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I hereby recommend that the thesis prepared under my supervision by Frank L. Strably

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QUANTITATIVE STUDY OF THE EFFECT OF LEAD UPON THE KLINGER REACTION

A dissertation submitted to the
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I. INTRODUCTION: HISTORY AND OBJECT

This research was undertaken to determine to what extent the reduction of nitrobenzene with sodium methylate in absolute methyl alcohol solution in the presence of lead would be comparable to the reducing action of aqueous sodium hydroxide and methyl alcohol in the presence of lead as previously investigated by Fry and Andress (1).

Since the history of the various methods of reducing nitrobenzene has been thoroughly reviewed in earlier theses from this laboratory, only a few of the more pertinent reductions will be noted.

The reduction of nitrobenzene has been known since 1845 when Zinin (2) prepared azoxybenzene by treating nitrobenzene with alcoholic potash. He postulated no equation to represent the character of the reaction. Alexeyeff (3) prepared azoxybenzene by adding sodium amalgam to an alcoholic solution of nitrobenzene acidified with acetic acid. He also stated that zinc dust, in the presence of small quantities of alkali, acts analogously to sodium amalgam.

Rosenack (4) found that azoxybenzene is formed when nitrobenzene is added in small quantities to a solution of sodium hydroxide and alcohol. He further noted that sodium or sodium amalgam has no effect on perfectly dry nitrobenzene, but a vigorous reaction follows when a few drops of water are added and azoxybenzene results.

Schmidt and Schultz (5) prepared azoxybenzene by the action of alcoholic potassium hydroxide on alcoholic nitrobenzene. They mention by-products of aniline, oxalic acid, and a dark resinous product similar to the biazoxybenzoic acid of Michler (6).

Klinger (7) devised a new method for the reduction of nitrobenzene to azoxybenzene by using sodium and methyl alcohol as the reducing ~~agents~~ agent, that is, sodium methylate. A yield of 85 - 89% was obtained.

Moltschonowsky (8) repeated Klinger's work, but obtained somewhat lower yields. Bruhl (9) prepared azoxybenzene in almost quantitative yield by suspending sodium methylate in xylene and then boiling the mixture with nitrobenzene for seven hours.

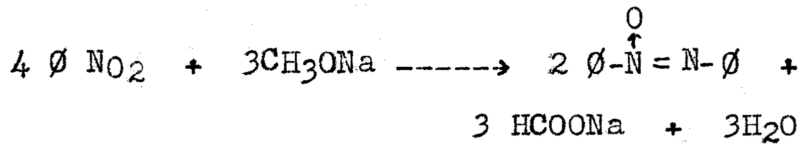
Lachman (10) repeated Klinger's method and obtained 95 - 97 percent yield. He stated that the water present in methyl alcohol has little effect upon the yield of azoxybenzene.

Evans and Fry (11) prepared azoxybenzene in 90 percent yield by the action of magnesium and methyl alcohol on nitrobenzene. The magnesium methylate has no reducing action; it is chiefly the hydrogen liberated when magnesium reacts with methyl alcohol that reduces the nitrobenzene.

Snowden (12) lists several known methods, chemical and electrical, for reducing nitrobenzene to azoxybenzene.

Of all the methods that have been cited, that of Klinger has been adopted as the standard method for preparing azoxybenzene from nitrobenzene.

As previously stated, Klinger found that nitrobenzene is reduced by sodium methylate, in methyl alcohol solution, to azoxybenzene. He proposed the equation,



$$4\,\varnothing\,NO_2 + 3CH_3ONa \dashrightarrow 2\,\varnothing\text{-}\overset{\overset{O}{\uparrow}}{N}=N\text{-}\varnothing + 3\,HCOONa + 3H_2O$$

but he gave no experimental data to substantiate the stoichiometric proportion of the equation. This reaction was quantitatively investigated by Fry and Cameron (13) and was found to be correct.

In the course of their investigation, Fry and Cameron proposed a mechanism for the reaction, involving the theory of acidic dissociation of sodium hydroxide, a discussion of which will subsequently follow. They found that increasingly large quantities of water, which promotes basic dissociation of sodium hydroxide, when added to the reaction mixture, lowered the percent reduction from the normal 88.45 per cent to 19 per cent. These results were in direct contradiction to the statement of Lachman to the effect that water present in methyl alcohol has little effect upon the yield of azoxybenzene. They further found that 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 establishment of the Klinger equation and this hypothesis, Fry and Bowman (14) carried on a further investigation to try the effect of various other organic bases upon the extent of the reducing action of sodium methylate on nitrobenzene. They found that increased molar quantities of organic bases (aniline, methyl aniline, dimethyl aniline, quinoline and isoamyl amine) caused increased per cent yield of sodium formate in each case.

Fry and Andress (1) found that nitrobenzene was quantitatively reduced to azoxybenzene by solutions of sodium hydroxide in methyl alcohol and water in the absence of lead with the accompanying evolution of large volumes of hydrogen. Furthermore, with increasing concentrations either of sodium hydroxide or of nitrobenzene, hydrogen was evolved in increasing volumes. These runs were repeated in the presence of lead and the following results were obtained:

(1) The volumes of hydrogen evolved were greatly in excess of those obtained in the absence of lead.

(2) The nitrobenzene was reduced to mixtures of azoxy- and azo-benzene.

(3) The lead reacting was converted into sodium plumbite.

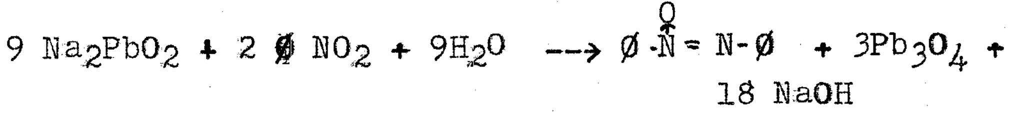
To determine whether nitrobenzene could be reduced by sodium hydroxide and lead in the absence of methyl alcohol or not, reactions were investigated wherein nitrobenzene was dissolved in pyridine and refluxed with lead and sodium hydroxide. In this instance the nitrobenzene was reduced chiefly to azoxybenzene and some azobenzene. The lead reacted to form sodium plumbite and red lead, presumably according to following equations:

$$\mathrm{Pb} + 2\,\mathrm{NaOH} \longrightarrow \mathrm{Na_2PbO_2} + 2\mathrm{H}$$

$$3\,\mathrm{Pb} + 4\,\mathrm{H_2O} \longrightarrow \mathrm{Pb_3O_4} + 8\,\mathrm{H}$$

No hydrogen was evolved. The available hydrogen was assumed to effect reduction.

They further found that sodium plumbite partially reduces nitrobenzene to azoxybenzene according to the following equation:



$$9\,\mathrm{Na_2PbO_2} + 2\,\text{Ø}\,\mathrm{NO_2} + 9\mathrm{H_2O} \longrightarrow \text{Ø}\text{-}\overset{\mathrm{O}}{\mathrm{N}}=\mathrm{N}\text{-}\text{Ø} + 3\mathrm{Pb_3O_4} + 18\,\mathrm{NaOH}$$

The intermediate formation of hydrogen peroxide on the interaction of lead, sodium hydroxide, and nitrobenzene in aqueous solution and also in the presence of methyl alcohol and water was shown to take place according to the following equation:

$$3\ Pb + 6\ NaOH + 4\ \phi\ NO_2 \dashrightarrow 3\ Na_2PbO_2 + 2\phi\text{-}\overset{O}{N}\text{=}N\text{-}\phi + 3H_2O_2$$

This research is a further study of the reduction of nitrobenzene under different experimental conditions, namely, dilute and nearly saturated solutions of sodium methylate in absolute methyl alcohol with and without lead. As previously noted, the study by Fry and Andress was conducted principally in alkaline aqueous media and under these conditions a variety of concurrent reactions were shown to take place. Since in the present study the initial reaction mixtures were anhydrous methyl alcohol solutions of sodium methylate, either in the absence or in the presence of lead, it was hoped that the occurrence of concomitant reactions might be eliminated and at the same time facilitate some quantitative correlation of the yields of sodium formate with the corresponding yields of the reduction products. It was desired to explain further, if possible, the effect of the presence of lead upon the nature and extent of the reduction.

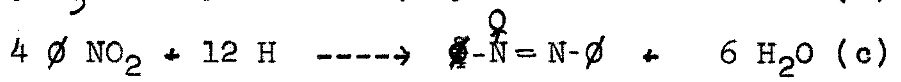
II. THEORETICAL

A. THE KLINGER REACTION AND THE MODIFIED KLINGER REACTION.

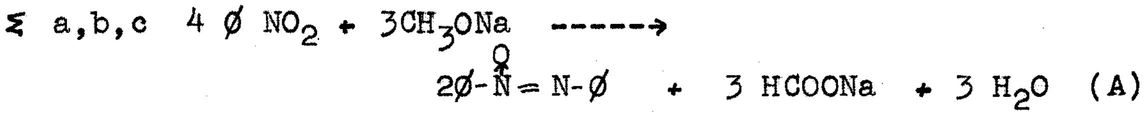
Although Klinger's reaction was adopted as the standard method for preparing azoxybenzene from nitrobenzene, no attempt was made to ascertain the mechanism of the reaction until Fry and Cameron(13) investigated it from a quantitative standpoint. The stoichiometric proportions suggested by Klinger were confirmed, and in addition, the following mechanism was proposed:

$$3CH_3ONa + 3HOH \dashrightarrow 3CH_3OH + 3HONa \quad (a)$$

$$3CH_3OH + 3HONa \dashrightarrow 3HCOONa + 12H \quad (b)$$



$$4\,\phi NO_2 + 12\,H \dashrightarrow \phi\text{-}\overset{O}{N}=N\text{-}\phi + 6\,H_2O \quad (c)$$



$$\Sigma\ a,b,c \quad 4\,\phi NO_2 + 3CH_3ONa \dashrightarrow 2\phi\text{-}\overset{O}{N}=N\text{-}\phi + 3\,HCOONa + 3\,H_2O \quad (A)$$

In dilute solutions of sodium methylate in methyl alcohol only azoxybenzene was obtained; but in a nearly saturated solution of sodium methylate in methyl alcohol, the nitrobenzene was reduced to a mixture of azo- and azoxybenzene.

