# Oxynitration of Benzene to Picric Acid

### **WOLFFENSTEIN-BÖTERS REACTION**

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The oxynitration of benzene to produce picric acid has been worked out as a practical procedure wherein 1.5 parts of the explosive can be obtained from one part of benzene and 1.4 to 1.6 parts of nitric acid. The procedure involves recovery of nitrogen oxides formed during the reaction. In order to conserve the expensive mercury catalyst the reaction liquors must be used repeatedly. If yield and quality of picric acid are to be maintained, the reaction liquor must be purified by steam distillation before it is used again.

**T** IS well known that some picric acid can be obtained from benzene in a single-stage reaction using a mercuric salt catalyst. A series of patents concerning this reaction was issued in 1906-09 to Wolffenstein and Böters (5, 31). Their claims embrace a general process for producing nitrophenols by heating aromatic compounds with ni-

tric acid or higher nitrogen oxides in the presence of a mercury salt; more particularly, for producing pierie acid by heating benzene with nitric acid and mercuric nitrate. In 1913 Wolffenstein and Böters published a paper containing somewhat generalized experimental directions for the preparation of pieric acid or 2,4-dinitrophenol (29). It was also reported that the same oxynitration takes place with benzoic acid (30). Accounts, more or less complete, are available of work on this reaction in several countries during the period 1914 to 1918 (3, 6, 7, 9, 10, 11, 19, 20, 22, 23, 24, 26) and shortly thereafter (4, 13, 32). Blechta and Patek (4) have extended the oxynitration reaction to toluene, and Davis (9) to naphthalene.

The purpose of the investigations reported here was, in general, to determine the suitability or unsuitability of the reaction as a means of



#### manufacturing picric acid and, in particular, to determine such points as the yield of picric acid, the consumption of nitric acid, the recoverability of unconsumed nitric acid, possible loss of the relatively valuable catalyst, and other economic and chemical features of the reaction which would have to be taken into account in a large scale operation. The reaction was tested on two scales: the first, using glass apparatus, produced about 150 grams of picric acid per run; the second, using metal-stoneware equipment, produced about 1900 grams of picric acid per run. The authors have found it convenient to divide the material for this paper into three main sections: a description of the small scale apparatus and procedure; some comments on this and a discussion of the reaction mechanism; and a description of the larger scale experiments.

#### **Small Scale Experiments in Glass Apparatus**

In the reaction yielding pieric acid, various workers are fairly

well agreed that: the optimum nitric acid concentration in the reaction mixture is about 50%; the yield is not improved by the presence of sulfuric acid: some nitrobenzene is always formed as a byproduct; the large volume of nitrous fumes evolved makes it difficult to prevent loss of unreacted benzene; and a large proportion of the benzene is destructively oxidized to oxalic acid, carbon dioxide, and possibly other products. There is a wide variation in the amount of mercury considered desirable; proportions from 10% of the weight of benzene up to 258% (a full molar equivalent) have been proposed. Other metals which have been patented as useful in the reaction include copper, silver, aluminum, and manganese (6, 23).

Vignon (26), Desvergnes (13), and others have worked with partial reaction runs where only a fraction of the benzene reacts in each run, the rest being recovered and recycled. Such a procedure

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Figure 2. Variations in Glass Apparatus Used When Reaction Mixture Was Not Stirred

appeared at the start of this work to be disadvantageous. Accordingly, all work reported here was done on the assumption that substantially complete reaction of benzene was desirable in each run.

The typical laboratory procedure, a result of several hundred experiments, was essentially an elaboration of an unpublished procedure of Reid and Lodge (24). The present authors have made detailed studies on the recovery of materials and on the purity of the product over a long series of consecutive runs carried out by repeated use of fortified reaction liquor. The procedure may be summarized very briefly as follows: The benzene was added over a period of time to the nitric acid-catalyst mixture, the reaction mixture boiled and concentrated by distillation and cooled, and the picric acid crystallized. The filtrate was then made up to strength to serve as the nitrating mixture for the next run.

APPARATUS. The fresh nitrating liquor consisted of 975 to 985 grams (750 ml., 7.8 moles) of 50 to 51% nitric acid, to which had been added 0.28 to 0.42 mole of mercury, 0.015 mole of manganese, and 0.005 mole of aluminum. The mercury was added either as nitrate or (with two equivalents of additional nitric acid) as oxide. Manganese and aluminum were added as the nitrates.

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through a 5-liter round-bottomed flask to provide time for oxidation of nitrie oxide, and then into the top of a 5-foot column, 20 mm. in diameter, packed with glass helices. The pulsator, or other lifting device, required to keep this packing wet with nitric acid (initially 35% nitric acid obtained as distillate from a former run) is not shown. The residual gases issued from the bottom of this absorber to a second absorber, packed with broken glass moistened with concentrated sulfuric acid, and circulated manually from the flask at the bottom to the dropping funnel at the top. The inert gas remaining passed through a dry ice trap, which, if the entire system was working correctly, condensed nothing.

PROCEDURE. With the reaction liquor at  $65 \,^{\circ}$  C., and the stirrer operating, 100 grams (1.28 moles) of benzene and 815 grams (575 ml., 9.06 moles) of 70% nitric acid were added continuously at a uniform rate over a 350-minute period to the acid-catalyst mixture. The quantity of 70% nitric acid added was that calculated to keep the acid in the reaction mixture at about 50%.

When these additions were complete, 35 grams (0.39 mole) of 70% nitric acid were added through the stopcock at the top of the reflux condensers, in order to wash down any condensed liquid. A sample from the reaction vessel was withdrawn, cooled, and centrifuged, and the strength of acid checked as described in the analytical methods.

The reaction mixture was stirred at  $65^{\circ}$  C. for 30 minutes at the end of this addition of acid, and was then heated, without stirring, with a fragment of porous tile added, to the boiling point (117° C.), over a 20-minute period, during which evolution of nitrogen oxides was vigorous. This evolution appeared to take place in two stages. From  $65^{\circ}$  to  $80^{\circ}$  C., the dissolved oxides were vaporized; from  $80^{\circ}$  to  $115^{\circ}$  C., oxides were produced (with a tendency toward foaming) presumably by oxidation of oxalic acid present in the reaction mixture. After the oxides had cleared into the absorbing system (reflux was water-white), 575 to 650 ml. were distilled through the take-off

575 to 650 ml. were distilled through the take-off stopcock over a period of 60 to 120 minutes. The shorter time is preferable to lessen oxidation of the product. The distillate separated into 15 to 21 grams of nitrobenzene and an aqueous layer consisting of 34 to 39% nitric acid. The reaction liquor was cooled to 80° C., siphoned from the

The reaction liquor was cooled to 80 ° C., siphoned from the 2-liter vessel, and further cooled with stirring to 18 ° C. The picric acid which crystallized was removed in a 5-inch stainless steel basket centrifuge, and centrifuge washed with two to six 50-ml. portions of 50 to 60% nitric acid, and then with two to six 50-ml. portions of water. After drying at 40 ° C., the picric acid weighed 130 to 135 grams. In the second and later runs, this yield increased to 150 to 155 grams (51 to 53% of theory on benzene), because the initial reaction mixture was then saturated with product. The filtrate from the centrifuge amounted to 560 to 635 ml. of 52 to 53% nitric acid. This was prepared for the next run by addition of wash acid and wash water until the volume was 750 ml. and the nitric acid concentration 50 to 51%. It was then chilled to 0 ° to 10° C. to precipitate (after the fourth rerun) a red semisolid oil (20 to 40 grams).

