phous carbon, it has been suggested that the nuclei of these acids contain groups of amorphous carbon.[11,5] A similar proposal was made by Wieluch in 1927,[12] but unfortunately Wieluch confused the issue by attempting to construct simple carbon compounds using both the normal (covalent) bond and a bond characteristic of the forces holding the graphite layers together in the crystal which he called the "inorganic" bond. At the same time he discarded the aromatic structure proposed for graphite[13] and considered that a hydroaromatic structure was better, again assuming that the "inorganic" bond between layers constituted the fourth bond of the hydroaromatic structure.

Fuchs immediately raised objections to these ideas,[14] but the fundamental concept that this class of carbonaceous compounds contains carbon as such in the nuclei of their molecules appears to be sound on the basis of their observed properties, regardless of whether an aromatic structure represents accurately the true structure of carbon or not. The presence of carbon in these molecules would account for their dark color, infusibility, pyrolytic behavior, oxidation to benzene carboxylic acids and their low molecular weight in catechol, assuming that the carbon layers are highly dissociated by this solvent. The larger molecular weights observed in other solvents would be explained simply by less dissociation of the layers. Trapping of solvent molecules between the layers would also account for the great tenacity with which many solvents are retained, especially water. Finally, the remarkable uniformity which the humic acid preparations appear to have, such as the inability of solvents to separate them into fractions with different properties or composition,[5] would be explained on the basis that the random association of carbon layers was not disturbed by the solvent used (acetone).

Without doubt the carbon structure must be modified considerably by the presence of other atoms, particularly oxygen, nitrogen, sulfur and small quantities of inorganic matter, which is removed with difficulty. However, an essentially carbon structure seems to account for the properties of the nuclei of the humic acid-like products obtained from bituminous coal. On the same basis, the nuclei of coal molecules, pitches and related carbonaceous products appear to have the same type of structure.

Summary

The pyrolysis of the humic acid-like oxidation products from a bituminous coal converted about 13% of the carbon to volatile substances, carbon dioxide, monoxide and methane. The amount of carbon dioxide corresponded to an equivalent weight of 242. Neither fusion nor the evolution of volatile aromatic fragments was observed. The remaining 87% of the carbon was non-volatile at 950° and approached pure carbon in composition.

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(11) Polansky, Kinney and Gauger, The Pennsylvania State College, Mineral Industries Experiment Station, Bulletin 44, p. 56 (1946).

(12) Wieluch, *Z. Oberschles. Berg- u. Hüttenmann. Ver. Katowice*, **66**, 2 (1927); **67**, 149 (1928); Wieluch's contributions were called to our attention by Drs. H. C. Howard and H. H. Lowry.

(13) von Stieger, *Ber.*, **53**, 666 (1920).

(14) Fuchs, *Brennstoff-Chem.*, **8**, 173 (1927).

[CONTRIBUTION FROM THE DIVISION OF FUEL TECHNOLOGY, THE PENNSYLVANIA STATE COLLEGE]

Ozonization of Humic Acids Prepared from Oxidized Bituminous Coal

BY MOFIZUD-DIN AHMED[1] AND CORLISS R. KINNEY[*]

On the assumption that the nuclei of the humic acid-like oxidation products of bituminous coal contain amorphous carbon, the humic acids described in the preceding paper have been subjected to ozonization. For comparison, carbon black, graphite oxide and the brown, water-soluble acids obtained from carbon black by hot nitric acid oxidation were ozonized under the same conditions.

Experimental

Procedure.—Ozone was prepared in apparatus described by Church, Whitmore and McGrew,[2] which had been further improved by replacing the mercury cups with spherical ground joints. Oxygen was passed through the ozonizer at a constant rate of 15 l. per hour and, since an alkaline solution was to be used in most experiments, the concentration of ozone was determined after passing through 150 ml. of 4% potassium hydroxide. The concentration was found to be quite constant at 0.056 g. (±0.001) per l. Samples weighing about 2 g. were dissolved or suspended in 150 ml. of 4% alkali. In certain cases where the substance was unreactive, 1-g. samples were used.

