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COMPARATIVE STUDIES IN THE OZONOLYSIS OF LIGNIN AND COAL

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ABSTRACT

The ozonizer used is illustrated and described. The experimental procedure for the ozonolysis of a spruce lignin sample and three bituminous coal samples in the temperature range 25—40°C is provided. The rate of reaction was found to vary between first and pseudo-zero order depending on the ozone concentration. (Supporting evidence was gained by paper chromatographic and potentiometric titrimetric studies of the reaction products.) A discussion on the structure of coal is given.

INTRODUCTION

Coal utilization could be extended immensely if its structure was known. Most investigators in this field of study agree that the structure of coal is complex and heterogeneous, with the major portion of the carbon network existing as a network of polynuclear aromatic compounds [1,2]. At its simplest, the coal molecule can be thought of as being composed of simple rings which are interconnected by various linkages to give a basic skeleton. Such structures break down when heated [3].

Ozone is found to be a suitable oxidizing agent for this purpose. It has advantages in that:

(i) the only by-product of this reagent is oxygen;

(ii) the reaction may be conducted at relatively lower temperatures.

The following conclusions are drawn from the UV and IR absorption spectra of coal [4].

(i) The hydroxyl concentration is very low but increases on oxidation. It reaches a maximum in a short time and then decreases.

(ii) Polycondensed aromatic ring systems are low in coal, but on oxidation they increase rapidly at first and then more slowly.

(iii) Simple aromatic rings are fairly high and increase only slightly on oxidation.

Tyler et al. [5] studied the kinetics of oxidation of special grade polycrystalline graphite with respect to partial pressure of oxygen. The effect of diffusion resistance on the rate was shown to be negligible. After the effects of self heating, burn-off and traces of gaseous impurities allowed for, the order of the reaction, n, was found to vary from 0.34 (at 720°C and $P_{O_2} = 16$

Torr) to 0.19 (at 690°C and $P_{O_2} = 245$ Torr).

Firm quantitative knowledge of the influence of ordinary kinetic parameters on the rate of oxidation of carbon is still scarce. There are several reviews to show that this is by no means due to the lack of experimental investigations [6—9]. The situation is particularly unsatisfactory for the reaction order with respect to oxygen. Tyler et al. [5] found that n varies from 0.19 to 0.34 for temperature changes between 690 and 720°C and oxygen pressure between 245 and 16 Torr. Sweeney [9] found that the rate of sorption in the temperature range 110—170°C was related to the "effective initial pressure", B_w, and the oxygen pressure at any time, P_i, by the equation

$$P_i = [K'_s t]^{0.60}\, B_w + B_w$$

or

$$-\mathrm{d}P_i/\mathrm{d}t = K''sP_i/(B_w - P_i)^{0.50}$$

It thus seems that there are variations in n with the type of carbon and its impurity content as well as with the temperature and range of O_2 concentration.

The main objective of this study is to determine the rate of reaction with ozone at lower temperatures on both coal and spruce lignin samples with the view to shedding some more light on the effect of oxidation on the structure (type of carbon) of coal.

METHODS

Instrumentation

The ozonizer

The ozonizer used was designed and constructed in this laboratory (Fig. 1). It consists of the following: an oxygen cylinder (A), a "smooth-outflow" 5-l bulb (B), a Fischer Laboratory flow meter (C), and a calcium chloride tower (D) with a glass wool plug in the top to remove moisture and dust. The dust-free oxygen was then passed into the ozonizer near the top. The ozonizer tube consists of two concentric lime glass tubes (E), and the system was cooled by means of a U-tube (F) and two spiral glass systems (G) carrying tap water. A chromel electrode (H) and a copper (sheet) electrode (I) were connected to the secondary of a high voltage transformer (J) which produced 15 000 V on its secondary coil. The transformer was grounded to the heating system in the laboratory. A triplet volt—Watt meter (K) was placed in line as shown. The ozonizer tube, cooling system, and electrodes were placed in a large bell jar filled with distilled water. The oxygen—ozone mixture was led out near the bottom.

