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I hereby recommend that the thesis prepared under my supervision by Harry J. Andrews, Jr.

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A STUDY OF THE KLINGER REACTION

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INTRODUCTION AND OBJECT

In a previous study of the reducing action of several metals on nitrobenzene in sodium methylate solutions(1), it was found that, as naturally expected, the nitrobenzene was quantitatively reduced, presumably by the sodium methylate in conformity with the Klinger reaction(2) to azoxybenzene. But, unexpectedly, many liters of hydrogen were liberated when this reaction was conducted in the presence of finely divided, metallic lead.

The problem thus presented was to explain the action of lead in effecting the evolution of such large volumes of hydrogen.

A preliminary approach to this problem was an investigation conducted to determine the effect of increasing concentrations of sodium hydroxide and of nitrobenzene, relatively and respectively, upon the nature and extent of the occurrence of the Klinger reaction in methyl alcohol solutions. It was indeed, quite a surprise to find that, with increasing concentrations either of sodium hydroxide or of nitrobenzene, hydrogen was evolved in increasing volumes. This entirely unexpected result has not previously been recorded in the literature.

The problem thus became twofold; first, to explain the evolution of hydrogen as an accompaniment of the Klinger reaction and second, to explain the more abundant liberation of hydrogen when the Klinger reaction was conducted in the presence of finely divided lead.

These explanations, in view of extended researches in this laboratory on the Klinger reaction, will naturally be based upon mechanisms of the reactions previously proposed by Fry and co-workers (3). The intermediate reactions, entailing the amphoteric dissociation of sodium hydroxide, their partial and complete summations, culminating in the final equation for the Klinger reaction, are represented as follows:

$$CH_3OH + NaOH \rightleftharpoons CH_3ONa + H_2O \qquad a$$

$$CH_3ONa + NaOH \longrightarrow CH_2(ONa)_2 + 2H \qquad b$$

$$CH_2(ONa)_2 + H_2O \longrightarrow CH_2O + 2HONa \qquad c$$

$$\sum a,b,c \qquad CH_3OH \longrightarrow CH_2O + 2H \qquad A$$

$$CH_2O + NaOH \longrightarrow HCOONa + 2H \qquad B$$

$$\sum A,B \qquad CH_3OH + NaOH \longrightarrow HCOONa + 4H \qquad C$$

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

$$\sum 3C,D \qquad 4C_6H_5NO_2 + 3CH_3OH + 3NaOH \longrightarrow 3HCOONa + 2(C_6H_5N)_2O + 6H_2O \qquad E$$

The above reaction mechanism scheme entails the oxidation of sodium methylate to sodium formate and the concomitant reduction of nitrobenzene solely to azoxybenzene. The hydrogen formed in the intermediate equations presumably is not liberated as gaseous hydrogen. As far as the reaction mechanism scheme is concerned, it immediately functions in the reduction of the nitrobenzene and there is nothing whatever in the reactions to indicate the possibility of the formation and liberation of hydrogen nor has any previous investigator observed or recorded same.

As noted, in preliminary experiments of the present study, it was found that when concentrated solutions of sodium hydroxide in methyl alcohol reacted with nitrobenzene, hydrogen was evolved in appreciable volumes. Furthermore, when finely divided lead was incorporated in the Klinger reaction mixtures, the volumes of hydrogen liberated were many times greater, and, let it also be noted that the nitrobenzene was further reduced to azobenzene in the higher concentrations of sodium hydroxide.

In order to arrive at a possible explanation of these unexpected observations, the first part of this research was limited to the Klinger reaction and the effect of increasing concentrations of sodium hydroxide and nitrobenzene in relation to the volumes of hydrogen liberated and the nature and quantities of the products of reduction.

The second part of the investigation embraced a repetition of experiments conducted in the first part, but with incorporation of varying molar quantities of finely divided lead in the various Klinger reaction mixtures. Here, marked variations in the volumes of hydrogen evolved and in the nature and extent of the reduction products obtained were observed.

HISTORICAL

The reduction of nitrobenzene to azoxybenzene has been known since 1845 when Zinin (4) first prepared azoxybenzene by the action of alcoholic potash on nitrobenzene. No equations were suggested for the reduction of nitrobenzene to azoxybenzene. Alexejew (5) used sodium amalgam to reduce nitrobenzene in alcoholic solution. He also states that zinc dust, in the presence of small quantities of alkali, acts in the same manner as sodium amalgam.

Rasenack (6) found that sodium hydroxide and alcohol would convert nitrobenzene to azoxybenzene if the nitrobenzene is added in small quantities while the solution is being refluxed. He noted that completely dry nitrobenzene is not attacked by sodium or sodium amalgam, but when a few drops of water are added, a reaction occurs at once and azoxybenzene results.

Schmidt and Schultz (7) prepared 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 Michler (8). In 1903, Weiler (9) prepared azoxybenzene by the use of iron and sodium hydroxide. Loesner (10), in 1909, used sodium hydroxide and arsenious acid to reduce nitrobenzene to azoxybenzene.

Klinger (2) devised a new method for the reduction of nitrobenzene to azoxybenzene in which he used sodium and methyl alcohol as the reducing agents. A yield of 85-89% was obtained.

Moltschonowsky (11) repeated Klinger's work and obtained somewhat lower yields. Bruhl (12) obtained almost quantitative yields by adding methyl alcohol to finely divided sodium in xylene

and then boiling the mixture with nitrobenzene for seven hours.

Lachman (13) also repeated Klinger's method and obtained much better yields, 95 and 97%. He states that the water present in the alcohol has little effect upon the yield of azoxybenzene.

Evans and Fry (14) obtained a 90% yield of azoxybenzene by the action of magnesium and methyl alcohol on nitrobenzene. The magnesium methylate formed has no reducing action. It is chiefly the hydrogen liberated when magnesium reacts with methyl alcohol that reduces the nitrobenzene.

Snowden (15) 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. Klinger's method is comparatively simple and 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 or hydrazobenzene.

An historical development of the Cannizzaro reaction may be found in the Ph. D. thesis of J. W. Price (U.C. 1931).

No references on the reduction of nitrobenzene by metallic lead and sodium hydroxide could be found in the literature.

THEORETICAL

(A) THE KLINGER REACTION

While a reaction mechanism scheme has been proposed for the Klinger reaction (herewith repeated for the sake of reference),

$$CH_3OH + NaOH \rightleftharpoons CH_3ONa + H_2O \qquad a$$

$$CH_3ONa + NaOH \longrightarrow CH_2(ONa)_2 + 2H \qquad b$$

$$CH_2(ONa)_2 + H_2O \longrightarrow CH_2O + 2H\,ONa \qquad c$$

$$\Sigma a,b,c \qquad CH_3OH \longrightarrow CH_2O + 2H \qquad A$$

$$CH_2O + NaOH \longrightarrow HCOONa + 2H \qquad B$$

$$\Sigma A,B \qquad CH_3OH + NaOH \longrightarrow HCOONa + 4H \qquad C$$

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

$$\Sigma 3C,D \quad 4C_6H_5NO_2 + 3CH_3OH + 3NaOH \longrightarrow 3HCOONa + 2(C_6H_5N)_2O + 6H_2O \qquad E$$

one cannot state with certainty which of the reactions A or B or their summation C is the source of the liberated hydrogen.

Since there is an excess of sodium hydroxide and methyl alcohol i.e., more than enough to reduce the amount of nitrobenzene used in conformity with the equation for the Klinger reaction E, it is possible that reactions A or B or their summation reaction C, is the source of the liberated hydrogen.

Hoping that further light might be shed upon this question, an extensive study was made to determine the effect of increasing concentrations of both sodium hydroxide and nitrobenzene upon the Klinger reaction.

(B) THE KLINGER REACTION IN THE PRESENCE OF LEAD

As previously noted, the addition of lead to the Klinger reaction mixtures not only (a) increases greatly the yield of

hydrogen, but also (b) with higher concentration of sodium hydroxide leads to the formation of azobenzene in addition to azoxybenzene. How does lead affect these changes? Several suggestions may be considered.

1. If lead catalyzes any or all of the intermediate reactions, A, B or C, the increased evolution of hydrogen may be thereby explained.

2. If all of the theoretically available hydrogen is not evolved, it would naturally effect more extensive reduction, thereby accounting for the formation of azobenzene in addition to the azoxybenzene. In fact, all runs with lead present yielded abundant quantities of hydrogen accompanied by the formation of azobenzene.

3. Another explanation for the increased formation of hydrogen is suggested by the possibility of the interaction between lead and sodium hydroxide according to the equation:

$$Pb + 2NaOH \longrightarrow Na_2PbO_2 + 2H \qquad F$$

While lead and an aqueous sodium hydroxide or methyl alcohol solution of sodium hydroxide do not react according to the above equation under the conditions that were employed, lead will react with fused sodium hydroxide. Accordingly, one would hesitate to postulate this reaction as the source of the hydrogen.

4. Lastly, an explanation may be found in the well-known property of lead in the presence of oxygen and water to form lead hydroxide and hydrogen peroxide in conformity with equations:

$$Pb + 2H_2O + O_2 \longrightarrow Pb(OH)_2 + H_2O_2 \qquad G$$

$$Pb(OH)_2 + 2NaOH \longrightarrow Na_2PbO_2 + 2H_2O \qquad H$$

It has been shown by Fry and Paine (16) that hydrogen peroxide will, in dilute solutions, oxidize methyl alcohol to formic acid with the liberation of hydrogen according to equations:

$$2CH_3OH + 2H_2O_2 \longrightarrow 2HCHO + 4H_2O \qquad a$$

$$2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2 \qquad b$$

$$\Sigma a,b \qquad 2CH_3OH + 3H_2O_2 \longrightarrow 2HCOOH + 4H_2O + H_2 \qquad I$$

Accordingly, in reaction mixtures of lead, sodium hydroxide, methyl alcohol, and nitrobenzene, it is conceivable that the nitrobenzene supplies the oxygen necessary for the above reaction and the hydrogen peroxide intermediately formed would in turn react with the methyl alcohol to yield hydrogen.

