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THE OXYNITRATION OF BENZENE TO NITROPHENOLS

by
Marvin Carmack
University of Pennsylvania

Report OSRD No. 4025
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Division 8
NATIONAL DEFENSE RESEARCH COMMITTEE
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OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

THE OXYNITRATION OF BENZENE TO NITROPHENOLS

Service Project: NO-117

Endorsement (1) from Dr. Ralph Connor, Chief, Division 8 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and noting:

> "In 1942 heavy demands for phenol threatened to reduce critically the amount of this material available for the production of picric acid and ammonium picrate. The Navy, therefore, requested Division 8 under Service Project NO-117 to reinvestigate the oxynitration of benzene. This process, the direct conversion of benzene to dinitrophenol and/or picric acid by treatment with nitric acid and mercuric nitrate, would eliminate the necessity for using either phenol or chlorobenzene for the manufacture of picric acid and ammonium picrate.
>
> "The work of Division 8 on the oxynitration of benzene has included both studies of the mechanism of the process and studies directed toward the development of preparative procedures. The mechanism of oxynitration has been established and has been described in OSRD-3154 and 4024. Preparative procedures, batch and continuous, have been developed and are described in OSRD-4026 and in the present report.
>
> "This report is concerned primarily with continuous oxynitration processes. The most successful of these is one in which excess benzene continuously extracts organic products from the reaction mixture. The yields equal or exceed those obtainable in batch operation, and the losses of mercury catalyst are minimized. Data on the effect of varying experimental conditions are described, and experiments on the mechanism of the process are presented.
>
> "Inasmuch as the expected phenol shortage did not develop, none of the procedures described in OSRD-4025 and 4026 was put into pilot plant operation.

Endorsement (Continued)

"On the basis of these laboratory investigations, it is believed that the oxynitration process can compete successfully on an economic basis with other known methods of making picric acid, but this can be established definitely only by pilot plant studies. In any case, serious consideration should be given to this process, if and when a need arises for the creation of picric acid facilities over and above those already in existence.

"This is the last report to be issued by Division 8 on the oxynitration reaction."

This is a progress report under Contract OEMsr-646 with the University of Pennsylvania.

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THE OXYNITRATION OF BENZENE TO NITROPHENOLS

A Formal Report of an investigation carried out under Contract OEMsr-646 in the Department of Chemistry of the University of Pennsylvania, Philadelphia, Pennsylvania, between October, 1942, and April, 1944.

Research Associates:

Manuel M. Baizer
G. Richard Handrick
Leonard W. Kissinger
Edward H. Specht

Official Investigator:

Marvin Carmack

Philadelphia
May 31, 1945

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ABSTRACT

An extensive reinvestigation of the oxynitration of benzene to 2,4-dinitrophenol and/or picric acid by reaction with nitric acid-mercuric nitrate solution has been carried out in collaboration with other groups.

A new procedure for continuous oxynitration of benzene to dinitrophenol (with some picric acid), utilizing the continuous liquid-liquid extraction principle, has been developed under this contract: an excess of the organic reactant, benzene, serves to remove benzene-soluble organic reaction products from the solution in which they are formed, eliminating the necessity of interrupting the operation of the reactor while products are removed. Yields of nitrophenols equal or exceed those obtained by batch procedures, and losses of mercury catalyst are minimized. Data illustrating the effects of experimental variations are described.

A number of batch oxynitration runs are described.

Previous work on the mechanism of the oxynitration reaction is reviewed, and new experiments which throw light on the mechanism have been carried out.

ACKNOWLEDGMENT

Experimental work on the oxynitration reaction under Contract OEMsr-646 was carried out by Dr. Manuel M. Baizer, Dr. G. Richard Handrick, Dr. Leonard W. Kissinger, and Dr. Edward H. Specht. Throughout the investigation Professor E. C. Wagner of the Department of Chemistry of the University of Pennsylvania offered many valuable suggestions, particularly with respect to the development of suitable analytical methods. Dr. Ralph Connor, Chief of Section 8.2, N.D.R.C., also contributed helpful advice. It is a pleasure to acknowledge the efforts of all of these persons.

Marvin Carmack
Official Investigator

TABLE OF CONTENTS

III. THE MECHANISM OF THE OXYNITRATION PROCESS

APPENDIX: ANALYTICAL METHODS

BIBLIOGRAPHY

INTRODUCTION

Definition of Oxynitration.- The oxynitration of benzene is a process involving the reaction of benzene with aqueous nitric acid containing mercuric nitrate as a catalyst to form 2,4-dinitrophenol and/or picric acid. The by-products are nitrobenzene, p-dinitrobenzene, o-dinitrobenzene, carbon dioxide, oxalic acid, and traces of other products. The reaction has been investigated especially as a method of manufacturing the military high explosive, picric acid.

Purpose and Results of the Present Investigation.- During 1942, the heavy demand for phenol seemed likely to create a shortage of this material for the manufacture of picric acid and ammonium picrate. A service project, NO-117, directed the reinvestigation of the oxynitration reaction as a possible means of manufacturing picric acid directly from benzene.

Work under Contract OEMsr-646 at the University of Pennsylvania was directed to a study of the oxynitration reaction during the period October, 1942, until the spring of 1944, when it became evident that the demands of the services for picric acid could be met from existing facilities. The work was carried out in collaboration with other NDRC contract groups at the Universities of Michigan[27,28] and Chicago.[25,26,27]

Studies at the University of Pennsylvania included a reinvestigation of earlier work on batch processes, an investigation of the reaction mechanism, and eventually the development of a new modification of the oxynitration reaction which has been called the Continuous Extraction Process. This report is devoted chiefly to a description of the Continuous Extraction Process.

The Continuous Extraction Process.- In this process benzene is introduced into the nitric acid-mercuric nitrate solution through a cluster of glass jets by which it is broken up into small droplets. The dispersed benzene droplets rise through the solution, partially dissolving and reacting. The excess undissolved benzene serves to extract the products of reaction from the solution. The supernatant benzene extracts are removed continuously, processed to remove reaction products, and the benzene is returned to the reaction mixture through the injection jets. The reaction mixture is fortified continuously with 98% nitric acid to maintain uniform acid concentration. The expansion in reaction volume is compensated by the removal of small portions of reaction solution, concentration of the catalyst by distillation, and return of the concentrated catalyst solution to the main reaction mixture. The yields and the quality of the nitrophenolic products appear to be comparable to the yields and quality obtained in batch runs under similar reaction conditions. It appears to be possible to reach and maintain an essentially steady state within the reactor with respect to the concentrations of reactants and products.

Types of Procedures Used for the Oxynitration of Benzene.- The nitric acid concentrations used for oxynitration in the present as well as in earlier studies have generally been in the range of 50 to 65% by weight (which is equivalent to 10 to 14 M solutions). The mercuric nitrate catalyst concentrations have usually been between 0.2 M and 0.5 M, although both higher and lower concentrations have been studied. Other substances have been added in some experiments.

Four main types of procedures can be distinguished:

Type 1. Complete Disappearance of Benzene. 2,4-Dinitrophenol (DNP) as the Major Product.

Benzene is agitated with a considerable excess of oxynitrating solution at temperatures usually in the range of 50-60°C. until all benzene disappears. Crystalline DNP is isolated either by chilling the solution to precipitate the product or by extracting with an immiscible organic solvent.

Type 2. Complete Disappearance of Benzene. Picric Acid (PA) as the Major Product.

Similar to Type 1 except that after completion of the first phase of reaction the temperature is raised gradually to the boiling point. At the higher temperatures, oxidative destruction of some of the by-products occurs and most of the DNP is nitrated to PA. When the mixture is chilled, crystalline PA separates.

Type 3. Partial Reaction of Benzene. 2,4-Dinitrophenol as the Major Product.

An excess of benzene is allowed to react with the oxynitration solution under mild conditions, usually in the temperature range of 50-60°C., with or without agitation. The reaction is terminated before all of the benzene is consumed. Some of the reaction products are found in solution in the benzene phase, the amount depending upon the relative volumes of the benzene and nitric acid phases present.

Type 4. Partial Reaction of Benzene. Picric Acid as the Major Product.

When high concentrations of nitric acid are used or when manganous nitrate is added as a catalyst or with any of several other special modifications of conditions, a considerable proportion of the DNP may be nitrated to PA even though some of the benzene is not consumed. This is true of certain variations of the Continuous Extraction Process.

Historical.- The oxynitration of aromatic hydrocarbons was discovered and patented by Wolffenstein and Böters[1] about 1906. Earlier patents described a mercury-catalyzed hydroxylation of aromatic compounds without nitration.[2] Subsequent publications of Wolffenstein and collaborators[3] provided further details of the reaction.

During and immediately following World War I, investigations of methods for the preparation of picric acid from benzene by the oxynitration method were carried out in France,[4,5] England,[6,7] Austria-Hungary,[8,9] the United States,[10,11,12] Canada,[13] and Germany.[14]

In 1917, three slightly different oxynitration processes were offered to the United States Government by Reid and Lodge, by Brewster, and by Lloyd. Brewster, Lodge, Lloyd, and their associates eventually formed a single company, The Contact Chemical Company of America, Inc., and together late in 1918 they carried out limited pilot plant investigations at the Nixon Nitration Works, Metuchen, New Jersey, with financial support of the United States Army Ordnance Department.[15] The results of several large-scale runs were considered promising, but apparently the number of technical problems still unsolved and the end of the war brought an end to the investigations before a completely satisfactory plant process had been worked out.

After World War I some further investigations of the oxynitration reaction were made at Picatinney Arsenal,[16] but were discontinued in 1921 because the results indicated that the consumption of nitric acid would be high and that costly special equipment would be needed.

More recently other papers on oxynitration have appeared from France,[17] Czechoslovakia,[18] and Russia.[19]

In 1940, W. C. Lodge of Canada, coinventor of a process offered to the U. S. Government in 1917, reinvestigated the oxynitration of benzene with particular emphasis on the reaction under mild conditions to form DNP. His reported yields were checked by Boyer[20] of McGill University.

G. F. Wright,[21] of the University of Toronto, began a study of the oxynitration reaction in 1940 which culminated by 1942 in the development of a process for producing picric acid on pilot plant scale. Adams and Marvel[22] of the N.D.R.C. checked and verified the yields of PA obtained under the conditions specified by Wright. A detailed evaluation of the Wright Process from an engineering point of view and an analysis of costs in comparison with other methods for picric acid manufacture were made by P. Ferencz[23] of the Research and Development Department, Canadian Industries Ltd.

The Barrett Company, New York City, has studied the oxynitration reaction to produce DNP. A memorandum report on the Barrett Process, dated March 11, 1942, appears in a report from Picatinney Arsenal[24] on the testing of the quality of picric acid prepared from DNP made by the Barrett Process.

<u>Conventions of Expressing Concentrations and Rates in This Report</u>.- The oxynitration reaction involves a very complex sequence of reaction steps, some of which are still obscure. For this reason a kinetic point of view has been adopted as far as possible in presenting the data of this investigation. Concentrations of reactants are usually expressed in terms of moles per liter of reaction volume (M) rather than in weight percentages, the units used in much of the previous work.

The use of weight percentages for solutions of organic and inorganic solutes in aqueous nitric acid is apt to lead to ambiguity. In some of the data sheets of this and other reports of oxynitration studies, when concentrations of nitric acid in aqueous solution containing various other solutes in addition to the acid were being considered, an empirical weight percentage has been used: the "percentage" of nitric acid is expressed in terms of the weight percentage for a solution of pure nitric acid in water having the same molar concentration. Although the conventions have not always been specifically stated, it is our impression that other workers have also used such "equivalent percentages" rather than true weight percentages.

Table I shows the relationship between the weight percentages of nitric acid solutions in water at 25°C. and the molar concentrations as used in this report. This table is the basis also for the calculation of equivalent percentages in reaction mixtures.

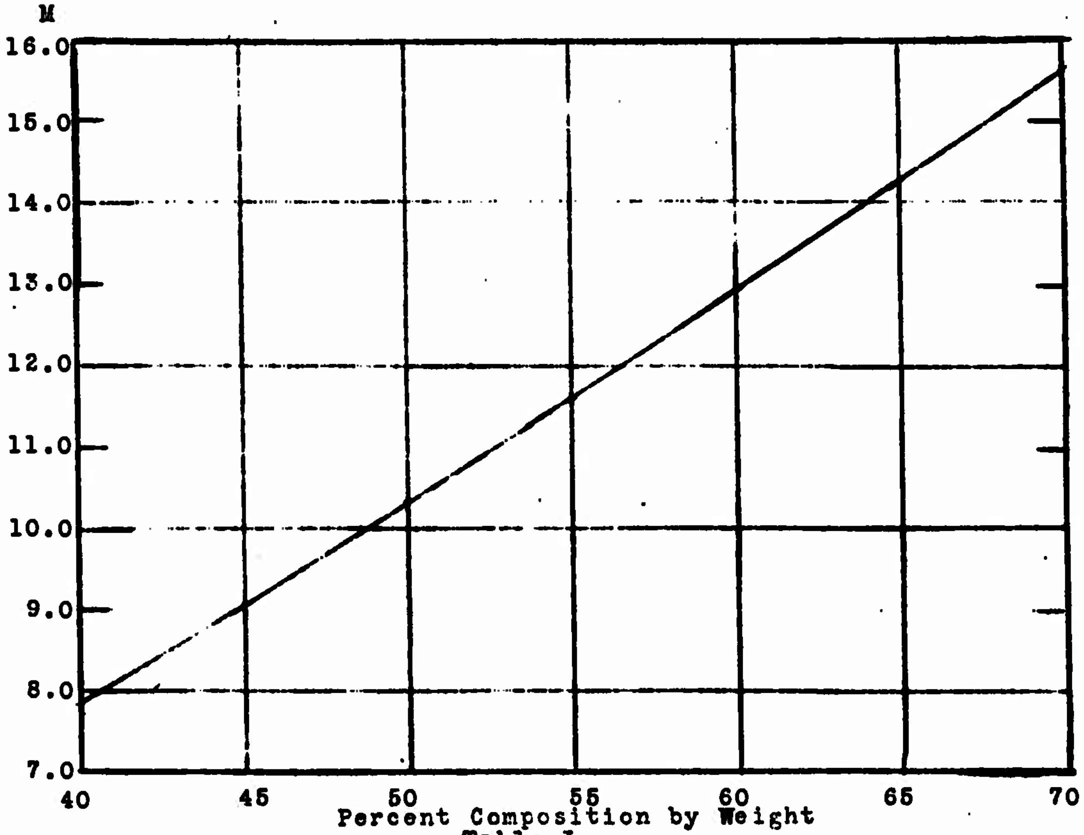


Table I
Relationship between the Molar Concentration and the Weight Per Cent for Solutions of Nitric Acid in Water at 25°C.

Reaction rates have been expressed in terms of grams of reaction product per liter of oxynitration solution per hour. This unit is easy to relate to the kinetic measurements of mercuration, etc., expressed in moles per liter per minute. Rates are based upon the volume of reaction mixture which actually produces product, at the temperature of the reaction.

The names of reaction products are abbreviated as follows:

2,4-Dinitrophenol = DNP
Picric acid = PA
p-Dinitrobenzene = p-DNB
o-Dinitrobenzene = o-DNB
Dinitrobenzene = DNB
o-Nitrophenol = o-NP
p-Nitrophenol = p-NP
Nitrobenzene = NB
2,4,2',4'-Tetranitrodiphenylamine = TNDA

I. THE CONTINUOUS EXTRACTION PROCESS

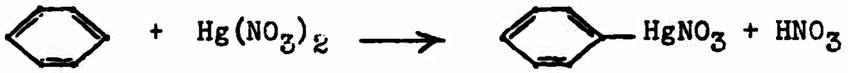
A. Theoretical

(1) Reaction Mechanisms.- A knowledge of the sequence of steps which occur in the oxynitration process is desirable for better understanding of the operation of the special procedures described in this report. The reactions now known to occur are outlined briefly in this section. Some of the work of establishing the steps was done by earlier investigators. Particular credit for work on the mechanism is due to the group under Westheimer[25,27] at the University of Chicago. The contributions of the group at Pennsylvania

will be discussed in greater detail in a later section (Section III -B-C-D-E).

It is known that at least two alternative paths can lead from benzene to dinitrophenol through the catalytic agency of mercuric salts. Two preliminary steps are common to both paths. The benzene first dissolves in the nitric acid, then reacts as follows:

(1)



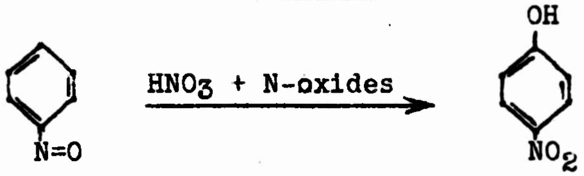
(2)

The mercuric nitrate is combined only momentarily and is regenerated as nitrosobenzene is formed. Other oxides of nitrogen than nitrogen tetroxide may be capable of reacting to cleave the phenylmercuric intermediate. The requisite oxides of nitrogen, if not present initially in sufficient quantity in the reaction mixture, are apparently generated by oxidative side reactions; once the reaction is started, it is possible that the later steps of the oxynitration reaction sequence continuously supply oxides to the mixture.

The nitrosobenzene can react by two alternative paths to form nitrophenols. Path A is the more important in concentrations of nitric acid above 50% and in low concentrations of nitrogen oxides. Yields are good.

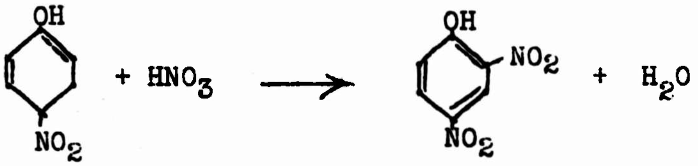
Path A

(3)

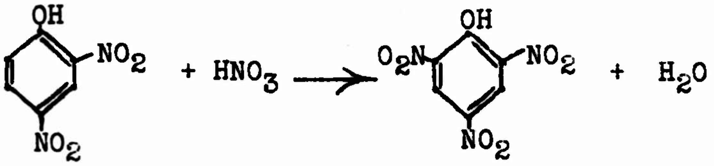


(Probably occurs in several steps; the OH group appears in the position para to the original nitroso group.)

(4)



(5)

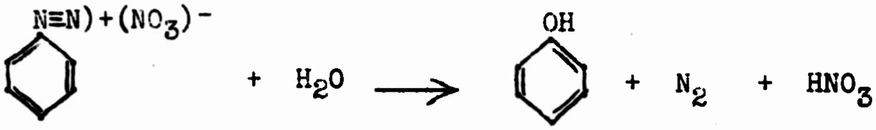


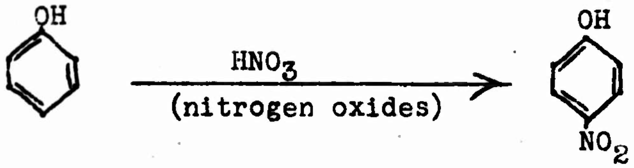
Path B is the predominant reaction course in concentrations of nitric acid below 50% by weight; it is favored when the solution is saturated or nearly saturated with nitrogen oxides. Even under most favorable circumstances, the overall yields in Path B are rather poor.

Path B

(6)

(7)



(8)  (and ortho)

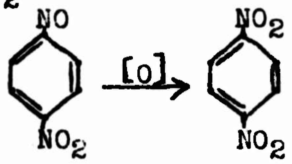
(4) Same as for Path A, leading to 2,4-DNP

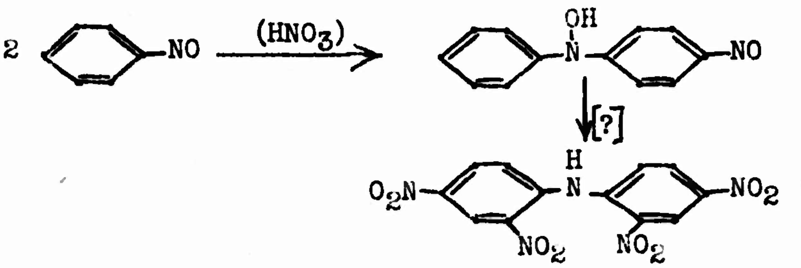
(5) Same as for Path A, leading to PA

Some of the known or possible side reactions are shown in the following equations:

(9) $C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2$

(10) $C_6H_5NO \xrightarrow{[O]} C_6H_5NO_2$

(11) $C_6H_5NO + HNO_3 \longrightarrow$  (and ortho)

(12)  (TNDA)

(13) $C_6H_5HgNO_3 + Hg(NO_3)_2 \longrightarrow C_6H_5(HgNO_3)_2 \longrightarrow$ polymercurials

(14) $C_6H_5OH + HNO_3$ (and N-oxides) $\longrightarrow$ [oxidation and condensation products of unknown structure]

(15) $C_6H_6 \xrightarrow{HNO_3}$ (unknown intermediates) $\left\{\begin{matrix} COOH \\ COOH \end{matrix}\right. \xrightarrow[Mn^{++}]{HNO_3} CO_2 + H_2O$ + N-oxides

(2) Important Variables.- The variables of the oxynitration reaction are numerous and not all of them are easily controlled. Before attempting a detailed discussion of the variations in experimental conditions, it is well to summarize some of the variables which our experience and the experience of other groups have shown to have the most important influence upon the yields and quality of products.

(a) Benzene Concentration.- The oxynitration reaction occurs in nitric acid solution. If a separate benzene phase is present in contact with the nitric acid-mercuric nitrate solution, only the benzene which is dissolved in the aqueous phase is effective in producing nitrophenols. The concentration of benzene dissolved at any given instant in the oxynitration solution is a very important factor in determining the yield of nitrophenol and the extent of side reactions. Numerous experiments in the present investigation and in other investigations have shown that saturation of the oxynitration solution with benzene gives relatively high proportions of neutral nitro products and colored by-products at the expense of nitrophenol formation, while low concentrations of benzene are much more favorable for the production of nitrophenols. Factors which indirectly influence the concentration of benzene dissolved in the oxynitration solution - the "effective benzene concentration" - are: the rate of addition of liquid benzene, the degree of agitation of benzene with the solution, the degree of dispersion of excess liquid benzene in the oxynitration solution, the rate of removal of benzene from solution by reason of chemical reaction.

(b) Nitric Acid Concentration.- The overall rate of oxynitration increases very rapidly as the nitric acid concentration increases. The kinetic studies of Westheimer have shown that this effect results from the great increase in the rate of benzene mercuration (Step 1 of the mechanism) as the acid strength increases. Below approximately 50% nitric acid (10.4 M) the oxynitration becomes impracticably slow and the diazonium mechanism (Mechanism B) giving relatively low yields is favored over the more efficient rearrangement mechanism (Mechanism A). Above 60% (13 M) strength the reaction is so rapid as to be difficult to control, and there is difficulty in maintaining constant reaction conditions. High concentrations of nitric acid also tend to favor the formation of nitrobenzene and the nitration of DNP to PA.

(c) Mercuric Nitrate Concentration.- Concentrations of catalyst have usually been in the range of 0.2 to 0.5 M. Other conditions being constant, the overall rate of oxynitration is roughly proportional to the molar concentration of catalyst.

(d) Temperature.- The overall rate of oxynitration increases by a factor of approximately 1.8 to 2.0 for each 10°C. rise in reaction temperature. The relative rates of the main and side reactions do not change at exactly the same rate; at higher temperatures - particularly above 60°C. - the formation of nitrobenzene and the nitration of DNP are favored.

(e) Concentration of Nitrous Acid.- Nitrogen oxides must be present in the solution, otherwise the oxynitration sequence proceeds no further than the mercuration of the benzene. In 50% nitric acid, Westheimer has estimated that a concentration of total oxides of nitrogen equivalent to that produced by the addition of 0.04 M nitrite would be the most satisfactory for high yields in the oxynitration reaction. This is probably about one-tenth the concentration of a solution saturated with oxides, and is about one-fifth that of the solution under the conditions of the best run of the Continuous Extraction Apparatus. Experimental difficulties have prevented a more critical evaluation of this variable.

(f) Concentrations of Reaction Products.- In batch runs the accumulation of reaction products necessitates the periodic interruption of operation to permit removal of reaction products. In the Continuous Extraction Process, organic products are removed at the same rate as formed once a steady state is reached and minimum residual concentrations of all products are built up. The removal of water formed in the reaction is provided for by the periodic withdrawal of small portions of reaction solution and concentration of these portions by distillation. Oxalic acid, a by-product, is prevented from accumulating beyond a definite minimal concentration by the presence of manganous nitrate, which catalyzes the oxidation of the oxalic acid to carbon dioxide by nitric acid.

A number of considerations limit the range of conditions under which the oxynitration process can be operated practically. It was mentioned under the heading Nitric Acid Concentration that a 50% (10.4 M) concentration is approximately the lowest that should be used. The factor which most limits the reaction in the direction of more concentrated nitric acid is the rate of accumulation of reaction products and by-products. The continuous extraction equipment developed under this contract is capable of removing the major organic reaction products at quite high rates of reaction.

The problem of the accumulation of the by-product, oxalic acid, is more difficult. A concentration of 0.5 M manganous nitrate was found to be just sufficient to destroy oxalic acid when the oxynitration was carried out at the rate of approximately 30 g. of dinitrophenol per liter of oxynitration solution per hour.

B. Final Laboratory Extraction Process in the No. 5A Jet Extractor

(1) General Description of Process.- The oxynitration solution is made up in the same way as for batch runs under optimum conditions (details are presented in a later section); numerous batch runs served to guide the choice of conditions. The benzene is injected into the reaction mixture near the bottom of the vertical cylindrical reaction vessel through a cluster of capillary glass jets in the No. 5A Apparatus (a coarse glass fritted disk was used in an earlier model). The size of the dispersed benzene droplets and the volume of throughput of benzene is regulated, following the experience of numerous pilot experiments, so that less then 10% of the benzene introduced actually dissolves in the acid solution. The undissolved benzene droplets rise through the reaction mixture by reason of their much lower density and extract the benzene-soluble reaction products. The droplets of benzene containing dissolved reaction products eventually merge upon the surface in a supernatant layer from which benzene is allowed to overflow continuously into a separate flask where the excess benzene is separated by distillation and is

recirculated through the reaction mixture. No agitation is used except that produced by convection currents and the movement of benzene droplets.

The laboratory procedure is described in detail for the No. 5A Extractor, the final of six different all-glass models which were studied. It employs a cluster of 22 glass capillary jets for the introduction of the benzene, and incorporates a number of refinements which were not present in earlier models.

Runs were made under a number of different conditions, but we consider Runs 5A-12 and 5A-14 to be representative of the "optimal results" achieved with this apparatus. Run 5A-12 was a run of sixty-five hours made to demonstrate that essentially constant conditions could be maintained continuously for a long period of time; Run 5A-14 was for ten hours under similar conditions to determine material balances.

In spite of the most careful efforts some loss of benzene occurs during the recovery of unreacted starting material, hence the following yield values should be regarded as minimal, since they are based on the total benzene which disappears in the reactor:

<u>Benzene Balance in Run 5A-14</u>

Benzene as DNP	44.1%	73.3%
Benzene as PA	29.2	
Benzene as NB	6.5	
Benzene as "DNB"	3.0	
Benzene as CO_2 (and CO*)	5.5	
Benzene as Oxalic acid	1.7	
Benzene not accounted for	10.0	
	100.0%	

*Traces

Some benzene which volatilized through the condenser with the nitrogen oxide fumes was measured but not counted in this balance, for it has been shown that loss by this route can be minimized by the use of more efficient condensers; the amount which is volatilized can be absorbed in an oxynitration solution, and is therefore not lost.

The rate of formation of dinitrophenol (or its equivalent in PA) was 30.7 g. per liter of oxynitration solution per hour. The ratio of DNP (or equivalent) to total neutral nitro compounds was 10.4 to 1 by weight. In the long Run 5A-12 the overall rate was almost identical with that in the run for balances, and the weight ratio of DNP to neutral nitro products was 9.5.

As a basis for comparison, it can be estimated from the data of Wright that the Wright Process for Picric Acid is capable of producing the equivalent of about 22-23 grams of DNP per liter of oxynitration solution per hour, calculated on the basis of the overall time cycle and the initial reaction volume.

It should be emphasized at this point that what we term "optimum conditions" are not the only conditions under which good results can be obtained. Wide variations can be made in the conditions, with attendant variations in the results. If, for example, a much higher rate of reaction were desired, the rate could be doubled or tripled by using more concentrated nitric acid and a larger quantity of mercury catalyst; this increase in rate, however, would introduce the problem of the destruction of the more rapidly accumulating oxalic acid. If nearly pure DNP were desired instead of the mixture of DNP-PA, manganous nitrate would have to be eliminated from the reaction mixture; this omission would make more difficult the long continued operation because of the increase in oxalic acid leading eventually to precipitation of the catalyst as the difficultly soluble mercuric oxalate. It is thus evident that any variations from the so-called optimum conditions, while holding considerable promise for special objectives, nevertheless introduce new problems which would have to be solved by further experimental work.

