429. *Studies in the Composition of Coal. The Constitution of the Ulmins.*

By FREDERICK HEATHCOAT and R. VERNON WHEELER.

THE ulmins form the major part of coal (see Safety in Mines Research Board Paper No. 28, p. 40, 1926). Knowledge of their constitution is therefore essential to a study of the composition of coal. Earlier researches (*loc. cit.*, and J., 1925, **127**, 2238) have shown that the ulmins of a bituminous coal, normally insoluble, can be obtained in a (modified) form soluble in alkalis by mild oxidation, *e.g.*, by air at 150°. The soluble ulmins thus produced would seem to be nearly homogeneous; they can be separated into a number of fractions by different solvents, but all the fractions are compounds of the same type and their analyses differ but slightly one from another.

The oxidation necessary to render the coal ulmins soluble in alkalis forms carboxyl groups which give them a definite acidic character allowing of salt formation. From the copper salt an average value of 170 is obtained for the equivalent. This should be compared with the figure, 350, given by Sven Odén (*Proc. Faraday Soc.*, 1921) for the equivalent of the soil ulmins. It is doubtful whether determinations of molecular weight have any meaning, the " molecule " of the coal ulmins, like that of carbon, probably being continuous. From the nitrogen content of the soluble ulmins (which is the same, in all the fractions obtained by different solvents), some idea can be obtained of the magnitude of any " molecular " unit there might be; a value 680 has been calculated in this way. The greater proportion of this nitrogen is inert, suggesting that its mode of occurrence is in a closed ring (cf. Pearson, *J. Soc. Chem. Ind.*, 1932, **42,** 71T).

In order to gain an insight into the character of the nuclear structure of the complicated molecular aggregate, Francis and Wheeler (J., 1925, **127**, 2236) attempted to disrupt it gradually in such a manner as to produce recognisable products of known constitution. They succeeded, by the careful use of hydrogen peroxide and dilute nitric acid, in isolating aliphatic dibasic acids, benzenepolycarboxylic acids and nitrophenols. Fischer and Schrader had earlier (*Abh. Kohle*, 1920, **5**, 135) isolated many benzenepolycarboxylic acids from the products of oxidation of coal under pressure of oxygen at 200—250° in the presence of alkalis. Francis and Wheeler therefore considered the nuclear structure of the ulmins to be essentially a compact system of annular six-membered groupings connected together by heterocyclic structures, such as pyrrole and furan or their derivatives, the aromatic acids and nitrophenols that they had obtained being derived from the six-membered ring structures and the aliphatic acids from the five-membered rings and connecting groupings. Bone and Quarendon (*Proc. Roy. Soc.*, 1926, **110**, 537) and, later, Bone, Horton, and Ward (*ibid.*, 1930, **127**, 480) have confirmed the benzenoid structure of the coal ulmins by the isolation of benzenepolycarboxylic acids in large yields from the products of oxidation of coal by alkaline potassium permanganate.

These elementary facts regarding the general nuclear structure of the ulmins, and some isolated observations pointing to the existence of certain reactive groupings, comprise the information so far obtained as to the constitution of the ulmins. The organic chemist is faced with the difficulty, when studying them, that the ulmins are colloids, of great complexity, in which internal condensation has proceeded so far that there are few reactive groupings. Even when such groupings are apparently detected, it might be argued that they have been formed during the reactions used for their detection. We have hitherto referred to such reactive groupings as " external," but it is doubtful whether that term is justified, for it implies the existence of definite ulmin molecules dissociable one from another.

The first part of this paper describes work on the detection of some of the simpler reactive groupings, such as may be presumed to exist in unstable ring formation, or as connecting linkages between stable nuclei. The second part deals with the nuclear arrangements.

(1) *Some Reactive Groupings in Coal Ulmins.*—The groupings attached to the nuclear structure of the ulmins determine their reactivity. With increasing degree of coalification, such attached groupings are progressively eliminated and the nuclear structure is correspondingly consolidated. Many of the groupings present, *e.g.*, in peat ulmins, may not, therefore, be found in the ulmins from bituminous coal.

