OXIDES OF NITROGEN AS CATALYST IN THE VAPOUR PHASE OXIDATION OF NAPHTHALENE.

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CONTENTS.

INTRODUCTION. The object of this investigation was to study in the vapour phase the oxidation of naphthalene without rupturing the naphthalene nucleus.

A great deal of work has been done on the oxidation in the vapour phase with the main object of obtaining phthalic anhydride, and the manufacture of phthalic anhydride industrially is the result of such work.

The exact mechanism of this reaction is not clear and the present work was started in the hope that with a less reactive catalyst, under certain conditions, the naphthalene nucleus could be oxidised step by step up to the point when rupture of the nucleus took place.

It was thought that a gaseous catalyst would be best suited for this purpose as any reaction product would pass along with the gas stream and so escape from the reaction zone before it had been completely changed by further reaction. On the other hand a solid catalyst would no doubt adsorb the primary reaction product, which might then be further acted on because of it remaining in the reaction zone. As it was oxidation that was to be studied the oxides of nitrogen as the gaseous catalyst suggested themselves, especially since Bibb and Lucas [1] had been successful in/

in obtaining phenol from benzene using these gases, whereas using solid catalysts, Weiss and Downs[2] have shown that higher oxidation products are obtained and only traces of phenol.

At the outset of this work it was proposed to bring naphthalene vapour and oxides of nitrogen together, under varying conditions of concentration and velocity, at as low a temperature as was possible to give a reaction, and afterwards to increase the temperature and study any change or changes which might be brought about.

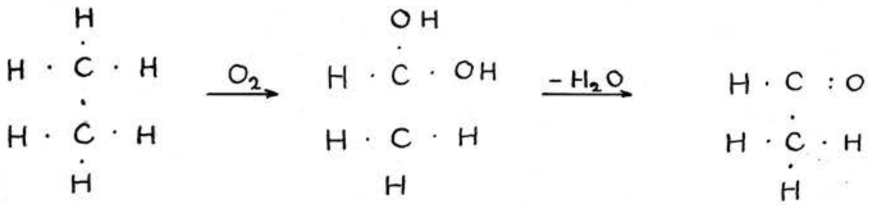
Owing to the nature of the reacting bodies when hot, the number of variations of change of concentration and velocity theoretically possible was limited practically because of the tendency to burn with slight explosions. However it was possible to investigate the reaction under varying conditions at two different temperatures, and this paper describes that work.

At the lower temperature α-nitro-naphthalene was formed and this reaction has been studied in detail.

At the higher temperature a different product of a most complicated structure was obtained which has involved a large amount of work to try to identify it.

LITERATURE. For the study of the possible intermediate products, stable or otherwise, in the oxidation of organic compounds the hydroxylation theory of Bone[3] is most useful.

Ethane on oxidation in the vapour phase is believed to undergo the following changes,

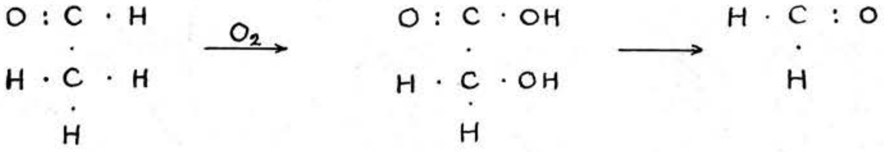


$$\begin{array}{c} H \\ H\cdot C\cdot H \\ H\cdot C\cdot H \\ H \end{array} \xrightarrow{O_2} \begin{array}{c} OH \\ H\cdot C\cdot OH \\ H\cdot C\cdot H \\ H \end{array} \xrightarrow{-H_2O} \begin{array}{c} H\cdot C:O \\ H\cdot C\cdot H \\ H \end{array}$$

ETHANE

ACETALDEHYDE

and acetaldehyde further oxidises to formaldehyde thus:-

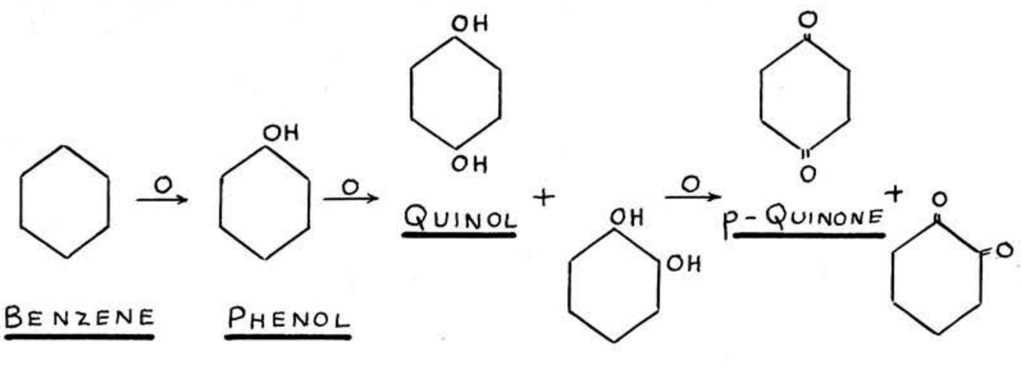


$$\begin{array}{c} O:C\cdot H \\ H\cdot C\cdot H \\ H \end{array} \xrightarrow{O_2} \begin{array}{c} O:C\cdot OH \\ H\cdot C\cdot OH \\ H \end{array} \longrightarrow \begin{array}{c} H\cdot C:O \\ H \end{array}$$

ACETALDEHYDE

FORMALDEHYDE

In the case of benzene similarly we would expect the following reactions:-



BENZENE

PHENOL

QUINOL

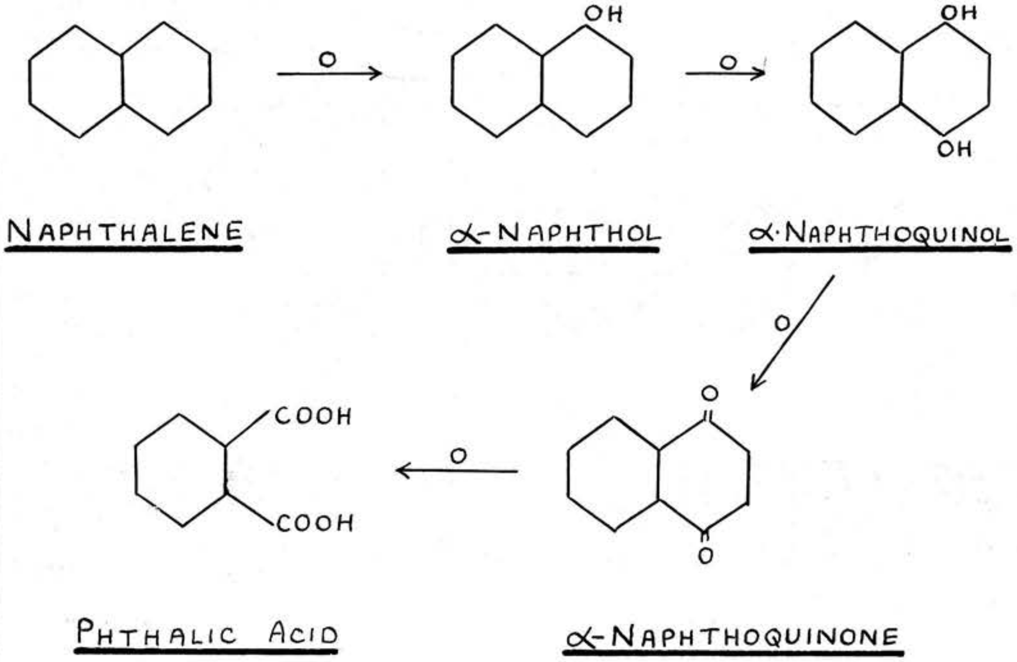
CATECHOL

p-QUINONE

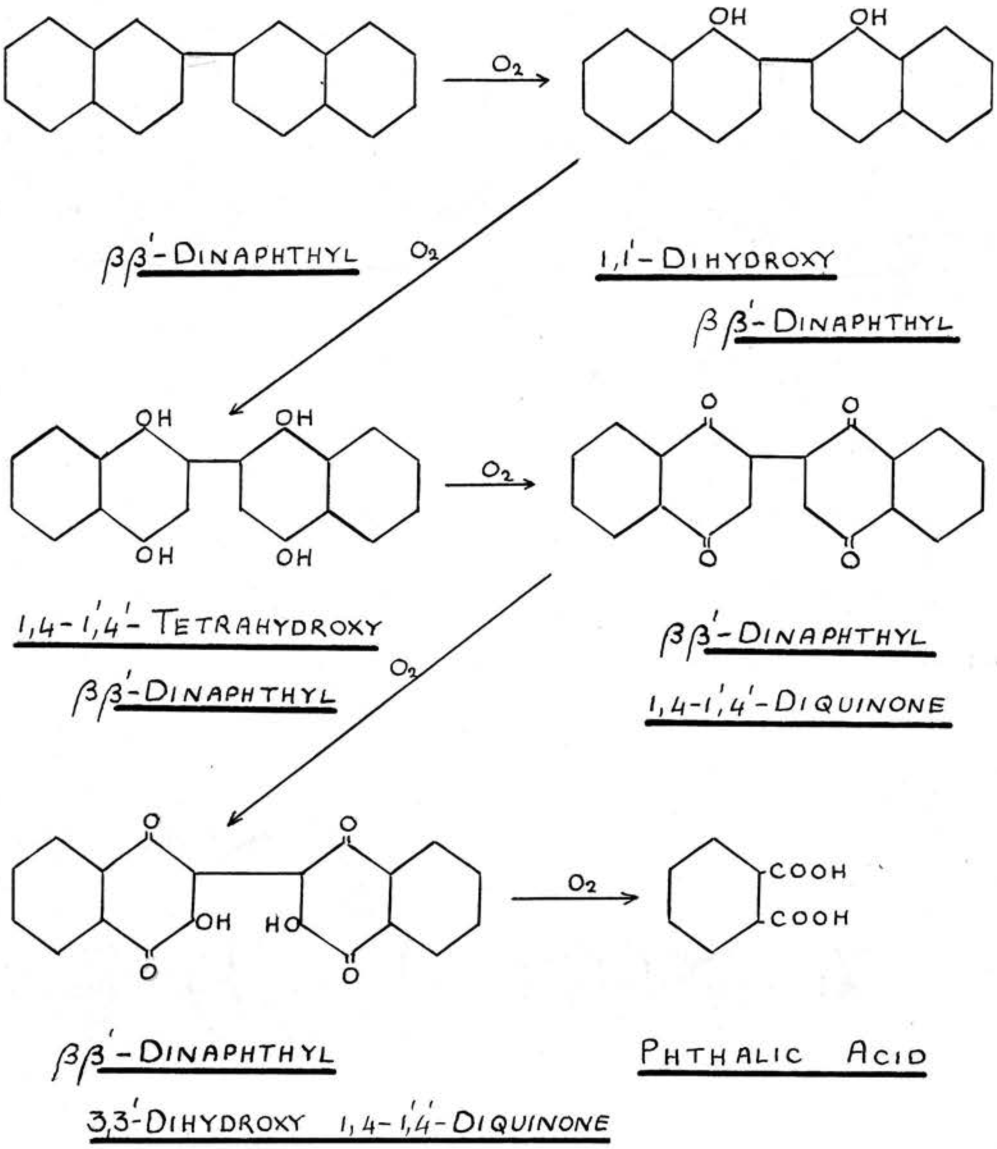
o-QUINONE

F. Fichter[4] believes that the above does explain the reactions which take place in the electrochemical oxidation of benzene, but that the reaction is too severe for one to detect measurable quantities of phenol, the first stage in the oxidation. Bibb and Lucas[1] having obtained phenol from benzene showed that it was possible by using a gaseous catalyst viz. oxides of nitrogen to obtain the first product of oxidation -.

