THE ACTION OF SUNLIGHT UPON PHENOLIC COMPOUNDS AND ANILINE.

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Certain benzene derivatives, such as most phenols and amino compounds have long been known to undergo change, in the light with the formation of colored compounds. The character of the colored compounds and the nature of the reactions involved have not been understood. A study of a number of these substances begun four years ago,[2] has shown the formation of the colored compound, in the case of the phenols, to be due to oxidation, which in every case examined results in the production of quinones. While decompositions and condensations set in, the first and most important colored compound formed is a quinone. Phenol forms quinone, and the methyl esters of *o*- and *m*-hydroxybenzoic acids and the methyl ester of gentisic acid should produce the same compound, namely, the quinone of methyl benzoate. This latter compound has been investigated and there is every indication that it exists and does not of necessity break down, giving off carbon dioxide as has been stated.[3] The monoxime has been isolated by D. S. Pratt. The mechanism of the reactions involved in the sunlight oxidation, is dependent upon the presence of the labile hydrogen atom, and the activity of the various phenols can be predicted by the presence of enol-keto tautomers, which Baly[4] and his co-workers have shown can be determined from a study of the absorption spectra of the compounds in solution. This tautomeric condition causes the formation of an absorption band which lies in the ultraviolet region of the spectrum and in the case of some of the compounds under consideration heads about the same region; for example, phenol 277 $\mu\mu$, the cresols 275 $\mu\mu$, *o*- and *m*-hydroxybenzoic acid 300 $\mu\mu$, aminophenol 300 $\mu\mu$, and aniline 285 $\mu\mu$. The tautomeric process occurring in acetylacetone and analogous aliphatic compounds causes a similar band in about the same region of the spectrum. When the enol-keto tautomers are in the pure state this band disappears and its presence

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[2] Gibbs, "The Compounds which Cause the Red Color in Phenol," *Philip. J. Science, Sec. A*, 3, 361 (1908); "The Oxidation of Phenol: the Effect of Some Forms of Light and of Active Oxygen upon Phenol and Anisole," *Ibid.*, 4, 133 (1909); "The Compounds which Cause the Red Coloration of Aniline. I. The Effect of Oxygen and Ozone and the Influence of Light in the Presence of Oxygen, *Ibid.*, 5, 9 (1910); II. The Effect of Sunlight in the Absence of Oxygen and Oxidizing Influences and a Comparison with the Behavior of Mono- and Dimethylaniline," *Ibid.*, 5, 419 (1910).

[3] Nef, *Ber.*, 18, 3499 (1885).

[4] Baly and Collie, *J. Chem. Soc.*, 87, 1339 (1905); Baly and Eubank, *Ibid.*, 1348; Baly and Desh, *Astrophys. J.*, 23, 118 (1906); Baly and Marsden, *J. Chem. Soc.*, 93, 2108 (1908).

is characteristic of the coexistence of the tautomers in dynamic equilibrium.

The intramolecular vibrations causing the band are synchronous with the light absorbed and cease when the incident light is removed, otherwise the substance would be self-luminous in the dark. The labile hydrogen atom can not be regarded as causing the absorption band, for the oscillation frequency of the light waves absorbed is nearly the same for all the substances examined irrespective of the nature or mass of the atom in the so-called labile condition, and the vibration frequency of the atom can not be the same as the oscillation frequency of the light absorbed. The frequency attributed to atomic vibration is never so high as that of the absorption band. The conclusion is therefore reached that the absorption of light is due to transformation which is expressed chemically by a change of linking taking place periodically. An important characteristic of the band due to the enol-keto tautomerism is a shifting toward the red produced by alkalies. This fact enables the identification of the condition when absorption bands due to other causes, as the internal motion of the benzene ring, fall in the same region.

The fixation of the labile hydrogen atom, precluding the formation of enol-keto tautomers, and in some cases the fixation of the hydrogen atom para to the hydroxyl group, causes changes in the behavior of the absorption band and chemically increases the stability of the molecule. For example, anisole and phenol show differences in the absorption band which indicate that phenol exists in the enol and the keto forms while anisole has only one form. The dimethyl esters of the dihydroxybenzenes show that only one form exists. Anisole is stable in the sunlight while phenol and the compound showing enol-keto tautomerism are rapidly oxidized. The same is undoubtedly true of the dihydroxybenzenes and their esters, the cresols and their esters, and many other compounds of a similar nature, although not all have been investigated. The ester of *p*-hydroxybenzoic acid is the only compound of this class which is stable in the light. Certain organic dyes are made more stable toward light by the substitution of methyl for the hydrogen of hydroxyl.

Aniline and methylaniline give absorption spectra which indicate the presence of the labile hydrogen atom. The persistence of the characteristic band, that is its existence over a wide range of dilution, is a measure of the reactivity, and indicates great activity in aniline, less in methylaniline and least in dimethylaniline. The behavior of these compounds in the sunlight bears out this conclusion and shows that in the case of aniline in the sunlight, oxygen is not necessary to produce change with the formation of colored compounds, but that the pure substance itself decomposes with the formation of azophenine, ammonia and benzene.

In the presence of moisture and oxygen the sunlight oxidation may be attributed to hydrogen peroxide, for the evidence all points to the formation of this oxidizing agent in the sunlight,[1] and it has been found that hydrogen peroxide and other oxidizing agents in the dark will produce the same results as those obtained in the sunlight.

