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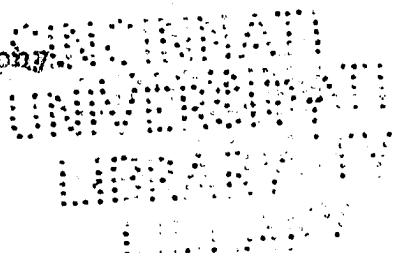
A QUANTITATIVE STUDY OF THE REDUCING ACTION
OF
ALKALI ALCOHOLATES ON AROMATIC NITRO COMPOUNDS.

A Thesis
by
Jessie Louise Cameron

Presented to the Faculty
of the
Graduate School
of the
University of Cincinnati

in fulfillment of part of the requirements for the degree of

Doctor of Philosophy.



Cincinnati, Ohio.

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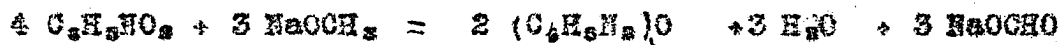
ACKNOWLEDGEMENT.

The writer wishes to express her appreciation for the helpful advice, suggestions and criticism given by Dr. H. Shipley Fry, under whose guidance this investigation was carried on. She also wishes to take this opportunity for thanking the Donor of the Anonymous Fellowship in Chemistry for his interest and assistance during the three years of her graduate research.

INTRODUCTION.

This investigation is intended to present a study of a well known reaction on a quantitative basis, with a definite statement of quantities of reacting substances, experimental conditions imposed, and of quantities of resulting substances. This work was considered of interest since so much of the literature of organic chemistry lacks standardization, many investigations being reported simply as a substance prepared, along with a brief account of the mode of preparation. The amounts of starting materials, the definite experimental conditions, the nature and amounts of various by-products obtained, and particularly the quantitative yields are too often omitted.

The reaction chosen for this investigation was the reduction of aromatic nitro-compounds by alkali alcoholates. The reduction of nitrobenzene, for instance, by sodium methylate in methyl alcohol solution has been known and used since 1882 when Klinger² first studied the reaction, but so far as can be learned from the literature, no attempt has been made to check the amount of anoxy benzene formed with the amount of sodium methylate oxidized to sodium formate. Klinger gave the equation for the reaction,



but no experimental data to show that sodium formate was the only product of the oxidation

of the methyate, and no investigation of this point has been recorded by any later investigator. Lachman, working with sodium hydroxide and methyl alcohol, stated that the amount of water present in the alcohol had little effect on the yield of azoxy benzene. He used a very concentrated solution of sodium hydroxide to obtain a quantitative yield. No definite study of the effect of water on the reduction of nitrobenzene had been made. Willgerodt stated that the yield of p-dichlorazoxybenzene is decreased, as the alcohol is diluted with water. He used an alcoholic solution of potassium hydroxide as reducing agent in his experiments.

In the present investigation, the amounts of azoxy benzene and of sodium methyate formed were determined when varying amounts of water or of pyridine were present in the reaction mixture. It was found that small amounts of these substances had a great effect on the extent of the reduction.

A comparison of the yields of azoxy compounds and of the sodium formate produced when the nitrotoluenes and the chloronitrobenzenes are reduced by sodium methyate is included in this study.

Finally, it was considered of interest to compare the effects of sodium methyate and of potassium methyate as reducing agents for nitrobenzene. This part of the investigation undertaken to secure data bearing upon the work of a special committee of the National Research Council to ascertain the feasibility and desirability of replacing

potassium compounds by sodium compounds in the operations of both pure and applied chemistry.

HISTORICAL.

¹
 Zinin, in 1845 heated alcoholic potassium hydroxide with nitrobenzene, and obtained azoxy benzene, along with a brown potassium salt insoluble in alcohol. Werigo² used sodium amalgam and / ^{nitrobenzene} in acetic acid and obtained azo benzene. Alexejeff³ treated nitrobenzene in alcoholic solution with sodium amalgam, made the solution acidic with acetic acid, and after heating obtained azoxybenzene and a small amount of azobenzene. Kekule discussed the relationships between the reduction products of aromatic nitro bodies. Alexejeff³ later extended his work with sodium amalgam and found further that zinc dust with potassium hydroxide had practically the same effect on an alcoholic solution of nitrobenzene as sodium amalgam.⁵ Raesneck reduced an alcoholic solution of nitrobenzene with sodium hydroxide and obtained azoxybenzene.⁶ Schmidt and Schultz⁶ obtained azoxybenzene by reducing nitrobenzene with an alcoholic solution of potassium hydroxide.⁷ Wallach and Wallach and Kiepenheur investigated the formation of the oxy azo-compound when azoxy benzene is treated with warm dilute sulphuric acid. Schmidt and Schultz⁶ in studies on azobenzene, recommended a preparation of azoxybenzene from nitrobenzene and alcoholic potassium hydroxide. The yield of their method, however, is low.

⁸
 Klinger discovered a new and better method for the reduction of nitrobenzene to the azoxy compound. He used

sodium methylate in a methyl alcohol solution and obtained a quantitative yield of practically pure azoxybenzene. He heated his reaction mixture to boiling, connected with a reflux condenser, on a water bath, and after five or six hours, distilled off the excess alcohol and poured the mixture into water, where the azoxy compound solidified. He represented this reaction as follows, but gave no experimental evidence for his conclusions:



Klinger remarked that a large excess of sodium methylate hastened the reaction, but a larger excess was necessary when potassium hydroxide was the reducing agent. Alcohols of higher molecular weight increased the vigor of the reaction.

9

Moltschanousky compared the different methods for preparing azoxybenzene, contrasted yields, and stated that he could not obtain as high a yield with Klinger's method as with Alexejeff's. Moltschanousky probably started with impure methyl alcohol.

10

Bruhl prepared alcohol free sodium methylate, and used it as a reducing agent for nitrobenzene suspended in xylol, obtaining a quantitative yield. He also prepared methylates of the borneols, menthols and camphors.

11

Lachman was led by the statement of Klinger, that ordinary methyl alcohol often contains much water, to return to Zinin's method for preparing azoxybenzene by the use of alkalis

in alcohol. Lachman used methyl alcohol and sodium hydroxide, stating that the alcohol must be ketone free, but that the amount of water present in the alcohol is relatively without influence. Lachman obtained a quantitative yield of azoxybenzene by the use of a very concentrated solution of sodium hydroxide. Lachman concludes his articles with a discussion of the various formulae proposed for azoxy benzene.

12

Evans and Fetsch reduced nitrobenzene in ethyl alcohol, with magnesium amalgam, and obtained azobenzene in quantitative yield.

13

Evans and Fry heated nitrobenzene in ethyl alcohol with magnesium amalgam. The product was a ninety per cent yield of azoxybenzene. When methyl alcohol was used as a solvent, azobenzene was obtained in a yield of 88.5 per cent. The difference in the reaction of the two alcoholic solutions was attributed to the fact that magnesium methyrate was formed in the latter case, and the nascent hydrogen reduced the product to the azo-stage, while in the former case, no ethylate was formed, and the reaction stopped at the azoxy-stage. To test this assumption, alcohol free magnesium methyrate and magnesium ethylate were prepared. While the methyrate is soluble in methyl alcohol, the ethylate is relatively insoluble in the corresponding alcohol, hence the former is more readily oxidized. When nitrobenzene was dissolved in methyl alcohol, magnesium amalgam added, and the whole procedure carried on without boiling, azoxy and azobenzene were obtained, the former in larger quantity. Thus the amalgam

reduces the nitrocompound to the azoxy-stage, and the nascent hydrogen formed with the methylate reduces the azoxy compound further. Fry also found that magnesium and methyl alcohol constituted a very effective reducing mixture.

Weisenheimer¹³ studied the effect of potassium methylate on nitrobenzene. At ordinary temperatures, there was no reaction. When heat was applied, the methyl alcohol boiled away (140°-150°C.), a reaction finally took place with great vigor, and a dark solid mass was left. When sodium methylate was used, the result was azoxybenzene. Allen¹⁴ used ferrous hydroxide as reducing agent, and made a very thorough analysis of his reduction products.

Petrieve¹⁵ reduced nitrotoluene with sodium amalgam in alkaline solution and believed the product to contain azoxytoluene. Since the o-m-and p-nitrotoluenes had not as yet been fully differentiated and recognized, and the properties of the azo-and azoxy-products were very imperfectly known, there is some doubt about these products. (See Rosenfeld, J. Chem. Soc. (1888) 825). Melms¹⁶ also used sodium amalgam.

Perkin¹⁷ prepared o-azotoluene by the action of potassium hydroxide on o-nitrotoluene. Klinger¹⁸ stated that when sodium methylate reacted with o-and p-nitrotoluenes the azoxy compounds were not formed. Later, with a definite concentration of sodium methylate, he obtained o-azoxytoluene, o-toluidin, and azoxy- or azo-acids, from the reaction mixture.

Guigermann¹⁹ reduced o-nitrotoluene with zinc dust in alcoholic sodium hydroxide, and obtained the azoxytoluene.

Evans and Fry²⁰ treated o-nitrotoluene in ethyl alcohol

with magnesium amalgam obtaining a 50 per cent yield of o-azoxytoluene. About 38 per cent of the o-nitrotoluene was recovered unused. When methyl alcohol was used, o-azotoluene was obtained as the chief product. The yield was 66.5 per cent. Nascent hydrogen, liberated when the methylate was formed, probably accounts for the difference in products formed.

22

Goldschmidt in a study of isomeric toluidines, heated m-nitrotoluene with alcoholic potassium hydroxide. He then distilled off the alcohol on a water bath, and then distilled the residue over an open flame. Azobenzene was the distillate. Here azoxybenzene was probably the first product, but this was converted to the azo-compound on distillation.

23

Barzilensky treated an alcoholic solution of m-nitrotoluene with sodium amalgam, and obtained m-azotoluene.

24

Elinger stated that m-nitrotoluene on reduction with sodium methylate formed a yellow amorphous compound.

25

Buehta and Schaebeck heated m-nitrotoluene with a solution of sodium hydroxide and methyl alcohol, obtaining m-azoxytoluene as the product.

26

Warigo treated p-nitrotoluene with sodium amalgam,

27

and azotoluene resulted. Janovsky found that when p-nitrotoluene was heated with sodium amalgam, p-azotoluene and a

28

small amount of p-azoxytoluene were formed. Patriev verified Janovsky's results, and added that in alcoholic solution the reduction produced the hydrate-compound also.

29

Melms found that the more concentrated the alcoholic solution treated with sodium amalgam, the more azoxy-compound

28

was formed. Petriew announced from some further experiments that "liquid" nitrotoluene is readily reduced to azoxytoluene, and thence in acid solution to toluidin, but that solid nitrotoluene does not readily undergo these changes.

30

Perkin prepared p-azoxytoluene by the use of sodium amalgam, and then tried the effect of alcoholic potassium hydroxide on p-nitrotoluene. The latter reaction did not yield the azoxy-compound, but a red amorphous insoluble compound which decomposed at high temperatures. Klinger obtained a red amorphous indifferent substance along with acids of undetermined composition, when he heated p-nitrotoluene with sodium methylate. Klinger attempted to assign a formula to the red substance. He considered it a condensation product formed from azoxytoluene with the loss of water. In later

31

articles Klinger set forth further studies on the structure of this and similar amorphous, colored, substances.

