Infrared Studies of Carbonised Coals.

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A weakly caking and a strongly coking coal, carbonised at temperatures up to 800°, have been examined by infrared methods. The most marked changes in the spectra are caused by heating to between 400° and 550°; they indicate a loss of aliphatic CH and phenolic OH groups. It is suggested that the different physical changes which occur in the two coals at temperatures between 400° and 460° result, in part, from the presence of phenolic material in the caking coal and its absence in the coking coal. A pyrolysis mechanism is proposed in which aliphatic groups are replaced mainly by C–C bonds between the aromatic systems; this begins in the temperature range 400—550°. The process is continued at higher temperatures with the loss of aromatic hydrogen, and some graphitisation ensues.

In the preceding paper the infra-red spectra of a range of vitrains were discussed. The present paper describes infra-red studies of heated coals. Infra-red methods have not been applied previously to the study of coal carbonisation although the spectra of several products have been published. They include the spectra of a " shock-heater " distillate (Cannon and Sutherland, *Trans. Faraday Soc.*, 1945, **41**, 279), a pitch (Gordon, Adams, and Jenkins, *Nature*, 1952, **170**, 317), and two pitch extracts (Cannon and Sutherland, *loc. cit.*).

Two coals have been studied in the present work, *viz.*, a " caking " and a " coking " coal. Briefly, a caking coal, when heated to 350—400°, first softens and contracts, and on further heating the particles sinter together and a slight swelling occurs; the shape of the product is similar to that of the unheated specimen. A coking coal, heated in the same temperature range, becomes semi-fluid (near 400°) and contracts slightly; then, at temperatures between 400° and 450°, it swells markedly and at higher temperatures the plastic mass, inflated by the gases evolved in its decomposition, sets to a solid with a highly developed bubble structure. In both cases the product is termed a semi-coke. Heating to temperatures beyond 550° transforms the semi-coke into a more compacted coke structure.

Little is known concerning the chemical changes which occur when coals are heated. Analyses show that the H/C and O/C ratios decrease with increasing temperature of carbonisation (see, *e.g.*, van Krevelen, *Fuel*, 1950, **29**, 269). The structure of the residual coal after carbonisation has been studied by *X*-ray methods (Blayden, Gibson, and Riley, Proc. Conf. Ultrafine Structure of Coals and Cokes, B.C.U.R.A., London, 1944, p. 342; Franklin, *Proc. Roy. Soc.*, 1951, **209**, *A*, 196); the process has been discussed in terms of a turbostratic system of graphitic crystallites in which the lamellæ change in size and degree of order.

The two coals studied in this work were carbonised at various temperatures up to 800°.

EXPERIMENTAL

The weakly caking coal selected was a Northumberland vitrain; its chemical composition on a dry mineral-matter-free basis (Parr formula) was C, 81·8; H, 5·3; N, 1·8; O (by diff.), 11·1%. Corresponding values for the Durham coking coal were 88·8, 5·1, 1·6, and 4·5%. Each was ground to −72 B.S.S. and heated in nitrogen at the rate of 1¼°/min. to temperatures of 300°, 400°, 460°, 550°, and 800°; they were kept at these temperatures for 1 hr. The method of preparation of the samples for infra-red examination, the instrument used in recording the spectra, and the procedure employed in drawing the background, were as described in the preceding paper. The spectra of the Northumberland coal are shown in Figs. 1*a* to 1*e*, and those of the Durham coking coal in Figs. 2*a* to 2*e*.