The following reaction mechanism scheme embodies the above changes:

$$4C_6H_5NO_2 \longrightarrow 2(C_6H_5N)_2O + 6O \qquad a$$

$$3Pb + 6H_2O + 6O \longrightarrow 3Pb(OH)_2 + 3H_2O_2 \qquad b$$

$$3Pb(OH)_2 + 6NaOH \longrightarrow 3Na_2PbO_2 + 6H_2O \qquad c$$

$$\Sigma a,b,c \qquad 3Pb + 6NaOH + 4C_6H_5NO_2 \longrightarrow 3Na_2PbO_2 + 2(C_6H_5N)_2O + 3H_2O_2 \qquad J$$

Thus, it is conceivable that lead and sodium hydroxide may effect the reduction of nitrobenzene to azoxybenzene accompanied by the formation of hydrogen peroxide (equation J). Furthermore, the hydrogen peroxide thus formed may oxidize the methyl alcohol to formic acid with the liberation of hydrogen according to the above noted reaction I.

Reactions J, I and D may occur simultaneously. The experimental part of this investigation is designed to test the validity of the above suggestions.

EXPERIMENTAL

All of the reactions investigated in this study were conducted in duplicate. In general, the reactions were run in one liter three-necked, round-bottomed flasks. The large center neck of the flask was connected with a mechanical stirrer through a mercury seal in order to provide constant stirring for the duration of the reaction. The flasks were securely attached to reflux condensers of thirty centimeters length. The upper end of the inner tube of the condenser was fitted with glass tubing to conduct the evolved hydrogen through a gas washing bottle into a graduated eight-liter bottle, serving as a gasometer. The third neck served for the introduction of the components of the reaction mixtures. All connections were made of heavy rubber tubing, wired and sealed to prevent any leakage of gas. The hydrogen was collected by displacement of water from the gasometer. The flasks containing the reaction mixtures were heated, in each experimental run, on constant-level water baths, kept at the boiling temperature, for the same length of time, four hours.

The volume of hydrogen evelved in each run was calculated to standard conditions and the identity and yields of the reduction products of the reactions were determined by methods that will be explained for each phase of the investigation.

(A) THE KLINGER REACTION

The Klinger reaction was studied with the view of determining not only the per cent theory yields of azoxybenzene, but, more especially, the volumes of hydrogen evolved when concentrations of both sodium hydroxide and nitrobenzene were relatively varied.

The volume of the reaction mixture in each of the runs, conducted in duplicate, was about 350cc. Three different concentrations of sodium hydroxide were used; namely, 100g., 150g., and 200g. dissolved respectively in a mixture of 200cc. of methyl alcohol and 100cc. of water. To each of these mixtures were added respectively, 0.2, 0.3, and 0.4 moles of nitrobenzene. Thus, this part of the investigation entails nine experimental runs in duplicate.

The following is a description of an experimental run:

Twenty-five grams (0.2 mole) of nitrobenzene was dissolved in 200cc. of absolute methyl alcohol contained in a one liter three-necked flask equipped with a mechanical stirrer and a return condenser. The mechanical stirrer was connected to the flask through a mercury seal to prevent loss of volatile products. The return condenser was connected by securely sealed glass tubing to the gasometer. 100g. of distilled water and 100g. of C.P. sodium hydroxide pellets were then added to the flask by means of the third neck. The flask was immediately sealed with a rubber stopper because sodium hydroxide reacts immediately with water. Considerable heat was liberated.

The flask containing the reaction mixture was then heated on a constant-level water bath at boiling temperature for four hours, at the end of which time the reactions were practically completed.

The excess methyl alcohol was distilled off and the reaction mixture steam-distilled to remove any remaining traces of unreacted nitrobenzene. The reaction residue, thus obtained, consisted of a hot concentrated aqueous solution of sodium hydroxide carrying the insoluble reduction product of nitrobenzene (azoxybenzene), in a melted state, floating on the surface.

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

Any hydrogen gas evolved during the reaction was collected in the gasometer and measured. A preliminary blank run was made to determine the volume of air forced into the gasometer by the methyl alcohol vapors. The volume of hydrogen, thus corrected, was computed to standard conditions.

The following table I indicates in column 1 the number of each duplicate run. The concentrations of sodium hydroxide and nitrobenzene are given in columns 2 and 3 respectively. Column 4 records the volume of hydrogen calculated to standard conditions. In order to compare as closely as possible the ratios of the increasing volumes of hydrogen liberated to the corresponding increasing quantities of nitrobenzene present in the several reaction mixtures, the volumes of hydrogen (column 4) were divided by a common divisor. The quotients are tabulated in column 5. Column 6 records the yield of azoxybenzene in grams, and column 7 records the corresponding per cent theory yield.

TABLE I

KLINGER REACTION DATA

1 Run	2 Conc. of NaOH g.	3 Conc. of $C_6H_5NO_2$ mols	4 Volume of H_2 (STP) cc.	5 Ratio of H_2 yields	6 Azoxy-benzene yield g.	7 Theory yield azoxybenzene %
I a	100	.2	163	1.61	18.8	93.0
b	100	.2	163	1.61	18.8	92.8
II a	100	.3	371	3.67	28.9	95.8
b	100	.3	335	3.31	28.8	95.6
IIIa	100	.4	410	4.06	37.9	94.2
b	100	.4	370	3.72	38.1	94.8
IV a	150	.2	622	2.54	19.1	94.9
b	150	.2	590	2.26	19.0	94.5
V a	150	.3	790	3.02	29.0	96.0
b	150	.3	772	2.96	29.0	96.0
VI a	150	.4	967	3.70	38.4	95.5
b	150	.4	967	3.70	38.3	95.2
VIIa	200	.2	1012	2.21	19.2	95.4
b	200	.2	976	2.16	19.2	95.4
VIIIa	200	.3	1322	2.92	29.0	96.0
b	200	.3	1282	2.83	29.0	96.0
IX a	200	.4	1776	3.93	38.5	95.7
b	200	.4	1776	3.93	38.4	95.5

Examination of the data of above table I reveals the following facts:

1. The per cent theory yields of azoxybenzene in all the runs were remarkably uniform, variations lying between 92 and 96% theory. This uniformity is undoubtedly due to the fact that in every run there was an abundant excess of the reducing agent, sodium methylate, present to insure complete reduction of the nitrobenzene to azoxybenzene.

2. With increasing concentrations of nitrobenzene and identical concentrations of sodium hydroxide, increasing volumes of hydrogen were obtained.

3. The quotients noted in column 5 comparing the increasing yields of hydrogen obtained with successively increasing concentrations of nitrobenzene, .2, .3, and .4 moles, respectively, show that there is no exact mathematical proportion existing between the concentrations of the nitrobenzene and the hydrogen evolved in the runs I, II, and III with 100 grams concentration of sodium hydroxide and in runs IV, V, and VI with 150 grams concentration of sodium hydroxide, but it is of particular note that the increasing yields of hydrogen in runs VII, VIII, and IX with 200 grams concentration of sodium hydroxide are virtually directly proportional to the increasing concentrations, .2, .3, and .4 moles of the nitrobenzene present.

4. With increasing concentrations of sodium hydroxide and identical concentrations of nitrobenzene, the volumes of hydrogen evolved also increased, but not in mathematical proportions.

This new discovery that hydrogen is evolved during the course of the Klinger reaction and that with increasing concentrations either of sodium hydroxide or of nitrobenzene, increasing quantities of hydrogen are evolved, is not easy to explain.

If the occurrence of any or all of the reactions A, B, and C in the reaction mechanism scheme is to serve as the explanation of the liberation of hydrogen, it is correct to conclude that increasing volumes of hydrogen would be liberated with increasing quantities of sodium hydroxide. But, none of the reactions A, B, and C entail nitrobenzene, increasing concentrations of which also promote increased yields of hydrogen.

If reaction C, $CH_3OH + NaOH \longrightarrow HCOONa + 4H$, the summation of reactions A and B, is concurrent with the Klinger reaction E, $4C_6H_5NO_2 + 3CH_3OH + 3NaOH \longrightarrow 3HCOONa + 2(C_6H_5N)_2O + 6H_2O$, then, since reaction C and E each yield sodium formate, it may be concluded that the yields of sodium formate obtained would be in excess of the yields of sodium formate in conformity with reaction E. In other words, if more sodium formate is obtained than would correspond to the yield of azoxybenzene (reaction E), then the excess sodium formate would be a product of reaction C which yields both sodium formate and free hydrogen.

In order to compare the yields of hydrogen, sodium formate, and nitrobenzene, several experiments were conducted. First, the Klinger reaction was conducted wherein 150g. of sodium hydroxide, .3 mole of nitrobenzene, 200cc. of methyl alcohol, 100cc. of water were heated for four and one-half hours. At the end of each successive ten minutes the yield of hydrogen was recorded.