The intermediate reactions, entailing the amphoteric dissociation of sodium hydroxide postulated by Fry and coworkers, culminating in the final equation for the Klinger reaction have herewith been modified to show the intermediate formation of nitrosobenzene and phenylhydroxylamine because the extent of the formation of these substances may have a bearing upon the relative yields of the concurrently azoxy- and azo-benzene with the higher concentration of sodium methylate. The revised reaction mechanism scheme for the reduction to azoxybenzene may be written as follows:

$$3\ CH_3ONa + 3\ HOH \longrightarrow 3\ CH_3OH + 3\ HONa \quad (a)$$

$$3\ CH_3OH + 3\ HONa \longrightarrow 3HCOONa + 12\ H \quad (b)$$

$$4\ \phi NO_2 + 8\ H \longrightarrow 4\ \phi NO + 4\ H_2O \quad (c)$$

$$2\ \phi NO + 4\ H \longrightarrow 2\ \phi N{<}^{H}_{OH} \quad (d)$$

$$2\ \phi NO + 2\phi N{}^{H}_{OH} \longrightarrow 2\ \phi\text{-}\overset{O}{\overset{\uparrow}{N}}{=}N\text{-}\phi + 2\ H_2O \quad (e)$$

$$\phi\ a, b, c, d, e\text{--}\ 4\ \phi NO_2 + 3CH_3OHa \longrightarrow 3\ HCOONa + 3\ H_2O + 2\ \phi\text{-}\overset{O}{\overset{\uparrow}{N}}{=}N\text{-}\phi$$

In using a higher concentration of sodium methylate, more extensive reducing conditions are imposed. Hence, one would expect an excess of phenylhydroxylamine to be formed by the reduction of the intermediate nitrosobenzene. Furthermore, an excess of phenylhydroxylamine is required for the formation of azobenzene, as noted in the following reaction mechanism scheme:

$$2\ CH_3ONa + 2\ HOH \longrightarrow 2\ CH_5OH + 2\ HONa \quad (a)$$

$$2\ CH_5OH + 2\ HONa \longrightarrow 2\ HCOONa + 8\ H \quad (b)$$

$$2\ \phi NO_2 + 4\ H \longrightarrow 2\ \phi NO + 2\ H_2O \quad (c)$$

$$2\ \phi NO + 4\ H \longrightarrow 2\ \phi N{<}^{H}_{OH} \quad (d)$$

$$\text{Ø N}\begin{smallmatrix}H\\OH\end{smallmatrix} + \text{Ø N}\begin{smallmatrix}H\\OH\end{smallmatrix} \longrightarrow \text{Ø N=N Ø} + 2\,H_2O \quad (e)$$

$$\Sigma\ a,b,c,d,e:\ 2CH_3ONa + 2\,\text{Ø}\,NO_2 \longrightarrow 2\,HCOONa + \text{Ø N=N Ø} + 2\,H_2O$$

In comparing the reaction mechanism schemes for the concurrent formation of azoxy- and azo-benzene, it should be noted that in the former, azoxybenzene is the product of the interaction between nitrosobenzene and phenylhydroxylamine, whereas, in the latter, the formation of azobenzene is the product of the interaction of two molecules of phenylhydroxylamine.

B. THE EFFECT OF LEAD UPON THE REDUCTION OF NITROBENZENE.

In the previous investigation by Fry and Andress(1), the presence of lead in the reaction mixture of sodium hydroxide, methyl alcohol and water, the reduction of nitrobenzene was shown to be accompanied by the liberation of hydrogen, the formation of sodium plumbite, red lead and hydrogen peroxide. In the equations, proposed and checked for these reactions, sodium formate was not formed. Since sodium formate accompanies the reduction by sodium methylate of nitrobenzene to either azoxybenzene, azobenzene, and even to hydrazobenzene, it is apparently concluded that the function of lead in effecting the reduction of nitrobenzene is as a direct reducing agent.

The possibility of correlating the quantities of lead reacting with the yields of the reduction product will be considered in the experimental part of this thesis.

III. EXPERIMENTAL

All reactions investigated in this study were conducted in duplicate in one liter three-necked round-bottomed flasks. The middle neck of the flask was connected with a mechanical stirrer through a mercury seal. Each flask was securely attached to a short Liebig condenser, which was, in turn, connected to a spiral condenser.

Regular type condensers were first used, but check results could not be obtained since methyl alcohol was not completely condensed. Spiral condensers were next used, but they "flooded" too readily. A combination of the two types as described above worked very efficiently. Most of the methyl alcohol vapors condensed in the Liebig condenser, and these vapors which passed on were condensed in the more efficient spiral condenser. The upper end of the inner tube of the spiral condenser.was fitted with glass tubing which led to an inverted 1000 ml. graduated cylinder filled with water serving as a gasometer.

The third neck of the reaction flask was fitted with a dropping funnel through which the nitrobenzene was added. All conections were made with rubber tubing, wired and sealed to prevent any leakage of gas. The reaction flasks were heated, in each experimental run, on constant level water baths, kept at the boiling temperature for the same length of time, namely, five hours.

A. REDUCTION WITH THE LOWER CONCENTRATION OF SODIUM METHYLATE
(The Klinger Reaction)

The Klinger reaction was studied with the view of determining not only the percent theory yield of reduction products of nitrobenzene; but, more especially, the yields of sodium formate when the concentrations of sodium methylate were varied by the addition of more or less absolute methyl alcohol. Three different concentrations of sodium methylate were used, namely: 17.3 grams of sodium dissolved in 250 ml., 300 ml., and 600 ml. of absolute methanol. To each of these solutions, 20.44 ml. (.2 moles) nitrobenzene were added.

The following is a description of a typical experimental run:

300 ml. of absolute methyl alcohol measured in volumetric flasks were poured into the liter three-necked flask, equipped as previously described.

17.3 g. of sodium, cut into small pieces, weighed under ligroin, was introduced into the reaction flask. When all the sodium was dissolved in the methyl alcohol, a dropping funnel containing 20.44 ml. (.2 mole) nitrobenzene was inserted in the third neck of the flask. The water bath was heated and the solution was brought to its boiling point. The solution was refluxed until no more air passed into the gasometer. The gasometer was refilled with water and then the 20.44 ml. of nitrobenzene in the dropping funnel were added, drop by drop, within a period of fifteen minutes.

The reaction mixture was refluxed for five hours. No gas (hydrogen) was evolved in any of the experimental runs of this section.

The reaction mixture was steam-distilled to remove the unreacted nitrobenzene and the excess methyl alcohol. Steam distillation was continued until the odor of nitrobenzene was no longer perceptible in the reaction mixture. About 800 ml. of distillate were collected.

The reaction residue, thus obtained, consisted of an aqueous solution of sodium formate and sodium hydroxide (obtained from the hydrolysis of sodium methylate) and the insoluble reduction product, azoxybenzene, which had settled to the bottom of the flask.

When this reaction mixture was poured into ice water, the azoxybenzene crystallized, was filtered off on a Buchner funnel, washed repeatedly with cold water, dried and weighed. Further purification of the reduction product was unnecessary since it melted at 36° C., the recorded melting point of pure azoxybenzene.

All the aqueous washings of the azoxybenzene were added to the main filtrate, which contained the sodium formate. The solution was diluted to 2000 ml. in a volumetric flask. The yield of sodium formate was determined by the alkaline permanganate method described by Oesper (15). The procedure employed was as follows:

50.00 ml. of the 2000 ml. dilution were transferred to a 500 ml. volumetric flask. A 100 ml. sample at this latter dilution is equivalent to a 10.00 ml. sample of the original 2000 ml. dilution. The formate determination was conducted as follows: 10 ml. of 30 per cent sodium hydroxide was added to 20.00 ml. 0.5 N $KMnO_4$ solution. 100.00 ml. of sample were added, followed by 30 ml. more of the sodium hydroxide solution. The mixture was allowed to stand ten minutes. 31 ml. sulfuric acid (1 : 1) and 10 ml. manganese sulfate solution (5%) were next added. After adding 20.00 ml. oxalic acid (34 g. per liter), the solution decolorized and it was quickly heated to 50° C. The excess oxalic acid was titrated with .1084 N potassium permanganate.

Only the titer of the .1 N potassium permanganate was determined independently. It was not necessary to accurately determine the normality of the .5 N $KMnO_4$ and the oxalic acid solution, since in the actual titration 20.00 ml. of each of the latter solutions were used in every determination. A "Blank run" was made as follows:

5 ml. of 1 : 1 sulfuric acid were added to 20.00 ml. oxalic acid (34 g./liter). The solutions was warmed to 50° C. and 10 ml. manganese sulfate solution and 20.00 ml. .5 N permanganate were added. All the permanganate was decolorized. The excess oxalic acid was titrated with .1084 N permanganate which was previously standardized against pure sodium oxalate. The volume of .1084 N permanganate used

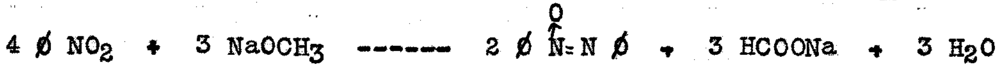
represents the blank consumption".

