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UNIVERSITY OF LOUISVILLE

THE VAPOR PHASE OXIDATION OF A BENZENE
SOLUTION OF PHENANTHRENE, USING SOLUBLE
CATALYSTS

A Thesis

Submitted to the Faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

By

Carey William Brackin

1940

THE VAPOR PHASE OXIDATION OF A BENZENE
SOLUTION OF PHENANTHRENE, USING SOLUBLE
CATALYSTS

Carey William Brackin

Approved by the Examining Committee:

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July 20, 1940

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ABSTRACT

This investigation was on the vapor phase oxidation of a benzene solution of phenanthrene, employing a series of soluble catalysts. The effect of cobalt linoleate, tetraethyl lead fluid, nitrobenzene, quinoline, and pyridine on the oxidation was investigated. The yield of dibasic acids resulting with the use of each of the above catalysts, under various operating conditions, was determined.

Only traces or small yields of dibasic acids were obtained in any of the runs which were made. The data obtained indicated too much complete oxidation of the benzene, with no appreciable oxidation of the phenanthrene to dibasic acids.

INTRODUCTION

INTRODUCTION

In the distillation of coal for the production of tar, there are a number of by-products obtained. Most of these by-products have been developed and are used today, as such or as the raw materials for other valuable products. Among the by-products which have found the least use, thus far, is phenanthrene.

Phenanthrene is obtained in the process of purification of the coal tar obtained on distillation of coal. The crude coal tar is scrubbed with hot coke-oven gas, which removes the light and heavy oils held by the tar. This gas, laden with the oils thus removed, is cooled and the oils condense out. The gas passes on, leaving the oils in the cooling vessel. The mixture of oils obtained is fractionated, usually into four fractions. If the distillation is carried out at atmospheric pressure, that fraction which boils between 270°C. (518°F.) and 320°C. (608°F.) contains anthracene, phenanthrene, and carbazol. This fraction solidifies on cooling, and it is then washed with solvent naptha and filtered. The naptha contains the phenanthrene, which may be separated by distillation.

Much work has been done in an effort to find profitable uses for the by-product phenanthrene, and much

research is still being carried on in this direction. Among the common processes which have drawn the most interest, in the treatment of the by-product, is the oxidation of the phenanthrene in an attempt to develop economical and profitable processes for obtaining satisfactory yields of oxidized products which would be more useful and valuable than the original material. Phenanthrene, as such, is of no value; it finds use only as a starting material for the production of other more desirable and useful end-products.

Considerable work has been carried out in the investigation of vapor phase oxidation of the phenanthrene with air, at high temperatures and with catalysts. However, all of this work has been pursued using solid catalysts and essentially pure mixtures of phenanthrene and air. Such a mixture is somewhat difficult to handle on account of the high boiling points of the raw material and the end-products. Moreover, the yields were none too high.

It was conceived that, if phenanthrene could be preferentially oxidized in the presence of benzene, a benzene solution of the phenanthrene would greatly facilitate handling of the material, especially at room temperature. Furthermore, the use of soluble catalysts in such a solution would greatly reduce the complications usually encountered in such oxidations with the use of

solid catalysts,--such complications as the rapid and efficient removal of accumulated heat from the catalyst mass.

The products that might most easily be expected would be the dibasic acids, which would result on the partial oxidation of the phenanthrene, principally phthalic acid, diphenic acid, and maleic acid. The dibasic acids are very much desired by the varnish and synthetic resin producers for the manufacture of various resins; this, of course, would be a ready market for the products of the oxidation mentioned above, if such products could be obtained cheaply enough to meet competitive prices from other sources.

The purpose of this investigation was to determine the possibilities of the vapor phase oxidation of a benzene solution of phenanthrene, using soluble catalysts.

HISTORICAL

HISTORICAL

Only in comparatively recent years has the distillation of coal for its tar and heavy oils received detailed attention. As the by-product coke became accepted more and more by the metallurgical industries, the old beehive coke ovens, which operated with the production only of coke, were gradually replaced by by-product coke ovens which conserved the more volatile by-products although yielding a coke which might not be as desirable as that produced by the bee-hive ovens. With the acceptance of the by-product coke, there resulted a large amount of research on methods of distillation of the coal tar. The result was the improved production of high melting point pitch and a large increase in yields of the constituent oils.

With the increased production of coal tar by-products, as the transfer was gradually made from bee-hive ovens to by-product ovens, the utilization of these by-products became an increasingly more important question. The tar, of course, was used in its finished form for road surfacing, waterproofing, etc. The light oils resulting from the distillation were used as solvents, fuels, and as intermediates for other products. The heavy oils, on the other hand, found little use in their finished form and

were practically entirely useless except as intermediates. For this reason, much research has been applied to the development and use of the heavy oils which contain, principally, anthracene, carbazol, and phenanthrene. In the technical production of these constituents, they are isolated into fairly pure states and may then be dealt with individually.

The first important investigations undertaken relative to the oxidation of these heavy oils by air were made by Gibbs and Conover, who did much work in the field in 1918 and the following years. In U. S. Patent 1,417,367, they protected the oxidation of anthracene to anthraquinone by air, in the presence of vanadium pentoxide. In collaboration with Lewis, Gibbs also obtained U. S. Patent 1,288,431, in 1918, covering the similar treatment of phenanthrene to yield phenanthraquinone.(10)

In 1922, Gibbs obtained another patent, relating to the oxidation of anthracene and phenanthrene mixtures, such as may be obtained by removal of carbazole by caustic fusion from anthracene press cake. This patent, U. S. Patent 1,444,088, claimed the production of a mixture of phthalic anhydride and anthraquinone when the vapors of the phenanthrene and anthracene were oxidized with oxygen in the presence of oxides of vanadium, molybdenum, or chromium.(17) This patent Gibbs assigned to E. I. du Pont

de Nemours and Company, Wilmington, Delaware.

