

972. *The Dehydrogenation of Coals with p-Benzoquinone.*

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Dehydrogenation of coals takes place on reaction with *p*-benzoquinone, considerable amounts of aliphatic hydrogen being removed. It is concluded that up to one-third of the carbon in coals occurs in the aliphatic part of hydroaromatic systems, the amount falling off with increasing carbon content of the coal. The hydroaromatic systems must be considerably substituted, particularly in coals of lower carbon content. Vitrinites and exinites do not differ greatly in the proportions of carbon in this hydroaromatic form. Besides dehydrogenation, a largely reversible addition of the quinone to the coal occurs, probably mainly to structures produced by the dehydrogenation; this permits some general statements to be made about the nature of some of the hydroaromatic systems.

WHEREAS the aromatic systems in coals have received considerable attention in the past few years, the non-aromatic material which is acknowledged to constitute an important fraction of the coal structure has received little investigation. In an attempt to obtain more information relating to the non-aromatic portions of the coal structure, the reaction between a series of coals and *p*-benzoquinone has been studied.

Quinones have been used widely as hydrogen acceptors in the aromatisation of hydroaromatic donors in solution under mild conditions, reaction being clean and not involving substituent groups (for a literature survey see ref. 1*a*). Braude, Linstead, and their co-workers¹ found practically quantitative reaction with a wide variety of hydrogen donors and acceptors under suitable conditions. Side reactions involving Diels–Alder addition of the quinone to the products of dehydrogenation sometimes took place.

Coals consist of a series of components, distinguished mainly by their appearance under the microscope, but also to some extent by their chemical properties. The petrological component exhibiting the most consistent and continuous variations in chemical properties with carbon content is vitrinite, and a series of hand-picked, vitrinite-rich (80–90%) coals, together with some purer vitrinites (90–98%) prepared by a flotation procedure,* have been used for this investigation. A series of pure exinites,* which contain considerably more hydrogen than vitrinites and are considered to be less aromatic,² have also been investigated.

Results.—The extent of reaction was estimated from the quinone consumed and quinol produced. In preliminary experiments both chloranil and quinone were used as hydrogen acceptors in dimethylformamide, phenetole, and 1,2,4-trichlorobenzene, but conventional methods for determination of the quinols were unsatisfactory owing to interference by the solvent or coal. However, the combination quinone–dimethylformamide had the advantages that both quinone and quinol could be determined simultaneously polarographically and that the reaction proceeded at a convenient rate at the b. p. (153°). This system was adopted for the present studies.

In the absence of added hydrogen donor, quinone in boiling dimethylformamide undergoes a slow reaction with the formation of some quinol in the later stages. In the presence of coal the quinone disappears rapidly and considerable amounts of quinol are formed. This behaviour is illustrated in Fig. 1. In most cases the quinol formation approached a limiting value after several hours (see Fig. 1), showing that a major proportion of the dehydrogenation was complete. After correction for the production of quinol in dimethylformamide alone (in most cases less than 15% of the total), the hydrogen removed from the coal was calculated. The results are collected in Tables 1 and 2.

* These samples were kindly supplied by Dr. G. W. Fenton, of the National Coal Board.

¹ (a) Braude and Linstead, *J.*, 1954, 3544; (b) Braude, Jackman, and Linstead, *ibid.*, (b) p. 3548; (c) p. 3564; (d) Braude, Brook, and Linstead, *ibid.*, p. 3569.

² Brown, "Macerals," B.C.U.R.A. Bulletin Review 183, 1959, and references therein.