The volume of .1084 N permanganate used in the actual titration minus the volume consumed in the blank run represents that volume of .1084 N permanganate equivalent to the sodium formate being determined.

The following table I records the data obtained to establish the normal yield of sodium formate and azoxybenzene for the reduction of nitrobenzene by sodium methylate in the three concentrations following the procedure described. Klinger's equation was used as the basis for calculating the theoretical yields. Column 1 indicates the number of each duplicate run. The volume of absolute methyl alcohol in which 17.3 g. of sodium were dissolved is given in column 2. The actual and theoretical yields of sodium formate are given in columns 3 and 4, respectively. Column 5 notes the per cent reduction of nitrobenzene calculated from the actual yield of sodium formate and the th theoretical yield according to the Klinger equation. Columns 6 and 7 record the actual and theoretical yield of azoxybenzene respectively. In column 8, the per cent reduction based on the yield of azoxybenzene is tabulated.

TABLE I

EXPERIMENTAL DATA BASED ON THE KLINGER REACTION:



$$4\ \phi\ NO_2\ +\ 3\ NaOCH_3\ \text{------}\ 2\ \phi\ \overset{O}{\overset{\uparrow}{N}}{=}N\ \phi\ +\ 3\ HCOONa\ +\ 3\ H_2O$$

(1) Run	(2) Con. methyl alcohol ml.	(3) HCOONa found (grams)	(4) HCOONa theory (grams)	(5) Percent Reduction	(6) Azoxybenzene found (grams)	(7) Azoxybenzene theory (grams)	(8) Percent Reduction
I. a.	250	8.80	10.20	86.30	17.19	19.80	86.85
b.	250	8.84	10.20	86.67	17.21	19.80	86.93
av.	250	8.82	10.20	86.48	17.20	19.80	86.89
II. a.	300	4.45	10.20	43.61	8.49	19.80	42.9
b.	300	4.42	10.20	43.31	8.53	19.80	43.1
av.	300	4.43	10.20	43.46	8.51	19.80	43.0
III. a.	600	.28	10.20	2.7	trace	19.80	
b.	600	.31	10.20	3.0	"	19.80	
av.	600	.30	10.20	2.9	"	19.80	

The above data leads to the following conclusions:

(1) In runs I and II, the yields of sodium formate and azoxybenzene are in exact conformity with the equation for the Klinger equation.

(2) In run III only a trace of azoxybenzene was formed, insufficient to be recovered.

(3) A marked difference in the extent of the occurrence of the Klinger reaction is noted in runs I, II, and III; namely in the 250 ml. dilution of sodium methylate, the yield of sodium formate and azoxybenzene is a little more than double (86.+%) that obtained with the 300 ml. dilution (43%), while with the 600 ml. dilution the extent of the reduction is practically negligible.

B. REDUCTION WITH HIGHER CONCENTRATION OF SODIUM METHYLATE.

The object in making the runs to be described in this section was twofold: first, to establish the extent of the occurrence of the Klinger reaction with a higher concentration of sodium methylate in the absence of lead to furnish data for the subsequent comparison with the extent of occurrence of reactions when conducted in the presence of lead; second, to establish a quantitative correlation of the total yield of sodium formate with the yields of both azoxy- and azo-benzene, which were the reduction products in the more concentrated solutions of sodium methylate.

Twice as much sodium, namely, 34.6 grams. was dissolved in 300 ml. absolute methyl alcohol. The solution was refluxed until no more air was collected in the gasometer. The gasometer was refilled with water and 20.44 ml. nitrobenzene was added dropwise over a period of fifteen minutes. The practically negligible volume of hydrogen evolved varied from 40 to 150 ml. in the various runs. Incidentally, the hydrogen evolved came over within twenty-five minutes after the addition of nitrobenzene was begun. It is to be noted that Fry and Andress found that when nitrobenzene is reduced in a solution of sodium hydroxide in water and methyl alcohol, the volumes of hydrogen evolved varied from 163 ml. to 1776 ml. with various concentrations of sodium hydroxide and nitrobenzene. They further found that 55% of the total volume of hydrogen was evolved within the first hour of the five-hour refluxing.

The formation of hydrogen described in the preceding research of Andress (1) in this laboratory is probably due to the amphoteric action of sodium hydroxide on methyl alcohol,

$$3\ CH_3OH + 5\ HONa \longrightarrow 3\ HCOONa + 12\ H \qquad (1)$$

Not all of this nascent hydrogen formed in the earlier part of the reaction period was utilized in the reduction of nitrobenzene. Parenthetically, in order to explain the evolution of hydrogen predominantly in the earlier period of the reaction, it may be logically assumed that the reduction of nitrobenzene to nitrosobenzene does not occur as readily as the subsequent reduction of nitrosobenzene to phenylhydroxylamine. Accordingly, any hydrogen evolved would be that fraction of the available hydrogen (reaction 1) which is not active in the reduction of nitrobenzene to nitrosobenzene. Therefore, one would expect most of the hydrogen, if any, to be evolved in the earlier stages of the reduction.

After the reaction mixture had refluxed five hours most of the excess methyl alcohol was distilled off. There was no need for steam distillation at this point since the odor of nitrobenzene was not present in the reaction mixture, showing that all nitrobenzene had been reduced. During the distillation about 200 ml. water were added. The reaction mixture was poured on to ice water: an orange precipitate (a mixture of azoxy- and azo-benzene) formed. This precipitate was filtered from the solution, washed thoroughly with ice water, air dried and weighed.

No hydrazobenzene was formed, as indicated by a negative benzidine test. The percentages of azoxy- and azo-benzene contained in each reaction residue were determined by the freezing point method described by Fry and Bowman. Their curve for the freezing points of mixtures of azo- and azoxy-benzene was used throughout this investigation.

The filtrate obtained from the azoxy- and azobenzene residue consisted of a solution of sodium formate, sodium hydroxide, methyl alcohol and possibly some unhydrolyzed sodium methylate. In order that the yield of sodium formate be determined accurately, it was absolutely necessary to free the solution of all remaining traces of methyl alcohol, since this substance is also oxidized by alkaline potassium permanganate solution.

The filtrate was diluted to 2000 ml. in a volumetric flask. 500 ml. of this solution were transferred to the three-necked reaction flask and steam distilled after the solution was made just acid by adding the calculated amount of sulfuric acid and then just basic by adding sodium carbonate. Previous experiments showed that if some of the alkali were not neutralized all the methyl alcohol would not completely distill off. This phenomenon is undoubtedly due to the fact that sodium methylate is not quantitatively hydrolyzed in a too strongly alkaline solution. It is essential that the solution be slightly alkaline before distilling because in acid solution formic acid is produced and this substance distils over. After some 300 ml. of distillate were collected, the contents of the distilling flask was diluted to 500 ml. and the yields of sodium formate in aliquot portions were determined as previously described.

In order to determine whether or not all methyl alcohol had been removed in the first distillation, advantage was taken of the fact that sodium formate reacts more readily with alkaline permanganate than does methyl alcohol. The test was conducted as follows. Duplicate samples of the sodium formate solutions were analyzed as previously described. One of the samples was allowed to stand ten minutes with the alkaline permanganate; the other sample was allowed to stand only a few seconds with the alkaline permanganate before the solution was acidified with sulfuric acid, and the determination was completed. In those instances wherein check results were not obtained, 250 ml. of the sodium formate solution were redistilled as before and then the sodium formate yield was determined on duplicate samples.

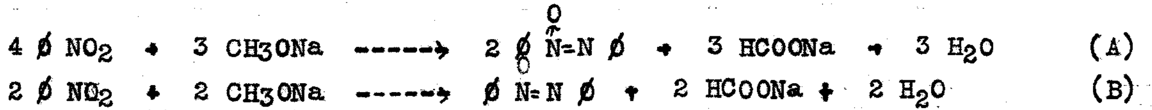
In the following table II, column 1 records the number of each run; column 2, the weight of azo- and azoxybenzene obtained. Columns 3, 4, and 5 record respectively the freezing points of the mixtures of azo- and azoxybenzene, the percents of azoxybenzene, and the percents of azobenzene. In columns 6 and 7, the corresponding weights of azoxybenzene and azobenzene in the reaction mixture are respectively tabulated. Columns 8 and 9 indicate the grams of sodium formate equivalent to the azoxybenzene and azobenzene formed, respectively, according to equations (A) and

(B). Column 10 indicates the total calculated yields of sodium formate formed by both reactions (A) and (B). Column 11 records the grams of sodium formate actually found. In column 12, the per cent theory yields of sodium formate calculated on the basis of the occurrence of the two reactions (A) and (B).