32

Bender and Schultz reduced p-nitrotoluene sulphonic acid with zinc and potassium hydroxide, and obtained not the azo-compound Heale described, but the toluidin compound.

33

Bender and Schultz also studied the red amorphous compound obtained by Klinger and others, and considered it a stilbene derivative.

34

Janovsky and Riemann prepared p-azotoluene, with a small amount of the azoxy-compound present, by the action of zinc dust in concentrated sodium hydroxide solution at 100°C. Janovsky continued the study in later work. He obtained two isomeric p-azoxytoluenes, one melting at 70°C. and the other

at 75°C., from the reaction of zinc dust and soda on pure p-nitrotoluene. These compounds were reduced to p-toluidine when treated with tin and hydrochloric acid. Studies of properties and crystal measurements were also made.

35

Fischer and Hepp heated p-nitrotoluene with sodium hydroxide in methyl alcohol, and obtained p-dinitrodibenzyl, a small amount of p-dinitrostilbene, dinitrostilbene and a large amount of the red amorphous compound first described by Perkin. This compound was obtained also when p-dinitrodibenzyl was reduced with sodium methylate. A discussion of this amorphous compound was given, along with some reactions of related compounds and references to various articles on dyes, etc. The constitution was still unsettled.

36

Schmidt treated p-nitrotoluene in ether with metallic sodium. When equivalent amounts of sodium and the nitrocompound were used, a small amount of p-azoxytoluene was obtained. The chief product was a brown substance which, when treated with hydrochloric acid, formed the red compound of Perkin and Klinger. Schmidt considered this to be p-azoxydihydrostilbene. When excess sodium was used, the yield was chiefly azotoluene with a small amount of the azoxy-compound.

37

Evans and Fry treated a solution of p-nitrotoluene in ethyl alcohol with magnesium amalgam. After prolonged boiling, the yield was found to be ninety per cent of the theoretical yield of p-azoxytoluene. When methyl alcohol was used instead of ethyl alcohol, p-azotoluene was obtained, in a yield of 23.9 per cent. Thirty-eight per cent of the p-azoxytoluene

was recovered unchanged, and p-azoxytoluene was obtained in a yield of 22.2 per cent. The reaction was thus affected by the formation of magnesium methylete, while in the first case no ethylete was formed

38

Green with his co-workers have made an intensive study of the red compound first obtained by Perkin and by Zlinger. They conclude, after much research, that the amorphous condensed compound is dinitrodibenzyl or dinitrostilbene or both. For this work, see the bibliography (number 38 for references).

39

Heumann remarked that the chlorine in chloronitrobenzene is so tightly bound to the ring that while potassium hydroxide reduces the nitro group, it does not affect the chlorine. He obtained an azoxy-compound on reduction but surmised that this was formed from p-chloronitrobenzene contained in the o-chloronitrobenzene with which he was working. Heumann and Geyger stated that sodium has no effect on an ethereal solution of "liquid" chloronitrobenzene. (Both the m- and the o-chloronitrobenzenes are liquid).

41

Lolry de Bruyn treated o-chloronitrobenzene in methyl-alcohol with sodium methylete, and obtained, after heating to 100°C. in a sealed tube, a yield of o-nitroanisole. The estimation of chlorine in the residue corresponded with the anisole formed, showing a quantitative yield. The bromine compound acts similarly.

42

Brand treated o-chloronitrobenzene with a mixture of sodium methylete in methyl alcohol. He found in this study that in strong methylete solution, o-dichlorobenzene was

formed. In moderately dilute solution o-dichlorazoxybenzene was obtained, and in a very dilute solution of sodium methylate, o-azoxyanisol and dianisidin were obtained.

43

Wohl found that sodium iodide had no catalytic effect on the replacement of the chlorine in o-nitrochlorbenzene and in p-nitrochlorbenzene by the -OCH₃ group of sodium methylate. In most of the organic chlorides studied, sodium iodide was a positive catalyst for this replacement.

43

De Meoy heated a mixture of o-nitrochlorbenzene and sodium methylate at 85°C. and obtained a quantitative yield of o-nitroanisol. This is interesting in that complete replacement of its chlorine by oxymethyl occurred with no reduction of the nitro group.

45

Landenheimer and Will heated m-chloronitrobenzene with an alcoholic solution of potassium hydroxide and obtained m-dichlorazoxybenzene as product. Likewise De Meoy⁴⁶ reduced m-chloronitrobenzene with sodium methylate and obtained the same product.

47

Heumann heated p-nitrochlorbenzene dissolved in alcohol with potassium hydroxide, obtaining p-chlorazoxy-

48

benzene. Hoffmann and Geyger dissolved p-chloronitrobenzene in ether and added sodium. The metal blackened and crumbled to a black powder. In water this substance formed di-

49

chlorazoxybenzene. Landenheimer and Will obtained p-dichlorazoxybenzene from the nitro-compound in an alcoholic solution of potassium hydroxide.

50

Willgerodt treated p-nitrochlorbenzene with potassium

hydroxide in methyl alcohol solution. He obtained p-nitroanisol and p-dichlorazoxybenzene. When an ethyl alcohol solution was used, the p-nitrophenetol was obtained. In dilute solution, potassium nitrophenylate was also formed. When the reaction mixtures were heated to 150°-200°, the reduction yielded p-dichlorazobenzene instead of the azoxy compound. Dilution of the alcohol with water diminished the yield of dichlorazoxybenzene.

51

Rotarsky and others prepared p-azoxyanisol by the reduction of p-nitroanisol with sodium methylate.

52

De Moco treated p-nitrochlorbenzene with sodium methylate and obtained a quantitative yield of p-nitroanisol.

He calculated the reaction velocity constants for the formation of the anisoles from chloronitrobenzenes.

53

Bloom studied the reaction and found that aqueous alcohol, at 70°C, inhibited the formation of dichlorazoxybenzene.

54

Richardson found that the amount of acetaldehyde present in the alcohol increases the yield of dichlorazoxybenzene. An increase in the concentration of the alkali, or a rise in temperature also favors the formation of the azoxy compound. p-chloroaniline is always formed in appreciable quantity when p-dichlorazoxybenzene is formed to large extent. Nitrophenol is always a by-product when chloronitrobenzene is heated with alcoholic alkali solution, and the yield is increased as temperature and strength of solution is raised, though slightly affected by the presence of water in the alcohol. Richardson used an alcoholic solution of

potassium hydroxide to reduce nitrochlorbenzene, and his object was to study the factors that inhibit the formation of the chlorazoxybenzenes.

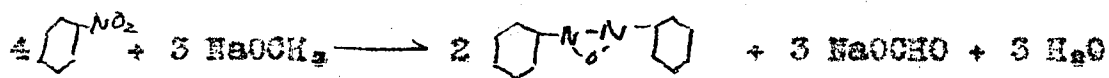
Other methods for the reduction of nitrobenzene and analogous compounds will be found listed in an article by Snowdon⁵⁵ on "The Electrolytic Reduction of Nitrobenzene", (J. Phys. Chem. 15, p 882). Many related compounds have been reduced by various methods similar to that used in this investigation, but these cannot be given here, since they are beyond the scope of the present work.

A list of references to colored compounds formed when nitro-compounds react in alkaline solutions will be found in the bibliography.⁶⁰ The yellow coloring matter obtained in most of the following experiments may be related to some of those described in the corresponding list, though there seems to be no definite knowledge on this point.

THEORETICAL.

8

Klinger investigated the action of different alcohols and alkalies on aromatic nitro-compounds, and for the preparation of azoxybenzene, recommended a method which is still the most generally used, namely the reduction by sodium methy-
late.



This reaction was chosen for study, because azoxybenzene is always the first and usually the chief product of the alkaline reduction of nitrobenzene while azobenzene and hydroazo-

benzene are some times formed. In acid solution, the reduction usually results in aniline, and in neutral solution phenyl-⁵⁶hydroxylamine is formed. Allen stated that in nearly every case the result of reduction was not a single product, but a mixture of products, often containing complex decomposition products. Hence a reaction was desirable which gave but one reduction product, and Klinger's reaction was chosen, and proved to yield only azoxybenzene by a comparison of the azoxybenzene and the sodium formate produced, and the confirmation of the fact that no sodium carbonate was produced during the reaction. In other words, the formate does not act as a reducing agent.

Since the effect of water on the reaction was to be studied, sodium and pure methyl alcohol were used instead of sodium hydroxide and aqueous methyl alcohol as Lachman¹¹ recommended, for these would react to form water, besides the water contained in the alcohol, and formed in the reduction. The amounts of the starting materials were chosen for convenience in manipulation, i.e. to give a relatively large yield of azoxybenzene within three hours of boiling, and yet the alcoholic solution was so adjusted that fairly large amounts of water or pyridine could be added without destroying the homogeneity of the solution.

THE OBJECT OF THE INVESTIGATION.

The purpose of this investigation is to present on a quantitative basis, the effect of alkali alcoholates on aromatic nitro bodies in various media. The reactions and the compounds are well known, but in the past thirty years, com-

paratively little attention has been given to this reduction reaction, especially to the conditions governing the extent of the reduction. For that reason it was considered of interest to study the effects of varying amounts, ~~first of~~ water and later of pyridine, on the extent of the reaction of sodium and of potassium methylates in methyl alcohol solution, in the presence of aromatic nitro-compounds. The effect of potassium methylate as compared with that of sodium methylate is interesting from the standpoint of the substitution of sodium for potassium wherever possible, as noted previously.

EXPERIMENTAL PART.

Apparatus.

The apparatus used was very simple. ~~The reduction mixtures and~~ All reactions here studied were carried out in duplicate, in 500 c.c. round-bottomed flasks of the same shape and ^{of} about the same surface area. The diameters of the bulbs of these flasks were equal in every case. These flasks were connected with reflux condensers having wide straight tubes throughout, so that thermometers could be suspended through them and dip into the reaction mixture. The water baths used had constant leveling devices, brass rings of equal diameter, and the flow of water through these was kept as slight and as uniform as possible. The burners used were of the low type and were chosen to give equal flames.

The steam distillation apparatus was of the usual type, utilizing kerosene cans for steam generators. T-tubes

were inserted between generators and the flasks containing the mixtures to make it possible to check back-suction whenever necessary.

For the titration work, burettes corrected at the German Bureau of Standards were used.

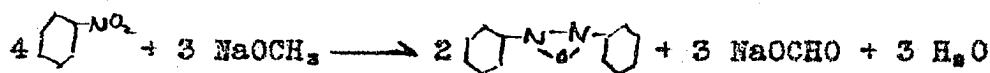
PROCEDURE.