(2) Description of the 5A Jet Extractor.-

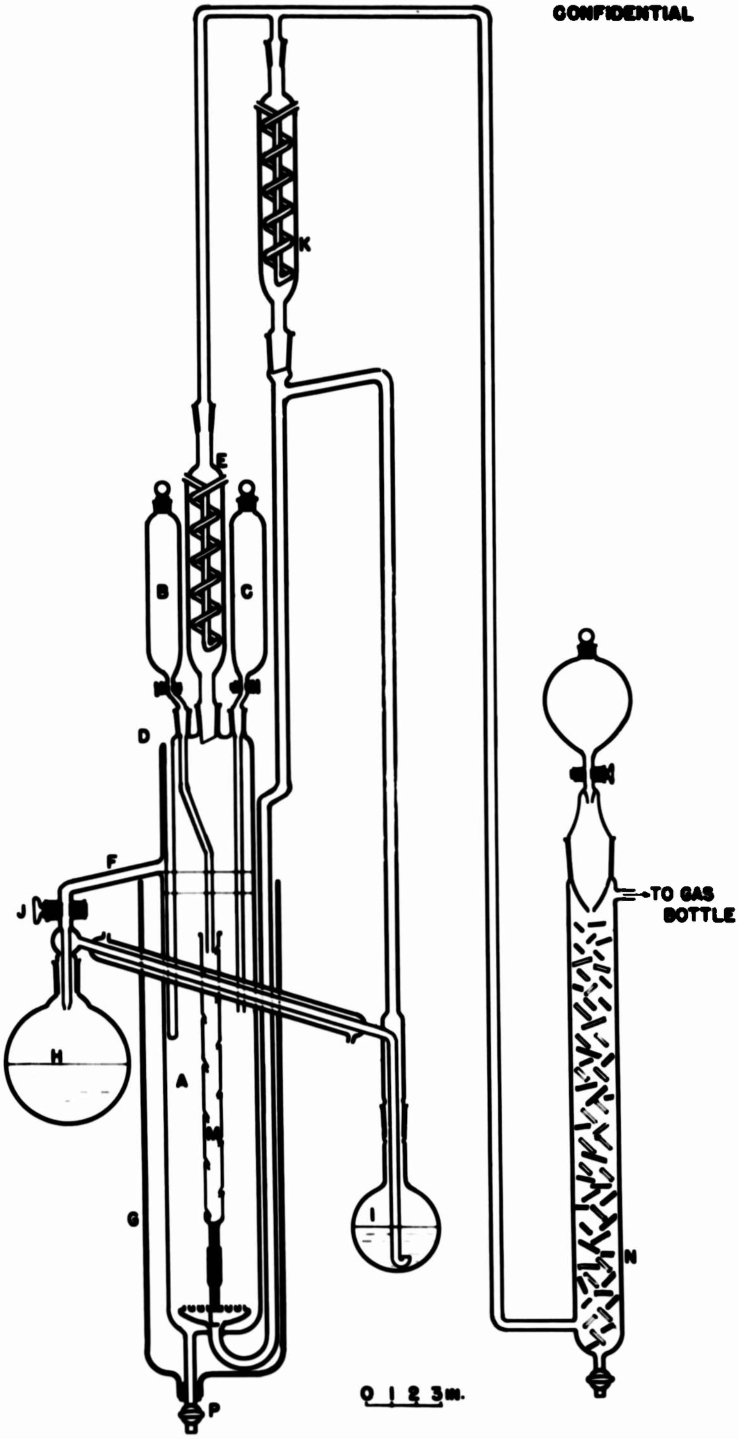
Figure 1 shows the all-glass 5A Jet Extractor Apparatus. The dimensions of the apparatus are indicated by means of a scale shown in the drawing. The various parts of the apparatus are indicated by letters, and the following key to Fig. 1 explains the nature and purpose of the various parts:

A. Reactor Unit containing approximately 2350 ml. of oxynitration solution (not counting a layer of supernatant benzene 2 or 3 cm. deep).

B. Dropping Funnel extending into Diluter M. This is used for the continuous introduction of fortifying nitric acid of approximately 98% strength during a run.

C. Dropping Funnel extending into reactor. This serves for the addition of fortifying catalyst solution and also for the removal, by application of suction, of samples of reaction liquor for analysis.

D. Thermometer Well.



LARGE JET EXTRACTOR APPARATUS

FIG. 1

E. Reflux Condenser. To condense benzene and some of the nitrogen oxides while permitting carbon dioxide, nitrogen, and nitric oxide to escape.

F. Overflow Tube. Supernatant benzene and dissolved reaction products overflow through this tube into Flask H.

G. Heating Jacket. The outer jacket, containing water, is warmed by a steam line and stirred by means of a stream of air. During the actual oxynitration runs, the heat of reaction is often sufficient to maintain the proper temperature. Occasionally slight cooling in the external jacket is required.

H. Evaporator Flask. The 1000-ml. flask serves to collect reaction products. It is heated at 115-120°C. by means of an oil bath, and benzene and nitrogen oxides distil into Flask I. The Stopcock J permits the Flask H to be cut off without interruption of the operation of the reactor while a new flask and fresh benzene are introduced into the system.

I. Boiler Flask. The use of this 500-ml. flask, heated in an oil bath at 105-110°C., is to aid in the distillation of benzene back into the reaction system through the jets. The second flask can be heated continuously even while Flask H is being changed.

J. Stopcock. To permit Flask H to be cut out of the system without interrupting operation of the reactor.

K. Condenser. Condenses the hot benzene vapors and some of the nitrogen oxides from the Boiler Flask I.

L. Jets. A cluster of 22 short lengths of glass capillary tubing, each with an internal diameter of approximately 0.5 mm. These are all carefully fused into a single plate so that the tips are in a horizontal plane, and the axes of the jets are all parallel and vertical. All jets were made from the same piece of capillary tubing to insure uniformity of internal diameter.

M. Diluter. The 98% nitric acid used in fortification is slightly more dense than the reaction mixture. The fortifying acid flows down inside the diluter tube, which is closed on the bottom and into which benzene droplets cannot enter; as the acid flows downward it is diluted by oxynitration solution entering the small tubular openings in the side of the diluter. Fortified solution flows out again through the small openings in the lower portion of the diluter. In this way, direct contact of benzene droplets with very concentrated nitric acid is prevented.

N. Gas Absorption Tower. The mixture of gases from the reactor contains carbon dioxide, air, benzene vapor, N_2, N_2O, NO, N_2O_4 and perhaps other oxides of nitrogen as well. All except CO_2, air, N_2, and N_2O are absorbed by passage upward through Tower N. A solution of concentrated sulfuric acid and 98% nitric acid is allowed to flow slowly downward through the absorption tower, dissolving and converting benzene to m-dinitrobenzene, and converting recoverable nitrogen oxides to nitrosyl sulfuric acid. Residual gases are passed into a large glass bottle over acidified water or brine; when complete balances are made these residual gases are analyzed.

P. Drain from Reactor. The drain with stopcock serves to remove small portions of the reaction mixture during a run as the formation of water causes the mixture to expand. At the end of a run it also serves to remove the reaction mixture and excess benzene without the necessity of dismantling the reactor.

(3) Operation of the 5A Jet Extractor.-

(a) Procedure for Runs Without Material Balance.- This procedure is typical of many runs which were made, in particular Run 5A-12. The concentrations of nitric acid and mercuric nitrate were varied in many other runs. Baker's C.P. Analyzed Benzene (Thiophene-free) was used in all runs in this report.

The solution charged into the reactor is made up as follows:

295.5	g.	Mercuric Oxide, C.P.
103	ml.	Nitric Acid, 98% (equivalent to catalyst)
1565	ml.	Nitric Acid, 70%
460	ml.	Water
288	ml.	Manganous Nitrate Hexahydrate Solution, 79% aq.

Such a solution is 0.5 M in mercuric nitrate, 0.5 M in manganous nitrate, and 10.1 M in nitric acid.

Benzene (600 ml.) is placed in the Evaporator Flask H and 300 ml. of benzene is placed in Flask I; the two flasks are heated in oil baths at, respectively, 115-120°C. and 105-110°C. The contents of the reactor are heated to the reaction temperature (55°C. in Runs 5A-12 and -14) by means of warm water in the Jacket G, stirred by an air current. The temperature of the jacket is adjusted to hold a constant internal temperature within the reaction mixture. When the Flask I is hot enough, benzene distils through the long vertical tube, condenses in Condenser K and thence flows into the bottom of the reactor through Jets L, which break up the benzene into a shower of fine droplets. The benzene builds up a head in the tube above the jets, and the height of the head serves as a rough indication of the rate of flow of benzene through the system.

When the flow of benzene has become steady, fortification with 98% nitric acid is begun through Dropping Funnel B, the rate being of the order of 2 ml. per minute. The rate of fortification is adjusted from time to time, on the basis of analyses of samples of mother liquor, so as to maintain the concentration of acid in the solution at the desired level.

The layer of supernatant benzene is maintained at an approximately constant depth of 1.5-2 cm. by periodic withdrawal of small portions of reaction solution through Stopcock P in the bottom of the reactor. Usually about 200-250 ml. of mother liquor is withdrawn during a three-hour period. The withdrawn solution is processed in the following way. The 200-250-ml. of solution collected over several hours is extracted with three 75-ml. portions of benzene, the benzene being saved and eventually combined with the final contents of the reactor for workup. The extracted nitric acid solution is then distilled at atmospheric pressure until the residual volume is about 50 ml. The concentrated solution, containing the mercuric nitrate and manganous nitrate, is re-introduced into the solution through Funnel C. The loss of catalyst is negligible. The dilute nitric acid recovered by distillation can either be saved for analysis or, if desired, could be used for the makeup of fresh starting mixture.

Samples of mother liquor are withdrawn at intervals by applying gentle suction at the top of Funnel C, and are analyzed for nitric acid, nitrous acid, oxalic acid, mercuric nitrate, manganous nitrate, etc., as desired. Adjustments are made in fortification rates as needed to maintain constant conditions.

About every eight hours, under conditions similar to those of Run 5A-12, the reaction products have accumulated in Flask H to such an extent that a new flask and fresh benzene must be used. The Stopcock J is closed and Flask H is allowed to cool somewhat until it can be exchanged for a new flask containing 600 ml. of fresh benzene. The new flask of benzene is heated to boiling and the flow of benzene started once more by cautiously opening Stopcock J. The reactor continues to operate without interruption.

Gases are passed through the Absorption Tower N. While in large-scale operation this unit would be replaced by a more efficient condensing system and an absorbing tower containing oxynitration solution, we have limited ourselves to the determination of entrained benzene and recoverable oxides by means of the mixture of concentrated sulfuric acid and 98% nitric acid (Bachmann, OSRD Report No. 4026, February 28, 1945, page 9). Benzene was determined as *m*-dinitrobenzene in an aliquot portion, and recoverable oxides of nitrogen could be estimated in a Lunge nitrometer.

A typical schedule of operations is shown below for a portion of the long Run 5A-12 (fourteen of a total of sixty-five hours):

Table II

Fortification		Vol. of soln. wthdn.	Time with-drawn	Time anal. smpl. wthdn.	Conc. HNO_3 M	Conc. Oxalic Acid M	Vol. Concd. soln. rtd. to reactor
Time	Vol. 98% HNO_3 added						
10:55-11:45	100 ml.			11:30	10.40		
11:45-12:35	100						
12:35- 1:25	100	233 ml.	1:25				51* ml.
1:25- 2:15	100						
2:15- 3:05	100			3:00		2.	
3:05- 3:55	100						
3:55- 4:55	100	241	5:00				
4:55- 5:35	100			5:30	10.31		35*
5:35- 6:25	100						
6:25- 7:15	100						
7:15- 8:05	100						
8:05- 8:55	100	200	8:30	8:45		2.	33*
8:55- 9:45	100						
9:45-10:35	100						
10:35-11:25	100	195	11:30				54*
11:25-12:15	100						
12:15- 1:05	100			12:30	10.35		

---

* A concentrate of the mother liquor previously withdrawn.

During the sixty-five hours of Run 5A-12, eight different evaporator flasks were used. Each of these flasks was worked up separately to determine the average rates of formation of products during each of the time intervals. In this way we were able to determine that both the rates of formation and of removal of products remained constant within the allowable variation over the whole reaction time. The data on weights of product are shown in the table below to illustrate the typical operation of the Jet Extractor.

Table III
Summary of Products in Run 5A-12

Evaporator Flask No.	1	2	3	4	5	6	7	8
Time Interval (hours)	0-10	10-18	18-26	26-34	34-42	42-51.5	51.5-59.5	59.5-65
Hours in Use	10	8	8	8	8	9.5	8	5.5
Weight of Nitrophenols (g.)	576	621	809	574	585	808	621	496
DNP (g.)	336	333	389	368	368	431	391	310
PA (g.)	240	288	420	206	217	377	230	186
Weight of Nitro Products (g.)	55.0	51.3	68.0	60.7	60.5	75.5	72.4	50.7
NB (g.)	33.9	30.8	41.0	41.0	33.0	48.8	43.5	31.5
"DNB" (g.)	21.1	20.5	27.0	19.7	27.5	26.7	28.9	19.2
Rate of DNP Formation (g. DNP/l./hr.)	20.8	28.0	35.8	26.5	26.8	30.6	28.5	33.1
Ratio: $\frac{\text{g. DNP}}{\text{g. NB + g. "DNB"}}$	9.1	10.4	10.0	10.0	8.5	9.2	7.6	8.6

At the end of the Run 5A-12 the reactor contained the following material: 88.9 g. DNP, 26.2 g. PA, 4.4 g. NB, and 4.0 g. "DNB." The total yield for the whole run was 5203 g. of DNP + PA (57.9% of this weight was DNP) and 503 g. of neutral nitro products (NB + "DNB").

At the beginning of a run, the initial pale color of the nitric acid solution rapidly darkens to a very deep red verging on black, the final intensity of the color being a function of the steady-state rate of oxynitration. After completion of a run, the mother liquid lightens again to a clear red color.

(b) Procedure for Runs with Material Balances in the 5A Jet Extractor.- Much valuable information was obtained by making a number of runs without complete material balances, as described in the preceding section. The data on rates of formation of products and especially the values of the ratio of grams of DNP (or equivalent) to grams of neutral nitro products (NB + DNB) enabled us to judge whether a given set of conditions was favorable without the necessity of going through the extremely laborious task of determining complete balances. In very long runs it was impractical to determine balances because of the greater proportional loss of benzene which resulted from the handling of a number of different evaporator flasks. For the determination of yields, runs of approximately ten hours' duration were made, using one Evaporator Flask H. The unreacted benzene was recovered as follows:

> The constituents of the original stock solution are carefully measured and the benzene is weighed directly into the evaporator and boiler. At the end of the ten-hour period of reaction, the heating units are removed from the flasks. Circulation of the benzene stops within a short time. Cold water is then circulated through the jacket surrounding the reactor until the temperature

of the oxynitration solution falls to 25°C. The acid solution is drained through the Stopcock P, but the benzene is left in the reactor. The evaporator and boiler units (H and I) are left attached to the apparatus until they have cooled to room temperature. Water is flushed through the Jets L to sweep the remaining benzene into the reactor well; the aqueous layer is separated through P and the rinsings are saved for analysis of nitric acid and mercuric nitrate.

The evaporator unit (H) is detached from the reactor and connected to an apparatus in which a gentle current of steam removes the benzene retained by the reaction products. Oxides of nitrogen evolved during the distillation are absorbed in a trap containing standard alkali so that the nitric acid balance can be completed. The benzene contained in the Boiler I is similarly collected by steam distillation. The benzene still remaining in the reactor unit is carefully drained into a round-bottomed flask and distilled with steam in the same way. Eventually all of the unreacted benzene is collected as nearly pure distillate together with some water in a single separatory funnel.

The benzene layer is washed with standard alkali to remove nitrogen oxides and nitric acid; titration of the wash accounts for a small amount of nitric acid, which is included in the nitric acid balance. The separatory funnel containing the colorless washed benzene is then allowed to stand over night, tightly stoppered, after which the lower aqueous layer is carefully separated and discarded. The solubility of benzene in water is disregarded because it is quite low; the solubility of water in benzene is likewise neglected. The benzene is weighed in the tared funnel as wet benzene; then it is dried over anhydrous calcium chloride and carefully distilled from a small Claisen flask with Vigreux column. A small residue of nitrobenzene obtained from the benzene layer is deducted from the weight of wet benzene and the difference is recorded as recovered benzene.

It is obvious that there are many chances for loss of benzene through films clinging to glass vessels and through volatility. There are no compensating errors which tend to make the weight of recovered benzene high, with the possible exception of water dissolved in the benzene layer, and this can be estimated as negligibly small. For this reason, our balances, based upon the difference between the weight of benzene introduced and the weight of benzene actually recovered as such, are conservative, minimal values. In the best run for balance in the 5A Jet Extractor (Run 5A-6) a total of 94.4% of the benzene was accounted for. In the two next best runs

(5A-11 and 5A-14) the percentages of benzene accounted for were 93.1% and 90.6%, respectively. Run 5A-14 is the one which most closely approaches the conditions of the sixty-five hour run (5A-12). We believe that these variations in the total amount of benzene accounted for are to be expected and are inherent in the very great experimental difficulties of recovering benzene in small glass apparatus of complicated design. We also feel that the varying amounts of benzene not accounted for include the sum of losses of various reaction products as well as the loss of benzene itself - that is, in the crystallization of the nitrophenols, the recovery of distilled neutral nitro compounds, gaseous compounds, traces of unidentified products, etc. We feel certain that the 5 to 10% of benzene not accounted for in the balances does not represent any single loss or any previously unsuspected by-product.

The recovery of reaction products was accomplished by the following procedure:

The residue remaining in the evaporator flask (H) after steam distillation of the benzene is poured into 500 ml. of ice water, and sufficient triethanolamine (TEA) is added to neutralize the nitrophenols; approximately ten per cent excess of TEA is added and the total volume is made up to approximately three liters with water. The solution is extracted with four 150-ml. portions of benzene to remove nitrobenzene and DNB. The extracted TEA solution is acidified with 1:1 nitric acid until further addition of acid produces no further change in color. The mixture is chilled for about twenty hours at 0-5°C. and the mixture of DNP-PA is filtered on a sintered glass funnel, washed thoroughly with ice water, and dried at 60°C. for twenty-four hours, after which it is weighed and analyzed for percentage of DNP by the Koppeschaar titration with bromine (See Appendix, page 126).

The benzene extracts of the TEA solution are combined, dried over calcium chloride, and distilled through a modified Claisen flask to remove benzene. A nitrobenzene fraction is removed over a boiling range of 207-215°C. The undistilled portion, which crystallizes as it cools to room temperature, is weighed and calculated as "DNB." Actually, the residue is a mixture, and its composition will be discussed in greater detail later. The assumption that it is "DNB" for calculation of yields introduces little or no error.

The acidified TEA filtrate remaining after removal of the main portion of nitrophenol is extracted in one-liter portions with three 100-ml. portions of benzene. The benzene extracts are combined, the benzene is removed by distillation, and the residue is dried in a stream of air for twenty-four hours and analyzed for DNP by the Koppeschaar method.

The mother liquor drained from the reactor is allowed to stand loosely stoppered over night. The precipitated DNP is filtered, washed with cold 50% nitric acid followed by water. The washings are analyzed for mercuric ion. A 750-ml. aliquot of the filtered mother liquor is diluted to 1500 ml. and extracted with four 150-ml. portions of benzene . The benzene extracts are washed with cold water, then extracted with several portions of 30% TEA. The alkaline extracts are acidified with 1:1 nitric acid, chilled to 5°C., and filtered. The DNP-PA, thoroughly washed with ice water, is dried and analyzed. Nitrobenzene in the benzene is recovered as described above.

Gases formed during the oxynitration reaction are passed through the all-glass absorption tower packed with short lengths of glass rodding and perfused with a mixture of concentrated sulfuric acid and 98% nitric acid. The gases emerging from the gas absorption tower are passed through a water bubbler to collect acidic nitrogen oxides, and residual gas is collected in 20-liter carboys over water acidified to methyl orange with hydrochloric acid. The total volume of residual gas is determined in runs for complete balance, and the gas composition is determined by Orsat analysis for carbon dioxide, oxygen, carbon monoxide; inert residual gas is assumed to be a mixture of nitrogen and nitrous oxide.

The acid absorption tower (N) is wet by a slow stream of a mixture of 65 parts of 98% nitric acid and 75 parts of 96% sulfuric acid. Benzene is absorbed and converted to *m*-dinitrobenzene. Recoverable oxides of nitrogen are also absorbed. The trap liquor is allowed to flow downward from the dropping funnel at a rate rapid enough to prevent the loss of brown oxides of nitrogen. The final volume of the tower acid is measured, and an aliquot sample is taken for the estimation of absorbed benzene. The acid is diluted with a large excess of ice and the crystalline m-dinitrobenzene filtered, washed, and weighed. Another aliquot portion of the trap acid is analyzed for total nitric acid and potential nitric acid by the Lunge Nitrometer method. Since the initial weight of 98% nitric acid in the tower is known, and the weight of nitric acid consumed by reaction with benzene can be calculated, these quantities of nitric acid can be deducted from the total determined by nitrometer, giving the number of grams of 100% nitric acid which could be recovered from the absorbed nitrogen oxides.

The water bubbler scrubs out nitric acid or higher nitrogen oxides carried over inadvertently from the trap. The acidity is determined and calculated as 100% nitric acid in the final balance. A negligible weight of sulfuric acid is carried over, tests with barium chloride show.

(4) Methods of Computing Yields.- Since confusion may result because of the use of three different methods of computing yields in the oxynitration process, some attention should be directed to the methods used in this and other studies which have been made.

The products of the oxynitration reaction which have been identified include: DNP, PA, NB, p-DNB, o-DNB, carbon dioxide, oxalic acid, and tetranitrodiphenylamine (TNDA; this product was first identified by the group under Bachmann at Michigan). Yields are in general reported for purified products, or for mixtures of products whose compositions are known by analysis.

Three different bases for calculations of yield have been used, each intended to emphasize a particular point. These bases can best be shown by the following tabulation:

	C	B	A
Benzene as DNP	│	│	│
Benzene as PA	│	│	│
Benzene as CO_2	│	│	│
Benzene as Oxalic Acid	│	│	│
Benzene Not Accounted For	│	│	│
Benzene as NB		│	│
Benzene as DNB		│	│
Benzene Volatilized through Condenser			│

100% of the Benzene Not Recovered as Benzene

In earlier publications yields of nitrophenols were based upon the total benzene added to the reaction mixture (the "A Basis" in the above scheme), since the minor products were seldom isolated, and unreacted benzene was not accounted for, although it was often noted that benzene was volatilized through the condenser. It was recognized that, without very efficient condensing, the loss of benzene by volatilization may be large, and the suggestion was early advanced that this loss could be minimized by proper design of the condenser.

The losses of benzene by vaporization are a function of the cooling temperature and area of cooling surface, and also of the volume of non-condensable gases evolved in the reaction. The amount of volatilized benzene can be cut down by efficient design of the condenser. Bachmann[28] has suggested that volatilized benzene be recovered by absorption in fresh oxynitration solution. Since the amount of benzene volatilized through the condenser bears no relation to the true yields of products resulting from reaction <u>within the reaction mixture</u>, most of our yields, as well as the yields of the group at the University of Michigan, have been computed on the <u>"B Basis,"</u> which excludes the volatilized benzene, determined as m-dinitrobenzene in the tower acid. Most yields recorded in the literature are on the "<u>A Basis</u>."

A third basis, the "<u>C Basis</u>," has been used in a few cases during this investigation, particularly in connection with the study of the reaction mechanisms. If the benzene converted to neutral nitro products by side reactions is excluded from the basis of yield calculations, as well as the benzene volatilized through the condenser, yield values for DNP and/or PA are obtained which give an idea of the efficiency of the oxynitration reaction as distinguished from the side reactions which lead to neutral products. This point will be discussed in greater detail in the section on mechanism (Section III). It was on the basis of a consideration of oxynitration efficiencies that Westheimer was led to postulate the existence of a "rearrangement mechanism" for the oxynitration process.

(5) Oxynitration Runs in the 5A Jet Extractor.-

Table IV summarizes the data on ten runs which were made under varying conditions in the 5A Jet Extractor.

(designated as Runs 5A-2 and 5A-5 in Table IV)
Runs 2 and 5/were made to establish a routine operational procedure for the Jet Extractor, following the experience with earlier models. In Run 2, 10.6 M nitric acid at 55°C. was used and, in Run 5, 12.1 M nitric acid at 45°C. It was felt that these represented close approximations to optimal conditions. Runs 6 and 8 were ten-hour checks of Runs 2 and 5, respectively, with material balances determined for benzene, nitric acid, and mercury. No manganous nitrate was used in any of these four runs. The concentration of oxalic acid was found to rise steadily in Runs 6 and 8, reaching 9.5 g. per liter in Run 6 and 15.1 g. per liter in Run 8. In neither case did precipitation of the mercury catalyst occur.