There is considerable evidence for the existence of true carboxylic groups in the ulmins from peat (see, *e.g.*, Marcusson, *Chem.-Ztg.*, 1920, **44**, 43; Fuchs, *ibid.*, p. 551). These " ulmic acids " decompose acetates (Fuchs, *Brennstoff-Chem.*, 1927, **8**, 337; Fuchs and Stengel, *ibid.*, **9**, 178; Fuchs and Horn, *ibid.*, 1930, **11**, 372) and can be exhaustively methylated (Fuchs and Stengel, *Brennstoff-Chem.*, 1929, **10**, 303). Marcusson (*Z. angew. Chem.*, 1921, **34**, 437) has suggested that during the transition of peats, through brown coals and lignites, to bituminous coals, the carboxylic groups condense to form anhydrides and ketones. This suggestion is supported by the decreasing solubility of the ulmins in alkalis. There appears to be no evidence of the existence of carboxylic groups in the ulmins as they occur naturally in freshly-mined bituminous coals.

The presence of hydroxyl groups in the ulmins of soils has been demonstrated by Roger and Vulquin (*Compt. rend.*, 1908, **147**, 1404) by acetylation. Fuchs and his co-workers (*loc. cit.*) also infer the existence of hydroxyl groups by methylation. We have obtained evidence of their survival in the ulmins of bituminous coals.

Strache and Harrancourt (*Brennstoff-Chem.*, 1924, **5**, 350) have devised a method for determining the carbonyl content of coals. In the brown coals and bituminous coals studied by them, the amounts varied between 0·37 and 0·14%.

Methoxyl groups have been detected in brown coals and lignites, but not in bituminous coals (Robertson, *Biochem. J.*, 1907, **2**, 458). Simak (*Brennstoff-Chem.*, 1928, **9**, 381) was unable to detect methoxyl groups in the ulmins of brown coals except in fractions soluble in ethyl ether, and concluded that the pure ulmins contain none. Buckley, working in these laboratories, found that when methylated sugars were condensed with amino-acids the methoxyl groups were progressively eliminated.

The fact that all these oxygen-containing groupings, if present at all, exist in the ulmins in small quantities only, suggests that the oxygen in the ulmins is bridged or nuclear. Marcusson (*loc. cit.*), who ascribed to the ulmin " molecule " a structure built up of benzene and furan rings, considered that the oxygen functions as oxonium in the latter. This " furan theory " was opposed by Fischer and Schrader (*Brennstoff-Chem.*, 1921, **2**, 37), who ascribed the production of phenols when coal is distilled to the pre-existence of hydroxyl groups. There is little doubt, however, that the greater part of the oxygen of bituminous coal is unreactive, and Jones and Wheeler's explanation (J., 1916, **109**, 708), that the phenols are derived for the most part from nuclei of furan type, would seem the more probable.

We considered that it should be possible to observe the gradual elimination of reactive groupings with increasing rank of a series of coals (*a*) by the action of a Grignard reagent, to estimate reactive hydrogen, and (*b*) by acetylation, to estimate hydroxyl.

The action of Grignard reagent. A Grignard reagent with dried coal would evolve methane from such groupings as $-OH$, $-CH_2{\cdot}CO-$ $(-CH{:}C{\cdot}OH-)$, $-CO_2H$, $-NH_2$, $-NHR$, $-CH{=}$, any of which might exist in the ulmin complex, but would not distinguish between such groupings.

With all the coals examined there was a measurable evolution of methane, the volume decreasing with the rank of the coal as judged by its carbon content or, better, its reactivity index (see Francis and Wheeler, J., 1931, 586). The results, which were obtained in closely-agreeing duplicate, are expressed in Table I as c.c. of methane at *N.T.P.* per g. of dried coal. Table I also records the percentages of hydroxyl equivalent to the quantities of methane evolved, not as necessarily indicating the sole origin of the reactive hydrogen but as giving direct significance to the results :

TABLE I.

The Action of Grignard Reagent on Coal.