Reaction flask and analytical train

Figure 2 shows the reaction flask (L) set in a constant temperature bath. A Bronwill Scientific Electronic Relay (M) and thermometer—heater—stirrer (N) regulate this bath. With this arrangement, the temperature could be maintained within 0.05°C.

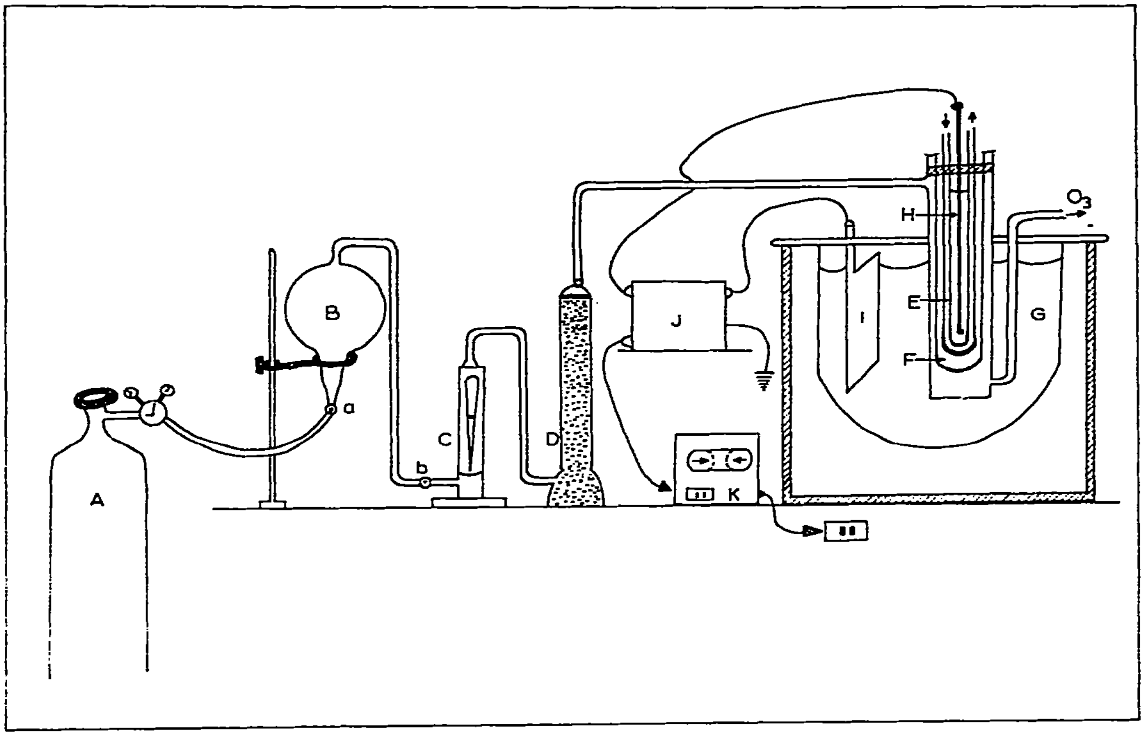


Fig. 1. The oxygen train and ozonizer.

The material to be reacted was suspended in 800 ml distilled water in the reaction flask, and was stirred with a magnetic stirrer (O) run by a motor (P). The ozone was led into the bottom of the flask, the escaping gases led out at the top to the analysis train. The third neck carried a glass tubing and stopcock (f). A system was arranged by means of stopcocks (c), (d) and (e) so that the ozone could be bypassed directly to bubblers (Q) and (R) which were used for the analysis of ozone and carbon dioxide, respectively. The two columns (S) contained glass wool soaked in 5% sodium hydroxide (solution) to destroy any ozone which might still be present in the oxygen stream. A filtration assembly, a vacuum distillation apparatus and the ascending paper chromatographic apparatus completed the basic instrumentation.

