammonium nitrate is in excess. Thus, it appears that the pH of the reaction solution governs the rate of formation and final yield of hexamine but not the course of the reaction.

Temperature exerts a dual effect on the reaction of formaldehyde with an ammonium salt. An examination of the data discloses that when the formaldehyde and ammonium nitrate are present in the theoretical proportions, an increase in the temperature not only increases the rate of formation and final yield of hexamine, but also leads to by-product formation. That is, the conversion of reactants to hexamine at elevated temperatures is less complete than at lower temperatures. When the ammonium nitrate is in excess, an increase in the temperature again results in an increased rate of formation but the tendency for by-product formation is decreased. When the formaldehyde is in excess, by-product formation becomes increasingly great as the temperature rises.

A further important observation disclosed by the kinetic study data is that doubling the formaldehyde concentration beyond that required by the theoretical proportions for hexamine formation produces a greater increase in the initial rate of hexamine formation than is produced by doubling the ammonium nitrate concentration. Also, the final hexamine yields are usually greater in excess formaldehyde at the lower temperatures. As the temperature is increased, however, the conversion of the reactants to hexamine becomes less complete, so that the yield of hexamine at the end point may be actually decreased.

By-product formation occurs when the formaldehyde is in excess, especially as the temperature is increased. An examination of the rate curves for the various experiments in which the formaldehyde was in excess shows that, initially, the three rate curves differ only slightly. With increasing time, however, the mercuric chloride curve indicates that an end point has been reached, while the formaldehyde and ammonia curves continue to rise. This shows that hexamine formation has ceased but formaldehyde and ammonia are still reacting. Evidently, during the initial stages of the reaction, the formation of hexamine is the preferred course of reaction. With increasing time, by-product formation becomes more extensive until hexamine formation ceases and the formaldehyde and ammonia still reacting are being converted almost entirely to by-product. These observations suggest that, under the reaction conditions investigated, the formation of hexamine is a more rapid reaction than that of by-product formation, evidently requiring a lower energy of activation.

There are two types of general behaviour to be considered. In the first, the ammonia curve lies above the other two curves, being closely followed by the formaldehyde curve; these two curves, however, lie considerably above the mercuric chloride curve. This situation is observed only in excess formaldehyde and is especially pronounced as the temperature is increased. The fact that both the formaldehyde and ammonia curves lie relatively closely together and above the mercuric chloride curve indicates that more formaldehyde and ammonium nitrate are consumed than appear as hexamine. Thus, it is evident that excess formaldehyde favours by-product formation, especially at elevated temperatures.

The second type of behaviour to be considered is where the ammonia curve lies below the mercuric chloride curve, but both of these curves lie above the formaldehyde curve. This situation is observed with formaldehyde and ammonium nitrate in the theoretical ratio at pH 6.0 and 20°C., pH 8.0 and 20°C. and in excess ammonium nitrate at pH 6.0 and 20°C. and at pH 8.0 and 0°C., 20°C. and 40°C. It is interesting to note that this phenomenon is never observed in excess formaldehyde, nor at pH 4.0, but it occurs mainly at pH 8.0. Since it is not possible to have more hexamine formed than can be accounted for on the basis of the formaldehyde consumed, it is evident that an explanation must be provided for these analytical results.

One possible explanation is that a by-product is formed. This by-product must be stable, since the three rate curves do not converge at the end point, and must also be precipitated with mercuric chloride, thereby adding extra weight to the "hexamine-mercuric chloride complex" and causing the calculated hexamine weight to be erroneously high to the extent of this co-precipitation. This would account for the high mercuric chloride curve. That the ammonia curve is also higher than the formaldehyde curve may be explained if the by-product co-precipitated with hexamine also contains ammonia, thereby resulting in an erroneously high consumption of ammonia. The fact that the formaldehyde curve lies below the ammonia and mercuric chloride curve may be explained by assuming that, in the analysis of the reaction solution for residual formaldehyde, formaldehyde is analyzed out of the by-product. If this analysis of formaldehyde out of the by-product is quantitative, the curve based on the consumption of formaldehyde should represent quite accurately the true rate of hexamine formation. If the formaldehyde contained in the by-product is not analyzed out, then the formaldehyde curve would also be erroneously high; in other words, the three curves would be in close agreement, although all three would be higher than the true values.

