THE EFFECT OF ORGANIC BASES UPON THE EXTENT AND MECHANISM OF THE REDUCING ACTION OF SODIUM METHYLATE ON (a) NITROBENZENE AND (b) AZOXYBENZENE

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I. ACKNOWLEDGMENT

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II. INTRODUCTION

Klinger[1] has shown that nitrobenzene is reduced by sodium methylate, in methyl alcohol solution, to azoxybenzene. To represent the reaction he proposed the equation

$$4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O.$$

The stoichiometric proportions of this equation have been investigated quantitatively by Fry and Cameron[2], and were found to be correct.

In the course of their investigation, Fry and Cameron proposed a mechanism for this reaction. This proposed mechanism involved the theory of the acidic dissociation of sodium hydroxide. A discussion of this mechanism will be given later in the theoretical discussion. They found that water, which promotes basic dissociation of sodium hydroxide, when added to the reaction mixture, greatly reduced the per cent reduction. On the other hand, pyridine, which being basic should promote acidic dissociation of sodium hydroxide, greatly increased the per cent reduction when it was present in the reaction mixture.

In view of this hypothesis and experimental finding it was accordingly deemed worthy of further investigation to try the effect of various other organic bases upon the extent of the reducing action of sodium methylate on nitrobenzene and also on azoxybenzene. The results to be obtained should show whether the increased reduction due to the presence of pyridine was an isolated instance, or whether organic bases in general increase the per cent reduction. This latter case would be evidence in favor of the proposed mechanism of the reaction and the proposed theory of the acidic dissociation of sodium hydroxide which has been clearly indicated to occur in fused sodium and potassium hydroxide media, but which here also apparently occurs in methyl alcohol solution.

III. HISTORICAL

The reduction of nitrobenzene to azoxybenzene has been known since 1845 when Zinin[3] treated one part of nitrobenzene with an alcoholic solution of dry potassium hydroxide in which the weight of potassium hydroxide was equal to the weight of nitrobenzene. This work was purely qualitative, no equations being postulated to represent the character of the reaction. In succeeding years various other experiments were conducted to accomplish this reduction.

Alexeyeff[4] added sodium amalgam to an alcoholic solution of nitrobenzene which was then acidified with acetic acid. After steam distillation to remove the alcohol and excess nitrobenzene, an oil was obtained from which the azoxybenzene was obtained pure by a number of crystallizations from alcohol. He also states that zinc dust, in the presence of small quantities of alkali, acts in the same manner as sodium amalgam.

Rasenack[5] found one part by weight of sodium hydroxide and five to six parts by weight of alcohol were sufficient to convert two parts of nitrobenzene into azoxybenzene if the nitrobenzene is added in small quantities while the solution is being refluxed. He states that completely dry nitrobenzene is not attacked by sodium or sodium amalgam, but when a few drops of water are added, rapid action occurs and azoxybenzene results.

Schmidt and Schultz[6] secured azoxybenzene by the action of alcoholic potassium hydroxide on alcoholic nitrobenzene. They mention by-products of aniline, oxalic acid and a dark resinous substance similar to the biazoxybenzoic acid of W. Michler[7].

Klinger[1] devised a new method in which ten parts of sodium in 250 parts of methyl alcohol were heated with 30 parts of nitrobenzene on a water bath for 5-6 hours. A yield of 85-89 per cent was obtained. Klinger proposed the equation

$$4C_6H_5NO_2 + 3NaOCH_3 \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3\ H_2O$$

which is the one used today to represent the reaction. He did not, as previously noted, give any quantitative evidence for selecting this equation.

Moltschanowsky[8] repeated Klinger's work and obtained somewhat lower yields.

Brühl[8] prepared sodium methylate by adding methyl alcohol to finely divided sodium in xylene and then boiling the mixture with nitrobenzene for seven hours. A quantitative yield of azoxybenzene was obtained. The sodium methylate thus prepared is free from alcohol of crystallization and according to Brühl is more active than the sodium methylate with alcohol of crystallization.

Lachman[10], because of Klinger's statement that ordinary methyl alcohol contains much water, tried Zinin's method once more in which sodium hydroxide is used in methyl alcohol solution. He obtained better results than Klinger. In one instance, yields of 95 and 97 per cent were obtained. He found also that acetone, present to the amount of 3 per cent, cuts down the reaction 30 per cent. Lachman states that the water present in the alcohol has little effect upon the yield of azoxybenzene.

Evans and Fetsch[11] heated a mixture of nitrobenzene, ethyl alcohol, and magnesium amalgam. The reaction proceeded quite vigorously and hydrogen was given off. Azobenzene was the product obtained. By increasing tenfold the relative quantity of ethyl alcohol used, Evans and Fry[12] obtained a 90 per cent yield of azoxybenzene. Hydrogen was given off in the reaction. When methyl alcohol was used as a solvent, azobenzene was obtained. In this latter case magnesium methylate is formed, but it has no reducing action. It is chiefly the hydrogen liberated when magnesium reacts with methyl alcohol that reduces the nitrobenzene to azo and azoxybenzene.

Meisenheimer[13] permitted the alcohol to boil off from a solution of nitrobenzene and alcoholic potash. When the temperature reached 140-150 degrees, a reaction of almost explosive violence occurred, and a hard black mass resulted. At intermediate temperatures azoxybenzene resulted. In the cold no reaction occurred.

Allen[14] studied the action of ferrous sulphate in an alkaline solution of nitrobenzene. He found that aniline, hydrazobenzene, and azoxybenzene can be obtained, depending on the conditions. If the ferrous sulphate is added slowly and in a quantity just sufficient to reduce theoretically to azobenzene, then 76 per cent of azoxybenzene and 14 per cent of aniline result. When electrolytic methods are used, stirring and low current density tend to promote the formation of azoxybenzene. Allen also states that a method of separating mixtures of azo and azoxybenzene on a basis of crystallization is hopeless. A determination of per cent composition of mixtures of azoxy and azobenzene, using a melting point curve is also of no value, he says, unless a mixture of absolutely pure components is obtained, since slight impurities invalidate results.

Snowden[15] lists the various known methods, chemical and electrical, for reducing nitrobenzene to azoxybenzene. He also proposes a method for determining the per cent of either azo or azoxybenzene in a pure mixture of the two by means of a melting point-per cent composition curve.

Rotarski[16] states that the action of alcoholates on aromatic nitrocompounds goes in two ways depending on the temperature:

(a) at low temperatures, $> O + CH_3ONa \longrightarrow NaOH + HCHO$

(b) at higher temperatures, $> O + CH_3ONa \longrightarrow HCOONa + H_2$.

Reaction (b) produces azo and azoxy compounds, while reaction (a) produces hydrazobenzene and aniline.

Heumann[17] by using zinc dust in dilute aqueous sodium hydroxide or ammonium hydroxide obtained azoxybenzene from nitrobenzene.

Dechen[18] reports that nitrobenzene yields azoxybenzene when heated to 105-110 degrees in a calcium chloride or sodium chloride solution. It is probable that he first got phenylhydroxylamine, which then decomposed to give aniline and azoxybenzene.

Loessner[19] obtained a 70 per cent yield of azoxybenzene when nitrobenzene was boiled with a sodium arsenite solution.

Wohl and Aue[20] mention that nitrobenzene reacts with dry potassium hydroxide to furnish azoxybenzene and o-nitro phenol.

Of all the methods that have been cited, that of Klinger has been adopted as the standard method, and is given in most of the books as the best method for preparing azoxybenzene from nitrobenzene. Klinger's method has the advantage over many of the other methods by virtue of the fact that there are formed no secondary reduction products such as azobenzene and hydrazobenzene.

IV. THEORETICAL

Although Klinger's reaction was adopted as the standard method for preparing azoxybenzene from nitrobenzene, no attempt was made to ascertain the mechanism of the reaction until Fry and Cameron[2] investigated the reaction from a quantitative standpoint. In this investigation the stoichiometric proportions as proposed by Klinger were confirmed, and, in addition, a proposed mechanism for the reaction was advanced. This mechanism was assumed to involve the reactions represented by the following equations:

$$3CH_3ONa + 3HOH \longrightarrow 3CH_3OH + 3HONa \qquad (x)$$

$$3CH_3OH + 3HONa \longrightarrow 3HCOONa + 12\ H \qquad (y)$$

$$4C_6H_5NO_2 + 12H \longrightarrow 2(C_6H_5N)_2O + 6H_2O \quad (z)$$

$$\Sigma\ (x),(y),(z)\quad 4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O.$$

The summation of the intermediate equations gives Klinger's equation.

It was assumed in equation (x) that there were traces of water present in the reaction mixture sufficient to produce the hydrolysis of the sodium methylate. Equation (y) deals with the oxidation of methyl alcohol to sodium formate, and involves the idea of the acidic dissociation of sodium hydroxide as postulated by Fry and co-workers.[21]

The theory of the acidic dissociation of sodium hydroxide is based upon experimental evidence obtained thru the action of fused caustic alkalies upon various organic compounds[22]. A general type reaction was formulated as follows:

$$R(H)_n + n(HOM) \longrightarrow R(OM)_n + nH_2 \quad (M = Na \text{ or } K).$$

As an example, the oxidation of methyl alcohol to carbonate will be given - $CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + 3H_2$ - which was assumed to involve the following type reactions:

$$CH_3OH + HONa \longrightarrow CH_3ONa + H_2O \qquad (a)$$

$$CH_3ONa + HONa \longrightarrow CH_2(ONa)_2 + H_2 \qquad (b)$$

$$CH_2(ONa)_2 + HONa \longrightarrow CH(ONa)_3 + H_2 \qquad (c)$$

$$CH(ONa)_3 + HONa \longrightarrow C(ONa)_4 + H_2 \qquad (d)$$

$$C(ONa)_4 + H_2O \longrightarrow Na_2CO_3 + 2NaOH \qquad (e)$$

$$\sum (a),(b),(c),(d),(e) \quad CH_3OH + 2HONa \longrightarrow Na_2CO_3 + 3H_2 \qquad (A)$$

This general mechanism has been employed to represent the oxidation of methyl alcohol to sodium formate by sodium hydroxide with the notable difference, namely that in the fused state the methyl alcohol was oxidized by the sodium hydroxide to the carbonate stage, but in methyl alcohol solution the oxidation proceeds only to the formate stage. Accordingly, equations (a), (b), (c) are the same as in the above summation, but with nitrobenzene in methyl alcohol solution the orthoformate of equation (c) reacts thus:

$$CH(ONa)_3 + H_2O \longrightarrow HCOONa + 2HONa \qquad (c')$$

and the summation of equations (a), (b), (c) and (c') represents the oxidation of methyl alcohol to formate with the liberation of hydrogen

$$\sum (a),(b),(c),(c') \quad CH_3OH + HONa \longrightarrow HCOONa + 2H_2 \qquad (B)$$

It is this hydrogen that reduces the nitrobenzene to azoxybenzene.

Hence the following scheme of reactions as employed by Fry and Cameron[2] to represent the reduction of nitrobenzene to azoxybenzene shows the completed scheme.

$$3CH_3ONa + 3HOH \longrightarrow 3CH_3OH + 3HONa \qquad (x)$$

$$3CH_3OH + 3HONa \longrightarrow 3HCOONa + 12H \qquad (y) \text{ or } (B)$$

$$4C_6H_5NO_2 + 12H \longrightarrow 2(C_6H_5N)_2O + 6H_2O \qquad (z)$$

$$\sum (x),(y),(z) \quad 4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O.$$

If this interpretation of the mechanism is correct, any conditions that hinder acidic dissociation will reduce the amount of hydrogen available for reduction and hence limit the extent of the reduction; while on the other hand, conditions favorable to the acidic dissociation should increase the extent of the reduction.

These conditions were tried experimentally by Fry and Cameron[2]. Since water promotes basic dissociation of sodium hydroxide, it naturally hinders acidic dissociation. It was found that water added in increasingly larger quantities lowered the per cent reduction from the normal 88.45 per cent to 19 per cent.