The methyl alcohol used in these experiments was Merck's C.P. methyl alcohol. The specific gravity at 21°C. was found to be 0.7965. The boiling point was between 65° and 66°C. It did not redden blue litmus. Tests for non-volatile matter, acetone, ethyl alcohol, empyreumatic substances, aldehydes, oxidizable substances (oxidizable by one-tenth normal potassium permanganate), chloroform, etc. were made, and it was concluded that in all cases the amounts of these substances present were negligible. The sodium used was well trimmed and scraped immediately before weighing. The nitrobenzene was Kahlbaum's product, and was redistilled occasionally, B.P. = 203° C.

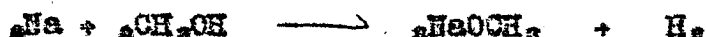
The other nitro-compounds -nitrotoluenes and chloronitrobenzenes, were all manufactured by Kahlbaum, the melting-points are given under Section (3).

The pyridine was Baker's product, redistilled, B.P. 114-115°C.

When nitrobenzene is reduced by sodium methylate in a solution of methyl alcohol, azoxybenzene and sodium formate are formed



About 150 c.c. of methyl alcohol were placed in each of two volumetric flasks of 200 c.c. capacity, cooled in an ice mixture. The sodium (17.3 gm. for each portion) was added slowly, in long slender strips, about 2.5 cm. long by 0.5 cm. in diameter. The methyl alcohol solution was kept near or at the boiling point by the vigor of the reaction until most of the sodium had been added.



When the action had slackened, the flasks were removed from the ice solution, and the reaction proceeded nearly to completion. The final two or three pieces of sodium were dissolved by the addition of small amounts of methyl alcohol. The solutions were now cooled to room temperature (about 21-23°C.) in cold water, and occupied, as a rule, a little over 150 c.c. volume. To each of these was added nitrobenzene (24.6 gm. or 20.44 c.c.) from a burette. The volumes were made up to 200 c.c. at room temperature, and the mixtures poured into the 500 c.c. round bottomed flasks. Two volumetric flasks of fifty c.c. capacity were now filled to the mark with methyl alcohol, and one of these used to rinse into the round bottomed flask each of the remaining amounts of reaction mixture in the volumetric flasks, so that in the end each round bottomed flask contained exactly 250 c.c. of solution. These flasks were then placed on the boiling water baths (constant level) so that equal surfaces were heated. In five to seven minutes the mixtures would

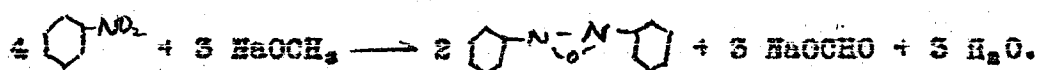
be boiling, and they were boiled, in every case, three hours, with reflux condensers fitted with thermometers, so that the temperatures could be watched. At the end of three hours the water baths were removed, the thermometers were raised part way up the condenser tubes and 100 c.c. cold distilled water poured into the mixtures to stop the reaction.

When cool, the contents of the flasks were subjected to steam distillation keeping the flask about half full of the mixture. The unused nitrobenzene and the methyl alcohol were completely separated from the azoxybenzene in the flask, when from 500 to 600 c.c. of distillate had passed over. However, azoxybenzene to a very small extent is volatile with steam. From 0.3 to 0.5 gm. would be found in the distillate on steam distillation of the latter and extraction with benzene.

The yellow, alkaline residue in the flasks, after steam distillation, contained azoxybenzene, sodium formate and much sodium hydroxide because excess sodium was used. Sodium carbonate was present only when carbon dioxide had been absorbed from the air, if the strongly alkaline solution had been left unstoppered. The azoxybenzene collected at the bottom.

The azoxybenzene was removed by shaking the residue in a one liter separatory funnel, with small portions of benzene, until the benzene was no longer colored by the yellow azoxybenzene. The alkaline solution remained deep orange-red. Benzene would not remove this color, nor was boil-

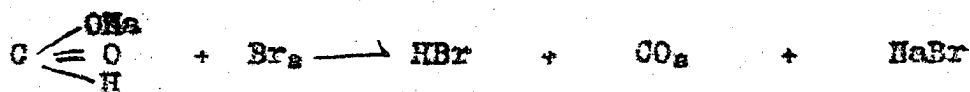
ing with charcoal satisfactory, as the formate to be determined *might* be adsorbed. The benzene solution of azoxybenzene was dried with calcium chloride and concentrated by distilling off part of the benzene. The remainder was placed in a weighed casserole, and the benzene allowed to evaporate in the air. The azoxybenzene soon reached constant weight, and was practically pure. The yield of azoxybenzene was calculated from the equation (first given by Klinger):



A leading motive of this research was to ascertain whether or not the yield could be determined from the amount of sodium formate formed. For this purpose the alkaline solution remaining after the extraction of the nitrobenzene was boiled to expel the remaining benzene. It is scarcely necessary to add that every drop of the solution was kept for this purpose, the round-bottomed reaction flask, and the separatory funnel, carefully washed, and the transference of the solution during extraction with benzene most carefully carried out, etc. The alkaline solutions were allowed to cool and then transferred to one liter volumetric flasks. These were then filled to the mark with distilled water, and aliquot portions used in the formate determinations.

Two different methods have been used for these formate determinations. Three others were tried and abandoned as impracticable in this case. The first method used was

57
 that of Joseph for the determination of formic acid. In this case 30-40 c.c. of the solution in a 500 c.c. Erlenmeyer ^{flask} were diluted to 100 c.c., made acid with sulphuric acid and heated to boiling with reflux condenser for five minutes to remove carbon dioxide. The reflux was rinsed and the solution allowed to cool. The solution was then made neutral with sodium hydroxide, (the indicator being a two per cent aqueous suspension of phenolphthalein), heated to boiling, and bromine water added until the color no longer disappeared immediately. The boiling was continued for half an hour after the color had faded. The hydrobromic acid formed according to the equation;



was titrated with standard tenth-normal potassium hydroxide. Bromine water boiled alone leaves a small quantity of free acid, so corrections were made according to blank runs, but these were really negligible. This method gave results checking from one to three per cent. The yellow coloring matter described above interfered slightly in the determination of the neutral point before the bromine was added. This in turn made the amount of standard potassium hydroxide either high or low. The yellow compound was decolorized by the bromine water and this also lessened the accuracy of the result. A better method was sought.

An attempt was made to separate the formic acid by distillation of the solution over phosphoric acid, but the

yellow compound reacted with the acid, and formed a volatile mixture. Part passed over with the formic acid, but after two days' boiling, the phosphoric acid solution was as yellow, apparently, as ever. No definite results could be obtained in this way.

The mercuric chloride method of Franssen and Greve as indicated in the following reaction 58



gave anomalous results. The yellow compound was probably oxidized by the mercuric chloride.

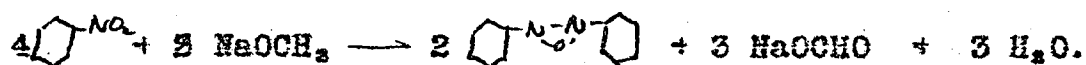
The ordinary permanganate method in which a solution of formic acid is made neutral with sodium carbonate and titrated to a faint pink with standard potassium permanganate did not work out any better than the bromine method, on account of the obscuring of the end point by the yellow compound. The results varied as much as two per cent, sometimes two-and-a-half per cent.

A modification of the permanganate method similar to that of Scott was at last found to be successful. Here 10 c.c. of the alkaline solution diluted to 100 c.c. in a 500 c.c. Erlenmeyer flask were made acid with sulphuric acid, then alkaline with sodium carbonate (as above). Litmus was used as an indicator. The solution was heated nearly to boiling, and a measured amount of one-tenth normal potassium permanganate run in drop by drop until some excess (2-3 c.c.) was present. The solution was then made acid by the addition of 10 c.c. of dilute sulphuric acid, well shaken and heated

several minutes near the boiling point. Then a measured amount of one-tenth normal oxalic acid was added slowly, until the solution became colorless. This was somewhat in excess. Next the mixture was heated for four minutes at about 90°C., with frequent shaking. Finally the solution was treated with the standard potassium permanganate drop by drop, until a faint pink appeared. The amount of permanganate solution equivalent to the amount of oxalic acid added is now subtracted from the total amount of permanganate added. The difference is the amount of permanganate equivalent to the formic acid in the sample, and thus the percent of formic acid can be accurately determined.

RESULTS. Section 1(a).

Nitrobenzene was reduced by sodium methylate with anhydrous methyl alcohol as solvent medium. This furnished a basis for the comparison of the effects of varying amounts of water, and later of pyridine, on the reduction. The reaction is usually considered to be as follows:



The sodium methylate solution was prepared, as previously described, by dissolving 17.3 gm. of sodium in about 150 c.c. methyl alcohol, and to this adding 20.44 c.c. of nitrobenzene (24.6 gm.) and enough methyl alcohol to make the total volume 250 c.c. According to the equation, 24.6 gm. of nitrobenzene is equivalent to 3.45 gm. of sodium. Five times this theoretical amount or 17.3 gm. was used in order to hasten

the reaction sufficiently to secure good yields by boiling for three hours. One-fifth of a mol of nitrobenzene was chosen for convenience, and so if the reaction actually proceeds as Klinger wrote it, we should have a theoretical yield of sodium formate of 10.2 gms. This compound will be contained in the alkaline solution, after the extraction of azoxybenzene with benzene.

The experiments were always run in duplicate and will be designated hereafter as A and B, meaning Run A and Run B.

The reaction mixtures for the reduction of nitrobenzene in anhydrous methyl alcohol were made up as follows: 17.5 gm. sodium were added in a little at a time to 150 c.c. of methyl alcohol cooled in an ice mixture. (For details see Procedure). When the sodium was all dissolved, and the mixture was at room temperature, 20.44 c.c. nitrobenzene were run in from a burette. The volume was then made up to 200 c.c. at room temperature, transferred to round bottomed flasks, the volumetric flasks rinsed out with just 50c.c. more of methyl alcohol, the rinsings added to the reaction mixture (which now totaled 250 c.c. volume). The flasks were connected with reflux condensers and heated to boiling on constant level water baths. The slightly yellow mixtures deepened in color to orange and then to cherry red as boiling continued. The temperatures of the boiling mixtures were between 81° and 83° C. at first, dropping about three degrees when sodium formate began to separate.

At the end of three hours' vigorous boiling, the reac-

tion was stopped by removal of the water bath and the immediate addition of 100 c.c. cold distilled water. On standing, the oily azoxybenzene and unused nitrobenzene separated to some extent, the azoxybenzene collecting as a cake at the bottom of the flask. The contents of the flasks were steam distilled, keeping their volume about 250 c.c., until all the methyl alcohol and unused nitrobenzene had passed over. (About 250 c.c. of impure methyl alcohol passed over first, with water, nitrobenzene, etc., and then about 350 c.c. water distillate brought over the rest of the nitrobenzene). The azoxybenzene is only slightly volatile. After the residues in the flasks had cooled, the alkaline mixtures, now orange yellow, were extracted with benzene until the benzene portions remained colorless and left no residue on evaporation. The benzene extracts were united, dried with shaking over calcium chloride, and then part of the benzene was recovered by distillation, the rest allowed to evaporate in the air from weighed casseroles. The azoxy benzene obtained was practically pure, melting at 35.5° C.