This explanation might be possible if the by-product or intermediate were considered to be a type such as $N(CH_2OH)_3$. A tertiary amine of this type might be expected to be precipitated by mercuric chloride in a manner analogous to hexamine itself. This would result in a high mercuric chloride curve. The ammonia curve would also be high, of course, since ammonia has been consumed. The formaldehyde curve, on the other hand, would not be affected, if in the analysis for residual formaldehyde which is conducted directly on the reaction solution and not on the solution from which the hexamine has been precipitated, the formaldehyde were analyzed back from the amine structure. This would be logical, since these structures are very unstable and only their derivatives have been isolated.

Another possible explanation for the fact that the mercuric chloride and ammonia curves lie above the formaldehyde curve is that the hexamine-mercuric chloride complex is contaminated with adsorbed ammonia. This might account for the fact that the mercuric chloride and ammonia curves lie above the formaldehyde curve. This argument is strengthened by the fact that the tendency for the mercuric chloride and ammonia curves to be higher than the formaldehyde curve is greatest at pH 8.0, where the ammonia of the ammonium nitrate would be expected to be largely present as free ammonia and that at pH 4.0, the three rate curves are in close agreement. The serious weakness in this argument lies in the fact that, if this effect is due to the adsorption of ammonia, then the adsorption would be expected to be greater in excess ammonia. Actually, however, excess ammonium nitrate does not produce a greater divergence in the curves.

The extent to which hexamine precipitated in the presence of ammonium nitrate is contaminated with adsorbed ammonia or ammonium nitrate, was estimated experimentally.

A calibration curve was established between known weights of pure hexamine dissolved in buffer solution at pH 8.0 and the weights of the resulting hexamine-mercuric chloride complex when the samples were analyzed for their hexamine content in the usual way. This calibration curve was then repeated, but this time the hexamine was dissolved in buffer solution at pH 8.0 which was also 0.20N in respect of ammonium nitrate. Again the solutions were analyzed for their hexamine content in the usual way. Thus, the amount of hexamine complex precipitated from pure buffer solution was compared with that precipitated in the presence of ammonium nitrate. It was found that, within the limits of experimental error, the two calibration curves were identical. Consequently, it may be concluded that when a sample of solution is analyzed for its hexamine content by the method used here, the weight of the hexamine-mercuric chloride complex is not increased by co-precipitation of ammonia or ammonium nitrate.

The above experiment eliminates the explanation that the mercuric chloride and ammonia curves lie above the formaldehyde curve because of contamination of the hexamine-mercuric chloride complex with adsorbed ammonia or ammonium nitrate.

In an investigation of the aqueous formaldehyde-ammonia system, Baur and Ruetschi (22) followed the course of the reaction by an acid titration of the ammonia. Rate constants were calculated from the consumption of ammonia and it was concluded that the reaction was third order. Since they only followed the rate of disappearance of ammonia and did not simultaneously follow the rate of disappearance of formaldehyde and the rate of appearance of hexamine in the solution, it is impossible to compare their results with those obtained in this kinetic study of the aqueous reaction of formaldehyde with ammonium nitrate. On the basis of limited data, they proposed two possible mechanisms of hexamine formation (p.8). They favoured a mechanism which involved the formation of methyleneimine and its subsequent trimerization to the postulated intermediate, cyclotrimethylenetriamine. As proof of the formation of the intermediate,cyclotrimethylenetriamine, they pointed to the fact that its tribenzoyl, dinitroso and trinitroso derivatives had been isolated from aqueous formaldehyde-ammonium salt solutions (18, 23, 24). However, it is now known, and was confirmed in this present work, that an aqueous solution of hexamine itself undergoes the Schotten-Baumann reaction (benzoylation) to yield tribenzoyltrimethylenetriamine in excellent yield. Also, when an aqueous solution of hexamine is treated with nitrous acid, trinitrosotrimethylenetriamine is formed. Consequently, the isolation of these derivatives from a reaction solution can no more be construed as proof of the presence of cyclotrimethylenetriamine as an intermediate in hexamine formation than as proof of the presence of hexamine in the solution.

