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The Action of Nitric Acid on a Bituminous Coal

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Bituminous coals can be converted almost completely into soluble products by treatment with nitric acid, under such conditions that great internal structural changes probably do not occur. A study of the character of the reaction and the nature of the products formed is of importance from the standpoint of our knowledge of the nature of these coals. Previous work[1] has been limited almost entirely to a study of the action of nitric acid on lignites and brown coals.

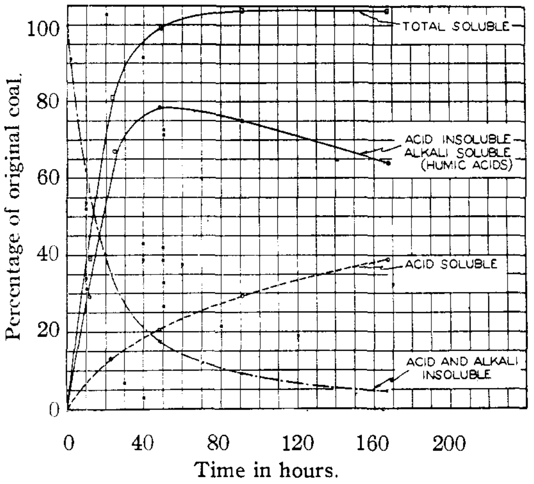

Fig. 1.—Yields of products of the reaction of 1 *N* nitric acid on coal as a function of time.

A preliminary study of the effect of acid concentration on the yield of soluble products, as a function of time showed that even with concentrations as low as one normal, five days' refluxing resulted in conversion of all but a small fraction of the original weight of the Pittsburgh seam coal used[2] into acid or alkali soluble products. At the end of an equal time with 0.1 *N* acid a residue of insoluble material of approximately 46% remained. Since a concentration of one normal appeared to be near the lower limit at which reasonably rapid reaction rates could be obtained, this concentration was chosen for detailed investigation.

Nature of the Reaction

The rates of formation of the products of the reaction, other than gaseous, are shown in Fig. 1. Acid-soluble products increase continuously with time, acid-insoluble, alkali-soluble, the so-called regenerated "humic acids," reach a maximum at about forty-eight hours and then decrease, presumably due to the fact that they are transformed to acid solubles more rapidly than they are formed from the coal. The total soluble material remains quite constant after the initial stages of the reaction are complete, since the principal reaction in the later stages is transformation of humic acids to soluble acids, with apparently little weight change, the decrease in weight due to loss of carbon dioxide during the transformation being approximately balanced by the increased oxygen content of the soluble acids formed.

The distribution of carbon and nitrogen in the oxidation products in a five- and a fifty-two-day oxidation is shown in Table I. It is evident that the reaction is chiefly an oxidation, since such a large fraction of the nitrogen in the nitric acid consumed appears as nitric oxide. The nitrogen in the organic acids decreases with time. Such behavior would be expected if a part of the nitrogen is held at first as isonitroso groups, as Fuchs[3] has suggested, which are removed by hydrolysis during the later stages of the oxidation. Transformation of the carbon of the humic acids to soluble acids with concomitant formation of carbon dioxide as the oxidation proceeds is also shown.

Table I

Distribution of Carbon and Nitrogen in Reaction Products

	5-Day oxidation, %		52-Day oxidation, %	
	C	N	C	N
Humic acids	67.6	9.2	15.0	0.8
Soluble acids	9.2	4.5	33.8	3.1
Carbonic acid	14.4	. .	36.2	. . .
Nitric oxide		82.5		102.0

The work on carbon balances was necessarily done in a closed system. In other oxidations carried out with free access of air to the system it was found that rates of formation of the various

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[1] Schellenberg, *Brennstoff-Chem.*, **2**, 386 (1921); Tropsch and Schellenberg, *Ges. Abhandl. Kenntnis Kohle*, **6**, 225 (1921); Strache-Lant, "Kohlenchemie," Akademische Verlagsgesellschaft, Leipzig, 1924, p. 308; Fuchs, *Brennstoff-Chem.*, **9**, 178 (1928); Fuchs and Stengel, *ibid.*, **10**, 303 (1929); *Ann.*, **478**, 267 (1930).