For several years, little further work was carried out in this field, but, in 1937, Yu. S. Zal'kind and V. V. Kesarev published the results of an extensive research, inquiring into the vapor phase oxidation of phenanthrene by air in the presence of solid catalysts. (24) Upon oxidizing of a 3% mixture of phenanthrene in air, at 400° C., in the presence of pumice impregnated with V_2O_5 , they obtained CO_2 , H_2O , and only 2% of phthalic acid. The largest yield, 11.5%, of phthalic acid was obtained at a reaction temperature of 370° C. with a reaction time of 4 seconds. Upon the addition of CO_2 to the air, no increase in yield was obtained; but increasing the moisture content yielded 14% of solid acids, melting at 177° C. The use of pumice impregnated with 25% NH_4VO_3 gave a yield of 21% of acids. Pure WO_3 had no catalytic effect on the reaction, and mixtures of this compound with vanadium oxides yielded only 12% of acids. Mo had little catalytic action, but U oxide, mixed with V_2O_5 , catalyzed the reaction to quite some extent, yielding 41% of solid acids. The optimum conditions for this catalyst (U 30 and V 70%) were 10 grams of catalyst, a contact time of 1.2 seconds, and a reaction temperature of from 430° C. to 440° C. A mixture of 60% V, 10% Mo, and 30% U yielded 30% of solid acids,

at a temperature of 350-80° C. and with a reaction time of 2 seconds. The mechanism proposed for the oxidation of the phenanthrene was: phenanthrene $\longrightarrow$ phenanthrene quinone $\longrightarrow$ 6,6'-diphenic acid $\longrightarrow$ o-phthalic acid $\longrightarrow$ BzOH $\longrightarrow$ maleic acid $\longrightarrow$ CO₂ + H₂O; and the formation of some fluorenone and fluorenenonecarboxylic acid during the oxidation was explained by the scheme: 6,6'-diphenic acid $\longrightarrow$ 2,6'-diphenic acid $\longrightarrow$ fluorenenonecarboxylic acid $\longrightarrow$ fluorenone $\longrightarrow$ o-phthalic acid.

At about the same time, J. K. Chowdbury and M. A. Saboor were carrying on similar researches on the vapor phase oxidation of naphthalene and of phenanthrene with air in the presence of tin and vanadium catalysts.(2) On oxidation of phenanthrene over tin vanadate-asbestos catalyst at 420° C., there resulted a yield of 22.35% phthalic anhydride, with the simultaneous formation of CO₂, CO, and traces of maleic acid, phenanthraquinone, and C₁₄H₉OH. It was found that lower temperatures and shorter time of contact favored the formation of the quinone.

Similar work on the oxidation of benzene was carried out immediately following the world war by Weiss and Downs, in an attempt to obtain phenol directly from benzene by the catalytic oxidation of that substance

with air. Instead of phenol, which appeared only in traces, they obtained appreciable quantities of maleic acid. (22)

After further research, Weiss and Downs developed the method, as described in U. S. Patent 1,318,632 of 1919, of oxidizing a mixture of benzene and benzoquinone in the vapor state under pressure by the use of a gas containing oxygen and in the presence of vanadium pentoxide. The temperatures prescribed fell between 300° and 700° C. After separation of the maleic acid produced, the residual benzene and benzoquinone were recirculated through the system for further oxidation. U. S. Patents 1,318,631 and 1,318,633 of 1919 claimed the production of maleic acid and benzoquinone upon the oxidation of benzene by air at 300-350° C. when passed over a suitable catalyst.

Whereas, like most researches on catalytic oxidation, all the instances mentioned have been concerned with solid catalysts, a large amount of work has also been pursued, in work on other materials, in developing soluble catalysts. Most of this work has been carried out in investigations on the oxidation of petroleum. The reason for this has been the fact that, in this field, it has been found necessary to have the catalyst in intimate contact with the oil during the oxidation in order for

the catalyst to be effective. A catalyst held in solution by the oil and vaporized simultaneously with it affords the most intimate contact and is the logical type for use in this instance. A series of catalysts has been developed and those in the patent literature which may be considered as the most important are: metal enolates as manganese acetyl acetone, oleates or stearates of manganese, copper, or iron, stearate or cinnamate of barium, calcium, magnesium, aluminum, resinates, oleates, enolates of the alkali metals, magnesium, aluminum, iron, and zinc, organic nitrogenous bases as hexamethylene-tetramine, aniline, pyridine, quinoline, etc. (17)

In the strictest sense, such materials, as they are used, can scarcely be regarded as catalysts as the term is usually defined. In the words of Marek and Hahn (17): "A catalyst is a substance which in minimal amounts will bring about the transformation of large quantities of the reacting substances and which will be found unchanged in its chemical composition at the end of the reaction." However, these materials do speed up the reaction rates of the oxidation at sufficiently low temperatures to prevent undue decomposition, and it is common usage to call them catalysts. Although they are often changed tremendously in their composition during the course of the

reaction, they still bring about the desired results in various manners as will be explained in the section on theory.