These Tables show that appreciable amounts of hydrogen are apparently removed from all the coals except those of highest carbon content. The extracts of the coals give figures closely resembling those of the parent coals. Since the former are in solution and resemble the parent coals chemically in most respects, this suggests that the heterogeneity of the reaction mixture when the coal is being used does not greatly retard reaction. The amount of hydrogen removed from sample VII which had been reduced by lithium-ethylamine compared with that from the parent coal agrees well with the amount of hydrogen introduced into the coal by the reduction which had previously been considered to reduce primarily the aromatic systems.³

TABLE 1. *Dehydrogenation of a lignite and a series of highly vitrainous coals and vitrinites.*

No.	Coal Colliery and seam	C (%) (dry mineral- matter free)	H (%)	Hydrogen removed (g./100 g. of coal)	
				(a) from quinol produced	(b) from analysis
V1	S. Arcot Lignite	64.9	5.5	2.3	—
V2	Binley, 9 foot (DO)	77.7	5.3	2.6	—
V3	Cannock Wood, Shallow	79.6	4.9	2.0	1.8
V4	Ellington High Main (DIII)	81.7	4.9	2.3	—
"	Acetylated ^a			2.0*	—
"	DMF extract ^b †	82.5	6.2	2.4	2.1
V5	Markham Main, Barnsley	82.3	5.0	3.0	—
V6	Maltby, Barnsley (DVI)	83.9	5.4	2.0	1.3
V7	Dinnington Main, Barnsley	85.1	5.3	1.4	—
V8	Sneyd, Coxhead (DIX)	86.0	5.3	1.7	} 0.8
"	Acetylated ^c	85.0	6.8	1.6	
"	DMF extract ^d †			1.4*	—
V9	Aldwarke Main, Silkstone	86.9	5.4	1.9	—
V10	Chislet, No. 5	88.6	5.3	2.1	—
V11	S. Garesfield, Victoria (DXIII)	88.9	5.1	1.7	—
"	Reduced with lithium	86.0	7.2	1.6	1.4
V12	Coegnant, Gellideg	91.4	4.5	3.5	3.0
V13	Blaenhirwaun, Pumpquart	93.8	3.1	0.5	—

* Allowance made for acetyl.

† DMF = Dimethylformamide.

^a Acetyl content of acetylated material was 13.1%. ^b 12% Extraction. ^c Acetyl content of acetylated material was 6.5%. ^d 19% Extraction.

TABLE 2. *Dehydrogenation of a series of exinites.*

No.	Coal Colliery and seam	C (%) (dry, ash-free basis)	H (%)	Hydrogen removed (g./100 g. coal) from quinol produced
E1	Cannock Wood, Shallow	81.0	7.0	4.7*
E2	Markham Main, Barnsley	81.6	7.6	2.7
E3	Dinnington Main, Barnsley	84.3	7.6	2.0
E4	Aldwarke Main, Silkstone	87.1	7.4	2.3
E5	Chislet, No. 5	89.1	6.2	2.5

* Value from analysis is 2.1 g.

It is not clear to what extent phenolic hydrogen would be removed in the reaction. Thus the oxidation of quinols of suitable oxidation potentials to quinones by benzoquinone has been reported,⁴ but not of monophenols. On the other hand, the oxidation of a large number of phenols by diphenylpicrylhydrazyl has recently been investigated.⁵ The mechanism of hydrogen abstraction by this reagent is not clear, but transfer of hydride ion has been inferred as for dehydrogenation by quinone.^{1b} In any case the oxidising power of diphenylpicrylhydrazyl is much greater than that of benzoquinone (oxidation

³ Given, Lupton, and Peover, Proc. Conf. Science in the Use of Coal, Inst. Fuel, 1958, A-38.

⁴ Urban, *Monatsh.*, 1907, **28**, 314; Valeur, *Ann. Chim. (France)*, 1900, **21**, 552.

⁵ McGowan, Powell, and Raw, *J.*, 1959, 3103.

potentials about 1.2 v and 0.71 v).⁶ The amount of hydrogen in coals associated with phenolic hydroxyl is in the range 2–8% of the total hydrogen.⁷ In an attempt to determine the effect of phenolic groups in coal, a number of acetylated coals were treated with quinone. Acetylation of the phenolic hydroxyl groups slows down the dehydrogenation; the final amount of oxidation is somewhat lower than for the unacetylated coal, but as the difference is small (10–15%) it is probably accounted for by the different rates of reaction.