[2] Described in detail in *Bur. Mines, Tech. Paper*, 525 (1932).

[3] Fuchs, "Chemie der Kohle," Verlag Julius Springer, Berlin, 1931, p. 202.

products were approximately the same as in the absence of air, but determination of nitric acid consumed showed that only about one-fourth as much nitric acid was required. The lower oxides of nitrogen first formed in the reaction are evidently converted, in the presence of air, to nitric acid. This indicates the possibility of carrying out such an oxidation with air, using a relatively small amount of oxides of nitrogen as carrier.

Oxidations were also carried out on the residue from a 260° benzene pressure extraction of this coal[4] and on the "cokes" from its thermal decomposition in a molecular still.[5] Acid-soluble products and humic acids were obtained from the oxidation of the extraction residue as in the oxidation of the original coal. The rate of oxidation, however, was considerably greater, as can be seen by comparison with Table I, a five-day oxidation of the residue yielding 57% of the carbon as humic acids, 13.7% as soluble acids, and 22.2% as carbon dioxide. The reaction products from oxidation of the cokes were not examined in detail, but it was found that in the oxidation of cokes prepared up to about 440°, the yield of soluble products was the same as for the original coal within the limits of error in the analytical method. In Fig. 2, yields of soluble oxidation products from the cokes, determined by difference, gas evolution and tar recovered during the vacuum carbonization, have been plotted. Gas evolution is in terms of pressure in the system at a constant rate of evacuation. The strong initial gas evolution at approximately the same temperature at which the coke residue begins to show resistance to oxidation would seem to indicate some fundamental change in the "coal molecule" over this temperature interval. Tar formation, on the contrary, appears to be relatively independent of any critical range.

Nature of the Products

If the oxidation proceeds for only a few days the chief product is, of course, the dark brown, colloidal humic acids. These regenerated humic acids are similar in composition and general properties to those extracted directly from peat and brown coal. They contain carboxyl and hydroxyl groups, but the latter in definitely smaller proportions than has been reported for humic acids from other sources. For acids from typical German brown coals,[6] the ratio of hydroxyl to carboxyl is given as 1.2, 3.9 and 2.6; for acids[7] from an Italian lignite and a peat 0.87; for those[8] from an Ontario lignite, 2.0; and for acids[8] prepared from sucrose, 1.0. The corresponding figure for the acids from this coal is 0.3 to 0.4.

As in the case of humic acids from other sources,[9] only from a half to two-thirds of the oxygen in these acids can be accounted for in specific groups (see Table II); the balance probably is in ether linkages. The amount of this oxygen of unknown form corresponds approximately to the oxygen of the original coal, thus indicating the presence of a relatively stable oxygen-containing unit both in the coal and in the acids regenerated from it.

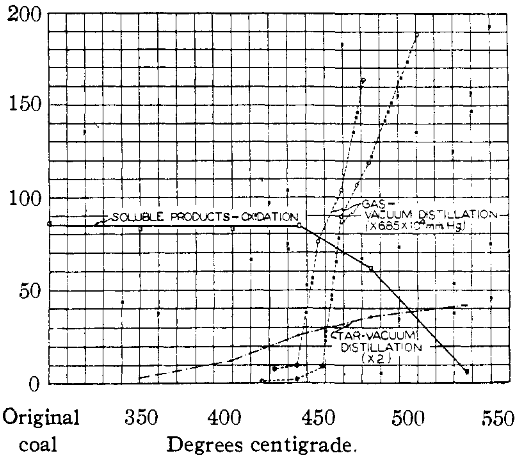

Fig. 2.—Yields of soluble oxidation products from the cokes, gas evolution and tar formation during vacuum pyrolysis as a function of temperature.