TABLE II

KLINGER REACTION DATA

(calculations based on Klinger (A) and modified Klinger Reactions (B))



$$4\ \phi NO_2 + 3\ CH_3ONa \dashrightarrow 2\ \underset{0}{\phi}\ \overset{O}{N}{=}N\ \phi + 3\ HCOONa + 3\ H_2O \qquad (A)$$

$$2\ \phi NO_2 + 2\ CH_3ONa \dashrightarrow \phi\ N{=}N\ \phi + 2\ HCOONa + 2\ H_2O \qquad (B)$$

(1) Run	(2) azoxy & azo-benzene yield (g.)	(3) F.P.	(4) Percent azoxy-benzene	(5) Percent azo-benzene	(6) azoxy-benzene (g.)	(7) azo-benzene (g.)	(8) HCOONa ≀≀ $(\phi)_2O$ Eq. A. g. calc.	(9) HCOONa ≀≀ $(\phi N)_2$ Eq.B. g.Calc.	(10) Eq. A & Eq. B. Calculated grams	(11) Total yield HCOONa Found (g.)	(12) Percent theory yield HCOONa
1	19.69	33.0°	95.5	4.5	18.80	0.89	9.68	.66	10.34	10.27	99.1
2	19.36	33.0°	95.5	4.5	18.49	0.87	9.52	.65	10.17	10.72	105.4
3	19.57	33.0°	95.5	4.5	18.69	0.88	9.63	.66	10.29	10.88	105.7
4	19.60	33.0°	95.5	4.5	18.72	0.88	9.56	.66	10.22	10.79	105.5

The data in the above table II lead to the following conclucions:

(1) At this higher concentration of sodium methylate, the nitrobenzene is completely reduced to a mixture composed of 95.5 per cent azoxybenzene and 4.5 per cent azobenzene.

(2) The total yield of sodium formate calculated from the yields of azoxy- and azo-benzene according to the reactions represented by equations (A) and (B) is, within the limits of experimental error, equal to the quantity of sodium formate actually formed.

(3) These results prove that in the higher concentration of sodium methylate solution nitrobenzene in conformity with the Klinger equation is reduced not only to azoxybenze,e but is also concomitantly reduced to azobenzene according to the modified Klinger equation, thereby supporting the occurrence of the two postulated reactions.

(4) It is of interest to note that in the previous research of Fry and Andress that either with increasing concentration of sodium hydroxide or increasing

concentration of nitrobenzene in methyl alcohol and water solution, increasing volumes of hydrogen were evolved but azobenzene was never formed. The yields of azoxybenzene varied from 93 to 96% theory.

C. Reduction with lower concentrations of sodium methylate in the presence of lead.

The Klinger reaction runs as described in part (A) were repeated with the addition to each reaction mixture of 0.4 moles (82.89 grams) of Baker's C.P. Analyzed granular lead. Duplicate runs were made wherein 17.3 grams sodium were dissolved in 300 ml. and 600 ml. of methyl alcohol.

The immediate purpose of this section was to determine the effect of the presence of lead upon the extent of the reduction of nitrobenzene in relation to the respective yields of azoxybenzene, azobenzene, lead monoxide, and sodium formate.

(a) Reaction with 300 ml. methyl alcohol, 17.3 g. sodium and 0.4 moles (82.89 g.) lead.

17.3 g. of sodium, cut into small pieces, were weighed over ligroin on the small laboratory balance. The ligroin was poured off and a current of carbon dioxide gas was used to dry perfectly the sodium and facilitate accurate weighing.

The sodium was dissolved piece by piece in the methanol and 82.9 gms. of finely divided lead were added to the solution. The mixture was heated to boiling on a constant level water bath and was allowed to reflux until no more air was expelled into the gasometer. The air in the gasometer was replaced with water; the mechanical stirrer was adjusted to a speed which provided mixing of the components and 20.44 ml. nitrobenzene was added dropwise over a period of fifteen minutes. The mixture was refluxed five hours. No gas was evolved in the runs at this concentration. Within a half hour, a light yellow precipitate (lead monoxide) formed in the reaction mixture.

At the end of the refluxing period the reaction mixture, which consisted of lead monoxide, unreacted lead, unreacted nitrobenzene, sodium formate, azoxy- and azobenzene, sodium plumbite and methyl alcohol, was filtered through a large Buchner funnel. The solid residue of lead monoxide and unreacted lead was washed several times with boiling water; the filtrate and water washings were transferred back to the original reaction flask. The lead and lead monoxide precipitate was next washed with ether until the filtrate was no longer colored (a colored ether washing indicates that nitrobenzene reduction products are being removed from the precipitate). The lead and lead monoxide residue was then washed with acetone and ether, dried and weighed. The ether and acetone washings were evaporated to dryness and the solid obtained was transferred to the main filtrate in which it dissolved.

The dried and weighed mixture of lead monoxide and unreacted lead was digested with 400 ml. freshly made 6N sodium hydroxide to dissolve all lead monoxide. After all the lead monoxide had gone into solution, the mixture was filtered. The remaining lead was washed with water, acetone and ether, dried and weighed.

The weight of lead monoxide formed was obtained by subtracting the weight of recovered or unreacted lead from the combined weights of lead monoxide and unreacted lead.

The remaining products of the reaction in the methyl alcohol filtrate, namely, azoxybenzene, azobenzene, sodium formate, sodium hydroxide, sodium plumbite, and unreacted nitrobenzene, was steam distilled until all methyl alcohol and unreacted nitrobenzene were removed.

The contents of the distilling flask (500 ml.) were added to the same volume of iced water. This effected the solidification of azoxy- and azo-benzene which was filtered off and washed with ice water. To remove slight traces of foreign matter, the azoxy-azobenzene residue was redissolved in ether. To remove traces of water from the filtrate, calcium chloride was added. The solution was again filtered and evaporated to dryness. The residue, which was found to be free from hydrazobenzene by the benzidine test, was weighed and the freezing point was taken in order to ascertain the percentage of azoxy- and azo-benzene present.

The aqueous filtrate obtained after filtering off the azo- and azoxy-benzene, contained sodium formate, sodium plumbite and sodium hydroxide. Before the yield of sodium formate could be determined, it was necessary to remove the sodium plumbite, since the latter substance interferes with the quantitative determination of the former. The filtrate was transferred to a 2-liter volumetric flask, made acid to litmus by adding the calculated amount of sulfuric acid. Lead sulfate was precipitated, but not quantitatively under these conditions.(16) Thus, to insure complete precipitation of all lead, 100 ml. of 2 N ammonium carbonate was added. The soluble lead sulfate was converted into insoluble lead carbonate. The solution was diluted to 2000 ml. in a volumetric flask with distilled water. After thorough mixing, the precipitate was allowed to settle (let stand overnight).

The content of sodium formate in the supernatant liquid was determined by the method previously described.

After the sodium formate determinations were made, the precipitate of lead sulfate and lead carbonate was filtered from the sodium formate solution. The filtrate, which was previously analyzed, was discarded. The lead, contained in the lead sulfate-lead carbonate precipitate, was determined by the method of Griffin (17) as follows:

The lead sulfate and lead carbonate precipitate was dissolved in boiling concentrated nitric acid containing a little bromine water. The solution was transferred to an Erlenmeyer flask and 15 ml. of concentrated sulfuric acid were added. The mixture was evaporated to strong fumes of sulfur trioxide. After cooling, 100 ml. water and 50 ml. ethyl alcohol were added. After standing one hour, the lead sulfate was filtered off in a weighed Gooch crucible, dried at 150° C. and weighed.

The data obtained in relation to the disposition of lead are given in the following table III.

TABLE III

DISPOSITION OF LEAD

	Run 1	Run 2
(1) Reaction Mixture: PbO + unreacted lead	81.76	75.70
(2) " " : unreacted lead	55.06	53.65
(3) " " : PbO sol. in NaOH(1-2)	26.70	22.05
(4) $PbSO_4$ from filtrate	3.94	10.90
(5) Pb $\approx$ PbO (3)	24.78	20.46
(6) Pb $\approx$ $PbSO_4$(4)	2.78	7.46
(7) Σ (2), (5), and (6)	82.52	81.57
(8) Initial weight of lead	82.89	82.89
(9) Lead reacting (8 - 2)	27.83	29.24

The above results indicate that all of the lead which participates in the reduction or in any other possible reaction is converted into lead monoxide. A portion of the lead monoxide first formed is subsequently converted into sodium plumbite by the alkaline solution.

It was found that if the stirrer motors were not adjusted at exactly the same speed, checks on duplicate runs could not be obtained. Therefore, it was decided to find out just how much effect the rate of stirring had upon the reduction of nitrobenzene under these conditions. Duplicate runs were made in which the motor was set at the same speed using the same stirrer and three-necked flask.

The data obtained for the disposition of lead when this higher rate of stirring was employed are as follows:

TABLE IV

DISPOSITION OF LEAD

(1) Reaction Mixture: PbO - unreacted Pb	80.90	81.85
(2) " " : unreacted lead	46.02	46.13
(3) " " : PbO soluble NaOH(1 - 2)	34.88	35.72
(4) $PbSO_4$ from filtrate	6.45	4.96
(5) $Pb \simeq PbO$	32.37	33.16
(6) $Pb \simeq PbSO_4$(4)	4.40	3.39
(7) Σ 2, 5, and 6	82.79	82.68
(8) Initial weight of lead	82.89	82.89
(9) Lead reacting (8 - 2)	36.87	36.76

By comparing the data of tables III and IV, it is seen that the more vigorously the reaction mixture is agitated the more lead enters into the reaction. At the lower speed , 28.5 grams(average) were converted into lead monoxide, whereas at the higher agitation speed 36.5 grams of lead entered into the reaction.

The orange colored reduction products obtained from runs at each agitation speed failed to give the benzidine test for hydrazobenzene. However, the freezing points obtained indicated that each sample was a mixture of azobenzene and azoxybenzene. Again the freezing point curve of Fry and Bowman(14) was used to determine the relative percentages of azo- and azoxy-benzene in the samples.

