[Contribution from the Coal Research Laboratory, Carnegie Institute of Technology]

Alkaline Permanganate Oxidation of Certain Condensed Cyclic Compounds Including Coal[1]

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The purpose of this investigation was to obtain information on the mechanism of oxidation of complex condensed hydrocarbons and related compounds, which would be of value in interpreting data already accumulated on the oxidation of coal. Certain types of condensed cyclic structures have been postulated as building units in coal.[4] Oxidative degradation[5] and hydrogenolysis[6] have demonstrated that coal is primarily composed of carbocyclic structures. Alkaline permanganate was selected as the reagent for oxidation since it has been used in a number of the investigations on coal.[5] One systematic study has been made with the same purpose in view as in this work, and it was concluded that the coal substance is composed of unreduced benzene rings linked through side chains or oxygen heterocycles and that fused reduced rings are probably not present to any great extent.[7]

In the present investigation the following compounds were oxidized: tetrahydronaphthalene, dodecahydrotriphenylene, triphenylene, decacyclene, trisdecahydrodecacyclene, naphthacene, pyrene, diphenylene oxide and carbazole. For comparison, a sample of Pittsburgh Seam coal was also oxidized under the same conditions. The rate and the total amount of permanganate consumption were determined by titrimetric methods. Micro and semi-micro techniques were employed since in all cases less than a gram of material was oxidized. Tetrahydronaphthalene was found to oxidize more rapidly than any other compound investigated. Next in order of ease of oxidation were Pittsburgh Seam bituminous coal, pyrene, and naphthacene. Diphenylene oxide and carbazole oxidized somewhat less rapidly. The hydrocarbons decacyclene and triphenylene were still less reactive and least reactive of all were the nearly saturated structures, dodecahydrotriphenylene and trisdecahydrodecacyclene. Carbon balances were determined and end products isolated and identified wherever possible.

Experimental

Oxidation Apparatus.—The apparatus used for the oxidation is shown diagrammatically in Fig. 1. It consisted of a 500-cc. four-necked round-bottom flask (A) immersed in a thermostated bath of glycerol (F). In the flask, a dropping funnel (C), a sampling tube (E), a West condenser (D), and a high speed stirring assembly (B) were inserted by means of standard taper glass joints. The stirrer, which was of glass, was cemented with Sauereisen into a hollow stainless steel shaft, which passed through Oilite bearings. A small pulley was attached to the upper end of the shaft and the assembly was belt-driven by a 1/30 h. p. Redmond, shaded pole, induction motor. A constant rate of stirring, 600 ± 10 r. p. m. was maintained. The reaction flask (A) was swept continuously with carbon dioxide-free air at the rate of 600 ml./hour. A high pressure cylinder (J), equipped with a pressure gage and reduction valve, supplied the air. The air was purified in the fore part of the train. This section of the train was made up of a pressure regulator (I) partly filled with concentrated sulfuric acid, a bubble counter and U-tube (H), filled with ascarite, and finally a bubble-counter (G) which contained concentrated sulfuric acid. The air entered the flask through a side-arm in the stirrer assembly (B), and left through the West condenser (D). The latter part of the train was made up in the following order. An ice-cooled U-tube trap (K) surrounded by a Dewar cylinder (L) was followed by a bubble-counter partly filled with concentrated sulfuric acid and U-tube packed with colorless drierite mixed with a small amount of indicating drierite. Two tared carbon dioxide absorption tubes (N) and (O) were attached after this. The carbon dioxide absorption tubes were filled by a method similar to that used for microchemical tubes, *i. e.*, about three-fourths of their length was filled with ascarite and the rest was filled with drierite. A protection tube (P) containing ascarite followed the absorption tubes and was placed before the Mariotte bottle (Q). The Mariotte bottle was filled with water, and its contents drained into a receiver bottle (R). The Mariotte assembly was equipped with a suction tube that allowed refilling of the bottle (Q) from bottle (R). During the refilling operation the train was broken after tube (P).

Extractors, Electrolysis Cell and Molecular Still.—Two liquid phase extractors[8] were used in recovering the water-soluble products. The larger had a total volume of 1 liter; the smaller, which was used in the final concentration of the organic acids, about 50 ml.

A small, 3-compartment electrolytic cell, similar in design to that used by Juettner, Smith and Howard,[5] was employed in some cases in the final purification of the organic acids. It was constructed of Lucite and had a capacity of 120 ml.

The molecular still was constructed with a cold finger type condenser,[9] which was cooled with a trichloroethylene–Dry Ice mixture. Evacuation was by a mercury vapor pump backed by a Hyvac oil pump. The body of the still was 12 cm. in length and 2.5 cm. in diameter and the condenser was 10 cm. long and 2 cm. in diameter.

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(4) J. Marcusson, *Ber.*, **54**, 542 (1921); *Z. angew. Chem.*, **34**, 437–438 (1921); W. Schrauth, *Brennstoff-Chem.*, **4**, 161–164 (1923); W. Fuchs, *ibid.*, **12**, 266–268 (1931).

(5) W. A. Bone, L. Horton and S. G. Ward, *Proc. Roy. Soc.* (London), **A127**, 480–510 (1930); B. Juettner, R. C. Smith and H. C. Howard, This Journal, **59**, 236–241 (1937); C. R. Kent, *Australian Chem. Inst. J. & Proc.*, **6**, 207–223 (1939).

(6) B. S. Biggs and J. F. Weiler, This Journal, **59**, 369–372 (1937); C. D. LeClaire, *ibid.*, **63**, 343–353 (1941).

(7) R. B. Randall, M. Benger and C. M. Groocock, *Proc. Roy. Soc.* (London), **A165**, 432–452 (1938).

(8) W. A. LaLande, Jr., and E. C. Wagner, *Ind. Eng. Chem., Anal. Ed.*, **6**, 300 (1934).

(9) J. A. Radspinner and H. C. Howard, *ibid.*, **15**, 566–570 (1943).

