

STRATHMORE PARCHMENT

100% RAG U.S.A.

THE VAPOR PHASE OXIDATION
OF NITROBENZENE

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OF NITROBENZENE

By

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INTRODUCTION

o-Nitrophenol would be a very important raw material for the synthesis of a considerable number of organic compounds such as picric acid, *o*-aminophenol and a number of dyestuffs, if it were possible to produce it cheaply in large quantities.

At present there is no known method by which it may be prepared efficiently except by processes involving several steps. These time-consuming factors and the rather high cost naturally limit its use in the synthesis of other chemicals. At present, technical grade nitrobenzene is priced at \$.60 per kg while *o*-nitrophenol is priced at \$2.95 per kg.

It can be seen therefore that, if an efficient method could be devised for producing *o*-nitrophenol, the cost could be reduced considerably, perhaps to one-half the present price, and the *o*-nitrophenol could thereby be used more widely in industry for the synthesis of other chemicals.

A successful process of oxidizing nitrobenzene in the vapor state to *o*-nitrophenol could be made continuous and thus eliminate most of the time-consuming steps of the present method. The practical aspects of vapor-phase oxidations are, in general, well established in the production of other chemicals, but this particular problem has been studied only superficially (16).

HISTORICAL

The practical aspects of vapor-phase oxidations are, for the most part, rather new in chemical history. The principle itself, however, has been known since the turn of the nineteenth century.

One of the first serious studies of this subject was made by Clement in 1806 when he used a mixture of oxides of nitrogen as an accelerator in the oxidation of SO_2 by air. In 1817, H. Davy studied the influence of platinum on combustible gases and vapors. Du Long in 1823 studied the influence of metals, in general, on gaseous reactions. Vapor-phase oxidations of aromatic compounds are fairly new and some few have been put on a commercial scale. Among these are the production of maleic acid, benzaldehyde, and benzoic acid from benzene, and of phthalic anhydride from naphthalene (15, 21, 6). McCants' thesis (16) has been the only published study on the vapor-phase oxidation of nitrobenzene to o-nitrophenol, although the liquid-phase oxidation has been studied by Druker and others (7, 31). The results of these studies indicated that it might be possible to devise a process for the production of o-nitrophenol from nitrobenzene and to make the production of practical importance.

Weiss and Downs (29) in an attempt to find a practical catalyst for the oxidation of benzene with air to phenol tried "every metal and metal oxide which would be stable under the conditions of the experiment--and in addition many mixtures" without any great success. Bibb (2, 3) described a process for the production of phenol from benzene wherein he used nitrogen oxides or nitric acid vapors as catalysts in the reaction zone.

This is the first report of a homogeneous catalyst being successfully used in the production of phenols. Schmidt and Roh (26) in a German patent describe the preparation of phenol and halogenated phenols by the treatment of benzene or halogenated benzenes with oxygen in the vapor phase.

Moyer and Klingelhoefer (18) found they could produce phenols by passing a mixture of air and benzene through a reaction zone devoid of contact masses. Porter (23, 24) also has patented a process for the production of phenol from benzene. Kriebble and Denton (12) have patented a method for continuous manufacture of phenol from crude benzene with oxygen-containing gas. Rust and Vaughan (25) have patented a method of oxidizing alkylated aromatic hydrocarbons and their partially hydrogenated derivatives in the presence of HBr to produce high yields of substituted phenols, aromatic carboxylic acids, aromatic ketones, and aromatic peroxides. Harmon (11) found gaseous iodine to be an excellent homogeneous catalyst for the production of phenols from benzene.

The production of phenols from benzene in the vapor phase is rather closely related to the problem studied in this work and thus it has been used as basis for, and a check upon, the work done here.

THEORETICAL CONSIDERATIONS

At the present time, there are a number of theories regarding the mechanism of vapor-phase oxidations with molecular oxygen. Bone and his co-workers (4) carried out extensive research in trying to prove the stepwise formation of oxygenated products. From this work has come the present hydroxylation theory, according to which oxidation proceeds through conversions of successive carbon-bonded hydrogens to hydroxyl groups followed by decomposition through successive stages to give water and carbon dioxide as final products. Norrish (20) has developed a modification of the hydroxylation theory suggesting a mechanism involving the formation of free radicals. The second theory, which Bach (1) was one of the first to advocate, is the peroxide theory. It assumes that the oxygen and the hydrocarbon first form a peroxide or moloxide which then acts as the active oxidizing agent.

It has been shown that molecules of hydrocarbons and oxygen do not always combine immediately with each other (22). The oxidation of hydrocarbons is marked by an induction period. That is, if a mixture of a hydrocarbon and oxygen is passed into a heated reaction chamber, there is usually a period during which no noticeable reaction takes place. Thereafter the reaction becomes noticeable and gradually accelerates, sometimes reaching explosive proportions. This leaves little doubt that such hydrocarbon oxidations are chain reactions.

There are two explanations possible for the induction period. One is that an unknown inhibiting substance is gradually destroyed; the other, that some active substance capable of propagating

chains is accumulated. Experimental evidence tends to favor the latter explanation.