Runs I and II were made at lower and higher speeds of agitation to afford data on the yields of reduction products, freezing points, the respective percentages of azoxy- and azo-benzene, the weight of each component present, andt the total yields of sodium formate. The data follows in table V.

TABLE V

YIELDS OF AZOXY-, AZO-BENZENE, AND SODIUM FORMATE. LEAD PRESENT IN 300 ML. DILUTION.

(1) Run No.	(2) Azoxy-Azo Benzene, g.	(3) Freezing Point	(4) Percent azoxy	(5) Percent azo	(6) Azoxybenzene, g.	(7) Azobenzene, gr.	(8) $HCOONa$ found g.
Ia. Lower Speed	11.81	27.6	84.2	15.8	9.95	1.86	4.56
Ib. Lower Speed	11.98	27.7	84.2	15.8	10.08	1.90	4.61
I-Average:	11.89	27.7	84.2	15.8	10.01	1.88	4.58
IIa. Higher Speed	14.00	28.4	86.3	13.7	12.08	1.92	5.50
IIb. Higher Speed	14.12	28.4	86.3	13.7	12.19	1.93	5.54
II-Average:	14.06	28.4	86.3	13.7	12.13	1.92	5.47

It may be noted that even though the percent of azobenzene formed at the lower speed is greater than the percent formed at the higher speed of agitation, the total reduction is only slightly greater at the higher speed. The conclusion may be drawn that the more lead which enters into the reaction, the greater is the extent of the reduction of nitrobenzene; but it has been found impossible on the basis of the equations proposed for reactions to correlate quantitatively the increased quantity of lead reacting with the increased extent of the reduction and the increased yield of sodium formate.

Nevertheless, a surprising relationship is found in the fact that the ratio of the combined weights of the reduction products (azoxy- and azo-benzene) obtained in runs I and II is identical with the ratio of the respective total yields of sodium formate, namely 0.895 to 1. The amounts of lead reacting, however, in runs I and II stand in the ratio of .765 to 1. This indicates that here also, as previously shown in section B, table II, the yields of reduction products are quantitatively related to the yields of sodium formate. This discrepancy in the lead ratios will be considered later

(b) Reaction with 600 ml. methyl alcohol, 17.3 g. sodium and .4 moles lead.

It was found in part (A) that when 20.44 ml. of nitrobenzene was reduced in a solution of 17.3 g. sodium in 600 ml. methyl alcohol, no lead being present, a negligible amount of reduction of nitrobenzene took place. Furthermore, in part C (a) it was found that the amount of reduction of nitrobenzene at 300 ml. dilution of sodium methylate was increased by the addition of lead. It was also found that the increased reduction was accompanied by the oxidation of lead to lead monoxide. To explain the increased reduction in relation to the concomitant formation of lead monoxide, several reaction mechanism schemes may be considered wherein it is assumed that lead is directly oxidized to lead monoxide by nitrobenzene.

It is conceivable that lead alone may effect reduction of nitrobenzene to azoxybenzene and to azobenzene in conformity with the following reaction mechanism schemes giving the summation equations (A) and (A'), respectively:

$$2\ \phi NO_2 \longrightarrow \phi\text{-}\overset{\overset{O}{\uparrow}}{N}\text{=}N\text{-}\phi + 3\ O \qquad (a)$$

$$3\ Pb + 3O \longrightarrow 3\ PbO \qquad (b)$$

$$\$\ a,b,\text{--}\ 2\ \phi\ NO_2 + 3\ Pb \longrightarrow \phi\text{-}\overset{\overset{O}{\uparrow}}{N}\text{=}N\text{-}\phi + 3\ PbO \qquad (A)$$

$$2\ \phi\ NO_2 \longrightarrow \phi\text{-}\overset{\overset{O}{\uparrow}}{N}\text{=}N\text{-}\phi + 4\ O \qquad (a')$$

$$4\ Pb + 4\ O \longrightarrow 4\ PbO \qquad (b')$$

$$\$\ a',b'\text{--}2\ \phi\ NO_2 + 4\ Pb \longrightarrow 4\ PbO + \phi\text{-}\overset{\overset{O}{\uparrow}}{N}\text{=}N\text{-}\phi \qquad (A')$$

It has also been shown by Fry and Andress that nitrobenzene is reduced in the presence of lead and sodium hydroxide to azoxybenzene with the formation of hydrogen peroxide rather than sodium formate in conformity with the following equation B:

$$3\ Pb + 6\ NaOH + 4\ \emptyset\ NO_2 \longrightarrow 3\ Na_2PbO_{22} + 2\ \emptyset\text{-}\overset{\overset{O}{\uparrow}}{N}\text{=}N\text{-}\emptyset + 2\ H_2O_2 \quad (B)$$

Further reduction of nitrobenzene to azobenzene accompanying the formation of hydrogen peroxide with no sodium formate may be represented by equation B':

$$2\ Pb + 4\ NaOH + 2\ \emptyset\ NO_2 \longrightarrow 2\ Na_2PbO_2 + \emptyset\text{-}\overset{\overset{O}{\uparrow}}{N}\text{=}N\text{-}\emptyset + 2\ H_2O_2 \quad (B')$$

The two following reaction mechanism schemes entailing the concurrent reduction of nitrobenzene, both by sodium methylate and metallic lead, lead to such summation equations C and C'.

$$CH_3ONa + HOH \longrightarrow CH_3OH + NaOH \qquad (a)$$

$$CH_3OH + NaOH \longrightarrow HCOONa + 4\ H \qquad (b)$$

$$4\ \emptyset\ NO_2 + 4\ Pb \longrightarrow 4\ PbO + 4\ \emptyset\ N\ \ O \qquad (c)$$

$$2\ \emptyset\ N\ \ O + 4\ H \longrightarrow 2\ \emptyset\ N{<}^{H}_{OH} \qquad (d)$$

$$2\ \emptyset\ N^{H}_{OH} + 2\ \emptyset\ N\ \ O \longrightarrow 2\ \emptyset\text{-}\overset{\overset{O}{\uparrow}}{N}\text{=}N\text{-}\emptyset + 2\ H_2O \quad (e)$$

$$\$\ a,b,c,d,e:\ CH_3ONa + 4\emptyset\ NO_2 + 4\ Pb \longrightarrow 4\ PbO + 2\ \emptyset\text{-}\overset{\overset{O}{\uparrow}}{N}\text{=}N\text{-}\emptyset + HCOONa + H_2O \quad (C)$$

$$CH_3ONa + HOH \longrightarrow CH_3OH + NaOH \qquad (a)$$

$$CH_3OH + NaOH \longrightarrow HCOONa + 4\ H \qquad (b)$$

$$2\ \emptyset NO_2 + Pb \longrightarrow 2\ PbO + 2\emptyset N\ \ O \qquad (c)$$

$$2\ \emptyset N\ \ O + 4\ H \longrightarrow 2\ \emptyset N \begin{smallmatrix}H\\OH\end{smallmatrix} \qquad (d)$$

$$\emptyset N \begin{smallmatrix}H\\OH\end{smallmatrix} + \emptyset N \begin{smallmatrix}H\\OH\end{smallmatrix} \longrightarrow \emptyset N = N \emptyset + 2\ H_2O \qquad (e)$$

$$\not{S}\ a,b,c,d,e:\ CH\ ONa + 2\ \emptyset NO_2 + 2\ Pb \longrightarrow$$

$$\emptyset N = N \emptyset + 2\ PbO + H_2O + HCOONa \qquad (C')$$

The object in making the runs of this section was to determine what other reactions were taking place in the runs of section C (a) (300 ml. methyl alcohol solution with .4 moles lead) in addition to the Klinger and modified K Klinger reactions. Other reactions effecting the reduction of nitrobenzene to azoxy- and azo-benzene undoubtedly occur since the yields of sodium formate were considerably lower than the calculated equivalent quantities required by the Klinger and modified Klinger equations.

Since at least four concomitant reactions were responsible for the formation of azoxy- and azo-benzene, it was not possible to determine from the yields of sodium formate and the weight of lead reacting to form lead monoxide which of the proposed reactions took place in addition to the Klinger and modified Klinger reactions.

To shed more light upon this question, it was decided to devise an experiment with lead wherein lead monoxide, sodium formate and only azoxybenzene were formed. Since it was previously found that when nitrobenzene was reduced with sodium methylate at a 600 ml. methyl alcohol dilution (Section III (A)), only a negligible amount of reduction took place in the absence of lead, it was hoped that if lead were introduced into this reaction mixture that azoxybenzene would be the only reduction product and thereby simplify the calculations.

To this end 17.3 g. sodium was dissolved in 600 ml. of absolute methyl alcohol and 82.89 gm. of finely divided lead and 20.44 ml. (.2 mole) nitrobenzene were added. The mixture was stirred and refluxed for four hours.

The data obtained relating to the disposition of lead are recorded in the following table VII:

TABLE VII

DISPOSITION OF LEAD

(1)	Reaction mixture: PbO + unreacted Pb	82.35	82.48
(2)	" " : unreacted lead	67.50	67.65
(3)	" " : PbO soluble (NaOH (1 - 2)	14.85	14.83
(4)	$PbSO_4$ from filtrate	1.932	1.943
(5)	Pb $\approx$ PbO	13.79	13.78
(6)	Pb $\approx$ $PbSO_4$ (4)	1.32	1.33
(7)	≤ 2, 5, and 6	82.61	82.76
(8)	Initial weight of lead	82.89	82.89
(9)	Lead reacting (8 - 2)	15.39	15.24

The above data indicate that all of the lead which reacts is converted into lead monoxide, part of which in turn is converted into sodium plumbite.