Boyd (32), in a kinetic study of the aqueous reaction of formaldehyde with ammonia, followed the rate of disappearance of the formaldehyde and ammonia as well as the rate of appearance of hexamine in the solution. It was found that, at 0°C., the three rate curves tended to approximate one another in a large excess of ammonia but were widely separated in excess formaldehyde. The reverse was true at 35°C. Increased temperature reduced the rate of hexamine formation in the early stages of the reaction. These observations led Boyd to propose a two-path mechanism of hexamine formation, one path being preferred in excess ammonia, the other in excess formaldehyde (p.13).

In this present kinetic study of the aqueous reaction of formaldehyde with ammonium nitrate at various controlled pH, it has also been found that the three rate curves tend to be in close agreement in excess ammonium nitrate but to diverge in excess formaldehyde. However, whereas Boyd (32) found that this effect was reversed at elevated temperature, the data in the present investigation indicate that elevated temperature merely accentuates the tendency for by-product formation, especially in excess formaldehyde. Since, in the work of Boyd, the pH of the different reaction solutions was not known nor controlled, it is difficult to say whether the difference between the results is fundamental. In any event, the present study at controlled pH gives no indication of alternative reaction paths leading to hexamine formation.

The very rapid initial rate of hexamine formation at the higher pH and also at elevated temperature makes it impossible to calculate accurately the specific rate constant for the reaction. Frequently, after only one minute, the reaction is already over 60 per cent complete and estimation of the residual reactants during the initial stages is subject to considerable experimental error. Calculation of specific rate constants beyond 60 per cent reaction, where by-product formation is becoming extensive, was not considered satisfactory. If it had been possible to calculate accurately the specific rate constants, it would have been interesting to calculate the energies of activation at the various controlled pH, to see whether or not they vary with the pH. However, it was felt that all such calculations would be subject to such large error as to be useless for an accurate interpretation.

It has been shown that the pH of the reaction solution is a very important factor governing both the rate of formation and the final yield of hexamine. At a given pH, the various ammonium salts give approximately the same rates of formation and final yields of hexamine, indicating that at given pH, different ammonium salts lose their individuality and become merely sources of ammonium ions or available ammonia as far as hexamine formation is concerned. The fact that the rate of formation and final yield of hexamine increase as the pH of the reaction solution increases suggests that an equilibrium involving hydrogen ion is present.

If it be assumed that the active reagent in the ammonium salt with which the formaldehyde reacts to form hexamine is ammonia, then the equilibrium involving ammonia and hydrogen ion will explain the effect of pH on the rate.

$$NH_4^+ \rightleftarrows NH_3 + H^+$$

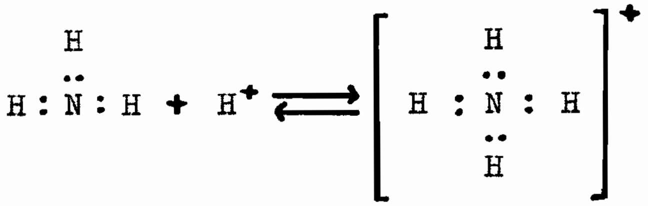
If the active reagent in the reaction of formaldehyde with an ammonium salt were the ammonium ion, the reaction should proceed readily under conditions favouring the formation of ammonium ions, that is, in acidic solution. This statement might be contested by citing the case of ammonium hydroxide, which exhibits a rapid rate of hexamine formation with formaldehyde and which is considered to contain ammonium and hydroxyl ions, but which is alkaline, not acidic, in its reaction. In this connection, therefore, it was interesting to observe that when an ammonium salt, such as ammonium nitrate which exhibits a slow rate of hexamine formation, was dissolved in water and then mercuric chloride added, no precipitate formed, even after long standing. On the other hand, when mercuric chloride was added to some dilute ammonium hydroxide or dibasic ammonium phosphate solution, both of which are alkaline and exhibit rapid rates of hexamine formation, a heavy white precipitate formed instantly. If, however, these solutions were acidified before adding the mercuric chloride solution, no precipitate was formed. These observations suggest that in alkaline solution there are free ammonia molecules, probably existing in a rapid dynamic equilibrium with ammonium ions. In acidic solution, the equilibrium is shifted so far in favour of ammonium ions that the presence of ammonia molecules can not be detected, and in accord with this is the fact that the rate is much slower in acidic solution.

