Anthracene,

and its isomer, Phenanthrene, and their Derivatives; with a short investigation of the methods for the quantitative estimation of Phenanthrene and Anthracene.

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Introduction.-

It is difficult to realize the idea that an article, which was as but yesterday unknown as a valuable product, should today assume the importance that we see in the product, coal-tar.- For, previous to 1858, coal-tar was a source of inconvenience to many gas-works, and today an article of great commercial industrial and chemical importance.-

Coal-tar.

This tar consists of fluid hydrocarbons:- Benzol, toluol, propyl, etc; of solid hydrocarbons:- Naphthalene, anthracene, etc; of acids;- Carbolic, acetic, rosolic, etc; of bases:- Aniline, picoline, toluidine, etc; and lastly of resinous, empyreumatic, and asphalte-forming compounds.- There are many other compounds, not mentioned here, which, so far as known, are included in a list given on pages

Anthracene is found in two product from coal-tar, both in the oily portion and in the pitchy residuum, which is left after the light oils have been distilled, as may be seen by reference to the following table:-

- Coal-tar
  - Light oils
  - Heavy oils
    - Solid-hydrocarbons
      - Anthracene $\frac{1}{2}$%
      - Chrysene,
      - Naphthalene, etc.
    - Oil.
  - Pitch
    - Oil
    - Solid hydrocarbons
      - Anthracene - 2%
      - Naphthalene, etc.
      - Resinous matter, Asphalte.
    - Coke

Solid Hydrocarbons) from Coal-tar.

At present anthracene is derived both from the heavy oils and the pitch.-

Anthracene is associated with a number of solid hydrocarbons, extremely similar to one another and presenting great difficulties to the process of separation.-

In the following table, I present a list of these solid hydrocarbons, their formulae, melting and boiling points, so far as known:-

Solid Hydrocarbons

Name	Formula	Melting pt.	Boiling pt.
Naphthalene	$C_{10}H_{8}$	179° C.	220° C.
Acenaphthene	$C_{12}H_{10}$	100°	285°
Fluorene	(?)	113°	305°
Phenanthrene	$C_{14}H_{10}$	95°	340°
Anthracene	$C_{14}H_{10}$	210°	360°
Pyrene	$C_{16}H_{10}$	180°	(?)
Chrysene	$C_{18}H_{12}$	248°	360°
Reten	$C_{18}H_{18}$	95°	400°
Benzerythrene	(?)	(?)	(?)

Relation of Anthracene to the Solid Hydro=Carbons.

The difference in the action of alcohol, ether, bisulphide of carbon, benzol, petroleum, and other solvents upon these hydrocarbons is merely a matter of degree.– Nitric and sulphuric acids, chlorine, and bromine, produce similar compounds of addition and substitution.– A solution of picric acid, mixed with a solution of these hydrocarbons, forms a series of compounds varying in color from yellow and light-orange to dark blood-red, but many of such

compounds are so unstable as to be even
decomposed into picric acid and the hydrocarbon in case an excess of the solvent is present.-

Variable quantities of these hydrocarbons are always present in commercial anthracene and therefore their complete separation is extremely difficult.—

I may say here, in passing, that anthracene has not yet been found in any of the natural pitch and bitumen deposits, or in fact any of the hydrocarbons of the benzol series.-

The yield of anthracene depends upon the quality of the coal and also decidedly upon the temperature to which the coal has been subjected in the gas manufacture.- It also depends upon the degree of heat to which the tar is exposed in the subsequent distillation.- It is scarcely doubtful whether the temperature to which the coal and tar are subjected does not influence and regulate the yield of anthracene.- The manufacture of anthracene must therefore be regarded as not so much a mechanical process, as heretofore, but rather as a chemical process requiring care and investigation both in the first step of obtaining the tar and in the separation of the anthracene therefrom. –

This suggests a very large and equally interesting field for investigation, as yet unexplored, ~~for there is some doubt that much~~ of these hydrocarbons, anthracene included, do ~~[illegible]~~ exist ready formed in the coal-tar, and during the distillation of the same are ~~merely~~ vaporized and afterwards condensed, ~~but that~~ they may be also the result of decomposition by heat of other and higher compounds of carbon & hydrogen. –

Relation to Alizarin.

A few years ago Messrs. Graebe and Liebermann in experimenting on madder-alizarin, heating it with Zinc dust, obtained the now familiar hydrocarbon, Anthracene. – They then attempted to reverse the process, and, after much labour, succeeded in obtaining a product which yields all of the brilliant and characteristic colors of the rubia root. –

This was and is the foundation for the commercial value of anthracene and is one of the most interesting and important applications of Chemistry to the arts that has been made of late years, following closely the discovery of the aniline dyes and bringing the heretofore almost waste-product, coal-tar, up to a commercial value and to deeper scientific investigation, and making the manufacture of anthracene an industry and a study.—

General History—

Anthracene has a history very interesting and also suggestive of the way many such subjects have been investigated and treated in years past.

Anthracene was discovered in 1832, by Dumas and Laurent, in the products of the distillation of coal-tar collected near the end of the operation, when the temperature of ebullition had been greatly passed.— They obtained thus an oily substance, holding in solution naphthalene and anthracene; on cooling this raw oil to −10° a crystalline deposit was formed.— By purification in alcohol their product melted at 180°, distilled at a temperature above 300°, and condensed, by sublimation, in distorted, laminated crystals.

The vapour density taken at 450° was 6.741.— After the elementary analyses they gave to it the formula $C_{15}H_{12}$; this being one and one-half times that of naphthalene, $C_{10}H_8$, they gave to this new hydrocarbon the name of Paranaphthaline.—

Later, Laurent having submitted this to new researches, changed its name to that of Anthracene and made known, in three memoirs, many important derivatives.- But Laurent evidently had impure quantities of the hydrocarbon at hand, which alone explains why he was not able to determine its true composition and to complete the history of the derivatives with advantage.- He investigated anthraquinone but misnamed it.

In 1857, Fritsche described a hydrocarbon having the formula $C_{14}H_{10}$, having separated the same from coal-tar products.- He remarked that this substance resembled somewhat the affinities of anthracene, except that its point of fusion was not at 18 180°, but at 210°-213° and notwithstanding the difference of formula.-

In 1862, Anderson published a most searching memoir on anthracene and its derivatives.- He indorsed the name which Laurent had given to it and fully established the identity of his anthracene to the hydrocarbon of Fritsche.-

In 1866, Limpricht made known that anthracene was formed when Benzyl Chloride is decomposed by water at 180°; and in the same year Berthelot commenced the publication of his researches on the action of heat on the hydrocarbons, on their origin, characteristics, and constitution.- He pointed to the circumstances in which anthracene was formed by the action of heat on other bodies

He found that toluol alone, or a mixture of styrolene and benzole, or benzole & ethylene, passed through a red-hot tube, furnished anthracene.- He confirmed the results of Anderson.-

But Fritsche, in 1867, declared positively that his hydrocarbon, $C_{14}H_{10}$, was neither identical with the anthracene of Anderson nor with that of Berthelot, and described at the same time many new properties of his hydrocarbon.–

This observation was as quickly rebuked by Berthelot, who, soon after, announced the products of the reaction of Hydroiodic Acid on Anthracene.–

Later, in 1870–3, Graebe & Liebermann made their very important and exhaustive researches on anthraquinone and artificial alizarine. And quite recently Castenger has shown that anthraquinone dichloride is obtained by the action of chloro-chromic acid on anthracene.–

What Berthelot, Limpricht, and Graebe considered as a perfectly definite hydrocarbon, identical with the anthracene of Anderson, $C_{14}H_{10}$, is, on the contrary regarded by Fritsche as a mixture of two substances to which he has given the names Photen and Phosene.- These and the anthracene of Anderson possess properties nearly identical.

They have the same point of fusion, same solubility in the various solvents, and no difference in their transformations and reactions.

The only difference rested in the forms of crystals and fluorescence.-

It is highly probable that Dumas and Laurent also operated on anthracene, not perfectly pure.-

Berthelot is inclined to think that those chemists have in reality obtained a homologue of Anthracene, the Methyl-Anthracene $C_{14}H_{10} + CH_2 = C_{15}H_{12}$, possessing precisely the formula of paranaphthaline which accords with the volatility, the point of fusion, and the density of the vapour observed.-

In support of this hypothesis he cites the point of fusion of Reten ($C_{18}H_{18}$).-

Reten can be considered as Anthracene-tetramethyl, $C_{14}H_{10} + 4CH_2 = C_{18}H_{18}$.-

Its point of fusion is 95°.- Between Reten and and Anthracene, which differs by $4CH_2$, the difference of the points of fusion is 110°, whence a quarter, which would correspond to $1CH_2$, is 28°.– We may then calculate for methyl-anthracene a fusing point of about 190°; and paranaphthalene has been considered as fusing at 180°.–

Berthelot has also shown that reten under a red heat furnished quantities of anthracene, as should be the case of a higher homologue.–

But this view is quickly combatted by Graebe and Liebermann for the following reasons:–

1°. Their analyses yield percentages of carbon and hydrogen that will but allow for $C_{14}H_{10}$ being present.

2°. The vapour density proof of Dumas is insufficient on account of an impure sample.

3°. The anthraquinone of Anderson is identical with the anthracenuse of Laurent.

4°. The analyses of Laurent correspond with the formula $C_{14}H_8O_2$, and not with the new formula $C_{15}H_8O_4$, which he has adopted.

In all their work, Graebe and Liebermann have never obtained "phosen" although photen is common in commercial anthracene.–

As Fritsche has not published the figures of the analysis of his "phosen" we can fairly draw our inferences of its existence.

The Anthracene of Anderson is then the most reliable as is also the work of Graebe and Liebermann, which was more extended than the former's but fully confirmed his records and views of Anthracene.

Preparation and Purification.

Although Anthracene can be prepared artificially it is always extracted from coal-tar.– It is found in the products which distil between 300°–400°C.– In distilling 100 parts of ordinary tar from the gas-works we obtain usually

3 pts. of light oils (naphtha, benzol, etc),
10-15 pts. of phenol,
25-30 pts. of heavy oils,
50-60 pts. of black pitch, and
10-15 pts. of gas, water, and residuum.

The pitch is about four times

as rich in anthracene as the heavy oils and the yield is very notably augmented if the pitch is reduced to a solid and if the distillation is pushed even to a complete carbonization of the material in the retort.-

Thus for the preparation of anthracene we are able to operate both on the heavy oils and on the dry pitch. ———

(a) From the heavy-oils of coal-tar.

The last products of the distillation which possess a consistency like that of butter are alone here operated upon.- The mass is sometimes greenish-yellow, resembling a little the crude palm-oil, and sometimes of a dirty greenish color and a little thicker.- It is allowed to remain in a cellar or a cool place for at least twenty-four hours, then it is thrown upon a cloth of close texture, allowed to drain during several days, and the semi-solid mass then submitted to the very gradual action of a press.- After one preliminary pressing in the cold, the press is heated to 60° and the mass is very strongly pressed at this heat. - A cake is thus obtained of a yellowish green color, dry, and which can be readily pulverized. - This is the raw commercial anthracene. -

An improvement in this method consists in fusing the product arising from the expression in the cold and allowing it to cool very slowly, then breaking it and submitting it to the warm press. -

If a purer anthracene is desired, the crude product is well pulverized and placed in petroleum naphtha. - After some hours it is removed and expressed first in the cold and then in the warm press. -

Anthracene is thus freed not only from the heavy and greasy oils but also from a very large portion of naphthalene, and the final product can be purified even to 80 - 85 % of anthracene. -

Benzol is separated from anthracene by fractional distillation. - Amido-compounds by washing with dilute acids and phenols by washing with alkalies. - If a

quinone is present we may pass the (15
vapour over Zinc dust. — The separation of Anthracene from its isomeride, Phenanthrene will be later described.

(6)
From the pitch of coal-tar.

The asphaltum or the asphaltum mixed with the heavy oils obtained in the final extraction can be treated at the time of the distillation of the coal-tar. — Two important precautions must be observed. —
1°. A still must be used very much broader than high, with a flat top and a very large neck. — In this way the tube for the removal of the vapours is brought nearer to the level of the liquid in ebullition and the vapors flow out with ease and do not condense in the still, without being obliged to rise to any considerable height. —
2°. It is also necessary to facilitate the departure of the vapours of the anthracen either by blowing in superheated steam at 200°-250° or by blowing in gas. —
Hydrogen or carbonic acid gas can be

used, or, more cheaply, atmospheric air
which has previously passed over red-hot charcoal, through a tube. - By this latter arrangement, not only is the oxygen of the air, which would cause an explosion in the still, by inflammation of the vapours, converted into carbonic-acid gas but this, and the nitrogen, is strongly heated before entering the retort. - Steam presents the advantage of condensing more easily and completely the products of the distillation.

A very moderate current of steam or gas is sufficient for the removal of the vapors.

The receiver should have a very large capacity and should be capable of being easily cooled. - The distillation is carried on as follows:- Everything being arranged, the temperature is quickly raised to 250°-260°; then the fire is slackened when distillation commences, which is indicated by the heating of the delivery tube. -

Nearly one-third of the material can be distilled without aid of steam or gas.

When the surface has sensibly lowered
so that the vapors are obliged to rise considerably in order to flow out, then the current is established, first very slowly, finally quite rapidly. - Care is taken not to heat the bottom of the retort to redness lest the orange vapours of chrysene and benzerythrene mix too much with those of anthracene. - In practice, on a large scale, the operation is stopped at a point when the black mass possesses just enough fluidity to run out of the retort, when inverted. - The receiver is detached, when cooled, and the mass, more or less greasy, shovelled into linen bags and pressed first in a cold, then in a warm press. - If a purer product is desired it is treated with petroleum naphtha, as in (a).

If a dry pitch is operated upon, especially being swept out with the aid of a gas, and distilled slowly, an anthracene is obtained in a pulverulent and crystalline state, the distillation being in this case a sublimation.

Preparation of Anthracene (not pure)

Anderson recommends redistilling crude anthracene in a retort, which he inclines as the distillation advances. – The first products are almost colorless but include naphthalene and the oily matter. – The later products are colored yellow. – There remains in the retort a black greenish residue of no value. The yellowish products are redistilled in order to destroy if possible the colouring matter. – The final purification is obtained by repeated crystallizations from benzol or alcohol, or by sublimations conducted very slowly. –

Fritsche states that the colouring matter which adheres so obstinately to anthracene is a peculiar hydrocarbon which he calls Chrysogen. – This chrysogen is of a yellow orange color, fusible between 280°–290° but blackens and sublimes at this temperature, with partial decomposition. – A characteristic of chrysogen is that of being purified and decolourized by exposure to the sunlight. – Thus Fritsche recommends

purification by successive crystallizations
from benzol in the sunlight. —

Berthelot recommends the redistillation of the crude anthracene, rejecting the first and last portions.- The remaining portion is purified by petroleum naphthas, volatile between 100°-120°, until it appears crystalline, formed of small laminae, white and shiny, of a micaceous appearance.-

Shiller, in 1870, proposed to purify anthracene by sublimation as follows:-

The anthracene is heated in a broad, large retort, gradually as far as to boiling; the neck of the retort is connected with a huge tubulated jar whose smaller opening is covered with a metallic cloth with small meshes.- A current of air is rapidly injected into the retort which soon expels the anthracene and there condenses in the retort a greenish-black mass. — In a few hours a quantity of anthracene is purified, which the purification by recrystallization and sublimation after the ordinary method (20 would have consumed days. - The resulting pulverulent form is also very favorable to the subsequent oxidation of anthracene. -

Graebe & Liebermann recommend recrystallization until a substance is obtained which melts at 210°-213°. -

The crystals are however always yellow. - In order to decolorize them one of the following methods is used:-

1°. By sublimation at the lowest possible temperature and subsequent washing with ether, which dissolves the yellow chrysogen; or,

2°. By decolourizing a hot solution by exposure to the direct rays of the sun, taking care that the anthracene does not pass into the state of Paranthracene. -

There is deposited by cooling, colorless crystals which present a fine blue fluorescence, described by Fritzche. -

Industrial preparation of Anthracene

In the distillation of coal-tar, the process is arrested when the residue in the still has a mobile consistency.-

The last distilled products, are designated in England by the name of "green-grease" and were used until recently for carriage and car-wheels.- This grease serves in the manufacture of anthracene and consists of heavy oils, naphthaline, and about twenty per. cent of anthracene.

If the distillation is carried further chrysen (chrysogen of Fritsche) and other solid hydrocarbons, quite objectionable, come over, yet by not doing so a quantity of anthracene is lost.-

For the extraction of anthracene from the green-grease it is put into a centrifugal machine or hydro-extractor in order to drive out the oily liquids.-

The residue, half solid, is submitted to the action of a hydrostatic press, first cold, then warm.- This cold pressing is to remove the oils, which, if warm,

will dissolve anthracene.- The resulting
material is the anthracene of 60%.-

By crystallization in naphtha and then sublimation a very pure anthracene is obtained - Even by dissolving the 60% anthracene in warm naphtha and then treatment of the cooled mass in a centrifugal machine a product of 70-80% anthracene may be obtained; this is usually done in America.

Commercial Anthracenes.

The crude anthracenes have a composition and a richness in anthracene very variable.

The quality of the anthracenes depends both on the mode of distillation of the tar and on the nature of the coal from which it was obtained - Usually the tars which furnish light benzene, furnish comparatively much anthracene, while the tars which furnish a considerable number of benzenes of a higher boiling point (consisting mainly of toluol, xylol, cumole, etc.) yield but little anthracene.-

The anthracenes of commerce are mainly poor, and it is to be regretted that the tar distiller does not purify his products more since it can be easily done at the place of distillation.

American Anthracene.

American anthracenes head the list and are very good, containing from 60-80% anthracene. - Our manufacturers are obliged to have their products among the best in order to make them worthy of exportation. - They usually recrystallize several times from naphtha. ——

English Anthracene.

Anthracenes of English origin vary from 35-65% of Anthracene. - This is due to careless work. - Of course the best and most valuable are those which have been most carefully purifid ——

French Anthracene.

The French anthracenes are variable, yet generally very poor. - This is due to the fact that more attention is paid to the obtaining of aniline and toluidine from coal-tar than to anthracene, anthracene being of secondary importance there. - They vary from 12-50% anthracene.

German Anthracene

German anthracenes are usually very good containing from 50-80% anthracene.