The sole reduction product of nitrobenzene was azoxybenzene (M.P. 36° C.) , which was isolated as previously described. The formate determinations were conducted as described in Section III (a).

The data presented in the following table VIII recording the quantities of lead reacting, the yields of azoxybenzene and sodium formate should be considered from the point of view of its being correlated with equation C.

TABLE VIII

DATA BASED UPON EQUATION C:

$$4\ Pb + CH_3ONa + 2\ \phi\ NO_2 \longrightarrow 2\ (\phi\ N)_2O + 4\ PbO + HCOONa + H_2O$$

① Run	② Pb reacted (g.)	(3) azoxy-benzene yield (g.)	(4) sodium formate yield (g.)	(5) azoxy-benzene yield Eq.C(g.)	(6) Pb reacted Eq. C. (g.)
I	14.05	4.272	.76	.73	6.71
II	13.90	4.251	.74	.73	6.65
Average	13.98	4.262	.75	.73	6.69

It will be noted that the actual yield of sodium formate, column 4, is practically identical with the theoretical yield, column 5, in conformity with equation C.

The corresponding yields of azoxybenzene, column 3, however, are considerably less than the yields required by equation C calculated on the basis of the quantity of lead reacting.

An explanation for this discrepancy is afforded by the fact that more lead reacts than is indicated by reaction C to form sodium plumbite without the accompanying formation of azoxybenzene. This has been proved to be the case by digesting finely divided lead with sodium hydroxide solution, whereupon appreciable quantities of lead undergo reaction. Sodium hydroxide while not initially present in the reaction mixture is formed during the course of the reduction.

It can also be shown that equation C can be derived as a summation equation entailing two reactions; namely, the direct reduction of nitrobenzene by lead concurrently with the Klinger equation. It has not been possible, however, to calculate the extent of the occurrence of each of these reactions as based upon the amounts of lead reacting, and the sodium formate and the reduction product formed.

D. Reduction with the Higher Concentration of Sodium Methylate in the Presence of Lead.

The experimental procedure employed in this portion of the research was substantially the same as that used in section C, except that the nitrobenzene was completely reduced and steam distillation was necessary only to get rid of the excess methyl alcohol. Previous experiments indicated that in those cases wherein a high concentration of sodium methylate was used the solution became so alkaline that the equilibrium,

$$NaOCH_3 + HOH \rightleftharpoons NaOH + CH_3OH$$

was not displaced quantitatively to the right, and therefore, all the methyl alcohol was not removed under these conditions. Since in the runs of this section twice the amount of sodium methylate as used in sections (A) and (C) was used, one half of the sodium methylate was neutralized with the calculated amount of sulfuric acid after the unreacted lead and lead monoxide were filtered from the reaction mixture. The procedure following steam distilling of the excess methyl alcohol was identical to that previously described in section C.

34.6 grams of sodium were dissolved in 300 ml. of absolute methanol. 82,89 g. of granular lead was added to the reaction mixture and 20.44 ml. nitrobenzene were added drop by drop through a dropping funnel. The mixture ~~was~~

was refluxed five hours. Hydrogen gas was evolved in almost a steady stream only for the first twenty minutes of refluxing. 650 and 675 ml. of hydrogen were collected in duplicate runs. By the time all the hydrogen had passed into the gasometer, a gradual color change from pale yellow to dark red took place in the reaction mixture.

Again it is pertinent to compare the volumes of hydrogen evolved in the reactions of this study with those volumes found by Fry and Andress to be evolved when lead was added to a Klinger reaction mixture under different conditions; namely, 82.9 g. lead, 100 grams sodium hydroxide, 200 ml. methyl alcohol, 100 ml. water and .2 moles nitrobenzene. They found that over two liters of hydrogen was evolved under these conditions (the quantity of sodium hydroxide -- 100 g. -- is practically equivalent to 34.6 g. sodium).

The lead which reacted was converted into lead monoxide. Part of the lead monoxide was isolated as such. The remainder of the lead monoxide reacted with the alkali present to form sodium plumbite. This soluble sodium plumbite was determined as lead sulfate by the method previously described. The data in relation to the disposition of lead in this reaction ~~is~~ are given in table X.

TABLE X

DISPOSITION OF LEAD

High concentration sodium methylate in the presence of lead.

		Run 1	Run 2
(1)	Reaction mixture: PbO + unreacted Pb	51.90	53.87
(2)	" " : unreacted Pb	40.49	41.50
(3)	" " : PbO soluble in NaOH ((1 - 2)	11.41	12.32
(4)	$PbSO_4$ from filtrate	46.40	44.17
(5)	Pb $\approx$ PbO (3)	10.59	11.43
(6)	Pb $\approx$ $PbSO_4$ (4)	31.70	30.18
(7)	Σ 2, 5, and 6	82.78	83.11
(8)	Initial quantity of lead	82.89	82.89
(9)	Pb reacting (8 - 2)	42.40	42.39

The nitrobenzene was completely reduced to a mixture of azo- and hydrazo-benzene. The qualitative test for hydrazobenzene was conducted as follows: a pinch of the orange reduction product was dissolved in about 10 ml. of 95% alcohol in a test tube. The solution was heated to about 50° and a few drops of concentrated sulfuric acid were added. Immediately a white precipitate of benzidine sulfate formed. Since hydrazobenzene was present, it became necessary to determine quantitatively the extent to which it was formed. The method devised by Fry and Rosen[18] for converting hydrazobenzene into benzidine was employed.

A 2.5 to 3.0 gram-sample of the reduction product was weighed into a 400 ml. beaker. The sample was moistened with 7 ml. water and 20 ml. concentrated hydrochloric acid was added with thorough stirring. This was covered and allowed to stand one hour, then heated to 70 - 80° for another hour. After cooling, the solution of benzidine hydrochloride was filtered from the solid residue, which may have been either a mixture of azoxy- and azo-benzene or just azobenzene. The residue, later shown to be azobenzene, was heated to melting with dilute hydrochloric acid, and then the solution was allowed to cool until the solid crystallized, when the acid solution was decanted off. The solid was washed three times in this manner to remove any traces of benzidine hydrochloride. The washings were added to the original filtered solution, which now had a volume of about 400 ml., and made alkaline with ammonia to liberate the benzidine which was extracted thoroughly with ether. A dark residue observed at this point was separated with the aqueous layer. Calcium chloride was added to the ether solution. After standing for a few minutes, the solution was filtered, evaporated to dryness in a weighed crystallizing dish, dried at 85-90° for 15 minutes in an oven, cooled, weighed, and recorded as the benzidine yield.

The solid obtained in the above determination after all the hydrazobenzene had been converted into benzidine was dissolved in ether. The ether extract was dried with calcium chloride, filtered and evaporated to dryness. The orange residue thus obtained was found to melt at 67.5°. The melting point of azobenzene is 67.8°. Therefore, it is evident that the organic reduction products of nitrobenzene in these runs were solely azobenzene and hydrazobenzene at these higher concentrations. No azoxybenzene was formed.

In table XI, the number of each run is given in column 1. Column 2 records the total yield of nitrobenzene reduction products (azo- and hydrazo-benzene); column 3, the weights of duplicate hydrazo- azobenzene sample taken for the determination of hydrazobenzene; column 4, the weights of benzidine equivalent to hydrazobenzene; obtained from the hydrazo- azo benzene samples by the above procedure; column 5, the percent of hydrazobenzene; columns 6 and 7, the yields of hydrazobenzene and azobenzene, respectively; and column 8, the yields of sodium formate.

TABLE XI

(1) Run No.	(2) Yield $(\phi N)_2$ + $(\phi NH)_2$	(3) Hydrazo-azo sample grams	(4) $(\phi NH_2)_2$ + $(\phi NH)_2$ found	(5) Per-cent hy-drazo	(6) Hydrazo benzene yield grams	(7) azo-benzene yield grams	(8) HCOONa yield grams.
		2.702	0.309	11.07	1.92	15.44	12.87
I	17.36	2.841	0.327	11.50	1.99	15.37	12.90
II	17.12	2.765	0.306	11.09	1.90	15.20	12.81
		2.931	0.342	11.69	2.01	15.11	12.88

At this higher concentration of sodium methylate in methyl alcohol in the presence of lead, nitrobenzene is reduced to mixture of 98.% azo- and 2.% hydrazobenzene with the concomitant formation of lead monoxide and sodium formate.

In the preceding section C, with the lower concentration of sodium methylate, 44.5 per cent of the lead present entered into the reaction while in this section D, with double the concentration of sodium methylate, 51.2 percent of lead present reacted. Here also it was not possible to correlate the yields of reduction products either with the amount of lead reacting and the sodium formate formed, apart from the significant finding that nitrobenzene yielded chiefly azobenzene and some hydrazobenzene, but no azoxybenzene.

E. Reduction with Sodium Methylate in pyridine and xylene.

The experimental procedure employed in this portion of the research was substantially the same as that used in previous sections, except that Mathieson Alkali Company's sodium methylate (95.4% pure) was used in 250 ml. of xylene and 250 ml. of pyridine, rather than sodium methylate made directly from metallic sodium and methyl alcohol. Sodium methylate equivalent to 17.3 g. sodium and 34.6 g. sodium were used in the various runs.

In all runs, the reduction product was azoxybenzene with the exception that in the solvent pyridine and the higher concentration of sodium methylate not more than 1 per cent of azobenzene was formed in addition to chief and practically sole product, azoxybenzene.

