Believing that the steric requirements for such a configuration could be met only under conditions of severe strain, we have submitted the proposed structure to an indirect empirical test.

In trimethylacetic acid the methyl group of acetic acid is replaced by the much more bulky *t*-butyl group; and the formation of the postulated tetramer would be considerably more difficult, if not impossible, in this instance. If it may be assumed that the higher polymerization of the paraffin acids follows the same general course, and if we accept Ritter and Simons' suggestion that the lamellar tetramer is the predominant higher polymeric species, then trimethylacetic acid ought to display a sharply reduced tendency toward higher polymerization, as compared with acetic acid. Actually, in a comparison using the same experimental and mathematical procedures, higher polymerization was found to be of the same order of magnitude in both instances and, if anything, trimethylacetic acid formed higher polymers more readily than acetic acid, under comparable conditions. This observation inclines us to view with considerable scepticism the postulated tetramer and, with it, one of the main arguments advanced for a tetrameric as against a trimeric species.

The structure of the trimer cannot now be decided with any degree of certainty. The heats of polymerization per mole of monomer indicate that there are three hydrogen bonds in the trimer, each of which is at least as strong as a dimer bond. Furthermore, the higher polymer structure whatsoever does not appear to suffer in stability from the presence of large hydrocarbon substituents to the paraffin acids: on the basis of the results for acetic and trimethylacetic acids, the *t*-butyl group may even enhance the higher association. This is in harmony with the observation that in formic acid, which is structurally unique in that there is no hydrocarbon substituent to the carboxyl group, a stable higher polymeric species does not appear to exist.

A trimer structure meeting these requirements might be a non-planar 12-membered ring with three hydrogen bonds. Realistic molecular models of these polymeric configurations are difficult to construct because of their effective requirement for divalent hydrogen, trivalent oxygen and very short O–H distances. To the extent that we have been able to realize these conditions in our models, we find that the trimer is as easily constructed as, and under no more strain than, the dimer.

Summary

A new method for the precise determination of the vapor densities has been applied in a study of the vapors of acetic and trimethylacetic acids. An accurate evaluation of the thermodynamics of the polymerization processes in these vapors has been secured. There is strong evidence for the formation of stable polymeric forms higher than the dimer—most notably, a trimeric species.

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

Pyrolysis of Humic Acids Prepared from Oxidized Bituminous Coal

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

Pyrolysis of the humic acid-like substances obtained from bituminous coal by oxidation has been studied particularly in connection with the constitution of these acids and indirectly the constitution of the coal from which they were made. Preliminary tests were made to isolate, if possible, any volatile aromatic fragments which might be expected if the humic acids have an aromatic structure[2] and an average molecular weight of about 250.[3] However, no aromatic substances or tar were obtained and consequently no provision was necessary for analyzing for such products. The volatile substances identified were water, carbon dioxide and monoxide, ammonia, hydrogen, methane, nitrogen and oxides of nitrogen. No diminution in the gas volume was observed with fuming sulfuric acid, indicating an absence of unsaturated hydrocarbons as well as aromatics. Likewise, no hydrogen sulfide, sulfur dioxide, nitric oxide or oxygen was detected.

Experimental

The humic acids used were a part of a sample prepared previously for other studies,[4,5] and were stored under nitrogen. Analyses of the coal, the humic acids and the pyrolytic residue at 950° are given in Table I.

TABLE I

ANALYSES, MOISTURE-FREE BASIS

	Raw coal, %	Humic acids, %	Residue at 950°, %
Ash	7.7	1.5	3.3
C	79.5	62.4	90.4
H	5.0	2.8	0.7
N	1.4	4.5	2.2
S	1.8	0.5	0.3
O	4.6	29.3	3.1

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* Harvard University Ph.D. 1925.

[1] Present address: University of Dacca, Dacca, E. Pakistan.

[2] Bone, Parsons and Groocock, *Proc. Roy. Soc.* (*London*), **A148**, 521 (1935).

[3] Smith and Howard, THIS JOURNAL, **57**, 512 (1935); Belcher, *J. Soc. Chem. Ind.*, **67**, 213 (1948).