The alkaline solution was boiled to expel the remaining benzene, cooled, and made up to 1 liter in a volumetric flask. From this, aliquot portions were extracted to test for formic acid content. The bromine method, (described under Procedure) was used in this case. The results from four runs i.e. two typical sets of duplicates, are given below.

Run	Azoxy- Benzene obtained g.	Azoxy- benzene: theory g.	per cent theory	Sodium formate obtained g.	Sodium formate: theory g.	per cent theory
A	17.00	19.80	85.85	8.74	10.20	85.90
B	17.20	19.80	86.86	8.85	10.20	86.82
A	17.30	19.80	87.36	8.80	10.20	86.30
B	17.20	19.80	86.86	8.84	10.20	86.68

From a consideration of these results, Klinger's equation is correct. That no carbon dioxide was formed in the reaction was proved as follows: 10 c.c. portions were extracted from the residue of the alkaline mixture left after steam distillation of a reaction mixture. The total volume remaining was measured later and that of the samples extracted added to this. The total volume was 257.3 c.c. The three samples were placed in Schroetter alkalimeters and the usual carbon dioxide tests made, adding 10 c.c. dilute hydrochloric acid, heating in boiling water for five minutes, cooling, passing dry air through, and weighing. The results obtained were:

A	Weight of alkalimeter, acids and sample before analysis	28.9796	gms.
	Weight after analysis	28.9791	gms.
	Loss (CO ₂ ?).....	.0005	gms.
B	Weight of alkalimeter before analysis..	29.3534	gms.
	Weight of alkalimeter after analysis...	29.3515	gms.
	Loss (CO ₂ ?).....	.0009	gms.
C	Weight of alkalimeter Before analysis..	31.7661	gms.
	Weight of alkalimeter after analysis...	31.7650	gms.
	Loss (CO ₂ ?).....	.0011	gms.

These experiments prove that the amount of sodium formate obtained in the reduction is in direct proportion

stoichiometrically to the azoxybenzene formed, and is thus a measure of the extent of the reaction. Accordingly, in most of the succeeding work, the amount of sodium formate was determined as a measure of the reduction.

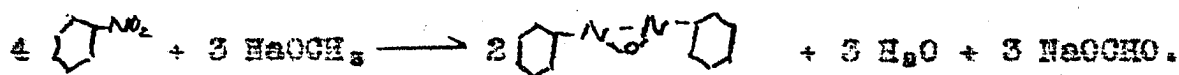
In some of the reactions to be described later the yields of azoxybenzene were so small that their complete recovery from the reaction mixture was not feasible. Since the quantity of formate, large or small, could usually be determined accurately, and since its quantity was proven to be stoichiometrically equivalent to the amount of azoxybenzene formed, the extent of the reducing action of the alkali methylates was measured in terms of the formate yields rather than by recovery of the azoxybenzene.

A STUDY OF THE EFFECT OF WATER ON THE EXTENT OF THE REDUCTION.

Section I. (b)

The effect of small amounts of water on the yield of azoxybenzene presents an interesting problem. Lachman stated that water in small quantities in the alcohol had no effect on the yield of azoxybenzene, but he was working with very concentrated solutions of alkali. If sodium methylate is used as reducing agent we should expect water to have a decided effect on the yield under the conditions of the present study. To determine the extent of the influence of water on the reduction, varying amounts of water were added to the sodium methylate before the addition of the nitrobenzene. The amounts used varied from $1/8$ mole to 3 mols, and thus from

the amount of water formed in the reaction, ~~in which the theo-~~



----- in which the theoretical amount of water would be 2.7 gm. from 24.6 gm. nitrobenzene) to 3 mols.

It was found by experiment that the maximum amount of water soluble in a total vol. of 250 c.c. containing also a methyl alcoholic solution of 17.3 gm. sodium and 20.44 g.c. nitrobenzene, was approximately equivalent to 54 c.c. or three mols. That is, the sodium was dissolved in about 150 c.c. methyl alcohol, 20.44 c.c. nitrobenzene added, and then 54 c.c. of water, with enough methyl alcohol to make a total of 250 c.c., were added. The solution was not entirely clear at room temperature but on slightly warming, solution was complete. Water tends to interfere with the solution of the azoxybenzene.

In the following experiments, amounts of water varying from one-eighth to three molecules were used, as follows: Exp. (1) 0.125 mols; Exp. (2) 0.25 mols; Exp. (3) 0.5 mols; Exp. (4) 1.0 mols; Exp. (5) 1.5 mols; Exp. (6) 2.0 mols; Exp. (7) 2.5 mols; and Exp. (8) 3.0 mols.

In each case, the sodium was first dissolved in the methyl alcohol, then the required amount of water added, *the mixture* well shaken and cooled to room temperature, then the nitrobenzene was added, the whole made up to a total of 250 c.c. with methyl alcohol and the remainder of the treatment was according to the general scheme.

The vigor of the reaction decreased greatly as the

amount of water added increased. When the experiment with three mols of water was performed, the amount of sodium formate formed was less than 20 per cent of the theory.

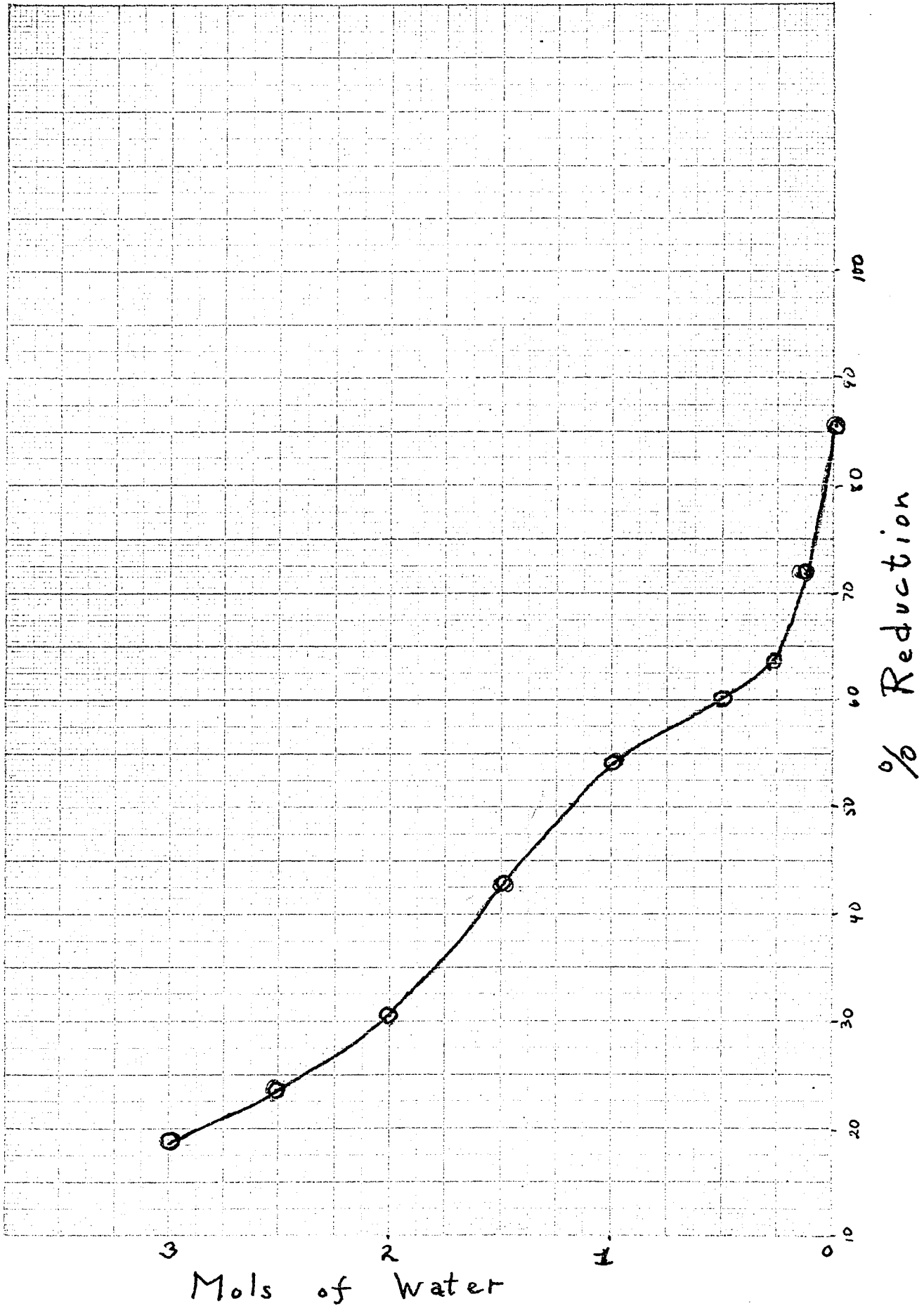
All the formate determinations for the experiments with water and with pyridine (to be described later) were made by the modified Potassium Permanganate Method described in the "Procedure". The results are given in the following table.

REPORT OF WORK ON REDUCTION.

Mols of H ₂ O :	Run :	Vol. taken :	2MnO ₂ :	H ₂ O ₂ :	KMnO ₄ :	H ₂ O ₂ :	KMnO ₄ :	Total KMnO ₄ :	Difference :
:	:	total :	0.1016N :	0.1000N :	0.1016 :	0.1016 :	0.1016 :	of KMnO ₄ :	of KMnO ₄ :
:	:	added :	added :	added :	to neutralize :	to neutralize :	to neutralize :	NaOH :	reduction :
:	:	first c.c. :	0.0 :	0.0 :	1.120 c.c. :	1.120 c.c. :	1.120 c.c. :	H ₂ O ₂ :	0.0 :
:	:	:	:	:	:	:	:	N=0.1000 :	:
:	:	:	:	:	:	:	:	:	:
1/8	A	10	39.00	32.00	3.75	42.75	21.64	21.11	71.42
		1000	40.00	34.00	4.89	44.89	23.61	21.23	71.97
1/8	B	10	34.79	15.52	1.47	36.26	15.28	20.98	71.08
		1000							
1/4	A	10	35.00	33.00	6.50	41.50	32.63	18.87	63.84
		1000	37.00	35.00	6.50	43.50	34.60	18.90	63.97
1/4	B	10	31.19	14.03	1.40	32.59	13.80	18.79	63.62
		1000	31.19	14.03	1.44	32.63	13.80	18.83	63.77
1/2	A	10	32.00	17.00	2.61	34.61	16.73	17.88	60.91
		1000	32.00	16.95	2.45	34.45	16.64	17.81	60.66
		10							
		1000							
1	A	10	30.00	17.00	2.95	32.95	16.73	16.22	64.81
		1000	33.00	21.00	3.86	36.86	20.66	16.20	64.90
1	B	10	33.00	21.00	4.00	37.00	20.66	16.24	64.94
		1000	28.17	13.02	0.60	28.77	12.82	15.95	64.01
1-1/2	A	10	25.00	15.00	2.50	27.50	14.76	12.74	43.10
		1000	25.00	15.00	2.55	27.55	14.76	12.79	43.31
1-1/2	B	10	21.00	10.00	1.60	22.60	9.80	12.76	43.21
		1000	25.00	15.00	2.42	27.42	14.76	12.67	42.90
2	A	20	32.00	16.00	1.55	33.55	15.75	17.80	30.11
		1000	33.00	18.00	2.35	35.35	17.72	17.63	29.84
2	B	20	34.00	19.00	2.40	36.40	19.69	17.71	29.95
		1000	24.00	19.00	2.40	26.40	18.69	17.71	29.95
2-1/2	A	20	23.00	11.00	1.60	24.60	10.82	12.78	23.36
		1000	25.00	13.00	1.46	26.46	12.79	12.67	23.13
2-1/2	B	20	26.00	17.00	2.45	28.45	16.73	13.72	23.20
		1000	27.00	16.02	2.48	29.48	15.74	13.74	23.25
3	A	20	20.13	10.02	1.04	21.17	9.86	11.31	19.14
		1000	21.13	10.52	0.50	21.63	10.25	11.28	19.07
3	B	20							
		1000							

Graph I

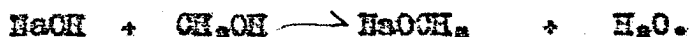
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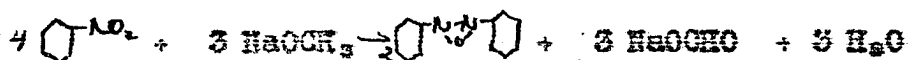
CONCLUSION.

