548. Polarographic Reduction of Carbonyl Groups in Solvent Extracts of Coals.

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Solvent extracts of coals in dimethylformamide solutions give distinct reduction waves in the range -0.4 to -0.7 v against the mercury pool owing to the presence of quinones. The height of the waves indicates that not all the molecules in these materials are quinones; some preferential extraction of the non-quinonoid substances is effected by certain solvents, but the effect in not marked. There are indications that the quinones present in different coals have similar structures.

ALL coals contain combined oxygen; in coals of carbon content up to 90% much of this [1,2,3] is in the form of phenolic hydroxyl; the intensity of the band at 1600 cm.$^{-1}$ in the spectra of coals is suggested to be due in part to quinone groups chelated to hydroxyl.[1] It was thought that reduction at the dropping-mercury electrode might provide an independent means of detecting and estimating quinone and other forms of carbonyl groups in the material extracted from coals by organic liquids. This possibility has been investigated, with the results reported here. Dimethylformamide, in which the polarographic behaviour of a number of aromatic carbonyl compounds was available for comparison,[4] was used as solvent. The proportion of coal extracted by the various solvents was not large (Tables 2 and 3). However, there are reasons (based, for example, on comparison of the infrared spectra of coals with the spectra of extracts of them [5]) for supposing that the soluble material does not differ essentially from the insoluble in basic chemical structure, so knowledge of the nature of the extract is relevant to the study of coals themselves.

EXPERIMENTAL

The apparatus, procedure, solvent, and electrolytes were as described previously.[4] Solvent extracts of four coals (Table 1) were studied; they were prepared as follows: the solvent and dried powdered coal (100 g. of coal to 1 l. of solvent) were irradiated with 25 kc./sec. ultrasonic

TABLE 1. *Analyses (%, w/w) of the coals (dry and ash-free).*

Coal	C	H	N	S	O (by diff.)
DO	77·8	5·3	1·2	2·6	13·1
DIII	81·1	5·2	1·8	1·6	10·3
DIX	86·1	5·3	2·2	0·7	5·7
DXIII	89·2	5·0	1·4	0·7	3·7

radiation (electrical power input 500—800 w) for 10 min. The insoluble residue, after filtration, was further extracted by heating with fresh solvent at 100° (or the b. p. of the solvent if lower) for 1 hr. The combined filtrates were either added directly to the supporting electrolyte solution or were evaporated to dryness in nitrogen at or below 100°. The ethylenediamine extract of the coal DIII, however, was prepared by shaking the powdered coal at room temperature for ½ hr. with solvent in a vessel provided with a porous-glass filter. After withdrawal of the liquid the residue was shaken with more solvent. The combined filtrates were diluted with much water, and hydrochloric acid was added to bring the pH to 3—4. The precipitate was thoroughly washed, then dried. The analyses of the products were similar to those of the original coals; they indicated in some cases a small retention of solvent but after allowance for this the extracts still appeared to contain somewhat more hydrogen and correspondingly less carbon (for typical figures see refs. 1, 2, 6, and 7).

[1] Wyss and Brown, *Chem. and Ind.*, 1955, 1118.
[2] Wyss, *ibid.*, 1956, 1095.
[3] Blom, Edelhausen, and van Krevelen, *Fuel*, 1957, **36**, 135.
[4] Given, Peover, and Schoen, preceding paper.
[5] Brown, *Fuel*, in the press.
[7] Rybicka, *Fuel*, in the press.
[8] Dryden, *Fuel*, 1952, **31**, 176.

Results.—The polarographic behaviour of solvent extracts of one coal (DIII) was studied; the extracting solvent was removed and the residue taken up in dimethylformamide (see Table 2). The term A' is $i_d/(c'm^{\frac{2}{3}}t^{\frac{1}{6}})$ where i_d is the diffusion current (μA), c' the concentration

TABLE 2. *Solvent extracts of coal DIII in dimethylformamide.*

Extracting solvent	Extract (% w/w of dry coal)	Concn. range (%)	$-E_{\frac{1}{2}}$ (v)	A'
Ethylenediamine	10	0·05—0·135	0·61	3·8
Butanone *	2	0·1	0·59	1·55
Acetone	3	0·1—0·17	0·57	1·4

* The coal had previously been extracted with acetone.