Lending support to the theory of Bone is the production of phenols from benzene by air oxidation (18). The presence of even small amounts of phenol indicates that phenol may be the initial oxidation product and shows that a hydroxylation mechanism, at least similar to that proposed by Bone, may occur in aromatic oxidation.

Marek, (14) in discussing methods and apparatus for the oxidation of hydrocarbons, states that aromatic hydrocarbons require high temperature and catalysts. He states, further, that the reaction proceeds in stages; therefore, a good yield of any intermediate oxidation product should be obtained if the process can be efficiently controlled.

Newitt and Burgoyne (19) reported that in the partial oxidation of benzene there are three stages before ring rupture takes place. They believe that, in the case of benzene, oxidation proceeds as a series of hydroxylations, yielding successively phenol, hydroquinone and finally quinone.

Tonomura (23) studied decomposition and oxidation products of toluene, ethylbenzene, n-propylbenzene, n-butylbenzene, isopropylbenzene, and tertiary butylbenzene, spectroscopically. These studies showed decomposition began with dehydrogenation, followed by demethylation, breaking off side chains, and the splitting of the nucleus. In oxidation of the alkylbenzenes, the reactive hydrogen in the side chain was oxidized, split off as hydroxyl and reattached in the original position. These

alcohols changed successively into the next lower alcohol and formaldehyde, producing finally phenol. At higher temperatures there was a formation of condensation products, all which were ortho isomers.

All of this indicates that the production of phenols from nitrobenzene is theoretically feasible and indicates the mechanism by which it may be accomplished. The exact mechanism for the production of the ortho isomer in the vapor-phase is not clearly defined, although it can be accounted for in the liquid phase by resonance of the molecule among ionic forms (7, 30). It is felt, however, that the o-nitrophenol, being the most volatile of three possible isomers, would be most likely to escape complete oxidation at higher temperatures.

One of the most important things to consider in a work of this sort is the question as to whether it is thermodynamically possible. Although this is not an absolute criterion, it is a starting point for further theoretical considerations.

An application of thermodynamic principles shows the oxidation of nitrobenzene to o-nitrophenol to be an exothermic reaction. Using data from the International Critical Tables the following calculations have been made:

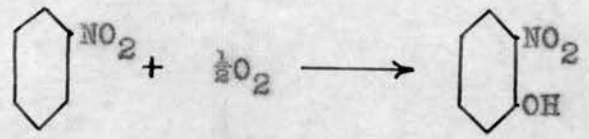
Heats of combustion of compounds in their standard states are

Nitrobenzene	-739,000 cal./mole (liquid)
o-Nitrophenol	-689,000 cal./mole (solid)

From the heats of combustions the heats of formation were calculated:

Nitrobenzene	4,000 cal./mole
o-Nitrophenol	-46,000 cal./mole

From the reaction



$$\Delta H_{\text{reaction}} = -46,000 - (4,000) = -50,000 \text{ cal.}$$

This shows the reaction to be exothermic. There are no available values for the entropy of o-nitrophenol; consequently, an estimated value was used to calculate the free energy of the reaction. The method of evaluation was by comparison of the known entropies of other reactions which were similar and whose products were phenols. The best estimated value for the entropy of the reaction is -35.0 eu/mole. As a maximum the entropy value probably does not exceed -60.0 eu/mole. The free energy calculations are based on these figures at 25° C.

$$\begin{aligned}
 \Delta F &= -50,000 - (298 \times -35.0) = -39,600 \text{ cal.} \\
 \Delta F &= -50,000 - (298 \times -60.0) = -32,100 \text{ cal.}
 \end{aligned}$$

Therefore for the above reaction

$$\Delta F \approx -35,000 \text{ cal.}$$

This compares favorably with the free energy values for the production of phenol from benzene, which was calculated to be about -40,000 cal.

Thus these calculations show that the free energy change is favorable for the reaction.

Kinetic studies on this reaction have not been made in heterogeneous systems; consequently, kinetic considerations have been omitted since they are impossible without some data from actual studies of the reaction.

In a reaction of this sort there are several variables which must be controlled to produce an efficient process. Moyer and Klingelhofer (18) showed that there was a definite correlation between the various reaction conditions of (1) temperature, (2) time of reaction or contact time, (3) pressure, and (4) ratio of oxygen to hydrocarbon. Since they used no catalysts, whereas catalysts were to be used in this work, there can be added two other factors--i.e. (5) preheating temperature, and (6) the catalyst.

APPARATUS AND PROCEDURE

The original problem in this work was to be an attempt to increase the yields of o-nitrophenol, using as a starting point the conditions McCants (16) found most favorable for production. It was the intent to vary conditions, one at a time, holding all others constant, to determine the effect of each. From this it was hoped to arrive at optimum operating conditions for an overall efficient process.

