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AIR OXIDATION OF PARA-NITROTOLUENE

BY

ALBERT E. MEISINGER JR.

A THESIS

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ABSTRACT

The original purpose of this paper was to investigate the reaction kinetics of the air oxidation of para-nitrotoluene (PNT) to para-nitrobenzoic acid (PNBA). The reaction was to be carried out at atmospheric pressure and at temperatures between 100 and 175° C, and in the presence of an oxidation catalyst. However the main problem became one of trying to find a catalyst that would work at these conditions. The catalysts used were nickel acetate, cobaltous acetate, manganous acetate and manganese naphthenate. Hydrogen peroxide was tried as an accelerator for the reaction. None of these worked since no yield greater than 0.01% PNBA was ever obtained even after runs of up to 29 hours.

Because such low yields were obtained it is concluded that the oxidation conditions were not vigorous enough and that much higher pressures should be used to carry out the liquid phase oxidation of PNT with gaseous oxygen. The high pressure oxidation could not be tried because suitable equipment was not available.

ACKNOWLEDGEMENT

I would like to thank Dr. Saul I. Kreps of Newark College of Engineering for his help and advice on this work.

I would also like to thank my sister, Sally, for her time and effort in typing up this report.

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MECHANISM OF OXIDATION

Oxidation, according to the modern concepts, is the loss of electrons by a substance. An oxidation of one type is shown in the following reaction with the ferrous ion being oxidized to the ferric ion by losing an electron.

$$Fe^{++} \longrightarrow Fe^{+++} + e$$

Most atoms and free radicals, with the exceptions of atomic hydrogen and metallic ions, have deficient electron shells and therefore may act as oxidizing agents by removing electrons from other species. Molecular oxygen may become an oxidizing agent by acting as the diradical -O-O- and abstracting electrons from other substances. (1)

The oxidation of a hydrocarbon can give a wide variety of products including water, carbon monoxide, carbon dioxide, acids, alcohols, aldehydes, peroxides and olefins. For the catalytic oxidation involving air or other substances containing oxygen there has been suggested various mechanisms. One mechanism suggests that an intermediate substance is formed, which has a stronger oxidizing potential with respect to the substance to be oxidized. In this mechanism the catalyst adsorbs oxygen and creates a compound which is a better oxidizing agent. It then gives off the adsorbed oxygen to the reactant and is regenerated in its original form, after which it is capable of adsorbing more oxygen. In this way small quantities of catalyst are capable of converting large quantities of reacting substance. (2) Some examples that show only a small amount of catalyst is needed are mentioned later on in the section "Selection of Air Oxidation Catalysts."

Catalytic oxidation using air or oxygen may be carried out in a gaseous or liquid medium. If the mixture of oxidizing gas and the vapor of the substance to be oxidized is passed through a catalyst at the required temperature there is danger of an explosion if the temperature is high enough. These gas phase reactions are believed to proceed by a free radical mechanism. One or more of the steps may give rise to an increase in the number of free radicals, such as the reaction below, where atomic hydrogen reacts with a molecule of oxygen to give rise to two radicals, OH and O.

$$H + O_2 \longrightarrow HO + O$$

If these reactions occur to a sufficient extent and the number of free radicals increases rapidly an explosion may occur. The explosion is caused because the reactions occur almost instantaneously. (3) Oxidations in the liquid phase are found to proceed also by this free radical mechanism and therefore the possibility of an explosion also exists.

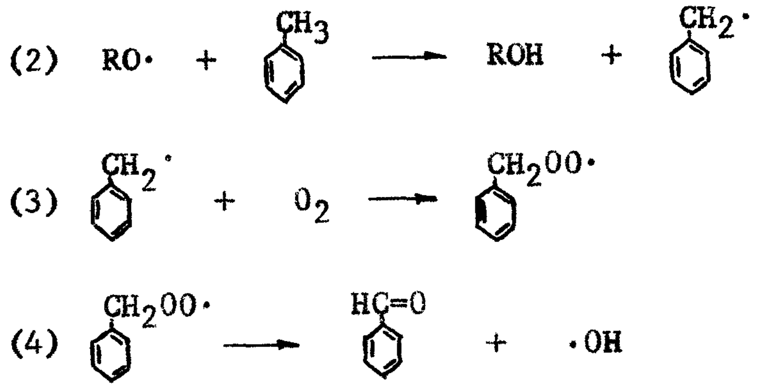
A reaction producing an increase in the total number of free radicals is known as a branching reaction and the overall process is known as a branching chain process. (4) The following is a general schematic set of reactions. It may be seen from these reactions that branching may give rise to an explosion.

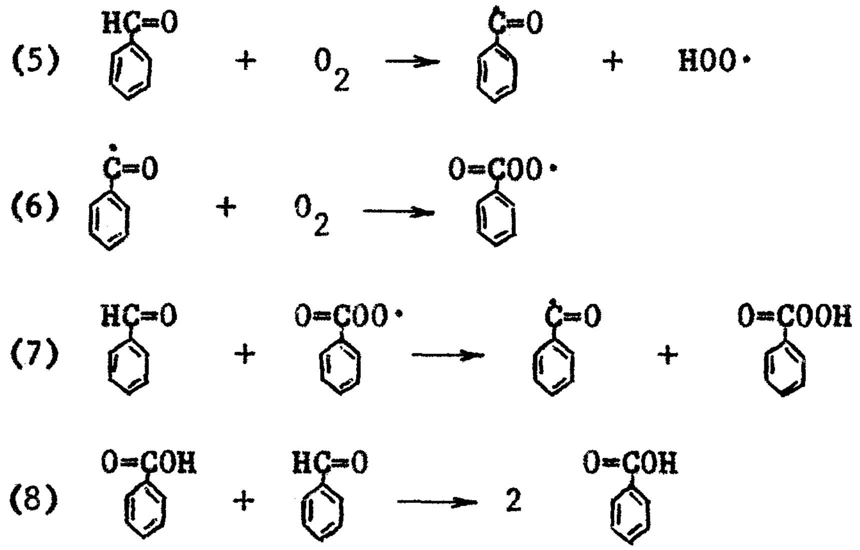
(1) $A \longrightarrow M$	Chain Initiation
(2) $M + B \longrightarrow \alpha N + \beta N$	Chain Branching
(3) $N + A \longrightarrow$ Products	Reaction to Give Products
(4) $M \longrightarrow ?$	Destruction at Surface of Reaction Vessel
(5) $N \longrightarrow ?$	Destruction in the Gas Phase of the Reaction

Reaction (1) is the chain-initiating step which produces the initial free radicals. This may be the type where $H_2 \longrightarrow 2H$, which produces two free radicals from one molecule. Reaction (2) is the chain-branching mechanism in which α plus β free radicals are produced from a collision of B and M. Reaction (3) is the formation of final products and the disappearance of some of the free radicals. In (4) and (5) the two general methods of destroying the left-over free radicals are shown. Free radicals M may revert back to molecule A by reacting on the surface of the reaction vessel. Free radical N may react with another free radical or a molecule in the gas phase of the reactor and form a molecule of product. The meaning of reaction (2) is that the total number of free radicals produced in the chain-branching step is greater than the number destroyed, so that no stationary state, where the number of free radicals is constant, is possible and an explosion may occur.(5)

A mechanism that might be proposed for the oxidation of toluene to benzoic acid is outlined below.(6) (7)

(1) Catalyst $\longrightarrow RO\cdot$





In reaction (1) the catalyst decomposes to give a free radical which can abstract a hydrogen atom from the methyl group in toluene to form the benzyl free radical. This is shown in the second reaction. The benzyl free radical then reacts with a molecule of oxygen to form the peroxide radical. In reaction (4) the peroxide radical decomposes to benzaldehyde and the ·OH free radical. The benzaldehyde then reacts with a molecule of oxygen losing an H atom to form a new free radical as shown in reaction (5). This benzoyl free radical reacts with another molecule of oxygen to form a benzoylperoxy free radical. In reaction (7) a molecule of benzaldehyde reacts with a benzoylperoxy free radical to form the perbenzoic acid plus the benzoyl free radical. A molecule of perbenzoic acid then reacts with a molecule of benzaldehyde to form two molecules of benzoic acid.