This oil was distilled with steam to remove mono- and dinitrobenzenes. The 3 to 6 liters necessary to complete the distillation can be reduced by use of superheat. The residual liquor was cooled to precipitate 15 to 30 grams of impure picric acid, removed by filtration. This impure picric acid was dissolved in the fortified de-oiled mother liquor for the subsequent run. The filtrate from which the impure picric acid came down was separated, and used to suspend the oil from subsequent runs. This re-use avoids loss of mercury.

A series of thirty consecutive runs was carried out according to this procedure, a mercury concentration of 0.42 mole per 100 grams of benzene being maintained throughout the series. The operating data for six consecutive runs near the end of this series are recorded in Table I. The nitric acid values in Table I, which is essentially a nitrogen balance sheet, are all expressed as grams of HNO<sub>3</sub>. A yield of 1.5 parts of picric acid could be produced consistently from 1 part of benzene and 2.51 parts of nitric acid.

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TABLE I. DATA ON RUNS IN GLASS APPARATUS										
Run number in series	22	23	27	28	29	30				
Nitric acid balance Acid in reaction vessel Fortifying acid Acid in take-off product Total HNO <sub>8</sub> added		$500 \\ 600 \\ 0 \\ 1100$	$ \begin{array}{c}As & G. \\ 505 \\ 600 \\ 9 \\ \overline{1114} \end{array} $	$     \begin{array}{r} HNO_{3} \\ 505 \\ 600 \\ 9 \\ \hline 1114 \end{array} $	$505 \\ 600 \\ 9 \\ \overline{1114}$	$505 \\ 600 \\ 9 \\ 1114$				
Acid in filtrate Acid in distillate Acid in fume-towers Total HNO₃ recovered for re-usé	349 267 227 843	355274227856	451 208 207 866	$     \begin{array}{r}             411 \\             222 \\             214 \\             \overline{847}         \end{array}     $	432 227 202 861	448 219 211 878				
●Total HNO <sub>2</sub> consumed	262	244	248	267	253	236				
Picric acid produced (as HNO <sub>3</sub> ) Nitrobenzene produced (as HNO <sub>3</sub> ) Dinitrobenzenes produced (as HNO <sub>3</sub> ) Total HNO <sub>3</sub> accounted for	125 $8$ $977$	131 8 3 998	125 9 2 1002	119 10 3 979	$125 \\ 11 \\ 1 \\ 988$	118 11 1007				
Other data Acidity of filtrate, % HNO <sub>3</sub> Volume of filtrate, ml. Yield of picric acid, g. % yield picric acid (based on benzene) Setting point, ° C. G. HNO <sub>3</sub> consumed/g. picric acid produced G. HNO <sub>3</sub> consumed/g. benzene used	$51 \\ 520 \\ 151 \\ 51.5 \\ 120.1 \\ 1.7 \\ 2.62$	$51 \\ 530 \\ 159 \\ 53.5 \\ 120.9 \\ 4 \\ 1.5 \\ 2 \\ 2.4 $	$53 \\ 640 \\ 151 \\ 51.5 \\ 121.9 \\ 3 \\ 1.64 \\ 4 $ 2.48	5260014449119.91.852.67	$52 \\ 630 \\ 152 \\ 51.5 \\ 121.8 \\ 1.66 \\ 2.53$	$53 \\ 635 \\ 143 \\ 9 \\ 121.0 \\ 1.65 \\ 2.36$				

As is shown later, the larger scale experiments resulted in a somewhat lower consumption of acid.

Slight deviations from the procedure outlined did, however, depress the yield, to values such as 40% (on benzene), and the quality, to material with setting points as low as  $119^{\circ}$  C. In addition, it was imperative that mercury losses be kept as low as possible. The factors influencing these requirements are discussed in detail in the next section. In evaluating these factors, a procedure was sometimes employed which differed, from that outlined above, in the absence of stirring. This variation imposed conditions which were far from ideal with respect both to quality and to duration of reaction, but did, however, permit reliable gas collection. The variations in the apparatus used when the reaction mixture was not stirred are shown in Figure 2, the two forms differing only in reflux cooling at  $10^{\circ}$  or  $-30^{\circ}$  C. Most of the factors discussed in the next section were examined by both stirred and unstirred procedures.

#### ANALYTICAL METHODS

REACTION MIXTURE. STRENGTH OF ACID. From the cooled and centrifuged sample from the reaction vessel, a 1-ml. portion was pipetted from the acid layer and diluted to 80 ml. Four milliliters of 2% aqueous potassium thiocyanate were added, and the sample was titrated with 0.5 N alkali, using 0.2% aqueous Congo red as indicator. The end point was fairly satisfactory, since the thiocyanate eliminated mercuric oxide precipitation at the end point, but it was advisable to add a drop of the indicator solution coincident with each drop of alkali toward the end of the titration.

MERCURY. The catalyst concentration must be followed carefully and any loss traced at once, if the process is not to become prohibitively expensive. The method of Desvergnes for determination of mercury (silver nitrate-potassium thiocyanate titration) was inexact, whereas sulfide precipitation was too tedious. Therefore the following method was developed:

For analysis of the reaction liquor, a homogeneous sample (nonaqueous phases contain mercury!) containing about 0.1 gram of mercury was weighed or delivered by pipet into a  $20 \times 2$  cm. test tube with a pouring lip<sup>1</sup>. To this sample were added 3 ml. of concentrated sulfuric acid and a boiling chip. The inclined tube was heated with a free flame, first cautiously, then as strongly as possible. When brown fumes were no longer seen, 10 drops of 70% nitric acid were added and the boiling was continued. Three such additions of nitric acid over a 10-minute period were generally sufficient. If the picric acid sublimed on the walls, the tube was rotated to wash this deposit back into the sulfuric acid. Three minutes after the picric acid was completely destroyed (solution might still be pale yellow), the tube was cooled and its contents were washed into a casserole with 100 ml. of water. After addition of 5 ml. of 6 N nitric acid and 1 ml. of ferric indicator, the

<sup>1</sup> Carmack of the University of Pennsylvania suggests insertion of a funnel to avoid loss by entrainment.

contents were titrated with 0.1 N thiocyanate to a deep orange color. When more dilute solutions (wash waters, etc.) were analyzed by this method, a preliminary concentration was necessary, as bumping was especially troublesome after the sulfuric acid had been added. This method gives results reproducible to 0.3 to 0.5%.

The product, picric acid, was analyzed for mercury by the same method. A 2-gram sample was required, together with 10 ml. of concentrated sulfuric acid and 5 ml. of 70%nitric acid, in a 100-ml. Kjeldahl flask. The procedure was otherwise identical, except that 0.05 N thiocyanate was used, since the mercury content would not be over 0.07\%. This analysis was reproducible to 2 to 3\%.

MANGANESE. The same sizes of sample were utilized for manganese determination as for mercury, and the method of decomposition was identical, except that sulfuric acid lost by volatilization had to be replaced to the nearest 0.1 gram. The sulfuric acid solution, freed from organic matter, was diluted with water to 100 ml. The A.S.T.M. method was then followed except that the mixed acid, which this method specifies, had to be altered to take into account the sulfuric acid already present in the mixture after digestion.