TABLE IV. OXYNITRATIONS OF BENZENE BY CONTINUOUS EXTRACTION METHODS

Expt. No.	Temp. °C.	Time hrs.	Conc. of Stock Soln. HNO3, moles/liter Initial	Final	Average	Hg M	Mn M	Fortification 90% HNO3 cc. added	Rate cc/1/hr	Hg. soln. added cc.	Mn soln. added cc.	Mother Liquor Removed Total cc.	Rate cc/1/hr	Rate of Benzene Flow cc/1/hr	Weights of Products Formed: Nitrophenols 1st crop g.	% DNP	2nd crop g.	% DNP	from M.L. g.	% DNP	Total g.	% DNP in prod.	[illegible] in evap. g.	in M.L. g.	[illegible] in evap. g.	in M.L. g.	Rate of Formation DNP g./l./hr.	Neutral Products g./l./hr.	Ratio g. DNP g.neut.prod.
Oxynitrations in Extractor No. 5A (Jet); Volume of oxynitrating solution is 2350 cc.																													
5A- 2	55	5	-	-	10.6	0.5	-	428	38	18/1	-	280	24	-	258	78	6	50	75	92	339	80.6	15	2	12	2	27.3	2.6	11.1
5A- [illegible]	55	"	-	-	12.1	0.6	-	570	51	51/	-	434	37	-	251	71	24	22	132	96	414	75.	36	6	11	3	33.	4.6	7.6
5A- [illegible]	55	10	-	-	10.7	0.5	-	878	38	59/3	-	591	25	-	557	53	23	32	93	88	703	56.7	55	3	19	3	26.8	2.1	12.8
5A- [illegible]	55	"	-	-	12.1	0.6	-	1170	51	88/3	-	775	33	-	695	53	33	22	150	89	879	58.0	61	4	18	3	33.5	3.7	9.3
5A- 9	"	29	11.6	12.2	11.9	"	-	3550	51	33/1	-	2192	32	-	-	-	-	-	-	-	2385	52.5	158	-	60	-	31.8	3.2	9.9
		(1) 6								Withdrawn Mother Liquor Concentrated to 348 cc. and Returned in Nine Portions.					652	57	-	-	-	-	-	-	58	-	14	-	31.1	3.8	8.3
		(2) 7													568	46	-	-	-	-	-	-	27	-	13	-	30.2	3.0	12.8
		(3) 7													663	52	-	-	-	-	-	-	40	-	17	-	35.8	3.5	10.5
		(4) 7													502	56	-	-	-	-	-	-	33	-	16	-	27.3	3.0	9.5
5A-10	55	10	-	-	10.5	0.5	-	880	38	47/2	-	614	26	-	493	70	23	22	98	90	614	71.3	25	3	19	2	24.1	2.1	11.5
5A-11	"	"	-	-	10.5	"	-	"	"	46/2	-	569	24	-	580	64	15	36	101	90	696	67.3	27	3	20	2	27.2	2.2	12.5
5A-12	"	65	10.1	10.3	10.3	"	0.5	7705	51	23/1	25/1	4784	31	-	-	-	285	28	115	77	5262	58.5	310	4	190	4	31.	[illegible]	[illegible]
		(1) 10								Withdrawn Mother Liquor Concentrated to 1113 cc. and Returned in Twenty Portions.					543	60	-	-	-	-	-	-	[illegible]	-	21	-	30.8	[illegible]	7.6
		(2) 8													586	55	-	-	-	-	-	-	51	-	21	-	28.0	2.8	10.6
		(3) 8													764	49	-	-	-	-	-	-	41	-	27	-	35.8	3.6	10.0
		(4) 8													[illegible]	[illegible]	-	-	-	-	-	-	41	-	20	-	[illegible]	[illegible]	[illegible]
		(5) 8													652	65	-	-	-	-	-	-	33	-	28	-	26.8	3.2	8.8
		(6) 9.5													762	56	-	-	-	-	-	-	45	-	27	-	30.6	3.4	9.0
		(7) 8													586	65	-	-	-	-	-	-	44	-	29	-	28.5	3.9	7.8
		(8) 5.5													458	65	-	-	-	-	-	-	32	-	19	-	33.1	3.9	8.8
5A-14	55	10	10.4	-	10.4	0.5	0.5	1170	51	68/3	77/3	525	35	-	654	57	36	18	116	77	806	54.7	38	5	24	3	30.7	3.0	10.4
5A-17	40	7	12.3	12.7	12.6	"	"	1050	64	75/3	84/3	901	55	236	148	85	4	25	108	79	260	81.5	118	39	4	5	14.9	10.1	1.5
Oxynitrations in Extractor No. 5 (Jet); Volume of oxynitrating solution is 2460 cc.																													
5- 2	65	5	9.74	9.1	-	0.5	-	188	3/dis.	-	-	-	-	-	-	-	-	-	-	-	193	62.5	16	2	8	3	14.5	2.4	6.7
5- 3	"	"	9.45	8.7	-	0.75	-	200	"	-	-	-	-	-	-	-	-	-	-	-	195	67.1	15	3	8	2	14.8	2.3	7.0
5- [illegible]	55	"	9.74	9.4	-	0.5	-	108	4/dis.	-	-	104	-	slow	41	94	25	51	45	90	111	83.4	7.2		3.2		8.6	0.9	9.7
5- [illegible]	"	"	"	9.3	-	"	-	"	"	-	-	91	-	-	73	97	32	60	44	86	148	85.8	11.1		5.6		11.5	1.6	8.0
5- [illegible]	"	3.5	12.9	11.5	-	"	-	300	"	-	-	170	-	rapid	75	83	123	35	162	82	360	65.1	41	8	8	5	39.0	7.2	5.4
5- 9	45	5	13.0	12.1	-	"	-	525	4/64	-	-	315	-	-	263	67	16	17	122	88	401	71.8	36	7	9	2	30.8	4.4	7.0
5-10	[illegible]	3.5	13.1	12.0	-	"	-	400	4/61	-	-	215	-	-	273	60	13	16	149	87	435	67.6	51	9	12	4	47.5	8.3	5.7
5-[illegible]	45	5	12.9	12.1	-	"	-	700	8/71	-	-	413	-	-	431	60	15	27	151	87	596	55.5	85	12	12	4	45.3	9.2	5.9
5-[illegible]	"	"	"	12.2	-	"	-	"	7/71	-	-	492	-	-	321	60	17	25	172	88	510	68.5	84	13	8	5	38.0	8.9	4.8
5-15	"	"	"	"	-	"	-	550	8/52	-	-	344	-	-	278	56	25	27	147	89	451	65.0	54	9	11	3	34.	6.2	5.5
5-16	55	"	10.3	10.5	-	"	-	360	6/37	-	-	250	-	-	182	82	3	-	77	93	262	84.0	12	4	9	2	20.6	2.1	9.7
5-17	"	"	10.5	10.6	-	"	-	"	29	-	-	231	19	-	192	82	11	44	81	89	283	82.5	15	3	7	2	22.2	2.2	10.0
5-[illegible]	45	"	11.9	12.5	-	"	-	590	57	-	-	457	37	-	203	64	9	67	129	81	340	73.2	28	8	4	3	26.2	3.6	7.4
5-[illegible]	"	"	11.7	12.1	-	0.6	-	"	"	24/1	-	489	40	-	224	70	11	50	116	97	351	78.3	25	7	6	3	27.4	3.3	8.2
5-[illegible]	40	"	12.5	13.2	-	0.5	-	850	61	68/3	-	820	67	-	202	63	8	53	154	86	363	72.1	65	25	5	4	28.0	7.9	3.6
5-[illegible]	"	"	"	13.0	-	0.7	-	"	"	109/3	-	840	68	-	296	51	13	46	186	94	495	67.1	28	26	8	5	37.7	9.8	3.9
5-[illegible]	"	"	12.6	12.8	-	1.0	-	"	"	157/3	-	855	69	-	247	50	15	35	161	90	423	65.5	27	36	6	5	36.	10.3	3.5
5-[illegible]	"	"	12.6	13.3	-	0.5	-	"	"	71/3	-	820	67	-	185	59	8	50	155	86	347	70.6	61	27	6	6	26.7	8.0	3.3
5-[illegible]	"	"	12.9	12.9	-	"	-	"	"	68/3	-	674	55	276	200	100	8	40	160	89	361	95.5	118	28	5	3	28.5	12.4	2.3
5-[illegible]	"	"	"	12.4	-	"	-	"	"	52/2	-	555	45	415	280	98	9	50	130	99	419	97.5	108	16	4	3	33.8	10.0	3.4
5-[illegible]	"	"	"	13.0	-	"	-	"	"	66/3	-	798	62	244	205	93	10	20	143	93	356	97.8	95	27	6	4	28.8	10.7	2.7
5-[illegible]	"	"	"	13.3	-	"	-	"	"	57/3	-	749	61	224	127	99	5	40	149	97	282	97.0	95	40	6	5	22.7	11.6	1.9

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Runs 10 and 11 were attempts to duplicate the very favorable balance for benzene obtained in Run 6. No. 11 repeated the yields essentially within the expected variation, but for an unaccountable reason Run 10 failed to duplicate the yields expected, probably because of an error in the recovery of products.

In Run 9 an attempt was made to keep the apparatus in continuous operation for at least fifty hours without the use of manganous nitrate. The run had to be discontinued after twenty-nine hours because of the precipitation of mercuric oxalate in the jets, clogging the inlets for benzene. It was obvious that a means had to be provided for the destruction of the oxalic acid.

Two methods for the destruction of oxalic acid were considered. One was to allow the oxalic acid to accumulate until precipitation of mercuric oxalate occurred (at a level of approximately 19-20 g. of oxalic acid per liter, according to data obtained by Bachmann at the University of Michigan[27,28]). The crystalline mercuric oxalate could be withdrawn at intervals from the bottom of the reactor and decomposed into mercuric nitrate and carbon dioxide by heating separately with nitric acid. Since this plan had some practical difficulties, the alternative was successfully adopted, from results obtained by the Michigan group, of adding relatively high concentrations of manganous nitrate to catalyze the reaction of nitric acid and oxalic acid to form carbon dioxide and nitrogen oxides. A concentration of 0.5 mole of manganous nitrate per liter of oxynitration solution proved to be adequate for the intended purpose in runs in the No. 5A Jet Extractor with approximately 10.4 M nitric acid at 55°C.

In Run 12, as has been previously described, the 5A Jet Extractor was kept in continuous operation for a total of sixty-five hours without interruption, and at the end of that period the run was discontinued when it seemed quite definite that an essentially steady state had been reached. The chief problem of the previous runs - namely, the destruction of oxalic acid - was solved by the use of 0.5 M manganous nitrate. Table V shows the results of periodic analyses of the mother liquor made at intervals during Run 12; the concentration of oxalic acid rose fairly rapidly at first, then more slowly, and finally became constant within the error of determination at a level of 11.9-12.0 g. per liter of oxynitration solution, which is safely below the level at which catalyst begins to precipitate.

Table V
Oxalic Acid Concentrations in Run 5A-12

Hours of Run	Grams $H_2C_2O_4$ per Liter
0	0.0
12	9.1
24	10.7
36	11.2
42.3	11.4
48	11.9
60.5	12.0
62	11.9

The manganese-catalyzed oxidation of oxalic acid causes somewhat more rapid reduction of nitric acid to nitrogen oxides than in the oxynitration reaction without manganous salt. For this reason the rate of fortification with 98% nitric acid was slightly higher in Run 5A-12 than in previous runs without manganese. Some of the extra nitric acid was required, however, to allow for the higher percentage of DNP nitrated to PA as a consequence of the activity of manganous nitrate as a nitration catalyst.

Run 5A-17 was an unsuccessful attempt to use a high concentration (12.6 M) of nitric acid at relatively low temperature (40°C). The relative rate of formation of neutral nitro compounds was high, and the yield of nitrophenolic product correspondingly low. This run was made with so-called "cold boiler"; that is, the benzene which passed through the reactor was collected in a flask at room temperature and was not recirculated through the reactor by distillation. Runs of this type were also made with other models of the extractor apparatus and yielded much valuable information.

The yields of nitrophenolic products are naturally of primary interest in a discussion of the extractor apparatus. Yield data for runs in the 5A Jet Extractor are summarized in Table VI below. The methods of calculating yields are those already described on page 28.

Table VI
Yields of Nitrophenols in the 5A Jet Extractor

Run No.	Yields of Nitrophenols			Weight Ratio of g. DNP/ g. Neutral Nitro Products
	Based on Benzene Disappearing in the Reactor "B Basis"	Based on Total Benzene Consumed "A Basis"	Oxynitration Efficiency "C Basis"	
2	74	68	80	11.1
6	81	77	87.5	12.8
10	73	69	78.5	11.5
11	78	75	85.5	12.5
5	66	64.5	75	7.4
8	72	70	81	9.3
14	73	69	81	10.4

Table VII shows the data on material balances obtained in five of the runs made in the 5A Jet Extractor. Since it is more convenient to discuss the subject of material balances in a single section for all of the extractor apparatus, the analysis of this table will be deferred to Section **I-F**, page 50 .

The weight ratio of "DNP/Neutral Nitro Products" is defined as the weight of dinitrophenol equivalent to the entire nitrophenolic product (DNP + PA) divided by the combined weight of the NB and DNB fractions. This ratio is computed to a constant DNP basis to avoid confusion resulting from the varying degree of nitration of DNP to PA. When the benzene was cycled by distillation from heated evaporator and boiler flasks, and especially when manganous nitrate was present in the reaction mixture, appreciable fractions of the DNP were nitrated to PA. The time of heating of solutions of DNP

TABLE VII
COMPLETE MATERIALS BALANCES
NO. 5A JET NITRATOR

CONFIDENTIAL

	Run No. 5A-6		Run No. 5A-8		Run No. 5A-10		Run No. 5A-11		Run No. 5A-14	
BENZENE BALANCE										
	g.	%	g.	%	g.	%	g.	%	g.	%
Benzene Input										
Benzene weighed in	635.3		798.5		671.5		630.4		871.4	
Benzene recovered unchanged	279.0		308.3		318.1		262.4		418.8	
Net benzene input	356.3	100.0	490.2	100.0	353.4	100.0	368.0	100.0	452.6	100.0
Benzene Output										
Benzene recovered as DNP	169.0	47.4	215.2	43.9	185.	52.4	199.0	54.2	188.1	41.6
" " " PA	104.0	29.2	126.0	25.7	60.0	17.0	77.4	21.0	124.1	27.4
" " nitrobenzene	17.9	5.0	41.3	8.4	18.1	5.1	19.0	5.2	27.8	6.1
" " "p-DNB"	10.2	2.9	9.8	2.0	10.0	2.8	10.4	2.8	12.6	2.8
" evaporated through condenser and recovered as m-DNB in oxide trap	16.0	4.5	16.0	3.3	16.9	4.8	15.5	4.2	26.4	5.8
" recovered as CO$_2$	11.4	3.2	13.7	2.8	12.6	3.6	13.3	3.6	22.8	5.0
" " " H$_2$C$_2$O$_4$	7.5	2.1	12.0	2.4	7.1	2.0	7.8	2.1	7.1	1.6
" " " CO	0.3	0.08	0.5	0.1	0.2	-	0.3	-	0.7	0.2
Benzene unaccounted for	20.0	5.6	55.7	11.4	43.5	12.3	25.3	6.9	43.0	9.4
Total	356.3	100.0	490.2	100.0	353.4	100.0	368.0	100.0	452.6	100.0
NITRIC ACID BALANCE										
Nitric acid input (as 100% HNO$_3$)										
In original stock solution	1558		1799		1534		1523		1944	
In fortification with 98% HNO$_3$	1291		1720		1278		1278		1297	
In mercury fortification	23		34		17		17		24	
Total nitric acid input	2872	100.0	3553	100.0	2829	100.0	2818	100.0	3265	100.0
Nitric acid output										
In final mother liquor	1928	67.1	2268	63.9	1956	69.2	1936	68.7	2044	62.7
In water trap	6	0.2	8	0.2	5	0.2	6	0.2	11	0.3
In alkali trap	5	0.2	9	0.2	5	0.2	2	0.1	4	0.1
As NO, N$_2$O$_3$, NO$_2$, N$_2$O$_5$(in H$_2$SO$_4$ tower)	217	7.6	302	8.5	270	9.7	250	8.9	402	12.3
In rinsings of apparatus	35	1.2	54	1.5	39	1.4	35	1.2	30	0.9
In titration samples	6	0.2	7	0.2	-	-	-	-	-	-
As N$_2$ or N$_2$O (residual gas)	60	2.1	66	1.9	57	2.0	60	2.1	72	2.2
As DNP	272	9.5	348	9.8	299	10.5	321	11.4	304	9.3
As PA	252	8.8	306	8.6	146	5.2	187	6.7	301	9.2
As nitrobenzene	14	0.5	33	0.9	15	0.5	15	0.5	22	0.7
as "p-DNB"	16	0.5	16	0.5	16	0.6	17	0.6	20	0.6
Unaccounted for	61	2.1	136	3.8	14	0.5	-	-	56	1.7
Total	2872	100.0	3553	100.0	2829	100.0	2829	100.9	3265	100.0
MERCURY BALANCE										
Mercury Input										
In original stock solution	240.3		287.3		241.4		240.9		234.6	
In mercury fortification	52.2		81.1		41.6		41.4		60.9	
Total input of mercury	292.5	100.0	368.4	100.0	283.0	100.0	282.3	100.0	295.5	100.0
Mercury Output										
In final mother liquors	285.1	97.5	363.7	98.7	278.8	98.6	279.8	99.0	292.4	99.0
In rinsings of apparatus	4.4	1.5	4.7	1.3	3.1	1.0	2.6	1.0	2.2	0.7
In titration samples	0.9	0.3	1.1	0.3	-	-	-	-	-	-
Unaccounted for	2.0	0.7	-	-	1.1	0.4	-	-	0.9	0.3
Total	292.5	100.0	369.5	100.3	283.0	100.0	282.4	100.0	295.5	100.0
MANGANESE BALANCE										
Manganese Input										
In original stock solution									62.1	
In manganese fortification									16.0	
Total input of manganese									78.1	100.0
Manganese Output										
In final mother liquors									77.4	99.1
In rinsings of apparatus									0.3	0.4
Unaccounted for									0.4	0.5
Total									78.1	100.0

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containing dissolved nitrogen oxides is also a factor in determining the extent of the nitration of DNP. Table VIII summarizes the data on the extent of nitration of DNP to PA in runs in the 5A Jet Extractor.

Table VIII
Composition of the Nitrophenolic Fraction in Runs in the 5A Jet Extractor

Run No.	% DNP	% PA
2	80.6	19.4
6	56.7	43.3
10	71.3	28.7
11	67.3	32.7
5	75	25
8	58	42
14	54.7	45.3

Some of the nitration of DNP to PA occurs in the evaporator flask in which the benzene solution of DNP is boiled in the presence of dissolved nitrogen oxides. Experiments with "cold boiler" in other models of the extractor apparatus have indicated that, in the absence of manganous nitrate and with good extraction efficiency, the product leaving the reactor is largely DNP with only small amounts of PA. If it were considered desirable to modify the extraction process to prepare DNP essentially without PA, then further study would need to be given to the problem of separating excess benzene from reaction products by means which do not include heating the product with nitrogen oxides.

As mentioned in the introduction, the presence of nitrogen oxides in the oxynitration solution is essential for the occurrence of the complete oxynitration sequence by either of the two known paths. No effort was made in runs in the 5A Jet Extractor to control the concentration of nitrogen oxides for two reasons: first, the equilibria existing among the various nitrogen oxides and nitric acid are extremely complex and a simple analytical method which would express the nitrogen oxide level in a single value would necessarily be somewhat empirical in the present state of knowledge of the system under the conditions of oxynitration; second, various schemes for controlling the nitrogen oxide level seem so complicated as to be impractical. In the runs made to date in the 5A Jet Extractor we have limited our investigations of the nitrogen oxide level to a single analysis for the concentration of "nitrous acid." Samples of mother liquor, when diluted with a great excess of water, can be used to diazotize an aromatic amine, and the amount of nitrous acid initially present can be determined colorimetrically by the coupling of the diazonium salt so formed. This method was used by Westheimer in his kinetic studies as the most satisfactory simple measure of the overall nitrogen oxide level. Table IX shows the values for the concentration of "Nitrous Acid" during Run 5A-19.*

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*Run -19, not described in the tables of data, was made for the express purpose of following the changes in nitrogen oxide level. The oxynitration conditions were similar to those in Runs 5A-12 and 5A-14.

Table IX
Concentration of Nitrous Acid in Oxynitration Solution in Run 5A-19*

Hours of Run	Concentration of Nitrous Acid in Moles per Liter
2	0.22
4	0.24
6	0.19
8	0.19
10	0.23, 0.21

It can be seen that the nitrogen oxide level became essentially constant during the first two hours of the run. It is obvious from visual observation of a reaction mixture that the induction period during which oxides of nitrogen are being formed at the beginning of a run is of rather short duration in normal runs under favorable conditions. This assumption is also borne out by the observation that the formation of nitrophenolic material begins within a few minutes and steadily increases to its maximum rate unless substances are present in the mixture which destroy oxides or prevent their formation.

Westheimer has estimated that a solution of 50% nitric acid saturated with nitrogen oxides/at 50°C. has a "nitrous acid" content of 0.35 mole per liter by the analytical method described.

C. The No. 5 Jet Extractor Apparatus

(1) Description of the No. 5 Jet Extractor.-

The No. 5 Jet Extractor was an earlier model of, and very

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*See foot note on page 36.

similar to, the 5A Apparatus except that it lacked certain refinements of the latter. There were only eight glass inlet jets for benzene instead of twenty-two, and the Dropping Funnel B of the No. 5A Apparatus (see Figure 1) was lacking. The Diluter M was also lacking. The operating volume was 2460 ml. of oxynitration solution.

(2) Operation of the No. 5 Jet Extractor.- The operation of the No. 5 Apparatus was essentially the same as with the No. 5A Apparatus, except for small differences due to the absence of an extra dropping funnel and diluter. The throughput of benzene was smaller because of the smaller number of jets, and this affected the rates of reaction and fortification somewhat, as might be expected.

(3) Oxynitration Runs in the No. 5 Jet Extractor.- Data for twenty-two runs made in the No. 5 Apparatus are summarized in Table IV along with the data for the 5A Extractor. Further data on material balances are shown in Table XI on page 50a.

The initial runs were made to translate the information obtained in smaller earlier models to the larger No. 5 Jet Extractor. In Runs 5-2 through 5-10, inclusive, the importance of maintaining a constant nitric acid concentration by continuous fortification was not fully appreciated, and hence the rate data are of dubious value because the strength of the oxynitration solution must have fluctuated greatly. Later, the practice was adopted of analyzing the mother liquor at intervals and adjusting the fortification rate to maintain the desired constant value.

In Runs 5-8, 5-9, 5-10, and 5-13, efforts to maintain a constant level of 13 M nitric acid proved to be unsuccessful, at temperatures in the range 45-55°C. With such a high acid concentration the reaction velocity is so high that great turbulence results, frequently causing the acid solution to spill over into the evaporator flask.

By reducing the reaction temperature to 40°C. it was possible to study the reaction under conditions of high acid strength. Although rates were satisfactorily high, the proportion of neutral nitro compounds was so great that experiments under these conditions of high acid strength were abandoned.

The amounts of carbon dioxide and oxalic acid formed in the oxynitration were not determined in runs made in the No. 5 Jet Extractor. Total percentages of benzene accounted for are therefore not as high as for some of the runs in the 5A Jet Extractor in which these determinations were made.

D. The No. 4 Fritted Disk Extractor

(1) Description of the No. 4 Fritted Disk Extractor.-- Figure 2 (page 39a) shows the No. 4 Fritted Disk Extractor Apparatus. The following key explains the functions of the various parts:

A. Reactor. The reactor is a vertical glass cylinder with internal dimensions of approximately 4.5 x 50 cm., with an operating volume of approximately 600 ml. of oxynitration solution.

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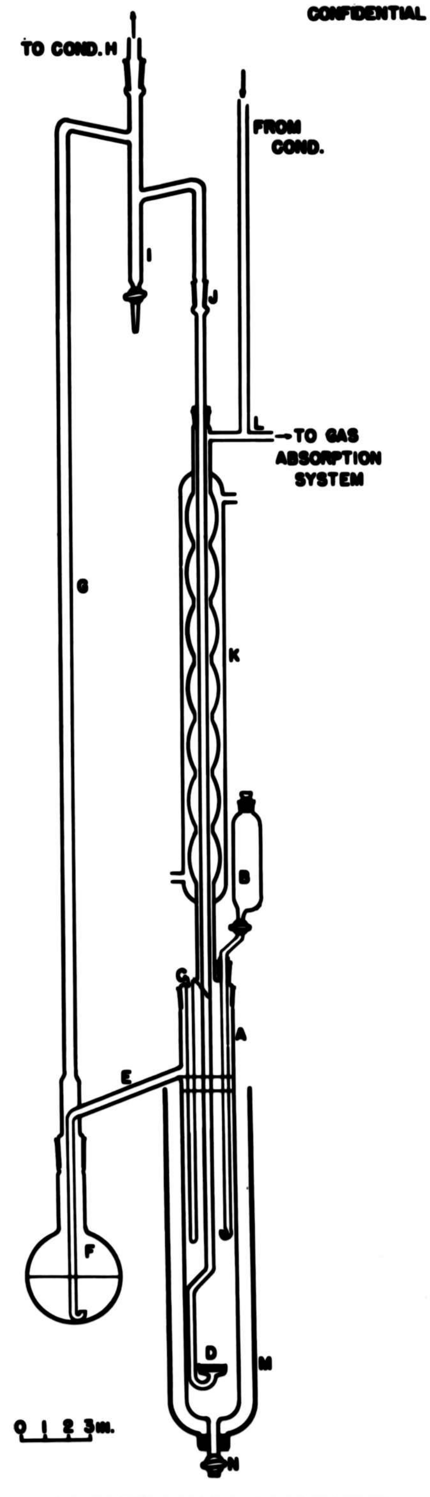

FRITTED DISC EXTRACTOR APPARATUS

FIG. 2

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B. Dropping Funnel. For the introduction of fortifying 98% nitric acid and for the withdrawal of specimens of oxynitration solution.

C. Thermometer Well.

D. Fritted Disk. A "Coarse" Pyrex Fritted Disk approximately 1 inch in diameter through which benzene is dispersed into the nitric acid as a shower of fine droplets.

E. Side-Arm Overflow. Supernatant benzene from the reactor overflows through this side-arm into the Boiler-Evaporator Flask F.

F. Boiling Flask. When benzene is recycled, this flask is heated in an oil bath to distil benzene and nitrogen oxides away from the reaction products back into the fritted disk injector by way of the Tube G.

G. Rising Tube. This tube was heated electrically by means of a spiral coil of resistance wire wound on thin asbestos paper; the use of supplementary heat on this rising tube allowed the Flask F to be heated at a lower temperature without undue condensation of the benzene vapors.

H. Upper Condenser. For the condensation of hot benzene vapors together with some nitrogen oxides.

I. Water Separator. Some aqueous acid vapors were carried along with the benzene and tended to accumulate as a separate phase beneath the fritted disk until this phase separator was installed. Occasionally the aqueous phase in the Separator I was withdrawn to prevent its overflow into the injector, since water was found to close the openings in the fritted disk to the passage of benzene.

J. Ground Joint. This joint was necessary to allow easy assembly and dismantling of the apparatus.

K. Condenser on Reactor. To condense benzene and some of the nitrogen oxides while permitting carbon dioxide and lower nitrogen oxides to pass through.

L. Side-arm to Gas Absorption Tube.

M. Heating Jacket. Filled with water and warmed by a gentle current of steam and air; also used to cool the contents of the reactor quickly to room temperature at the end of a run.

N. Outlet in Reactor. To drain the contents of the reactor and for withdrawal of mother liquor as the volume expanded during a run.

The Fritted Disk Extractor was designed for the purpose of studying the oxynitration reaction under the extreme condition in which the solution would approach saturation with benzene. The high dispersion of benzene was considered favorable for a rapid rate of solution of benzene and also was expected to result in a very high extraction efficiency.

(2) Operation of the No. 4 Fritted Disk Extractor.- The Fritted Disk Apparatus was operated in two ways. One method was very similar to that used with the two jet extractors previously described (Nos. 5 and 5A). Benzene was distilled from the reaction products in the boiling flask (F) and returned to the reaction mixture continuously along with some of the nitrogen oxides carried out in the benzene extracts. In many of the earlier runs with the Fritted Disk Extractor, unreacted benzene was recovered at the end of a run by a procedure similar to that already described (page 24ff). It was found, however, that it was difficult to obtain quantitative recovery of benzene from the fritted disk, and the percentage yields based upon benzene were uniformly lower in this apparatus than in the larger jet extractors.

For this reason, and also in order to conserve time, all runs beginning with Run No. 4-32 were made by a "cold boiler" procedure. The boiler flask was replaced by a large receptacle and the overflowing benzene extracts were collected without heating or without distillation of the benzene back into the system. Fresh benzene was constantly fed into the system through Joint *J* at a predetermined rate. This method required a larger volume of benzene than when the benzene was constantly recycled, and the determination of a complete benzene balance was impractical. However, it was easy to determine the rates of formation of dinitrophenol and of neutral nitro compounds, and also the weight ratio of DNP (or equivalent) to neutral nitro compounds. Experience with batch runs had indicated that these data provide good indications of the performance of the equipment; the ratio of dinitrophenol to neutral products especially is a good index of the order of efficiency of the oxynitration, since a high ratio is indicative of a high oxynitration yield.

Some difficulty was experienced as the result of using a fritted glass disk for the dispersion of benzene. In many of the runs a progressive clogging of the disk reducing the rate of flow of benzene was noted; sometimes the head of benzene above the disk rose so high as to fill the side tube completely, and in such cases the runs had to be terminated.

Several explanations were advanced to account for the clogging: (1) fine particles of mercuric oxalate precipitated in the pores of the fritted disk or on its surface; (2) nitric acid solution gradually wetted the surface of the fritted disk preferentially, excluding the benzene from penetrating the capillary openings; and (3) pockets of gaseous products collected on the under side of the glass disk.

None of these theories was completely verified, but it was noted that in runs with relatively high concentrations of manganous nitrate less difficulty was experienced with clogging, and since the chief function of manganous nitrate is to promote the destruction of oxalic acid or mercuric oxalate the observation seems to give support to the idea that clogging is caused by particles of mercuric oxalate.

In any adaptation of the extraction principle to large-scale operation, it would seem desirable to avoid the use of an injection device, such as a fritted disk, having fine openings. It would be preferable to provide some means of varying the degree of dispersion at will.

(3) Oxynitration Runs in the No. 4 Fritted Disk Extractor.- Table X summarizes the data concerning a total of forty-six runs made in the Fritted Disk (No. 4) Extractor. Twenty of the runs (including Run 4-32 and runs with higher serial numbers) were made by the "cold boiler" procedure - that is, without recycling of benzene by distillation.