The majority of the investigations described were performed in sealed tubes, the glass being thin and permeable to ultraviolet light of about the wave length 285 $\mu\mu$ which is considerably beyond the limits of the sun's spectrum.

Experimental.

Phenol and Anisole.

The coloration of phenol has been attributed to various causes,[2] but the first real light was thrown upon the question by Hanko[3] and by Kohn and Fryer,[4] the latter proving that the coloration was due to the action of the more refrangible light rays in the presence of air and moisture, or hydrogen peroxide in the dark, and that metallic impurities accelerated the color formation.

I have confirmed the view that the principal reaction involved is oxidation and have further proved that the presence of moisture is not necessary, that the first product of the oxidation is quinone, and that the brilliant red condensation product phenoquinone is probably present. It is thus easy to account for the facts recorded by Reuter[5] and Kremel[6] that sulfur dioxide and stannous chloride retard the formation of the color.

Ten sealed tubes, containing the following mixtures exposed to the sunlight, proved that oxygen is necessary to the formation of the color:

I. Phenol (about 2 grams), freshly boiled water 3 drops, sealed in a hydrogen atmosphere.

II. Phenol (about 2 grams), freshly boiled water 1 cc., heated to boiling in a hydrogen atmosphere and then sealed.

III. Same as I, except sealed in nitrogen.

IV. Same as II, except sealed in nitrogen.

V. Same as I, except sealed in carbon dioxide.

VI. Same as II, except sealed in carbon dioxide.

VII. Phenol (about 2 grams), water 3 cc., boiled in a carbon dioxide atmosphere and sealed.

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[1] Gibbs, "The Question of the Production of Hydrogen Peroxide by the Action of Sunlight on Water and Oxygen," *Philip. J. Science, Sec. A*, **7**, No. 2 (1912).

[2] Müller, *Dingl. Pol. J.*, **179**, 462 (1866); Hager, *Chem. Centr.*, **11**, 178 (1880); Sicha, *J. Soc. Chem. Ind.*, **1**, 397 (1882); Meyke, *Jsb. Chem.*, **1883**, 875; Ebel, *Ber.*, **17**, 69, Ref. (1884); Hager, *Chem. Centr.*, **16**, 120 (1885); Kremel, *J. Soc. Chem. Ind.*, **5**, 160 (1886); Mylius, *Chem. Centr.*, **18**, 251 (1887); Fabini, *J. Soc. Chem. Ind.*, **10**, 453 (1891); Bidet, *Bull. soc. chim.*, [3] **5**, 13 (1891); *Compt. rend.*, **108**, 521 (1889); Boes, *Chem. Centr.*, **73**, 50 (1902).

[3] *Ber.*, **25**, 386, Ref. (1892).

[4] *J. Soc. Chem. Ind.*, **12**, 107 (1893); *Chem. News*, 68, 163 (1893).

[5] *J. Soc. Chem. Ind.*, **18**, 360 (1899).

[6] *Loc. cit.*

VIII. Phenol (about 3 grams), boiled in a carbon dioxide atmosphere and sealed.
IX. Same as I, except sealed in atmospheric air.
X. Same as II, except sealed in atmospheric air.

Tubes IX and X showed a distinct color in a few minutes and were light red in two hours. These are the only tubes which have shown any color and they have been exposed to the light for about four years.

In order to prove that the presence of moisture was not essential, an elaborate apparatus constructed entirely of glass was devised, in which dried and purified phenol was twice distilled over metallic sodium in an atmosphere of dry hydrogen, and then condensed in tubes in which the hydrogen could be displaced by dry air and the tubes sealed. Tubes of phenol thus prepared, colored quite rapidly in the sunlight when the temperature was allowed to rise. When the phenol was kept cold so that no liquid formed on the crystals the coloration did not appear. This indicates that phenol crystals are the enol form while the melted compound is a mixture of the two tautomers.

The presence of moisture, as Kohn and Fryer and Richardson[1] believed necessary, since the latter attributed the reaction solely to hydrogen peroxide oxidation, is thus proved not to be one of the essentials.

The rays of the quartz mercury lamp color pure phenol, in the presence of oxygen, with remarkable rapidity. Samples exposed in small dishes covered with quartz plates are colored light red after an exposure of one minute.[2] The lamp employed was manufactured by W. C. Heraeus, Hanau,[3] and during these experiments was run at 120 volts and 12 amperes.

Methods for separating small quantities of quinone from large quantities of phenol were all found to be rather unsatisfactory; however, the presence of quinone in phenol reddened in the sunlight was proved by the hydrocerulignon reaction of Liebermann,[4] and catechol was isolated.[5]

The presence of hydrogen peroxide will readily account for the reactions, for Cross, Bevan and Heiberg[6] have produced phenol, catechol, quinol and quinone by the hydrogen peroxide oxidation of benzene, and Martinon[7] has found that quinone, quinol and catechol are the products of the reactions between phenol and the same oxidizing agent. In

[1] *J. Soc. Chem. Ind.*, **12**, 415 (1893).

[2] Berthelot and Gaudechon (*Compt. rend.*, **152**, 376 (1911)) have recently studied the action of ultraviolet light upon certain typical aromatic compounds and could observe no chemical action in the cases of benzene, phenylacetylene, phenol, benzyl alcohol, benzaldehyde, benzoic acid, dibasic acids, $C_6H_4(COOH)_2$, and the hexabasic acid, $C_6(COOH)_6$. It is not entirely clear from their articles that they worked in the absence of oxygen, but such must have been the case, at least with benzene and phenol.

