If oxygen is present in the fluid, the discharge leads to activation, with formation of hydrogen peroxide or direct chemical reaction of activated oxygen with certain compounds present in solution such as aminophthalichydrazide. Sonic chemiluminescence then results, as shown by Flosdorf, Chambers and Malisoff.[6] Sonoluminescence is remarkably independent of substances dissolved in the water phase but is quenched by high vapor pressure of water (from rise in temperature) or by specific volatile organic compounds.

Oxidation of Carbonaceous Materials to Organic Acids by Oxygen at Elevated Pressures[1]

BY R. C. SMITH, R. C. TOMARELLI AND H. C. HOWARD

Coals, cokes, and pitches yield significant amounts of organic acids when subjected to controlled oxidation with oxidizing reagents such as alkaline permanganate and nitric acid,[2] and small amounts of aromatic acids have also been isolated from oxidation products formed by the action of air, at elevated temperatures and pressures, upon suspensions of coal in aqueous alkali.[3]

In the present investigation oxidations were carried out in aqueous alkali at temperatures from 100 to 250° and oxygen partial pressures from approximately 100 to 375 pounds (7–25 atm.). Below 225°, reaction rate was very slow. Bituminous and anthracite coals and low temperature coke can be oxidized completely to carbon dioxide and water or to any desired intermediate stage. High temperature coke and graphite are partially oxidized under the same conditions, 50–60% of the carbon appearing as carbon dioxide, but much smaller amounts of organic acids are recovered. In the case of graphite no significant amount is obtained because mellitic acid is the principal organic acid formed in the oxidation degradation of these higher rank carbonaceous materials,[4] and it has been found to be unstable under the conditions of this oxidation.

Increase in area of gas–liquid interface, by introduction of packing material into the bomb, has been found to increase significantly the reaction rate in the early stages of the degradation.

Of some nineteen different catalysts investigated, only copper and cobalt salts affect reaction rate significantly, and these chiefly in the later stages of the oxidation.

Carbon balances show that under the proper conditions approximately 50% of the carbon of bituminous and anthracite coals can be converted to water soluble organic acids, the rest of the carbon appearing as carbon dioxide. Of the carbon recovered in the form of organic acids about one-fourth is oxalic acid and the balance aromatic acids. The actual amount of the latter recovered by oxidation of a Pittsburgh Seam coal was 30–40 g. per 100 g. of coal.

Experimental.—The oxidations were carried out in an all-nickel bomb of 1-liter capacity of identical design with those supplied for hydrogenation,[5] except that a silver gasket was used. The bomb was heated externally by an electric furnace and agitated in the usual way by oscillation approximately 30° above and below the horizontal, about a transverse axis. Oxygen was introduced through a spiral of high pressure tubing from an oxygen reservoir of constant pressure. Since maintenance of the oxygen partial pressure depended upon absorption of the carbon dioxide formed, the amount of coal oxidized at one time was limited primarily by the amount of alkali which could be introduced. The maximum amount of coal which could be used was 50 g. and with materials of higher carbon content such as graphite it was necessary to reduce the size of the sample. The material to be oxidized was ground to −200 mesh and in most cases was suspended in a solution of 335 g. of potassium hydroxide in 350 cc. of water. In a few oxidations the potassium hydroxide was replaced by equivalent amounts of sodium hydroxide or calcium oxide.

In the early experiments considerable difficulty was encountered with the alkaline solution working back into the pressure tubing which supplied the oxygen. To prevent this a trap was provided in the pressure line just before it entered the head of the bomb and the line was continued inside the bomb and turned upward at the tip,

(1) Presented before the Division of Gas and Fuel Chemistry at the 96th meeting of the American Chemical Society, Milwaukee, Wisconsin, September, 1938.

(2) Bone and co-workers, Proc. Roy. Soc. (London), A110, 537 (1926); A127, 480 (1930); A148, 492 (1935); Juettner, Smith, and Howard, THIS JOURNAL, 59, 236 (1937); 57, 2322 (1935).