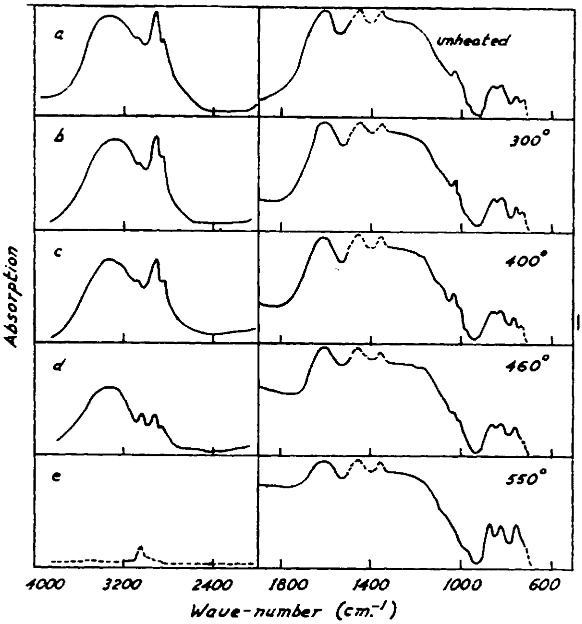
DISCUSSION

(a) *Unheated Coals.*—The analysis of the spectra of the unheated coals follows directly from the interpretation of the spectra of a range of vitrains given in the preceding paper. The most significant features in the spectrum of the Northumberland coal are strong absorption bands arising from hydrogen-bonded OH (near 3300 cm.$^{-1}$) and aliphatic (or alicyclic) CH groups (2920 and 2850 cm.$^{-1}$). Much weaker absorption bands, arising from the out-of-plane motion of aromatic CH bonds, are observed near 750, 820, and 860 cm.$^{-1}$, *i.e.*, in the positions previously found for other coals with similar carbon content (82%). The spectrum of the unheated coking coal (Fig. 2*a*) shows all the characteristics of a vitrain of carbon content near 89%, *viz.*, a weak hydrogen-bonded OH absorption band, and a ratio of the optical densities of aromatic CH to aliphatic CH stretching absorption bands, $D_{\mathrm{ar.}}/D_{\mathrm{al.}}$, of approx. 0·25. The out-of-plane aromatic CH bands lie at 750, 814, and 870 cm.$^{-1}$. The spectrum of the coking coal shows a well-defined background absorption which, from previous work (Cannon, *Nature*, 1953, **171**, 308; Brown, *loc. cit.*), has been tentatively ascribed to an electronic effect associated with polycyclic aromatic structures. A very pronounced absorption band at approx. 1030 cm.$^{-1}$ in the spectrum of the coking coal may be associated with inorganic material (the ash content was 2·6%).

(b) *Coals heated at* 300° *and* 400°.—There is very little change in the spectra of the coals heated to 300° and 400°. The hydrogen-bonded OH absorption band in the spectrum of the unheated caking coal (Fig. 1*a*) has decreased in intensity, but is still very pronounced. The decrease may have been a result of the removal of absorbed water or some other hydroxylic material, or it may have been due to a chemical change, *e.g.*, formation of ether linkages from phenolic structures. No change is observed in the intensities or positions of the aromatic CH absorption bands between 900 and 700 cm.$^{-1}$. The spectra of both coals at 300° and 400° show a decrease in the intensity of the aliphatic (or alicyclic) CH stretching absorption bands. The decrease could not be estimated for the Northumberland coal owing to the overlapping OH absorption band; however, the reduction in intensity is not marked. A quantitative estimate of the ratio $D_{\mathrm{ar.}}/D_{\mathrm{al.}}$ was made for the Durham coking coal; at 300° the value is 0·27 and at 400° 0·33, compared with 0·25 for the unheated sample.

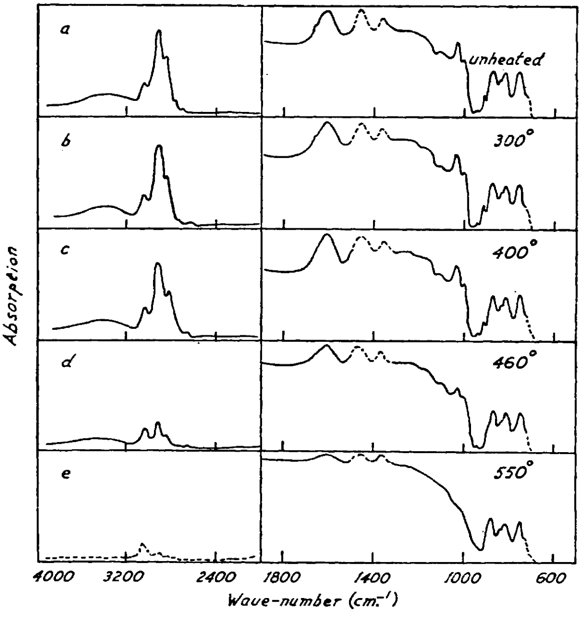
(c) *Coals heated at* 460°.—At 460° marked changes in the spectra are apparent. There is a very pronounced decrease in the intensity of the aliphatic CH stretching absorption bands in the spectra of both coals (Figs. 1*d* and 2*d*). The $D_{\mathrm{ar.}}/D_{\mathrm{al.}}$ ratios have been estimated for the two products; in each case the value is near 1. A further decrease in

FIG. 1. *Infrared spectra of a carbonised caking coal (Ellington High Main).*



----- Uncertain intensities (left portions).
----- Nujol absorption bands (right portions).