[3] Bodenstein, *Z. Elektrochem.*, 10, 123 (1904).

[4] *Ber.*, 10, 1615 (1877).

[5] Details previously published. *Loc. cit.*

[6] *Ber.*, **33**, 2017 (1900).

[7] *Bull. soc. chim.*, **43**, 155 (1885).

the absence of water, and consequently hydrogen peroxide, it is evident that oxygen will, of itself, act in the sunlight when the enol-keto condition of tautomerism exists.

It has also been shown that the union of oxygen and phenol takes place in the dark, the temperature being an important factor of the rate.

About 50 grams of pure phenol were introduced into a distilling flask which was arranged with a tube reaching to the bottom, sealed in at the top of the neck. The phenol from the time of its purification was protected from the light and from contact with substances which might introduce impurities, and the distilling flask was likewise protected from the diffused daylight of the room by asbestos wrappings. No corks or stoppers were used in the distilling flask, glass seals only being employed. The sample was distilled with a current of purified, dry, atmospheric air slowly bubbling through the tube reaching to the bottom of the flask. The air was purified by passing through the purifying chain which included a heated combustion tube filled with copper oxide.

The distillation was stopped when about 10 cc. of phenol remained in the distilling flask. The phenol had been at the boiling temperature 20 minutes, and during this time had assumed a light reddish yellow color, about the shade usually produced by a few hours' exposure to the sun, in contact with atmospheric air, at a temperature of about 40°. On changing the air current to oxygen and heating to the boiling point, the rate of coloration was much more rapid, a brilliant red being produced in a few minutes.

A tube of pure dry phenol, prepared by the method of distillation in hydrogen, and sealed in contact with purified atmospheric air, was protected from the action of light by heavy wrappings of tin foil, and placed in a steam bath at 100° in the dark. The steam bath was heated for seven hours a day during six days of the week. The tin foil covering was carefully removed once a week for the shortest possible length of time, to allow examination of the phenol. At the end of the second week a faint reddish yellow was observed. This color deepened constantly as time proceeded.

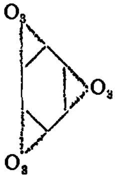
The rate of combination of the phenol molecule with oxygen, and consequently the formation of the color, will undoubtedly be augmented with a gas mixture containing a higher percentage of oxygen than atmospheric air.

It is evident from these experiments, that for the production of the purest phenol, the distillation should not be conducted with access to oxygen. While the temperature of the phenol is elevated, it should come in contact only with an indifferent gas.

Ozone will react with phenol, as first observed by Otto[1] who noted

[1] *Ann. chim. phys.*, [3] 13, 136 (1898).

that phenol was colored red by ozone. He isolated no reaction products. Dry ozone is, in general, not reactive, but is much more active when traces of moisture are present.[1] Pure, dry, ozonized oxygen will react at once with pure, moisture-free phenol in the liquid state and more slowly when the phenol is in the form of crystals. The reactions which take place are largely influenced by the temperature. At the room temperature, 30°, the first action is the production of quinone, and possibly quinol, as indicated by the coloration. As the reaction proceeds, an ozonide is undoubtedly produced. This is evidenced by the copious evolution of carbon dioxide and the formation of glyoxylic acid, a reaction analogous to the breaking down of the triozonide of benzene,



$$+ 3H_2O = 2CHO.CHO + 2CO_2 + 4H_2O,$$

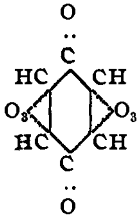
as demonstrated by Harries and Weiss.[2]

When ozone acts upon dry phenol, the water which seems to be necessary to the breaking down of the ozonide, and which also accelerates the reaction, is produced during the formation of quinone as follows:

$$C_6H_5.OH + 2O = C_6H_4O_2 + H_2O.$$

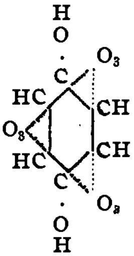
When ozone reacts upon moist phenol, the same reaction products are produced, quinol resulting in larger quantities than quinone.

Whether it is the diozonide of quinone or the triozonide of quinol which breaks down according to the reactions,



$$+ 2H_2O_2 = 2HOOC.CHO + 2CO_2 + 2H_2O$$

or



$$= 2HOOC.CHO + 2CO. + H_2O,$$

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[1] Uhrig, Richarz, *Physik. Z.*, **6**, 1 (1905).

[2] *Ber.*, **37**, 3431 (1904).

has not been determined. When dry ozone comes in contact with dry phenol, cooled in an ice bath, the velocity of the reaction is very much reduced; the products, however, appear to be the same. Carbon dioxide is evolved and no ozonide can be isolated. No attempts have been made to work at lower temperatures and employ solvents for the phenol with the view of isolating an ozonide.

Oxygen liberated at the anode in contact with phenol solutions produces considerable quantities of quinone. No complete investigation of the reactions involved has been attempted.

Anisole is not colored by a rapid current of ozonized oxygen bubbling through it for two days at 30°, or by exposure to direct sunlight in the presence of moisture and oxygen for two months, the temperature occasionally rising above 40°.