In order to promote acidic dissociation, a basic substance, pyridine, was added, and, as was expected, the per cent reduction increased. In fact, the reduction with higher concentrations of pyridine was carried beyond the azoxybenzene stage to azobenzene. By way of further evidence, it was shown that starting with azoxybenzene, in the presente of pyridine, it is reduced somewhat by sodium methylate to azobenzene, presumably according to the equation,

$$2(C_6H_5N)_2O + CH_3ONa \longrightarrow 2C_6H_5N{=}NC_6H_5 + HCOONa + H_2O.$$

It was also shown by Fry and Cameron[2] that the sodium formate formed in the reaction is a direct measure of the degree of reduction of the nitrobenzene. This was calculated from Klinger's equation,

$$4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + H_2O$$

when nitrobenzene was reduced with sodium methylate, but when pyridine was present, both of the preceding equations representing reactions for production of formate were taken into account.

It thus appears that when no basic carbon compounds are present in the reaction mixture, Klinger's reaction only occurs, but when basic carbon compounds are present, azoxybenzene may be further reduced to azobenzene and in this case sodium formate is also the final product of the oxidation of the methyl alcohol. This means that when both azoxybenzene and azobenzene are formed, the total yield of formate is commensurate with the sum of the quantities of azoxybenzene and azobenzene obtained.

V. OBJECT OF THE INVESTIGATION

The object of this investigation was to determine the effects of a selected number of organic bases upon the extent of the reducing action of sodium methylate on nitrobenzene and azoxybenzene in methyl alcohol solution as measured by the amount of sodium formate produced.

It has been shown that pyridine added to the reaction mixture - nitrobenzene, sodium methylate, methyl alcohol - causes increased reduction of the nitrobenzene. The present investigation was to determine to what extent, as evidenced by quantitative determinations, other organic bases such as aniline, monomethyl aniline, dimethyl aniline, quinoline, and isoamylamine, would produce similar results.

The basic substances selected were of different basic strength, although the choice was restricted considerably due to considerations as to cost and availability. It was also the purpose of this investigation to determine if there was any relation between the extent of the reduction and the basic strength of the added base.

VI. EXPERIMENTAL

A. Preparation of Freezing Point-Composition Curve for Azobenzene-Azoxybenzene

Before the actual runs were begun, it was thought advisable to secure data for plotting a melting point-composition curve for mixtures of azo and azoxybenzene, since mixtures of these compounds were expected to be obtained as products of the reaction. Mixtures of known content of pure Kahlbaum azo and azoxybenzene were made and the melting points determined.

The first method for determining the melting points employed a thin walled glass tube, about 1 mm. in diameter, which was partially filled with the powdered substance. The tube, attached to a thermometer, was suspended in a beaker of water and the temperature of the water raised gradually. The point at which the substance in the tube melted was noted. There was no sharp melting as stated by Snowden[15], but liquid and solid coexisted over a range of several degrees. This is to be expected in the light of experience with substances forming eutectics. The method, therefore, was abandoned.

The second method was to secure time-temperature cooling data for the various mixtures. In this method a sufficient quantity of the substance was pladed in a test tube so that on melting there was one inch of liquid in the tube. A thermometer, graduated to 0.2 degrees, and a copper stirrer were inserted. The mixture was melted and the temperature of it taken at timed intervals during the cooling while the mixture was stirred. When the solid first starts to separate, the temperature either remains constant or the rate of cooling is so changed that on plotting time-temperature values, the point at which solidification begins can easily be determined. An air jacket or the open test tube was used as the circumstance demanded.

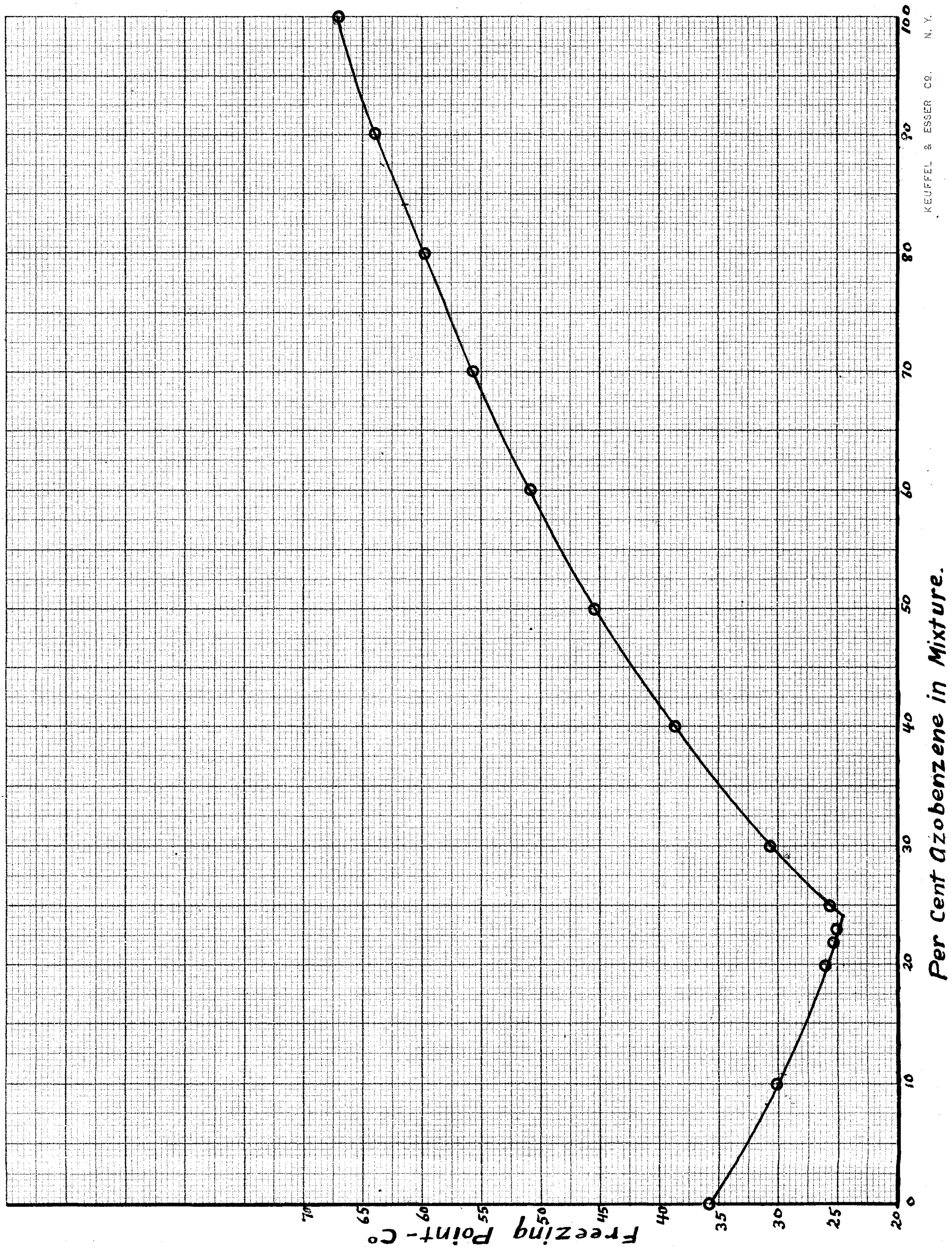
Hartley and Stuart[23] employed this method for obtaining data used in plotting a freezing point diagram of azo and azoxybenzene mixtures. They also state that the melting point is not sharp and cannot be obtained with accuracy. The results obtained in this investigation agree with those of Hartley and Stuart.

The following data, Table I, were obtained in this investigation for the freezing point-composition diagram.

TABLE I

Freezing Points of Mixtures of Azobenzene and Azoxybenzene

Per cent by weight of azobenzene	Per cent by weight of azoxybenzene	Freezing point of mixture
0	100	35.60
10	90	30.20
20	80	26.00
22	78	25.40
23	77	25.15
25	75	25.60
30	70	30.70
40	60	38.60
50	50	45.40
60	40	50.80
70	30	55.60
80	20	59.80
90	10	63.80
100	0	67.20


Per Cent Azobenzene in Mixture.
0
10
20
30
40
50
60
70
80
90
100
Freezing Point - C°
20
25
30
35
40
45
50
55
60
65
70
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B. General Procedure and Determination of Normal Per Cent Reduction

Before going ahead with any runs in which the organic bases were present, it was necessary to establish the normal conditions and yields obtained in the reaction. For this purpose the procedure standardized by Fry and Cameron[2] was used with slight modifications. All runs were made in duplicate throughout the entire investigation.

The sodium methylate was freshly prepared each time it was used. The sodium was Kahlbaum's "analytical grade." The methyl alcohol was Merck's "C.P. grade", specific gravity 21°-0.7911, acetone free, and free from other oxidizable material. In preparing the sodium methylate the sticks of sodium were first scraped while under ligroin to free them from any oxide. Then 17.3 grams were weighed out in ligroin to within 0.1 grams on an ordinary laboratory balance. The sodium was cut in quarters and dropped through a reflux condenser into a 500 c.c. flask containing 100-125 c.c. of methyl alcohol. The reaction at first was so vigorous as to cause the solution to boil. When the reaction became less vigorous, the sodium was cut into thinner and thinner slices to expedite its solution. Finally, when all the sodium was added, about 50 c.c. more of methyl alcohol were added and a hot plate inserted under the flask to aid in getting the last traces of the sodium into solution.

When cool, the sodium methylate solution was poured into a 250 c.c. measuring flask into which had previously been run 20.44 c.c. of Kahlbaum nitrobenzene, boiling point 208-209 degrees. This is the equivalent of 24.6 grams or 0.2 moles of nitrobenzene. The 500 c.c. flask that originally held the sodium methylate was rinsed out with methyl alcohol, which was then poured into the 250 c.c. measuring flask. Sufficient methyl alcohol was then added to the 250 c.c. measuring flask to fill it to its graduated capacity. Then 10 c.c. of the alcohol were pipetted out before the liquid in the 250 c.c. flask was poured back into the 500 c.c. flask. These 10 c.c. were used to rinse the liquid in the 250 c.c. flask into the 500 c.c. flask.

Pieces of broken glass were then added to the mixture to aid in preventing bumping during the heating period. The flasks were connected to reflux condensers and heated on constant level water baths for 5 hours. Special care must be taken at this part of the operation to secure uniform heating. The flasks, of course, should be of the same shape and capacity. They should be lowered into the water to the same depth and the water should be boiling at about the same rate in each bath. To insure uniform boiling, the rate at which water is run into the baths should be the same, and burners with the same size flame should be used.

Particular attention must be given to the condensers. Each one should be connected directly to a water supply to insure proper cooling. Methyl alcohol is very volatile and easily escapes. This is especially true in this case, since during the boiling, sodium formate forms with subsequent bumping. In order to prevent any vapors from escaping thru the condensers, it was necessary to use condensers with a jacket one meter long. Normal length condensers were first used but check results could not be obtained since alcohol was escaping out of the top. To be sure that the reaction was complete, the boiling was continued for five hours.

At the end of this time, the flasks were removed from the water baths. Solid formate was on the bottom. One hundred cubic centimeters of cold water were then added to stop the reaction. The flasks were cooled with tap water. On standing, azoxybenzene settled out on the bottom as an oil. The solution was now strongly alkaline due to the reaction,

$$CH_3ONa + H_2O \longrightarrow CH_3OH + NaOH.$$

The next step in the procedure was to remove the excess nitrobenzene and alcohol by steam distillation. The usual steam distillation apparatus was set up using liter flasks for steam generators. Most of the alcohol and nitrobenzene came over within a period of three quarters of an hour. Many text books say that azoxybenzene is not carried over in steam distillation. This is not true, since as much as 0.55 grams of azoxybenzene has been recovered from the distillate after a two hour period of distillation.

At the end of the steam distillation the solutions were cooled and the azoxybenzene was separated from the strongly alkaline solution containing the sodium formate by extraction with benzene. In general, five extractions were made on each sample using 25, 20, 15, 15, 15 c.c. of benzene for each extraction. The first benzene extract is rather viscous and hence entraps some of the solution containing formate. Consequently, it is advisable to shake the united extracts in a separatory funnel with water to recover the formate solution. This water solution is then added to the original solution.

The benzene extract containing the azoxybenzene was dried over night with fused calcium chloride sticks. The benzene was then evaporated and the resulting product weighed and its freezing point determined by the method previously described.

The alkaline solution containing the sodium formate was boiled to expel the benzene held by it. The solution has a tendency to bump while boiling and must be heated carefully to prevent loss through splashing. This alkaline solution always had a yellow color in all the determinations in this investigation. The solution was cooled, and then diluted to one liter.