If the oxidation is carried on for several weeks, water-soluble, non-volatile acids to the extent of 35–40% of the weight of the coal can be recovered, forming a pale yellow to orange-red, amorphous, highly hygroscopic mass. These acids are lower in carbon and higher in oxygen than the humic acids, the average empirical composition for typical preparations, calculated on the basis of six carbon atoms, being $C_6H_{3.6}O_{4.8}$ for the former, and $C_6H_{3.8}O_{2.2}$ for the latter. A comparison of typical preparations of the two kinds of acids is made in Table II. The soluble acids are definitely smaller in molecular and equivalent weights, contain on the average only small amounts of

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[4] Asbury, *Ind. Eng. Chem.*, **26**, 1301 (1934).

[5] Juettner and Howard, *ibid.*, **26**, 1115 (1934).

[6] Fuchs, Ref. 3, p. 197.

[7] Ubaldini and Siniramed, *Ann. chim. appl.*, **23**, 585 (1933).

[8] Plunguian and Hibbert, THIS JOURNAL, **57**, 528 (1935).

[9] Fuchs, Ref. 3, p. 121.

hydroxyl, and nearly all the oxygen found by ultimate analysis can be accounted for in carboxyl groups. We have observed that whether the attack on coal be made by hydrogenation or oxidation, soluble, crystallizable or distillable products are obtained only when this non-determinable oxygen is largely eliminated, thus indicating the importance of the role played by this element in the coal polymer.

TABLE II

PROPERTIES OF HUMIC AND SOLUBLE ACIDS

	Humic acids	Soluble acids
Molecular weight	200–300	120–140
Equivalent weight	233	68
Carboxyl oxygen, %	13.7	47
Hydroxyl oxygen, %	2.2	<1
O in functional groups, %	15.9	47
Total O (by combustion), %	29	49

The presence in the soluble acids of mellitic and benzene-pentacarboxylic acids was shown by isolation of their methyl esters. The amount of ester recovered was in each case less than 1% of the weight of the coal. German workers,[10] by oxidation of brown and bituminous coals, with oxygen under pressure and with nitric acid, obtained similar soluble acids from which they isolated various benzene carboxylic acids from benzoic to mellitic. The maximum yield of pure benzenoid acids reported was 10.4 g. per 100 g. of coal. Bone[11] and his co-workers state that alkaline permanganate oxidations of English bituminous coals yield 39–46% of the carbon as "crude benzenoid" acids, approximating the tricarboxylic in composition and corresponding to 65–81 g. of crude acids per 100 g. of coal. No figures are given on the actual quantity of pure acids isolated.

It was recognized that the isolation, in good yields, of the individual benzenoid acids from a mixture of the twelve possible, constituted a very difficult problem, hence some more general criterion of the benzenoid nature of these products was sought. Since they all contain the benzene ring as a nucleus, decarboxylation followed by recovery of the benzene formed appeared suitable.[12] Fischer's[13] method of heating the sodium salts with water to high temperatures under pressure was studied with the following known acids: benzoic, the three phthalics, and one each of the tri and tetra acids and the penta. With small samples, $^1/_{16}$ mole, recoveries ranged from 56% with iso-phthalic to 73% with benzoic. With a 1 mole sample of benzoic acid the recovery of benzene was 94%. Application of this method of decarboxylation to the soluble acids obtained in our work yielded approximately 10 cc. of steam-volatile hydrocarbons per 100 g. of acids, corresponding to 9 g. per 100 g. of coal oxidized to soluble acids. Fractionation of these hydrocarbons yielded 40% boiling in the range of benzene, 78–81°, of refractive index 1.496 at 25°. Solid hydrocarbons denser than water appeared in the higher fractions, indicating the presence of aromatic nuclei more complex than the benzene ring. This material contained diphenyl, which also appeared, in small amounts, in the decarboxylation of the known benzenoid acids, and presumably is the result of secondary reactions of the benzene. The residue in the bomb after a decarboxylation smelled strongly of cresol and of aromatic organic bases, and about 2.5% of a tarry residue was recovered by extraction with ether. If all the steam-volatile hydrocarbons are assumed to be benzenoid, approximately one-tenth of the carbon in the coal oxidized to soluble acids was recovered in the form of C_6 rings.