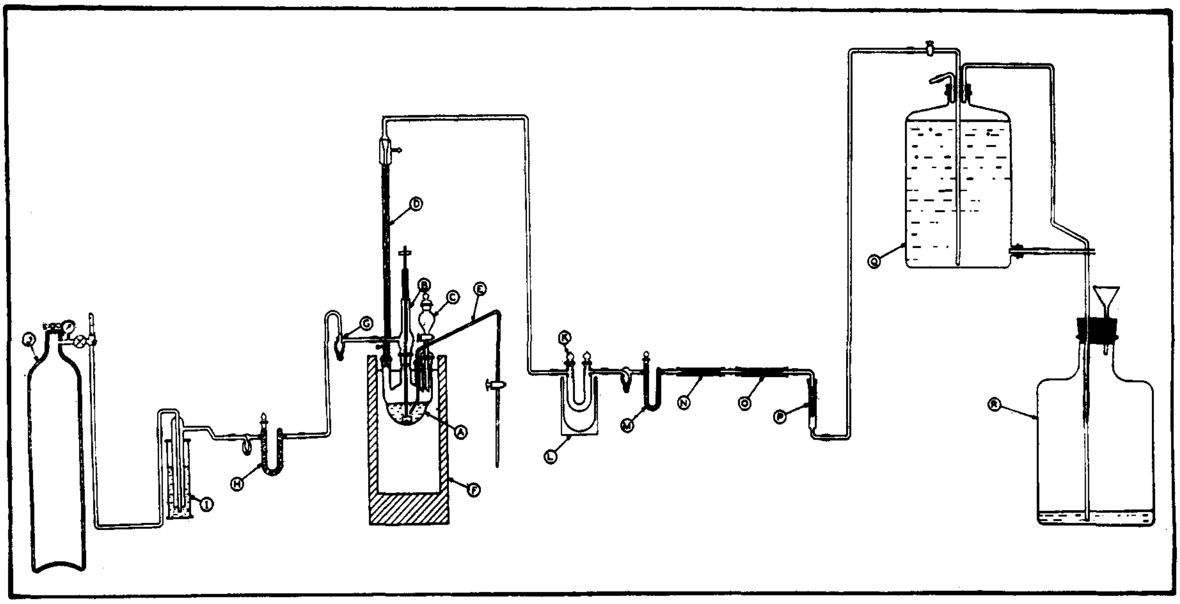

Fig. 1.—Oxidation apparatus.

Preparation and Standardization of Solutions.—Standard potassium permanganate, 0.1 *N*, was prepared and standardized using the procedure of Fowler and Bright.[10] Mallinckrodt "Primary Standard Analytical Reagent" sodium oxalate was used for the primary standard.

The 0.6 *N* potassium permanganate in 1% potassium hydroxide was prepared as follows: 169.5 g. of potassium hydroxide, Mallinckrodt "Analytical Reagent," containing 3% potassium carbonate as a maximum amount of impurity was dissolved in 85 ml. of distilled water and to this solution 146 ml. of saturated barium hydroxide solution was added (4.29 g, of barium hydroxide per 100 g. of water). The barium carbonate precipitate was removed by filtering through a Büchner funnel fitted with filter paper. The filtrate showed an excess of barium ion. The concentration of the solution was shown to be 477 g. per 1 liter of potassium hydroxide when titrated with 1.0 *N* hydrochloric acid solution using methyl orange indicator. The carbonate content of the alkali after the barium hydroxide precipitation was determined by the evolution method and was found to be 3.5 mg. of carbon dioxide per 10 ml of solution. 31.605 g. of Mallinckrodt "Analytical Reagent" potassium permanganate was dissolved in distilled water and 21 ml. of the potassium hydroxide solution was added. This alkaline permanganate solution was diluted to 1 liter at 20° and standardized with sodium oxalate[10] as follows: 1 ml. of the permanganate solution was pipetted into 40 ml. of dilute sulfuric acid solution (5 ml. of concentrated sulfuric acid + 95 ml. of water) which contained about 10 ml. of 0.1 *N* sodium oxalate solution. The mixture was heated to 50–60° and the excess oxalate was determined by titration with 0.1 *N* potassium permanganate. Special care was taken in pipetting the 1 ml. of solution so as to insure a reproducible technique. Four determinations showed a maximum variation of five parts per thousand.

Purification of Materials

Pyridine.—Baker C. P., after standing over barium oxide, was purified according to the method of Mahan and Bailey.[11] The purified material gave a negative Beilstein test, distilled between 114.0 and 114.3°, and showed n^{21}D 1.5084.

Benzene.—A sample of Mallinckrodt "Analytical Reagent" was distilled in a 250-ml. Claisen flask through a short column and the middle fraction collected as the sample for the oxidation study; n^{20}D 1.5008.

Tetrahydronaphthalene.—30 ml. (Eastman Kodak) was vacuum-distilled from a 50-ml. Claisen flask with a fractionating column. The first 10-ml. fraction was discarded and the second fraction of 10 ml. boiling at 105.2° (36 mm. mercury pressure) was collected and taken for the oxidation study.

Decacyclene.—A sample of Fränkel and Landau product was recrystallized twice from cumene: melting point reported 387°, found 390° (uncor.).

Anal. Calcd. for $C_{36}H_{18}$: C, 95.97; H, 4.03. Found: C, 95.75; H, 4.39.

Trisdecahydrodecacyclene.—Obtained by hydrogenating decacyclene in decahydronaphthalene at 230° and 200 atmospheres hydrogen pressure with Raney nickel catalyst. The hydrogenated product, after separation from the catalyst, was recrystallized from glacial acetic acid several times; melting point reported 212–215°, found 217–219° (cor.).

Anal. Calcd. for $C_{36}H_{48}$: C, 89.94; H, 10.06. Found: C, 89.78; H, 10.06.