ALUMINUM. The estimation of aluminum in the reaction liquor was troublesome owing to the iron and chromium which accumulated from the stainless steel stirrer. In general, manganese has been considered as presumptive for aluminum.

#### **Comments on Procedure**

ADDITION OF REAGENTS. Patents have been issued for introduction of gaseous benzene in a carbon dioxide or air stream (20). The authors' experience suggests that such a procedure would be disadvantageous. In any case, the liberation of large amounts of nitrogen and its oxides, as well as carbon dioxide, causes unavoidable loss of some of the volatile benzene. In order to reduce this loss to a minimum, the benzene should be added at the approximate rate at which it is consumed. The extent of benzene loss by vaporization can be estimated by the yield of dinitrobenzenes in the sulfuric scrubbing acid. Indeed, it is troublesome here, since the dinitrobenzenes tend to clog the tower.

It seems unimportant whether the fortifying 70% nitric acid is added above or below the surface of the reaction liquor. The 70% concentration of acid used seems roughly to be optimum. Stronger nitric acid will tend toward direct nitration of benzene. Furthermore, the final volume must be sufficient to ensure substantial removal of the nitrobenzene by distillation.

. The yield of picric acid is markedly larger if the benzene is added slowly during the reaction rather than all at the beginning. This suggests that it is desirable to minimize, or avoid, a nonaqueous phase. This suspicion was confirmed by several experiments wherein varying quantities of nitrobenzene were added at the beginning. The production of nitrobenzene, at the expense of picric acid yield, increased with the amount of nitrobenzene initially present. The deleterious effect of the oily byproduct, described later, is probably due to the fact that it promotes the separation of an organic phase.

REACTION TEMPERATURE. The authors' experience confirms the opinion of Reid and Lodge that  $65^{\circ}$  C. is optimum. At  $75^{\circ}$  C. the ratio of nitrobenzene to picric acid is several times higher than at  $65^{\circ}$  C. The ratios at  $55^{\circ}$  and  $65^{\circ}$  C. are practically the same, but the rate at the lower temperature is slower by 25 to 30%. It would seem, then, that  $65^{\circ}$  C. is the temperature at which the maximum yield of picric acid can be produced in the shortest time.

If 100 grams of benzene are added at once to 750 ml. of stirred acid with catalyst at 25° C., the temperature rises spontaneously but slowly to 50° C. In the reaction at 65° C., with gradual benzene addition, however, heat evolution is barely observable.

COMPLETION OF REACTION AT 117° C. This final heating completes the nitration of dinitrophenol to picric acid, and the oxidation of oxalic acid. As the distillate is taken off, it is advisable to collect it in two roughly equal fractions, the first containing 22 to 28% and the second 37 to 44% nitric acid. Otherwise there is sometimes difficulty in separating the nitrobenzene layer because nitrobenzene has the same density as 34% nitric acid. The distillation, as well as removal of the nitrobenzene, increases the nitric acid concentration in the reaction vessel, to 52 to 53%, so that clean pieric acid will separate after cooling to  $18^{\circ}$  C.

Normally at least 75% of the total destructive oxidation, as measured by nitrogen oxide evolution, takes place before the reaction temperature reaches  $117^{\circ}$  C. However, some further oxidation does occur, especially toward the end of the distillation. This sharp increase sets in after about 575 ml. have come over. It is not due to higher acid concentration, for whether the distillation is stopped at this point or continued until 650 ml. have been distilled, the final concentration in the pot is 52 to 53%.

The effect of this secondary oxidation on the picric acid was evaluated during an abortive attempt to fractionate the nitric acid during the distillation. This fractionation, which required the maximum 2-hour period at 117 °C., rather than the minimum 1-hour period, reduced the concentration of the distillate only by 2 to 3%, and produced an increase in nitrogen oxide evolution. The strength of the residual acid was still 52 to 53%, but about 20 grams of picric acid were destroyed. It would appear from this observation that the distillation time should tend toward the minimum of 1 hour. It is important, however, that the residual liquor be entirely clear (even though deep red); otherwise the picric acid, when crystallized, will have a red-brown tinge.

The destruction of pieric acid by this secondary oxidation is not completely understood. If a solution of pieric acid in 58%nitric acid containing mercuric and manganic salts is boiled 2 hours, only 2% of the pieric acid is destroyed. Under similar conditions, 7% of nitrobenzene is destroyed in the same time.

INTRODUCTION OF OXYGEN. An effort was made to conserve nitric acid by introduction of oxygen during the addition period. No particular effect on the yield of picric acid was observed. Exaggerated nitrogen oxide evolution during the final heating, however, suggests that this variation is undesirable.

FILTRATION OF PRODUCT. Filtration of the crystalline picric acid by suction is not satisfactory. The mother liquor, rich in catalyst and organic by-products, tends to cling to the crystals. A centrifuge is much better; in the laboratory a 5-inch stainless steel basket centrifuge lined with glass cloth was used.

If the picric acid is washed directly with water, an orange-red oily material is precipitated on the surface. It should be washed first with 50 to 60% nitric acid which does not precipitate this oil. A washing schedule used (on approximately 150 grams of picric acid) comprises six 50-ml. portions of nitric acid, followed by seven 50-ml. portions of water. The first acid and first water washes are then used to increase the volume of the mother liquor to the 750 ml. necessary for the next run. The second wash liquids become the first in the next run, so that eventually the crude picric acid is washed with five portions of acid, each used previously a fewer number of times, and finally with a portion of fresh acid, which will appear as a clear wash without pink color. The same progression is used in the water washing. The first water wash contains 25 to 35% nitric acid, the last, 1.5 to 2%. Under the conditions used for nitric acid titrations, saturated aqueous picric acid titrates about 0.5% when calculated as nitric

acid, so that the picric acid washed by this procedure contains residual nitric acid. Some of this still remains when washing is continued until the titer of the filtrate is lowered to 0.5%. This can be demonstrated by slight nitrogen oxide evolution from the molten picric acid at 140 ° C. Steaming of the centrifuge-washed material, however, gives a product which is nitric acid-free by this test. This steam purification will also remove residual dinitrobenzene as discussed under by-products.

PURITY OF PRODUCT. Large crystals of pieric acid tend to occlude mother liquor, so that rapid agitation with rapid cooling of the final reaction mixture is advisable. The setting point of the product is affected strongly by *p*-dinitrobenzene; 3.1% of *p*-dinitrobenzene lowers the setting point to  $115^{\circ}$  C., 1.1% lowers it to  $119.5^{\circ}$  C. Steaming, which distills out the *p*-dinitrobenzene, as mentioned above, will raise this setting point to  $121^{\circ}$  C.

The setting points were determined on a 4- to 7-gram sample in a  $6 \times 1$  inch test tube, after heating the melt to  $142^{\circ}$  to  $145^{\circ}$  C. for one hour. The setting point of the yellow melt checked to 0.1° C., after this period. A slight brown flocculent precipitate sometimes appeared. If the crystalline picric acid contained pink spots owing to insufficient washing, the surface of the steamed product became brown, and at 140° C. the melt was red-brown, but the setting point was not affected.

GAS EVOLUTION DURING REACTION. There is a copious evolution of fume throughout the reaction, part of which may be returned to the reaction vessel from the reflux. Part (nitrogen trioxide, tetraoxide, and nitric oxide if air is present) will be absorbed in the two acid towers, and part (nitrogen, nitrous oxide, carbon dioxide and a possible trace of carbon monoxide) will be lost to the system.