No special attempts were made to purify the anisole. A sample which had been in this laboratory for some time was distilled once and the middle fraction employed in the experiments. It remained practically colorless throughout the experiments. The fixation of the labile hydrogen atom of phenol prevents oxidation under the conditions of the experiment.

The Cresols.

The three hydroxytoluenes all color in the sunlight; the meta most rapidly, and the ortho and para compounds much more slowly. The methyl ether of *p*-cresol remains colorless in the sunlight. Although this is the only one investigated it can be predicted with certainty that the ethers of all of the cresols will behave the same.

Tubes containing freshly distilled specimens of *o*-, *m*- and *p*-cresol and the methyl ether of *p*-cresol were sealed with atmospheric air and placed in the sunlight. The meta compound colored in one hour, the ortho and para compounds in one day, and the ether of *p*-cresol remained colorless for months.

The Hydroxybenzoic Acids and Their Esters.

During the preliminary investigations of methyl salicylate,[1] it was discovered that this ester colored quite rapidly in the sunlight, forming a yellow solution. The colored compound is insoluble in water, soluble in dilute alkalies, reduced to a colorless compound by sulfur dioxide, and the color restored by hydrogen peroxide and other oxidizing agents and is not volatile in steam. It is formed either in the presence or absence of water in the sunlight and requires the presence of oxygen in the sunlight or oxidizing agents in the dark, such as ozone, hydrogen peroxide, oxygen liberated at the anode, chromic or persulfuric acid, or other oxi-

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[1] Gibbs, "Methyl Salicylate:" Part I, "The Separation of Salicylic Acid from Methyl Salicylate and the Hydrolysis of the Ester." *Philip. J. Sci., Sec. A*, 3, 101 (1908) and THIS JOURNAL, 30, 1465 (1908); Part II, "The Solubility in Water at 30°," *Philip. J. Sci., Sec. A*, 3, 357 (1908).

TABLE I.—SEALED TUBES CONTAINING THE HYDROXYBENZOIC ACIDS AND THEIR ESTERS AND OTHER SUBSTANCES EXPOSED TO THE SUNLIGHT AND CONTROLS KEPT IN THE DARK.

Tube number.	Date sealed.	Date of final examination.	Contents.	Duration of exposure to sunlight.	Remarks.
1z	Feb. 29, 1908	March 27, 1908	Methyl salicylate 1 cc. 0.1 *N* sulfuric acid 10 cc. Atmospheric air	95 hours	Aqueous layer colorless Ester layer bright lemon yellow
2z	Feb. 29, 1908	March 27, 1908	Methyl salicylate 1 cc. 0.1 *N* sulfuric acid 10 cc. Atmospheric air	None. Wrapped in tin foil	Clear and colorless
3z	Feb. 29, 1908	March 27, 1908	Methyl salicylate 1 cc. 0.1 *N* hydrochloric acid 10 cc. Atmospheric air	95 hours	Aqueous layer colorless Ester layer bright lemon yellow
4z	Feb. 29, 1908	March 27, 1908	Methyl salicylate 1 cc. 0.1 *N* hydrochloric acid 10 cc. Atmospheric air	None. Wrapped in tin foil	Clear and colorless
5z	Feb. 29, 1908	March 27, 1908	Methyl salicylate 1 cc. 0.1 *N* citric acid 10 cc. Atmospheric air	95 hours	Aqueous layer colorless Ester layer bright lemon yellow
6z	Feb. 29, 1908	March 27, 1908	Methyl salicylate 1 cc. 0.1 *N* citric acid 10 cc. Atmospheric air	None. Wrapped in tin foil	Clear and colorless
7z	Feb. 29, 1908	March, 27 1908	Methyl salicylate 1 cc. 0.2 *N* sodium carbonate 10 cc. Atmospheric air	95 hours	Aqueous layer brown Ester layer colorless
8z	Feb. 29, 1908	March 27, 1908	Methyl salicylate 1 cc. 0.2 *N* sodium carbonate 10 cc. Atmospheric air	None. Wrapped in tin foil	Aqueous layer very light brown Ester layer colorless
9z	Feb. 29, 1908	March 27, 1908	Methyl salicylate 0.5 cc. Atmospheric air	95 hours	Yellow but not as bright as tubes containing acids

TABLE I (*Continued*).

Tube number.	Date sealed.	Date of final examination.	Contents.	Duration of exposure to sunlight.	Remarks.
1a	March 9, 1911	September, 1911	Methyl salicylate 10 cc. Atmospheric air about 20 cc.	6 months	Yellow
2a	March 9, 1911	September, 1911	Methyl salicylate 10 cc. In vacuum	6 months	Colorless
3a	March 9, 1911	September, 1911	Methyl salicylate 10 cc. Water 5 cc. Atmospheric air about 15 cc.	6 months	Aqueous layer colorless Ester layer light yellow
12a	March 11, 1911	September, 1911	Methyl salicylate 2 cc. Water 5 cc. Atmospheric air about 23 cc.	6 months	Aqueous layer colorless Ester layer yellow
13a	March 11, 1911	September, 1911	Methyl salicylate 2 cc. Water 5 cc. Hydrogen atmosphere	6 months	Colorless
4	March 9, 1911	Aug. 31, 1911	Methyl salicylate 10 cc. Formaldehyde, 5 cc. of a 40% solution Atmospheric air 15 cc.	Between 5 and 6 months	Very slight color
5	March 9, 1911	Aug. 31, 1911	Methyl salicylate 10 cc. Formaldehyde, 1 cc. of a 40% solution	Between 5 and 6 months	A little color but more than last tube
16	March 9, 1911	Aug. 31, 1911	Methyl salicylate 10 cc. Methyl alcohol 10 cc. Gases, practically none	Between 5 and 6 months	Colorless
7	March 9, 1911	Aug. 31, 1911	Methyl salicylate 10 cc. Methyl alcohol 5 cc. Water 5 cc. Atmospheric air 10 cc.	Between 5 and 6 months	Light yellow