McCants (16) showed in his work that platinum gauze was the most efficient catalyst under the conditions at which he operated. He reported using an operating temperature of about 360° C. and obtaining a yield of about 1.5 per cent o-nitrophenol based on total input of nitrobenzene. It was for this reason that platinum gauze was chosen for the catalyst in these experiments. The gauze actually chosen had the composition, 98.3 per cent platinum, 1.6 per cent rhodium, and 0.1 per cent cobalt, this corresponding to one of the several types of platinum catalysts used industrially.

The contact time should be set at about 0.15 second at the start, since industrial experience shows this to be the average optimum contact time for this type reaction (11, 14). This could be controlled by regulating the pressure, the rate of flow through the apparatus, and the number of layers of platinum gauze.

The oxygen-nitrobenzene ratio was set at 2.5 volumes of oxygen to one volume of vaporized nitrobenzene, at the start, which gives slightly more oxygen than theoretically necessary. This was to be accomplished by bubbling heated air through heated nitrobenzene and passing the resulting mixture into the reaction

chamber. Theoretically, from the vapor pressure curves, the temperature at which the air would pick up the correct amount of nitrobenzene is 158° C.

With these factors arbitrarily fixed, the first step in the investigation was to determine the effect of variations in preheating and reaction temperature.

The first apparatus constructed was of a rather large design to accommodate all of the features considered essential. Figure 1 shows a cross-section view of the apparatus. The nitrobenzene-air mixer consisted of a 150 ml. flask which contained the nitrobenzene, a fritted glass spoon, 4 feet of copper tubing, and an oil bath. The fritted glass spoon was sealed into the flask to serve as a saturator for the incoming air. The copper tubing was coiled around the flask and immersed in the oil bath. One end of this tube served as an air inlet and the other end was attached to the glass spoon with a silver chloride seal. This construction served to preheat the incoming air and disperse the air in small bubbles through the nitrobenzene, thus saturating the air with nitrobenzene vapors. The air and nitrobenzene mixture was then passed into the reaction chamber through a heated side arm. This heated section was to serve as a preheater for the incoming gases as well as to prevent condensation of the nitrobenzene. The reaction chamber was a glass tube $2\frac{1}{2}$ inches in diameter and 18 inches long. The gas inlet was 6 inches from the top of the tube and the platinum gauze was placed on a stainless steel platform 6 inches from the bottom. The middle portion of the tube served as a further preheater and mixer. The whole tube, as well as the side