Stated very briefly, it is our opinion that the dispersion of benzene into the reaction mixture in such finely divided form as from the fritted disk is not a practical or desirable procedure, although surprisingly high rates of oxynitration and very satisfactory extraction efficiency can be attained in this way. The difficulty is that the oxynitration reaction proceeds in poorer yield and with a higher proportion of by-products when the solution is kept

TABLE X

OXYNITRATIONS OF BENZENE IN CONTINUOUS EXTRACTOR NO. 4 (FRITTED DISK)

Expt. No.	Temp. °C	Time hrs.	Vol. Soln. Taken cc.	Conc. of Stock Soln.: HNO3, moles/liter Initial	HNO3, moles/liter Final	HNO3, moles/liter Average	Hg N	Mn N	Fortification: Nitric Acid Conc. %	Nitric Acid cc. added	Nitric Acid Rate cc/l/hr	Hg soln. added cc.	Mn soln. added cc.	Rate of Benzene Flow cc/l/hr	Mother Liquor Removed. Total cc.	Mother Liquor Removed. Rate cc/l/hr	Weights of Products Formed: Dinitrophenol 1st crop g.	% DNP	2nd crop g.	% DNP	from M.L. g.	% DNP	Total	% DNP in prod.	PhNO2 g.	[illegible]-DNB g.	Rates of Formation: DNP g./l./hr.	Neutral Products g./l./hr.	Ratio g. DNP per g. Neutral Products
4-2	45	5	600	9.6	-	-	0.12	-	-	none	-	-	-	-	-	-	10	-	2	-	-	-	12	-	0.7	0.7	3.9	0.5	6.2
4-3	"	"	"	"	-	-	"	-	-	"	-	-	-	-	-	-	11	-	1	-	-	-	12	-	1.4	0.4	3.9	0.6	6.4
4-4	"	"	605	"	-	-	0.24	-	-	"	-	-	-	-	-	-	18	-	-	-	-	-	18	-	2.4	-	6.1	0.8	7.6
4-5	"	"	590	"	-	-	"	0.033	-	"	-	-	-	-	-	-	15	-	3	-	-	-	18	-	5.4	0.7	6.1	2.0	3.0
4-6	"	"	"	"	-	-	"	"	-	"	-	-	-	-	-	-	12	-	2	-	-	-	14	-	5.2	1.2	4.6	1.9	2.3
4-7	"	"	"	"	-	-	0.36	"	-	"	-	-	-	-	-	-	17	-	2	-	-	-	19	-	6.9	0.8	6.4	2.6	2.5
4-8	"	15.5	"	"	-	-	0.24	"	98	45	3/dis.	-	-	-	30	-	52	-	4	-	-	-	56	-	8.9	1.8	6.0	1.2	5.0
4-10	55	5	580	"	-	-	"	-	70	30	1/dis.	-	-	-	"	-	40	-	3	-	-	-	43	-	11.0	1.3	14.7	4.1	3.6
4-12	"	"	"	"	-	-	0.36	-	"	"	"	-	-	-	"	-	45	-	4	-	-	-	49	-	12.5	1.5	16.8	4.8	3.5
4-13	"	"	"	"	-	-	0.48	-	"	"	"	-	-	-	"	-	55	-	4	-	-	-	59	-	15.1	2.5	20.0	6.0	3.3
4-14	"	"	"	"	-	-	0.06	-	-	none	-	-	-	-	-	-	13	-	1	-	-	-	14	-	3.1	1.2	4.9	1.4	3.4
4-15	"	"	585	"	-	-	0.12	-	70	30	1/dis.	-	-	-	30	-	26	-	2	-	-	-	28	-	5.5	0.8	9.6	2.1	4.5
4-16	"	10	580	"	-	-	0.36	0.17	"	120	3/dis.	-	-	-	90	-	77	-	5	-	-	-	82	-	20.9	6.5	14.0	4.7	3.0
4-17	65	5	"	"	-	-	"	"	"	"	"	8/3	-	-	"	-	57	-	30	-	6	-	93	-	31.2	5.8	32.0	13.0	2.5
4-18	65	10	585	"	-	-	"	-	"	40	1/dis.	-	-	-	20	-	33	-	20	-	4	-	57	-	11.7	2.4	9.7	2.4	4.0
4-20	65	5	575	"	-	-	"	0.17	"	120	3/dis.	8/3	-	-	90	-	85	-	4	-	6	-	95	-	31.3	5.5	35.4	13.0	2.7
4-21	55	"	580	"	-	-	"	-	"	40	1/dis.	3/1	-	-	30	-	42	-	2	-	5	-	49	-	6.1	2.5	17.	2.9	5.8
4-22	"	"	585	"	-	-	"	-	"	"	"	"	-	-	"	-	39	-	3	-	4	-	46	-	9.1	3.0	17.7	4.6	3.8
4-23	"	"	560	7.4	-	-	"	-	-	none	-	-	-	-	-	-	10	-	-	-	4	-	-	-	7.2	0.8	-	3.4	-
4-24	"	"	570	9.6	8.7	-	"	-	70	40	1/dis.	3/1	-	-	30	-	34	-	4	-	9	-	47	-	4.2	2.4	16.4	2.3	7.0
4-25	"	"	"	12.8	9.9	-	"	-	"	"	"	"	-	-	"	-	78	-	8	-	9	-	95	-	10.1	4.0	33.5	5.0	6.7
4-26	"	"	575	9.6	7.8	-	0.72	-	"	65	"	-	-	-	55	-	63	-	6	-	6	-	75	-	7.9	6.9	26.	5.1	5.1
4-27	"	"	570	7.4	-	-	0.36	-	-	none	-	-	-	-	-	-	10	-	4	-	3	-	17	-	6.6	2.3	6.2	3.1	2.0
4-28	"	"	"	12.8	9.9	-	"	-	70	140	4/dis.	9/4	-	-	120	-	93	98	14	15	23	75	131	84	11.2	4.4	46.	6.5	7.1
4-30	"	"	"	13.0	10.2	-	"	-	"	220	4/dis.	16/4	-	-	155	-	129	90	10	35	14	80	153	85	21.0	4.4	52.	8.9	5.8
4-31	"	"	"	"	10.8	-	0.18	-	"	"	"	8/4	-	-	120	-	97	97	9	29	17	71	123	88	21.2	5.0	43.	9.2	4.6
4-32	"	"	575	12.8	9.8	-	0.36	-	"	"	"	16/4	-	327	115	-	153	90	11	27	14	78	179	85	21.7	8.5	61.	10.3	6.0
4-33	"	"	"	"	10.1	-	"	-	"	"	"	"	-	143	"	-	126	99	9	45	14	71	149	93	17.2	6.5	51.	8.2	6.2
4-34	45	"	"	"	9.6	-	0.72	-	75	"	"	"	-	244	"	-	148	100	6	53	13	69	167	92.5	13.2	7.2	58.5	7.1	8.2
4-35	"	"	565	"	11.0	-	0.5	-	98	204	83	-	-	283	65	23	144	99	6	50	35	74	185	93	15.4	6.7	63.	7.8	8.1
4-36	"	4	"	"	12.1	-	"	-	"	336	155	-	-	266	200	89	131	99	7	57	70	87	207	94	23.0	6.8	90.	13.1	6.9
4-37	"	3	"	"	13.0	-	"	-	"	360	250	-	-	333	175	103	142	99	13	23	55	67	210	92	32.9	11.1	120.	27.	4.7
4-38	"	5	580	12.9	11.2	-	1.0	-	"	288	199	-	-	306	63	64	192	95	-	-	40	80	232	93	18.4	12.4	137.	17.7	7.6
4-39	"	6.5	"	12.0	12.0	-	0.5	0.18	"	556	186	30/2	13/1	294	395	105	294	95	-	-	78	89	372	94	34.7	10.6	97.5	12.	8.1
4-40	"	10	"	"	11.5	-	"	0.36	"	972	"	54/3	45/3	320	663	93	498	96	-	-	95	85	593	94.5	40.5	20.3	101.5	19.	5.3
4-41	"	15	"	11.8	11.6	-	"	0.54	"	1475	"	85/5	105/5	352	1015	117	692	96	-	-	80	51	773	91	127.2	15.7	88.	16.4	5.4
4-42	"	4	575	12.1	11.8	-	"	-	"	298	"	17/1	"	378	236	107	162	99	6	48	-	-	168	97	25.7	5.7	72.6	13.6	5.3
4-43	"	2	573	12.1	11.9	-	"	-	"	162	"	-	"	740	73	64	65	99	2	47	-	-	67	98	16.7	-	58.	14.5	4.0
4-44	"	4.5	580	-	-	11.7	0.32	0.54	"	384	155	7/1	13/1	274	156	63	155	94	-	-	38	93	193	93	50.3	10.1	72.6	23.0	3.2
4-45	"	"	"	-	-	"	"	"	"	405	155	12/1	23/1	204	273	105	138	93	-	-	46	89	185	92	51.4	5.0	70.0	21.6	3.2
4-46	"	"	"	-	-	11.8	"	0.54	"	405	155	11/1	21/1	455	244	94	153	96	-	-	27	92	190	95	57.9	5.4	72.4	24.2	3.0
4-47	"	"	"	-	-	11.95	"	0.25	"	393	150	12/1	12/1	286	258	99	137	95	-	-	34	94	172	95	46.	-	65.	18.5	3.5
4-48	"	"	"	-	-	11.5	"	0.95	"	496	190	11/1	39/1	276	295	113	170	92	-	-	37	93	208	92	89.4	5.8	79.5	36.6	2.1
4-49	"	"	"	-	-	12.4	"	-	"	375	143	13/1	-	290	248	95	150	91	-	-	38	97	188	92	32.4	6.0	70.9	14.7	4.8
4-50	"	2.5	"	-	-	11.2	1.00	0.54	"	405	280	19/1	22/2	450	224	148	243	94	-	-	40	96	283	94	33.4	12.1	103.	31.4	3.3
4-51	35	4.5	"	-	-	12.7	0.5	-	"	475	182	11/1	-	345	265	110	160	97	-	-	50	99	210	97.5	64.5	10.4	80.	28.6	2.8

near the saturation level with benzene than when the **steadystate** concentration of benzene is considerably below saturation. Numerous runs by the batch procedure. bear out this idea.

The runs made in the Fritted Disk Extractor are, however, of great interest and value in establishing the limiting conditions for the process.

By the use of rather high concentrations (11-13 M) of nitric acid in the Fritted Disk Extractor, maintained by continuous fortification with 98% nitric acid, and with concentrations of mercuric nitrate up to 1.0 M, rates of oxynitration as high as 193 g. of DNP (or equivalent in PA) per liter of oxynitration solution per hour were obtained. If this rate were maintained, a given weight of oxynitration solution could produce its own weight of DNP approximately every seven hours, and in addition would produce a considerable amount of neutral nitro compounds as by-products.

Extremely high rates of oxynitration do not appear to us to be practical, for the following reasons: (1) mechanical difficulties complicate the operation at high rates - for example, turbulence caused by rapid evolution of gas, dissi ation of heat of reacti the difficulty of introducing fortifying nitric acid to maintain a constant uniform concentration throughout the solution, and the lack of suitable means of destroying oxalic acid at the very rapid rates of reaction; (2) high reaction rates are obtained under reaction conditions which favor the undesired reactions leading to neutral nitro products and colored materials of unknown structure.

A brief resume of the runs in the Fritted Disk Extractor follows. Runs 4-2 through 4-7, inclusive, 4-10 through 4-15, inclusive, and 4-26 were preliminary runs to establish the modus operandi for the Fritted Disk Extractor. The chief difference from operation in the jet type extractor is the different rate of fortification necessitated by the more rapid reaction rates in the fritted disk type.

Run 4-8 established that with 9.8 M nitric acid, 0.24 M mercuric nitrate, and no manganous nitrate, the Fritted Disk Extractor could be operated continuously for fifteen and one-half hours before clogging of the disk occurred. With more vigorous reaction conditions and more rapid oxynitration, clogging occurred more promptly. Run 4-16 showed that manganous nitrate has a favorable action in delaying the clogging of the disk, although in the concentration used clogging could still occur.

Runs 4-17 and 4-20 proved that, although the Fritted Disk Extractor can be operated at a temperature as high as 65°C., the turbulence at the higher temperature is so great that operation is very difficult.

Runs 4-21, 4-24, and 4-30 were designed to study the effect of the rate of throughput of benzene but were inconclusive because the extreme importance of a constant nitric acid concentration was not fully appreciated. In later runs with more careful acid control, 4-44, 4-45 and 4-46, the results seemed to indicate that the throughout rate has little or no effect upon the results obtained provided the minimum requirements of the solution for reaction and extraction of products are provided. An exception to this statement was observed in Run 4-23 using 7.4 M nitric acid; in this run the rate of oxynitration was so slow (because of the low concentration of nitric acid) that the intermediate, phenylmercuric nitrate, was extracted by the benzene and carried over into the side flask. Extraction of mercurial intermediates does not occur to an appreciable extent when 10 M or higher nitric acid is used.

Run 4-22 duplicated 4-12 except that a deeper layer of supernatant benzene remained in the reactor. This modification had no apparent effect.

Runs 4-23, 4-25, 4-27, and 4-28 show the great influence of nitric acid concentration upon the overall rate of formation of DNP. The reaction rate increases rapidly with increasing acid strength, especially in the range 11-12 M. The magnitude of the change of rate with concentration is so large that the importance of maintaining constant nitric acid concentration can hardly be over-emphasized. The reaction velocity increases so rapidly above 12 M nitric acid that it is difficult to add 98% nitric acid fast enough to maintain a constant acid strength in that range. The formation of neutral nitro products is greatly favored in the range of 12-13 M nitric acid.

Run 4-31 showed that in relatively strong nitric acid with low mercuric nitrate level the rate of formation of nitrobenzene remains high, while the rate of formation of nitrophenols is lower than with higher concentrations of mercuric nitrate in the same strength of acid.

The use of the "cold boiler" procedure was adopted in Run 4-32 and all subsequent runs. The original objective of the "cold boiler" was to determine whether a considerable portion of the nitrobenzene is formed in the hot boiler flask. In the Fritted Disk apparatus, at least, the conclusion seems to be that the nitrobenzene arises almost entirely in the reactor.

Runs 4-35 through 4-41, inclusive, were made to determine what concentration of manganous nitrate will prevent clogging of the fritted disk. For runs of fifteen hours, a minimum of 0.5 M manganous nitrate was required. Runs 4-42 and 4-43 were like 4-41 except that manganous nitrate was omitted. The disk clogged in four hours and two hours, respectively, indicating clearly that manganous nitrate is effective in delaying the clogging. The addition of manganous nitrate after clogging in Run 4-42 failed to clear the disk, even when the temperature was raised to 58°C. The disk was quickly cleared, however, by immersion in dilute hydrochloric acid, an indication that mercuric oxalate is responsible for the clogging.

Runs 4-44, 4-47, 4-48, and 4-49 showed that the manganous nitrate, in the concentrations used, has a pronounced catalytic action on the rate of formation of nitrophenolic products. The manganous salt, however, promoted the formation of nitrobenzene to an even greater degree so that less favorable weight ratios of DNP to neutral products were obtained in the presence of manganous nitrate.

In Run 4-50 a high mercuric nitrate concentration (1.0 M) was used in conjunction with 0.54 M manganous nitrate concentration and 11.2 M nitric acid. This combination gave the highest overall oxynitration rate achieved in This Laboratory, 193 g. of DNP per liter of solution per hour. The operation was complicated by turbulence of the solution, and the run had to be discontinued after two and one-half hours because of clogging of the disk.

The use of a lower temperature (35°C.) in Run 4-51 appeared to offer no advantage.

E. Other Extraction Apparatus

(1) The No. 1 and No. 2 Extractors.- The idea of carrying out the oxynitration reaction in a continuous extraction apparatus grew out of the work of Dr. Baizer on the mercuration of benzene in nitric acid, a study which was intended to explain the role of the mercuric nitrate catalyst in the oxynitration process. Dr. Baizer observed that mercuration of benzene occurs very readily in nitric acid solution - so readily that if the primary product, phenylmercuric nitrate, is not removed from the solution physically or by chemical reaction it will undergo further reaction with mercuric nitrate to form di-mercuric, tri-mercuric, and even tetra-mercuric derivatives. The preparation of monomercurated

benzene derivatives was later carried out successfully in a continuous extraction apparatus, utilizing the fact that monophenylmercuric nitrate is somewhat soluble in benzene whereas polymercurials are insoluble.

During the experiments on the mercuration of benzene and in the course of early attempts to prepare mercurials by continuous extraction, it was discovered that the continuous extraction principle could be successfully applied to the oxynitration reaction itself. The first extractor (referred to as No. 1) was designed for other purposes and was relatively inefficient; it was capable of operating only at 75°C. The result were sufficiently promising to justify the construction of a series of five additional models of extraction apparatus.

The advantages of a continuous process are obvious: (1) the operation does not have to be interrupted for the removal of products, an operation which may require more time and labor than the actual oxynitration itself; (2) the reaction products remain in contact with the oxynitration solution for a minimum of time, hence are less likely to undergo undesirable side reactions, such as mercuration; (3) the removal of reaction products by continuous extraction largely eliminates the chance that mercury catalyst will be retained in the products, inasmuch as mercuric nitrate is not extracted by benzene. The direct filtration of solid product from the oxynitration solution, used in most earlier processes, even when followed by careful washing, always leaves a residue of the mercuric salt in the product.

The No. 2 Extractor, like the first model, was capable of operation at only one temperature.

(2) The No. 3 Extractor.- The No. 3 Extractor was a smaller version of the No. 5 Jet Extractor. The reactor was a cylinder 8.5 cm. in diameter by 19 cm. in height, with a capacity of 760 ml. of oxynitration solution. Four glass jets served to introduce the benzene. Rates of reaction were lower in this apparatus than in later models because of the low rate of throughput of benzene.

Although many runs were made in the No. 3 Extractor, many of them with complete benzene and nitric acid balances, the data are not included in this report, for most of the results were repeated with more elaborate attention to detail in the later extractor models. The results were valuable in guiding the design and operation of the later models.

F. Material Balances in Continuous Extractors

Specific data regarding the runs in continuous apparatus have been discussed under the headings of each of the various models (Sections I-B, -C, -D). The methods of computing yields have been described in Section I-B-(3)(c). The purpose of this section is to summarize some of the data on overall material balances in the various continuous extractor apparatus.

Table XI (page 50a) summarizes data on the benzene balance for runs made in Extractors 4, 5, and 5A. Table VII (page 34a) summarizes balances in Extractor 5A for benzene,

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TABLE XI
BALANCE SHEET
OXYNITRATIONS OF BENZENE BY CONTINUOUS EXTRACTION METHODS

Expt. No.	Benzene Not Recovered g.	Benzene Net Reacting g.	Per Cent Yields of Products Based on Net Benzene Reacting				Fate of All Benzene Not Recovered as Benzene							
			DNP	PA	PhNO$_2$	"p-DNB"	DNP	PA	PhNO$_2$	"p-DNB"	Volatilized through condenser	Oxalic acid	CO$_2$ and CO	Total C$_6$H$_6$ Acctd. for
3-29	106	96	72	-	6.1	2.1	65.8	-	5.6	1.8	9.5	-	-	82.7
3-30	116	107	70	-	7.0	2.8	65.3	-	6.5	2.6	7.4	-	-	81.8
5- 2	127	114	45	21	10.2	4.4	-	-	-	-	-	-	-	83.3
5- 3	133	118	47	18	9.8	3.9	-	-	-	-	-	-	-	82.2
5- 4	74	68	58	9	6.7	2.7	53.9	8.9	6.3	2.5	6.7	-	-	78.3
5- 5	96	87	62	8	8.1	3.0	56.0	7.5	7.3	2.7	9.8	-	-	83.3
5- 8	251	221	46	19	14.2	3.5	40.0	16.5	12.4	2.4	12.4	-	-	83.7
5- 9	258	225	55	17	12.1	2.2	47.3	14.9	10.6	1.9	12.7	-	-	87.4
5-10	292	266	47	18	14.2	2.0	42.5	16.4	13.0	1.8	9.0	-	-	82.7
5-13	436	402	41	18	15.3	1.8	38.0	16.0	14.1	1.7	7.8	-	-	77.6
5-14	391	357	42	15	17.2	1.7	37.8	14.	15.7	1.5	8.7	-	-	77.7
5-15	308	279	45	19	14.2	2.3	40.3	17.3	12.9	2.0	9.6	-	-	82.7
5-16	186	170	55	8	5.8	3.0	50.1	7.6	5.3	2.7	8.4	-	-	74.1
5-17	179	168	59	10	6.9	2.5	55.3	9.4	6.4	2.3	6.1	-	-	79.6
5-18	229	221	48	14	10.4	1.6	46.1	13.6	10.0	1.5	3.6	-	-	74.8
5-20	211	202	58	13	10.1	2.0	56.0	12.3	9.7	1.9	4.0	-	-	83.9
5-21	258	249	45	14	22.9	1.2	43.1	13.3	22.1	1.7	3.4	-	-	83.1
5-23	327	318	44	18	21.5	1.2	43.0	16.9	20.8	1.7	3.0	-	-	85.4
5-24	332	323	37	15	24.1	1.5	35.4	15.0	23.4	1.5	2.7	-	-	78.0
5A- 2	204	189	62	12	5.5	3.3	56.6	11.0	5.1	3.0	7.8	-	-	83.5
5A- 5	260	257	52	14	9.9	2.6	51.0	13.5	9.7	2.5	1.2	2.9	1.9	82.7
5A- 6	356	340	50	31	5.3	3.0	47.4	29.2	5.0	2.9	4.5	2.1	3.2	94.4
5A- 8	490	474	45	27	8.7	2.1	43.9	25.7	8.4	2.0	3.3	2.4	2.9	88.6
5A-10	353	337	55	18	5.4	3.0	52.4	17.0	5.1	2.8	4.8	2.0	3.6	87.7
5A-11	368	352	56	22	5.4	2.9	54.1	21.0	5.2	2.8	4.2	2.1	3.6	93.1
5A-14	453	426	44	29	6.5	3.0	41.6	27.5	6.1	2.8	5.8	1.6	5.2	90.6
4-10		36	50	-	19.	1.6								
4-12		40	51	-	20.	1.2								
4-13		49	50	-	19.	2.4								
4-16		71	49	-	18.5	4.3								
4-17		74	53	-	26.	3.6								
4-18		41	58	-	18.	2.6								
4-20		80	51	-	25.	3.2								
4-21		38	55	-	10.	3.0								
4-22		35	57	-	17.	4.0								
4-24		32	61	-	8.3	3.5								
4-25		65	62	-	9.9	2.8								
4-26		57	56	-	3.7	5.6								
4-27		15	51	-	28.0	6.8								
4-28		79	67	-	8.3	2.6								
4-30		97	65	-	13.7	2.1								
4-31		82	63	-	16.4	2.8								

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nitric acid, mercuric nitrate, and manganous nitrate.

In Table XI the weight of Benzene Not Recovered represents the difference between the weight of benzene added to the reactor and that recovered as benzene by the methods previously described. This value includes any benzene lost by volatilization or accident. The column headed Net Benzene Reacting is equal to the weight of benzene not recovered minus the weight of benzene volatilized through the condenser and estimated by conversion to m-DNB in the gas absorption tower. This figure is assumed to approximate the weight of benzene which actually enters into reaction in the reactor; actually, this weight is somewhat high for the reason already mentioned - that some benzene is unavoidably lost in handling. The yields of products in the next column are based upon the weight of net benzene reacting; this is the "B-basis" of yield calculation described on page 28. The final tabulation under the heading of Fate of All Benzene Not Recovered as Benzene is made on the "A-basis" as explained on page 28.

The weight of benzene volatilized through the condenser and determined as m-DNB varied in a range of 1.2% to 12.7%. The weight of benzene which escapes in this way bears no direct relationship to that which undergoes oxynitration, and is dependent upon the design and temperature of the condenser and the volume of non-condensable gaseous reaction products.

The most careful accounting of benzene was made in runs in the 5A Jet Extractor, as summarized in Table VII (page 34a). In a series of six runs the lowest percentage of benzene accounted for was 82.7% and the highest 94.4%. In spite of the most careful efforts, the total of benzene accounted for fluctuated, a fact which is not surprising in view of the volatility of the benzene and the complicated manipulations that were required. If the lowest value is disregarded (as low because of accidental loss), the average total percentage of benzene accounted for was 90.9%. The benzene not accounted for was undoubtedly lost in small amounts during the workup of each of the reaction products; we do not believe that there is any single large loss or previously unsuspected by-product.

For the entire series of runs made in the 5A Jet Extractor, the average yield of DNP + PA based upon benzene reacting in the acid solution was 73.9%; based upon the benzene not recovered as such, the average figure was 70.2%. Run 5A-6 was the most satisfactory, with 81% of DNP + PA based upon benzene reacting, or 76.6% based upon total benzene not recovered as benzene; this run was made in 10.7 M nitric acid, 0.5 M mercuric nitrate, and no manganous nitrate. Run 5A-14 was made under very nearly similar conditions except that 0.5 M manganous nitrate was used; the yield of DNP + PA was 73% based upon benzene in the reaction mixture, or 69.1% upon total benzene introduced but not recovered. It should be noted that these yield values are conservative because they are based upon weights of benzene which include all losses in handling.

Table VII further summarizes data on nitric acid consumption in the 5A Jet Extractor. In most of the runs, 98-100% of the nitric acid was accounted for. Taking Run 5A-14 as typical, about 2/3 of the total nitric acid introduced during the ten-hour period was still present in the oxynitration solution or in washings, about 20% had been converted into reaction products, about 12% had been evolved as nitrogen oxides recoverable as nitric acid, while only about 2% of the total nitric acid was lost as elementary nitrogen or non-recoverable oxides; 1.7% of the nitric acid was not accounted for.

Mercury and manganese were accounted for quantitatively, within the accuracy of the analytical methods for their determination, in the oxynitration solution or in the rinsings from the apparatus. Carryover of mercury catalyst into the evaporator flask in the benzene extracts is apparently negligible under the conditions of operation used in the 5A Jet Extractor, as qualitative tests for mercury made at intervals on the material in the evaporator flask were almost always negative. The only remaining operation which might result in loss of mercury catalyst is the concentration of portions of withdrawn mother liquor to small volume by distillation, and losses from this source would result only from carelessness in handling. Data on manganese balances are available for only one run; it is natural to assume that losses of manganese would not be greatly different from losses of mercury. The methods of sampling and analysis admit of appreciable error, but as nearly as can be determined (± 1%), the loss of both metallic salts is small.

G. Discussion of Results of Runs in Continuous Extractors

(1) Effect of Nitric Acid Concentration.-

Westheimer[25] has studied the kinetics of mercuration of benzene in nitric acid saturated with benzene. He has shown that, under the usual conditions of practical oxynitration, the mercuration step (cf. page 9) is the rate-controlling one. Since the rate of mercuration is extremely low in very dilute nitric acid and increases rapidly as the strength of acid increases, one would expect the overall rate of oxynitration to vary similarly. This has been observed experimentally in the continuous extractors.

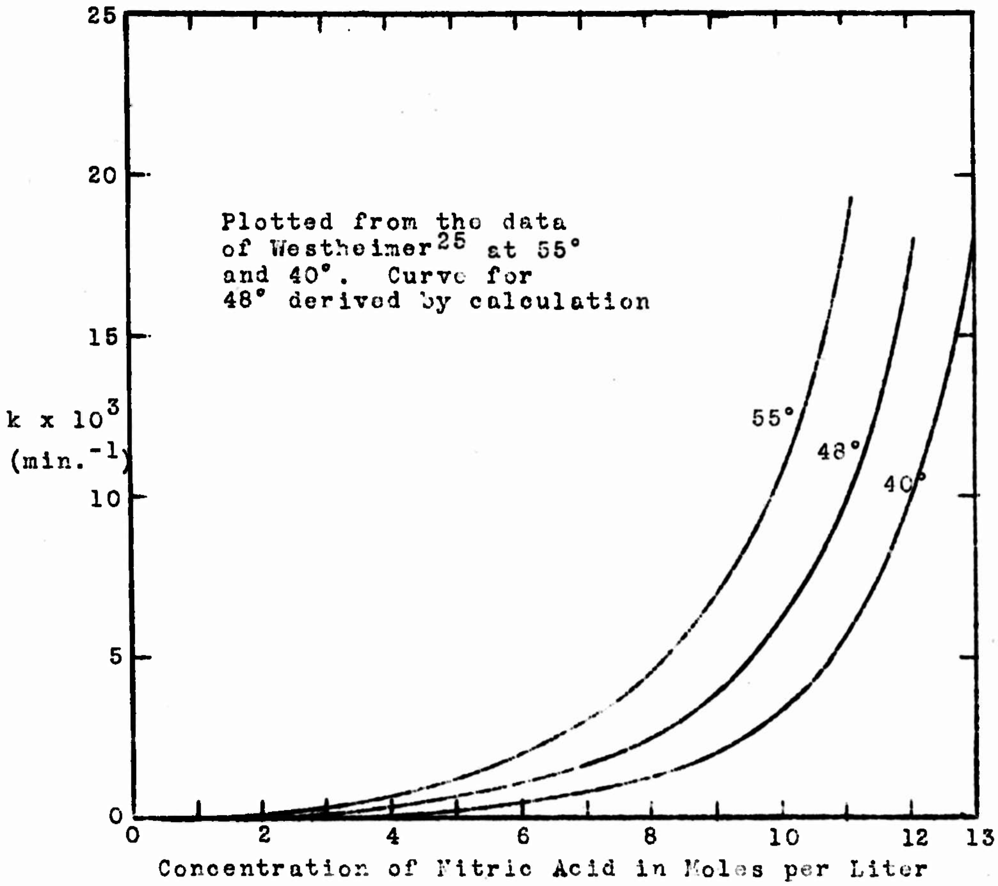
The great change in oxynitration rate with change in nitric acid concentration makes careful control of the acid strength by analysis and continuous fortification essential. Early batch runs were usually made with a fixed amount of nitric acid present; it is not surprising that yields were usually low, since the reaction then proceeded in constantly decreasing acid strength.

Figure 3 shows some of the data of Westheimer on the apparent rate constants for mercuration of benzene plotted against the molar concentration of nitric acid.

The constants, k, are defined by the equation

$$\frac{d\left[C_6H_5HgNO_3\right]}{dt} = k\left[Hg^{++}\right]$$

for solutions constantly kept saturated with benzene.



