

Not for Publication
Presented Before the Division of Gas and Fuel Chemistry
American Chemical Society
Chicago, Illinois, Meeting, September 7-12, 1958

The Photo-Oxidation of Polycyclic Hydrocarbons

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Summary

Solutions of anthracene and tetracene in acetic anhydride and other solvents in the presence of air and ultra-violet light at room temperature photo-oxidize to the 9,10 and 5,12 quinones respectively. Other polycyclic hydrocarbons such as chrysene, pyrene and triphenylene do not photo-oxidize under these conditions. With naphthalene and phenanthrene oxidation takes place but the reaction appears to continue past the quinone stage. The photo-oxidation reaction is catalyzed by bases and is not inhibited by sodium hydrogen sulfite indicating that the mechanism is probably not a free radical chain reaction.

Discussion

In an investigation now underway in the Coal Research Laboratory involving the vapor phase acetylation of various coals with acetic anhydride it was noted that with certain coals a very slow reaction (weeks) was superimposed on the main reaction (days) so that after a relatively rapid weight change, the weight of the coal sample increased gradually over a period of many weeks. As the main reaction can be assumed to be the acetylation of the hydroxyl and traces of amino groups present in the coal it became necessary to consider the possibility that gaseous acetic anhydride was reacting directly with hydrocarbon structures present in the coal.

The acetylation of coal is being carried out using an adsorption type apparatus. The course of the acetylation is followed directly by use of McBain-Baker spring balances. All experiments are being made at 45°C. with the relative pressure of acetic anhydride being fixed at unity. The very slow reaction is particularly noticeable when small amounts of oxygen are present so that most experiments have been made with 5 mm of oxygen gas present in the system. Under these conditions the coal sample is present in large excess relative to the acetic anhydride. Acetic acid resulting from the acetylation process is also present. In an attempt to determine the type or types of hydrocarbon structures which would react with mixtures of acetic anhydride and acetic acid a series of experiments using various polycyclic hydrocarbons have been made in which the experimental conditions approximate those utilized in the work on coal.

If a saturated solution of anthracene in acetic anhydride is allowed to stand in a Pyrex flask, loosely stoppered so that air has access to the flask, and exposed to light there appears a light tan, crystalline precipitate which on isolation proved to be anthracene-9,10-quinone. No other product in appreciable amounts could be isolated from the reaction mixture except starting material. As the reaction involving anthracene progresses the solution becomes light yellow in color. With other hydrocarbons the solution becomes deeply colored. The coloring material is present in such small amounts that it can not be isolated

and might well be due to traces of impurities present in the starting material. A systematic investigation of this reaction was undertaken to determine the conditions under which it takes place.

Effect of oxygen: Saturated solutions of anthracene in acetic anhydride are placed in small Pyrex tubes, evacuated, and sealed. The tubes are then exposed to sunlight and to the radiation from a 3605L fluorescent lamp. After several months exposure at room temperature to the ultra-violet radiation the solutions remained colorless. A white crystalline product which precipitated from the solution proved to be the photo-dimer of anthracene. These experiments indicate that oxygen from the air is the oxidizing agent for anthraquinone formation.

Effect of light: Solutions of anthracene in acetic anhydride saturated with air and kept in the dark at room temperature for several months remain colorless and no quinone (negative vat test) is present. A solution of anthracene in acetic anhydride was refluxed three weeks under conditions where little light reached the system. The solution becomes red in color but no quinone is present. After cooling the mixture was exposed to the radiation from a 3603L lamp. After several weeks anthracene-9,10-quinone precipitated and the red color gradually disappeared. These experiments indicate that the dark reaction is very slow. The cause of the color is not known.

Effect of temperature and light intensity: From qualitative experiments samples kept at room temperature appeared to react slower than samples exposed to sunlight and kept outdoors during the winter months. The temperature coefficient of the photo-oxidation, as one would expect, must be small. Since sunlight represents much higher intensities than the radiation from lamps it seems likely that the rate of the reaction increases with increasing intensity of incident light.

Catalysts: It has been found that the rate of anthracene-9,10-quinone formation is increased by the addition of bases to the acetic anhydride solution. Suitable catalysts are the sodium or potassium salts of organic acids such as formic, acetic, phthalic, and benzoic acids and pyridine bases such as pyridine, quinoline, and acridine.