Experimental procedure

The samples were ground to 10 μm particle size and dried in a vacuum oven at 40°C for 28 h. The ozonizer was cooled, and ozone was passed through 800 ml of distilled water in the reaction flask for a period of at least 2 h.

The bath was heated to the required temperature (25, 30, 35 and 40°C). After ensuring that the water was ozone saturated at the particular temperature, an accurately known weight of approximately 1 g sample was introduced into the reaction flask and the system was closed. Ozone was passed through the reaction mixture, and the time at which the first bubble was

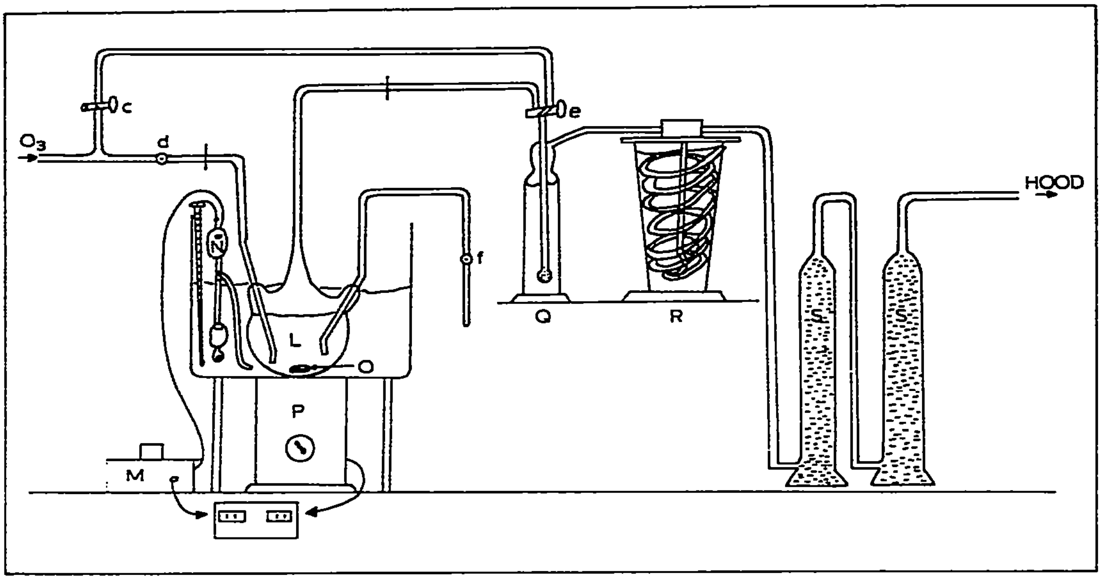


Fig. 2. The reaction flask and analysis train.

noticed in bubbler (Q) (which contains 20% ferrous ammonium sulphate solution) was recorded as zero time. [Bubbler (R) contained 0.1 M baryta water.] The rate of ozone production was predetermined by two methods, viz. (i) KI and (ii) $FeSO_4(NH_4)_2SO_4$.

During the run, the rate of ozone absorption by the sample was determined by method (ii), since in kinetic studies involving CO_2, method (i) introduces some errors. At the end of the run, nitrogen was bubbled through the solution. Beginning at zero time and generally extending over a period of 8—10 h, gas washer (R) was removed at half-hour intervals and analysed for CO_2.

RESULTS AND DISCUSSIONS

All of the solid lignin material had reacted by the 32nd hour of ozonolysis, but the carbon dioxide evolution continued at approximately the same rate for the next 13 h, at which time the reaction was stopped. This same pattern was observed for the McBean Seam coal except that it took a longer time of ozonolysis for the solid material to react completely. It was therefore concluded that the reaction rate is dependent on the ozone concentration but was independent of the concentration of the sample. The ozone concentration was maintained constant throughout. The reaction was found to be first order becoming pseudo-zero order when the ozone concentration was held constant.