THEORY

THEORY

The definition of a few general terms will first be given, as a clear understanding of these terms is necessary in a discussion of catalytic theory. The bulk of the theory to be given here has been abstracted from the material presented on the subject in two rather comprehensive works in the field: "Industrial Catalysis" by Green, and "Catalytic Oxidation of Organic Compounds in the Vapor Phase" by Marek and Hahn.

Catalysis is a general term under which Berzelius, in the early part of the nineteenth century, classed numerous diverse chemical reactions. In his words, a catalyst may be considered as "a substance that, by its presence, and not by its affinity, has the power to arouse latent affinities, so that compound substances undergo interaction, and a greater electrochemical neutralisation occurs". (10) When in the course of a reaction, the reaction develops substances which, themselves, may affect the progress of the reaction, the process is then commonly known to be "auto-catalytic".

In distinction from "positive catalysis", which implies the action of a catalyst to accelerate a reaction, is "negative catalysis", which is defined as the action of a catalyst to slow down or prevent the progress of a reaction.

It is generally accepted that a true catalyst is supposed in general to have the same effect on the rate of two inverse reactions and that, accordingly, the final state of equilibrium in any given system of chemical reaction is independent of the presence of the catalyst. This, then, leads to the implication that the nature and quantity of the catalyst does not affect the ultimate state of equilibrium. A good example of the proof of this fact may be found in the manufacture of sulfuric acid by the contact process, where the equilibrium of the reaction is affected in no way; only the velocity of the attainment of this equilibrium is affected.

The action of a catalyst in a reaction varies greatly, dependent upon the type and the complexity of the reactions considered. The functions of a catalyst may be grouped, in a general way, under two headings: "1. to increase the rate of a given reaction or, as is usually the case, to lower the temperature at which a reaction will occur at a desirable rate, and 2. to direct a reaction along a particular path when several are possible".(17) A sharp line between these two functions can not be clearly drawn, since it is quite common for a catalyst to function in both ways. In industrial practice, both of these functions are naturally very important, since it is desirable and even necessary to obtain high yields of the products quickly

as well as to obtain them in as pure a form as possible. In various individual cases, however, the selection of a suitable catalyst depends often on its ability to perform only one of these functions.

If the catalyst is changed to any great extent in either its chemical nature or in its physical structure during the course of a reaction in which it is present, it may be readily imagined that the state of equilibrium of the reaction no longer would remain independent of the nature and quantity of the catalyst present. Such has been found to be the case. For this reason, such a material is not generally accepted in the strictest sense to be a "catalyst". However, it is common usage to include them in the general classification, and the action of such materials is so often the same as that of many true catalysts that such inclusion can not be considered to be actually so very erroneous.

Two further classifications of catalysis are often recognized, according to the state of aggregation of the catalyst and the reactants. "Homogeneous catalysis" is catalysis in which the components of a reaction are all in the same state, as when all are in the form of gases or all are in the form of liquids. "Heterogeneous catalysis", on the other hand, is catalysis in which all components are not in the same state, as when a solid catalyst acts on a reaction between two gases. The

latter type of catalysis is the type most often employed in industrial practice.

Whereas, in heterogeneous catalysis, a true mixture of the reactants and the catalyst is never realized, homogeneous catalysis does involve the true and close admixture of the components. Therefore, the action of the catalysts is different in the two types of catalysis. In homogeneous catalysis, the catalyst acts by virtue of its mass, and it is quite common to find that the concentration of the catalyst directly affects the velocity of the reaction.

The intelligent application of theoretical principles to the prediction of effect of individual catalysts on given reactions is quite useful, but it is only in very isolated and special cases that the suitability of any particular catalyst for a given reaction can be determined by the application of theoretical reasoning. In only a very few cases, as in the synthesis of ammonia from hydrogen and nitrogen, in the presence of nickel, has it been possible to make such predictions directly from a theoretical basis. Usually, even in these cases, the predictions are made on the basis of empirical facts, already determined experimentally, known to hold for very closely related conditions. Thus, in the synthesis just mentioned the nickel was known to accelerate the reverse reaction, and it was logical to assume that it would

have the same affect on the desired reaction, if the external forces were controlled properly. Except in such occasional cases as have been mentioned, the only way to determine actually the affect of a catalyst on a given reaction is to experimentally run the reaction under the desired conditions and observe the empirical results. This is the most direct way to arrive at conclusions, and any other speculations are little more than pure guesswork. It is very common that the results obtained are not what might have been expected, but are entirely new and different from any predictions that might have been made. For this reason, the advancement of knowledge of catalytic action can be expected only on the accumulation of an increasing amount of experimental data, and not on the mere speculations that may be made on what little data is available at the present time.' (17)

In attempting to explain the mechanism of catalysts in homogeneous reactions, one general type of theory has been fairly generally accepted. This theory is based on the auto-oxidation of the catalyst to give some unstable form of oxide, and the subsequent decomposition of this intermediate product to give up the oxygen and return the catalyst to its original form. Thus, in the use of stearates, oleates, and similar unsaturated salts, oxygen is given up by a peroxide which first forms on

the mixing oxygen with the catalyst. The union of the oxygen and the unsaturate seems to take place at the double bond of the latter. The nascent oxygen thus liberated is very active and much more reactive than it was in its original condition. Furthermore, the direct reaction between the peroxide and the material being oxidized may take place with the subsequent freeing of the salt into its original form and the final formation of the desired oxide by the oxygen left behind.