Ozonization of Humic Acids.—The absorption of ozone by the humic acids (described in the preceding paper) was measured and the results are shown in Fig. 1. The effect on the humic acids is shown in Fig. 2 in which the percentages were calculated on the basis of the carbon present in the sample. The "unreacted" acids were considered to be those acids obtained by acidifying an aliquot part of the alkaline solution after ozonization. Carbon dioxide was determined on the acidified aliquot by carrying the carbon dioxide into excess standard barium hydroxide with a stream of carbon dioxide-free nitrogen and titrating the excess with standard oxalic acid. Carbon dioxide blanks were run on the original alkaline solution. The quantity of steam volatile acids, apparently entirely acetic acid and calculated as such, was determined from the amount of standard alkali required for neutralization. After steam

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[*] Harvard University Ph.D. 1925.

(1) Present address: University of Dacca, Dacca, E. Pakistan.

(2) Church, Whitmore and McGrew, THIS JOURNAL, **56**, 176 (1934).

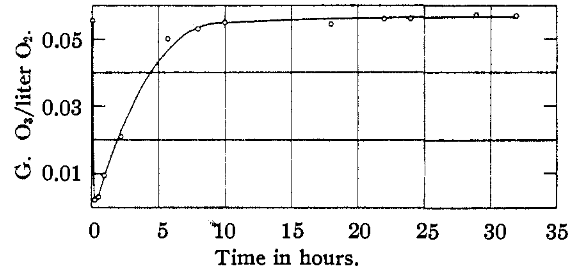

Fig. 1.—Absorption of ozone by humic acids.

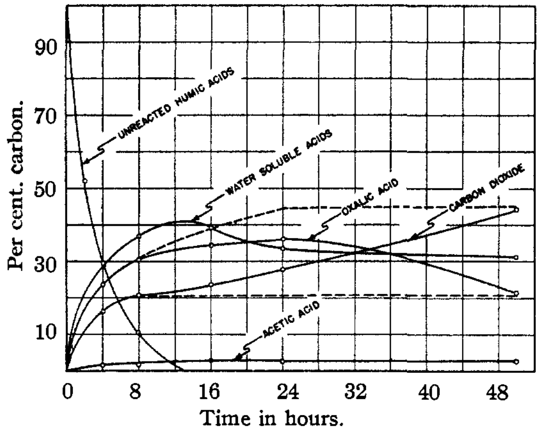

Fig. 2.—Yields of ozonization products.

distillation, oxalic acid was determined on the residue by precipitation as calcium oxalate and titration with acid permanganate. The percentages of the remaining water-soluble acids, obtained by difference, are given in Fig. 2. Tests made for carbonyl compounds with 2,4-dinitrophenylhydrazine were negative.

A 1.0849-g. sample of the humic acids was also ozonized in aqueous suspension. The ozonized oxygen stream from the humic acids was then led through alkali to recover carbon dioxide. After twenty-eight and one-half hours, 0.1406 g. remained unattacked. This was ground with water, returned to the original solution and ozonized for an additional eleven hours. At this time only 0.0065 g. of grayish-black residue remained which was less than the ash content of the starting material. The percentages of carbon in the sample converted to carbon dioxide were 46.6%, acetic acid 0.8%, oxalic acid 17.4%, and the balance, water-soluble, ozone-resistant acids, 33.1%.

A 0.7061-g. sample of 950°-carbonized humic acids was ozonized for twenty-four hours in alkaline suspension. Only 0.3% of the carbon was converted to carbon dioxide and no oxalic acid was detected. The unattacked residue amounted to 94.8%.

Action of Ozone on Related Substances.—Oxalic acid, weighing 2.07 g., was ozonized for twelve hours. The amount of carbon dioxide formed was 0.63 g. and the weight of oxalic acid unchanged was 1.35 g.

Phthalic acid was ozonized for twelve hours and from 2.014 g. the yields of carbon dioxide and oxalic acid were 0.111 g. and 0.0104 g. or 2.6 and 0.2%, respectively.