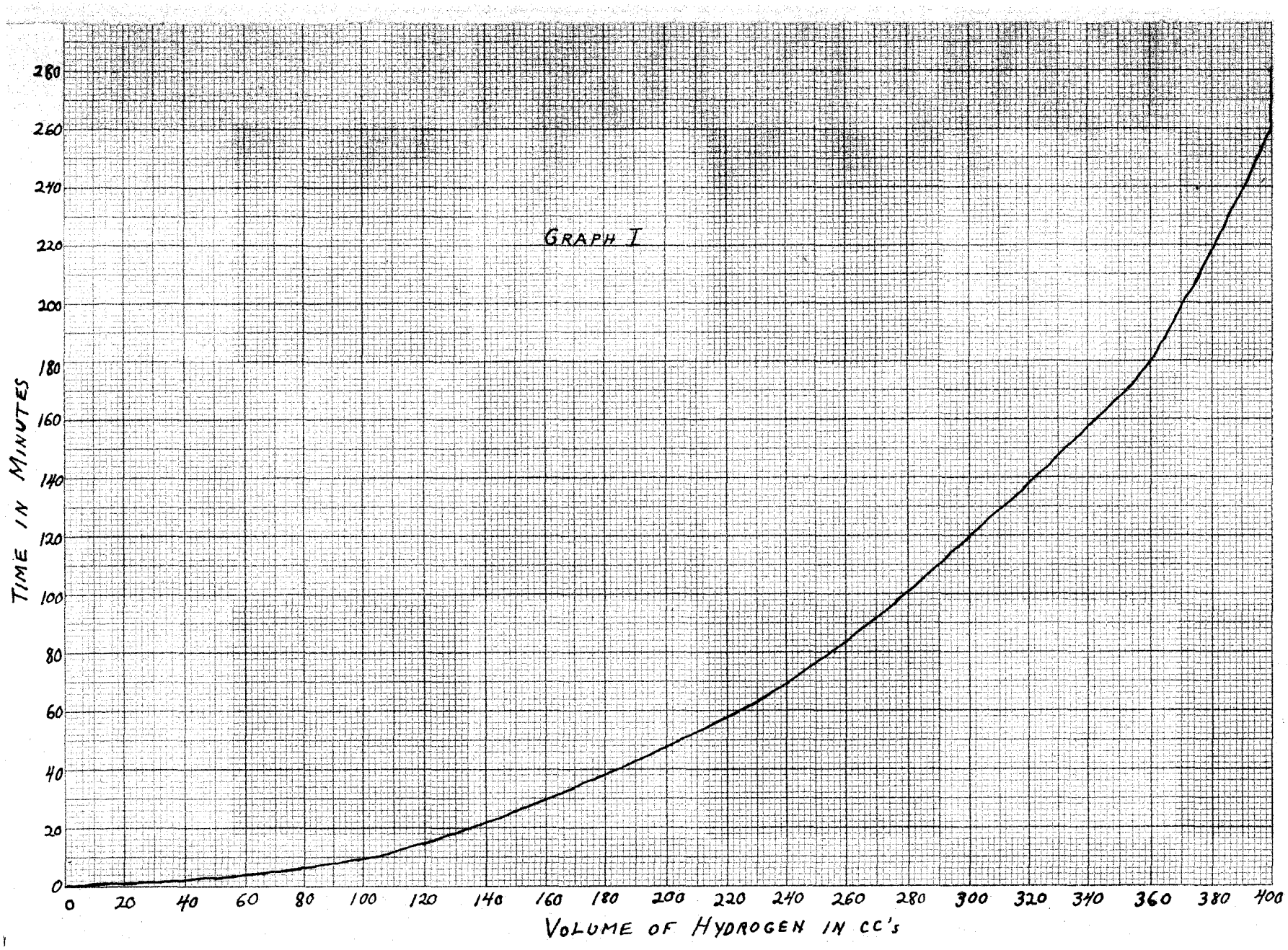
The following Table II and Graph I revealed that of the total volume (400cc.) of hydrogen obtained, more than 55%, namely , 225cc., was evolved in the course of one hour. At the end of two hours, 300cc. or 75%, and at the end of three hours, only 360cc. or 90% of the total yield of hydrogen was obtained. The data show conclusively that the reactions responsible for the formation of hydrogen predominantly occur during the earlier part of the total time required for the completion of the reaction.

Second, in order to determine the ratio between the yields of sodium formate and hydrogen, the above reaction mixture was again used in four experimental runs of one, two, three, and four hours duration. At the end of each run, the reaction was stopped by diluting the reaction mixture with cold water to a

volume of one liter. The reduction product (azoxybenzene) was removed by repeated (four) extractions with ether. The diluted reaction mixture was then boiled to expel any ether that remained dissolved in the water, cooled and made up to a volume of exactly two liters. An aliquot part, 50cc. of this solution, was pipetted off and made up to a volume of 500cc.. The yields of sodium formate were determined employing 50cc. samples of the latter solution which corresponds to a 1:400 dilution. The aliquot portion was first acidified with dilute sulfuric acid and then made alkaline with sodium carbonate. The solution was then heated to boiling and potassium permanganate run in slowly until there was about 2-3cc. excess as shown by a pink color. The solution must be kept on a hot plate during the titration. Enough dilute sulfuric acid is added to the solution to make it definitely acid and then oxalic acid is run in slowly until all the manganese dioxide has disappeared. Finally, the solution is titrated with potassium permanganate until the end-point is reached.

For a complete description of the alkaline permanganate-oxalate method for the determination of the yields of sodium formate, the method employed by Bowman (17) was used.

The following table gives in column 1 the number and length of time for each duplicate run. Column 2 indicates the volume of potassium permanganate used. Column 3 indicates the volume of oxalic acid used. Column 4 records the volume of potassium permanganate equivalent to the volume of oxalic acid (column 3). The volume of permanganate equivalent to sodium formate is given in column 5. The total yield of sodium formate for each run is indicated in column 6. Column 7 records the volume of hydrogen



liberated, and column 8 shows the ratio of sodium formate (column 6) to hydrogen (column 7).

TABLE II

1	2	3	4	5	6	7	8
Run hrs.	Total $KMnO_4$ (.0975N) cc.	$H_2C_2O_4$ (.1000N) cc.	$KMnO_4$ (.0975N) $H_2C_2O_4$ cc.	$KMnO_4$ (.0975N) HCOONa cc.	Total yield HCOONa g.	Yield of H_2 (STP) cc.	Ratio $\frac{HCOONa}{H}$
Ia ½	23.80	9.20	9.44	14.36	19.040	200	.0950
a 1	23.80	9.20	9.44	14.36	19.040	200	.0950
b 1	24.80	10.20	10.46	14.34	19.016	200	.0950
b 1	24.80	10.20	10.46	14.34	19.016	200	.0950
IIa 2	24.75	10.00	10.26	14.49	19.212	270	.0710
a 2	24.75	10.00	10.26	14.49	19.212	270	.0710
b 2	24.70	10.00	10.26	14.44	19.147	270	.0710
b 2	24.70	10.00	10.26	14.44	19.147	270	.0710
IIIa3	24.80	10.00	10.26	14.54	19.280	325	.0593
a3	24.75	10.00	10.26	14.49	19.212	325	.0593
b3	24.85	10.00	10.26	14.59	19.348	325	.0593
b3	24.80	10.00	10.26	14.54	19.280	325	.0593
IVa 4	24.85	10.00	10.26	14.59	19.348	356	.0543
a 4	24.85	10.00	10.26	14.59	19.348	356	.0543
b 4	24.85	10.00	10.26	14.59	19.348	356	.0543
b 4	24.80	10.00	10.26	14.54	19.280	356	.0543

The data show that while the ratio of the sodium formate to the hydrogen successively decreases, the total yield of sodium formate is practically constant--a variation of only one and one-half per cent between the minimum yield, 19.000 grams, and the maximum yield, 19.348 grams.

While it has never been found possible to determine accurately the yield of azoxybenzene, unless the nitrobenzene has been practically completely reduced, and the nitrobenzene was never completely reduced unless the reaction period was at least of four hours duration, it is particularly important to record that the 19 gram yield of sodium formate obtained at the

end of one hour, when the nitrobenzene was far from completely reduced, is much in excess of the yield of sodium formate(15g), which would be formed in conformity with the Klinger reaction E. These experimental observations lead definitely to the conclusion that the evolution of the hydrogen during the course of the Klinger reaction must be due to the concurrence of another reaction wherein sodium formate is formed, namely, reaction B between formaldehyde and sodium hydroxide, $CH_2O + NaOH \longrightarrow HCOONa + H_2$,

Since a 15 gram yield of sodium formate corresponds to practically complete reduction of nitrobenzene according to the Klinger equation, and a19 gram yield of sodium formate was obtained, the 4 grams excess sodium formate should be the equivalent to a hydrogen yield according to equation B, of 1317cc. hydrogen. It will be noted in Table II that the yields of hydrogen varied from 200cc. to 356cc., only a small fraction of the hydrogen theoretically obtainable in conformity with reaction B. This fact leads to the conclusion that the low yield of hydrogen may be due to participation of the greater part of the theoretically available hydrogen in another reaction occurring independently of the reduction of nitrobenzene.

This other concurrent reaction may be assumed to be the reduction of the intermediately formed formaldehyde. The intermediate formation of formaldehyde according to equation A in the reaction mechanism scheme __ $CH_3OH \longrightarrow CH_2O + 2H$, has been proven to occur by the research of Fry and Bowman (17) on the effect of organic bases upon the extent and mechanism of the reducing action of sodium methylate on nitrobenzene and azoxybenzene, for when isoamylamine was added to the Klinger reaction mixture, a compound of formaldehyde with isoamylamine, presumably isoamyl methyleneimide was found.