Triphenylene.—A sample from Fränkel and Landau was purified by dissolving in hot benzene–absolute alcohol, treating with activated charcoal, filtering and crystallizing from the cool solution; melting point reported 198° found 197.7–198° (cor.).

Dodecahydrotriphenylene.—This compound was prepared in two ways: (1) by the condensation of cyclohexanone according to the method of Mannich,[12] melting point reported 232–233°, found 231–232° (cor.); (2) by the catalytic hydrogenation of triphenylene: 15 g. of triphenylene in 75 ml. of cyclohexane was treated for four hours at 185° with hydrogen at 1700 lb. per sq. in.; 168 g. of Raney nickel catalyst was used; 12 g. of hydrogenated product, melting at 232–233°, was obtained. A mixed melting point of the material prepared from the condensation of cyclohexanone and that prepared from the catalytic hydrogenation of triphenylene showed no depression in melting point.

Diphenylene Oxide.—Eastman Kodak Co. material was twice recrystallized from absolute alcohol; melting point reported 86–87°, found 85–86° (uncor.).

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(10) R. M. Fowler and H. A. Bright, *J. Research Natl. Bur. Standards*, 15, 493–501 (1935).

(11) R. I. Mahan and J. R. Bailey, THIS JOURNAL, 59, 2449–2450, (1937).

(12) C. Mannich, *Ber.*, 40, 155 (1907).

Naphthacene.—The Fränkel and Landau product was twice recrystallized from cumene; melting point reported 341°, 335–336°, 331°; found 331–334° (uncor.).

Anal. Calcd. for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.84; H, 5.25.

The following compounds were obtained through the courtesy of Dr. Herman Pines of the Universal Oil Products Company and originated with the Gesellschaft für Teerverwertung.

Pyrene.—The compound was twice recrystallized from absolute alcohol melting point reported 149–150°; found, 150–151° (uncor.).

Carbazole.—The material was twice recrystallized from benzene; melting point reported 245–246°; found, 244–245° (uncor.).

Bituminous Coal.—The sample was from Edenborn Mine, Pittsburgh Seam.[13]

The Oxidation Procedure and Method of Obtaining Carbon Balances.—A weighed sample of the substance was introduced into the reaction flask (A), Fig. 1. The weight taken was calculated to consume 300–400 ml. of standard permanganate assuming oxidation to water, carbon dioxide and a benzene carboxylic acid. Ten per cent. excess of permanganate over the calculated amount was used.

The flask containing the weighed sample was clamped into the thermostated bath (F). The carbon dioxide absorption tubes (N) and (O) were tared by the same method used for microchemical absorption tubes. The side-arm of the Mariotte bottle, (Q) was adjusted so that a stream of carbon dioxide-free air continuously passed through the system at the rate of 10 ml./minute. The apparatus was checked for gas leaks by closing the stopcocks on the U-tube (K), and observing the bubble-counter (G) for any gas passage. When the apparatus was proved to be gas-tight for a period of at least five minutes, the calculated amount of 0.6 *N* potassium permanganate solution was added through the opening at (C), and the following series of operations quickly performed: the time was noted, the stopcocks on the U-tube (K) were opened, the stirrer was started, water was turned into the West condenser (D), and the primary heater of the thermostated bath was turned on, the resistance in the primary circuit heater having been reduced previously to hasten heating, and the Dewar cylinder (L) was packed with ice. The bath usually reached the reaction temperature of 99.60° in one hour and forty-five minutes after the heater had been started. When this temperature was reached the resistance in the main bath heater circuit was increased so that a steady state of several degrees below 99.60° was maintained. By means of a thermoregulator and relay circuit operating a secondary heater, the bath temperature was maintained constant at 99.6 ± 0.05°. Bath temperature and speed of the reaction sitrrer were checked several times daily. The starting time was taken when the bath heater was started.

At given time intervals, depending upon the rate of reaction, a 3-ml. sample was removed from the flask and filtered through a 2-ml. Pyrex glass fritted funnel by an arrangement similar to the automatic suction filter described by Pregl,[14] and the normality of the potassium permanganate solution was determined using the method already described. In this way the rate of oxidation was determined. The experiment was discontinued when the change in normality was less than 0.02 unit in twenty-four hours.

When the oxidation was completed, the thermostated bath heaters were turned off and the bath temperature was allowed to cool to 38°. (This required about twenty-four hours.) The carbon dioxide absorption tubes were weighed and the increase in weight during this part of the run was determined. A final sample was taken for the normality determination of the potassium permanganate. Then a solution of sulfuric acid (5 ml. of concentrated sulfuric acid and 20 ml. of water) was added dropwise to the flask through the separatory funnel (C). The bubble-counter (G) was watched during the addition to make sure that no excessive pressure developed in the system. After the solution was acid, a calculated amount of 15% hydrogen peroxide was added dropwise to reduce the excess potassium permanganate. This addition had to be made carefully since the oxygen evolved during the reaction created considerable pressure in the system. Any excess hydrogen peroxide was oxidized by the solid manganese dioxide. The system was then swept with carbon dioxide-free air at the rate of 600 ml./hour for twenty-four hours. The carbon dioxide absorption tubes were re-weighed and the total increase in weight found.

The exterior surface of the condenser (D), stirrer assembly (B), dropping funnel (C), sampling tube (E), and the upper part of the reaction flask (A) were thoroughly wiped with a damp cloth and then with a dry towel to remove any sublimate from the glycerol-bath. The apparatus was then taken apart and the flask contents poured into an 800-ml. beaker. The flask and auxiliary parts were washed with hot distilled water to remove any water-soluble material and the washings were added to the beaker containing the manganese dioxide suspension.