The rate of evolution of recoverable nitrogen oxides is fairly uniform (0.3 to 0.4 gram as 100% nitric acid per minute) through the addition period, increases greatly (10- to 15-fold) while the reaction mixture is heated to boiling, and then falls off during the distillation, though it is still 2 to 4 times faster than the rate of evolution during addition. These approximate rates were ascertained by analysis of the absorbing tower liquors from the oxynitration of 100 grams of benzene.

There is a considerable amount of nitric oxide present in the fume, which of course must be oxidized before it can be absorbed, and oxidation is slow because of the large amount of carbon dioxide diluting the gas. If a gas sample is drawn directly from the reaction vessel through a dry ice trap to remove nitrogen sesquioxide and tetroxide, the effluent gases analyze about 50% carbon dioxide, 5% nitric oxide (15), and 45% nitrogen plus nitrous oxide during the addition stage, whereas this changes to 60%carbon dioxide, 30% nitric oxide, and 10% nitrogen plus nitrous oxide during the boiling and distillation stage. The actual volumes of these three gases (from 100 grams of benzene) are 20 liters during the addition period and 20 to 25 liters during the boiling and distillation. When the 5-liter vessel shown in the fume system in Figure 1 was by-passed, the nitric acid recovery was 46% as acid of 55% strength, 46% as nitrosylsulfuric acid, and 8% loss. With the 5-liter reservoir installed, the amount of weak acid increased to 53% recovery, and the nitrosylsulfuric acid remained the same, with 1% loss. This latter loss was not decreased by use of a second 5-liter reservoir.

The large amount of inert gas produced, which of course is augmented by the necessary addition of oxidizing air, results in a very low partial vapor pressure of any benzene passing into the fume. The difficulty in obtaining a benzene balance to within 10 to 12% of the total is apparent.

The sulfuric acid absorption tower scours the oxidized fume efficiently, although it receives a heavy load during the boiling-up period. The temperature of the acid averages about  $40^{\circ}$  C. during the first stages of the reaction, but rises to  $65^{\circ}$  to  $70^{\circ}$  C. during the boiling and distillation stages. The most concentrated acid which can be obtained from the bottom of the sul-

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furic acid tower during efficient absorption analyzed (Du Pont nitrometer) for 32 weight % as 100% nitric acid, but there was an appreciable vapor pressure of nitrogen oxides from this sample at 25° C. The total recovery of nitrogen oxides from both towers approximates 1.5 parts (as 100% nitric acid) per part of pieric acid produced (Table I).

The variation during the run in nitric oxide percentage necessitates control of the incoming air. The approximate amount necessary to ensure a small percentage of oxygen in the tail gas was estimated by repeated gas analyses: during reagent addition, 80 cc. per minute; during the heating from 65° to 117° C., 600 cc. per minute; and during distillation, 400 cc. per minute.

If the reflux condenser is operated at  $-30^{\circ}$  C., so that both nitrogen sesquioxide and tetroxide will be returned entirely to the reaction, the nitric oxide content of the gas above the condenser increases to about 65% during the addition period. The total quantity of recovered oxides (as 100% nitric acid) remains about the same, so that the retention in the reaction vessel of the nitrogen trioxide plus nitrogen tetroxide seems, by escape of nitric oxide, only to shift to the right the equilibrium:

$$N_2O_3 \rightleftharpoons NO_2 + NO$$

and it may be significant that the amount of inert gas (nitrogen plus nitrous oxide) does not increase if the reflux is at  $-30^{\circ}$  C.

A typical analysis of the tail gas emerging from the sulfuric acid tower (reaction gases plus gases from introduced air) is: carbon dioxide, 52%; nitric oxide, none; oxygen, 1.4%; nitrous oxide, 11%; carbon monoxide, less than 0.5% (present?); and nitrogen, 35% by difference.

The quantities of nitrous oxide and nitrogen (ratio approximately 1 to 2) liberated in unstirred runs together represent 1.0 to 1.5 atoms of nitrogen per mole of picric acid formed, or 0.3 to 0.5 part of 100% nitric acid per part of picric acid which is entirely lost. This is of the same order of magnitude as the loss of 0.29 part (as 100% nitric acid) per part of picric acid produced by nitration of phenol (21).

BY-PRODUCTS. The by-products in the reaction (apart from the gaseous by-products) may be classified into those appearing in the distillate and fume-recovery systems, and those remaining in the reaction mixture with the picric acid. In the first class is nitrobenzene, which, as mentioned in the procedure, comes over during the distillation stage. About 18 parts of nitrobenzene, containing traces of benzene and dinitrobenzene, are produced per 150 parts of picric acid. The mixed acid in the sulfuric acid tower yields, when poured on ice, 1.5 to 3.0 grams of *m*-dinitrobenzene, evidently formed from the benzene and nitrogen tetroxide carried by the effluent gases to this tower:

 $N_2O_4 + H_2SO_4 \longrightarrow NO_2SO_3H + HNO_8$  $2HNO_3 + C_6H_6 \longrightarrow C_6H_4(NO_2)_2 + 2H_2O_3$ 

There is no implication in this work that all the benzene passing into this tower is converted to dinitrobenzene. By-products remaining in the reaction mixture include all three dinitrobenzenes (3 parts per 100 parts of benzene at start) which may be obtained from the mother liquor by steam distillation. Normally, only the para isomer is found in the crystallized picric acid, presumably because of its relative insolubility.

These by-products, remaining in the reaction mixture, are not evident until the reaction liquor has been used about five times, at which point they have accumulated sufficiently that they separate as an oily layer when the cooled liquor is made up to volume for the next run. Coincident with this, the yield and setting point of the picric acid decrease progressively. After ten more runs, if the oil was left in the reaction liquor, the yield dropped from 1.5 parts of picric acid per part of benzene to 1.1 parts, and the setting point from  $121.5^{\circ}$  to  $114^{\circ}$  C.



Figure 3. Four-Pound Batch Reactor

Examination of the oil indicated that it was a mixture of picric acid, all three dinitrobenzenes (chiefly the meta isomer), nitrobenzene, and some nitric acid with catalyst. The dinitrobenzenes, which were evidently the undesirable components of this mixture, probably accumulate because of the solubilizing effect of the picric acid and other, unknown, components. The dinitrobenzenes could not be steam-distilled satisfactorily if the oil was suspended in a small volume of water. However, if 50 parts by volume of oil were suspended in enough water or better, aqueous picric acid-mercuric nitrate solution (2400 parts by volume) to dissolve it all (based on the assumption that it was all pieric acid), then distillation with superheated steam (160° to 200° C.) brought over about 6000 parts of water, 5 to 6 parts of nitrobenzene, and 10 to 20 parts of mixed dinitrobenzenes melting at about 60° C. A green color in residue and distillate was noted at the beginning of the distillation, but no nitroso compounds have been isolated.

When the residual liquor from the steam distillation was cooled to  $20^{\circ}$  C., picric acid and a brown gum, rich in mercury, separated out. This entire precipitate was returned to the reaction liquor; the aqueous phase was retained for steam distillation of the next by-product oil. Since mercury and manganese tended to accumulate in this liquor, the rate of catalyst withdrawal from the reaction liquor had to be determined regularly by analysis.