From these results it is evident that water has a great effect on the reduction of the nitrobenzene and that the presence of small amounts of water in the methyl alcohol has a serious inhibiting effect.

The earlier investigators who used potassium and sodium hydroxides in methyl or ethyl alcohols were introducing water by the reaction:



They also held the belief that small amounts of water had no effect on the reaction. On the contrary, if the water formed in the reaction,



were removed, the reaction would probably be more complete. The amount of water formed at the completion of the reaction is approximately equal to the 1/8 molecule added in the experiment. (1/8 mol = 2.25 gm., theoretical amount of water = 2.7 gm.)

Graph I in which the per cent reduction was plotted as abscissae and the number of molecules of water as ordinate, shows that at first increasing amounts of water have a very

great deterrent action on the reduction, but that from one molecule on, the decrease in reduction is roughly proportional to the amount of water present. After three mols of water have been added the water present ceases to have so great an effect on the reduction. The mixture is no longer homogeneous. At one molecule of water, most of the sodium methylate has been broken down to sodium hydroxide and water. This fact is shown by the decrease in the amount of reduction for a given amount of water added. From this point to that for three molecules of water, we have simply the effect of sodium hydroxide and aqueous methyl alcohol, no excess methylate is present.

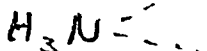
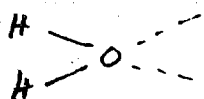
THE EFFECT OF PYRIDINE ON THE RATE OF THE REDUCTION.

Section I. (a).

Pyridine is frequently used as a catalyst in organic chemistry to bring about reactions which involve the separation of hydrochloric or hydrobromic acid; as a carrier in the chlorination and bromination of aromatic hydrocarbons; and in both the Claisen reaction and in the formation of the Grignard reagent. It is supposed that intermediate compounds are formed with the pyridine in some or all of these reactions, and that they then break down, forming the final product and pyridine. The nature of the effect of pyridine, quinoline, etc., in these cases is not well understood as yet.

Pyridine forms solutions analogous to aqueous solutions. This is significant, since pyridine is chemically similar to water in several respects. For instance, there are two unsaturated valencies on the oxygen atom in water,

which lead to the formation of oxonium compounds, and two free valencies on the nitrogen atom in pyridine, quinoline, etc., due to the saturation of which substances analogous to the ammonium compounds are formed:



For these reasons, it should be interesting to study the effect of pyridine in small amounts on the yield of azoxybenzene in these standard experiments. Amounts of pyridine equivalent to 1/8 mol, ^{1/4 mol} 1/2 mol, and 1 mole were used, so that these results could be compared directly with the effects of equivalent amounts of water on the reaction.

The procedure was the usual one for these experiments, the sodium was dissolved in the minimum amount of methyl alcohol, the desired amount of pyridine was added from a pipette, the mixture was shaken and cooled and then 20.44 c.c. of nitrobenzene added, the mixture made up to 250 c.c. with methyl alcohol, and boiled vigorously for three hours. On steam distillation of the reaction mixture, the pyridine distilled over with the alcohol and unused nitrobenzene. The rest of the analysis was the same as that in previous experiments.

In these experiments, the formate began to separate from the solution earlier than in the experiments with water, and in the cases where 1/2 mole of pyridine, and 1 mol of pyridine were used, the separation began within the first fifteen minutes. The solutions darkened as soon as the pyridine was

added, and in the end were darker red than in the previous experiments.

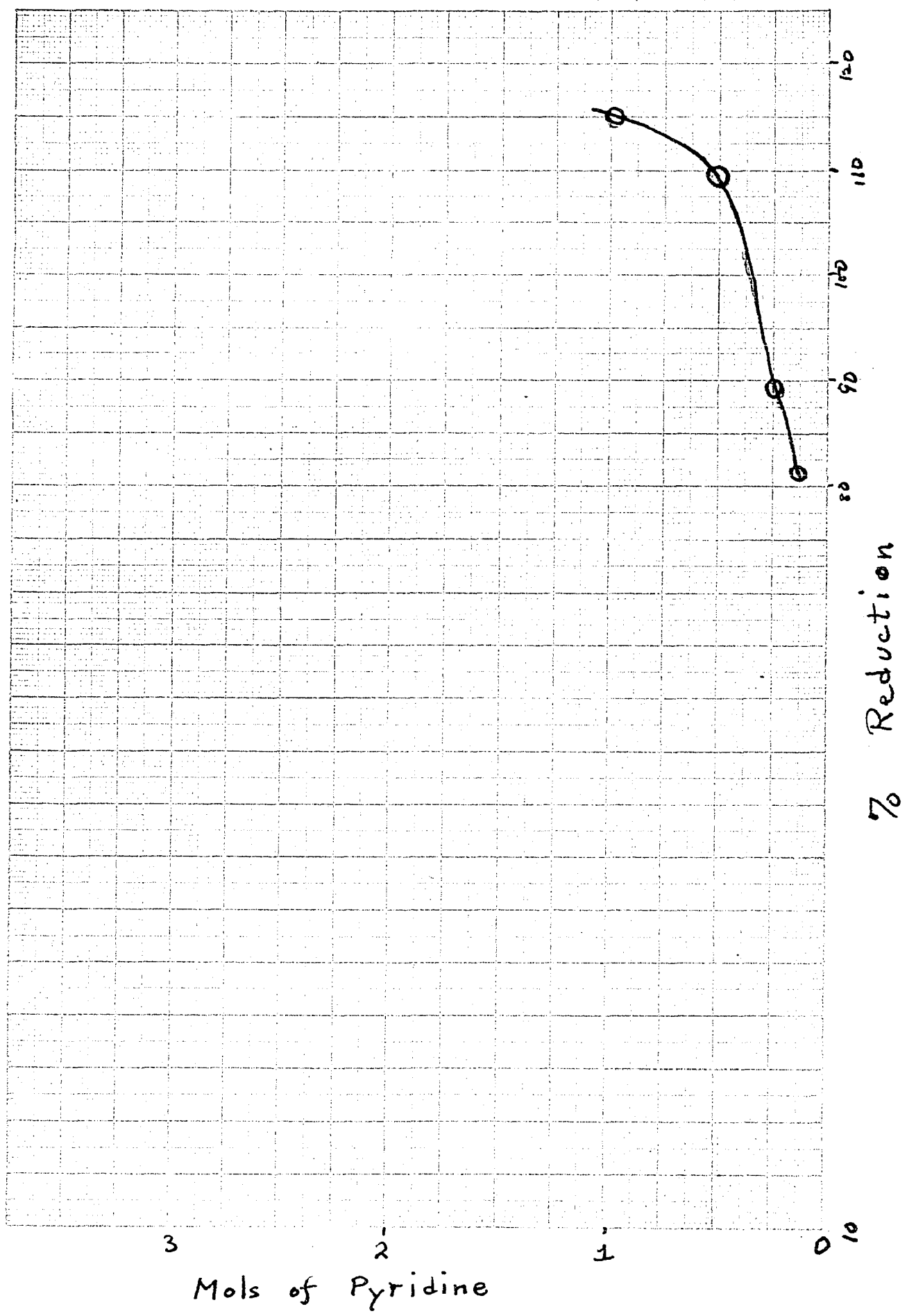
More than one mol of pyridine could not be used because, at the standard volume selected in all these experiments, 250 c.c. it was not possible to dissolve the sodium, the nitrobenzene, and the pyridine to form a homogeneous mixture, since one mol of pyridine occupies 79.87 c.c., the nitrobenzene occupies 20.44 c.c., and the sodium is not soluble in much less than 150 c.c., even with several hours heating on a water bath, with a reflux condenser.

The reaction was found to be more pronounced as the amount of pyridine was increased, but this effect slackened after half a molecule and there was little further increase in reduction (as explained later), for increase of amount of pyridine. After one molecule the mixture is no longer homogeneous.

It is inferred that the reduction goes farther than the azoxy stage when pyridine is present, since more than the equivalent of 100 per cent of sodium formate calculated on the basis of azoxybenzene was found in the case of 1/2 and 1 molecules of pyridine. This would naturally be assumed to be due to the formation of azobenzene but no azobenzene has as yet been separated from the mass of azoxybenzene formed. This work is being continued, and the presence and amount of azobenzene in the mixture will be determined by comparison of the melting points obtained with those of known mixtures of azo and azoxy-³⁵benzene. The first to advocate this method was Snowden, but he failed to publish the melting points of his standard mixtures.