If the ammonium ion were the active reagent of the ammonium salt in hexamine formation, it would be expected that a decrease in the pH of the reaction solution would be favourable to hexamine formation. Actually, however, the rate of formation and final yield of hexamine are decreased when the pH is decreased. This suggests that the active reagent in the ammonium salt for hexamine formation is the available ammonia. The ammonia will become more readily available as the pH is increased and consequently, an increase in the pH of the reaction solution would be expected to increase the rate of hexamine formation. The experimental data confirm this hypothesis, and, furthermore, an aqueous solution of dibasic ammonium phosphate, which is alkaline and which exhibits a very rapid rate of hexamine formation, demonstrates the presence of ammonia by forming a mercury-ammonia complex on the addition of mercuric chloride solution.

On the other hand, it might be that the ammonium ion can also react with formaldehyde to form hexamine, in view of the fact that it is possible to write the equation:

$$4NH_4^+ + 6CH_2O \longrightarrow (CH_2)_6N_4 + 4H^+ + 6H_2O$$

This equation would also explain the effect of pH on the rate of formation and yield of hexamine, for it can be seen that as the H ions are removed from the solution by the buffer, hexamine formation will be favoured by Le Chatelier's Principle. A closer examination of this equation shows that, initially, there are four ammonium ions and after their reaction with formaldehyde, four hydrogen ions are eliminated. In other words, only three of the four hydrogens constituting each ammonium ion are attacked by formaldehyde in the formation of hexamine, the fourth being liberated. That is, if the ammonium ion does react with formaldehyde, it reacts only to the extent of three hydrogens. The difference between the hydrogens in ammonia and those in the ammonium ion can be seen from a consideration of the electronic configurations.



$$\begin{array}{c}\mathrm{H}\\ \cdot\cdot\\ \mathrm{H:N:H}\end{array} + \mathrm{H}^{+} \rightleftharpoons \left[\begin{array}{c}\mathrm{H}\\ \cdot\cdot\\ \mathrm{H:N:H}\\ \cdot\cdot\\ \mathrm{H}\end{array}\right]^{+}$$

In ammonia, the nitrogen to hydrogen bonds are covalent. When the hydrogen ion combines with ammonia to form the ammonium ion, it is held by a co-ordinate covalent bond, both electrons being supplied by the nitrogen.

As was shown in numerous examples in the introduction to this work, when formaldehyde reacts with an active hydrogen atom in an addition reaction, a methylol group, $-CH_2OH$, occupies the position formerly held by the active hydrogen atom. If the formaldehyde reacts in a condensation reaction, as ~~is the~~ case in hexamine formation, water is subsequently eliminated and methylene groups are substituted for the hydrogen atoms.

Ammonia is strongly co-ordinating, since the nitrogen atom possesses an unshared pair of electrons. As the hydrogen atoms of the ammonia become substituted by methylene groups, $-CH_2-$, as occurs in the formation of the tertiary amine, hexamine, the nitrogen atom becomes less strongly co-ordinating. This is due to the fact that the alkyl groups are electron donors relative to hydrogen. Consequently, as the hydrogen atoms of the ammonia become successively substituted by methylene groups, the power of the nitrogen atom to co-ordinate is greatly reduced until finally the proton is released. Facilitating the continual removal of these protons by buffering the solutions at higher pH promotes the reaction and this is made manifest by an increased rate of formation and final yield of hexamine.

Mechanism of the Reaction

In proposing a mechanism of hexamine formation from the reaction of formaldehyde with an ammonium salt in aqueous solution, there are several reactions which must be considered. The foregoing remarks suggest that the formation of hexamine, whether it be in the aqueous reaction of formaldehyde with an ammonium salt or in a formaldehyde-ammonia solution, probably reverts to the reaction of formaldehyde with ammonia.