Name of coal.	C, % on ash-free dry coal.	Re-activity index.	CH_4 evolved per g., c.c. at *N.T.P.*	Reactive groupings calc. as –OH, %.
Ellistown Main	77·9	89	46·0 (54·8)*	3·5
Deep Hards	82·8	72	28·7	2·2
Waterloo	82·1	63	25·2	1·9
Deep Softs	82·6	77	25·0	1·9
Tupton	83·3	62	24·2	1·8
Swallowood Softs	82·6	56	20·0 (24·7)	1·5
East Kirkby	82·5	62	16·1	1·2
Parkgate Brights	85·4	56	15·7	1·2
Two Foot Nine	89·8	25	10·5	0·8
Kent No. 5	86·8	41	8·1 (14·9)	0·6
Silkstone	86·9	22	6·7	0·5
Busty	88·3	34	5·7 (14·4)	0·4
Anthracite	92·5	5	4·4 (7·4)	0·3

* The values in parentheses were obtained on the residues from the coals after extraction with pyridine.

The results cannot be regarded as quantitative because, although all the determinations were made under standardised conditions, the action of a mild reagent such as the Grignard on a colloidal complex such as coal is subject to modification dependent on the physical state of the substance, and this varies from one coal to another. The values obtained with some of the coals after their extraction with pyridine illustrate the effect of alteration in their physical condition.

For comparison with the coals, the following results obtained with allied fuels are of interest : CH_4, c.c. (at *N.T.P.*) per g. : Dopplerite, 103·5 ; Morwell brown coals, 93·0 ; Lancashire peat, 90·4.

The Grignard reagent was prepared, in the usual manner, from 12·2 g. of Mg and 7·1 g. of MeI dissolved in 500 c.c. of amyl ether. Each coal was prepared by grinding so as to pass a 120- and remain on a 200-mesh sieve, dried to const. wt. at 105°, heated at 150° under 15 mm. press. during 2 hr., and transferred to a vac. desiccator containing conc. H_2SO_4. The determinations were carried out by the method due to Hibbert and Sudborough (J., 1904, **85**, 933 ; see also, Zerewitinoff, *Ber.*, 1907, **40**, 2023).

Acetylation. Several coals were acetylated, the products hydrolysed, and the liberated acids measured by titration after steam distillation. The results are recorded in Table II.

TABLE II.

The Acetylation of Coal.

Name of coal.	C, % on ash-free dry coal.	Reactivity index.	-OH, %.
Ellistown Main	77·9	89	3·75
Alfreton	80·4	—	2·80
Swallowood Softs	82·6	56	1·75
Parkgate Brights	85·4	56	0·85
Anthracite	92·5	5	0·45

Where comparison can be made with the values calculated on the assumption that all the reactive hydrogen measured by the Grignard reaction was of hydroxylic origin, it is seen that with all but one of the coals acetylation gave a higher value. Presumably, with acetylation there is a greater penetration of the ulmin complex than can be effected by the Grignard reagent. Although neither set of results can be accepted as quantitative, yet together they prove the presence of free hydroxyl groups in the ulmins of bituminous (and anthracitic) coals and show that their quantity decreases as the rank of the coal increases.

The coals were ground as before, and 4 g. of each with 4 g. of NaOAc and 200 c.c. of Ac_2O were refluxed during 2 hr.; H_2O (400 c.c.) having been added cautiously, the mixture was boiled during 15 min., filtered, and the residue washed once with H_2O. It was transferred to a beaker with a large excess of H_2O, boiled during 15 min., filtered, and thoroughly washed; it was then dried, hydrolysed during 6 hr. with 100 c.c. of 10% $Ph{\cdot}SO_3H$ aq., and distilled in steam. The distillate was titrated with $N/10$-NaOH.

(2) *The Nuclear Structure of the Coal Ulmins.*—The fact that the nuclear structure of the coal ulmins is of aromatic character led Fischer and Schrader (*Abh. Kohle*, 1920, **5**, 200) to believe that the coal ulmins are derived solely from lignin, the carbohydrates, which form such an important part of the original plant materials, being supposed to be transformed by bacterial fermentation entirely into gaseous products, as indeed they are under certain conditions. Under anærobic conditions, the celluloses are not necessarily destroyed but may be converted into substances which can play an important part in the formation of coal. Marcusson (*loc. cit.*) has consequently argued in favour of a cellulosic origin of coal, and has elaborated a scheme whereby sugars can form ulmins having aromatic nuclei with bridged oxygen linkages. The researches of Willstätter and Kalb (*Ber.*, 1922, **55**, 2648) and of Schrauth (*Z. angew. Chem.*, 1922, **35**, 617; 1923, **36**, 149) furnish examples of the relationship existing between the carbohydrates and their aromatic derivatives, and of the reactions which permit of the passage of the one type of compound into the other.

