[CONTRIBUTION NO. 42 FROM COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Exhaustive Chlorination of a Bituminous Coal

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Further support of the concept that coal is essentially benzenoid[1] in character was sought by subjecting a bituminous coal from the Pittsburgh seam, Edenborn Mine, to exhaustive chlorination in antimony pentachloride, this reaction converting aliphatic substances to carbon tetrachloride and hexachloroethane while removing only the side chains of benzenoid substances, leaving the ring structures intact.[2]

The coal, suspended in carbon tetrachloride at 76°, in phosphorus oxychloride at 107°, stannic chloride at 114°, and antimony pentachloride at 100, 150, 200 and 400°, was treated with chlorine. The reaction in the first three media did not proceed so far as in the antimony pentachloride, and the data obtained are not reported herein. About 10% of the reaction product in antimony pentachloride at 200° was volatilized easily and consisted of carbon tetrachloride, hexachloroethane and hexachlorobenzene. The non-volatile residue was too complex for identification. Elementary balances were made of both the volatile and non-volatile products.

Experimental

A sample of 200 mesh coal, dried *in vacuo* at 105° to constant weight and weighing about 7 g., was placed in a reaction flask connected with a trap cooled with dry ice and 50 cc. of antimony pentachloride added. Chlorine was led through the apparatus at the rate of about 3 cc. per minute while the temperature was maintained at the desired point by a furnace with automatic temperature control. As the chlorination proceeded volatile products were condensed in the trap.

At the conclusion of the chlorination the apparatus was disconnected and the trap allowed to warm up to 10° so as to evaporate the chlorine that had condensed there. Water was then added slowly and with good cooling to hydrolyze the antimony pentachloride that had condensed in the trap.

The volatile contents of the trap were then swept through a combustion train by means of a current of oxygen. Cerium dioxide on silica gel served as the combustion catalyst; it was followed by a layer of silver wool to remove halogens.

The non-volatile portion of the reaction product was treated in a Soxhlet extractor with 20% hydrochloric acid for six days in order to remove antimony, and then dried *in vacuo* over phosphorus pentoxide at room temperature.

Microelementary analyses of these non-volatile residues were made. The samples still contained enough antimony to vitiate the carbon–hydrogen determinations when the usual combustion tube filling was used. It was found possible, however, to adapt the red lead filling used to retain arsenic in macrocombustions[3] so that correct analyses were obtained on organic compounds containing antimony.[4]

Results and Discussion

Data are summarized in Table I in the form of elementary balances for the various experiments performed.

The criteria for following the extent of chlorination with time and temperature were the values for non-volatile chlorinated residue, for the carbon content of the volatile products, and the chlorine and hydrogen contents of the residue. The amount of non-volatile residue showed no significant change in the various experiments but the carbon in the volatile products increased greatly as the temperature rose from 100 to 150 to 200°, then increased but slightly as the time at 200° increased from one to four to six days. The rate of increase of chlorine content and decrease of hydrogen content with time and temperature fell off abruptly at the four-day 200° chlorination. Apparently the coal was exhaustively chlorinated after four to six days' chlorination at 200°.

As a further test of the extent of the chlorination one-half of a sample of coal chlorinated for six days at 200° without driving off the volatile reaction products was reheated with antimony pentachloride in a sealed tube at 400° for four days. Both halves of the sample were then extracted for twelve hours each, successively, with ether, chloroform and chlorobenzene, in a Soxhlet. Both products showed practically the same solubility, indicating that the chlorination at 200° had been nearly complete. The ether removed 21%, the chloroform 22% and the chlorobenzene 18%, leaving an insoluble residue of 39%. Analyses and empirical formulas for the fractions from the material chlorinated at 200° only are given in Table II. The empirical formulas are calculated

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(1) W. A. Bone, L. Horton and A. Ward, *Proc. Roy. Soc.* (London), **127A**, 508 (1930).