FIG. 2. *Infrared spectra of a carbonised coking coal (South Garsfield Victoria Seam).*



----- Uncertain intensities (left portions).
----- Nujol absorption bands (right portions).

intensity of the hydrogen-bonded OH absorption band occurs in the spectrum of the weakly caking coal (Fig. 1*d*); it is accompanied by a shift in frequency of one of the aromatic CH bending absorption bands at 862 cm.$^{-1}$ in the spectrum of the coal at 400° to 870 cm.$^{-1}$ at 460°. A slight increase in intensity of the 750-cm.$^{-1}$ absorption band is also observed. There are no corresponding changes in the spectrum of the coking coal, although a decrease in intensity of several absorption bands in the region 1100—900 cm.$^{-1}$ (in particular, that at 1030 cm.$^{-1}$) is apparent. Both the caking- and the coking-coal spectra show an increase in the structureless background absorption which, from a previous discussion of the effect (preceding paper), is interpreted as indicating a growth in size of the aromatic lamellæ.

At 460°, the caking coal had contracted and agglomerated; the coking coal, in contrast, had swollen and was in the initial stages of forming a semi-coke. The spectrum of the caking coal shows that hydrogen-bonded OH groups still formed a significant part of the structure, whereas they were in very small concentration in the coking coal. It is possible that hydroxylic material (probably mainly phenolic) in the caking coal during the caking process (*i.e.*, between 400° and 460°) was responsible for the difference in the physical changes which occurred. The simple explanation that the strong intermolecular forces associated with hydrogen-bonding restricted the ability of the caking coal to become plastic and swell is not satisfactory as it is not in accord with a number of facts known about the coking process (*e.g.*, the destruction of coking power by solvent extraction).

(d) *Coals heated at* 550°.—At 550° there is a further marked decrease in the intensity of the aliphatic CH stretching absorption bands; in both spectra (Figs. 1*e* and 2*e*) they are very weak. Further, the hydrogen-bonded OH absorption band has disappeared from the spectrum of the Northumberland coal (Fig. 1*e*) and thus the difference between the two coals in this respect is eliminated. The disappearance of OH groups from the weakly caking coal is accompanied by a marked change in the pattern of absorption between 900 and 700 cm.$^{-1}$. There is an overall increase in intensity, and the 750-cm.$^{-1}$ absorption has now become of approximately the same strength as the other two main absorption bands in this region. Also, the 870-cm.$^{-1}$ absorption band (present in the spectrum of the coal at 460°) has moved to 876 cm.$^{-1}$. The changes in the region 900—700 cm.$^{-1}$ are very similar to those observed in the spectra of a range of unheated vitrains (preceding paper) where they were correlated with the disappearance of phenolic OH groups from the structure; thus the two observations are in good agreement.

The coking coal spectrum (Fig. 2*e*) shows less change between 460° and 550° because there were insufficient OH groups present in the structure to produce, on their elimination, any appreciable change in position of the aromatic CH absorption bands.

The level of background absorption in both spectra has increased; in the caking coal heated to 550° it is similar to that of unheated coals with carbon contents in the range 90—93% (coking ⟶ dry steam coals). In the coking coal spectrum the level corresponds closely to that observed in unheated anthracites (94% of carbon). The higher level of background absorption in the coking coal spectrum indicates, on the previous interpretation of the effect (preceding paper), a larger graphitic crystallite size. The spectrum of the heated coking coal resembles that of an unheated anthracite, not only in the background level but also in the weakness of the aliphatic CH stretching absorption bands and the almost structureless nature of the absorption at frequencies above 1000 cm.$^{-1}$. The similarity suggests that the formation of anthracites may have occurred at temperatures in the region of 500°. Measurements of H/C and O/C ratios of carbonised semi-anthracites (van Krevelen, *Fuel*, 1951, **30**, 253) show that these follow the same course as that observed in the coalification process, and therefore provide some support for the above conclusion.

(e) *Coals heated at* 800°.—No spectra are shown for the coals heated to 800°, for the samples were opaque to infra-red radiation throughout the region 4000—650 cm.$^{-1}$, even in very thin sections. A similar effect has been observed for mulls of powdered graphite (Cannon, *loc. cit.*); in both cases the structureless background absorption extends across the spectrum and no absorption edge is observed. This suggests that between 550° and 800° some graphitisation has occurred. Electrical resistance measurements of coals carbonised in the above temperature range (Sandor, Proc. Conf., etc., *loc. cit.*, p. 342) also support this view.