ALTERNATE METHODS OF OXIDATION

In liquid phase oxidation it is possible to use either gaseous oxygen or compounds having oxidizing power. Some of the compounds having the ability to oxidize other compounds are discussed below. (8)

Permanganates

Permanganic acid forms solid salts that are powerful oxidizing agents. Potassium permanganate is one of the commonest and most useful agents used for oxidizing organic compounds. The oxidizing strength of the potassium permanganate depends upon the pH of the solution in which it is used. In acid solution potassium permanganate yields a very powerful oxidizing agent useful only in the preparation of very stable compounds. The acidic oxidation may proceed by either of the following mechanisms depending on the compounds involved. There may be direct oxidation by the permanganate ion or there may be the formation of the Mn^{++} ion and the subsequent oxidation by hydroxyl radicals produced by the Mn^{++} ion and water. (9) Permanganate is used to oxidize both aliphatic and aromatic sulfides to their corresponding sulfonic acids. It is also used for the oxidation of side chains on benzene and thus it would be good for the oxidation of PNT to PNBA.

Dichromates

Most commonly employed is dichromic acid in aqueous sulfuric acid (sodium dichromate and sulfuric acid) or chromic anhydride (chromium trioxide) dissolved in glacial acetic acid. These produce an electron deficient species which may be a positive ion or a molecule with an electron deficient atom. Dichromic acid oxidizes by way of the $[^{+}CrO_3H]$ ion which may be produced in the following equilibrium.(10)

$$H_2Cr_2O_7 + 3H_2SO_4 \longrightarrow 2[^{+}CrO_3H] + 3[HSO_4^{-}] + [H_3O^{+}]$$

Chromic acid is an excellent oxidizing agent for organic compounds.

Peroxides

The four main inorganic peroxides used as oxidizing agents are those of lead, manganese, hydrogen and some peracids. Lead peroxide (PbO_2) is used with acetic, sulfuric or hydrochloric acids. One mole of lead peroxide mixed with an acid yields one atom of oxygen and the salt of the acid, as shown below;

$$PbO_2 + H_2SO_4 \longrightarrow PbSO_4 + H_2O + (O)$$

Manganese dioxide is used with sulfuric acid to release one atom of oxygen per mole of MnO_2. One of its major uses is to oxidize toluene to benzaldehyde. The major use of hydrogen peroxide is in the bleaching of textiles, paper and pulp. Also most silks, woolen goods, rayon fabrics and light cotton goods are bleached with hydrogen peroxide. (11)

Nitric Acid

Nitric acid can be used as an oxidizing agent but it has the disadvantage of also having the tendency to act as a nitrating agent and some of the product may be nitro derivatives. However it is very good for oxidizing substances that are already nitrated. Oxidation of benzene homologues with dilute acid to form the carboxylic acid is slow. Nitrogen tetroxide is also a good oxidizer of hydrocarbons and substituted hydrocarbons. (12)

Fuming Sulfuric Acid (Oleum)

Fuming sulfuric acid (H_2SO_4 + SO_3) mixed with mercury salts is a very powerful oxidizing agent. Fuming sulfuric acid is used to add hydroxyl groups in anthroquinone derivatives for making different alizarin dyes. (13)

Ozone

In addition to the oxygen in the air, ozone is another good gaseous oxidizing agent. Ozone is used in the vapor phase oxidation of olefins and it is also used for several different oxidations in drug manufacture. (14)

Besides oxidation by gaseous air or ozone, or by oxygen containing compounds there is another way to carry out an oxidation. This is by electrolytic means. However according to Shamy (15) the electrolytic oxidation process to produce p-nitrobenzoic acid from p-nitrotoluene is not economically feasible at this time. This is because the cost of raw materials for the electrolytic process is about 94% of the PNBA selling price, but to be economically feasible the raw material cost should not exceed 50% of the product's selling cost.

A method for carrying out oxidations that would be much cheaper than any of the previously mentioned methods would be to use the oxygen from the air. However while this method is potentially one of the cheapest it is also one of the most difficult to control. Most of the air oxidations are carried out under high pressure which causes this method to loose a lot of its economic advantage because of the expensive high pressure equipment required. However if the oxidation could be carried out under atmospheric pressure then it would have both a technical and a large economic advantage over other methods.

SELECTION OF AIR OXIDATION CATALYSTS

Catalysts function in an oxidation not only by increasing the rate of a reaction at a certain temperature, but also to reduce the temperature and energy of activation required to carry out the reaction. The catalyst and the selected physical conditions regulate the velocity and direction of the oxidation and also the extent of the reaction.

To obtain even a small yield of PNBA under the conditions to be used a catalyst is necessary. Even oxidations carried out at high pressures of about 75 atmospheres require catalysts, therefore under our conditions of just atmospheric pressure an oxidation catalyst would be essential.

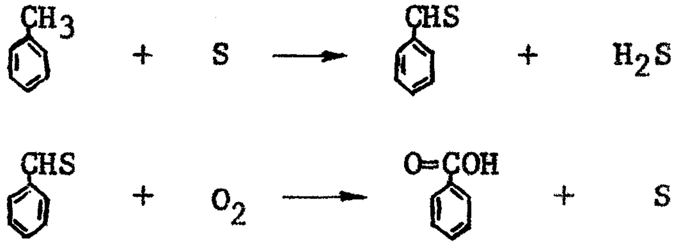
Temperature seems to be the most important factor influencing the rate of oxidation. However the rate is also very pressure dependent, proceeding faster at the higher pressures. Also effecting the rate, besides the type of catalyst, is the concentration of the catalyst over a wide concentration range.(16)

The amount of catalyst would depend upon the particular catalyst being used. Conner (17), for his oxygen containing gas oxidation of p-cymene varied the weight of catalyst from 0.05 to 10% by weight of aromatic compound. However his most desired range was from 1 to 3%. The catalysts tried by Conner were alkali metal and alkaline earth metal oxides and hydroxides.

Hull (18), in his oxidation of aromatic compounds (toluene to benzoic acid, ortho-xylene to ortho-toluic acid, acetophenone to benzoic acid, allyl benzene to benzoic acid) using pressures from 1 to 10 atmospheres, varied the weight of catalyst (cobalt acetate) from 3 to 6% by weight of aromatic compound.

It is known that metals of the platinum group and oxides and salts of elements that can exist in several oxidation states, such as oxides of tungsten, vanadium, molybdenum and thorium are most suitable as catalysts of heterogeneous oxidation processes. The transition elements which stand at the minima of the atomic volume curve are the best catalysts for oxidation reactions in their oxide form. The ions of these transition elements can absorb electrons to complete their outermost shell. The elements are characterized by the ease with which electrons can be removed both from the outermost shell of electrons and the next inner shell to form bivalent and trivalent ions. (19) Some of the most useful metals for oxidation are; cobalt, cerium, manganese, iron, copper, uranium, nickel, lead and chromium.(20) Substances that also can act as promoters are the salts of barium, magnesium and potassium. Peroxides, peracids, aldehydes, ketones, olefins or organic substances forming peroxides can be used as initiators to help start the reaction.(21) The type of metal salts that seem to be best for this oxidation include; stearates, benzoates, naphthenates, oleates and acetyl acetonates. (22) Many variations and additions are possible with the standard oxidation catalysts mentioned above.

One different type of catalysis was performed by Mills(23), who for the oxidation of alkyl aromatics added elemental sulfur. During the oxidation the sulfur reacts with the alkyl group to produce hydrogen sulfide and an unstable dehydrogenation product. This dehydrogenation product is very susceptible to oxidation and ultimately forms a carboxyl group. The reactions are shown below.



The H_2S which is produced is to a large extent converted back to elemental sulfur by oxidation by means of the oxygen gas in the reaction medium.

$$2\ H_2S + O_2 \longrightarrow 2\ S + 2\ H_2O$$

The amount of sulfur was varied from 0.005 to 0.1 mole sulfur per mole of charge stock. In addition to the sulfur other metallic catalysts could be used at the same time. Mills used pressures that varied from 1 atmosphere to 500 psig and temperatures that ranged from 250 to 400°F. He used 300°F and 10 psig for the liquid phase oxidation of m-xylene using 0.05 wt. % of cobalt naphthenate as a catalyst.