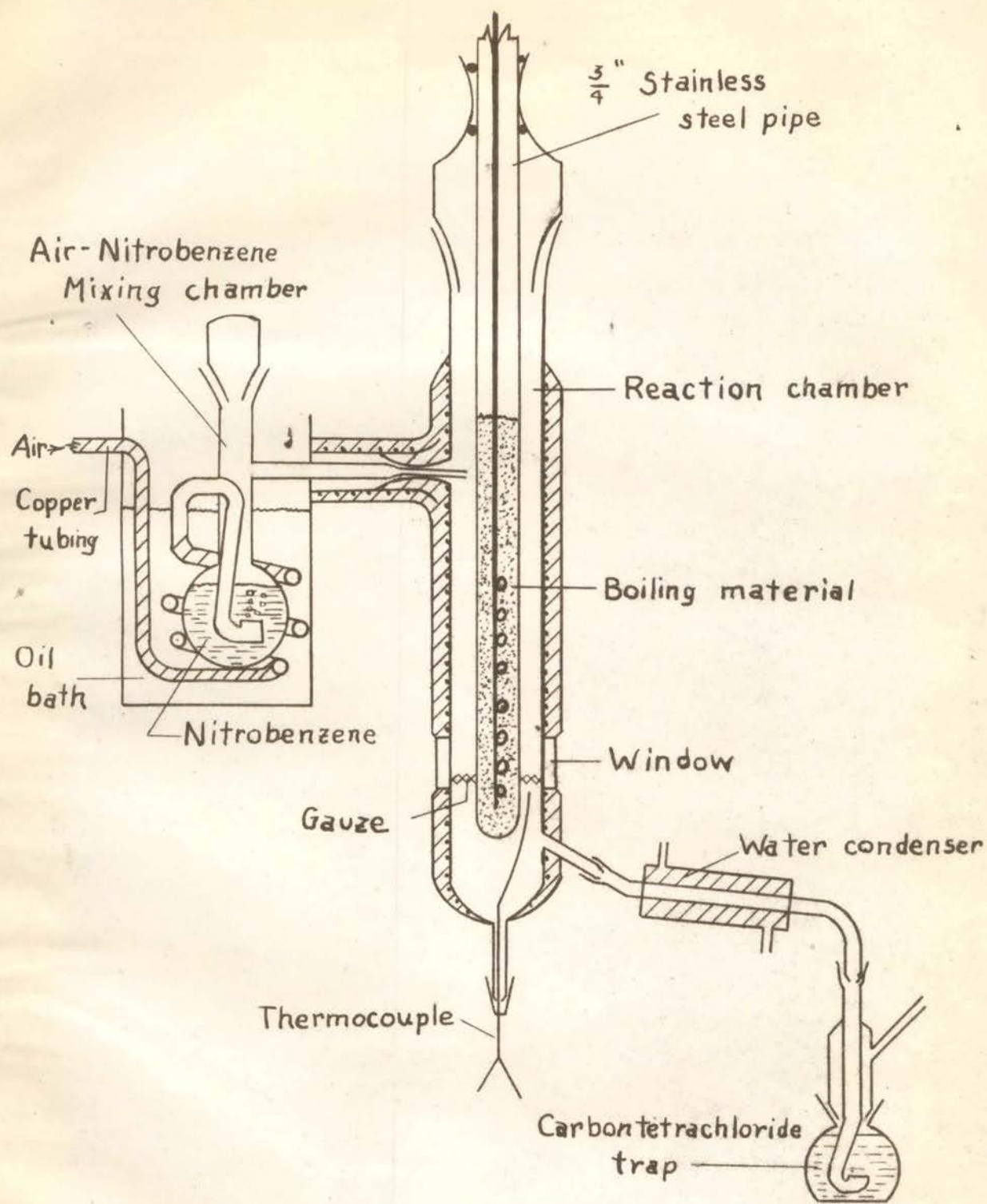


Figure 1
Cross Sectional View

arm, was heated electrically with two nichrome wire heating elements wrapped on the outside of the reaction tube. These heating elements were arranged to work independently or together to give better temperature control. A series of adjustable resistances was used to control the temperature of the nichrome heating elements. Running through the center of the reaction chamber was a 3/4-inch stainless steel pipe, welded shut at one end, to serve as a boiler, the upper part of this pipe serving as an air condenser. The tube was held in place in the reaction chamber through a ground glass joint attached to the pipe by a silver chloride seal. In the stainless steel pipe was placed a material whose boiling point was approximately equal to the temperature at which the reaction was to be carried out. The material was heated electrically by means of a nichrome heating coil inserted into the material inside the stainless steel tube. By boiling the liquid, the reaction mixture could be brought up to the operating temperature and once the reaction started the boiling liquid would serve as a temperature control by dissipation of the excess heat from the reaction to the liquid and thus to the outside air. Into the bottom of the reaction chamber was fitted a constantan-iron thermocouple extending to a position just below the gauze. This was to measure the temperature of the gases passing through the gauze. The whole reaction tube was insulated with magnesium-asbestos plastic insulating material except for a small section around the catalyst which was insulated by a dead air space provided by a glass sleeve imbedded in the insulating material. This was done to form a window through which the catalyst could

be observed at all times. Near the bottom of the reaction chamber was placed a product take-off arm to which was attached a large-capacity water condenser for cooling the gases. The gases were then passed through a fritted glass spoon immersed in a flask containing CCl_4 . This was the method which McCants (16) found most efficient for condensing the mists and vapors formed.

Air under pressure was needed in these experiments; consequently an air pump with a surge tank was used as a source of air. Between the surge tank and the air inlet into the air-nitrobenzene mixer was placed an open-end mercury manometer, a calcium chloride drying tower, and a nitrobenzene-filled flow meter. These were for regulation of the pressure and rate of flow through the reaction tube.

The first experimental attempts with this apparatus were run along the lines previously outlined. The catalyst was platinum gauze, 80 mesh, of the composition described earlier. The gauzes were cut in the form of rings which exactly filled the space between the walls of the reaction chamber and the stainless steel boiler tube. Two thicknesses of platinum gauze were used.

The contact time was determined by assembling the apparatus without nitrobenzene in the air-nitrobenzene mixing chamber, bringing the temperatures up to operating conditions, and measuring the volume of gas passed through the apparatus per unit time. From the measured volumes of gas and the volume of the platinum gauzes, the contact time was calculated. The actual contact time used was 0.14 second with a pressure of 11.5 cm. of mercury (above atmospheric pressure) and a flow meter reading of 16 cm.

of nitrobenzene. The actual volume of gas passed through the catalyst, under these conditions, was 10 cc. per second.

The air-nitrobenzene mixer bath was maintained at 160° C. to give the proposed oxygen-nitrobenzene ratio.