[4] Charmbury, Eckerd, LaTorre and Kinney, THIS JOURNAL, **67**, 625 (1945).

[5] Herbert, Charmbury and Kinney, *Fuel*, **27**, 168 (1948).

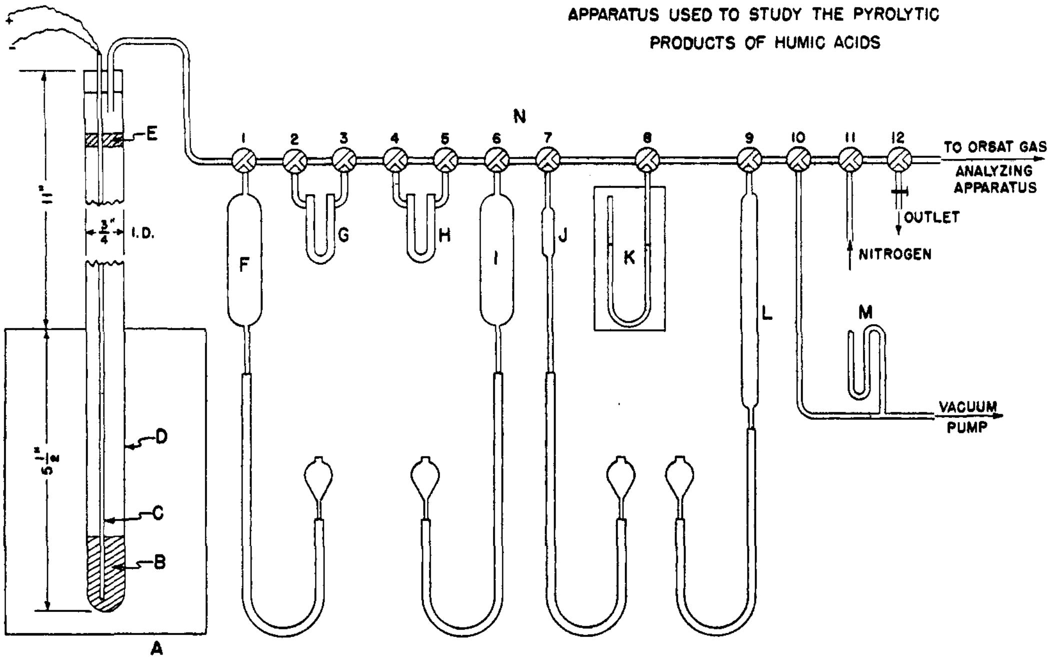

Fig. 1.—A, Hoskins furnace; B, sample; C, pyrometer; D, silica tube; E, glass wool plug; F, gas pipet; G, KOH tube: H, $CaCl_2$ tube; I, J, gas pipets; K, M, manometers; L, gas buret; N, manifold.

The apparatus used is shown diagrammatically in Fig. 1. The sample of humic acids, 3.9630 g., was placed in Tube D and heated in stages of 100° from 150 to 950°. Heating at each stage was continued until less than 0.5 ml. of gas was evolved per hour. This required from eight to twelve hours. The quantities of products were determined as follows. Water, carbon dioxide, oxides of nitrogen and nitric acid were absorbed on solid potassium hydroxide in tube G and the increase in weight obtained. After dissolving the caustic in water, the carbon dioxide was determined on an aliquot part by acidifying, distilling the carbon dioxide into excess standard barium hydroxide and titrating the excess with standard oxalic acid. A blank carbonate determination was also made on the original sample of caustic and used in calculating the quantities of carbon dioxide produced.