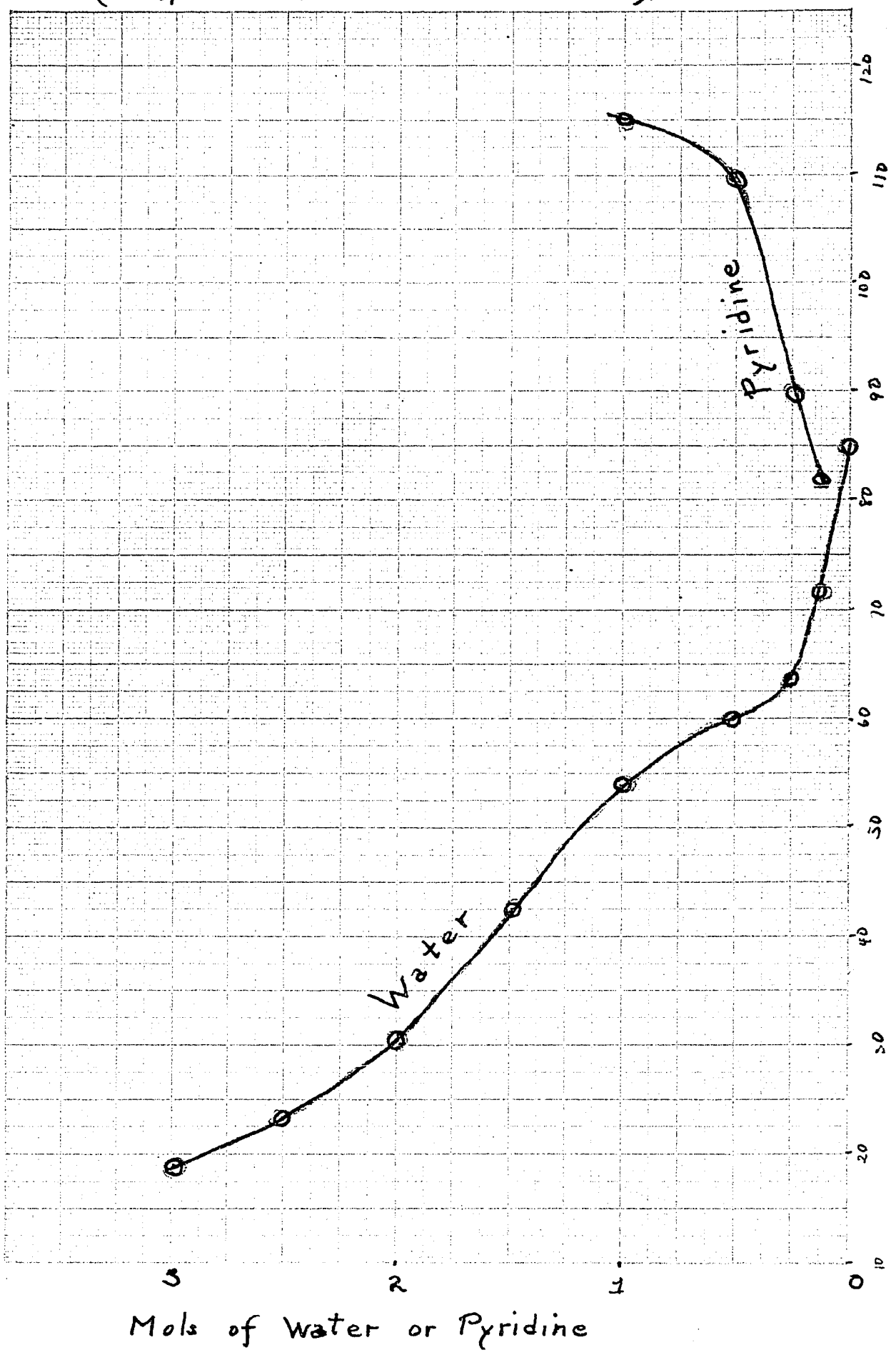
Graph II

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Graph III
(Graph I superimposed on Graph II)

Department of Chemistry, College of Engineering



CONCLUSION.

Small amounts of pyridine in the reaction mixture increased the extent of the reduction very greatly. Amounts of pyridine exceeding 1/2 mol, however, cause a relatively smaller increase in the extent of the reaction, and Graph II indicates that after 1 mol of pyridine, further addition of pyridine has little or no effect on the reduction. A comparison of the effects of water and of pyridine on the reduction of nitrobenzene is given in Graph III. Under certain conditions pyridine is reduced (as by nascent hydrogen from sodium and alcohol, etc.), to *piperidine*, but there is no free sodium in the reaction mixture, so there can be no nascent hydrogen. The cause of the increased reduction is still an open question.

THE REDUCING ACTION OF SODIUM METHYLATE ON
AZOXYBENZENE IN THE PRESENCE OF PYRIDINE.

In order to determine whether or not azoxybenzene is reduced by sodium methylate in the presence of pyridine, an experiment was carried on in which pure azoxybenzene, instead of nitrobenzene, was heated with sodium methylate and pyridine. 20 gm. of azoxybenzene (Kahlbaum) was dissolved in a minimum amount of methyl alcohol, and added to the mixture of 17.3 gm. sodium dissolved in methyl alcohol, with 1/2 mol (40 c.c.) of pyridine. The total volume was made 250 c.c. after boiling for three hours, during which the yellow color of the mixture deepened to orange, but no sodium formate separated, the product was steam distilled until all of the pyridine and methyl alcohol were removed. The residue was extracted with benzene to remove the azoxybenzene, boiled to remove the remaining benzene, and diluted to one liter. This solution had a pale straw color, showing that a small amount of the yellow compound had been produced. Formate determinations gave the following results:

THE EFFECT OF PYRIDINE ON THE REDUCTION OF AZOBENZENE.

Mols of pyridine:	Vol. used : total vol.:	KMnO ₄ : H ₂ C ₂ O ₄ : H=0.1004:	H ₂ C ₂ O ₄ : H=0.09993:	KMnO ₄ : H=0.1004:	Total KMnO ₄ : vol.:	KMnO ₄ : H ₂ O:	Per cent reduction
1/2	A 10 1000	4.00	8.00	1.60	5.60	4.75	2.84
1/2	A 10 1000	4.00	8.00	1.61	5.61	4.75	2.88
1/2	B 10 1000	4.00	8.00	1.60	5.60	4.75	2.84
1/2	B 10 1000	4.00	8.00	1.58	5.58	4.75	2.78

CONCLUSION.

From these results it is evident that azoxybenzene is reduced by sodium methylate in the presence of pyridine, to a small but constant extent. It is very probable that this extent is greater when the azoxybenzene is freshly prepared, (in the nascent state), than when pure azoxybenzene is used as a starting substance, as it was in this experiment. Hence in the usual standardized experiments previously described, the greater reduction can be readily explained.

The yellow compound may also be considered a product of the nascent azoxybenzene, rather than of azoxybenzene in its usual inactive state, for very little of the yellow compound was formed in this blank experiment.

Since it had been proved that azoxybenzene is reduced by sodium methylate in the presence of pyridine, it may be assumed that the product of this reduction is azobenzene. It remains to determine the amount of azobenzene formed when 1/8, 1/4, 1/2 and 1 mol of pyridine is present in the reaction mixture. The benzene extracts from the alkaline residues of steam distillation were used for these determinations (see page 37).

Azobenzene and azoxybenzene are miscible in all proportions, and no efficient method was found for their separation, since they are soluble to about the same extent in most organic solvents, and their boiling points, though very distinct, are too high to be useful in a separation. From these considerations, Snowden⁵⁵ was led to suggest the use of the melting points of known mixtures of the two components as a means for determining the amounts of each substance in a mixture of these two substances. Snowden did not include the melting points of various mixtures of azo- and of azoxybenzene in his paper, so these data had to be determined in connection with this study of the effect of pyridine on reduction. The melting points of known mixtures of pure (Kahlbaum) azobenzene and azoxybenzene are given in the following table. The desired amount of each substance was carefully weighed,

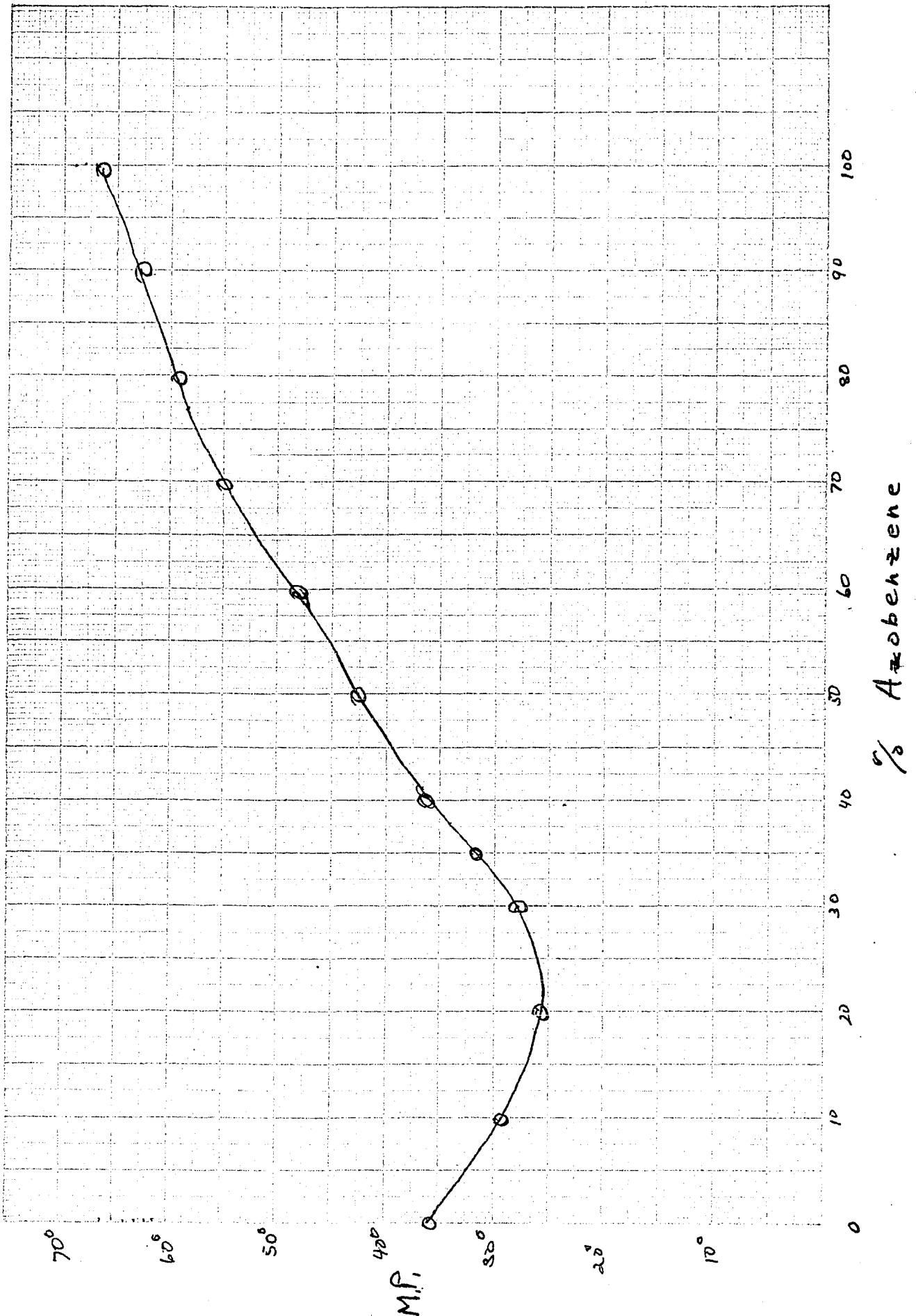
the two substances melted together in a casserole, cooled on ice, ground intimately, and the melting points determined with the usual apparatus, using a water bath and specially prepared thermometers, calibrated to two-tenths of a degree.

MELTING POINTS OF MIXTURES OF AEO- AND AZOXYBENZENE.