(2) G. Ruoff, *Ber.*, **9**, 1483 (1876); V. Merz and W. Weith, *ibid.*, **16**, 2870 (1883); F. Hartmann, *ibid.*, **24**, 1025 (1891); A. Eckert and K. Steiner, *Monatsh.*, **36**, 175 (1915).

(3) M. Falkov and G. W. Raiziss, THIS JOURNAL, **45**, 998 (1923).

(4) F. C. Silbert, unpublished.

TABLE I

ELEMENTARY BALANCES OF CHLORINATED PRODUCTS

Grams per 100 Grams of Coal

In product from chlorination for	Non-volatile chlorinated residue per 100 g. coal, g.	C In residue	C In volatile	C Total	H	O	N	S	Cl	Ash
(Original coal)	...	..	..	77.4	5.32	6.95	1.36	0.87	..	8.12
4 days—100° (2)[a]	176	71.2	0.86	72.1	2.92	21.1	1.48	1.02	71.9	6.44
4 days—150° (2)	185	71.6	2.1	73.7	2.32	19.7	1.70	0.87	81.2	6.98
1 day—200° (1)	172	69.6	3.6	73.2	2.08	13.1	1.60	0.29	78.8	6.55
4 days—200° (3)	177	66.3	3.8	70.1	1.86	15.6	1.65	0.64	86.1	4.96
6 days—200° (2)	181	67.2	4.0	71.2	2.54	11.1	2.00	1.05	88.7	6.29

[a] Figures in parentheses refer to number of experiments; the values given in the table are averages.

TABLE II

SOLVENT FRACTIONATION OF COAL CHLORINATED AT 200° FOR SIX DAYS

	C	H	Cl (ash free)	N	S	O	Empirical formula
Ether soluble	38.97	1.89	48.20	0.64	0.39	9.91	$C_6H_{2.4}Cl_{2.5}(OH)_{1.1}$
$CHCl_3$ soluble	38.76	0.89	50.94	.94	.37	8.10	$C_6H_{0.7}Cl_{2.7}(OH)_{0.9}$
C_6H_5Cl soluble	44.66	1.11	44.68	1.14	.63	7.78	$C_6H_{1.0}Cl_{2.1}(OH)_{0.8}$
Residue	43.65	1.46	36.61	1.10	.36	16.82	$C_6H_{0.8}Cl_{1.7}(OH)_{1.7}$

arbitrarily on the basis of six carbon atoms and the oxygen is assumed to be hydroxyl oxygen.

The mean molecular weights of these fractions were determined cryoscopically in catechol by the method of Smith and Howard[5] but the results were not sufficiently reproducible to indicate more than the order of magnitude. The three soluble fractions gave values from 130 to 190; the insoluble residue gave values from 230 to 270. These values were too low to be consistent with the physical behavior of the substances and it may have been that the substances underwent a dissociation similar to that reported by the above authors for humic acids.

The ether soluble fraction was light brown in color. When heated considerable amounts of hexachlorobenzene sublimed off and then the material charred with evolution of hydrogen chloride. The ratio of carbon to attached substituents was nearly one to one, indicating the absence of appreciable amounts of condensed ring structure in this fraction.

The chloroform and chlorobenzene soluble fractions and the residue were black and infusible, losing hydrogen chloride on heating. The ratio of carbon to attached substituents was approximately 6 to 4 in each fraction, indicating the presence of a preponderance of condensed ring structure.

The fraction of each of the constituent elements of the coal which make up the stable ring structures as represented by the non-volatile residues from the 200° chlorinations may be obtained from the elementary balances in Table I.

The carbon balances show that the non-volatile residue accounted for 85% of the carbon of the original coal. Approximately 5% was accounted for in the volatile reaction products which consisted wholly of carbon tetrachloride, hexachloroethane and hexachlorobenzene, while 10% was unaccounted for. The 10% was probably lost as carbon dioxide. The results indicate that approximately 85% of the carbon of this coal is present in a large, condensed ring structure not destroyed by chlorination, the other 15% being present in side chains or ring structures broken by chlorination.