Applying the hydroxylation theory to naphthalene we should expect the reaction to proceed as follows:-



and similarly for a dinaphthyl the following:-



The use of oxides of nitrogen along with naphthalene in the vapour phase might lead to the formation of α-nitronaphthalene at lower temperatures than those at which oxidation takes place. This was found to be the case. No mention of this having been studied is to be found in the literature.

As regards the vapour phase oxidation of naphthalene all the work so far carried out has been directed towards/

towards preparing phthalic anhydride in good yield i.e. to the rupturing of the naphthalene nucleus under the best conditions.

Conover and Gibbs[5] have done a considerable amount of research on the vapour phase oxidation of naphthalene to phthalic anhydride using many different solid catalysts, the most successful of which was found to be Vanadium Pentoxide, while Platinum and Magnesium Oxide were almost useless. They obtained good yields of phthalic anhydride along with small quantities of benzoic acid, and what they believed to be naphthols and naphthoquinones as by-products.

Much research along this line has been carried out resulting in the many patented processes, but nothing can be gathered from the work to clearly indicate how the reaction proceeds i.e. what intermediate products if any are formed.

One must consider also the possibility of the formation of dinaphthyls under the conditions of these experiments and the oxidation products obtained from them. In fact a mixture of the three possible isomeric dinaphthyls has been obtained up to a 15% yield by merely passing naphthalene vapour alone, or along with either antimony trichloride or stannic chloride through a hot tube.[6] No work appears to have been done on the vapour phase oxidation of the dinaphthyls.

The/

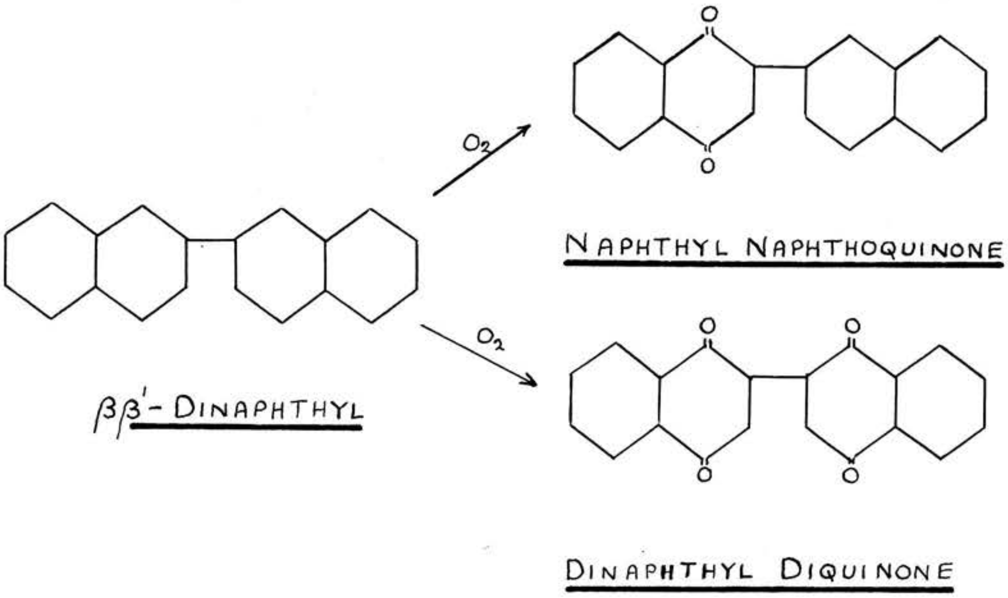
The oxidation in solution of naphthalene by various reagents has been studied in some cases in great detail, and a short summary of the products formed will now be given.

Phthalic acid or its anhydride can be produced by a number of methods:-

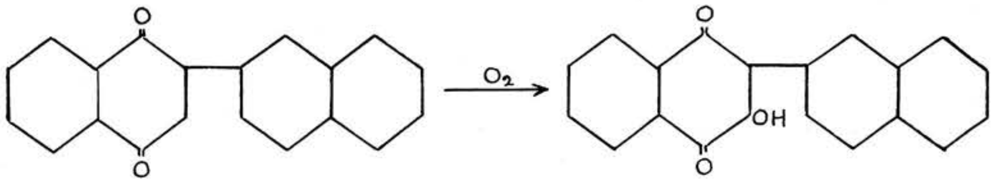
(1) By treatment with dilute nitric acid at 130°C.[7]

(2) Until the introduction of the modern vapour phase processes, the industrial preparation was carried out by oxidising with concentrated sulphuric acid in presence of mercuric sulphate as catalyst, and in later years oxides of metals such as molybdenum, chromium or vanadium[8].

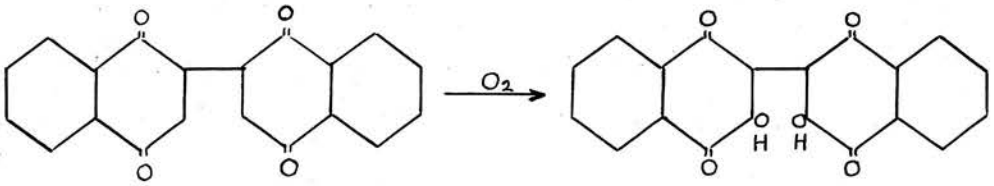
(3) By boiling with either acid permanganate[9] or chromic acid mixture[10]. The latter agent also produces some ββ'-dinaphthyl in a side reaction. ββ'-Dinaphthyl may be oxidised farther with chromic acid in acetic acid solution, yielding according to conditions either naphthyl-naphthoquinone or dinaphthyl diquinone.[11]



These quinones dissolve in alkaline solutions with absorption of atmospheric oxygen yielding hydroxy derivatives[11] -



NAPHTHYL NAPHTHOQUINONE   NAPHTHYL HYDROXY NAPHTHOQUINONE



DINAPHTHYL DIQUINONE   DINAPHTHYL DIHYDROXY DIQUINONE

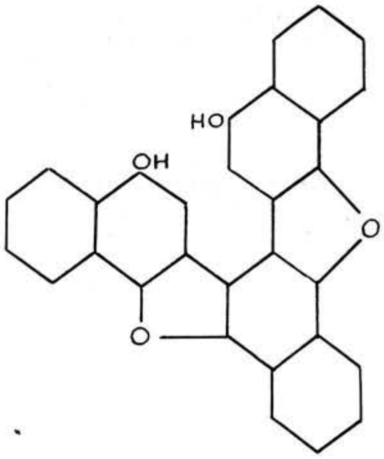
On further oxidation in alkaline solution with potassium permanganate naphthyl hydroxy naphthoquinone gives a mixture of β-naphthoic acid and phthalic acid, while dinaphthyl-dihydroxy-diquinone yields only phthalic acid[11].

It has been pointed out that oxidation with acid potassium permanganate yields phthalic acid as the principal product[9]. If however the solution be neutral or alkaline a less vigorous action takes place resulting in the formation of phthalonic acid.[12]

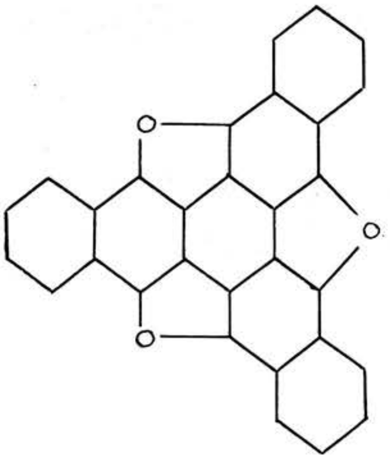
The conversion of naphthalene to α-naphthoquinone may be achieved by oxidation at room temperature in glacial acetic acid solution with chromic anhydride/

anhydride.[13] Phthalic acid appears as one of the chief by-products.[7] Oxidation in acid solution with ceric salts[14] and electrolytic oxidation[15] in presence of cerous salts[16] also convert naphthalene into α-naphthoquinone and phthalic acid. It should be noted that the tendency for side reactions to occur renders the yields poor. The best method of preparing α-naphthoquinone is now considered to be by oxidation of 1-amino 4-naphthol.[17]

α-Naphthoquinone on further oxidation with chromic acid or potassium permanganate yields phthalic acid, but treatment with acid or dilute alkali brings about oxidation to 2-hydroxy-1-4-naphthoquinone[18] which then polymerises forming a mixture of the so called "naphthoquinone humic acids". Erdtman[19] recently isolated two of these polymers and has put forward structural formulae for them