In all cases where appreciable amounts of quinol were produced, an excess of quinone was consumed, as can be seen, for example, from Fig. 1. Hence not only dehydrogenation occurred. Weight increases usually of 15–20%, but sometimes up to 30%, were found in the products, and elementary analyses showed decreased hydrogen contents but also decreased carbon and increased oxygen contents. This side reaction with quinone made characterisation of the products difficult.

The infrared spectra of the products from the coals V4 (acetylated), V5, E1, and E5 showed reduced aliphatic C–H absorption (in the case of V5 and E1 greatly reduced). Also

FIG. 1. Reaction of benzoquinone in boiling dimethylformamide: (a) alone; (b) with V5 coal. — Quinol production; - - - quinone disappearance.

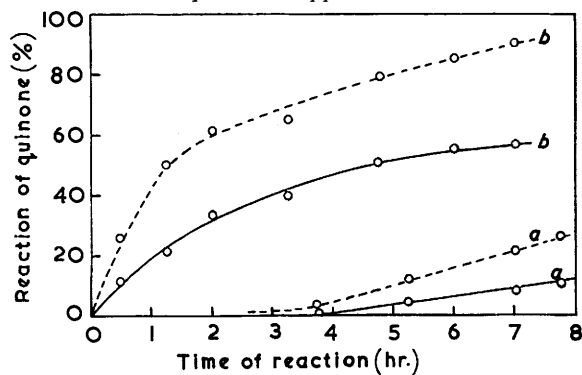
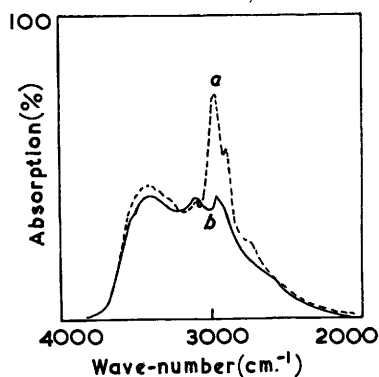


FIG. 2. Infrared spectrum between 2000 and 4000 cm^{-1} of (a) V4 coal and (b) same after treatment with triphenylmethyl perchlorate. (Mulls in hexachlorobutadiene.)



two intense new bands had arisen at about 1510 and 1680 cm^{-1} , associated with aromatic and carbonyl absorption, respectively. The presence of these bands in the acetylated sample eliminated the possibility of molecular complexes of the quinhydrone type, but Diels–Alder addition of the quinone to existing structures in the coal or to those produced by dehydrogenation would account for the observed results. The two new bands were eliminated from the E5 product by boiling it in α -naphthol, whereas the reduction in aliphatic C–H absorption was as marked as formerly. The use of a lower temperature (boiling 1,2,4-trichlorobenzene) was unsuccessful in bringing about division; also the bands could not be eliminated completely from the V5 product by treatment in α -naphthol.

On the assumption that only dehydrogenation together with some addition of quinone occurred in the reaction,* the analyses of the products could be corrected for the addition

* I am indebted to a Referee for pointing out that, in view of known addition of amines to benzoquinone giving 2-alkyl- or aryl-aminoquinols (Hofman, *Proc. Roy. Soc.*, 1863, **13**, 4; H. and W. Suida, *Annalen*, 1918, **416**, 118), there is a slight possibility that phenolic structures in coal might by an analogous reaction phenoxyate benzoquinone. If this occurred the phenoxy-quinols produced, not being in solution, should not influence the polarographic analysis—unless they are capable of reducing benzoquinone.

⁶ Braude, Brook, and Linstead, *J.*, 1954, 3574.

⁷ Blom, Edelhausen, and van Krevelen, *Fuel*, 1957, **36**, 135.

on the basis of the increased oxygen contents, thus obtaining the amount of hydrogen removed. These values are included in Table 1 and 2 and are in most cases in fair agreement with those calculated from the quinol production, which should measure only the dehydrogenation and not be affected by Diels–Alder addition

Since the body of this work was completed, Bonthron and Reid⁸ have published details of dehydrogenations using the triphenylmethyl cation in the form of triphenylmethyl perchlorate as hydrogen acceptor. The application of this method to V4 coal gave a product whose infrared spectrum showed changes in hydrogen content similar to those in the quinone-treated sample but with little evidence of side reactions. A portion of the spectrum showing the changes in relative intensities of aliphatic and aromatic C–H absorptions at 2900 and 3030 cm^{-1} is given in Fig. 2. The further use of this reagent is being explored.