Some earlier work on coal using oxygen at elevated temperatures led to the conclusion that the oxidation was a true surface reaction [9—11]. Their determined order of oxidation reaction, however, varied from fractional [9] to first order [10], to first order regarding oxygen and zero order regarding coal [11].

TABLE 1

Data for the ozonolysis of lignin at 25° C

Time (h)	$CO_2 \times 10^2$ g	Total $CO_2 \times 10^2$ g
0.5	1.08	1.08
1	1.22	2.30
1.5	1.26	3.56
2.5	2.66	6.22
3	1.48	7.70
3.5	1.42	9.12
4.5	2.70	11.82
5	1.70	13.52
6	1.52	15.04
6.5	1.52	16.56
7.5	3.04	19.60

Data for the kinetic analysis of three coals, "McBean Seam", "Old Sydney Collieries", and "Western Dominion Klimax lignite", and the lignin sample, an alkali-permanganate extract from "spruce", were obtained for 1 g samples at 25, 30, 35 and 40° C for 7.5 h ozonolyses. The results obtained were quite similar, and therefore only a representative table (Table 1) is given.

Two steps were followed in the determination of the rate constants.

(i) *Quantitative data:* the reaction constant, K, was determined from the slopes of the plot of carbon dioxide concentration vs. time (Figs. 3—8).

(ii) *Corrected constants:* Corrections were made for the reaction dependence on the amount of ozone in solution by making use of the re-arranged form of the differential equation for the reactions, i.e. $K = \text{slope}/[O_3]$. The

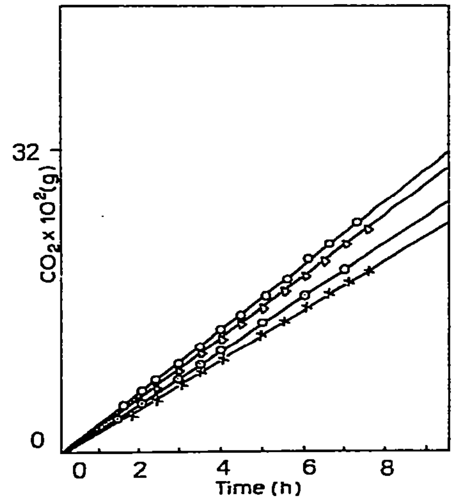


Fig. 3. $CO_2 \times 10^2$ (g) vs. time (h) for spruce lignin. × = 25°C; △ = 30°C; ⊗ = 35°C; ⊙ = 40°C.

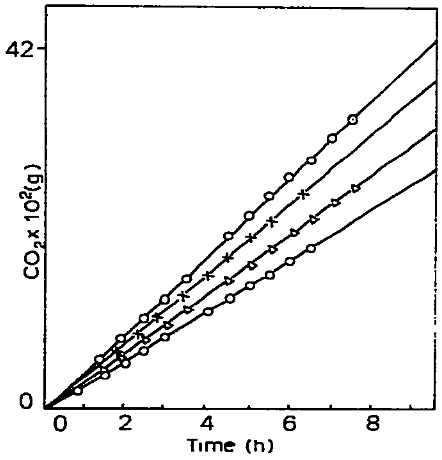
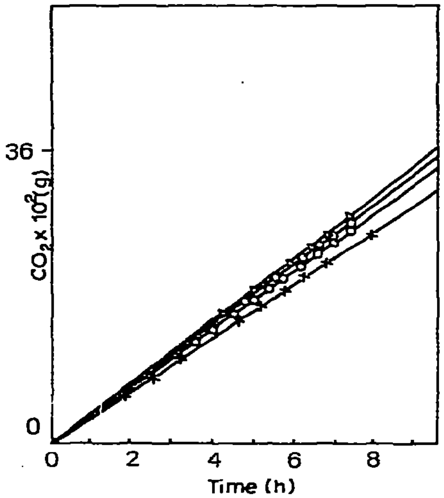


Fig. 4. $CO_2 \times 10^2$ (g) vs. time (h) for McBean Seam coal. ⊗ = 25°C; ⊙ = 30°C; △ = 35°C; × = 40°C.