Since formaldehyde is readily reducible to methyl alcohol by hydrogen, it follows that the Cannizzaro reaction with formaldehyde may occur. This reaction has been shown by Fry, Uber, and Price (18) to occur in two independent steps;

$$HCHO + NaOH \longrightarrow HCOONa + 2H \qquad B$$

$$\underline{HCHO + 2H \longrightarrow CH_3OH}$$

$$2HCHO + NaOH \longrightarrow HCOONa + CH_3OH$$

In other words, the first step of the Cannizzaro reaction mechanism, equation B, will explain the excess yield of sodium formate and while a part of the hydrogen formed is liberated, the remainder functions in the reduction of formaldehyde to methyl alcohol which is the second step of the Cannizzaro reaction mechanism.

The foregoing facts may serve to explain why increased concentrations of nitrobenzene in the Klinger reaction lead to increasing yields of hydrogen. As stated by Fry and Bowman (17), the finding of formaldehyde in the reaction mixture is confirmation of the intermediate type reaction equations previously postulated. Their summation may be indicated as follows:

$$3CH_3OH + 3NaOH \longrightarrow 3CH_3ONa + 3H_2O \qquad a$$

$$3CH_3ONa + 3NaOH \longrightarrow 3CH_2(ONa)_2 + 6H \qquad b$$

$$3CH_2(ONa)_2 + 3H_2O \longrightarrow 3CH_2O + 6NaOH \qquad c$$

$$2C_6H_5NO_2 + 6H \longrightarrow (C_6H_5N)_2O + 3H_2O \qquad c'$$

$$\sum a,b,c,c' \quad 2C_6H_5NO_2 + 3CH_3OH \longrightarrow 3CH_2O + (C_6H_5N)_2O + 3H_2O \qquad K$$

This summation equation K accounts for the intermediate formation of formaldehyde in the reaction mixture. Accordingly, increasing concentrations of nitrobenzene would yield more formaldehyde intermediately, which in turn would function in the Cannizzaro reaction as described above in equation B to

increase the yield of free hydrogen.

Part(A) may be summarized briefly as follows: in the various Klinger reaction mixtures investigated;

1. The nitrobenzene was practically quantitatively reduced to azoxybenzene.

2. The yields of sodium formate obtained were invariably in excess of the yield required by the equation for the Klinger reaction.

3. The evolution of hydrogen occurred in each reaction.

4. Increasing yields of hydrogen were obtained when increasing concentrations either of sodium hydroxide or nitrobenzene were employed.

5. An explanation for the evolution of hydrogen and the excessive yields of sodium formate has been suggested, based upon the intermediate formation of formaldehyde and its participation in the concurrent Cannizzaro reaction.

(B) THE KLINGER REACTION IN THE PRESENCE OF LEAD

The Klinger reaction runs as described and conducted in part (A) were repeated with the addition to each reaction mixture of .4 moles of Baker's C.P.Analyzed granular lead. The mechanical stirrer was adjusted to such a speed as would insure adequate mixing of the components of the reaction mixture for the length of time of each complete run.

In each run conducted, the nitrobenzene was completely reduced to mixtures of azoxy- and azobenzene. The reaction mixtures were diluted to a volume of one liter with distilled water and decanted from the unreacted lead. The lead was repeatedly washed with water, acetone, then dried and weight recorded. The azoxy- and azobenzene were extracted with ether

from the alkaline reaction mixture containing the reacted lead in the form of soluble sodium plumbite. After evaporating off all the ether used in the extraction, the residue consisted of a mixture of azoxy- and azobenzene. The percentages of azoxy- and azobenzene contained in each reaction residue were determined by the freezing point method described by Bowman (Ph.D.Thesis U.C. 1929). Bowman's curve of the freezing points of mixtures of azoxy- and azobenzene was used throughout this investigation.

In every run conducted in the presence of lead, hydrogen was more abundantly evolved than in the runs of part (A) in the absence of lead.

The following table III indicates in column 1 the number of each run with duplicate data. Columns 2 and 3 record the concentrations of sodium hydroxide and nitrobenzene, respectively. Column 4 records the weight of lead used at the beginning of each reaction. Column 5 indicates the weight of lead recovered at the end of each reaction. Column 6 indicates the weight of lead reacted. Column 7 records the total volume of hydrogen liberated calculated to standard conditions.

In order to indicate the ratios of the increasing volumes of hydrogen liberated accompanying the corresponding increasing quantities of nitrobenzene present in the several reaction mixtures, total volumes of hydrogen evolved (column 7) were divided by a common divisor. The quotients are tabulated in column 8. Similarly, column 10 records the quotients for the excess volumes of hydrogen (column 9).

Since more hydrogen is obtained in each run with lead present than when lead was absent, column 9 records the excess volumes of

hydrogen evolved when lead was present. In other words, for each and every run the amount of hydrogen evolved, as noted in Table I of part (A), was subtracted from the corresponding runs wherein lead was present. Column 11 indicates the combined yield in grams of the reduction products, azoxy- and azobenzene. The percentages of azoxy- and azobenzene in the total yield of reduction products are recorded in column 12.

TABLE III

KLINGER REACTION IN THE PRESENCE OF LEAD

1 Run	2 Conc. of NaOH	3 Conc. of $C_6H_5NO_2$	4 Pb used	5 Pb recovered	6 Pb reacted	7 Total volume of H_2 (STP)	8 Ratio of H_2 yields	9 Excess volume of H_2 (STP)	10 Ratio of H_2 yields	11 Total yield reduction products	12 Percentage ratios (azoxy:azo) azoxybenzene	azobenzene
	g.	mols	g.	g.	g.	cc.		cc.		g.	%	%
I a	100	.2	82.9	64.5	18.4	2217	1.98	2054	2.03	18.8	76.0	24.0
b	100	.2	82.9	64.6	18.3	2285	2.05	2122	2.09	18.9	76.0	24.0
II a	100	.3	82.9	64.4	18.5	3329	2.98	2976	2.94	27.9	76.0	24.0
b	100	.3	82.9	64.5	18.4	3387	3.04	3034	3.00	28.0	76.0	24.0
IIIa	100	.4	82.9	64.6	18.3	4399	3.95	4009	3.95	37.7	76.0	24.0
b	100	.4	82.9	64.3	18.6	4390	3.94	4000	3.95	37.9	76.0	24.0
IV a	150	.2	82.9	54.1	28.8	1818	2.08	1212	1.99	18.5	31.5	68.5
b	150	.2	82.9	54.2	28.7	1774	2.03	1168	1.92	18.6	31.5	68.5
V a	150	.3	82.9	54.4	28.5	2622	3.01	1841	3.03	26.5	31.5	68.5
b	150	.3	82.9	54.1	28.8	2674	3.07	1893	3.07	26.3	31.5	68.5
VI a	150	.4	82.9	54.2	28.7	3406	3.91	2439	4.01	35.0	31.5	68.5
b	150	.4	82.9	54.1	28.8	3365	3.87	2398	3.94	34.9	31.5	68.5
VIIa	200	.2	82.9	49.7	33.2	2153	2.07	1159	1.98	18.6	20.0	80.0
b	200	.2	82.9	49.7	33.2	2118	2.04	1124	1.92	18.7	20.0	80.0
VIIIa	200	.3	82.9	49.6	33.3	3063	2.95	1761	3.01	26.5	20.0	80.0
b	200	.3	82.9	49.7	33.2	3098	2.98	1796	3.07	26.6	20.0	80.0
IX a	200	.4	82.9	49.6	33.3	4159	4.00	2383	4.07	35.2	20.0	80.0
b	200	.4	82.9	49.6	33.3	4093	3.94	2317	3.96	35.0	20.0	80.0

The data of the above table leads to the following observations:

1. With respect to the quantities of lead undergoing reaction, a comparison of the data of columns 2, 3, 4, 5, 6, and 7 reveals that:

a. With a fixed concentration of sodium hydroxide and increasing concentrations of nitrobenzene, identical amounts of lead have reacted. With concentrations of 100, 150, and 200 grams of sodium hydroxide the quantities of lead reacting are in the ratios of 18.4, 28.7, and 33.25 grams,

respectively. These quantities may be expressed in simple ratios of 2.06:3.21:3.71 which are of the same relative order but not the exact ratios of the sodium hydroxide gram concentrations, 2:3:4. In other words, the increasing amounts of lead reacting depend directly upon the increasing quantities of sodium hydroxide in the reaction mixtures and not upon the increasing concentrations of nitrobenzene.

2. With respect to the volumes of hydrogen liberated, the data of column 7 reveals that:

a. The total volumes of hydrogen obtained when lead is present are far in excess of the total volumes of hydrogen formerly liberated when lead is absent (column 4, Table I, part A). If the yields of hydrogen obtained in the runs without lead be subtracted from the total yields of hydrogen evolved with lead, the differences (column 9, Table III) reveal the excess liberation of hydrogen occasioned by the presence of lead.

b. With a fixed concentration of sodium hydroxide, both the total volumes of hydrogen (column 7) and the excess volumes of hydrogen (column 9) evolved are found to increase as the concentration of nitrobenzene is increased.

c. The quotients in columns 8 and 10 indicating the ratios of the relative amounts of hydrogen evolved with increasing concentrations of nitrobenzene are, indeed, significant in revealing that, in the runs with any given concentration of sodium hydroxide (100g., 150g., and 200g.), the yields of hydrogen with increasing molar concentrations of nitrobenzene (.2, .3, and .4) stand to each other in the same ratios 2:3:4. Deviations from these whole numbers are within the limits of experimental error. This noteworthy relationship holds not only

for the total volumes of hydrogen but also for the excess volumes of hydrogen evolved.