15	March 9, 1911	Aug. 31, 1911	Methyl salicylate 2 cc. Formaldehyde, 5 cc. of a 10% solution Hydrogen atmosphere	Between 5 and 6 months	Colorless
17	March 9, 1911	Aug. 31, 1911	Methyl salicylate 2 cc. Methyl alcohol, 5 cc. of a 20% solution Hydrogen atmosphere	Between 5 and 6 months	Colorless
2x	Oct. 14, 1908	Aug. 3, 1909	Salicylic acid 0.1 gram 0.1 *N* sulfuric acid, 10 cc. Atmospheric air	About 14 months	Colorless
5x	Oct. 14, 1908	Aug. 3, 1909	Sodium salicylate 0.1 gram Water 10 cc. Atmospheric air	About 14 months	Brown
7	Oct. 14, 1908	Aug. 3, 1909	Salicylic acid 0.1 gram 0.1 *N* sulfuric acid 10 cc. Chloroform 2 cc. Atmospheric air	About 14 months	Chloroform colored light yellow
5c	Jan. 23, 1912	Feb. 13, 1912	Salicylic acid 0.2 gram Water 5 cc. Carbon tetrachloride 2 cc. Atmospheric air	21 days	Aqueous layer reddish yellow Carbon tetrachloride colorless
6c	Jan. 23, 1912	Feb. 13, 1912	Same as last except no carbon tetrachloride	21 days	Yellow
13c	Jan. 23, 1912	Feb. 13, 1912	*m*-Hydroxybenzoic acid 0.2 g. Water 5 cc. Carbon tetrachloride 2 cc. Atmospheric air	21 days	Aqueous layer yellow Carbon tetrachloride colorless
14c	Jan. 23, 1912	Feb. 13, 1912	Same as last except no carbon tetrachloride	21 days	Yellow with red deposit

TABLE I (*Continued*).

Tube number.	Date sealed	Date of final examination.	Contents.	Duration of exposure to sunlight.	Remarks.
11c	Jan. 23, 1912	Feb. 13, 1912	Ethyl *m*-hydroxybenzoate 0.2 g. Water 5 cc. Carbon tetrachloride 2 cc. Atmospheric air	21 days	Aqueous layer colorless Carbon tetrachloride yellow
12c	Jan. 23, 1912	Feb. 13, 1912	Same as last except no carbon tetrachloride	21 days	Yellow with a few drops of dark colored oil
15c	Jan. 23, 1912	Feb. 13, 1912	Methyl *m*-hydroxybenzoate 0.2 g. Water 5 cc. Carbon tetrachloride 2 cc. Atmospheric air	21 days	Water colorless Carbon tetrachloride yellow Layer of red liquid between water and CCl_4
16c	Jan. 23, 1912	Feb. 13, 1912	Same as last except no carbon tetrachloride	21 days	Yellow with a few drops of a dark red oil
9c	Jan. 23, 1912	Feb. 13, 1912	*p*-Hydroxybenzoic acid 0.2 g. Water 5 cc. Carbon tetrachloride 2 cc. Atmospheric air	21 days	Colorless
10c	Jan. 23, 1912	Feb. 13, 1912	Same as last except no carbon tetrachloride	21 days	Colorless
7c	Jan. 23, 1912	Feb. 13, 1912	Ethyl *p*-hydroxybenzoate 0.2 g. Water 5 cc. Carbon tetrachloride 2 cc. Atmospheric air	21 days	Colorless
8c	Jan. 23, 1912	Feb. 13, 1912	Same as last except no CCl_4	21 days	Colorless
17c	Jan. 23, 1912	Feb. 13, 1912	Methyl *p*-hydroxybenzoate 0.2 g. Water 5 cc. Carbon tetrachloride 2 cc. Atmospheric air	21 days	Colorless
18c	Jan. 23, 1912	Feb. 13, 1912	Same as last except no CCl_4	21 days	Colorless

dizing agents. The preparation of this colored compound in any considerable yield is difficult and the purification of sufficient quantities for analysis has not been successful. All indications, however, point to the conclusion that it is the same compound formed by the oxidation of the methyl ester of *m*-hydroxybenzoic acid and the methyl ester of gentisic acid. It is further considered under the heading of the latter acid.

The ester of *m*-hydroxybenzoic acid colors very rapidly in the sunlight, the ester of *o*-hydroxybenzoic acid less rapidly and the corresponding *p*-compound not at all. The free acids behave in about the same manner, but color much less rapidly than the esters.

Since it has been shown[1] that the methyl alcohol, produced by the hydrolysis of the ester in presence of water or acids, will be oxidized to formaldehyde in the sunlight, the question of the formation of colored form-

TABLE II.—THE ACTION OF HYDROGEN PEROXIDE (3% SOLUTION) UPON METHYL SALICYLATE IN THE DARK.