Discussion.—The results show that considerable amounts of aliphatic hydrogen can be removed from coals by reaction with quinone. The nature of the hydrogen-abstraction by quinone from known compounds creates the presumption that with coals this occurs from hydroaromatic systems. Moreover, the alicyclic part of these systems must be fused to an aromatic ring, as in tetralin, since fully saturated structures are not dehydrogenated by this technique.

Although aliphatic hydrogen is removed in the reaction with quinone, the amount of aromatic hydrogen is not noticeably increased. This can only partly be accounted for by the lower extinction coefficient of aromatic C–H bonds, and it must be concluded that the hydroaromatic systems are considerably substituted.

The rate of dehydrogenation of coals by quinone is surprisingly high; in this respect it most nearly resembles that of 1,4-dihydronaphthalene,¹⁹ one of the more reactive hydroaromatic compounds. When applied to 1,4-dihydronaphthalene, 9,10-dihydroanthracene, and tetralin, the procedure used in this work resulted in 91%, 31%, and ~10% dehydrogenation after 7 hr. But there is no evidence for the presence of ethylenic bonds in coals,⁹ and recent work,¹⁰ using nuclear magnetic resonance, suggests the absence of significant numbers of methylene bridges. Possibly the presence of hydroxyl and other substituents may have a bearing on this reactivity.

Evidence for the presence of hydroaromatic material in coals has been presented by Mazumdar *et al.*,¹¹ who found that hydrogen sulphide was evolved when coals were heated with sulphur. However, other workers¹² have shown that unsubstituted polycyclic aromatic compounds also yield hydrogen sulphide under similar conditions. The reaction is thus not sufficiently selective to establish the presence of hydroaromatic features from the evolution of hydrogen sulphide alone.

It is of interest to know whether the addition of quinone, which takes place simultaneously with dehydrogenation, is confined to structures already present in the coal or to those produced by dehydrogenation. Treatment of one coal with maleic anhydride (a more reactive dienophile than quinone) in boiling dimethylformamide gave no indication of a significant amount of reaction, suggesting that it is the products of dehydrogenation which are reactive in this respect. Since analogues of anthracene and perylene are the only aromatic compounds known to give adducts under the conditions used,¹³ our conclusion points to the production of these aromatic systems from hydroaromatic structures.

In considering the significance of the data for hydrogen abstraction in Tables 1 and 2, it must be borne in mind that complete reaction may not have taken place; also, any ring

⁸ Bonthron and Reid, *J.*, 1959, 2773.

⁹ Brown, *J.*, 1955, 744; Brown and Hirsch, *Nature*, 1955, 175, 229.

¹⁰ Brown and Ladner, *Fuel*, 1960, 39, 87.

¹¹ Mazumdar, Choudhury, Chakrabarty, and Lahiri, *J. Sci. Ind. Res. India*, 1958, 17, B, 509.

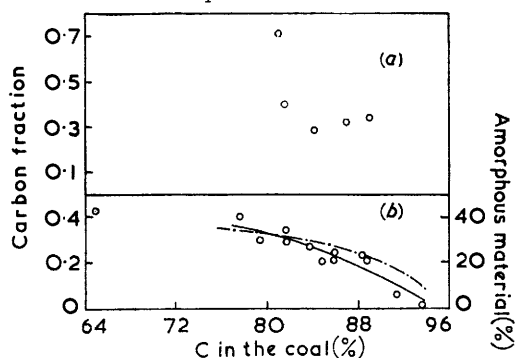
¹² van Krevelen, Goedkoop, and Palmen, *Fuel*, 1959, 38, 256; Pinchin, personal communication.