The gas, approximately 20 liters of which was recovered per 100 g. of acids, consisted of 25% methane, 60% hydrogen, and small amounts of ethane and unsaturates. The presence of considerable amounts of the lower aliphatic hydrocarbons and hydrogen, in the gases from decarboxylation, would indicate the presence of aliphatic acids such as oxalic, malonic and succinic, which were, however, not found; hence it appears these gaseous products must have come from the thermal decomposition of acids of more complex nucleus.

Experimental

Determination of Yields of Oxidation Products.—For determination of the rates of formation of the non-volatile oxidation products, 0.5-g. samples of 200 mesh coal[2] were refluxed with 100 cc. of 1 *N* nitric acid in 250-cc. round-bottomed Pyrex flasks connected to water condensers by ground joints. At the end of the determined period the contents of the flask were filtered through weighed Jena fritted glass crucibles with asbestos pads. The insoluble material was thoroughly washed with 1 *N* nitric acid, filtrate and washings evaporated to dryness on the water-

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(10) For a review see Horn, *Brennstoff-Chem.*, **10**, 362 (1929).

(11) Bone, Parsons, Sapiro and Groocock, *Proc. Roy. Soc.* (London), **A148**, 521 (1935).

(12) Kerkovius and Dimroth [*Ann.*, **399**, 120 (1913)] recovered benzene, naphthalene and fluorene by heating the barium salts of acids formed by oxidation of charcoal with fuming nitric acid.

(13) Fischer and Schrader, *Ges. Abhandl. Kenntnis Kohle*, **5**, 307 (1922); Schrader and Wolter, *ibid.*, **6**, 79 (1923); Schrader and Friedrich, *ibid.*, **6**, 108 (1923).

bath in weighed porcelain dishes and finally dried at 110° and weighed. This material constituted the yellowish-orange soluble acids. The acid-insoluble material in the Jena crucibles was dried at 110°, weighed, and then thoroughly washed with cold concentrated ammonium hydroxide. By this means the dark brown, acid-insoluble, alkali-soluble humic acids were extracted. This extraction, however, was never entirely complete; air oxidation continuously formed traces of soluble products during the extraction operation. The acid and alkali insoluble material remaining in the Jena crucibles was dried again at 110° and the weight of humic acids determined by difference. In the experiments on the oxidation of the cokes, the same method was used as for coal, except acid and alkali soluble products were removed in one step by treatment with concentrated ammonium hydroxide, followed by centrifuging and filtration, and the insolubles determined at once by drying the insoluble residue at 110°. Total soluble material was then obtained by difference. In all cases duplicate determinations were carried out, and the agreement was usually within 5 parts per 100.

In those experiments where gaseous products were recovered, to obtain carbon and nitrogen balances, oxygen was completely eliminated from the system by evacuation followed by flushing with nitrogen. The tube for collection of gas samples was sealed directly to the top of the reflux condenser and delivered through the usual U bend immersed in mercury, into mercury filled gas sampling tubes. No attack on the mercury was observed as long as oxygen was carefully excluded. Analyses of gaseous products were made in an Orsat apparatus using standard methods for carbon dioxide, unsaturates, carbon monoxide, hydrogen and methane. Nitric oxide was absorbed in freshly prepared acidified ferrous sulfate.[14] Tests were made for condensable hydrocarbons and nitrous oxide by passage of the gas through a liquid nitrogen trap before absorption in the ferrous sulfate. Negligible amounts of material condensed.

Molecular and Equivalent Weights.—Molecular weights were determined cryoscopically by a technique similar to that already described,[15] the only modification being the use of an atmosphere of dry nitrogen above the fused catechol during the measurements. Equivalent weights were determined electrometrically, using the antimony electrode,[15] and also by the method of Ubaldini and Siniramed,[7] in which the humic acid reacts with a mixture of calcium acetate and carbonate and the evolved carbon dioxide is absorbed and weighed. The latter gave somewhat higher values and the agreement between duplicate determinations was less satisfactory. For a typical regenerated humic acid, values of 233 ± 2 were obtained electrometrically, and 251 ± 4 by the Italian workers' method.