(% w/v), m the mass (mg.) of mercury flowing per sec., and t the drop-time (sec.). Also, a series of pyridine and dimethylformamide extracts of 4 coals were studied, without removal of the original solvent: the extract was so added to the base solution that the concentration of the

FIG. 1. *Polarograms in lithium chloride–dimethylformamide of (a) 12 : 12'-dimethoxy-dibenzanthrone and (b) ethylenediamine extract of coal DIII.*
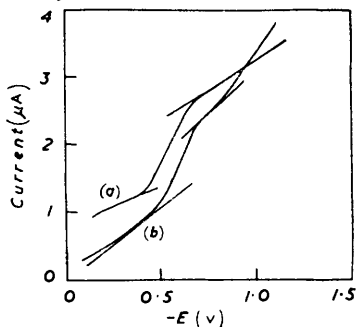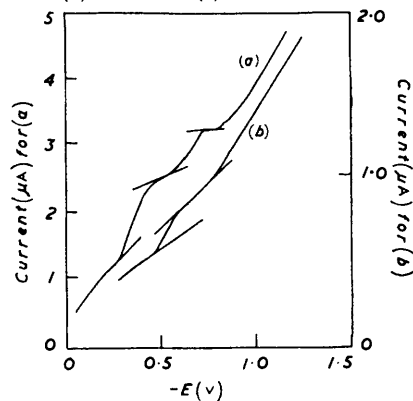

FIG. 2. *Polarograms in lithium chloride–dimethylformamide of pyridine extracts of coals (a) DIII and (b) DO.*

mixture was 0·05—0·2% in coal (see Table 3) and did not exceed 20% in pyridine. Pyridine itself gave no waves in the range of voltage studied, but it did influence the polarographic behaviour of the coals. Half-wave potentials are referred to the mercury pool, and all the results quoted were obtained with 1·0N-lithium chloride as supporting electrolyte. A few of the materials were also studied in 0·1N-tetraethylammonium iodide; the results were very similar, except that diffusion currents were higher.

TABLE 3. *Solvent extracts of four coals in dimethylformamide.*

Coal	Extracting solvent	Extract (% w/w of dry coal)	Concn. range (%)	$-E_{\frac{1}{2}}'$ (v)	$-E_{\frac{1}{2}}''$ (v)	A'
DO	Pyridine	10	0·05—0·1	N	0·57	2·9
	Dimethylformamide	10	0·094	N	N	—
DIII	Pyridine	10·5	0·08—0·16	0·36	0·67	3·5
	Dimethylformamide	3·7	0·12	N	0·67	1·8
DIX	Pyridine	12·5	0·05—0·11	N	0·67	2·2
	Dimethylformamide	9·9	0·08—0·17	N	0·68	1·4
DXIII	Pyridine	2·7	0·05—0·12	0·42	0·70	4·1

$E_{\frac{1}{2}}'$ and $E_{\frac{1}{2}}''$ are first and second waves respectively; N = no wave.

Polarograms of all the solvent extracts of coals showed considerable increases in current as the applied voltage increased in the range −0·2 to −1 v, and most of them showed distinct but not well-defined waves between −0·3 and −0·7 v (see examples in Figs. 1 and 2) which shifted slightly to more negative potentials with increasing concentration. The waves were

difficult to read (the method recommended by the makers of the instrument [9] was adopted as a standard procedure) and the reproducibility of diffusion currents was not good.