Tube No.	Duration of action.	Temperature.	Contents of tube.	Remarks.
1	6 days	30°	0.1 *N* sodium carbonate Methyl salicylate 0.5 cc. Atmospheric air	Aqueous layer light brown Ester layer colorless
2	6 days	30°	0.1 *N* sodium carbonate Methyl salicylate 0.5 cc. Hydrogen peroxide 2 cc.	Aqueous layer muddy brown, much darker than 1 Ester layer colorless
3	6 days	30°	0.1 *N* sulfuric acid 10 cc. Methyl salicylate 0.5 cc. Hydrogen peroxide 2 cc.	Aqueous layer colorless Ester layer yellow
4	6 days	30°	Water 10 cc. Methyl salicylate 0.5 cc. Hydrogen peroxide 2 cc.	Aqueous layer colorless Ester layer brilliant yellow
5	......	100°	Methyl salicylate 2.0 cc. Hydrogen peroxide 10 cc. Traces sulfuric acid	Aqueous layer colorless Ester layer yellow Color appeared in a few minutes
6	......	100°	Methyl salicylate 0.5 cc. Chloroform 2.0 cc. Hydrogen peroxide 10 cc.	Aqueous layer light yellow. Chloroform layer yellow. Color appeared in a few minutes.
22	10 days	100°	Methyl salicylate 2 cc. Formaldehyde, 40% solution, 5 cc.	Colorless
26	2 days	100°	Methyl salicylate 2 cc. Hydrogen peroxide 2 cc.	Ester layer rapidly colored yellow
29	2 days	100°	Methyl salicylate 2 cc. Hydrogen peroxide 2 cc. Formaldehyde, 40% solution, 2 cc.	Ester layer colored yellow but more slowly than No. 26

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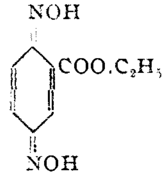
[1] Gibbs, "The Action of Sunlight on Methyl Alcohol," *Ibid.*, 7, No. 2 (1912).

aldehyde-quinone, -quinol, or -phenol condensation products accounting for the coloration was studied and it was found that the principal colored compounds were not of this class. Typical examples of over one hundred and fifty tubes exposed to the sunlight by R. R. Williams and myself, in Manila, are given in Table I.

Hydrogen peroxide in the dark will produce the same results as oxygen and sunlight, and formaldehyde retards the rate of color formation, as shown by the experiments in Table II.

Quinolcarboxylic Acid (Gentisic Acid).

The esters of this compound are the most rapidly affected by sunlight, oxygen, and other oxidizing agents, of all the compounds studied. The oxidation is easily effected in the cold by hydrogen peroxide, very dilute solutions of potassium dichromate and potassium persulfate acidified with dilute sulfuric acid, and other oxidizing agents. Potassium persulfate with dilute sulfuric acid seems to produce the best result, although it is very difficult, in all cases, to carry the reaction to completion without at the same time causing decomposition. No evidence of decomposition to *p*-quinone has been detected in the cold. The oxime



described by Jeanrenaud,[1] has not been prepared, but the monoxime, $C_6H_3:O:NOH.COOCH_3$, has been prepared by D. S. Pratt in the following manner:

The calculated amount of hydroxylamine hydrochloride was added to an alcoholic solution of the methyl ester of gentisic acid and, while heated on the water bath, small amounts of hydrogen peroxide were added at intervals until further additions produced no increased darkening of the color. After heating eight hours the dark red solution was poured into water, which caused the precipitation of a heavy oil. This was washed with water until free from hydroxylamine, then with small amounts of ethyl ether until practically free from unoxidized ester. Further purification was effected by precipitation with dilute sulfuric acid from a solution in dilute alkali, in which the oil was very soluble. The brown flocculent product thus obtained was centrifuged, washed with cold water to remove inorganic salts, and dried at 100°. It is an amorphous, dark chocolate colored, almost black, powder.

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[1] *Ber.*, **22**, 1283 (1889).

The analysis was effected by the following method which Dr. Pratt[1] has tested with various oximes and found satisfactory: The —NOH group is first reduced to the hydroxamic acid group by means of dilute sulfuric acid and zinc dust and then the nitrogen determined by the Kjeldahl method.

Calculated for $C_6H_3:O:NOH,.COOCH_3$; N, 7.73; found, 7.28.

Considering the difficulties experienced in purifying the small yield, the analysis is satisfactory and further establishes the fact that the methyl ester of gentisic acid forms a quinone without the loss of carbon dioxide.

Aniline.

The cause of the formation of the red color in aniline has been attributed to impurities and to oxidation[2] and the various text-books have chosen either one or the other of these explanations.

I have found that the cause of the coloration of pure aniline in the presence of oxygen is oxidation. Azobenzene, dianilinoquinone, dianilinoquinoneanil, and azophenine have been isolated from the red aniline, but are by no means the only substances produced by the oxidation. Since the oxidation, because of the presence of the quinone derivatives, has been shown to go as far as quinone, it is reasonable to expect that intermediate products are formed at least as transition compounds, and that these exist in the aniline solution if they escape further oxidation and do not readily form condensation products.

The fact that the three quinone condensation products, dianilinoquinone, dianilinoquinoneanil, and azophenine, have been isolated would seem to indicate that they all exist in the aniline solution. This, however, is by no means proved for the reason that the methods employed for their isolation may convert, at least in part, one derivative into another.