The number of each run is recorded in column 1 of table XII. Column 2 notes the solvent used in each run; column 3, the grams of sodium methylate used; columns 4 and 5, the actual yield of azoxybenzene and the theoretical yields, respectively; column 6, the percent theory yields; columns 7 and 8, the actual and theoretical yields of sodium formate; column 9, the percent reduction based on the theoretical yield of sodium formate calculated on the basis of Klinger equation.

TABLE XII

EXPERIMENTAL DATA BASED ON KLINGER EQUATION:

$$4\,\phi\,NO_2 + 3\,CH_3ONa \dashrightarrow 2(\phi N)_2O + 3\,HCOONa + 3\,H_2O$$

(1) Run	(2) Solvent	(3) NaOCH$_3$ (95.4% pure) (grams)	(4) Azoxy-benzene found (grams)	(5) Azoxybenzene theory (grams)	(6) Percent theory yield	(7) HCOONa found (grams)	(8) HCOONa theory (grams)	(9) Percent theory yield
Ia	xylene	42.55	17.23	19.81	87.0	8.91	10.20	87.3
b	xylene	42.55	17.18	19.81	86.8	8.82	10.20	86.5
IIa	xylene	85.11	18.72	19.81	94.5	9.73	10.20	95.4
b	xylene	85.11	18.81	19.81	94.9	9.70	10.20	95.1
IIIa	pyridine	42.55	15.31	19.81	77.3	8.25	10.20	80.9
b	pyridine	42.55	15.72	19.81	79.4	8.27	10.20	81.1
IVa	pyridine	85.11	19.11	19.81		10.37	10.20	101.
b	pyridine	85.11	18.85	19.81		10.33	10.20	101.

Conclusions:

1. Even though sodium methylate is only slightly soluble in either xylene or pyridine, nitrobenzene is reduced in either of these mixtures in accordance with the Klinger equation.

2. In all runs, the percent theory yields of azoxybenzene and sodium formate are in conformity with the Klinger equation.

3. At the lower concentration of sodium methylate in xylene and pyridine, .2 mole nitrobenzene is reduced to pure azoxybenzene in 87 per cent and 81 per cent theory yield, respectively.

4. At the higher concentration of sodium methylate in xylene, a 95 percent theory yield of azoxybenzene was obtained.

5. At the higher concentration of sodium methylate in pyridine, a practically quantitative yield of azoxybenzene (freezing point 35°) was obtained.

6. It is of particular interest to note that in the previous sections, A and B, wherein higher concentrations of sodium methylate in methyl alcohol as solvent medium yielded both azoxy- and azo-benzene in conformity with the Klinger and modified Klinger reactions, respectively, but with the higher concentration of sodium methylate in either pyridine or xylene as solvent medium, azoxybenzene is

the sole product of the reduction. Accordingly, it appears that the modified Klinger reaction yielding azobenzene occurs only in methyl alcohol medium, with the occurrence to a very minimum extent of the modified Klinger reaction with the higher concentration of sodium methylate in pyridine. (This is shown by slightly lower f.p. of the reaction product and the slight excess yield of sodium formate above that for the straight Klinger reaction).

7. No hydrogen was evolved during the course of any of the foregoing reactions.

F. Reduction with Sodium Methylate in Pyridine and Xylene in the Presence of Lead.

It should now be noted that it was impossible in preceding reductions of nitrobenzene by sodium methylate in methyl alcohol in the presence of lead to obtain data correlating the amounts of lead reacting and the quantities of sodium formate formed with the yields of the reduction product. This inability was attributed to the fact that definite quantities of lead apparently interacted with the solvent or in other unknown reactions. Accordingly, the immediate purpose of conducting reductions in the presence of inert solvents, xylene and pyridine, was to preclude the possibility of the occurrence of side reactions between the lead and the solvent medium and thereby secure data which could be correlated quantitatively with the assumed reactions.

The runs of section E, reductions with sodium methylate in pyridine and xylene, were repeated with the addition of 82.89 g. of lead to the respective reaction mixtures. The experimental procedure was substantially the same as that used in sections C and D, in methyl alcohol solution, except that powdered sodium methylate in 250 ml. of xylene and 250 ml. of pyridine were used.

In the runs of this section appreciable volumes of hydrogen were evolved in contrast to the almost negligible volumes obtained in previous sections. The source of this hydrogen is attributed to the concurrence of the reaction

$$CH_3ONa + HOH \longrightarrow HCOONa + 2H_2 \qquad (E)$$

which is one of the intermediate summation equations postulated in the reaction mechanism schemes postulated for the Klinger and modified Klinger reactions.

The data obtained ~~is~~ are recorded in the following table XIII. Column 1 notes the number of each run; column 2, the solvent used; column 3, the grams of sodium used; column 4, the grams of lead reacting; columns 5 and 6, the yields of reduction products and the freezing points of the azoxy-azo mixtures, respectively; columns 7 and 8, the yields of azoxy- and azo-benzene, respectively; column 9, the volumes of hydrogen evolved (N.T.P.); column 10, the grams of azoxybenzene equivalent to the weight of lead reacting according to equation (A); column 11, the grams of azobenzene equivalent to the lead reacting (equation B); column 12, the grams of sodium formate equivalent to the azoxybenzene, formed in excess of the lead reaction A in conformity with Klinger equation C; column 13, the grams of sodium formate equivalent to the azobenzene formed in excess of the lead reaction B, in conformity with the modified Klinger reaction, D; column 14, the grams of sodium formate equivalent to the volume of hydrogen evolved (N.T.P.); in accordance with equation E; column 15, the sum of the yields of sodium formate from equations C, D, and E; and column 16, the actual yield of sodium formate found.

T A B L E X I I I

REDUCTION WITH $NaOCH_3$ IN PYRIDINE AND XYLENE IN THE PRESENCE OF LEAD

(based upon the following equations)

$3\ Pb + 2\ \phi NO_2 \longrightarrow (\phi N)_2 + 3\ PbO$ (A)

$4\ Pb + 2\ \phi NO_2 \longrightarrow (\phi N)_2 + 4\ PbO$ (B)

$3\ CH_3ONa + 4\ \phi NO_2 \longrightarrow 2\ (\phi N)_2O + 3\ HCOONa + 3\ H_2O$ (C)

$2\ CH_3ONa + 2\ \phi NO_2 \longrightarrow (\phi N)_2 + 2\ HCOONa + 2\ H_2O$ (D)

$CH_3ONa + HOH \longrightarrow HCOONa + 2\ H_2$ (D)

(1) Run	(2) Solvent	(3) $NaOCH_3$ (g.)	(4) Pb reacting (g.)	(5) azoxy and azo yield (g.)	(6) F. P. Mixture	(7) azoxy. benzene yield (g.)	(8) azo benzene yield (g.)	(9) H_2 evolved N.T.P. Liters	(10) azoxy ≀≀ Pb Eq.(A) (g.)	(11) azo ≀≀ Pb Eq.(B) (g.)	(12) HCOONa ≀≀ azoxy Eq.(C) (g.)	(13) HCOONa ≀≀ azo Eq.(D) (g.)	(14) HCOONa ≀≀ hydrogen (Eq.E) (g.)	(15) HCOONa ‖ gram Eq.C,D,E Theory	(16) HCOONa found (g.)
Ia	pyridine	85.11	34.80	17.79	66.4	.54	17.25	2.9	-	7.65	.28	7.16	4.45	11.89	13.50
b	pyridine	85.11	34.65	18.01	66.0	.81	17.20	2.9	-	7.62	.42	7.15	4.45	12.02	13.62
IIa	pyridine	42.55	32.37	17.13	64.4	1.38	15.75	1.65	-	7.14	.85	6.44	2.51	9.80	11.37
b	pyridine	42.55	32.62	17.42	65.0	1.39	16.03	1.60	-	7.16	.83	6.62	2.49	9.94	11.58
IIIa	xylene	85.11	17.90	13.36	28.8	11.52	1.84	3.0	5.71	-	2.99	1.37	4.55	8.91	8.86
b	xylene	85.11	17.72	13.51	28.5	11.62	1.87	2.9	5.66	-	3.08	1.41	4.45	8.94	8.72
IVa	xylene	42.55	10.98	13.70	29.4 ~~13.70~~	12.20	1.50	1.7	3.50	-	4.48	1.12	2.58	8.18	8.86
b	xylene	42.55	11.10	13.81	29.5 ~~13.81~~	12.18	1.63	1.65	3.53	-	4.45	1.22	2.51	8.17	8.48

The data in the above table XIII lead to the following interpretations and conclusions:

(1) In the runs using pyridine as solvent, the nitrobenzene reduction product was chiefly azobenzene with very little azoxybenzene whereas in xylene the principal reduction product was azoxybenzene with very little azobenzene.

Since azoxybenzene and azobenzene may arise not only from the concurrence of reactions A and B, respectively without the formation of sodium formate but also through the concurrence of reactions C and D with the formation of sodium formate, it is impossible to correlate the yields of each of the reduction products with the quantities of lead reacting (equations A and B) and the yield of sodium formate (equations C and D). In order to approach as far as possible a desired correlation, calculations were made relative to the reduction first in pyridine on the basis of the predominant occurrence of the one lead reaction (B), yielding azobenzene according to equation B. On the other hand, in xylene, calculations were made relative to the reduction on the basis of the predominant occurrence of the other lead reaction (A), yielding azoxybenzene.