Inhibitors: Most of the common organic inhibitors would be expected to react with acetic anhydride. Small amounts of sodium hydrogen sulfite added to the acetic anhydride solutions appear to have little or no effect upon the rate of quinone formation. It is therefore unlikely that the photo-oxidation reaction is a chain reaction.

Types of hydrocarbons: The following polycyclic hydrocarbons have been employed: naphthalene, anthracene, phenanthrene, tetracene, pyrene, chrysene, and triphenylene. With anthracene and tetracene the only products are anthracene-9,10-quinone and tetracene-5,12-quinone. It has been previously reported (1) that

L. C. Dufraisse and R. Horclois, Bull. Soc. Chim. France (5) 3, 1880 (1936)

tetracene in xylene solution photo-oxidizes to the 5,12 quinone. Pyrene, chrysene and triphenylene gave no appreciable amount of any reaction product although the solutions became colored. Naphthalene and phenanthrene gave a mixture of reaction products which have not been completely characterized. Solutions in acetic anhydride of phenanthrene-9,10-quinone are not stable in the presence of oxygen and ultra-violet light but apparently undergo further oxidation. On the other hand saturated solutions of anthracene-9,10-quinone in acetic anhydride have been exposed to the radiation from the 3608L lamp for several months and no reaction has been noticed. The ultraviolet absorption spectra of naphthalene and phenanthrene begins rather far in the ultra-violet region (2) where the

2. E. Clar, *Aromatische Kohlenwasserstoffe*, Springer, Berlin 1952, pages 134 and 142

absorption by Pyrex is appreciable and where the intensity of such radiation from the 360BL lamp is low. The photo-oxidation reactions for the two hydrocarbons will need to be investigated in quartz flasks with lower wave length radiation.

Solvents: The photo-oxidation of anthracene proceeds in the following solvents: acetic anhydride, acetic acid, mixtures of acetic acid and anhydride, carbon disulfide, methanol, pyridine, quinoline, and dimethylformamide. The formation of anthracene-9,10-quinone was proven by its isolation in all cases except dimethylformamide. For this solvent a positive vat test for quinone was obtained using sodium hydrosulfite as the reducing agent. The formation of anthracene-9,10-quinone is very slow in benzene and cyclohexane as indicated by the vat test. It has been shown (3) that the photo-oxidation of anthracene in carbon disulfide

3. C. Dufraisse and M. Gerard. *Bull. Soc. Chim. France* 4, 2052 (1937)

solution leads to the formation of a photo-oxide. Carbon disulfide is one of the few solvents which inhibits the formation of the photo-dimer of anthracene. According to H. E. Ocampo (4), the photo-oxidation of anthracene in nitrobenzene

4. H. E. Ocampo, *C. A.* 40, 6458 (1946)

solution gives anthracene-9,10-quinone.

Mechanism: The most recent investigation of the photo-oxidation of anthracene has been made by E. J. Bowen and his collaborators (5). Their work was done

5. E. J. Bowen et al., *Trans. Faraday Soc., Discussions* 14, 143, 146 (1953); *Trans. Faraday Soc.*, 51, 475 (1955)

primarily in benzene solution although solvent mixtures were also used. According to Bowen the irradiation of benzene solutions of anthracene saturated with oxygen gives the following reactions: 1. Formation of the photo-dimer, 2. Formation of the photo-oxide, and 3. Reaction with certain added solvents such as CCl_4 . Our work indicates that with long exposure times there is a fourth possibility, the formation of the quinone. The experimental conditions for the two sets of experiments are quite different. Bowen used benzene as his primary solvent which as has been indicated inhibits quinone formation, used high light intensities, used shorter times of radiation (hours relative to days), used higher oxygen pressures, and used dilute solutions of anthracene. Bowen postulated that the formation of the photo-oxide of anthracene is a non-chain process. From the results with sodium hydrogen sulfite it is believed that quinone formation is a non-chain process. In the work described here the photo-dimer was not detected in the photo-oxidation reaction. The photo-dimer is known to show a photo-stationary state indicating that the reverse reaction, dissociation of the dimer into anthracene, has a finite velocity constant at room temperature. During the long exposure times used in this work any photo-dimer could be eventually converted completely into the quinone.