Plotted from the data of Westheimer[25] at 55° and 40°. Curve for 48° derived by calculation

Figure 3

Relationship between Mercuration Rate Constants and Nitric Acid Strength

It is obvious that if mercuration is the first step of the oxynitration sequence, whatever the final path may be to nitrophenol from the mercurial, the maximum possible overall rate of oxynitration will be attained if the solution is constantly saturated with benzene and if all of the benzene which undergoes mercuration is converted in 100% yield to DNP. It is possible on this basis to estimate the maximal rate of oxynitration under a given set of conditions from mercuration kinetic data provided by Westheimer. Some interesting correlations so obtained will be discussed in Section I-G(9). Actually, of course, the rates of oxynitration observed in the extractor apparatus are usually less than the limiting values, since the solution is less than saturated with benzene and since there are side reactions which produce neutral by-products at the expense of nitrophenols An interesting exception to this statement has been noted (cf. page 73).

The maintenance of a constant level of nitric acid concentration is of greatest importance. Fortunately, there exists a convenient automatic compensating effect which simplifies the problem of maintaining a constant acid strength. When the fortifying acid is added continuously, the rate of fortification is found to determine eventually the steady-state nitric acid concentration in a long run. Once the proper fortification rate is discovered by experiment, it becomes a fairly simple matter to hold the acid level constant.

If, for example, the acid strength rises slightly momentarily, the resulting sharp increase in the mercuration rate and in turn the oxynitration rate begins to use up nitric acid more rapidly and the acid strength is reduced again. Conversely, a temporary fall in the acid strength produces a corresponding decrease in overall reaction rate so that nitric acid is consumed somewhat less rapidly and the fortification is able to restore the original strength. This compensating action is of course only effective within limits, and it is essential to establish approximate optimum conditions by the use of pilot runs.

There is another reason why the maintenance of a constant nitric acid concentration is very important: it was shown by Westheimer that the Path A "Rearrangement Mechanism" occurs as the major process in concentrations of nitric acid above about 50% by weight (10.4 M), especially when the concentration of nitrogen oxides is low, but below 50% nitric acid strength, and particularly when the level of nitrogen oxides is high, the Path B "Diazonium Mechanism" is the predominating process. The yields and quality of nitrophenols produced are superior in the Path A mechanism.

(2) Importance of Method and Rate of Benzene Addition.- The development and successful operation of the continuous extraction apparatus have depended very largely upon the correctness of the fundamental idea that benzene is only oxynitrated when it is dissolved in the aqueous nitric acid solution containing mercuric nitrate catalyst. Benzene present as a separate liquid phase is not effective in the oxynitration process except as it helps to maintain a suitable concentration of dissolved benzene in the acid phase.

Westheimer[27] has shown that the solubility of benzene in 50% (10.4 M) nitric acid at 40°C. is 6.4 g. per liter. In any actual apparatus the concentration of dissolved but unreacted benzene will vary between 0 and the level of saturation. The concentration will be the resultant of the rate of solution and the rate of disappearance of benzene to form reaction products.

Numerous experiments by earlier investigators as well as by other groups in the NDRC and in this Laboratory have convincingly demonstrated that the oxynitration reaction gives poor yields of nitrophenolic product, with relatively high yields of nitrobenzene and dark by-products, when the solution is kept saturated by vigorous agitation of an excess of liquid benzene with the solution. Bachmann and others have shown, on the other hand, that the yield of nitrophenol and also its quality increase sharply as the time of addition of a fixed weight of benzene is increased, but the yield eventually levels off and becomes constant as the time of addition is increased; stated in other words, there is an optimum rate of addition of benzene, and this is found to be related to the rate at which the solution is capable of oxynitrating benzene under a given set of conditions.

The mere presence of excess benzene is not in itself disadvantageous except when vigorous agitation is used. Vignon[5] was able to obtain high yields of nitrophenolic material in unstirred runs with excess benzene, and the Barrett Company found that the rate of agitation has an influence upon the yields when an excess of the starting material is present.

We have found that the manner of introduction of the benzene is a variable of great importance in the continuous extraction process. This is undoubtedly due to the fact that when such a large excess of benzene is used (usually more than ten times the weight of benzene which reacts) the rate of throughput of benzene and the degree of dispersion in the solution determine very largely the steady-state concentration of dissolved but unreacted benzene (the rate of transformation of the benzene to intermediates is the other determining factor). No stirring is used in the present models of the continuous extractors other than that provided by the upward movement of benzene droplets, the downward movement of fortifying acid, and the convection currents. These seem to be quite adequate in apparatus of the scale herein described. On a larger scale it would perhaps be advantageous to provide some gentle swirling motion in order to insure against the formation of pockets with excessively low or high acid concentration and to facilitate the uniform extraction of products. It should be emphasized, however, that the stirring should not be so violent as to break up the droplets into a very fine state of subdivision.

In practice it was found that a cluster of 22 fine glass jets gave better results than a coarse fritted glass disk, for two reasons: the jets do not clog easily and they do not disperse the benzene too finely. The fritted disk - even the coarse grade - gives a shower of extremely fine droplets which rise very slowly through the solution. Such a condition facilitates the dissolving of the benzene, and the results appear to indicate that with the fritted disk extractor the solution operates very near the saturation level. The jet extractor, on the other hand, breaks up the benzene into a smaller number of larger droplets which rise fairly rapidly through the solution. The observed reaction rates suggest that the solution is about one-third saturated with benzene, and this apparently is a very favorable level to produce good yields of nitrophenols with relatively small amounts of neutral products and colored by-products.

In the 5A Jet Extractor, the 22 glass jets have internal diameters of approximately 0.2-.3mm. The rate of throughput of benzene is such that about 3-5% of the benzene dissolves and reacts.

In summary it can be said that the variables which affect the steady state concentration of dissolved but unreacted benzene are as follows:

(1) The rate of injection of benzene into the oxynitration solution, usually expressed in terms of ml. of benzene per liter of oxynitration solution per hour.

(2) The degree of dispersion of benzene in the oxynitration solution, expressed most conveniently perhaps as the average size of the benzene droplets in the solution.

(3) The average time of contact of the droplets of benzene with the reaction mixture. Naturally the smaller drops rise more slowly and remain in contact with the solution longer. The dimensions of the apparatus also affect the time of contact.

(4) The concentrations of nitric acid, mercuric nitrate, and manganous nitrate which determine the rate of mercuration, and hence the limiting rate of oxynitration, of the solution.

(5) The use of supplementary means of agitation will to some extent influence the amount of benzene which dissolves and reacts.

Not all of these variables have been investigated in detail. The results described should, however, provide a useful guide for the construction of larger scale equipment.

(3) Effect of Mercuric Nitrate Concentration.- In the kinetic expression for the rate of mercuration given by Westheimer[25] the rate is directly proportional to the molar concentration of mercuric salt. It would be expected that the overall rate of oxynitration will be similarly dependent upon the catalyst concentration. When all other conditions are carefully kept as nearly constant as possible, this assumption seems to be true. The influence upon the results produced by variations of the catalyst concentration in the range of 0.2 to 0.7 M, or perhaps even greater, are relatively small as compared with the very great effect of variations of acid strength or of the manner of adding benzene, so that the maintenance of an

exact concentration of catalyst is not of tremendous importance.

In most of the runs in the Jet Extractor, a concentration of 0.5 M mercuric nitrate has been found to give very good results. Doubling the catalyst concentration helps to increase the oxynitration rate, but since the moderate rates obtained with 0.5 M concentration are most convenient from the standpoint of operation, the attainment of high reaction velocities is not an objective.

The thought has been expressed that the use of higher catalyst concentrations should favor oxynitration over the side reactions leading to neutral reaction products. We have been unable to prove this because the effect, if any, must be small and easily obscured by variations in other factors.

(4) Effect of Temperature.- The overall rate of oxynitration increases roughly by a factor of 1.8 to 2 with each 10°C. rise in reaction temperature. The reaction appears to be qualitatively about the same in the range from room temperature to about 55-60°C. Above approximately 60°C. the conditions favor the nitration of benzene to nitrobenzene somewhat more than the conversion to nitrophenols, and the reaction of DNP to form PA begins to occur at increasingly important rates, particularly when the concentration of nitrogen oxides is high. The temperature range of 50-60°C. has been found to give the most satisfactory results in general.

(5) Effect of Manganous Nitrate.- The oxalic acid which is formed as a by-product in the oxynitration process reacts slowly with nitric acid to form carbon dioxide and nitrogen oxides, but the rate of destruction in the absence of catalysts is unable to keep pace with the rate of formation, with the result that eventually enough oxalic acid accumulates to cause precipitation of the insoluble solid mercuric oxalate. Precipitation occurs at a concentration of approximately 20 g. of oxalic acid per liter; the mercuric oxalate tends to supersaturate the solution, but precipitation occurs fairly rapidly when once started.

The catalytic action of manganous nitrate upon the reaction between oxalic acid and nitric acid is well known.[37] Manganous nitrate has been added to oxynitration mixtures to serve both as a catalyst for the oxynitration reaction and also to hasten the destruction of the by-product.[21] Bachmann[28] has made a careful study of the kinetics of the catalyzed destruction of oxalic acid. He has shown that the rate of decomposition of oxalic acid increases with increase of both the manganous salt and the oxalic acid concentrations. At any given rate of oxynitration, with a given concentration of manganous nitrate, there is a definite concentration of oxalic acid for which the rate of destruction is equal to the rate of formation. The problem is to select the proper concentration of manganous nitrate so that the steady-state level of oxalic acid will remain safely below the level at which precipitation of catalyst begins. The data of Bachmann allowed us to select a suitable salt concentration with a minimum of experimentation. It was found that, under optimum conditions in the 5A Jet Extractor, 0.5 M manganous nitrate is able to hold the level of oxalic acid concentration to approximately 12 g. per liter of oxynitration solution.

There appears to be a definite increase in the rate of formation of DNP + PA resulting from the use of 0.5 M manganous nitrate. This is best shown in results obtained in the Fritted Disk Extractor, and will be discussed in detail in Section I-G-(9). The rate of formation of nitrobenzene also appears to be increased; the proportional increase in the rate of formation of nitrobenzene seems, unfortunately, to be greater than the increase in the rate of formation of nitrophenolic material.

The catalytic effect of manganous nitrate on the nitration of o-nitrophenol and p-nitrophenol in aqueous nitric acid was noted in this Laboratory early in the course of the present investigation.[27] Bachmann[28] investigated the catalytic action of manganous salts on the nitration of DNP to PA in aqueous nitric acid. The fact has been repeatedly verified that a higher proportion of PA is formed when manganous nitrate is present than when it is absent. Some experiments to illustrate this effect are shown in the next section dealing with the effects of nitrogen oxides.

A comparison of data for runs made in the extractor apparatus with and without the added manganese salts will confirm the observations made in separate experiments with nitrophenols.

If it were considered desirable to adapt the continuous oxynitration reaction to the production of 2,4-dinitrophenol free, or nearly free, of picric acid, further study would need to be made of catalytic means of destroying oxalic acid without at the same time promoting the nitration of DNP. There are indications in the literature[37] that substances other than manganous nitrate are capable of promoting the destruction of the by-product, but as yet none of these has been studied in the oxynitration process. The possibility of allowing mercuric oxalate to precipitate from the mixture so that it can be separated mechanically for recovery of catalyst in a separate unit has been suggested, but has not been tested experimentally because of the complications of operation which this practice would entail.

(6) Effect of Nitrogen Oxide Concentration.- Westheimer has defined the complex equilibria which obtain in a solution of nitrogen oxides in approximately 50% nitric acid in terms of an analytical value for nitrous acid.[25] Since most of the oxides of nitrogen in nitric acid solution are in equilibrium with nitrous acid, or are convertible to

nitrous acid upon dilution, this somewhat empirical measure of the nitrogen oxide level has been adopted in this Laboratory to follow the changes in nitrogen oxide concentration in the Jet Extractor (5A). The analytical method used by Westheimer involves the dilution of a measured volume of the oxynitration solution with a large (known) volume of water, then the determination of the amount of nitrous acid in an aliquot by diazotizing an aromatic amine, coupling it with a color-forming agent, and measuring the intensity of the resulting color in a photoelectric colorimeter.

This procedure gives an overall measure of the oxide level, but does not accurately measure the concentrations of the individual nitrogen oxides. The present knowledge of the mechanism of the oxynitration process is not sufficiently detailed to provide exact information as to which oxides are needed in each of the steps, nor what the optimum concentrations are for each separate step. Westheimer has calculated[38] that a level of nitrogen oxides corresponding to approximately 0.04 M nitrous acid should be optimal for the reaction in 50% (10.4 M) nitric acid at 50°C., or 0.35 M nitrous acid in 60% nitric acid and with low mercuric concentration.

In Run 5A-19 the nitrogen oxide level was found to rise promptly to a nearly constant value equivalent to 0.22 M nitrous acid, which is somewhat higher than Westheimer's calculations would predict as the most favorable (cf. page 13). This level is less, however, than that in a 50% nitric acid solution saturated with nitrogen oxides (0.35 M, 50% HNO_3, 50°C). We have made no effort to vary the nitrogen oxide level in the 5A Jet Extractor, since the experimental modifications required for such a purpose would greatly complicate the construction and operation of the continuous extractors. We have obtained data in batch runs and in other models of the extractor apparatus, however, which indicate that both the extremes of very low and very high nitrogen oxide levels are unsuitable for the oxynitration reaction. When nitrogen oxides were passed into batch oxynitration reaction mixtures from an external source, the yields of DNP (and/or PA) were invariably lower than for similar runs without added oxides; the addition of oxides also promoted the formation of dark red by-products which were very difficult to remove from the nitrophenolic product. Westheimer has shown[25] that a high nitrogen oxide concentration favors the mechanism sequence involving an intermediate diazonium compound (Path B, page 10); since this mechanism is known to give poor yields of nitrophenols and considerable dark by-products, a low concentration of nitrogen oxides and relatively high nitric acid concentration are preferred because these conditions are unfavorable for the diazonium mechanism and favorable for the alternative Path A mechanism (v.s.).

The effect of eliminating nitrogen oxides in the continuous extraction apparatus is very interesting, since it leads to the formation of phenylmercuric nitrate without the occurrence of the subsequent steps of the oxynitration sequence. Phenylmercuric derivatives were isolated from reaction mixtures in rather dilute nitric acid (in which the oxynitration reaction is very slow) early in the investigations in this Laboratory.[27] Westheimer later showed that good yields of phenylmercuric nitrate could be isolated when urea is added to a typical oxynitration reaction mixture to destroy nitrogen oxides.

A reaction was carried out in the No. 3 Jet Extractor using the usual oxynitration mixture but with the inclusion of urea in the starting acid. The product extracted from the solution was not the usual mixture of nitrobenzene and nitrophenols, but instead consisted of nearly pure phenylmercuric nitrate, which is somewhat soluble in benzene. When the urea was present the solution remained practically colorless, and no nitrogen oxides were evident. The use of the continuous extraction principle for the preparation of phenylmercuric nitrate in aqueous nitric acid is, we believe, new, and should afford a convenient method for the manufacture of that mercurial. The mercuration was not studied in detail in the continuous reactors; only a single run was made in the No. 3 Extractor, as described below:

<u>The Preparation of Phenylmercuric Nitrate by Continuous Extraction</u>.- The stock solution introduced into the No. 3 Jet Extractor contained 70 g. of mercuric oxide, 41 ml. of 70% nitric acid, 5 g. of urea, and sufficient 50% nitric acid to make the volume up to 750 ml. Benzene was circulated through the apparatus by distillation, as previously described; except for the inclusion of urea, the procedure did not differ from that of oxynitration. The extractor was operated at

55°C. for five hours. The evaporator flask was found to contain 54.3 g. of phenylmercuric nitrate, m.p. 129-131°. When the mother liquor in the reactor was diluted with water and sodium chloride was added to the solution, 37.2 g. of white solid, m.p. 225-250°, precipitated. This was considered to consist principally of phenylmercuric chloride (equivalent to 40.3 g. of phenylmercuric nitrate). Unreacted benzene was recovered as carefully as possible. A total of 24.2 g. of benzene was unaccounted for.

The experiment of mercuration clearly demonstrates that the catalytic function of the mercuric nitrate involves the formation of a reactive phenylmercuric derivative, and also proves the necessity for the presence of nitrogen oxides. Under normal circumstances there appears to be no difficulty in the prompt formation of at least the minimal concentration of nitrogen oxides, even though little or no oxide is present in the starting mixture. The induction period for fresh oxynitration solutions appears to be a matter of minutes, as judged by the rapid darkening of the initially pale solution, and, in the extractors, by the prompt beginning of the extraction of reaction products from the solution.

Nitrogen oxides, or perhaps nitrous acid in equilibrium with nitrogen oxides, also aid in the nitration of nitrophenols, as, for example, in the conversion of DNP to PA. The higher the concentration of nitrogen oxides the more rapid the conversion of DNP to PA appears to be.

In order to demonstrate that the nitrogen oxides are involved in the nitration of nitrophenols and have an important influence on the rates of nitration, a series of experiments was carried out in which 30-g. samples of pure DNP were heated at 55°C. for seven hours in 700-ml. volumes of nitric acid. Different concentrations of nitric acid were used. In one group of experiments a gentle stream of air was drawn through the mixture while in another group of experiments nitrogen oxides generated from the action of sulfuric acid upon moist sodium nitrite were passed through the reaction mixtures. The results, summarized in Table XIa below, clearly show that the presence of added oxides greatly increases the extent of conversion of DNP to PA. In the case of the very strong nitric acid (70%, or approximately 15 M), some of the DNP was destructively oxidized with the formation of nitrogen oxides internally, and extensive nitration occurred even though no nitrogen oxides were added from an external source.

Table XIa
Effect of Nitrogen Oxides in Promoting Nitration of Dinitrophenol in Nitric Acid

	No Nitrogen Oxides			Nitrogen Oxides Added			
Average Concentration of Nitric Acid (M)	10.2	12.7	15.2	10.0	11.9	14.2	14.4*
Per cent conversion of DNP to PA	0.7%	7 %	63 %	30 %	55 %	70 %	99+ %

*In this experiment introgen oxides were added to the nitric acid which contained a concentration of 0.5 M manganous nitrate. It is clear that manganous nitrate promotes the nitration of DNP to PA.

Some of the nitration of DNP to PA which is observed in the extraction process probably occurs in the evaporator flask during prolonged heating of the DNP in hot benzene solution containing dissolved nitrogen oxides.

(7) Effects of Other Variables.- Wright has recommended the use of small concentrations of aluminum nitrate in the oxynitration process. In batch runs we have been unable to observe any effect due to aluminum salts in the concentrations recommended by Wright. This salt was consequently not used in the continuous extraction process.

(8) Rates of Extraction of Reaction Products.- The successful operation of the continuous extractors during long periods without interruption depends upon the capacity of the excess benzene to extract the organic reaction products from the reaction mixture at rates equal to their respective rates of formation. At the beginning of a run, when little or no products are present, the rates of extraction will of course be very small but will increase as the weights of dissolved reaction products increase. For successful results the rates of removal of products must increase until they equal the rates of formation; when this steady state is reached there will be a constant residual level of each product dissolved in the oxynitration solution.

Fortunately, the factors which determine the efficiency of removal of products also partially determine the amount of benzene which dissolves and reacts. The rates of extraction have in general been found adequate under optimum conditions of oxynitration in all of the models of extractor apparatus.

In the 5A Jet Extractor, the efficiency of extraction is quite satisfactory at the optimum rate of formation of DNP of approximately 30-35 g. per liter of oxynitration solution per hour. The extraction efficiency would still be ample for an appreciably higher rate of oxynitration if this were desired. The No. 4 Fritted Disk Extractor obviously has a greater extraction efficiency than the jet types, and is suited for the removal of reaction products even when the oxynitration rate greatly exceeds 100 g. of DNP per liter of solution per hour.

To determine whether the efficiency of extraction is adequate for any given set of conditions, it is only necessary to change the evaporator flask at regular intervals and work up the separate portions to determine whether the rates of extraction are constant and equal to the rates of formation of products. This was done in Run 5A-12, and the data of Table III (page 23) show how the removal of products kept pace with the reaction rates.

Figure 4 shows graphically the relationship between the formation and extraction of any single reaction product. The solid curves a, b, and c represent the plots of total weight of product formed (vertical axis) against total time of reaction (horizontal axis). The slope of the curve at any time, t, gives the rate of formation of the product at

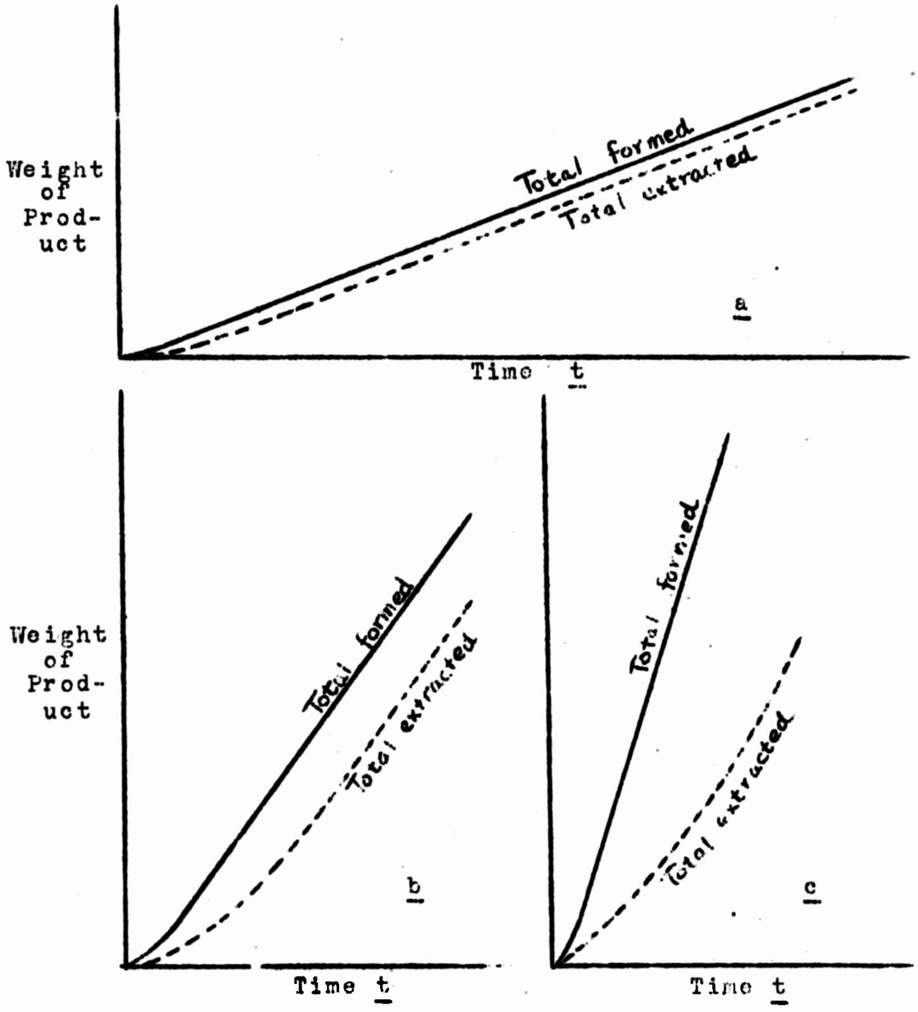


Figure 4

Relationship between the
Rates of Formation and Extraction
of Reaction Product

that time. The dotted curves show the total weight of product extracted plotted against time, and the slope of the dotted curves at any point indicates the rate of extraction of the product at that time. The vertical distance between any pair of curves at any given time represents the weight of the product remaining in solution in the reactor at that time. Curves a represent the situation in which a moderate rate of formation of product prevails, and the extraction efficiency is high. Here the induction period is short, and the residual concentration of unextracted product is small. Curves b represent the situation in which there is a rather rapid rate of formation with fair extraction efficiency. In this case the rate of extraction of product eventually becomes equal to the rate of formation, but the residual concentration of unextracted product is fairly great. Curves c represent the situation in which the rate of formation of product is greater than the capacity of the apparatus to remove the product; the result is that the rate of extraction never catches up with the rate of formation, and eventually this situation must lead to the separation of the unextracted reaction product as a separate solid or liquid phase.

(9) Comparison of Observed Rates of Oxynitration With Theoretical Rates.- As explained in Section I-A-(1) (page 8), the first step of the oxynitration sequence is the mercuration of benzene, and under the conditions used in the present practical processes it is the rate controlling step. On the basis of several simple assumptions it is

possible to estimate from the kinetic data of Westheimer the maximum rates of overall oxynitration for a given acid concentration, temperature, and mercuric nitrate concentration. The expression for the mercuration of benzene as given by Westheimer is

$$\frac{d\,[C_6H_5HgNO_3]}{dt} = k\,[Hg^{++}]\ ,$$

for solutions of nitric acid saturated with benzene. In the expression above, $[C_6H_5HgNO_3]$ and $[Hg^{++}]$ are the concentrations of intermediate and of mercuric ion in terms of molarity, and **k** is the velocity constant in $min.^{-1}$ Some of the data of Westheimer are plotted in Figure 3 (page 55) to show the magnitude of the influence of nitric acid concentration on rate of mercuration. The assumptions involved in the calculation of maximum oxynitration rates are as follows:

(1) The acid is kept saturated with unreacted benzene.

(2) Side reactions to form neutral nitro products can be neglected.

(3) All the benzene which is mercurated is eventually converted to DNP in 100% yield.

(4) When a steady state is reached in the continuous reactors, the rate of formation of DNP in moles per liter per hour will be equal to the rate of formation of phenylmercuric intermediate.

In making the calculations of the theoretical maximum oxynitration rates, the final values for the rates of DNP formation in moles per liter per minute are converted by the appropriate factor to units of grams of DNP per liter of oxynitration solution per hour. Table XII shows the comparison of calculated rates of oxynitration with observed rates of formation of DNP in Extractors 4, 5, and 5A, in solutions containing only nitric acid, mercuric nitrate, and benzene as starting materials.

Table XII
Comparison of Observed and Calculated Rates of Formation of DNP in Continuous Extractors in the Absence of Manganous Nitrate

Run No.	Temp. °C.	Molarity		Rates of DNP Formation		Ratio of Obs./Calcd. Rates
		HNO_3	Hg^{++}	Obs.	Calcd.	
4-49	45°	12.4	0.32	71	70	1.0
4-37	45°	12.9	0.50	120	150	0.8
4-38	45°	12.0	1.00	137	170	0.8
5-26	40°	12.9	0.50	29	95	0.30
5-16	55°	10.5	0.50	21	74	0.27
5-23	40°	12.8	0.70	38	125	0.30
5-24	40°	12.7	1.00	32	165	0.20
5A-2	55°	10.6	0.50	27	80	0.34
5A-6	55°	10.7	0.50	27	85	0.31
5A-10	55°	10.5	0.50	24	75	0.32
5A-11	55°	10.5	0.50	27	75	0.36
5A-5	45°	12.1	0.60	33	105	0.31
5A-8	45°	12.1	0.60	34	105	0.32

It should be recognized that the calculated rates are only approximate because of the number of assumptions which are made in arriving at the values. Furthermore, the comparison may not be strictly accurate because of unavoidable variations in the acid strength during a run which would appreciably influence the average reaction rate for the whole run. In spite of these uncertainties, the ratios of observed to calculated oxynitration rates remain surprisingly constant for each different type of reactor. The rates observed in the Fritted Disk Extractor (No. 4) approach the theoretical limit rather closely, suggesting that the solution in the Fritted Disk Extractor is kept nearly saturated with benzene at all times, as previously suspected.

The Jet Extractors show reaction rates of roughly one-third the limiting value, and this may be accounted for by the assumption that the solutions in the jet extractors are much below the saturation level of benzene.

Surprising and interesting results are obtained by similar calculations for runs made with oxynitration solutions containing manganous nitrate. Some of these data are summarized in Table XIII.

Table XIII
Comparison of Observed and Calculated Rates of Formation of DNP in Continuous Extractors in the Presence of Manganous Nitrate

Run No.	Temp. °C.	Molarity			Rates of DNP Formation		Ratio of Obs./Calcd. Rates
		HNO_3	Hg^{++}	Mn^{++}	Obs.	Calcd.	
4-47	45°	12.0	0.32	0.25	65	53	1.2
4-46	45°	11.8	0.32	0.54	72	48	1.5
4-45	45°	11.7	0.32	0.54	70	45	1.55
4-44	45°	11.7	0.32	0.54	73	45	1.6
4-50	45°	11.2	1.00	0.54	193	105	1.84
4-48	45°	11.5	0.32	0.95	80	40	2.0
5A-12	55°	10.3	0.50	0.50	31	70	0.44
5A-14	55°	10.4	0.50	0.50	31	75	0.42
5A-17	40°	12.6	0.50	0.50	15	80	0.18

In all runs made in the Fritted Disk Extractor (No. 4) the observed rates were consistently higher than the calculated values by factors ranging from 1.2 up to 2.0. In Runs 5A-12 and 5A-14 the ratios of observed to calculated rates are less than unity, but are higher than for similar runs in the same apparatus in the absence of manganese. The low value in Run 5A-17 is easily explained by consulting the data for that run; under the unfavorable conditions used in that run a large portion of the benzene which underwent reaction formed nitrobenzene, so that the observed rate of nitrophenol formation was correspondingly lower than it might have been.