It has been shown in this present work that hexamine is formed in the reaction of formaldehyde with numerous ammonium salts, for example:

$$4NH_4NO_3 + 6CH_2O \longrightarrow (CH_2)_6N_4 + 4HNO_3 + 6H_2O \qquad (1)$$

On the other hand, when hexamine is heated with a dilute acid, it is hydrolyzed.

$$(CH_2)_6N_4 + 4HNO_3 + 6H_2O \longrightarrow 4NH_4NO_3 + 6CH_2O \qquad (2)$$

Apparently, these two reactions are in equilibrium in the reaction solution. There is another reaction which must be considered, namely, that heating the ammonium salt of a mineral acid with formaldehyde in aqueous solution yields the salts of methylamines.

$$NH_4Cl \xrightarrow{CH_2O} CH_3NH_2\cdot HCl + (CH_3)_2NH\cdot HCl + (CH_3)_3N\cdot HCl + nHCOOH \quad (3)$$

Equation (1) illustrates a condensation reaction, whereas the reaction in equation (3) is oxidation-reduction. The oxidation-reduction reaction, which leads to the formation of methylamines, is favoured at elevated temperatures.

Chemnitius (47) in 1928, in an investigation of the preparation of hexamine from formaldehyde and ammonium hydroxide solution, found that hexamine formation was favoured in excess ammonium hydroxide but that the use of formaldehyde in excess led to the formation of trimethylamine. These observations present an interesting analogy to those found in this present kinetic study of the reaction of formaldehyde with ammonium nitrate at various controlled pH levels. In both cases, an excess of ammonia or ammonium nitrate favoured hexamine formation, whereas excess formaldehyde favoured by-product formation. These observations of Chemnitius confirm another fact found in this present study, namely, that the pH of the reaction solution does not alter the course of the reaction. For example, hexamine is formed in both aqueous formaldehyde-ammonium salt solutions, which are acidic, and in formaldehyde-ammonium hydroxide solution, which is alkaline. Similarly, methylamines are formed in both of these reaction solutions.

In the reaction of formaldehyde with ammonium chloride to form methylamine hydrochloride,

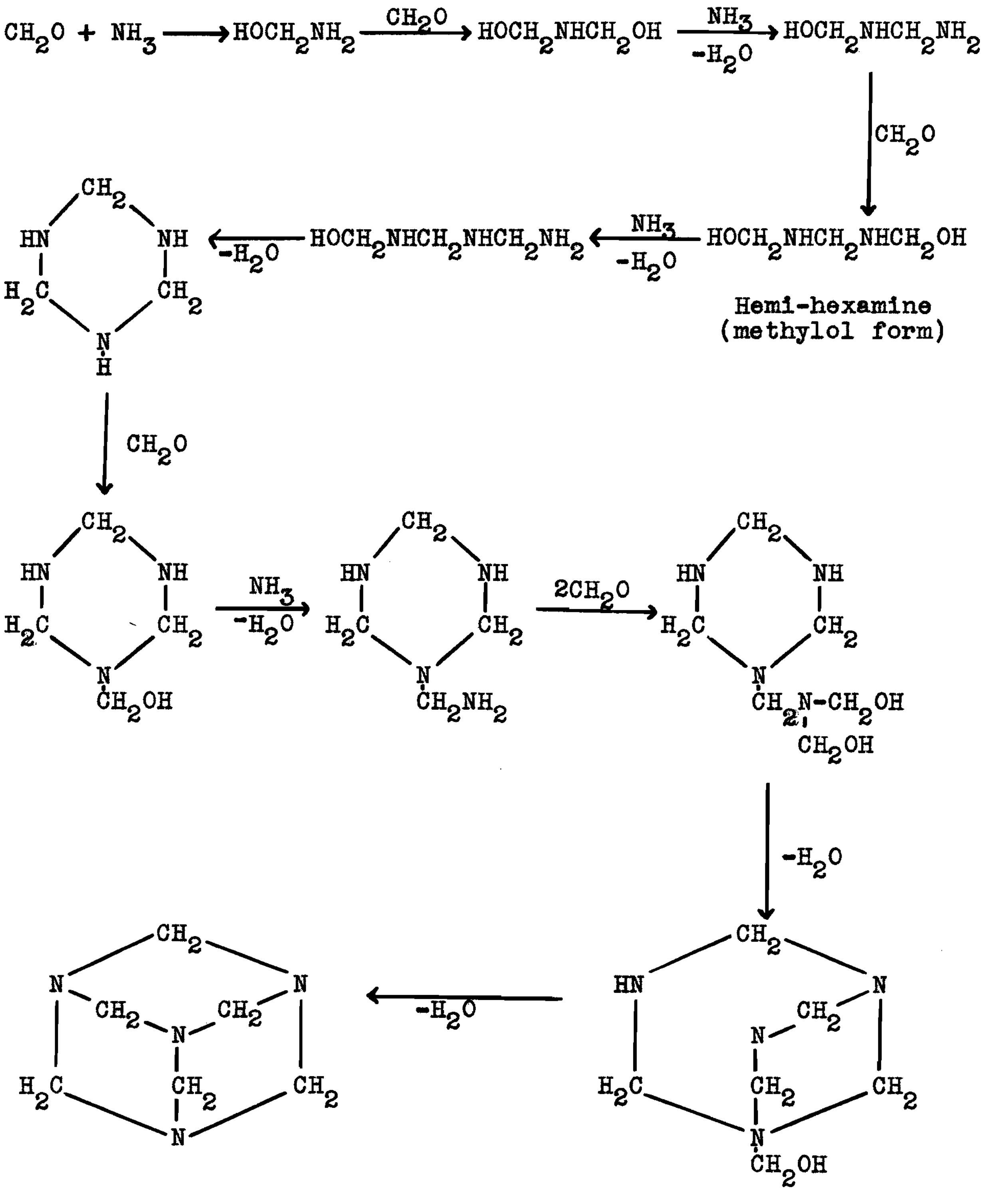
$$NH_4Cl + 2CH_2O \longrightarrow CH_3NH_2 \cdot HCl + HCOOH$$