The percentages of nitrogen oxides and nitric acid were found as follows. Total nitrogen was determined on an aliquot sample by the standard Devarda method. The per cent. of nitrite was found by using Lunge and Ambler's permanganate method. From the total nitrogen and the amount of nitrite, the per cent. of nitrate was calculated and, from the quantities of nitrite and nitrate and using the following equations, the percentages of nitrogen trioxide, tetroxide and nitric acid were calculated.

$$N_2O_3 + 2KOH = 2KNO_2 + H_2O \quad (1)$$

$$N_2O_4 + 2KOH = KNO_2 + KNO_3 + H_2O \quad (2)$$

$$2HNO_3 + 2KOH = 2KNO_3 + 2H_2O \quad (3)$$

Since both nitrite and nitrate were formed but in unequal amounts, it was assumed that, when there was an excess of nitrite over nitrate, nitrogen trioxide and tetroxide were present and conversely, when an excess of nitrate was produced, that the products were the tetroxide and nitric acid.

Water evolved from the humic acids was calculated as the difference between the total increase in weight of the potassium hydroxide tube G and the calculated weights of carbon dioxide, nitrogen oxides and nitric acid.

Ammonia was collected and weighed on calcium chloride in tube H. The remaining gases were measured using buret L at atmospheric pressure and then analyzed in standard Orsat equipment not shown in the diagram. The gases were manipulated by means of leveling bulbs attached to pipets F and I. At the beginning of the run, decomposition tube D and the manifold N were filled with a known quantity of pure dry nitrogen. The remainder of the apparatus was filled with mercury. This amount of nitrogen was taken into account when calculating the quantities of products. The gas unaccounted for at the end of each analysis was reported as nitrogen.

The data obtained are compiled in Table II.

TABLE II

PYROLYTIC PRODUCTS FROM HUMIC ACIDS

Grams/100 Grams of Humic Acids Dried at 110°

Temp., °C.	H_2O	CO_2	N_2O_3	NO_2	NH_3	H_2	CO	CH_4[b]	N_2
110–150	2.9	1.9	...	0.2[a]	Residual gas was too small to be analyzed				
150–250	3.7	5.1	0.8	.7	...	...	0.1	...	...
250–350	2.6	8.8	.1	.3	...	...	.1	...	...
350–450	2.6	3.6	...	...	...	...	.1	...	0.2
450–550	1.3	0.4	...	...	0.2	...	.2	0.1	.4
550–650	..	.2	...	...	.3	0.2	.5	.8	.7
650–750	..	.1	...	...	.1	.4	.4	.4	.3
750–850	..	..	...	...	.1	.4	.4	.2	.1
850–950	..	..	...	...	...	.2	.3	...	.1
Total	13.1	20.1	0.9	1.2	0.7	1.2	2.1	1.5	1.8

[a] Plus 0.2 g. of nitric acid. [b] (C_nH_{2n+2}).

Discussion

Water was evolved continuously up to 750° (Table II), consequently it is impossible to distinguish by thermal means alone water of decomposition from sorbed water. However, the appearance of nitric acid, nitrogen tetroxide and carbon dioxide in the 110–150° range indicates that decomposition began at this temperature. The appearance of the oxides of nitrogen also suggests that further oxidation was possible and that a part of the carbon dioxide and water formed at this temperature may have resulted from oxidation. The extent of this is suggested by the quantity of lower oxides of nitrogen produced. From these data it seems probable that the water and carbon dioxide evolved below 150° resulted from oxidation reactions in addition to the elimination of some sorbed water. The nitric acid evolved may be either sorbed or combined chemically.

The maximum evolution of carbon dioxide occurred at 250–350° and over 98% was evolved below 550°. Since this is the normal temperature range at which decarboxylation occurs, it seems probable that most of this carbon dioxide came from carboxyl groups. On this assumption, the equivalent weight of the humic acids may be calculated to be 242. This compares favorably with an experimental value of 241 obtained by electrometric titration. Fuchs and Sandhoff[6] obtained 235 by the same method on a similar preparation, 240 from the potassium content of the potassium salt and 284 from the maximum methoxyl content of 10.9% obtained on methylation. On alkaline hydrolysis of the methylated acids, the methoxyl content decreased to 5.2%. Fuchs and Sandhoff considered that the latter was phenolic methoxyl and that a part of the acidity of these humic acids was due to phenolic groups. Since it is difficult to account for the evolution of such large amounts of carbon dioxide from any other structure than carboxyl and since the use of hot concentrated nitric acid should not favor the formation of phenolic groups, it seems likely that the acidity was due entirely to carboxyl groups. In this case it would be necessary to assume that either Fuchs and Sandhoff's methylation or hydrolysis was incomplete.