¹³ Alder, "Newer Methods, of Preparative Organic Chemistry," Interscience Publ. Inc., New York, 1948, p. 485.

bearing two substituents on one aliphatic carbon atom would not react completely,* and fully saturated systems could not be determined at all. For these reasons the values represent minimum amounts of hydrogen that can be removed from the coals by dehydrogenation. The dehydrogenation does not constitute an analytical determination of hydroaromatic structures in coal, as Mazumdar *et al.* chose to regard their dehydrogenation with sulphur. Nevertheless, the results are useful in limiting the possible structures that can be assigned to coal. The results cannot give directly the total amount of hydrogen in hydroaromatic systems, since this requires a knowledge of the degree of substitution of these systems which is not available. However, since each hydrogen atom lost is derived from one carbon atom in the hydroaromatic system, the (minimum) proportion of hydroaromatic carbon is given directly by $(\% \text{ hydrogen removed} \times 12)/(\% \text{ carbon in coal})$.

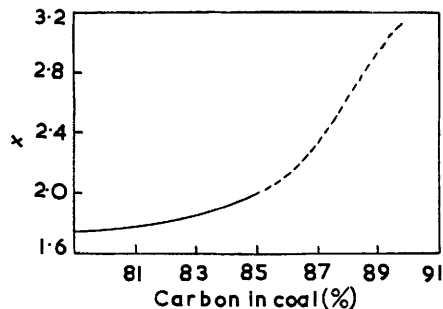
These minimum values for hydroaromatic carbon fractions are plotted in Fig. 3 against the carbon content of the coals. There is a marked decrease in the fraction with increasing

FIG. 3. Minimum fraction of carbon in hydroaromatic form in a series of coals as determined by reaction with benzoquinone.



- (a) Exinites, dry ash-free basis.
 (b) Vitrinites, dry mineral matter-free basis.
 ----- Hirsch's "amorphous material" (%).⁹

FIG. 4. Variation of maximum value of x in CH_x with carbon content for a series of vitrains.



carbon content of the vitrains, notably in the region 90—94% carbon, where the aromatic systems are thought to increase in size rapidly.¹⁴ The fraction of "amorphous material" as deduced by Hirsch, Cartz, and Diamond¹⁴ from X-ray studies, which may also contain contributions from oxygen atoms, is also shown in Fig. 3 for comparison. The point in Fig. 3(a) corresponding to a carbon fraction of 0.7 refers to the exinite E, and may be too high due to experimental error (See Table 2); a more probable value is 0.36—0.38.

The minimum values of hydroaromatic carbon obviously set maximum limits to the fraction of aromatic carbon.

The average composition CH_x of the hydroaromatic portion of the coals can be calculated on the assumptions: (1) that Brown's estimates,⁴ based on infrared intensities, of the ratio of aromatic to aliphatic hydrogen in coals are correct (if incorrect they are likely to be too low^{9,10,15}) and that extrapolation of his data below 84% carbon is permissible; (2) that the hydroaromatic carbon contents calculated above are not minima; (3) that all the aliphatic material in coal is hydroaromatic. Since incorrectness of any of

* Since this was written it has been shown (Braude, Jackman, Linstead, and Lowe, *J.*, 1960, 3123), that one alkyl group in certain *gem*-dialkyl hydroaromatics migrates to the *ortho*-position under the conditions used, making dehydrogenation impossible.

¹⁴ Hirsch, Proc. Conf. Science in the Use of Coal, Inst. Fuel, 1958, A-38 and references therein.

¹⁵ Given, *Fuel*, 1960, 39, 147.

these assumptions would make the calculated values of x lower, they are maximum figures. The values of x are plotted in Fig. 4. The low, maximum, values of x for coals of low carbon content show that the hydroaromatic rings are considerably substituted or fused into multi-ring structures in agreement with the conclusions from the infrared spectra noted earlier. On the other hand, no useful conclusions can be drawn where $x > 2$; such values only show that one or both of assumptions (2) and (3) do not hold for coals of higher carbon content (but the conclusion drawn when $x < 2$ merely acquire greater force if these assumptions are invalid).