The data are not sufficiently accurate to justify any emphasis of the importance of these data. It seems definite, however, that manganous nitrate has an appreciable influence upon the rate of formation of DNP, and that in the Fritted Disk Extractor, which operates near the saturation level of benzene, the observed rates are greater than predicted from mercuration studies made in the absence of manganous nitrate. The explanation for this observation is not immediately obvious. The manganous salt may catalyze the mercuration step, or increase the rate of solution or solubility of benzene in the reaction mixture, or perhaps it influences the equilibria of nitric acid and nitrogen oxides in such a way as to promote the overall reaction or affects the analyses for nitric acid upon which the calculated rates are based.

The use of the kinetic data is also of indirect value in affording a means of predicting roughly the rates which may be achieved under combinations of conditions which have not been studied in actual oxynitration runs.

H. Proposed Methods of Separating Reaction Products

The investigation of the continuous extraction process in laboratory models has been carried out with the primary objective of obtaining data as accurate as possible on the yields of products formed in the reactor. To do this, very elaborate precautions have been taken to isolate the products as nearly quantitatively as possible and to analyze mixtures for the individual components. The separation of DNP + PA from neutral products was made by the use of aqueous solutions of triethanolamine (TEA), which forms water-soluble salts with nitrophenols (a method suggested by G. F. Wright). It was realized that the methods suitable for the laboratory investigation would not be suitable for large-scale production, and that sooner or later an investigation of methods for the separation of the reaction mixtures would need to be undertaken if the continuous extraction process were to be developed to pilot plant scale.

We have considered a number of possible separation methods and have carried out some preliminary experimental work along this line. The investigation was terminated, however, before any final procedure had been developed, hence this portion of the work is still incomplete. Before this phase of the problem can be completed it will be necessary to select a definite objective for the products to be produced, since that decision will to a great extent determine the method of separation used.

For example, it would be possible to adapt the process to yield a mixture of DNP + PA, or pure PA, or perhaps to produce practically pure DNP. The production of DNP would, however, require further study of methods for the destruction of oxalic acid.

The products produced during a five-hour interval of Run 5A-12 were as follows:

225	g.	DNP
167	g.	PA
28.6	g.	NB
4.6	g.	p-DNB
0.7	g.	o-DNB
4.2	g.	Unidentified products, including TNDA (tetranitrodiphenylamine), excess benzene, and dissolved nitrogen oxides.

In preliminary experiments on methods of separation suitable for large scale operation, mixtures of pure compounds approximating the composition given above for an actual reaction mixture were made up and were separated by the procedures described below.

<u>(1) Method of Separation Leading to PA as a Final Product</u>.- The solution of reaction products and nitrogen oxides dissolved in benzene is warmed gently to cause the distillation of most of the oxides together with a little benzene. If the heating is done carefully, very little nitration of DNP or other material occurs.

After the bulk of the nitrogen oxides has been distilled, the mixture of benzene and reaction products is stirred vigorously for ten minutes with a quantity of hot 5% sodium hydroxide solution equivalent to the nitrophenolic material present; this treatment is carried out under reflux with the benzene boiling. The layers are then separated, the alkaline layer retaining the nitrophenols as salts, while the benzene solution holds the neutral products. Acidification of the aqueous layer precipitates a mixture of solid DNP + PA, which is filtered after the solution has been cooled. The mixture of DNP + PA can be nitrated in almost quantitative yield to PA by treatment with concentrated sulfuric acid and 98% nitric acid (procedure of Bachmann[28]).

The benzene is removed by fractional distillation from the neutral fraction, and nitrobenzene is collected at a higher temperature. A high-boiling residue which solidifies upon cooling contains polynitro compounds and TNDA. The p-dinitrobenzene, o-dinitrobenzene, and TNDA which largely compose this residual fraction can be converted into nitrophenols by an alkaline treatment described below, or direct separation of the pure components can be made by fractional crystallization.

In the separation of phenolic from neutral products, the use of sodium hydroxide solution stronger than 6% is not recommended because of the tendency for the sodium nitrophenolate salts to be "salted out" of such solutions. It is advisable to restrict the amount of alkali used in the separation to the theoretical amount or slightly less, since TNDA (2,4,2',4'-tetranitrodiphenylamine) and perhaps other minor by-products are very weakly acidic and will dissolve in an excess of strong base. If an excess of strong base is not used, these highly colored by-products remain in the neutral fraction where they cause less trouble in the separation of pure nitrophenols.

(2) Method of Separation Leading to Ammonium Picrate.- The solution of reaction products and nitrogen oxides in benzene, as isolated from the evaporator flask of an extractor apparatus, is steam distilled with a rapid current of steam to remove benzene and nitrogen oxides. Distillation is discontinued as soon as there is evidence of the presence of DNP in the distillate. The remaining residue is heated in a bath at 120-130°C. until no further distillation occurs.

The residual cake of DNP-PA containing neutral products is warmed with sufficient concentrated sulfuric acid to cause complete solution at 75°C. The solution is then cooled to 25°C. and nitrated to PA by addition of 98% nitric acid according to the procedure of Bachmann.[28] The PA contains some neutral by-products, and melts at 115-117°C.

Ten parts of the crude PA is vigorously stirred with 100 parts of benzene while concentrated aqueous ammonia (6.7 parts) is added slowly during the course of ten minutes. Stirring is continued for a few minutes longer, after which the solid ammonium picrate is filtered and washed with water (two portions of 10 parts each).

In laboratory experiments the recovery of dried product in the first crop represented 97.5% of the nitrophenol originally present. Analysis of the ammonium picrate for ammoniacal nitrogen gave 5.63% (Ordnance specification, 5.64% minimum) and tests showed 0.06% insoluble matter (Ordnance specification, no more than 0.2%). No investigation was made to determine whether the benzene filtrates could be re-used directly for the precipitation of other batches of product.

(3) Separation Based upon Continuous Alkaline Extraction of the Nitrophenolic Products.- A few preliminary experiments were carried out with the plan of passing the benzene extracts directly from the oxynitration reactor countercurrently through a column of aqueous alkali (perhaps through a unit similar in design to the reactor itself) so as to remove the acidic nitrophenols while allowing the neutral products to pass through with the benzene. Time did not permit a careful test of this method.

The main drawback to such a separation is that a considerable quantity of nitrogen oxides is extracted from the oxynitration solution by the benzene. Normally the oxides redistil back into the reactor and hence are not lost from the system. If the benzene extracts are passed directly into an alkaline extractor, a large amount of alkali would be required to neutralize the nitrogen oxides, and the consumption of nitric acid would be correspondingly increased. If a simple means of separating the nitrogen oxides first and returning them to the reactor could be found, this difficulty would disappear.

The choice of an alkaline agent for the extracting solution would not be simple; sodium and potassium hydroxide are not very suitable because of the low solubility of their picrate salts. Triethanolamine would probably be suitable for laboratory use, but its cost would be high on large scale.

(4) The Possibility of Producing Pure DNP.- The present investigation of the oxynitration reaction was undertaken under a directive specifically concerned with means of producing picric acid. No special consideration was given therefore to the possibility of adapting the final procedure of the extraction process to yield DNP free, or nearly free, of PA. Under some reaction conditions, it was determined that the predominant product in the nitrophenolic fraction is DNP. This is particularly true in cold-boiler runs (benzene not recycled by distillation) in nitric acid of moderate strength (10.5-11 M) containing no manganous nitrate.

In most runs in the extractors some nitration of DNP to PA occurred, the extent of nitration depending upon a number of factors some of which were not easily controllable. If there were interest in a method of producing DNP, we believe that the results are promising enough to warrant a thorough study of methods of suppressing the nitration of DNP to PA without unduly inhibiting the oxynitration reaction or complicating the operating procedure.

The results indicate that the product of oxynitration under optimal conditions is almost exclusively DNP. Although mononitrophenols are assumed to be intermediates they are not isolated under the conditions of the extraction process herein described. The subsequent formation of PA is due to the prolonged contact of DNP with nitric acid or nitrogen oxides, especially in the presence of manganous nitrate. Nitration may also occur in benzene solution. The critical factors which seem to determine the extent of nitration to PA are the concentration of nitrogen oxides, the concentration of manganous salt, the temperature, and the time of contact of the DNP with the nitrating solution or with the hot benzene solutions containing oxides of nitrogen. We have been able to establish that the use of 98% nitric acid for fortification is not a contributing factor in the nitration of some of the DNP to PA.

I. By-Product Investigations

The products of the oxynitration reaction in the extractors were separated into three main categories for the purpose of determining yields. These main groups were the nitrophenols (DNP + PA), nitrobenzene (distilled at 207-215°C. at atmospheric pressure), and a fraction called "DNB," which comprised the residue remaining after distillation of nitrobenzene.

Illustrative of a typical run are the weights of products for Run 5A-12 in which the 5A Jet Extractor was kept in continuous operation for sixty-five hours. A total of 5262 g. of DNP + PA was isolated, 314 g. of distilled nitrobenzene, and 194 g. of "DNB."

(1) <u>Analysis of the Mixture of High-Boiling Neutral Nitro Products</u>.- The high-boiling fraction designated as "DNB" is of interest because it corresponds to nearly 3% of the weight of benzene consumed in the reaction.

By a combination of methods, including fractional distillation, fractional crystallization, differential solubility, and chemical reactions, the high-boiling "DNB" fraction was estimated to contain approximately the following components:

38%	Nitrobenzene
31%	p-Dinitrobenzene
5%	o-Dinitrobenzene
?%	2,4,2',4'-Tetranitrodiphenylamine (TNDA)

The values are approximate, since the methods of separation allow of considerable error. The results agree fairly well with the results obtained by Bachmann[28] for analogous mixtures obtained in batch oxynitration runs.

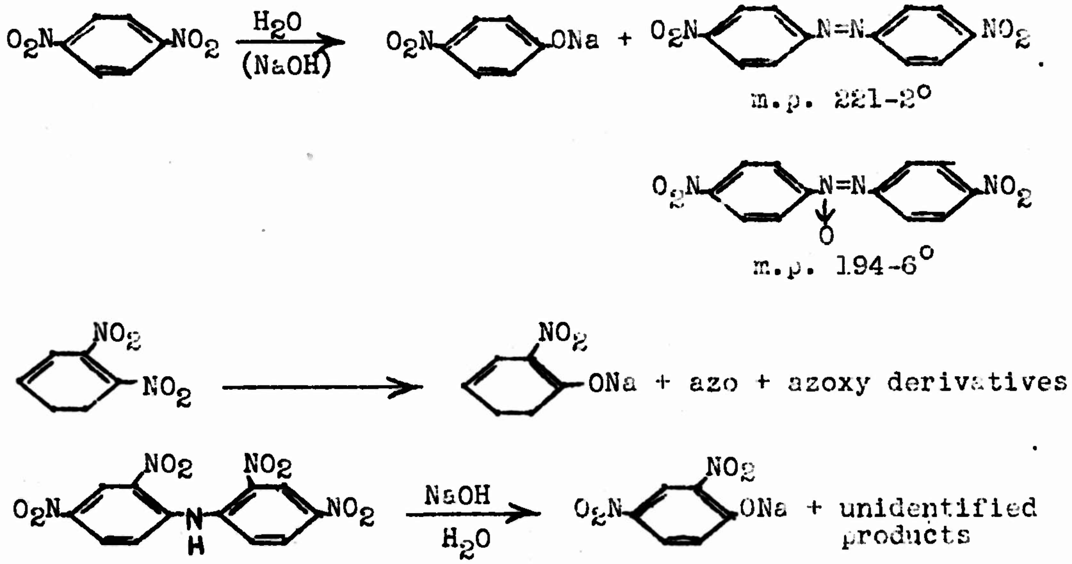
An examination of the 314-g. fraction of distilled nitrobenzene showed that it contained small amounts of p-DNB and o-DNB (a minimum of 1.5% and 0.07%, respectively).

By methods described in the following section, it would be possible to convert the DNB isomers to mononitrophenols and the TNDA to 2,4-dinitrophenol.

(2) <u>Conversion of p-DNB, o-DNB, and TNDA to Nitrophenols by Hydrolysis</u>.- p-DNB and o-DNB can be hydrolyzed

to p- and o-nitrophenol, respectively, and TNDA can be hydrolyzed to 2,4-DNP by the action of hot dilute aqueous alkali.[39]

The chemical reactions involved are shown in the following equations:



The conversion of p-dinitrobenzene to sodium p-nitrophenolate takes place in 95% yield when just slightly more than the theoretical amount of boiling 2% sodium hydroxide solution is used. The use of more concentrated alkali or a large excess of alkali above the required two moles per mole of DNB leads to the formation of the red azo and azoxy by-products shown above. Three hours' treatment with the boiling alkali is sufficient for complete conversion of the nitro compound to the final products.

The hydrolysis of o-DNB is not as smooth as that of the p-isomer. A maximum yield of 65% of o-nitrophenol (or a derivative) was isolated from the action of 5% alkali (3.7 moles) on o-DNB for three hours at reflux temperature.

The action of 10 moles of boiling 5% sodium hydroxide solution upon one mole of tetranitrodiphenylamine gave a hydrolysis mixture from which, by acidification, steam distillation, and filtration of the chilled distillate, a 24% yield of 2,4-dinitrophenol was obtained. In another experiment with 7.5 moles of 2% sodium hydroxide the yield of 2,4-dinitrophenol was 43%.

Most of the experiments with the hydrolysis reactions described above were carried out on small scale, and the nitrophenolic products were isolated, identified, and weighed as the bromo derivatives.

The results showed that the 2% alkali gave the lowest yields of azo and azoxy compounds with the dinitrobenzenes. An attempt was made to use exactly one molecular equivalent of 2% sodium hydroxide in the hydrolysis of p-DNB instead of the required two moles; only a 52% yield of p-nitrophenol was obtained and nearly half of the starting material was recovered unchanged, indicating that a slight excess of alkali is required for the occurrence of the cleavage; the excess should be as small as possible to avoid the side reactions leading to azo and azoxy derivatives.

The experiments were not continued to determine the yields of hydrolysis products on large scale runs.

Since the p- and o-dinitrobenzenes are rather difficult to prepare by straightforward methods, they would probably have a higher value as such than as nitrophenols.

II. OXYNITRATION OF BENZENE IN BATCH RUNS

A. Discussion

During the early part of the present investigation, a very large number of batch oxynitration runs were made to determine which variables are critical and approximately the optimum conditions for high yields of dinitrophenol or picric acid and low yields of neutral nitro compounds. Other objectives were to find, if possible, conditions which would materially reduce the percentage of benzene destructively oxidized and the amount of highly colored minor by-products.

In spite of the variety of conditions reported in previous investigations before 1936, it was difficult to evaluate the importance of the different variables because of the incompleteness of the reported data and the lack of interpretive discussions.

No effort will be made to present all of the experimental data of the many batch runs; instead, the important conclusions which were drawn from them will be given, with illustrative data on the final batch runs which were made. Work on the batch process was discontinued in favor of the continuous extraction process. Because of the more nearly steady-state conditions which prevail in the continuous extraction process, that modification affords a better insight into the effects of the variables than the batch process in which constantly changing conditions are inevitable. Detailed reports of the entire investigation can be found in the Interim Reports of Division 8.[27]

(1) Procedure in Batch Runs.- Most batch runs followed a fairly standardized procedure. A solution of nitric acid, usually in the neighborhood of 50% concentration by weight (equivalent to 10.4 M), was made up with anywhere from 0.2 mole to 0.5 mole per liter of mercuric nitrate. The possible catalytic or promoter effects of other substances were also tested. Benzene was added to the vigorously stirred mixture either in a single portion, or in smaller portions at spaced intervals, or continuously from a dropping funnel; with dropwise addition the benzene was introduced either below the surface or upon the surface of the solution. The whole reaction mixture was warmed at the desired temperature, usually in the range of 40-60°C. In early runs no effort was made to fortify the solution with nitric acid during a run, but as the importance of constant nitric acid strength became more evident during the early runs, the practice of intermittent and later continuous fortification was developed. The use of 98% nitric acid was shown to be the most satisfactory because of the relatively small increase in the volume of the reaction mixture resulting from its use.

(2) Nitric Acid Concentration.- As in the continuous extraction process, best results were obtained in

concentrations of nitric acid of at least 50% (10.4 M). The rate of oxynitration increases rapidly as the acid concentration increases, but the range of 50-55% strength appears to combine adequate reaction rates with optimum convenience of operation and favorable ratios of nitrophenolic to other reaction products. Above 60% nitric acid (13.0 M) the rate of oxynitration is very rapid, and the formation of nitrobenzene is favored more than in 50-55% acid. Results are very much more favorable when provision is made to maintain a constant, or approximately constant, acid concentration by fortification.

(3) Mode of Addition of Benzene.- The feeding of benzene to the reaction mixture is a factor of great importance in determining the relative yields of nitrophenols as compared with neutral products and oxidation products. Agitation of a large excess of liquid benzene with the solution is the worst possible condition for high yields of pure nitrophenols. Very slow dropwise addition of benzene below the surface of the reaction mixture is the best. For a given set of reaction conditions (acid strength, mercuric nitrate concentration, temperature, rate of agitation, etc.) there is an optimum rate at which benzene should be added; within certain limits it does not seem to make a great deal of difference whether the addition is continuous and dropwise or whether it is in small intermittent portions. The optimum rate of addition of benzene is most easily determined by experiment, although kinetic data on rates of

mercuration determined by Westheimer provide a guide to the selection of approximately correct conditions (see pages 9, 54 ff.).

Bachmann[27] was the first to point out that drop-wise addition of benzene below the surface of the reaction mixture gives the best yields of nitrophenols. The importance of the rate of introduction of benzene was shown also in experiments at the University of Pennsylvania which involved the introduction of a single fixed portion of benzene at the beginning of each run of a series in which increasing volumes of reaction solution were used. There was a sharp increase in the yield of nitrophenols and corresponding decrease in the yield of nitrobenzene when the ratio of the weight of oxynitration solution to the weight of benzene increased. An eventual limit to the yield of nitrophenol seemed to be reached when the molar ratio was of the order of 30-40 to 1.

It was shown that the presence of an excess of liquid benzene did not necessarily lead to a low yield of nitrophenolic product if the excess was not violently agitated or otherwise finely dispersed through the reaction mixture. This fact is utilized in the continuous extraction process discussed in Section I.

(4) Mercuric Nitrate Concentration.- Under the conditions found to be most favorable for the batch oxynitration, the concentration of catalyst was not critical. Concentrations between 0.2 and 0.5 M were found to give qualitatively similar results. Evidence obtained mostly in the continuous extraction apparatus had indicated that, when other factors are constant,

the rate of formation of nitrophenols is roughly proportional to the concentration of catalyst, and that the oxynitration is favored slightly over side reactions as the mercuric salt concentration is increased.

(5) Temperature.- With 50% nitric acid the optimum temperature was found to be in the range 50-55°C.

(6) Time of Reaction.- The rate of oxynitration is so greatly dependent upon the various reaction conditions that the time for complete reaction must be determined for each set of conditions. From results obtained in continuous extractors, however, it can be stated that in 50% (10.4 M) nitric acid, 0.5 M mercuric nitrate, at 55°C., benzene reacts at an optimum rate of approximately 0.05-0.1 mole per liter oxynitration solution/per hour. As the acid strength, the temperature, or the catalyst concentration increases, the potential rate of consumption of benzene increases.

(7) Effect of Manganous and Aluminum Nitrates.- Aluminum nitrate in concentrations recommended by previous workers did not appear to have any significant effect in our batch experiments. Manganous nitrate in the low concentrations previously used likewise seemed to have little if any appreciable effect, but fairly high concentrations, of the order of 0.5 M or higher, seem to catalyze both the oxynitration reaction and the formation of nitrobenzene, as well as the nitration of dinitrophenol to picric acid.

(8) Re-Use of Mother Liquors.- Experiments showed that it is possible to remove the bulk of the dinitrophenol

(and picric acid) at the end of a batch run by chilling the mixture and filtering directly. Some nitrobenzene may separate along with the solid, particularly if the solution has been used previously for other runs, and this necessitates a purification procedure for the crude product. The filtered oxynitration solution can be restored to its proper acid and catalyst strength by fortification with 98% nitric acid and mercuric nitrate, and can then be used again to complete another cycle of reaction by the addition of fresh portions of benzene. There is a small expansion of reaction volume during each cycle of reaction resulting from the formation of water in the reaction and the small amount of water introduced with the reagents. After several cycles the amount of nitrobenzene retained in the filtrate becomes essentially constant.

B. Batch Oxynitration Runs with Re-Use of Mother Liquors

The experience of many previous runs is included in and illustrated by seven series of batch oxynitration runs made with re-use of the filtered mother liquors. The first three series, A,B,C, were made with a procedure which involved the addition of the benzene within the first fifteen or twenty minutes of each reaction cycle; the individual series differed only in the proportion of benzene to acid in each cycle and in the scale of the experiments. Balances were determined for mercury and partial balances for nitric acid.

Four subsequent series, D,E,F, and G, utilized the more efficient dropwise addition of benzene (cf. Bachmann[28]), and were also designed to test the effects of manganous nitrate and aluminum nitrate in the batch runs.

(1) Apparatus.- In each series a three-necked, round-bottomed flask appropriate to the volume of reaction mixture was used. It was equipped with 60-cm. bulb condenser, mechanical paddle stirrer, and Y-tube which served for the introduction of benzene to the mixture and also for the insertion of a thermometer into the oxynitration solution. The mechanical stirrer was made gas-tight by a graphite packing in an aluminum housing. The relatively small volume of fumes was led into the hood or into a water absorption trap.

(2) Procedure.- The compositions of the reaction mixtures are shown in Table XIV for Series A, B, and C, and in Table XVIII for Series D, E, F, and G. The reaction was heated to 55°C. and the weighed portion of benzene (as indicated in the tables) was added from a dropping funnel during the first fifteen or twenty minutes of the run for Series A, B, and C, and over longer periods as indicated in the subsequent series. In the first three series the time of reaction was three hours; in subsequent series the time varied from three to eight hours, as indicated. The mixture rapidly assumed a deep reddish-brown color. After the reaction period, the mixture was chilled at 0-5°C. for several hours to cause separation of the bulk of the 2,4-dinitrophenol; the solid was filtered on a fritted glass Büchner funnel and washed with cold 50% nitric acid to remove as much as possible of adhering nitrobenzene, then washed with ice water. Washings were not combined with the main volume of reaction mixture but were worked up separately for nitrobenzene and analyzed for nitric acid and mercury. In the first run or two of a series, the filtered product consisted of almost pure DNP with a light tan color, melting at 109-113° or better. In later runs nitrobenzene was always retained in the solid even after the wash with 50% nitric acid.

The mixture of DNP and nitrobenzene was separated as follows: The solid was treated with a slight excess of 5% sodium hydroxide solution and steam distilled to remove nitrobenzene. Acidification of the residual solution precipitated fairly pure DNP. A small amount of picric acid formed in the reaction under the conditions of these experiments remained for the most part in the mother liquors in early runs of a series. As the picric acid built up in the mother liquors it eventually began separating with the DNP in later runs, resulting in somewhat lowered melting points of the alkali-purified products.

After the filtration of the chilled reaction mixture following each reaction cycle, the volume of the filtrate was measured and an analysis made for nitric acid. The required volume of 98% nitric acid to restore the desired acid concentration was added and a new reaction cycle was started.

The last mother liquor of each series had to be worked up for the residual reaction products still retained in solution. In Series A the final mother liquor was thoroughly extracted with benzene, the nitrophenolic products were removed from the benzene solution with alkali, and the nitrobenzene was obtained after removal of the benzene by distillation. The residue remaining from the distillation of the nitrobenzene was a crude mixture of dinitrobenzenes in which the para isomer predominated. In Series B and C the final mother liquors were subjected to a boil-off, during which their volumes were reduced to approximately one-half the original and the mixtures of nitrophenolic compounds were converted to picric acid. The picric acid was isolated by filtration and by benzene extraction after dilution and chilling of the residual solution from the boil-off. Nitrobenzene was isolated from the distillates by benzene extraction (Series B) and by steam distillation (Series C).

Mercury analyses were made on the final mother liquor in each of the first three series and on the combined washings from each of these series. (For procedure, see Appendix, page 123). In Series A and B the procedure gave somewhat low results because of losses during the decomposition of organic matter, but this was corrected in Series C, in which the loss was relatively low, considering the weight of product which was produced at the same time.

Various details of the runs of Series A, B, and C are presented in Tables XIV, XV, XVI, and XVII. Data for Series D, E, F, and G are presented in Table XVIII and notes. It will be noted that the predominating product in these runs is dinitrophenol. In the last four of the series, particularly when manganous nitrate was present, some picric acid was formed. Since the product which precipitated directly from the reaction mixture contained only a little PA, the latter product was found largely in the extracted nitrophenolic material; the extracted portion is tabulated separately in the tables, and a range of percentage yields is given for the assumptions that the extracted product is either all PA or all DNP. This is given in most of these runs in lieu of a precise analysis of the relative amounts of DNP-PA in the relatively small extracted fraction. When these runs were made, convenient analytical methods for the two nitrophenols had not yet been completely worked out.

Table XIV
Composition of Initial Oxynitrating Solutions

	Series A	Series B	Series C
Mercuric oxide, g.	86.6	54.2	130.0
98% Nitric acid, ml.	----	21.2	51
70% Nitric acid, ml.	51	798	1915
50% Nitric acid, ml.	1200	----	--
Water, ml.	----	451	1080
Volume (20°C.), ml.	1260	1220	2910
Sp. gr., 60°/60° F.	1.382	1.371	----
Moles C_6H_6 per run	0.4	0.25	1.0
Molarity of $Hg(NO_3)_2$	0.31	0.205	0.34
Ratio: Moles HNO_3/Moles benzene	31	50	50

Table XV
Oxynitration with Re-use of Mother Liquors

Details of Separate Runs

Series A Run No.	Yield of DNP g.	%	m.p., °C.	Volume of Mother Liquor ml.	Fortification for next run, ml. of 98% HNO_3
1	32.9	45	109-113	1260	80
2	41.4	56	109-113	1285	60
3	40.4	55	108-113	1305	58
4	39.2	53	110-113	1325	46
5	37.0	50	109-113	1340	54
6	37.4	51	109-113	1355	54
7	34.7	47	110-113	1380	55
8	36.1	49	110-113	1405	--
Series B Run No.					
1	21.1	46	110-113	1190	47
2	26.1	57	109-113	1200	36
3	26.1	57	111-113	1215	33
4	23.9	52	111-113	1220	44
5	24.3	53	110-113	1230	39
6	22.4	49	110-113	----	--
Series C Run No.					
1	88.0	48	112-114	2835	197
2	101.5	55	111-113	2915	146
3	103.0	56	109-113	2985	140
4	106.5	58	108-112	3035	121
5	101.0	55	108-112	3060	151
6	104.0	57	104-112	3120	130
7	106.5	58	108-112	3150	155
8	103.0	56	106-113	3220	140
9	103.5	56	106-112	3275	140
10	104.0	57	95-111	3330	---

Table XVI
Oxynitration with Re-use of Mother Liquors

Summary of Products in Series A, B and C

		Series A	Series B	Series C
2,4-Dinitrophenol	g.	299.0*	143.9	1021.0
	%	51.0	52.2	55.6
Picric acid (after boil-off)	g.	---	24.1	77.3
	%	---	7.0	3.4
Nitrobenzene	g.	49.0	15.0	147.6
	%	12.4	8.1	12.0
Dinitrobenzenes (crude)	g.	3.0	0.7	4.4
	%	0.6	0.3	0.3
Total benzene accounted for	%	64.0	67.7	71.3

* This figure does not include 23 g. of alkali-soluble, low-melting material recovered by benzene extraction of the final mother liquor; estimated on the basis of analyses in later experiments, it corresponded to a 3-4% yield of a mixture of 2,4-dinitrophenol and picric acid.