The concluding operation of each run was the determination of the amount of formate in aliquot portions of the solution obtained from the reaction. It has been shown by Fry and Cameron[2] that the sodium formate obtained is a measure of the reduction occurring in the reaction. They also tried various methods for determining the sodium formate in the solution and concluded that the alkaline permanganate-oxalic acid method described by Scott[24] gave the best results. The same method was used in this investigation.

It was found, however, that the most careful manipulation and observance of time sequence was necessary in order to obtain concordant results in this formate determination. All operations were timed with a watch and carried out in the same manner each time. If these precautions were not observed, variations were observed of over 2 per cent in results with samples from the same solution.

There is so much formate in the solution that only a 10 c.c. sample from the liter can be used. To eliminate errors in reading the burette, a 50 c.c. sample was taken and then diluted to 500 c.c. A 100 c.c. portion from this diluted solution was used for titration.

To the sample were added 2 c.c. of dilute sulphuric acid to acidify it, then sufficient sodium carbonate to make the solution slightly alkaline. The solution was heated to boiling and potassium permanganate (0.1 N) was run in at the rate of 15 c.c. per minute for 2 minutes, then 10 c.c. for one minute and the balance slowly so that the required amount was added within 5 minutes. Time must be allowed for stopping the flow of permanganate while one lets the manganese dioxide settle to see if excess permanganate has been added. About 2-3 c.c. excess as shown by a pink color was sufficient. During the addition of the potassium permanganate, the flask was kept hot on a hot plate. This is important.

The solution was let stand for one minute, then heated to boiling and 12 c.c. of the dilute sulphuric acid were added and the solution again heated to boiling. This takes about one minute. Oxalic acid (0.1 N) was then run in rapidly at first and then more slowly toward the last until the manganese dioxide disappeared. From this point on, the time factor is not important. Once more the solution was heated to boiling and permanganate run in until a faint pink color appeared.

The amount of oxalic acid added was calculated in terms of its equivalent in permanganate which was then subtracted from the total quantity of permanganate used to give the cubic centimeters equivalent to the formate in the solution. Since the results were multiplied by 100, any difference between duplicate samples is greatly magnified.

The data given in Table II were obtained to establish the normal yield for the reduction of nitrobenzene by sodium methylate following the procedure just described. Klinger's equation was used as the basis for calculating the theoretical yields. The average yield based on three duplicate check runs was found to be 88.45% theory.

TABLE II

Reduction of Nitrobenzene by Sodium Methylate. Determination of Normal Yield

Run		Vol. taken / Total vol.	cc. $KMnO_4$ 0.1062 N added	cc. $H_2C_2O_4$ 0.1011 N added	cc. $KMnO_4$ 0.1062 N $\Bumpeq$ cc. $H_2C_2O_4$	cc. $KMnO_4$ $\Bumpeq$ HCOONa	Per Cent Reduction
1	A	$\frac{10}{1000}$	44.60	20.68	19.69	24.91	88.17
	B	$\frac{10}{1000}$	44.65	20.64	19.65	25.00	88.50
2	A	$\frac{10}{1000}$	45.75	21.95	20.90	24.85	87.97
	B	$\frac{10}{1000}$	46.78	22.95	21.85	24.93	88.25
3	A	$\frac{10}{1000}$	50.42	26.60	25.32	25.10	88.85
	B	$\frac{10}{1000}$	45.75	21.62	20.61	25.14	88.99
						Average	88.45

C. Determination of the Effect of Added Bases upon the Extent of the Reduction of (a) Nitrobenzene, (b) Azoxybenzene

1. Preliminary Discussion

The next step was to determine what effect an added organic base, such as aniline, quinoline, etc. would have on the extent of the reduction of nitrobenzene by sodium methylate. A series of runs was made in which increasing quantities of the organic base were incorporated in the standard reaction mixture, namely, 17.3 grams of sodium dissolved in methyl alcohol and 0.2 moles of nitrobenzene, and this mixture after the organic base was added, diluted to 250 c.c. with methyl alcohol. The organic bases chosen were used in the following order: aniline, monomethyl aniline, dimethyl aniline, quinoline, and isoamylamine.

In this group there are both aromatic and aliphatic bases. The aniline group was selected because it forms a series - aniline, monomethyl aniline, dimethyl aniline - of increasing basic strength. Consequently, the per cent reduction should be expected to increase in like manner. For each compound selected, a series of runs was made in which the quantity of base added to each run was 1/8, 1/4, 1/2, and 3/4 moles respectively. The maximum of 3/4 moles was chosen in order to limit the total volume of the solution to 250 c.c.

A second series of four runs was similarly made with each of the bases wherein the standard reaction mixture consisted of 19.8 grams of pure Kahlbaum azoxybenzene, 17.3 grams of sodium dissolved in methyl alcohol, the organic base and the whole diluted to 250 c.c. with methyl alcohol. The same bases were selected as in the previous runs with nitrobenzene and for each series the same relative quantities - 1/8, 1/4, 1/2, and 3/4 moles of base were added.

The purpose of this second series of runs was to determine the effect of the organic base on the further reduction of azoxybenzene to azobenzene by sodium methylate. Fry and Cameron[2] have shown that pure azoxybenzene when refluxed with sodium methylate in the presence of 1/2 mole of pyridine gave azobenzene according to the following equation.

$$2(C_6H_5N)_2O + CH_3ONa \longrightarrow 2C_6H_5N{=}NC_6H_5 + H_2O + HCOONa$$

This equation was used as the basis for calculating the yields of formate and the consequent per cent of this secondary reduction.

<u>This secondary reduction explains why the per cent reduction in some of the runs amounts to more than one hundred per cent yield of sodium formate.</u>

Before each individual series of runs is described and discussed, the general appearance and behavior of the reaction mixture will be described for all the runs.

When nitrobenzene was initially present, the solution became dark red within a few minutes after heating.

At the end of thirty minutes to one hour, solid sodium formate precipitated from the solution and collected on the side and bottom of the flask. Foaming and bumping resulted at this stage. At the end of the reaction period, the solution varied in color from a light cherry to a dark cherry red depending on the quantity of base added. When 3/4 of a mole of base was present, the reaction mixture was quite viscous and boiled very slowly.

When no nitrobenzene was initially present, the solutions did not color as rapidly nor as deeply. At the end of the reaction period, the color in all cases was an orange yellow. No solid formate settled out, but in some cases a very fine cloud appeared visible in the reaction mixture.

In all runs with nitrobenzene and with azoxybenzene, the addition of water at the end of the reduction period caused the precipitation of an oil from the solution.

During steam distillation it was necessary in some cases to stop the distillation before all of the base was volatilized. This was necessary since appreciable quantities of azoxybenzene come over during a long distillation. The balance of the base was removed from the azoxybenzene by shaking the benzene extract with dilute sulphuric acid.

2. The Effect of Aniline on the Extent of the Reduction of (1) Nitrobenzene, (2) Azoxybenzene

(a) Observations

The method as outlined under "Procedure" was followed in which there were added to the standard reaction mixture 1/8, 1/4, 1/2, and 3/4 moles of aniline. When 3/4 mole of aniline was added, the solution was homogeneous before refluxing, but not at the end of the five-hour period. The oil separating was dark cherry red in color.

Nitrobenzene with 1/8 and 1/4 moles of aniline present yielded 96.85 and 99.26 per cent theory of sodium formate respectively, but the yields were slightly decreased to 98.28 per cent and 94.26 per cent in the presence of 1/2 and 3/4 moles of aniline respectively. While the reduction in the presence of aniline is considerably greater than in the normal run without aniline, it is surprising to find that with increasing quantities of aniline the yields of formate decrease with the higher concentrations of aniline.

This anomaly may be due to two possible secondary reactions. (1) When the nitrobenzene is reduced, it is first reduced to nitrosobenzene which unites with the aniline already present to form azobenzene as represented by the equation[25] $C_6H_5NO + NH_2C_6H_5 \longrightarrow C_6H_5N{=}NC_6H_5 + H_2O$. (2) The other possibility is that nitrobenzene reacts with the aniline in the presence of a little sodium hydroxide, formed through the hydrolysis of some of the sodium methylate, to yield azobenzene[26], as represented by the following equation:

$$2C_6H_5NO_2 + 4C_6H_5NH_2 \longrightarrow 3C_6H_5N{=}NC_6H_5 + 4H_2O.$$

The freezing points of the products obtained decreased from 32.4° with 1/8 mole of aniline present to 27.6° with 3/4 mole of aniline present. These temperatures indicate on the freezing point - per cent composition curve compositions of 5.6 per cent azobenzene for a freezing point of 32.4° and 17.2 per cent for a freezing point of 27.6°.

To show that this decrease in freezing point is actually due to azobenzene, the product freezing at 27° was steam distilled for seven hours. A mixture of azo and azoxybenzene rich in azobenzene was obtained which had a freezing point of 39°. After numerous fractional crystallizations from methyl alcohol, a red crystalline product was obtained with a melting point of 66.5°. This proves conclusively that azobenzene was formed in this reaction, since its melting point is 67.2°.

With no nitrobenzene but azoxybenzene initially present, a slight reduction of the azoxybenzene occurred, 3.52-5.46 per cent, in which the per cent reduction increased as increasing amounts of aniline were incorporated in the reaction mixture.

The data for these two series of runs (1) and (2) are given on the succeeding pages in tables III and IV respectively.

TABLE III

Reduction of Nitrobenzene by Sodium Methylate in the Presence of Aniline

Moles of Aniline added	Run	Vol. taken / Total Vol.	cc. KMnO$_4$ 0.1102 N added		cc. $H_2C_2O_4$ 0.1025 N added		cc. KMnO$_4$ 0.1102 N ≎ cc. $H_2C_2O_4$		cc. KMnO$_4$ ≎ HCOONa		Per cent. Reduction		F.P. of Azo-Azoxybenzene Mixture °C.
1/8	A	$\frac{10}{1000}$	47.38	48.15	22.42	23.33	20.85	21.70	26.53	26.45	97.48	97.18	32.4
	B	$\frac{10}{1000}$	47.68	48.43	23.03	23.93	21.41	22.25	26.27	26.18	96.52	96.20	32.4
											Average 96.85		
1/4	A	$\frac{10}{1000}$	48.90	48.17	23.51	22.61	21.86	21.03	27.04	27.04	99.35	99.35	30.8
	B	$\frac{10}{1000}$	48.27	48.05	23.01	22.81	21.40	21.21	26.87	26.84	98.73	98.62	30.2
											Average 99.26		
1/2	A	$\frac{10}{1000}$	50.78	47.60	26.01	22.40	24.19	20.83	26.59	26.77	97.70	98.45	29.2
	B	$\frac{10}{1000}$	49.75	48.83	24.59	23.75	22.88	22.09	26.87	26.74	98.73	98.25	29.1
											Average 98.28		
3/4	A	$\frac{10}{1000}$	47.87	46.51	23.93	22.57	22.25	20.99	25.62	25.52	94.14	93.77	27.6
	B		47.20	47.20	23.01	23.15	21.40	21.53	25.80	25.67	94.80	94.32	27.6
											Average 94.26		

TABLE IV

Reduction of Azoxybenzene by Sodium Methylate in the Presence of Aniline

Moles of Aniline added	Run	Vol. taken / Total Vol.	cc. $KMnO_4$ 0.1102 N added		cc. $H_2C_2O_4$ 0.1025 N added		cc. $KMnO_4$ 0.1102 N ≡ cc. $H_2C_2O_4$		cc. $KMnO_4$ ≡ HCOONa		Per cent. Reduction		F.P. of Azo-Azoxybenzene Mixture °C.
1/8	A	50/1000	8.50	7.41	7.57	6.40	7.04	5.95	1.46	1.46	3.22	3.22	35.00
	B	50/1000	6.93	6.90	6.08	6.07	5.65	5.65	1.28	1.25	2.82	2.82	35.00
											Average 3.00		
1/4	A	50/1000	8.15	6.95	7.07	5.71	6.58	5.31	1.57	1.64	3.46	3.61	34.95
	B	50/1000	8.72	7.30	7.77	6.30	7.23	5.86	1.49	1.44	3.29	3.18	35.00
											Average 3.40		
1/2	A	50/1000	9.20	8.15	7.70	6.60	7.16	6.14	2.04	2.01	4.49	4.43	35.05
	B	50/1000	9.88	8.48	8.71	7.22	8.10	6.71	1.78	1.77	3.92	3.90	35.05
											Average 4.18		
3/4	A	50/1000	7.55	8.54	5.56	6.71	5.17	6.24	2.38	2.30	5.24	5.07	34.80
	B	50/1000	9.37	9.83	7.75	8.30	7.21	7.72	2.16	2.11	4.77	4.65	34.85
											Average 4.93		

(c) Summary

Due to the fact that there is a side reaction involving aniline when nitrobenzene and aniline are initially present, it is not possible to draw any definite conclusions as to the effect of aniline upon the regular reduction of nitrobenzene by sodium methylate apart from the noteworthy fact that reduction in the presence of aniline is far more extensive than in its absence, that is, it runs to 99.26 per cent of the theoretical yield of formate as compared with the normal yield of 88.45 per cent of theory.