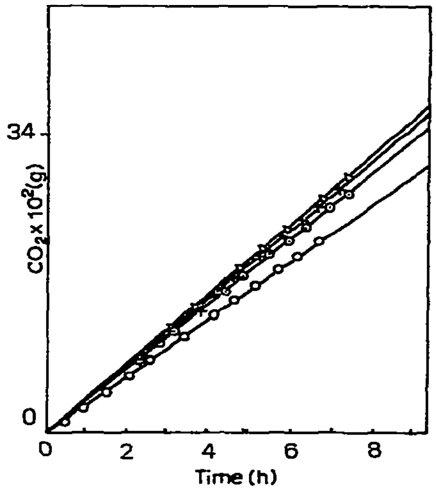


Fig. 5. $CO_2 \times 10^2$ (g) vs. time (h) for Western Dominion Klimax lignite. ⊗ = 25°C; ⊙ = 30°C; △ = 35°C; × = 40°C.

Fig. 6. $CO_2 \times 10^2$ (g) vs. time (h) for Old Sydney Collieries. ⊙ = 25°C. △ = 30°C; × = 35°C; ⊗ = 40°C.

reaction rate constants (Table 4) were calculated from the data given in Tables 2 and 3.

There is a close similarity between the energies of activation of the lignin

TABLE 2

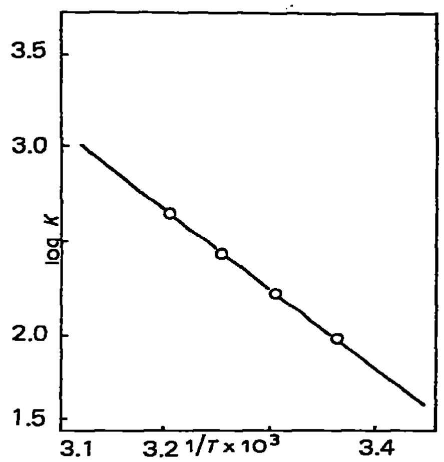
Saturated aqueous ozone concentrations at different temperatures

Temp. (°C)	Ozone concentration	
	(mg l^{-1})	$\times 10^4$ (mole l^{-1})
25	15.99	3.331
30	10.78	2.245
35	6.80	1.416
40	4.21	0.877

TABLE 3

Slopes, *n*, obtained for spruce lignin and bituminous coals at temperatures between 25 and 40°C

Samples	$n \times 10^2$			
	25°C	30°C	35°C	40°C
Lignin	2.73	3.35	2.99	3.53
McBean Seam	2.78	4.27	3.28	3.89
Western Dominion Klimax lignite	3.37	3.85	4.02	3.94
Old Sydney Collieries	3.58	3.85	3.33	3.77



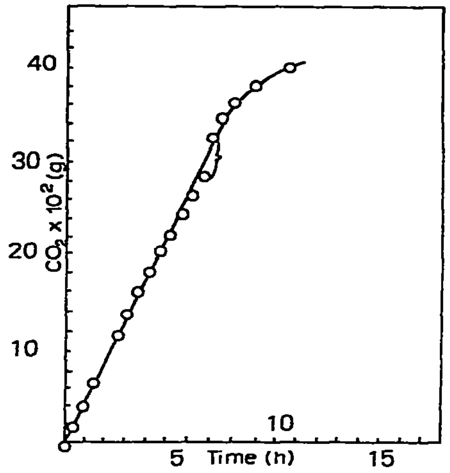


Fig. 7. Log K vs ${}^1/T \times 10^3$ for Western Dominion Klimax lignite (a typical graph).

Fig. 8. Oxalic acid. $CO_2 \times 10^2$ (g) vs. time (in hours) for the ozonolysis of oxalic acid. Note the break in linearity when the solution is allowed to stand over-night and not maintained saturated with ozone.