Table XVII
Nitric Acid and Mercury Balances

Nitric acid (as 100% HNO_3)		Series A	Series B	Series C
Initial oxynitrating soln.,	g.	786	796	1922
Fortification	g.	601	294	1660
Rinsing in benzene	g.	12	8	20
Total HNO_3 added	g.	1399	1098	3602
HNO_3 (or equivalent) in final mother liquor	g.	831	782 [a]	2105 [a]
HNO_3 consumed	g.	568	316	1497
Total DNP produced	g.	299 [b]	163 [c]	1098 [c]
Ratio: g. HNO_3/g. DNP		1.90	1.94	1.36
Moles HNO_3/mole DNP		5.55	5.66	3.98
Mercury (as HgO)				
Initial oxynitrating soln.,	g.	86.6	54.2	130.0
In final mother liquor	g.	78.0	47.75	113.9
In washings	g.	5.3	4.33	14.3
Total HgO accounted for	g.	83.3	52.08	128.2
HgO unaccounted for [d]	g.	3.3	2.12	1.8
HgO unaccounted for	%.	3.8	3.9	1.4

Notes:

a Before boil-off.

b Only the weight of good quality 2,4-dinitrophenol is included in this figure.

c The weight of picric acid obtained after the boil-off was converted into the equivalent weight of 2,4-dinitrophenol and included in this figure.

d The amount of mercury unaccounted for, as given above, is high in Series A and B in which the mercury analyses were performed before the final, more accurate modification of the analytical procedure was adopted. The figure given for Series C was obtained using the modified procedure (see p. 123).

Table XVIII
Oxynitration with Continuous Drop-wise Addition of Benzene Effect of Al^{+++} and Mn^{++} and of Hg^{++} Concentration

		Series			
Composition of Initial Oxynitrating Solution:		D	E	F	G
Mercuric oxide,	g.	240	130	130	390
70% Nitric acid,	ml.	2164	2000	2000	2130
$Mn(NO_3)_2 \cdot 6H_2O$ 75% solution,	ml.	13.6	--	13.6	--
$Al(NO_3)_3 \cdot 9H_2O$,	g.	8.4	--	8.4	--
Water,	ml.	to make 3 l.	850	850	935
Concentration: HNO_3,	M	10.6	10.4	10.4	10.5
Hg^{++},	M	0.37	0.2	0.2	0.6
Procedure: [a]					
Benzene per addition,[b]	g.	40	78	78	78
Time of addition,	hrs.	2	6	6	6
Additional stirring,	hrs.	1	2	2	1
Number of additions		4	2	2	4
Fortification, 98% HNO_3,		72ml at 3-hr. intervals	35ml at 2-hr. intervals	as in Series E	35ml at 2-hr. intervals during addn. of benzene
Summary of Products: [c]					
DNP, filtered,[d]	g.	213.5	172.5	179.5	458.0
	%	56.5	46.9	48.8	62.3
DNP-PA, extracted,[e]	g.	64.0	65.4	61.5	69.6
	%	13.6-16.9	15.6[f]	13.4-16.7	6.9-9.5
Total nitrophenols,	%	70.1-73.4	62.5	62.2-65.5	69.2-71.8
Nitrobenzene,[g]	g.	14.2	26.2	25.8	17.5
	%	5.6	10.7	10.5	3.6
Dinitrobenzenes,[h]	g.	4.3	5.9	6.5	14.4
	%	1.2	1.8	1.9	2.1
Total benzene accounted for	%	76.9-80.2	75.0	74.6-77.9	74.9-77.5

Notes (Table XVIII)

a The apparatus used was essentially the same as that described for Series A, B and C, p. 94 . Series D was run according to the procedure, PND-6, reported by Bachmann et al.,[27] but using four times the quantities.

b For the continuous, drop-wise addition of benzene a cylindrical funnel with a drop-counter was employed. The temperature was maintained at 50° during the addition and subsequent stirring.

c Products were allowed to accumulate in the reaction mixture until after the final addition of benzene except in Series G, in which after the second addition crystalline 2,4-dinitrophenol was removed by filtration before continuing the series.

d After the final addition of benzene and subsequent stirring period, light yellow, crystalline 2,4-dinitrophenol, melting in the range 111-114°, was removed by filtration of the chilled (0-3°) reaction mixture.

e An aliquot of the filtered mother liquor was diluted with an equal volume of water and extracted with portions of benzene. A deep yellow mixture of 2,4-dinitrophenol and picric acid, melting within the range 80-105°, was removed from the benzene solution by alkaline extraction. In Series D, F and G analyses were not performed and the percentage yields given in each series represent the range of values obtained when the yield was based separately upon each constituent.

f The extracted material (Note e) from Series E was analyzed by the Koppeschaar titration (p. 126) and found to contain 37.9% 2,4-dinitrophenol and 62.1% picric acid, the latter by difference. Calculated from these values, the yields of the two nitrophenols were 6.7% and 8.9%, respectively, a total of 15.6% of combined nitrophenols as recorded in the table.

g The benzene solution remaining after removal of nitrophenols (Note e) was distilled and nitrobenzene collected at 205-212° (uncorr.).

h The crude residue remaining after distillation of nitrobenzene is recorded in the table as <u>Dinitrobenzenes</u>.

III. THE MECHANISM OF THE OXYNITRATION PROCESS

At the outset of the present investigation it appeared, from an examination of the literature bearing on the oxynitration process, that a study of the fundamental chemistry of the complex reactions involved would offer the best hope of modifying the reaction conditions to produce high yields of nitrophenols and low yields of by-products. Accordingly, considerable attention was given to the elucidation of the mechanism. This phase of the work under Contract OEMsr-646 was suspended, however, when results in the Continuous Extraction Process showed promise enough to justify our full-time effort.

A. Historical

(1) Darzens' Diazonium Mechanism.- The French chemist, Darzens, was apparently the first to propose a detailed mechanism for the oxynitration process, essentially as follows:

Step 1: $C_6H_6 + Hg(NO_3)_2 \longrightarrow C_6H_5HgNO_3 + HNO_3$

Step 2: $C_6H_5HgNO_3 + 2\,N_2O_3 \longrightarrow (C_6H_5N{\equiv}N)(NO_3)$

Step 3: $(C_6H_5N{\equiv}N)(NO_3) + H_2O \longrightarrow C_6H_5OH + N_2 + HNO_3$

Step 4: $C_6H_5OH + 3HNO_3 \longrightarrow C_6H_2(NO_2)_3OH + 3H_2O$

Although this reaction mechanism appears to have been proposed in 1914, the only report of it in the literature is a brief outline in the article by Desvergnes in 1929.[17] No experimental evidence supporting the mechanism was given, and Desvergnes in the same article proposed his own quite different alternative mechanism.

(2) Desvergnes' Mercurial Intermediate.- Desvergnes[17] postulated (on the basis of experiments by Broders) the formation of the compound, 2,4,2',4'-tetranitrodiphenylmercury, as an intermediate, and cited the isolation of a dark solid analyzing for that composition as evidence in favor of his mechanism. He also discussed the possibility that nitrosobenzene may be formed in the reaction mixture through the intermediate of phenylmercuric compounds, but he apparently considered nitrosobenzene as a source of some of the by-products rather than as an essential intermediate of the major reaction.

(3) T. L. Davis' "Black Solid."- Davis and co-workers[11] described the isolation of a "black solid" in the oxynitration of benzene to picric acid, and they postulated from the analytical results showing the presence of mercury, and from the fact that picric acid was formed on treatment of the black solid with nitric acid, that the solid is a mercurial intermediate in the oxynitration reaction.

(4) Blechta and Patek's Nascent Benzene Mechanism.- Blechta and Patek[18] studied the behavior of mercury derivatives of benzene and toluene and came to the conclusion that a phenylmercuric compound is formed in the oxynitration reaction, but that the aqueous nitric acid causes a rapid cleavage back to benzene and inorganic mercuric salt; they postulated that, at the instant of its regeneration, the benzene possesses unusually high reactivity, making it susceptible to oxidation by the nitric acid.

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(5) G. F. Wright's Evidence Against the Darzens Mechanism.- G. F. Wright[21] found the Darzens Diazonium Mechanism attractive, but concluded that the experiments on material balance in his laboratory did not support that reaction mechanism. The diazonium mechanism predicts that a minimum of one mole of nitrogen is formed for each mole of picric acid, but the observed quantities of nitrogen gas fell considerably short of this amount. Since some nitrogen was found, the diazonium mechanism was not completely excluded from consideration.

B. Mercuration As the First Step in Oxynitration

(1) Examination of Davis' "Black Solid."- It seemed highly probable that mercuration of benzene is the initial step in the oxynitration process. We prepared specimens of T. L. Davis' "Black Solid," presumed to be a mercurial intermediate, following as nearly as possible the scanty published directions. The black solids which we obtained consisted largely of dinitrophenol coated with an insoluble dark tarry substance containing some mercury; there was evidence also for the presence of oxalic acid. No well-defined compound other than DNP was found in the black solid; the dark color apparently was due to carbonaceous decomposition products.

(2) Mercuration of Benzene in Aqueous Nitric Acid.- It was found that mercuration of benzene occurs readily in aqueous nitric acid. When the acid concentration is 35% or

lower, oxynitration does not proceed readily to completion unless the temperature is raised or a long reaction time is used, and it is easy to isolate and identify mercury derivatives. Under conditions only slightly milder than a typical batch oxynitration, an 8.6% yield of basic phenylmercuric nitrate was isolated.

Procedure for Basic Phenylmercuric Nitrate from Benzene.- Benzene (0.2 mole) was stirred with a solution containing 0.2 mole of mercuric nitrate in 200 ml. of 35% nitric acid at 62°C. for seventy-five minutes. Upon cooling and diluting with water, a precipitate of 5.4 g. of basic phenylmercuric nitrate, m.p. 182-183°C., was obtained (8.6% of the theoretical based upon benzene).

Mercuration occurs even in quite dilute nitric acid, but the reaction is slow and the insoluble, infusible products consist of complex mixtures of mono-, di-, tri-, and tetra-mercurated derivatives. A typical experiment is described below.

Mercuration of Benzene in 6.5% Nitric Acid.- Benzene (50 ml.) was agitated with a solution of 65 g. of mercuric nitrate dihydrate dissolved in 207 ml. of 6.5% nitric acid; the temperature was 65°C. and the time of reaction nine hours. The mixture was cooled and 39.9 g. of nearly colorless solid material was filtered. Titration of the filtrates showed that approximately 40% of the mercuric ion remained uncombined. The product was shown to consist of a mixture of mono- and poly-mercurated benzene derivatives, as illustrated with the typical procedure described in the following paragraph.

Examination of the Products of the Mercuration of Benzene in Dilute Nitric Acid.- A quantity of 50 g. of mixed mercurial derivatives prepared by a procedure similar to that described in the preceding paragraph was treated with a slight excess of bromine in an agitated aqueous suspension at temperatures below 30°C. The organic reaction products were extracted with benzene and separated by careful fractional distillation (under reduced pressure for the higher boiling constituents). The presence of bromobenzene, p-dibromobenzene, 1,3,5-tribromobenzene, and a solid tentatively identified as 1,2,4,5-tetrabromobenzene was shown in the distillate; it is very probable that other isomeric di-, tri-, and tetrabromobenzene derivatives were present but could not be isolated in pure state. The distillate was divided into fractions corresponding in boiling range to mono-, di-, tri-, and tetrabromobenzenes; the approximate mole percentage composition of the mixture of bromo derivatives, and by inference the mole percentage of corresponding mercurial derivatives in the original mixture, was estimated to be:

Mole Percentage Composition

53% mono-bromo ~ (mono-mercurated benzene)
38% di-bromo ~ (di-mercurated benzenes)
7% tri-bromo ~ (tri-mercurated benzenes)
2% tetra-bromo ~ (tetra-mercurated benzenes)

The weight of recovered mercuric bromide (54.4 g.) corresponded to approximately 88% of the expected weight on the basis of the composition indicated above. The method of cleavage with bromine was checked with pure phenylmercuric acetate; under comparable conditions, it yielded 80% of the theoretical bromobenzene (distilled), and 84% of the calculated weight of mercuric bromide was recovered; there was no evidence of formation of polybromo compounds. Similarly, m-diacetoxymercuribenzene gave 78% of the calculated m-dibromobenzene and 84% of the calculated mercuric bromide.

It was further shown that the treatment of basic phenylmercuric nitrate with hot solutions of mercuric nitrate in dilute nitric acid led to the formation of mixtures very similar to those prepared as described above directly from benzene, containing polymercurated benzene derivatives.

(3) Conversion of Phenylmercuric Compounds to Dinitrophenol.- Experiments with phenylmercuric acetate, phenylmercuric nitrate, basic phenylmercuric nitrate, and with the mixture of mono and polymercurated compounds formed by mercuration of benzene in dilute nitric acid showed that each of the monomercurated benzene compounds reacts with hot

nitric acid of approximately 50% concentration by weight to form dinitrophenol (and some picric acid) in varying yields.

Our earliest experiments carried out in 1942 always failed to produce as high yields of DNP from phenylmercuric salts as from equivalent quantities of benzene and mercuric nitrate under comparable conditions of time, temperature, and nitric acid concentration. In these early experiments the mercurial was added in one portion at the beginning of a run, as was also the benzene in the control experiments. Yields of DNP from pure phenylmercuric compounds amounted in the best experiments to only 29%. The yields of DNP from the mixture of mono and polymercurated derivatives obtained by mercuration in very dilute nitric acid were lower, and the yield figures were of such a magnitude as to suggest that only the monomercurated derivatives in the mixture are capable of being converted into DNP.

Subsequent work showed that the low yields obtained with phenylmercuric derivatives resulted from the choice of unfavorable experimental conditions. When phenylmercuric acetate or basic phenylmercuric nitrate was slowly added to 54.6% nitric acid at 45°C. over a period of two hours, the yield of DNP rose to 54.9%, with a 2.7% yield of dinitrobenzene and a trace of nitrobenzene; when all of the phenylmercuric acetate was added in one portion in a control experiment the yield of very impure, dark DNP was only 21.1%. When the addition of phenylmercuric acetate in very small portions was extended over a period of six hours nitric acid of approximately 50% concentration by weight to form dinitrophenol (and some picric acid) in varying yields.

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Several experiments were carried out to determine to what extent reversal of mercuration by the nitric acid can occur under conditions of oxynitration, and whether or not cleavage of the intermediate mercurial compound to benzene has an important role in the oxynitration process. It is known that hot dilute acids can cleave arylmercury compounds to the parent hydrocarbons and inorganic mercury salts, as illustrated in the following equation:

$$C_6H_6 + Hg(NO_3)_2 \rightleftharpoons C_6H_5HgNO_3 + HNO_3.$$

Basic phenylmercuric nitrate was suspended in warm 40% nitric acid and steam was passed through the mixture. Control experiments with benzene and nitric acid containing mercuric nitrate showed that benzene, when present in such a mixture, is swept out before it has time to undergo appreciable oxynitration. With basic phenylmercuric nitrate a certain amount of benzene (from 23 to 47% of the theoretical) was distilled during the first five minutes, but none subsequently. Dinitrophenol or PA was always found in the residue in varying yields. The yield of benzene was increased and the yield of nitrophenols was lowered when the concentration of nitric acid was decreased. When an excess of mercuric nitrate was added to the suspension before steam was passed through, the extent of cleavage of benzene was decreased and the yield of nitrophenol was increased. These observations would all be consistent with the view that the mercurial does not revert to benzene before being oxynitrated; that the cleavage to benzene is favored as the nitric acid concentration is decreased while at the same time the oxynitration is inhibited; that cleavage of the mercurial is inhibited by the presence of an excess of mercuric nitrate in solution.

Serious consideration was given to the possibility of carrying out the oxynitration in two separate stages, the first being a controlled mercuration of benzene and the second stage consisting of the conversion of the mercurial intermediate into DNP or PA. It was hoped that by thus dividing the overall process into separate steps it would be possible to adjust the reaction conditions more favorably for each phase. All modifications of such a two-stage process failed to attain the best yields of a one-stage oxynitration. The failure is to be attributed to the fact that polymercuration occurs very readily if the mono-mercurated benzene derivative is allowed to build up an appreciable concentration in the mixture. The complex polymercurials which are formed do not yield more than small amounts of DNP or PA upon treatment with nitric acid. In an actual oxynitration it appears that the monomercurated intermediate reacts so rapidly to form nitrosobenzene that only a low steady-state concentration is present and the extent of polymercuration is small.

(4) Mercuration of Benzene in Nitric Acid Containing Urea.- The demonstration that phenylmercuric compounds are formed under conditions very close to those used in actual oxynitration, and the experiments in which phenylmercuric compounds were converted into DNP by nitric acid constituted fairly convincing evidence that mercuration is the first step in the oxynitration process. The theory of Blechta and Patek,[18] involving the idea of "nascent benzene" regenerated from phenylmercuric nitrate as an intermediate, was not, however, excluded as a possible path from benzene to DNP.

Westheimer[25,27] was able to provide direct experimental evidence in support of the Darzens mechanism. He showed that phenylmercuric nitrate is converted in the presence of nitrogen oxides to benzenediazonium nitrate, which can then break down to phenol and thence to DNP in the presence of the proper concentrations of nitric and nitrous acids.

Of particular interest was Westheimer's demonstration that the mercuration of benzene occurs at normal rates in nitric acid containing urea, but all subsequent steps of the oxynitration are inhibited in the absence of necessary nitrogen oxides. Using solutions containing urea as an oxynitration inhibitor, he was able to measure the rates of formation of phenylmercuric nitrate from benzene in different concentrations of nitric acid and at various temperatures, and to show that the rate of mercuration is probably the rate-controlling step in the oxynitration process under the usual preparative conditions.

Westheimer's batch preparation of phenylmercuric nitrate in nitric acid containing urea suggested to us later the possibility of preparing phenylmercuric nitrate in the continuous extraction apparatus. Since phenylmercuric nitrate is somewhat soluble in benzene, we were able to prepare that compound conveniently by use of the fritted disk extractor (No. 4) with solutions of mercuric nitrate in nitric acid containing urea. Details of this preparation have already been described on page 68 for the No. 3 Jet Extractor.

C. Nitrosobenzene as an Intermediate in Oxynitration

At a meeting of contract groups (Michigan, Chicago, Toronto, and Pennsylvania Universities) held in Detroit in April, 1943, Dr. Westheimer presented his report of March 15 - April 12 describing the first direct experimental evidence confirming Darzens' proposed conversion of phenylmercuric nitrate to benzenediazonium nitrate. In the discussion which followed Dr. Westheimer's report, attention was called to reports in the literature[29] which indicate that arylmercury compounds are cleaved with great ease to nitroso compounds, and that aryl nitroso compounds are in turn readily converted to diazonium nitrates by the action of nitric oxide.[30] The possibility was suggested that nitrosobenzene may be a true intermediate in the oxynitration sequence, instead of a precursor of some of the by-products, as suggested in the article by Desvergnes.[17] That nitrosobenzene is a true intermediate was later confirmed by experimental work of the three NDRC contract groups.

The conversion of nitrosobenzene to DNP by the action of nitric oxide and nitric acid, without the use of mercury, was shown at the University of Pennsylvania in the following experiment.

Oxynitration of Nitrosobenzene without Mercuric Nitrate.- A solution of 80 ml. of 30% nitric acid was stirred at 30°C. and 10.7 g. of finely powdered nitrosobenzene was added gradually during one hour, nitric oxide was passed through the solution constantly during the whole reaction period. The mixture was stirred for an additional fifteen minutes, then 67 cc. of 70% nitric acid was slowly added with stirring to increase the acid concentration to 50% by weight (approximately). The temperature rose rapidly to 50-55°C. The mixture was stirred for two hours, then chilled and filtered to remove 9.7 g. (52.7%) of DNP.

D. Evidence Leading to Westheimer's "Rearrangement Mechanism."

(1) Evidence for the Darzens Diazonium Mechanism.-

The Darzens Diazonium Mechanism, extended by the inclusion of nitrosobenzene as an intermediate, was accepted as a working hypothesis by the NDRC contract groups for some time. The strongest evidence supporting it was that every postulated step could be demonstrated experimentally. Furthermore, the rates of the individual steps as determined by Westheimer accounted very well for the observed rates of oxynitration in concentrations of nitric acid below 50% by weight (10.4 M). Another feature of the diazonium mechanism was that it gave a plausible explanation for the observation that 20 to 30% of the benzene was consumed by oxidative side reactions. The nitration of phenol, pictured as an intermediate, is known to give poor yields.

The diazonium mechanism requires nitrogen oxides as essential reactants in the oxynitration process, and since normally the preparative oxynitration is carried out without the addition of nitrogen oxides from an external source, it follows that the nitrogen oxides required for the reaction would have to be formed internally by the reduction of nitric acid. Since benzene is the only organic material introduced, it also follows that the reduction of nitric acid must occur at the expense of the oxidation of benzene or compounds derived from it. On the assumption that benzene would have to be oxidized to form N_2O_3, Westheimer proposed a stoichiometric equation to define the most efficient possible utilization of starting materials, as follows:

$$19\ C_6H_6 + 75\ HNO_3 \longrightarrow \underset{\text{(picric acid)}}{15\ C_6H_2(NO_2)_3OH} + 24\ CO_2 + 15\ N_2 + 72\ H_2O.$$

This equation assumes that lost benzene is oxidized completely to carbon dioxide to form only the needed nitrogen oxides with none left over, and that in addition the oxidation of benzene occurs before conversion to benzenediazonium nitrate. On this basis the maximum yield of picric acid would be 15/19 or 79%, and 21% of the benzene, at the very least, would be lost by oxidation.

As an alternative, the group at the University of Pennsylvania proposed the following stoichiometric equation:

$$7\ C_6H_6 + 24\ HNO_3 \longrightarrow \underset{\text{(DNP)}}{5\ C_6H_3(NO_2)_2OH} + 12\ CO_2 + 7\ N_2 + 23\ H_2O$$

The assumption inherent in this equation is that the organic material oxidized to produce carbon dioxide and nitrogen oxides first undergoes the oxynitration steps through phenol and that it is phenol which is oxidized; the number of moles of nitrogen formed will by this assumption be equal to the number of moles of benzene used up rather than to the number of moles of dinitrophenol formed. On the basis of the latter equation, the maximum yield of DNP (or PA) would be 71.5%, with a minimum of 28.5% of the benzene destroyed.

The actual yields of DNP and PA isolated in a large number of batch and continuous oxynitration runs approached the limits set by the above stoichiometric equations, and this was considered for a time as tending to confirm the correctness of the diazonium mechanism.

(2) Evidence Against the Diazonium Mechanism.- G. F. Wright and co-workers discarded the diazonium mechanism largely on the ground that they were able to find only about three-fourths of a mole of nitrogen for each mole of picric acid formed,[31] rather than the predicted minimum of one mole. The low yield of nitrogen was later confirmed in the continuous extraction apparatus (No. 5A) at the University of Pennsylvania (ODP-14, Division 8, NDRC, January 15, 1944, page 11). Under the relatively mild conditions of the extraction process, in Run 5A-6, slightly less than one mole of inert residual gas ($N_2 + N_2O$) was obtained during the production of a total of 3.5 moles of DNP and PA; this finding provided definite proof that under optimum conditions of oxynitration only a part of the nitrophenolic material can arise through the intermediate of benzenediazonium nitrate. Data on the consumption of nitric acid in the continuous extractors (ODP-13,[27] Division 8) also showed that, even when the loss in the fume is counted, the total consumption of nitric acid in some of the runs with material balance was less than the minimum of four moles of nitric acid required by the diazonium mechanism for the formation of each mole of DNP.

Several months before material balance data were available to prove the existence of an alternative mechanism, there were indications that the diazonium mechanism was inadequate. When the yields of DNP + PA were calculated for runs in the continuous extractors, eliminating from the basis of calculation the benzene volatilized through the condenser and that which was converted to nitrobenzene and dinitrobenzene by side reactions, the "oxynitration efficiency" yields so computed were found to exceed the limit of 71.5% set by the Pennsylvania stoichiometric equation, and in a few runs even the figure of 79% implicit in Westheimer's stoichiometric equation (see page 28 for a further discussion of the methods of calculation). This could only be possible if an alternative mechanism existed which would not require nitrogen oxides as reactants in the amounts demanded by the diazonium mechanism.

In spite of our repeated efforts, all experiments designed to improve the yields of nitrophenols in oxynitrations by the addition of nitrogen oxides from an external source failed. In the presence of high concentrations of nitrogen oxides, whether the oxides were added from an external source or generated in the mixture by addition of sodium nitrite or hydroquinone, the yields of DNP were always low (50% or less) and considerable amounts of highly colored by-products were formed.

On the basis of kinetic studies of the various steps of the diazonium sequence, Westheimer was led to predict (ODP-8, Division 8, NDRC, July 15, 1943, page 45) that above 50% (10.4 M) nitric acid strength the oxynitration reaction would suffer due to the sharp increase in the rate of dimerization of the intermediate, nitrosobenzene. He had previously shown that the rate of diazotization of nitrosobenzene was not favored by an increase in acid strength. We found that, contrary to the prediction, good yields of nitrophenols could be obtained in both batch and continuous oxynitrations carried out even in 60% nitric acid, (ODP-10,[27] September 15, 1943, page 9).

From a consideration of the inconsistencies not explained by the diazonium mechanism, Westheimer proposed (ODP-11,[27] Division 8, NDRC, October 15, 1943, page 27) that, while the diazonium mechanism accounts for the formation of a portion of the nitrophenolic material under some reaction conditions, an alternative mechanism capable of giving higher yields obtains under other conditions, particularly in nitric acid above 50% concentration by weight. His alternative mechanism has already been outlined (Path A, page 10). In subsequent reports Westheimer provided evidence which proved in a very convincing and elegant manner the correctness of the essential features of his alternative "Rearrangement Mechanism," which shares with the original Darzens mechanism the initial steps of mercuration of the benzene and conversion of the mercurial to nitrosobenzene. The Westheimer mechanism is the predominant one under optimal operating conditions of the oxynitration process.

E. Miscellaneous Studies Relating to Mechanism

(1) Preparation of Basic Phenylmercuric Nitrate.- A new method for the preparation of basic phenylmercuric nitrate was developed which is much more convenient than the method of Woolett and Coulter.[32]

Procedure: Powdered phenylmercuric acetate (100 g.) is gradually added to a solution of 125 ml. of concentrated ammonium hydroxide in 400 ml. of water heated on a steam bath. An additional 20 ml. of concentrated ammonium hydroxide is added, after which the solid is almost all in solution. The mixture is heated to boiling and filtered into 75 ml. of 70% nitric acid which is continuously and vigorously stirred with a mechanical stirrer. An additional 5 ml. of 70% nitric acid is introduced and the solution, containing a suspension of some white solid, is boiled for one minute. It is cooled to 5°C., filtered, and the solid washed with ice water. The yield of pure colorless basic phenylmercuric nitrate, m.p. 181-2° dec., is 73.3 g. (77.5%).

(2) Diazotization of Phenylmercuric Compounds in Glacial Acetic Acid.- In line with an idea that the mercuration step might be carried out separately from the subsequent steps of the oxynitration, some experiments were made on the diazotization of phenylmercuric acetate in glacial acetic acid. Diazotization could be accomplished with either sodium nitrite and sulfuric acid or by the introduction of nitrogen oxides, as shown by the isolation of coupled products, but phenol could not be isolated, and conditions could not be found by which the resulting mixture could be converted in good yield to DNP.

(3) The Reaction of *m*-Diacetoxymercuribenzene with Nitric Acid.- The possibility that dimercurated benzene derivatives might be formed in the oxynitration mixture led us to examine the nature of the reaction of *m*-diacetoxymercuribenzene (prepared by standard methods from the benzene-disulfonyl chloride) with 50% nitric acid under conditions similar to the usual batch oxynitration conditions. Of the amount introduced, 60% could not be accounted for as definite products, 6% of a mixture of mono- and dinitrobenzenes was obtained, and a 31% yield of DNP was isolated.

(4) Conversion of Benzenediazonium Nitrate to DNP and PA.- Diazotized aniline was converted to a mixture of DNP and PA in a yield between 61.6 and 66.7% in a one-step procedure similar to the usual oxynitration.

> Procedure: Aniline (0.2 mole) was diazotized in 75 ml. of 50% nitric acid with 15 g. of sodium nitrite in 25 ml. of water. By means of a chilled dropping funnel, the solution of diazonium salt was added to 600 ml. of 10.4 M (50%) nitric acid; the solution was vigorously stirred at 50°C. The acid strength was held constant during a three-hour period by addition of 98% nitric acid. A yield of 15.1 g. of solid DNP was filtered and 9.45 g. of a mixture of DNP and PA was extracted; total yield, between 61.6% and 66.7% (no analysis on the composition of the extracted mixture).

(5) Conversion of p-Nitrobenzenediazonium Nitrate to DNP.- In an effort to break down the oxynitration process into its component steps, some model studies were carried out with p-nitrophenyl derivatives. In one experiment it was shown that diazotized p-nitroaniline can give a small yield of DNP under conditions approximating the oxynitration. There is no reason to believe that the nitro diazonium compound is an intermediate in the oxynitration of benzene.

> Procedure: p-Nitroaniline (0.2 mole) was diazotized by the same procedure described in the preceding section, and was in turn treated with warm 50% nitric acid for four hours at 50°C. Upon cooling the mixture,

tests were obtained for unchanged diazonium compound. Extraction with benzene and purification with alkali led to the isolation of 3.2 g. (8.7%) of quite pure DNP, m.p. 113-4°.