The manganese dioxide, formed during the reaction, was separated from the aqueous solution of the oxidation products in the following manner: the suspension was transferred to a 250-ml. centrifuge cup and after centrifuging for five minutes, the supernatant liquid was decanted into a beaker and suction-filtered through a 75-ml. medium porosity Pyrex fritted glass funnel. The manganese dioxide was washed by decantation with three 50-ml. portions of water, the supernatant wash water being added to the solution from the oxidation. Finally, the manganese dioxide was transferred from the centrifuge cup to the fritted glass funnel and further thoroughly washed by suction. In order to remove any remaining water soluble products, the manganese dioxide was dried and transferred to a 60-ml. alundum Soxhlet thimble and extracted with water in a Soxhlet apparatus for twenty-four hours. The thimble had been previously heated to 900° for several hours to oxidize any organic impurity it may have contained. In the case of non-volatile compounds, the funnel containing the water-washed manganese dioxide was dried at 120° for three hours. With volatile compounds such as diphenylene oxide, the manganese dioxide was dried over anhydrous calcium chloride at room temperature. Mechanical carry-over of manganese dioxide during extraction was prevented by packing the thimble opening with glass wool. The aqueous extract was added to the filtrate from the manganese dioxide suspension.

In order to remove unreacted hydrocarbon, the thimble containing the manganese dioxide and the Soxhlet apparatus were dried and the manganese dioxide extracted with a suitable organic solvent for forty-eight hours. In the case of diphenylene oxide, diethyl ether was used as a solvent; with decacyclene and trisdecahydrodecacyclene, chlorobenzene was found to be a suitable solvent, and with the remaining compounds benzene was used. The greater part of the solvent was distilled off and the last portion allowed to evaporate in an oven at 110°. The increase in weight of the extraction flask was determined by weighing. The extract was analyzed for carbon, hydrogen and ash by microchemical methods. The manganese dioxide that had been extracted with water and organic solvent was dried thoroughly, then pulverized and transferred to a 300-ml. flask. The flask and contents were dried to remove any traces of organic solvent and the manganese dioxide analyzed for carbon by a wet combustion method using chromic and sulfuric acid. The carbon dioxide evolved was weighed on a semi-micro analytical balance and in a semi-micro carbon dioxide absorption tube similar to that used in the oxidation procedure.

The 2-ml. Pyrex glass fritted funnel used for filtering the samples taken for determining the potassium permanganate normality was extracted with a suitable organic sol-

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(13) For a detailed description of this coal see U. S. Bur. Mines, Tech. Paper no. 525 (1932).

(14) F. Pregl, "Die quantitative organische Mikroanalyse." Julius Springer, Berlin, 3rd ed., 1930, p. 160.

vent and the weight of extract determined. The carbon content of this extract was determined by the wet combustion method in the same flask used for the extraction.

In the meantime the filtrate and washings from the manganese dioxide suspension were concentrated by distillation in a 1-liter round-bottom flask which was fitted with a Kjeldahl distillation head. The distillation was stopped when the volume was reduced to 80 ml. since salts usually began to separate from the cooled solution when concentrated to this volume. The distillate was titrated with 0.1 N potassium hydroxide solution using phenolphthalein indicator, and the acidity calculated as acetic acid. The residue from the distillation was transferred quantitatively to the macro extractor. Sufficient concentrated sulfuric acid was added to make the solution 8 N and, after cooling, the solution was extracted from thirty to forty hours with diethyl ether. The extracted liquor was drained from the macro extractor and its volume measured. Fifty ml. of this liquid, after complete elimination of ether, was analyzed for carbon by the wet combustion method. The ether was separated from the extract by distillation on the water-bath and the residue, containing the free acids and potassium salts, was carefully neutralized with 0.1 N potassium hydroxide solution using phenolphthalein indicator. The neutralized solution was sucked into a tared Jena tube. The water was evaporated off in a Reich-Rohrwig[15] micro steam-bath, and the salts dried at 120° for thirty minutes. The salts were then allowed to stand in air for twenty- four hours and weighed as an air-dried sample. The salt mixture was ground in an agate mortar and analyzed for carbon by the following special micro procedure: a sample of the potassium salts, approximately 3 mg., was weighed out in a platinum boat and 3 drops of sulfuric acid (2 parts of concentrated sulfuric acid, 5 parts of water) were added. The sulfuric acid was then carefully volatilized in the combustion apparatus after which the sample was burned. On completion of the second pass with the movable burner the boat was heated with the full strength of a Bunsen burner directed against the bare combustion tube for five minutes. In this way the determination of carbon and of potassium sulfate was done in one apparatus in a single operation. The water from the sulfuric acid was held up in the water absorption tube and oxides of sulfur were retained by the silver and lead chromate in the combustion tube filling. The following results were obtained with a synthetic mixture of potassium mellitate and potassium sulfate

Weight of sample, mg.	5.290
Weight of carbon dioxide (obtained), mg.	4.759
Weight of carbon dioxide (calcd.), mg.	4.895
Per cent. carbon, found	24.55
Per cent. carbon, calcd.	25.25

After completing thirty analyses by this procedure the combustion tube filling was examined. The first silver wad was heavily coated and discolored and the yellow color, due to lead chromate, was changed to a greenish color for a distance of about 1.5 cm. at the front end of the tube filling. The green color was probably due to copper sulfate. The silver in the rest of the tubing remained as bright as it had been initially so there was little possibility that any oxides of sulfur had passed through the entire tube; they were apparently all removed at the very front portion of the tube. The determination of carbon in the oxidation products from carbazole required the removal of oxides of nitrogen from the train before entering the carbon dioxide absorption tube. This was accomplished by using a modification of the method of Elving and McElroy.[16] An Abrahamczik tube, as modified by Stillson and Clark, was inverted and the lower part was half-filled with 0.02 N potassium permanganate[17] in concentrated sulfuric acid. The upper part, which was separated from the lower by a wad of glass wool, was filled with anhydrous magnesium perchlorate. The solution of potassium permanganate became clear and formed a brown precipitate after three determinations. The results obtained using the above method with *p*-aminoacetophenone and with benzoic acid were as follows: *p*-aminoacetophenone, calcd., C, 71.09; found, 70.86; benzoic acid: calcd., 68.84; found, 69.20.