Little effort has been made to explain the use of certain soluble organic catalysts which are coming into more common usage in the catalytic vapor phase oxidation of petroleum. Such catalysts which have met with quite a degree of success are nitrogen-containing compounds such as pyridine, quinoline, nitrobenzene, aniline, etc. These catalysts, present in small amount, seem to be quite active in promoting certain oxidations. The secret of their action, although not clearly understood, must lie in the decomposition of the catalysts, themselves, by oxygen to yield nitrogen oxides, which are really the active catalysts in the oxidation.

The oxides of nitrogen have been found in a number of cases to be quite suitable as oxidation catalysts in homogeneous reactions. Notable among the instances of the employment of these oxides as catalysts are the use

in the oxidation of methane to formaldehyde(1), in the oxidation of acetylene(14), in the production of phenol from benzene(8), and in various methods of oxidation of anthracene(20, 21). In all of these cases, it is assumed that the catalytic effect is due to the alternate formation and decomposition of nitrogen peroxide. Thus, in the oxidation of benzene to phenol, the nitrogen peroxide present decomposes to yield nitrogen oxide and active oxygen, which then unites with benzene to yield the phenol:

or, it may be that, without dissociation into nitric oxide and oxygen, the reaction is direct between the nitrogen peroxide and the benzene:

In either case, the nitric oxide is then oxidized to nitrogen peroxide and the cycle may be repeated:

It is often found in the trial of catalysts for the acceleration of oxidations that only extremely small amounts of the materials under trial are required to exert a tremendous influence on the speed of the reaction. The quantities of catalysts are so small in some cases that it would seem they could scarcely be carriers and activators for all of the oxygen that enters into the

oxidation. It has been thought that perhaps such reactions require only a little initiation from some outside source to cause them to start; once started, they proceed easily even without the influence of the outside force. That is, there seems to be what is sometimes known as a period of induction, in which a small amount of the catalyst will exert the small amount of initial activity necessary to cause the oxidation to proceed of itself. After a small amount of the product is formed, the equilibrium shifts toward the further production of the product, with resultant acceleration of the reaction.

In the progress of a catalyzed reaction, there are often what are known as points of resistance. Intermediate products may be formed very easily, but any further action on these products is very difficult to obtain. The presence of various catalysts often has the power of exerting a considerable influence on these points of resistance in specific cases. Sometimes the intermediate products are favored by the catalyst, and further action is greatly reduced by the presence of the catalyst. On the other hand, such points of resistance are sometimes overcome by the presence of a particular catalyst, resulting in the continued action on the intermediate products to produce greater yields of end products. The partial oxidation or combustion of

hydrocarbons to obtain valuable intermediate products is one of the most important fields in which such points of resistance become significant. In the words of Green(10): "The effect of partial combustion is to oxidize away one portion of the molecule, that is, the least stable under the particular working conditions, while the remainder of the molecule is resolved into a compound stable under the same conditions. Such a sharply-defined result, discriminating between the stability of different parts of the same molecule, requires a highly specific catalyst, and one, moreover, which, while it induces an attack on the starting material, has a much slower or inappreciable action on the product."

In the oxidation of phenanthrene with air in the presence of solid catalysts, Chowdbury and Saboor postulated the mechanism already given (see "historical") for the oxidation through the intermediate products to carbon dioxide and water, the final oxidation products. Their scheme seems quite logical and probably gives a close representation of the actual path of the reaction. As may be seen, there are about five or six intermediate products that would be likely to form, and there is the possibility that there might be a catalyst that would favor the production of any one of these products. A search for catalysts among the homogeneous, or soluble,

group would require a large amount of trial and error research, as there is little data in this field available. Furthermore, variance of conditions exert a tremendous effect on the action of the catalyst. With such little basis for speculation as to possible results, the best that can be done in such cases is the systematic and continued search for results with various catalysts under diverse conditions of reaction. With this idea in mind, the following investigation was carried out, in an effort to find some soluble catalyst that, under the proper conditions, would favor the partial combustion of phenanthrene in a benzene solution, with a minimum oxidation of the benzene and a maximum yield of the three possible intermediate dibasic acids, formed in the decomposition of the phenanthrene by air to CO_2 and H_2O . These three acids, as has already been noted, are diphenic acid (6,6'- or 2,6'-), o-phthalic acid, and maleic acid.

APPARATUS

FIGURE I. APPARATUS FOR VAPOR PHASE
OXIDATION

APPARATUS

The apparatus used in the following investigation was made principally of pipes and pipe fittings and was constructed in the school laboratory. The essential parts of the apparatus are shown in Figure I. They are: a liquid reservoir (A), a liquid flowmeter (B), an air flowmeter (C), a reaction chamber (D), a condenser (E), a receiving vessel (F), a reflux condenser (G), and a gas scrubber (H). The air supply was obtained from a small air pump, which also supplied the pressure to cause the liquid to flow through the system.

The flowmeters were of the orifice type. The orifice plate consisted of a small metal disc perforated with a small hole and placed between the two sections of a 1/8-inch union. Tees were coupled by nipples to either side of the union; to these tees the two arms of a manometer were attached through drilled caps and short nipples. Packings of lead foil were found to be necessary around the liquid manometer arms in order to prevent leakage. Sections of meter sticks were used as scales for the manometers. To facilitate readings during runs, when the manometers were held constant, sliding markers of metal were attached to the manometer arms by rubber bands. Mercury was used in the air flowmeter;

mercury and glycerol were used, as necessary, in the liquid flowmeter. Flow rates which did not give a sufficient differential with mercury were measured with glycerol in the liquid manometer.