BIS-ANHYDRO-TRINAPHTHO QUINOL



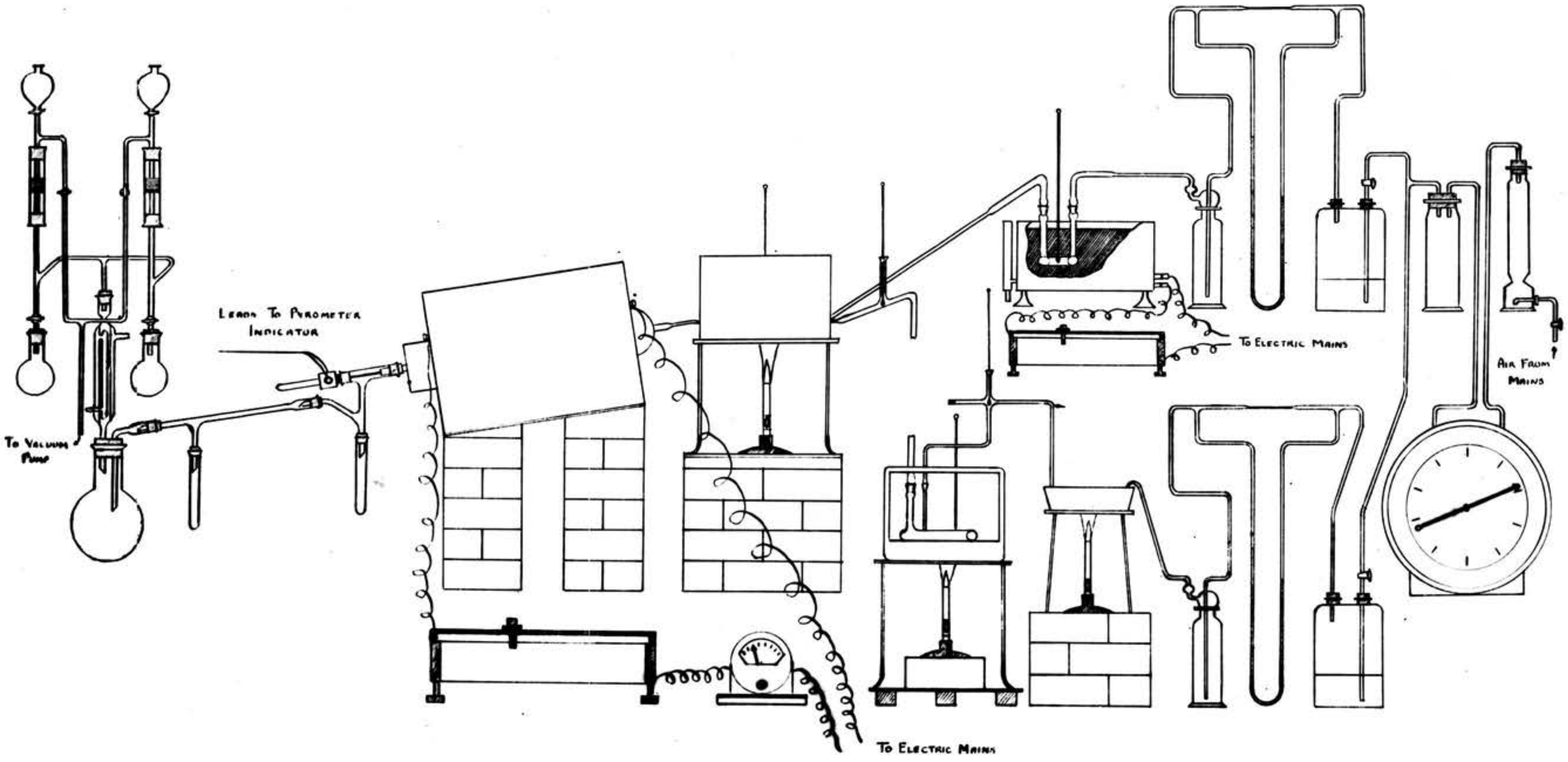
TRINAPHTHOBENZENE TRIOXIDE

These are crystalline bodies whereas the "quinone humic acids" are generally amorphous. Erdtman believes the amorphous products to have even more complicated structures than those shown above.

In 1881 Leeds[20] claimed to have produced β-naphthol by boiling naphthalene in acetic acid solution with hydrogen peroxide. He stated that there was on prolonged boiling no tendency to form resinous bodies, or to oxidise farther. He also claimed the production of phenol in similar experiments with benzene. As a result of more recent investigations this work has been shown to be very inaccurate. Charrier and Moggi[21] carrying out similar experiments obtained phthalic acid as the main and only identifiable product of oxidation.

Treatment of naphthalene with concentrated sulphuric acid and potassium chlorate produces a mixture of phthalic acid, dichlornaphthalenes and syrupy oxychloronaphthalic acid $C_{10}H_7ClO_5$,[22] while with chromyl chloride dichloronaphthoquinones are formed.[23] Aqueous hypochlorous acid and naphthalene form an addition compound with the formula $C_{10}H_8(HOCl)_2$, which on treatment with alcoholic potash is converted to tetrahydroxytetrahydronaphthalene.[24]

DIAGRAM OF LAYOUT



NOT DRAWN TO SCALE

THE APPARATUS. In the apparatus of Bibb and Lucas[1] the oxides of nitrogen were obtained by bubbling a stream of air through flasks containing nitric acid, some of the vapour of which was picked up and carried on into an electric furnace, at the high temperature of which it was decomposed into oxides. A similar stream of air was bubbled through flasks containing benzene, and this vapour was also passed into the furnace. The resulting products were condensed, last traces being removed by absorption in lubricating oil.

An apparatus somewhat similar to that used by Bibb and Lucas[1] was set up and gradually improved upon until fairly satisfactory under working conditions. A diagram of the layout is shown on the opposite page.

The air used was that supplied by the compressed air system at 5 lbs/□″ guage pressure, and in order to remove oil and dust it was first passed up a tower packed with alternate layers of cotton wool and glass wool. The air then passed through a large capacity reservoir in the form of a gas meter to smooth out the effects of any sudden fluctuation of air pressure on the mains. The next stage was to dry the air by passing through sulphuric acid wash bottles, but to avoid the risk of acid running back into the gas meter through a sudden failure of the air supply, or a back pressure in the apparatus, a trap was placed in between the meter and the wash bottles.

The/

The air was divided into two streams each controlled by a tap, and after being dried passed through flowmeters, the calibration curves for which are shown opposite page 16. After some preliminary work it was found necessary to put traps between the flowmeters and the rest of the apparatus, to catch the liquid should it be accidentally driven over.

The naphthalene vaporiser consisted of two parts, a preheater and a vaporiser proper.

Conover and Gibbs[5] in their work on the oxidation of naphthalene to phthalic anhydride used as their naphthalene vaporiser a horizontal U-tube immersed in an oil bath. The ends were turned up at right angles to the plane of the U so as to project out of the oil, while the naphthalene only partly filled the tube, thus providing the minimum of resistance to the air flow.

A similar vaporiser was used in the present apparatus and was heated in an oven which could be lowered for detachment of the U-tube for weighing or filling. In the bottom of the oven was a layer of 1½ inches of sand covered with a thin iron plate on which the U-tube rested. The oven was gas heated, the temperature being controlled by a thermometer whose bulb projected through the metal plate into the sand, while the portion of the scale concerned projected through the top of the oven. The inlet and outlet tubes which were/

were provided with ground glass joints passed through holes in the top of the oven. The door of the oven is not shown in the diagram.

The air preheater was a copper coil heated in a sand bath to a high temperature, and although the heat transfer was poor the temperature of the cold incoming air was raised by 25-45°C. which was all that was required. It was connected to the vaporiser through a cross piece in one leg of which was fixed a thermometer to measure the temperature of the preheated air. The fourth leg, provided with a stopper at the end, was used as a by pass for the air when necessary, as for example during heating up or cooling down of the apparatus. As shown in the diagram, the outlet tube from the vaporiser was made with a downward slope towards the mixer and preheater. The temperature of the naphthalene air mixture was recorded on a thermometer fixed in a side tube sealed into the sloping tube described above.

The preheater and mixer simply consisted of a Y-tube strongly heated in a sand bath. Briefly the bath consisted of a round tin box about 10" in diameter and 5" high whose walls were lined with asbestos. Sand filled the bottom up to the level of the tubes, while on top was another layer of asbestos. The result aimed at was maintainance of a uniform temperature, which could at the same time be repeated in the next/

next experiment. To have some means of control a thermometer was placed so that its bulb lay immersed in sand at the fork of the Y-tube.

The nitric acid vaporiser consisted of a similar detachable U-tube, immersed in an electrically heated water bath wired in series with a variable resistance. The temperature of the bath was recorded on a thermometer graduated in $\frac{1}{10}$ths of a degree. The acid used was the constant boiling 68% acid, and so the difficulty of frequent replacements was avoided.

The outlet from the preheater led directly to the tube of an electric furnace, which was controlled by a variable resistance and ammeter. The tube was of $\frac{1}{2}$" internal diameter fused silica and was not packed in any way. A glass T-piece placed over the lower end of the furnace tube provided an exit for the products, while holding in position a thermocouple projecting into the heated zone of the tube. This couple was a platinum-rhodium one encased in a silica sheath, and the temperatures were read off on an indicator calibrated in degrees centigrade.

A tube to trap high boiling products was fitted to the end of the vertical leg of the T-piece, while a side tube led off the vapour as yet uncondensed to an air condenser, near the lower end of which was a second trap. The air condenser led into a wide mouthed flask of about 500 ccs. capacity fitted with an upright double surface water cooled condenser.

From/

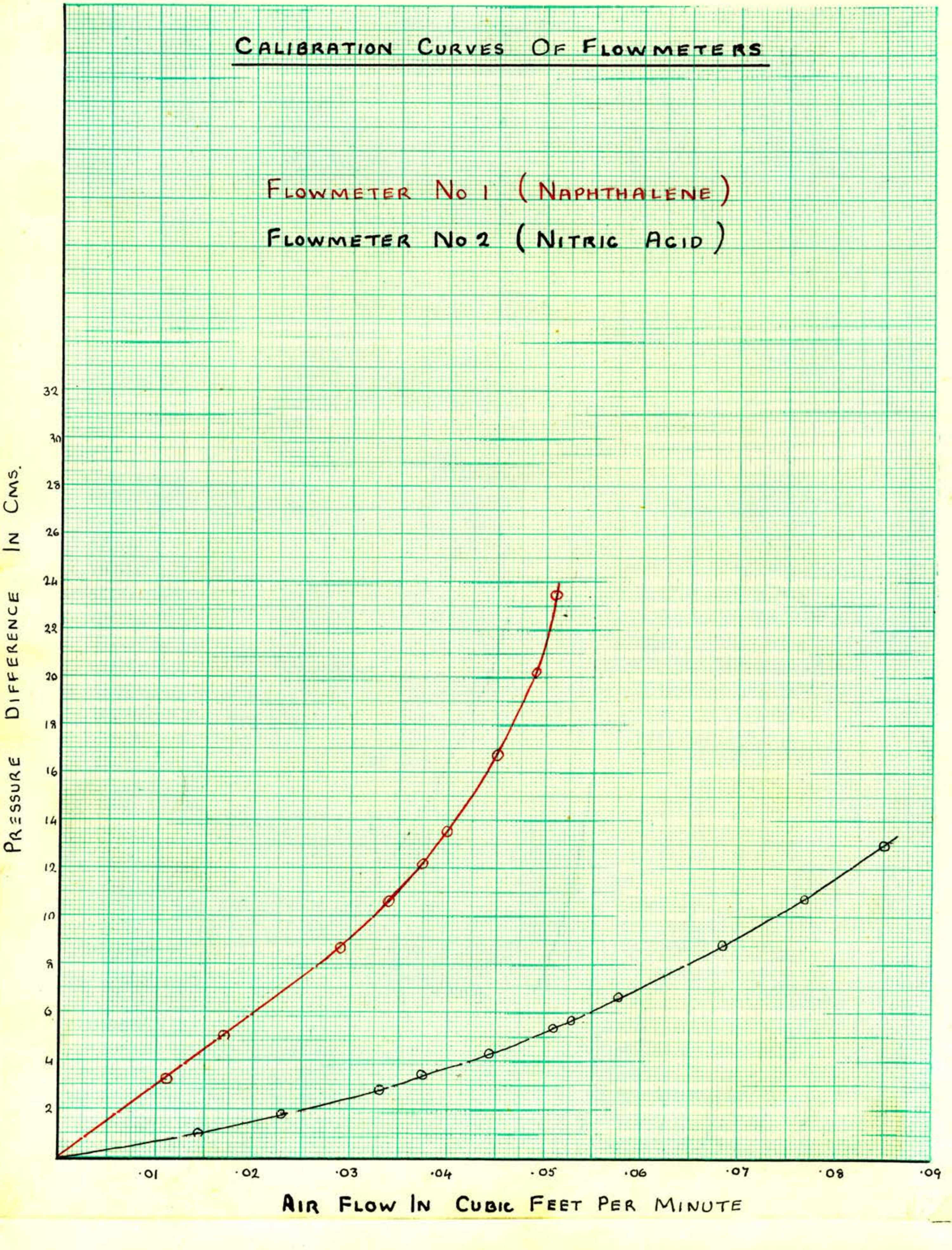
From the top of the latter the exit gases passed to the mist settling device which was a duplicate system, only one unit however being in operation at one time. The essential part of the system was a "scrubber" consisting of a tube about $\frac{3}{4}$" in diameter containing four or five perforated porcelain discs similar to those used in a Gooch crucible. The discs were kept apart about $\frac{1}{8}$ inch by rings of rubber tubing fitting closely to the sides of the glass.