The following results were obtained by determining the carbon and hydrogen in benzoic acid and *p*-aminoacetophenone using the Abrahamczik tube filled with 0.02 N potassium permanganate in concentrated sulfuric acid but omitting the addition of sulfuric acid to the sample: *p*-aminoacetophenone, calcd.: C, 71.09; H, 6.71. Found: C, 71.00; H, 6.77. Benzoic acid, calcd.: C, 68.84; H, 4.95. Found: C, 68.94; H, 4.94.

There was an unavoidable carbon loss in taking the samples from the reaction vessel, and the magnitude of this was estimated by assuming that the fraction of the carbon removed in the sample was proportional to the fraction of the total permanganate reduced at that time and to the volume of the sample taken, or

$$\frac{c}{C} = \frac{(N_0 - N_t)v}{(N_0 - 0.1)V}$$

where

c = mg. carbon in sample removed
C = mg. carbon in original
N_0 = initial normality of permanganate
N_t = normality of permanganate at time sample was taken
v = volume of sample in ml.
V = total volume of permanganate added

Recovery and Characterization of the Oxidation Products.—In order to determine optimum conditions for the recovery in the ether extraction of the organic acids formed in the oxidations, preliminary experiments were carried out with synthetic mixtures of mellitic acid, sulfuric acid and potassium sulfate. Samples of saturated potassium sulfate solution of 375 ml. were treated with the required amounts of sulfuric acid to produce solutions of 1 to 8 N, and 200 mg. of mellitic acid was added to each. The rate of extraction of mellitic acid was found to be an approximately linear function of the sulfuric acid concentration up to the highest concentration studied, 8 N. The rate of extraction of the sulfuric acid increased in a similar way so that a mixture of the organic acid and sulfuric acid was obtained in the extract. The separation of these acids was found to be difficult. A satisfactory separation on synthetic mixtures was, however, obtained by precipitation with barium nitrate, at *p*H about 0.2, using acid cresol red indicator. At this acidity the barium mellitate is soluble, the sulfate relatively insoluble. By electrolysis of the filtrate from the barium sulfate precipitation and evaporation of the anode solution pure mellitic acid was recovered. This procedure, however, when applied to the oxidation products, did not give consistently satisfactory results. Other methods resorted to were fractional crystallization from fuming nitric acid and esterification followed by fractional distillation. Differential titration was not feasible because of the similar acid strengths of mellitic and sulfuric acids.[18] Attempts at a separation as the benzidine salts were also unsuccessful.

Discussion

Reaction Rates.—A blank experiment to establish the stability of the alkaline permanganate solution under the experimental conditions showed a small but significant increase in strength of the oxidant as a function of time from an initial value of 0.583 N to 0.587 N after seventy-two hours at 98.1°. This effect was no doubt due to the loss of water vapor from the system. Preliminary experiments were carried out to deter-

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[15] W. Reich-Rohrwig, *Mikrochemie*, **12**, 189–192 (1932).

[16] P. J. Elving and W. R. McElroy, *Ind. Chem., Anal. Ed.*, **13**, 660–663 (1941).

[17] R. O. Clark and G. H. Stillson, *ibid.*, **12**, 494–498 (1940).

[18] W. R. Maxwell and J. R. Partington, *Trans. Faraday Soc.*, **31**, 922–935 (1935).

mine whether benzene or pyridine were sufficiently stable to permit their use as solvents in the oxidation reactions. Pyridine was rapidly oxidized; 5 ml. completely reduced 250 ml. of 0.6 N alkaline potassium permanganate in five hours at 98.2°. Benzene reacted less rapidly; 5 ml. reduced 82 ml. of 0.6 N permanganate in twenty hours, but its use was undesirable also because it volatilized into the cold trap, where it froze out and blocked the train. Since it appeared improbable that any solvent could be found which would be stable enough to be satisfactory, all the oxidations were carried out simply by agitating the hydrocarbon with the aqueous permanganate. The kinetics of the process were no doubt influenced to some extent by physical factors such as the degree of subdivision of the material being oxidized. With some of the solids there was a marked tendency to coalesce into sizable lumps with resulting reduction in surface.

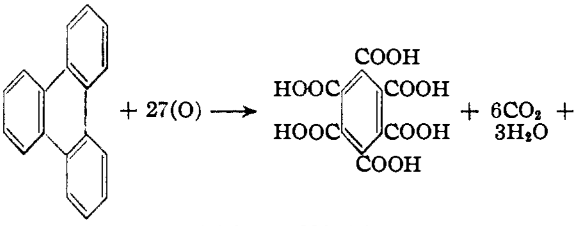
The alkaline permanganate oxidation of polycyclic hydrocarbons may result in the formation of oxalic and benzene keto-carboxylic acids along with carbon dioxide and the simple carboxylic acids. Since the presence of the first two acids would complicate the analytical procedure, they were eliminated by the oxidation step in the acid medium. Undesired further oxidation was avoided by carrying out the reaction in the acid medium at 38–40° and promptly destroying the excess permanganate by hydrogen peroxide. Excess peroxide was in turn rapidly removed by the solid manganese dioxide present.

Complete rate data for a typical oxidation are shown in Table I. Rates of consumption of permanganate for all the compounds studied, except trisdecahydrodecacyclene, and for a bituminous coal are summarized in the curves of Fig. 2. N_0 is the initial concentration of the permanganate and N_t that at the specified time. The difference between these two quantities is the permanganate consumed. The curves show that tetrahydronaphthalene, which combines an aromatic and hydroaromatic structure, oxidized more rapidly than any other substance investigated. Next in order of ease of oxidation were bituminous coal, pyrene and naphthacene. The heterocyclic compounds—diphenylene oxide and carbazole—follow, both oxidizing rather rapidly to simple products. The completely aromatic hydrocarbons, decacyclene and triphenylene, were less reactive and least reactive of all were the nearly completely saturated structures, dodecahydrotriphenylene and trisdecahydrodecacyclene. The last named, not shown in the figure, consumed, after one hundred and forty-four hours, only 5% of the theoretical amount of permanganate required for oxidation to mellitic acid, carbon dioxide, and water.