They are usually associated with but few hydrocarbons, being obtained by slow distillation and by excellent processes, which are mainly as previously stated, by filtration, redistillation, hydraulic pressure, and recrystallization.

Preparation of Chemically-pure Anthracene

Anthracene, purified by simply washing with alcohol, or redissolved and recrystallized from light oils, is sufficiently pure to serve in the industrial preparation of its derivatives but it is still very far from being chemically pure. -

Berthelot suggests the following:- The commercial anthracene is distilled with care; what passes over from 340° to the boiling point

of mercury, is gathered.- The product thus
obtained is redistilled until the thermometer stands at 340°-350°; the operation is stopped; the black mass remaining behind is mainly anthracene.- This is boiled with light naphthas (boiling between 120°-150°); the solution decanted; filtered, if necessary; cooled, and the crystalline mass thus obtained is pressed until the substance ceases to moisten blotting paper.- This operation is repeated several times until the product appears in very clearly defined, laminated rhombohedrons capable of producing Fritsche's reaction of binitroanthraquinone:- viz:- rose-violet crystals in alcohol or benzol, very characteristic, which are dwelt upon later in my essay.-

Then this product is sublimed very gradually several times until the sublimate is purely white.-

Davis, in 1872, gave the following method, which, Bolley, in 1875, indorses:-

Digest the crude anthracene with bisulphide of carbon, filter by means of a

Bunsen pump and wash upon the filter until the filtrate comes away colorless; then dry upon the filter by means of the pump.- Warm the residue to 30° with petroleum naphtha and, when cool, filter.- Wash the residue with naphtha.- The same operation is then carried on with ether until it filters colourless.- The residue is boiled with 80% alcohol and a little ether, cooled and filtered.- Then it is carefully sublimed and the sublimate washed with cold ether and alcohol and then crystallized.- By two crystallizations an anthracene giving a percentage of 99.8 - 99.95% anthracene by the method of Lück is obtained.- The method of Lück I shall fully ventilate before closing my theme.-

Of course such a tedious process as the above is only valuable as a standard against which to compare the common products and for purposes of careful scientific investigation.

Properties of Anthracene

Semi-pure anthracene crystallizes by slow cooling from boiling alcohol in the form of laminated crystals, white and brilliant, bearing a micaceous aspect.- These laminae examined under a microscope are folded and irregular, and assume often the form of crooked polygons of five or six unequal sides.-

The crystals appear to belong to the monoclinic system with the prism oblique to the base rectangle.

Slowly sublimed anthracene gives laminated, transparent crystals, extremely thin, and turned on the edges, somewhat analogous to those of naphthalene but smaller and less brilliant.

Rapidly sublimed anthracene gives a sublimate in the form of a fine powder or light flakes, easily carried away by the currents of air, always irritating to the throat and eyes.-

At the ordinary temperature anthracene is ~~not~~ volatile; but at 100° it commences to volatilize; fusing at 210°-213°, boiling at 340°-360°.- Once melted it solidifies at a temperature very variable, according as it has been more or less superheated and as the cooling has been more or less rapid.- (28

When once melted and resolidified, the temperature at which it melts again depends upon not merely the conditions already indicated but even on the temperature more or less above the point of fusion, to which it has been subjected, and also on the time which has elapsed since the first fusion.-

The hydrocarbon chrysene is usually associated with it and communicates to its solutions a peculiar fluorescence.- This is usually freed, as noticed previously, by exposure to the sunlight which precipitates chrysene in colourless crystals.- But by so doing the isomeric modification of anthracene called paranthracene is formed in the shape of hexagonal plates.-

(This is the paraphoton of Fritsche.)

Paranthracene has a great stability, being almost insoluble in alcohol, benzol, and ether and is not altered by nitric acid, bromine in CS_2 or bromine free, at 100°.- By fusion (at 244°) it is reconverted into anthracene.

Anthracene is sparingly soluble in alcohol, ether and bisulphide of carbon at the ordinary temperature.- It is quite soluble in boiling alcohol, benzol, naphtha, but separates out on cooling.- Its best solvent is oil of turpentine. In the cold, alcohol dissolves .6%; benzol .9%; and bisulphide of carbon 1.7% of anthracene.-

At 15° anthracene is dissolved as follows:-

Alcohol (80%)	.472 by volume	.591 by weight.
" (83%)	.408 " "	.491 " "
" (84%)	.387 " "	.460 " "
" (85%)	.360 " "	.423 " "
Ether	.858 " "	1.175 " "
Chloroform	2.587 " "	2.736 " "
Bisulphide Carbon	1.180 " "	1.478 " "
Glacial Ā acid	.472 " "	.444 " "
Benzole	1.470 " "	1.661 " "
Petroleum	.291 " "	.394 " "

Anthracene is insoluble in water and alkalies and not altered by boiling with the same.- It dissolves in concentrated sulphuric acid and forms conjugated monosulpho- or bisulpho-acids according to the temperature employed.-

Chlorine and bromine give rise to substitution products.- Nitric acid acts on it with great violence, with formation of anthraquinone, dinitroanthraquinone, and other compounds according to the temperature and proportion of the substances taken.- With picric acid, anthracene forms forms a compound, crystallizing in very bright, ruby-red prisms.-

To prepare the picrate of anthracene, a saturated solution of picric acid in water at 26°C is mixed with a saturated solution of anthracene in boiling alcohol; on cooling, the compound is deposited in a crystalline state.- It is very quickly decomposed by an excess of alcohol, into picric acid and the hydrocarbon.-

This remarkable compound is used to distinguish anthracene from naphthalene and other hydrocarbons, which under like circumstances give rise to various shades of yellow needles; the picrate of naphthalene forms in fine golden-yellow needles, and the picrate of chrysene forms in clusters of small, yellow needles.—

This compound of anthracene presents a very marked characteristic, formed with a solution of binitroanthraquinone in benzol or toluol, as observed by Fritsche.— If a drop of this solution is placed under a microscope there immediately appears, upon spontaneous evaporation, beautiful laminated rhombohedrons of a magnificent violet tint.

If the anthracene is not pure, then a compound is derived in the form of small, brown, laminated prisms.

To a degree of purification a little less advanced still, the anthracene furnishes a fine blue appearance.—

Finally, when the foreign materials are most abundant, all these special reactions with binitroanthraquinone cease.

These crystals have the formula $C_{14}H_{10} + C_{14}H_6O_2(NO_2)_2$.—

Chemically pure

anthracene is a crystalline body having a shiny, laminated appearance and a very fine, violet fluorescence, which, although interesting, I must not dwell upon.-

It melts at 210°, begins to sublime at 100°, slightly decomposed at the boiling point of mercury.- With the solvents it acts as previously stated.-

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Formation and Synthesis.

Anthracene can be formed artificially in several ways, which, although it is not probable that any of the methods will be practically employed, are yet very instructive and interesting from a scientific point of view.

1°. From Toluol-

1°. By means of toluole or toluene (C_7H_8).

This toluol is found in notable quantities in common benzol and is isolated by fractional distillation.- Mr. Warren's process, well known, is excellent for this separation.- Toluol, passed in vapour through a red-hot porcelain tube gives rise to a tarry liquid which yields besides benzol, benzyl, naphthalene, chrysene, benzerythrene, and unaltered tolual, always a certain quantity of anthracene.–

$$2(C_7H_8) = C_{14}H_{10} + 6H$$

~Tolual~ ~Anthracene

2°. From Benzyl Chloride–

2°. By heating Benzyl Chloride with water to 200° C.–

Tolual treated with chlorine gives rise to two products of the same composition but very different characteristics, depending on the temperature at which it was treated.–

(I) In the cold Monochlorotoluene is formed:– $C_7H_7Cl = \underline{C_6H_4Cl.CH_3}$.– In this compound the chlorine is strongly retained, not being attacked by water at 200°, alcohol at 100°, or by ethylate, sulphite, or sulphydrate of soda in alcohol at 100°–150°.–

(II) If chlorine is allowed to act on warm tolual, kept at 110°, there is formed Benzyl Chloride, $C_7H_7Cl = C_6H_5.\underline{CH_2Cl}$.–

In this compound the chlorine is only feebly retained and it is attacked by water at 180°, by heating with the same for eight hours with double its volume of water.–

3°
From
Benzl-
=Toluene.-

3° By passing the compound $C_{14}H_{14}$, Benzyl Toluene, over red-hot pumice, anthracene is formed.-

4° By the reaction of ethene and styrolene on benzol; or by heating diphenyl or chrysene vapour with ethylene gas in closed tubes.

4°
Reaction
of
Ethene
and
Styrol.-

In passing ethene and benzol through a red-hot porcelain tube, the principal product is styrolene, $C_8H_8 = C_6H_5.C_2H_3$.-

$$C_6H_5.H + C_2H_3.H = C_6H_5.C_2H_3 + 2H$$

~Benzol~ ~Ethene~ ~Styrolene~

There is also formed, phenyl, ace=naphtene, naphthaline, and also anthracene:-

$$2C_6H_5.H + C_2H_3.H = 2C_6H_4.CH + 6H$$

~Benzol~ ~Ethene~ ~Anthracene~

But the anthracene is not produced immediately at the expense of these two hydrocarbons but styrolene is formed first and this reacts in turn on a molecule of benzol:-

$$C_6H_5.C_2H_3 + C_6H_5.H = 2C_6H_4.CH + 4H$$

~Styrolene~ ~Benzol~ ~Anthracene~

5°
Polymeric condensation of Acetylene.

5° Anthracene is formed, according to Berthelot, by the polymeric condensation of acetylene C_2H_2.–

Acetylene first forms benzole; this reacts on acetylene forming styolene, and finally styrolene treated anew with benzol and acetylene is partly transformed into anthracene:–

(1) $3C_2H_2 = C_6H_6$
~Acetylene~ ~Benzole~

(2) $C_6H_6 + C_2H_2 = C_8H_8$
~Benzol~ ~Styrol~

(3) $C_8H_8 + C_6H_6 = C_{14}H_{10} + 2H$ or
~Styrol~ ~Anthracene~

Anthracene here then is a tertiary product.

6°
Reaction of Chrysene on Ethene.

6°.– By the reaction of ethene on chrysene:–
$C_2H_4 + C_{18}H_{12} = C_{14}H_{10} + C_6H_6$.–
~Ethene~ Chrysene~ ~Anthracene~

7°
From Benzol and Naphthalene

7°.– By the reaction of benzol on naphthalene:–
$3(C_6H_6) + C_{10}H_8 = 2(C_{14}H_{10}) + 6H$.–
–Benzol– ~Naphthalene~ Anthracene

8°. From the Hydrides

8°.– In passing the hydrides of anthracene, $C_{14}H_{12}$ and $C_{14}H_{16}$, through a red-hot tube, both being converted into anthracene and hydrogen.

9°. From its chromate by calcination

9°.– By calcining bichromate or bichloride of anthracene with lime or soda-lime.–

10°. General reduction of oxygenated derivatives

10°.– With great ease if the oxyen derivatives (alizarin, etc.) are treated with energetic reducing agents.–

Hydro=genated Derivatives

~Hydrogenated derivatives of Anthracene~

There are several hydro-derivatives which demand notice.

I. Anthracene Bihydride

I.– Bihydride of Anthracene.–

$$\sim C_{14}H_{12} = C_{14}H_{10}.H_2 \sim$$

This may be obtained either (1°) by the action of Hydriodic acid on anthracene or (2°) by the action of sodium=amalgam on anthracene in alcoholic solution.

(1°.) The powdered anthracene is heated with ten times its weight of alcohol in a balloon connected with a spiral condenser and the amalgam thrown in from time to time. - It is well to neutraliz the alkali thus formed with hydrochloric acid as the reduction progresses very slowly in a strong alkaline solution. - The balloon is heated for 12-20 hours, depending upon the quantity of anthracene used. - To test the bihydride thus formed, add it to a picric acid solution in benzol and if the characteristic red color of picrate of anthracene is not seen then the anthracene is all converted into bihydride. -

The larger part of bihydride may be separated by boiling alcohol from which it separates on cooling, purified by recrystallizing.

It crystallizes in monoclinic plates, soluble in strong alcohol, melting at 160°, and boiling at 305°, but subliming at a lower temperature. At a dull-red heat it is resolved into anthracene and hydrogen.

(2°). The anthracene is heated with a quarter of its weight of amorphous phosphorus and about five times its weight of concentrated hydriodic acid (boiling at 127°),

in sealed tubes, for 10-12 hours at a
temperature of 160°-170°. - The phosphorus is added in order to reconvert the iodine formed, again into hydriodic acid and thus to keep the solution rather concentrated. -

By so doing almost all of the phosphorus disappears and the anthracene is converted into a hydrocarbon which solidifies on cooling.

In opening the tube phosphoretted hydrogen gas is liberated, especially if the temperature had exceeded 170°. — By washing with water, the hydriodic acid is separated and by solution in and crystallization from alcohol the bihydride or dihydro-anthracene is separated.

It is insoluble in water, soluble in alcohol, ether, and benzol. - Volatilizes slowly with the vapour of water or alcohol. - The solid is not ~~att~~ all fluorescent but the solutions of the same present a fine blue fluorescence. - It forms no picric acid compound.

Passed through a red-hot tube it is decomposed into anthracene and hydrogen.

Concentrated sulphuric acid oxidizes it even at 100°; Sulphurous acid is evolved and anthracene is formed; further oxidation converts it into a sulpho.-acid:-

$$C_{14}H_{10}.H_2 + H_2SO_4 = C_{14}H_{10} + 2H_2O + SO_2$$

~Bihydride of Anthracene~ ~Anthracene~

~ Bromine acts directly on bihydride but not, as in these previous cases, in forming anthracene and freeing hydrogen, but forming bibromanthracene and evolving hydrobromic acid:-

$$C_{14}H_{12} + 6Br = C_{14}H_8Br_2 + 4HBr.-$$

Anthr. bihydride~ ~Bibromoanthracene~

The bihydride is not acted on by iodine.

Oxidizing agents, such as bichromate of potash and sulphuric acid, or nitric acid, transform it into anthraquinone:-

$$C_{14}H_{10} + 4O = C_{14}H_8O_2 + 2H_2O.$$

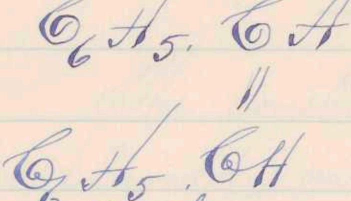
~Bihydride~ ~Anthraquinone~

Nitric acid forms also nitro-compounds.

~Iodohydric acid (conc.) heated with the bihydride in sealed tubes at 160° does not change; but at 200°-220°, it is attacked and transformed into the hexahydride of anthracene, $C_{14}H_{10}.H_6$.

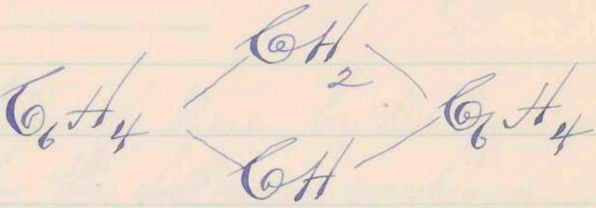
Bihydride of Anthracene is isomeric with stilbene, whose formula is also $C_{14}H_{12}$

~Rational Formulae~



$$\begin{array}{c} C_6H_5.CH \\ \| \\ C_6H_5.CH \end{array}$$

~Stilbene~



~Athracene $^{2}_{1}$Bihydride~

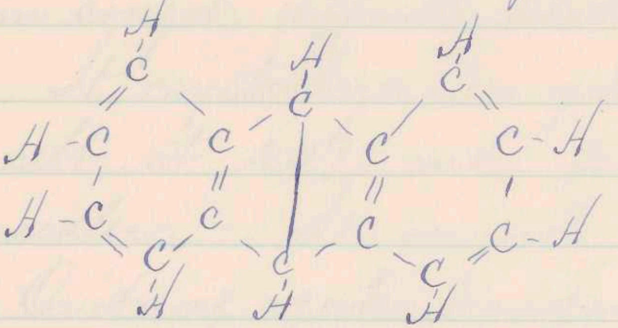
II. Hexa-hyride of Anthracene.

II. The hexahydride of anthracene, $C_{14}H_{16} = C_{14}H_{10}.H_6$, is formed by heating one part bihydride with 1/4 part of red phosphorus and 5 parts concentrated hydroiodic acid in a sealed tube for 10-12 hours at a temperature of 200°-220°.- A good deal of phosphoretted hydrogen gas is formed.- The product is washed with water, dissolved in alcohol, filtered, evaporated to drive off the alcohol, and strongly expressed to eliminate a little oily matter; finally, it is distilled.- The part that comes over at 290° is collected and crystallized from alcohol. It is deposited in colorless laminae, melting at 63°, boiling at 290°.- It is very soluble in alcohol, ether, and benzol; more stable in the presence of nitric acid than the bihydride.

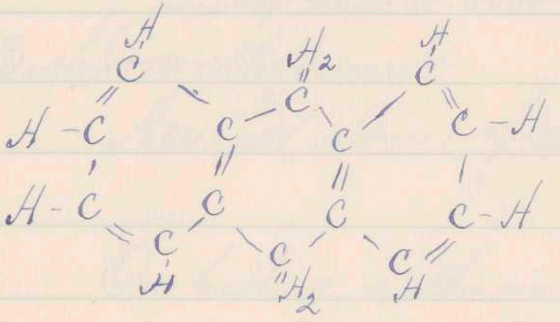
Decomposed at a red heat as before stated.

Constitution of Anthracene graphically considered.

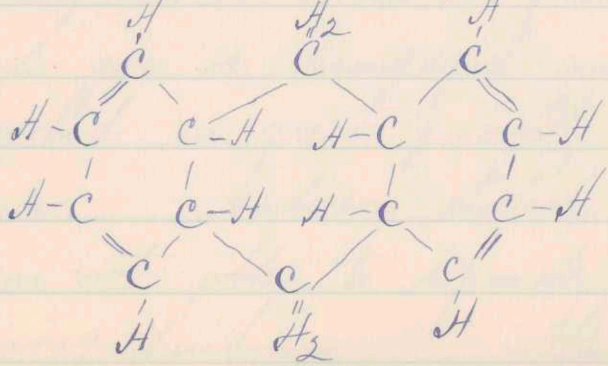
The constitution of these hydrides is explained as by the following graphical formulae:-



Anthracene.