(3) For a review of the work of F. Fischer and co-workers see Horn, Brennstoff-Chem., 10, 362 (1929).

(4) Juettner, THIS JOURNAL, 59, 1472 (1937).

(5) American Instrument Company, Silver Spring, Md.

so that even during oscillation the end of the pressure line was above the liquid level in the bomb. Bomb and pressure tubing were filled with 100–300 pounds (7–21 atm.) of oxygen, depending upon the final pressure to be used, before starting heating or agitation. After the bomb reached the desired temperature the full oxygen pressure was applied and agitation started. The temperature of the bomb was measured by a chromel–alumel couple placed in a well extending from the head to the middle of the bomb. Temperatures were maintained constant to ±2° by a Leeds and Northrup controller.

Total pressures were measured with a Bourdon tube gage placed in the oxygen inlet line near the trap. Oxygen partial pressures were calculated by taking the difference between total gage pressure and the aqueous vapor pressure, at the temperature of the oxidation, of a sodium hydroxide solution of equivalent concentration to the potassium hydroxide actually used, since no data are available for the latter. For this reason the absolute value of the oxygen partial pressure is somewhat uncertain.

In the preliminary experiments the rate of the reaction was followed by oxygen absorption, in the later ones, analytically, through examination of the products formed at the end of definite time intervals.

The analytical procedure was as follows. After cooling, the alkaline solution from the bomb was drained into a 2000-cc. volumetric flask, and bomb, head, and packing material, when used, were washed carefully and the washings and contents of the bomb combined in the volumetric flask, made up to volume and mixed thoroughly. After standing to permit any insoluble matter to settle to the bottom of the flask, which in most cases consisted of inorganic material, aliquot portions were withdrawn from the clear supernatant liquid for determination of total carbon, carbonate carbon, oxalate carbon and, in a few cases, carbon in the form of volatile acids. The volatile acids were never found to constitute more than 1 to 2% of the carbon of the material oxidized and in the later experiments this determination was omitted. The methods used for the determination of the various forms of carbon have been described in a previous publication.[6]

The greater part of the work was done with a Pittsburgh Seam coal, Edenborn Mine, but for comparison oxidations were also carried out on Illinois No. 6, High Splint coal, Pocahontas No. 3, a Pennsylvania anthracite, 500° and 700° cokes, prepared in this Laboratory from the Pittsburgh coal, a commercial high temperature coke, Acheson electrode graphite, and a pitch from a high temperature carbonization process.[7]

In order to obtain sufficient material to examine the aromatic acids in detail, eleven oxidations of Edenborn coal were carried out. Fifty grams of −200 mesh coal was treated at 225° with an oxygen partial pressure of approximately 380 pounds (25 atm.), total pressure 600 pounds (40 atm.), for a period of eighteen hours. The alkaline solution from the bomb was filtered to remove insoluble material, chiefly inorganic, the filtrate was neutralized with sulfuric acid, and excess acid added until the concentration was about 3 N. This acid solution was treated with manganese dioxide in an amount about twice

the theoretical required to oxidize the oxalic acid present. The excess manganese dioxide was filtered off, the filtrate and washings concentrated to 1500 cc. and the acidity again adjusted to about 3 N. A total carbon determination at this point showed, on the average, 85% of the carbon present which was previously calculated to be aromatic from the analytical data, so that presumably this method of removal of oxalate also attacks some aromatic carbon.

This solution was then subjected to ether extraction in a continuous extractor[8] for a period of a week. Of the aromatic carbon which was placed in the extractor an average of 80% was recovered in the seven-day extraction. The greater part of this was recovered in the first twenty-four hours.