% azobenzene	% azoxybenzene	M. P.
0	100	35.4 ^o
10	90	29.2
20	80	25.5
30	70	27.5
40	60	35.5
50	50	42.0
60	40	48.0
70	30	55.0
80	20	59.0
90	10	62.5
100	0	66.2

Graph IV

University of Cincinnati, College of Engineering



The melting points of the mixtures of azo- and azoxybenzene obtained when $1/8$, $1/4$, $1/2$ and 1 mols of pyridine, respectively, were used, were determined, and from these, the per cent of azobenzene in the mixture could be found by reference to the preceding table and graph. In the area in which double values occur, the melting point after the addition of a small amount of either component will locate the desired point on the curve. When the composition of the mixture is known, the extent of the reduction may be determined by adding the amount of sodium formate equivalent to the azoxybenzene to that equivalent to the azobenzene, thus obtaining the total amount of formate formed during the reaction. These values are shown in the following table, along with the total amounts of formate found by the usual formate analysis of the alkaline residues of steam distillation.

Mols pyridine	Total wt. gms.	% azobenzene from graph	azobenzene gms.	azoxybenzene gms.
1/8	15.70	3	0.47	15.23
1/4	17.05	5	0.85	16.20
1/2	20.00	6.5	1.30	18.70
1	20.90	7.0	1.46	19.44

Mols pyridine	gms. NaOCHO azo- benzene	gms. NaOCHO azoxy- benzene	total for- mate azo- & azoxy- benzene	total for- mate obtained in analysis (p.37)
1/8	0.35	7.84	8.194	8.26
1/4	0.64	8.35	8.99	9.13
1/2	0.97	9.63	10.60	11.27
1	1.09	10.01	11.10	11.74

CONCLUSION.

From the preceding table, it will be observed that a close relation exists between the total formate values obtained from melting point data and the values from formate determinations. This substantiates the idea that azobenzene is produced when sodium methylate reduces nitrobenzene in the presence of pyridine, though no separation and weighing of the azobenzene formed is possible. Further, the high formate yields recorded on page 37 are thus accounted for. It has been shown that pyridine has a very decided effect in promoting reduction beyond the azoxy-stage to the azo-stage, and also an effect tending to increase the yield of azoxybenzene.

Section (2).

The reduction of the three nitrotoluenes and the three nitrochlorbenzenes by sodium methylate in methyl alcohol solution was studied under the standard conditions established in this series of experiments.

O-NITROTOLUENE.

Sodium (17.3 gm.) was dissolved in about 150 c.c. methyl alcohol, and the mixture made up to 200 c.c.; 23.46 c.c. or 27.4 gm. of o-nitrotoluene were made up to 50 c.c. in a volumetric flask, with methyl alcohol, and the two solutions were united and boiled in the regulation method for three hours. The solution was pale yellow at first but changed to orange, to red and then rapidly blackened as the temperature of the mixture rose to the boiling point, 85° - 86° C. The mixture remained thin and *mobile*, no formate separated during the boiling, and the temperature of boiling dropped to 83° C. toward the end. Distilled water was added (100 c.c.) to stop the reaction, and the mixtures were steam distilled. Much unused o-nitrotoluene passed over with the methyl alcohol and with the watery distillate. The alcohol portions were resteam distilled to remove the alcohol, then diluted and extracted with benzene. The water distillates were also extracted with benzene, the benzene extract dried, the benzene partly removed by distillation, and finally evaporated in the air. The amounts of o-nitrotoluene recovered were A:48.43 per cent (13.27 gm.) B:50.32 per cent (13.79 gm.)

The residues from the steam distillation were black and tarry, showing that side reactions had taken place. They were placed in 2 liter beakers, and the oil did not settle out. From A about 10 c.c. were removed to test for various properties. On acidification of a portion a copious brown precipitate separated. This was not the toluidine ^{of} Klinger and Pitschke (B 18 2551) for ~~it~~ ^{that} would have been soluble in the acid, reprecipitating when alkali should be added. Instead, ~~on~~ ^{after} filtering out the brown precipitate, the solution was made alkaline, and ^{it then} became a lighter yellow than when acid, and remained clear.

The two residues were then acidified and filtered on Büchner funnels, the precipitates thoroughly washed with distilled water. The filtrate was yellow, and the coloring matter was not soluble in the organic solvents; ligroin, benzene, carbontetrachloride, and ether. The extracts were colorless and left no residue on evaporation.

The acid filtrates grew cloudy on standing. More acid did not dissolve the substance, but on rendering them alkaline, the cloudiness disappeared. Coconut charcoal, finely powdered, was added and the mixture boiled and filtered. But little of the coloring matter was removed. The filtrates were made up to 2 liters and 2 100 c.c. portions removed to test for formate. After dilution, acidification and boiling to remove carbon dioxide, the mixtures were made neutral ^{to litmus} by sodium hydroxide, and then bromine water added. Immediately a light brown precipitate formed, which darkened on standing. Thus the

formate could not be determined in this way. Extraction with benzene of the mixture before the formate determination was of no help, for nothing was extracted. The same light precipitate was formed. Some bromide insoluble in ordinary organic solvents was probably formed.

The brown precipitates obtained after steam distillation and acidification of the alkaline residue were in very small amounts - 3 to 5 gms. and no pure compound was isolated on recrystallization from alcohol. Larger portions were needed for this investigation.

m-NITROTOLUENE.

The sodium was dissolved as before in about 150 c.c. methyl alcohol and made up to 200 c.c. volume, 23.46 c.c. (27.4 gm.) m-nitrotoluene were added and the total volume made up to 250 c.c. The orange red mixtures were then boiled for three hours, turning deep red. The temperatures rose to 85° C. as boiling point for the mixture. When sodium formate began to separate, the temperature fell to 81° C. Water was added as usual at the end of three hours' boiling, to stop the reaction and the mixtures were steam-distilled until over 500 c.c. had passed over.

Formate determinations were made by the bromine method. The results were as follows:

Run	Azoxy compound found g.	Theoretical yield g.	per cent theory	Sodium formate found g.	Theoretical yield g.	Per cent theory
A	17.30	22.60	76.54	7.89	10.20	77.32
B	17.60	22.60	77.67	7.66	10.20	77.02

The azoxytoluene was recovered from benzene extracts of the alkaline mixture remaining after steam distillation. They formed yellow needles melting at 57° C.

P-NITROTOLUENE.

To the sodium methylate methyl alcohol solution in about 150 c.c. volume, was added 27.41 gm. of p-nitrotoluene dissolved in methyl alcohol. The volume was made up to 250 c.c. and the mixture was boiled for three hours. The mixture began to darken, even before heating, first becoming brilliant red, then very dark red, then wine color, thickening rapidly and giving off heat. On heating, the color became brownish, then more yellowish, with a very dark brown suspension, and the temperature rose to 76° C. as boiling temperature. After the three hours' boiling, water was added and the whole mixture steam distilled. The alcohol was easily separated, but it was difficult to get more distillate to pass over when the alcohol was gone.

A brick red precipitate settled over night. After acidifying with dilute sulphuric acid, the mixture was filtered, and the product dried on a Büchner filter, then to constant weight at 100° C. The red substance decomposed without melting when heated on a platinum spatula. This substance was described by Klinger and other investigators (See the Historical Section), and is considered to be in some way related to stilbene. The weights obtained were: A 20.3 gm., B 21.00 gm. The theoretical yield for p-azoxytoluene would be 22.5 gm.

The filtrate from the red amorphous compound was extracted with benzene, but its yellow coloring matter could not be separated in that way. The solutions were then made up to 2 liters, and portions tested by the bromine method for sodium formate content:

Run	Sodium formate obtained : g.	Sodium formate theory : g.	Per cent theory.
A	2.99	10.20	29.26
B	3.00	10.20	29.41

These results are not in accord with those obtained with nitrobenzene and with m-nitrotoluene, and this behavior will be discussed later, in the conclusion.

O-CHLORONITROBENZENE.

The experiments on o-m- and p-nitrotoluenes showed that only in the case of the m-compound were the azoxy compounds formed to any extent. It was considered of interest to determine the behavior of o-chloronitrobenzene, m-chloronitrobenzene and p-chloronitrobenzene on reduction with sodium methylate, under the conditions used in the previous experiments.

The sodium was dissolved in methyl alcohol, as usual, and to this 31.5 g. o-nitrochlorobenzene was added, dissolved in a little methyl alcohol, the total volume being made up to 250 c.c. When the nitro-compound was first added to the sodium methylate, there was a gradual darkening to brownish

color, but as the substance was heated, the color changed to orange red, and on boiling to dark purple, with a reddish orange foam and solid separating along with colorless sodium formate. The temperature rose to 79° C., then dropped slowly to 74° - 75° C. When the mixture had boiled three hours, water was added and the mixture allowed to cool. A mass of yellow crystals was found at the bottom of the flask, after standing over night.

Steam distillation was carried on until about 800 c.c. water distillate had passed over in addition to the alcoholic distillate, because a small amount of yellow oil, supposed to be *o*-nitroanisol was passing over. This substance froze at 0° C. in an ice mixture, and melted at 8.5° C. The melting point for *o*-nitroanisol is given as 9.0° C., therefore, the identity was established. Not enough of the oil was obtained for weighing.

During the steam distillation the yellow crystalline substance was partially decomposed, for a purple or blackish tarry residue separated, and was partially removed by filtration. The residue was extracted, but a brown tarry oil was recovered which would not solidify, and which darkened on heating. It is very soluble in benzene.

The alkaline solution, after extraction, was of a reddish brown color, but clear. Formate determinations were made by the permanganate method, and were found to be over 100 per cent if calculated on the basis of azoxy compound formation.

The formation of the tarry substances probably accounts for the high formate values. The values are given as follows:

Run	: Formic acid : : found g. :	Theoretical : : yield g. :	Per cent theory.
A	8.18	6.9	118.5
B	8.19	6.9	118.7
A	8.17	6.9	119.4
B	8.21	6.9	119.0

These results show that it is impossible to correlate the yields of reduction products of *o*-chloronitrobenzene with the quantity of formate obtained. This is analogous to previously described results obtained when *o*- and *p*-nitrotoluene were studied.

METACHLOR-NITROBENZENE.

The sodium methylate solution was made as usual. 31.5 gm. *o*-chloronitrobenzene were added, and the volume made up to 250 c.c. The mixture was heated to boiling for three hours. The reaction mixture turned yellow and then darkened, and the boiling point was 82° C. The boiling point dropped gradually to 79° C. and a light yellow or white crystalline precipitate separated and attached itself to the walls of the flask. This was not the usual jelly-like sodium formate precipitate. At the end of the reaction, water was added, and the mixture subjected to steam distillation.

The residues in the flasks on cooling contained hard yellow masses of crystals at the bottom. The liquid portions were poured off and retained, and small amounts of water were added to the solid masses of crystals, to wash them. The washings were added to the alkaline solution for formate determination. The masses of crystals were melted by boiling in water, and on cooling under the tap and shaking vigorously, they solidified in small pieces which could be removed from the flask with ease. The hard yellow masses were filtered on Büchner funnels, washed, dried, pulverized and weighed when thoroughly dry. The substance was recrystallized twice from alcohol, yielding pure *m*-dichlorazoxybenzene, melting at 96° C.