The benefit of removing the by-product oil and steam distilling out the dinitrobenzenes was illustrated by carrying this out after the fourteenth run in a series from which no previous separation had been made. The fourteenth run had yielded 1.20 parts by weight of picric acid and 0.24 part of nitrobenzene per part of benzene. The fifteenth run gave 1.57 parts of picric acid and 0.15 part of nitrobenzene, yields comparable to those obtained in the first few runs of a series.

#### **REACTION MECHANISM**

EFFECTS OF CATALYSTS. The efficient catalysis of this reaction appears to involve a combination of effects. When benzene and 50% nitric acid containing mercuric nitrate are shaken together in a separating funnel at  $25^{\circ}$  C. and the layers allowed to separate, the entire acid layer begins to darken slightly after 30 minutes. If, instead, the benzene is poured on top of the acid without shaking, the darkening starts at the interface and extends slowly down through the acid. After several weeks, the acid layer becomes lighter in color, and crystals, largely dinitrophenol, separate. There is some evidence that this latter stage is accelerated photochemically. The two stages might reasonably be interpreted as the formation of an intermediate mercurial, followed by its decomposition. Actually, Desvergnes (13) reports the isolation of both nitrosobenzene and an unstable product which analyzed for tetranitrodiphenylmercury.

The temptation to draw an analogy between the intermediate in this reaction and the diazonium salt intermediate obtained from anthraquinone in its conversion to quinizarin with a mercury catalyst (1, 16) is very strong, particularly in view of the known conversion of diphenylmercury to phenylmercuric nitrate and benzene diazonium nitrate by nitrogen trioxide (2). Indeed, the authors found that when phenylmercuric nitrate was dissolved in 50% nitric acid, the solution darkened after about 30 minutes, and when the mixture was boiled, cooled, and extracted with ether, a mixture of picric acid and nitrobenzene was isolated. However, this can be interpreted either as diazonium salt formation, or as hydrolysis of the mercurial to benzene, followed by the Wolffenstein-Böters reaction.

If the diazonium salt formation were an intermediate step in the Wolffenstein-Böters reaction, then one mole of nitrogen should be evolved per mole of picric acid produced, according to the following scheme:

$$C_{6}H_{6} \xrightarrow{H_{g}(NO_{3})_{2}} C_{6}H_{5}H_{g}NO_{3} \xrightarrow{N_{2}O_{3}} C_{6}H_{5}N_{2}NO_{3} \xrightarrow{H_{2}O} C_{5}H_{5}OH + N_{2}$$

$$C_{6}H_{5}OH \xrightarrow{3HNO_{3}} C_{6}H_{2}(NO_{2})_{3}OH$$

However, in unstirred runs, the authors were in no case able to isolate in the oxynitration reaction more than  $^{3}/_{4}$  the volume of inert gas required by these equations, and about  $^{1}/_{3}$  of this inert gas turns out to be nitrous oxide, which could not have been produced from a diazonium salt. In view of the fact that substantial quantities of nitrogen and nitrous oxide are produced even in ordinary mixed acid nitrations without mercury catalyst—for example, in nitrating phenol (21)—the gases evolved in the oxynitration cannot substantiate the diazonium salt mechanism.

This conclusion does not exclude intermediate mercurial formation. Indeed, the work of Smith and Taylor (25) would indicate that if nitrosobenzene were an intermediate in the oxynitration, it would probably arise via a mercurial<sup>2</sup>. The authors have not been able to identify nitrosobenzene in the main reaction at  $65^{\circ}$  C. However, the green colors obtained on steam distillation of the by-product oil, and from the acid washing of the crude pieric acid, strongly suggest the presence of a nitroso compound. Furthermore, the dinitrobenzenes obtained from the steam distillation of the by-product oil contain a much larger percentage of the para isomer than is formed in direct nitration of benzene. This *p*-dinitrobenzene could arise from the following reaction sequence:



Nitrosobenzene can be converted in 7% yield to impure dinitrophenol. Three hundredths of a mole of nitrosobenzene were added at 25° C. to 0.20 mole of 50% nitric acid and 0.007 mole of mercuric oxide. The compound dissolved without noticeable heat evolution, and the solution turned a very dark brown. After 15 minutes the temperature had increased spontaneously to 45° C., at which point it was checked, and maintained at 30° C. for 12 hours while nitrous fumes were evolved. After 5 days, the greasy solid was filtered off and washed with *p*lcohol

<sup>2</sup> Carmack and co-workers (8) have isolated basic phenylmercuric nitrate from reaction mixtures weak in nitric acid, ori n which nitrous acid is absent. to leave a solid (melting point  $80^{\circ}$  to  $108^{\circ}$  C.) which was crystallized from water to a purity (melting point  $112^{\circ}$  C.) adequate for mixed melting point identification as 2,4-dinitrophenol. Steam distillation of the mother liquor produced about 5% of theory of nitrobenzene in the distillate, and 21 weight % of an unidentified brown powder melting from  $145^{\circ}$  to  $200^{\circ}$  C.

The yields and general behavior are strongly remindful of the reaction with benzene carried out under the same conditions. When, however, the reaction with nitrosobenzene was carried out at  $65^{\circ}$  C. under otherwise identical conditions, thus simulating the actual reaction whereby picric acid is produced from benzene, only a trace of crystalline material was obtained, in addition to mercuric oxalate. The authors therefore have no valid evidence for postulating either nitrosobenzene or benzene diazonium nitrate as reaction intermediates, and hence have no adequate explanation for the action of the mercury catalyst<sup>3</sup>.

Likewise, they cannot explain the accelerating action of aluminum salts in the presence of mercury. However, the bleaching and precipitation stage in the test reaction at 25° C. seems definitely to be accelerated by traces of aluminum, but not by any other elements tried. These included arsenic (as arsenious oxide), boron (as boric acid), calcium, cerium, chromium, iron, lead, magnesium, nickel, selenium (as selenic acid), silicon (as sodium silicate), silver, sulfur (as elemental sulfur), tantalum, and tin, none of which exerted any significant effect. Copper seems to inhibit slightly, and vanadium (as vanadic acid) inhibits completely. The amount of these elements (as nitrate salts unless otherwise specified) used in unstirred

runs at  $65^{\circ}$  C. was 8% of the weight of mercury, which, in turn, was 60% of the weight of benzene used.

The action of manganese is catalytic, but not for the main reaction. It serves to catalyze the complete oxidation of oxalic acid, which otherwise contaminates the product with insoluble mercuric oxalate. The catalytic effect of manganese in this reaction is well known (12, 14, 17, 18, 27). The authors have actually isolated and identified mercuric oxalate from reactions where manganese was not present.

The best catalyst mixture found comprised the nitrates of mercury, aluminum, and manganese. Stirred runs containing 30 parts of mercuric oxide (0.14 mole) and 4 parts of manganese nitrate (20.7% manganese) per 100 parts of benzene required 15 hours for completion. Inclusion of 2 parts of aluminum nitrate monohydrate (7.2% aluminum) shortened this time to 10 hours, although a larger amount did not benefit further. When the quantity of mercuric oxide was doubled to 60 parts (0.28 mole) per 4 and 2 parts, respectively, of the other salts, the reaction time was shortened to 6 hours. Further addition of mercury did not increase the yield or shorten the reaction time, but in practice it was found convenient to carry 90 parts of mercuric oxide (0.42 mole) in order to ensure, without immediate analysis, that the mercury was not temporarily withdrawnfor example, in the by-product oil-to leave a concentration below the necessary minimum of 0.23 mole per 100 grams of

benzene. If the process is to work reproducibly within the 8-hour cycle given in the procedure, it is evident that the catalyst concentration must be followed carefully.