Anthracene Dihydride.



Anthracene Hexahydride.

~Chlorinated derivatives of Anthracene.~

~Action~ of Chlorine on Anthracene.

Laurent has obtained pale yellow needles, proving to be the substitution of 2Cl for 2H in anthracene, with evolution of HCl, by allowing chlorine to act on cold powdered anthracene.–

~Bichlor=anthracene

This bichloranthracene is easily soluble in benzol, difficultly soluble in alcohol and ether. It crystallizes in yellow spangles which melt at 209° and sublime finally in yellow needles. – It is not attacked by alkalies. Oxidizing agents transform it into anthraquinone

$$C_{14}H_8Cl_2 + 2O = C_{14}H_8O_2 + 2Cl$$

~Bichloroanthracene~ Anthraquinone.–

Here two atoms of oxygen replace two of chlorine.

Tetra=chloride of Bichlor=anthracene

On heating anthracene to 170°–180° and passing over it a current of chlorine, hydrochloric acid gas is disengaged and chlorine is absorbed in great quantity as the material fuses. – Anderson studied this reaction but was not able to separate exactly the products arising therefrom. – After continuing the

the action of chlorine for eight days he obtained a semi-solid product which mainly dissolved in cold ether. By evaporation, an oily chlorine compound separated out and then a crystalline compound.- This latter was soluble in benzol, alcohol, and ether; its analysis corresponded to the empirical formula, $C_{14}H_9Cl_5$.-

The oily chlorine compound, treated with alcoholic-alkaline solution gave products not yet, so far as I am able to ascertain, studied.

It is more than probable that the crystalline compound was mainly tetrachloride of bichloranthracene: $C_{14}H_8Cl_6 = C_{14}H_8Cl_2.Cl_4$ still mixed with a little anthracene and perhaps a little bichloranthracene, $C_{14}H_8Cl_2$:- for, if we suppose a mixture of one part of $C_{14}H_{10}$ (Anthracene) with 5 parts of $C_{14}H_8Cl_6$ (Tetrachloride of bichloranthracene) we have:-

$$C_{14}H_{10} + 5(C_{14}H_8Cl_6) = C_{84}H_{50}Cl_3 =$$

$= 6(C_{14}H_{8\frac{1}{3}}Cl_5)$ which approaches very nearly the empirical formula from the analyses of Anderson, $C_{14}H_9Cl_5$.-

The dibromanthracene tetrabromide is known without a doubt and probably the corresponding chlorine compound will soon be obtained pure enough to establish its identity by analysis.-

Mono=
=chlor=
=anthracene.

By submitting anthracene for a long time to a rapid current of chlorine or by treating bichloride of anthracene with an alcoholic solution of caustic potash, Mr. Anderson thought that he had obtained monochloranthracene, $C_{14}H_9Cl$, in the form of small hard crystalline scales, very soluble in alcohol, ether, and benzol but it is questioned even by himself.

Theoretically there should be such a compound.-

Bi=
=chloride
of
Anthracene

If a current of chlorine is passed very slowly and not too long over cold anthracene, chlorhydric acid gas is evolved and the principal product is bichloride of anthracene, $C_{14} H_{10} Cl_2$:-

This product is soluble in benzol and separates from it on cooling in radiating groups of needles, often very long, melting at 209°; very soluble in alcohol, less soluble in ether. - Its solutions exhibit a splendid blue fluorescence. -

Tetra=
=chlor=
=anthracene.

The tetrachoranthracene, $C_{14} H_6 Cl_4$, was obtained by Graebe and Liebermann by treating the preceding crystalline product, $C_{14} H_9 Cl_5$,[3] of Anderson with an alcoholic solution of caustic potash and purifying the product by recrystallization in benzol. -

It crystallizes in needles of a golden yellow lustre, grouped in tufts; sparingly soluble in alcohol, more soluble in boiling benzol, from which it separates by cooling, in crystals which melt at 200° C. -

Nitric acid converts it into bichlor=
=anthraquinone:-

$$C_{14} H_6 Cl_4 + O_2 = C_{14} H_6 Cl_2 O_2 + 2 Cl.$$

Tetrachloranthracene - Bichloranthraquinone -

The history of the chlorine derivatives of anthracene is not at all complete and satisfactory as all of these previous reactions and several others need to be confirmed and verified by new researches.–

~Action of Bromine on Anthracene~

History

The action of bromine was studied with care by Anderson who described two distinct compounds to which he assigned the formulas:– $C_{14}H_{10}Br_6$ and $C_{14}H_8Br_4$.– The first was prepared by the action of an excess of bromine on powdered anthracene and was considered as an addition product resulting from the combination of six atoms of Br with one atom of $C_{14}H_{10}$.– The second, prepared by the action of alcoholic caustic potash on the first, was called by Anderson bibromide of bibromanthracene.

Berthelot, having observed that HBr was evolved in the first reaction, proposed to subtract two atoms of bromine from the formula of

Anderson, confirmed lately by Graebe (47 and Liebermann, and also changed the hydrogen.–

Bibrom=
=anthracene

Bibromanthracene, $C_{14}H_8Br_2$, is easily obtained by dissolving anthracene in bisulphide of carbon and adding bromine drop by drop to sufficient quantity.–

Graebe & Liebermann have lately proved that if less bromine is used, the monobromanthracene is never formed, but a mixture of anthracene and the bibromanthracene, easily separated by alcohol in which the bromine compound is absolutely insoluble.– Again, if an excess of bromine is used, a compound is never formed richer in bromine.–

By crystallizing from boiling toluol or xylol the bibromanthracene crystallizes in beautiful golden needles, fusible at 22°; subliming later without decomposition.

Very insoluble in alcohol and ether; rather soluble in hot benzol and petroleum-naphtha but separates out from the same on cooling.- It is not affected by alkali, whether aqueous or alcoholic, hot or boiling.-

But an alcoholic solution heated with it at 170° in a closed tube produces anthracene and simultaneously aldehyde and acetic acid:-

$C_{14}H_8Br_2 + 2KOH + C_2H_6O = C_{14}H_{10} =$

Bibromanthracene- -Anthracene

$= + 2KBr + C_2H_4O + H_2O$.-

It also furnishes anthracene by calcination with quick lime.-

Oxidizing agents (Nitric acid or chromic acid in glacial acetic acid) convert it into anthraquinone:-

$C_{14}H_8Br_2 + 2O = C_{14}H_8O_2 + 2Br$.-

Chlorine has no affect upon it but if exposed to the vapours of bromine it absorbs them and the tetrabromide of bibromanthracene is formed.-

Fuming sulphuric acid dissolves it with a green coloration forming a sulpho-compound, bibromanthracene bisulphonic acid:-

$C_{14}H_8Br_2 . 2SO_3$:-

Tetra=
bromide
of
Bibrom=
anthracene

Tetrabromide of bibromanthracene,
$C_{14}H_8Br_2.Br_4$, is obtained by placing powdered anthracene in a capsule which in turn is placed inside of a larger capsule filled with bromine and finally all is covered with a glass jar.- After twenty-four hours the absorption is complete and the product is treated with boiling benzol which on cooling deposits the compound in small white crystals, sharply defined, belonging to the orthorhombic system.- These crystals are insoluble in water, little soluble in ether, alcohol, or benzol, more sol. in hot benzol.-

This hydrocarbon melts at 170-180° and is changed to tribromanthracene with disengagement of hydrobromic acid gas.

$$C_{14}H_8Br_6 = C_{14}H_7Br_3 + HBr + 2Br$$

Tetrabr. of bibromanthracene. Tribromanthracene.-

The tetrabromide treated with a warm alcoholic solution of caustic potash loses two atoms of HBr and tetrabromanthracene is formed:- $C_{14}H_8Br_6 + 2KOH = C_{14}H_6Br_4 + 2KBr + 2H_2O$.

Bibromanthr. tetrabromide- Tetrabromanthracene.

Tribrom=
=anthracene

Tribromanthracene, $C_{14}H_7Br_3$, is obtained by heating tetrabromide of bibrom=
=anthracene to 200° as long as vapors of HBr and Br are given off; then recrystallizing several times from benzol.- It crystallizes in yellow needles, little soluble in alcohol, easily soluble in benzol.- It melts at 169°. and sublimes to yellow needles.-

Oxidizing agents, employed cold, change tribromanthracene to monobromanthraquinone:-

$C_{14}H_7Br_3 + O_2 = C_{14}H_7Br(O_2) + 2Br$.-

Treated with bromine it readily forms tetrabromide of tribromanthracene:-

$C_{14}H_7Br_3 + 4Br = C_{14}H_7Br_7$

Tribromanthracene— Tetrabr. of tribromanthracene

This last compound has alone been indicated by Graebe and Liebermann in their recent work with bromine and has not, so far as I can ascertain, been fully studied.-

Tetra=
=brom=
=anthracene

Tetrabromanthracene, $C_{14}H_6Br_4$, is easily prepared by heating tetrabromide of

bibromanthracene in alcohol with an
aqueous or alcoholic solution of caustic potash.
It is obtained by crystallization in benzol as long yellow needles, melting at 254°, very little soluble in cold benzol, alcohol or water. - 100 pts of boiling benzol dissolve 1 part of the compound. - It always changes to a brown color on fusion and a change in its composition begins. - As in the case of bi- and tribromanthracene oxidizing agents replace 2 atoms of Br by 2 atoms of O.

Soluble in glacial acetic acid and converted by chromic acid into bibrom-anthraquinone:-

$$C_{14}H_6Br_4 + O_2 = C_{14}H_6Br_2(O)_2 + 2Br.$$

Tetrabromanthracene - - Bibromanthraquinone

The bromine derivatives are of great interest since in them, especially the tetrabromidanthracene, the first step was taken towards obtaining the artificial alizarin of today. -

Action of Iodine on Anthracene ~ (52

Iodo= =compounds

Iodine does not produce definite compounds by direct action on anthracene. At 100° it forms a brown, insoluble substance containing a certain quantity of iodine in combination. – On heating the same higher, hydroiodic acid is evolved and the matter is charred.–

Action of Hydriodic Acid on Anthracene

Anthracene heated to 280° in sealed tubes with 100 times its weight of HI, forms three hydrocarbons, which are:–

1°. Hydride of tetradecenylene, $C_{14}H_{30} = C_{14}H_{28}.H_2$. – This is the principal product, which boils at 240°.–

2°. Hydride of heptylene, $C_7H_{16} = C_7H_{14}.H_2$ This boils at 95°.–

3°. An oily hydrocarbon, almost solid, very abundant, which does not distil below 360° and which has the formula $C_{28}H_{58}$ and has the properties of the series C_nH_{2n+2} i.e. it is not acted on by sulphuric or nitric acids, bromine or chlorine.–

By operating in the same manner

on anthracene but only using 20 parts of hydroiodic acid, at 280°, Berthelot obtained:-

1°.- A considerable quantity of toluol, C_7H_8.-

2°. A trace of benzol, C_6H_6.-

3°. A very large quantity of a liquid hydrocarbon, offering the properties of a hydride of anthracene giving the formula, $C_{14}H_{10}.H_4$.-

On pages 37 & 38 attention is called to the fact that Graebe and Liebermann, by heating anthracene with red phosphorus and hydroiodic acid for ten hours, obtained the bihydro-anthracene, $C_{14}H_{12} = C_{14}H_{10}.H_2$, fusible at 106° and boiling at 302°, isomeric with stilbene of Laurent.—

~The Action of Oxidizing Bodies~

~History~

The history of the action of oxidizing bodies on anthracene is very confused from the fact that many chemists have worked on anthracene not perfectly pure, thus forming many secondary resinous products, of very variable composition, which render the purification of the principal products difficult. — When they have employed nitric acid it has produced, beyond the simply oxidized bodies, a series of complex nitro-compounds, very troublesome; when sulphuric acid was in any way employed, a mono- or a disulpho-acid was formed. — The product of the oxidation of anthracene is the anthraquinone $C_{14}H_8O_2$" identical with the anthracenuse of Laurent and the oxyanthracene of Fritsche.

Anthra=quinone.

Anthraqinone

Relation to Quinone

In my study of this subject, I have seen, especially in English journals, this substance having the formula $C_{14}H_8O_2$, spoken of as anthrachinon. — The difference between this mode of spelling and the one that I have endeavored to use in my treatise of the subject, is a small matter it may seem but yet the relation between this product, $C_{14}H_8O_2$, and the hydrocarbon, $C_6H_4O_2$, called Quinone, is such as will sustain me in insisting upon the use of the latter method of spelling, viz. anthraquinone. for anthraquinone bears the same relation to anthracene as quinone does to benzol, naphthalene intermediate:-

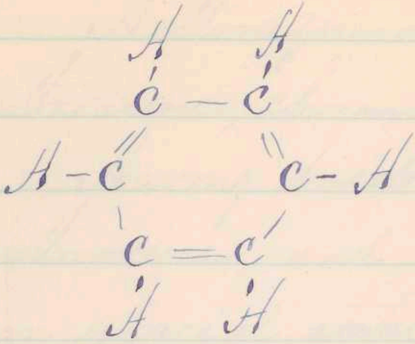
Benzol - C_6H_6 — Quinone - $C_6H_4O_2$.

Naphthalene $C_{10}H_8$ — Naphtoquinone $C_{10}H_6O_2$.

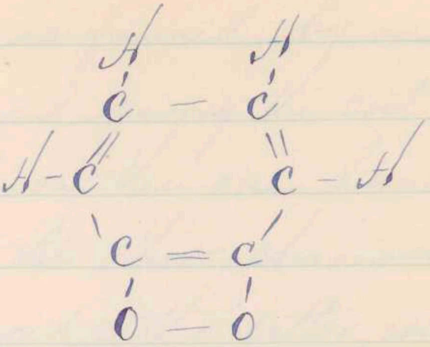
Anthracene $C_{14}H_{10}$ — Anthraquinone $C_{14}H_8O_2$.

In the three hydrocarbons H_2 is replaced by O_2, the two atoms of O being so situated as to represent an equivalent of two atoms of H.-

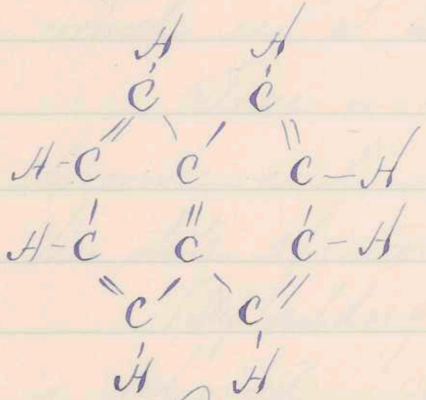
On page 56, the relation of these hydrocarbons, is graphically considered.



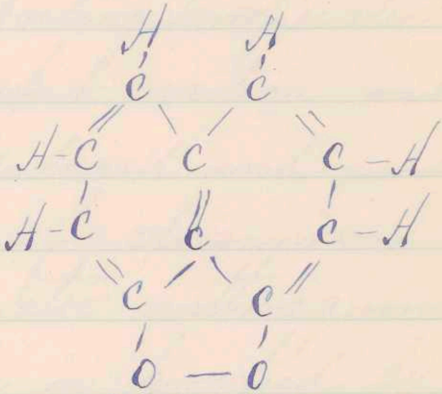
Benzol



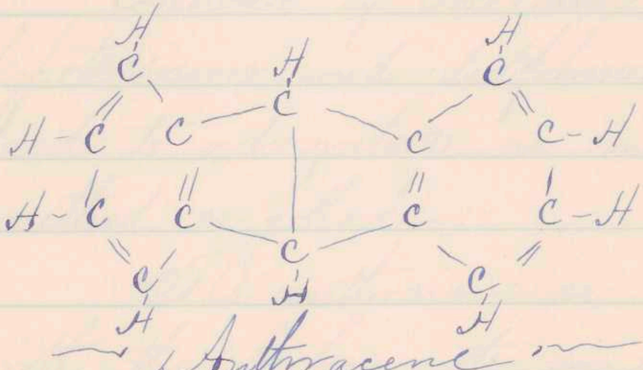
Quinone



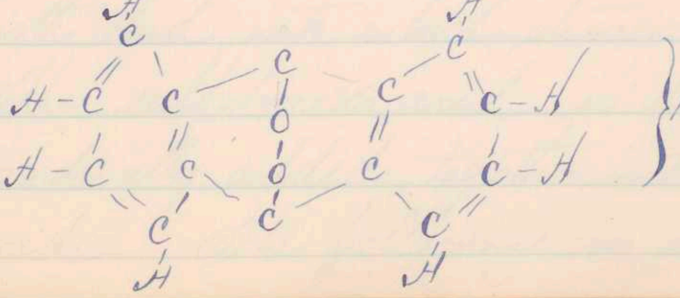
Naphthalene



Naphtoquinone



Anthracene



Anthraquinone

Formation of Anthra=quinone

Anthraquinone is formed by oxidizing anthracene, chromic acid giving the best results.

Having dissolved on the one hand anthracene, and on the other chromic acid, in glacial acetic acid, the latter solution is poured gradually into the former which is at the boiling temperature.

General Method

There is a rapid reaction and the chromic acid is reduced and passes into the state of acetate of chromium.–

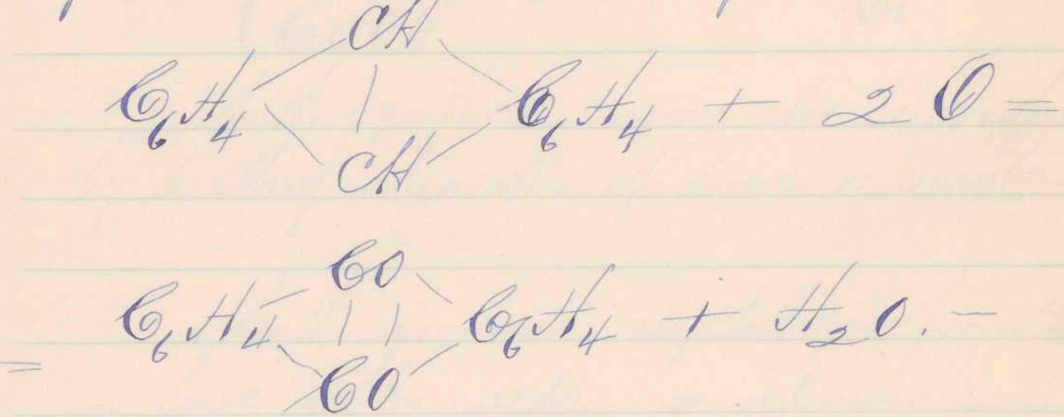
By adding water anthraquinone is deposited.– This is purified by sublimati

Industrial Method.