3. Concerning the effects of varying concentrations of sodium hydroxide and nitrobenzene, reacted lead, and volumes of total and excess hydrogen evolved upon the respective yields of azoxy- and azobenzene, the following observations are pertinent:

a. In every experimental run, the nitrobenzene was practically completely reduced to yield mixtures of azoxy- and azobenzene.

b. In duplicate runs I, II, and III, with 100 grams of sodium hydroxide and .2, .3, and .4 moles, respectively, of nitrobenzene: (i) the same quantity of lead, 18.4 grams average, was converted into sodium plumbite; (ii) very small differences were found between the total volumes and excess volumes of hydrogen evolved; (iii) the composition of each reaction mixture product was identical, i.e., each contained 76% azoxybenzene and 24% azobenzene.

c. In duplicate runs IV, V, and VI with 150 grams of sodium hydroxide and .2, .3, and .4 moles, respectively, of nitrobenzene: (i) identical but greater quantities of lead, 28.7 grams average, were converted into sodium plumbite; (ii) the total volumes of hydrogen evolved were, in general, 50% greater than the volumes of excess hydrogen; and (iii) the composition of each reaction mixture product was identical but contained less azoxybenzene and more of azobenzene, i.e., 31.5% of the former and 68.5% of the latter.

d. In duplicate runs VII, VIII, and IX with 200 grams of sodium hydroxide and .2, .3, and .4 moles, respectively, of nitrobenzene: (i) even greater identical quantities of lead, 33.25 grams average, were converted into sodium plumbite; (ii) the total volumes of hydrogen evolved were, in general, 80% greater than the volumes of excess hydrogen; and (iii) the composition of each reaction mixture product was identical, but contained less azoxybenzene and more azobenzene, 20% of the former and 80% of the latter.

(C) FURTHER STUDY OF THE EFFECT OF LEAD

To study further the effect of the presence of lead in Klinger reaction mixtures, experimental runs were conducted as exactly as described in part (B), employing a constant initial concentration of nitrobenzene, .2 moles, with increasing concentrations of sodium hydroxide, namely, 100, 150, and 200 grams, but in the successive reaction mixtures decreasing quantities of lead, .4, .3, .2, .1, .065, .03, .02, and .01 moles, were incorporated.

The data thus obtained is embodied in the following tables, IV, V, and VI.

In each table, column 1 records the number of each run in duplicate; column 2, the weight of lead used; column 3, the weight of lead reacted; column 4, the total yield of reduction product; column 5, the total volume of hydrogen evolved; column 6, the excess volume of hydrogen, i.e., the difference between the total volume and the corresponding volume of hydrogen evolved concurrently with the Klinger reactions conducted in the absence of lead, as noted in Table I, Part (A); and columns 7 and 8, the percentages of azoxybenzene and azobenzene, respectively, present in the reaction mixtures.

TABLE IV

(Reaction mixture: 100 grams NaOH, .2 moles $C_6H_5NO_2$)

1		2	3	4	5	6	7	8
Run		Total Pb used g.	Pb reacted g.	YIeld reduction products g.	Total H_2 (STP) cc.	Excess volume of H_2(STP) cc.	Azoxy-benzene %	Azo-benzene %
I	a	82.88	18.37	18.8	2217	2054	76.0	24.0
	b	82.88	18.29	18.9	2285	2122	76.0	24.0
II	a	62.16	18.06	18.8	2013	1850	76.0	24.0
	b	62.16	18.10	18.8	2105	1942	76.0	24.0
III	a	41.44	18.16	18.8	1955	1792	78.0	22.0
	b	41.44	18.04	18.8	2035	1872	78.0	22.0
IV	a	20.72	10.22	18.7	1974	1811	82.5	17.5
	b	20.72	10.38	18.8	1973	1810	82.5	17.5
V	a	13.47	7.67	18.8	1782	1619	87.5	12.5
	b	13.47	7.76	18.9	1816	1653	87.5	12.5
VI	a	6.22	2.72	19.0	1140	977	96.5	3.5
	b	6.22	2.67	19.0	1149	986	96.5	3.5
VII	a	4.14	2.69	19.0	1116	953	96.5	3.5
	b	4.14	2.66	19.1	1120	957	96.5	3.5
VIII	a	2.07	1.37	19.1	761	598	96.5	3.5
	b	2.07	1.32	19.0	783	619	96.5	3.5

TABLE V

(Reaction mixture: 150 grams NaOH, .2 moles $C_6H_5NO_2$)

1 Run		2 Total Pb used g.	3 Pb reacted g.	4 Yield reduction products g.	5 Total H_2 (STP) cc.	6 Excess H_2 (STP) cc.	7 Azoxy-benzene %	8 Azo-benzene %
I	a	82.88	28.80	18.8	1818	1212	31.5	68.5
	b	82.88	28.70	18.8	1774	1168	31.5	68.5
II	a	62.16	27.66	18.8	1773	1167	36.0	64.0
	b	62.16	27.59	19.0	1758	1152	36.0	64.0
III	a	41.44	19.24	18.8	1485	879	41.0	59.0
	b	41.44	19.34	18.9	1519	913	41.0	59.0
IV	a	20.73	12.42	18.8	1447	841	58.0	42.0
	b	20.73	12.49	18.9	1415	809	58.0	42.0
V	a	13.47	7.47	18.9	1429	823	80.0	20.0
	b	13.47	7.56	18.9	1401	795	80.0	20.0
VI	a	6.22	2.42	19.0	809	203	94.5	5.5
	b	6.22	2.38	19.0	818	212	94.5	5.5
VII	a	4.14	2.64	19.1	813	207	94.5	5.5
	b	4.14	2.61	19.1	815	209	94.5	5.5
VIII	a	2.07	1.27	19.0	734	128	94.5	5.5
	b	2.07	1.29	19.1	744	138	94.5	5.5

TABLE VI

(Reaction mixture: 200 grams NaOH, .2moles $C_6H_5NO_2$)

1		2	3	4	5	6	7	8
Run		Total Pb used g.	Pb reacted g.	Yield reduction products g.	Total H_2 (STP) cc.	Excess H_2 (STP) cc.	Azoxy-benzene %	Azo-benzene %
I	a	82.88	33.24	18.5	2153	1159	20.0	80.0
	b	82.88	33.28	18.5	2118	1124	20.0	80.0
II	a	62.16	25.36	18.5	1844	850	24.5	75.5
	b	62.16	25.45	18.5	1868	874	24.5	75.5
III	a	41.44	19.54	18.6	1625	631	36.0	64.0
	b	41.44	19.60	18.6	1660	666	36.0	64.0
IV	a	20.72	15.32	18.7	1526	532	52.5	47.5
	b	20.72	15.44	18.7	1557	563	52.5	47.5
V	a	16.58	11.18	18.8	1369	375	68.0	32.0
	b	16.58	11.25	18.8	1378	384	68.0	32.0
VI	a	12.43	7.45	18.9	1246	252	76.0	24.0
	b	12.43	7.59	18.9	1261	267	76.0	24.0
VII	a	6.22	1.41	18.9	1045	51	92.0	8.0
	b	6.22	1.38	18.9	1041	47	92.0	8.0
VIII	a	4.14	1.40	19.0	1089	95	94.0	6.0
	b	4.14	1.44	19.0	1095	101	94.0	6.0
IX	a	2.07	1.32	19.0	1001	11	94.5	5.5
	b	2.07	1.30	19.0	998	4	94.5	5.5

The data recorded in the tables IV, V, and VI, may be summarized as follows:

1. In all runs, the nitrobenzene was completely reduced to yield mixtures of azoxy- and azobenzene.

2. In all runs, with decreasing amounts of lead, both the total volumes and the excess volumes of hydrogen (columns 5 and 6) successively decrease, but not in exact mathematical ratios.

3. In all runs, with decreasing amounts of lead, the percentage of azoxybenzene increases, and the percentage of azobenzene decreases. In other words, increasing amounts of lead present in the reaction mixture increase the extent of the reduction, but not in mathematical proportion.

These observations will be subsequently discussed.

(D) REDUCTION OF NITROBENZENE BY LEAD AND SODIUM HYDROXIDE

Since it has been shown in parts (B) and (C) of this research, that the presence of lead in Klinger reaction mixtures not only augments the evolution of hydrogen but also furthers the extent of reduction of nitrobenzene, a study was undertaken to determine whether or not metallic lead and sodium hydroxide in the absence of methyl alcohol would effect reduction of nitrobenzene.

In order to secure homogeneous reaction mixtures, 200cc. of pyridine as a solvent for the nitrobenzene were substituted for the previously used 200cc. of methyl alcohol to which were added 100cc. of water, 100 grams of sodium hydroxide, 25 grams, or .2 moles of nitrobenzene, and 82.88 grams or .4 moles of lead. Reaction, duplicate runs, was conducted as previously described.

At the end of the runs the supernatant liquid containing unreacted nitrobenzene, azoxy- and azobenzene, sodium plumbite, red lead, pyridine and water was agitated by swirling. This held in suspension the finely divided red lead while the heavier unreacted lead remained in the bottom of the flask. The swirling liquid was then poured into a Buchner funnel. The unreacted lead was repeatedly washed with water and the washings also poured into the Buchner funnel. The remaining lead was subsequently dried and weight recorded.

The red lead remaining on the funnel was also washed, dried, and weighed. The filtrate was acidified with hydrochloric acid, thereby converting the pyridine into pyridinium hydrochloride and the sodium plumbite into soluble lead chloride. The unreacted nitrobenzene and the products of reduction were extracted with ether in a separatory funnel.

The ether extract was subjected to steam distillation, thereby separating the ether and nitrobenzene from the reduction products which were found to consist of azoxy- and azobenzene--the mixture of the two weighing 5.32 grams and 5.45 grams, in the respective duplicate runs. The freezing point determinations showed that these mixtures contained 4.52 grams of azoxybenzene with 0.80 grams of azobenzene and 4.63 grams of azoxybenzene with 0.82 grams of azobenzene.