The maximum evolution of water occurred between 150 and 250°. Over 99% was evolved below 550°. The ease of eliminating a considerable part of the water at relatively low temperatures suggests the presence of a large number of alcoholic hydroxyl groups. However, Juettner, Smith and Howard[7] have reported only 2.2% hydroxyl oxygen by indirect methods. Direct acylation appears to give negative results.[8] Consequently, it seems that the main sources of the water are the unreactive ether linkages which are believed to be present.[7]

In addition to water, carbon dioxide and oxides of nitrogen, relatively small amounts of ammonia, hydrogen, carbon monoxide, methane and nitrogen were split out as shown in Table II.

The yield of methane calculated from the data was 0.098 mole per 100 g. of humic acids. The yield of acetic acid obtained by dichromate–nitric acid oxidation[9] of these acids was found to be 0.107 mole per 100 g. This correlation appears to show the presence of methyl groups in the humic acids and that the source of methane on carbonization is the methyl group. The original coal[9] gave 0.264 mole of acetic acid from the amount of coal (112 g.) required to yield 100 g. of humic acids. Consequently, nearly 60% of the acetic acid yielding structures was oxidized away during the conversion of the coal to the humic acids, while on carbonizing the coal at 550° 86% of these structures was destroyed. On the other hand, carbonizing the humic acids to 550° gave only 4% of the total methane evolved to 950°, the remainder being evolved above 550°. This shows that the methyl groups remaining in the humic acids are relatively stable thermally as well as resistant to oxidation by hot nitric acid. Based on the yields of methane and acetic acid, the empirical weight containing one methyl group is about 1000. Since this appears to be too large to be the molecular weight, it may be assumed that not all molecules contain methyl groups.

The distribution of the chemical elements in the products of pyrolysis is given in Table III.

TABLE III

DISTRIBUTION OF ELEMENTS IN PRODUCTS

	% of total element in products			
Product	C	H	O	N, (Kjeldahl)
H_2O		52.5	40.1	
CO_2	8.9		49.9	
CO	1.5		4.2	
CH_4	1.9	13.8		
NH_3		4.7		12.5
H_2		43.8		
N_xO_y			5.3	16.1
N_2				39.2
Residue	84.1	1.5	5.9	28.0
Totals	96.4	116.3	105.4	95.8

These data show that the accuracy of the analyses given in Table II is of the order of about 5–10%. Nevertheless, it is apparent that over 87% of the carbon, based on that accounted for, remained in the residue at 950° while only 13% was split out in the form of single carbon atom products. Of the hydrogen, about 45% was split out as water, while 54% was eliminated as methane, ammonia and free hydrogen and 1% remained in the carbon residue. In the case of oxygen nearly all appeared as carbon dioxide and water, only 4% appeared as carbon monoxide and 5% remained in the residue. Of the nitrogen, nearly 30% remained in the residue, the remainder being evolved as nitrogen oxides, ammonia and free nitrogen.

The pyrolytic behavior of the humic acids is highly significant in respect to their structure. In some ways their behavior is similar to that of certain large molecules such as Bakelite, but their apparent solubility in a variety of organic solvents,[10] and low apparent molecular weight, requires some other explanation. Because many of their properties are similar to those of amor-

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(6) Fuchs and Sandhoff, *Fuel*, **19**, 45, 69 (1940).

(7) Juettner, Smith and Howard, THIS JOURNAL, **57**, 2322 (1935).

(8) Unpublished work.

(9) Kinney, THIS JOURNAL, **69**, 284 (1947).

(10) Polansky and Kinney, *Ind. Eng. Chem.*, **39**, 925 (1947).

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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[1] Present address: University of Dacca, Dacca, E. Pakistan.

[2] Church, Whitmore and McGrew, This Journal, **56**, 176 (1934).