two moles of formaldehyde are required for each mole of ammonium chloride. On the other hand, for hexamine formation, the equation is:

$$4NH_4Cl + 6CH_2O \longrightarrow (CH_2)_6N_4 + 4HCl + 6H_2O$$

Thus, when the reactants are present in the theoretical proportions for hexamine formation, there is a deficiency of formaldehyde as far as the methylamine reaction is concerned. The use of ammonium salt in further excess of these proportions would be expected, and does, further decrease the tendency for methylamine formation. Conversely, an increase in the formaldehyde concentration is more favourable for methylamine formation.

As was stated in the introductory remarks to this work, Linstead (6), in 1943, proposed a mechanism of hexamine formation to account for the possibility that hexamine dinitrate may be an intermediate in the formation of RDX from paraform and ammonium nitrate. That mechanism is presented here in order that it may be discussed in detail and compared with other proposed mechanisms, notably that of Baur and Ruetschi (22).


CH2O + NH3
HOCH2NH2
CH2O
HOCH2NHCH2OH
NH3
-H2O
HOCH2NHCH2NH2
CH2O
HOCH2NHCH2NHCH2OH
Hemi-hexamine
(methylol form)
NH3
-H2O
HOCH2NHCH2NHCH2NH2
-H2O
CH2
HN
NH
H2C
CH2
N
H
CH2O
N
CH2OH
NH3
-H2O
CH2NH2
2CH2O
CH2N-CH2OH
CH2OH
-H2O
N
CH2
-H2O

Hexamine

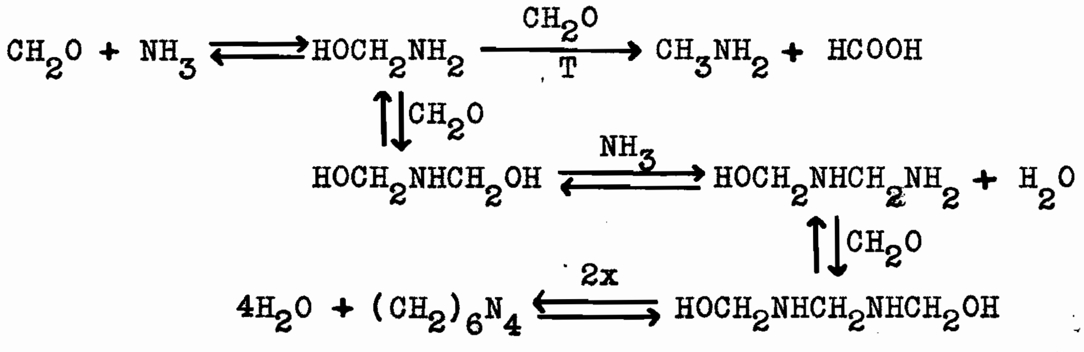
This mechanism involves a series of successive condensation reactions between formaldehyde and ammonia leading to the formation of the intermediate cyclotrimethylenetriamine. Baur and Ruetschi (22) (p.8) considered that this intermediate was formed by the trimerization of methyleneimine, $CH_2{=}NH$. Linstead then proposes that only one of the imino groups of the cyclotrimethylenetriamine is attacked by formaldehyde and that successive condensation reactions continue along this side chain until finally the elimination of water leads to hexamine formation by further ring closure. Baur and Ruetschi, on the other hand, proposed that each of the imino groups of cyclotrimethylenetriamine is attacked by a formaldehyde molecule and that subsequent reaction of these three methylol groups with ammonia leads to hexamine formation.