Lignin and cellulose differ markedly in their chemical properties and it is reasonable to assume that the ulmins derived from each might also differ. Eller (*Annalen*, 1923, **431**, 177) has shown that the chlorination of sugar ulmins and artificial ulmins formed from quinol yields compounds of different types (containing 22·8% and 43·5% Cl respectively); and Thaysen, Bakes, and Bunker (*Fuel*, 1926, **5**, 217) have recorded the formation of two different types of compounds by the chlorination of peat, the one, soluble in ethyl ether and containing 40·7% Cl, which they related to ulmins from lignin, and the other, insoluble in ethyl ether and containing 21% Cl, which they related to ulmins from cellulose.

The chlorination of coal therefore seemed a possible means of separating the ulmins into compounds of different types. We have used chlorine dioxide for this purpose.

Chlorination of coal. A bituminous coal of fairly high rank (Swallowood Softs, C, 82·6; H, 5·7%) was extracted with C_5H_5N and the residue (α-fraction) chlorinated with a standard quantity of dil. Hoffmeister's reagent in a pressure-bottle. The product was extracted with Et_2O, and both the extract and the residue re-chlorinated. Under this treatment, the Cl content of the extract increased, and a further quantity of the residue became sol. in Et_2O. By successive chlorinations of the residue in this manner, there was obtained a series of compounds, sol. in Et_2O, containing, in the order of their extraction, 31·0, 31·5, 26·7, 27·6, and 25·1% Cl, when fully chlorinated. These compounds were all stable, amorphous powders of a golden-yellow colour.

The α-fraction of a bituminous coal of lower rank (Ellistown Main, C, 77·9; H, 5·35%) was treated in a different manner, the product of a single (incomplete) chlorination being extracted successively with different solvents (acetone, EtOH, Et_2O and H_2O). In this way a number of fractions was obtained, but each fraction after being fully chlorinated had nearly the same Cl content and was sol. in Et_2O.

Nitration of these highly chlorinated compounds does not proceed far, owing to their saturated condition: a mixture of conc. H_2SO_4 and fuming HNO_3 introduced 4·6% of nitro-groups into the chloro-ulmin from the β-fraction of the Swallowood Softs. The product (containing 37·4% Cl) was an amorphous, yellow-red solid, sol. in Et_2O, acetone, and EtOH but insol. in C_6H_6. When "unstable" Cl had been removed from the chloro-ulmin by treatment with alkali, 13·6% of nitro-groups could be introduced.

Although the earlier fractions obtained on chlorinating the α-fraction of the Swallowood coal contained more chlorine than the later, the difference is not marked and the work as a whole confirms our original belief that the ulmins of a bituminous coal can be regarded as homogeneous. Earlier workers, who have claimed to have separated chloro-ulmins into fractions of different character by means of solvents, seem to have been misled by their omission to subject the fractions to exhaustive chlorination. The effects they have observed have been partly physical, the outer layers of the coal particles having been chlorinated to a higher degree than the inner and having become more readily soluble in organic solvents.

Sulphur and nitrogen in the nuclear structure. Exhaustive treatment of the α- and β-fractions, separately, of the Swallowood Softs coal with chlorine dioxide yielded compounds of the following compositions (% on the ash-free, dry substances) compared with that of the original coal :

	Original coal.	Chlorinated α-fraction.	Chlorinated β-fraction.
C	82·6	36·3	39·0
H	5·7	1·8	2·0
Cl	—	40·6	39·8
N	1·81	0·54	0·74
S (organic)	0·54	nil	nil

The complete removal of the organic sulphur by chlorination–oxidation, a preferential removal although the ulmins still remain highly complex, suggests its existence in the nuclear structure in a fairly readily accessible condition, *e.g.*, in connecting linkages as postulated by Francis and Wheeler (Safety in Mines Research Board Paper No. 28, p. 34). On the other hand, a considerable proportion of the nitrogen of the coal survives chlorination–oxidation, showing that it is in a highly stable form and an essential constituent of the nucleus.