When azoxybenzene is refluxed with sodium methylate, in the presence of aniline, it was found (i) reduction of azoxybenzene occurs and (ii) the amount of the reduction increases with increasing amounts of aniline added.

Due to the fact that the amount of reduction varies by only a few per cent, and since small traces of impurities affect the freezing point to a great degree, it was found impossible to calculate the per cent of azo and azoxybenzene in the mixture obtained from the reduction of azoxybenzene. The difference in freezing point of a mixture which contains 3 per cent azobenzene and one containing 4.93 per cent is one degree. This could easily be obscured by a small amount of impurity.

Azobenzene is also more volatile with steam than azoxybenzene, so that some of it is lost in the steam distillation. This further complicates any attempt to calculate the amounts of azobenzene present.

3. The Effect of Monomethyl Aniline on the Extent of the Reduction of (1) Nitrobenzene (2) Azoxybenzene

(a) Observations

For this series of runs, Kahlbaum's monomethyl aniline, boiling point 194° C., was used. The mixtures were homogeneous before refluxing except when 3/4 mole of monomethyl aniline was present. The usual quantities of base were introduced into the mixture, namely, 1/8, 1/4, 1/2, and 3/4 moles of monomethyl aniline. The method as described under "Procedure" was used.

The color of the cakes of azoxybenzene obtained from the runs when nitrobenzene was initially present became darker in color as more monomethyl aniline was added. They had a reddish brown color. Those obtained when no nitrobenzene was present also changed color, but the shade was not so dark.

In both the series of runs, the per cent reduction increased as increasing quantities of monomethyl aniline were present.

The data for these two series of runs (1) and (2) are given in the following Tables V and VI respectively.

TABLE V

Reduction of Nitrobenzene by Sodium Methylate in the Presence of Mono-Methyl Aniline

Moles of Mono Methyl Aniline added	Run	Vol. taken / Total Vol.	cc. $KMnO_4$ 0.1108 N added	cc. $H_2C_2O_4$ 0.1014 N added	cc. $KMnO_4$ 0.1108 N ≎ cc. $H_2C_2O_4$	cc. $KMnO_4$ ≎ HCOONa	Per cent. Reduction	F.P. of Azo-Azoxy-benzene Mixture °C.
1/8	A	$\frac{10}{1000}$	47.50 47.45	24.60 24.68	22.51 22.58	24.99 24.87	92.27 91.82	30.60
	B	$\frac{10}{1000}$	47.62 46.50	25.05 23.77	22.92 21.75	24.70 24.75	91.20 91.38	30.40
							Average 91.66	
1/4	A	$\frac{10}{1000}$	48.48 49.08	23.60 24.33	21.59 22.26	26.89 26.82	99.28 99.02	29.70
	B	$\frac{10}{1000}$	48.47 48.30	24.00 23.70	21.96 21.69	26.51 26.61	97.88 98.25	29.00
							Average 98.61	
1/2	A	$\frac{10}{1000}$	54.93 54.10	29.55 28.75	27.04 26.31	27.89 27.79	102.97 102.67	27.70
	B	$\frac{10}{1000}$	55.27 52.90	29.81 27.28	27.28 24.96	27.99 27.94	103.34 103.26	27.60
							Average 103.06	
3/4	A	$\frac{10}{1000}$	59.25 54.13	33.70 28.21	30.84 25.81	28.41 28.32	104.89 104.56	30.00
	B	$\frac{10}{1000}$	56.05 56.84	30.35 31.37	27.77 28.70	28.28 28.14	104.41 103.88	30.40
							Average 104.44	

TABLE VI

Reduction of Azoxybenzene by Sodium Methylate in the Presence of Mono-Methyl Aniline

Moles of Mono Methyl Aniline added	Run	Vol. taken / Total Vol.	cc. $KMnO_4$ 0.1108 N added		cc. $H_2C_2O_4$ 0.1014 N added		cc. $KMnO_4$ 0.1108 N ≎ cc. $H_2C_2O_4$		cc. $KMnO_4$ ≎ HCOONa		Per cent. Reduction		F.P. of Azo-Azoxy-benzene Mixture °C.
1/8	A	50/1000	12.65	10.43	12.13	9.78	11.11	8.96	1.54	1.47	3.39	3.24	34,80
	B	50/1000	11.60	11.10	10.90	10.20	9.98	9.34	1.62	1.76	3.57	3.88	34.80
											Average	3.52	
1/4	A	50/1000	11.57	9.68	10.65	8.72	9.76	7.99	1.81	1.69	3.99	3.72	34.80
	B	50/1000	10.48	11.48	9.33	10.55	8.55	9.66	1.93	1.82	4.27	4.01	34.80
											Average	4.00	
1/2	A	50/1000	10.70	9.57	9.13	8.00	8.36	7.33	2.34	2.24	5.15	4.91	34.65
	B	50/1000	9.38	10.80	8.03	9.53	7.36	8.73	2.02	2.07	4.45	4.56	34.55
											Average	4.77	
3/4	A	50/1000	8.10	8.92	6.20	7.20	5.68	6.60	2.42	2.32	5.33	5.11	34.20
	B	50/1000	12.55	10.67	10.90	8.80	9.98	8.06	2.57	2.61	5.66	5.75	34.10
											Average	5.46	

(c) Summary

The results obtained in both of these series of runs in which monomethyl aniline has been incorporated show (i) the addition of monomethyl aniline causes increased reduction with reference to the established normal reduction, 88.45 per cent. (ii) Increased quantities of monomethyl aniline present produce increased reduction - 91.66, 98.61, 103.06, 104.44 per cent theory yields of formate.

The amount of reduction of the azoxybenzene, when nitrobenzene was absent, was slightly greater than was the case in the previous series when aniline was used. This is to be expected since monomethyl aniline is more basic than aniline.

An attempt was made to separate the azobenzene from the azoxybenzene in these runs by steam distillation, followed by fractional crystallization from methyl alcohol of the product from the steam distillate.

4. The Effect of Dimethyl Aniline on the Extent of the Reduction of (1) Nitrobenzene (2) Azoxybenzene

(a) Observations

Kahlbaum's dimethyl aniline, boiling point 192°, was used in both series of runs. Four runs in each series were made to which the usual quantities of organic base were added, namely 1/8, 1/4, 1/2, and 3/4 moles of dimethylaniline. In this series of runs , the solutions were not homogeneous when 1/2 and 3/4 moles of base were present.

When nitrobenzene was added to the dimethyl aniline before refluxing, an orange color developed. While the steam distillation was carried on to remove the nitrobenzene and dimethyl aniline, it was noticed that as long as nitrobenzene was present, the oil in the distillate was orange. When no nitrobenzene was present, the oil was greenish yellow in color.

Using this color change as a test, together with the absence of any nitrobenzene odor, the conclusion was reached that when 1/2 and 3/4 moles of dimethyl aniline were present, no nitrobenzene remained in the mixture after refluxing. This is a qualitative check on the measure of reduction as obtained from formate titration. In each of the cases, the titration showed a reduction of over one hundred per cent. Hence there should be no nitrobenzene left over, which fact checks with the observed conditions.

The data for these two series of runs (1) and (2) are given in the following Tables VII and VIII respectively.

TABLE VII

Reduction of Nitrobenzene by Sodium Methylate in the Presence of Dimethyl Aniline

Moles of Dimethyl Aniline added	Run	Vol. taken / Total Vol.	cc. $KMnO_4$ 0.1062 N added	cc. $H_2C_2O_4$ 0.1011 N added	cc. $KMnO_4$ 0.1062 N ≡ cc. $H_2C_2O_4$	cc. $KMnO_4$ ≡ HCOONa	Per cent. Reduction	F.P. of Azo-Azoxybenzene Mixture °C.
1/8	A	10/1000	48.26 48.21	23.10 22.93	21.99 21.83	26.27 26.38	93.00 93.38	33.70
	B	10/1000	49.23 49.37	23.67 23.72	22.53 22.58	26.70 26.79	94.51 94.82	33.70
							Average 93.93	
1/4	A	10/1000	53.78 56.86	27.12 30.10	25.82 28.66	27.96 28.20	98.98 99.82	33.75
	B	10/1000	53.00 54.73	26.50 28.20	25.23 26.85	27.77 27.88	98.31 98.69	33.80
							Average 98.95	
1/2	A	10/1000	56.97 57.90	28.41 29.48	27.05 28.06	29.92 29.84	105.91 105.63	33.70
	B	10/1000	58.50 60.00	30.13 31.84	28.67 30.31	29.83 29.69	105.59 105.10	34.00
							Average 105.56	
			$KMnO_4$ 0.1109 N	$H_2C_2O_4$ 0.1014 N		$KMnO_4$ 0.1109 N		
3/4	A	10/1000	56.23 57.40	29.83 30.91	27.30 28.28	28.93 29.12	106.94 107.64	33.10
	B	10/1000	56.48 57.54	30.03 31.33	27.48 28.67	29.00 28.87	107.20 106.72	33.20
							Average 107.12	

TABLE VIII

Reduction of Azoxybenzene by Sodium Methylate in the Presence of Dimethyl Aniline

Moles of Dimethyl Aniline added	Run	Vol. taken / Total Vol.	cc. $KMnO_4$ 0.1109 N added		cc. $H_2C_2O_4$ 0.1014 N added		cc. $KMnO_4$ 0.1109 N ≡ cc. $H_2C_2O_4$		cc. $KMnO_4$ ≡ HCOONa		Per cent. Reduction		F.P. of Azo-Azoxybenzene Mixture °C
1/8	A	$\frac{50}{1000}$	10.12	9.14	9.25	8.20	8.46	7.50	1.66	1.64	3.67	3.63	34.7
	B	$\frac{50}{1000}$	8.53	11.78	7.78	11.25	7.12	10.29	1.41	1.49	3.12	3.30	34.8
											Average 3.43		
1/4	A	$\frac{50}{1000}$	6.50	7.28	5.25	6.14	4.80	5.62	1.70	1.66	3.76	3.67	34.45
	B	$\frac{50}{1000}$	7.15	7.60	6.21	6.73	5.68	6.16	1.47	1.44	3.26	3.19	34.60
											Average 3.47		
1/2	A	$\frac{50}{1000}$	10.80	13.87	8.14	11.50	7.45	10.52	3.35	3.31	7.42	7.33	34.50
	B	$\frac{50}{1000}$	10.90	10.68	8.30	8.15	7.59	7.46	3.31	3.22	7.33	7.13	34.30
											Average 7.30		
3/4	A	$\frac{50}{1000}$	10.68	10.01	7.33	6.68	6.71	6.12	3.97	3.89	8.80	8.62	33.6
	B	$\frac{50}{1000}$	10.47	11.02	7.10	7.78	6.50	7.12	3.97	4.00	8.80	8.65	33.7
											Average 8.72		

(c) Summary

The results obtained from these two series of runs in which dimethyl aniline was present in increasing quantities in the reaction mixture are of the same general nature as those obtained using monomethyl aniline, namely, (i) the addition of dimethyl aniline produced an increased per cent reduction with reference to the normal extent of the reduction; (ii) This increased per cent reduction grows in magnitude as the quantity of dimethyl aniline present increases - 93.93, 98.95, 105.56, and 107.12 per cent theory.