The reaction chamber, which was the heart of the unit, was constructed of a 10-inch section of 3-inch iron pipe, threaded on both ends. Both ends were capped, one cap being drilled and threaded to take a one-inch nipple, centrally placed, the other cap being drilled and threaded to take two 1/2-inch nipples placed on either side of the center of the cap. Through the large nipple a section of 1/2-inch pipe was passed and was secured to the nipple by means of a tapped and drilled cap which closed the end of the nipple. In a similar manner, sections of 1/4-inch pipe were secured to their respective nipples at the opposite end of the chamber. As may be seen from the sketch, all three pipes extended through the length of the chamber. The two 1/4-inch pipes, which were used to introduce the air and the liquid into the chamber were thus led through the high temperature zone of reaction, which permitted preheating of the reactants before they were mixed. This arrangement also secured the efficient mixing of the gases, as it was necessary for them to reverse in flow and travel the length of the chamber before their products could escape through the larger pipe at the

opposite end of the chamber.

The temperature measurement was made possible by the placement of three thermocouples along the length of the chamber. These thermocouples consisted of short sections of 1/8-inch iron pipe with the ends of sections of constantan wire welded into the ends of the pipes. These thermocouples were placed with the welded tips at approximately the diametrical center of the 3-inch pipe and were welded at the surface of the holes in the large pipe through which they passed. A single wire, of iron, was firmly grounded to one of the short sections of iron pipe and served as a common connection for the iron branches of the thermocouples.

Auxiliary features of the unit were the pressure-equalizing chamber (I) and the pressure manometer (J) , used to smooth out and measure the pressure of the reaction in the reaction chamber.

Rates of flow of the reactants were controlled, for the liquid by means of the needle valve (K), and for the air by means of the air cock (L).

Heating of the reaction chamber was accomplished by means of the gas burner constructed of a section of 1/2-inch pipe, drilled at 2-inch intervals with 1/16-inch holes, capped at one end, and fitted at the other end with a gas cock. This burner was placed about two inches below the reaction vessel and ran the length of it. Both

the burner and the vessel were supported by means of iron strap, bent into suitable shape.

The various connecting lines were of standard 1/8-inch iron pipe and pipe fittings. All joints were made liquid-tight by the use of a dope of graphite base.

The condenser was constructed of a thirty-inch length of one-inch iron pipe and a water jacket of 2-inch iron pipe fixed about the 1-inch pipe by means of drilled caps. Small pieces of threaded 1/8-inch pipe threaded into holes at either end of the water jacket served as connections for the rubber tubing which brought the water to the condenser and carried it away.

A large wide-mouth glass jar was used for the receiving vessel and two smaller wide-mouth bottles were used for the liquid reservoir and for the scrubber.

The reflux condenser was an ordinary laboratory glass water condenser.

The waste gases coming from the scrubber were led away by means of a length of rubber tubing.

PROCEDURE

PROCEDURE

It having been decided that benzene should be used to carry the phenanthrene in this investigation, the solubility of the phenanthrene in the benzene was first determined. A series of test tubes were taken and into each was poured a 10-cc portion of benzene (8.69 gm.). Samples of the commercial phenanthrene to be used were then weighed out into the test tubes. Into the first was weighed exactly 1.0 gm. of phenanthrene, into the next was weighed 2.0 gm., etc., through the series. The mixtures were well shaken and left at room temperature. The following day, the solutions were observed. It was found that the tube containing 2.0 gm. of phenanthrene was clear, without any excess phenanthrene present; all of the tubes containing more than 2.0 gm. were saturated as evidenced by an excess of the phenanthrene remaining on the bottoms of the tubes. This, then, showed that the commercial 90%-grade phenanthrene was soluble to the extent of approximately 20 parts in 100 parts, by weight, of benzene, or of approximately 20 gm. of phenanthrene per 100 cc of benzene. A stock solution of the phenanthrene in benzene was made up. In the preparation of this solution, 217 grams of phenanthrene were weighed into 1,000 cc of benzene, and the resulting total

volume was observed to be 1170 cc. Thus, the solution contained 0.1855 gm. of phenanthrene per cc of solution. This solution will be referred to, hereafter, as "Solution I".

After the preparation of the stock solution, it was essential that an accurate calibration of the flowmeters be made. The air flowmeter, therefore, was first calibrated. Mercury was placed in the manometer of the flowmeter, and the air pump was started. With the liquid control valve closed, the air cock was partially opened to permit a rate of flow of air represented by the head of mercury in the manometer. The air passing through the apparatus was collected in an inverted liter graduate, and the volume of air collected was measured by reading the meniscus of water downwardly displaced from the graduate. By means of a stopwatch, the time required to collect a definite amount of air was determined. This procedure was repeated at various settings of the aircock. The duration of the run in seconds, the head of mercury in millimeters, and the volume of air collected were recorded. From this data, the rate of flow of air, in cc per second, was calculated for each manometer reading. This data was plotted as rate versus manometer reading. The plot is shown in Figure II.

A similar calibration plot was made for the flow of the solution through the liquid flowmeter. In this

Figure II. CALIBRATION OF AIR FLOWMETER

Figure III. CALIBRATION OF LIQUID FLOWMETER
USING MERCURY

Figure IV. CALIBRATION OF LIQUID FLOWMETER
USING GLYCEROL

case, the liquid was collected by allowing it flow directly into an empty upright 100-cc graduated cylinder. Plots were made, using mercury in the manometer, then, substituting glycerol for the mercury. A sufficient differential was not attained with the use of mercury for very small rates of flow, and glycerol was found to be satisfactory in that region. These calibration plots are shown in Figure III and Fig. IV.