TABLE I

TYPICAL OXIDATION DATA

Triphenylene



Mol. wt., 228.276

1 gram requires 54/228.2 ≃ 0.236 eq. oxygen ≃ 393.3 ml. of 0.6 N $KMnO_4$ (alkaline basis)

Hydrocarbon, mg.	723.48	721.18
Initial normality of $KMnO_4$, N_0	0.603 0.606	0.597 0.596
Volume $KMnO_4$ used (10% excess), ml.	314.8	313.9
Temperature, °C.	99.6	99.6
Stirring rate, r. p. m.	600 ± 10	600 ± 10

t, time in hours	N_t[a]	$N_0 - N_t$[b]	N_t	$N_0 - N_t$
4	0.596	0.007	0.596	0.0005
	.598		.596	
24	.550	.054	.550	.047
	.551		.548	
48	.488	.114	.481	.116
	.492		.479	
72	.431	.173	.429	.166
	.432		.431	
96			.370	.225
			.372	
103	.366	.239		
	.365			
144	.299	.307		
	.296			

[a] N_t = normality at time, t. [b] Mean values of N_0 and N_t used.

Certain aromatic hydrocarbons have been reported to be so highly resistant to boiling alkaline permanganate that they were regarded as practically unoxidizable by it.[7] Among these were benzene and decacyclene. Under the conditions employed in this investigation both of these were found to oxidize at a significant rate. Further, the results on the oxidation of triphenylene, pyrene and naphthacene are not in agreement with the view[7] that "unreduced and unsubstituted aromatic hydrocarbons containing more than three "fused" rings are practically unattacked, a circumstance possibly due to their insolubilities in the reagent."

Examination of the data indicates that in condensed polycyclic hydrocarbons the "double bond character" of the molecule is an important factor in the rate of oxidation. A measure of "double bond character" is the ratio of the number of resonance structures which place a double bond between any two carbon atoms to the total number of resonance structures which can be written for the molecule.[19] Such a treatment, applied to

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(19) Henry Gilman, Editor, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, 2nd ed., Vol. II, p. 1973.

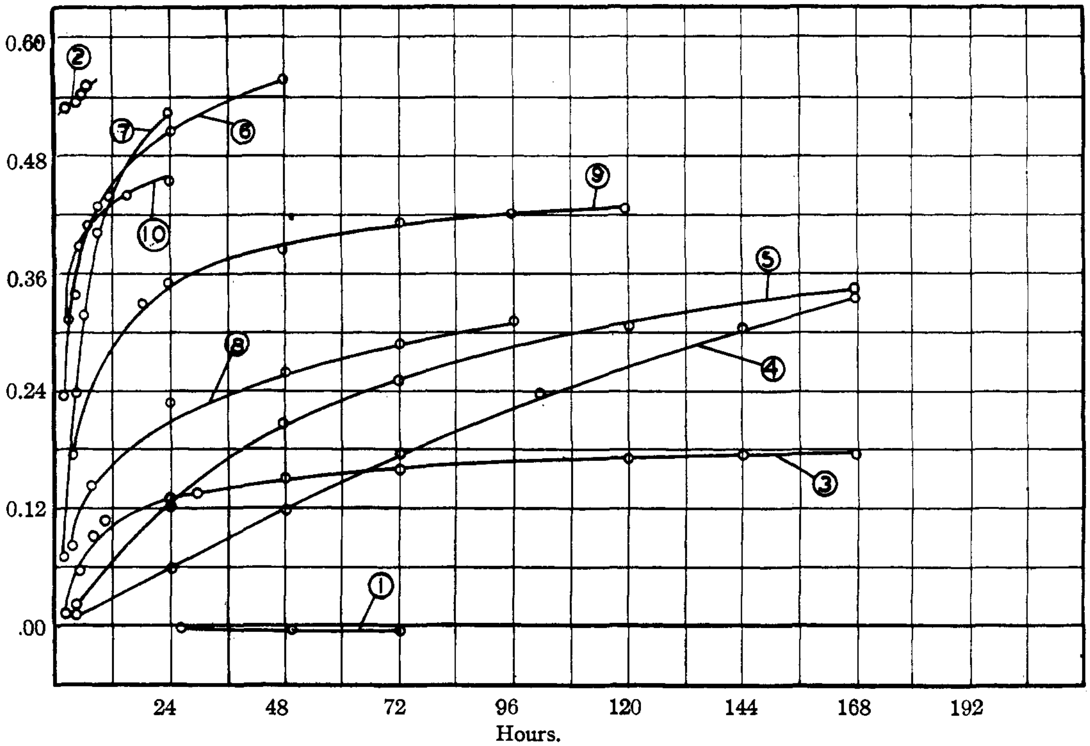
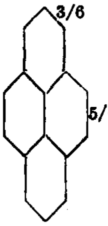
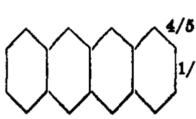


Fig. 2.—Rates of permanganate consumption: 1, blank; 2, tetrahydronaphthalene; 3, dodecahydrotriphenylene; 4, triphenylene; 5, decacyclene; 6, naphthacene; 7, pyrene; 8, diphenylene oxide; 9, carbazole; 10, Pittsburgh seam coal.

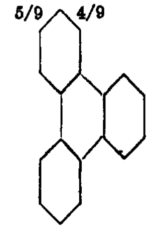
the molecules pyrene, naphthacene and triphenylene, gives the following results



Pyrene



Naphthacene



Triphenylene

The high values of the ratios for certain bonds in the pyrene and naphthacene molecules, as compared with those in triphenylene, are in accord with the much higher rates of reaction of the two first named compounds. It is also of interest to observe that the high reaction rate of the bituminous coal places it among the condensed polycyclic structures with "high double bond character."