The yield of aromatic acids actually obtained in this way, from 50 g. of Edenborn coal, ranged from 15 to 20 g. They were orange to pale yellow in color; slightly hygroscopic; easily soluble in water, except about 1%, which was found to be terephthalic acid; easily soluble in acetone and alcohol; moderately soluble in ether and ethyl acetate, and almost insoluble in benzene.

A sample from a 225°, twenty-four hour oxidation, dried to constant weight at 85°, showed the following average properties: C, 51.91%; H, 2.87%; N, 0.45%; S, 1.03%; residue on ignition, 0.58%; equiv. wt., by titration using phenolphthalein, 73.1; mol. wt. by boiling point elevation in acetone, 230. This average composition, except of course for nitrogen and sulfur, is close to that of a benzenetricarboxylic acid: C, 51.41%; H, 2.85%.

The yellow color was found to be a function of the severity of the oxidation treatment, lighter colored acids resulting from prolonged treatment. Samples of the more deeply colored acids had higher average equivalent and molecular weights ranging up to 76 and 260, respectively.

The methods of barium salt fractionation, esterification and vacuum fractionation of the esters were like those previously described,[6] except that a somewhat more effective design of molecular still was employed and longer time periods were used for distillation of the ester fractions. Terephthalic acid (1,4-benzenedicarboxylic acid), because of its relative insolublity in water, was separated readily before the barium salts were formed. Trimellitic acid (1,2,4-benzenetricarboxylic acid) was found in the water-soluble barium salt fraction and was purified by crystallization from concentrated nitric acid, followed by vacuum distillation. The purified acid melted 215–225°, was converted to the anhydride by heating at 250° and the anhydride vacuum distilled. The m. p. of the anhydride was 166°.

Anal. Calcd. for $C_9H_4O_5$: C, 56.25; H, 2.08. Found: C, 56.02; H, 2.37.

The tetramethyl ester of prehnitic acid (1,2,3,4-benzenetetracarboxylic acid) was isolated from the ester fraction distilling at 125° prepared by the action of diazomethane on the fraction of acids forming barium salts insoluble in water, but soluble in acetic acid; m. p. 130°.

Anal. Calcd. for $C_{14}H_{14}O_8$: C, 54.19; H, 4.52. Found: C, 54.16; H, 4.55.

(6) Juettner, Smith and Howard, THIS JOURNAL, **59**, 236 (1937).

(7) The sources of these materials are given in ref. 4.

(8) Discussed in ref. 6.

The tetramethyl ester of pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid), was isolated from the ester fraction distilling at 125° prepared by the action of diazomethane on the fraction of acids forming barium salts insoluble in water and acetic acid, but soluble in formic acid; m. p. 141°.

Anal. Calcd. for $C_{14}H_{14}O_8$: C, 54.19; H, 4.52. Found: C, 53.90; H, 4.73.

Results and Discussion

Early in the work it was found that the rate of oxidation, measured by the amount of carbon dioxide formed per unit of time, was relatively independent of the weight of coal present. This indicated that the rate was determined by some constant factor, and in view of the rather low oxygen partial pressure employed and the correspondingly low solubility of oxygen, it appeared that the oxidation must be taking place chiefly at the gas-liquid interface and that the area of this interface was the rate controlling factor. Experiments in which the area of this interface was increased by the introduction of packing material confirmed this analysis and showed definitely increased reaction rates, and, as was to be expected, the packing was much more effective at lower oxygen partial pressures (see Table I). The packing con-

TABLE I

OXIDATION OF PITTSBURGH SEAM COAL[a]