The average composition of the aliphatic parts of coal, apart from its obvious value in limiting possible structures, is of some importance in the derivation of structural parameters such as f_a , the fraction of aromatic carbon. It has been usual to assume that the average composition of the aliphatic material does not vary with rank and is CH_2 or a little greater.^{9,11,16} The present work shows that the first of these assumptions is incorrect, and the second could only be valid for coals of higher carbon content.

A comparison of the series of exinites and vitrains (see Fig. 3) shows that the exinites contain a somewhat greater fraction of carbon in hydroaromatic structures. Infrared spectroscopic studies of exinites indicate that they contain a greater proportion of hydrogen in aliphatic systems than vitrinites;^{2,9} but our results do not enable us to say how much of the hydrogen is in ring systems capable of dehydrogenation.

EXPERIMENTAL

Materials.—Benzoquinone, m. p. 112—113°, was purified by steam-distillation from a laboratory-grade specimen. Dimethylformamide was fractionated, and phenetole purified by distillation from sodium. 1,4-Dihydronaphthalene was prepared by the method of Bamberger and Lodter.¹⁷ Other materials were either "AnalaR" where available or a laboratory grade.

The solvent extracts of the coals were made by Soxhlet-extraction for 16 hr., followed by evaporation of the solvent. Acetylations were performed with a boiling mixture of acetic acid and acetic anhydride containing a trace of perchloric acid for 4 hr.

Details of the coals are given in refs. 3, 18, 19. The "D" coals appearing in Table 1 are those previously used for investigations in this laboratory.

Procedure.—In general, 0.1 g. of the dried powdered coal and 0.3 g. of benzoquinone were refluxed in 10 ml. of dimethylformamide under nitrogen, with stirring. At intervals, 1 ml. of the mixture was withdrawn for analysis.

Determination of Quinone and Quinol.—In buffered solution, the reduction of quinones and oxidation of quinols are strictly reversible at the dropping-mercury electrode.²⁰ The diffusion currents are proportional to the concentrations of the quinol or quinone, being slightly larger for the latter. Thus when a mixture of the two is polarographed, only one wave is formed whose half-wave potential is independent of the concentration of either species, the position of zero current on the wave indicating the amounts of oxidisable and reducible components (quinol and quinone respectively) in the solution. The formation of oxidisable and reducible soluble products other than quinol would result in waves at different potentials and therefore need not be determined.

The aliquot parts from the reaction mixture were diluted to give an approximately 10⁻⁴ solution in a 50% methanol buffer²¹ from which oxygen had been removed with oxygen-free nitrogen. Methyl Red was added as a maximum suppressor. Polarograms were made on a Tinsley Mark 14/3 polarograph against a saturated calomel electrode with a 0.1N-potassium nitrate-agar bridge. Well-defined single waves were always found, with invariant half-wave potential of +0.16 v. From the position of the galvanometer zero, the heights of the cathodic

¹⁶ Dryden, *Fuel*, 1958, **37**, 444.

¹⁷ Bamberger and Lodter, *Ber.*, 1887, **20**, 705.

¹⁸ Brown, Given, Lupton, and Wyss, *Proc. Conf. Science in the Use of Coal*, Inst. Fuel, 1958, A-43.

¹⁹ Given, Peover, and Wyss, *Fuel*, 1960, **39**, 323.

²⁰ Kolthoff and Lingane, "Polarography," Interscience Publ. Inc., New York, 1952, p. 699.

²¹ Smith, Kolthoff, Wawzonek, and Ruoff, *J. Amer. Chem. Soc.*, 1941, **63**, 1018.

and anodic portions of the wave were determined, and hence the concentrations of quinone and quinol, the diffusion current constant of the latter being 1.33 times that of the former.²¹

Isolation of Products.—For analysis and infrared determination, the quantities given in the preceding section were trebled and the mixture was refluxed for 5 hr. The coal was filtered off and washed repeatedly with methanol. The extracts were precipitated with water and washed with water.

Division of the Adducts.—The product (0.3 g.) was refluxed in 10 g. of α -naphthol under nitrogen for 3 hr. The solid mass produced on cooling was broken up, and the naphthol dissolved out with methanol. The product was washed repeatedly with methanol.

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