McIntyre (24), discusses the use of bromine or a bromine containing compound as a catalyst. For organic compounds with a benzene ring he used hydrogen bromide, ethyl bromide, sodium bromide, manganese bromide or copper bromide to carry out the oxidation. The best type to use was a metallic bromide, using one of the common oxidation metals mentioned before. This type of compound would supply both the metal and bromine ion. However the reason why the bromine ion helped the oxidation was not given.

For the production of benzene dicarboxylic acids, Spear (25) carried out the oxidation in the liquid phase with air or O_2 at temperatures between 120 and 200°C and pressures ranging from 2 to 30 atmospheres. He improved the yield by oxidizing in the presence of a lower saturated aliphatic alcohol. In his patent methanol was used. The alcohol was introduced into the reaction at the rate of 0.5 to 5% by weight of xylene to be oxidized per hour. Neither the mechanism for this reaction nor the reason why the methanol helped the oxidation were given.

Roebuck and Wales (26), increased the amount of alkyl aromatic hydrocarbon oxidized by the introduction of an inorganic adsorbent, such as alumina, an alkaline earth oxide or fuller's earth. The adsorbent may act to remove the poisons which normally build up and stop the reaction. The time of the addition of the adsorbent will depend upon the particular reaction being carried out. With this procedure a good yield of toluic acid from p-xylene was obtained using copper acetyl acetonate as a catalyst, at a relatively low temperature of 100°C and a low pressure of 1 atmosphere.

Ohta and Tezuka (27) performed an air oxidation of PNT. They used manganese, copper and cobalt naphthenates as catalysts. Yields ranging from 50 to 75% PNBA were obtained when the reaction was carried out under pressure. However the exact values for the temperatures and pressures used for their runs could not be obtained.

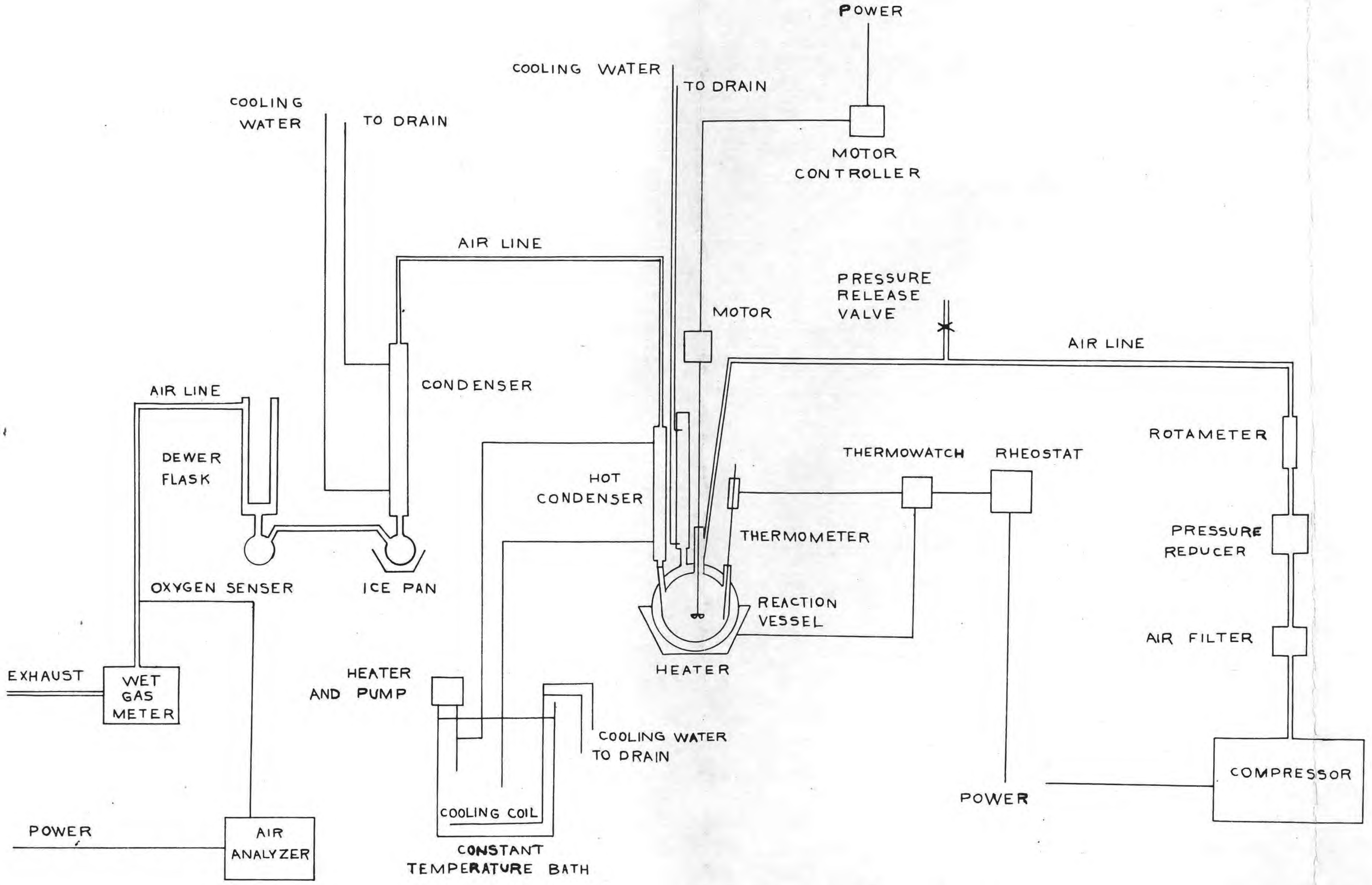
APPARATUS

The flow diagram of the apparatus used for the air oxidation of PNT is shown in fig. 1. Air was first compressed and stored in the compressor tanks at between 30 and 50 psig. The air was then filtered through an air filter to remove any oil, grease or dust that might have been entrained. The pressure of the air was then reduced to 2 psig. This pressure head was just high enough to keep the air flowing through the rest of the apparatus.

An air rotameter was placed next in the line to measure the rate of air flow. However when the reaction was being carried out the rotameter ball bounced up and down so much that it was impossible to take an accurate reading. To overcome this, a flow rate was set on the rotameter before the reactor stirrer was started and this was then taken as the average flow rate. Installed next in the line was a pressure release valve. This was opened when samples were taken to prevent the liquid PNT from backing up into the hollow shaft of the stirrer and solidifying and thus stopping the air flow.