Instead of chromic acid, bichromate of potassium and sulphuric acid can be used to advantage as in the industrial method as follows:–

The anthracene is mixed intimately with the bichromate in large vats lined with lead into which steam is passed. The sulphuric acid is diluted and gradually added, together with some acetic acid.– The following is an approximate formula:- 1 part anthracene; 2½ parts bichromate of potash; 4 parts pyroligneous acid; after heating sometime 6 parts of sulphuric acid are added. - The yield is almost what theory requires. - It is purified by dissolving the crude product in sulphuric acid (cold) and reprecipitating with water; collecting, washing and pressing, and drying at 50°. -

The formation of anthraquinone from anthracene is thus formulated:-



$$C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4 + 2O =$$

$$= C_6H_4\left\langle\begin{matrix}CO\\|\\CO\end{matrix}\right\rangle C_6H_4 + H_2O. -$$

Pthalic Acid and Anthra=quinone.

I may say in passing that the manufacture of alizarin from anthracene has been somewhat checked for want of anthracene but there is now prospect of obtaining the anthraquinone in

Synthesis-

1°

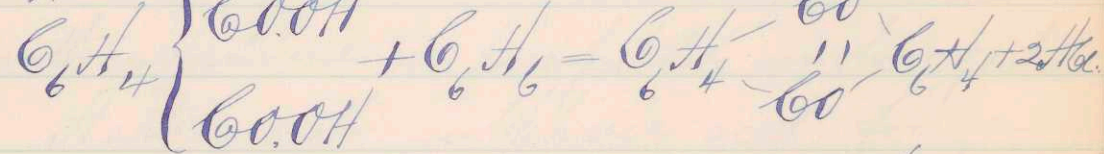
From Pthalic =Chloride and Benzol.

quantity by another method.- Pthalic acid, $C_8H_6O_4$, is produced by oxidizing naphthalene. - Benzol, C_6H_6, is also abundant in coal-tar. - If the chlorine compound of pthalic acid $C_8H_4O_2Cl_2$, is heated with benzol for twelve hours to 220° anthraquinone is readily obtained.

$$C_8H_4O_2Cl_2 + C_6H_5.H = C_{14}H_8O_2 + 2HCl$$

~Pthalic Chloride~ Benzol Anthraquinone-

or



$$C_6H_4\begin{cases}CO.OH\\CO.OH\end{cases} + C_6H_6 = C_6H_4\begin{matrix}CO\\ \|\\ CO\end{matrix}C_6H_4 + 2HCl.$$

2°.

From Alizarate.

Anthraquinone may also be prepared by distilling alizarates of lime or baryta-

General Properties

Anthraquinone crystallizes from alcohol in long silky needles, sometimes in prisms of a slight-yellowish gold tint.- The color should be very light, almost white, when precipitated from chromic acid by water.

It is insoluble in water, little soluble in alcohol and ether, more soluble in boiling benzol but diff. soluble in cold benzol.-

It melts at 270° and distils at a much higher temperature without alteration.- It is very stable, resisting energetic oxidizing agents.

Soluble in hot nitric acid (sp. gr. 1.4) separating out on cooling.- But treated with a mixture of nitric and sulphuric acids, binitroanthraquinone is formed.-

Soluble in conc. sulphuric acid with an orange coloration; by heating the liquid, a red color appears but on adding water, the anthraquinone is precipitated unchanged.

Heated with sulphuric acid for a long time sulpho-compounds are formed.

Reactions with Caustic Alkalies

Anthraquinone is insoluble in solutions of caustic alkalies but if fused with KOH

1°

1°. At 250° with the solid caustic potash the mass becomes blue, as if alizarin was formed; but on adding water to the mass, the liquid is decolorized and the anthraquinone precipitated again unchanged in flakes.-

2°

2°.- If this fusion is prolonged and then added to water, benzoic acid is is precipitated as a white crystalline deposit.—

3° 3°. Fusing as before, at a certain time the mass becomes suddenly peculiarly green. If now it is added suddenly to water, the water is coloured a magnificent red. By filtering, the red color slowly disappears and the white flakes of anthraquinone are again deposited.— By adding acid to the red solution a yellow amorphous precipitate is formed which rapidly is converted into anthraquinone on exposure to the air.—

4° 4°. By fusing still stonger, there is finally a disengagement of hydrogen and the anthraquinone is transformed into a series of products as yet unstudied.—

Bromine acts on neither the crystals or a solution in bisulphide of carbon in the cold but by heating the same in closed tubes at 100°, a bromine compound, bibromanthraquinone, is formed.

Anthraquinone can be distilled very quickly without alteration.— It is not, as naphtoquinone and quinone are, acted upon by Sulphurous acid.- Iodohydric acid only changes it to bioxyanthracene.-

But if the same be heated in closed tubes to 150° the needles disappear and white flakes are obtained.- These are not bioxyanthracene, $C_{14}H_8\begin{cases}OH\\OH\end{cases}$ but simply regenerated anthracene, $C_{14}H_{10}$.—

Anthraquinone is readily reduced to anthracen by heating 1 pt. with 10 pts. powd. zinc in a tube.

The reduction is operated by the hydrogen of the water of the hydrated oxide of zinc, which is always found in powdered zinc which has been exposed to the air.-

$$C_{14}H_8O_2 + 2H + 2Zn = C_{14}H_{10} + 2ZnO.$$

~Anthraquinone~ ~Anthracene~

Quinone and Anthra=quinone.

Quinone, $C_6H_4O_2$, treated with reducing agents, is converted into hydroquinone, $C_6H_6O_2 = C_6H_4O_2.H_2$.-

By mixing solutions of quinone and hydroquinone, green crystals of a combination of the two substances, called quinone hydrone, are formed. — Quinone is a crystalline body of a golden yellow color; hydro-quinone is colorless; quinone-hydrone is a true colouring matter, of crystals of a brilliant beetle-green lustre.-

Anthraquinone is capable of many transformations, quite similar to the preceding.

Anthra=
=hydro=
=Quinone.

Nascent hydrogen changes it to anthrahydroquinone, $C_{14}H_{10}O_2 = C_{14}H_8O_2.H_2 = C_{14}H_8\left\{\begin{matrix}OH\\OH\end{matrix}\right.$. This latter combines with anthraquinone forming anthraquinone hydrone:-

Anthra=
=Quinone
Hydrone.

$C_{14}H_8O_2 + C_{14}H_8O_2.H_2 = C_{28}H_{18}O_4 =$
~Anthraquinone~ Hydroanthraquinone
$= 2(C_{14}H_9O_2) = 2(C_{14}H_8\left\{\begin{matrix}O\\OH\end{matrix}\right.$
~Anthraquinone hydrone~

In speaking of the action of fused caustic potash on anthraquinone (p. 61) producing a red color when the green mass (3°. p. 61) was added to water. This is probably due to anthraquinone hydrone, which is quite unstable, absorbing oxygen from the air and changing thus into anthraquinone.- In this case of fusion with caustic potash a quantity of hydrogen is given off which explains the formation of the anthraquinone hydrone.- The hydrogenation of the anthraquinone is more easily realized by the use of powdered zinc and a solution of alkali.-

Boettger noticed that the same solution gave a red color, and Graebe has lately studied and explained the same.-

Anthrahydroquinone may be obtained by mixing a solution of anthraquinone in alcohol with sodium amalgam and caustic soda.

Isomerides of Anthra=quinone.-

There are two isomers of anthraquinone.

1°.

1° Schutzenberger, while oxidizing chlorinated anthracene obtained the paranthraquinone, $C_{14}H_8O_2''$, a sublimable body, crystalline, beautifully red-coloured resembling alizarine, but distinguished by its insolubility in ammonia and potassa. It is converted into anthraquinone by heating the vapour to 300°.-

2°.

2° By treating red orange-anthracene, a

nitro-compound, with tin and hydrochloric acid, a precipitate of silky plates of the iso-anthracene falls.- By oxidizing these, iso-anthraquinone, $C_{14}H_8O_2''$ is formed in beautiful red needles, melting at 235° and dissolving in sulphuric acid with a pure indigo-blue colour.-

Action of Bromine on Anthra=quinone

Bromine acts on anthraquinon directly at 100° in closed tubes forming bibromanthraquinone; $C_{14}H_8O_2 + 4Br =$
~Anthraquinone~
$= C_{14}H_6Br_2O_2 + 2HBr$.
~Bibromanthraquinone~ This method is not so satisfactory since masses of bibromanthraquinone form on the outside of the anthraquinone and protect it from the action of the bromine.-

Bibrom=anthra=quinone.

It is more easily obtained by means of the tetrabromanthracene, by heating the same with 2 parts of $K_2Cr_2O_7$ and 5-6 pts of nitric acid (sp. gr. 1.4).- The reaction is very energetic and bromine is freed.

The product is purified by throwing

into water, washing, and crystallizing from benzene.- Chromic acid in acetic acid may also be used.-

Bibromanthraquinone crystallizes and sublimes in clear yellow crystals, little soluble in alcohol, more soluble in benzene and chloroform.- Not acted upon by KOH until above 200°C when it forms alizarin as a final product.-

$$C_{14}H_6O_2Br_2 + 2KOH = C_{14}H_6O_2(OH)_2 + 2KBr.$$

~Bibromanthraquinone~ ~Alizarin~

Bibromanthrahydroquinone.

If this reaction is urged with caution and stopped when an intense green color is observed and then added to hydrochloric acid, green flakes are deposited.- These flakes are probably the bromanthrahydroquinone, corresponding to the hydroquinone of anthracene, bromatized.

Monobromanthraquinone.-

By oxidizing tribromanthracene, by a reaction exactly like the last, monobromanthraquinone may be obtained:-

$$C_{14}H_7Br_3 + O_2 = C_{14}H_7Br(O)_2'' + 2Br$$

~Tribromanthracene~ ~Monobromanthraquinone

This crystallizes in pale yellow needles, melting at 187° and sublimes without decomposition.— Little soluble in alcohol or cold benzol, but readily soluble in boiling benzol.—

Alkaline hydrates readily convert the same into alizarin with the formation of a little monoxyanthraquinone,

$C_{14}H_8O_3 = C_{14}H_7(HO)(O)''_2$.—

Action of Chlorine on Anthraquinone.—

Monochloranthraquinone.

Monochloranthraquinone, $C_{14}H_7Cl(O)''_2$, has never been prepared, so far as I can learn, and the trichloranthracene, $C_{14}H_7Cl_3$, from which it might be derived by oxidation has not yet been obtained by this method but has been obtained with PCl_5 (See p. 84)

Bichloranthraquinone

Bichloranthraquinone, $C_{14}H_6Cl_2O_2$, is obtained in a manner similar to that by which bibromanthraquinone is obtained, by oxidation of the tetrachloranthracene by means of nitric acid or chromic acid in acetic acid.—

It resembles the bromine compound, crystallizing in yellow needles, difficultly soluble in alcohol and ether, more soluble in benzene.— Fused with caustic potash it furnishes alizarin as a final product.—

Action of Nitric Acid on Anthracene or Anthraquinone.

Anthracene is slowly acted on by nitric acid, if cold; but if hot, very energetically, and, depending on the concentration of the acid and length of the reaction, various products are obtained, as anthraquinone and various nitro-compounds of the same and of anthracene, which are very difficult to separate.—

Mono=nitro=anthracene.

Mononitroanthracene, $C_{14}H_9NO_2$, is obtained by dissolving 1 pt. anthracene in boiling alcohol and adding 1 pt. nitric acid (sp. gr. 1.33) and leaving the same for some time exposed to the rays of the sun. — There is gradually deposited from this solution, the nitro-compound, in orange-red crystals in groups of needles. — These are washed on a filter with cold alcohol.

They are little soluble in alcohol or benzene; are easily sublimed.—

Dinitro=anthracene.

If instead of exposure to the sun, the solution is heated, the same crystals are obtained, but mixed with another white crystalline precipitate, more easily soluble in alcohol and also sublimable.

This latter compound is I claim, the binitroanthracene, $C_{14}H_8(NO_2)_2$, since late analyses give to it 10.51% of N and the theoretical requires 10.46% of the same. — Some writers, especially Schmidt, claimed as late as 1871 that this compound was an isomer of red mononitroanthracene but such is lately proven not to be the case.—

The mononitroanthracene, $C_{14}H_9NO_2$

is easily reduced by hydrogen to a resinous brown matter which on being sublimed gives colorless crystals which melt at 275° and have the formula:-

Nitroxy=
=anthracene.

$$C_{28}N_2OH_2 = \left\{\begin{matrix}C_{14}H_6N\\C_{14}H_6N\end{matrix}\right\}O \text{ called} =$$

= Nitro-oxyanthracene:~ This body is soluble in conc. sulphuric acid but by the addition of water, it separates again in the form of a black amorphous powder.

By heating the sulphuric acid a soluble sulpho-acid is formed.

Nitroxyanthracene is also soluble in conc. nitric acid and by cooling the same, there separates from it a substance in the form of yellow needles which compound has not yet been studied.

Mono=
=nitro=
=anthra=
=quinone.

Mononitroanthraquinone, $C_{14}H_7(NO_2)O_2$ is formed by dissolving anthracene in nitric acid (Sp. gr. 1.5) and boiling for ½ hour.

By adding water, the above is precipitated in pale yellow flakes, which melt at 230°, highly electric, subliming at the same temperature in delicate needles.-

Insoluble in water, sparingly soluble in ether and alcohol; more freely in acetic ether, benzol, chloroform, oil of turpentine and glacial acetic acid.— Easily soluble in nitro-benzol, conc. sulphuric acid and aniline.- A mixture of nitric and sulphuric acids convert it into dinitroanthraquinone.-

Dinitroanthraquinone.

Anderson, by treating anthraquinone with fuming nitric acid obtained binitroanthraquinone, $C_{14}H_6N_2O_6 = C_{14}H_6O_2''(NO_2)_2$

It may be prepared with a mixture of nitric and sulphuric acids as stated on page 70.- This was isolated by Anderson by treating the mass with small quantities of boiling alcohol; by cooling, it was deposited as a red powder somewhat crystalline, melting at 230° and subliming at 250° in yellow needles.-

By cooling and collecting the nitric

Anthr=
=acenic
Acid.

acid decanted from the resinous mass (72 and the wash water, evaporating with care and crystallizing, Anderson obtained a yellow crystalline substance, an acid, which he has called Anthracenic acid.

This acid has been but little studied Anderson has alone stated that it is very soluble in water and that it forms with potash and ammonia, crystallizable salts, which precipitate lead and barium salts by double decomposition.-

Dinitro=
=anthra=
=quinone
(Continued)

It is quite probable that there are several isomeric dinitroanthraquinones, presenting different properties.- Boettger prepares it as follows:- 1 pt. of anthraquinone is dissolved in 16 parts of a mixture of H_2SO_4 of 66° Baumé and fuming HNO_3 of sp. gr. 1.5, at a moderate heat.

The anthraquinone is completely dissolved; the brownish-green liquid is turned on to a filter containing a little cold water when the dinitroanthraquinone is deposited in yellow and almost pure flakes.

These are washed with water and dried.

This compound, called by Boettger dinitroanthraquinone, and by Graebe & Liebermann isobinitroanthraquinone has the formula:-

$$C_{14}H_6N_2O_6 = C_{14}H_6O_2''(NO_2)_2.$$

It is almost insoluble in water, a little more soluble in ether, difficultly soluble in alcohol, benzol but quite soluble in chloroform. - It crystallizes in pale yellow microscopic prisms.

Submitted to the action of heat, dinitroanthraquinone browns, softens, agglomerates at 250° and sublimes in part to yellow needles, the rest carbonized. By heating quickly it deflagrates.

Diamido=anthra=quinone.

Submitted to the action of energetic reducing agents (Stannate of Soda, Sulphydrate of soda or ammonia) it is converted into "orange-anthracene" which is the diamidoanthraquinone:-

$$C_{14}H_{10}N_2O_2 = C_{14}H_6O_2'(NH_2)_2. -$$

This compound, which is deposited in small cinnabar-red flakes from a boiling solution of Stannate of Soda, melts at 256° to a cherry-red liquid.— It sublimes at this temperature in magnificent crystalline needles, which, under the microscope appear to be elongated rhombs or rectangles.— This amide presents only a very limited basic character and scarcely dissolves in boiling mineral acids; by cooling, it is deposited from the same, in a pulverulent form.— With caustic potash it forms alizarine.— It becomes highly electric by grinding or rubbing.—

Action of Nitrous Acid on Diamidoanthraquinone

By passing nitrous acid gas (HNO_2) into a solution of "orange-anthracene" in alcohol, its colored solution passes from hyacinth-red to violet and finally to a yellow-brown and then some brownish flakes are deposited.— By adding water whitish flakes are deposited which are merely anthraquinone reformed.—

If ethyl or acetic ether is substituted for alcohol, the nitrous acid almost immediatelty precipitates a quantity of a brownish-violet powder which gives by analysis, the formula:-

~ $C_{14}H_8N_4O_4$ ~

This may be considered in several ways, as:-

1° Dinitrosoamidoanthraquinone:~
~ $C_{14}H_6\left(N\left\{\begin{matrix}NO\\H\end{matrix}\right.\right)_2O_2''$;

or,

2° Dioxyimidoamidoanthraquinone:-
~ $C_{14}H_6\left(N\left\{\begin{matrix}NH\\O\end{matrix}\right.\right)_2O_2''$;

or,

3° Tetrazoanthraquinone Hydrate:-
~ $C_{14}H_6(N_2OH)_2O_2$;

or,

4° Diazo-anthraquinone Nitrate; (???
~ $C_{14}H_6NO{=}N_2{=}NO_3$ ~ (?) see p. 77

Tetrazo=
=anthra=
=quinone
Hydrate

This compound, $C_{14}H_8N_4O_4$ is readily soluble in cold water with a fine reddish-violet color. By carrying this solution to boiling, orange anthracene is regenerated and also a brown body, not yet studied, is precipitated while a quantity of nitrogen is set free. — By treating the same compound, $C_{14}H_8N_4O_4$, with a solution of caustic soda, the same reaction is affected. — By heating to 70° it is decomposed with explosion and carbon is left behind. —

Tetrazo-anthraquinone Nitrite

By treating "orange-anthracene" in chloroform with HNO_2, a brown body is deposited, almost insoluble in water, a little soluble in alcohol and whose composition is expressed by the formula: — $C_{14}H_6N_6O_6$. — This compound is quite unstable, decomposed by exposure to the air, to alkalies, or to heat. — It can be considered as Tetrazo-anthraquinone Nitrite =

$$C_{14}H_6(NO_2)_2''N_2''O_2$$

This and the preceding compound, which I have called Tetrazo-anthraquinone Hydrate, give alizarine when treated with alkalies. —

Schorlemmer, in his treatise of Carbon compounds, calls the compound

$C_{14}H_8N_4O_4$, of page 75 (Schorlemmer, p. 447) the "Diazo-anthraquinone Nitrate" and gives the formula: $C_{14}H_7O_2''N_2''NO_3$, which is typographically an almost total error.—

Tetrazo=
=anthra=
=quinone
Nitrate

By boiling orange anthracene in acetic ether and passing nitrous acid into the solution, a brownish, resinous, very nitrogenous compound is formed, quite unstable:— It gives by analysis, the formula:— $C_{14}H_6N_6O_8$, and may be considered as Tetrazo-anthraquinone Nitrate. (Schorlemmer's account, etc., is a mixture of the history and formulae of this and of the corresponding hydrate for and also of the orange anthracene.)