The scrubber was developed from a very much simpler one consisting of two discs in a tube attached to a filter pump. With this device a mist of ammonium chloride was very effectively dealt with, but the holes became choked in a very short time, and so when the idea was adapted to the oxidation apparatus duplicate scrubbers were provided in order that operation might be continuous, one scrubber being cleaned while the other was in service.

The actual effect of the discs was considered to be baffling of the mist particles. The effect of the first disc was to produce a sudden increase of velocity in the mist. Some of the particles shooting through would tend to strike the surface of the second disc with considerable impact, thereby adhering to the surface for sufficient length of time to prevent them going off again as mist.

By means of the taps shown in the diagram either unit could be switched in or out of circuit at will. When/

CALIBRATION CURVES OF FLOWMETERS



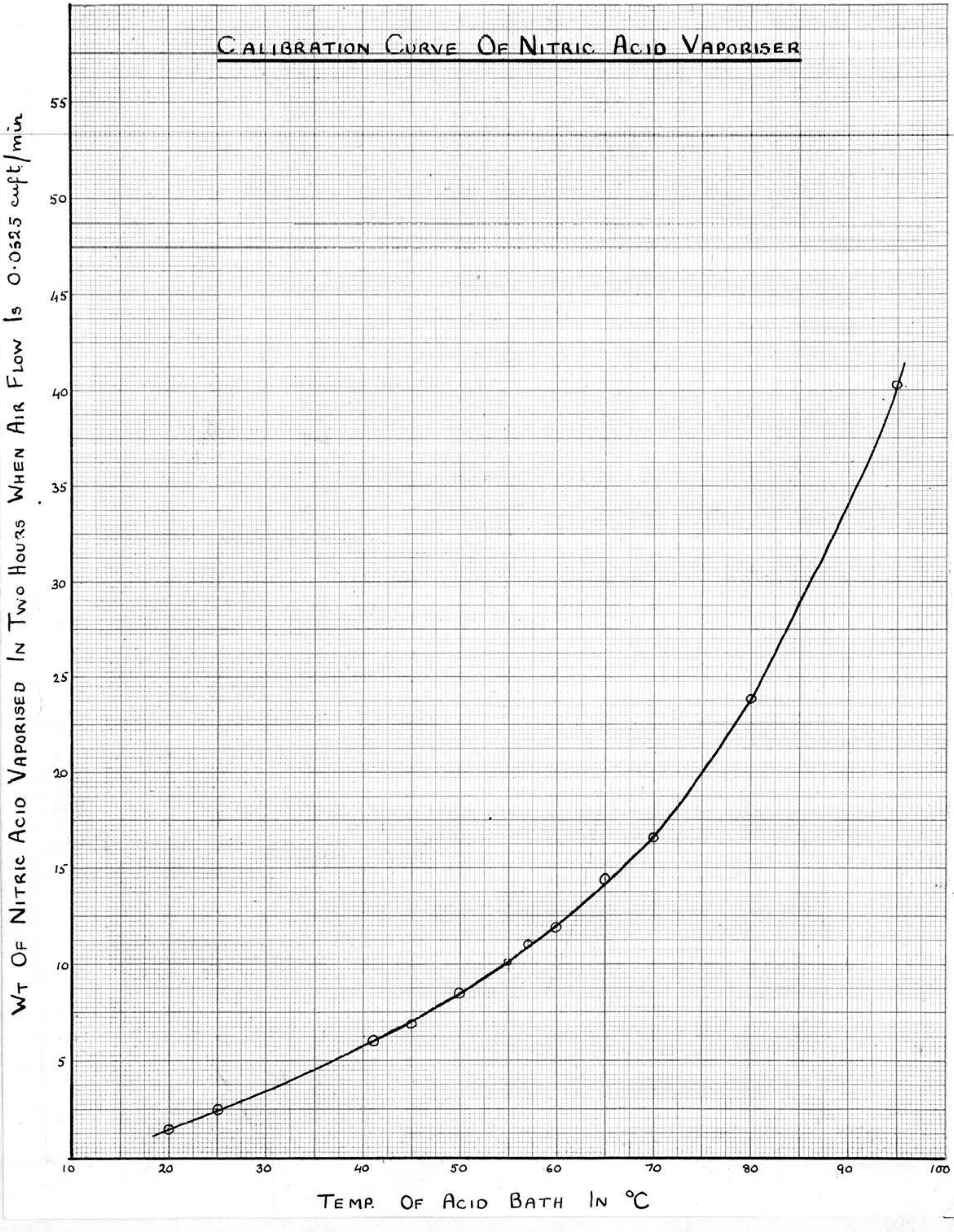
When one of the scrubbers became choked it was switched out, and cleaned by running down a small quantity of ether from the separating funnel attached to the top, the liquid running down and collecting in the flask attached at the foot. It was then ready for use again.

As the discs created a considerable resistance it was necessary to pull the gases through with the aid of a water pump. The amount of vacuum applied was controlled by adjustment of a tap which admitted air to the pump when opened.

Calibrations:- The flowmeters were calibrated against a gas meter, and the curves obtained are shown opposite.

The weights of naphthalene vaporised, even with constant air flow, showed large discrepancies at times, and no reliable calibration curve could be obtained. Conover and Gibbs[5] had a similar experience and believed the discrepancies to be due to variations in room temperature and draughts from day to day.

The amounts of acid vaporised were dependent on the air flow through the vaporiser and the temperature of the surrounding bath, and did not like the naphthalene appear to be influenced by variations in atmospheric temperature and draughts. As the temperatures/


Calibration Curve Of Nitric Acid Vaporiser
Wt Of Nitric Acid Vaporised In Two Hours When Air Flow Is 0·0525 cuft/min
55
50
45
40
35
30
25
20
15
10
5
10
20
30
40
50
60
70
80
90
100
Temp. Of Acid Bath In °C

temperatures were very much lower this was not unexpected. It was assumed that within experimental variations the weight of acid vaporised would be directly proportional to the air flow. This proved to be the case. The weights of acid vaporised in a number of experiments were reduced to the weight for an air flow of 0.0625 cubic feet per minute and the values so obtained plotted against the corresponding bath temperatures. The points were all found to lie on the curve shown on the opposite page. By means of this curve the amount of acid to be vaporised under a given set of conditions could be forecast with a fair degree of accuracy.

Table of Observations made on Nitric Avid Vaporiser.

No.of Expt.	Flowmeter Reading.	Cuft. of Air per minute	Temp. of Acid Bath	Wt. of Acid used.	Wt. of acid for .0625 cuft/min.
97	8.0 cms.	.0650	95°C.	39.27 gms.	37.80 gms.
115	7.5 cms.	.0625	80°C.	23.84 gms.	23.84 gms.
114	7.5 cms.	.0625	70°C.	16.62 gms.	16.62 gms.
104	7.5 cms.	.0625	65°C.	14.46 gms.	14.46 gms.
111	7.5 cms.	.0625	60°C.	11.96 gms.	11.96 gms.
101	7.5 cms.	.0625	57°C.	10.76 gms.	10.76 gms.
99	8.0 cms.	.0650	55°C.	10.10 gms.	9.74 gms.
110	7.5 cms.	.0625	55°C.	10.00 gms.	10.00 gms.
105	7.5 cms.	.0625	50°C.	8.49 gms.	8.49 gms.
107	7.0 cms.	.0600	45°C.	6.60 gms.	6.87 gms.
106	7.0 cms.	.0600	41°C.	5.55 gms.	5.78 gms.
120	7.5 cms.	.0625	25°C.	2.49 gms.	2.49 gms.
121	7.0 cms.	.0600	20°C.	1.48 gms.	1.55 gms.

Development Of The Apparatus:- In the preliminary work a simpler form of apparatus was used. The capacity was however small owing to a $\frac{3}{4}$" internal diameter furnace tube, and quantitative measurements were not possible as the vaporisers could not be detached for weighing, and no suitable method of calibration could be found.

The acid vaporiser consisted of two large capacity wash bottles connected in series and heated in a water bath, while the naphthalene vaporiser consisted of a distilling flask. The air stream was passed down the neck of the latter, and the mixed vapours passed out by the side tube into the mixer and preheater.

The absorption system was also somewhat different, though quite efficient in settling the mist. First came a settling bottle followed by two scrubbing towers connected as before to a filter pump. The exit gases were passed up the towers which were packed with glass wool, while the absorbing liquid was run down from the top. The liquid used initially was 8% sodium hydroxide solution, while later glacial acetic acid was substituted for this. The difficulty of recovering the products from the latter solvent was however rather great and therefore useless for quantitative work.

RESULTS. After testing the apparatus for leakages and carrying out a few preliminary experiments in order to determine suitable working temperatures and air speeds, it was observed that at a temperature of 400°C as recorded by the thermocouple in the gas mixture, (hereinafter referred to as the furnace temperature) a product distinct from naphthalene collected in the receiver. On purification this proved to be α-nitronaphthalene. Below 400°C reaction was very slight, and this temperature was taken therefore as the lowest at which an appreciable reaction would occur. Accordingly this reaction was studied in detail at this temperature under varying conditions.

The time of contact had to be fixed within fairly narrow limits at about 1.25 seconds. With longer periods flame combustion took place, while shorter periods reduced the amount of reaction to a very large extent. The relative amounts of naphthalene and nitric acid could however be varied within a fairly wide range, although the ratio of naphthalene to air had to be kept low in order to avoid flame combustion.

Variation of the molecular ratio of Nitric acid vaporised to Naphthalene vaporised was possible up to a ratio of about $\frac{5}{1}$. Beyond this firing occurred. Within/

Within these limits the main product was α-nitronaphthalene along with very small amounts of a dark coloured alkali soluble body. Even with high ratios of acid to naphthalene no trace of dinitro or trinitro derivatives was found.

The reaction was next studied quantitatively i.e. the variation in yield with differing acid to naphthalene ratios.

After removal of alkali soluble impurities the solid was dissolved in alcohol, and the weight of α-nitro-naphthalene in a sample was found by reduction with titanous sulphate, according to a modification of the method used by Callan and Henderson.[25]

The details are described in the Experimental Section.