The values for hydrogen were erratic; the non-volatile residue contained approximately 35–50% of the hydrogen present in the original coal. Assuming that the increase in the oxygen content of the residue was due to replacement of chlorine by hydroxyl during the hydrochloric acid extraction and correcting for the hydrogen thus introduced, the hydrogen content of the residue before extraction was approximately 25–40% of that of the original coal. The 60–75% hydrogen not accounted for in the non-volatile residue is probably not entirely peripheral hydrogen[6] but includes such nuclear hydrogen as has undergone reaction.

The nitrogen balances show that the chlorinated residues contained more nitrogen than the original coal, the excess having increased with increased chlorination until it amounted to 50%.

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(5) R. C. Smith and H. C. Howard, THIS JOURNAL, **57**, 512 (1935).

(6) A. Eccles, G. H. Kenyon and A. McCulloch, *Fuel*, **10**, 6 (1931).

The nitrogen could not be traced to the reagents or to the small amount ($<0.5\%$) of antimony in the residue. It is possible that the chlorination alters the nature of the nitrogen bonds in the coal so that nitrogen, previously inert to the Kjeldahl reagents, becomes susceptible to conversion to ammonium sulfate. It was observed that the chlorinated residue went into solution during the Kjeldahl digestion much more readily than the original coal. The presence of the total original nitrogen of the coal in the non-volatile chlorinated residue is in agreement with the findings of Heathcoat and Wheeler[7] and would indicate that the nitrogen is an integral part of the stable ring structure of coal.

The sulfur balances, although the values are erratic, show a trend toward less sulfur in the more highly chlorinated residues. It is possible that the antimony in the residue caused some error in the microanalyses, which were done by combustion in oxygen.

The oxygen balances show that the residues from the mildest chlorinations contained threefold the amount of oxygen contained in the original coal. The oxygen content decreased uniformly as the time and temperature of chlorination increased, until it was only 1.5 times that of the original coal. The increase in oxygen is probably due to hydrolysis during the hydrochloric acid extraction. In the earlier stages of chlorination the amount of chlorine susceptible to hydrolysis would be greatest, diminishing with increased temperature and time of chlorination due to splitting out as hydrogen chloride.

The chlorine balances show that the non-volatile residues from the four- and six-day chlorinations at 200° contained approximately 50% chlorine.

The ash content of the coal has been lowered somewhat, probably as much the result of the hydrochloric acid extraction as of the chlorination.

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Summary

Coal has been chlorinated exhaustively with chlorine and antimony pentachloride for six days at 200°. Additional chlorination at 400° for four days did not materially increase the breakdown of the coal substance. The volatile reaction products obtained at 200° consisted of carbon tetrachloride, hexachloroethane and hexachlorobenzene, and contained only about 5% of the carbon of the original coal. This 5% and an additional 10% unaccounted for were probably formed from the peripheral material of the coal substance.

The non-volatile residue is considered to originate from the stable nuclei of the coal substance. Elementary balances showed that the residue contained: (1) 85% of the carbon of the original coal, (2) 40% of the hydrogen of the original coal, (3) an excess of 50% nitrogen over that of the original coal, (4) approximately double the oxygen of the original coal due to hydrolysis of the more active chlorine atoms, and (5) a ratio of carbon to attached substituents that indicates a condensed ring structure.

The residue was separated into ether, chloroform and chlorobenzene soluble fractions; each showed a mean molecular weight (cryoscopic in catechol) of approximately 160; the insoluble residue which remained had a mean molecular weight of about 250.

From these data it may be concluded that approximately 85% of the carbon of a bituminous coal from the Pittsburgh seam is part of a large condensed ring system of which the nitrogen in the coal is probably an integral part.

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(7) F. Heathcoat and R. V. Wheeler, *J. Chem. Soc.*, 2839 (1932).