Experimental

Apparatus: The experiments described here were made in Pyrex flasks using the radiation from a 360BL fluorescent lamp. A few experiments used sunlight. The transmission characteristics of Pyrex glass and the distribution of radiation from the 360BL lamp have been published by L. R. Koller (6). The radiation of this

6. L. R. Koller, *Ultraviolet Radiation*, John Wiley and Sons, Inc., New York, 1952, pages 68 and 147.

lamp is in the region 3200-4400 Å and peaks at 3600 Å. Pyrex glass cuts off around 3000 Å. It is probable that the effective radiation is in the region 3000-4000 Å although with the long periods of exposure used appreciable amounts of shorter wavelength radiation might have passed through the solutions.

Chemicals: The hydrocarbons used were in stock at the Coal Research Laboratory and were originally from American and foreign manufacturers. Anthracene (blue-white fluorescence) was an Eastman product and was used without further purification. All other hydrocarbons were recrystallized at least once and in some cases two or three times. Recrystallizations were continued until the melting point of a given hydrocarbon was less than one degree from the melting point cited by E. Clar (2) for this hydrocarbon. All solvents were freshly distilled before use.

Procedure: The general procedure was to make a saturated solution of the hydrocarbon in the desired solvent and place it in a Pyrex flask, loosely stoppered with an aluminum foil covered cork so that air had access to the solution. The flask was then placed one foot from the 360EL lamp. The contents of the flask were at room temperature. At times small portions of the solution were withdrawn and added to an alkaline aqueous solution of sodium hydrosulfite. The mixture was then heated and the color changes observed. After exposure to the radiation for usually a period of a week or more, the flask was placed in a water bath and the solvent evaporated under vacuum with a water aspirator. With solvents of lower volatility the water bath was warmed to about 50°C. The solid residue was washed with water to remove catalyst, if the salt of an organic acid was used, and then dissolved in methanol or some other suitable solvent such as benzene. The product was recrystallized at least twice in all cases. Yields of product were as high as 70% of theoretical and depended mainly on the time of exposure and the intensity of the light source. Sunlight always gave the higher yields for equal exposure times.

The product from the anthracene oxidation melted at 287-289°C. which was identical with the melting point of an authentic sample of anthracene-9,10-quinone. A mixture of authentic sample and reaction product gave the same melting point, 287-289°. Using the reaction product from the photo-oxidation of anthracene, benzanthrone (1,9-10) was prepared by reacting the product with glycerol in 92-93% sulfuric acid-water solution using iron powder as the reducing agent and a reaction temperature of 113 to 120°C. After one hour heating the reaction mixture was poured in water, precipitated solid recovered and recrystallized from methanol. The purified benzanthrone was bright yellow, melted at 167-169°, gave an orange colored solution in sulfuric acid which shows a bright red-orange fluorescence. These properties agree with the properties of benzanthrone cited by J. Houben (7), who lists 170° as being the melting point of this compound.

7. J. Houben, *Das Anthracen und Die Anthrachinone*, G. Thime, Leipzig, 1920, page 575.

For tetracene the reaction product from acetic anhydride solution was compared with the reaction product using xylene solution. The reaction product from the photo-oxidation of tetracene in xylene has been identified as tetracene-5,12-quinone (1). The reaction product from acetic anhydride had a melting point of 293-295° and that from xylene had a melting point of 296-297°. The melting point for a mixture of the two products was found to be 295-296°.

The reaction product which precipitated by radiation of an anthracene solution in acetic anhydride which had been placed in an evacuated and sealed tube gave a melting point of 245-250°C. J. Houben (8) lists for the photo-dimer

8. J. Houben, loc. cit., page 135

of anthracene the melting points, 242-244°, 244°, 272-274°, and 270-280°. The wide variation is attributed to the fact that on heating, the photo-dimer dissociates slowly into anthracene and the melting point obtained depends on the rate of heating. The sample on being allowed to cool and reheated gave a melting point of 208°. This behavior together with the white color and the lack of fluorescence by the solid, can be considered as evidence that the reaction product obtained in the absence of O₂ is the photo-dimer of anthracene.