Incidentally, to confirm the formation of the red lead, the weighed quantities recovered in the duplicate runs were respectively treated with dilute nitric acid, and the respective quantities of lead dioxide thereby formed were filtered, washed, dried, and weighed, and found to be equivalent in quantity to the initial amounts of red lead.

To explain the reduction of nitrobenzene, it is here assumed that sodium plumbite and red lead may be formed according to the following reactions (equations o and p):

$$Pb + 2NaOH \longrightarrow Na_2PbO_2 + 2H \qquad o$$

$$3Pb + 4H_2O \longrightarrow Pb_3O_4 + 8H \qquad p$$

While these reactions do not occur under ordinary circumstances, it is assumed that the hydrogen so formed effects the reduction of the nitrobenzene to azoxy- and azobenzene.

The extent of the occurrence of reaction p and the amount of hydrogen available for reduction therefrom can be calculated from the yields of red lead. The quantity of lead reacting according to equation o was calculated by subtracting the quantity of lead yielding red lead (equation p) from the total amount of lead participating in the reaction. Hence, the amount of hydrogen available for reduction according to equation o may be calculated from the amount of lead participating.

The reduction of nitrobenzene by hydrogen to azoxy- and azobenzene are represented by the following equations:

$$2C_6H_5NO_2 + 6H \longrightarrow (C_6H_5N)_2O + 3H_2O \qquad q$$

$$2C_6H_5NO_2 + 8H \longrightarrow (C_6H_5N)_2 + 4H_2O \qquad r$$

Thus, data available for calculating the theoretical quantity of hydrogen formed according to equations o and p and the total amount of hydrogen which would be required to effect the reduction of nitrobenzene to the found quantities of azoxy- and azobenzene were obtained.

Accordingly, if the quantity of hydrogen available through occurrence of reactions o and p is equal to the quantity of hydrogen required for the reactions q and r, then the assumptions proposed above are thereby substantiated.

The following Table VII records the above data and related equivalents.

TABLE VII

REDUCTION OF NITROBENZENE BY LEAD AND SODIUM HYDROXIDE

(Reaction mixture: $C_6H_5NO_2$, 25g.; C_6H_5N, 200cc.; NaOH, 100g.; H_2O, 100cc.; Pb, 82.88g.)

1	2	3	4	5	6	7
Run	Pb reacted g.	Pb_3O_4 found g.	$H_2 \simeq Pb_3O_4$ (equation p) (STP) cc.	$H_2 \simeq Na_2PbO_2$ (equation o) (STP) cc.	Azoxybenzene found g.	Azobenzene found g.
I	17.17	4.18	561	1434	4.52	.80
II	17.28	4.25	568	1438	4.63	.82

1	8	9	10	11	12
Run	$H_2 \simeq (C_6H_5N)_2O$ (equation q) (STP) cc.	$H_2 \simeq (C_6H_5N)_2$ (equation r) (STP) cc.	Total H_2 available cc.	Total H_2 reducing cc.	Theory H_2 used (11)÷(10) %
I	1534	392	1995	1926	96.9
II	1568	403	2006	1971	98.2

Examination of the data in the above table reveals that the volumes of the hydrogen used (column 12) in effecting the reduction of nitrobenzene to azoxy- and azobenzene (columns 6 and 7) are approximately 96.9 and 98.2 per cent, in respective runs I and II, of the total available hydrogen (column 10) through the concurrence of equations o and p.

Accordingly, it may be concluded that a mixture of lead and sodium hydroxide in the solvent medium of pyridine and water effects reduction of nitrobenzene chiefly to azoxybenzene and some azobenzene. While the quantity of nitrobenzene used, 25 grams, was not completely reduced, it may be calculated from the yields of azoxy- and azobenzene that approximately 27% of the nitrobenzene was reduced in conformity with the postulated reactions.

(E) THE REDUCTION OF NITROBENZENE BY SODIUM PLUMBITE

Since in the preceding part (D), the interaction of lead and sodium hydroxide with nitrobenzene was accompanied by the formation not only of sodium plumbite but also red lead, another investigation was suggested, namely, to determine whether or not sodium plumbite in alkaline solution would effect the reduction of nitrobenzene and be concomitantly oxidized to red lead.

In preliminary experimental tests, a solution of sodium plumbite was prepared by reacting .3 moles of lead chloride with 1.2 moles of sodium hydroxide in conformity with the equation, $PbCl_2 + 4\,NaOH \longrightarrow Na_2PbO_2 + 2NaCl + 2H_2O$. When nitrobenzene was added to the solution of sodium plumbite, heated to boiling and vigorously stirred, the nitrobenzene was reduced to azoxybenzene and the sodium plumbite was oxidized to red lead.

Since red lead is the equivalent to lead monoxide or sodium plumbite plus lead dioxide, the following equation would represent the oxidation of sodium plumbite to red lead and accompanying reduction of nitrobenzene to azoxybenzene:

$$9Na_2PbO_2 + 2C_6H_5NO_2 + 9H_2O \longrightarrow (C_6H_5N)_2O + 3Pb_3O_4 + 18NaOH$$

To test the validity of this assumption, duplicate runs were conducted as noted in the description of the preliminary tests above.

The reaction mixture was actively stirred and boiled for four hours. After cooling, the unreduced nitrobenzene and reduction product were extracted with ether. Steam distillation of the ether extract carried over both the ether, the nitrobenzene, and the residual azoxybenzene, which after

drying and weighing, was found to melt correctly at 36°C.

The red lead formed was filtered, dried and weight recorded. As before, the identity of the red lead was confirmed by treatment with dilute nitric acid which converted it into the equivalent quantity of lead dioxide.

The following table VIII records the data thus obtained:

TABLE VIII

REDUCTION OF NITROBENZENE BY SODIUM PLUMBITE

(Reaction mixture: $C_6H_5NO_2$, 25g.; Na_2PbO_2, 85.56g.; H_2O, 100cc.)

1	2	3	4	5
Run	Pb_3O_4 found g.	Pb_3O_4 theory yield (equation S) %	Azoxybenzene found g.	Azoxybenzene theory yield (equation S) %
I	67.72	98.8	6.10	92.4
II	67.61	98.7	6.15	93.2

The data reveal that nitrobenzene is reduced to azoxybenzene by sodium plumbite in aqueous solution in conformity with the proposed equation S. The reduction was not extensive since the average yield of 6.125 grams of azoxybenzene is equivalent to 7.61 grams of nitrobenzene which is 34% of the initial quantity of nitrobenzene.

(F) THE REDUCTION OF NITROBENZENE BY FORMALDEHYDE
I. IN THE ABSENCE OF LEAD
II. IN THE PRESENCE OF LEAD

In the reaction mechanism scheme for the Klinger reaction, the action of sodium hydroxide upon the intermediately formed formaldehyde was represented by the following equation:

$$NaOH + HCHO \longrightarrow HCOONa + H_2 \qquad B$$

If the hydrogen available is assumed to effect reduction of the nitrobenzene to azoxybenzene according to the equation,

$$2C_6H_5NO_2 + 6H \longrightarrow (C_6H_5N)_2O + 3H_2O \qquad D$$

then the summation of equation B and this latter equation D represents the reduction of nitrobenzene by formaldehyde as follows:

$$3NaOH + 3HCHO \longrightarrow 3HCOONa + 3H_2 \qquad 3B$$

$$\underline{2C_6H_5NO_2 + 6H \longrightarrow (C_6H_5N)O + 3H_2O} \qquad D$$

$$\Sigma\, 3B,D \quad 2C_6H_5NO_2 + 3HCHO + 3NaOH \longrightarrow (C_6H_5N)_2O + 3HCOONa + 3H_2O \qquad T$$

To determine the occurrence of this reaction and the effect of the presence of lead upon the extent of its occurrence, experiments were conducted with reaction mixtures consisting of 15 grams of nitrobenzene, 300cc. of water, 100 grams of sodium hydroxide, and 10 grams of formaldehyde as trioxymethylene (I) in the absence of lead, and (II) in the presence of lead, 25 grams.

The previously described experimental procedure for conducting the reactions and recovering the azoxybenzene, the sole product of the reduction, was employed.

In run I, without lead, the reduction of the nitrobenzene can be attributed only to reaction T (above) but in run II, in the presence of lead, it is conceivable, since an appreciable quantity of lead was reacted to form sodium plumbite with the liberation of hydrogen, that some of the nitrobenzene would be reduced by this hydrogen to azoxybenzene. Accordingly, the equation for the interaction of lead, sodium hydroxide, and nitrobenzene may be represented by the following reaction mechanism scheme:

$$3Pb + 6NaOH \longrightarrow 3Na_2PbO_2 + 6H \qquad 3o$$

$$\underline{2C_6H_5NO_2 + 6H \longrightarrow (C_6H_5N)_2O + 3H_2O} \qquad D$$

$$\leq 3o,D \quad 3Pb + 6NaOH + 2C_6H_5NO_2 \longrightarrow 3Na_2PbO_2 + (C_6H_5N)_2O + 3H_2O \qquad U$$

Thus, in run II, with lead, nitrobenzene is reduced according to the equations T and U. The extent of the occurrence of the reaction according to equation U will be in conformity with the amount of lead reacted.

The data obtained in reactions without and with lead are recorded in the following Table IX.