TABLE 4

Corrected reaction rate constants for spruce lignin and bituminous coals

Samples	K_1 (l h^{-1})			
	25°C	30°C	35°C	40°C
Lignin	1.86	3.39	4.80	9.15
McBean Seam	1.89	4.32	5.26	10.08
Western Dominion Klimax lignite	2.30	3.89	6.45	10.20
Old Sydney Collieries	2.44	3.89	5.35	9.78

The energies of activation were calculated in the normal manner, i.e. by plotting log k_1 vs. $1/T$ (Fig. 5). The results are given in Table 5.

TABLE 5

Activation energies (kJ $mole^{-1}$) for a spruce lignin and three bituminous coal samples

Sample	Slopes ($\times 10^{-3}$)	Activation energies (kJ $mole^{-1}$)	
		Low temp. ozonation	High temp. oxidation
Lignin	—4.32	82.72	
McBean seam	—4.545	87.07	
Western Dominion Klimax lignite	—4.119	78.87	74.68
Old Sydney Collieries	—4.00	76.61	78.53

and these coals (Table 5). It appears, therefore, that there are considerable similarities in the structures of coal and lignin, and that there is at least one pertinent grouping common to both structures. It had been shown [12] that coniferyl alcohol is a building structure of lignin which, on drastic oxidation, is completely degraded into carbon dioxide, acetic acid, oxalic acid and other similar substances. It now appears that coniferyl alcohol is also common to the structure of coal.

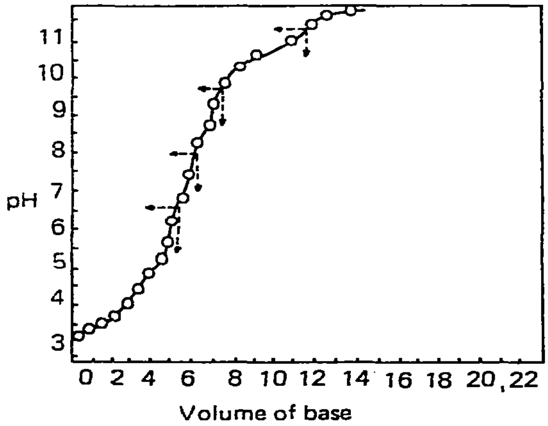
OTHER METHODS, RESULTS AND DISCUSSIONS

Paper chromatography

The paper chromatographic method was applied to known mixtures of several complex organic (carboxylic) acids, and on the water-soluble humic acids produced from the ozonolysis of the lignin and coal samples. Table 6 shows the R_F values and identified acids obtained from these investigations.

It was observed that the seven acids identified from the lignin product were all part of the 11 found in both McBean Seam and Old Sydney Collieries coals. Five of the eight acids found in Western Dominion Klimax lignite coal were common to all substances. In the latter, however, there were no "J", "K", "H" (or R_F 0.64) acids, and it was the only sample to show the presence of "M" and "N" acids. Ten of the 11 acids identified in McBean Seam and Old Sydney Collieries coal reaction products were identical. The exception was that unidentified, R_F 0.64, acid of the former was replaced by acid "H" (R_F 0.68) of the latter.

From these results it is safe to assume that the structures of lignin and coal are quite similar, but that the structure of coal is somewhat more complex.



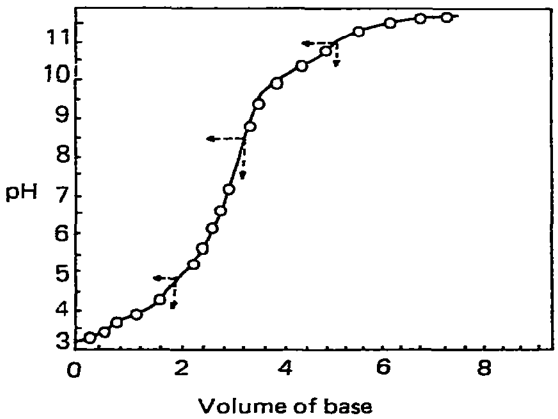


Fig. 9. Potentiometric titration curve for an aqueous solution obtained from the ozonolysis of spruce lignin.