Plots of some of the data on the assumption of first order reaction with respect to permanganate concentration are shown in Fig. 3. Non-linear first order plots were obtained with the other compounds and with coal.

Carbon Balances.—The analytical procedure used permitted the determination of the distribution of the carbon among the following reaction products: carbon dioxide, water soluble products and water insoluble products. The data are summarized in Table II. The figures are the averages of not less than two experiments and in many cases as high as five. The summations are satisfactory, ranging from 96 to 103%, with the exception of the very slightly reacted trisdecahydrodecacyclene which gives a value of 109%.

In calculating the theoretical permanganate consumption, the reaction products postulated for each of the compounds, in addition to carbon dioxide and water, were as follows: tetrahydronaphthalene–*o*-phthalic acid; dodecahydrotriphenylene–mellitic acid; triphenylene–mellitic acid; decacyclene–mellitic acid; trisdecahydrodecacyclene–mellitic acid; pyrene–hemimellitic and prehnitic acids; naphthacene–pyromellitic and *o*-phthalic acids. Complete oxidation was postulated for the heterocyclic compounds and for coal. The large proportions of the carbon appearing as carbon dioxide along with significant amounts of unreacted material were not anticipated since in macro experiments it has been found possible to oxidize such hydrocarbons as triphenylene to mellitic acid with 45% of the theoretical yields, corresponding to a recovery of 30% of the carbon as the acid.[20] Juettner, Smith and Howard showed that alkaline permanganate oxidation of Pittsburgh Seam bituminous coal on a macro scale results in conversion of 50–60% of the carbon of the coal to a mixture of water soluble acids.[5] In this work, only with tetrahydro-

(20) B. Juettner, THIS JOURNAL, 59, 1472-1474 (1937).

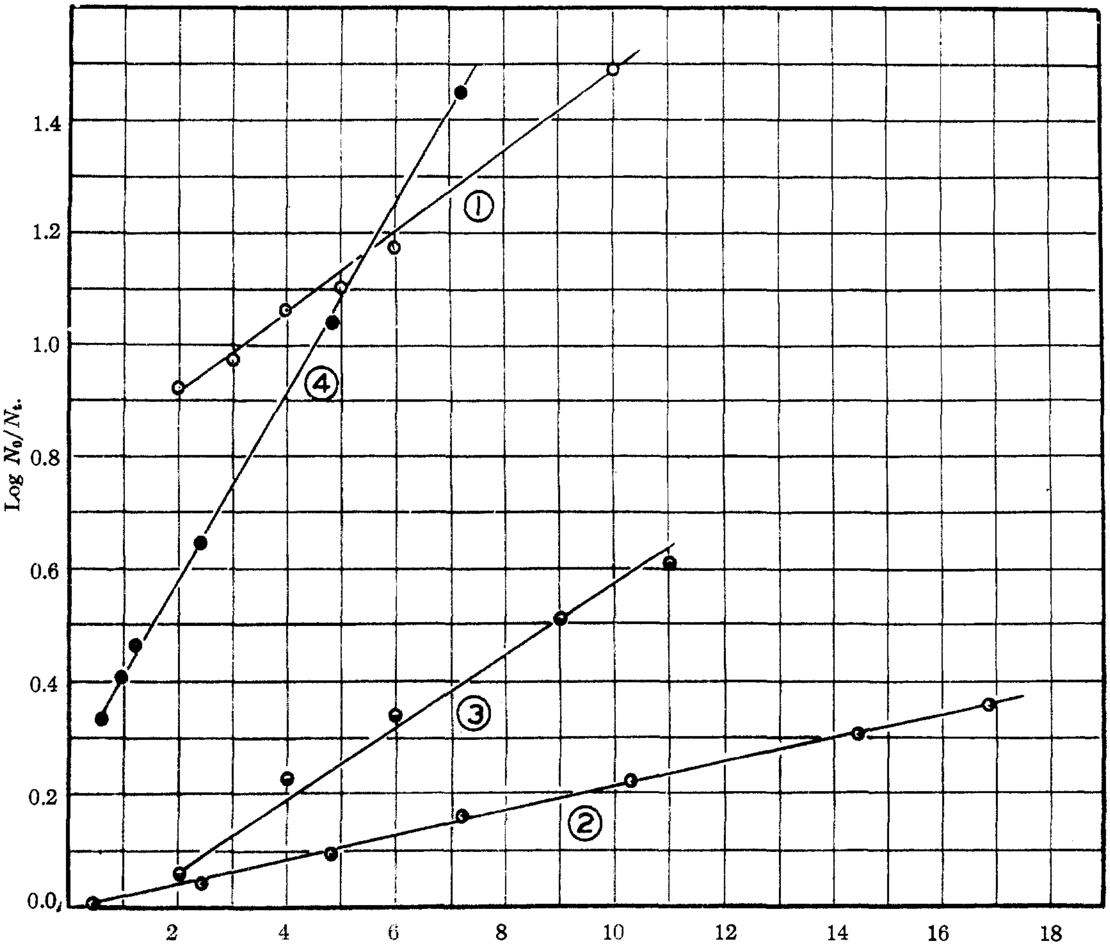


Fig. 3.—First order plots: 1, tetrahydronaphthalene, abscissa in hours; 2, triphenylene, abscissa in hours × 10^{-1}; 3, pyrene, abscissa in hours; 4, naphthacene, abscissa in hours × 10^{-1}.

naphthalene, naphthacene and pyrene did the yield of organic acids approach that postulated.