Temp., °C.	Total pressure, lb.	Estimated oxygen p. p., lb.	% of carbon[b] of coal as CO_2 12 hrs.	24 hrs.	Remarks
250	500	137	23.0	32.5	No packing[c]
250	500	137	34.9	49.5[d]	
225	600	377	40.7	43.6	No packing
225	600	377	43.1[f]	48.5	
225	600	377	53.0	75.8	Copper sulfate
250	500	137	49.0	78.9[e]	Copper sulfate
250	500	137	..	69.5	No packing, copper sulfate
250	500	137	..	66.7	Cobalt sulfate
200	375	250	35.4	38.3	
225	450	227	31.5	44.2	
250	600	237	46.4	64.2	
225	325	102	..	31.5	
225	375	147	..	26.9	
225	450	227	..	44.2	
225	600	377	..	48.5	
225	600	377	32.7	42.3[e]	Sodium hydroxide
225	700	377	..	43.0	Sodium hydroxide

[a] −200 mesh, 50-g. sample; 350 cc. water; 335 g. potassium hydroxide or its equivalent. [b] Values represent single measurements except where otherwise noted. [c] Packing was used in all experiments except where otherwise noted. [d] Mean of 30 oxidations; all values within ±2% of mean. [e] Mean of 2 oxidations. [f] Mean of 3 oxidations.

sisted of 69 pieces of 2.5 × 20 cm. 6-mesh monel screen twisted into stick form, 6 mm. in diameter.

In a study of the effect of the addition of various anions and cations upon the course of the reaction, 5 g. per 50 g. of coal of the following substances was used: copper sulfate, silver sulfate, zinc sulfate, mercuric chloride, titanium sulfate, cerium sulfate, thorium nitrate, antimony trichloride, chromic sulfate, tungstic acid, uranium nitrate, selenium, manganous sulfate, ferrous sulfate, nickel nitrate, cobalt sulfate, potassium permanganate, potassium chromate, and sodium nitrate. The values for percentage carbon converted to carbonic acid in the oxidations when additions were made did not vary more than a few units from the average of those without additions, run under identical conditions, except in those experiments where copper or cobalt salts were used. Two experiments with addition of copper sulfate gave 79.3 and 78.5% carbon converted to carbonic acid, and one experiment with cobalt sulfate gave 66.7%, as compared with 49.5% for the average of experiments without catalysts. Unfortunately these catalysts appear to have little effect on the rate of initial oxidation of the coal, but accelerate markedly the conversion of the soluble acids to carbon dioxide and water. When an attempt was made to preserve the soluble acids by shortening the oxidation period, considerable coal remained unattacked. The catalytic effect of copper and cobalt also was observed in oxidations of cokes. A 500° coke gave 61.3 and 91% for uncatalyzed and copper-catalyzed reactions, respectively; a 700° coke, 59.8 and 86.8%. No effect was found with graphite.

The oxidations at 200, 225 and 250°, at an approximately constant oxygen partial pressure, showed that the effect of increased temperature was most marked in the later stages of the reaction, after the coal had been largely converted to the alkali-soluble "humic acids." At 200° the amount of soluble carbon and the carbonate carbon both remained nearly constant over the last twelve hours; at 225° there was definite evidence of attack on the "humic acids," over the same period; and at 250°, there was a large increase in the fraction of the carbon appearing as carbon dioxide, with a corresponding marked drop in the carbon in the form of organic acids. The color of the alkaline solutions of the oxidation products obtained at the different temperatures, as well as their behavior on acidification, were very charac-

teristic; those prepared at 200° were deep brown and contained acid precipitable products, "humic acids"; those from the 250° oxidations were pale yellow and no acids precipitated on acidification; while those formed at 225° were intermediate in color and showed variable behavior on acidification.

The data on the effect of oxygen partial pressure at a constant temperature of 225° and an oxidation period of twenty-four hours indicate an increase in rate of formation of carbon dioxide with higher oxygen partial pressures.

Replacement of the potassium hydroxide by sodium hydroxide was found to reduce the rate of oxidation markedly; the fraction of the carbon converted to carbon dioxide was 25% lower at the end of twelve hours. It seems probable that this is due to differences in solubility of the sodium and potassium salts of the organic acids formed in the early stages of the reaction, where the rate of oxidation must be greatly affected by the rate at which fresh coal surfaces are exposed by solution of the initial oxidation products.