Fig. 10. Potentiometric titration curve for an aqueous solution obtained from the ozonolysis of McBean Seam coal.

Potentiometric titrations

Potentiometric titrations were done on 50 ml of the water-soluble acids vs. 0.05 M sodium hydroxide solution. The data presented in this section are limited to two graphs (Figs. 9 and 10) to emphasize the similarities between the ozonolysis products of lignin and coal.

The initial pH values of the solutions are almost identical; neutralization points quite similar, indicating a strong acid in each case, two rather concentrated mixtures of weak acids, and other indentations significant of the presence of other acids either too diluted to be pronounced, or whose pK_a values are too close together to be distinguished separately. A dissimilarity is also observed, viz. that the total equivalents required for lignin is much greater than that for McBean Seam coal. Comprehensive studies on weak acid poly-

TABLE 6

R_F values obtained for known acids and for reaction products of lignin and coal samples

Sample (hours ozonized) at 30°C	R_F	Acids [a]
Known	0.0; 0.15	A; B
	0.28; 0.42	C; D
Lignin (7.5 h)	0.0; 0.15	A and/or I; B
	0.27; 0.28	E; C
	0.44; 0.54	D; G
Lignin (4.5 h)	0.0; 0.15	A and/or I; B
	0.27; 0.28	E; C
	0.44; 0.54	D; G
	and also 0.66	and L
McBean seam (7.5 h)	0.0; 0.15	A and/or I; B
	0.27; 0.28	E; C
	0.44; 0.54	D; G
	0.61; 0.64	F; 0.64
	0.80; 0.82	J; K
McBean seam (66 h)	0.0; 0.15	A and/or I; B
	0.27; 0.28	E; C
	0.44; 0.54	D; G
	0.64; 0.80	0.64; J
Western Dominion Klimax lignite (7.5 h)	0.0; 0.15; 0.28	A and/or I; B; C
	0.44; 0.61	D; F
	0.73; 0.87	M; N
Old Sydney Collieries (7.5 h)	0.0; 0.15	A and/or I; B
	0.27; 0.28	E; C
	0.44; 0.54	D; G
	0.61; 0.80	F; J
	0.82; 0.68	K; H

[a] Acids: A = mellitic; B = benzene-pentacarboxylic; C = prehnitic; D = pyromellitic; E = mellophanic; F = trimellitic; G = hemimellitic; H = trimesic; I = oxalic; J = terephthalic; K = adipic; L = malonic; M = phthalic; N = benzoic.

electrolytes in aqueous solution on substances similar to these can be found in published articles by Gamble [13,14] and others.

Ozonolysis of oxalic acid

A sample of pure oxalic acid was ozonized by the same procedure as the lignin and coal samples. From the data obtained it was observed that oxalic acid is ozonized to CO_2 at a rate similar to that for coal and lignin. This apparently accounts for the reaction rate in the later stages of the ozonolyses of coal and lignin.

It is the author's opinion that ozonides are formed instantaneously from the rupture of ethylenic double bonds which constitute a linkage between large benzenoid systems in the original structure of coal and lignin. These ozonides are simultaneously decomposed by the aqueous medium to form benzene-polycarboxylic acids, oxalic acid and carbon dioxide. McCaulay [15] identified methylene and isopropyl groups as bridging structures in coal.

Water solubles

While at the end of 7.5 h ozonolysis the colour of the water-solubles was yellow for lignin and dark brown for coal, at the end of 45 h and 66 h, respectively, the solutions were colourless. This is supporting evidence for the assumption that those structures responsible for the colour were formed early in the ozonlysis and were in turn ozonized. These systems are possibly fused aromatic systems, since aliphatics would undergo almost instantaneous degradation to carbon dioxide or similar substances.

SUMMARY

From the previous discussions, certain conclusions have been drawn relative to the constitution of coal.