The air then went into the stirring assembly shown in

FIGURE I, LINE DIAGRAM OF AIR OXIDATION ASSEMBLY



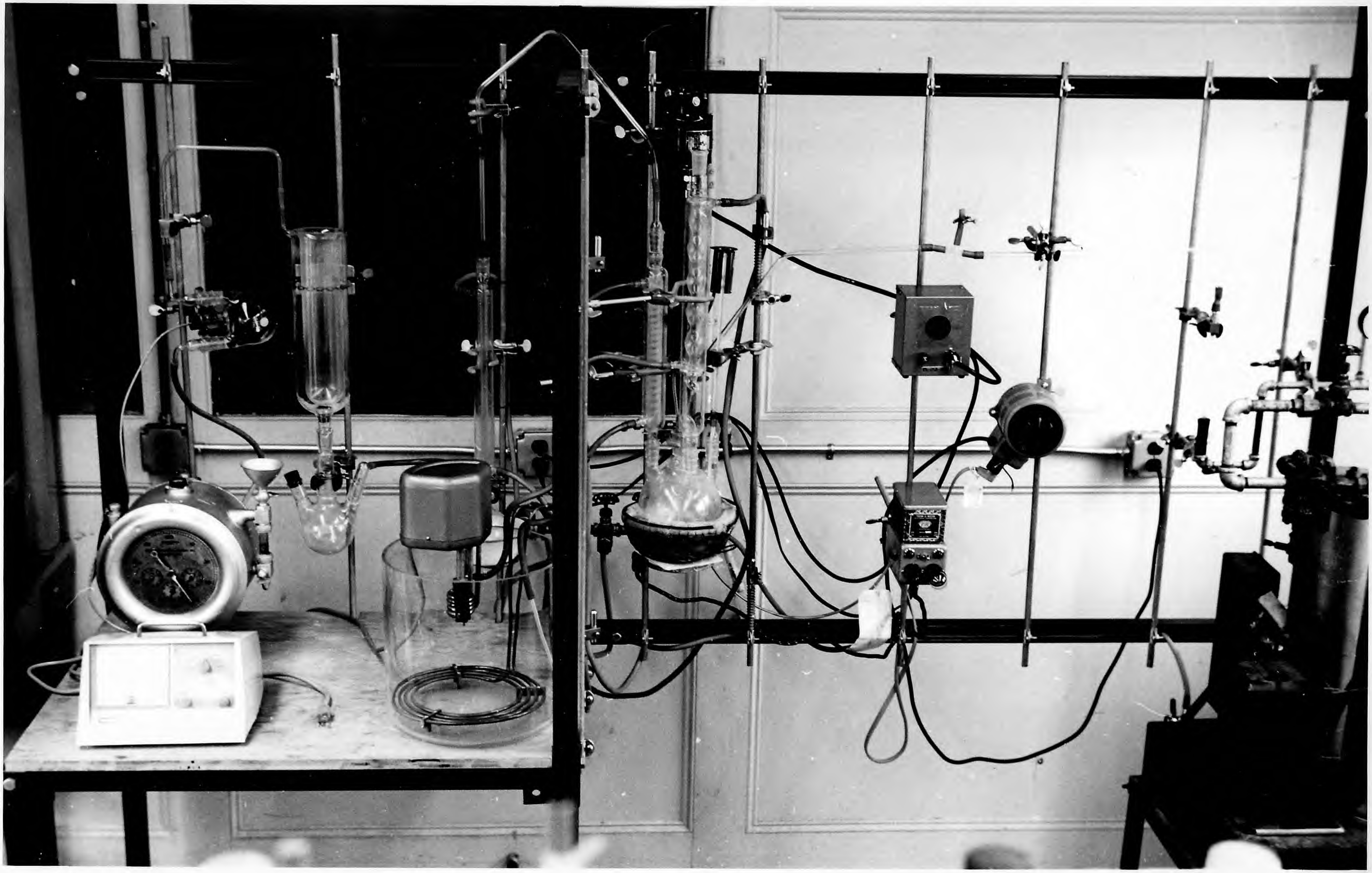


FIGURE 2 AIR OXIDATION APPARATUS ASSEMBLY

FIGURE 3

STIRRING ASSEMBLY

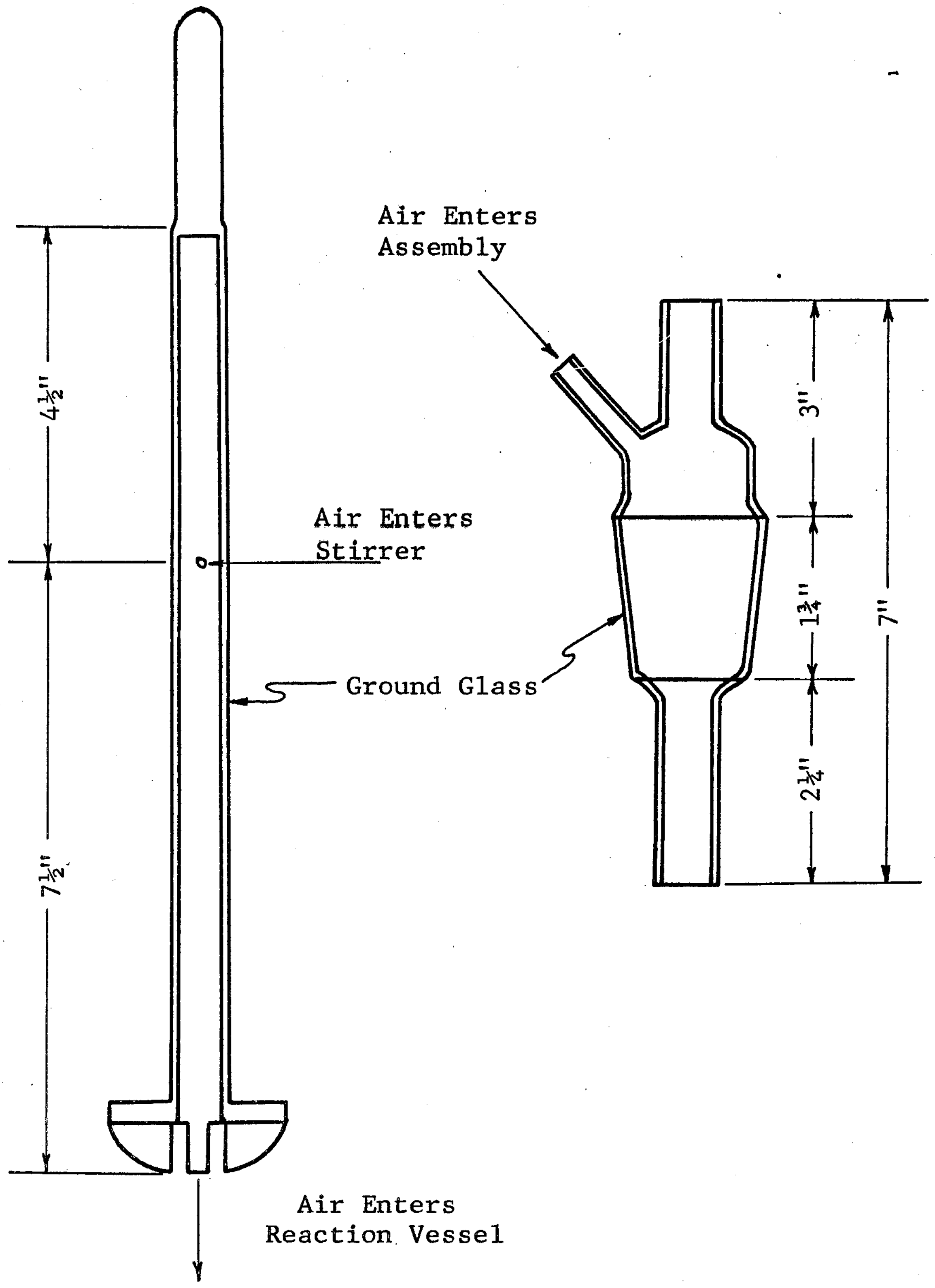


fig. 3. First the air went into the stirrer holder and then down the hollow shaft of the glass stirrer. It was then dispersed into the liquid PNT in the reaction vessel by the high speed stirrer. The reaction vessel is shown in fig. 4. It was a 1000-ml creased morton flask sealed within a 2000 ml jacket. The inside flask had three openings and the outside jacket one opening. The three openings for the inside flask, which contained the PNT and the catalyst, were; one for the stirrer through which the air also entered, one for the outgoing air and one for the thermometer. The stirrer was driven by a constant speed motor. The outside jacket was filled with a liquid whose boiling point was the operating temperature desired. The liquid was kept at its boiling point by a heating mantle which was automatically controlled by a Thermowatch temperature controller which was mounted on the thermometer as shown in fig. 4. This arrangement kept the reaction mixture at the desired temperature with an accuracy of $\pm 2^{o}C$.

The air upon leaving the reaction vessel entered a hot condenser, which was kept at about the melting point of the PNT ($53^{o}C$) so that whatever PNT was carried over by the air flow would condense here and drip back into the reaction