#### Larger Scale Experiment in Metal Apparatus

The work described in this section was in a sense of a supplementary nature and consisted of testing the reaction on a larger scale, using the optimum conditions developed in the small scale experimental work. The main purpose was to determine whether the reaction, when run under conditions simulating actual conditions which might be encountered in practice, dis-

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<sup>&</sup>lt;sup>8</sup> Westheimer (23) has since shown that nitrosobenzene, derived from phenylmercuric nitrate, can be considered as the principal intermediate in the Wolffenstein-Böters reaction.

played any features which had not been apparent on the small scale, and which might cause operating troubles. The scale decided upon was 12.5 times that of the small scale operations, so that about 4 pounds of picric acid were produced per run.

APPARATUS. In designing the equipment for this work, the first step was to carry out corrosion tests on a variety of materials in order to determine the material suitable for the reaction vessel. These tests were carried out on 1- to 20-gram samples of known surface area, by boiling for 30-day periods immersed in 50% nitric acid containing the catalysts. These tests were not sufficiently stringent, perhaps because pieric acid and nitrobenzene were not included, but they indicated that the following were unsatisfactory: chemical stoneware, high-manganese iron, enameled iron, Nichrome, and Durimet D. Allegheny 18-8 stainless steel showed reaction equal to an annual rate of penetration of 0.007 inch, Allegheny 25-20 stainless steel corroded at a rate of 0.005 inch per year, and no observable corrosion could be discovered for tantalum, Duriron, or Corrosiron. As a result of these tests, and because of availability of equipment, the reaction vessel used was Duriron.

The apparatus as assembled is partly illustrated in Figure 3 and wholly diagrammed in Figure 4. Reference to the diagram shows a jacketed Duriron kettle, C, fitted with a conventional steam gage, valves, and trap installation (not shown). The kettle was stirred by a stainless steel (18-8) stirrer, H, driven at 400 revolutions per minute by a quarter horsepower motor, F. It was equipped with a thermometer, E, a calibrated dropping funnel, D, and a drainage valve, V-9. The vapor outlet (2-inch diameter) from the kettle was equipped with a spray trap, K, of conventional design, which conducted the gases to the reflux condenser, J. The latter consisted of three parallel 6-foot lengths of vertical Duriron pipe. This manifold was tilted slightly to permit the withdrawal of condensate through valve V-10, during the distillation, and was shrouded with cloths to retain water spray from the nozzles. The nozzles, spaced 2 inches apart, impinged on the Duriron pipes. The top of the condenser manifold was equipped with valve V-11, through which the last portion of fortifying acid was added to wash down the reflux tubes.

The fumes from the top of this condenser were combined at the beginning of a stainless steel pipe, W, 4 inches in diameter and 22 feet long, with air supplied at V-12 by a compressor and measured by a gas meter. The optimum air flow was estimated as 7 cubic feet per hour during benzene addition, 18 cubic feet per hour during the heating period, and 8 cubic feet per hour during distillation. This stainless steel pipe, W, (2 cubic feet capacity) led into the 6.25-cubic foot sewer tile tower, N, which was packed with



Figure 4. Apparatus for Large Scale Experiment

stainless steel scrap and fed in the top and out the bottom with 35% nitric acid from a previous run. This acid was continuously recirculated at a rate of 3 to 4 liters per minute by a stainless steel centrifugal pump, O. The gases from the base of tower N passed into an empty 6.25-cubic foot capacity sewer tile tower, M, which provided time to complete the nitric oxide oxidation, and thence to the 18-foot by 2-inch diameter stainless steel (18-8) tower, R. This tower was packed with stainless steel scrap, consisting of 0.25-inch by 3-inch stamped strips bent into V-shape of internal angle  $45^{\circ}$ . Concentrated sulfuric acid was circulated through tower R, in at V-13 and out at V-14, at rates of 0.13 and 2.0 liters per hour during the addition and boiling stages, respectively. The effluent gas from this tower was passed through a bottle of 0.5 N alkali and thence through an aspirator pump, the titer of the alkali evaluating the final fume loss of nitric acid.

For filtration of the cooled reaction mixture, a stoneware nutsch with glass filter cloth and the 5-inch stainless steel basket centrifuge used previously were employed. Steam distillation of the by-product oil was carried out in a 12-gallon jacketed stainless steel vessel with a stainless steel tube condenser, which latter condensed about 150 liters of distillate at the rate of 30 liters per hour.

These are two deviations from the design of the glass apparatus shown in Figure 1. First, the design of the kettle made it necessary to add the 70% nitric acid and benzene intermittently through the same funnel. Even though these additions were spaced over the 35-minute period available, according to a 374minute addition schedule, there was a greater benzene loss than should have occurred.

The second variation from the glass apparatus involved the use of empty nitric, oxide oxidizers both before and after the tower through which the 35% nitric acid circulated. Both these empty towers may not be necessary; the apparatus as first assembled was furnished with a short 2-inch-diameter paraffined iron pipe in place of the 4-inch stainless steel pipe, W. Although the empty tower, M, is over three times larger (relative to the amount of benzene oxynitrated) than the 5-liter glass reservoir shown in Figure 1, the gas absorption was much less efficient, and no reasonable nitric acid balances could be obtained with it alone as oxidizing chamber. When the stainless steel pipe, W, was installed, this relatively small (2 cubic feet) additional delay reservoir so improved the air oxidation, that less than 1% of fume loss was observed at the end of the sulfuric acid tower, R. Tower Ralso operated much cooler, thus indicating that less oxidation was occurring within it. We interpret this to mean that nitric oxide is more readily oxidized, before it is moistened by the 35% nitric acid, when it is relatively dry from the top of the reflux condenser.

> PROCEDURE. Except for the variations noted above, the operation of the Duriron stoneware equipment was essentially 12.5 times that used for the glass equipment. The reactor was heated to  $65^{\circ}$  C. with 9375 ml. of liquor consisting of 50 to 51%nitric acid, with 693 grams of mercury, 10 grams of manganese, and 2 grams of aluminum (weights calculated as the metals). Before commencing the addition of benzene, the take-off pocket above valve V-10 in the reflux condenser was filled by introduction of 250 to 340 ml. of 70% nitric acid through valve V-11.

> The addition cycle included 30 minutes for introduction of 125 ml. of benzene and then 5 minutes for addition of 694 ml. of 70% nitric acid. This cycle was repeated nine times, but the eighth and ninth additions of nitric acid were 787 ml., while the tenth nitric acid addition of 288 ml. was effected through valve V-11. This brought the titer of the reaction liquor at the end of the addition period to 49% nitric acid. Temperature control of the heating jacket was necessary to prevent a 2° to 3° C. rise in temperature during the first two additions of benzene, but little subsequent attention was necessary.

> After the drainage of the kettle jacket, steam was introduced, initially at 5 pounds per square inch and gradually raised to 27 pounds per square inch over the 2-hour distillation period. The charge, about

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Figure 5. Corrosion of Duriron Reactor Vessel

7.1 liters, was then cooled to  $80^{\circ}$  C. by passing air through the jacket, and run out into a 12-liter flask equipped for fume return to the absorbing system. The steam consumed during the distillation was about 70 pounds.