Five out of the six equivalents of potassium hydroxide could be replaced by equivalent amounts of calcium hydroxide without adverse effect on the reaction rate. With calcium hydroxide alone only a small fraction of the carbon of the coal, less than 3%, was converted to soluble products, under the same conditions where complete conversion took place with potassium hydroxide.

The distribution of the carbon of a Pittsburgh Seam coal, among the various oxidation products, as a function of time, was studied in detail. The results, which are shown in Fig. 1, are similar to those obtained with oxidizing agents such as nitric acid and alkaline permanganate.

The results of a study of the behavior of several different types of carbonaceous materials, using a standard oxidation procedure, are summarized in Table II. Under these conditions all of the coals
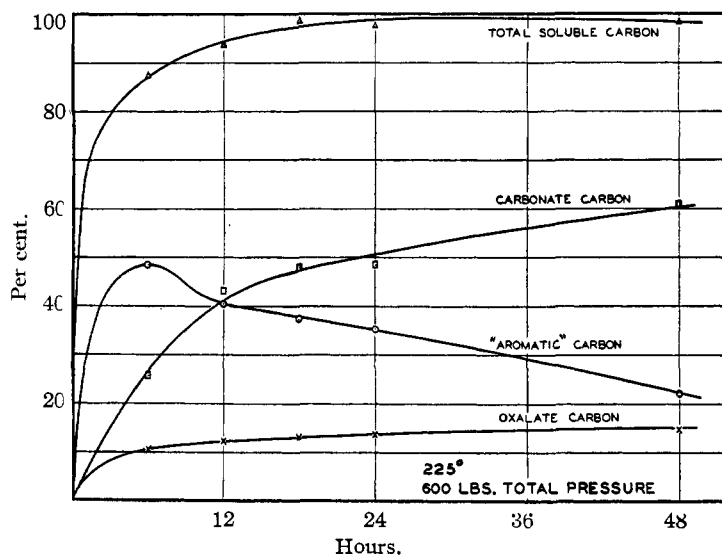

Fig. 1.

investigated and the 500° coke can be oxidized completely to water-soluble products. The 700° coke, the high temperature coke, and the pitch are incompletely oxidized and the soluble products consist largely of carbonic acid. In the case of graphite, carbonic acid is the only soluble acid present in significant amounts. It has been

TABLE II

OXIDATIONS OF VARIOUS CARBONACEOUS MATERIALS[a]

	Total soluble carbon, %	Carbonate carbon, %	Oxalate carbon, %	"Aromatic" carbon, %	Carbonate / Soluble C	Carbonate carbon, g.	"Aromatic" carbon, g.
Illinois No. 6	100.2	58.1	9.33	32.8	0.58	20.3	11.4
Pittsburgh	98.8	49.7	12.90	36.2	.50	19.2	14.0
High Splint	102.2	57.7	8.03	36.5	.56	22.7	14.3
Pocahontas No. 3	100.6	57.0	4.50	39.1	.52	24.2	16.6
Anthracite	100.5	59.3	3.40	37.8	.59	24.5	15.6
500° coke	99.5	61.3	5.20	33.0	.62	24.5	13.2
700° coke	85.5	59.8	4.15	21.5	.71	24.6	8.2
High temp. coke	72.7	63.1	2.90	6.7	.87	25.6	2.7
Graphite (40 g.)	62.1	57.9	1.90	2.3	.92	28.8	1.1
Pitch (30 g.)	80.5	44.0	6.45	30.0	.55	12.0	8.2

[a] The sources of these materials are given in ref. (4). Oxidized for twenty-four hours at 250°; estimated oxygen partial pressure 137 lb. (9 atm.); −200-mesh, 50-g. sample, except where noted.

shown[4] that graphite on oxidation with nitric acid and alkaline permanganate furnishes mellitic and carbonic acids exclusively and studies on the behavior of mellitic acid in the bomb, under the same conditions which were used for the oxidation of graphite, showed that 97% of the carbon of a 25-g. sample was converted to carbon dioxide in twenty-four hours.