In the absence of oxygen, that is, *in vacuo* or in contact with indifferent gases such as nitrogen or hydrogen, the coloration takes place with remarkable rapidity in the sunlight of this locality and is first visible in about seven minutes. The principal colored compound formed is azophenine and, since ammonia and benzene have also been identified, the reaction may be represented by the equation

$$9C_6H_5.NH_2 = C_6H_2.(N.C_6H_5)_2.(NH.C_6H_5)_2 + 4C_6H_6 + 5NH_3.$$

The aniline employed in these experiments was obtained from three different sources and was purified by several different methods.

First.—Acetanilide, purified by recrystallization, was decomposed

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[1] Gibbs, Williams and Pratt, "Methyl Salicylate:" Part III, "The Coloration of Methyl Salicylate and Some Allied Compounds in the Sunlight." *Philip. J. Sci., Sec. A*, **7**, No. 2 (1912).

[2] Rosenstiehl, *Compt. rend.*, **82**, 380 (1876); Bidet, *Ibid.*, **108**, 520 (1889); Werner, *Soc. Chem. Ind.*, **9**, 278 (1890); Hantzsch and Freese, *Ber.*, **27**, 2529, 2966 (1894).

by potassium hydroxide. The aniline was distilled with steam, separated from the water by extraction with ether, and fractionated several times after the ether was expelled. Portions of this aniline were further treated with acetone by the method of Hantzsch and Freese[1] which is designed to remove sulfur compounds. The final drying was accomplished by distillation over sodium.

Second.—Kahlbaum's aniline, from the sulfate, was purified by distillation and only the middle fractions of constant boiling point were employed. Portions of this aniline were further purified by the method of Hantzsch and Freese.

Third.—Nitrobenzene, made from thiophene-free benzene as a starting point, was reduced by tin and hydrochloric acid and the resulting aniline purified by distilling in steam from potassium hydroxide solution. The aniline was extracted with ether, fractionally distilled and finally dried by distilling over sodium.

In these samples of aniline I have not been able to observe any very great differences in the behavior in sunlight or any variation in the compounds formed, although some of the samples obtained do color more rapidly than others.

The separation and identification of the products of the reaction of aniline in the presence of oxygen and sunlight was effected in several different ways. On pouring 20 cc. of the colored aniline into a large volume of very dilute sulfuric acid, the aniline all dissolves as aniline sulfate, and in the highly colored insoluble portion 2,5-dianilinoquinone was identified. Other separations were made by extracting the dilute sulfuric acid solution, without removing the suspended precipitate, with small quantities of ether. Dianilinoquinone and dianilinoquinoneanil were separated from this solution and identified. The residue after evaporating the ether gave, on distilling with steam, a few drops of an orange red oil, which solidified to orange red crystals. These crystals were readily reduced in alcoholic solution to hydrazobenzene. Azobenzene must, therefore, be present. Twenty cc. of the colored aniline were slowly poured into 100 cc. of 50% acetic acid, and on cooling with ice large numbers of crystals of azophenine separated. These were recognized under the microscope, the marked tendency to twinning being very characteristic. A few crystals of dianilinoquinone were also observed.

Since the microscope affords the best means for identifying 2,5-dianilinoquinone and azophenine, the description of the crystals as furnished me by W. D. Smith of the Bureau of Science is given.

2,5-Dianilinoquinone crystallizes in the tetragonal system and occurs in very thin plates, generally under a millimeter in length. The usual forms are prism, pyramid and base, diamond and square. In mass and

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[1] *Ber.*, 27, 2966 (1894).

by reflected light these plates have a decided purple hue. By ordinary transmitted light many of them are quite colorless. The crystals are trichroic. The accompanying Fig. 1 gives the form, and Figs. 2 and 3 show the pleochroism:

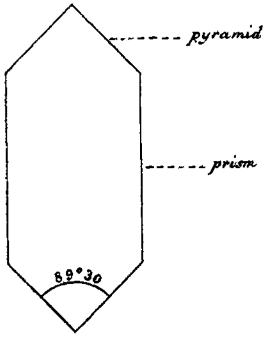

Fig. 1.

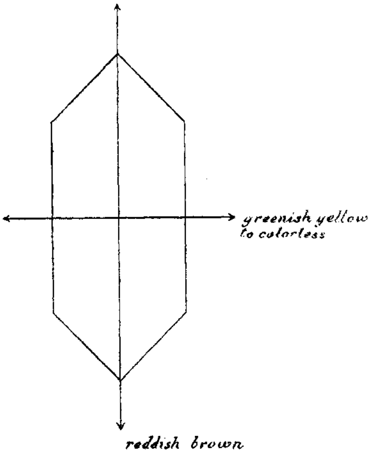

Fig. 2.

These plates show parallel extinction in polarized light. The index of refraction is medium and the double refraction is low. First order colors.

2,5-Dianilinoquinonedianil (azophenine) crystallizes in the monoclinic system and by reflected light appears garnet red. The crystals, which appear almost invariably as shown in Fig. 4, measure much under a millimeter in length, one of the longest in a group measuring 0.18 millimeter. They are very pleochroic varying from colorless through yellow to garnet

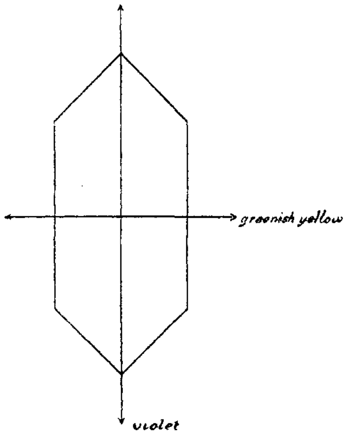

Fig. 3.