Since dimethylaniline is more basic than monomethyl aniline, the increased per cent reduction should be larger in the case of the dimethyl aniline. This was found to be the case when nitrobenzene was initially present and also when azoxybenzene was used and no nitrobenzene was present. With 1/8 and 1/4 moles of organic base present, there was little difference in the extent of the reduction produced by monomethyl and dimethyl aniline.

5. The Effect of Quinoline on the Extent of the Reduction. (1) Nitrobenzene, (2) Azoxybenzene.

(a) Observations

Kahlbaum's quinoline, boiling point 237° C, was used. The quantities of quinoline added in each series of runs were 1/8, 1/4, 1/2, and 3/4 moles respectively, and in all the runs the reaction mixtures were homogenous before and after refluxing.

The runs were conducted according to the method outlined under "Procedure." Not all of the quinoline was removed, even by four hours steam distillation. In order to reduce the time required for steam distillation and thus prevent much of the azo-azoxybenzene mixture from passing over, the greater part of the quinoline was removed thru extraction with dilute sulphuric acid. This was accomplished after the oil had been separated from the reaction mixture with benzene. Even with this procedure, a faint odor of quinoline persisted in the final product.

The data for these two series of runs (1) and (2) are given in the following Tables IX and X respectively.

TABLE IX

Reduction of Nitrobenzene by Sodium Methylate in the Presence of Quinoline

Moles of Quinoline added	Run	Vol. taken / Total Vol.	cc. $KMnO_4$ 0.1102 N added	cc. $H_2C_2O_4$ 0.1025 N added	cc. $KMnO_4$ 0.1102 N ≡ cc. $H_2C_2O_4$	cc. $KMnO_4$ ≡ HCOONa	Per cent. Reduction	F.P. of Azo-Azoxybenzene Mixture °C.
1/8	A	$\frac{10}{1000}$	46.39 46.63	21.85 22.00	20.32 20.46	26.07 26.17	95.79 96.16	33.75
	B	$\frac{10}{1000}$	46.99 47.73	22.63 23.45	21.05 21.81	25.94 25.92	95.31 95.24	34.00
							Average 95.62	
1/4	A	$\frac{10}{1000}$	47.50 47.92	20.88 21.50	19.42 20.00	28.08 27.92	103.17 102.59	34.25
	B	$\frac{10}{1000}$	47.41 47.57	20.81 21.22	19.45 19.73	27.96 27.84	102.61 102.29	34.30
							Average 102.66	
1/2	A	$\frac{10}{1000}$	52.17 53.47	24.70 26.01	22.97 24.19	29.20 29.28	107.29 107.58	34.00
	B	$\frac{10}{1000}$	51.89 51.50	24.23 23.85	22.53 22.18	29.36 29.32	107.88 107.73	34.20
							Average 107.62	
3/4	A	$\frac{10}{1000}$	54.47 54.55	25.72 25.61	23.92 23.82	30.55 30.73	112.25 112.91	33.10
	B	$\frac{10}{1000}$	54.09 54.95	24.98 25.85	23.23 24.04	30.86 30.91	113.39 113.57	33.15
							Average 113.03	

TABLE X

Reduction of Azoxybenzene by Sodium Methylate in the Presence of Quinoline

Moles of Quinoline added	Run	Vol. taken / Total Vol.	cc.$KMnO_4$ 0.1112 N added		cc.$H_2C_2O_4$ 0.1015 N added		cc.$KMnO_4$ 0.1112 N $\equiv$ cc.$H_2C_2O_4$		cc.$KMnO_4$ $\equiv$ HCOONa		Per cent. Reduction		F.P. of Azo-Azoxybenzene Mixture °C.
1/8	A	$\frac{50}{1000}$	15.34	11.73	14.98	11.08	13.67	10.11	1.67	1.62	3.71	3.60	35.0
	B	$\frac{50}{1000}$	15.58	12.32	15.41	11.80	14.07	10.77	1.51	1.55	3.36	3.45	35.05
											Average	3.53	
1/4	A	$\frac{50}{1000}$	9.53	9.58	7.98	8.17	7.29	7.45	2.24	2.13	4.98	4.73	34.95
	B	$\frac{50}{1000}$	13.70	8.78	12.62	7.32	11.52	6.68	2.18	2.10	4.84	4.67	34.95
											Average	4.80	
1/2	A	$\frac{50}{1000}$	14.07	11.35	12.11	9.30	11.06	8.49	3.01	2.86	6.66	6.36	34.80
	B	$\frac{50}{1000}$	12.50	10.98	10.63	9.03	9.71	8.24	2.79	2.74	6.21	6.09	34.85
											Average	6.33	
3/4	A	$\frac{50}{1000}$	11.45	10.27	8.95	7.68	8.17	7.01	3.28	3.28	7.30	7.30	34.60
	B	$\frac{50}{1000}$	11.53	10.29	8.90	7.60	8.13	6.94	3.45	3.35	7.67	7.45	34.55
											Average	7.43	

(c) Summary

A study of the results obtained when quinoline is present in increasing amounts in the reaction mixture shows that quinoline also increases the per cent reduction above that determined as the normal per cent reduction. This per cent reduction grows larger as increasingly larger quantities of quinoline are added - 95.62, 102.66, 107.62, and 113.03 per cent theory.

Since quinoline is more basic than monomethyl or dimethyl aniline, it should give a larger per cent reduction than the other two. This was found to be the case when nitrobenzene was initially present, but not when azoxybenzene was the initial compound.

When azoxybenzene was used, the per cent reduction with quinoline is greater than that with monomethyl aniline, but less than that with dimethyl aniline. The reason for this has not been determined. A search for ionization constants that might be used as a measure of the relative basic nature of the compounds concerned failed to reveal any that were determined at the temperature of the reaction, namely 85° C. Just why quinoline as compared with dimethyl aniline should produce a greater per cent reduction when nitrobenzene is initially present and a smaller per cent reduction when no nitrobenzene is present is not at all clear. It serves as an interesting point for future study.

6. The Effect of IsoamylaAmine on the Extent of the Reduction. (1) Nitrobenzene, (2) Azoxybenzene.

(a) Observations

Kahlbaum's isoamylamine, boiling point 95° C, was used in this series of runs. As usual, there were added to the standard reaction mixtures 1/8, 1/4, 1/2, and 3/4 moles of isoamylamine. The mixture was then treated as described under "Procedure." In all the runs the reaction mixtures were homogeneous before and after refluxing.

While steam distilling, an odor of nitrobenzene was noticed in the distillate from the mixtures to which 1/8 and 1/4 moles of isoamylamine had been added, but the odor was absent in the distillate from the runs in which 1/2 and 3/4 moles of isoamylamine were present. This observation agrees with the observation made in previous runs.

It was noticed that after five hours refluxing, the mixture to which 1/8 mole of isoamylamine had been added did not seem to contain as much solid formate as usual. Upon analysis it was shown that the per cent reduction was only 63.45 per cent in terms of yield of sodium formate. This was surprising since isoamylamine being more basic than the aromatic amines should have produced a correspondingly larger per cent reduction. The reason for this will be considered shortly.

When 1/4 and 1/2 moles of isoamylamine were present in the reaction mixture, there was hardly any solid formate produced in the reaction mixtures, and the per cent reduction as showed by formate titration decreased to 40.70 and 38.22 per cent respectively. When 3/4 mole of isoamylamine was present, the per cent reduction increased somewhat to 51.75 per cent. The data from which these figures were obtained are given in Table XI.

TABLE XI

Reduction of Nitrobenzene by Sodium Methylate in the Presence of Isoamylamine

Moles of Iso-amyl-amine added	Run	Vol. taken / Total Vol.	cc. $KMnO_4$ 0.1112 N added	cc. $H_2C_2O_4$ 0.1015 N added	cc. $KMnO_4$ 0.1112 N $\Bumpeq$ cc. $H_2C_2O_4$	cc. $KMnO_4$ $\Bumpeq$ HCOONa	Per cent. Reduction	F.P. of Azo-Azoxy-benzene Mixture °C.
1/8	A	$\frac{10}{1000}$	36.19 35.09	21.00 19.70	19.17 17.99	17.02 17.10	63.10 63.40	34.05
	B	$\frac{10}{1000}$	36.52 26.44	21.13 21.15	19.29 19.31	17.23 17.13	63.82 63.49	34.05
							Average 63.45	
			$KMnO_4$ 0.1102 N	$H_2C_2O_4$ 0.1025 N				
1/4	A	$\frac{10}{1000}$	25.85 22.40	15.77 12.06	14.67 11.22	11.18 11.18	41.08 41.08	33.6
	B	$\frac{10}{1000}$	26.95 22.82	17.20 12.71	16.00 11.82	10.95 11.00	40.23 40.41	33.6
							Average 40.70	
			$KMnO_4$ 0.1112 N	$H_2C_2O_4$ 0.1015 N				
1/2	A	$\frac{10}{1000}$	22.95 21.98	13.92 12.80	12.72 11.69	10.23 10.29	37.93 38.15	33.8
	B	$\frac{10}{1000}$	20.23 21.65	10.84 12.34	9.90 11.26	10.33 10.39	38.30 38.52	33.8
							Average 38.22	
			$KMnO_4$ 0.1102 N	$H_2C_2O_4$ 0.1025 N				
3/4	A	$\frac{10}{1000}$	24.18 25.90	10.78 12.66	10.02 11.77	14.16 14.13	52.03 51.92	33.7
	B	$\frac{10}{1000}$	25.38 23.70	12.25 10.37	11.39 9.64	13.99 14.06	51.39 51.66	33.5
							Average 51.75	

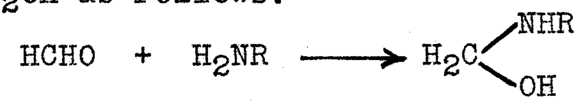
This behavior was entirely different from that of all the other runs. Another peculiar feature was the fact that the yields of azoxybenzene were way in excess of the amounts as indicated by the per cent reduction obtained from formate titration.

It was noticed in the first run that the odor of isoamylamine persisted in the steam distillation distillate after three hours of steam distilling. This seemed unusual in view of the low boiling point of isoamylamine.

Then, too, the oil obtained after adding water to the refluxed reaction mixture was of a very dark cherry red color. This color was removed when the benzene solution of the oil was extracted with dilute sulphuric acid. The acid solution took on a reddish brown color and smelled strongly of formaldehyde. Whenever the acid solution was made alkaline, the odor of isoamylamine was present and an oil formed in the solution.

Since isoamylamine is soluble in water, the oil was not isoamylamine. This suggested that a compound had formed in the reaction mixture, possibly between formaldehyde and isoamylamine, and that the sulphuric acid decomposed this compound with the liberation of formaldehyde. In other words, the sulphuric acid combining with the isoamylamine of the isoamylamine-formaldehyde compound yielded the isoamylamine sulphate and liberated formaldehyde. That a compound of isoamylamine and formaldehyde has been formed as an intermediate product is quite likely in view of the work of L. Henry[27] which is pertinent to the present investigation.

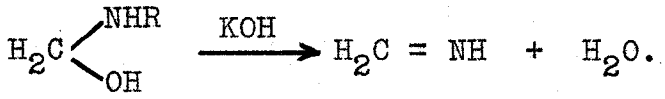
Henry states that formaldehyde in aqueous solution reacts energetically with primary and secondary amines to give addition products of the general formulas $RNHCH_2OH$ and R_2NCH_2OH as follows:



$$HCHO + H_2NR \longrightarrow H_2C\begin{cases}NHR\\OH\end{cases}$$

The members of the methyl and ethyl series are slightly soluble in water and separate as light oils, but the higher members are liquids which are difficultly soluble in water or not soluble at all. Henry has prepared $C_5H_{11}NHCH_2OH$, isoamylamidomethyl alcohol, which has a specific gravity of .8922 at 11.6° C. These products can be distilled without decomposition.

Strong caustic potash withdraws water from the compounds, derived from primary amines, and changes them into colorless liquids of a basic character, which are undecomposable by boiling and possess the general formula $RN = CH_2$, corresponding to an alkyl imide. The following equation represents this change:



$$H_2C\begin{cases}NHR\\OH\end{cases} \xrightarrow{KOH} H_2C = NH + H_2O.$$

Henry further states that the action of dilute acids decomposes by hydrolysis the imide compound and regenerates the formaldehyde and the amine. This reaction can be represented as follows:

$$H_2C = NR + H_2O \longrightarrow HCHO + H_2NR.$$

The formation in the reaction mixture of isoamylmethyleneimide through the reaction of formaldehyde and isoamylamine can be regarded as an explanation for the peculiar results obtained in the series of runs with nitrobenzene initially present.