The method used for isolation of the individual acids, barium salt fractionation, followed by esterification and vacuum fractionation of the esters, was essentially the same as applied to the acids prepared by the action of alkaline permanganate on the Pittsburgh Seam coal. As in that work, it was found that a significant fraction of the methyl esters will not distil under conditions where the least volatile of the esters of the benzene carboxylic acids, the hexamethyl mellitate, distils rapidly.

ing in rank from an Illinois bituminous coal to artificial graphite, have been oxidized to simple acids by oxygen at elevated pressures, at temperatures of 200 to 250°, in the presence of aqueous alkali. With the lower rank materials a significant fraction of the carbon can be recovered as simple organic acids. From the materials of rank higher than a low temperature coke, decreasing recoveries of organic acids are obtained, and with graphite the soluble products consist almost exclusively of carbonic acid. The effects of temperature, time, oxygen partial pressure, catalysts, surface, and nature of the alkali on the course of the oxidation of a Pittsburgh Seam coal have been studied. Oxalic, trimellitic, pyromellitic, prehnitic, and terephthalic acids have been identified. A significant fraction of the acids forms non-distillable methyl esters, indicating the presence of structures more complex than the benzenecarboxylic acids.

Summary

Several types of carbonaceous materials, rang-

The Stereochemistry of Complex Inorganic Compounds. IV. The Introduction of Racemic Organic Molecules into Some Optically Active Complex Ions of Cobalt and Chromium[1]

BY JOHN C. BAILAR, JR., C. A. STIEGMAN, J. H. BALTHIS, JR., AND E. H. HUFFMAN

The penetration of a molecule of an optically active diamine, dibasic acid or amino acid into an optically active complex of the type $[MA_2X_2]^2$ offers several stereochemical possibilities. In some cases, all of the possible stereoisomers of the reaction product are realized. Thus, levo-1,2-trans-diaminocyclopentane reacts with racemic dichlorodiethylenediaminocobaltic chloride, [Coen₂Cl₂]Cl, to give both the D and the L forms of [Coen₂-l-Cptdn]Cl₃.[3]

Sometimes, however, the entrance of the new group takes place only in certain preferred ways; this gives part, but not all, of the possible stereo-

isomers. The reaction of racemic diaminocyclopentane with racemic dichlorodiethylenediaminocobaltic chloride gives only two of the four possible isomers; each of the antipodes of the [Coen₂Cl₂]Cl reacts preferentially with one form of the diaminocyclopentane. This effect is certainly not absolute, and may be very slight. It suggests, however, that the reaction between an optically active complex and an *excess* of a racemic coördinating substance might be selective to some extent—that is, that the complex might accept one antipode of the coördinating material preferentially, thus effecting a resolution. Some studies of this possibility are reported here. The results indicate that the preference of the complex for one antipode over the other is slight in these reactions.

The reactions studied were those of propylenediamine and alanine with cobalt complexes containing two molecules of levo-propylenediamine, that of leucine with dichlorodiethylenediaminocobaltic chloride, and that of phenylalanine with

(1) Abstracted from portions of the doctorate theses of C. A. Stiegman, J. H. Balthis, Jr., and E. H. Huffman.

(2) The following symbols are used in this paper: M = metal ion, A = coördinating group occupying two corners of the octahedron, X = an acido group occupying one corner, en = ethylenediamine, pn = propylenediamine, Cptdn = 1,2-trans-diaminocyclopentane, Hala = alanine, Hleu = leucine. D and L refer to the dextro and levo configurations of the complex ion, and d and l to the configurations of the "A" groups.

(3) Jaeger and Blumenthal, Z. anorg. allgem. Chem., 175, 161–230 (1928).