(a) The kinetic analysis indicated that there are marked similarities in the respective structures — the rate of carbon dioxide evolution followed a similar pattern; the ozonolysis constant is similar; and the solutions of the water-solubles are coloured after 7.5 h ozonolysis and colourless after a considerable length of time. A logical assumption based on these results and observations would be that the structure of coal is similar to that of alkali lignin.

(b) Paper chromatographic separations of the water-solubles have revealed that the water-soluble acid mixture from coal is much more complex than that from lignin. The lignin acids were benzene-polycarboxylics plus oxalic acid, the amount of which varied with the length of ozonolysis. The coal acids consisted of identical benzene-polycarboxylics and oxalic acid, as well as some benzene-dicarboxylics, benzene-tricarboxylics and the aliphatic acid, adipic acid, which is stable to ozone reaction.

From these arguments, it was concluded that the structure of coal is similar to that of spruce lignin, and that the former is more complex than the latter. The larger variety of benzene-polycarboxylic acids formed in all cases indicates that these structures are predominantly benzenoid in nature. Further, since it was established that the structure of lignin was a benzenoid nucleus with oxidizable side chains [16], a structure with phenylpropane as skeleton [17—19], coniferyl alcohol and naphthalene structures with phenyl substituents [20], it is reasonable to assume that the structure of coal has as its building structure some such compounds, and is linked together by a $(CH_2)_4$ saturated straight chain with possible unsaturation at either end accounting for the presence of adipic acid $[COOH(CH_2)_4COOH]$.

The results of this work seem to be in agreement with Nelson's [21] X-ray results that the size of the aromatic ring system in coal is not larger than four fused rings, since at the end of the ozonolysis there was no sign of any aromatic nucleus greater than one in the water-soluble acids of either lignin or coal. Larger condensed ring systems are not likely to be almost instantaneously degraded to one ring system. It is evident that if a large number of fused rings existed they would either have to be degraded instantaneously to benzene-carboxylic acids, oxalic acid or similar products, or remain unchanged in the original samples. The samples are completely degraded. It is unlikely that a larger number than four-membered rings would be instantaneously degraded, and therefore, it is the author's opinion that the maximum number of fused-ring systems in the structure of coal is four.

The results should not be taken too literally, however, for they portray a simplified picture of the overall structure of ozone-treated lignin and coals. It is known that they are quite heterogeneous in structure and composition, and that they show some differences depending on their original sources. For example, the structure of lignin shows differences dependent on the plant from which it originates, as do coals of different rank.

Anthracites possess rather different graphitizing properties to other coals, because they combine a relatively high degree of parallel layer alignment together with considerable three-dimensional crosslinking [22]. (Oberlin and Terriere [23] have demonstrated the alignment of layers in anthracites treated at various temperatures.) Aronson [24] shows that lignite and bituminous coals exhibit similar behaviour which is different from that of anthracite coal.

CONCLUSION

Because of its complexity, several details of the structure of coal are still contentious. By means of X-ray diffraction studies [25] and matrix techniques [26], it was concluded that 50—60% of the total carbon in coal form the aromatic nuclei which are extensively interlinked by nonaromatic structures. Little order is shown beyond the region of an average-sized (5—6 Å) aromatic nucleus, and therefore rule out larger aromatic entities.

Friedel et al. [27] consider the linkages to be noncrystalline pseudographic, but not necessarily aromatic C—C configurations. The existence of aromatic and aliphatic C—H, cyclic $—CH_2—$ and $—CH_3$ groups in coal have been established [28]. There are few, if any, olefinic or acetylenic configurations, and in coals with greater than 80% carbon, there is no —COOH or —OCH_3 linkages.

The syntheses of information derived from elemental and functional group analyses, X-ray diffraction, IR and NMR spectroscopy, molecular weight determinations and chemical degradations of coal substances have, however, enabled several investigators to develop "illustrative" skeletal structures for a typical coal [29].

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