The conditions and results for a number of experiments are shown in the following tables.

TABLE I.

No. of Expt.	Flowmeter Readings		Cuft. of Air/Min		Total Vol. of Air.	Temp. of Acid Bath.
	HNO_3	$C_{10}H_8$	HNO_3	$C_{10}H_8$		
106	7.0 cms.	3.5 cms.	.0600	.012	8.64 cuft.	41°C
101	7.5 cms.	3.5 cms.	.0625	.012	8.95 cuft.	56-57°C
109	7.0 cms.	3.5 cms.	.0600	.012	8.64 cuft.	50°C
112	7.5 cms.	3.5 cms.	.0625	.012	8.95 cuft.	65°C
110	7.5 cms.	3.5 cms.	.0625	.012	8.95 cuft.	55°C
111	7.5 cms.	3.5 cms.	.0625	.012	8.95 cuft.	60°C
105	7.5 cms.	3.0 cms.	.0625	.010	8.70 cuft.	50°C
114	7.5 cms.	3.5 cms.	.0625	.012	8.95 cuft.	70°C
104	7.5 cms.	3.5 cms.	.0625	.012	8.95 cuft.	65°C
115	7.5 cms.	3.0 cms.	.0625	.010	8.70 cuft.	80°C
108	7.0 cms.	3.0 cms.	.0600	.010	8.40 cuft.	75°C

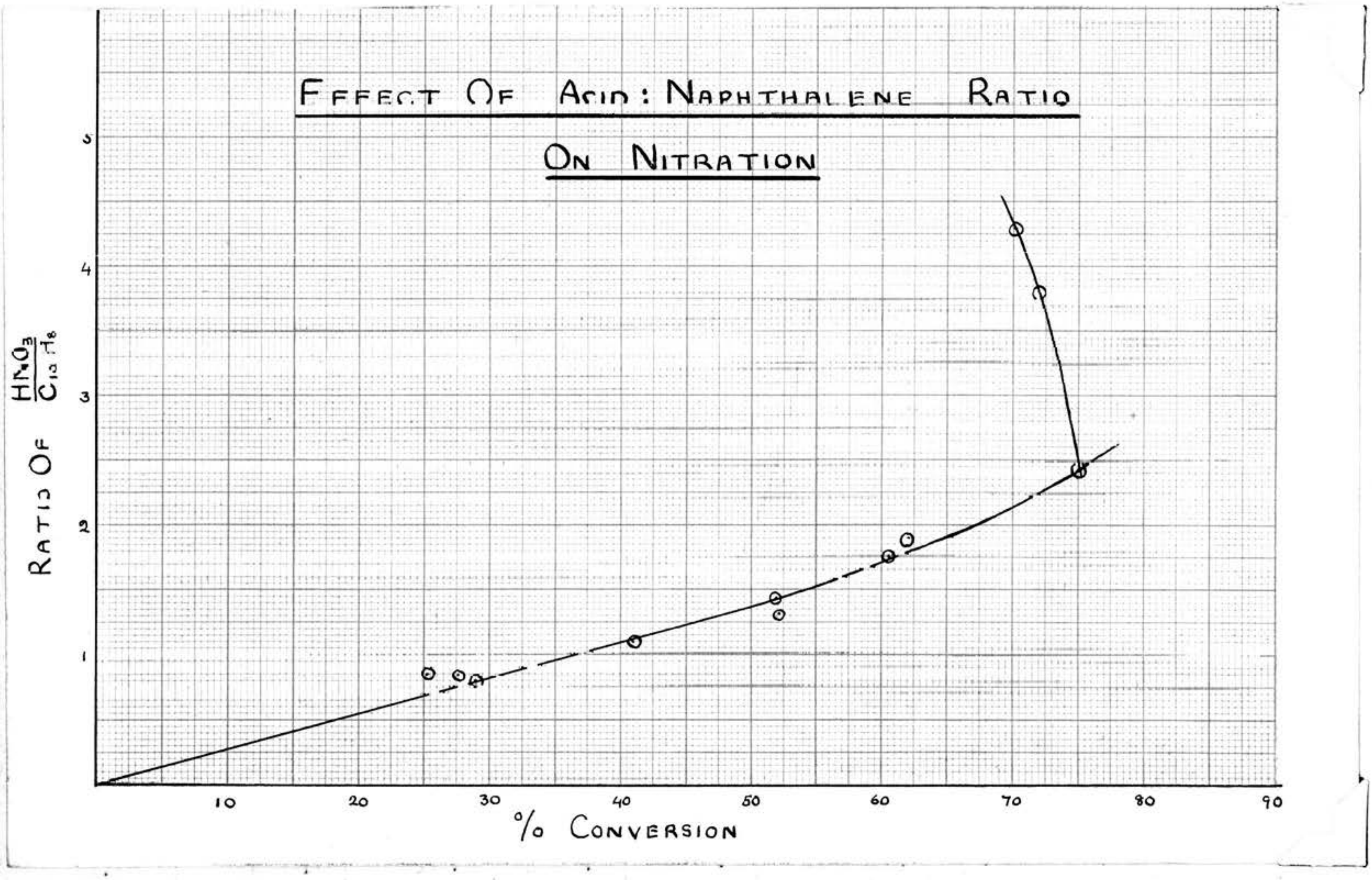
Other conditions were constant as follows:-

1.	Time of each run	120 mins.
2.	Temperature of furnace . .	$400^{\circ}C$
3.	Temperature of air oven . .	$250^{\circ}C$
4.	Temperature of mixture preheater	$250^{\circ}C$
5.	Temperature of preheated air .	$45^{\circ}C$

The respective weights of nitric acid and naphthalene vaporised are shown in table II.

TABLE II.

No.of Expt.	Wt.of HNO_3 used.	Wt.of $C_{10}H_8$ used.	Mols.of HNO_3	Mols.of $C_{10}H_8$	Mol.Ratio $\frac{HNO_3}{C_{10}H_8}$	Mols.of $C_{10}H_7NO_2$ formed.	% Conversion.
106	5.55 gms.	9.39 gms.	0.060	0.0733	0.820	0.0212	28.9
101	10.76 gms.	17.64 gms.	0.116	0.138	0.843	0.0380	27.6
109	6.72 gms.	10.91 gms.	0.0725	0.0852	0.852	0.0214	25.2
112	14.79 gms.	19.10 gms.	0.152	0.149	1.080	0.0609	40.8
110	10.00 gms.	10.49 gms.	0.108	0.0819	1.320	0.0426	52.0
111	11.96 gms.	11.78 gms.	0.129	0.0920	1.400	0.0483	52.0
105	8.49 gms.	6.68 gms.	0.0915	0.0522	1.755	0.0316	60.5
114	16.62 gms.	11.92 gms.	0.1793	0.093	1.930	0.0564	62.0
104	14.46 gms.	8.19 gms.	0.156	0.064	2.440	0.0481	75.2
115	23.84 gms.	8.65 gms.	0.2575	0.0676	3.810	0.0487	72.0
108	16.89 gms.	5.42 gms.	0.1825	0.0423	4.310	0.0298	70.3



EFFECT OF ACID : NAPHTHALENE RATIO ON NITRATION

It will be seen from the results and the graph of % conversion against molecular ratio of nitric acid vaporised to naphthalene vaporised shown on the opposite page, that the conversion increased to a maximum of 75% at 2.44 mols. of acid to one mol. of naphthalene. Above this ratio the yield decreased. It was probable that beyond this point some degree of oxidation took place forming carbon dioxide and water, as no appreciable quantity of either phthalic anhydride or the dark coloured alkali soluble body was observed in the products.

The fact that under the best conditions a large excess of acid was required to produce the mononitro derivative would seem to be explained by bad mixing, though this appeared very unlikely as the vapours were in turbulent motion, and the distance to be travelled before entering the furnace was at least nine inches. On the other hand the time of contact might have been too short.

Having studied the reaction at 400°C the temperature was raised. At 600°C with an acid ratio not exceeding 0.6 to 1 of naphthalene the reaction led to the formation of an oxidation product and not α-nitronaphthalene. Beyond this ratio firing occurred. Indeed at the higher temperature the reaction was very sensitive to change of conditions, and it was found that/

that the variables, time of contact etc. had to be maintained within the same limits as those used during nitration at 400°C in order to avoid flame combustion.

The oxidation product had the appearance and properties of a hydroxyquinone, and seemed to be identical with the by-product obtained in small amounts along with α-nitronaphthalene in the previous experiments. This body along with very small amounts of phthalic anhydride was the main product. The dark coloured substance distilled over as an oil mixed with naphthalene, and condensed in the trap just outside the furnace.

The reaction taking place at 600°C was studied quantitatively in detail with varying acid to naphthalene ratios.

The product was readily soluble in sodium hydroxide solution and was separated in this way from naphthalene and any small amount of insoluble impurities. After acidifying the red brown precipitate was filtered, washed with a large volume of water, dried and weighed. The weight obtained was taken as the yield. The results were calculated on the product having a molecular weight of 346 as it was believed to be a dinaphthyl-dihydroxy-diquinone, $C_{10}H_4O_2(OH).C_{10}H_4O_2(OH)$.