The mechanism of Baur and Ruetschi (22) is based on the formation of methyleneimine and its trimerization to cyclotrimethylenetriamine which would involve an improbable third order reaction. Moreover, as was pointed out in the introductory remarks, aqueous formaldehyde probably exists in the hydrated form, $HOCH_2OH$, which is methylene glycol. Thus, methylol derivatives are considered to be the primary formaldehyde reaction products, as was illustrated by numerous examples. If, however, it be argued that methylol compounds only exist in alkaline media and that in acidic media they lose water, forming methylene derivatives, such as methyleneimine, then it follows that a mechanism such as that proposed by Baur and Ruetschi would be valid only in acidic solutions. Consequently, there appear to be two possibilities: either the hexamine is formed by one mechanism in both alkaline and acidic solutions, or, by one mechanism involving methylol derivatives in alkaline solutions and by another mechanism involving methylene compounds, such as methyleneimine, in acidic solutions. These two mechanisms might be analogous, except for the step involving the trimerization of methyleneimine, for which there would be no counter-part with methylol derivatives. As has already been stated, the present kinetic data at controlled pH levels do not give cause to suspect a change in reaction mechanism.

It is interesting to analyze the conditions which would seem to be necessary for the Baur and Ruetschi and Linstead mechanisms to be operative. Both of these mechanisms have cyclotrimethylenetriamine as a focal point. This would have to react with three formaldehyde molecules and one of ammonia. Regardless of the mode of representation, it seems necessary to assume rapid reaction between formaldehyde and the imino group of the cyclotrimethylenetriamine so that three methylol groups become attached to the ring, only one of these reacting with ammonia to form the amine necessary for ring closure in the manner shown by Baur and Ruetschi. If the rate of reaction of ammonia with methylol groups were rapid, it would be expected that a diamine or even triamine should result as the dimethylol or trimethylol compound were formed.

No ring closure to form hexamine would be possible under these conditions, in either the Baur and Ruetschi or the Linstead mechanism. If now it be assumed that the reaction of formaldehyde to form the methylol group is, in fact, rapid, then in the series of reactions leading to the formation of cyclotrimethylenetriamine, the reaction of ammonia with the methylol intermediates would presumably be the rate-governing reaction. Consequently, a proportionately greater increase in the rate should be noted with excess ammonia as compared with the increase observed with excess formaldehyde. Experimentally, the reaction rate is more sensitive to an increase in the formaldehyde concentration, indicating that the reaction of formaldehyde with the amino group is slower than the reaction of ammonia with methylol groups.

On the basis of this argument, it seems, therefore, that the major portion, at least, of the hexamine formed is not by way of cyclotrimethylenetriamine as intermediate. A possible alternative is through dimerization of hemi-hexamine.

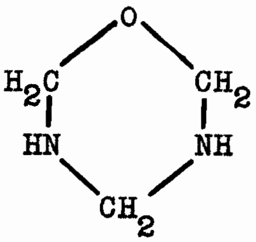


$$\begin{tikzcd}
CH_2O + NH_3 \arrow[r, shift left] & HOCH_2NH_2 \arrow[l, shift left] \arrow[r, "CH_2O", "T"'] \arrow[d, shift left, "CH_2O"] & CH_3NH_2 + HCOOH \\
 & HOCH_2NHCH_2OH \arrow[u, shift left] \arrow[r, shift left, "NH_3"] & HOCH_2NHCH_2NH_2 + H_2O \arrow[l, shift left] \arrow[d, shift left, "CH_2O"] \\
 & 4H_2O + (CH_2)_6N_4 \arrow[r, shift right] & HOCH_2NHCH_2NHCH_2OH \arrow[u, shift left] \arrow[l, shift right, "2x"']
\end{tikzcd}$$