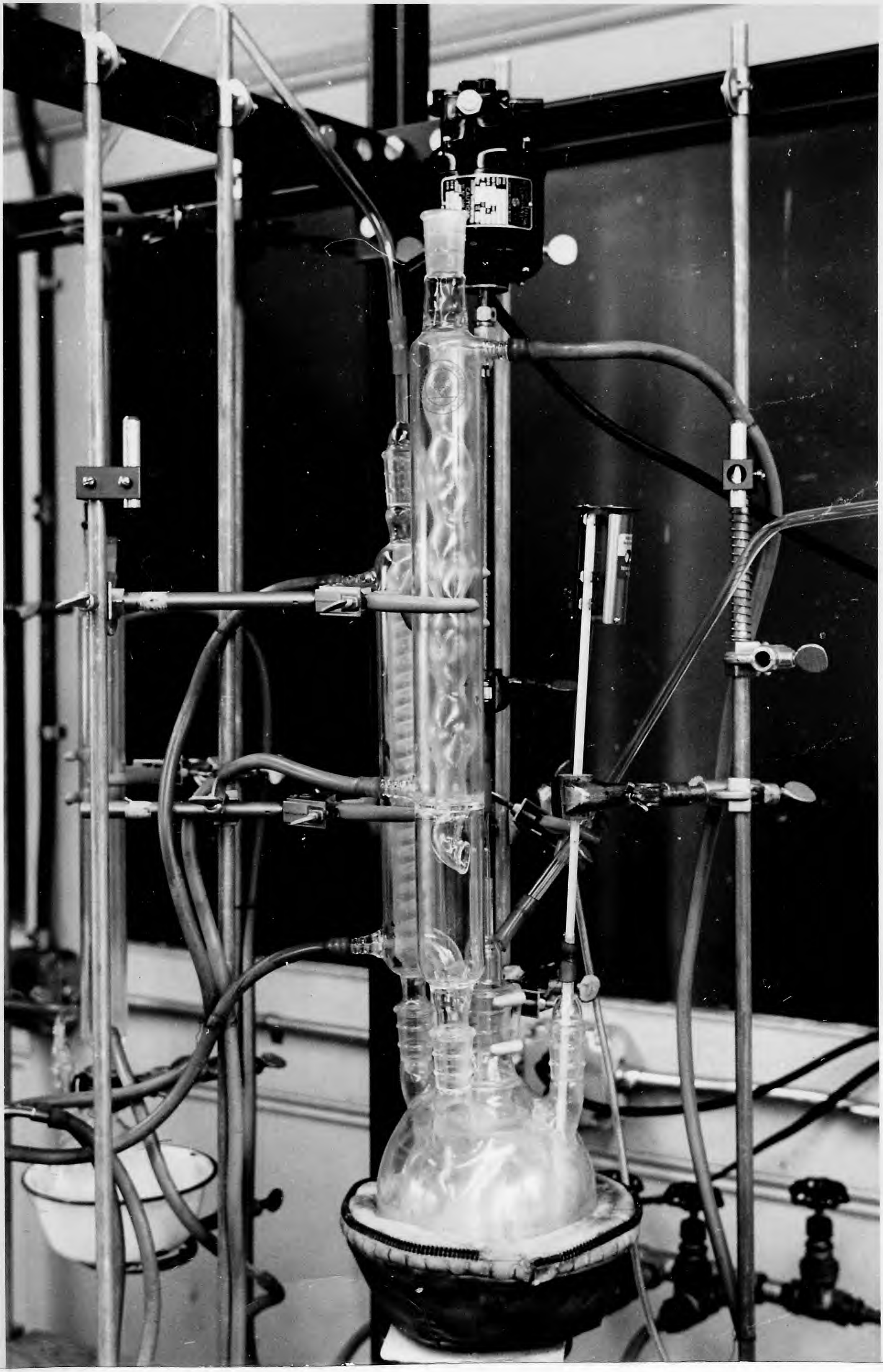


FIGURE 4 REACTION VESSEL ASSEMBLY

vessel without solidifying. The constant temperature bath that supplied this condenser contained a cooling coil so that cold water could be run through it to remove some of the heat of the exothermic oxidation reaction, thus keeping the temperature from going above 53°C.

After the hot condenser there was a cold water condenser to solidify any PNT still in the air. This connected to a condensing flask which was immersed in ice water. The air then flowed to another condensing flask and then up through a Dewar flask that was filled with ice water. Last in line was a wet gas meter to measure the total volume of air that passed through the system. Inserted in the line between the Dewar flask and the gas meter was the sensing element of a Beckmann Oxygen Analyzer. This could give the percent oxygen in the air to an accuracy of ±1% and thus tell if oxidation was taking place. The exit gas was then led through a tube out the nearest window.

EXPERIMENTAL PROCEDURE

An amount of PNT, between 650 and 750 grams, was weighed out and put into the 1000 ml reaction vessel. PNT has a density of 1.286 so this gave a volume when the PNT was liquid of between 500 and 600 ml. The catalyst was then added, the amount of catalyst used varied between 2 and 10% by weight. These were both added through the opening that held the thermometer. After the PNT and catalyst were put in, the thermometer was inserted and the Thermowatch sensing head was attached to it. The liquid in the 2000 ml jacket was added, this was equivalent to about 800 ml. For a constant temperature of 100° C distilled water was used and for a temperature of 137-140° C a mixture of o, p and m-xylene was used. After turning on the two heaters, the two cold condensers and adding the necessary ice to the system the oxygen analyzer was turned on and the senser inserted into the air stream. The compressor was then started.

When the PNT melted the stirrer was turned on to a slow speed until the PNT was heated up to the desired temperature. A sample at the initial conditions was then taken. With the pressure release valve open and the stirrer off the desired flow setting was made on the rotameter. The pressure release valve was then closed and the stirrer was turned up to "five" on the motor controller, which gave a speed of about 5000 RPM. When the stirrer was turned up to high speed the timing of the reaction was started. In early runs, before the oxygen analyzer was used, samples were taken every half-hour at the start of the reaction, then every hour and then every two hours as the reaction proceeded. With the oxygen analyzer in the system samples were taken about every five hours.

Sample Taking

Samples were taken through the joint in the reaction vessel that was used to hold the thermometer. After removing the thermometer a sample was taken and placed in an accurately weighed flask (±0.0001 gram). Duplicate samples were taken at each time interval and these samples usually weighed about 0.1 gram. The thermometer and Thermowatch head were replaced and the reaction vessel which had usually fallen in temperature a couple of degrees was allowed to heat up again before the pressure release valve was closed and the reaction started again.

The samples were allowed to cool and then were weighed, again to ±0.0001 gram. To the sample flask was added 25 ml of neutral ethanol and the solution was warmed to allow the

PNT and PNBA to dissolve. Three drops of phenolphthalein were added and the solution was then titrated with standard NaOH. The percent PNBA was then calculated by the method shown in Appendix A.

Recovery of PNBA from PNT

When the run was finished the molten charge of PNT was poured into an equal weight of cold water while the water was being slowly stirred. Sodium hydroxide was added to this mixture which was again stirred and warmed until the acid had gone into solution. The liquid was then decanted from the solid PNT. The PNT was washed in 10% HCl and then in water several times. It was then air dried so that it could be used again. To the original decanted liquid a slight excess of 10% H_2SO_4 was added over the amount of NaOH originally used. The precipatate formed was the PNBA which was filtered, washed, dried and then weighed.

DISCUSSION OF RESULTS

The total amount of oxidation of PNT to PNBA in each run is listed in Table 2B. The method of calculating the percent oxidation is shown in Appendix A. Shown in Table 1B are the operating conditions for each run including the type and amount of catalyst used. The catalysts tried for this oxidation were nickel acetate, cobaltous acetate, manganous acetate, 30% hydrogen peroxide and manganese naphthenate. The weight of catalyst varied from 1.16 to 8.053 per cent based on the weight of the catalyst plus the PNT.

The initial reaction vessel temperature was set at 100° C, but when it was found that practically no PNBA was being obtained, the temperature was changed to 137-40° C by changing the heating liquid from water to xylene.

The amount of oxidation of PNT to PNBA as shown in Table 2B was never greater than 0.01% which would mean about 0.06 grams of PNBA was formed during the reaction time. However in all the attempts to recover the acid nothing was obtained. This could mean either of two things; the amount of acid was just too small to make any recovery possible or that because of the heating and air bubbling through it the catalyst was being changed so as to give the increase in the milliequivalents of NaOH required to titrate the samples. One observation that would seem to favor the second belief is that during all the reactions there was a change in the color of the reaction mixture. For example in Run No. 4 when manganous acetate was used, at the start of the reaction when the mixture was first melted it was a green color. As the reaction was carried out the mixture started to turn brown until at the end of the reaction period (26 hours) the mixture was a very dark brown. This brown solid could have been an oxide of manganese because several are brown in color, such as $Mn(OH)_3$ and MnO_2. However the compound was not checked to see if it was one of these oxides.

The oxygen analyzer was used to measure the percentage oxygen in the air leaving the reaction vessel. The instrument was calibrated at 21% by flowing air through the apparatus when it was all set to run except that the stirrer was not running. The needle drifted slightly to either side of 21% during the reaction but it took no big dips. The drifting stayed within ±0.5% all during the reaction. The variation of percent oxygen with time is shown on the graph in fig. 5, for Run No. 5 when manganese naphthenate was used as the catalyst. This variation could have been in the machine and not caused

FIGURE 5

REACTION TIME VS PERCENT OXYGEN

by any oxidation because it was not a steady variation but a slight back and forth oscillation.