An explanation for the formation of an isoamylamine-formaldehyde compound is found in the previously proposed scheme of reactions wherein methyl alcohol is first oxidized to the formaldehyde stage and then the latter to the formate stage. At the formaldehyde stage more or less of the iso-amylamine-formaldehyde compound would be formed and any formaldehyde not combining in this manner would then be oxidized to sodium formate. Consequently, the amount of sodium formate generated is low.

The previously proposed mechanism for the oxidation of methyl alcohol to sodium formate is represented by the following equations:

$$CH_3OH + HONa \longrightarrow CH_3ONa + H_2O \qquad (a)$$

$$CH_3ONa + HONa \longrightarrow CH_2(ONa)_2 + H_2 \qquad (b)$$

$$CH_2(ONa)_2 + HONa \longrightarrow CH(ONa)_3 + H_2 \qquad (c)$$

$$CH(ONa)_3 + H_2O \longrightarrow HCOONa + 2HONa \qquad (c')$$

$$\Sigma\ (a),(b),(c),(c') \quad CH_3OH + HONa \longrightarrow HCOONa + 2H_2. \qquad (B)$$

Since there is a trace of water present in the reaction mixture, it is logical to assume that this water can react with the product of reaction (b) as well as with the product of reaction (c) as previously postulated. This reaction of the water with the product of reaction (b) can be represented as follows:

$$CH_2(ONa)_2 + H_2O \longrightarrow HCHO + 2NaOH \qquad (b')$$

If there is no isoamylamine present to unite with the formaldehyde, the formaldehyde is oxidized to sodium formate by the sodium hydroxide as noted in the above scheme.

$$OCH_2 + HONa = HCOONa + H_2$$

Reaction (b') is similar to reaction (c') and also to reaction (e) previously shown[21] as the last step in the oxidation of methyl alcohol to carbonate by sodium hydroxide. <u>This is therefore additional evidence that the proposed mechanism for the oxidation of methyl alcohol by sodium hydroxide to form successively formaldehyde, formic acid, and carbonic acid, involving the theory of the acidic dissociation of sodium hydroxide, is correct</u>. This is shown by the fact that an intermediate compound of formaldehyde and isoamylamine has been isolated in methyl alcohol as the reaction medium.

That the aldehyde stage is not dependent upon the use of methyl alcohol is shown by the fact that Suter and Dains[28] isolated benzaldehyde as a product of the reaction when the alcoholate of benzyl alcohol was used in benzyl alcohol solution for reducing nitrobenzene.

If the union of formaldehyde with isoamylamine is the correct explanation for the low yields of formate obtained when isoamylamine is present, then the more isoamylamine present, the more formaldehyde would be held in combination with the isoamylamine. Consequently, the amount of formate should be lower. To check this assumption, a determination of the amount of formaldehyde present should show larger quantities of formaldehyde as the amount of sodium formate becomes smaller.

(b) Quantitative Determination of Formaldehyde Combined with Isoamylamine.

In order to have some estimate of the amount of formaldehyde combining with the isoamylamine during the reaction, it was necessary to devise a method for determining the amount of formaldehyde set free by the sulphuric acid treatment noted above.

To estimate this quantity of formaldehyde, the reaction of L. Vanino and E. Seitter[29] was first tried. This reaction depends upon the oxidation of the formaldehyde to carbon dioxide by potassium permanganate in a strongly acid solution. Excess permanganate is added and the excess titrated with hydrogen peroxide. A 5 c.c. portion of a 1 per cent solution of formaldehyde should be used.

To test out the method a known sample was made up by taking 13.4416 grams of a 37 per cent solution of formaldehyde and adding to it 14.0753 grams of isoamylamine, approximating equimolar quantities. The whole was diluted to 500 c.c. after being made strongly acid with dilute sulphuric acid. This gave a solution approximating the one to be analyzed as found in the reaction mixture.

When 2.5 c.c. of this known solution was analyzed for formaldehyde by Vanino and Seitter's method, the amount found corresponded to 123 per cent of that added. This high yield is due chiefly to the presence of the amine which is also oxidized by the permanganate. This method also tried on a pure formaldehyde sample of known content gave results about 4 per cent too high. Therefore, the method was abandoned.

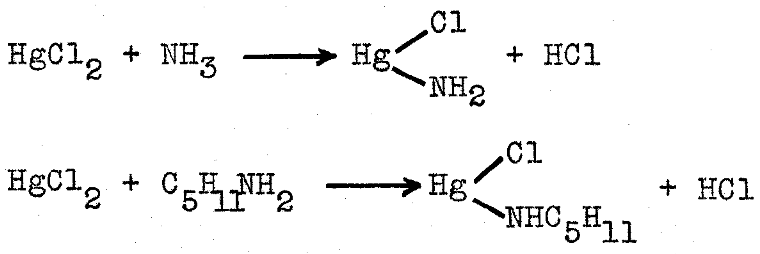
The second method tried was to separate the formaldehyde by steam distillation. In this case only 80 per cent of the formaldehyde came over from a standard sample. Wilkinson and Gibson[30] have shown that when a solution containing formaldehyde was distilled, the formaldehyde polymerized in the solution and a portion of it always remained in the residue in the distilling flask. The greater the concentration of formaldehyde, the more remained behind. Therefore, this method of separating formaldehyde through steam distillation was abandoned.

The third method using hydrogen peroxide as the oxidizing agent is recommended by the Association of Official

Agricultural Chemists[31] as good for impure samples of high formaldehyde content. The method is as follows. To 50 c.c. of normal sodium hydroxide in an Erlenmeyer flask add 50 c.c. of neutral hydrogen peroxide (3% solution) and 3 c.c. of the formaldehyde solution under examination. Heat 5 minutes on the steam bath with occasional shaking. Cool, and titrate the excess sodium hydroxide with standard dilute sulphuric acid using litmus as an indicator.

The one objection to this method was that it is carried out in an alkaline medium. As soon as the solution was made alkaline, the isoamylamine was set free and united with the formaldehyde, which was then no longer available for oxidation. It was therefore necessary to eliminate the amine before separate estimation of the formaldehyde could be effected.

It was found that mercuric chloride does not react with formaldehyde, but, as is well known, it does react with amines to form mercuric amidochlorides[32], analogously to the reaction of ammonia with mercuric chloride. The parallel equations are as follows:



$$HgCl_2 + NH_3 \longrightarrow Hg\begin{matrix} Cl \\ NH_2 \end{matrix} + HCl$$

$$HgCl_2 + C_5H_{11}NH_2 \longrightarrow Hg\begin{matrix} Cl \\ NHC_5H_{11} \end{matrix} + HCl$$

To bring about such a separation the following procedure was adopted. The benzene extract of the reaction mixture contained the formaldehyde-isoamylamine compound. It was treated with dilute sulphuric acid which gave an aqueous solution of isoamylamine sulphate and free formaldehyde. This solution was diluted to 500 c.c. and 10 c.c. of the resulting solution was used for analysis. Twenty-five cubic centimeters of a saturated solution of mercuric chloride were added and in addition 2-3 grams of solid mercuric chloride to insure a sufficient excess. In order to keep the volume small, no more of the saturated solution was added.

Dilute sodium hydroxide (2.5 N) was next added, rapidly at first until a white precipitate began to form, then 3 or 4 drops at a time with constant shaking. The sodium hydroxide added decomposed the isoamylaminesulphate liberating the isoamylamine which combined with the mercuric chloride, as previously noted, to give the white precipitate of mercuric isoamylamidochloride. When all the isoamylamine sulphate had been decomposed, further addition of sodium hydroxide precipitated yellow mercuric oxide which soon turned brick red as more sodium hydroxide was added. If sodium hydroxide was added beyond this point, the precipitate became black and the determination was ruined. This was likely due to the fact that mercuric oxide is reduced by formaldehyde in the presence of an excess of alkali.

The precipitated mercuric oxide, mercuric isoamylamido chloride, and the excess solid mercuric chloride were filtered off on a Buchner funnel using suction. Dilute sodium hydroxide was added, drop by drop, to the filtrate containing formaldehyde and mercuric chloride until the last of the mercuric chloride was precipitated as mercuric oxide. If too much sodium hydroxide was added, the precipitate again became black and the determination was ruined. The precipitate of mercuric oxide was filtered off as before and the filtrate, after neutralizing the alkali present, was ready for analysis of its formaldehyde content. This was carried out as previously described.

A solution containing known quantities of formaldehyde and isoamylamine was made up and tried out by this new method. The per cent of the theoretical amount of formaldehyde obtained was 98.67, 103.4, 95.6, 104.3, 101.70 giving an average of 100.73. The reason for this variation was due to the fact that in titrating the excess alkali, one drop of acid in excess made a difference of 1.5 per cent. There were two other places where neutralization occurred and at these points one drop in excess might also be allowed.

It was also found that if too large quantities of solution of aldehyde were used, low results were obtained. Double quantities of the original solution as used above were analyzed and the results obtained only came to 84 per cent of the theoretical.

The solution from the run in which 1/8 mole of isoamylamine was present was then analyzed. This showed

0.419 and 0.427 per cent of formaldehyde.present. This corresponds to 2.2714 grams of formaldehyde in the original reaction mixture. When the solution from the run containing 1/2 mole of isoamylamine was analyzed for formaldehyde, the samples showed 0.905 and 0.942 per cent which corresponds to 4.969 grams in the original mixture or over twice as much as before. The data from which these results were obtained are given in Table XII.

TABLE XII

Data for Determination of Formaldehyde Combined with Isoamylamine

Moles of Isoamylamine present	Run	Vol. taken / Total Vol.	cc.NaOH (0.9903 N) added		cc.H_2SO_4 (0.95.86 N) added		cc.NaOH ≎ HcHO		gms. HcHO in 500 cc.	
1/8	A	$\frac{20}{500}$	37.08	24.58	35.20	22.08	3.02	3.20	2.2454	2.3792
	B	$\frac{20}{500}$	10.13	10.14	7.40	7.35	2.97	3.03	2.2082	2.2528
1/2	A	$\frac{10}{500}$	11.14	10.35	8.11	7.35	3.29	3.24	4.8923	4.8179
	B	$\frac{10}{500}$	10.30	11.12	7.14	7.91	3.39	3.46	5.0410	5.1450

These results will now be used to calculate the actual per cent reduction of the nitrobenzene, but it will first be necessary to consider the source of the hydrogen that reduces the nitrobenzene. This hydrogen comes not only from the reaction in which part of the methyl alcohol is oxidized in the normal way to sodium formate as previously postulated in equation (B), which is the summation of equations (a), (b), (c), and (c') in the proposed mechanism scheme, but some of the hydrogen comes from the oxidation of that part of the methyl alcohol which is oxidized to the formaldehyde stage whereupon the formaldehyde combines with the isoamylamine. The formation of this quantity of hydrogen from the oxidation of methyl alcohol to the formaldehyde stage is represented as the summation of equations (a), (b), and (b'), which gives the equation (D):

$$CH_3OH \longrightarrow CH_2O + H_2 \qquad (D)$$

The hydrogen from equations (B) and (D) reacts with nitrobenzene according to equation (z), previously noted to give azoxybenzene and water. When equations (B), (x), and (Z) are combined, Klinger's equation (C) results wherein 2 molecules of azoxybenzene are produced for each 3 molecules of sodium formate. When equations (D) and (z) are combined the following equation (E) is obtained:

$$2C_6H_5NO_2 + 3CH_3OH \longrightarrow 3CH_2O + C_6H_5N_2OC_6H_5 + 3H_2O \qquad (E)$$

wherein one molecule of azoxybenzene is formed for each 3 molecules of formaldehyde.

Using these stoichiometrical ratios of the sodium formate to azoxybenzene ($3HCOONa:2(C_6H_5N)_2O$) and formaldehyde to azoxybenzene ($3CH_2O:(C_6H_5N)_2O$), the quantities of azoxybenzene that should be formed in the two reactions (C) and (E) respectively were calculated and compared with the total quantity of azoxybenzene actually found.