Graphite oxide was prepared by Staudenmaier's method.[3] The product, after drying, contained 18.6% moisture and, on the moisture-free basis, gave the following analysis. *Anal.* Found: C, 63.5; H, 0.9; O, 35.6. Although this analysis approximated that of the humic acids except for hydrogen, the product was insoluble in dilute alkali and had a grayish-black, instead of a brownish-black, color. A 1.0054-g. sample was suspended in 150 ml. of 4% potassium hydroxide and ozonized for twenty-four hours. At the end of this time, 0.5% of the carbon had been converted to carbon dioxide and none to oxalic acid. The oxide was recovered unchanged to the extent of 95.6%.

Carbon black,[4] heated to 950° for seven minutes to remove 17% of adsorbed gases, was suspended in alkali and ozonized for twenty-four hours. Only 0.2% was converted to carbon dioxide and no oxalic acid was detected.

An attempt was made to prepare humic acid-like oxidation products by the method used to prepare the humic acids from coal; but, although a brown color was obtained with dilute alkali, no precipitated acids were obtained on acidification. Consequently, 100 g. of carbon black was boiled with 400 ml. of concentrated nitric acid, to which a little fuming nitric acid was added occasionally, for fifteen days. The nitric acid was then removed by distillation and the residue extracted with 300 ml. of hot water. The water-insoluble residue weighed 1.2 g. and the water-soluble acids 28.8 g. The moisture content of the dried acids was 1.7%. The following analysis, calculated on a moisture-free basis and assuming the balance was oxygen, was obtained. *Anal.* Found: C, 33.7; H, 1.5; N, 1.8; O, 63.0.

A 2.0213-g. sample of the acids was ozonized in the usual way in alkaline solution. The brown color was quickly destroyed. The percentages of the carbon converted to carbon dioxide, acetic acid and oxalic acid were 6.6, 1.3 and 5.0%, respectively. The remaining acids, 87.1%, appeared to be similar to the ozone-resistant acids from the humic acids.

Pyrenequinone was prepared from pyrene by the method of Bamberger and Philip.[5] A 0.8693-g. sample of the recrystallized product, melting at 283–285° and consisting of a mixture of the 3,8- and 3,10-quinones, was ozonized for thirty-three hours in dilute alkali. Positive tests for carbonate and oxalate were obtained, but negative tests for carbonyl derivatives were observed with 2,4-dinitrophenylhydrazine. Oxalic acid was precipitated as calcium oxalate and the filtrate evaporated to dryness. The residue was redissolved in a little dilute hydrochloric acid and again evaporated to dryness. The product was extracted with acetone in a Soxhlet, yielding 0.56 g. of crystalline acid which softened at 225° and melted at 236° with decomposition. The expected acid, 1,2,3,4-benzenetetracarboxylic acid, has reported melting points of 238 and 241° with decomposition. For identification, the methyl ester was made by the silver salt–methyl iodide method and, after recrystallization from methanol, melted at 134°.

Discussion

The humic acids absorbed almost all of the ozone passed into the solution during the first half-hour, as shown in Fig. 1. Following the initial rapid absorption, the rate decreased until at eight hours relatively little was being absorbed. However, the reaction continued as is shown in Fig. 2, because the per cent. of "unreacted" humic acids fell from about 10% at eight hours to zero in something less than sixteen hours. The yields of oxalic and water-soluble acids rose to maxima at about twenty-four and twelve hours, respectively, while the amount of carbon dioxide continued to rise to fifty hours. Since it was found that oxalic acid was oxidized to carbon dioxide by ozone under the conditions used, it is obvious that the observed yield of oxalic acid was not the total amount produced. Assuming that the observed rate of oxidation of oxalic acid (31.1% in twelve hours) also occurred during the ozonization of the humic acids, the

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[3] Staudenmaier, *Ber.*, **31**, 1481 (1898); see also Hamdi, *Kolloid-Beihefte*, **54**, 554 (1943).

[4] Carbolac 1 supplied by Godfrey L. Cabot, Inc., Boston, Mass.