The half-wave potentials in the Tables all lie within a narrow range; all the coal extracts show a wave at -0.63 ± 0.07 v, and two of them a second wave at about -0.4 v. The effect of the presence of some pyridine in the base solution is not consistent: with coal DO, one wave is seen in the presence of pyridine and none in its absence, with DIII a second wave appears, and with DIX no effect is observed. These effects may be due to pyridine's being a base. If a little piperidine was added to the dimethylformamide solution of the extract of DIII, the behaviour became the same as that of the solution containing pyridine. There is no reason to suppose that pyridine and dimethylformamide extract essentially different materials from the coals.

Plots of log $i/(i_d - i)$ against the voltage E_{de} were made from a number of the polarograms (i is the current at any potential E_{de} of the dropping electrode). Satisfactory straight lines were obtained, whose slopes corresponded approximately to $n = 1$ [*e.g.*, 0·90, 0·93, 0·98, 1·0 (3 times), 1·2 (twice), 1·3].

An electrolytic reduction of a dimethylformamide extract of the coal DIII at a controlled potential of -1.5 v (*vs.* saturated aqueous calomel electrode) was carried out by M. Peover in a cell similar to that described by Lingane, Swain, and Fields.[10] The solvent extract was dissolved in dimethylformamide with tetraethylammonium iodide as supporting electrolyte. When the current had fallen to less than 1 mA excess of acetic anhydride was added and the solution left for two days. The product, after removal of the solvent and supporting electrolyte, was much lighter in colour than the starting material and easily soluble in chloroform. Its infrared spectrum (determined by Dr. J. K. Brown) showed a marked weakening of the band at 1600 cm.$^{-1}$ (previously associated with the presence of quinones; see below), two intense phenolic acetate bands near 1200 and 1760 cm.$^{-1}$, and very weak hydroxyl absorption. This spectrum was very similar to that of the product of the reductive acetylation of a similar extract of the same coal with zinc, acetic acid and anhydride, and sodium acetate [1] in whose polarogram no wave was observed, and the steady increase in current with increasing applied voltage, which was marked with all the untreated coal extracts, was only slight.

DISCUSSION

Controlled potential electrolysis makes it clear that the polarographic waves shown by solvent extracts of coals in the range -0.4 to -0.7 v (against the mercury pool) are due to the presence of carbonyl groups. Comparison of the half-wave potentials observed with values for known carbonyl compounds studied under the same conditions [4] shows that the carbonyl groups in the solvent extracts of coals must be strongly conjugated to aromatic systems. Of the known compounds studied, only quinones have half-wave potentials as low as those found for the coal extracts. We therefore conclude that these materials contain quinones, as did Wyss and Brown [1] from a comparison of the infrared spectra of solvent extracts of a coal with the spectra of the products of reductive acetylation. A strong band close to 1600 cm.$^{-1}$ is prominent in the spectra of all coals and their solvent extracts,[11] the assignment of which to a functional group is equivocal on spectroscopic grounds alone. Wyss and Brown,[1] however, showed that its intensity is markedly weakened if solvent extracts of a coal are reductively acetylated, from which they deduced that the assignment to quinonoid carbonyl strongly chelated to hydroxyl is correct (the weak benzene-ring skeletal vibration at the same frequency would also contribute). This concord between the different methods establishes the presence of quinone groups in coals. This band is of very nearly constant frequency for all coals, and its intensity decreases only slightly with increasing carbon content up to about 93% of carbon. This constancy indicates that the carbonyl groups have a closely similar molecular environment in all

[9] Anon., Polarography with Tinsley Polarographs, Instruction Book No. ETP 460, Evershed and Vignoles Ltd., London, 1955.
[10] Lingane, Swain, and Fields, *J. Amer. Chem. Soc.*, 1943, **65**, 1348.
[11] Brown and Hirsch, *Nature*, 1955, **175**, 229.

coals and is matched by the narrow range of voltage within which lie the half-wave potentials of extracts of four coals. Although a possible explanation of the fact that the waves are superimposed on a steadily rising diffusion current is that a series of quinones are present in coals, having a range of half-wave potentials, and that the waves observed merely represent preferred values of the potentials, yet two pure compounds, 12 : 12'-dimethoxy-dibenzanthrone (see Fig. 1) and 1 : 2 : 5 : 8-tetrahydroxyanthraquinone, also give poorly defined waves superimposed on a steadily rising current, though the effect is less marked.[4]