Hemi-hexamine
(methylol form)

The first intermediate represented is methylolamine, $HOCH_2NH_2$. If formaldehyde reacts with methylolamine in an addition reaction, dimethylolamine, $HOCH_2NHCH_2OH$, is formed. If, however, formaldehyde reacts with it in an oxidation-reduction reaction, methylamine is formed as a by-product. The formation of methylamine increases at higher temperatures and is represented as an irreversible reaction, since it has been shown that hexamine is not formed from it. If it be considered that the methylolamine reacts with ammonia instead of with formaldehyde, methylenediamine, $H_2NCH_2NH_2$, would be formed. This, on reaction with formaldehyde, would also yield the methylol form of hemi-hexamine.

It is interesting to observe that, if instead of dimerizing, the methylol form of hemi-hexamine were to lose the elements of water between its terminal methylol groups, the resulting structure would be cyclonite oxide, a known product in the formation of RDX.



Cyclonite oxide

The experimental observation that the rate of hexamine formation is more sensitive to change of formaldehyde concentration than to change of ammonia concentration, is then readily explained if it be assumed simply that the rate of reaction between formaldehyde and amino groups is rate-governing. The reactions leading to hexamine formation are represented as reversible, suggesting an extensive equilibrium system, since heating an aqueous solution of hexamine results in hydrolysis, with the liberation of formaldehyde and ammonia.

SUMMARY

1. Hexamine has been prepared from the reaction of formaldehyde with various ammonium salts, in both aqueous and glacial acetic acid media. The isolation of hexamine in good yield depends on the neutralization of the acid formed in the reaction before the solution is evaporated to dryness.

2. The rate of formation and the final yield of hexamine vary greatly with the different ammonium salts. The rate is most rapid with dibasic ammonium phosphate which forms the solution of highest pH and it is slowest with ammonium chloride which forms the solution of lowest pH.

3. A rate study reveals that the pH of the reaction solution is an important factor governing both the rate of formation and the final yield of hexamine. Both the rate and the yield are increased by an increase in the pH of the reaction solution.

4. When buffered at given pH, the different ammonium salts exhibit rates of formation and final yields of hexamine which are approximately similar. Apparently, at given pH, the different ammonium salts lose their individuality and become merely sources of ammonium ions or available ammonia, as far as hexamine formation is concerned.

5. Rate curves have been determined for the reaction of formaldehyde with ammonium nitrate in aqueous solutions buffered at pH 8.0, 6.0 and 4.0, at temperatures of 0°C., 20°C. and 40°C. and over a range of initial mole ratios (formaldehyde:ammonium nitrate) of 2 ratio 0.75 to 3.0. For each set of conditions, three rate curves have been obtained on the basis of ammonia consumed, formaldehyde consumed and material precipitated with mercuric chloride.

6. In excess formaldehyde, a stable by-product is formed and its formation increases as the temperature is increased. It is suggested that this by-product is methylamine.

7. In excess ammonium nitrate, by-product formation is decreased.

8. The data illustrate an interesting fact from the point of view of chemical kinetics, namely, that the course of the reaction is essentially unaltered by pH.

9. A mechanism of hexamine formation depending on the formation of hemi-hexamine and its subsequent dimerization to hexamine is suggested.

CLAIMS TO ORIGINAL RESEARCH

1. The rate of hexamine formation has been studied in the reaction of formaldehyde with different ammonium salts in aqueous solution.

2. The effect of pH on the rate of formation and final yield of hexamine in aqueous formaldehyde-ammonium salt solutions has been investigated.

3. A kinetic study of the formation of hexamine in aqueous formaldehyde-ammonium nitrate solutions at various controlled pH levels has been made. Previous rate studies were made on aqueous formaldehyde-ammonia solutions and the pH was not controlled.

4. The course of the aqueous formaldehyde-ammonium nitrate reaction is essentially unaltered by pH.

5. A mechanism of hexamine formation depending on the formation of hemi-hexamine and its subsequent dimerization to hexamine has been suggested.

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