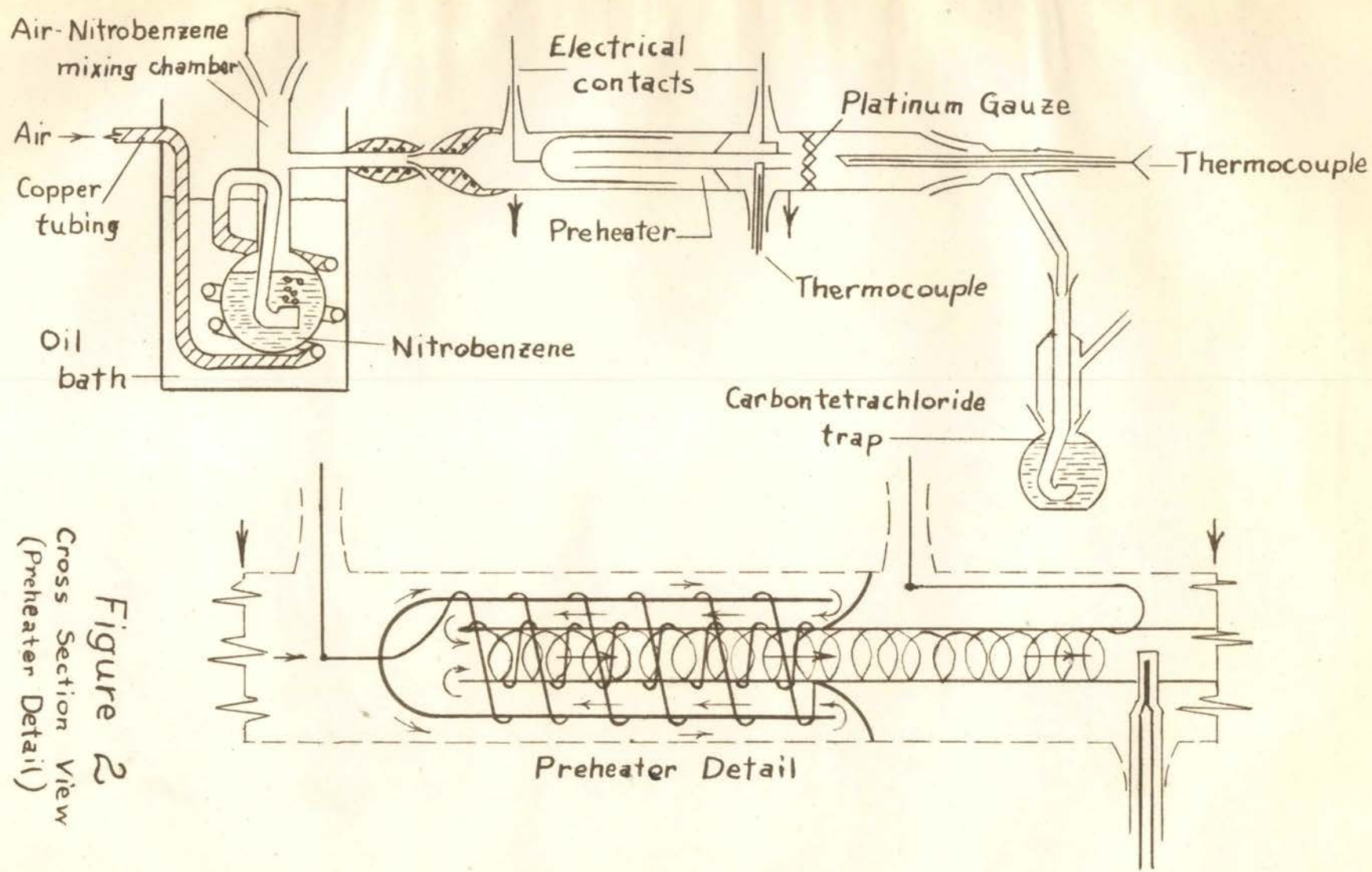
All of these conditions were maintained throughout operation of the first apparatus. The temperatures of the preheater and the reaction chamber were the only variables changed. The preheater temperature was maintained about midway between that of the air-nitrobenzene mixer bath and the temperature of the reaction chamber.

Using the apparatus in this manner, tests were made at a number of temperatures (reaction chamber) from 320° to 470° C. with no detectable results. On the fifth attempt, while the apparatus was being brought up to operating temperature, a sudden explosion occurred. The temperature recorded at this point was only 220° C. In view of the fact that no reaction had been obtained previously at much higher measured temperatures, these results were interpreted as indicating local superheating due to improper design of the apparatus. In view of this, the original problem of increasing the production of o-nitrophenol from nitrobenzene was changed to the problem of designing apparatus capable of being used for further more carefully controlled studies.

Consequently, a second apparatus was designed and built on a smaller and simpler scale to reduce the problem of construction and to gain greater control over operating conditions. It was felt that the problem of efficiently heating the air-nitrobenzene to a high enough, controlled preheat temperature had not been

accomplished in the first apparatus, since it appeared to be in the preheater that the explosion centered. The second apparatus was designed to study this problem.

The pressure system and the air-nitrobenzene mixer was the same as that used in the first piece of apparatus described. The essential difference in this apparatus was the preheater, whose details are shown in Figure 2. The inlet tube to the preheater was jacketed and heated electrically to keep vapors from condensing before they reached the preheater. The preheater itself consisted of two glass tubes wrapped with nichrome wire to serve as the heater, electrical contacts to the outside being made through platinum wires sealed through the glass wall. The first tube was sealed at the end meeting the incoming gas and was just small enough to slide into the main reaction tube and allow for air passage between them. The second tube was of still smaller diameter, slipping into the first and having a flared section near its outer end which was just large enough to fit snugly into the reaction tube. The second tube was long enough to allow free air flow through the front end and to extend to a point approximately one-fourth inch from the gauze. Near the outlet was a hole in the tube which allowed a thermocouple to be inserted into the stream of preheated gases just before they reached the gauze. This permitted measurements to be made of the temperature of the preheated gases. One section of the nichrome heating spiral was placed on the inside of the smaller tube. A second spiral was wound back over the outside of the small tube, and a third over the outside of the larger tube. The three spirals were connected



in series. This design gave a maximum of heating and mixing in a minimum of distance. The platinum gauze was placed directly in front of the preheater outlet and was supported by two nichrome expansion rings. The gauze was of the same material previously described and was cut in a disk to fit inside the reaction tube. Two thicknesses of the gauze were again used. Directly behind the gauze was placed a thermocouple to measure the temperature of the gases immediately after they passed through the gauze. At the exit end of the reaction chamber was placed another fritted-glass spoon immersed in carbon tetrachloride to catch the products --the same arrangement as that used in the first apparatus.