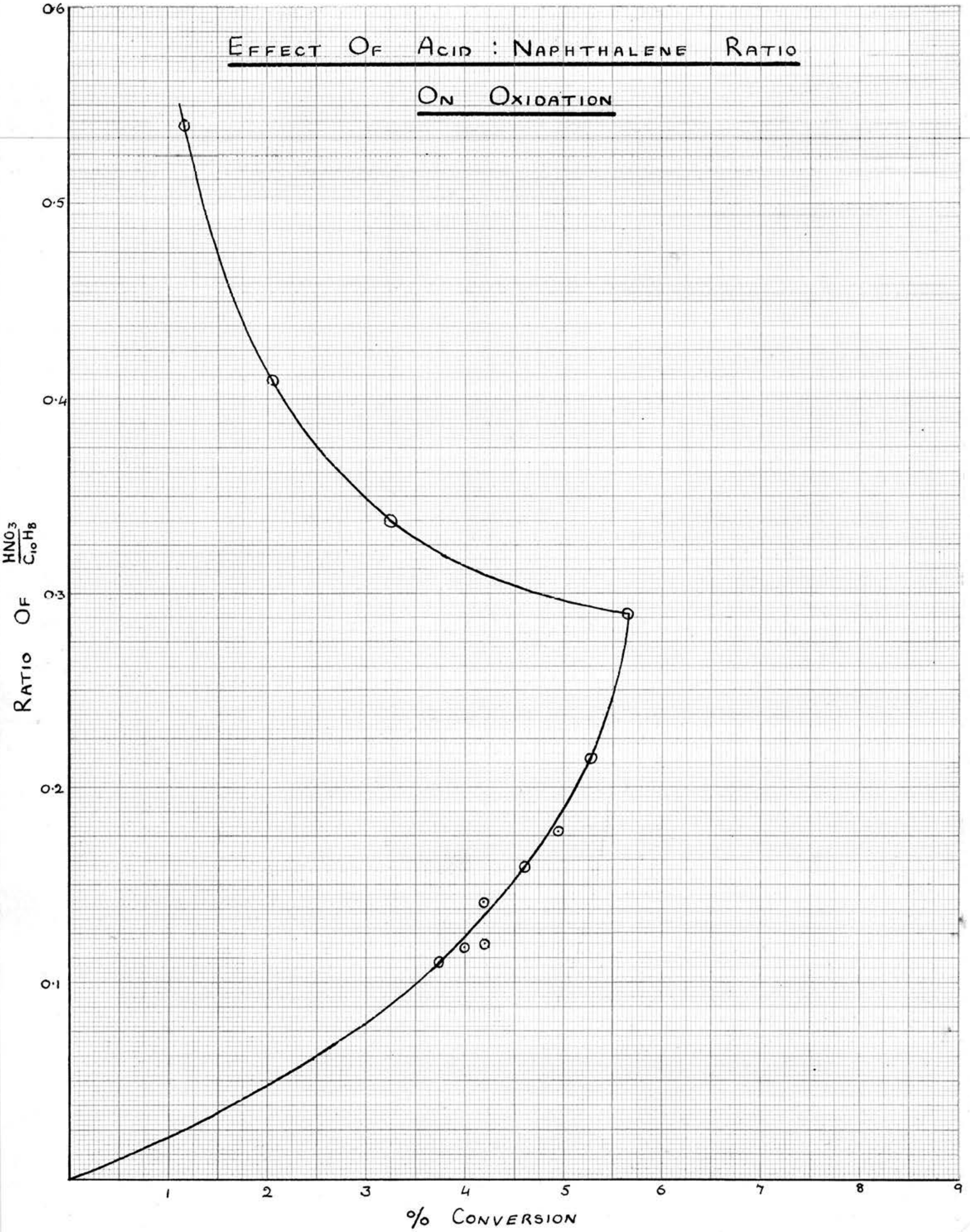
The conditions and results for a number of experiments are shown in the following tables:-

TABLE III.

No.of Expt.	Flowmeter Readings		Cu.Ft.of Air/Min.		Total Vol. of Air.	Temp. of Acid Bath.
	HNO_3	$C_{10}H_8$	HNO_3	$C_{10}H_8$		
130	7.5 cms.	3.0 cms.	0.0625	0.010	8.70 cu.ft.	20°C.
145	7.5 cms.	3.0 cms.	0.0625	0.010	8.70 cu.ft.	19°C.
127	7.0 cms.	3.5 cms.	0.0600	0.012	8.64 cu.ft.	19°C.
126	7.0 cms.	4.0 cms.	0.0600	0.014	8.88 cu.ft.	20°C.
146	7.0 cms.	3.0 cms.	0.0600	0.010	8.40 cu.ft.	18°C.
131	7.5 cms.	3.0 cms.	0.0625	0.010	8.70 cu.ft.	20°C.
128	7.5 cms.	2.5 cms.	0.0625	0.0085	8.52 cu.ft.	20°C.
143	8.0 cms.	3.5 cms.	0.0650	0.012	9.24 cu.ft.	25°C.
129	7.5 cms.	2.5 cms.	0.0625	0.0085	8.52 cu.ft.	20°C.
147	7.5 cms.	3.0 cms.	0.0625	0.010	8.70 cu.ft.	19°C.
144	7.5 cms.	1.5 cms.	0.0625	0.005	8.10 cu.ft.	25°C.
142	7.5 cms.	2.0 cms.	0.0625	0.007	8.34 cu.ft.	17°C.

Other conditions were constant as follows:-

1. Time of each run . 120 mins.
2. Temperature of furnace . 600°C.
3. Temperature of air oven . 250°C.
4. Temperature of mixture preheater 250°C.
5. Temperature of preheated air 55°C.



EFFECT OF ACID : NAPHTHALENE RATIO ON OXIDATION

TABLE IV.

No.of Expt.	Wt. of HNO_3 used.	Wt. of $C_{10}H_8$ used.	Mols.of HNO_3	Mols.of $C_{10}H_8$	Mol.Ratio of $\frac{HNO_3}{C_{10}H_8}$	Mols.of Product formed	% Conversion.
130	1.47 gms.	18.44 gms.	0.0159	0.1440	0.110	.00273	3.78
145	1.34 gms.	15.79 gms.	0.0145	0.1230	0.118	.00246	4.00
127	1.24 gms.	14.22 gms.	0.0134	0.1110	0.121	.00234	4.22
126	1.40 gms.	13.60 gms.	0.0151	0.1062	0.142	.00222	4.18
146	1.20 gms.	10.37 gms.	0.0129	0.0810	0.160	.00186	4.59
131	1.39 gms.	10.85 gms.	0.0150	0.0848	0.177	.00211	4.96
128	1.58 gms	10.22 gms.	0.0171	0.0798	0.215	.00211	5.28
143	1.83 gms.	9.93 gms.	0.0198	0.0776	0.255	.00178	4.59
129	1.48 gms.	7.05 gms.	0.0160	0.0551	0.291	.00156	5.66
147	1.35 gms.	5.55 gms.	0.0146	0.0433	0.337	.00070	3.24
144	2.07 gms.	7.00 gms.	0.0224	0.0546	0.410	.00056	2.06
142	1.14 gms.	2.91 gms.	0.0123	0.0228	0.540	.00014	1.17

It will be seen from the figures and the graph of % Conversion against acid to naphthalene ratio shown on the opposite page that the conversion reached a maximum of 5.66% at 0.291 mol. of acid to one of naphthalene. Above this ratio the yield decreased, rapidly at first, and then more slowly till the firing point was reached.

Working with ratios higher than that giving the maximum/

maximum yield the production of phthalic anhydride was quite noticeable. Long white needles were observed in the condenser and traps. These were removed with tweezers and shown to be phthalic anhydride. The yields of the latter were not determined as this was outside the scope of the present work, but the quantity produced appeared to increase as the acid to naphthalene ratio was raised.

Identification of the Oxidation Product:- The oxidation product contained only carbon hydrogen and oxygen, and when dry was an amorphous powder showing no traces of crystalline form under the microscope and, depending on the state of division, varied in colour from light brown to almost black. It was only very sparingly soluble in cold water when freshly precipitated and totally insoluble after being dried. In benzene and petroleum ether the solubility was very small, but solution took place more readily in acetic acid, acetone, nitrobenzene and most of the other common organic solvents. It separated with difficulty from hot absolute alcohol as a dark red brown powder. The product dissolved in concentrated sulphuric acid giving a dark brown solution and was reprecipitated unchanged on pouring into water.

The fact that the substance dissolved readily

in/

in solutions of sodium or ammonium hydroxide and was not reprecipitated on saturating the solution with carbon dioxide suggested a carboxy acid. The substance however did not attack sodium bicarbonate and was therefore thought more likely to be a hydroxy quinone or a polymerised hydroxy quinone, i.e. a "quinone humic acid". From the appearance of the substance and the method of preparation such a compound seemed quite likely.

If the product from the furnace was a quinone treatment with alkali would bring about oxidation to a hydroxy quinone. The product from the furnace was however purified without dissolving in alkali and found to be the same as the alkali treated substance, thus showing that the oxidation in the furnace was complete.

A molecular weight determination in camphor gave a value of approximately 390. The exact melting point of the camphor solution was difficult to determine owing to the dark colour of the solute.

The "naphthoquinone humic acids" are considered[19] to be at least termolecular polymers and the value of 390 corresponded more nearly to the molecular weight of a dinaphthyl derivative. The problem was accordingly attacked along these lines.

Although soluble in alkali the substance in aqueous solution gave no reaction towards litmus. This,/

This, together with the fact that solution in water only occurred with a freshly precipitated sample suggested colloidal properties. Examination in the ultramicroscope showed that an aqueous solution was colloidal.

No information was obtained from distillation with either soda lime or zinc dust, while treatment with phenyl hydrazine yielded no satisfactory result.

A combustion gave Carbon = 69.0% Hydrogen = 3.1%. This would indicate three oxygen atoms for each naphthalene nucleus. A dinaphthyl dihydroxy diquinone $C_{10}H_4O_2(OH).C_{10}H_4O_2(OH)$ requires 69.2% of Carbon and 2.9% of Hydrogen.

An analysis of the ammonium salt gave 4.73% of NH_3. The monoammonium salt of a dinaphthyl dihydroxy diquinone $C_{10}H_4O_2(ONH_4).C_{10}H_4O_2(OH)$ requires 4.68% of NH_3.

The silver salt was prepared from the ammonium salt and analysed. The % of silver found 22.7% agreed well with that required 23.8% for the monosilver salt of a dinaphthyl dihydroxy diquinone $C_{10}H_4O_2(OAg).C_{10}H_4O_2(OH)$.

Attempts to determine the number of hydroxyl groups were made, but owing to the colour of the alkaline solution any volumetric method using an indicator was impossible. Titration at a hydrogen electrode proved unsatisfactory.

Attempts to acetylate by various methods were unsuccessful.

A more accurate determination of the molecular weight by boiling point elevation methods also failed. In acetic acid no elevation was observed, and the solution appeared to be colloidal although the particles were probably comparatively small. Examination in the ultramicroscope gave rather indefinite results, while the Tyndall Effect was only exhibited to a slight extent. Congo Red which is known to be definitely colloidal in aqueous solution gives no Tyndall Effect nor can the aggregates be seen in the ultramicroscope. In the case of Congo Red the colloidal particles consist of only about ten molecules and are therefore too small to scatter light. With other solvents the behaviour of the substance was similar to that in acetic acid.

On oxidation with both acid and alkaline permanganate the substance was converted to phthalic acid along with a very small amount of a bright red substance unattacked by potassium permanganate. Chattaway[11] prepared a $\beta\beta'$-dinaphthyl dihydroxy diquinone which on further oxidation yielded only phthalic acid along with a small amount of an unidentified red coloured material.

This quinone as prepared by Chattaway darkened on/

on heating to about 200°C. then sintered, and finally melted at about 215°C. The present substance behaved similarly melting actually at 227°C. The exact temperature was difficult to determine owing to the dark colour and depended on the rate of heating. Decomposition appeared to take place at or near the melting point.

Chattaway makes no mention of attempting to reduce his quinone. The present substance did not appear to reduce by any of the several methods tried out.

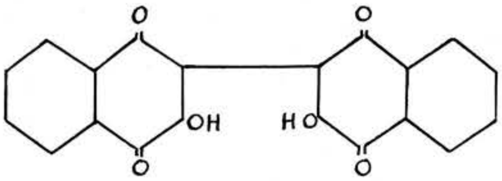
Bromination by some of the usual methods was unsuccessful.

The hot tube method of obtaining the dinaphthyls from naphthalene leads to a predominance of the ββ' form, and for this reason one would expect the present compound to be the ββ' form. On the other hand if the reaction proceeds either through the nitro compound or α-naphthol as the first stage, then one would expect an αα'-dinaphthyl derivative.