Run	Weight of :azoxy com- : pound : found g.	Theoretical : Yield : g.	Per : cent : theory:	:	:	:
A	25.59	26.70	95.83			
B	25.70	26.70	96.25			

The alkaline solution was made up to 1 liter and 20 c.c. portions used in formate determinations by the bromine method. The results were over 100 per cent theory showing that some other substance, besides the formate, had been oxidized - possibly the ever-present yellow compound. This compound could not be removed by extraction with organic solvents. The permanganate method had not yet been applied to formate determinations in these experiments.

P-CHLORONITROBENZENE.

The sodium methylate solution was treated with 31.5 gm. p-chloronitrobenzene, the total volume made up to 250 c.c. (after heating to dissolve the nitro-compound, and cooling) and the whole boiled three hours. The mixture darkened, the temperature rose to 81° C. as the boiling point, then fell to 77° - 78° C. as the formate began to separate. At the end of the reaction the mixture was a deep orange color clear when hot, but after adding water and cooling the solution was full of light yellow crystals.

The mixtures were steam distilled. Three liters of distillate had to be collected before all the volatile matter had passed over. P-chloronitrobenzene was found to a small extent in the first fractions. Colorless very fine needle crystals were also present, which were filtered, dried, and found to melt at 54° C. These were p-nitroanisol. The second and third portion contained large amounts of this compound which would crystallize in the condensers and had to be steamed down occasionally. The liquid then ran into the watery distillate collectors and hardened in pellets and ribbons. This substance was pure p-nitroanisol, melting at 54° C. It was filtered out, the containers washed out with benzene, the alcoholic portions re-steam distilled, and the residues extracted with benzene. The extracts were united and evaporated. The yields were as follows, the crystals melting at 54° C.

Run	Gms. of p-nitroanisol	Theoretical yield for p-nitroanisol	Per cent theory.
:	G.	G.	:

A	20.20	30.6	66.03
B	20.00	30.6	65.36
A	20.20	30.6	66.03
B	20.65	30.6	67.48

The residues from steam distillation were filtered, and the filtrates extracted with benzene. Small amounts of yellow crystals melting at 127° C., obviously not homogeneous, were obtained. Between 4 and 5 gm. of these crystals were obtained in each case. By fractional recrystallization from alcohol of the united yields it was found that one part was relatively insoluble in alcohol and possessed a higher melting point than the other. After five recrystallizations in fractions a component (the less soluble) was isolated which melted at 153.5° C. and was thus proved to be p-di-chlor-azoxybenzene, (M.P. 155°C.). The other, more soluble component melted at 115° C. after several recrystallizations, evidently p-azoxyanisol, (116° C.).

The filtrates from the azoxy compounds were intensely yellow, and an attempt was made to remove the yellow compound. Organic solvents do not extract this to any extent, from water solution. The A portion had stood longer after steam distillation, than the B portion, and long yellow

needle crystals separated. In filtering these with the azoxy compound, part of this filtrate was lost, so that later formate and chloride tests were impossible for the A portion. The yellow needles were very soluble in water and several were saved in washing the azoxy residue for testing. They decompose before melting, and when heated on a nickel spatula turn red, and then explode with a little puff, being probably the sodium salt of some organic acid, ^{probably containing nitrogen.} When acid is added to a solution of these crystals in water, the intense color fades to pale straw. This proves that the compound is related to those colored compounds noticed in all preceding experiments which were formed during the reduction, intensely colored usually yellow in alkaline solution, slightly colored in acid, much more soluble in water than in organic solvents, and oxidizable by bromine in neutral or acid solution.

About half of the alkaline solution A was made just acid with hydrochloric acid, and evaporated dry on a steam bath. The residue weighed 21.9 gms. after drying to constant weight. The crystals (mostly sodium chloride with some pale pink ones) were placed in a Soxhlet extractor and extracted with benzene for 5 - 6 hours. On cooling the liquid contained a feather shaped mass of pale yellow crystals. These were dried after washing with a little benzene, and melted at 115° - 116° C. The weight was 2.9 gm. so that the whole solution probably contained about 6 gm. of the substance, or more if all had not been extracted.

This acid compound is soluble in water, especially in alkaline solution. It is not very soluble in alcohol, benzene and less so in ligroin and chloroform. It contains no halogen.

The chlorine in the alkaline solution B was determined by the Volhard method. If all the p-nitrochlorobenzene had been converted to p-nitroanisol, p-azoxyanisol, or both, there would have been 7.09 gm. of chlorine liberated. The yield obtained is given below:

	: Chlorine : : liberated: : 5. :	Theory for : chlorine. : 5. :	Per cent theory
A			
B	6.34	7.09	89.40
A	6.34	7.09	89.40
B	6.41	7.09	90.45

The filtrates from the azoxy compounds were also tested for sodium formate, but the yields were over 100 per cent theory, showing that some other substance besides nitrobenzene had been reduced. As in the cases of the o- and p-nitrotoluenes and the o-chloronitrobenzene, no correlation could be made between the azoxy compound and the formate.

CONCLUSIONS.

The reduction of the nitrotoluenes and the chloronitrobenzenes were studied under the same conditions imposed for nitrobenzene in the first part of this thesis. The meta

compounds reacted in the same manner as the nitrobenzene itself, toward the reducing agent sodium methylate, but the o- and p-derivatives, where the methyl group or chlorine functions negatively, underwent complex reactions, giving several products in each case, and therefore were not so well suited to analysis by the formate method. When the azoxy compound was the sole product, the formate method was adequate to measure the extent of the reduction.

Since, as previously noted, on the one hand, only 4 gms. of azoxy compounds were obtained while on the other, there was approximately 90 per cent of the chlorine liberated as sodium chloride, it is very probable that in p-chloronitrobenzene, the chlorine atom is the reactive part of the molecule, being replaced by $-OCH_3$, while the nitro group is slightly affected by the reducing action of $NaOCH_3$.

SECTION III.

The reducing action of potassium methylate on nitrobenzene is of interest, since it is of great practical importance to substitute sodium for potassium wherever feasible. Meisenheimer (see page 9), stated that potassium methylate had no effect on nitrobenzene until the alcohol had boiled away.

In this experiment potassium was cleansed by dipping each ball of the metal into a mixture of one part of methyl alcohol to nine parts of benzene, then rinsing well in pure benzene. The balls were weighed by difference under benzene. Two samples of 29.4 gm. each were cut into small pieces under benzene, and dropped through reflux condensers into 150 c.c. portions of methyl alcohol in 500 c.c. flasks, cooled in an ice mixture. The solutions were then transferred to 200 c.c. volumetric flasks, 20.44 c.c. (24.6 gm.) of nitrobenzene added, and the whole made up to 250 c.c. volume with methyl alcohol. The solution began to redden immediately. It boiled at 85° C. at first, dropping slowly to 79°, darkened to deep red-brown, but no formate separated during the reaction.

On the addition of distilled water at the end of three hours' boiling, the solution became a deep orange in color.

Formate determinations (given in the following table), proved that reduction had taken place in the presence of the methyl alcohol.

THE EFFECT OF POTASSIUM METHYLATE ON HYDROPEROXIDE.

Run	Vol. used: KMnO ₄	H ₂ O ₂	KMnO ₄	Total: KMnO ₄	KMnO ₄	Per cent reduction.
	: N=0.1004	: N=0.09993	: N=1.004	: N=	: N=	
	Vol. : c.c.	: c.c.	: c.c.	: H ₂ C ₂ O ₄	: HCOOH	
A	$\frac{10}{1000}$	49.00	26.00	4.14	53.14	25.88 27.26 91.03
A	$\frac{10}{1000}$	48.00	26.00	5.18	53.18	25.88 27.30 91.09
B	$\frac{10}{1000}$	48.00	26.00	5.08	53.08	25.88 27.20 91.28
B	$\frac{10}{1000}$	48.00	26.00	5.10	53.10	25.88 27.22 91.37

CONCLUSION.

The preceding results show that potassium methylate exerts a slightly greater reducing action on nitrobenzene than does sodium methylate. The solubility of the potassium formate in methyl alcohol solution probably exerts some opposition to the reduction of nitrobenzene, but this effect is over-balanced by the greater activity of potassium.

The effect of potassium methylate is so like that of sodium methylate, that there is little need for the use of potassium in this reaction.

GENERAL CONCLUSIONS.

(a). The equation given by Klinger for the reduction of nitrobenzene by sodium methylate in methyl alcohol solution has been verified quantitatively. No carbon dioxide is formed during the reaction, and the sodium formate obtained is equivalent to the amount of nitrobenzene reduced to azoxybenzene, and can therefore be used as a measure of the extent of the reduction.

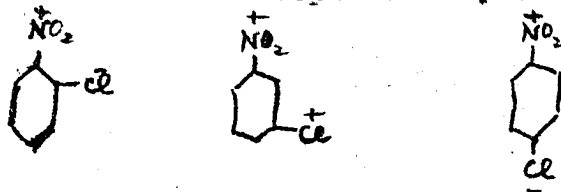
(b). The effects of varying amounts of water on the reduction have been determined. Small amounts of water decrease the speed of the reaction to a decided degree. This effect becomes less marked as the amount of water is increased. When an amount of water equivalent to all the sodium methylate

present has been added, further additions of water cause a proportional decrease in the reduction, or the extent of reduction is inversely proportional to the amount of water added, until we reach an amount of water which renders the mixture heterogeneous. Further additions of water have little effect.

(c). The effects of varying amounts of pyridine on the reduction have been studied. In this case small amounts of pyridine cause a relatively large increase in the reduction. As the solution becomes more concentrated with respect to pyridine, the effect diminishes, and probably ^{little} further effect, would be noted when the solution becomes heterogeneous. The amounts of sodium formate obtained in the last two experiments with pyridine indicate reduction to a lower stage than azoxybenzene, or reduction of the pyridine itself. Since nascent hydrogen is usually considered necessary for the reduction of pyridine, the catalytic effect of pyridine on the reduction presents an interesting problem for future research.

(d). The reduction of the nitrotoluenes and the chloronitrobenzenes have been studied under the standardized conditions for conducting these experiments. It was found in these experiments, that the behavior of the m-compounds was normal, and comparable to that of nitrobenzene, while the o- and p-compounds underwent side reactions, and formed little or no azoxy compounds. This behavior is in accordance with what we might expect from a consideration of the electronic formulae. For instance, in the o- and p-chloronitrobenzene, the

chlorine is negative and replaceable by the negative methylate radical $-OCH_3$, while in the *m*-chloronitrobenzene, the chlorine is positive and not replaceable, thus:



It is well known that in all chlorine substituted organic compounds in which the chlorine functions positively, boiling with sodium methylate will not displace the chlorine from the nucleus, while in those compounds containing negative chlorine, the latter is readily displaced from the nucleus by sodium hydroxide.

(e) The effect of potassium methylate, as compared with that of sodium methylate, upon nitrobenzene in methyl alcohol solution, has ^{also} been investigated.

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	Janoysky	M 7	124	
		B 19	2158	
		B 24	971	
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		Rec. Trav. Chim.	14	89
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