Comparison of Tables 2 and 3 shows that there is some variation in the half-wave potentials and the diffusion currents of the series of solvent extracts of the coal DIII with the fraction of coal extracted. Some fractionation is evidently effected by extraction with different solvents, but not into materials of radically different structure. The behaviour of the ethylenediamine extract is of interest because the heat of immersion of coal DIII in it is so high (65 cal./g. at 25°; cf. 25 cal./g. for methanol [12]) that specific interaction must be suspected. Moreover an ethylenediamine extract, precipitated with hydrochloric acid, retains a small amount of solvent even after prolonged washing, as is shown by the higher nitrogen content of the dried extract (3·4%) in the material prepared for the present work than in that of the original coal (2·0%). The diamine possibly reacts with carbonyl groups in the coal giving a glyoxaline ring or other heterocyclic system. But as the only type of carbonyl group in coals for which there is evidence is the quinonoid, and if they had so reacted the polarographic behaviour could hardly have been that observed, some other explanation of the interaction must be sought.

The diffusion current constants, $i_d/(cm^{\frac{2}{3}}t^{\frac{1}{6}})$, of all the quinones of known structure studied in lithium chloride–dimethylformamide were abnormally low and had about the value expected for a one-electron addition, although two waves were observed in most cases;[4] the wave heights were more normal in tetraethylammonium iodide solutions. Where a coal extract has been studied in both lithium chloride and tetraethylammonium iodide solutions, the diffusion current was lower in the former. A more serious uncertainty in the diffusion current constants arises from the fact that the waves were superimposed on a steadily rising current. If one takes merely the height of the waves one may be neglecting part of the current due to reduction of quinones. On the other hand the rise in current between, say, 0 and −1 v may be not wholly diffusion current. One cannot therefore estimate quinone contents accurately from diffusion current constants by means of the Ilković equation. However it appears, from diffusion coefficients of the coal extracts in dimethylformamide, measured by Coggan and Given,[13] and the polarographic wave heights, that the pyridine extracts contain 2 g.-atoms of oxygen as quinone per 3000—5000 g. If one takes instead the rise in current between −0·1 and −1 v these weights of coal are about halved. Since the molecular weights of the materials, estimated from the diffusion coefficients, are about 2000 for the extract of coal DO and 600—900 for the others, it appears that not all the molecules in the materials are quinones. One might therefore expect quinones or non-quinones to be preferentially extracted from coals by some solvents. Some such effect can be observed in the varying diffusion current constants of the extracts of coal DIII (see Tables 2 and 3; the term $D^{\frac{1}{2}}$ appearing in the Ilković equation does not differ greatly for these extracts).

For comparison, we mention some other estimates of the quinone contents of coals and their solvent extracts. Wyss and Brown estimated a figure of 2 g.-atoms of oxygen as quinone per 6400 g. for the acetone extract of coal DIII. Peover, from the quantity of electricity passed in electrolytic reduction of another extract of the same coal (see above), obtained a figure of 1300 g. Blom et al.[3] attempted to determine carbonyl groups in coals by oximation. They found that the uptake of hydroxylamine, calculated from the difference in nitrogen content of the oximated product before and after hydrolysis, was much greater (3—16 times) than the amount liberated from the product by hydrolysis;

[12] Bangham and Dryden, *Fuel*, 1950, **29**, 291.
[13] Coggan and Given, unpublished measurements.

the latter was determined by reduction with titanous chloride and estimation of the ammonia produced. Their method did not give satisfactory results with a number of known compounds. They report carbonyl contents, which they regard as minimum figures, corresponding to 2 g.-atoms of oxygen as carbonyl per 5300—16,000 molecular-weight units, depending on the carbon content of the coal.