The experiments with this apparatus showed results on the first run. The conditions of operation were the same as those used with the first apparatus, except that now there was no direct method of controlling the reaction temperature. It was expected to control the temperature by changing the rate of flow of gases through the equipment.

In the first run it was found that it would be necessary to keep the temperature of the nichrome preheating coil low if the burning of the nitrobenzene vapors was to be prevented. This was accomplished by using external resistances to keep the nichrome heater wire below the temperature which produced a dull red glow. At the end of about five minutes of operation under these conditions, however, there suddenly occurred a light blue flash of fire, running along the inner tube preheater coil. After several such flashes, the flame settled upon a small section of the coil, burning in this section, producing enough heat to cause the coil

to become white-hot. At this point, although all the heating current through the preheater was cut off, the wire continued to glow as before.

The flame was extinguished and the preheater temperature was considerably lowered. At the recorded temperatures of 180° C. for the preheater and of 95° C. for the gas behind the gauze, there appeared a formation of fog--a phenomenon which seemed to occur whenever reaction took place. Even at these recorded temperatures, when an excess of oxygen was allowed in the reaction chamber small explosions occurred. A test of the products (with alkali) showed phenols to be present. A series of new runs confirmed the results observed in the first run.

The recorded temperatures appeared to be suspiciously low in view of the fact that runs made at much higher recorded temperatures in the first apparatus showed no detectable results. Therefore, it was felt that perhaps the nichrome heating coil was overheating and that reaction was occurring at the heating coil rather than at the platinum gauze. Consequently, the next runs were made without the platinum catalyst in place. These experiments were designed to determine if phenol could be produced without the platinum catalyst, under the same conditions. It was found that, under identical conditions, all the results obtained in the first set of experiments with this equipment were reproducible even without the platinum gauze. Thus it appeared that the nichrome wire, when heated electrically, was itself a catalyst for this reaction--though not necessarily a good one.

As was obvious both from thermodynamic calculations of free

energy change and from the observed flame, the reaction is exothermic. It seemed reasonable, therefore, that if the preheater wire were sufficiently hot to initiate a small amount of reaction, the heat produced would raise the temperature of the wires still more. This heating would be aided by the fact that heat loss from the wire would be decreased and the current would heat the wire to still greater temperatures. Direct electrical heating, therefore, seemed to be inadvisable. As a result a preheater was designed which would (1) eliminate metal surfaces in the preheating zone, and (2) have a certain amount of heat capacity to oppose rises in temperature. Figure 3 shows a cross-sectional view of the preheater. The preheater coil consisted of a pyrex glass tube 8 mm. in diameter, in the form of a spiral. The spiral was about four inches in diameter and consisted of 9 turns spaced about one-half inch apart. The inlet end began at the top of the bath and spiraled to the bottom, the outlet tube coming vertically up from the bottom in a position to allow the gases to enter a reaction chamber or to permit the use of this vertical portion itself as a reaction tube, if desired. The whole spiral was immersed in a bath which contained oil, for lower preheat temperatures, or a mixture of molten salts for higher temperatures. In the center of the bath was placed a motor-driven propeller-type stirrer.

With this design a wide range of preheat temperatures could be covered for study. If the length of heating tube in the coil proved insufficient, a second coil of smaller diameter could be nested in the first and the two connected in series.