Recovery of Acids from the Oxidation Products.—Because of the small amounts of starting materials and the low fraction of the carbon appearing as organic acids, only with tetrahydronaphthalene, naphthacene, and pyrene were sufficient organic acids isolated to be characterized. With the exception of the phthalic acids all of the benzene polycarboxylic acids are very soluble in water, and their recovery from mixtures of large amounts of inorganic salts is a difficult problem. A preliminary concentration was effected by the two sizes of liquid phase extractors

TABLE II

DISTRIBUTION OF CARBON IN THE OXIDATION PRODUCTS

	% C as CO_2		% C as water soluble products		% C as water insoluble products
	Found	Calcd.[a]	Found	Calcd.[a]	Found
Tetrahydronaphthalene	26.1	20.0	60.8	80	13.1
Dodecahydrotriphenylene	26.2	33.3	10.1	66.7	60.1
Triphenylene	46.8	33.3	16.2	66.7	37.2
Decacyclene	53.0	33.3	10.5	66.7	39.2
Trisdecahydrodecacyclene	18.7	66.7	5.0	33.3	85.5
Carbazole	65.5	..	8.5	..	29.4
Diphenylene oxide	64.3	..	5.2	..	28.3
Pyrene	54.3	37.5 43.5	36	62.5[b] 56.3[c]	7.7
Naphthacene	60.5	44.4 55.6	35.3	55.6[d] 44.4[e]	3.0
Bituminous coal	71.1	..	19.2	..	4.5

[a] The theoretical reactions postulated are described in the discussion. [b,c,d,e] Oxidation assumed to: hemimellitic, prehnitic pyromellitic and *o*-phthalic acids, respectively.

or by electrolytic decomposition of the salts in a three-compartment cell. Final purifications were by crystallization from fuming nitric acid or by esterification with diazomethane followed by distillation in the small molecular still. The ultimate composition and equivalent weight of the acids recovered from the tetrahydronaphthalene oxidation were in satisfactory agreement with the theoretical values for *o*-phthalic acid. The products recovered from the pyrene oxidation and purified by crystallization from fuming nitric acid gave values of ultimate composition and equivalent weight corresponding to a mixture of tetra- and tricarboxylic acids, presumably phrenitic and hemimellitic acids. The products recovered from the naphthacene oxidation by a similar procedure, judged by ultimate composition and equivalent weight, consisted of a mixture of a di- and a tetracarboxylic acid, presumably *o*-phthalic and pyromellitic acids, and with the dicarboxylic acid predominating.

Summary

Apparatus has been devised and analytical methods have been worked out for following quantitatively the rate of reaction of condensed cyclic compounds with alkaline permanganate, for determining the carbon balances in the process, and for recovering and characterizing the soluble products of the oxidations. The semi-micro apparatus and methods used permitted the work to be done on samples of 500 to 800 mg. The following substances were studied: tetrahydronaphthalene, dodecahydrotriphenylene, triphenylene, decacyclene, trisdecahydrodecacyclene, naphthacene, pyrene, diphenylene oxide and carbazole. For comparison, a sample of a typical bituminous coal was investigated under identical conditions.

Under the conditions of this oxidation tetrahydronaphthalene oxidized most rapidly; bituminous coal, pyrene and naphthacene were next; then followed the heterocyclic compounds, diphenylene oxide and carbazole; the completely aromatic compounds—decacyclene and triphenylene—were less reactive, and the nearly saturated structures were least reactive of all. A qualitative correlation between the rates of oxidation and "double bond character" of certain polycyclic hydrocarbons was found. On the basis of this evidence the bituminous coal possesses a high "double bond character." Satisfactory first order relations with respect to alkaline permanganate were found in the reactions with tetrahydronaphthalene, pyrene, naphthacene and triphenylene, showing that with these compounds the reaction with the oxidant is the rate controlling factor. Significantly higher rates of oxidation were found than have been previously reported for some of the same compounds. This may be ascribed to the excess permanganate present in the early stages of the reaction.

Only with tetrahydronaphthalene, pyrene and naphthacene did the fraction of the carbon recovered as organic acids approach that postulated from theoretical equations.

The results of this investigation are in accord with the view that bituminous coals are condensed cyclic structures of "high double bond character."

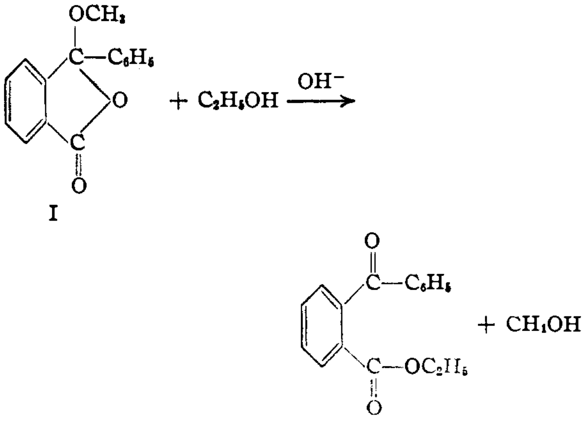
PITTSBURGH, PA. RECEIVED SEPTEMBER 14, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Kinetics of the Base-Catalyzed Reaction of Pseudo *l*-Menthyl *l*-*o*-Benzoylbenzoate with Methanol[1]

BY JOHN R. SCHAEFGEN,[2] FRANK H. VERHOEK AND MELVIN S. NEWMAN

Pseudo methyl *o*-benzoylbenzoate (I) has been found to react with great rapidity with aqueous methanol in the presence of a small quantity of sodium hydroxide to yield its normal isomer, and with alkaline aqueous ethanol to yield normal ethyl *o*-benzoylbenzoate (II).[3] This reaction therefore involves both a change from a pseudo, or lactol ether, structure to a keto ester structure and an ester interchange with the solvent. The rapidity with which this reaction took



I

II

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[1] Presented before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, September, 1944. The material in this paper is contained in the Ph.D. thesis of J. R. S., The Ohio State University, March, 1944.

[2] Present address: Goodyear Tire and Rubber Co., Akron, Ohio.

[3] McCleary, Ph.D. Dissertation, 1940, The Ohio State University.