The analysis would also agree with an αα'-dinaphthyl-dihydroxy-diquinone. Korn[26] obtained αα'-dinaphthyl-2,2'-dihydroxy-3,4-3',4' - diquinone by polymerisation of β-naphthoquinone and subsequent oxidation with alkali. This compound is however a yellow crystalline body melting at 245-250°C, so that one must rule out the likelihood of the present compound/

compound being an $\alpha\alpha'$-dinaphthyl derivative.

Taking the evidence as a whole, one is led to support the formula:-

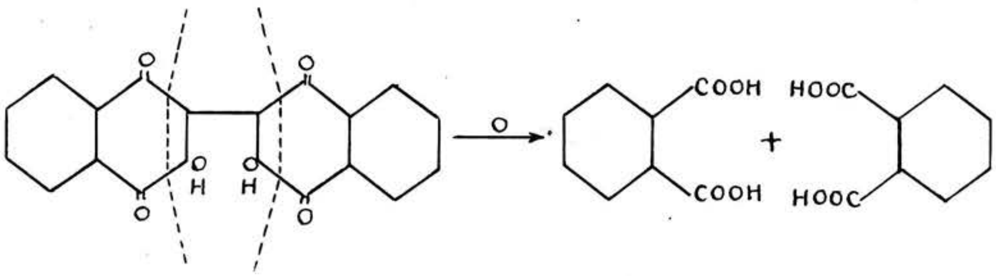


$\beta\beta'$- DINAPHTHYL 3,3'- DIHYDROXY 1,4-1'4'- DIQUINONE

The analysis of the ammonium and silver salts suggest only one hydroxyl group. It is quite possible however that due to steric hindrance only one ·OH group might react with ammonia. On the other hand if both ·OH groups were substituted one of them might on boiling revert to ·OH giving off ammonia.

The failure of the quinone to reduce might also be explained by steric hindrance the -OH and = O groups being in the ortho position to each other.

As further oxidation leads to phthalic acid

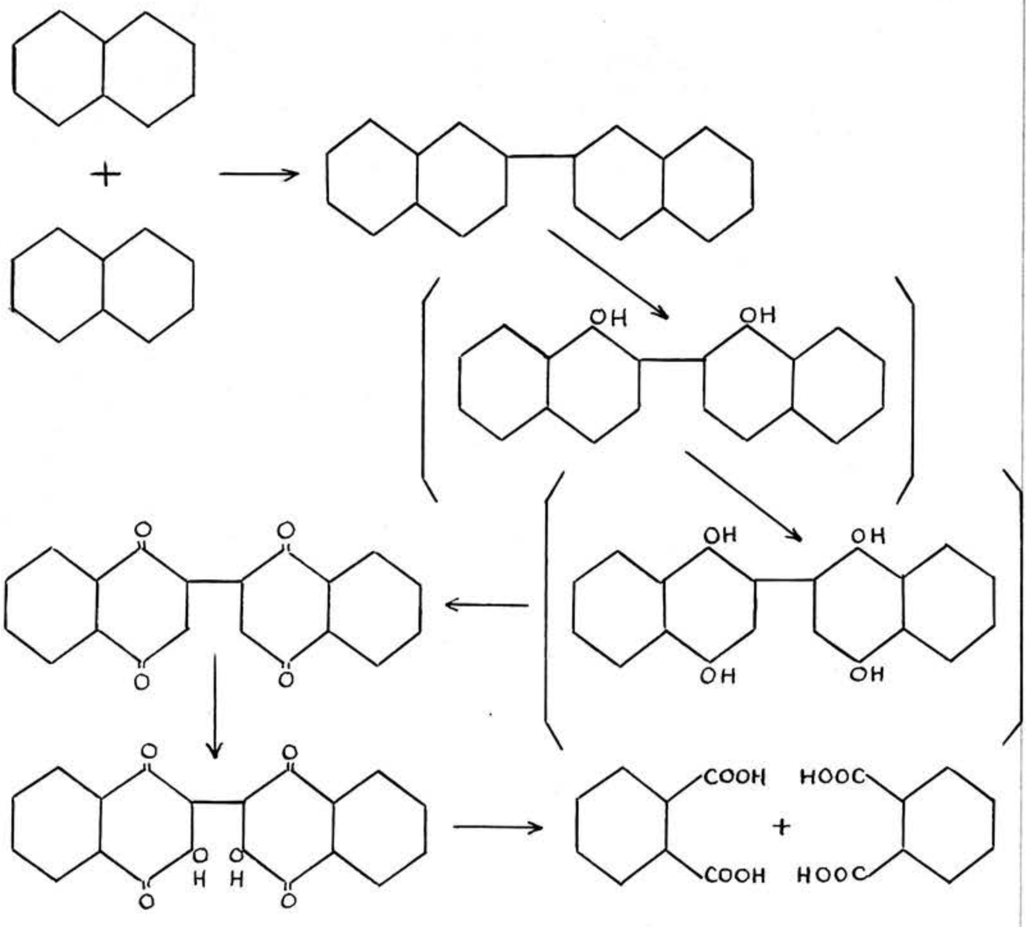


one/

one is led to put forward the theory that in the oxidation of naphthalene to phthalic anhydride ββ'-dinaphthyl dihydroxy diquinone is the last intermediate stage before rupture of the ring. With catalysts more active than oxides of nitrogen this compound would be oxidised to phthalic acid as fast as it was formed, and could therefore never appear in any but the smallest concentrations.

Such a theory is also supported by the fact that pyrolysis of naphthalene leads to the formation of ββ'-dinaphthyl which oxidises very readily to quinonoid derivatives.

The oxidation of naphthalene to phthalic anhydride may therefore proceed by the following stages:-



EXPERIMENTAL. The apparatus was first of all tested for leakages under the full pressure of the air supply mains, and found to be satisfactory.

Preliminary experiments showed that some of the reaction product came over as a heavy mist, difficult to remove, but which was successfully dealt with on the introduction of the scrubbers. It was observed that most of the oily product collected in the traps, while the solid material deposited in the air condenser, flask and upright condenser, and the mist was completely taken out by the scrubbers.

To test the efficiency of the absorption apparatus the nitric acid was removed from the vaporiser and a run carried out using only naphthalene and air at a furnace temperature of 400°C. After a weighed quantity of naphthalene had been put through the apparatus the recovered product from all parts of the absorption system was dissolved in alcohol. To recover the product quantitatively from the alcohol by evaporation was not possible because of the volatility of the naphthalene, so a method of estimation of the latter in alcoholic solution was sought for.

The methods detailed in the literature are all for estimation of naphthalene in coal gas, and consist essentially of conversion to the picrate which can then/

then be weighed or determined by volumetric methods.

Kuster's[27] method was tried out but proved cumbersome and rather unreliable. The method consists in passing the coal gas through a known volume of standard picric acid solution. Impure naphthalene picrate is always formed. The absorption flask is then exhausted of air and heated on the water bath for two hours. On cooling the pure solid now formed is filtered off, and the excess of picric acid in the filtrate titrated with standard alkali.

The method was tried out by heating in vacuo weighed quantities of naphthalene with a known excess of picric acid. The results were however unsatisfactory. Colman and Smith(28) and later Gair(29) made various improvements on the method, introducing washing of the precipitate with various solvents, and new methods of titration. Gair later dissolved the precipitate of impure naphthalene picrate in the minimum quantity of absolute alcohol along with a slight excess of picric acid. To the alcoholic solution he then added a large volume of saturated aqueous picric acid whereby pure naphthalene picrate was precipitated. His subsequent procedure was somewhat unnecessarily laborious however.

The method adopted for the present work was a combination of the methods of all the workers mentioned. It/

It was hoped to use it in later work to determine the amount of naphthalene unattacked in the oxidation apparatus.

Estimation of Naphthalene as the Picrate:-

Weighed quantities of naphthalene together with a moderate excess of picric acid were placed in a 250 cc. beaker along with 10 ccs. of alcohol R.S. The mixture was warmed gently to assist solution. When all the solid had disappeared the solution was cooled, and then while stirring vigorously a nearly saturated aqueous picric acid solution was run into the beaker up to the 250 cc. level. After standing for a few minutes the precipitated picrate was filtered off through a Hirsch funnel, the beaker being rinsed with the picric acid solution mentioned above. This solution was made up by adding 200 ccs. of water to 2500 ccs. of saturated picric acid. The solution being now below the saturation point could take up the excess of picric acid in the alcoholic solution.

The precipitate in the funnel was sucked as dry as possible with the pump, and was then washed with 7 to 8 ccs. of cold distilled water to displace picric acid from the cake. Naphthalene picrate is soluble in water, but insoluble in strong aqueous picric acid solutions, hence the reason for precipitating in the latter medium.

After/

After again sucking dry, a jet of hot water was used to transfer the solid to a beaker where the mixture was titrated with N/10 sodium hydroxide, using phenolphthalein as indicator. When the solution turned orange or pink in colour, thus seeming to indicate the end point, the beaker was warmed when the colour generally changed back to pale yellow. More alkali was added and the end point taken only when the colour was seen to be permanently pink or orange on boiling the mixture. The method was found to be accurate within 1%.

Using this method it was determined that the weight of naphthalene recovered in the "efficiency test" was 1.90 grams against 1.89 grams vaporised, i.e. a recovery of 100.7%.

This showed then that as far as naphthalene was concerned the absorbing system was very efficient, and no doubt efficient for catching any mist that might come along.

A series of experiments was now carried out with a furnace temperature of 400°C under varying conditions. The details are shown in the Results.

It was observed that a yellow coloured oil collected in the traps in the receiver. On standing the oil solidified in a crystalline form.

The/

The solid was taken out and warmed with water in order to remove acid. Ice was then added while stirring rapidly so that the product solidified in a granular form. The granules were then filtered off and washed with a large quantity of cold water. The solid was next remelted with a 1% sodium hydroxide solution and again granulated, filtered and washed. This removed the last traces of nitric acid and in addition phthalic acid, quinones, nitronaphthols etc. if they happened to be present. Finally the product received another treatment by melting in hot water to remove last traces of alkali. The solid was then dissolved in a small quantity of hot alcohol, and well boiled for a few minutes with animal charcoal. After filtering hot, the solution on cooling deposited yellow needles. After one or two recrystallisations from alcohol or light petroleum the melting point remained steady at 56.5°C, the melting point of pure α-nitronaphthalene (corrected)(30). A mixed melting point with pure α-nitronaphthalene showed no depression, while a combustion gave 8.0% of nitrogen. α-Nitronaphthalene requires 8.1%.

Under varying ratios of nitric acid vaporised to naphthalene vaporised obtained by altering the temperature of the nitric acid bath, α-nitronaphthalene appeared to be the main product. The presence of naphthols could not be detected, while the yield of the/

the quinone body recovered from the alkaline extract by acidifying, was always small. Nitration therefore appeared to be the main reaction at 400°C.

The reaction was next studied quantitatively under the same conditions.

After each experiment the product was carefully removed by washing into a beaker with water or ether, the washings of the scrubbers being also added.