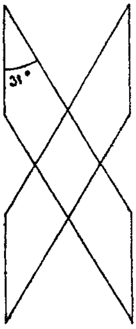

Fig. 4.

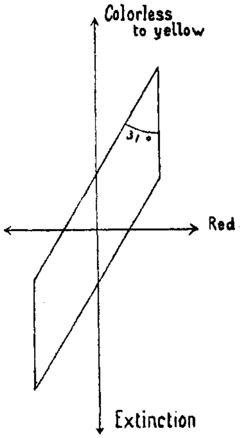

Fig. 5

red. The crystals usually occur in halves, the normal crystallization being as shown in Fig. 7. In Fig. 6, a twin is shown, the twinning angle being 31°, the same as the extinction angle. The index of refraction is medium. The double refraction is strong, the interference colors are reds and blues of the second order.

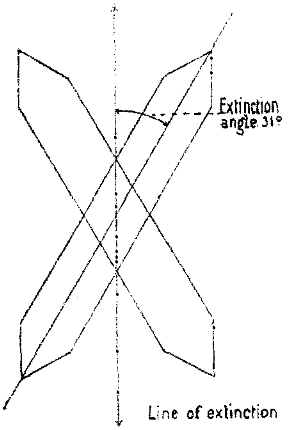

Fig. 6.

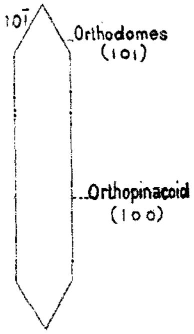

Fig. 7.

All of the compounds which have been isolated are soluble in aniline with the production of colored solutions. The following is a brief study of the solubilities.

Azophenine is somewhat soluble in alcohol and aniline and is readily crystallized from either solvent. The solutions are brilliant red.

2,5-Dianilinoquinoneanil is soluble in alcohol and aniline, the solutions being brilliant red.

2,5-Dianilinoquinone is practically insoluble in alcohol and soluble in aniline, forming a brilliant red solution.

Azobenzene is very soluble in aniline forming a reddish yellow solution.

The power of the first three compounds of coloring colorless aniline is intense and exceeds by many fold the coloring power of the last compound.

The reaction products formed by the action of sunlight upon aniline in the absence of oxygen, that is *in vacuo*, or in hydrogen or nitrogen atmospheres, were isolated and identified by the following methods:

Small portions of the aniline were placed in small crystallizing dishes in a vacuum desiccator over sulfuric acid. In about one week beautiful crystals of azophenine began to separate. The large crystals measured 0.18 millimeter and the characteristic twins formed in large numbers. Continued crystallization until the mass was solid failed to reveal the presence of any solid other than azophenine. Tests for ammonia gave positive results.

Ten cc. were heated in a very small distilling flask, the delivery tube of which dipped under 5 cc. of 0.1 *N* hydrochloric acid, colored with a drop of methyl orange, in a test tube. As the temperature of the aniline rose, evolution of gas took place. Before the boiling point was reached and before any but the smallest traces of aniline could have passed over, the heat was removed. The top layers of the hydrochloric acid solution became alkaline as shown by the change in color of the indicator. On shaking the solution it was found still to be acid. This solution was evaporated over calcium chloride in a desiccator at room temperature. Ammonium chloride crystals separated and on treatment with potassium hydroxide solution the unmistakable odor of ammonia was very strong. No odor of aniline was detected.

A second portion was distilled until about 20 drops of aniline had passed over into the hydrochloric acid. The excess of aniline was then removed by distillation in steam, the solution filtered and the filtrate evaporated to dryness on a water bath. This residue sublimed ammonium chloride on gentle heating, and on treating with a few drops of potassium hydroxide gave a strong and unmistakable odor of ammonia. The small amounts of aniline salt present did not interfere at all with the tests.

A third portion was heated in a distilling flask very and slowly carefully until 0.5 cc. had passed over. This distillate on nitration developed the characteristic odor of nitrobenzene. A control experiment in which an equal quantity of pure aniline was treated in the same way developed no odor of nitrobenzene.

A fourth portion was distilled in the same manner and the first three drops collected. The refractive index of the distillate was decidedly lower than that of aniline and on nitration the odor of nitrobenzene was strong.

Methylaniline and Dimethylaniline.

Methylaniline colors rapidly in the sunlight and methylamine was identified as one of the reaction products. No colored compound could be isolated and identified.

Dimethylaniline showed a slight coloration after 60 days exposure to the sunlight, which may have been due to impurities since no especial care was employed in its purification.

Summary.

In this paper a study of the action of sunlight upon phenol, anisole, the cresols, the methyl ether of *p*-cresol, the three hydroxybenzoic acids and their esters, gentisic acid and its esters, aniline, methylaniline and dimethylaniline is recorded.

The labile hydrogen atom, the existence of which can be detected from a study of the absorption spectra of the substances in solution, is the determining factor in the reactivity of these compounds in the sunlight.