In operating the unit, the burner was lit and the reaction vessel was brought to the desired temperature, which was measured by means of the thermocouples and a potentiometer. The 200-cc sample of the liquid had previously been placed in the liquid reservoir. While the reaction chamber was being heated, the sliding markers on the manometers were set at the readings which corresponded to the rates of flow desired. As soon as the chamber reached the desired temperature the air pump was started and the needle valve was adjusted so that the liquid manometer fluid matched the readings set with the markers. Immediately, then, the air cock was so adjusted that the mercury in the air flowmeter matched the markers of that manometer. The temperature and the manometer readings were closely watched and held constant during the run. The gases issuing from the condenser were passed through a layer of water placed in the bottom of the receiving vessel before they were permitted to

pass through the reflux condenser and scrubber. In this way the escape of some of the products as a mist was eliminated, and this product was collected in the receiver along with the material which drained from the condenser. The needle valve and the air cock were closed at the instant that the 200-cc sample was consumed. A small amount of residual spray coming from the reflux condenser was trapped in the scrubber, and this was added to the product in the receiver. In this manner a large number of runs were made under varying conditions of operation.

At the end of each run, the total volume of the product was measured and put into a stoppered bottle for later analysis. The hydrocarbon product was easily separated from the water in which it was caught, as it formed a distinctly separate layer above the water, which was siphoned from beneath it.

In the analysis, the total acids were determined in the manner used by Sheely and King (19) in their work on the oxidation of cleaners' naptha. A 5-cc sample of the oxidized product was shaken for five minutes with 25 cc of standard NaOH, 0.13 N, and allowed to stand overnight. Two cc of the alkali layer were taken and titrated with standard 0.01 N HCl, using phenolphthalein as an indicator, to determine the amount of unused base. From this

titration, the acids formed during the course of each run was determined and calculated as percentage yield, based on the amount of dibasic acid that, theoretically, could be obtained. This basis was backed by the fact that all proposed and accepted mechanisms thus far offered for the oxidation of benzene or for phenanthrene have yielded only acids which are dibasic. A few preliminary runs were made with uncatalyzed solution as a basis for comparison. These runs were made at each of four temperatures, arbitrarily chosen: 375° C., 400° C., 450° C., and 500° C. A series of runs, at these temperatures, was made, first using exactly the theoretical proportion of air to phenanthrene required for oxidation of the phenanthrene to diphenic acid. A second series of uncatalyzed runs, at these same temperatures, was then made with the same solution but with double the amount of air.

Five different catalysts were then investigated: cobalt linoleate, tetraethyl lead fluid, nitrobenzene, quinoline, and pyridine. The cobalt linoleate represents a type of catalyst which, supposedly, operates by the addition of oxygen at the double bonds and by the subsequent surrender of this oxygen, in a more active state, with resultant oxidation of the material being reacted. The tetraethyl lead fluid was used in an attempt to see if its well-known property of retarding oxidation would

slow down any oxidation of the benzene and allow selective oxidation of the phenanthrene to take place. The other three catalysts (nitrobenzene, quinoline, and pyridine) were of the nitrogen group and were suggested by their successful use in the oxidation of petroleum products, as previously explained. The linoleate was weighed out and added to the benzene solution in proportions of 0.5 gm. linoleate to 100 cc of "Solution I". It was found that the linoleate was incompletely soluble, even in these proportions, however; nevertheless, the mixture was well shaken just before the runs were made and the resulting suspension was run through the apparatus. The other four catalysts, all liquid, were added to the solution in proportions of 2% catalyst, 98% solution, by volume. They were all readily miscible with the solution.

The runs made with the catalyzed solutions were at the same temperatures as the uncatalyzed runs, i.e., at 375°, 400°, 450°, and 500° C. A series of runs, at these temperatures, were made for the solutions of pyridine, quinoline, and nitrobenzene, using the theoretical amount of air required for oxidation of the phenanthrene to diphenic acid. The reaction time, which is the time that the mixture remained in the heated reaction vessel before it was quickly cooled, was three seconds in these runs; for the corresponding uncatalyzed

runs the reaction time was also three seconds.

Additional runs were made with solutions of all five catalysts at temperatures of 400° C. and 450° C. with double the theoretical air and with a reaction time of five seconds.

To observe the effect of increased air ratio, a series of runs was made with four times theoretical air, at 450° C., using the solutions of cobalt linoleate, nitrobenzene, quinoline, and pyridine.

In the analyses, identical samples of the catalyzed solutions were treated in a manner similar to that in which the oxidized products were treated, to serve as blanks.

DATA AND RESULTS

DATA AND RESULTS

The phenanthrene used in this investigation was of commercial quality and was obtained from Reilly Tar and Chemical Company. It was 90% grade; that is, it contained an average of 90% phenanthrene, 10% anthracene, and a very small amount of carbazole as impurity.

The solution, referred to as "Solution I", used in all the runs was a benzene solution of phenanthrene containing 0.1855 gm. of the commercial phenanthrene per cubic centimeter of the solution. In the runs using cobalt linoleate as catalyst, 0.5 gm. of the linoleate was added per hundred cubic centimeters of "Solution I". In all of the other catalyzed runs, 4.0 cc of the catalyst was added to 196 cc of "Solution I" to make a total of 200 cc of catalyzed solution used in the run. In the case of the uncatalyzed runs, the solution was used just as it was prepared, 200 cc per run.

The results of the runs are given in Tables I, II, and III, showing the conditions of the runs, the recovery of hydrocarbon, and the yield of acids in each run, calculated as the percentage of dibasic acids theoretically possible to be obtained from the phenanthrene put through the apparatus for the run.