After evaporating off the ether by warming gently on the steam bath the solid was purified as described previously, by melting with (a) water, (b) 1% sodium hydroxide and (c) water. The solid was now removed carefully to a beaker, and dissolved in about 200 ccs. of alcohol, heat being applied to assist solution if necessary. The alcoholic solution was then filtered into a graduated flask, the washings of beaker, funnel etc. were added, and the solution made up to the mark.

The method of estimation used was that recommended by Callan and Henderson,(25) namely reduction by a known excess of standard titanous sulphate solution in presence of sulphuric acid, followed by back titration with standard iron alum using ammonium thiocyanate as indicator.

The titanous sulphate solution which was of approximately 1% strength was first standardised with pure α-nitro naphthalene prepared by the method of De Aguiar.(31)

Preparation of α-Nitronaphthalene

64 gms. naphthalene

150 ccs. glacial acetic acid

33 ccs. concentrated nitric acid

The naphthalene was dissolved in the acetic acid in a one litre flask fitted with a reflux water condenser and a tap funnel. The mixture was heated to the boiling point and the acid then slowly run in from the tap funnel. After the addition of acid was completed the mixture was boiled for half an hour. On cooling the nitro compound crystallised out. It was filtered off, washed free from acid with water, and after one recrystallisation from alcohol the sharp melting point of 56.5°C showed the compound to be pure.

Estimation of the α-Nitronaphthalene Formed:-

(a) Standardisation of the Titanous Sulphate Solution:- The reaction was carried out in a 250 cc. round bottomed flask fitted with a reflux water condenser and a tube through the stopper for admission of carbon dioxide. The carbon dioxide was generated in a Kipp and purified by passing firstly through sodium bicarbonate solution and secondly concentrated sulphuric acid.

25 ccs. of 40% sulphuric acid (A.R.) were run into the flask, which was then connected up and flushed out/

out with carbon dioxide for five minutes. The flask was then carefully detached and 50 ccs. of the titanous sulphate solution run in. The flask was connected up once more and a flame applied. When the solution was boiling 5 ccs. of alcohol were slowly run in from the top of the condenser, and the solution boiled for seven minutes. The flask was then cooled, and when quite cold was detached and a bent glass tube reaching nearly to the surface of the liquid was placed in the flask. The other end was attached to the carbon dioxide apparatus. The cold solution was then titrated with iron alum solution of about 0.03 N. strength, using 20 ccs. of a 20% solution of ammonium thiocyanate as indicator. This gave the relationship of the titanous sulphate solution to the iron alum solution under the exact conditions of a genuine reduction.

(b) This procedure was then repeated in a second experiment only this time a standard solution of α-nitronaphthalene in alcohol was run in, the strength being approximately 0.05 N.

From the difference in the back titration between the blank and the actual reduction, the relationship between iron alum, titanous sulphate and α-nitronaphthalene was determined.

(c) Determination of the nitronaphthalene in an unknown:- The procedure was as described above. A portion of the original alcoholic solution was made up/

up to 100 ccs. in a graduated flask, and 5 ccs. of this new solution were run into the boiling mixture. From the result of the back titration and the normalities of the standard solutions already determined, the amount of α-nitronaphthalene present was calculated.

It was found by experiment that the presence of naphthalene in no way impaired the accuracy of the method.

It was hoped to determine also the amount of unchanged naphthalene by the method already described. α-Nitronaphthalene forms a picrate which decomposes in presence of moisture, and although a great deal of work was done to try and produce the latter in quantitative yields by the precipitation method, reproducible results were not obtained.

The estimation of the unchanged naphthalene had therefore to be abandoned.

On raising the furnace temperature to 600°C a dark brown oil consisting of naphthalene and an alkali soluble material of the hydroxyquinone type collected in the receiver.

The yields of the latter under varying conditions of nitric acid to naphthalene ratio were determined. The details are shown in the results.

After/

After each experiment the product was as before, washed into a beaker with water or ether, and the washings of the scrubbers added. After evaporating off the ether layer on the steam bath the resulting mixture was made alkaline with sodium hydroxide. The solution was warmed to the boiling point to melt the naphthalene, and thus set free any included alkali soluble matter. After cooling, the naphthalene along with a very small amount of insoluble impurity was removed by filtration. The resulting solution was then evaporated down on the water bath till the volume was about 250 ccs. On acidifying with hydrochloric acid the oxidation product was precipitated as a red brown flocculent material.

If the precipitation was carried out slowly the product filtered fairly easily, but if carried out too rapidly the substance came down in a gelatinous form almost impossible to filter.

In order to assist coagulation of the particles, the mixture after precipitation was maintained at about 80°C on the water bath for half an hour. After cooling the product was filtered off and washed with a large volume of cold water, a medium in which it was almost insoluble. It was then dried to constant weight in a vacuum dessicator. Although the material was probably not quite pure the weight obtained was taken as the yield.

Under/

Under certain conditions white needles were observed to form in the condenser and traps. Some of these were removed and examined. They were proved to be phthalic anhydride by fusion with a little resorcinol and a few drops of concentrated sulphuric acid, when fluorescein was produced. The needles melted at 128°C, while a mixed melting point with pure phthalic anhydride (melting point 130°C) melted at 129°C.

Identification of the Oxidation Product:-

The oxidation product was purified by repeated precipitation from alkaline solution, until the indefinite melting point showed no further rise.

In some cases purification was effected by separation from hot alcohol, but the melting points of the specimens obtained were no higher.

To prove that the substance was unaffected chemically by the treatment with alkali the crude material from the traps was worked up by other methods.

(a) In order to remove any free acid the crude material from the traps was dissolved in the minimum quantity of glacial acetic acid, and thrown out by addition of water. After filtering and washing with water the solid was subjected to steam distillation to remove the naphthalene. During this last process some slight decomposition appeared to take place so the/

the product was again taken up in glacial acetic acid and filtered free from insoluble matter. On dilution with water a red brown amorphous material separated. After being dried, this possessed the same melting point and properties as the alkali treated product.

(b) Another specimen was freed from acid as described above and after drying was heated to about 190°C under a pressure of one millimetre. The naphthalene sublimed out, while a small amount of oil distilled off. The residue after separation from a small quantity of decomposed matter was similar to the alkali treated specimens.

Treatment with Phenyl Hydrazine:-

A portion of the oxidation product was heated for several hours in acetic acid solution with phenyl hydrazine hydrochloride. A tarry material separated on pouring into water. No recognisable products,other than the original materials could be extracted from this tar. In aqueous alcoholic solution, and in acetic acid solution in presence of sodium acetate, similar results were obtained.

Analysis of Ammonium Salt:- A weighed quantity of the oxidation product was dissolved in very dilute aqueous ammonia and the resulting solution boiled until the escaping steam was free from ammonia. The combined ammonia was then determined by the direct method in the usual way.

Analysis of Silver Salt:- An excess of silver nitrate was added to a solution of the ammonium salt, prepared as above. The silver salt which separated was filtered off and washed with water till free from nitrate. The salt was then dried in an oven at 110° to 120°C. A weighed specimen of the dry salt was then converted to metallic silver by ignition.

Titration at a Hydrogen Electrode:- A weighed quantity of the substance was dissolved in a known volume of standard sodium hydroxide, and titrated back at a hydrogen electrode with standard sulphuric acid. The end points were however unreliable due no doubt to the nature of the compound, and the method had to be abandoned.

Treatment with Acetic Anhydride:- The "Thiele Acetylation"[32] method for quinones was tried out. A quantity of the substance was slowly added to a mixture of ninety parts of acetic anhydride and ten of concentrated sulphuric acid. With benzoquinone, naphthoquinone etc. heat is developed during this process, and the mixture has to be cooled in order to control the reaction. In this case no evolution of heat occurred, and therefore the mixture was heated to 80°C on the water bath for several hours. On pouring into water a tarry material separated. This was filtered off and extracted with hot alcohol. The alcoholic solution/

solution was boiled with animal charcoal and filtered hot. The solid which separated on cooling, was however soluble in alkali and did not differ from the starting material.

Another method was tried out by boiling in a mixture of five parts of pyridine and one of acetic anhydride. After one hour the mixture was poured into water and the precipitate collected and washed. It proved to be the original substance unchanged.

Treatment with Potassium Permanganate:- A quantity of the oxidation product was dissolved in 1% sodium hydroxide. The resulting solution was heated on the water bath, and then while stirring vigorously a solution of potassium permanganate was run in till the colour of the resulting turbid mixture was seen to be tinged with purple.

After cooling, the mixture was acidified with sulphuric acid, and the excess of permanganate along with the precipitated manganese dioxide destroyed with sulphurous acid. The resultant solution was almost colourless and was extracted with ether. The ether was removed and the resulting viscid mass boiled with a small quantity of water. A small amount of a red material remained undissolved. This was filtered off hot. The solid which separated was phthalic acid; this was confirmed by the formation of fluorescein on/

on fusing with resorcinol in presence of concentrated sulphuric acid.

The red substance insoluble in hot water was soluble in alkali and reprecipitated on acidifying, and was not further attacked by alkaline permanganate.

Phthalic acid was also produced by oxidation with acid permanganate. In this case the substance was dissolved in boiling glacial acetic acid, and the permanganate, dissolved in acetone, run in as before. The subsequent procedure was similar to that described above.

Treatment with Reducing Agents:- 1 An alkaline solution was shaken with 5% sodium amalgam in an atmosphere of hydrogen. No colour change took place and on acidifying the original compound was reprecipitated unchanged.

2 An alkaline solution shaken with zinc dust in an atmosphere of hydrogen gave similar results.

3 Boiling with zinc dust and hydrochloric acid was also unsuccessful.

4 An acetic acid solution was boiled with titanous sulphate solution. On pouring the mixture into water the original substance was recovered unchanged.

5 Boiling with zinc dust in acetic acid gave similar results.

6 An alkaline solution was treated with sodium hydrosulphite. On acidifying the starting material was recovered.

7 An alcoholic solution boiled with stannous chloride also gave negative results.

Treatment with Bromine:-

1 An acetic acid solution of the oxidation product was treated with bromine. No reaction appeared to take place but to test this point the solution was poured into water. The solid which separated was filtered off and well washed with water. It was found to contain no bromine.

2 A solution in concentrated sulphuric acid was treated with bromide-bromate solution. No absorption of the bromine liberated took place.

3 Bromine was added to an alkaline solution of the oxidation product. On acidifying a solid which did not contain bromine was thrown down.

SUMMARY.

By passing naphthalene vapour and oxides of nitrogen along with air through a zone heated to 400°C. with a short time of contact, α-nitronaphthalene was obtained up to a yield of 75%.

Under similar conditions at a temperature of 600°C. naphthalene was oxidised to ββ'-Dinaphthyl 3,3'-Dihydroxy 1,4-1',4'- Diquinone. Yields up to 5.66% were obtained.

In the vapour phase oxidation of naphthalene to phthalic anhydride it is probable that ββ'-Dinaphthyl 3,3'-Dihydroxy 1,4-1',4'- Diquinone is formed in the stage before rupture of the ring takes place.

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