The chlorination of a series of coals. Although the ulmins in a given coal could not be separated into different types of compound by chlorination, it appeared possible that different types could be recognised in different coals. The α-fractions of a series of coals, including an anthracite, were therefore chlorinated exhaustively in the manner previously described for the Swallowood Softs. All the compounds so produced were completely soluble in ethyl ether. They ranged in colour from light yellow, when from the coal of lowest rank, to brown, when from the anthracite. The analyses of the coals used and of the chlorination products are recorded in Table III.

TABLE III.

The Chlorination Products of Coals.

	Analysis, % on ash-free dry coal.				Chlorination product, %.*				
Coal.	C.	H.	Ratio, C/H.	Re-activity index.	C.	H.	Cl.	N.	Ratio, C/H.
Ellistown Main	77·9	5·35	14·5	8·9	30·8	3·10	30·1	0·35	9·9
Kent Thick	84·0	5·30	15·9	58	36·3	2·40	32·9	0·30	15·1
Silkstone	86·0	5·40	15·9	22	36·8	1·95	37·4	0·45	18·9
Tilmanstone	86·5	5·05	17·2	41	38·5	1·85	35·3	0·30	21·0
Brockwell	88·8	5·10	17·4	71	38·6	1·75	36·9	—	22·0
Anthracite	92·5	3·55	26·1	5	41·3	1·51	35·3	0·50	27·4

* The content of S was nil throughout.

The Silkstone and Brockwell coals were included in the series because their reactivity indices were markedly anomalous.

It will be noted that the " rank " of the coals, as judged by the carbon contents, has been preserved in the chlorination products. The C/H ratio has been considerably reduced in the chlorination product of the coal of lowest rank but is not much altered in that of the anthracite. This ratio would be reduced if carbon in reactive groupings or in unstable ring formation were oxidised, but would be increased if chlorination were taking place by substitution of hydrogen. The results show that there is more carbon present in reactive groupings in coals of lower than in those of higher rank, and that in anthracite more carbon is present in stable ring formation. A similar conclusion can be drawn from the chlorine contents of the products, for the analyses show that the reaction has involved oxidation to a greater degree with the coals of lower rank.

In order to determine the proportions of " stable " chlorine in the chlorination products, each was treated with boiling *N*/6-NaOH during an hour, causing complete solution. The solutions were acidified and the colloidal precipitates filtered, washed, dried, and analysed. The analyses are recorded in Table IV.

TABLE IV.

Chlorination Products of Coals after Treatment with Alkali.

	Analysis of chlorination product.			
Coal.	C, %.	H, %.	Cl, %.	Ratio C/H.
Ellistown	51·9	3·20	12·0	16·3
Kent Thick	50·8	2·95	12·4	17·5
Silkstone	50·0	2·65	14·3	19·0
Tilmanstone	50·6	2·85	13·4	17·9
Brockwell	50·7	2·45	14·3	20·6
Anthracite	49·9	2·10	18·3	24·0

The most striking feature of these results is the remarkable uniformity in the carbon contents of the products, despite the widely different character of the coals from which they were obtained. It should be noted that the coals of which the reactivity indices were abnormal—Silkstone and Brockwell—do not now exhibit any abnormality. We believe this to be due to the fact that all reactive groupings were removed during the drastic treatment of oxidation–chlorination, the abnormality of the coals residing in their reactive groupings.

The amount of " stable " chlorine is greater in the products from the coals of higher rank. Since this chlorine has been introduced into the nuclear structure of the ulmins, it follows that the ulmins of coals of higher rank possess higher proportions of stable nuclei.

There is no indication that ulmins of different types exist in different coals.

We thank the Department of Scientific and Industrial Research for generous grants towards the cost of carrying out this research, which is being continued.

DEPARTMENT OF FUEL TECHNOLOGY, SHEFFIELD UNIVERSITY.

[*Received, October 6th,* 1932.]