In Run No. 4 manganous acetate was used as a catalyst. When after 15½ hours it was found that negligible oxidation had taken place, two milliliters of 30% hydrogen peroxide were added to the reaction vessel. However this did not help increase the amount of oxidation and a yield of less than 0.01% PNBA was obtained for the entire run.

One of the major problems encountered during the experimental runs was the carry over of the PNT from the reactor into the air line. The air flowing through the reactor would carry the PNT out of the reactor, through the hot condenser and deposit it in the glass air line. This tube constantly plugged up and had to be cleaned at intervals during the run. This carry over prevented the use of large air flows at any temperature. But in order to use medium air flows the temperature of the PNT could not be raised too high so as to keep down the vapor pressure of the PNT and limit this carry over.

HAMMETT EQUATION

The Hammett equation is used to relate structure to equilibrium constants and rate constants for the reactions of meta and para substituted benzene derivatives. For a series of aromatic compounds, all with the same reaction center in the side chain but with a different substituent located meta or para to the reaction center, the Hammett equation says that the rate constant for any reaction in this series can be determined from a constant specific for the parent compound and from two parameters. The first parameter (σ) is determined only by the nature of the substituent and is independent of the reaction. It represents the relative ability of the group to attract or repel electrons. The second parameter (ρ) is characteristic of the reaction series and relates the sensitivity of the series to ring substitution.(28)

The Hammett equation may be written as follows, where K and K_o are the rate constants for the reaction of the substituted and unsubstituted compounds respectively.

$$\log\left(\frac{K}{K_o}\right) = \sigma\rho$$

The value of ρ is fixed at unity for the ionization of benzoic acid and σ is defined on the basis of this standard. If equilibrium constants are used rather than rate constants σ may be obtained by the following equation;

$$\sigma = \log \left(\frac{K \text{ compound}}{K_o \text{ Benzoic acid}} \right)$$

A positive σ indicates a stronger electron attractor than hydrogen and a negative σ shows a weaker electron attractor than hydrogen. Values of ρ are obtained for a given series by measuring the rate or equilibrium constants for a number of compounds, all having the same reaction center and each having a different ring substituent with a known σ value. The slope of the plot of the following equation;

$$\log K = \sigma \rho + \log K_o$$

with the logarithms of the measured constants plotted against the corresponding σ values, gives the ρ value for the reaction series being studied. Positive ρ's mean the reaction is aided by electron withdrawal from the benzene ring and negative ρ's mean the reaction is made more difficult by electron withdrawal. (29)

Honold $^{(30)}$, used the Hammett sigma (σ) values to determine the first group that would oxidize in the partial oxidation of monosubstituted p-xylenes. In these oxidations Honold used for his oxidizing agents alkaline potassium permanganate and chromium trioxide in glacial acetic acid with and without sulfuric acid as a catalyst. He summed up the meta and para σ values for each group on the benzene ring. However the important effects at the ortho positions were not taken into account in these calculations. The following example of the partial oxidation of 2-nitro-p-xylene to 3-nitro-p-toluic acid shows how these calculations were done.

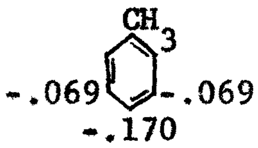
σ for p CH_3 = -0.170

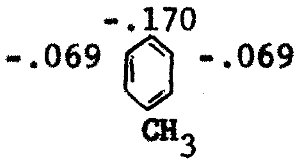
σ for m CH_3 = -0.069

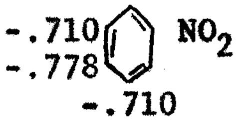
σ for p NO_2 = +0.778

σ for m NO_2 = +0.710

For the different positions the σ values are substituted.





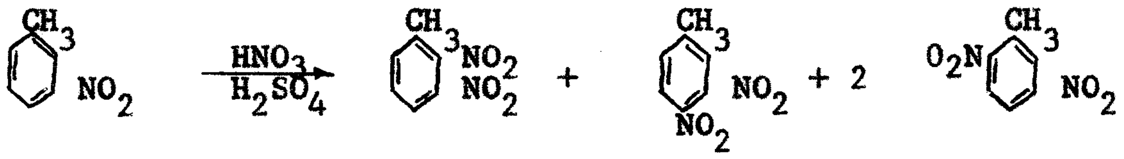


Summing up the sigma values for each position of the benzene ring.

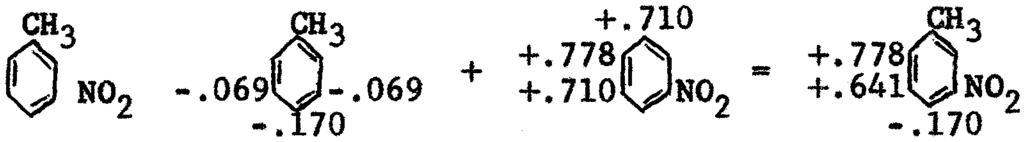
POSITION	$\Sigma\sigma$
1	-0.170
2	-0.069
3	-0.069
4	+0.540
5	+0.709
6	+0.641

From these values and his experimental work he found that it was the position with the lowest calculated electron density that was oxidized first. Thus position (4) was oxidized instead of position (1). However oxidation is the loss of electrons and therefore according to the Hammett sigma values it should have been the (1) position, which has the highest electron density, that should have been oxidized first.

To show that these values are not good to use take the examples of the nitration of m-nitrotoluene as shown.

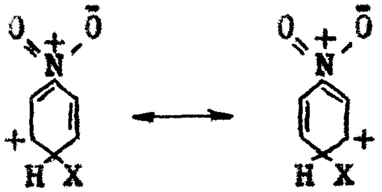


The nitro group enters into the 2,4 and 6 position but not the five position.(31) Summing up the σ values for the m-nitrotoluene.



The lowest electron density, position (6), and the highest electron density, position (4), were nitrated but the in between position (5) was not. Therefore it can be seen that the summation of σ values is not good to use where ortho affects appear.

A much better way to do these calculations would be to use the σ $^+$ values which take into account the resonance interaction between the substituent group and the reaction center.(32) The σ constants were obtained for the benzoic acids which do not take into account resonance structures such as the following which may exist during substitution where there is resonance between the reaction center and the substituent group. These are the resonance structures when the groups are para to each other,



Because of the extra resonance the p-nitro substituent acts as a stronger electron withdrawer group making the oxidation of PNT much more difficult than the oxidation of a $-CH_3$ group where there is no $-NO_2$ group present such as in toluene.

Ohta and Tezuka (33) made a study of the liquid phase air oxidation of PNT under pressure in which they compared the ease of oxidation of PNT to toluene. In their experiments it was found that the oxygen absorbed by the PNT when oxidized at 200° C and 8 atmospheres was about the same as that absorbed by toluene oxidized at 150°C and 3.14 atmospheres. The $-CH_3$ group when in toluene was therefore oxidized easier than when in the PNT.

SUMMARY

A nitro group located in the para position relative to a methyl group makes it very difficult to oxidize the methyl group because of the electron withdrawing and resonance effects set up by the nitro group. This is seen by the fact that little para-nitrobenzoic acid was obtained, no yield being greater than an indicated 0.01% PNBA. It is concluded that the oxidizing conditions employed were not vigorous enough to provide the energy of activation required for the oxidation reaction to proceed.

RECOMMENDATIONS

The best way to get oxidation of PNT to PNBA by using air would be to carry out the reaction under pressure and by the batch instead of by a flow process. The pressure could range from 25 to 75 atmospheres. These reactions at high pressures might also be carried out at a little higher temperature than was tried. Temperatures of 150 to 200° C would be very good. These higher temperatures might also be tried at atmospheric pressure if some method to prevent the carry over of the PNT can be found.

If the reaction was still to be carried out at one atmosphere some of the catalysts discussed in the beginning that were not used should be tried. These would include the use of elemental sulfur at the same time one of the metal salts was being used. Also a metallic bromide might work at atmospheric pressure. The catalyst copper acetyl acetonate should be tried because of the fact that good yields were obtained at a low temperature and pressure when it was used along with an adsorbent.

APPENDIX A

CALCULATIONS

Typical calculations showing the procedure for calculating the percent PNBA for each run are shown.