TABLE IX

THE REDUCTION OF NITROBENZENE BY FORMALDEHYDE
I. IN THE ABSENCE OF LEAD
II. IN THE PRESENCE OF LEAD

1	2	3	4	5	6
Run	Pb reacted	$(C_6H_5N)_2O$ found	$(C_6H_5N)_2O$ theory yield (equation U)	$(C_6H_5N)_2O$ yield (equation T)	$(C_6H_5N)_2O$ theory yield (equation T)
	g.	g.	g.	g.	%
I a	0.0	1.50	0.0	1.50	6.80
b	0.0	1.00	0.0	1.00	4.54
II a	11.1	8.40	3.53	4.87	22.14
b	11.0	8.30	3.50	4.80	21.83

The data reveal the following facts:

1. In run I, without lead, the nitrobenzene underwent very little reduction as noted in per cent theory yield of azoxybenzene according to equation T (column 6).

2. In run II, with lead, 11 of the initially used 25 grams of lead were reacted in conformity with equation U yielding 3.53 and 3.50 grams of azoxybenzene (column 4). The differences between the yields of azoxybenzene with lead (column 3 minus column 4) give the yields of azoxybenzene formed according to equation T (column 5).

3. The per cent theory yields of azoxybenzene (column 6) obtained with lead are three to four times greater than the yield of azoxybenzene without lead as effected by the reducing action of trioxymethylene alone. In other words, it is evident that the presence of lead catalyzes the reducing reaction action of formaldehyde on nitrobenzene. (It should be observed that in the absence of the formation of red lead the intermediately formed sodium plumbite under the present experimental conditions did not effect any reduction of the nitrobenzene as shown in part (E).)

(G) THE INTERMEDIATE FORMATION OF HYDROGEN PEROXIDE ON INTERACTION OF LEAD, SODIUM HYDROXIDE AND NITROBENZENE IN AQUEOUS SOLUTION

It has been noted in part (B), paragraph d, that the formation of hydrogen may be related to the intermediate formation of hydrogen peroxide according to the following equation which represents a well known property of lead:

$$Pb + 2H_2O + O_2 \longrightarrow Pb(OH)_2 + H_2O_2 \qquad G$$

This reaction occurs when lead in contact with water is exposed to the atmospheric oxygen. To determine whether or not nitrobenzene might act as an oxidizing agent accompanied by the formation of hydrogen peroxide according to the previously derived reaction represented by the equation:

$$3Pb + 6NaOH + 4C_6H_5NO_2 \longrightarrow 3Na_2PbO_2 + 2(C_6H_5N)_2O + 3H_2O_2 \qquad J$$

Reaction mixtures containing nitrobenzene, lead, sodium hydroxide solution, and potassium iodide were heated with vigorous stirring for four hours. The nitrobenzene was thereby reduced to azoxybenzene. An excess quantity of potassium iodide was incorporated in the reaction mixture for the purpose of

reacting with the intermediately formed hydrogen peroxide to liberate iodine. The iodine, in turn, would immediately react with the sodium hydroxide to form sodium iodide and sodium iodate. The equations for these reactions are as follows:

$$H_2O_2 + 2KI \longrightarrow 2KOH + I_2 \qquad a$$

$$3I_2 + 6NaOH \longrightarrow 5NaI + NaIO_3 + 3H_2O \qquad b$$

To determine the quantities of sodium iodate formed, 50cc. aliquot portions of the total reaction mixture, diluted to a volume of one liter were acidified with dilute sulfuric acid to effect the release of the iodine according to the equation:

$$NaIO_3 + 5NaI + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 3H_2O + 3I_2 \qquad c$$

The iodine liberated was extracted with benzene and subsequently estimated by titration with standard 0.1N sodium thiosulfate solution.

According to the proposed equation-- $3Pb + 6NaOH + 4C_6H_5NO_2 \longrightarrow 3Na_2PbO_2 + 2(C_6H_5N)_2O + 3H_2O_2$, the quantity of lead reacting to form azoxybenzene and hydrogen peroxide should check with the quantity of iodine found in conformity with the stoichiometrical equivalents, $3Pb \rightleftharpoons 2(C_6H_5N)_2O \rightleftharpoons 3H_2O_2 \rightleftharpoons 3I_2$

Two runs were conducted, (I) and (II). Reaction mixtures in both sets of duplicate runs contained 41.44 grams of lead, 25 grams of nitrobenzene, and 300cc. of water, but in (I), 35 grams of potassium iodide and 150 grams of sodium hydroxide were incorporated while in (II), 50grams of potassium iodide and 200 grams of sodium hydroxide were used.

The data obtained are recorded in the following Table X.

TABLE X

INTERMEDIATE FORMATION OF HYDROGEN PEROXIDE ON INTERACTION OF LEAD, SODIUM HYDROXIDE AND NITROBENZENE IN AQUEOUS SOLUTION

$(3Pb + 6NaOH + 4C_6H_5NO_2 \longrightarrow 3Na_2PbO_2 + 2(C_6H_5N)_2O + 3H_2O_2$ ---J)

$(3H_2O_2 + 6KI \longrightarrow 6KOH + 3I_2$ ----------a)

1	2	3	4	5	6	7	8
Run	Pb reacted	$(C_6H_5N)_2O$ found	$(C_6H_5N)_2O$ theory (equation J)	$(C_6H_5N)_2O$ theory (equation J)	$I_2 \Rightarrow H_2O_2$ found	$I_2 \Rightarrow H_2O_2$ theory (equation a)	$I_2 \Rightarrow H_2O_2$ theory (equation a)
	g.	g.	g.	%	g.	g.	%
I a	17.20	10.45	10.96	95.8	20.10	21.09	95.3
b	17.25	10.50	10.96	96.0	20.18	21.15	95.4
II a	28.35	17.20	18.00	95.5	33.32	34.74	95.9
b	28.40	17.25	18.00	95.8	33.41	34.81	95.9

It should be noted that approximately 50% of the nitrobenzene initially used was reduced to azoxybenzene. However, the quantity reduced is equivalent to the quantity of lead reacted and the equivalent quantity of intermediately formed hydrogen peroxide, all in conformity with the ratios, $3Pb:2(C_6H_5N)_2O:3H_2O_2:3I_2$, required by the postulated equations J and a. The per cent theory yields of azoxybenzene (column 5) and iodine equivalent to hydrogen peroxide (column 8) check within 95-96% of the theory, thereby confirming the fact that the interaction of lead, sodium hydroxide, and nitrobenzene in aqueous medium yields azoxybenzene accompanied by the intermediate formation of hydrogen peroxide.

(H) THE INTERMEDIATE FORMATION OF HYDROGEN PEROXIDE ON THE INTERACTION OF LEAD, SODIUM HYDROXIDE, AND NITROBENZENE IN METHYL ALCOHOL SOLUTION

Since it has been proven that hydrogen peroxide is a product of the interaction of lead, nitrobenzene, and sodium hydroxide in aqueous solution, the question arises as to its intermediate formation when lead interacts with nitrobenzene and sodium hydroxide in methyl alcohol solution. In other words, is hydrogen peroxide formed as an intermediate product when the Klinger reaction is conducted in the presence of lead?

To answer this question, two sets, I and II, of duplicate runs were conducted with reaction mixtures containing: lead, 41.44 grams; nitrobenzene, 25 grams; sodium hydroxide, 150 grams; water, 100cc.; and methyl alcohol, 200cc. No potassium iodide was added to reaction mixture I, but to reaction mixture II, 35 grams of potassium iodide were added to react with any intermediately formed hydrogen peroxide to liberate iodine which, in turn, reacted with the sodium hydroxide present to yield the sodium iodide--sodium iodate mixture, wherein the iodine content was subsequently determined in conformity with the reactions and experimental procedure noted in part (G).

The reduction products in both runs were mixtures of azoxy- and azobenzene. The liberation of hydrogen accompanied their formation.

The formation of hydrogen peroxide in the preceding part (G) was represented by the equation,

$$3Pb + 6NaOH + 4C_6H_5NO_2 \longrightarrow 3Na_2PbO_2 + 2(C_6H_5N)_2O + 3H_2O_2 \qquad J$$

Analagously, the concomitant formation of azobenzene and hydrogen peroxide may be represented by the equation,

$$2Pb + 4NaOH + 2C_6H_5NO_2 \longrightarrow 2Na_2PbO_2 + (C_6H_5N)_2 + 2H_2O_2 \qquad L$$

Since both azoxy- and azobenzene were formed, and, in each of the above equations J and L, one molecule of hydrogen peroxide is formed for every molecule of lead reacting, then the iodine equivalent for the intermediately formed hydrogen peroxide may be calculated in terms of the quantity of lead reacted.

The following table XI embodies the data obtained.

TABLE XI

INTERMEDIATE FORMATION OF HYDROGEN PEROXIDE ON INTERACTION OF LEAD, NITROBENZENE, AND SODIUM HYDROXIDE IN METHYL ALCOHOL SOLUTION

$(3Pb + 6NaOH + 4C_6H_5NO_2 \longrightarrow 3Na_2PbO_2 + 2(C_6H_5N)_2O + 3H_2O_2$ ------- J)

$(2Pb + 4NaOH + 2C_6H_5NO_2 \longrightarrow 2Na_2PbO_2 + (C_6H_5N)_2 + 2H_2O_2$ ------- L)

$(3H_2O_2 + 6KI \longrightarrow 6KOH + 3I_2$ ----------a)

1		2	3	4	5	6
Run		KI used g.	Pb reacted g.	Reduction products g.	Azoxy-benzene %	Azo-benzene %
I	a	0.0	19.24	18.85	41	59
	b	0.0	19.33	18.85	41	59
II	a	35.0	19.25	18.80	58	42
	b	35.0	19.30	18.80	58	42

1		7	8	9	10
Run		$I_2 \Rightarrow H_2O_2$ found g.	$I_2 \Rightarrow H_2O_2$ theory (equations JL) g.	$I_2 \Rightarrow H_2O_2$ theory (equations JL) %	H_2 evolved (STP) %
I	a	0.0	0.0	0.0	1485
	b	0.0	0.0	0.0	1519
II	a	22.50	23.60	95.3	1480
	b	22.62	23.66	95.6	1498

1. Since the quantity of lead reacted in run II gave a 95% theoretical yield of hydrogen peroxide (column 9), it follows that lead does react with sodium hydroxide and with nitrobenzene to form hydrogen peroxide in conformity with equations J and L.