Carboxyl and Hydroxyl Groups.—Carboxyl oxygen was calculated from the equivalent weights. Hydroxyl groups were determined by exhaustive methylation followed by alkaline hydrolysis of the ester methoxyl and a volumetric microdetermination[16] of the unhydrolyzable methoxyl. Several methods of methylation were employed; diazomethane, dimethyl sulfate plus 40% alkali, and Waliaschko's[17] procedure of rubbing the potassium salt in a mortar with dimethyl sulfate. The last gave the highest results, both for total methoxyl and ether methoxyl. Hydroxyl groups in humic acids can also be estimated indirectly by the difference between the carboxyl content, calculated from equivalent weights, and the total acidity carboxyl plus phenolic hydroxyl, determined by the method of Ubaldini and Siniramed.[7] Two determinations for oxygen in hydroxyl in a typical humic acid preparation gave an average of 3.4% by this difference method, compared with an average of 2.2% determined by methylation and hydrolysis.

Examination of the Soluble Acids.—To obtain sufficient amounts of the soluble acids to attempt the isolation of individual compounds, larger quantities of coal were oxidized. In order to avoid handling large volumes the ratio of coal to acid was considerably increased, up to about 7 g. per 100 cc. of acid, and the nitric acid concentration maintained by the addition of fresh acid when required, as determined by periodic titration with standard alkali of small aliquots from the reaction mixture. After a suitable period of oxidation, thirty to sixty days, the insoluble material was separated by sedimentation and filtration and washed with water until peptization started. Filtrate and washings were concentrated to a small volume on the water bath at pressures of 10 to 20 mm. and finally freed completely of nitric and other volatile acids by prolonged evacuation at 50°, using a Megavac pump behind a liquid nitrogen trap. In two experiments of thirty-two days' duration, 33 and 34 g. of acid solubles per 100 g. of coal were recovered. The dried, ground acids were exhaustively extracted in a Soxhlet with ether, acetone and finally methyl alcohol. Approximately 40% of the material did not dissolve. Methylation of the soluble acids with an ether solution of diazomethane, in the usual manner, followed by distillation in a molecular fractioning still, up to bath temperatures of 300°, yielded 10.8 g. of distillable esters per 100 g. of coal. No pure compounds have yet been isolated from these mixed esters.

The esters of mellitic and benzene-pentacarboxylic acids were isolated as follows: 100 g. of the dried, ground acids was treated with 1 liter of concentrated ammonium hydroxide at 0° for an hour. The insoluble ammonium salts were filtered off and treated with an excess of barium hydroxide solution, at the boiling point, until all ammonia was displaced. The barium salts were filtered off, the acids liberated with dilute sulfuric acid, using brom thymol blue indicator, were separated, methylated with diazomethane and the esters fractionated as before. From the fraction evaporating at a bath temperature of 220–300°, pressure of about 1 micron, 1 g. of the methyl ester of mellitic acid, m. p. 187.4°, and 0.2 g. of the benzenepentacarboxylic methyl ester, m. p. 147.9°, were isolated. *Anal.* Hexamethyl mellitate. Calcd.: C, 50.71; H, 4.23. Found: C, 50.68; H, 4.26. Pentamethyl ester of benzenepentacarboxylic acid. Calcd.: C, 52.18; H, 4.34. Found: C, 52.34; H, 4.69. The identity of the penta compound was confirmed by a mixed melting point with the ester prepared by the action of ethereal diazomethane on a sample of Eastman benzenepentacarboxylic acid. The appearance of the penta acid along with the mellitic was

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(14) Moser, *Z. anal. Chem.*, **64**, 81 (1924).

(15) Smith and Howard, THIS JOURNAL, **57**, 512 (1935).

(16) Vieböck and Brecher, *Ber.*, **63**, 3207 (1930).