SAMPLE CALCULATIONS ARE SHOWN FOR RUN NO. 5

Catalyst- Manganese Naphthenate
Amount PNT- 695 gms.

Calculation of Percent Catalyst

Weight Catalyst- 60.9 gms.

$$\text{Percent Catalyst} = \frac{60.9}{695 + 60.9} \times 100 = 8.053\%$$

Two samples were taken at each time but only one is shown in the calculations.

Sample No.	Time Hrs.	Sample gms.	Catalyst free Sample gms.	NaOH N	NaOH ml.
7	0	0.9234	0.8490	0.0255	5.6
13	15	1.1052	1.0162	0.0255	11.8

The weight of the catalyst is deducted from each sample

Percent sample without catalyst = 100 - 8.053 = 91.947%

Weight catalyst free sample-

Sample (7) 0.9234 gms. × 0.91947 = 0.8490 gms.

Milliequivalents NaOH required to neutralize standard sample (7) with no acid

Volume × Normality = 5.6 ml. × 0.0255 N = 0.1428 meq.

Milliequivalents NaOH required to neutralize standard + Acid Sample (13)

Volume × Normality = 11.8 ml. × 0.0255 N = 0.3009 meq.

The milliequivalents of NaOH is then divided by the sample weight (catalyst free) to obtain milliequivalents per gm. of sample

$$\text{Sample (7)} \qquad \frac{0.1428 \text{ meq.}}{0.8490 \text{ gms.}} = 0.1681 \text{ meq./gm.}$$

$$\text{Sample (13)} \qquad \frac{0.3009 \text{ meq.}}{1.0162 \text{ gms.}} = 0.29610 \text{ meq./gm.}$$

The meq./gm. for the standard is then subtracted from each sample to obtain meq. acid

$$\text{Sample (13)} \left[0.29610\right] - \text{Sample (7)} \left[0.1681\right] = 0.1280 \text{ meq.PNBA}$$

<u>To find percent PNBA</u>

$$\frac{\text{meq. PNBA} \times \dfrac{0.1612 \text{ mgm.}}{1 \text{ meq. PNBA}} \times \dfrac{1 \text{ gm.}}{1000 \text{ mgm.}}}{1 \text{ gm. Sample}} \times 100 = \%\ \text{PNBA}$$

$$\frac{0.1280 \text{ meq.} \times \dfrac{0.1612 \text{ mgm.}}{1 \text{ meq. PNBA}} \times \dfrac{1 \text{ gm.}}{1000 \text{ mgm.}}}{1 \text{ gm. Sample}} \times 100 = 0.00206\%\ \text{PNBA}$$

APPENDIX B

SUMMARY OF RESULTS

Table 1B	Operating conditions for each run.
Table 2B	Final tabulations of percent oxidation of PNT to PNBA and the time of each run.

TABLE 1B

OPERATING CONDITIONS

Run Number	Catalyst	Weight Catalyst-gms.	Weight % Catalyst	Weight PNT-gms.	Reaction Temp. °C	Motor Mixing Speed Setting	Rotameter & Setting
1	1	5.90	1.16	503	100	5	A 2
2a	2	10.25	1.54	655	100	5	B 10
2b	2	10.25	1.54	655	137-40	5	B 10
3	2	14.83	1.963	744	137-40	5	B 5
4a	3	14.08	2.00	690	137-40	5	B 5
4b	3+4	14.08 +2 ml H_2O_2	2.00	690	137-40	5	B 5
5	5	60.87	8.05	695	137-40	5	B 3

All runs - Air Inlet Pressure- 2 psig, Constant Temperature Bath Temperature-54°C

Catalysts; 1-Nickel Acetate, 2-Cobaltous Acetate, 3-Manganous Acetate, 4-30% Hydrogen Peroxide, 5-Manganese Naphthenate

TABLE 2B

FINAL TABULATIONS

Run Number	Gm.Moles PNT	Volume Air-ft^3	Volume Air STP-Liters	Gm.Moles Air	Reaction Time-Hrs.	Percent PNBA
1	3.67	6.20	163	7.28	3¼	<0.01
2a	4.775	43.91	1152	51.6	14½	<0.01
2b	4.775	42.04	1107	49.4	14½	<0.01
Total 2	4.775	85.95	2259	101.0	29	<0.01
3	5.42	4.92	129.3	5.78	3¼	<0.01
4a	5.03	22.96	604	26.95	15½	<0.01
4b	5.03	17.17	451	20.1	10½	<0.01
Total 4	5.03	40.13	1055	47.05	26	<0.01
5	5.07	15.64	411	18.85	15	<0.01

APPENDIX C

EQUIPMENT

Graph 1C Speed of the stirrer for the various controller settings.

Graphs 2 and 3C Calibration of the two rotameters used.