About two thirds of the total fume was used to fortify the 35% nitric acid to 54 to 56%, the remainder being absorbed by 7 kg. (3.80 liters) of 94% sulfuric acid. Not more than 0.5 to 1.0% of the fume escaped this system. About 60 grams of dinitrobenzene were formed in the sulfuric acid tower per 1250 grams of benzene oxynitrated.

The subsequent operations closely paralleled those used for the glass equipment. After cooling to  $18^{\circ}$  C., a portion of the picric acid was filtered off using the centrifuge, and the remainder filtered in the nutsch, using washing procedures identical with those described previously. The by-product oil was steam-distilled, and the reaction liquor made up for the next run in a manner similar to the methods used on the small scale.

The yields and setting points of the product averaged 49%and  $121.1^{\circ}$  C., respectively, over the last 16 of a 38-run series. With the larger scale of operation, recovery of nitric acid was more favorable than had been the case with the glass apparatus. The operating data for eight consecutive runs are given in Table II, the average nitric acid consumption being 1.44 parts of nitric acid per part of picric acid produced, compared to 1.68 parts of nitric acid on the smaller scale. CORROSION. Although the preliminary corrosion tests (on samples furnished by the company) indicated that Duriron was resistant to the nitric acid-catalyst mixture, a great deal of trouble was encountered with the reaction vessel. After 50 runs had been carried out (400 hours in operation) the equipment was dismantled for examination. Figure 5 shows that the entire surface below the liquid level line was corroded to a depth of about  $1/1_{16}$  inch. Deep blow-holes can be seen in the bottom of the vessel. The type of corrosion is shown on a section at the liquid level about  $6 \times 10$  inch photographed in Figure 6. A sample chipped from the well washed interior contained 0.5% mercury. In contrast, the 18-8 stainless steel stirrer was dark blue but showed no pitting, no line of demarcation at the liquid level, and no sharpening at the edges, characteristic of corrosion.

EFFECT OF CORROSION PRODUCTS. Though the nitric acid consumption remained fairly uniform over the series of runs, it became progressively more difficult to obtain a good yield of high quality pieric acid with each succeeding run. This tendency is shown in Table II, and although it can be compensated for by excess washing (runs 33 and 34), the yield is necessarily diminished. The tendency was correlated with a change in distillation behavior; the acid strength of the distillate began to increase from an average 35% to an average 41%, whereas the residual liquor correspondingly decreased from an average of 54% to an average of 48.5%.

The authors had discovered previously that picric acid of high quality will not crystallize from liquor with nitric acid content as low as 47 to 48%. This was confirmed by adding, to a liquor which gave picric acid of setting point 120.9° C., enough strong nitric acid to raise the concentration to 51.3%. The setting point of the picric acid obtainable was raised to 121.9° C.

This unfavorable behavior of the reaction liquor was not attributable to organic impurities. When the entire waterinsoluble residue (obtained by drowning a part of the reaction liquor) was transferred to a fresh nitric acid-catalyst solution, the resulting liquor, after the reaction, behaved normally and gave good picric acid. It was found, however, that when the organic material in the unsatisfactory liquor was destroyed by boiling mixed acid, the resulting solution contained 86% more 'ash than could be accounted for by the catalyst mixture, so evidently inorganic material, presumably corrosion products, was present.

Acting on the assumption that these inorganic salts were causing the anomalous behavior, four solutions of 1350-ml. vol-

Run number in series	27	28	29	30	31 HNO	32	33	34		
	As G. HNU									
Nitric acid balance Acid in reaction vessel Fortifying acid Washing acid used By-product residue in Total HNOs added	$\begin{array}{r} 6220 \\ 7728 \\ 833 \\ 175 \\ \hline 14956 \end{array}$	$ \begin{array}{r} 6250 \\ 7912 \\ 830 \\ \hline 14992 \\ \end{array} $	$\begin{array}{r} 6230 \\ 7843 \\ 828 \\ 172 \\ \hline 15073 \end{array}$	$\begin{array}{r} 6280 \\ 7938 \\ 1344 \\ 121 \\ \hline 15683 \end{array}$	$ \begin{array}{r} 6260 \\ 8035 \\ 1340 \\ 146 \\ 15781 \end{array} $	$ \begin{array}{r} 6250 \\ 8026 \\ 1328 \\ \hline 1328 \\ \hline 15604 \\ \end{array} $	6160 8669 1369	6228 8526 1406		
Acid in filtrate Acid in distillate Washing acid recovered Acid in fume towers in H <sub>2</sub> SO <sub>4</sub> Acid in fume towers in dil. HNO <sub>3</sub> Total HNO <sub>3</sub> recovered for re-use	$3840 \\ 4375 \\ 1180 \\ 700 \\ 1968 \\ 12063$	$3918 \\ 4470 \\ 1160 \\ 716 \\ 2167 \\ 12431$	$\begin{array}{r} 4360 \\ 4290 \\ 1130 \\ 610 \\ 1955 \\ \hline 12345 \end{array}$	$3960 \\ 4610 \\ 1760 \\ 810 \\ 1856 \\ 12996$	$3760 \\ 4725 \\ 1670 \\ 895 \\ 1861 \\ \hline 12911$	$3940 \\ 4546 \\ 1570 \\ 834 \\ 2193 \\ \overline{13083}$	$4075 \\ 4600 \\ 1835 \\ 843 \\ 2193 \\ \hline 13546$	3743 4950 2147 1288 1856 13984		
Total HNO <sub>3</sub> consumed	2893	2561	2728	2687	2870	2521	2552	2176		
Picric acid produced (as HNOs) Nitrobenzene produced (as HNOs) Dinitrobenzenes produced (as HNOs) By-product residue	$1700\\140$	$1486 \\ 151 \\ 332$	$1605 \\ 178 \\ 130 \\ 143$	$1533 \\ 125 \\ 84 \\ 179$	$1561 \\ 130 \\ 57 \\ 171$	$\substack{\substack{1463\\122\\0}\\\dots}$	$\begin{array}{c}1382\\112\\17\end{array}$	$1330 \\ 128 \\ 17$		
Total HNO₂ accounted for	14135	14400	14401	14917	14850	14668	15057	1545		
Other data Acidity of filtrate, % HNOs Volume of filtrate, ml. Yield of picric acid, g. % yield picric acid (based on benzene) Setting point, ° C. G. HNOs consumed/g. picric acid produced	51.4 3675 2054 56.0 119.9 1.41	50.5 5903 1801 49.2 121.6 1.42	$51.5 \\ 6420 \\ 1945 \\ 53.0 \\ 119.9 \\ 1.41$	50.6 5972 1860 50.7 120.9 1.45	$\begin{array}{r} 49.4 \\ 5835 \\ 1894 \\ 51.5 \\ 119.9 \\ 1.51 \end{array}$	$\begin{array}{r} 48.9\\6180\\1773\\48.2\\120.9\\1.42\end{array}$	$\begin{array}{r} 48.4\\5615\\1676\\45.6\\121.9\\1.52\end{array}$	$\begin{array}{r} 48.2\\5293\\1617\\44.2\\121.9\\1.35\end{array}$		

#### COMMENTS ON PROCEDURE

Amount of Sulfuric Acid. A considerable amount of 94% sulfuric acid would be required to concentrate the 35% nitric acid from the absorption tower to the 95%nitric acid content needed for make-up to 70% fortifying acid. More 94% sulfuric acid would be needed than the 7 kg. used in the sulfuric acid tower. Hence the capacity could be increased; this would cause it to run cooler than the 65° C. maximum observed. If the tower temperature were reduced below 50° C., the formation of the dinitrobenzenes would be markedly decreased.