(17) Waliaschko, *Arch. Pharm.*, **242**, 242 (1904).

unexpected, since it is only the latter which forms an insoluble ammonium salt. It is probable that the amount of the penta acid recovered represents only a small fraction of that present.

Decarboxylation.—One hundred grams of the dried acids, 200 g. of sodium hydroxide, and 100 cc. of water were placed in a 1-liter American Instrument Company bomb furnished with a nickel liner. The temperature was raised to 450° in about four hours, maximum pressure 3800 lb. After cooling, and withdrawal of a gas sample, the pressure head of the bomb was replaced by a head carrying a delivery tube for attachment to a water condenser and an inlet for steam. The steam-volatile hydrocarbons, after passage through the water condenser, were collected over a strong calcium chloride solution acidified with hydrochloric acid, and measured in a small buret calibrated to 0.05 cc. After further drying over anhydrous calcium chloride the hydrocarbons were fractionated through a 51-cm. vacuum jacketed column.

The volume of gaseous products formed in the decarboxylation was calculated from the pressure and volume of the system and their composition determined in an Orsat apparatus by standard methods.

Acknowledgment.—The authors are indebted to F. C. Silbert and T. B. Smith for determinations of ultimate composition, and to J. M. Scott for gas analyses.

Summary

The action of dilute (1 *N*) nitric acid in converting bituminous coal into soluble products has been shown to be chiefly an oxidation. The yield of humic acids reaches a maximum in a few days, while that of the soluble acids increases slowly with time. If the reaction is carried out in the presence of air, only about one-fourth as much nitric acid is consumed as in its absence.

The residue from the benzene pressure extraction of this coal oxidizes more rapidly than the original coal. Oxidation of the cokes obtained by thermal decomposition of the coal in vacuum shows no difference from the original coal with cokes up to about 440°. Cokes prepared above this temperature show markedly greater resistance to oxidation. It has been pointed out that this temperature coincides with that at which gas evolution becomes rapid.

Determinations of ultimate composition and functional groups on both types of acids formed in this oxidation show the regenerated humic acids to contain markedly less hydroxyl than is reported for other humic acids, while the soluble acids contain negligible amounts. In the humic acids only approximately half the oxygen determined by ultimate analysis can be accounted for in functional groups, while in the soluble acids only small amounts of oxygen are thus unaccounted for. The presence, in the soluble acids, of benzenepentacarboxylic and mellitic acids was shown by isolation of their esters. Of the carbon of the coal which was oxidized to soluble acids, approximately one-tenth was recovered as steam-volatile, aromatic hydrocarbons, by decarboxylation. The presence of acids more complex than the benzene carboxylics is indicated.

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NOTES

Decomposition of *p*-Iodoaniline

BY F. B. DAINS, R. Q. BREWSTER AND JOHN A. DAVIS

A sample of *p*-iodoaniline was prepared and carefully purified by one of us.[1]

The product stood for three years in a glass-stoppered bottle (hence a limited supply of air) in semi-diffused light, at room temperature; it had then changed to a black liquid, which was found to contain a trace of free iodine and a small amount of aniline. Further examination showed the presence of 2,4-diiodoaniline and unchanged *p*-iodoaniline. The *p*-iodoaniline was removed as its hydrochloric acid salt by extraction of the liquid with hot, dilute acid. The salt crystallized from the solution as it cooled and the free base was liberated with alkali and recrystallized from ligroin, b. p. 90–100° (m. p. 62°). The 2,4-diiodoaniline was extracted from the acid insoluble residue with hot alcohol leaving a black insoluble mass, some 80 g., which was not identified. Dark needles of the 2,4-diiodoaniline crystallized from the alcohol as it cooled. These, when recrystallized from ligroin, gave a light tan colored product (m. p. 95°). In all, 95 g. of 2,4-diiodoaniline

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(1) R. Q. Brewster, "Organic Syntheses," John Wiley and Sons, Inc., New York City, 1931, Vol. 11, p. 62.