The relation between these preceding bodies can be represented as follows:—

(see p. 78)

Anthraquinone, $C_{14}H_{80}O_{2} = C_{14}H_{6}O_{2}\left\{\begin{matrix}H\\H\end{matrix}\right.$
(see p. 70)

Relation of these Azo=-compounds.

Dinitroanthraquinone, $C_{14}H_{6}N_{2}O_{6} = C_{14}H_{6}O_{2}\left\{\begin{matrix}NO_{2}\\NO_{2}\end{matrix}\right.$
(see p. 72)

Diamidoanthraquinone, $C_{14}H_{10}N_{2}O_{2} = C_{14}H_{6}O_{2}\left\{\begin{matrix}NH_{2}\\NH_{2}\end{matrix}\right.$
(see p. 73)

Tetrazoanthraquinone Hydrate, $C_{14}H_{8}N_{4}O_{4} = C_{14}H_{6}O_{2}\left\{\begin{matrix}N_{2}OH\\N_{2}OH\end{matrix}\right.$
(see p. 75)

Tetrazoanthraq. Nitrite, $C_{14}H_{6}N_{6}O_{6} = C_{14}H_{6}O_{2}\left\{\begin{matrix}N_{2}NO_{2}\\N_{2}NO_{2}\end{matrix}\right.$
(see p. 76)

Tetrazoanthraq. Nitrate, $C_{14}H_{6}N_{6}O_{8} = C_{14}H_{6}O_{2}\left\{\begin{matrix}N_{2}NO_{3}\\N_{2}NO_{3}\end{matrix}\right.$
(see p. 77)

Action of Sulphuric Acid on Dinitro=anthra=quinone

If one part of dinitroanthraquinone, (see p. 71 and 72) is dissolved in 16-18 parts of sulphuric acid and heated, at about 200° SO_2 gas is abundantly given off and the liquid becomes brownish-red. By turning this solution into cold water a brownish-red precipitate is deposited.– By washing, dissolving in dilute alkali and again precipitating with acid once or twice a pure product is obtained.– This gives a violet substance having the formula

$$C_{14}H_8N_2O_4 = C_{14}H_6O_2\left\{\begin{matrix}NHO\\NHO\end{matrix}\right. .$$

which is called

Diimido=hydroxyl=anthra=quinone

Diimidohydroxylanthraquinone.– (In the purification of the above, a blackish substance is separated which dissolves only in concentrated alkalies) This compound, $C_{14}H_8N_2O_4$ may also be prepared by means of an excess of sulphuric acid and a little HNO_3 according to recent experiments of Graebe and Liebermann and Gutzkow.

This compound is little soluble

in water, easily soluble in alcohol, benzol, (80 chloroform, ether, or glycerine giving fine red-violet colored solutions. - Acetic acid dissolves it to a fuchsine-red color, sulphuric acid to a hyacinth red, and alkalies to a bluish-violet color, which dye wool and cotton.

By heating, it melts to a violet liquid, fuses, bubbles, then sublimes in violet fumes of a peculiar odor very similar to that of indigo; part condenses, some is carbonized. - It will be seen that the formula differs from that of Indigotin, $C_{16}H_{10}N_2O_2$, by 2 CH. -

Its Isomer; called Alizarine Biimide

Caustic alkalies dissolve it with liberation of ammonia and alizarin is formed. - This body body therefore should be considered as Alizarine Biimide

Alizarine :-

$$C_{14}H_8O_4 = C_{14}H_6O_2\left\{\begin{matrix}OH\\OH\end{matrix}\right.$$

Alizarine Biimide:-

$$C_{14}H_8N_2O_4 = C_{14}H_6O_2\left\{\begin{matrix}NH\\NH\end{matrix}\right\}O_2$$

Oxyimido=
=hydroxyl=
=anthra=
=quinone

By treating a solution of this compound in ether-alcohol with HNO_2 brown flakes are deposited.- Then driving off the ether and adding to cold water remain orange flakes are deposited which melt to a brown liquid at 142°.- These are sublimed and condense in yellowish red orthorhombic crystals, very brilliant, soluble in cold alcohol; in ether to a yellow color; in sulphuric acid to an orange solution; in alkalies to red; by fusion with alkalies, alizarine is formed:-

Peterson gives to this formula $C_{14}H_7NO_5$ which may be called Oxyamidohydroxyl= =anthraquinone:-

$$C_{14}H_7NO_5 = C_{14}H_6O''_2\left\{\begin{matrix}NH\\O\end{matrix}\right\}O_2$$

Dinitro=
=dihydroxyl=
=anthra=
=quinone-

By treating the isomeric compound of Diimidohydroxylanthraquinone, the compound Alizarine Biimide of p. 80, with conc. nitric acid, the solution changes from violet to reddish-brown and by addition of water, orange flakes are deposited which are very electric and soluble in caustic alkali to an intense red solution.- This compound by analysis gives a formula:-

$$C_{14}H_6N_2O_8 = C_{14}H_6O_2\left\{\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O_2$$

and may be called Dinitrodihydro-anthraquinone.-

Action of Oxychloride of Carbon on Anthracene-

By heating a mixture of anthracen and oxychloride of carbon ($COCl_2$) in closed tubes for 10-12 hours at a temp. of 180°-200° a reaction takes place.-

The tubes are well cooled before opening when great quantities of HCl gas are evolved.- The tubes contain 1°. yellowish crystals, 2°. a brown resinous mass, which are both treated with a solution of caustic alkali which dissolves the crystals only.-

By filtering into an acid yellow flakes of impure anthracene-carbonic acid are deposited.- These crystals are purified by successive recrystallizations in alcohol.-

Anthracene=
=Carbonic
Acid.

Anthracene-carbonic acid, $C_{15}H_{10}O_2 = C_{14}H_{10}(CO_2) = C_{14}H_9.COOH$, presents very characteristic acid properties. It is soluble in alcohol, ether, glacial acetic acid, rather soluble in hot water. It melts at 206° and is slowly resolved at the same temperature into anthracene and carbonic acid. The same decomposition is observed when the acid is heated with soda lime.

Chromic acid converts it into the anthraquinone. Nitric acid does the same.

$$C_{14}H_9.CO_2H + 3O = C_{14}H_8O_2 + CO_2 + H_2O$$

~Anthracenecarbonic Acid ~ Anthraquinone~

~Salts of Anthracenecarbonic Acid.-

~Barium
Salt.

The Barium salt of this acid, $(C_{14}H_9CO_2)_2Ba$ is prepared by saturating the acid with barium carbonate. - It is more soluble in hot than cold water, crystallizing from the same in small yellow crystals, which at 170° lose nothing and are probably free from water of crystallization or constitution.-

Silver Salt.

The Silver Salt, ($C_{14}H_9.CO_2Ag$), is prepared by saturating the acid with recently precipitated oxide of silver. – This salt is readily soluble in water. – By evaporating the aqueous solution a crystalline powder is obtained made up of microscopic prisms. –

Action of Perchloride of Phosphorus on Anthraq.

The action of perchloride or quinquichloride of phosphorus, PCl_5, on anthraquinone is analogous to that observed when trichloroquinone, $C_6HCl_3O_2''$, or the dichloronaphthoquinone, $C_6H_4Cl_2O_2''$, is treated with PCl_5. – This adds new strength to the view of a group of quinones expressed on pp. 54, 55, and 56. –

Tri=
=chloro
Anthracene

Trichloro-anthracene is formed by the replacement of two atoms of chlorine for two atoms of oxygen in anthraquinone accompanied by a further substitution by the free chlorine liberated in the first reaction, as may be seen in the following reactions:

1°.- $C_{14}H_8O_2 + PCl_5 = C_{14}H_8Cl_2 + Cl_2 + 2(POCl_3)$
~Anthraquinone~ ~Bichloranthracene~

2°.- $C_{14}H_8Cl_2 + Cl_2 = C_{14}H_7Cl_3 + HCl$.-
~Bichloranthracene~ ~Trichloranthracene~

These reactions are carried on in sealed tubes as usual, the insoluble product resulting being recrystallized in alcohol. Yellow crystals are thus obtained, sublimable without decomposition, not altered by solution of alkalies; difficultly soluble in alcohol and ether readily soluble in benzol.-

~Action of Sulphuric Acid on Anthracene~

Two acids are formed when anthracene is treated with sulphuric acid, viz:- 1°. Monoanthracenesulphonic Acid:-

$$C_{14}H_{10}.SO_3 = C_{14}H_9.SO_3H$$

and

2°. Anthracenebisulphonic Acid:-

$$C_{14}H_{10}.2SO_3 = C_{14}H_8.\left\{\begin{array}{l}SO_3H\\SO_3H\end{array}\right.$$

Let me say, in passing, that great commercial importance has of late been attached to these acids since the latest and best results in the manufacture of alizarin artificially have come through these acids instead of through a bromine compound.- Still very little is known of these acids or is known of their salts from a scientific point of view.

~Anthracene=
=mono=
=sulphonic
Acid.~

The first, anthracenemonosulphonic acid, is obtained by dissolving anthracene in sulphuric acid at the ordinary temperature.-

By separating the excess of acid (sulphuric) with acetate of lead, and the excess of acetate of lead with ammonium carbonate, the impure ammonium salt is obtained which is very soluble in water and reacts on lead, sodium and other salts with the formation of anthracenemonosulphonic salts, not yet studied.- The sodium salt fused with caustic soda forms anthracene again.-

The acid oxidized with chromic acid or with nitric acid is transformed into the anthraquinone monosulphonic acid, $C_{14}H_8O_2SO_3$

Anthracene=
=bi=
=sulphonic
Acids.

Anthracenebisulphonic Acid,

$C_{14}H_{10}(SO_3)_2 = C_{14}H_8\begin{cases}SO_3H\\SO_3H\end{cases}$, is formed when anthracene is treated with sulphuric acid in excess at a high temperature.

Mayer has recently obtained the same with good results.- The sulphuric acid in excess is separated with barium carbonate and the barium anthracenebisulphonate is in solution, yet impure.- Acetate of lead is added which separates the impurities more fully; finally the excess of lead salt is precipitated by means of Hydrogen sulphide.-

By evaporating the solution the barium salt is obtained in the crystalline state.— By dissolving this in water and adding just enough sulphuric acid the $BaO.SO_3$ is precipitated and the acid liberated.- It is very soluble in water, separating therefrom in yellowish-orange laminae.-

~Salts~

The barium salt, crystallizing in brilliant brown laminae; the ammonium, brownish-orange, and the calcium and sodium salts are readily soluble in water.

The bisulphoanthracenates, or even the acid, treated with oxidizing agents (nitric acid or chromic acid, or sulphuric acid and oxide of manganese) are converted into anthraquinone bisulphonic acid, $C_{14}H_6O_2\left\{\begin{matrix}SO_3H\\SO_3H\end{matrix}\right.$ which will be later considered.-

Action of Sulphuric Acid on Anthraquinone-

Sulphuric acid acts on anthraquinone forming two very interesting acids which is one step further in the alizarine manufacture as will soon be seen.-

Anthra-quinone-mono-sulphonic Acid.

Anthraquinone monosulphonic Acid, $C_{14}H_8O_2.SO_3 = C_{14}H_7O_2.SO_3H$, is formed by heating anthraquinone (1 part) with conc. sulphuric acid (2-3 pts) to 200°-220°.

It is freed from the excess of sulphuric acid by carbonate of calcium, the calcium salt being quite readily soluble in warm water, and the acid set free again by means of sulphuric acid.- It is also produced from the monosulpho-acid of anthracene by means of oxidizing agents.—

It crystallizes in yellow plates extremly soluble in hot water, soluble in cold water and alcohol, but insoluble in ether and mineral acids.–

~Salts~

Barium Salt.

The Barium salt, $(C_{14}H_7O_2 . SO_3)_2 Ba + H_2O$ crystallizes in yellow microscopic laminae; very little soluble in cold, more soluble in hot water.– It loses its water of crystallization at 150°.–

Calcium Salt.

The Calcium salt, $(C_{14}H_7O_2 . SO_3)_2 Ca$, is more soluble in water than the barium salt and crystallizes in small, indefined yellow crystals.–

Sodium Salt.

The Sodium salt, $C_{14}H_7O_2 . SO_3 Na$, is obtained by double decomposition with carbonate of soda.– It is very soluble in hot water; difficultly soluble in cold water. It crystallizes in yellow crystals.– Its aqueous solution is however orange.

Anthra=
=quinone
=bisulfonic
Acid.–

Anthraquinone-bisulphonic Acid,

$$C_{14}H_8O_2 . 2SO_3 = C_{14}H_6O_2\left\{\begin{array}{l}SO_3H\\SO_3H\end{array}\right.$$

is prepared as previously indicated by treating anthraquinone with an excess of sulphuric acid at 270°-290°.–

The acid is very difficultly soluble in sulphuric acid and separates from it by cooling the solution.– It is also prepared by oxidizing the anthracenebisulphonic acid by means of chromic acid, nitric acid, nitrate of mercury, bichromate of potash, or oxide of manganese and sulphuric acid.

The acid thus formed is transformed into a soluble calcium salt by means of chalk. – By filtration and expression the impurities are removed.– The acid is freed from the barium salt by sulphuric acid.

It crystallizes in small yellow crystals, more soluble in water than the monosulphonic acid.– The salts are yellow when dry; in solution, orange; more orange in the case of salts of alkalies.

~Salts~

The Barium salt, $C_{14}H_6O.Ba(SO_3)_2$ (91 is little soluble in cold, more soluble in cold water. ~Crystallizes in small, yellow needles.–

The Lead salt, $C_{14}H_6O_2.Pb(SO_3)_2$, crystallizes in confused yellow crystals, soluble as the barium salt.–

~Alizarin from Anthraquinone bisulph. Ac.

Anthraquinone-bisulphonic acid is the foundation of the manufacture of alizarine by fusing with caustic potash.– But there is an intermediate step which has been observed when either the mono- or disulphonic acid is thus treated.– In reality one of the SO_3H is substituted by OH first and thus there is formed

Oxanthra=
=quinone=
=Sulphonic
Acid.

Sulphoxanthraquinonic Acid:–

$$C_{14}H_8O_3.SO_3 = C_{14}H_6O_2\begin{cases}OH\\SO_3H\end{cases}$$

~Alizarine:–

$$C_{14}H_8O_4 = C_{14}H_6O_2\begin{cases}OH\\OH.\end{cases}$$

~Anthracene-Bisulphonic Acid~

$$C_{14}H_8O_2(SO_3)_2 = C_{14}H_6O_2\begin{cases}SO_3H\\SO_3H\end{cases}$$

By heating Anthracenebisulphoquinonate of potassium with caustic potash, a point is noticed when the mass assumes an orange-red color and then is converted gradually to blue. — At the last moment (blue) the anthraquinoneoxysulphonate of potassium is found formed:—

$$C_{14}H_6O_2\left\{\begin{matrix}SO_3K\\SO_3K\end{matrix}\right. + 2KOH = C_{14}H_6O_2\left\{\begin{matrix}OK\\SO_3K\end{matrix}\right. + \text{etc.}$$

~Anthraq. bisulp. potassium.~ Sulphalizarate or Anthraquinoneoxysulphonate potash.

By prolonged heating beyond the blue a violet color appears when alizarate of potassium is formed:—

$$C_{14}H_6O_2\left\{\begin{matrix}OK\\SO_3K\end{matrix}\right. + 2KOH = C_{14}H_6O_2\left\{\begin{matrix}OK\\OH\end{matrix}\right. + SO_3K_2 + H_2O.$$

Sulphalizarate K~ ~Alizarate of Potassium.

By decomposing alizarate of potassium with an acid alizarine, so called, is formed:—

$$C_{14}H_6O_2\left\{\begin{matrix}OK\\OK\end{matrix}\right. + 2HCl = C_{14}H_6O_2\left\{\begin{matrix}OH\\OH\end{matrix}\right. + 2KCl.$$

Alizarine =
= sulphonic =
Acid.

Anthraquinone-oxysulphonic or alizarin = sulphonic acid, $C_{14}H_8O_3.SO_3 = C_{14}H_6O_2\left\{\begin{matrix}OH\\SO_3H\end{matrix}\right.$ is prepared by fusing the anthraquinone disulphonic acid with KOH until a blue color gradually appears.-

The mass is dissolved in water and an excess of hydrochloric acid added to decompose any alizarate that may have formed.- Barium chloride is added to the filtrate and the barium salt purified by recrystallizations and then decomposed by sulphuric acid.

The acid forms yellow crystals, easily soluble in alcohol or water but insoluble in ether.- It is a bibasic acid and forms two series of salts

- Salts -

The neutral salts, in which the H's of the OH and SO_3H are both replaced by the metal, are all blue.-

The acid salts, in which the H of the SO_3H is alone replaced by the metal, are yellowish-orange colored.-

Thus the blue potassium

salt, soluble with the same color in water has the formula:—

$$C_{14}H_6K_2O_3.SO_3 = C_{14}H_6O_2\left\{\begin{matrix}OK\\SO_3K\end{matrix}\right.$$

Potassium Salt.