Figure 6. Type of Corrosion on Duriron Reactor Vessel

ume were distilled from a 2-liter flask, and samples for titration were withdrawn at 100-ml. intervals. The first solution (A) was the reaction liquor from run 38. B was a solution, in 50%nitric acid, of 90 grams of mercuric oxide, manganese, aluminum, and 105 grams of ferric nitrate; the weight equivalent of the contaminant inorganic salts in solution A. Solution C was identical with B, except that no ferric nitrate was added. Solution D was similar to C, except that the amount of mercuric oxide was reduced to 60 grams, the minimum amount of mercury required for satisfactory operation.

The interesting parts of the distillation data are shown in Figure 7. In the presence of inorganic solute, the composition of the 68.0% (735 mm.) constant boiling nitric acid can never be attained in the residue. The practical maximum concentration in the residue is indicated by the ordinate at which the concentration lines for distillate and residue cross. Comparison of B, C, and D shows that the solute concentration should be held to a minimum, since D, containing 60 grams of mercuric oxide does not fall off until 850 ml. have distilled, whereas C dropped off at 775 ml., and B at 725 ml. Although none of these artificial reaction mixtures drop off as quickly as A (the old liquor, for

which the lines cross at 660 ml.), it must be remembered that some of the inorganic impurities may be univalent and bivalent, and hence more effective than ferric salt; furthermore, the dissolved picric acid will likewise contribute to this effect.

These findings confirmed the suspicion that the unsatisfactory distillation behavior toward the end of the 34-run series was due to inorganic salt contamination caused largely by corrosion of the Duriron reaction vessel, though some may have been introduced from the stoneware towers. The results further indicate that optimum distillation behavior will be obtained if the catalyst concentration is held close to the minimum 60 grams mercuric oxide per oxynitration of 100 grams of benzene. This

would necessitate a check of the reaction liquor for mercury content before every run. It would also be advisable to run ash determinations from time to time, although little difficulty need be anticipated in this regard if stainless steel rather than Duriron were used for the reaction vessel.

CATALYST LOSSES. The practical success of the oxynitration process must depend ultimately on retention in the system of the expensive mercury catalyst. The experiments in glass apparatus established that no loss should occur according to the chemistry of the process. Actually the losses in the Duriron stoneware equipment averaged 5.1 gram of mercury per run over a 12-run series. This would correspond to about 1 cent per pound of pieric acid produced. However, the following five sources of loss could in practice largely be eliminated:

The mercury contained in the picric acid produced was determined on that part filtered in the centrifuge; the remainder, filtered on the nutsch, undoubtedly contained more mercury. Although identical washing procedures were employed, the setting point of the centrifuged product was 0.3° to 0.4° C. higher.

Some trouble with mercury entrainment was encountered both in the boil-off period and in the steam distillation of the by-product oil; efficient spray traps would eliminate this.

The gasket which secured the lid of the Duriron kettle contained 36 grams of mercury at the end of the series, and a break in this gasket (Figure 5) accounted for 0.5 gram per run. Metal chipped from the well washed interior of the Duriron

kettle contained 0.5% mercury at the end of this series of runs. All analyses involving evaporation of dilute solutions of mer-cury (acid distillate and steam distillate) were found, by a check run with a known amount of mercury, to be low by 10 to 15%.

#### HEALTH HAZARDS

A final question concerning the oxynitration is that of the health hazard involved in a process employing a mercury catalyst. George Lucas and Arthur Ham of the departments of pharmacology and anatomy of this university conducted 3month tests on three men working 60 hours per week on this project. The tests showed that mercury poisoning was not encountered, but that a slight anemia developed in one worker. This anemic condition was characteristic of dinitrobenzene poisoning.





#### Summary

The preparation of picric acid by simultaneous oxidation and nitration of benzene (the Wolffenstein-Böters reaction) has been investigated over a series of several hundred experiments. The procedure involved the reaction of benzene with a nitric acidcatalyst mixture, separation of the product from the cooled reaction mixture, and make-up of the latter to serve as the reaction liquor for the next run. The reaction was tested on two scales, the first in glass apparatus using 100 grams of benzene per run, and the second in metal equipment using 1250 grams of benzene per run. The main results obtained may be summarized as follows:

The yield of picric acid of satisfactory setting point consistently obtained was 1.5 parts from 1 part of benzene (a 50% yield). The consumption of nitric acid was 1.68 parts of nitric acid per

part of picric acid produced in the small scale runs, and 1.44 parts of nitric acid per part of picric acid in the larger scale runs. The difference may be attributed to a more efficient fume-recovery system in the latter case.

The optimum amounts of the catalyst metals were 0.28 mole of mercury, 0.015 mole of manganese, and 0.005 mole of aluminum, for reaction with 100 grams of benzene. The mercury concentration was somewhat critical; amounts below that specified necessitated a longer reaction time, and larger amounts increased the inorganic salt content of the reaction mixture to a point where concentration by distillation was interfered with.

The by-products of the reaction included significant amounts of dinitrobenzenes as well as the nitrobenzene previously known to be produced. The dinitrobenzenes, if allowed to accumulate in the reaction liquor, contaminated the product, lowered yield and setting point noticeably, and when separated after each run carried with them a substantial quantity of mercury. Avoidance of these difficulties constituted the most troublesome part of this investigation.

The evolution of oxides of nitrogen was not at a uniform rate, but relatively high toward the end of each run. This necessitated a fume-recovery system of a size out of proportion to the reaction vessel. This might in practice be dealt with by having one fumerecovery system common to two or more reactors.

Corrosion troubles were encountered with the Duriron equipment used for the larger scale work, and stainless steel would apparently have been much more satisfactory.

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## Variations in B.O.D. Velocity Constants of Sewage Dilutions

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N A RECENT study (1) of the biochemical oxygen demand (B.O.D.) of sewage from military areas, in which this laboratory cooperated, it was found that the mean velocity constant was considerably higher than the value of 0.1 at  $20^{\circ}$  C., which is generally accepted for domestic sewage. It was also noted that the K values for military sewage dilutions varied considerably. These findings were not in agreement with the generally accepted theory that the 5-day B.O.D. is directly proportional to the strength of the sewage. Also, although military sewage might be stronger than domestic sewage, on the basis of the general theory of biochemical oxidation there should be no essential difference in the rates of biochemical oxidation of domestic or military sewages. To determine the causes of the high K values and the

variation in these values, an intensive study was made of some of the factors that might be involved, such as time of storage, condition of storage, dilution water, and application of blank corrections. Some of the more important data and findings are assembled in this report.

In this study the B.O.D. at 20° C. of fifty-nine samples of domestic, military, and hospital sewage was measured daily over a period of 10 days. The domestic sewage used was a Cincinnati sewage originating from a densely populated section of the city. It was essentially free of industrial waste, had a 5-day B.O.D. of approximately 450 parts per million (p.p.m.), and was received in a fresh state. The hospital sewages were obtained from two sources, the U.S. Public Health Service Narcotic Hospital,