If the sum of these two calculated quantities of azoxybenzene is equal or nearly equal to the actual yield of azoxybenzene, then it may be concluded that the proposed mechanism for the reduction of nitrobenzene according to summation equations (C) and (E) has been substantiated. This is evidenced by the data in the following Table XIII.

TABLE XIII

Data Confirming Independent Reactions (C) and (E)

Moles of Isoamylamine present	HCHO formed (grams)	HCOONa formed (grams)	$(C_6H_5N)_2O \equiv HCHO$ (Eq. E) (grams)	$(C_6H_5N)_2O \equiv HCOONa$ (Eq. C) (grams)	Total $(C_6H_5N)_2O$ Calculated (grams)	$(C_6H_5N)_2O$ Found (grams)	Wt. Calc. / Wt. Found %
1/8	2.2714	6.4747	4.9971	12.5685	17.5656	17.53	100.20
1/2	4.9690	3.8992	10.9318	7.5680	18.4998	18.79	98.45

These data confirm the assumption that nitrobenzene in methyl alcohol solution of sodium methylate and isoamylamine is reduced to azoxybenzene in conformity with the two independent reactions as represented by the following equations:

$$4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3\,H_2O \qquad (C)$$

$$2C_6H_5NO_2 + 3CH_3OH \longrightarrow (C_6H_5N)_2O + 3CH_2O + 6\,H_2O \qquad (E)$$

(c) Determination of Distributed Reduction of Nitrobenzene.

Regarding equations (C) and (E) as simultaneous and independent, it is possible to calculate the extent to which each of these reactions proceeds in the presence of 1/8 and 1/2 moles of isoamylamine.

When 1/8 and 1/2 moles of isoamylamine were present in the reaction mixture, the quantity of nitrobenzene reduced according to the reaction represented by equation (C) was calculated from the sodium formate produced using the stoichiometric ratio $4C_6H_5NO_2$: 3HCOONa, and the nitrobenzene reduced according to the reaction represented by equation (E) was calculated from the formaldehyde using the ratio $2C_6H_5NO_2$: 3HCHO. From these calculated quantities of nitrobenzene, the proportion of the total nitrobenzene present that was reduced according to each reaction can be calculated. These results are included in Table XIV.

When 1/4 and 3/4 moles of isoamylamine were present in the reaction mixture, the quantities of nitrobenzene reduced according to the reactions represented by equations (C) and (E) were readily claculated as follows. From equation (C) the quantity of azoxybenzene corresponding to the quantity of sodium formate obtained was calculated using the ratio $3HCOONa:2(C_6H_5N)_2O$. The calculated quantity of azoxybenzene thus obtained was subtracted from the total azoxybenzene actually obtained and the difference was the azoxybenzene produced according to the reaction represented by equation (E).

Now in order to know how much of the original 0.2 mole of nitrobenzene were reduced and also how much was reduced according to equations (C) and (E), the following ratios, $2(C_6H_5N)_2O:4C_6H_5NO_2$ and $(C_6H_5N)_2O:2C_6H_5NO_2$ were employed. Furthermore, the quantities of formaldehyde corresponding to the quantities of azoxybenzene produced were calculated from equation (E) using the ratio $(C_6H_5N)_2O:3HCHO$. The data from these calculations are embodied in Table XIV.

TABLE XIV

Data Relative to Distributed Reduction of Nitrobenzene in the Presence of Isoamylamine according to Equations (C) and (E)

Moles of Isoamylamine	Distribution of reduction	HCOONa formed grams Eq. C	HCHO formed grams Eq. E	$(C_6H_5N)_2O$ formed (Calc.) grams	$C_6H_5NO_2$ reduced (Calc.) grams	$C_6H_5NO_2$ reduced %	Total Reduction %
1/8	Equation C	6.4747		12.5685	15.6213	63.50	88.74
	Equation E		2.2714	4.9971	6.2085	25.24	
1/4	Equation C	4.1517		8.0591	10.0129	40.70	87.22
	Equation E		4.1868	9.2109	11.4438	46.52	
1/2	Equation C	3.8992		7.5680	9.4039	38.22	93.43
	Equation E		4.9690	10.9318	13.5812	55.21	
3/4	Equation C	5.2786		10.2467	12.7310	51.75	86.61
	Equation E		3.1379	6.9033	8.5768	34.86	

The results given in the above table clearly show that as the quantity of isoamylamine present increases from 1/8 to 1/4 to 1/2 mole, the per cent of nitrobenzene reduced according to equation (C) decreases while the per cent reduced according to equation (E) increases. This is quite in agreement with the proposed interpretation of the conditions under which the reaction occurred, from which it may be concluded that isoamylamine promotes the extent of the reaction of equation (E) and limits the extent of the reaction of equation (C) through its tendency to form the isoamylamine-formaldehyde compound thus preventing participation of some of the formaldehyde in further oxidation.

When 1/8 mole of isoamylamine was present, the total per cent reduction of the nitrobenzene was slightly above the normal per cent (88.45) and with 1/4 mole present the total per cent reduction was slightly below the normal per cent. When 1/2 mole was present, the per cent reduction increased markedly to 93.43, but with 3/4 mole present it decreased to 86.61 which is below the normal per cent reduction. The reason for this decrease is not evident at present.

Since with 3/4 mole of isoamylamine present the extent of the reduction is slightly below normal, the inference may be drawn that this excess of isoamylamine present reduces the molar concentration of the methyl alcohol present and therefore reduces the extent of its reducing action. The marked anomaly, however, lies in the fact that the extent of the reaction of equation (C), 51.75 per cent reduction, is so much greater than that of the reaction of equation (E), 34.86 per cent reduction. From this it is evident that while the excess of isoamylamine decreases the concentration of methyl alcohol, it at least does not inhibit the occurrence of the proposed intermediate type reactions, but rather promotes them through its basic properties. In other words, the nearly normal extent of the reaction is the result of a balance, so to speak, between two opposing tendencies, one of which is the lowered concentration of the methyl alcohol, the other the increased acidic dissociation of the sodium hydroxide.

(2) Azoxybenzene

The effect of isoamylamine upon the extent of the reduction of azoxybenzene by sodium methylate is very noticeable. In this series of runs the per cent reduction remained almost constant with increasing quantities of isoamylamine present. There was, in fact, a slight decrease in the per cent reduction which indicates that here also, isoamylamine withholds some of the formaldehyde from being oxidized to sodium formate. These results are given in Table XV.

TABLE XV

Reduction of Azoxybenzene by Sodium Methylate in the Presence of Isoamylamine

Moles of Isoamylamine added	Run	Vol. taken / Total Vol.	cc. $KMnO_4$ 0.1112 N added		cc. $H_2C_2O_4$ 0.1015 N added		cc. $KMnO_4$ 0.1112 N ≡ cc. $H_2C_2O_4$		cc. $KMnO_4$ ≡ HCOONa		Per cent. Reduction		F.P. of Azo-Azoxybenzene Mixture °C.
1/8	A	$\frac{50}{1000}$	16.62	13.19	16.71	13.00	15.26	11.87	1.36	1.32	3.02	2.93	35.10
	B	$\frac{50}{1000}$	14.48	12.10	14.51	11.82	13.05	10.79	1.43	1.31	3.12	2.91	35.10
											Average	3.00	
1/4	A	$\frac{50}{1000}$	15.11	12.80	15.21	12.70	13.89	11.60	1.22	1.20	2.71	2.67	34.9
	B	$\frac{50}{1000}$	16.31	13.02	16.60	13.03	15.15	11.90	1.16	1.12	2.58	2.49	35.0
											Average	2.61	
1/2	A	$\frac{50}{1000}$	13.80	9.45	13.67	8.93	12.48	8.15	1.32	1.30	2.93	2.90	35.15
	B	$\frac{50}{1000}$	13.96	9.59	14.00	9.23	12.78	8.43	1.18	1.16	2.62	2.58	35.15
											Average	2.76	
3/4	A	$\frac{50}{1000}$	13.62	9.70	13.60	9.30	12.42	8.49	1.20	1.21	2.67	2.69	35.00
	B	$\frac{50}{1000}$	12.32	9.27	12.30	9.02	11.23	8.23	1.09	1.04	2.42	2.32	35.10
											Average	2.52	

(d) Summary

The results from the two series of runs with isoamylamine present are different from the results of the runs with the other organic bases present. This arises from the fact that isoamylamine unites with some of the formaldehyde, as it is formed during the oxidation of the methyl alcohol, and thus prevents the formation of sodium formate which is used as a measure of the per cent reduction.

Formaldehyde was isolated from the reaction mixture and quantitatively determined. This fact is additional evidence for the proposed mechanism of the oxidation of methyl alcohol to sodium formate by sodium hydroxide, which involves the theory of the acidic dissociation of sodium hydroxide and postulates the intermediate formation of formaldehyde.

A method was developed for determining quantitatively the formaldehyde combined with the isoamylamine in the reaction mixture, and from the yields of formaldehyde and sodium formate it was possible to calculate the extent and the distribution of the reduction of the nitrobenzene in conformity with two summation equations (C) and (E).

Before recording the final summary and conclusions, the following Tables XVI and XVII of summarized data of all of the runs made with nitrobenzene and azoxybenzene respectively are inserted.

TABLE XVI

Summary of Data Obtained from Runs with Reaction Mixtures of Nitrobenzene, Organic Base, Sodium Methylate, and Methyl Alcohol.

Moles of Organic Base present	Aniline Extent of Reduction %	Monomethyl Aniline Extent of Reduction %	Dimethyl Aniline Extent of Reduction %	Quinoline Extent of Reduction %	Isoamylamine Extent of Reduction %
1/8	96.85	91.7	93.93	95.62	88.74
1/4	99.26	98.61	98.95	102.66	87.22
1/2	98.28	103.06	105.56	107.62	93.43
3/4	94.26	104.44	107.12	113.02	86.61

TABLE XVII

Summary of Data Obtained from Runs with Reaction Mixtures of Azoxybenzene, Organic Base, Sodium Methylate, and Methyl Alcohol.

Moles of Organic Base present	Aniline Extent of Reduction %	Monomethyl Aniline Extent of Reduction %	Dimethyl Aniline Extent of Reduction %	Quinoline Extent of Reduction %	Isoamylamine Extent of Reduction %
1/8	3.00	3.52	3.43	3.53	3.00
1/4	3.38	4.00	3.47	4.80	2.61
1/2	4.18	4.77	7.30	6.33	2.76
3/4	4.93	5.46	8.72	7.43	2.52

VII. GENERAL SUMMARY AND CONCLUSIONS

A. General Summary

The object of this investigation was to determine the effect of organic bases, when present in the reaction mixture in increasing molar quantities, upon the extent and mechanism of the reduction of nitrobenzene and azoxybenzene by sodium methylate in methyl alcohol solution.

Nitrobenzene is reduced to azoxybenzene by sodium methylate in conformity with Klinger's equation for the reaction

$$4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3\,H_2O.$$

The yield of sodium formate is a direct quantitative measure of the extent to which this reaction proceeds. Since Fry and Cameron[2] have shown that Klinger's equation may be the summation of several reactions involving the acidic dissociation of sodium hydroxide, conditions which prevent this, such as addition of water, limit the extent of the reduction. On the other hand, conditions which favor acidic dissociation, such as the addition of basic carbon compounds, e.g., pyridine, actively increase the extent of the reduction as attested by yields of sodium formate greater than 100 per cent. The excessive yield is due to further reduction of azoxybenzene to azobenzene in conformity with the following equation:

$$2(C_6H_5N)_2O + CH_3ONa \longrightarrow 2C_6H_5N{=}NC_6H_5 + H_2O + HCOONa$$

In addition to the sectional summaries relating to the specific conclusions on the effects of the various amines described in the body of this thesis, the following general summary may be added.

1. The results obtained when monomethyl aniline, dimethyl aniline and quinoline were present in the reaction mixture containing nitrobenzene, when compared with Fry and Cameron's results[2] obtained with pyridine present, show the same general characteristics, namely,

(a) The per cent reduction is always considerably greater than the normal per cent reduction.

(b) The per cent reduction for each series always increased as the quantity of base present was increased from 1/8 to 3/4 moles.