By adding a little chlorhydric acid to the solution, the blue changes to orange and the acid potassium salt is formed having the formula:—

$$C_{14}H_7KO_3.SO_3 = C_{14}H_6O_2\left\{\begin{matrix}OH\\SO_3K\end{matrix}\right.$$

By adding a large excess of chlorhydric acid, the acid is set free:—

$$C_{14}H_8O_3.SO_3 = C_{14}H_6O_2\left\{\begin{matrix}OH\\SO_3H\end{matrix}\right.$$

Barium Salt.

The barium salts are obtained by double decomposition of the potash salts:

1°. The acid salt is soluble in water, less so in chlorhydric acid.—

2° If hydrate of barium is added to an acid aqueous solution of the preceding a blue precipitate is formed, which is the neutral salt:—

$$C_{14}H_6BaO_3.SO_3 = C_{14}H_6O.\left.\begin{matrix}O\\SO_3\end{matrix}\right\}_2 Ba$$

Action of Sulphuric Acid on Bichloranthracene.

Bichloranthracene can be prepared as already indicated on page 42, by either the direct action of chlorine on anthracene or by passing a current of chlorine through a solution in benzol.-

Bichlor=
=anthracene=
=bisulphonic
Acid.

By treating bichloranthracene with fuming sulphuric acid it is converted into bisulpho-bichloranthracenic acid and turning the resulting mass into water, precipitating the sulphuric acid with carbonate of barium and concentrating the filtrate from the barium sulphate, the bichloranthracene-bisulphonic acid separates out :-

$$C_{14}H_8Cl_2 . 2\underline{SO_3} = C_{14}H_6Cl_2\left\{\begin{matrix}SO_3H\\SO_3H\end{matrix}\right.$$

It is readily soluble in water to a yellow-orange solution.- Insoluble in sulphuric or chlorhydric acids.- The dilute aqueous solution is remarkable for the beauty and intensity of its blue fluorescence.-

The acid is bibasic and

forms salts represented by the general formula:—

$$C_{14}H_6Cl_2\left\{\begin{matrix}SO_3M\\SO_3M\end{matrix}\right. :—$$

~Salts~

Some neutral salts are as follows:—

The Sodium salt, $C_{14}H_6Cl_2(SO_3Na)_2$ crystallizes in small yellow crystals, easily soluble in water.

The Barium salt, $C_{14}H_6Cl_2.(SO_3)_2Ba$ is yellow.— Insoluble in hydrochloric acid, little soluble in water. — Obtained by the double decomposition of the sodium salt, in an excess of chlorhydric acid.

The Calcium and Strontium salts are readily soluble in water, crystalline, yellow.—

Acid- -oxidized.

The acid is readily converted by oxidizing agents into anthraquinone-bisulphoni acid, even by sulphuric acid if heat is applied; the liquid assumes an intense red color which soon disappears with disengagement of hydrochloric and sulphurous acids. (See p. 91)

The transformation into

anthraquinone-bisulphonic acid is then finished. - The following reactions are expressive :-

Oxidized to Anthra=quinone=bisulpo. Acid

$$\text{I. } C_{14}H_8Cl_2 + 2(SO_4H_2) = C_{14}H_6Cl_2\begin{cases}SO_3H\\SO_3H\end{cases} + H_2O$$

~ Bichloranthracene ~ Bichloranthracene bisulp. Acid

$$\text{II } C_{14}H_6Cl_2\begin{cases}SO_3H\\SO_3H\end{cases} + SO_4H_2 = C_{14}H_6O_2\begin{cases}SO_3H\\SO_3H\end{cases} + 2HCl$$

~ Bichloranthracenbisulphonic Ac ~ ~ Anthraq. bisulphonic Ac. ~

Chromic acid, oxide of manganese and sulphuric acid, or nitric acid, affect this change much more rapidly than sulphuric acid alone. -

~ Action of Sulphuric Acid on Bibromanthracene.

Bibromanthracene, treated with sulphuric acid, resembles the preceding. -

Bibrom=anthracene=bisulphonic Acid.

At the ordinary temperature it dissolves in sulphuric acid to a green solution, forming bibromanthracene bisulponic acid. - By heating the same solution the color changes to a red and fumes of bromine are given off. -

The following equations represent

the reactions:)-

I. $C_{14}H_8Br_2 + 2H_2SO_4 = C_{14}H_6Br_2\begin{cases}SO_3H\\SO_3H\end{cases} + 2H_2O$

~Bibromanthracene.- Bibromanthracenebisulphonic Acid.-

II. $C_{14}H_6Br_2\begin{cases}SO_3H\\SO_3H\end{cases} + 2H_2SO_4 = Br_2 + 2SO_3 +$

$+ 2H_2O + C_{14}H_6O_2\begin{cases}SO_3H\\SO_3H\end{cases}$

~Anthraquinonebisulphonic Acid.~

~ Salts ~

The salts of bibromanthracenebisulphonic Acid resemble exactly the salts of the chloro-acid.- The bromo-acid separates in crystals, soluble in water; its aqueous solution, as well as that of its salts, presenting a blue fluorescence.-

The Sodium salt, $C_{14}H_6Br_2(SO_3Na)_2$ crystallizes in small microscopic needles, very soluble in water.

The Barium salt, is obtained, by double decomposition of the preceding, as a yellow precipitate, little soluble in water.

~Alizarin~

From the sulphoric derivatives of anthracene and anthraquinone ($C_{14}H_{10}$ and $C_{14}H_8O_2''$) alizarine is formed, as has been previously stated.

This alizarin, which gives to anthracene its interest today, is simply the anthraquinone, $C_{14}H_8O_2''$, in which two atoms of H are replaced by two atoms of OH giving the formula:-

~Alizarine:- $C_{14}H_8O_4 = C_{14}H_6O_2\left\{\begin{matrix}OH\\OH.\end{matrix}\right.$ ~Alizarine

Prep= =aration.

In practice the commercial anthracene is dissolved in an excess of hot sulphuric acid, thereby forming anthracene-bisulphonic acid.- Then oxide of manganese is added, which gives the anthraquinone-bisulphonic acid:-

$C_{14}H_{10}.2SO_3 + 3MnO_2 + 3H_2SO_4 =$

~Anthracenebisulphonic Ac.~

$= C_{14}H_8O_2.2SO_3 + 3(MnSO_4) + 4H_2O.$

~Anthraquinonebisulphonic Ac.

Then this anthraquinonebisulphonic acid

is fused with potassium hydrate in excess (100
which gives as, a final product, alizarine.

Alizarine is also produced by fusing the dibromanthraquinone (page 65), or dinitro- or diamidoanthraquinone (pages 71 and 73) with caustic potash until the mass assumes a violet color

$$C_{14}H_6O_2''\begin{cases}Br\\Br\end{cases} + 2KOH = C_{14}H_6O_2''\begin{cases}OH\\OH\end{cases} + 2KBr.$$

~Dibromanthraquinone~ ~Alizarine~

Properties

Alizarine crystallizes from alcohol in yellowish-red needles, which melt at 215° and sublime to brilliant red needles.- By crystallizing in slightly aqueous ether, alizarine hydrate ($C_{14}H_8O_4 + 3H_2O$) is formed, containing 18.3% of water of crystallization, in golden yellow plates, shiny, resembling gold.-

By crystallization from alcohol, benzol, naphtha, or ether alizarin crystallizes anhydrous, in the form of prismatic needles, tipped with orange.- Alizarine is almost insoluble in cold water. It is slightly soluble in sulphide of carbon.

It is soluble, even in the cold, in glycerine, acetone, anhydrous or monohydrated acetic acid. – Chlorydric, phosphoric or sulphuric acids do not affect it, even though boiling. –

Nitric acid attacks it energetically giving of nitrous fumes and forming pthalic acid and oxalic acid:–

$$C_{14}H_8O_2 + 2O = C_8H_6O_4 + 3(C_2H_2O_4)$$

~Alizarine~ ~Phthalic Acid~ ~Oxalic Acid.

A similar oxidation is affected by ferric nitrate or chloride.

Salts of Alizarin, or Alizaric Acid.

Alizarin, or alizaric acid, has strong acid properties. – It forms very soluble salts with the alkalies, less soluble in alcohol, insoluble in ether.

The alizarate of sodium, $C_{14}H_6Na_2O_4$, crystallizes in fine needles of a very deep, almost black color. – The phosphates, pyrophosphates, arsenicates, arsenites, borates and silicates of the alkalies dissolve alizarine, giving up part of their base to it, with a red violet color.

**Alizar=
=amide.-**

Ammonia water, heated with (102
alizarine in closed tubes to 100° for some hours, exerts a remarkable reaction on alizarine. - If the tube is opened and an acid is added, violet flakes of alizaramide fall:-

$$C_{14}H_8O_4.H_3N - H_2O = C_{14}H_9N\underline{O_3}$$
$$= C_{14}H_6O_2.N\left\{\begin{matrix}H\\H\\H\end{matrix}\right\}O.-$$

This is sensibly soluble in boiling water, soluble in alcohol or ether. By rapid evaporation from alcohol, it is precipitated in the form of a crystalline powder, which when heated is decomposed as it sublimes)

**Salts
(continued)**

The Alizarate of calcium, $C_{14}H_6CaO + H_2O$, is prepared by double decomposition. It loses its water at 100°. - It is precipitated as a magnificent purple powder while wet, almost black when dry. - Ground in a mortar it presents a metallic lustre. - The Barium salt resembles the calcium salt. - By adding various salts to solutions of alizarate of sodium or ammonium, various colored precipitates are formed, as follows:—

Acetate of Lead	Reddish-purple.
Sulphate of Aluminum	Rose-red.
Sulphate of Strontium	Violet, slightly red.
Sulphate of Magnesium	Blue-violet.
Sulphate of Zinc	Dark red-violet.
Chloride of Magnesium	Reddish violet.
Ferrous Chloride	Blackish "
Ferric Chloride	Brownish "
Chloride of Chromium	Brownish black.
Sulphate of Copper	Brownish-red violet.
Nitrate of Mercury	Very dark violet.
Ammoniacal Cupric Sulphate	Reddish violet.
Mercuric Chloride	Deep violet.
Tartrate of Potash & Antimony	Yellow violet.
Stannous Chloride	Reddish violet.
Stannic Chloride	Pure violet.

Conclusion of Derivatives of Anthracene

The further reactions of alizarin, with methyl, ethyl and acetyl salts I must pass by and call your attention very briefly to the principal isomeride of anthracene and its principal derivatives.

An Isomeride of Anthracene called Phenanthr

In August, 1872, Prof. Fittig of Leipzig (104 brought forward a communication upon a new hydrocarbon in coal-tar.- He then stated that his analysis led to the formula $C_{16}H_{12}$ but at the same time called attention to the fact, that the whole behaviour of this hydrocarbon was rather in accordance with the view that it was an isomeride of anthracene, which indeed subsequent researches have shown to be the case.

-History-

This isomeride of the hydrocarbon, anthracene, is called Phenanthrene, and was obtained from the liquid portion of coal-tar oil boiling above 300°, by fractional distillation, refrigeration of the middle distillates, pressing the crystalline mass, and repeated recrystallization from alcohol to remove anthracene and other bodies; or, 2ndly, the crude phenanthrene is dissolved in alcohol of 80-85% and a little nitric acid is added which oxidizes the anthracene present more readily than the phenanth; or, 3rdly, by forming the picric acid compound of phenanthrene, a stable compound, and the decomposing with ammonia.

Preparation

Properties

This hydrocarbon, crystallizes in colorless (105 shining, occasionally rather-large, crystalline scales; melts at 96°–98°; begins to sublime at 100° and passes over unchanged at a higher temperature; boils above 300°. — It is readily soluble in hot and moderately in cold alcohol; readily soluble in ether, benzene, acetic acid, and bisulphide of carbon.—

Its solutions display a fine blue fluorescence.

Synthesis

Phenanthrene is obtained synthetically by, 1°. Passing stilbene through a red-hot tube filled with pieces of glass:—

$$\begin{array}{l} C_6H_5.CH \\ C_6H_5.\overset{\|}{C}H \end{array} = \begin{array}{l} C_6H_4.CH \\ |\,C_6H_4.\overset{\|}{C}H \end{array} + 2H$$

~Stilbene~ ~Phenanthrene~

2°. By heating toluene to 180° with amorphous phosphorus and iodohydric acid, stilbene, etc., being first formed, and finally, phenanthrene:—

$$(A)\ 2C_6H_5.CH_3 - 4H = \begin{array}{l} C_6H_5.CH \\ C_6H_5.\overset{\|}{C}H \end{array}$$

~Toluol~ ~Stilbene

$$(B)\ \begin{array}{l} C_6H_5.CH \\ C_6H_5.\overset{\|}{C}H \end{array} = \left.\begin{array}{l} C_6H_4.CH \\ |\,C_6H_4.\overset{\|}{C}H \end{array}\right\} \text{Phenanthrene.}-$$

3° Also, in a similar manner from dibenzyl (106 which is first resolved into stilbene and toluene:-

$$2\left\{\begin{array}{l} C_6H_5.CH_2 \\ \quad | \\ C_6H_5.CH_2 \end{array}\right. = \begin{array}{l} C_6H_5.CH \\ \quad \| \\ C_6H_5.CH \end{array} + 2(C_6H_5.CH_3)$$

~Dibenzyl~ ~Stilbene~ ~Toluol~.

Picric
Acid
Comp'd.

The picric acid compound, of formula $C_{14}H_{10}.C_6H_2(NO_2)_3OH$, is prepared by dissolving 1 pt. phenanthrene and $1\frac{1}{3}$ pts. of picric acid in hot naphtha.- On cooling, the above compound separates out in fine yellow prisms melting at 145°.- This may be boiled with a large excess of alcohol without decomposition. (The anthracene picrate is immediately decomposed by an excess of alcohol. (See p. 30)

Water resolves it slowly and alkalies quickly into its two constituents.-

Hydrides
of
Phenanthrene

There are two hydrides of phenanthrene but neither corresponds to those of anthracene, the Tetrahydrophenanthrene, $C_{14}H_{14}$, and the Octohydride of phenanthrene, $C_{14}H_{18}$. (See pp. 36, 40)

Tetra=
=hydride
of
Phenanthr

– Tetrahydride of Phenanthrene is obtained just as the hexahydride of Anthracene (p. 40) is formed, viz. by heating with red phosphorus and iodohydric acid to 240°. – It is a liquid, having a faint but peculiar smell, boiling at 310°.

Octo=
=hydride
of
Phenanthr

– Octohydride of phenanthrene, $C_{14}H_{18}$, is formed by using a large excess of phosphorus and heating above 240°. – This also gives a liquid but boiling below 300°–

– A hydride has not yet been obtained even by prolonged action with sodium-amalgam which converts anthracene so readily into the anthracene bihydride (See p. 36.)

– Action of Bromine on Phenanthrene –

If well cooled solutions of phenanthrene and bromine in bisulphide of carbon are mixed

Dibromide
of
Phenanthr

phenanthrene dibromide, $C_{14}H_{10}Br_2$, is formed in well-defined four-sided prisms which even in closed vessels undergo rapid decomposition. – It melts at 98°, with loss of HBr, being converted at this time and at this temperature into a substitution product,

Mono=
=bromo=
=phenanthrene.

Monobromphenanthrene, $C_{14}H_9Br$, which is also easily produced by boiling the preceding dibromide with alcohol or water. - This comp'd forms thin, white prisms melting at 63° and subliming without decomposition. - On adding bromine to its solution in bisulphide of carbon, it is converted into

Dibromo=
=phenanthrene.

~Dibromphenanthrene, $C_{14}H_8Br_2$, which crystallizes in white, warty needles. - On heating a solution of these with bromine, as before,

Tribromo=
=phenanthrene

~Tribromophenanthrene, $C_{14}H_7Br_3$, is formed in silky needles, melting at 126°. -

The mother liquor contains an insoluble bromo-compound in the form of a yellowish powder, melting at 202°. -

~Action of Nitric Acid on Phenanthrene~

Nitric acid dissolves phenanthrene to a green Solution. - When water is added, the

Mono=
=nitro=
=phenanthrene

Mononitro-compound, $C_{14}H_9NO_2O$, is precipitated in yellow crystals which melt at 76°. -

Dinitro=
=phenanthrene.

If the nitric acid is heated to 100°, dinitro-phenanthrene, $C_{14}H_8(NO_2)_2$, is formed, which crystallizes in yellow needles, melting at 150°-160°. -

No chlorine compound has been studied as yet. - (109

~ Action of Sulphuric Acid on Phenanthrene ~

Mono-Sulpho-Acid

When phenanthrene is heated with sulphuric acid to 100°, a mono-sulphonic acid, $C_{14}H_9.SO_3H$ is formed. - This is obtained pure by preparing the lead salt, which is readily soluble in water, and decomposing the same with hydrogen sulphide.

It separates out as a crystalline mass, more soluble in hot than in cold water.

Salts

~ The calcium salt $(C_{14}H_9.SO_3)_2Ca + 4H_2O$, crystallizes in small plates, readily soluble in alcohol and hot water.

~ The lead salt $(C_{14}H_9SO_3)_2Pb + 2H_2O$, as also the barium salt, is readily soluble in water.

~ Phenanthrene Quinone ~

Phenanthrene-quinone

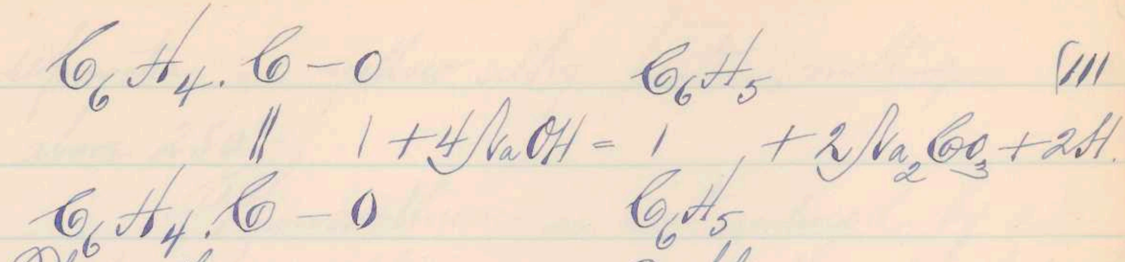
Phenanthrene-quinone, $C_{14}H_8O_2$, is produced together with carbonic acid (?), by dissolving the hydrocarbon in hot glacial acetic acid and adding a solution of chromic acid in acetic acid, or, by heating the hydrocarbon with a mixture of one part bichromate of potash, one and one-half parts of sulphuric acid, diluted with three parts of water, heating so as to to keep the solution just at the boiling point (110 for sometime.- On distilling off a greater part of the acetic acid and adding water to the residue, a crystalline precipitate of the phenanthrene-quinone is obtained.- This is purified by crystallization from acetic acid or from alcohol, though more conveniently by disolving it in a solution of acid sodium sulphite and reprecipitating with an acid.