The straight benzene solution was of a clear

yellowish-green nature. The hydrocarbons obtained from the runs varied from light orange to a dark brown in color. The color seemed to indicate the formation of some quinones, possibly phenanthraquinone, or possibly some anthraquinone resulting from the anthracene present in the commercial phenanthrene.

In some of the runs, a considerable amount of volatile, insoluble gas passed the scrubber. It was in the form of white fumes that lay heavily in the air, similar to cigarette smoke. In all of the runs made, some of this gas was noticeable. The amount evolved, however, varied; and the variance in volume produced ran very parallel to the amount of solution lost by complete combustion, as evidenced by the amount of material not recovered in the receiver and scrubber.

TABLE I

Air in theoretical proportion for the oxidation of the phenanthrene to diphenic acid. Mol ratio of oxygen to phenanthrene of 2:1; mol ratio, or volume ratio, at reaction temperature, of air to solution vapors of 1:1.236. Reaction time of 3 seconds.

Run	Solution fed to reaction chamber	React. temp.	CC of hydrocarbon recovered	% yield of dibasic acids
1	200 cc Solution I	375°C.	165	0%
2	200 cc Solution I	400°C.	165	0.20%
3	200 cc Solution I	450°C.	145	0.78%
4	200 cc Solution I	500°C.	180	1.00%
5	196 cc Solution I	375°C.	130	0.48%
6	+ 4 cc pyridine			
6	196 cc Solution I	400°C.	130	0.32%
	+ 4 cc pyridine			
7	196 cc Solution I	450°C.	130	0.40%
	+ 4 cc pyridine			
8	196 cc Solution I	500°C.	115	0.21%
	+ 4 cc pyridine			
9	196 cc Solution I	375°C.	110	0.20%
	+ 4 cc quinoline			
10	196 cc Solution I	400°C.	110	0.20%
	+ 4 cc quinoline			
11	196 cc Solution I	450°C.	120	0.30%
	+ 4 cc quinoline			
12	196 cc Solution I	500°C.	120	0%
	+ 4 cc quinoline			
13	196 cc Solution I	375°C.	110	0.34%
	+ 4 cc nitrobenzene			
14	196 cc Solution I	400°C.	105	0.25%
	+ 4 cc nitrobenzene			
15	196 cc Solution I	450°C.	100	0.49%
	+ 4 cc nitrobenzene			
16	196 cc Solution I	500°C.	85	0.67%
	+ 4 cc nitrobenzene			

TABLE II

Air in twice theoretical proportion for the oxidation of the phenanthrene to diphenic acid. Mol ratio of oxygen to phenanthrene of 4:1; mol ratio, or volume ratio, at reaction temperature, of air to solution vapors of 1:2.472. Reaction time of 5 seconds.

Run	Solution fed to reaction chamber	React. temp.	CC of hydrocarbon recovered	% yield of dibasic acids
1	200 cc Solution I	375°C.	170	0.41%
2	200 cc Solution I	400°C.	170	1.00%
3	200 cc Solution I	450°C.	160	0.58%
4	200 cc Solution I	500°C.	160	0.41%
5	196 cc Solution I	375°C.	165	0.60%
6	+ 4 cc tetraethyl lead fluid	400°C.	165	0%
7	+ 4 cc tetraethyl lead fluid	450°C.	165	0%
8	+ 4 cc tetraethyl lead fluid	500°C.	165	0.10%
9	+ 4 cc tetraethyl lead fluid	400°C.	185	0%
10	+ 1.0 gm. cobalt linoleate	450°C.	145	0.60%
11	+ 1.0 gm. cobalt linoleate	400°C.	105	0.89%
12	+ 4 cc nitrobenzene	450°C.	95	0.52%
13	+ 4 cc nitrobenzene	400°C.	85	0.89%
14	+ 4 cc quinoline	450°C.	110	1.49%
15	+ 4 cc quinoline	400°C.	100	0.86%
16	+ 4 cc pyridine	450°C.	95	0.23%
	+ 4 cc pyridine			

TABLE III

Air in four times theoretical proportion for the oxidation of the phenanthrene to diphenic acid. Mol ratio of oxygen to phenanthrene of 8:1; mol ratio, or volume ratio, at reaction temperature, of air to solution vapors of 1:4.944. Reaction time of 5 seconds.

Run	Solution fed to reaction chamber	React. temp.	CC of hydrocarbon recovered	% yield of dibasic acids
1	200 cc Solution I + 0.5 gm. cobalt linoleate per 100 cc solution	450° C.	90 cc	0.49%
2	196 cc Solution I + 4 cc nitrobenzene	450° C.	45 cc	0.72%
3	196 cc Solution I + 4 cc quinoline	450° C.	25 cc	0.72%
4	196 cc Solution I + 4 cc pyridine	450° C.	45 cc	0.32%

SUMMARY

SUMMARY

The use of five soluble organic catalysts, namely, cobalt linoleate, tetraethyl lead fluid, nitrobenzene, quinoline, and pyridine, was investigated relative to their influence on the oxidation of a phenanthrene solution by air in the vapor phase. The solution was a benzene solution saturated with commercial phenanthrene, 0.1855 gm. of phenanthrene per cc of solution. From this stock solution several catalyzed solutions were prepared and reacted with air at elevated temperatures: a solution of 0.5 gm. of cobalt linoleate added to 100 cc of stock solution, a set of four solutions, each containing 98% of the stock solution and 2% of one of the following, by volume--tetraethyl lead fluid, nitrobenzene, quinoline, and pyridine.