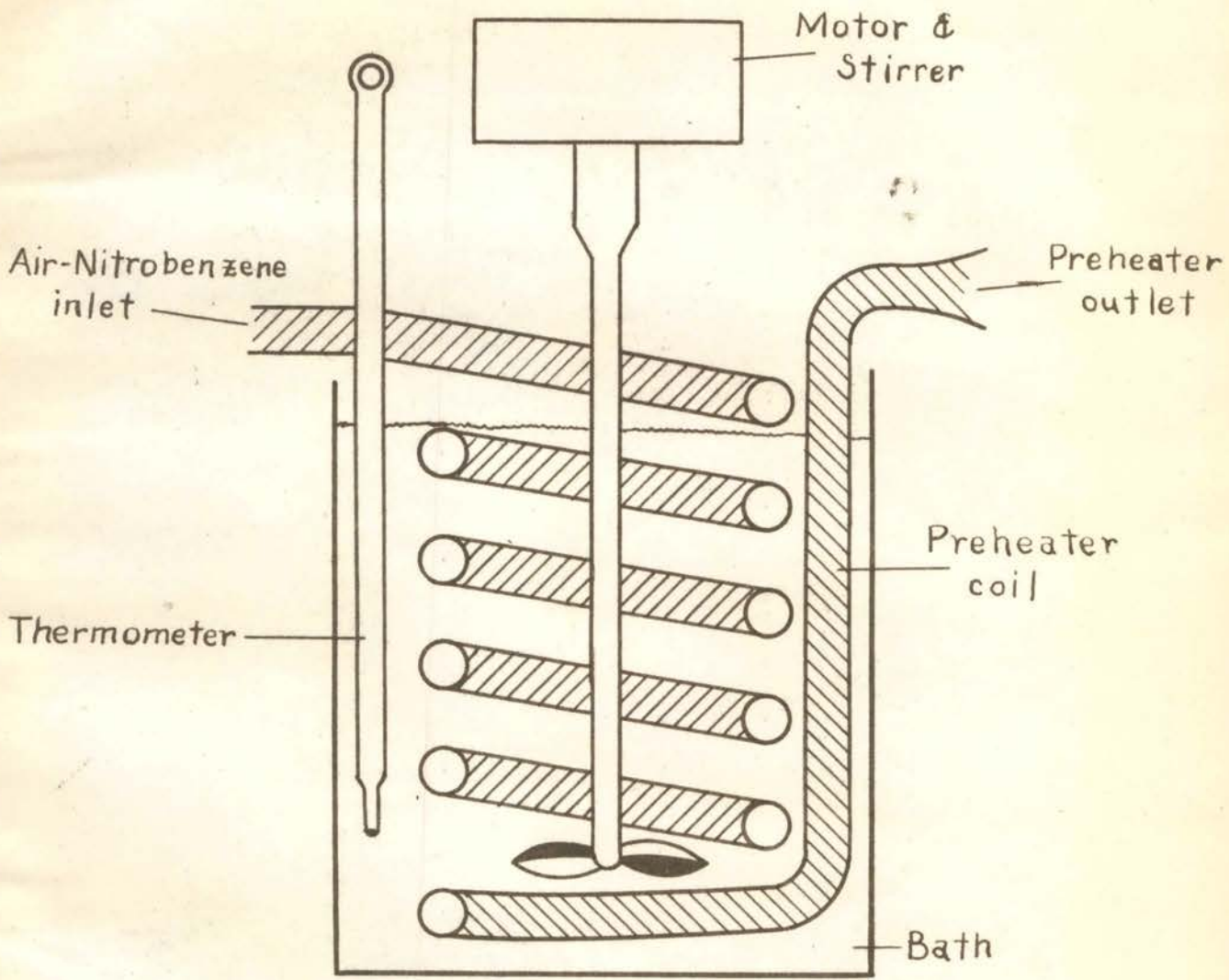


Figure 3
Cross Section view
Preheater

It was found in actual operation of this preheater, that an equivalent of 4 feet of the tubing, or three turns of the coil, were sufficient for heating the gases to the desired temperature of operation over a pressure range of 2 cm. to 11 cm. of mercury. These runs were made using the full capacity of the pressure system without the two glass spoons or other restricting objects in the system, so that it was felt the capacity of this preheater was entirely adequate. In arriving at this conclusion, several bath components were used. The first runs were made with hydrogenated melting-point wax as a heating liquid, at a series of temperatures between 197° C. and 250° C. In trying to determine the exit temperature of the gases from the preheater, it was found that the temperatures measured at a point within the tube near the outlet appeared to increase almost linearly with increasing pressure and flow. This indicated that the cooler portions of the glass exit tube were cooling the gases as they left the level of the bath liquid. Consequently, measurements of temperature were made at different levels in the vertical exit tube. It was found that the temperatures did not vary as the rate of flow was changed if the thermocouple was in the tube at or any place below the liquid level. Consequently, checks were made simultaneously of bath and exit gas temperatures with the thermocouple in the exit tube just at liquid level, and with only three turns of the coil immersed in the liquid. Under these conditions the results listed in Table 1 were obtained. For higher temperatures (above 325° C.) a bath of molten lead replaced the wax bath.

As the results of these tests indicated that the new pre-

heater was working with the desired efficiency, two test runs were made with catalysts in the apparatus and with the air-nitrobenzene mixture described earlier.

Table 1

Results of Preheater Tests

Rate of Flow ¹	Temperature (°C)		Difference in Temperature (°C)
	Bath	Exit Gases	
12 cm.	197°	185°	12°
12 cm.	209°	200°	9°
3 cm.	217°	210°	7°
12 cm.	217°	210°	7°
2 cm.	227°	220°	7°
4 cm.	227°	220°	7°
6 cm.	230°	225°	5°
7 cm.	250°	240°	10°
3 cm.	340°	305°	35°
6 cm.	375°	350°	45°
3 cm.	410°	350°	60°

¹In this work it was assumed that the rate of flow would be proportional to the pressure of the gas supplied. The values given here are pressure values expressed as centimeters of mercury.