While thus omitting equation A in the solvent pyridine and equation B in the case of xylene, the calculations made in terms of the predominant reactions just noted lead to the following conclusions; which are indicative of the nature and extent of the occurrence of the predominant reactions:

2. In all the pyridine and xylene runs the total yield of sodium formate is very nearly equal to the sum of the yields of sodium formate, formed in conformity with and thereby confirming the occurrence of reactions represented by equations C, D, and E.

3. In all runs the total amount of lead reacting was accounted for in terms of equation B, in the case of pyridine, and equation A, in the case of xylene.

4. From 2 and 3, it follows that the concurrence of reactions in conformity with equations A, B, C, D and E is confirmed.

Other observations may be noted:

5. With the two concentrations of sodium methylate (one double the other) in pyridine there was little difference in the weights of lead reacting and the composition of the reduction products.

6. As should be expected, the volumes of hydrogen evolved were greater with the higher concentration than with the lower concentration of sodium methylate used. Furthermore, in runs with both solvents the ratio of the yields of hydrogen with the higher concentration to the yields with the lower concentration of sodium methylate was

practically identical, namely 1.75 to 1.

7. The quantities of lead reacting in pyridine solvent were approximately from two to three times as great as the quantities of lead reacting in xylene solvent. This may be due to the fact that pyridine acts as a catalyst in many and varied reactions.

IV. SUMMARY AND CONCLUSIONS

I. Reduction in the Absence of Lead.

The nature and extent of the reduction of nitrobenzene with sodium methylate in anhydrous solvents- methyl alcohol, pyridine, and xylene - was studied in order to determine and explain the effect, thereupon, of the presence of lead in these various reaction mixtures. The most important observations and conclusions are as follows:

1. Nitrobenzene is reduced in methyl alcohol solution, dependent upon the concentration of sodium methylate, either to azoxybenzene in conformity with the Klinger reaction:

$$4\,\varnothing\,NO_2 + 3CH_3ONa \dashrightarrow 2\,\varnothing\,\overset{O}{N}{=}N\,\varnothing + 3HCOONa + 3H_2O$$

or to a mixture of azoxy- and azo-benzene, in conformity withthe Klinger reaction and the concurrent modified Klinger reaction:

$$2\,\varnothing\,NO_2 + 2CH_3ONa \dashrightarrow \varnothing\,N{=}N\,\varnothing + 2HCOONa + 2H_2O$$

2. There is no record in the literature that both products of reduction were formed when a high concentration of sodium methylate in anhydrous methyl alcohol was used. It has also been shown that the total yield of sodium formate accompanying the respectively determined yields of azoxy- and azo-benzene may be correlated according to the Klinger and modified Klinger reaction.

and modified Klinger reaction.

3. Powdered sodium methylate suspended in either of the inert solvents, pyridine or xylene, effected reduction of nitrobenzene to azoxybenzene in quantitative conformity with the Klinger reaction. The extent of reduction varied from 80 to 95 per cent of the theoretical yield of azoxybenzene and sodium formate, depending upon the concentration of sodium methylate.

With the higher concentration of sodium methylate in pyridine a very small amount (not greater than 1%) of azobenzene was formed through the concurrence of the modified Klinger reaction.

4. It is particularly interesting that with a high concentration of sodium methylate in methyl alcohol (conclusions 1 and 2) both the Klinger and modified Klinger reactions occurred but with the same concentration of sodium methylate in the pyridine and xylene reaction mixtures, reduction was practically limited to the occurrence of the Klinger reaction.

II. Reductions in the presence of lead.

Experimental runs conducted in the absence of lead were repeated in the presence of lead.

1. With a low concentration of sodium methylate in methyl alcohol, both azoxy- and azobenzene were formed.

2. With high concentration of sodium methylate in methyl alcohol azo- and hydrazo-benzene were formed.

3. Results (1) and (2) conclusively show that the presence of lead in the reaction mixture markedly affects both the nature and extent of the reduction.

4. While it was possible to correlate quantitatively the yields of azoxy- and azo-benzene with the yields of sodium formate in conformity with the Klinger and modified Klinger reaction in methyl alcohol solution, similar correlations could not be revealed when reductions occurred in the presence of lead. This difficulty may be attributed to the fact that appreciable quantities of lead effected reduction of nitrobenzene to azoxybenzene and to azobenzene with the formation of lead monoxide according to the concurrent reactions:

$$3\,Pb + 2\,\varnothing NO_2 \longrightarrow \varnothing\text{-}\overset{O}{\overset{\uparrow}{N}}=N\text{-}\varnothing + 3\,PbO$$

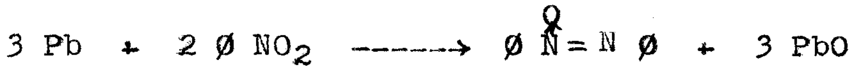
$$4\,Pb + 2\,\varnothing NO_2 \longrightarrow \varnothing\text{-}N=N\text{-}\varnothing + 4\,PbO$$

Furthermore, lead apparently reacted with sodium hydroxide (formed during the reaction) yielding sodium plumbite and hydrogen

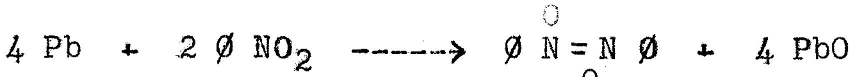
$$Pb + 2\,NaOH \longrightarrow Na_2PbO_2 + H_2$$

which hydrogen could also effect reduction.

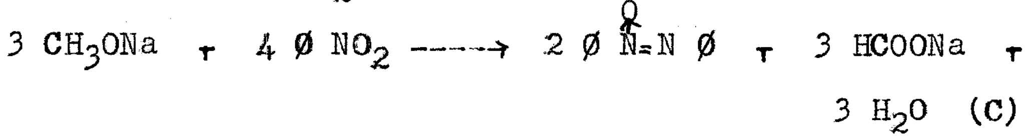
To restrict or limit the occurrence of the various concomitant reactions reductions with powdered sodium methylate in pyridine and xylene in the presence of lead gave data leading to the following conclusions based upon the occurrence of the following reactions:



$$3\,Pb + 2\,\phi NO_2 \longrightarrow \phi\overset{O}{N}=N\phi + 3\,PbO \quad (A)$$



$$4\,Pb + 2\,\phi NO_2 \longrightarrow \phi\overset{O}{N}=N\phi + 4\,PbO \quad (B)$$



$$3\,CH_3ONa + 4\,\phi NO_2 \longrightarrow 2\,\phi\overset{O}{N}=N\phi + 3\,HCOONa + 3\,H_2O \quad (C)$$

$$2\,CH_3ONa + 2\,\phi NO_2 \longrightarrow \phi N=N\phi + 2\,HCOONa + 2\,H_2O \quad (D)$$

$$CH_3ONa + HOH \longrightarrow HCOONa + 2H_2 \quad (E)$$

5. In pyridine medium, both with the lower and higher concentrations of sodium methylate, azobenzene was the predominating reduction product with very little azoxybenzene whereas in xylene the principal reduction product was azoxybenzene with very little azobenzene. Accordingly,

6. From pyridine medium reaction data calculations were based upon the concurrence of reactions B, C, D, and E., and from xylene medium, reaction data, calculations were based upon the concurrence of reactions A, C, D, and E. Accordingly, ommitting equation A (pyridine medium) and equation B (xylene medium) the following conclusions may be noted:

7. The total yield of sodium formate was very nearly equal to the sum of the yields of sodium formate, formed in conformity with and thereby confirming the

occurrence of reactions represented by equations C, D, and E.

8. In all runs the total amount of lead reacting was accounted for in terms of equation B, in the case of pyridine, and equation A, in the case of xylene.

Finally, the predominating reactions occurring in the reduction of nitrobenzene by sodium methylate in pyridine and xylene in the presence of lead have been correlated quantitatively with the respectively proposed reactions represented by equations A, B, C, D, and E.

ADDENDUM: A MODIFIED PREPARATION OF AZOXYBENZENE.

Since in section III (E) it was shown that nitrobenzene dissolved in xylene or pyridine was readily and almost completely reduced to azoxybenzene when heated with powdered sodium methylate, the following modified method for the laboratory preparation of azoxybenzene is recorded.

Suspend 90 g. Mathieson sodium methylate (95.4% pure) in 250 ml. xylene (U.S.P.) in a 1-liter three-necked flask. Fit a mercury sealed mechanical stirrer to the central neck and a Liebig condenser to each of the two side necks of the flask. Add 50 ml. of nitrobenzene (C.P .) through one of the condensers. Heat with a free flame until the reaction mixture turns brown. Extinguish the flame. This color change marks the beginning of the reaction. After fiften or twenty minutes, the reaction subsides and an additional 50 ml. nitrobenzene is added, a few ml. at a time, over a period of fifteen minutes at such a rate as to maintain constant and gentle refluxing of the solvent. After all the nitrobenzene is added, the reaction flask with contents is placed in an oil bath and heated for one and one half hours cautiously at first and finally the temperature of the bath is gradually raised to 130-140° C. The reaction mixture is refluxed, a total of two hours.

Remove the oil bath and add 100 ml. water to the reaction mixture. Continue stirring until the brown solid mass dissolves. The xylene and unreacted nitrobenzene is removed by steam distillation. Pour the reaction mixture onto ice and water. Azoxybenzene solidified. Filter, air dry, and weigh. The azoxybenzene is pure (M.P. 34.5 - 35.0° C.), and the yield is 90 - 92 g. (93 - 95 percent theory).

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