A series of runs, with air in theoretical proportion for the oxidation of the phenanthrene to diphenic acid, was made at the following temperatures: 375° C., 400° C., 450° C., and 500° C. The solutions which were treated in this manner were uncatalyzed stock solution and the catalyzed solutions containing the pyridine, the quinoline, and the nitrobenzene. Only traces and small amounts of acid were produced. The largest yield of acids was obtained with uncatalyzed solution at 500° C.; the yield was 1.00% dibasic acids. The oxidation of the benzene,

as evidenced by the disappearance of solution due to complete oxidation, was greatly increased by the presence of the catalysts. Although the acids found decreased, the increase in loss of solution, due to complete oxidation, ran from 15% to 30% upon the introduction of the catalysts. The smallest recovery obtained, indicating the largest amount of total oxidation, was obtained with the nitrobenzene solution when treated at 500° C.; the recovery of hydrocarbon was only 45% of the amount fed to the reaction chamber. The relative tendencies of the catalysts in favoring the production of acids, as far as could be deduced from the small yields, were, ranging from the catalyst having greatest tendency for production of acids to catalyst having least tendency, as follows: nitrobenzene, pyridine, then quinoline.

A series of runs made under the same temperature conditions, but with double the amount of air, indicated increased yields of acids, with increased activity noted in the case of the quinoline solution. In this series of runs, the greatest yield, 1.49% dibasic acids, was obtained with the use of the quinoline solution at 450° C. In addition to the catalyzed solutions used in the first series, additional runs were made using the cobalt linoleate solution and the solution containing the tetra-ethyl lead fluid; also, blank runs were again made, using

uncatalyzed solution. This time, the uncatalyzed solution yielded more acid than any of the other solutions except the quinoline solution, the run made at 400° C. with no catalyst giving a yield of 1.00% dibasic acids. The tetraethyl lead fluid seemed to almost entirely inhibit what oxidation occurred without catalysts. This appears consistent with the use of the fluid as an "anti-knock" in petroleum products. In this series of runs, once more, a greatly reduced recovery was again noted upon the addition of the catalysts to the solution.

A third series of runs was made at 450° C. on each of the catalyzed solutions except the one containing the tetraethyl lead solution, this time with the use of four times theoretical air. The result was no increase in acid yield but a tremendous increase in total oxidation, indicated by the reduced recovery of hydrocarbon. The smallest recovery noted was for quinoline, again indicating its catalytic power in the oxidation to be the greatest of the catalysts used.

In general, it may be said that the catalysts investigated were altogether unsuccessful in their action to promote acid yield. Their presence greatly increased the total oxidation of the solution used. This oxidation was chiefly on the benzene, as indicated by a great drop in the volume of hydrocarbon recovered, when the catalysts were introduced into the solution.

INTERPRETATION OF RESULTS

INTERPRETATION OF RESULTS

The attempt to preferentially oxidize phenanthrene, in the presence of benzene with the use of the catalysts investigated was unsuccessful. The only yield obtained with the use of the catalyzed solutions that was greater than the corresponding yield with uncatalyzed solution was obtained at 450° C. with twice theoretical air and employing quinoline as a catalyst. In this case, even, the recovery of hydrocarbon was only 55% of the original volume fed into the reaction chamber. In all cases, only small yields, sometimes no yields whatsoever, of acids were obtained.

It would seem, upon observation of the results, that the catalysts investigated exert catalytic power in the direction only of total oxidation of the benzene. A large yield of products of total or almost total oxidation of the benzene was obtained in the case of nearly every run using catalysts, except in the case of the tetra-ethyl lead, which seemed to exert, in general, an inhibiting effect on the oxidation. This fact gives a basis for the belief that the use of any similar catalysts would result only in increased oxidation of the benzene. The benzene, as a carrier, seems to be too easily attacked by the oxygen of the air to permit any appreciable

oxidation of the phenanthrene, as was desired. Whereas it was hoped, at the outset, that the catalysts might promote preferential oxidation of the compound of the larger molecule, the actual effect was just the opposite, with the benzene being preferentially oxidized.

From the data obtained, the catalytic effect of the materials used, as indicated by the consumption of benzene, was readily noticeable. The catalyst exerting the greatest influence was found to be the quinoline, with the nitrobenzene and pyridine falling shortly behind. The cobalt linoleate did not seem to have a great deal influence on the reaction, and the tetraethyl lead seemed to exert an inhibiting effect on the oxidation.

From these results, it may be deduced that the solution used was unsatisfactory. The benzene, being so active, reacted with the oxygen to yield total oxidation products, principally; while the phenanthrene was practically unaffected. Some formation of quinones was evident, but the yield of acids was practically nil. A similar investigation, using some carrier which would not be as active as the benzene might meet with considerably better success. Such a carrier would have to be much less easily attacked by oxygen and might be found among the halogenated solvents, such as, for example, carbon tetrachloride. Whatever catalysts were chosen

would, in addition, have to carry appreciable amounts of phenanthrene in solution to be feasible.

Although the carrying of the phenanthrene in solution, as in this investigation, considerably facilitates the handling of the material, which has a melting point of 100° C., the successful oxidation seems to be more easily attained with the use of the pure material, as employed by earlier investigators. The series of soluble catalysts, when added to a melt of the pure material, might be found to be suitable in influencing vapor phase oxidation by air. Doubtless, their use would probably promote the oxidation to some extent, as their influence has been noted in this investigation.

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