2. In the Klinger reaction with lead in the absence of potassium iodide (run I), the ratio of the yields of azoxy- to azobenzene are practically 4:6. This ratio is reversed when potassium iodide was present in the reaction mixture (run II).

3. The volumes of the hydrogen evolved (column 10) are practically identical, either in the presence of or the absence of potassium iodide.

SUMMARY AND CONCLUSIONS

(A) The nature and extent of the reduction of nitrobenzene in standardized solutions of sodium hydroxide, methyl alcohol, and water was conducted to determine the effects of increasing concentrations of sodium hydroxide and of nitrobenzene. The following facts were noted:

1. It was discovered that hydrogen was evolved during the course of the reaction and that with increasing concentrations either of sodium hydroxide or of nitrobenzene increasing volumes of hydrogen were evolved.

2. The nitrobenzene was practically completely reduced to azoxybenzene and sodium formate was formed in conformity with the equation for the Klinger reaction.

3. With fixed concentrations of sodium hydroxide, increasing concentrations of nitrobenzene led to the evolution of increasing volumes of hydrogen. With the maximum concentration of sodium hydroxide used, the yields of hydrogen were practically proportional to the molar concentrations of the nitrobenzene.

4. An investigation of the rate at which the hydrogen was evolved and sodium formate formed during the course of the reaction showed that, while the ratio of the sodium formate formed to the hydrogen evolved successively decreased, the total yield of sodium formate was not only practically constant, but in excess of the quantity formed according to the equation for the Klinger reaction. This led to the conclusion that---

5. The evolution of hydrogen was due to the concurrence of certain reactions postulated in the reaction mechanism scheme.

6. It has been suggested that the increasing yields of hydrogen with increasing yields of nitrobenzene were due to the previously proven intermediate formation of formaldehyde according to the reaction mechanism scheme. Furthermore, it has been shown that formaldehyde reacts with sodium hydroxide to yield hydrogen and sodium formate.

(B) The Klinger reaction runs as described and conducted in part (A) were repeated with the addition to each reaction mixture of .4 moles of pure granular lead.

1. In all runs, the volumes of hydrogen evolved were greatly in excess of the volumes of hydrogen liberated in the absence of lead, part (A).

2. The nitrobenzene was reduced to yield mixtures of both azoxybenzene and azobenzene.

3. With fixed concentrations of sodium hydroxide and increasing concentrations of nitrobenzene, identical amounts of lead reacted to yield sodium plumbite.

4. With increasing concentrations of sodium hydroxide, correspondingly increasing quantities of lead reacted as in 3, but the quantities of lead reacting were not affected by the increasing concentrations of nitrobenzene.

5. With a fixed concentration of sodium hydroxide, both the total volumes and the excess volumes of hydrogen evolved were found to increase in direct proportion to the increasing concentrations of nitrobenzene employed.

6. With fixed concentrations of sodium hydroxide and increasing comcentrations of nitrobenzene, the ratio of the yields of azoxybenzene to azobenzene were constant.

7. With increasing concentrations of sodium hydroxide and fixed concentrations of nitrobenzene, the ratios of the yields of azoxybenzene to azobenzene uniformly decreased, i.e., the extent of the reduction was more pronounced. Hence, --

8. This result (7) was attributed to the presence of lead (increasing concentrations of sodium hydroxide in part (A) never effected the formation of azobenzene.)

(C) A further study of the effect of lead (in quantities ranging from .4 to .01 moles) revealed the following facts in all runs:

1. The nitrobenzene was completely reduced to yield mixtures of azoxybenzene and azobenzene.

2. With decreasing amounts of lead, both the total volumes and the excess volumes of hydrogen decreased but not in mathematical proportion.

3. With decreasing amounts of lead, the percentage yields of azoxybenzene increased while those of azobenzene decreased but not in mathematical proportion.

4. Since the lead initially present, even in the minimum molar amounts, was never completely reacted, the formation of both azoxy- and azobenzene revealed that lead augments the volumes of hydrogen evolved and promotes the extent of the reduction.

(D) An investigation of the reduction of nitrobenzene by lead and sodium hydroxide in the absence of methyl alcohol showed that:

1. The nitrobenzene was reduced chiefly to azoxybenzene and some azobenzene. The lead reacted to form sodium plumbite and red lead presumably according to the following equations:

$$Pb + 2NaOH \longrightarrow Na_2PbO_2 + 2H \qquad o$$

$$3Pb + 4H_2O \longrightarrow Pb_3O_4 + 8H \qquad p$$

2. Since no hydrogen was liberated, the available hydrogen (equations o and p) was found to be equivalent to the quantities of azoxybenzene and azobenzene formed.

(E) Since sodium plumbite was formed in all of the runs, a separate investigation of the reduction of nitrobenzene by sodium plumbite alone revealed that:

1. The nitrobenzene was partially reduced solely to azoxybenzene with the concomitant formation of red lead.

2. The equation developed for this reaction --

$$9Na_2PbO_2 + 2C_6H_5NO_2 + 9H_2O \longrightarrow (C_6H_5N)_2O + 3Pb_3O_4 + 18NaOH \qquad S$$

was confirmed by the yields of azoxybenzene and red lead.

(F) Since the proposed reaction mechanism scheme for the Klinger reaction indicated the intermediate formation of formaldehyde, the reduction of nitrobenzene by formaldehyde and sodium hydroxide in the absence of methyl alcohol was investigated both in the absence of lead and in the presence of lead. An application of the reaction mechanism scheme to the reduction of nitrobenzene by formaldehyde gives the equation:

$$2C_6H_5NO_2 + 3HCHO + 3NaOH \longrightarrow (C_6H_5N)_2O + 3HCOONa + 3H_2O \qquad T$$

In the presence of lead, another concomitant reaction is represented by the equation:

$$3Pb + 6NaOH + 2C_6H_5NO_2 \longrightarrow 3Na_2PbO_2 + (C_6H_5N)_2O + 3H_2O \qquad U$$

Experimental runs conducted in the absence of lead and in the presence of lead revealed that:

1. In the absence of lead, the extent of the reduction was very small--an average of 5.5% theory yield of azoxybenzene.

2. In the presence of lead, the per cent theory yields of azoxybenzene were three to four times greater than the yields of azoxybenzene without lead. Hence, --

3. The presence of lead catalyzes the reducing action of formaldehyde upon nitrobenzene.

(G) The facts that the presence of lead in Klinger reaction mixtures increased the volumes of hydrogen liberated, the extent of the reduction and, that the increased concentrations of nitrobenzene also proportionately increased the yields of hydrogen, may possibly be related to a well-known property of lead to undergo oxidation by atmospheric oxygen yielding hydrogen peroxide according to the equation:

$$Pb + 2H_2O + O_2 \longrightarrow Pb(OH)_2 + H_2O_2 \qquad G$$

If it can be proven that nitrobenzene oxidizes the lead and is thereby reduced to azoxybenzene with the formation of hydrogen peroxide in conformity with the derived equation,

$$3Pb + 6NaOH + 4C_6H_5NO_2 \longrightarrow 3Na_2PbO_2 + 2(C_6H_5N)_2O + 3H_2O_2 \ , \qquad J$$

it could be further assumed that the intermediately formed hydrogen peroxide may lead to the formation of hydrogen in conformity with the previously confirmed reaction represented by the equation-- $2CH_3OH + 3H_2O_2 \longrightarrow 2HCOOH + 4H_2O + H_2$ I

The validity of this assumption has been attested by proving the intermediate formation of hydrogen peroxide on the interaction of lead, sodium hydroxide, and nitrobenzene in aqueous solution in conformity with the above equation J.

(H) The intermediate formation of hydrogen peroxide on the interaction of lead, sodium hydroxide, and nitrobenzene was also proven to occur in methyl alcohol solution. Azoxybenzene and hydrogen peroxide were formed in these reaction mixtures in conformity with equation J. Furthermore, azobenzene and hydrogen peroxide were formed in conformity with the following equation: $2Pb + 4NaOH + 2C_6H_5NO_2 \rightarrow 2Na_2PbO_2 + (C_6H_5N)_2 + 2H_2O_2$ L

The total yields of hydrogen peroxide (equations J and L) were found to be equivalent to the total amounts of lead reacting in conformity with equations J and L.

In conclusion, it has not been possible to correlate the quantities of lead reacting with the yields of hydrogen, azoxybenzene, and azobenzene in the various runs because the hydrogen may arise from the several sources described. However, experimental data indicate that lead definitely catalyzes one or more of the reactions whereby hydrogen is formed, some of which may be liberated and some of which may effect not only the reduction of nitrobenzene both to azoxy- and azobenzene but also function in the reduction of the intermediately formed formaldehyde.

The assumptions proposed for the several concurrent reactions have been confirmed by the experimental data which serve to explain the increased yields of hydrogen and the increased extent of reduction as being, in general, commensurate with the increasing quantities of lead reacting and the increasing concentrations of nitrobenzene employed in the various experimental runs.

Further investigations relating to the foregoing problems are being conducted in this laboratory.

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