(c) The maximum per cent reduction occurred with 3/4 moles of organic base present and amounted to 104.44 per cent for monomethyl aniline, 107.12 per cent for dimethyl aniline, and 113.02 per cent for quinoline. These results follow the order of increasing basic strength of the added compounds.

2. When azoxybenzene was the initial compound subjected to reduction, the following results were obtained:

(a) The same general trend of reduction noted with nitrobenzene also occurred with azoxybenzene, that is, the extent of reduction increased as increasing quantities of organic base were added.

(b) The maximum reduction occurred when 3/4 mole of organic base was present and amounted to 4.93 per cent with aniline, 5.46 per cent with monomethyl aniline, 7.43 per cent with quinoline and 8.72 per cent with dimethyl aniline.

3. The extent of the reduction with different organic bases present, appears to bear some relationship to their basic character. Thus with nitrobenzene, the increased extent of the reduction is in the order of increasing basic character as follows : aniline, monomethyl aniline, dimethyl aniline, quinoline. However, with azoxybenzene, the order is the same with the exception that quinoline precedes dimethyl aniline. The explanation for this has not as yet been determined.

4. The extent of the reduction of nitrobenzene with aniline present was complicated by a side reaction in which azobenzene was formed. Even in this case, however, the per cent reduction was considerably greater in the presence of aniline than in its absence.

5. The series of runs with isoamylamine present in the nitrobenzene reaction mixture furnished the most significant feature of this research. The following significant observations were noted and investigated.

(a) The intermediate formation of formaldehyde,

$$CH_2(ONa)_2 + H_2O \longrightarrow HCHO + 2NaOH$$

assumed in the proposed scheme of reactions summarized in

Klinger's equations and formulated on the basis of the acidic dissociation of sodium hydroxide as the key to the reaction mechanism, has been verified.

(b) This verification resulted through the identification of an intermediately formed compound of formaldehyde with isoamylamine, namely, isoamylmethyleneimide.

(c) The formation of isoamylmethyleneimide restricts the amount of the intermediately formed formaldehyde available for further reduction of the nitrobenzene which results in decreased yields of sodium formate.

(d) A new method, based upon the precipitation of isoamylamine as mercuric isoamylamidochloride upon addition of mercuric chloride, was developed for quantitatively determining the formaldehyde combined with the isoamylamine in the reaction mixture.

6. From the observations in paragraph 5, it may be concluded that the reduction of nitrobenzene in the presence of isoamylamine proceeds in conformity with and is distributed between two simultaneously independent reactions represented by the following equations (C) and (E).

$$4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O \qquad (C)$$

$$2C_6H_5NO_3 + 3CH_3OH \longrightarrow (C_6H_5N)_2O + 3HCHO + 6H_2O \qquad (E)$$

7. The quantities of formaldehyde and sodium formate produced, when 1/8 and 1/2 moles of isoamylamine were present, were calculated to their equivalent amounts of azoxybenzene, as based upon the stoichiometrical ratios in equations (C)

and (E). The amounts so calculated were in remarkably good agreement with the total quantity of azoxybenzene actually found. The application of this method of calculation showed that as the quantities of isoamylamine present increased from 1/8 to 1/4 to 1/2 mole, the per cent of nitrobenzene reduced according to equation (C) decreases, while the per cent reduced according to equation (E) increases.

B. General Conclusions

The general conclusions drawn from this investigation are:

1. The presence of an organic base increases the extent of the reduction of nitrobenzene to azoxybenzene by sodium methylate.

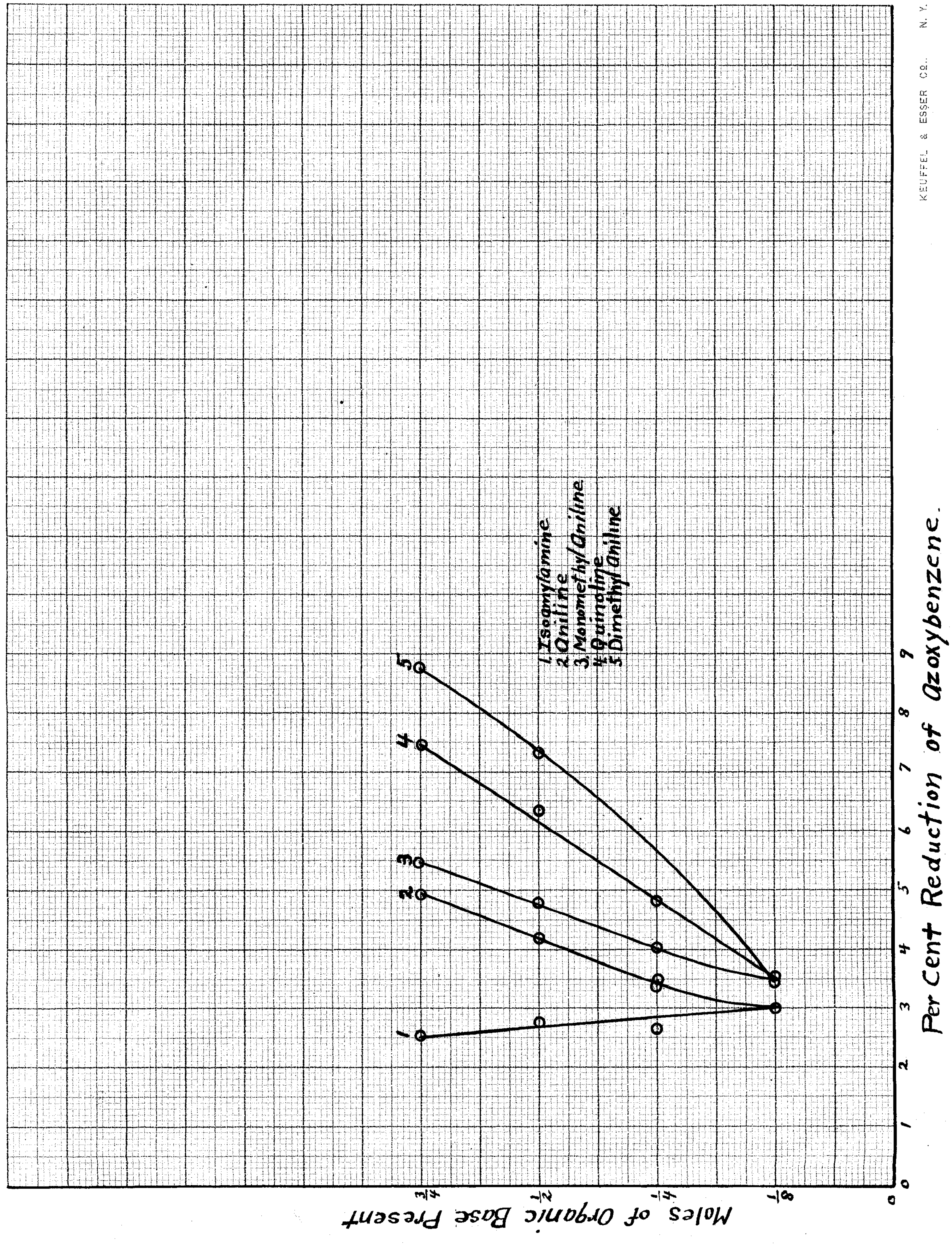
2. The presence of organic bases causes further reduction of azoxybenzene to azobenzene.

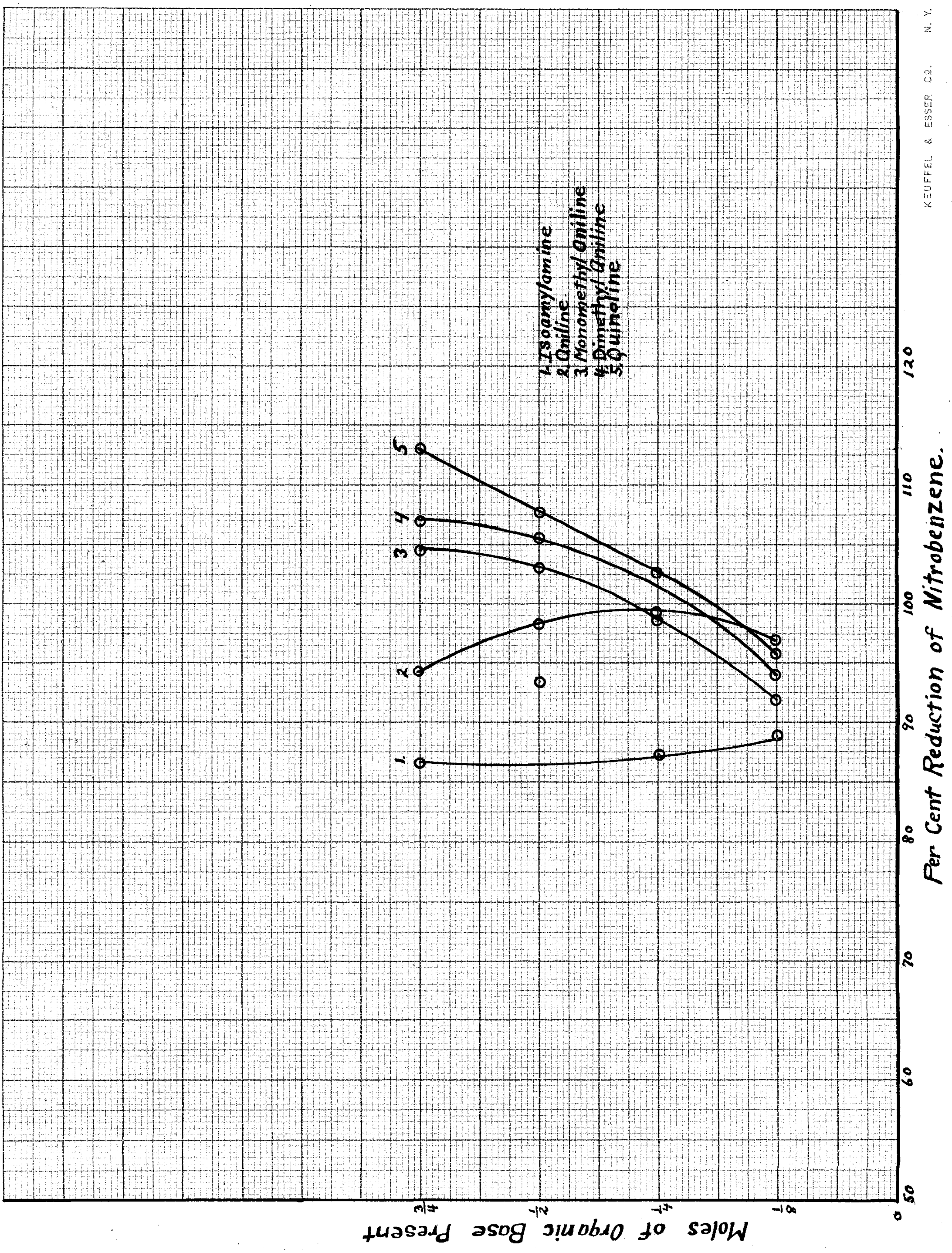
3. Increasing molar quantities of organic bases present in the reaction mixtures caused increased per cent reduction of nitrobenzene and azoxybenzene.

4. Formaldehyde is intermediately formed in the reaction mixture containing isoamylamine during the oxidation of methyl alcohol to sodium formate and some of it combines with the isoamylamine present to form isoamylmethyleneimide.

5. The formaldehyde combined with the isoamylamine can be isolated from the reaction mixture and quantitatively determined according to a newly proposed method.

6. The distribution of the extent of the reduction of nitrobenzene in the presence of isoamylamine has been calculated according to equations (C) and (E) previously mentioned.


Per Cent Reduction of Azoxybenzene.
0
1
2
3
4
5
6
7
8
9
Moles of Organic Base Present
3/4
1/2
1/4
1/8
0
1
2
3
4
5
1. Isoamylamine
2. Aniline
3. Monomethyl Aniline
4. Quinoline
5. Dimethyl Aniline


1. Isoamylamine
2. Aniline
3. Monomethyl Aniline
4. Dimethyl Aniline
5. Quinoline
1.
2
3
4
5
Per Cent Reduction of Nitrobenzene.
50
60
70
80
90
100
110
120
Moles of Organic Base Present
3/4
1/2
1/4
1/8
0

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