Properties.

Phenanthrene-quinone is more soluble in alcohol than anthraquinone and dissolves readily in benzene, ether, and glacial acetic acid, but is almost insoluble in cold water.

It crystallizes in tufts of long yellowish-orange needles, melting at 198° and subliming at a higher temperature, with partial decomposition, to brilliant, transparent, orange-red plates.- It boils above 360°.- It is reduced to phenanthrene by heating with zinc dust and by passing it over red-hot soda-lime it is converted into diphenyl.-

The reaction is represented by the following equation:-



$$\begin{array}{l} C_6H_4.C-O \\ \qquad\ \ \| \qquad | \\ C_6H_4.C-O \end{array} + 4NaOH = \begin{array}{l} C_6H_5 \\ \ \ | \\ C_6H_5 \end{array} + 2Na_2CO_3 + 2H.$$

~Phenanthrenequinone~ ~Diphenyl~

[Anthracenequinone yields with soda lime chiefly Benzol: These reactions go to prove that the two aromatic nuclei are linked together directly in phenanthrene but not so in anthracene.]

Phenanthren=quinone=Sulphonic Acid. Phenanthrenequinone dissolves in sulphuric acid without change until above 100° when phenanthrenesulphonic acid is formed.

Dibromo=Phenanthren=quinone. Phenanthrenequinone heated with bromine and water to 180° yield Dibromo=phenanthrenequinone, $C_{14}H_6Br_2O_2$, in yellow crystals, melting at 230°.

Phenanthrenequinone dissolves in nitric acid to a red solution but the quinone is reprecipitated by water.— A boiling mixture of nitric acid and sulphuric acid converts it into nitro-compounds, prominent among which is the Dinitro=

Dinitro=phenanthrene=quinone =phenanthrene-quinone, $C_{14}H_6(NO_2)_2O_2$, which separates in yellow silky plates, melting above 280°.-

Phenanthrahydroquinone.

Phenanthrene is not reduced by a solution of sulphurous acid in the cold but if an aqueous solution of the same is heated with the quinone to 100°, it is slowly reduced to the phenanthrahydroquinone, $C_{14}H_8(OH)_2$ which separates out in long, colourless crystals, needles, melting at 202°.- An alcoholic solution of SO_2 reduces it more rapidly.- This hydro compound in a moist state absorbs oxygen from the air and is thereby oxidized but when dry is more stable.-

By boiling with water, in the presence of air, it is first converted into a brownish-black quin-hydrone and then to the quinone.

This last reaction takes place when it is treated by ferric-chloride, nitric acid, chromic acid, and several other similar compounds yielding oxygen.

Sodium-sulphite Compound.

Phenanthrenequinone dissolves readily in a warm solution of acid sodium sulphite, the phenanthrenequinone=

= sodium sulphite, $C_{14}H_8O_2 . NaHSO_3 + 2H_2O$, being formed. – This crystallizes in colourless plates, which are slowly decomposed by water, quickly by acids and alkalies.

The potassium salt is similar. –

Diphenic Acid

Phenanthrenequinone is readily oxidized to a well characterized bibasic acid, called Diphenic acid, of the formula: –

$$C_{14}H_{10}O_4 = \begin{array}{l} C_6H_4 . CO.OH \\ | \\ C_6H_4 . CO.OH \end{array}$$

and this acid is always formed in small quantity in the preparation of phenanthrene-quinone. –

In this respect phenanthrene differs in the process of oxidation for although in anthracene we produce a quinone, yet we cannot oxidize the same any further. – In attempting to do so we split up the compound into two molecules of Benzol and two molecules of carbonic acid.

Diphenic acid is most conveniently prepared by heating the impure hydrocarbon, containing anthracene, with a chromic acid solution and crystallizing the quinones from alcohol; and again treating with the oxidizing mixture, which does not act on the anthraquinone, but does convert the phenanthrenequinone to diphenic acid.–

Properties

Diphenic acid is sparingly soluble in cold water, more freely in hot water, and readily in alcohol and ether.– It crystallizes on cooling the solution, in shining little plates but if the solution cools more slowly, it is obtained in transparent compact prisms containing no water.– By evaporating a solution in dilute alcohol it is obtained in very large transparent crystals containing two molecules of water.– The acid melts at 226°, and sublimes in long transparent needles; when heated above its melting point, it blackens, being decomposed.–

Salts

Barium diphenate, $C_{14}H_8O_4Ba+4H_2O$ is readily soluble in water and forms large transparent crystals.–

Calcium diphenate, $C_{14}H_8O_4Ca+2\frac{1}{2}H_2O$, is readily soluble in water, does not crystallize well. — Magnesium, copper, ferrous and ferric diphenates, are readily soluble in water. —

Silver diphenate, $C_{14}H_8O_4Ag$, is a bulky white precipitate, dissolving in a large quantity of hot water. —

Diphenyl Ketone

When the acid itself, or the calcium salt, is heated with quick-lime it does not yield diphenyl, as might be expected, but it is converted into Diphenylene Ketone: —

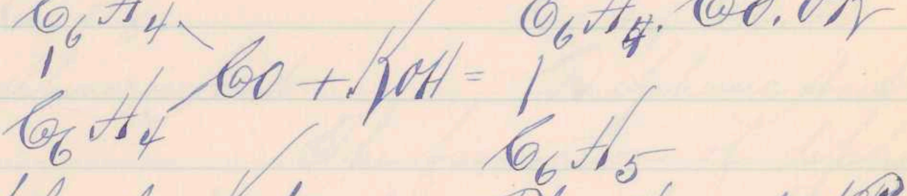
$$\begin{array}{l} C_6H_4.COOH \\ \mid \\ C_6H_4.COOH \end{array} = \left.\begin{array}{l} C_6H_4 \\ \mid \\ C_6H_4 \end{array}\right> CO + CO_2 + H_2O.$$

— Diphenic Acid — — Diphenylene Ketone —

Properties

This Ketone crystallizes from alcohol in large, transparent, pale-yellow plates or thick compact crystals, melting at 84° and boiling above 300°. — It volatilizes with the vapour of water and dissolves in concentrated sulphuric acid with a wine-red color, being however precipitated again unchanged, by water, if the sulphuric acid solution had not been boiled. —

When diphenylene Ketone is added gradually to fused caustic potash it is converted into phenyl-benzoate of Potassium $C_{13}H_9KO_2$.–



$$\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right\rangle CO + KOH = \begin{array}{l}C_6H_4.CO.OK\\ |\\ C_6H_5\end{array}$$

~Diphenylene Ketone~ ~Phenylbenzoate of Potassium

The free acid can be readily obtained from its salts in a state of purity.

Phenyl=benzoic Acid

Phenylbenzoic Acid, $\begin{array}{l}C_6H_4.CO.OH\\ C_6H_5\end{array}$ is almost insoluble in cold water, sparingly soluble in hot water, and freely soluble in alcohol.– From a hot aqueous solution it crystallizes in small ramified needles, resembling frost, melting at 110°.– On slowly cooling, it solidifies to a crystalline mass, but when rapidly cooled, remains viscid and transparent for days, when, if stirred with a rod, it immediately crystallizes.– By heating this acid with lime, diphenylene Ketone is regenerated.– The formation of

The formation of these hydrocarbons (117 shows that phenylbenzoic acid and diphenic acid have the following constitution:–

$$\begin{array}{l} C_6H_4.CO.OH \\ | \\ C_6H_5. \end{array} \qquad \begin{array}{l} C_6H_4.CO.OH \\ | \\ C_6H_4.CO.OH \end{array}$$

~Phenylbenzoic Acid~ ~Diphenic Acid~

The formation of diphenylene ketone is quite analogous to that of dimethyl ketone, or acetone, from acetic acid:–

$$2\left(\begin{matrix} C_2H_3O \\ H \end{matrix}\Big\} O\right) = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array} + CO_2 + H_2O.$$

~Acetic Acid~ ~Dimethyl Ketone~

$$\begin{array}{l} C_6H_4.CO.OH \\ | \\ C_6H_4.CO.OH \end{array} = \begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\Big\rangle CO + CO_2 + H_2O.$$

~Diphenic Acid~ ~Diphenyl Ketone~

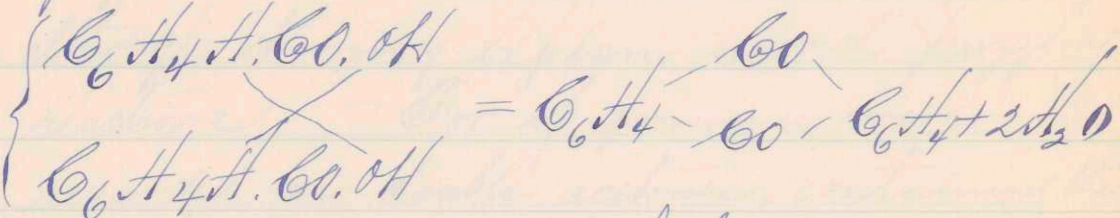
Quinone theories contrasted

~Quinone Theories.

Fittig regards the quinones as double acetones, believing it more than probable that the formula of diphenyl ketone is $C_{26}H_{16}O_2$.– For Kekulé has lately shown that on heating calcium <u>benzoate</u>

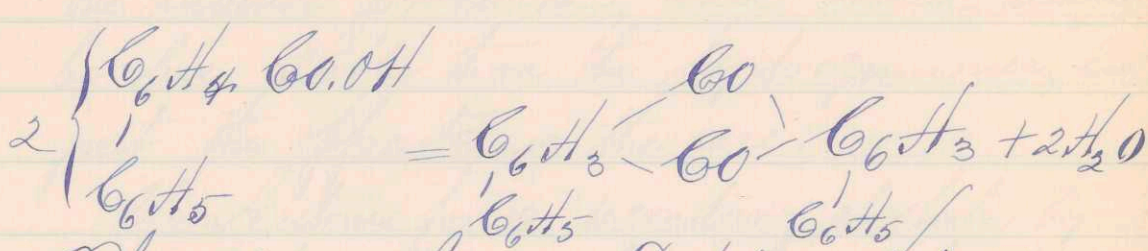
a small quantity of anthraquinone is formed, and Jaffé, Barth & Senhofer have found that di- and tri-oxybenzoic acids are readily converted into derivatives of anthracene.

Phenyl-benzoic acid behaves in a very similar manner, as the following equations show:-



$$\left\{\begin{matrix} C_6H_4H.CO.OH \\ C_6H_4H.CO.OH \end{matrix}\right. = C_6H_4\begin{matrix} CO \\ CO \end{matrix}C_6H_4 + 2H_2O$$

-Two mol. Benzoic Acid- -Anthraquinone-



$$2\left\{\begin{matrix} C_6H_4.CO.OH \\ | \\ C_6H_5 \end{matrix}\right. = \underset{C_6H_5}{C_6H_3}\begin{matrix} CO \\ CO \end{matrix}\underset{C_6H_5}{C_6H_3} + 2H_2O$$

-Phenylbenzoic Ac.- -Diphenyl Ketone-

Thus Fittig regards Diphenyl-Ketone as diphenyl-anthraquinone. - On fusing again with caustic potash, it yields diphenyl-benzoic acid, just as anthraquinone is under like action resolved into two molecules of benzoic acid. - He also claims that

diphenic acid must be regarded as a
diphenyl in which two atoms of hydrogen are replaced by a "chain"

$-CH=CH-$

and this group yielding, by oxidation

$-CO-CO-$.

~The theory however which regards the quinones as double acetones is objectionable although it may explain several puzzling reactions. For if quinones were regarded as double acetones, containing the group, CO, twice they would belong to the additive products, and would therefore be less stable than the hydroquinones, but just the opposite is the case.

2°.- Acetones form secondary alcohols by taking up 2 atoms of H for each atom of O, but quinones take up only 1 atom of H for each atom of O.

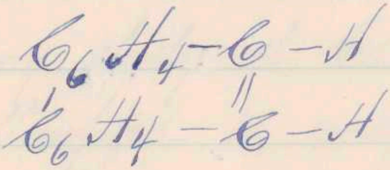
3°.- In acetones each atom of O may be replaced by 2 of Cl, while in quinones 2 of Cl are replaced by 2 of O.-

4°.- Quinones are formed by replacing

2 atoms of H by 2 of O; whereas acetones are produced by replacing only ~~two~~ of H by one of O.

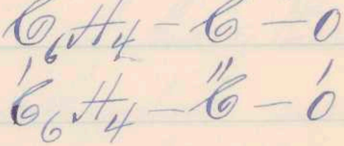
These reactions have been so ably ventilated by the exhaustive theoretical discussions of Graebe that they cannot be, in spite of the ingenious argument of Fittig, any doubt but that the present theory is right which regards the quinones as containing the dyad group −O—O− and thus we may at present best consider as follows:–

~Phenanthrene~



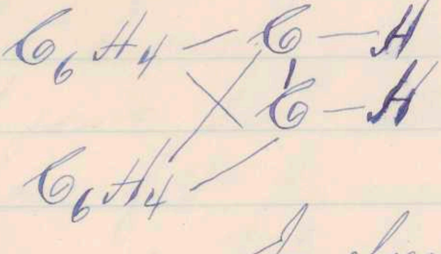
$$\begin{array}{l} C_6H_4-C-H \\ \,| \qquad\quad \| \\ C_6H_4-C-H \end{array}$$

~Phenanthraquinone~

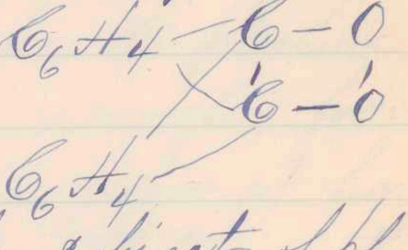


$$\begin{array}{l} C_6H_4-C-O \\ \,| \qquad\quad \| \qquad | \\ C_6H_4-C-O \end{array}$$

~Anthracene~



~Anthraquinone~



Conclusion of Phenanthrene

In closing the subject of phenanthrene let me say that many facts need new and further investigation as also is the case ~~with~~ anthracene, which I shall soon speak of.–

Before proceeding to lay before you a brief account of as brief an account of original research, for want solely of time, let me say that many of the previous reactions of anthracene I have studied in the laboratory with sufficient success as to be valuable to me in my attempt to get a clear understanding of anthracene and phenanthrene as they stand scientifically considered to day. - But I must consider this treatise mainly the result of work in my study at Chelsea. - I have therein attempted to write an exhaustive essay on anthracene which will be of value to some investigator in the future, hoping that I may possibly have the pleasure of some such extended research, for I have felt the need of a paper at hand in my study of the quantitative methods for determining anthracene and phenanthrene that I lay before you at present in this thesis.

The derivatives of Anthracene have been studied by many of the ablest

investigators that the world affords and (122
although in my brief study during the past three months I have probably not been able to discover all the results of investigation upon this subject yet I have gleaned many reliable and exhaustive ones.

Allow me to add, on pages 122, 123, 124, the following references to sustain my study, also hoping that they may be of value to whomsoever may hereafter pursue a study or research upon this very interesting hydrocarbon, Anthracene:-

Also, may I add, a list of such branches that call the loudest for investigation:-

Derivatives of Anthracene needing investigation.

1° Heat on higher homologues and on coal-tar.
2° Tetrabromide of Tribromanthracene (p.50)
3° Action of Iodine, p.52.
4° Fusion with caustic potash, p.61.
5° Nitrooxyanthracene and nitric acid, p.70.
6° Anthracenic acid. p.72.
7° Reactions of Diimido-hydroxylanthraquinone and Indigotin, pp. 79 & 80. - 8° Monosulphonates, p 86.

– References on Anthracene, etc. –

– Annalen der Chemie und Pharmacie –

cxxii, pp. 294, 296; – cxxix, p. 308; – clxi, p. 305
clxii, p. 325; – clxiii, p. 163; – clxvii, p. 162, 363; –
clxvi, pp. 147, 149, 150; – clxix, pp. 207, 214. –

German References.

– Berichte Der Deutschen Chem. Gesellschaft –
1868, pp. 104, 186; – 1869, pp. 14, 332; –
1870, pp. 545, 547, 548, 634, 637; –
1871, pp. 109, 226, 229, 301, 671; 1873, p. 167

– Journal für Praktische Chemie –
Cv, p. 129; – CVI, p. 274; –
1872, nos. 17 and 18. –

– Wagner's Jahresbericht –
1871, p. 795; – 1872, p. 698; – 804, 807, – 1873; –
1874, pp. 880, 883, 886. –

– Fres. Zeitschrift für Chemie –
Vol. XII, p. 350. –

~Jahresbericht der Chemie~

1858, p. 440; —1861, p. 676; —1864, p. 532; —
1868, pp. 395, 404; —1869, p. 501; —1870, pp. 416,
513, 569, 630; —1872, pp. 425, 431; 1873, pp. 501, 1122.

~Dr. Elsner's Technischen Mittheilungen—
1869, pp. 13 and 14.—

~Oppler's Handbuch der Fabrikation
mineralischer Oele:—1862, pp. 60, 89.—

~Bolley's Handbuch der tech. chem. Untersucher—
1876 – p. 501.—

French References

~Moniteur Scientifique~
1869, pp. 465, 1138; —1870, p. 753; —
1871, pp. 531, 691; —1872, pp. 33, 319, 681; —
1873, pp. 14, 224.—

~Des Derives de la Houille; Girard et DeLaire
1875 – pp. 80, 167, 169.—

~Bulletin de la Société Chimique de Paris

t. vi, pp. 268, 272, 280, 467, 474;-
t. vii, pp. 32, 43, 222, 274, 288;-
t. viii, pp. 191, 192, 195, 223, 232, 238, 279, 288;-
t. ix, p. 295;-
t. x, pp. 337, 341, 482, 483;-
t. xi, pp. 178, 271, 335, 374, 516;-
t. xii, pp. 414, 450;-
t. xiii, pp. 464;-
t. xiv, pp. 63, 68, 70, 413, 419, 422, 456;-
t. xv, pp. 3, 315, 318;-
t. xvi, p. 154;-
t. xvii, pp. 89, 90, 93;-
t. xix, pp. 30, 77, 166, 259, 383, 413, 518, 519;-
t. xx, pp. 217, 302;-
t. xxii, pp. 86, 216, 404.-

English References.