The apparatus was the same as used previously except that the exit arm of the preheater coil was used as the reaction chamber and the former reaction chamber was used as an air condenser. The preheater bath container was lagged with magnesia-asbestos mixture to prevent excessive heat losses at the outside of the lead bath, and the bath was heated by a gas flame. Using two thicknesses of platinum gauze as the catalyst, runs were made over a temperature range from about 350° to 500° C. bath temperature. The gas temperatures were 300° to 450° C. It was found that at a bath temperature of 460° and gas temperature of about

400° C., the characteristic fog of reaction appeared. A second run was made using the above procedure with, however, in place of the platinum gauzes, a nichrome spiral three inches long. The nichrome previously had been oxidized by heating to redness in the open air, an electrical current being used for this purpose. At recorded temperatures of 330° C. for the preheater bath and about 300° C. for the gas temperature, this apparatus produced the characteristic fog also. It was further noted in these experiments that there was no apparent reaction of the nitrobenzene at the highest temperatures used except in the presence of a catalyst. The glass walls of the tube seemed to have little or no catalytic action.

These experiments showed that the new apparatus, and particularly the preheater, was efficient in overcoming the difficulties hitherto encountered. These tests show further that the preheating temperature is a very vital factor in producing an efficient process.

DISCUSSION OF RESULTS

There is much work that remains to be done on this problem before an exact and efficient process can be developed. The equipment developed in this work has proved efficient, in actual operation, for studies of the vapor-phase oxidation of nitrobenzene to o-nitrophenol. It is also an apparatus which could well be used to study other vapor-phase oxidations.

As was found in this work, two main tasks needed to be accomplished: (1) the development of a preheater in which the gaseous reaction mixture could be heated to an accurately known temperature in the absence of any catalyst which might cause reaction at this point, and (2) the development of a reaction chamber in which the catalyst could be supported and which would provide some compensation for the heat produced by the reaction.

The first of these aims seems to have been accomplished in the bath-type preheater last described. The hot liquid in the bath has sufficient heat capacity to heat the gases efficiently, but it is impossible for hot-spots to be developed within this part of the system. The all-glass preheater coil apparently has no catalytic effect; consequently, any reaction which might be observed must be at the surface of the catalyst in the reaction chamber.

The second aim was accomplished by means of the simple reaction chamber illustrated in Figure 2. If the outlet from the preheater is brought close to the gauze the gases will be at their full preheat temperature as they strike it. The gauze may be heated by an external heater of a liquid-jacket type if the re-

action is found to need such control. The gauze itself could be electrically heated by passing a current directly through it to initiate the reaction.

No attempt was made at analysis of oxidation products other than testing for phenols and for CO_2 , since the immediate needs of this research were met by determining whether oxidation had taken place within the apparatus.

Kinetic studies of this reaction would be very valuable in determining further changes in the design of apparatus for this reaction. Other problems which might well be worth studying are the possibilities of nickel and cobalt, either the metals or their oxides, by themselves or in mixtures, acting as a catalyst for this reaction. Also studies of homogeneous catalysts such as oxides of nitrogen, gaseous halogens, and gaseous hydrogen halides should be undertaken. For studies of the latter, the preheater unit itself might well serve as a reaction chamber.

SUMMARY

A review was conducted of available literature pertaining to vapor-phase oxidation of aromatic compounds to phenols.

Several apparatuses for the study of the vapor phase air-oxidation of nitrobenzene were constructed and the good and poor points of each studied.

It was decided that such an apparatus must have the following features: (1) good preheating temperature control, (2) means for controlling the heat of reaction at the catalyst, (3) walls of the apparatus must exhibit no catalytic action, (4) an adequate means for controlling air-nitrobenzene ratios without allowing condensation of the nitrobenzene to take place before it reaches the catalyst, and (5) the reaction chamber must contain a means of supporting a catalyst and have a mechanism for dissipating the excess heat of reaction.

An apparatus was developed which embraced the above features. Tests of this apparatus showed that results were much better than those obtained with earlier designs.

Suggestions have been made which should be of value in further work on this problem.

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BIOGRAPHY

Clifton Norton Sechrist was born at Liberal, Missouri, March 29, 1920. He completed grade school, junior high school, and high school at Neosho, Missouri, with a science major in the spring of 1938. That fall he entered Oklahoma A. and M. College at Stillwater, Oklahoma and received a Bachelor of Science degree in 1942.

In August of 1942 he was employed by the E. I. DuPont Company of Wilmington, Delaware and assigned as chemist in their Wabash River Ordinance Plant at Terre Haute, Indiana where he remained until August, 1944. On June 12, 1944 he received a commission as Ensign in the United States Naval Reserve and was placed on active duty August, 1944. After attending officers school in Plattsburg, New York, he was sent to the Pacific Theater of Operations with the Third and Fifth Fleet. He returned to the United States in December, 1945. After release to inactive duty in May, 1946, he returned to his home in Neosho, Missouri.

In September, 1946, he entered the Graduate School of Oklahoma A. and M. College where he has been employed as a graduate fellow in the Department of Chemistry until the present time.

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