[5] Bamberger and Philip, *Ann.*, **240**, 165 (1887).

percentage of oxalic acid that would have been obtained, had no oxidation occurred, was calculated and is indicated in Fig. 2 by the dashed line. The calculated yield of oxalic acid at twenty-four hours is 44.2% of the carbon and at fifty hours, 45.7%. On the same basis the estimated yield of carbon dioxide would remain nearly constant at about 20%. It will also be observed that the yield of water-soluble, ozone-resistant acids became nearly constant with about a 32% conversion of the carbon. Considering the demonstrated resistance of phthalic acid to ozonization under the conditions used and the fact that benzene carboxylic acids have been isolated from other extensive oxidations of bituminous coals, it appears likely that benzene carboxylic acids are present in the ozone-resistant acids. Finally a small but constant amount of acetic acid was formed.

These results would be expected from a polynucleararomatic structure and, experimentally, pyrenequinone was found to yield carbon dioxide, oxalic acid and 1,2,3,4-benzenetetracarboxylic acid. However, the appearance of about 20% of the carbon of the humic acids in the form of carbon dioxide in the first eight hours and apparently none thereafter, except from the oxidation of the oxalic acid present, would not be expected from a polynuclear aromatic structure. Carbon dioxide was obtained from carbon black and the humic acids carbonized to 950°, but only traces in twenty-four hours and no oxalic acid. This resistance to ozonization may be considered to be proof that the humic acids contain no amorphous carbon, but there is also the possibility that the marked insolubility of these carbons was the cause of their unreactivity. Consequently, the humic acids suspended in water in which they are quite insoluble, were ozonized and, although the rate was much slower, the end-products were the same. Also, graphite oxide was ozonized, but was insoluble and unreactive like the carbons. Finally, a sample of the dark brown, water-soluble acids, obtained by oxidizing carbon black with boiling nitric acid, was ozonized. In this case, the brown color was readily destroyed and carbon dioxide, oxalic acid, and ozone-resistant acids were obtained.

Assuming that the brown color of the water-soluble acids was due to unoxidized islands of amorphous carbon, it appears that ozone is capable of attacking such carbon atoms under favorable conditions. Since the structure of amorphous carbon appears to be closely related to the polynuclear aromatic structure,[6] the identification of carbon dioxide, oxalic acid and benzenecarboxylic acids was not surprising. Furthermore, the similarity in behavior of the humic acids and the brown, carbon-black acids toward ozone suggests the possibility that the two acids have similar structures. Whether these are basically aromatic structures or the somewhat more complex structure of amorphous carbon cannot be decided definitely on the basis of the results obtained.

Summary

Both carbonic and oxalic acids appear to be primary products in the ozonization of the humic acids and account for about 65% of the carbon. Practically all of the remaining carbon was converted to almost colorless, water-soluble, ozone-resistant acids. Although carbon black and graphite oxide did not react with ozone appreciably, the brown, water-soluble acids prepared by oxidizing carbon black with nitric acid did react like the humic acids, giving carbonic, oxalic and ozone-resistant acids.

[6] von Steiger, *Ber.*, **53**, 666 (1920).

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1,3-Anhydro-2,4-methylene-D,L-xylitol and Related Compounds

BY RAYMOND M. HANN,[1] NELSON K. RICHTMYER,* HARRY W. DIEHL AND C. S. HUDSON†

An earlier paper[2] from this Laboratory has described the preparation and properties of 2,4:3,5-dimethylene-D,L-xylitol and some of its derivatives, together with its transformation to 2,4-methylenexylitol (a *meso* form) and some of its derivatives. The present communication will describe the results of further research in these two series of compounds.

In the first set of reactions the 2,4-methylenexylitol, upon treatment with benzaldehyde and zinc chloride, yielded a mixed acetal which has been named, in accordance with the system used in the earlier paper, 2,4-methylene-3,5-benzylidene-D,L-xylitol. The free hydroxyl group was readily tosylated, and the tosyloxy group replaced in succession by an iodine and then a hydrogen atom. Subsequent removal of the benzylidene group by acid hydrolysis produced the expected 1-desoxy-2,4-methylene-D,L-xylitol as prisms melting at 52–53°. This value is 103°

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* Harvard University Ph.D. 1927.

† Editorial Board 1938-1944.

[1] Deceased, April 30, 1949.

[2] R. M. Hann, A. T. Ness and C. S. Hudson, THIS JOURNAL, **66**, 670 (1944).