~Journal of the Chemical Society of London~
1872, pp. 139, 444;- 1873, pp. 956, 1263.-

~Wagner's Chemical Technology~
1874, pp. 584, 667.-

~Chemical News~
1870, pp. 37, 139; – 1871, p. 171; – 1874, p. 264; –
1875, pp. 46, 177, 190, 209. –

~Chemistry of Carbon Compounds~
Schorlemmer.
pp. 340, 436, 443 – 451. –

~Cooke's New Chemistry~
1875, pp. 320, 324.

~Wurtz Dict. der Chemie~
1873, p. 494; p. 744; p. 795.

~Discussion of Methods for Quan. Estimation:~

In the brief time at my disposal I have criticized the methods of determining phenanthrene and anthracene quantitatively, both by study and experiment in the laboratory.

For the purpose I took a sample known to be rich in phenanthrene, marked A, and another supposed to contain a large quantity of anthracene, marked B.-

A had been previously separated from a crude anthracene by fractional distillation and purification by two crystallizations in alcohol, leaving B in the still.-

A was **dark** brown and melted at 114°.-

B was light brown, melting above 200°.-

Quantitative
Estimation
of
Phenanthrene-

I attempted to determine the amount of phenanthrene in A by

1° Oxidizing the phenanthrene to Diphenic acid and precipitating the silver salt.

1° As
Silver
Diphenate.

Taking one gram of A, I treated for twelve hours with Chromic acid in glacial acetic acid, in excess, and precipitated the excess of chromic acid and sulphuric acid with Barium Nitrate, previously decomposing the acetate of Chromium with carbonate of ammonium. — In the filtrate the diphenic acid was in the state of diphenate of ammonium and I added Silver nitrate to precipitate the diphenate of silver in a bulky, white precipitate, somewhat soluble in water.

For want of time I was not able to find to what extent it was soluble.

2°. As Phenanthrene-quinone.

2°. By oxidizing phenanthrene to the phenanthrene-quinone. —

This method cannot be very accurate since the phenanthrene-quinone is somewhat oxidized to diphenic acid.

I attempted to ascertain what proportions of bichromate of potassium and of sulphuric acid would yield the best results. — I treated with a boiling solution, one gram of the A product, the amount of anthracene being previously determined. — By heating in all cases for fifteen (15) minutes; then adding cold water, filtering, etc., I obtained the following results:–

~–A– product.~

Product:-	$K_2Cr_2O_7$	H_2SO_4	H_2O	Result.
I. 1 grm.	2 grms	2 c.c.	6 c.c	72.77%
II. 1 grm.	3 grms.	2 c.c	6 c.c.	70.32%
III. 1 grm.	4 grms.	3.5 c.c	10 c.c	70.67%
IV. 1 grm.	5 grms	4. c.c.	12 c.c.	69.96%
V. 1 grm.	6 grms.	5 c.c.	15 c.c.	62.54%
VI. 1 grm.	8 grms.	6 c.c.	18 c.c.	58.83%

It will thus be seen that by using equal quantities of bichromate of potash and sulphuric acid that the best results are obtained. – I will say that Schmidt, Fittig, and Graebe have also obtained the best results with like proportions.

3°. By a colorimetrical method.

3°. By a colorimetrical test after Laubenheimer:-

In the Berichte der Deut. Chem. Ges., vol. VIII, 224, Laubenheimer mentions the following reaction.- On mixing 5 c.c of a solution of phenanthrenequinone in glacial acetic acid with 1 c.c. of toluol, adding 4 c.c conc. sulphuric acid drop by drop, and keeping the liquid cold, a bluish green colour is produced. - When the liquid, after a few minutes, is poured into water, a turbid purple solution is obtained, from which, if ether is added, there appears a fine reddish-violet color.

Laubenheimer says that this reaction is so delicate that even .0005 grammes of the quinone may be detected by it.

On evaporating the ether, a black substance is left behind, which in thin scales present an indigo blue color.

In order to investigate these reactions I prepared pure phenanthrene-quinone as follows. First prepared phenanthrene by Schmidt's process given (131 in the Bericht D. C. G. Mar. 9, 1874.–

If mixtures of hydrocarbons containing phenanthrene are dissolved in alcohol of 80-85%, and the filtrate is boiled for some time with an amount of nitric acid equivalent to the hydrocarbon, and allowed to cool, all the anthracene separates out as anthraquinone and dinitroanthraquinone, and on further cooling, the liquid congeals to a crystalline paste of unchanged phenanth

I treated sixteen samples of one gram each with nitric acid, after this method, using all the way from 15 c.c HNO_3 to ½ c.c HNO_3 but invariably got nitro-compounds of phenanthrene. Finally by using from 10 drops HNO_3 down to 3 drops I got a phenanthrene melting at 104°–106°, but this being too impure I gave up this method and attempted to purify by successive recrystallizations in alcohol.

After five successive recrystallizations I obtained a product melting at 96–98°.

I oxidized this pure phenanthrene to the corresponding quinone and crystallized the same twice in alcohol to free from impurity.

But after this labor I was not able to get the colors, previously described, sufficiently characterized as to be of value as a colorimetrical test of phenanthrene as the quinone.- I am prone to believe that Laubenheimer's phenanthrenequinone was not free from anthraquinone which accounts for the similarity of the residue, from the evaporation of the ether solution, and the diimidohydroxylanthraquinone of which mention is made on pages 79 and 80.

I hope to compare these and investigate further the product of this test of Laubenheimer before long.-

In the case of phenanthrene, then, I must say that no method is at present better than the quinone method of p. 128 which is open the fault of being weak thro. the oxidation of the quinone to diphenic acid and also another point spoken of on p. 141.

Quantitative Estimation of Anthracene.

There are also three methods by which the per centage of anthracene may be obtained, in practice, in a commercial sample, viz: 1°. The Alcohol test,
2°. The Bisulphide of Carbon test,
and 3°. The Quinone method

The first two are valueless, the third excellent. – A short account of these methods will bear out this opinion.–

1°. The Alcohol test by
Dr. Gessert of Elberfield.–

Alcohol Test

This is based on the opinion that the commercial value of a sample might be ascertained with sufficient accuracy by determining the percentage of hydrocarbon insoluble in alcohol, together with its melting and solidifying point. – The test is as follows:

Take 20 grammes of the well mixed sample, heat it in a beaker glass with 150 c/c of alcohol, sp. gr. .83, till it boils gently; then cool to 15° C, bring it on a filter, and wash with so much alcohol that the filtrate of alcohol measures

400 c.c. – Dry the filter and residue in a water bath, detach the residue from the filter and weigh; this weight multiplied by 5 gives the percentage. – Then ascertain the melting point by heating a little of the substance, in a test tube, in a bath of sulphuric acid, in which a thermometer is placed and indicates the temperature of the bath. – After noting the melting point, heat a little more; then remove the heat and note the point when the liquid becomes solid. – The mean of the two points gives the correct one.

This method is worthless owing to the solubility of anthracene in alcohol;

2.° Owing to the possibility of impurities being present in such proportions as to melt at the correct point, 212. –

3.° The fact that anthracene, as previously noticed, if melted and superheated, solidifies at a variable point.

Bisulphide of Carbon Test.

II. The bisulphide of carbon is also based on the same idea as the alcohol test and is open to as many objections

I made no determinations by either of these methods, considering them a priori unreliable.-

Quinone Method.

The last, or quinone method, was proposed by Mr. Lück, publishing the same in the Berichte D. C. G, 1874 and also in Fres. Zeit. Vol. XII, p. 350.-

It was there given as follows:-

Heat in a flask 1 grm. of anthracene together with 45 c.c. glacial acetic acid till it gently boils; add gradually and at intervals of a few seconds, a solution of 10 grms. chromic acid in 5 c.c glacial acetic acid and 5 c.c. of water. To prevent any loss of acetic acid, the flask is mounted with a condenser, which allows the condensed acid to constantly flow back.- After boiling some minutes add 150 c.c. of water and allow to stand 12 hours.- Then filter, wash with water, then with dilute alkali till the filtrate runs through colourless; and lastly wash well with water and dry.- Remove the quinone when dry from the filter, and weigh.

This method has since been investigated and it has been found that 50 c.c of glacial acetic acid in 150 c.c of water, used in this method, dissolves 0.01 gramme of anthraquinone, which must be added to the weight actually found.

Lücks method is objected to by many chemists on the ground that it gives too high results in consequence of incomplete oxidation. These high results are probably due to too hasty oxidation in many cases.

The following method is presented to cover this point:-

The solution of the sample in acetic acid and the gradual oxidation is as given above by Lück. - The anthraquinone thus obtained, washed with water only, is washed from the filter into a dish with 1-2 cc caustic soda solution and boiled for five minutes with 1 c.c solution of permanganate of potash, the whole stirred well.

Should the red color disappear, more is added until an excess of permanganate is visible. – After cooling, the liquid is rendered slightly acid by H_2SO_4, and a few crystals of oxalic acid may be added which will effect the solution of the manganese compounds.–

The anthraquinone is then collected on a filter and washed with water, then with dilute alkali, again with water, and finally dried at 100°C.–

The treatment of anthraquinone with the permanganate occupies merely a short time, and ensures a complete removal of all coal-tar impurities, anthraquinone alone remaining.

To avoid errors involved in collecting on weighed filters, or filters counterpoised in the usual way, I suggest the following, which though original with myself, has, I see quite recently, obtained priority in Mr. Davis, an English chemist.

It is as follows:– Two filters of

Equal size are selected and folded; the point, or cone of one is cut off, so that when folded together, the cone of the inner projects through the cut portion of the other to the extent of half an inch; these two filters are counterpoised by cutting off small portions of the larger one. The solution to be filtered is passed through both filters; after washing, they are dried and the inner one, containing the anthraquinone is placed on one pan of the balances and the outer filter on the other, adding weights till the counterpoise is perfect.

The advantages are, that this method obviates errors:- 1°. From solution of the substance of the paper in the chromic and acetic acids, since both filters are treated alike.

2°. From scraping off some of the filter in case the anthraquinone adheres to the paper filter;

3°. From unequal absorption of moisture while weighing, both filters being exposed in all cases to like circumstances. - I have used this method with filters for the past two months with excellent success.

I have determined the amount of anthracene in a commercial sample and also in the A and B products of p. 127 by this quinone method with the following results:-

~Commercial Anthracene (Warren's), very dark colored.

		~Wt. taken~
I.	Anthracene, 56.58%	
II.	" , 56.7%	1 grm

~A-product.~

~Wt. taken~	~Percentage of Anthracene~
(1) .9136 grms	8.49 %
(2) 1.1262 "	8.67 %
(3) 1.1536 "	8.61 %

~B-product.~

(1) 1.4634 grms	43.28 %
(2) 1.099 "	43.52 %
(3) 1.1582 "	43.47 %
(4) 1.176 "	43.46 %

The per cent of phenanthrene in A on p. 129.

According to Bolley and Lucas, anthrace is associated with the following hydrocarbons:-

1° Naphthalene, $C_{14}H_8$ ~
2° Acenaphthalene, $C_{12}H_8$ ~
3° Fluorene, (?)
4° Phenanthrene, $C_{14}H_{10}$ ~
5° Anthracene, $C_{14}H_{10}$ ~
6° Pyrene, $C_{16}H_{10}$ ~
7° Chrysene, $C_{18}H_{12}$ ~
8° Reten, $C_{18}H_{18}$ ~
9° Benzerythrene (?)

Argument in favor of the Quinone Method.

In the process of oxidation the first, Naphthaline, is easily easily oxidized to Naptoquinone and then to Pthalic Acid. and if any trace of this acid should remain mixed with the anthraquinone it would be washed out by dilute alkali used in the after part of Lück's process.:-

2° The next, acenaphthene, is converted by the chromic acid into naphthalic or naphtho-pthalic acid, the sodium salt being readily soluble in water.-

3.° The next, fluoren, is uncommon and of it little is known; but, as it is associated with acenaphthene, and melts at a little above 100° we have every reason for believing that it is also eliminated in the process of oxidation.

4.° Phenanthrene, an isomer of anthracene, is oxidized by chromic acid in acetic acid solution to phenanthrenequinone and after sometime is oxidized to diphenic acid a body having the same percentage composition as alizarin, and soluble in dilute alkali.

5.° On anthracene, it is repetition to dilate. It is readily oxidized to anthraquinone and this product is insoluble in dil. alkali.

6.° Pyrene is acted upon very energetically by chromic acid, with the formation of pyroquinone, which is, according to Lucas converted by an excess of chromic acid into a soluble compound.-

7.° Chrysene is converted by oxidation into chrysoquinone and by further action into a compound soluble in dilute alkali.

8° Reten is a polymer of acetylene and $C_{14}H_2$ when heated with chromic acid, splits up. A compound called Dioxretisten, $C_{16}H_{14}O_2$ is the result together with a little pthalic acid. According to Bolley, the former is soluble in alcohol, and by futher treatment with chromic acid is further oxidized to a compound soluble in alkali.

9° Benzerythrene, is readily soluble in dilute alkali and moreover is not found in large quantities in commercial anthrace.

Besides these named, there sometimes exist in poor qualities of anthracen a dark green substance which requires a very long time for oxidation and sometimes cannot be oxidized.— But it is not common and we may consider this quinone method of Lück, with the subsequent modifications of using an *excess* of chromic acid in the first oxidation, the subsequent oxidation with permanganate of potash, and the

method of counterpoising filters, as the
best quantitative method at present employed
it being equal to many excellent methods
of inorganic determination.

Conclusion in favor of the last.

In calculating the per centage of anthracene from the observed weight of anthraquinone this weight must be multiplied by the decimal .8558 to reduce to anthracene. –

I cannot close without expressing thanks to my Professor, C.H. Wing, for his kind assistance during my study and to Prof. J. M. Ordway for the loan of books.

Very respectfully submitted,
Chas. R. Fletcher.

The following table gives a list of the (144 products obtained by the distillation of Coal gas & Coal tar:-

~Name~	~Formula~	Gas or vapor, Sp. gr.	Boiling pt.
Atmospheric air		1.000	......
Hydrogen	H	.069	.....
Nitrogen	N	.971	...
Oxygen	O	1.106	...
Ammonia ..	NH_3	.590	33
Aqueous vapor ..	H_2O	.622	100
Carbonic oxide ..	CO	.967	- - -
Carbonic anhydride	CO_2	1.529	43
Cyanogen	CN	1.801	...
Sulphurous anhydride	SO_2	2.2112	10
Carbon disulphide	CS_2		

~Marsh Gas Series~

Methyl Hydride	CH_4	.5596	...
Ethyl "	C_2H_6	1.037	...
Propyl "	C_3H_8	1.522	...
Butyl "	C_4H_{10}	2.005	9
Amyl "	C_5H_{12}	2.489	30
Hexyl "	C_6H_{14}	0.669	65
Octyl "	C_8H_{18}	0.726	108

~Olefiant Gas Series~

~Name~	~Formula~	~Vapor density~	~Boiling pt.
Methylene	CH_2	0.484	39
Ethylene (olefiant gas)	C_2H_4	0.9784	.....
Propylene (tritylene)	C_3H_6	1.452	−17.8
Butylene	C_4H_8	1.936	+35
Amylene	C_5H_{10}	2.419	55
Caproylene (hexylene)	C_6H_{12}	2.97	61.3
Oenanthylene	C_7H_{14}	3.320	99

~Acids~

Hydrosulphocyanic	$H(CN)S$	....	85
Hydrosulphuric	H_2S	1.175	....
Carbolic (phenol)	$H(C_6H_5)O$	1.065	188
Rosolic	$C_{20}H_6O_3$	....	....
Brimolic		....	....
Hydrocyanic	HCN	0.706	26.5
Acetic	$C_2H_4O_2$	2.079	120

~Alcohols~

Cresylic alcohol	C_7H_8O	....	203
Phlorylic "	$C_8H_{10}O$	.....	.....

~Benzole Series~

~Name~	~Formula~	Gas or vapor, ~Sp. gr.~	Boiling pt.
Benzole	C_6H_6	2.695	82
Toluole	C_7H_8	3.179	110
Xylole	C_8H_{10}	3.179	129
Cumole	C_9H_{12}	4.147	149
Naphthalene	$C_{10}H_8$	4.423	212
Anthracene	$C_{14}H_{10}$	6.741	melts at 210°
Chrysene	$C_{18}H_{12}$	....	....
Pyrene	$C_{16}H_{10}$		....
Aniline	$H_2(C_6H_5)N$	(Sp. gr. $H_2O=1$) 1.020	182
Pyridine	$(C_5H_5)N$	....	115
Picoline	C_6H_7N	.0961	134
Lutidine	C_7H_9N	.921	154
Collidine	$C_8H_{11}N$	....	170
Parvoline	$C_9H_{13}N$	....	188
Coridine	$C_{10}H_{15}N$	....	211
Rubidine	$C_{11}H_{17}N$	....	230
Viridine	$C_{12}H_{19}N$	1.017	251
Lecoline	C_9H_7N	....	235
Lepidine	$C_{10}H_9N$	....	260
Cryptidine	$C_{11}H_{11}N$	....	256
Pyrrol	C_4H_5N	....	133

Anthracene, a coal-tar product.

An Abstract, by Chas. R. Fletcher.

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Relation of Anthracene to Alizarin. –
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3°. From Benzyl Toluene.–
4°. From Ethene and Styrol.–
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6°. Reaction of Chrysene and Ethene.–
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~ Action of Chlorine on Anthracene.–

Bichloranthracene.– Bichloranthracene=Tetrachloride.– Monochloranthracene.– Anthracenebichloride.– Tetrachloranthracene.

~ Action of Bromine on Anthracene.–

Bibromanthracene.– Tetrabromide of Bibromanthracene.– Tribromanthracene. Tetrabromanthracene.–

Action of Iodine on Anthracene.–

Action of Hydriodic Acid on Anthracene.

Action of Oxidizing Bodies on Anthracene:–

Anthraquinones:– Relation to Quinone.

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