(6) Reaction of Nitrophenylmercuric Salts with Nitric Acid.- Nitrobenzene was mercurated with mercuric acetate in acetic acid, giving, according to literature reports, a mixture of o-, m-, and p-nitrophenylmercuric acetates. In a series of experiments which it was hoped would throw light on the mechanism of oxynitration, portions of the mixture of mercurated derivatives were treated with 50-55% nitric acid at 70-80°C. for three hours during which small portions of sodium nitrite were added. From the reaction mixtures we were able to isolate small amounts of o- and p-dinitrobenzene and an unidentified mercury-free crystalline compound, m.p. 248-250°. In another experiment at 100-110°C. small yields of o- and p-dinitrobenzene were obtained, but no nitrophenols were identified.

(7) The Nitration of Phenol.- When it was still considered probable that the diazonium mechanism was the important one, a careful literature search was made to determine the yields to be expected from the nitration of phenol with approximately 50% nitric acid. (Literature review, ODP-8,[27] Division 8, NDRC, July 15, 1943.) The conclusion was that the nitration of phenol is always attended by considerable losses due to formation of dark condensation products and because of oxidation. Confirmatory experiments under conditions approximating those of the oxynitration reaction,

gave a maximum of 65-70% of DNP containing some PA. Dark by-products were always formed.

(8) The Catalytic Effect of Manganous Nitrate in the Nitration of o-Nitrophenol and of p-Nitrophenol.- In a series of experiments intended to determine whether mercuric, manganous, and aluminum nitrates have any catalytic action of the nitration of mono- and dinitrophenols, we found that mercuric and aluminum nitrates apparently have no effect, but manganous nitrate definitely increases the rate of conversion of the mono-nitrophenols to DNP. Bachmann [27,28] subsequently showed that manganous nitrate catalyzes the nitration of DNP to PA. These nitrations are all sensitive to the concentration of nitrogen oxides, and it is possible that the catalytic effect of manganese, which is quite pronounced, is due to an effect on the nitrogen oxide equilibria. Although manganous nitrate has been recommended previously for the oxynitration reaction, we are not aware that its role as a catalyst in direct nitration has been pointed out before.

APPENDIX
ANALYTICAL METHODS

List of Analytical Procedures Described:

Determination of Acidity in Oxynitration Solutions

Analysis for Mercuric Ion in Oxynitration Stock Solutions, Mother Liquors, Fortifying Solutions, Washings, and Rinsings; Analysis of DNP and PA for Mercuric Ion

Manganous Ion Analysis in Stock Solutions, Mother Liquors, Fortifying Solutions, Washings and Rinsings

Analysis of DNP-PA Mixtures for DNP Content

Analysis of PA in DNP-PA Mixtures

Analysis of Acid in Gas Absorption Trap for Nitric Acid and Potential Nitric Acid

Analysis of Gases Evolved in Oxynitration

Analysis of Oxynitration Liquors for Oxalic Acid

Analysis of Oxynitration Liquors for Nitrous Acid

Analysis for Acidity

1. Solutions

Potassium Thiocyanate, 1.0 N (96.8 g. KSCN/1.)
Congo Red, 0.4% aqueous (4 g. congo red/1.)
Standard Sodium Hydroxide, 0.5 N (20.0 g./1.)
(Standardized against potassium acid phthalat

2. Procedure

The method employed is that described by Downing and Wright.[21] For the stock solution and mother liquor a sample is withdrawn with a 1-ml. pipette (Note 1) and drained into 100 ml. of water in an Erlenmeyer flask. Six milliliters of potassium thiocyanate solution (Note 2) and four drops of congo red are added. The solution is titrated with standard sodium hydroxide to a definite red end point (Note 3). Acidity is expressed as molarity of nitric acid.

$$M\text{-}HNO_3 = \frac{N\text{-}NaOH \times vol.\ NaOH}{vol.\ sample}$$

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$$\text{M-HNO}_3 = \frac{\text{N-NaOH x vol. NaOH}}{\text{vol. sample}}$$

3. Notes

(1) For less concentrated solutions than 10-12 M HNO_3, a proportionate sample can be taken.

(2) Addition of potassium thiocyanate prevents the precipitation of HgO. When Mn is absent, only 3 ml. are required. With the mercury fortifying solution (1 g. HgO per ml.) it is necessary to use 30 ml. of KSCN to prevent the precipitation of HgO in a 1-ml. sample.

(3) Ordinarily this is an exceedingly sharp end point. The color is hard to determine, however, when nitrophenols are present. In these cases, near the end point a drop of indicator is added after each drop of alkali; the end point is reached when there is no color change.

Analysis for Mercuric Ion in Solutions

1. Solutions

Sulfuric Acid, conc.
Nitric Acid, conc.
Nitric Acid, 6 N (290 ml. conc. HNO_3/l.)
Ferric Alum, sat'd. (140 g. $FeNH_4(SO_4)_2.12H_2O$ dissolved in 400 ml. of hot water. When cool, filter, and make up to 500 ml. with 6 N HNO_3.)
Standard Ammonium Thiocyanate, 0.1 N (7.61 g. NH_4SCN/l.) (Standardized against a known solution of HgO in nitric acid.)

2. Procedure

The mercury concentration is determined in the manner described by Downing and Wright.[21] A 2-ml. sample of the unknown (Notes 1 and 2) is pipetted into a large test tube (25 x 200 mm.) and 3 ml. of conc. sulfuric acid is added. A burette funnel is inserted into the mouth of the tube (Note 3) clamped in an inclined position on a ring stand, and the solution is boiled until fumes of sulfur trioxide are evolved. The solution is allowed to cool somewhat, about 0.5 ml. of conc. nitric acid is added cautiously, and the solution again fumed. The addition of nitric acid and fuming are repeated until all organic matter has been destroyed and the solution is colorless (Note 4). Two such fumings are usually sufficient. The solution is cooled under the tap and washed into a 250-ml. Erlenmeyer flask with 100 ml. of water. The resulting solution should be colorless.

Two milliliters of ferric alum indicator and 5 ml. of 6 N nitric acid are added, and the solution cooled below

20°C. It is then titrated with standard ammonium thiocyanate to the appearance of a permanent pale-brown color (Note 5). The mercury concentration is expressed in moles per liter (Note 6).

$$M\ Hg^{++} = \frac{N\ NH_4SCN \times \text{vol. } NH_4SCN}{2 \times \text{vol. sample}}$$

3. Notes

(1) For solutions less concentrated than 0.5 M Hg^{++}, a larger sample may be taken. In such cases it is advisable to evaporate the sample to a small volume in an evaporating dish before the digestion period. Concentration in the test tube is virtually impossible because of the violent bumping.

(2) It is desirable to determine the concentration of the mercury fortifying solution by weight. A 0.4 g. sample is weighed out from a Lunge pipette and titrated with ammonium thiocyanate standardized against a known weight of HgO.

(3) The use of a burette funnel reduces to a large degree the loss of mercury by entrainment in the sulfur trioxide fumes.

(4) Sometimes a pale yellow color persists after all the nitrophenol is destroyed. If manganese is present a pink color may develop. The destruction of organic matter is complete, however, if the solution is colorless when diluted. In the absence of organic matter, this digestion may be omitted.

(5) It is desirable to carry out this titration in a cold concentrated solution. The end point is more easily observed against the background of white HgSCN which precipitates near the end point.

(6) For the very small amounts of mercury (.01-.05%) which may be present in the nitrophenolic products a modified procedure is employed, as follows:[21]

A weighed sample (about 2 g.) is decomposed with 10 ml. of conc. sulfuric acid and 5 ml. of 70% nitric acid in a pyrex 100-ml. Kjeldahl flask. The mixture is boiled carefully, with addition of a boiling chip, to the appearance of sulfur trioxide fumes. The solution is allowed to cool somewhat, 2 ml. of conc. nitric acid is added, and the boiling to sulfur trioxide fumes is repeated. The digestion is repeated until the solution is nearly colorless. It is then diluted, and titrated with 0.05 N ammonium thiocyanate in a microburet, using ferric alum as the indicator. The results are expressed as per cent Hg^o by weight.

$$\% \ Hg^o = \frac{\text{vol. } NH_4SCN \times N \ NH_4SCN \times 10.08}{\text{wt. sample}}$$

Analysis for Manganous Ion in Solutions

For small concentrations of manganese, Downing and Wright[21] have described a satisfactory method of analysis, modified from the ASTM ammonium persulfate-arsenite method. With the higher concentrations of manganese used in the continuous extraction method of oxynitration, the well-known sodium bismuthate method proved to be more convenient and accurate.33

1. Solutions

Sulfuric Acid, conc.
Nitric Acid, conc.
Sodium Bismuthate, solid (82% $NaBiO_3$; Baker's Analyzed)
Nitric Acid, wash (30 ml. conc. HNO_3/l. water)
Standard Ferrous Ammonium Sulfate, 0.15 N (59.1 g. $Fe(NH_4)_2(SO_4)_2.6H_2O$/l. + 12 ml. conc. H_2SO_4) (Standardized against standard $KMnO_4$)
Standard Potassium Permanganate, 0.15 N (5.0 g. $KMnO_4$/l. Boil for 30 minutes; cool; let stand 24 hrs.; filter through Gooch or sintered glass crucible) (Standardized against sodium oxalate)

2. Procedure

A 2-ml. sample (Notes 1 and 2) is pipetted from the unknown solution and the organic matter is destroyed in the manner described for the mercury analysis. The cold sulfuric acid solution is then washed into a 500-ml. iodine flask with 75 ml. of water, and 25 ml. of conc. nitric acid is added. The solution is cooled to 10-15°C. in an ice bath, and 1.4 g. of sodium bismuthate is added all at once. The contents of the flask are agitated briskly for 1 minute, 100 ml. of water is added, and the excess sodium bismuthate is separated by filtration through a sintered glass funnel. The flask is rinsed out and the precipitate washed with 60 ml. of dilute nitric acid (3%) until the wash is colorless.

To the combined filtrates is added 50.00 ml. of standard ferrous ammonium sulfate. The nearly colorless solution is back titrated with standard potassium permanganate to a pink end point.

A blank run is carried out by mixing 50.00 ml. of standard ferrous ammonium sulfate with 125 ml. of water, adding 25 ml. of conc. nitric acid diluted with 60 ml. of wash nitric acid, and titrating against standard potassium permanganate. From this value is subtracted the volume of permanganate used in the determination of the unknown, to give the volume of permanganate equivalent to the manganese present in the unknown sample. The concentration of manganese is expressed in moles per liter.

$$M\ Mn^{++} = \frac{N\ KMnO_4 \times \text{vol. } KMnO_4 \text{ required}}{5 \times \text{vol. sample}}$$

3. Notes

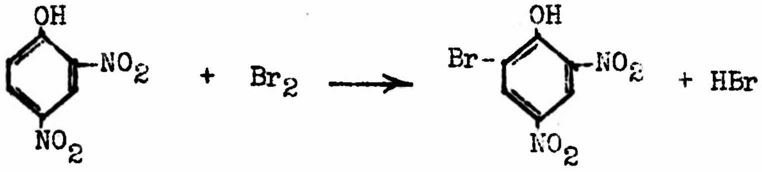
(1) For solutions less concentrated than 0.5 M Mn^{++}, a larger volume of unknown was taken for analysis.

(2) For manganese fortifying solution, the determination is carried out on a sample (0.5 g.) weighed from a Lunge pipette.

Analysis for DNP in Mixtures of DNP-PA

The determination of dinitrophenol in the acidic products is based upon the Koppeschaar titration method as worked out by Dr. E. C. Wagner of this laboratory. The following reactions are involved:

$$5\ KBr + KBrO_3 + 6\ HCl \longrightarrow 3\ Br_2 + 6\ KCl + 3\ H_2O$$



$$\text{(excess) } Br_2 + 2\ KI \longrightarrow I_2 + 2\ KBr$$

$$I_2 + 2\ Na_2S_2O_4 \longrightarrow 2\ NaI + Na_2S_4O_8$$

1. Solutions

Sodium Hydroxide, 0.5% (5 g. NaOH/1.)
Hydrochloric Acid, conc.
Koppeschaar Solution, 0.15 N (4.2 g. $KBrO_3$ + 60 g. KBr/1.) (Standardized against Standard Sodium Thiosulfate)
Potassium Iodide, 50% (400 g. KI/400 ml. H_2O)
Standard Sodium Thiosulfate, 0.1 N (24.8 g. $Na_2S_2O_3.5H_2O$/1.) (Standardized against potassium iodate[34])
Starch Solution, 0.5% (2.5 g. soluble starch/500 ml. H_2O)

2. Procedure

A weighed sample (about 0.2 g.) (Note 1) of the unknown is placed in a 500-ml. iodine flask and dissolved in an excess of dilute sodium hydroxide (about 15 ml.) by heating to the boiling point (Note 2). The walls of the flask are washed down with 25 ml. of water and the contents of the flask boiled until solution is complete. A drop of phenolphthalein is added to determine if an excess of alkali is present. The solution is then diluted with 100 ml. of water and cooled to 15-20°C. (Note 3).

To the cold alkaline solution is added 25.00 ml. of Koppeschaar solution from a pipette, and then 5 ml. of conc. hydrochloric acid (Note 4). The flask is stoppered immediately, the contents mixed by swirling, and allowed to stand in a dark place for 10 minutes (Note 5) with occasional shaking. At the end of this time the stoppered flask is cooled to create suction. Five milliliters of potassium iodide solution is placed on the flange of the iodine flask, and allowed to drain into the flask by loosening the stopper slightly. In the same manner the walls of the flask are washed down with a small amount of water. The stoppered flask is shaken to dissolve all bromine vapors.

The liberated iodine is titrated with standard sodium thiosulfate solution. Near the end point 5 ml. of starch solution is added. The end point is reached when the starch-iodine color disappears and is replaced by a pale to bright yellow color. The pale yellow precipitate which usually appears is 6-bromo-2,4-dinitrophenol, and causes no interference.

A blank is carried out in exactly the same manner, omitting the sample, to determine the volume of standard sodium thiosulfate equivalent to 25.00 ml. of standard Koppeschaar solution. (It is not necessary that the blank determination stand longer than 5 minutes.) The volume of sodium thiosulfate solution required for the blank minus the volume required for the unknown sample is equivalent to the bromine consumed by the DNP present. The result is expressed as per cent DNP by weight.

$$\% \text{ DNP} = \frac{100 \text{ x vol. } Na_2S_2O_3 \text{ x N } Na_2S_2O_3 \text{ x } 0.092055}{\text{weight of sample}}$$

3. Notes

(1) For samples containing less than 50% DNP larger samples (about 0.3 g.) of the unknown are desirable.

(2) Do not boil unless there is an excess of alkali present, since DNP is lost by steam volatilization.

(3) A secondary reaction occurs at a higher temperature in which one of the nitro groups is replaced by bromine. Likewise the nitro groups in picric acid are attacked by bromine, the rate of reaction being accelerated above 30°C.

(4) The hydrochloric acid can be measured into a test tube beforehand and added all at once.

(5) A period of reaction longer than 10 minutes gives high results in mixtures containing PA, presumably caused by the replacement of the nitro groups in the molecule by bromine. Although the bromination of DNP is a very rapid reaction, it is advisable to let it proceed for the length of time specified, in order to get more accurate and reproducible results.

Analysis for PA in DNP-PA Mixtures

Two methods are available for the estimation of PA in the nitrophenolic products from the oxynitration reaction. The more accurate one involves precipitation with nitron and weighing as nitron picrate. DNP is determined by difference. The workers at Michigan have used this method exclusively. Nitric acid or nitrates will interfere, as does DNP if the conditions for precipitation are not carefully controlled. Since the experimental work at Pennsylvania has been concentrated on the production of DNP rather than PA, resulting in products high in DNP content, it seemed more advisable to determine DNP directly by the Koppeschaar titration method, and to calculate the PA content by difference.

The other method for the determination of PA is used in conjunction with the Koppeschaar titration method.

It involves adding an excess of standard acid to a solution of the nitrophenolic unknown dissolved in an excess of standard alkali, and back titrating with standard base to a phenolphthalein end point. The disadvantage of this indirect method is the difficulty in determining the true equivalent point, and the dependency on the DNP determination. The method fails when the unknown is very high in DNP. This method was worked out by Dr. E. C. Wagner.

1. Solutions

Standard Sodium Hydroxide, 0.1 N (4.0 NaOH/l.)
(Standardized against potassium acid phthalate)
Standard Hydrochloric Acid, 0.1 N (9 ml. conc. HCl/l.) (Standardized against Standard Sodium Hydroxide)
Phenolphthalein Solution (1 g. phenolphthalein dissolved in 50 ml. of alcohol and diluted with 50 ml. of water)

2. Procedure

A weighed sample of the unknown is placed in a 500-ml. flask (see procedure for determination of DNP) and dissolved in an excess of standard sodium hydroxide (about 20.00 ml.) by heating to the boiling point. The walls of the flask are washed down with 20 ml. of water, and the solution is boiled gently until the sample is dissolved. Three drops of phenolphthalein are added, making certain an excess of alkali is present. The solution is diluted with 100 ml. of water, cooled to room temperature, and an excess of standard hydrochloric acid is added. It is then back-titrated with standard sodium hydroxide to the phenolphthalein end point (Note 1). The determination of DNP as described above can then be carried out on the sample from this point. The PA content is calculated in terms of per cent by weight.

$$\% \text{ PA} = (\text{Total vol. NaOH req.} - \text{vol. NaOH req. for DNP}) \times \frac{\text{N NaOH} \times 2.291}{\text{wt. sample}}$$

$$\text{vol. NaOH req. for DNP} = \frac{\% \text{ DNP} \times \text{wt. sample}}{\text{N NaOH} \times 1.841}$$

3. Notes

(1) This end point is invariably difficult to determine. It is advisable to overrun the end point in both directions until the observer is satisfied that he knows where it is located. It is also advantageous to have a color standard for comparison, made up of known quantities of material.

Analysis of Acid in Gas Absorption Trap for Nitric Acid and Potential Nitric Acid

The gases produced in the oxynitration reaction (CO_2, oxides of nitrogen, O_2, CO, nitrogen, entrained benzene) are passed through a trap consisting of conc. sulfuric acid and 98% nitric acid. The oxides of nitrogen (except nitrous oxide) and the entrained benzene are absorbed as nitrosylsulfuric acid and m-dinitrobenzene respectively. The remaining gases are passed through a water trap to scrub out any acid fumes which may have been carried over, and collected in 20-l. carboys by the downward displacement of a strong salt solution. The neutral gases are analyzed as described below.

For a nitrogen balance it is necessary to ascertain the amount of nitrous gases absorbed in the acid fume-trap. This is accomplished by analyzing a known weight of the acid solution before and after use, by the Lunge nitrometer method. This method depends upon the quantitative conversion of nitrates and nitrites (including nitrosylsulfuric acid) into nitric oxide, in the presence of mercury and conc. sulfuric acid, as follows:[35]

$$2\ KNO_3 + 4\ H_2SO_4 + 3\ Hg = K_2SO_4 + 3\ HgSO_4 + 4\ H_2O + 2\ NO$$

1. Solutions and apperatus

   Sulfuric Acid, conc.
   Lunge Nitrometer filled with mercury

2. Procedure

The procedure is the same as that described by Lunge and Ambler.[35] It involves placing a weighed sample of the unknown (from a Lunge pipette) which will give about 30 ml. of gas in the upper cup of the nitrometer, mixing with 5 ml. of conc. sulfuric acid, drawing the mixture into the nitrometer through a stopcock, rinsing the cup with 2 ml. of conc. sulfuric acid, drawing this into the nitrometer, closing all stopcocks, shaking the graducted tube until the evolution of nitric oxide ceases, and measuring the volume of gas produced, as soon as the gas comes to room temperature and is adjusted to atmospheric pressure. At S.T.P. one ml. of nitric oxide is equivalent to 2.816 mg. of nitric acid. For convenience the result is expressed in terms of 100% nitric acid, per cent by weight in the trap solutions. The nitric acid equivalent to the oxides of nitrogen (except nitrous oxide) formed during the reaction is equal to the difference in HNO_3 content before and after the experiment.

$$V' = \frac{V \times P}{760\ (1 + 0.00367\ t)}$$

where V' = volume at STP, ml.
V = observed volume, ml.
P = barometric pressure, mm.
t = observed temperature of gas, °C.

$$\%\ HNO_3 \text{ by wt.} = \frac{100 \times .002816 \times V'}{\text{wt. sample}}$$

Analysis for Gases Evolved in Oxynitration

The residual, neutral, and insoluble gases collected in the run, consisting of CO_2, CO, O_2, N_2O, and N_2, are sampled and analyzed in an ordinary Orsat apparatus in the usual manner.[36]

1. Solutions

For CO_2: Potassium Hydroxide (600 g. KOH/l. H_2O; for use dilute 3 vols. with 2 vols. H_2O)
For O_2 : Alkaline Pyrogallol (300 g. pyrogallic acid/l. H_2O; for use dilute 1:1 with KOH, 600 g./l. H_2O)
For CO : Acidic Cuprous Chloride (340 g. $CuCl_2 \cdot 2H_2O$ dissolved in 600 ml. conc. HCl and reduced by adding 190 ml. sat'd solution $SnCl_2$ or until solution is colorless. The stannous chloride is prepared by treating 200 g. metallic tin in 500-ml. flask with conc. HCl until no more tin goes into solution.)

The gas remaining after CO_2, O_2, and CO have been absorbed consists of N_2O and N_2 which do not need to be determined separately for nitrogen balances.

The results are expressed in terms of per cent by volume.

Analysis of Oxynitration Solutions for Oxalic Acid

The analytical procedure for determining oxalic acid in the oxynitration liquor reported by Bachmann[27] gave low results in this laboratory. After several modifications of the original procedure continued to give low results, it was found that the presence of manganese in the oxynitration liquor catalyzed the decomposition of oxalate ion during the determination. Accordingly the following procedure was adopted in which the method was calibrated against solutions containing known amounts of oxalic acid and known varying amounts of manganese.

Solutions

<u>(a) Oxalic Acid Solution</u>. Nine grams of oxalic acid hexahydrate was dissolved in 100 ml. of distilled water and the exact oxalate ion concentration was determined by the permanganate titration as described in part b of the Procedure.

<u>(b) Nitric Acid</u>. Four hundred milliliters of 70% nitric acid was added to 54 ml. of distilled water.

<u>(c) Mercuric Nitrate - Nitric Acid Solution</u>. One hundred grams of mercuric oxide was dissolved in enough 70% nitric acid to make the total volume 100 ml.

<u>(d) Manganous Nitrate Solution</u>. Baker's CP 79% manganous nitrate hexahydrate aqueous solution was used.

<u>(e) Sodium Acetate - Calcium Nitrate Solution</u>. A solution containing 400 g. sodium acetate trihydrate and 40 g. of calcium nitrate trihydrate per liter was prepared.

Procedure (Calibration of Method)

<u>(a) Precipitation of Calcium and Mercury Oxalates</u>. Five milliliters of nitric acid solution (b) was pipetted into a small beaker. One milliliter of oxalic acid solution (a) was added followed by 0.60 ml. of the mercuric nitrate solution (c) with stirring. The desired quantity of manganous nitrate solution (d) was then quickly added, followed quickly with 27 ml. of the sodium acetate - calcium nitrate solution (e). The suspension was allowed to stand at room temperature in the dark for 35-40 minutes. The solid mixture of oxalates was collected by filtration on a fine sintered glass funnel and the residual contents of the small beaker were washed into a 250-ml. Erlenmeyer flask to be used for the subsequent titration. The residue on the filter was dissolved in three 20-ml. portions of 2 N hydrochloric acid. The filtrate was added to the contents in the Erlenmeyer flask, diluted with 100 ml. of distilled water, and the sample was titrated with standard permanganate as described below.

<u>(b) Permanganate Titration</u>. Since it was found in separate experiments that sulfuric acid did not completely dissolve the mixed oxalates on the filter (see part a above),

hydrochloric acid was used instead. The following modified permanganate titration was therefore used. The solution to be titrated was warmed to 40° and the 0.1 N permanganate solution was added dropwise until a pink end point lasting longer than one minute was obtained.

The permanganate solution was standardized against weighed amounts of primary standard sodium oxalate dissolved in 150-175 ml. of distilled water containing 10 ml. of concentrated hydrochloric acid. The titration was carried out at 35-40° C. in a dropwise fashion as described above. Standardizations by this procedure usually agreed with standardizations by the usual hot titration method within 0.1 per cent.

Variation of Results in the Presence of Manganese. The amount of oxalate found varied considerably with the amount of manganese present. The method outlined above was found to give duplicable results which varied with the manganese content as follows:

Mn^{++} conc. (molar) (in oxynitration soln.)	Per cent oxalic acid accounted for
0.0	100 ± 1
0.29	96.5 ± 1
0.55	94 ± 1
0.70	89 ± 1
1.19	70 (one determination)
1.57	0 (no precipitation)

It was shown that the effect of manganese was due to the destruction of oxalate in the presence of manganese as well as to incomplete precipitation of calcium and mercury oxalates when manganese was present. In several experiments the sample was prepared as described in a of the procedure, the filtrate from which the calcium and mercury oxalates had been removed was titrated with permanganate as was the precipitated mixed oxalates. While the oxalate content of this filtrate was appreciable (at 0.70 M manganese and higher), the sum of its titration and the titration of the precipitated oxalates was not equivalent to 100% of the oxalate originally present, indicating destruction of the oxalate ion during the determination. The sum of the determinations of the oxalate in the filtrate and in the precipitated oxalates usually ranged between 85-95%.

Determination of Oxalic Acid in Used Oxynitration Liquor. The following procedure was used to determine the oxalic acid content during and after several runs made in

Extractor No. 5A: About 15 ml. of sample was removed and chilled to 15°, filtered, and 5 ml. of the filtrate at 20-21° was pipetted into 25 ml. of the sodium acetate - calcium nitrate solution (d). The suspension was allowed to stand at room temperature in the dark for thirty-five minutes after which the precipitated oxalates were collected by filtration and determined as outlined above. Corrections for the effect of manganese were obtained from the table above.

A rough check was made on the accuracy of the oxalate determination in a used oxynitration liquor. A liter portion of the oxynitration liquor from Run 5A-6 was heated under reflux in the presence of manganous nitrate solution. The evolved gases were passed through the absorption train described on page 19 and the neutral gases were collected and analyzed in the Orsat gas analysis apparatus. Assuming that all the carbon dioxide found was formed from the oxalic acid present at the end of the run, the oxalic acid concentration was 12.5 g. per liter. Since it is probable that compounds other than oxalic acid decomposed to carbon dioxide in this experiment, this quantity is in fair agreement with the concentration of 9.3 g. per liter found by the precipitation method.

Analysis of Oxynitration Solutions for Nitrous Acid[40]

Solutions

α-Naphthylamine Acetate - Boil a suspension of 0.5 g. of α-naphthylamine (recrystallized from dilute methanol) in 100 ml. of water for five minutes, filter through cotton into 250 ml. of glacial acetic acid, and dilute to 1000 ml.

Sulfanilic Acid - Dissolve 3.3 g. of sulfanilic acid (recrystallized from water) in 750 ml. of water by heating, and add 250 ml. of glacial acetic acid.

Standard Sodium Nitrite, 0.0001 M - Dissolve 3.45 g. of sodium nitrite (99.8%) in water and dilute to 500 ml. Dilute 2.00 ml. of this solution to 2000 ml. Standardize by titration against a standard solution of Chloramine-T.

Procedure

Standard color - Add 2.0 ml. of standard sodium nitrite to a mixture of 5 ml. of α-naphthylamine solution and 5 ml. of sulfanilic acid solution. After 10 minutes at 20° determine log I_0/I at 525 mμ, using a spectrophotometer such as the Beckman. Successive dilutions of the standard sodium nitrite solution give the following concentrations of solutions used for calibration:

1×10^{-5} Molar
2×10^{-5} "
5×10^{-5} "
10×10^{-5} "

Unknown - A 2.0 ml. sample (approx. 0.35 M HNO_2) is diluted to 500 ml. with water containing 4 ml. of 6 N sodium hydroxide (to neutralize the strong nitric acid), and 25.0 ml. of this sample is diluted to 250 ml. A 2.00-ml. sample of this solution is treated with the developing reagents as with the standard solution of sodium nitrite. The concentration of HNO_2 is determined from the calibration graph.

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An extensive investigation of the oxynitration of benzene to 2.4 -dinitrophenol and/or picric acid by reaction with nitric acid-mercuric nitrate solution was carried out. A new procedure for continuous oxynitration of benzene to dinitrophenol (with some picric acid), utilizing the continuous liquid-liquid extraction principle was developed. An excess of the organic reactant, benzene, serves to remove benzene-soluble organic reaction products from the solution from which they are formed, eliminating the necessity of interrupting the operation of the reactor while products are removed. Yields of nitrophenols equal or exceed those obtained by batch procedures, and losses of mercury catalyst are minimized.

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