FIGURE 6

SPEED OF MIXER FOR VARIOUS CONTROLLER SETTINGS

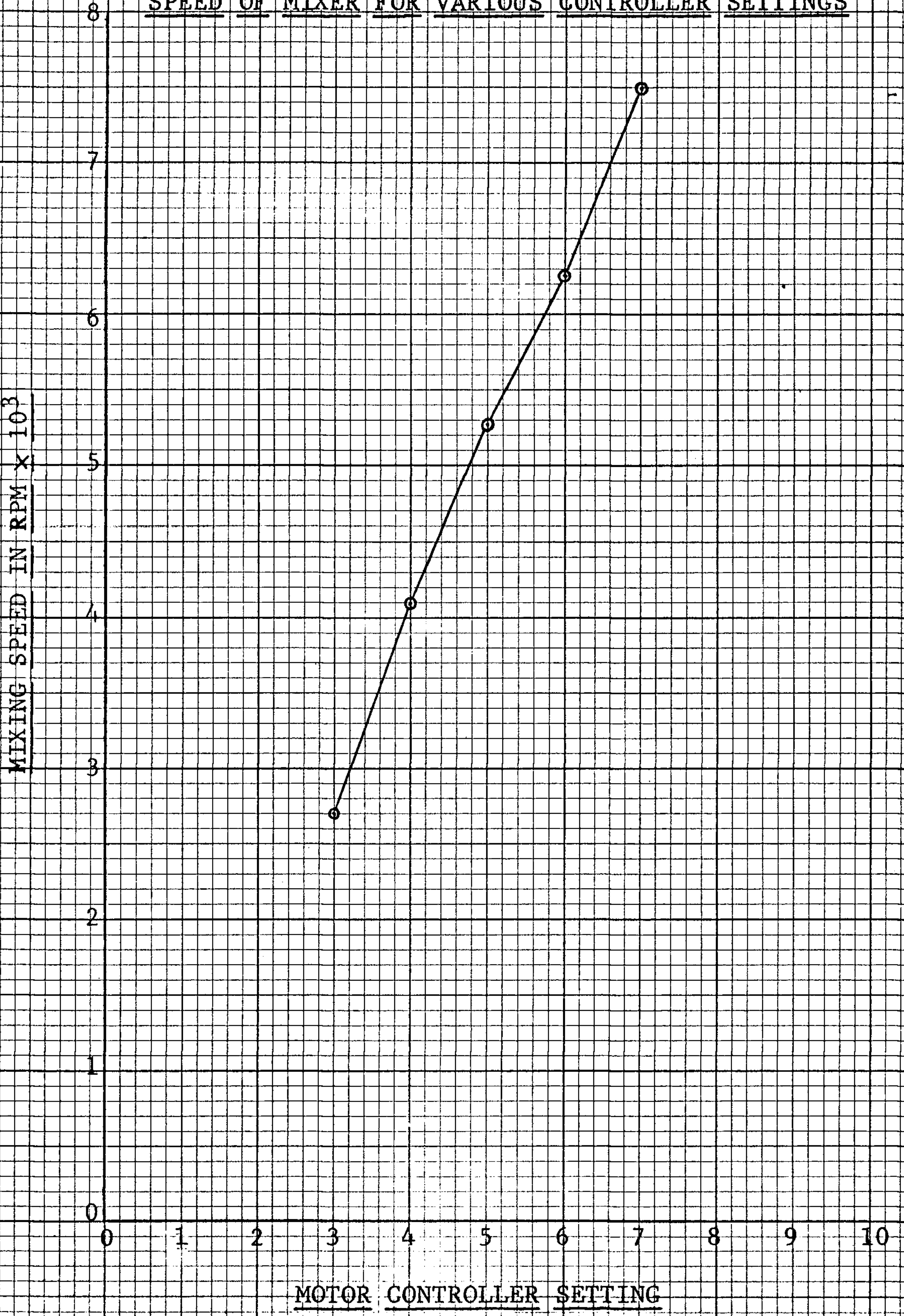


FIGURE 7

ROTAMETER B CALIBRATION CURVE

06-150/13 TUBE, 3/32" DIA. STAINLESS STEEL FLOAT

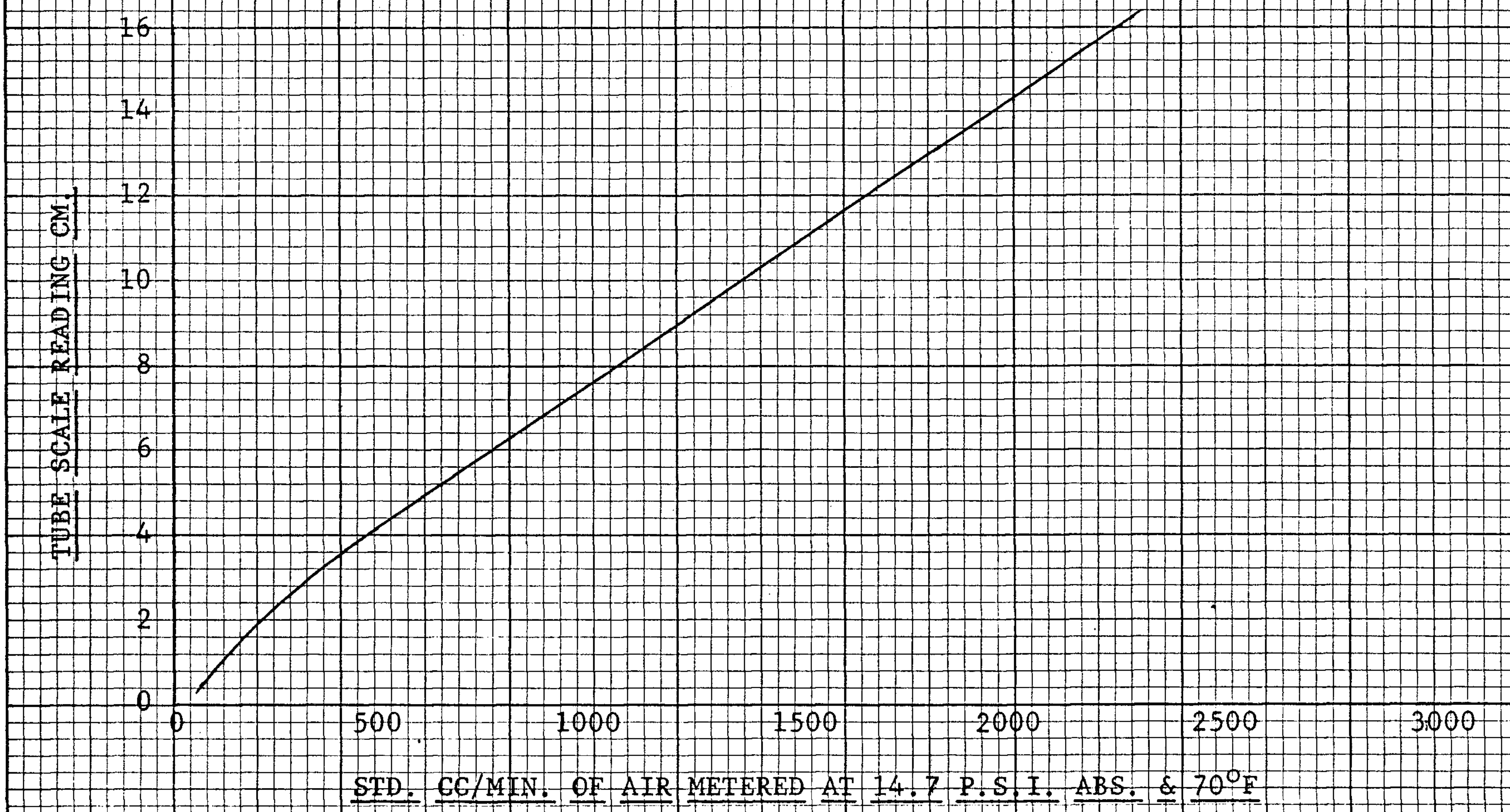
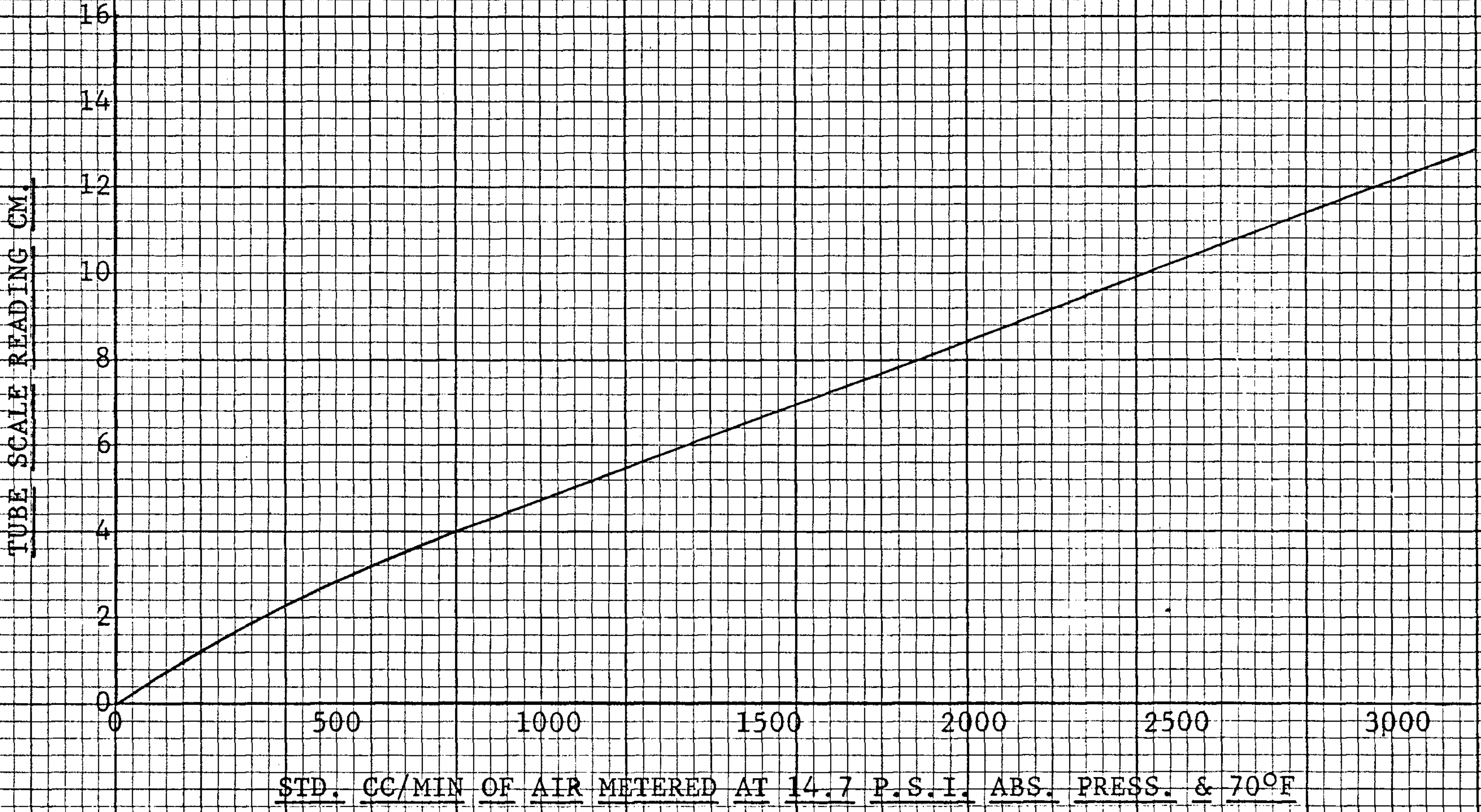


FIGURE 8

ROTAMETER A CALIBRATION CURVE

2-L-150 TUBE, ¼" DIA. GLASS FLOAT



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