(f) *Constant Features of the Spectra.*—The previous discussion has concentrated mainly on the *changes* that occur in coal structure at different temperatures. Two features of the spectra undergo remarkably little change. One is the pronounced 1600 cm.$^{-1}$ absorption band which occurs in the spectra of both coals. In the preceding paper the intensity of this absorption band was ascribed to the presence of oxygen in aromatic ether linkages or in hydroxylated quinone structures. The present work shows that, whatever type of oxygen grouping is associated with the strong 1600-cm.$^{-1}$ absorption band, this grouping must be a very stable one. The second feature occurs only in the spectrum of the Durham coking coal; this is the pattern of absorption bands between 900 and 700 cm.$^{-1}$ which shows very little variation in shape or intensity throughout the range of temperatures. This is surprising because, as stated earlier, the intensity of the aliphatic (or alicyclic) CH stretching absorption bands decreases very markedly in the spectra of samples heated at temperatures above 400°; they are very weak in the spectrum of the 550° sample. Two alternative suggestions can account for these observations: (i) the aliphatic (or alicyclic) material does not form a major part of the structure, but occurs only in units of low molecular weight. Either the spectrum of these units is very similar in the region 900—700 cm.$^{-1}$ to that of the rest of the coal, or it is completely masked by it. On being heated to 550°, the material of low molecular weight is distilled away and leaves aromatic systems largely unsubstituted. In the second alternative (ii) the aliphatic material is associated with the main part of the coal structure and is decomposed on heating. The removal of the aliphatic material leaves unsatisfied valencies on the edges of the aromatic systems, which, however, are not replaced by hydrogen atoms (causing a change in the pattern between 700 and 900 cm.$^{-1}$) but principally by C–C bonds, *i.e.*, the systems become cross-linked.

Evidence from the spectra of solvent extracts (Brown, unpublished work) suggests that aliphatic (or alicyclic) material forms part of the main coal structure, and therefore, at the present stage, explanation (ii) is the more acceptable. This means that, in the temperature range 400—550°, cross-linking of the aromatic systems is initiated.

Independently of the foregoing evidence, the infra-red data suggest strongly that cross-linking occurs at temperatures higher than 550°. Both spectra show that the amount of aliphatic (or alicyclic) material is very small, and yet, as the temperature is increased the H/C ratio continues to fall (van Krevelen, *loc. cit.*); the decrease in the ratio presumably arises from the elimination of hydrogen from the ring systems during the linking process.

Conclusions.—The above analysis shows that coals undergo not only marked physical changes but also important modifications in chemical structure in the temperature range 400—550°. Aliphatic (or alicyclic) material is removed, most probably by simple distillation and chemical decomposition; hydrogen-bonded phenolic OH groups are also eliminated, the change being most marked in the temperature range 460—550°. The data suggest that the formation of C–C cross-links between the aromatic systems accompanies the loss of aliphatic groups, and that at temperatures above 550° the process is continued with the removal of aromatic hydrogen. Presumably, as the temperature is increased, cross-linking extends throughout the structure; the very steep fall in the electrical resistance of coals carbonised at temperatures between 600° and 650° may be a consequence of this change. The opacity of the specimens heated to 800° suggests that some graphitisation has occurred.

Van Krevelen (*Fuel*, 1951, **30**, 253) considers the essential mechanism in the pyrolysis of coal to be a slow primary decomposition which reaches a maximum rate between 400° and 460°; this decomposition comes to an end at about 550°. A secondary reaction then sets in during which hydrogen is split off. This view, which is supported by kinetic studies, is given further significance by the present infra-red work; this suggests that the secondary reaction is a cross-linking of the aromatic systems which results in some graphitisation as the temperature is increased.

A difference between the structure of the caking and coking coal has been found which is apparent in the unheated specimens. This is that hydroxylic material (probably mainly phenolic) is in much higher concentration in the caking coal. Previous infra-red work on unheated coals (preceding paper) has shown that the development of coking properties is accompanied by a decrease in the amount of hydroxylic material in the structure. The present studies show that this material persists in the temperature range 400—460° and may be an important factor in determining the different physical changes which occur in caking and coking coals.

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